Energy Transport in Organic Phosphors

S. C. Ganguly and N. K. Chaudhury

Solid Physics Laboratory, Jadavpur University, Calcutta, India

CONTENTS

1. INTRODUCTION

THE mechanism of energy transfer from one constituent to the other in solids, solutions, and gaseous mixtures has created considerable interest during recent years. Until very recently these discussions[1,2] were confined mostly to the inorganic phosphors in general, and alkali halides in particular. Along with the inorganic atoms and molecules, more than a few experimental results on benzene and benzene derivatives are also reported in the literature.[3-6] For instance, the fluorescence of indigo vapor is not excited by light of wavelength between 2700 to 2400 A, but in the presence of aniline vapor it gives violet indigo fluorescence. The incident light is first absorbed by the aniline vapor and then the absorbed energy is transferred to the indigo vapor. Similarly, aniline in presence of benzene vapor gives strong fluorescence under weak excitation. Zinc radiation at 2500 A produces only a very weak fluorescence in aniline vapor extending from 2850 to 2500 A. In a mixture of aniline and benzene vapor the benzene fluorescence is weak though it is easily excited by primary light of wavelength 2500 A, while the aniline fluoresces strongly. Apparently, the transfer of excitation energy from the benzene to the aniline molecules has high efficiency. These are instances of sensitized fluorescence which are commonly described as the process whereby an impurity atom or molecule (activator) devoid of any appreciable absorption band in a given spectral region is made to radiate upon absorption of excitation energy in this region by the host lattice or an impurity atom or molecule (sensitizer) embedded in it. In all cases of sensitization, the problem which is of the most fundamental significance is as follows: What is the mechanism of propagation of the excitation energy from the sensitizer to the activator and its ultimate transfer? Where the sensitizer and the activator are close to each other, the excitation energy does not have to move far and the processes of propagation and transfer both take place at nearly the same position in the lattice. There are also cases of sensitized luminescence where absorption of the exciting energy takes place all over the matrix lattice while the luminescence transitions occur in or near the few activators. These cases are characterized by propagation of energy through the lattice over a considerable distance before transfer of the excitation energy can occur. There are four distinct processes by which transfer of the excitation energy can take place. They are (a) photon absorption and reabsorption, known as photon cascade; (b) collision; (c) exciton migration; and (d) electron and hole migration. We discuss them briefly, bringing out the conditions to which each is subject. Particular emphasis is given to the discussion of anthracene-naphthacene and anthracene-naphthalene systems in crystals.

(a) Photon Absorption and Reabsorption

This mechanism of energy transfer, also called the photon cascade process, becomes of quantitative importance in a system if there exists strong overlap between the emission and the absorption spectra and

[1] F. A. Kroger, *Some Aspects of the Luminescence of Solids* (Elsevier Publishing Company, Inc., Houston, Texas, 1948).
[2] H. W. Leverentz, *Introduction to Luminescence of Solids* (John Wiley & Sons, Inc., New York, 1950).
[3] P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1950).
[4] M. Furst and H. Kallmann, Phys. Rev. 94, 503 (1954).
[5] M. Furst and H. Kallmann, Phys. Rev. 97, 583 (1955).
[6] M. Furst and H. Kallmann, J. Chem. Phys. 23, 607 (1955).

if the system has a high absorption coefficient in the area of overlap, comparable with that at the wavelength of excitation. The system may be a pure one containing no foreign constituents, the region of overlap being between the emission and the absorption spectra of the constituents of the pure system. If the system is an impure one, containing impurity atoms or molecules embedded in it, the region of overlap may be provided by the emission spectrum of the pure system and the absorption spectrum of impurity constituents. If we consider such a crystal system, the part of the primary molecular fluorescence that is emitted in the region of overlap, is practically reabsorbed by the crystal within a small fraction of its thickness. This reabsorbed radiation is re-emitted as fluorescence by the molecules which absorbed it. A fraction of it suffers reabsorption by succeeding layers of molecules, these processes of emission and reabsorption follow each other until all the excitation energy is either transformed into fluorescence outside the region of overlap so as to escape from the crystal as technical fluorescence or is thermally dissipated by internal conversion.

A quantitative formulation of the mechanism was developed by Birks[7] to explain the photofluorescent and scintillation properties of organic materials. Let us consider a mixed crystal containing solute molecules A immersed in solvent molecules S. On the photon cascade theory, the processes shown in Table I occur in the crystal, assuming that the exciting radiation is absorbed totally by S and that S does not absorb the fluorescence radiation of A.

When only processes 2 and 3 (see Table I) compete, there results the molecular fluorescence of S. Its quantum efficiency η_{0s} is given by

$$\eta_{0s} = \frac{1}{1 + (K_{is}/K_{fs})}. \tag{1}$$

When the competing processes are described by 2, 3, 4, 5, and 9, the primary fluorescence of S is reabsorbed and re-emitted and only a part of the primary fluorescence S escapes from the crystal as technical fluorescence. The quantum efficiency η_{es} of this is given by

$$\eta_{es} = \frac{\eta_{0s}}{1 + (K_S/K_{es}) + (K_A/K_{es})[A]}$$
$$+ \frac{K_S}{K_{es}} \left\{ \frac{\eta_{0s}}{1 + (K_S/K_{es}) + (K_A/K_{es})[A]} \right\}^2$$
$$+ \left(\frac{K_S}{K_{es}}\right)^2 \left\{ \frac{\eta_{0s}}{1 + (K_S/K_{es}) + (K_A/K_{es})[A]} \right\}^3$$
$$= \frac{\eta_{0s}}{1 + (1 - \eta_{0s})(K_S/K_{es}) + (K_A/K_{es})[A]}. \tag{2}$$

[7] J. B. Birks, Phys. Rev. 94, 1957 (1954).

TABLE I. Photon transfer process.

Process	Relative ratio[a]	Description of process
1. $S + h\nu \rightarrow S^*$	1	Excitation by light
2. $S^* \rightarrow S + h\nu_s$	$K_{fs}[S^*]$	Fluorescence of S
3. $S^* \rightarrow S$	$K_{is}[S^*]$	Internal quenching of S
4. $S + h\nu_s \rightarrow S^*$	$K_s K_{fs}[S^*]$	Self-absorption of S
5. $A + h\nu_s \rightarrow A^*$	$K_A K_{fs}[S^*][A]$	Absorption of A
6. $A^* \rightarrow A + h\nu_A$	$K_{fA}[A^*]$	Fluorescence of A
7. $A^* \rightarrow A$	$K_{iA}[A^*]$	Internal quenching of A
8. $A + h\nu_A \rightarrow A^*$	$K_A K_{fA}[A^*][A]$	Self-absorption of A
9. $h\nu_s \rightarrow$	$K_{es} K_{fs}[S^*]$	Escape of $h\nu_s$
10. $h\nu_A \rightarrow$	$K_{eA} K_{fA}[A^*]$	Escape of $h\nu_a$

[a] Here Brackets stand for concentrations in molecules per solvent molecule, S^* and A^* for excited molecules of S and A, and $K = (1/t)$ for the probability of a process of decay time t, i.e., number of events describing the process, that happen per unit time.

In the absence of internal quenching $K_{is} = 0$ and $\eta_{0s} = \eta_{0A} = 1$, so that (2) is reduced

$$\eta_{es} = \frac{1}{1 + (K_A[A]/K_{es})}. \tag{3}$$

The quantum yield for transfer, i.e., the ratio of the number of photons transferred per second from S to A to the number of photon absorbed by S per second, neglecting nonradiative transactions in S becomes, in the case of molecular fluorescence,

$$\eta_{0T} = K_A[A]/K_S. \tag{4}$$

The molecular fluorescence quantum efficiency η_{0A} of A is given by

$$\eta_{0A} = \frac{1}{1 + (K_{iA}/K_{fA})}. \tag{5}$$

The quantum efficiency (η_{eA}) of escape of (A) technical fluorescence is given by

$$\eta_{eA} = \frac{\eta_{es}\eta_{0A}(K_A/K_{es})[A]}{1 + (1 - \eta_{0A})(K_A'/K_{eA})[A]}. \tag{6}$$

In the absence of internal quenching, $K_{iA} = 0$ and $\eta_{0s} = \eta_{0A} = 1$ so that we have for (6)

$$\eta_{eA} = \eta_{es}(K_A/K_{es})[A] = 1 - \eta_{es} = \frac{(K_A/K_{es})[A]}{1 + (K_A/K_{es})[A]}. \tag{7}$$

Here the quantities K_{es}, K_S, and $K_A(A)$ are inter-related by

$$K_{es} + K_S + K_A(A) = 1.$$

They are dependent upon the relative absorption coefficients of S and A for the fluorescence of S and on the crystal size.

In pure crystal phosphors, processes 1, 2, 3, 4, and 9 are in operation. The molecular quantum efficiency (suffix S is now dropped) remains unchanged while the

technical quantum efficiency η_e takes the form

$$\eta_e = \frac{\eta_0}{1+(1-\eta_0)(K/K_e)} = \frac{1}{1+(K_i/K_e K_f)};$$

$$[\because \quad K+K_e=1].$$ (8)

If internal quenching is not present, the molecular photofluorescence decay time $(t_f)_{00}=1/K_f$; internal quenching, if present, reduces it to $(t_f)_0$ given by

$$(t_f) = \frac{(t_f)_{00}}{1+[(t_f)_{00}/t_i]} = \eta_0(t_f)_{00}.$$ (9)

In case of a large thick crystal, stepwise self-absorption lengthens the duration of the interval between the moment of primary excitation and the moment of escape of fluorescence so that the technical photofluorescence decay time t_f is increased to

$$t_f = \frac{(t_f)_{00}}{K_e+[(t_f)_{00}/t_i]}.$$ (10)

When internal quenching is small enough to make $(t_f)_{00} \ll t$; (8) and (10) may be expressed approximately as follows:

$$t_f = \eta(t_f)_0$$ (11)

and

$$\eta_e = (\eta_0)^N.$$ (12)

Here $N=1/K_e$ represents the average number of steps of molecular emissions passed before escape of technical fluorescence. The molecular and technical photofluorescence quantities $(t_f)_0$ and (t_f) can be obtained from measurements on microcrystalline and thick crystal specimens and thus N can be determined. Comparison of the molecular and the technical photofluorescence spectra leads to a determination of N.

(b) Collision Process

This mechanism was proposed by Cario and Franck[8] and to account for the disappearance of fluorescence of a gas due to the presence of foreign gas molecules. In this process when an excited atom or molecule collides during the lifetime of its excited state with a slow electron, it may give away its excitational energy to the electron, without any radiation, the products of the collision being an electron with enhanced kinetic energy and an unexcited atom or molecule. When the collision partner is a normal atom or molecule, the excited atom or molecule may give away a quantum of energy (E_2-E_1) to the unexcited one and the latter may take up the energy either as energies of translation, excitation or both; there being no loss of energy during the process as radiation. Such radiationless transfer of excitation energy is called a collision of the

second kind, as distinguished from a collision of the first kind in which excitation is produced. The mechanism, demonstrated in gases by Franck, Cario, and many others, has been shown to take place also in some organic solutions.[3,9]

The quantum-mechanical theories of this transfer process as formulated by Perrin[10] and Forster[11] are based on resonance between allowed electric dipole transitions in the sensitizer and the activator. The resonance theory is extended by Dexter[12] to include cases of energy transfer in which an activator having a suitable emission spectrum can be made to fluoresce with energy transferred from an absorbing sensitizer despite the fact that the activator is forbidden direct absorption of energy. The transfer mechanisms of importance are by overlap of the electric dipole fields of the sensitizer and the activator, overlap of the dipole field of the former and the quadrupole field of the latter, and exchange effects, producing, respectively, sensitization of about 10^3-10^4, about 10^2, and about 30 lattice sites in a crystal surrounding each sensitizer. Dexter's theory is applicable to impurity sensitization both in solid and liquid systems. He adopts the physical model of a crystal in which the sensitizing impurity atoms or ions, of atomic concentration x_s, and the activators of atomic concentration x_a, are randomly arranged at suitable lattice sites, without mutual interaction. The time-dependent perturbation method of quantum mechanics gives the probability of transition of a system from its initial to final state as

$$(2\pi/\hbar)|\langle H_1\rangle|^2 \rho_E,$$ (13)

where $\hbar$ is Planck's constant divided by 2π, H_1, the matrix element of the perturbation to the Hamiltonian and ρ_E the density of final states. In this case the initial state ψ_1 is identified with the configuration of the system in which the sensitizer S is in the excited state ψ_s' while the activator A is in its ground state ψ_a and the final state ψ_2 is the configuration in which S is in its ground while A is excited to the state ψ_a'. Thus the probability that the energy of excitation is transferred from a particular sensitizer S to a particular activator A has the form,

$$P_{sa} = (2\pi/\hbar)\rho_E \left| \int \psi_1^* H_1 \psi_2 d\tau \right|^2,$$ (14)

as long as the states ψ_1 and ψ_2 are of the same energy.

To take account of the lack of definition of the initial and final levels of S or A caused by lattice vibrations, the wave functions are normalized on an energy scale and the density of states factor ρ_E is included within the

[8] G. Cario and J. Franck, Z. Physik 17, 202 (1928).

[9] J. Franck and R. Livingston, Revs. Modern Phys. 21, 505 (1949).

[10] F. Perrin, J. phys. radium 7, 1 (1936).

[11] Th. Forster, Ann. phys. 2, 55 (1948); Z. Electrochem. 53, 93 (1949).

[12] D. L. Dexter, J. Chem. Phys. 21, 836 (1953).

normalization parameters. It is convenient to normalize the initial states of S and A (ψ_s' and ψ_a) and to express by the functions $p_s'(w_s')$ and $p_a(w_a)$ the probabilities that S is in the particular energy state denoted by w_s' and that A is in the state w_a so that

$$\int |\psi_s'(w_s')|^2 d\tau = \int |\psi_a(w_a)|^2 d\tau,$$

$$\int_0^\alpha p_s'(w_s')dw_s' = \int p_a(w_a)dw_a = 1. \qquad (15)$$

The final states of S and A (ψ_s and ψ_a') are normalized on the energy scale by the following:

$$\frac{1}{\Delta w}\int_w^{w+dw} dw_s \int |\psi_s(w_s)|^2 d\tau = 1$$

$$\frac{1}{\Delta w}\int_w^{w+\Delta w} dw_a' \int |\psi_a'(w_a')|^2 d\tau = 1. \qquad (16)$$

The properly antisymmetrized initial and final states wave functions describing S and A can now be written as

$$\psi_1(w_s',w_a) = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_s(\bar{r}_1,w_s') & \psi_s'(\bar{r}_2,w_s') \\ \psi_a(\bar{r}_1,w_a) & \psi_a(\bar{r}_2,w_a) \end{vmatrix}$$

$$\psi_2(w_s,w_a') = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_s(\bar{r}_1,w_s) & \psi_s(\bar{r}_2,w_s) \\ \psi_a'(\bar{r}_1,w_a') & \psi_a'(\bar{r}_2,w_a') \end{vmatrix}, \qquad (17)$$

where only two electrons are involved in the transitions.

According to the Franck-Condon principle, an electronic transition in which the electronic excitation energy is lost to the lattice has small probability of occurrence, because of the condition of energy equality of the states ψ_1 and ψ_2. Under these conditions the transition probability P_{sa} should contain a Dirac delta function $\delta(E_1 - E_2)$, as a factor where $E_1 = w_s' - w_s$ and $E_2 = (w_a' - w_a)$ are the excitation energy on S in the state ψ_1, and that on A in the state ψ_2, respectively. The total probability of energy transfer from S to A becomes

$$P_{sa} = \left(\frac{2\pi}{\hbar}\right) \sum_1 \sum_2 (g_s'g_a)^{-1}$$

$$\times \int dw_a' \int dw_s \int dw_a p_a(w_a) \int dw_s' p_s'(w_s')$$

$$\times |\langle H_1(w_s', w_a; w_s, w_a')\rangle_{12}|^2$$

$$\times \delta[(w_s' - w_s) - (w_a' - w_a)], \qquad (18)$$

where g_s' and g_a are the degeneracies of the level of S and of the level of A, respectively.

Calculating by means of the S function and sub-

stituting $E = E_1 = E_2$, we have

$$P_{sa} = \left(\frac{2\pi}{\hbar}\right) \sum_1 \sum_2 (g_s'g_a)^{-1}$$

$$\times \int dE \int dw_a p_0(w_a) \int dw_s' p_s'(w_s')$$

$$\times |\langle H_1(w_s', w_a; w_s' - E, w_{a+E})\rangle|^2. \qquad (19)$$

The interaction between A and S can be expressed as the sum of all the Coulomb interactions of the outer electrons and the core of A with those of S, properly reduced by the dielectric constant K of the medium. Expansion of this sum in a Taylor series around the vector $\mathbf{R}$, which separates the nuclei of A and S, reduces the interaction Hamiltonian to the form

$$H_1(\bar{R}) = \left(\frac{e^2}{KR^3}\right)\{\bar{r}_s \cdot \bar{r}_a - 3(\bar{r}_s \cdot \bar{R})(\bar{r}_a \cdot \bar{R})/R^2\}$$

$$+ \left(\frac{3e^2}{2KR^4}\right)\{\sum_{i=1}^3 (R_i/R)r_{ai}{}^2 r_{si}(-3 + 5R_i{}^2/R^2)$$

$$+ 10(XYZ/R^3)(x_a y_a z_s + x_a z_a y_s + y_a z_a x_s)$$

$$+ \sum_{i\pm j}^3 \sum_{}^3 [(R_j/R) - 5R_i{}^2 R_j/R^3]$$

$$\times [-r_{ai}{}^2 r_{sj} - 2r_{ai} r_{aj} r_{si}]\}, \qquad (20)$$

where $\bar{r}_s = \sum_m \mathbf{r}_{s0m}$ refers to all electrons on S measured from its nucleus and so with $\mathbf{r}_a = \sum_n \mathbf{r}_{an}$.

