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The Luminescence of Organic Molecular Crystals

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INTRODUCTION AND SCOPE

SOLID-STATE physics and organic crystal spectroscopy often deal with very similar phenomena. The apparent lack of communication between experimentalists in the two areas is therefore surprising. The physicists' terminology can be confusing to the chemist, and vice versa, especially in view of the semantic problems which arise through the use of identical terms to describe different models.

This article describes a particular terminology currently used by chemists and chemical physicists in relation to the spectroscopy of molecular crystals. In so doing, the present status of the theoretical models, the experimental results, and the relation between theory and experiment are critically examined.

The author feels that the two groups have much to offer each other in the solid-state field both from the theoretical and experimental standpoints. Notwithstanding the apparent complexity of the organic molecules which compose molecular crystals, the states of the free molecules involving π-electron excitation are well understood. Unlike ionic and valence crystals, the excited states of organic crystals can be derived in principle from the free molecule states by relatively simple perturbation theory. However, the existing rigid lattice models fail to account for many of the observed phenomena. The theoretical description of lattice imperfections, impurity centers, surface effects, intermolecular electron transfer, or even the influence of crystal vibrations on the electronic spectra of organic crystals, has barely begun. It is hoped that this article will serve to interest experimental and theoretical solid-state physicists in some of the intriguing problems of molecular crystal spectroscopy.

I. SOME ASPECTS OF THE THEORY OF EXCITONS IN RELATION TO THE LUMINESCENCE OF CRYSTALLINE ORGANIC COMPOUNDS

1. Introduction

The experimental verification of the rigid lattice theory of molecular excitons is found in the absorp-

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tion spectra of molecular crystals of aromatic molecules. The Davydov theory[1] accounts for the existence of several uniquely polarized electronic states of the crystal corresponding to each nondegenerate electronic level of the free molecule. In a higher approximation[2] this theory accounts for such phenomena as redistribution of intensity among the various crystal states and polarization ratios which deviate from the oriented gas model (Sec. I-2). According to theory, the natural radiative lifetime of the crystal is of the same order of magnitude as that for the free molecule. The exciton states should therefore radiate *if excitons are not caused to decay, through other processes, at rates which are much faster than the natural radiative rate of the optically produced excitons.* Thus, to a second-order approximation of perturbation theory, such crystals should exhibit uniquely polarized emission bands corresponding to transitions from the various exciton band origins (crystal states) to the crystal ground state. Moreover, if, as the theory allows, the exciton wave spreads with a group velocity that is large in comparison to the frequency of intramolecular vibrations, then these emission bands should be broadened only to the extent of the interaction of excitons with phonons in the ground and excited states.

However, the emission spectra of most organic crystals are not uniquely polarized (i.e., with reference to the crystallographic axes and symmetry planes); do not consist entirely of sharp lines; do not mirror the absorption spectra from the viewpoint of polarization; and indeed the gross features of the spectra parallel the fluorescence of the isolated molecules to a great extent. The spectra are diffuse except sometimes at lower than 20°K when some sharpening is evident; they are erratically polarized, often conforming to the oriented gas model; they are usually built on numerous close origins; the absorption and emission origins do not always coincide; and the spectra show pronounced vibrational structure with Franck-Condon envelopes that often match the free molecule spectrum. In addition, the absorption and emission bands do not always undergo the same shifts with temperature, which for the free molecule would indicate some specific interaction in the excited state. In other cases the vibrational structure is absent, although evident for the free molecule, and there is an apparent Stokes shift of 0.2 to 0.5 eV.

It is the purpose of this paper to classify certain of these and other phenomena and to set up criteria which may help in the understanding of organic molecular crystal luminescence. The discussion will be confined to molecules containing π-electron optical systems which are best exemplified, in view of the available experimental material, by aromatic molecules.

2. Definitions

Crystal luminescence and *luminescence from a crystal* are not to be taken as synonymous. *Pure crystal luminescence* originates from an electronic level of the crystal as a whole, the wave function of which belongs to an irreducible representation of the lattice translation group. This does not imply that the luminescence always originates from completely delocalized levels. The wave function describes the delocalization of the exciton and this may or may not be extensive, depending on the lattice direction and the extent of the interaction with phonons or the degree of coupling with molecular vibrations. Consequently, pure crystal luminescence might be defined as that having the final state corresponding to a pure crystal state. There are exceptions to this definition; for example, when an exciton is caused to emit under the perturbation of a local disturbance in the crystalline order. The emission from this region is pure crystal emission although the exciton band in the vicinity of the disturbance may not have the three-dimensional symmetry of the lattice. To guard against exceptions of this nature it is fitting to define pure crystal emission as that involving the spontaneous transformation of excitons into photons, with or without the participation of phonons. All the other luminescent properties of the crystal involve the exciton only indirectly and the transformation to a photon occurs only after the excitons have first decayed into another excited level. Thus, impurities, imperfections, and surface regions may give rise to emitting sites but the energies and wave functions of these "impure" states cannot easily be described in the three-dimensional symmetry of the pure crystal lattice. The trapping of excitons at these levels may result in *emission from the crystal* which, in the absence of chemical impurities of a certain type, may be called *defect emission.*

All the molecules under consideration have closed shell ground states and the most probable emission process is *fluorescence* between *singlet states* of the array. Here, the term *phosphorescence* of the free molecule describes the process of triplet-singlet emission; analogous emission is observed from some molecular crystals and must be classified as either *exciton phosphorescence* or *defect phosphorescence.* These multiplicity forbidden transitions have radiative proba-

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[1] A. S. Davydov, J. Exptl. Theoret. Phys. (U.S.S.R.) **18**, 210 (1948).