Electric Dipole-Dipole Interaction

The first curly brackets in Eq. (20) are the dipole-dipole interaction term. Inserting this into Eq. (17), one can have

$$P_{sa}(dd) = \left(\frac{2\pi}{\hbar}\right) \sum_1 \sum_2 \left(\frac{e^4}{K^2 R^6}\right)(g_s'g_a)^{-1}$$

$$\times dE \int dw_a p_a(w_a) \int dw_s' p_s'(w_s')$$

$$\times \langle \bar{r}_s\rangle\langle \bar{r}_a\rangle - 3(\langle \bar{r}_s\rangle \cdot R)|(\langle r_a\rangle R)|^2, \qquad (21)$$

where the matrix element, $\langle \bar{r}_s\rangle$ stands for

$$\langle \bar{r}_s(w_s', w_s' - E)\rangle_{i s f s}$$

and so with $\langle r_a\rangle$. Average of the absolute square of the matrix element in Eq. (21) over all possible orientations of $\mathbf{R}$ is $(2/3)|\langle r_s\rangle|^2|\langle r_a\rangle|^2$, where $|\langle r\rangle|^2 = |\langle x\rangle|^2 + |\langle y\rangle|^2 + |\langle z\rangle|^2$ so that

$$P_{sa}(dd) = \frac{4\pi e^4}{3\hbar K^2 R^6 g_s g_a} \sum_1 \sum_2 \int dE$$

$$\times \left\{ \int dw_s' p_s'(w_s')|\langle \bar{r}_s\rangle|^2 \right\}. \qquad (22)$$

By using the usual expressions for Einstein's A and B coefficients to evaluate the matrix elements contained here in terms of the experimentally measurable quantities such as oscillator strengths, absorption coefficients, and decay times, Dexter reduces Eq. (22) to the form,

$$P_{sa}(dd) = \frac{3\hbar^4 c^4 Q_a}{4\pi R^6 n^4 \tau_s} \left(\frac{\mathscr{E}}{K^{\frac{1}{2}} \mathscr{E}_c}\right)^4 \int \frac{f_s(E) F_a[E]}{E^4}, \quad (23)$$

with the absorption data for A and the emission data for S or to the form,

$$P_{sa}(dd) = \frac{3\hbar c^2 Q_a Q_s}{4\pi^3 n^2 R^6} \left(\frac{g_s}{g_s'}\right) \left(\frac{\mathscr{E}}{K^{\frac{1}{2}} \mathscr{E}_c}\right)^4 \int \frac{f_s(E) f_a(E)}{E^2} dE, \quad (24)$$

which also contains the emission data for s, where Q_s, Q_a = areas under the absorption bands of S, A; r_s = decay time for S emission; $\mathscr{E}$ = electric field at an isolated atom; $\mathscr{E}_c$ = electric field within the crystal; K = dielectric constant of the medium; $f_s(E)$ = shape of the observed S-emission band normalized so that $\int f_s(E) dE = 1$; $F_a(E) = \sigma_a(E)/Q_a$; $\sigma_a(E)$ = absorption cross section of energy E by A, measurable at low concentrations of A, as the absorption coefficient per unit impurity (A) density in the medium.

This result is similar to Forster's[11] expression for the probability of $(d\text{-}d)$ transfer between systems S and A at a distance R_{sa} apart,

$$P_{sa} = \frac{2c}{\pi^4 n^2 \bar{N}^2 \bar{\nu}^2 R_{sa}^6} \int f_s(\bar{\nu}) \rho_a(\bar{\nu}) d\bar{\nu}, \quad (25)$$

where $\bar{N} = 6.06 \times 10^{23}$, $\bar{\nu}$ = wave number in cm^{-1}, $f_s(\bar{\nu})$ = molar emission intensity of S at $\bar{\nu}$, $\rho_a(\bar{\nu})$ = molar extinction coefficient of A at $\bar{\nu}$.

The transfer probability thus depends upon the strengths of the individual transitions as determined by decay times, absorption band areas Q, and the energy overlap of the emission and absorption bands of A and S. Neglecting nonradiative transfers in S and transfers from S to S, the following expression for the quantum yield for transfer is obtained,

$$\eta_T = p_{sa}\tau_s/(1 + p_{sa}\tau_s). \quad (26)$$

By writing $\beta = (P_{sa}\tau_s)^{\frac{1}{3}} v$, where v is defined as $(4/3)\pi R^3$, one obtains $\eta_T = (\beta^2)/(v^2 + \beta^2)$. Let C^+ be the number of density of lattice sites that can accommodate A and let v_0 be the volume excluded by the presence of the sensitizer. Writing $y = x_a C^+ \beta$ one finds the average yield as

$$\bar{\eta}_T = y \exp(x_a C^+ v_0)\{y^{-1}[\exp(-x_a C^+ v_0) - 1]$$
$$+ C_i(y) \sin y - S_i(y) \cos y + (\pi/2) \cos y\}, \quad (27)$$

where C_i and S_i are cosine and sine integral functions. For concentrations $x_a \lesssim 1\%$ if $C^+ = 2.26 \times 10^{22}$ cm^{-3} ($y \lesssim 20$); $\beta = 8.26 \times 10^{-20}$ cm^{-3} the factors $\exp \pm (x_a C^+ v_0)$
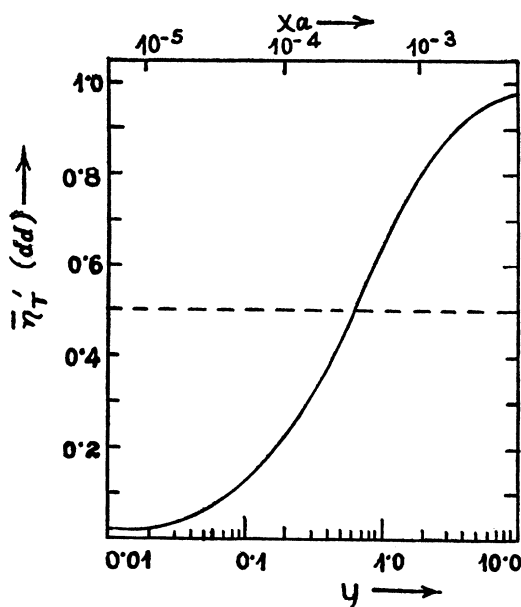

Fig. 1. Quantum yield for dd transfer as a function of the reduced concentration y of the activator. The upper abscissa represents the numerical values of the atomic concentration x_a in the typical case of NaCl crystals (after Dexter).

may be set equal to unity and one obtains

$$\bar{\eta}_{T'} = y\{C_i(y) \sin y - S_i(y) \cos y + (\pi/2) \cos y\}. \quad (28)$$

This function is shown in Fig. 1. For concentrations small enough that $y \ll 1$, $\bar{\eta}_{T'}$ varies as $y(\pi/2 + y \ln y - 0.4228y)$ so that for small x_a, $\bar{\eta}_T$ increases linearly with concentration. For concentrations high enough to make $y \gg 1$, $\bar{\eta}_{T'} \to 1$.

The temperature dependence of the transfer probability can be understood from Eqs. (23) and (24). Generally Q_a, Q_s, or τ_s are not very dependent on temperature so that the main temperature dependence is determined by the temperature dependence of the energy overlap integral $\int f_s(E) F_a(E)/E^4$. Both f_s and F_a generally possess temperature broadening. In the event of perfect overlapping at all temperatures, the transfer probability decreases with increasing temperature. If, however, the absorption and emission bands have well separated centers, temperature broadening of the bands acts to produce greater overlap, and therefore grater transfer probability. At low temperatures the broadening being negligible as compared to natural zero-point widths, the transfer probability should not depend on temperature.

Electric Dipole-Quadrupole Interaction

When S makes an allowed dipole transition and A a prohibited quadrupole transition to calculate the transfer probability, one can insert in Eq. (19) the absolute square of the matrix element $\langle H_1 \rangle$ computed from the second bracket of Eq. (20) and averaged over all

orientations of $\bar{R}$. Inserting

$$\langle|\langle H_1\rangle|^2\rangle_{Av}=\frac{9e^4\alpha}{4K^2R^8}|\langle r_s\rangle|^2|\langle N_a\rangle|^2 \quad \text{in Eq. (19),}$$

where $\alpha=1.266$ and $|\langle N_a\rangle|^2=|\langle x_a{}^2\rangle|^2+|\langle y_a\rangle|^2+|\langle z_a\rangle|^2$ $+2|\langle xy\rangle|^2+2|\langle yz\rangle|^2+2|\langle zx\rangle|^2$ one obtains the following expression for the transfer probability:

$$P_{sa}(dq)=9e^4\pi\alpha/2\hbar K^2R^8 g_s{}'g_a \sum_1 \sum_2 \int dE$$

$$\times\left\{\int dw_s{}'p_s{}'(w_s{}')|\langle \bar{r}_s(w_s{}', w_s{}'-E)\rangle|^2\right\}$$

$$\times\left\{\int dw_a p_a(w_a)|\langle N_a(w_a, w_a+E)\rangle|^2\right\}. \quad (29)$$

Relating, as before the bracketed quantities to either emission or absorption data when measurable or significant, for A or S, Dexter obtains

$$P_{sa}(dq)=\frac{135\pi\alpha\hbar^9 c^8 g_a{}'}{4\eta^6 R^8 \tau_s \tau_a g_a}\left(\frac{\mathscr{E}}{K^{\frac{1}{2}}\mathscr{E}_c}\right)^4 \int \frac{f_s(E)F_a(E)}{E^8}dE. \quad (30)$$

If τ_s is not measurable or has no significance, one can use the expression

$$P_{sa}(dq)=\frac{135\alpha\hbar^6 c^6 Q_s}{4\pi n^4 R^8 \tau_a}$$

$$\times\frac{g_a{}'g_s}{g_a g_s{}'}\left(\frac{\mathscr{E}}{K^{\frac{1}{2}}\mathscr{E}_c}\right)^4 \int \frac{f_s(E)F_a(E)}{E^6}. \quad (31)$$

The ratio that $P_{sa}(dq)$ bears to $P_{sa}(dd)$ is calculated from Eqs. (30) and (23) to be $(45\alpha/4\pi^2)(n\lambda/R)^2\tau_a(d)/\tau_a(q)$. Since a quadrupole radiative transition has a probability of the order of $(a/\lambda)^2$ times a dipole radiative transition, one can put $\tau_a(d)/\tau_a(q)$ so that $P_{sa}(dq)$: $P_{sa}(dd)$ is of the order of $(a/R)^2$. Thus, resonance transfer can occur from a sensitizer to a nearby activator having a quadrupole transition in the proper frequency interval whereas direct absorption of radiation by the activator takes place with a probability only $\sim 10^{-7}$ of that in an impurity with an allowed transition.

After defining γ by the relation $P_{sa}(dq)=\gamma^{8/3}v^{8/3}\tau_s$ and putting $y=\gamma C^+x_a$, one finds

$$\bar{\eta}_T=y\exp(x_a C^+v_0)\left\{y^{-1}[\exp(-x_a C^+v_0)-1]\right.$$

$$\left.+\int_0^\alpha (e^{-vt}/1+t^{8/3})dt\right\} \quad (32)$$

and

$$\bar{\eta}_T{}'=y\int_0^\alpha (e^{-vt}/1+t^{8/3})dt. \quad (33)$$
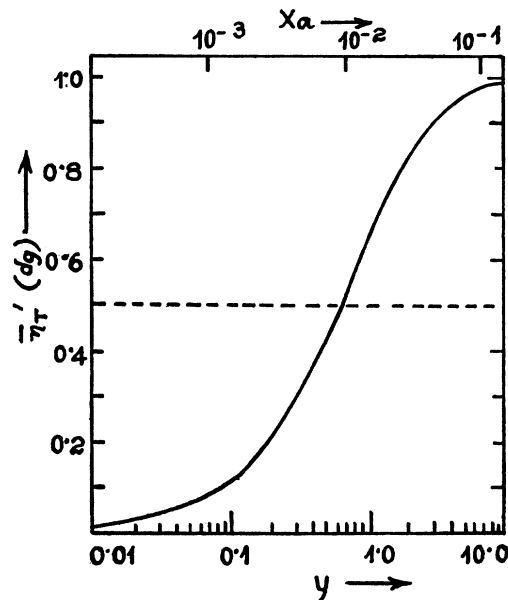

FIG. 2. Quantum yield for dq transfer as a function of the reduced concentration y of the activator, as in Fig. 1. The upper abscissa scale shows atomic concentrations in the typical case of NaCl crystals. The variation of $\bar{\eta}_T{}'$ with concentration is more rapid in the dq case than in the dd case (after Dexter).

This function is shown in Fig. 2. Since $P_{sa}(dq)$ depends on R more strongly than $P_{sa}(dd)$, $\bar{\eta}_T$ depends upon x_a more rapidly in the dq case than in the dd case.

The function $F_a(E)$ which is the absorption shape function of A cannot be experimentally determined because the absorption would not be observed.

Exchange Effects and Other Forbidden Transitions

Considering only the effects of electron spin, one can write out explicitly the matrix element of H_1 as $\psi(\bar{r},\bar{\sigma})=\varphi(\bar{r})\chi(\sigma)$ where $\chi(\sigma)$ are the spin wave functions.

$$\langle H_1\rangle=\int \varphi_s{}'^*(\bar{r}_1)\varphi_a{}^*(\bar{r}_2)H_1\varphi_s(\bar{r}_1)\varphi_a{}'(\bar{r}_2)$$

$$\times\chi_s{}'^*(\bar{\sigma}_1)\chi_a{}^*(\bar{\sigma}_2)\chi_s(\bar{\sigma}_1)\chi_a{}'(\bar{\sigma}_2)$$

$$-\int \varphi_s{}'^*(\bar{r}_1)\varphi_a{}^*(r_2)H_1\varphi_a{}'(\bar{r}_1)\varphi_s(\bar{r}_2)$$

$$\times\chi_s{}^*(\bar{\sigma}_1)\chi_a{}^*(\bar{\sigma}_2)\chi_a{}'(\bar{\sigma}_1)\chi_s(\bar{\sigma}_2). \quad (34)$$

The first term in $\langle H_1\rangle$ is the Coulomb term treated before, and the second integral is an exchange integral with $H_1=e^2/Kr_{12}$. If the X's are left for the moment the integral can be understood as representing the electrostatic interaction between the two charge clouds

$$Q'(r_1)=\varphi_s{}'^*(\bar{r}_1)\varphi_a{}'(\bar{r}_1) \quad \text{and} \quad Q(\bar{r}_2)=\varphi_a{}^*(\bar{r}_2)\varphi_s(\bar{r}_2).$$

Each function φ dies off exponentially with distance from S or A and each product Q will not be sizeable throughout all space except when r_{12} is small so that

the integral $\int Q'(\bar{r}_1)(1/r_{12})Q(\bar{r}_2)d\tau_{12}$ may be of sizeable value (R being small) even though the overlap integral $\int Q(r)d\tau$ which enters in normalization, is small enough to be neglected.

The transfer probability by exchange mechanism may be expressed as

$$P_{sa}(ex)=\left(\frac{2\pi}{\hbar}\right)Z^2\int f_s(E)F_a(E)dE, \qquad (35)$$

where

$$Z^2=\sum_1\sum_2\frac{e^4}{g_s'g_a\kappa^2}\left|\int Q'(r)\frac{1}{r_{12}}Q(\bar{r}_2)d\tau_{12}\right|^2_{1,2}$$

cannot be directly connected to optical experimental quantities.

The exchange mechanism has an efficiency in energy transfer slightly less than the dq transfer.

Electric Dipole-Magnetic Dipole Interaction

The transfer mechanism arising from an electric dipole-magnetic dipole interaction may be treated by including magnetic fields in the Hamiltonian. The most important in a so-constructed H_1 is $e\hbar/2mc\bar{H}\cdot(\bar{r}_a\times\bar{\nabla}_a+i\bar{\sigma}_a)$, where H is the magnetic intensity at A produced by motion of charge at S. The largest term in H being of the order $(e/c)\bar{R}\times\bar{V}_s/R^3$ or $(e\hbar/mc)\bar{R}\times\bar{\nabla}_s/R^3$. Thus $\langle H_1\rangle$ has the magnitude $(e^2\hbar^2/2m^2c^2R^2)\langle\bar{\nabla}_s\rangle$ or because $\langle\bar{\nabla}_s\rangle=mE\langle\bar{r}_s\rangle/\hbar^2$ one finds

$$|\langle H_1(em)\rangle|^2/|\langle H_1(dd)\rangle|^2\sim(e^2/hc)^4E^2/(e^2/R)^2. \qquad (36)$$

Thus for the nearest neighbors $P_{sa}(em)$ is of the order of 10^{-8} times $P_{sa}(dd)$, small enough to be neglected.

Host Sensitization

Most of the discussion of impurity sensitization applies also to host sensitization, i.e., sensitization of an activator by the lattice itself in which it is embedded. In this case X_s, being equal to unity, is not small enough to forbid S-S transfer. When S has an allowed transition the transfer mechanism from S to S would be a (d-d) process, and depending on the degree of forbiddenness of transitions in A, either a dd process, a competition between dq and exchange or exchange from S to A.

Transference of excitation energy by dipole-dipole interaction should be carefully distinguished from a cascade phenomenon. In the latter process where a photon emitted by S is reabsorbed by A, the quantum yield for transfer depends not only on the concentration (A) but also on the size and shape of the system, as seen from (16).

The quantum yield for transfer by the cascade mechanism can be expressed as follows in terms of the

crystal dimension,

$$\bar{\eta}_T(C)=Av\int f_s(E),$$

where A, v, $f_s(E)$, C, and (E) are as defined before and the average is taken over the linear dimension l of the sample. $1-\eta_{0T}$ is the probability that a photon emitted by S will escape from the system and is then equal to η_{es}. The quantity $C(A)l$ represents the number of impurity molecules A per cm² projected on a plane perpendicular to the path of the photon. If we compare a spherical system containing a concentration (A) of A with the same system spread out in a thin film as regards quantum yield, it will be greater in the former case than in the latter, if the transfer takes place by the cascade process whereas it will be independent of the shape and size of the sample if the transfer takes place by dipole-dipole interaction.

(c) Exciton Migration

Exciton or excitation wave, a concept first introduced by Frenkel[13] to mean quick transfer of excitation energy from one constituent to another of a crystal lattice, is a product of the mathematical problem of calculating the excited states of a lattice of interacting atoms or molecules. The physical model used by Frenkel, Peierls,[14] and subsequently, by Slater and Shockley[15] was simple. It consists of a system of identical atoms each containing one electron arranged in simple crystalline array. The electron spin is neglected and both the lowest and the first excited states are assumed to possess no degeneracy. Let atoms be located at the points defined by

$$\mathbf{r}(n)=n_1\tau_1+n_2\tau_2+n_3\tau_3, \qquad (37)$$

where the τ are the primitive translations of the lattice and the n range over all integral values. Let ψ_1 and ψ_2 denote the normal and the excited wave functions of the particular electron at $\mathbf{r}(n)$ and assume that there is so little overlapping of the wave functions on different atoms that the ψ are practically the same as the atomic wave functions. Consequently, ψ_n and ψ_n' are orthogonal to each other and to the wave functions of electrons on other atoms. A wave function for the lowest state of the entire crystalline array, which may be expressed as a determinant of the form

$$\psi_0=\frac{1}{(N!)^{\frac{1}{2}}}\begin{vmatrix}\psi_1(\bar{r}_1)\cdots\psi_1(\bar{r}_N)\\\psi_N(\bar{r}_1)\cdots\psi_N(\bar{r}_N),\end{vmatrix} \qquad (38)$$

where N is the total number of electrons and atoms. The mean energy of this state is $E_0=\int\psi_0{}^*H\psi_0d\tau$, where H is the Hamiltonian of the entire system.

Let us now consider the wave function ψ_f of the entire system for the state in which one atom is excited from

[13] J. Frenkel, Phys. Rev. 37, 1276 (1931); Physik. Z. Sowjetunion, 9, 158 (1936).
[14] R. Peierls, Ann. Physik 13, 905 (1932).
[15] J. C. Slater and W. Shockley, Phys. Rev. 50, 705 (1936).

the state ψ_f to the state ψ_f'

$$\psi_f = \frac{1}{(N!)^{\frac{1}{2}}} \begin{vmatrix} \psi_1(\bar{r}_1)\psi_1(\bar{r}_2) \cdots \psi_1(\bar{r}_N) \\ \psi_2(\bar{r}_1)\psi_2(\bar{r}_2) \cdots \psi_2(\bar{r}_N) \\ \cdots\cdots\cdots\cdots\cdots\cdots\cdots \\ \psi_f(\bar{r}_1)\psi_f(\bar{r}_2) \cdots \psi_f(\bar{r}_N) \\ \psi_N(\bar{r}_1)\psi_N(\bar{r}_2)\cdots\psi_N(\bar{r}_N). \end{vmatrix} \quad (39)$$

We cannot regard this system of wave functions as proper representations of the excited states of the crystal because they do not make

$$E_{gf} = \int \psi_g^* H \psi_f d\tau \quad (40)$$

vanish when $m \neq n$.

The N-dimensional matrix constructed from the E_{gf} can be diagonalized by finding those linear combinations ψ' of the ψ_f which are of the form

$$\psi' = \sum a_f \psi_f, \quad (41)$$

where the a_f satisfy the following equation

$$\sum_g a_g E_{gf} = E_{\alpha f}'. \quad (42)$$

Since crystal symmetry makes E_{gf} dependent only upon the difference between g and the f values, the N equation (42) can be reduced to the same form if we substitute

$$a_g = a_k e^{2\pi i k \cdot r(g)} \quad (43)$$

where K is a vector in the reciprocal lattice of the crystal. This reduces (42) to

$$E_K' = E_{ff} + \sum E_{f,f+s} e^{2\pi i k \cdot r(s)} \quad (44)$$

where $E_{f,f+s} = E_{g+m,g+m+s}$ where m, s are arbitrary integer sets.

After substituting Eq. (44) in (41), we have the normalized wave function

$$\psi_K = \frac{1}{N^{\frac{1}{2}}} \sum e^{2\pi i k \cdot r(f)} \psi_f. \quad (45)$$

A wave function of this type represents the fact that the locality where the atom is excited, moves about the lattice with a wave number k. In other words, the excited state is not localized on the particular atom that is excited, but is handed over from one constituent of the lattice to its neighbors.

By virtue of the assumption of weak overlapping we assume that E_{gf} vanishes for all but the nearest neighbors. If E_{gf} has the value ϵ in this case, (44) reduces to

$$E_K' = E_{ff} + \epsilon \sum e^{2\pi i k \cdot r}, \quad (46)$$

where r is to range over the nearest neighbors.

For a cubic lattice with lattice constant a, Eq. (46) takes the simple form

$$E_K' = E_{ff} + \epsilon(\cos 2\pi k_x a + \cos 2\pi k_y a + \cos 2\pi k_z a). \quad (47)$$

This means that the excited levels constitute a band having a spread of the order of magnitude ϵ.

It can be shown that the wave of excitation moves with a group velocity,

$$V = (1/h)\ \mathrm{grad}_K E, \quad (48)$$

and also that it carries no current. We may thus look upon the excitation wave as if it were an uncharged particle created by exciting the crystal and capable of moving about the lattice. This concept is due to Frenkel who called the wave of excitation an exciton.

It is instructive to look into Wannier's[16] model of treating the excitation bands in insulators because of its simplicity. If an electron is removed from the highest filled band of an insulator a positive charge, or positive hole, results. This positive hole may be filled up by an electron from an adjacent lattice constituent, and thus the positive hole may be able to roam about freely in an undistorted lattice. Though the Bloch picture endows the excited electron with freedom of movement independently of the positive hole, one should attract the other with a force that is Coulomb-like at large distances. It has been shown by Wannier that at the discrete levels of the hydrogen atom the excitation bands arise because of the motion of the electron and hole, one about another in closed states, and the different levels in a band behave as if they were different transitional levels of an excited hydrogen atom. This picture allowed Wannier to obtain a set of simple equations from which to derive the wave functions and energy levels of an exciton.

The migration of excitation energy by the exciton method should be carefully distinguished from that by dipole-dipole interaction. When excitons are generated in a crystal, the excitation energy is propagated through the lattice with a given wave-number vector K and the total wave function of the crystal describes a moving state of excitation energy of previously defined momentum, but indeterminate coordinates. The interaction Hamiltonian which describes the moving state of excitation energy is in form the same as that which determines the probability of transfer in a quantum mechanical collision process. The fundamental difference between them is that the former process is the result of interaction between an excited atom or molecule and all other like units, while the latter process results from interaction between one excited sensitizer and a normal activator. The latter is thus a one-step process which may take place over a distance of many angstroms in a neutral solvent, while the former may be regarded as a stepwise propagation of excitation energy from molecule to molecule covering many successive independent acts and terminates by one of a number of possible events. The motion of an exciton may be terminated by trapping at an impurity, by decay with characteristic emission of the solvent, or by

[16] G. H. Wannier, Phys. Rev. 52, 191 (1937).

a radiationless transition. The transfer of energy to an impurity by exciton migration obeys a concentration dependence that is entirely different from that in case of the single step process of collision. The theory of exciton propagation in an insulating crystal has been extended by Heller and Marcus[17] to include cases where appreciable overlapping of the electronic wave functions of nearby crystal constituents is absent. Whereas in the primary works of Frenkel, and later Slater and Shockley the ease of exciton propagation was ascribed to the overlap of the excited state wave functions of the neighboring crystal constituents, Heller and Marcus have shown that very good propagation may result, notwithstanding poor overlap, from the coupling produced by the dipole-dipole terms of the interaction Hamiltonian which give rise to the van der Waals interactions in second-order perturbation theory. When one of the lattice constituents is excited to such a state that transition between it and the ground state is associated with a large oscillator strength, the strong coupling between this excited constituent and its identical neighbors in the ground state allows the migration of energy through lattice. This happens because the translational symmetry of the lattice permits of solution of the corresponding Schrödinger equation in the form of moving waves of excitation, analogous to Frenkel's exciton waves. One of their important results is that even in an idealized cubic crystal there exists anisotropy in the propagation of excitons. Two interesting cases of exciton propagation are distinguished, those in which the induced dipole moment $\mathbf{\mu}$ is parallel and perpendicular, respectively, to the vector $\mathbf{k}$ of the exciton wave (Fig. 3). Provided there is no interference from polar modes of lattice vibration, exciton waves of the type $\mathbf{\mu}\cdot\mathbf{k}=\pi/2$ are excited by absorption of light waves, since in that case the electric vector and the propagation vector for light quanta are normal to each other. Conversion of excitons from the type $\mathbf{\mu}\cdot\mathbf{k}=\pi/2$ into the type $\mathbf{\mu}\cdot\mathbf{k}=0$ and vice versa may result from scattering collisions with phonons or other imperfections in the lattice. It is of interest to note that the excitons for which $\mathbf{\mu}\cdot\mathbf{k}=\pi/2$ have an energy increasing with k for all prominent directions of propagations, namely (100), (110), and (111) in a simple cubic lattice, and thus these excitons created by light waves behave as if they possess a positive mass. Those excitons which are polarized parallel to $\mathbf{k}$ behave in the reverse way and as if they possess a negative mass. The magnitude m' of the effective mass of an exciton is given by

$$m' \simeq mR_0/fn_0 a_e,$$

where m is the electronic mass, f is the oscillator strength of the transition between the ground state and the excited state, a_e is the equivalent Bohr radius for the excited atom, and $R_0 = (3\pi/4n_0)^{\frac{1}{3}}$, n_0 being the atomic density. Thus, the larger the oscillator strength

---

[17] W. R. Heller and A. Marcus, Phys. Rev. **84**, 809 (1951).

the quicker is the propagation of radiationless migration of excitation energy from one atom or complex to another atom or complex, attributed by Cario, Franck, and Forser to dipole coupling. The speed of migration varies inversely as the sixth power of their separation. In the case of exciton propagation, by virtue of the very high density of states, the stationary state cannot be located on one particular excited atom at a time and so the appropriate model is much like the electron wave packet in metals, in which collisions changing $\mathbf{\mu}$ and $\mathbf{k}$ will take place during the lifetime of the excitations. Following this approach one can think of a typical maximum diffusion distance of an exciton wave packet d as given by

$$d \leq (\langle v^2_{\text{thermal}} \rangle \tau_{\text{thermal}} \tau_{\text{optical}})^{\frac{1}{2}}$$

$$\approx (10^{14} \times 10^{-14} \times 10^{-8})^{\frac{1}{2}} = 10^{-4} \text{ cm}.$$

The total length of the path traversed may be of the order of centimeters. The exciton may be deprived of its energy long before the optical lifetime has expired by a competing process.

All these conclusions are reached on the basis of the assumption of a small amount of overlapping of the excited wave functions of the electrons. In certain ionic and molecular crystals in which the electron wave functions are strong at the widely spaced lattice sites and weak in between, this assumption is an appropriate qualitative description of the state of affairs.
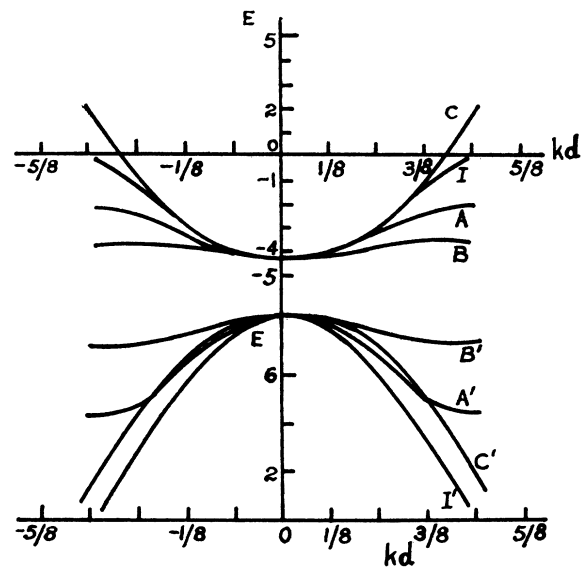

Fig. 3. The energy of exciton waves as a funcion of wave number (after Heller and Marcus). The upper curves refer to excitons for which the electric dipole moment is perpendicular to the direction of propagation, whereas the lower family refers to excitons characterized by polarization parallel to the wave number vector k, d is $(2n_0)^{-\frac{1}{3}}$ where n_0 is the density of ions contributing to the exciton propagation. The energy unit is $\mu_0^2 n_0$ where μ_0 is the electric dipole moment of the excited state. Curves A, B, C in the upper diagram and A', B', C' in the lower are for k vectors in the (100), (110), and (111) directions, respectively. Integral approximations in which the excitons behave isotropically are shown in curves I and I'.

(d) Electron and Hole Migration

Production of electrons and holes and their migration were first suggested by Mott and Gurney[18] to account for electronic behavior in insulating crystals. Such a crystal is characterized by a full band of energy levels, named the valence band, separated by a finite energy gap W from an empty conduction band (Fig. 4). If absorption of a quantum of radiation raises an electron to the conduction band, the resulting vacancy in the valence band, called a positive hole, may be filled up by an electron from another constituent whose full band lies above the starting band of the absorption processes in Fig. 5(a) and thus may be caught in a trap. When the free electron from the conduction band finally recombines with its holes trapped in the new host, there results a new emission. It may also happen that the excited electron temporarily falls into an intermediate vacant band below the conduction band as in Fig. 5(b) and the holes become mobile through the lattice until it recombines with its trapped counterpart with the emission of a new band. The energy set free by the trapping of the electron or its hole may be emitted as infrared radiation or dissipated as heat. The traps of the electrons or holes are localized—the
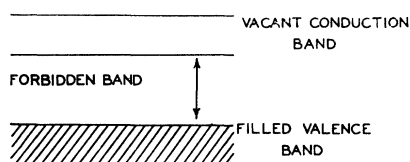

FIG. 4. Schematic representation of the filled and unfilled levels.

energy levels being produced by an activator or lattice flaws, or cracks. Such crystals exhibit photoconductivity because of the mobility of an electron in the conduction band or because of its positive holes in the valence band.

When energy transfer takes place over a long distance, each of these processes requires a transport mechanism:

(1) In a quantum mechanical collision process, the collision partners themselves may become vehicles of long distance transportation of energy.

(2) The excitation energy may travel through the lattice by the migration of an excited electron and its holes freed from each other.

(3) In the exciton mechanism, the transport of energy through the lattice takes place in the shape of excitation wave.

(4) Photon absorption is not a localized process but may occur over larger distances.

Although the same mechanism may account for energy transport and its transfer such as in CaWo—Sm (mechanism 3) and the Zn—S luminiphors (mechanism 2), this is not indispensable. It is not improbable that
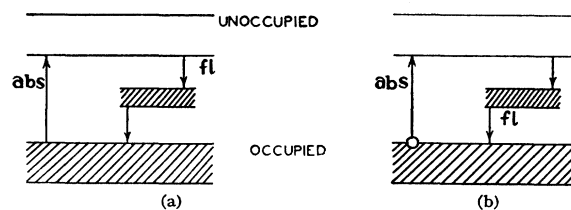

FIG. 5. The excited electron falls into an intermediate vacant band below the conduction band.

excitation energy is transported by say migration of electrons and holes, whereas the final transfer is effected by, say, a collision process.

2. FLUORESCENCE TRANSFER IN ORGANIC MIXED CRYSTALS

In 1949 Franck and Livingston[9] summarized the facts on fluorescence in organic mixed crystals brilliantly. Since then many more publications have appeared and considerable new results are now at hand, so it seems desirable to discuss the subject afresh. The present discussion is confined to organic crystals in general and naphthacene in anthracene in particular for the following reasons: (a) a considerable amount of experimental results and theoretical discussion have been published on it which have made it a matter of controversy; (b) we are studying the matter in this laboratory and some interesting quantitative results have been obtained by us and our collaborators.

(a) Exciton and Absorption

Interest in transfer of energy from one molecule to another in an aromatic solid seems to grow continuously from the anthracene-naphthacene problem. Many workers[19–22] have observed that in the pure crystalline state naphthacene hardly fluoresces, whereas dissolved in solid anthracene or chrysene, it fluoresces brilliantly with its characteristic yellow-green color and the quenching of host crystal fluorescence. The quantum yield of its photofluorescence increases from 0.04 in a pure crystal to about 1 in anthracene.[23] Bowen[20] suggested that the mechanism of transfer of excitation energy from anthracene to naphthacene molecules embedded in the anthracene lattice possesses a close resemblance to that observed in a typical inorganic phosphor, and that the energy of excitation travels by the exciton mass. On the other hand, Ganguly's[24] investigations into the absorption and fluorescence phenomena of these aromatic hydrocarbons under different physical conditions, particularly the depend-

[18] N. F. Mott and R. W. Gurney, *Electronic Process in Ionic Crystals* (Oxford University Press, New York, 1949).

[19] Dufraisse and Horclois, Bull. soc. chim. 1888 (1936).
[20] E. J. Bowen, Nature 142, 1081 (1938).
[21] S. C. Ganguly, Nature 151, 3841 (1943).
[22] S. C. Ganguly, Nature 153, 652 (1944).
[23] E. J. Bowen and A. H. Williams, Trans. Faraday Soc. 35, 765 (1939).
[24] S. C. Ganguly, J. Chem. Phys. 13, 128 (1945); Indian J. Phys. 19, 22B (1945). Doctoral thesis, Calcutta University, 1949.
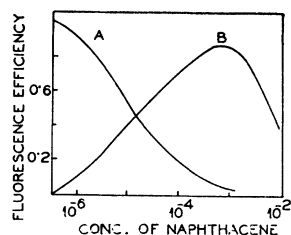
FIG. 6. Dependence of fluorescence efficiency of naphthacene concentration in the naphthacene contaminated anthracene crystal. A is for anthracene fluorescence, B is for naphthacene fluoroescence (after Bowen).

ence of the latter upon the wavelength of exciting radiation suggests that the exciton mechanism is unnecessary in this case and that the enhanced fluorescence of naphthacene could be related to the excitation of the naphthacene molecules by way of absorption of the exciting radiations as well as the fluorescent light of anthracene. This suggestion was based on the following observations:

(i) When excited by light of wavelength from 4030 to 4350 A, green anthracene crystal or a green chrysene crystal emits the characteristic naphthacene fluorescence, except that it is shifted toward the red due to the solvent effect. Naphthacene molecules absorb these exciting wavelengths but the anthracene lattice does not.

(ii) Since the absorption region of naphthacene overlaps the emission region of anthracene (3650 to 5000 A), the naphthacene molecules absorb not merely the exciting radiation 3650, but must also absorb the fluorescence radiations of anthracene.[22]

(iii) There is positive evidence for photon absorption by naphthacene molecules followed by photon emission, and lack of evidence for the exciton mechanism.

Almost simultaneously Bowen and his co-workers[25-28] were investigating the effect of naphthacene concentrations, particle size etc., on the intensities of anthracene and naphthacene fluorescence. They observed the following.

(i) At a concentration of 10^{-5} naphthacene molecule per anthracene molecule, the green naphthacene fluorescence is visible and at 10^{-4} naphthacene molecules per anthracene molecule it grew strong. Lack of molecular proximity and orientation in liquid solution inhibited the transfer so that a green crystal of anthracene with a low concentration of naphthacene when dissolved in benzene did not give the characteristic green fluorescence of naphthacene under the same excitation.

(ii) The curves (Fig. 6) relating the intensities of anthracene and naphthacene fluorescence to the concentration of naphthacene in an anthracene crystal could be represented by $n=1/1+kx$ and $1-\eta=kx/1+kx$, where $n=$ quantum efficiency of fluorescence of host lattice; $k=a$ constant for a pair of compounds in the host and

guest relation, excited by a particular radiation; and $x=$ guest concentration in g per g of the host. For solid solutions of anthracene in naphthalene k was found to be 5×10^4 when excited by 2900 to 3200 A radiations at 20°C, for naphthacene in anthracene crystal excited by 2900 to 3200 A, k was found to be 2×10^5 at 20°C.

(iii) The curves of intensities of fluorescence vs naphthacene concentrations in anthracene crystal do not differ greatly from those in solutions precipitated from one solution. When separate mixtures of the two are taken, there is produced a great difference.

(iv) The intensity ratio of the 0—1 and 0—2 bands in the fluorescence of anthracene remains unaltered for all concentrations of naphthacene in anthracene crystals.

(v) The intensity of the 0—1 band compared to that of the 0—2 band in the fluorescence of anthracene increases as the particle size is diminished and finally approaches that for dilute solution in benzene.

These observations were regarded by Bowen and his co-workers as evidence supporting the exciton mechanism in these crystals. Later it was shown by Birks[7] that the observations (i) and (ii) could not lead to this unambiguous conclusion.

Lipsett and Dekker's[29] investigtions are of interest in that, apart from using an improved technique of measurement, they studied band-wise the spectral intensity of fluorescence under x-ray excitation emitted by solid solutions of naphthacene, 1,2,5,6-dibenzanthracene in naphthalene and in anthracene as a function of concentration. The relative band intensity of impurity fluorescence increased with the rise of concentrations in the host lattice, reached its maximum, and then fell off in a manner shown in Fig. 7, for 1,2,5,6-dibenzathracene in naphthalene. Considering the high efficiencies of energy transfer at concentrations as low as 1.01×10^{-4} mole naphthacene per mole naphthalene and 2.93×10^{-4} mole naphthacene per mole anthracene
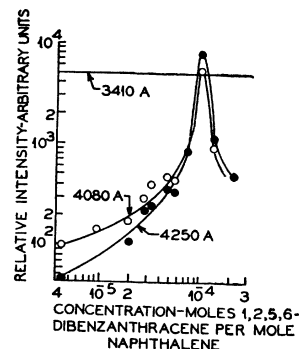
FIG. 7. Intensity of the 4080 and 4250 A bands of 1,2,5,6-dibenzanthracene fluorescence relative to the 3410 naphthalene fluorescence band as function of concentration (after Lipsett and Dekker).

[25] E. J. Bowen, Nature 153, 663 (1944).
[26] E. J. Bowen and E. Mikiewicz, Nature 159, 706 (1947).
[27] E. J. Bowen and P. D. Lawley, Nature 164, 572 (1949).
[28] Bowen, Mikiewicz, and Smith, Proc. Phys. Soc. (London) A62, 26 (1949).

[29] F. R. Lipsett and A. J. Dekker, Nature 173, 736 (1954).

for maximum transfer, they discard the absorption and re-emission as unlikely and regarded the exciton mechanism as more probable. Subsequently, they observed that the intensity of fluorescence under x-ray excitation of anthracene molecules embedded in the naphthalene lattice increased steadily with concentration even after the naphthalene fluorescence was quenched. They attributed this complex behavior to a vigorous fluorescence of anthracene molecules by themselves in addition to the transferred excitation energy from naphthalene molecules to anthracene molecules by way of exciton. The anthracene bands at 3505 and 3700 A arose primarily from the transferred excitation energy and those at 3895, 4200 A, etc., from a combination of transferred excitation energy and molecular fluorescence.

Recent investigations of fluorescence of solid solutions of nine aromatic hydrocarbons in anthracene and pyrene by Northrop and Simpson[30] have supplied significant quantitative information as regards the transfer of excitation energy from solvent to solute molecule. The degree of energy transfer is discussed in terms of two experimentally determined quantities, namely, the quenching factor and the transfer efficiency, defined by

$$Q=(S-S')/S \quad \text{and} \quad T=I/(S-S'),$$

where $S=$ integrated emission of pure solvent molecules, $S'=$ integrated emission of a pure solvent containing solute molecules, and $I=$ integrated emission of solute molecules. These investigators found (Fig. 8) that for anthanthrene dissolved in anthracene the quenching factor is proportional to concentration up to 10^{-2} M and at higher concentration becomes less than what is expected from the proportionality relation. The behavior of transfer efficiency with increasing concentra-
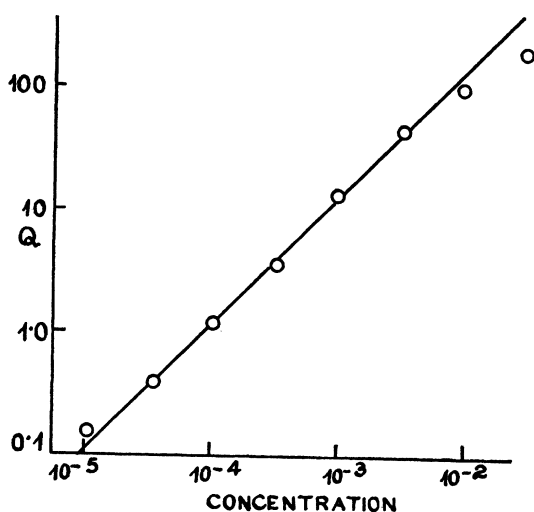

Fig. 8. Dependence of the quenching factor Q on the concentration of impurity (after Northrop and Simpson).

[30] D. C. Northrop and O. Simpson, Proc. Roy. Soc. (London) A234, 136 (1956).

TABLE II.

C	0	10^{-5}	3.3×10^{-5}	10^{-4}	3.3×10^{-4}	10^{-3}	3.3×10^{-3}	10^{-2}	3.3×10^{-2}	10^{-1}
T	0	0.57	0.75	0.81	0.95	1.02	0.93	0.75	0.50	01.4

tion C is given in Table II. Thus all the quanta quenched in anthracene fluorescence do not reappear as anthranthrene fluorescence. There is an optimum concentration, 10^{-3} M in this case, at which T is maximum, unity in this case. For molecules of smaller size studied by them such as naphthacene, pentacene, perylene, etc., T was greater at 10^{-3} M than at 10^{-4} M. Larger molecules such as iso-violanthrene and ovalene display a reversed tendency. The concentration dependence of Q is semi-quantitatively explained by Northrop and Simpson on the basis of exciton migration. When the matrix lattice of the solvent is not contaminated with impurity molecules a solvent molecule may return to the ground state by emitting fluorescence, by nonradiative transitions causing internal quenching, or by transferring its excitation energy to a like neighbor and let α, β, and γ be the probabilities per unit time of the individual processes, respectively. Considering that an exciton continues to move through the crystal until it ends its life it is potentially able to cause fluorescence, they obtained the total probability of emission of one fluorescence quantum per one molecule initially excited as $S=\alpha/(\alpha+\beta)$ where the matrix lattice contains foreign molecules of concentration c, there is a probability, q, say, that the exciton may be captured during its propagation by an adjacent foreign molecule. This reduces the probability of emission by a solvent molecule to

$$S'=\alpha/\alpha+\beta+\gamma cq,$$

where s and s' are proportional to S and S'. Therefore,

$$Q=\frac{S-S'}{S}=\frac{s-s'}{s}=\frac{\gamma cq}{\alpha+\beta},$$

which predicts that Q is proportional to c in agreement with the experimental results.

The investigations of Northrop and Simpson point out that there is no correlation between quenching and the overlap between solvent emission and impurity emission and impurity absorption. There is very little overlap in the case of iso-violanthrene embedded in the anthracene lattice and yet iso-violanthrene quenches anthracene fluorescence strongly with $Q=11$ and 31 at $C=10^{-4}$ and 10^{-3} M, respectively. Naphthacene has a very strong absorption overlapping the emission of pyrene but there was observed no quenching or transfer when at high concentration. These facts are of great importance as they rule out the possibility of energy transfer by collision processes. The probability of energy by collision is proportional to $\int v^{-4}E(v)A(v)dv$, where $E(v)$, $A(v)$ are the fluorescence spectrum of the excited molecule and the absorption spectrum of the acceptor molecule.

3. ELECTRONIC STATES OF AROMATIC CRYSTALS

One of the glaring features of early investigations of energy transfer is that the question whether transference of excitation energy by way of the exciton in aromatic crystals is feasible in view of weak intermolecular binding in them, was not attacked by a consideration of the nature of electronic states in these crystals. In spite of the works of Heller and Marcus,[17] some[7,9] had the idea that exciton propagation required strong intermolecular coupling. As there existed at that time little evidence of such intermolecular coupling in these crystals, often the possibility of exciton propagation was ruled out.

Theoretical works on the electronic states of molecular crystals, begun not long ago, are all based on the elementary theory of excited states of a lattice of interacting atoms or molecules given by Frenkel,[13] later by Slater and Shockley[15]; and improved by Peierls[14] to include the effect of lattice vibrations. One of the principal results of this theory is that in aromatic hydrocarbon crystals beneath conduction bands there occur nonconducting excited states called exciton bands. Just as the conduction bands are analogous to ionization levels of atoms or molecules, these excitation bands in a crystals are analogous to the excited states of free atoms or molecules and are characterized by the fact that the optical excitation to these bands is accompanied by propagation of this state of excitation from one lattice constituent to another, by what is called an "exciton."

Nonconducting excited states or exciton states as they are generally called, arise in two ways. In weakly bound solids (molecular crystals such as anthracene, etc.), the exciton bands correspond closely to the lowest excited states of the constituent atoms or molecules in the free state. Secondly, the strongly bound ionic or covalent crystals, where the constituents have lost their individuality, arising in the ionic case from the removal of an electron from one atom to a neighbor, or by the sharing of electrons with neighbors in the covalent case. An application of Frenkel's exciton theory to the calculation of energy states of molecular crystals was made first by Davydov.[31] He envisaged a weak coupling model of a molecular crystal characterized by an intermolecular interaction energy small compared to the intramolecular energy so that crystallization does not appreciably affect the electronic structure of a molecule. This is required by the fact that the broad features of the visible and ultraviolet spectra are but little changed by the process of crystallization. One of the most significant results reached by his calculations is that from each excited level of a free molecule there originates a band of energy levels in the crystal. And what is more important, corresponding to a transition in the free molecule there may take place several optical transitions in the crystal, notwithstanding the

nondegeneracy of the free molecular levels. This results in multiplicity of lines corresponding to one optical transition in the free molecule. This effect, called Davydov splitting, must be carefully distinguished from the two other well-known effects of crystal field. One of these is the splitting of levels that are degenerate in the free molecule by the crystal field. This effect has been discussed by Bethe. It has found wide application in the interpretation of the spectra of rare earth crystals. The other is the occurrence of crystal-field-induced transitions which are altogether forbidden in the free molecules.

We now discuss the extent to which the exciton effects occur in the crystals of aromatic hydrocarbons in accordance with theoretical predictions.

(a) Benzene Crystal

The benzene crystal being the simplest of the aromatic crystals, its importance in interpreting the nature of the solid state of the aromatic hydrocarbons is unique. The electronic spectra have been investigated both experimentally and theoretically. The first transition in solid benzene was first observed by Kronenberger.[32] The spectrum exhibited some degree of fine structure not accountable without assuming some crystal effects, either Davydov splitting, or combination with lattice modes. Recently Broude et al.[33] have investigated the absorption spectrum of single crystals of benzene using polarized light and detected two perpendicularly polarized lines, separated by 25 cm^{-1} and corresponding to the lowest excited singlet state of the free molecule. Inasmuch as these workers identified the crystal axes by comparing the intensities of light absorbed by the crystal in these directions, it is desirable that their results should be confirmed by similar experiments with crystals in which the axes are independently determined. The fluorescence spectrum of solid benzene at $-253°C$ and at $180°C$, investigated by Kronenberger[32] and Starkiewicz[34] exhibits frequency intervals which have been tentatively ascribed to combination with lattice modes. These experimental observations are understood best by comparison with theoretical predictions on the electronic spectra of the benzene crystal made by Davydov,[31] Winston,[35] and recently by Fox and Schnepp[36] on the assumption that the lower excited states in the free molecule are converted into exciton states in the crystal. According to Davydov's calculations the state B_{1u} of the free molecule gives rise to the representations A_{1u} (inactive), B_{2u} (b polarized) and the molecular state represented by B_{2u} to B_{1u} (a polarized) and B_{3u} (c polarized). Winston confirmed

[31] S. S. Davydov, J. Exptl. Theoret. Phys. (U.S.S.R.) 18, 210 (1948); 21, 673 (1951).

[32] A. Kronenberger, Z. Physik 63, 494 (1930).
[33] Broude, Medvedev, and Prikhotjko, J. Exptl. Theoret. Phys. (U.S.S.R.), 21, 665 (1951).
[34] J. Starkiewicz, Compt. rend. soc. polon. phys. 4, 201 (1929).
[35] H. Winston, J. Chem. Phys. 19, 156 (1951).
[36] D. Fox and O. Schnepp, Phys. Rev. 96, 1196 (1954); J. Chem. Phys. 23, 76, 7 (1955).

these results and also found that the forbidden 0−0 transition of the free molecule is not prohibited in the crystal. Fox and Schnepp calculated the exciton band energies and band widths in the benzene crystal corresponding to the B_{1u} and the B_{2u} states of the free molecule, to which dipole transitions from the ground state are allowed. They used the x-ray determination of the benzene crystal structure made by Cox and Smith,[37] more recent, and exciton wave functions, more general, than those used by Davydov. Their results are tabulated in Tables III and IV for exciton functions constructed from molecular states of symmetry B_{1u} and B_{2u}. The foregoing results belie our expectation of identifying the B_{1u} and B_{2u} band from polarization measurement because in each band the transitions are a, b, and c polarized in the same order of energy. The band widths are 720 and 58 cm⁻¹. The two optically active levels observed by Broude et al. with a separation

TABLE III. Symmetry and energy of states in the B_{1u} band and polarization and intensity of transition from the ground state to these states.

Representation in D_{2h}	Polarization of transition	Band splitting in cm⁻¹	Intensity ratio
B_{2u}	b	180	8×10⁻⁴
B_{3u}	c	−180	17×10⁻⁴
A_{1u}	forbidden	+360	0
B_{1u}	a	−360	29×10⁻⁴

TABLE IV. Symmetry and energy of translationally invariant states in the B_{2u} band and polarization of transition from the ground state to these states.

Representation in D_{2h}	Polarization of transition	cm⁻¹
B_{3u}	c	−7
B_{2u}	b	+29
B_{1u}	a	−29
A_{1u}	forbidden	+7

of 25 cm⁻¹ confirm the splitting qualitatively though not qualitatively and thus lend experimental support to the exciton nature of these bands in the benzene crystal.

(b) Naphthalene Crystal

Quantum mechanical treatment of the naphthalene crystal on the basis of the exciton theory has been carried out by Davydov and more recently by McClure and Schnepp.[38] The results are that the free molecular energy levels are split by crystal forces, each into α and β components such that transitions from the ground state to them are perpendicularly polarized. The exciton theory intensity figures for these transitions in terms of free molecular intensity are given in Table V.

The a- and b-axis polarized absorption spectra of

TABLE V.

Symmetry		Intensity	
Molecular	F. group	a axis	b axis
B_{3u}	$A_u(\beta)$	0	0.045
B_{3u}	$B_u(\alpha)$	0.19	0
B_{2u}	$A_u(\alpha)$	0	0.76
B_{2u}	$B_u(\beta)$	0.1025	0

TABLE VI.

Upper electronic state	0−0 band cm⁻¹			F. group splitting cm⁻¹	Band shift cm⁻¹
	a pol	b pol	gas		
B_{3u}	31 476	31 642	32 021	166	462
B_{2u}	33 783	33 610 or 33 460	35 910	170 or 320	2210 or 2290

single crystals of naphthalene were investigated by Prikhotjko,[39] Craig and Lyons,[40] and more recently by McClure and Schnepp. The latter workers made an attempt to interpret the observed structure of the a- and b-polarized spectra at 20, 77, and 298°K using single crystals of naphthalene of thickness 10 mm to 0.5 μ. Table VI depicts the observed effects of crystallization on the electronic transitions to the upper states in a naphthalene molecule. They are displacement and dichroic splitting of the 0−0 band in both transitions. The observed polarization behavior of the crystal absorption is described and compared with the exciton theory predictions in Table VII.

The fluorescence spectrum of the naphthalene crystal at 20°K, investigated in great detail by Obreimow and Sabaldas[41] and more recently by McClure and Schnepp, is polarized along the a and b axes of the crystal. Factor group splitting of vibrational level absent in the mixed crystal is evident in the doubling of the line 1384 cm⁻¹ in the one and two vibrational quanta and of some

TABLE VII.

Observer	Region of study cm⁻¹	Temperature of study	Measured $I_b:I_a$ ratio	Exciton theory predictions	
				$Ag - B_{2u}$	$Ag - B_{3u}$
Craig and Lyons	37 000 3150	Room temp.	4.5 5:1		
	37 000 3150	20°K	4.5 5:1	7.5:1	1:4.2
	0−0 band	20°K	100:1		
Craig	37 000 33 780		2−3:1		
McClure and Schnepp	37 000 33 780	20°K	Qualitative agreement with above		

[37] E. G. Cox and J. A. S. Smith, Nature 173, 75 (1954).
[38] D. S. McClure and O. Schnepp, J. Chem. Phys. 23, 1575 (1955).
[39] A. Prikhotjko, J. Phys. U.S.S.R., 8, 257 (1944); Akad. Nauk U.S.S.R. Ser. Fiz 12, 499 (1948).
[40] D. P. Craig and L. E. Lyons, J. Chem. Phys. 20, 1499 (1952).
[41] W. Obreimov and K. Sabaldas, J. Phys. U.S.S.R. 7, 168 (1943).

v	Wave number in cm^{-1}		Vibrational wave number in cm^{-1}		
	Pure crystal	Mixed crystal	Pure crystal	Mixed crystal	Splitting
0	31 060.8	31 551.6	0	0	
1	29 681.2	30 174.2	1379.6	1377.4	8.2
	29 673.0		1387.8		
2	28 284.9	28 799.0	2765.9	2752.6	6.2
	28 288.7		2772.1		

combination lines involving 1384 cm^{-1} in the pure crystal. Measurements on the 1348 series are entered in Table VIII.

Thus the gross features of the absorption and the fluorescence spectra satisfy the predictions of the exciton theory for molecular crystals.

(c) Anthracene Crystal

The energy levels of the anthracene crystal were first treated by Davydov as an application of his theory of light absorption in molecular crystals. The absorption spectrum has been investigated by Obreimov and Prikhotjko[42] at 20°K, by Craig and Hobbins,[43] Lyons,[44] and Sidman.[45] The fluorescence spectrum has been studied by Obreimov, Prikhotjko, and Sabaldas[46] at 20°K, Pesteil and Barbaron[47] at 14°K, and Sidman[48] at 4°K. Craig and Hobbins, following Davydov, calculated the splitting, shift, and polarization ratio associated with an electronic transition in the anthracene crystal. Davydov's theory predicts that the second absorption system of anthracene will be split in the crystal by 16 000 cm^{-1} if it were due to a long axis transition and by 1000 cm^{-1}, if due to a short axis transition. Craig and Hobbins investigated the a- and b-polarized absorption spectra of the crystal and observed that the peak of the b spectrum in the second system occurred at 2680 A so that for $A_g - B_{3u}$ (long axis) assignment, the peak of the a spectrum should fall at 1900 A. Though they could not detect it, they observed a continuous rise of absorption until the spectrum was cut off at 2300 A in a crystal of thickness 0.1 μ so that the peak was expected beyond 2300 A. Recently, Lyons[44] reported that experiments with polarized light in the vacuum ultraviolet located the split components at 2200 A and at 1890 a.u. and the absorption is greater perpendicular to the b axis than parallel to it. This allows one to interpret the 1890 a.u.

[42] I. W. Obreimov and A. F. Prikhotjko, Physik. Z. Sowjetunion 9, 48 (1936).
[43] D. P. Craig and P. C. Hobbins, J. Chem. Soc. 2309 (1955).
[44] L. E. Lyons, J. Chem. Phys. 23, 1973 (1955).
[45] J. W. Sidman, Phys. Rev. 103, 96 (1956); J. Chem. Phys. 25, 115 (1956).
[46] Obreimov, Prikhotjko, and Sabaldas, J. Exptl. Theoret. Phys. (U.S.S.R.) 6, 1062 (1936).
[47] P. Pesteil and M. Barbaron, J. phys. radium 15, 92 (1954).
[48] J. W. Sidman, Phys. Rev. 102, 96 (1956).

absorption as the a component of the vapor $A_g - B_{3u}$ transition polarized along the long molecular axis.

On the basis of the exciton theory, Craig and Hobbins calculated by first-order perturbation the polarization ratio of the a-b polarized spectrum in the second system and obtained theoretically molar extinction coefficients in the crystal from the solution values. The predicted value was 9100±500 for the b-crystal absorption, taking the solution extinction coefficient as 232 000 while the experimental value obtained by Bree and Lyons[47] was 9450. The polarization ratio $(I_b : I_a)$ 1.8:1, observed by Craig and Hobbins for the first absorption system in anthracene, later confirmed by Ganguly et al.,[49] was quantitatively interpreted by Craig on the basis of exciton theory modified by crystal-induced mixing of two excited electronic states to be due to $A_g - B_{2u}$. This interpretation leads to a value 21 000 of molar extinction coefficient while the experimental value is 22 800 as measured by Bree and Lyons.

Thus, the observed behavior of electronic transition in the anthracene crystal confirms the predictions of the exciton theory. Calculations of Craig and Hobbins were made by considering the dipole-dipole interaction between molecules not more than 20 A apart. Craig showed that the influence of distant molecules made no difference in their calculated results because the interaction summation converges within a distance of 20 A in the anthracene crystal. Fox and Yatsiv[50] also critically discussed the dependence of the calculated splitting and shift on the shape, size, and direction of propagation of the exciton wave packet. They found that the observed splitting could not lead to an unambiguous long axis assignment for the second absorption system since by reasonable assumptions as to the shape and size of exciton wave packet, one may interpret the observed splitting on the basis of a short axis assignment while by these assumptions one may interpret the observed frequency shift as confirming long axis assignment.

The long wavelength absorption and fluorescence have been investigated in greater detail in the ab plane at 4°K by Sidman.[45] The absorption spectrum is found to consist of at least two regions, one which extends from 25 400 to 30 000 cm^{-1} in both the a- and b-polarized spectra and the other which extends downward from 2540 to 3000 cm^{-1} and appears only in the b polarization. The former, which consists of strong, broad absorption bands, the first band peak being located at 25 400±20 cm^{-1} by Sidman, at 25 380 cm^{-1} by Obreimov and Prikhotjko,[51] and at 25 350 cm^{-1} by Craig and Hobbins, as electronic vibrational transition to the two transitionally allowed levels of the free exciton band derived principally from L_a, B_{2u} state of an

[49] Ganguly, Chaudhury, and Mukherjee, 44th Session, Indian Science Congress (1957).
[50] D. Fox and S. Yatsiv, J. Chem. Phys. 24, 1103 (1956).
[51] I. W. Obreimov and A. F. Prikhotjko, Physik. Z. Sowjetunion 11, 948 (1936).

anthracene molecule. The latter regions which consist of many weak bands and lines such as at 24 809, 24 836, and 24 989 cm^{-1} detected by Sidman is assigned by Sidman to transitions from the ground electronic state to the trapped exciton states of the crystal, predicted by Frenkel[12] and Davydov.[52] In addition to the phenomenon of propagation of a free exciton, Frenkel considered the case where the crystal lattice may suffer distortion in the neighborhood of a migrating exciton. His result is that the exciton may be trapped at the site of the local distortion produced by it, if the energy of the trapped exciton is less than that of the free exciton. The low intensity of absorption in this region is caused by a nonvertical Franck-Condon transition of the lattice, since the orientation of the molecule in the lattice is different in the upper and lower electronic states.

The fluorescence spectrum as observed by Sidman at 4°K consists of broad bands superimposed with sharp structures. The fluorescence spectrum has several origins, principally below 24 975 cm^{-1}, which do not coincide with the origin of strong absorption at 25 400 cm^{-1}. This gap of several hundred cm^{-1} between the origins of fluorescence and absorption has been verified by all workers and is significant. It shows that radiationless transference of excitation energy from free exciton levels to trapped exciton levels is rapid so that no fluorescence takes place from the free exciton levels at 25 400 cm^{-1}. This gap between the origins of absorption and fluorescence has been found to exist in crystalline naphthalene and phenanthrene and is similarly accounted on the basis of the trapped exciton theory of Frenkel. Sidman also points out that calculations of Craig[43] applied to Frenkel's prediction show that the relative shift of electronic transition in vapor mixed and pure crystals can be interpreted as a semiqualitative proof of the existence of trapped exciton.

(d) Naphthacene Crystal

The first absorption system of tetracene single crystals under light polarized parallel and perpendicular to the b axis of the crystal was investigated by Achis.[53] The maxima in one spectrum are displaced from those in other, so that Davydov splitting is compared. There seems to be no published absorption data on the second and third systems. Bree and Lyons[54] recently investigated the polarized ultraviolet spectrum of tetracene single crystals by the photoconductance method and confirmed splitting in the first absorption system as shown in Fig. 14. The flatness of the photoconductance curve in the second and the third absorption system does not give any information about splitting there. The absorption and photoconductance of the first

TABLE IX.

Peak parallel to	A[a]	19 235	20 715	22 320
b direction	P[b]	19 160±50	20 750±50	22 270±300
Peak perpendicular	A	19 810	21 145	22 545
to b direction	P	19 860±50	21 190±50	22 370±400
Splitting between	A	575	430	225
components	P	700±100	440±100	

[a] A = absorption spectra.
[b] P = photoconductance curve.

system are entered in Table IX. Recently, the absorption and fluorescence spectra of tetracene in solid substitutional solutions at 20°K have been investigated by Sidman.[55] The lowest excited singlet state at 20 246 cm^{-1} has been found to be B_{2u}, L_a since the transition with the ground state is polarized along the short axis of the molecule.

(e) Phenanthrene Crystal

The a- and b-polarized absorption and fluorescence spectra of single crystal of phenanthrene have been investigated at 20°K by McClure.[56] The absorption spectra show that the strong a-polarized 28 613 cm^{-1} band and the strong b-polarized 28 660 cm^{-1} band act as if they are the two components of the 0−0 band split by intermolecular resonance. The former belongs to the B_u representation and the latter to the A_u representation of the factor group C_{2h} of the crystal so that the factor group splitting is 47 cm^{-1}. The vibrational frequency 1378 cm^{-1}, a C−C stretching mode also becomes split into 1370 and 1386 in the crystal. The total width of the exciton band is 280 cm^{-1}, the band beginning at 28 540 cm^{-1} and terminating at 28 820 cm^{-1}.

The weak absorption bands at 28 315 and 28 408 cm^{-1} on the red side of the 0−0 band are not regarded by McClure as a part of exciton band. Similar bands also occur in the crystals of anthracene and stilbene as observed by Sidman. The fluorescence originates at or near the weak absorption band at 28 315 cm^{-1}. Sidman has recently interpreted these low lying emitting levels as the trapped exciton bands of Frenkel.

(f) Hexamethyl Benzene Crystal

The molecular plane in the hexamethyl benzene crystal lies almost parallel to the ab plane of the crystal, the b axis of the crystal being in the plane of the benzene ring. The absorption spectra of the hexamethyl crystal under polarized light were investigated by Scheib et al.[57(a)] They concluded that the polarized light absorption in the near ultraviolet takes place predominantly

[52] A. S. Davydov, Lzvest. Akad. Nauk S.S.S.R. Ser. Fiz. 12, 608 (1948).
[53] A. Y. Achis, quoted by A. S. Davydov, Akad. Nauk. Pamyati S. I. Vavilov, 197 (1952).
[54] A. Bree and L. E. Lyons, J. Chem. Phys. 22, 1630 (1954).

[55] J. W. Sidman, J. Chem. Phys. 25, 122–124 (1956).
[56] Donald S. McClure, J. Chem. Phys. 25, 481–485 (1956).
[57] (a) Scheibe, Hartwig, and Muller, Z. Electrochem. 49, 376 (1943). (b) O. Schnepp and D. S. McClure, J. Chem. Phys. 26, 83 (1957).

in the plane of the benzene ring; though they report a definite absorption perpendicular to the ring planes, amounting to about ten percent of parallel absorption at room temperature. A detailed investigation of the absorption parallel and perpendicular to the ring plane was recently made by Schnepp and McClure[57(b)] at high resolution at 20°K in the 2800 A region. The hexamethyl benzene crystal contains one molecule per unit cell and because the excitation exchange energy between the neighboring molecules should be small, one can expect that the spectrum should be free from all the complications resulting from the presence of two or more molecules per unit cell and that the spectrum exhibits molecular properties and not crystal properties. The analysis shows that the 0—0 transition placed at 35 136 cm^{-1} is much stronger under light polarized perpendicular to the benzene ring than under light polarized in the plane. The in-plane absorption is due to a forbidden transition. Detailed quantum mechanical calculations show that the observed behavior, of the 0—0 band under polarized light is caused not by crystal effects but by the destruction of molecular symmetry by the unsymmetrical positions of the methyl groups in the S_6 structure. This distortion gives rise to weak perturbation of the π electron state by the perpendicular non-π electron states.

The fluorescence spectra, investigated by Schnepp and McClure at medium resolution, exhibit polarization of bands but not as complete as in absorption. As the 0—0 band, calculated from the fluorescence spectrum by use of Raman frequency, is located at 35 140±8 cm^{-1}, it is concluded that both absorption and fluorescence originate from 35 136 cm^{-1}. If this is so, then the crystalline band in this crystal must be either very narrow or the allowed level of the band must lie very near the bottom of the band.

Thus nonconducting excited states or exciton states do occur in most of the insulating aromatic crystals investigated as a result of excitation in the fundamental absorption band. The excited regions—called excitons— are believed to be mobile and capable of transporting energy through a crystal. The existing experimental evidence for exciton migration in these crystals rests mainly on indirect observations.

The work of Apker and Taft,[58,59] shows that excitons are able to create and destroy F centers. Exciton migration has been shown by Northrop and Simpson[30] to account quantitatively for the fluorescence quenching of aromatic hydrocarbons containing impurities; Sidman[45] has presented evidence derived from differences in the absorption and fluorescence spectra of anthracene which implies that excitons can be trapped at lattice imperfections. All these experiments depend on the interaction of excitons with particular centers of the lattice. That there occurs actual migration of ex-

citons through the anthracene lattice has been recently demonstrated by the investigation of Simpson.[60] He devised a method which enabled him to measure the exciton motion directly. The observed diffusion length in the case of anthracene is found to be 460 A. In an isotropic medium this would correspond to a root-mean-square displacement of 1120 A between the points of origin and decay of an exciton.

Dexter[61] points out that a phosphor containing luminescence centers can be used as a detector of excitons. Thus it is possible to detect the diffusion of excitons from an activator free crystal into a contiguous crystal, if the latter contains centers capable of trapping the excitons. One surface of a thin specimen is covered by an exciton detector, the opposite face of the specimen is illuminated in the fundamental absorption band. The luminescence emitted by the detector is drived partly from excitation by that fraction of the primary radiation not absorbed in the specimen and partly from excitons originating in the specimen. A separate measurement of the transmission of the specimen suffices to separate the two contributions; hence to determine the flux of excitons into the detector.

The allowance for reabsorption of anthracene fluorescence by naphthacene, was found by measuring the emission from specimens which were made with the anthracene and detector deposited on separate glass plates, and then put together with a small air gap between. In this arrangement transfer by exciton diffusion was suppressed.

4. INFLUENCE OF CRYSTAL SIZE ON THE SPECTRAL NATURE AND DECAY TIME OF FLUORESCENCE

Though the matters discussed in the previous section bear testimony to the exciton nature of the electronic bands and to the migration of excitation energy by way of excitons, some experimental facts give evidence of energy migration by photon reabsorption. In this case efficiency of fluorescence escape from aromatic crystals shows a dependence upon crystal size, in contradiction with predictions of exciton theory.

The long-known fact that overlap of emission and absorption spectra of a system is apt to alter the spectral character of fluorescence due to self-absorption and re-emission, is given proper consideration in the case of organic crystals by the investigations of Kortum and Finckh,[62] Bowen and Lawley,[63] and Little and Birks.[64] They show that the transmitted photofluorescence spectrum of an organic crystal is critically influenced by crystal thickness. That this fact cannot be ignored is evident from the fluorescence spectrograms of anthra-

[58] L. Apker and E. Taft, Phys. Rev. 79, 954 (1950).
[59] L. Apker and E. Taft, Phys. Rev. 82, 814 (1951).

[60] O. Simpson, Proc. Roy. Soc. (London) A238, 402 (1956–1957).
[61] D. L. Dexter, J. Chem. Phys. 21, 836 (1953).
[62] G. Kortum and B. Finckh, Z. physik. Chem. (Leipzig) B52, 263 (1942).
[63] E. J. Bowen and P. D. Lawley, Nature 164, 572 (1949).
[64] W. A. Little and J. B. Birks, South African Association for the Advancement of Science Congress, Cape Town, South Africa (July, 1952).

cene, trans-stilbene, para-terphenyl, and diphenylacetyl-
ene for thick crystals recorded by Koski,[65] Koski and
Thomas,[66] and Sangster.[67]

Birks and Little[68] studied the spectral change in the
fluorescence of each of these compounds as they
changed the fluorescent specimen from single crystals
of 1-cm thickness to microcrystalline layers deposited
on a thin glass plate by evaporation of a dilute solution
of the compound in xylene and the mode of observation
from transmission to reflection. The fluorescence spec-
trum of anthracene (Fig. 9) gets extended into the ultra-
violet as far as 3700 A and about 80% of this primary
fluorescence suffers reabsorption in a one centimeter
thick crystal. These observations were carefully re-
examined by Birks and Wright[69], who used improved
technique and made relative quantum intensity meas-
urements on one centimeter thick crystal specimens and
very thin microcrystalline layers deposited on quartz
plates. They observed that the microcrystalline fluores-
cence spectrum corresponds to the complete molecular
emission; 76% of the primary molecular emission from
a 1-cm thick anthracene crystal could not escape re-
absorption so that the probability of escape of molecular
fluorescence, K was 24. In a thick trans-stilbene crystal
40% of the molecular fluorescdnce was reabsorbed.

These investigations lend support to the photon
cascade theory formulated by Birks[70] and later on
supported by Fowler and Roos.[71] Based on the fact that
the absorption coefficient of an organic crystal is high,
exceeding 10^3 in the first absorption band system of
anthracene, and that there is overlap between the emis-
sion and absorption spectra, this theory proposes that
in a thick crystal, the part of the primary molecular
fluorescence which is emitted in the region of absorp-
tion is practically reabsorbed in a path length of a few
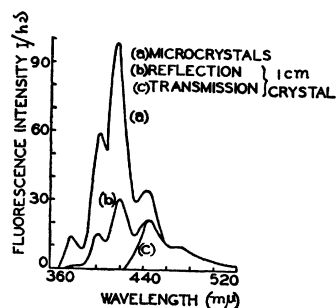wavelengths. This reabsorbed radiation is re-emitted as

FIG. 9. Anthracene
fluorescence spectra ex-
cited by 2537 A (after
Birks and Wright).

[65] W. S. Koski, Phys. Rev. 82, 230 (1951).
[66] W. S. Koski and C. O. Thomas, J. Chem. Phys. 19, 1286 (1951).
[67] R. C. Sangster, Massachusetts Institute of Technology Tech. Rept. No. 55 (1952).
[68] J. B. Birks and W. A. Little, Proc. Phys. Soc. (London) A66, 921 (1953).
[69] J. B. Birks and G. T. Wright, Proc. Phys. Soc. (London) B67, 657 (1954).
[70] J. Birks, Scintillation Counters (Pergamon Press, London; McGraw-Hill Book Company, Inc., New York, 1953).
[71] J. M. Fowler and C. E. Roos, Phys. Rev. 98, 996 (1955).

fluorescence, a fraction of which is again absorbed by
succeeding layers, these processes of absorption and
emission following each other until all the excitation
energy either escapes from the crystal or is dissipated
thermally by internal conversion. Thus the inter-
molecular energy transfer takes place by expansion of
the excitation column, not by the mechanism of exciton
migration but by the absorption and reabsorption of
the primary fluorescence. This is an extension of
Ganguly's[22] theory of transfer of energy from the
anthracene lattice to the naphthacene molecules em-
bedded in it through absorption of anthracene fluores-
cence by naphthacene molecules. But our recent meas-
urement on the coefficient of absorption of naphthacene
shows that the probability of naphthacene excitation
by absorption of fluorescence of anthracene is remote.

The photon cascade theory seems to be strengthened
by surprisingly few existing photofluorescence decay
time measurements of organic crystals. Liebson[72] found
that for anthracene the photofluorescence decay time
t_f changed from 2.0 ± 0.5 mμsec for a $\frac{1}{2}\%$ solution in
benzene to 17 mμsec, for a crystal. For terphenyl it is
increased from 2.5 ± 0.5 mμsec for a $\frac{1}{2}\%$ solution to 11
mμsec for a crystal. For stilbene and diphenylacetylene
crystals, they measured t_f to be 3.1 and 2.5 mμsec,
respectively. The effect of crystal size on t_f was in-
vestigated by Birks and Little[73] who used the phase-
shift method and observed t_f for thick single crystals
exceeded by many times that for microcrystalline
specimens. The data for anthracene and terphenyl
represent two extreme cases. Whereas in the former the
t_f increases from 3.5 ± 1.0 mμsec for microcrystalline
specimens to 14 ± 2.0 mμsec for 1-cm^3 single crystals,
in the latter it changes from 3.5 ± 1.0 mμsec for powder
to 3.8 ± 1.0 sec for 2-mm thick single crystals. Account-
ing for the observed increase in decay times in crystals
by self-absorption and re-emission of the primary
molecular fluorescence, they calculate the decay time
t_f of technical fluorescence at 12.6 ± 3.5 mμsec which
agrees, within experimental error, with the experimental
value 14 ± 2.0 mμsec. They calculated the decay time
$(t_f)_{00}$ of primary molecular fluorescence to be $3.1 + 0.8$
mμsec in agreement with the experimental value
3.5 ± 1 mμsec. Bose et al.[74] have observed that under
x-ray excitation the decay times of anthracene and
naphthacene emissions in a green anthracene crystal
isolated by suitable filters were practically identical.

Splendid as the success of the photon cascade theory
seems to be in interpreting the energy transfer mecha-
nism in pure aromatic crystals, it is not so in mixed
crystals. In fact, in mixed crystals it is more qualitative
than quantitative and must be considered with caution.
The basic fact utilized by the theory, viz., that the
primary photons emitted in the region of the first ab-

[72] S. H. Liebson, Nucleonics 10, 41 (1952).
[73] J. B. Birks and W. A. Little, Proc. Phys. Soc. (London) A66, 921 (1953).
[74] H. N. Bose et al., Proc. Natl. Inst. Sci. India 18, 397 (1952).

sorption band system of a crystal are reabsorbed completely in this region due to very high absorption coefficients (10^2-10^3) is violated in the case of energy transfer from the host lattice to impurity molecules in mixed crystals. In spite of very high absorption coefficients of impurity molecules the effective absorption by a mixed crystal in the region of impurity absorption is much short of being total, unlike in pure crystals, because of the very low concentrations ($10^{-4}-10^{-5}$) mole solute/mole solvent at which the transfer of energy is almost total. The fluorescent spectrum studied by reflection, instead of transmission, to eliminate the small absorption effect of a thin microcrystalline layer of anthracene containing low percentage of naphthacene deposited from xylene solution on a fused quartz plate exhibits the naphthacene fluorescence bands in high intensity.[75] The result of drawing a parallelism between absorption effects due to the host lattice and impurity molecules is evident from the following considerations.

The relation

$$q_{ex}=\frac{1}{1+(K_y[Y]/K_{ex})}=\frac{1}{1+K[Y]},$$

where q_{ex}= technical fluorescence quantum efficiency of the host crystal X, K_y= probability of photon capture by the impurity y, K_{ex}= probability of photon escape in X crystal fluorescence, and $[Y]$= concentration of Y, derived on the photon cascade theory in the absence of internal quenching, is similar to $N_x=1/(1+K[Y])$, where N_x= technical quantum efficiency of X-crystal fluorescence, K= exciton capture probability of Y relative to that of X, derivable from the exciton theory. In both of them the important quantity is the energy transfer parameter k which determines the efficiency of the process. The value of k determined by Bowen et al. from the experimental N_x vs $[Y]$ curve for anthracene-contaminated naphthalene crystals excited by 2900 to 3000 A was 5×10^4 and the value obtained by Wright who used 2540 A as the exciting radiation was 4×10^4. In the relation $K_{ex}+K_x+K_y$, $[Y]=1$ where K_x= photon capture probability of X, given by the cascade theory, putting $Y=2.5\times10^{-5}$ mole, anthracene per molar naphthalene for equal intensities of the components and assuming the most favorable but experimentally unrealized condition $K_y=1$, we have $K_{ex}+K_x$ $+2.5\times10^{-5}=1$. As the theory assumes no interaction between the host and the guest molecules, K should not differ from its value in a pure crystal. Substituting $K_x=0.9565$ from scintillation data which always gives a somewhat larger value, we have $k_{ex}=4.3475\times10^{-2}$ and $k=23$ far away from the experimental value. The only support for the theory in mixed crystals is Bowen and Mikiewicz's[76] result that the intensities of anthracene naphthacene fluorescence components become

equal at 1.8×10^{-5} g naphthacene/g anthracene in anthracene-naphthacene crystals and at 9.10^{-5} g/g in solution, giving a ratio 0.2. The explanation that this difference results from the reduction of the effective absorption coefficient in solutions due to random alignment by a factor 0.25 relative to that in crystals where the Y molecules align parallel to X molecules applies to all such crystals and is not supported by the experimental facts that light in a double refracting crystal is bifurcated into two perpendicularly polarized components and that the absorption coefficients of a substance such as anthracene in solution are greater[77] than those in crystal by a factor ~8. Moreover, the disagreement by 25% is glaring.

5. SCINTILLATIONS FROM ORGANIC CRYSTALS

The scintillation property of fluorescent organic crystals has made them of great use in scintillation counting of nuclear radiations, but there seems to have been little attempt to understand its nature until the recent work of Taylor et al.,[8] Franzen et al., Hopkins, Birks, etc.[78-82] We review the fundamental facts in the scintillation process because any satisfactory theory of the fluorescent process in these crystals must not ignore them. That the energy transfer mechanism in organic crystals under photon or corpuscular excitation is qualitatively independent of the mode of excitation seems to be borne out in Birk's[83] experiments. Using crystals of naphthacene containing different concentrations of anthracene he investigated their scintillation response to alpha particles. The intensities of naphthalene (N) and anthracene (A) emissions were measured separately by introducing suitable filters between the crystals and the photo tube. His plots of (N) and (A) fluorescence intensities, relative to pure crystal, against A concentrations, show that not only the N fluorescence is progressively suppressed with A concentration but also the quantity suppressed in N reappears in A (Fig. 10). The experimental curves were excellently reproduced in the theoretical curves obtained from the relation $n=1/(1+kx)$ derived by him from the exciton theory of energy transfer where n= relative intensity of radia-
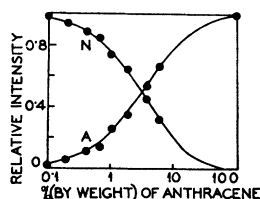
Fig. 10. Fluorescence emission from the mixed crystals of naphthalene containing anthracene as a function of anthracene concentration. A and N represent anthracene and naphthacene fluorescence, respectively (after Birks).

[75] N. S. Bayliss, Rev. Pure Appl. Chem. 1, 64 (1951).
[76] E. J. Bowen and E. Mikiewicz, Nature 159, 706 (1947).

[77] N. S. Bayliss, Rev. Pure Appl. Chem. 1, 64 (1951).
[78] Franzen, Peele, and Scherr, Phys. Rev. 79, 742 (1950).
[79] Taylor, Remley, Jentschke, and Kruger, Phys. Rev. 83, 169 (1951).
[80] Frey, Grim, Preston, and Gray, Phys. Rev. 82, 372 (1951).
[81] Jentschke, Eby, Taylor, Remley, and Kruger, Phys. Rev. 82, 170 (1951).
[82] J. I. Hopkins, Rev. Sci. Instr. 22, 29 (1951).
[83] J. B. Birks, Proc. Phys. Soc. (London) A63, 1044 (1950).

tions, $k=$ the exciton capture probability of an anthracene molecule relative to that of a naphthalene molecule, $x=$ anthracene concentration in moles per mole of naphthalene; with $k=43$ for α particles. These curves are similar to those obtained by Bowen et al.[84] and Wright et al.[85] in case of photofluorescence of anthracene in naphthalene with $k=5\times10^4$.

A similar relation was derived by Birks and Black[86] on the exciton to account successfully for the irreparable deterioration in anthracene scintillation response produced by a prolonged intense α-particle bombardment so as to cause a permanent molecular damage as reported by Birks[87] and Wright.[88] They regard the damaged molecules as quenching centers just as quenching impurity molecules in a host lattice and found a value 1000 for k which is the exciton capture probability of a damaged molecule relative to an undamaged anthracene molecule.

The investigations of the scintillation response S of anthracene to protons of $E\leq17$ Mev by Franzen et al.,[78] Taylor et al.,[79] and Frey et al.[80] to electrons of E from 1 Kev to 3 Mev by Jentschke et al.[81] and Hopkins,[82] to α particle of $E\leq2.1$ Mev by Birks[87] and Taylor et al.,[79] to deuterons of $E\leq11$ Mev by Taylor et al., show that the response S of anthracene to an ionizing particle of energy E and residual range r, depends on the nature of the particle and is proportional to E above a certain energy level. Measurements of the relative response of other organic crystals such as naphthalene,[87] stilbene,[79] terphenyl,[89] etc., and of organic solutions[90] to different particles show that they behave in the same manner as anthracene so that the behavior of anthracene can be regarded as typical of the organic substances studied. The $S-E$ curves of anthracene for different ionizing radiations are shown in Fig. 11(a). Birks' investigations[91] deserve special mention in that, unlike others, he compared the scintillation response S of anthracene and other crystals to different ionizing particles, by considering not the $S-E$ curve but the variation of the specific fluorescence ds/dr (expressed in arbitrary units of volts/cm air equivalent) with the specific energy loss dE/dr (measured in Mev/cm air equivalent) where r (measured in air equivalent) is the residual range of the particle within the crystal. He showed that the nonlinear portion of the $S-E$ curves was due to the nonlinear variation of the specific fluorescence with the specific energy loss. At low values of dE/dr (electrons of $E>125$ Kev) ds/dr increases linearly with corre

(a)
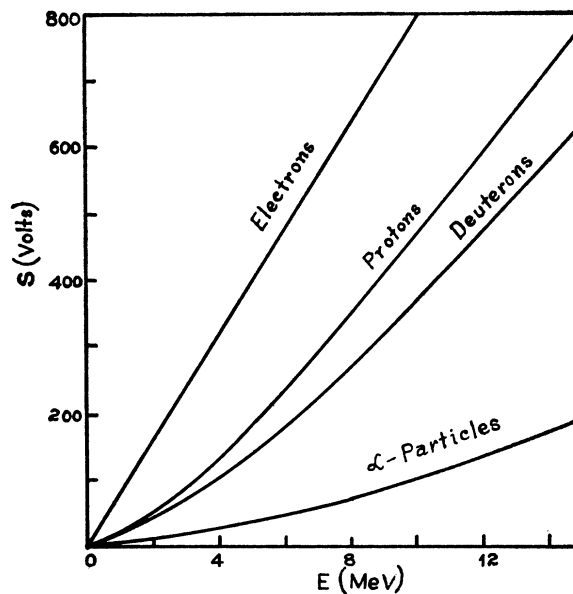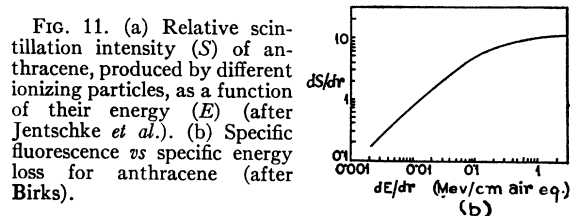
FIG. 11. (a) Relative scintillation intensity (S) of anthracene, produced by different ionizing particles, as a function of their energy (E) (after Jentschke et al.). (b) Specific fluorescence vs specific energy loss for anthracene (after Birks).

(b)

spondence to S being proportional to E. At high values of dE/dr (α particles of $E<5$ Mev) ds/dr is practically constant so that the scintillation S is proportional to the residual range r of the particle rather than to its energy E. This linearity in the $S-r$ curves for anthracene, terphenyl, and stilbene was found to hold good for r about 8 mm. The ds/dr vs dE/dr curve for anthracene and $S-r$ curve for stilbene are shown [Fig. 11(b) and Fig. 12].

The exciton theory was extended by Birks[92] to account for the foregoing experimental facts. The passage of an ionizing particle through the crystal produces along its path a local concentration of damaged or ionized molecules and he regards them as quenching agents for the excitons produced by the ionizing particle. The linear density of excitons produced and the local concentration of nonradiative molecules at any point on the particle track are both proportional to the specific energy loss of the particle and can be put equal to $A(dE/dr)$ and $B(dE/dr)$ molecules per undamaged molecule, respectively. Denoting by k the exciton capture probability of a damaged molecule relative to

[84] E. J. Bowen, Nature 142, 1081 (1938); E. J. Bowen and E. Mikiewicz, Nature 159, 706 (1947); E. J. Bowen and P. D. Lawley, Nature 164, 572 (1949); Bowen, Mikiewicz, and Smith, Proc. Phys. Soc. (London) A62, 26 (1949).
[85] G. T. Wright, Proc. Phys. Soc. (London) A66, 777 (1953).
[86] J. B. Birks and F. A. Black, Proc. Phys. Soc. (London) A64, 511 (1951).
[87] J. B. Birks, Proc. Phys. Soc. (London) A63, 1294 (1950).
[88] G. T. Wright, Proc. Phys. Soc. (London) A66, 777 (1953).
[89] R. Hofstadter, Nucleonics 6, 72 (1950).
[90] Reynolds, Harrison, and Hill, Phys. Rev. 82, 317 (1951).
[91] J. B. Birks, Proc. Phys. Soc. (London) A64, 874 (1951).
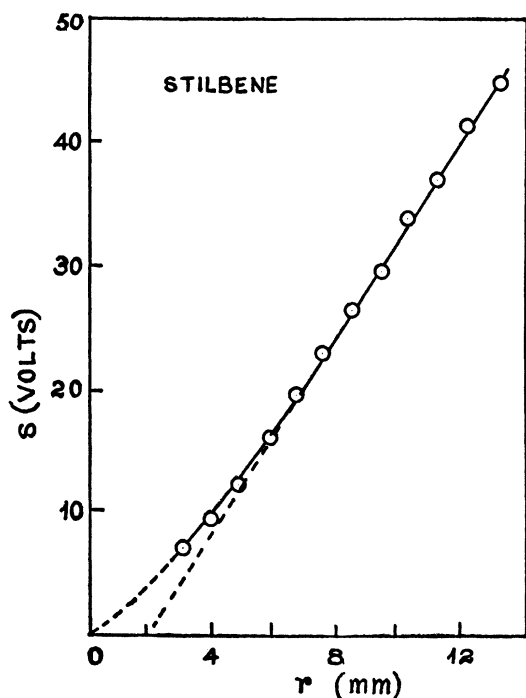
[92] J. B. Birks, Phys. Rev. 84, 354 (1951).

FIG. 12. Scintillation response of stilbene to α particles as a function of their air range r (after King and Birks).

an undamaged one, he deduces the relation,

$$\frac{ds}{dr} = \frac{A\,(dE/dr)}{1 + KB(dE/dr)}, \qquad (49)$$

which is reduced to $ds/dr = A\,(dE/dr)$ at low values of dE/dr and to $ds/dr = A/KB =$ constant, at high values of dE/dr in agreement with observed facts. The experimental values of dE/dr and ds/dr used for substitution in Eq. (49) were obtained from the observations of Birks,[87] Curie,[93] Livingstone and Bethe,[94] and Bethe[95] and gave for $A = 82.5$, $KB = 7.15$ in anthracene.

The variation of dS/dr with dE/dr calculated from (49) agrees well with the experimental curve obtained for anthracene by Jentscke et al.[81] as shown in Fig. 11. The $S - E$ curve for electrons, protons, α particles, etc., calculated from (49) are in excellent agreement with those obtained experimentally.[96]

To account for the observed nonlinearity in the $S - r$ curves for $r < 8$ mm, Birks[96] introduced a multiplying factor ϕ in (49) in consideration of the different behavior of excitons produced near the crystal surface. The function ϕ is given by

$$\phi = 1 - \tfrac{1}{2}\left\{\exp\left(-\frac{r}{a_0}\right) - \left(\frac{r}{a_0}\right)E_i\left(\frac{r}{a_0}\right)\right\},$$

where a_0—mean free path of an exciton and $E_i(r/a_0)$ exponential integral. The experimental $\phi - r$ curve for electrons in anthracene agrees well with the theoretical one.

The absolute efficiency of scintillation, i.e., the total energy of fluorescence emission/total energy of scintillation particles, of anthracene was measured by Birks and Szendrei[97] to be $3.76(\pm 0.07)\%$ for thick anthracene crystals at room temperature, excited by fast electrons. This corresponds to an energy expenditure $E = 70.5(\pm 3.8)$ ev per fluorescence photon. The cascade theory formulated by Birks gave $E = 68$ ev per photon in agreement with the experimental value.

Liebson[72] investigated the temperature dependence of the scintillation response S and the scintillation decay time t for anthracene from $103°$ to $283°$K. His results show that a linear relationship between $\log_{10}S$ and t_1 holds good. Birks[98] worked out the relationship between S and t_1 on the photon cascade theory in $\log S = \log A + Bt_1$ where A is a constant and $B = \log q_0 t_0$, q_0 being the quantum efficiency of photon emission, occurring in cascade and of molecular decay time t_0. Substituting the experimental value of B from the graph and $q_0 = 0.9$, Birks found $t = 3.8$ mμsec for the molecular decay time of anthracene at room temperature in excellent agreement with the experimental value 3.5 ± 1.0 mμsec obtained by Birks and Little.[73]

Sangster and Irvine[99] have studied the scintillation and photofluorescence behavior of a large number of crystalline organic compounds and the utility of Birks's photon cascade theory of the scintillation process has been demonstrated.

6. PHOTOCONDUCTIVITY OF ORGANIC CRYSTALS

Byke and Bork,[100] and Volmer[101] observed that anthracene crystals begin to photoconduct under the irradiation with wavelengths shorter than 4000 A. Later works of Putseiko, Akamato and Inokuchi, Vartanyan, Inokuchi, Eley et al.,[102] Mette and Pick,[103] Northrop and Simpson,[104] and Lyons and Morris[105] have confirmed that not only photoconduction but also semiconduction takes place in some aromatic crystals. This photoconductivity effect raises the question whether production and migration of holes have anything to do with the transport of excitation energy

[93] Mme. P. Curie, Radioactivity (Herman et Cie, Paris, 1935).
[94] M. S. Livingston and H. A. Bethe, Revs. Modern Phys. 9, 245 (1937).
[95] H. A. Bethe, Revs. Modern Phys. 22, 213 (1950).
[96] J. B. Birks and J. W. King, Phys. Rev. 86, 569 (1952).

[97] J. B. Birks and M. E. Szendrei, Phys. Rev. 91, 197 (1953).
[98] J. B. Birks, Phys. Rev. 95, 277 (1954).
[99] R. C. Sangster and J. W. Irvine, Jr., J. Chem. Phys. 24, 670 (1956).
[100] Byke and H. Bork, Ber. deut. physik. Ges. 8, 621 (1910).
[101] M. Volmer, Ann. Physik 40, 775 (1913).
[102] E. K. Putseiko, Doklady Akad. Nauk S.S.S.R. 71, 641 (1949); A. T. Vartanyan, ibid. (1950); H. Akamato and H. Inokuchi, J. Chem. Phys. 18, 810 (1950); H. Inokuchi, Bull. Chem. Soc. Japan 29, 131 (1956); Eley, Parfitt, Perry, and Taysum, Trans. Faraday Soc. 49, 79 (1953).
[103] H. Mette and H. Pick, Z. Physik 134, 566 (1953).
[104] D. C. Northrop and O. Simpson, Proc. Roy. Soc. (London) A234, 124 (1956).
[105] L. E. Lyons and G. C. Morris, Proc. Phys. Soc. (London) B69, 1162 (1956).

through the anthracene lattice, even though want of any evidence of ionization in the anthracene lattice led Franck and Livingston[9] to discard the electron migration mechanism. Recent studies of the photoconductivity of anthracene have been made by Carswell,[106] Carswell and Lyons,[107] Chynoweth and Schneider,[108,109] and Bree, Carswell, and Lyons.[110] Carswell and Lyons' experimental arrangement uses a single anthracene crystal sublimed in a CO_2 atmosphere, mounted with Aquadag on platinum electrodes and irradiated with monochromatic radiation. Their important observations are: (a) plot of photocurrent vs frequency[106] of exciting radiations closely reproduces the optical absorption spectrum (Fig. 13), (b) the ratio of the current produced with light polarized parallel to the b-crystal axis to that parallel to the a-crystal axis was 1.5, using a mercury 3650 A light source[111]; (c) the photocurrent is proportional to the intensity of light; (d) quantum efficiency is approximately 10^{-4}, under his experimental conditions, constant over the near ultraviolet, and nearly equal to the fluorescence quantum efficiency; (e) the intentional incorporation of naphthacene as an impurity in the anthracene lattice so as to change the relative heights of the 5325 A and 4425 A fluorescent bands to 37:1 apparently affects neither the photocurrent nor the time constant.[111] The investigations of Chynoweth and Schneider[109] are of great significance in that their results support the adoption in organic crystals of the conventional energy band picture usually associated with inorganic crystals. The fact that irradiation of anthracene crystals within the fundamental absorption spectrum cannot liberate electrons com-

FIG. 14. Photocurrent in naphthacene single crystal as a function of frequency, in two ranges of wavelengths. In 1, light is polarized $||b$; in 2, $\perp b$; in 3, unpolarized. In the lower diagram "$||$, $\perp$" are with respect to a direction which makes 12° with the b crystallographic axis (after Bree and Lyons).
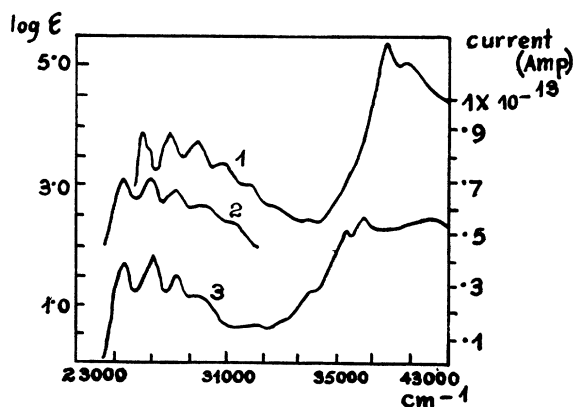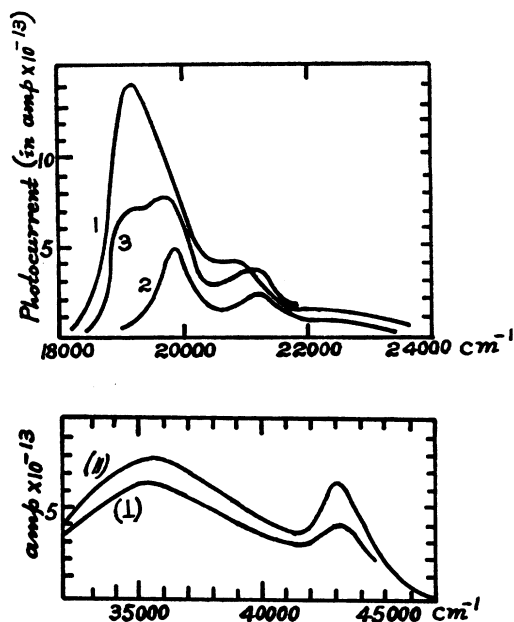

FIG. 13. (1) Solution absorption spectrum of anthracene. (2) Crystal absorption spectrum of anthracene. (3) Spectral photocurrent curve in anthracene crystal. Plot of photocurrent vs frequency of exciting radiations showing reproduction of the optical absorption spectrum (after Carswell).

pletely,[112] combined with their observation that the majority of the carriers are positive holes suggests to them the following mechanism: light absorption raises the electrons either directly or through the intermediate process of exciton formation, into a metastable level from which they can either recombine with their holes, emitting fluorescence, or are trapped in a relatively stable level. Under the action of the field the holes drift through the lattice, but the drift velocity depends upon hole traps of different depths. Under steady-state conditions the rate of creation of carriers equals the rate of recombination between positive holes in the full band and the trapped electrons, as also the rate of trapping of carriers equals the rate of detrapping.

If this mechanism is to be adopted for the emission of characteristic fluorescence of anthracene, it remains to be seen how it explains the want of reproduction of some photoconductivity phenomena in corresponding fluorescent phenomena as noted in (d) above. Leaving aside the question of transport of energy through the lattice of anthracene, the observation (e) made by Carswell suggests that immediate transfer of energy to naphthacene or pentacene in an impure anthracene crystal takes place by a mechanism other than hole migration.

The correspondence between the optical absorption spectrum and the photoconductance curve of an anthracene crystal, as observed above, led Bree and Lyons[54] to study the ultraviolet polarized spectrum of tetracene

[106] D. J. Carswell, J. Chem. Phys. **21**, 1890 (1953).
[107] D. J. Carswell and L. E. Lyons, J. Chem. Soc. 1734 (1955).
[108] A. G. Chynoweth and W. G. Schneider, J. Chem. Phys. **22**, 1021, (1954).
[109] A. G. Chynoweth, J. Chem. Phys. **22**, 1029 (1954).
[110] Bree, Carswell, and Lyons, J. Chem. Soc. 1928 (1955).
[111] D. J. Carswell (private communication to S. C. Ganguly, 1954).
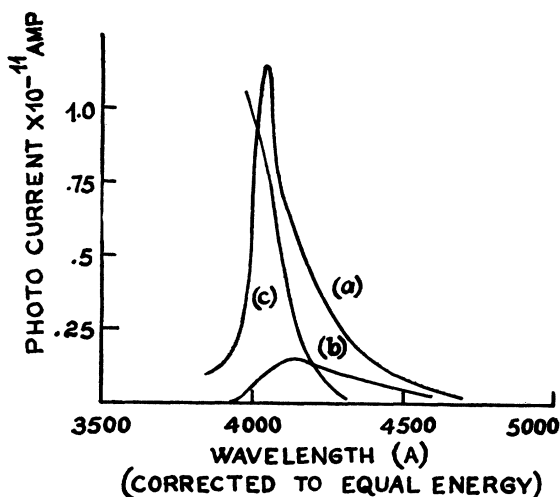
[112] E. J. Bowen, Nucleonics **10**, 14 (1952).

FIG. 15. Wavelength dependence of photocurrent in sandwich cell; (a) illuminated electrode positive, (b) illuminated electrode negative, (c) approximate edge of photosensitivity in surface cell (after Compton *et al.*). The observed effect produced by reversal of polarity of electrodes indicates that the charge carriers are mostly positive holes.

single crystals by the photoconductance method. They observed that the first system is definitely *b*-axis polarized and exhibits Davydov splitting (Fig. 14) as discussed in Sec. 3. Lyons and Morris[105] investigated the spectral dependence of photocurrent in naphthalene, phenanthrene, diphenyl, and *p*-terphenyl and compared it with the solution absorption spectra in the compounds. The photoconductivity takes place in the absorption region and not outside it. The measurements of Riehl,[113] Bree, Carswell, and Lyons[110] suggest that there is no true bulk photocurrent in anthracene and that the photoconductivity in anthracene is a surface phenomenon. This led Lyons[114] to explain the spectral dependence of photoconductivity in a surface cell on the assumption that the light energy absorbed by the crystal creates excitons, and that only those excitons that can migrate from their points of origin to the surface layer can generate charge carriers. The number *n* of excitons reaching the surface is given by

$$n = KI_0\left[\frac{E}{1-q} - \frac{E_q^2}{2}\left\{2(1-q)^2 + \frac{1}{1-q}\right\} + E^3\right], \quad (50)$$

where E denotes the optical density of a molecular layer, I is the intensity of the incident light, q is the probability that an exciton crosses a layer of molecules, and k is a constant depending upon the specimen. If E is small, then neglecting higher powers of E, $n = KI_0E/(1-q)$ and the photocurrent is given by

$$i = e\mu V = K'I_0VE/(1-q), \quad (51)$$

where μ is the mobility of the charge carrier and V is the

applied voltage. The photocurrent is linearly dependent on (a) the optical density of the crystal, (b) the incident light intensity, and (c) the applied voltage. The linear dependence on the incident light intensity and on the applied voltage was demonstrated by the investigations of Carswell and Lyons[107] and Chynoweth and Schneider,[108] respectively. Lyons[114] showed that, in the case of the tetracene crystal, the plot of optical density of the crystal against photocurrent was a straight line and thus exhibited the predicted dependence.

A recent detailed investigation of surface and bulk photoconductivity of anthracene was undertaken by Compton, Schneider, and Waddington.[115] They used three types of crystals, namely, large scintillation crystals, thin layer crystals grown from dimethyl-
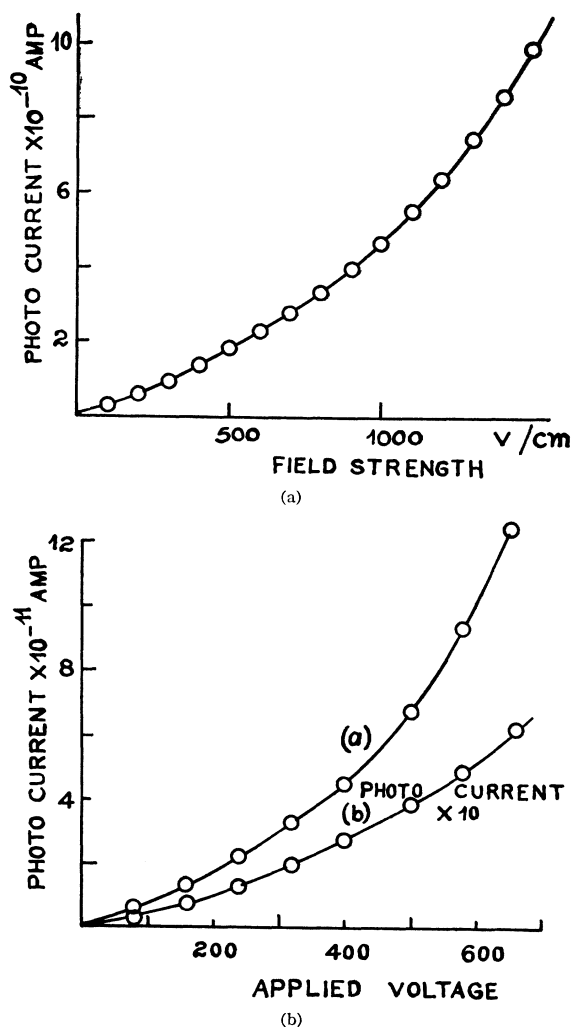

(a)

(b)

FIG. 16. (a) Photocurrent as a function of field strength (surface cell); (b) Photocurrent as a function of applied voltage (sandwich cell), (a) illuminated electrode positive, (b) illuminated electrode negative, crystal thickness 2 m (ordinate scale values are multiplied by ten) (after Compton *et al.*).

[113] N. V. Riehl, Zhur. Fiz. Khim. **29**, 959 (1955).
[114] L. E. Lyons, J. Chem. Phys. **23**, 220 (1955).

[115] Compton, Schneider, and Waddington, J. Chem. Phys. **27**, 160 (1957).

formamide solutions, and sublimation flakes, and practically got rid of the space-charge effect, observed by earlier workers, by using electrodes of colloidal graphite, evaporated metals, and silver paste to secure better contacts with the crystal. To investigate the bulk photocurrent, they constructed a sandwich cell fitted with a guard ring on the surface separating the two electrodes. [One of the electrodes, called the front electrode, which was transparent, conducting and receiving the exciting light, was connected to a stabilized source of power; the other electrode, called the rear electrode, was connected to a microammeter.] If the guard ring is earthed, surface current is prevented from reaching the rear electrode.

Besides confirming the reported spectral dependence of surface photoconductivity and that the photocurrent is mostly caused by the mobility of positive holes, they arrived at the following results:

(1) Anthracene crystals exhibit a true bulk photoconductivity which is not affected by the nature of ambient gases. The bulk photocurrent in an anthracene
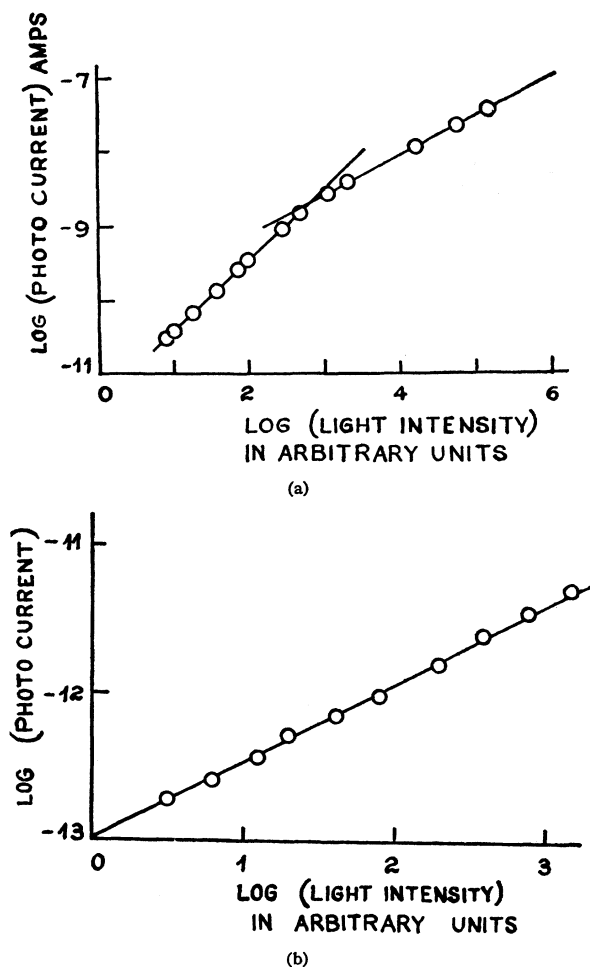
FIG. 18. Photocurrent as a function of temperature (after Compton et al.).

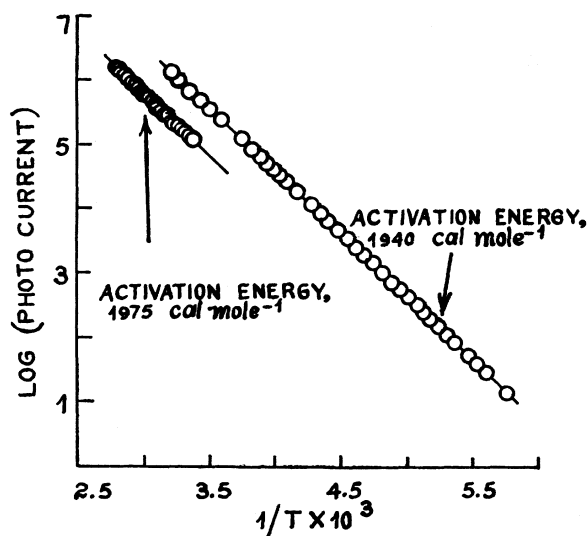FIG. 17. Photocurrent as a function of light intensity (a) surface cell and (b) sandwich cell (after Compton et al.).

sandwich cell is much less than the photocurrent in a surface cell under comparable conditions. The spectral dependence of bulk photocurrent is unlike that of surface photocurrent in that the maximum photocurrent occurs on the long wavelength side of the anthracene absorption band (Fig. 15).

(2) The surface and bulk photocurrent in anthracene, generally nonohmic, exhibits an ohmic dependence on applied voltage at very low strength (less than 60 v cm^{-1} in a surface cell) and increases at a rate higher than linear at higher field strengths. The photocurrent, i, showed no sign of saturation, even with 25 kv cm^{-1} in a surface and 20 kv cm^{-1} in a sandwich cell (Fig. 16). Plots of V/i against V, in the case of a surface cell were straight lines, indicating that i is proportional not to V, as demanded by Lyons' theory, but to $V/(a-bV)$.

(3) In the surface cell the photocurrent shows a linear dependence on the light intensity except at very high level of intensity, whereas in a sandwich cell it varies as the square root of the light intensity (Fig. 17).

(4) The photocurrent displays an interesting dependence on crystal orientation; it is greatest in the b direction, about ten times smaller in the a direction, and one-hundred times so in the c direction. This indicates that the charge carriers are more mobile in the b direction than in the a and c directions by factors 10 and 100, respectively.

(5) The photocurrent studied in a surface cell or in a sandwich cell over a temperature range from 55 or 70°C to −130°C in an atmosphere of pure dry argon, follows the relation

$$i = i_0 e^{(-E/KT)},$$

where $E = 0.172 \pm 003$ ev in a surface cell and 0.176 ± 010 ev for a sandwich cell (Fig. 18).

(6) The photocurrent in an anthracene surface cell exhibits a decay time, which is less than 30×10^{-5} sec. The decay shows a tail of some seconds, which is about 10^{-3} times the original photocurrent. As this varies markedly from crystal to crystal, the tail is most likely due to flaws.

(7) When tetracene or acridine is incorporated into an anthracene crystal in the approximate concentration 10^{-3} mole per mole of anthracene, it is found that the voltage dependence of photocurrent is unaltered, its intensity dependence is linear in the surface cell, and the photocurrent produced by excitation in the 3800 A system is reduced.

(8) There is little evidence for the existence of trapping levels in an anthracene crystal, as postulated by many workers. Irradiation with infrared light produces very small effect on surface photoconductivity. The electrical analog of the thermoluminescent glow curve shows that the concentration of traps of depth from 0.15 to 0.5 ev is less than 10^8 cm^{-3} in a pure anthracene surface or sandwich cell, and this is not dependent on the nature of the ambient gas. These experimental results are explained on the following model: The carriers of charge, which are positive holes, are generated in the bulk as well as on the surface, the carrier mobility being greater in the latter case than in the former. Lyons' calculations can be applied with the modification that q denotes the probability of charge carrier crossing a molecular layer. The photocurrent thus remains proportional to the optical density as observed by Lyons but the smaller the optical density is, the greater is the proportion of carriers formed at a good depth below the surface. This gives rise to the long wavelength tail of surface current in thick crystals and becomes of great importance in a sandwich cell. The photocurrent in the bulk is recombination limited, i.e., the charge carriers (positive holes) end their life by recombination before reaching the electrodes.

In the surface cell these carriers migrate to the surface along the shortest route, but because the surface in a real crystal is not perfectly flat, this route at many points will not be perpendicular to the field direction. Thus, the probability q of a charge carrier crossing a molecular layer is affected by V and if the phenomenon is averaged over the distance between electrodes, q can be expressed as $q=a+bV$. The equation for i becomes

$$i = \frac{KVI_0E}{1-a-bV} = \frac{KVI_0E}{a'-bV},$$

which explains the experimental fact that V/i depends linearly on V. The mechanism of formation of charge carriers in anthracene and other organic crystals is not clearly understood. Though photoconductivity is produced by absorption of light, it is not a primary product of light absorption because the first excited states of anthracene crystal are exciton states where the electrons and holes, created by the act of light absorption, mi-

grate remaining bound to each other and produce no photocurrent. The experimental facts that the quantum efficiency for photoconductivity is of the order of 10^{-4}, and that the photocurrent is profoundly influenced by impurities (as observed by Carswell and Lyons[107] and Compton et al.[115]), and reduced by neutron irradiation (as observed by the latter group), cannot be explained on such an assumption.

In many photoconductors in which infrared irradiation has little effect on the photocurrent, optical and thermal formation of charge carriers requires identical energies and the absorption edge occurs corresponding to the energy E in the equation for semiconductivity $\sigma = \sigma_0 e^{-E/2kT}$. This relation is obeyed by the aromatic[113] hydrocarbons such as anthracene, naphthacene, pentacene, etc. If the generation of charge carriers is not a primary product of light absorption in anthracene, one cannot expect that the energy parameter E would have the energy value corresponding to the absorption edge. In fact, the energy 3.2 ev associated with an exciton in the 3800 system is greater than the activation energy of semiconductance 1.63 ev as found by many workers[103,104] from the temperature dependence of semiconductivity. In all the aromatic hydrocarbons investigated, the measured activation energies are lower than the fundamental absorption energy ^1E. This produces a difficult situation, because the theory of conductivity leads one to suppose that all conduction bands must have energies greater than E. Any doubt as to whether the values of the energy parameter E derived from semiconductivity are really activation energies is removed by the fact that there is good agreement between the impurity activation energy parameter ϵ and the triplet state energies ^3E of free molecules. This led Northrop and Simpson[104] to conclude that in the absence of an applied electric field, the number of electrons populating the conduction band is too small to account for the observed conductivity. Conductivity is due to the fact that there is greater population of electrons in the low lying bound states and there is a finite probability of ionization from the bound excited states due to the applied field. The mechanism is described by them as dissociation of the exciton in an applied field.

The exponential dependence of photoconductivity on temperature suggests that the charge carriers are formed through a molecular triplet so that for the actual separation for the uncoupled electrons, thermal energy is required. This explains the energy parameters E as activation energy having the same value 0.17 in both types of cell.

The question of the origin of the charge carriers has been somewhat controversial and much of the controversy derives from the effects of gases on the photocurrent. It has been observed by many[116] that the surface current is profoundly enhanced due to the presence of adsorbed gases such as O_2, SO_2, etc. This led Bree

[116] H. J. Zinzer, Z. Naturforsch. 11a, 306 (1956).

and Lyons to suggest that oxygen serves as a catalyst in the formation of a triplet level which reacts to form the biradical intermediate AOO. When the AOO dissociates into ions, charges are liberated and the positive holes move through the lattice. This scheme of formation of charge carriers is, however, not properly equipped to explain the origin of bulk photocurrent established by Compton *et al.* who regard fluorescence and photoconductivity as processes competing with each other when an exciton ends its life. This is supported by experimental investigations of Zinzer[116] who found that prolonged α-ray bombardment reduces the fluorescence and the surface photocurrent and by those of Compton *et al.* who observe that neutron bombardment reduces both bulk and surface photocurrent as well as fluorescence. Compton *et al.* observe that the incorporation of tetracene into anthracene lattice also reduces the photocurrent in the 3800 system of anthracene, though Carswell and Lyons find that introduction of 10^{-4} M tetracene into anthracene increases the photocurrent, especially in the region of the second electronic transition (40 000 cm). Many workers[21,2] observed that incorporation of tetracene or acridine into the anthracene lattice suppresses or quenches the fluorescence. The quantum efficiency of photoconductivity of anthracene is 1. The former figure may mean that the range of charge carriers is small compared with the electrode separation which is suported by the observed lack of saturation in the photocurrent. A knowledge of the carrier mobility is required to convert detected currents into quantum efficiency of charge formation, and it remains to be seen whether there is quantum equivalence between absorption and photoconductivity.

7. SOME NEW RESULTS

The contents of the Secs. 3, 4, and 5 seem to indicate that, in most of the aromatic crystals investigated, the energy of excitation can migrate away from the place of excitation in the form of excitons, and that if the exciton is annihilated deep in such a crystal with the emission of fluorescence radiation, the emitted radiation may be absorbed in a photon cascade process by the crystal having intense absorption band in the region of emission. But the sections do not furnish any detailed information regarding the place of terminus of the energy transport, and it is not known how the final stage of the transfer is executed in a pure crystal, nor in an impure one. Polarization properties of crystal absorption and emission are expected to yield valuable information in this regard. If the crystal fluorescence is due to the reverse of photon absorption, fluorescence should give the same polarization ratio as absorption, provided both correspond to the same electronic transition. Experimental observations show that the polarization ratio of absorption (3800 A) and the fluorescence (corresponding to the same electronic transition) spectra are very different.

The polarization ratio for absorption of light in the c' direction of an anthracene crystal, when c' is perpendicular to the a and b crystallographic axes, has been measured by Craig and Hobbins[43] to be 1.8:1 and by Ganguly, Chaudhury, and Mukherjee[49] to be 1.5:1. The ratio of fluorescence intensity along the same directions, observed in the c' direction, has been determined by Ferguson and Schneider[117] to have the value 5:1 and the value obtained by Chaudhury[118] who corrected for all probable errors, is 4.3:1. Ganguly and Chaudhury[119] calculated on the basis of an oriented gas model that the polarization ratio (I_b/I_a) is given by the square of the cotangent of the angle which the active molecular axis (projected on the ab face) makes with b axis of the crystal. Craig and Hobbins[43] showed that the first-order perturbation methods applied to the exciton theory gives the same result. For an anthracene crystal it is 7.8:1 which is reduced to 6.5:1 on making allowance for torsional oscillations. Ferguson and Schneider argue that if the value 1.8:1 for absorption is accounted for, as was done by Craig,[120] by assuming a crystal induced mixing of the first two excited states of an anthracene molecule, the value of 4–5:1 for fluorescence, being nearer the exciton theory prediction, implies that the fluorescence is emitted from a molecule situated at a lattice dislocation where the symmetry elements of the lattice are not maintained. The different values for absorption and fluorescence I_b/I_a may be due to the fact that fluorescence is emitted from a molecule situated at a place where the principal directions of transition are rotated with regard to those of crystal absorption. Thus, these facts seem to establish the idea that an exciton in an anthracene crystal ends its life by being captured by a molecule situated at a dislocation from where the fluorescence is emitted.

When naphthacene molecules are present in an anthracene crystal that is excited by ultraviolet radiation, the naphthacene molecules may fluoresce by any one of the processes described in Sec. 1. If the photon cascade process is responsible, the decay time for fluorescence of anthracene would be different from the decay time of fluorescence of naphthacene in a crystal containing naphthacene as impurity. Unfortunately, there are hardly any useful data on decay times of fluorescence in mixed crystals, except those of Bose[74] which are not free from ambiguity. In this laboratory we have measured the optical densities of an anthracene crystal containing naphthacene molecules and calculated the effect of naphthacene absorption on anthracene fluorescence, according to the formula[118]

$$\frac{f_r}{f_0} = \frac{\mu_1 t}{\mu_1 t + \mu_2 t} \left\{ \frac{1 - e^{-(\mu_1 + \mu_2)t}}{1 - e^{-\mu_1 t}} \right\},$$

[117] J. Ferguson and W. G. Schneider, J. Chem. Phys. **25**, 780 (1956).

[118] N. K. Chaudhury, Z. Physik. **151**, 93–105 (1958).

[119] S. C. Ganguly and N. K. Chaudhury, Phys. Rev. **95**, 1148 (1954).

[120] D. P. Craig, J. Chem. Soc. 2302 (1955).

where f_r is the backward fluorescence intensity of anthracene if there is absorption, f_0 is the same for no absorption; $\mu_1 l$ is the optical density of this crystal at the exciting wavelength λ_1, $\mu_2 l$ that at the emitted wavelength λ_2. In our measurements, $l = 9.9 \times 10^{-3}$ cm, $\mu_1 l \sim 10^3$ at $\lambda_1 = 3650$ A; $\mu_2 l \sim 1$ at $\lambda_2 = 4898$ A where the absorption intensity of naphthacene molecules is the greatest in the fluorescence region of anthracene and $f_r/f_0 \simeq 1$. Thus absorption cannot be held responsible for transfer of energy from anthracene to naphthacene.

It has also been observed in this laboratory that when naphthacene molecules are incorporated within the anthracene lattice, not only the absorption and fluorescence spectra of naphthacene molecules show polarization, but also the polarization ratio of absorption spectra of these molecules remains unaltered from that of pure anthracene crystal. This means that the naphthacene molecules are embedded in an anthracene lattice as substitutes for anthracene molecules, and also that they are coupled to the anthracene lattice in the same way as anthracene molecules themselves. Thus it may be inferred that if the fluorescence of anthracene occurs at molecules situated in imperfect regions of crystal lattice, so it is for naphthacene fluorescence. The transfer of excitation energy from anthracene to naphthacene molecules is half complete at a concentration of $c = 1.8 \times 10^{-5}$ mole naphthacene per mole anthracene.[28] If the naphthacene molecules occur at lattice dislocations at the same concentration as anthracene molecules, which is quite reasonable in view of the foregoing facts, the probability that a naphthacene molecule receives the excitation energy, and emits it in the form of fluorescence, should be at least 5×10^4 times as great as that of an anthracene molecule.

When the intensity ratio of the polarized fluorescence band at 4450 A of an anthracene crystal along the b axis to that along the a axis is plotted against different concentrations of naphthacene in the crystal, it is observed that the ratio at first gradually increases, attains a maximum value, then decreases with increase of concentration of naphthacene. This increase of intensity ratio with increase of concentration of naphthacene at low concentration region excludes absorption process. But the fall of the intensity ratio of fluorescence of anthracene at high concentration region of naphthacene is difficult to explain if the absorption process is prohibited altogether.

8. SUMMARY

Though our knowledge of energy transfer in aromatic crystals has increased considerably, it has not reached the state of maturity required for a definite formulation of a general rule. Many aspects of the problem remain almost untouched. Except for Bowen et al. and Birks et al., very few workers have measured the effect of crystal size and shape on the fluorescence intensity, nor the efficiency of transfer of energy in these crystals.

Because a quantum mechanical resonance transfer process is independent of crystal size and shape, the importance of such measurements in distinguishing the photon cascade from resonance transfer cannot be overemphasized. More and more careful measurements would be worthwhile. There exist few data on the efficiency of energy transfer from a host molecule to an impurity as a function of the exciting wavelength. It is also not known whether naphthacene fluoresces with the same efficiency by transferred excitation energy as by direct absorption, though in a recent paper Simpson[60] has shown that the intensity of naphthacene fluorescence excited by absorption of fluorescence of anthracene is smaller than that under exciton excitation. Because of complete quenching of the fluorescence of anthracene, it cannot be concluded whether the fluorescence efficiency is or is not the same in both the cases. Careful study of the results show that the agreements between the predictions of the exciton theory of the molecular organic crystal and the observed spectroscopic data are only over all and not in details. Again, cascade theory cannot explain many experimental results, though it gives satisfactory solutions to the problem of mechanism of energy transfer in pure crystal. This shows that either data of greater precision or some modification in the theories must be introduced. Measurements of absorption coefficients have not been made in many of these crystals, pure or impure, with the result that values of the absorption coefficients in solutions are quoted in support of a theory in solids. The importance of temperature in emission and absorption cannot be denied, but it has been almost completely ignored. More data are required on photoconductivity. Results obtained by different workers on the same crystals not only differ but are sometimes contradictory: how the mobility is influenced by various factors needs to be known for clearer understanding of the subject. It is expected that the study of temperature effect on the efficiency of fluorescence, coefficients of absorption, energy transfer, and polarization will reveal facts of far-reaching consequences. We have undertaken some of the studies in this laboratory.

Note added in proof.—After the review had been sent for publication, some new works having some bearing on the subject matter of the review appeared. They are briefly described below.

Electronic states of aromatic crystals (Sec. 3).—The near ultraviolet polarized absorption spectra of some aromatic crystals of pyrene have been investigated by Ferguson[121] at room temperature and at 77°K, of 1,3,5-trichlorobenzene by Schnepp[122] at 42°K, of hexachlorobenzene by Schnepp and Kopelman[123] at liquid nitrogen and liquid helium temperature, and of durene by Schnepp and McClure[124] at 20°K. Whereas in the case of pyrene, Davydov splitting could be detected as a separation of 18 cm^{-1} between the a- and b-polarized components, the a component being of higher energy in 1,3,5-trichlorobenzene, hexachlorobenzene, and durene

[121] J. Ferguson, J. Chem. Phys. **28**, 765 (1958).
[122] O. Schnepp, J. Chem. Phys. **30**, 863 (1959).
[123] O. Schnepp and R. Kopelman, J. Chem. Phys. **30**, 868 (1959).
[124] O. Schnepp and D. S. McClure, J. Chem. Phys. **30**, 874 (1959).

crystals, no such splitting could be detected. If present, the splitting must not be greater than 5 cm^{-1} in the trichlorobenzene and hexachlorobenzene and 3 cm^{-1} in the durene crystal. In the case of the hexachlorobenzene crystal, the energy of separation between the two $K=0$ levels in the exciton band has been calculated to be 0.7 cm^{-1}.

Thus it appears that at least one of the low-lying excited electronic states of the pyrene crystal has the nature of exciton states, though in the case of the 1,3,5-trichlorobenzene, hexachlorobenzene, and durene crystals any such conclusion would be too hasty in view of the paucity of experimental data.

Photoconductivity of organic crystals (Sec. 6).—In a recent paper[125] Northrop and Simpson have published values of photocurrents of pure hydrocarbon crystals. They observed that the impurity molecules embedded in pure crystals which quench the fluorescence of pure substance reduce the photocurrent in the same ratio. Their other observations regarding dependence of photocurrent with light intensity, applied voltage, etc., are in agreement with previous publications. From these observations they propose that the interaction of two excitons is required to produce a single ionized molecule. Thus the production of charge carriers is explained. Compton *et al.*[126] studied photocurrent of anthracene crystals before and after neutron bombardment and concluded

that conductivity was greatly reduced on bombardment. They further observed that dependence of photocurrent on wavelength and intensity of incident light remained unaltered after bombardment. Before bombardment the photocurrent was markedly non-ohmic, after bombardment it was ohmic up to a field of 25 000 volts cm^{-1}. Before neutron bombardment the sample shows change of photocurrent when polarity of electrode is reversed, but this asymmetry disappears after irradiation. Kommandeur and Schneider[127] studied the photoconductivity in greater detail with very pure specimens of anthracene crystals and obtained results very different from previous ones. They observed that the maximum value of photocurrent corresponds to the minima of the absorption spectra. They also observed that the intensity dependence of photocurrent changes with wavelength, field direction, and even with magnitude of the applied field. These authors finally concluded that spectral response, voltage, and intensity dependence of photocurrent depend on the source and treatment of the crystals used, i.e., it depends on the density of imperfections of the crystals.

9. ACKNOWLEDGMENTS

[125] D. C. Northrop and O. Simpson, Proc. Roy. Soc. (London) A244, 377 (1958).
[126] Compton, Schneider, and Waddington, J. Chem. Phys. 28, 741 (1958).

[127] J. Kommandeur and W. G. Schneider, J. Chem. Phys. 28, 582, 590 (1958).

Irreversible Thermodynamics of Nonlinear Processes and Noise in Driven Systems*

WILLIAM BERNARD† ‡ AND HERBERT B. CALLEN

University of Pennsylvania, Philadelphia 4, Pennsylvania

1. INTRODUCTION

THIS paper reviews and extends the theory of irreversible thermodynamics. The irreversible behavior of a system driven by externally applied forces has been studied extensively, but attention has been focused primarily on the first-order term in the driven response. Here we also consider the higher-order terms in the driven response and the random fluctuations, or noise, occurring during an irreversible process. In addition to the well-known relations between the linear response and the equilibrium fluctuations, several new relations are proved involving the nonlinear response, the driven noise, and the equilibrium fluctuations.

The method of analysis is statistical mechanical and general, neither assuming a specific model nor postulating Markoffian behavior. The purposes of the analysis

are thermodynamic; that is, to investigate interrelationships among macroscopically observable characteristics of systems undergoing irreversible processes. In this sense the aim should be clearly differentiated from those other approaches which might be characterized as kinetic or statistical mechanical rather than thermodynamic.

The most direct approach to the problem of irreversibility is the kinetic approach, in which a specific model is immediately introduced. The essential features of the model may be expressed in terms of molecular collision probabilities, giving rise to the Boltzmann equation, or to some similarly detailed kinetic equation. This is the standard method of "transport theory," and it is the method characteristic of the theory of the solid state.

A considerably more general approach is one which we term the irreversible statistical mechanical approach. The purpose there is to develop a general formalism, analogous to the partition sum algorithm of equilibrium statistical mechanics, which would provide a systematic recipe for the calculation of any macroscopically ob-