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

bilities of 10^{-4} to 10^{-8} times the corresponding fluorescence process. However, it is most convenient to label the emissions from crystals with reference to spectral location rather than to lifetime, because some crystals exhibit a *slow fluorescence* component of the normal fluorescence band. These classifications are useful only when the crystal and the free molecule emission spectra are closely analogous. As will be shown later, this is usually, but not always, the case.

The *polarization ratio* is defined here as the ratio of the intensity of the emitted light polarized parallel to each of two crystal axes. This quantity has fundamental significance only when one of these axes is a symmetry axis of the crystal (e.g., the *b* axis of the monoclinic group). Some workers have referred data to the dielectric axes in which case the polarization ratio will vary with wavelength. In absorption spectra the polarization ratio, equivalent to the above, is the ratio of the optical densities along each of two axes. An *oriented gas ratio* corresponds to the polarization ratio for an ideal crystal of completely noninteracting molecules. This ratio is obtained from x-ray data which provide information on the orientation of molecules in the unit cell.

Impurities which occupy substitutional sites in the *host* lattice are referred to as *guest* molecules. Owing to the planarity and similar dimensions of aromatic molecules, there is a wide range of host-guest pairs available for study. The details of why certain pairs of molecules form substitutional solid solutions while others do not are not yet known.

3. The Dynamic Approach to the Exciton Problem

Familiarity with the zeroth-order description of the wave functions and energies of the ground and excited states of an aggregate, in the framework of the Heitler-London or tight-binding approximation is assumed. The wave functions for the crystal states corresponding to the *f*-free molecule states are

$$\Psi^f = (N)^{-1/2} \sum_{i=1}^{N} a_i \Phi_i$$

where the a_i are periodic in the lattice. The Φ_i are antisymmetrized Heitler-London product functions. One such product function is

$$\chi_i^f = \varphi_i^f \prod_{k \neq i} \varphi_k^0$$

where the superscript 0 indicates the ground state, and χ_i^f is the wave function with only the *i*th molecule excited. The χ_i^f are single site excitation functions. The φ_i are the wave functions for the unperturbed states of the isolated *i*th molecule.

The wave functions and energies for stationary states of the crystal can be obtained in the manner of Frenkel,[3] Peierls,[4] and Davydov[1] using first-order perturbation theory. There are numerous reviews on this topic,[5–7] so we shall only be concerned with the physical (interpretive) aspects of the theory. In general, any state of the crystal is characterized by a function

$$\Psi(\mathbf{r},\mathrm{R},\mathbf{k}) \tag{1}$$

which depends on the internal corrdinates $\mathbf{r}$ of the molecules; on the location $\mathbf{R}$ of molecules in the crystal; and on a lattice wave vector $\mathbf{k}$ which modulates the excitation wave. The expression (1) is usually written as a modified Bloch function wherein the variables are separated into a product of functions characterizing molecular electronic states ($\mathbf{r}$); resonance interaction between the excited molecule and the rest of the molecules in the crystal ($\mathbf{R}$); the vibrational state of the lattice ($\mathbf{R}$); and a phase factor ($\mathbf{k}$,$\mathbf{R}$). To each of these states there corresponds an energy of excitation ΔE which is given by

$$\Delta E = E_{\mathrm{mol}} + \epsilon(\mathbf{k}) + \text{environmental stabilization} \tag{2}$$

where $\epsilon(\mathbf{k})$ is periodic in the lattice (see Sec. I-6 for further details). These states are stationary states of the crystal only when the time of excitation transfer to a neighboring molecule is small compared with the time for displacement of molecules in the lattice. This stationary condition is disturbed for energy transfer related to a change in the wave vector of the exciton within the Brillouin zone.

The nonstationary condition leads to the broadening of excited levels, owing to the shortening of their lifetime. Further, the velocity (momentum) of the exciton is changed and a significant change in the probability of transference of exciton energy into lattice vibrational energy can occur.

For values of the wave vector $\mathbf{k} = 0$, the symmetry problem is considerably simplified[8] and the symmetry properties of the crystal states can be obtained from the known space group, molecular point group, and the number of molecules per unit cell. Fortu-

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[3] J. Frenkel, Phys. Rev. **37**, 17, 1276 (1931).

[4] R. Peierls, Ann. Phys. **13**, 905 (1932).

[5] D. S. McClure, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 8, p. 1.

[6] H. C. Wolf, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1959), Vol. 9, p. 1.

[7] J. Tanaka, Suppl. Progr. Theoret. Phys. (Kyoto) **12**, 183 (1959).

[8] H. Winston, J. Chem. Phys. **19**, 156 (1951).

nately the *observed electronic states* lie in the region $\mathbf{k} = 0$, and the resulting agreement between theory and experiment in regard to absorption spectra is extremely satisfactory.

The absorption process involves the annihilation of a photon of momentum $\hbar\mathbf{Q}$ and the production of an exciton with momentum $\hbar\mathbf{k}$, where $\mathbf{k}$ is the wave vector of the reciprocal lattice. Consequently, the optical selection rule $\mathbf{k} = \mathbf{Q}$ expresses the conservation of momentum. The photon momentum or wave vector is of the order of 10^{-3} times the reciprocal lattice constant so momentum is conserved when $\mathbf{k} \sim 0$. This expresses the selection rule for optical transitions involving only excitons and photons and permits considerable simplification of the theory of molecular crystal spectra.

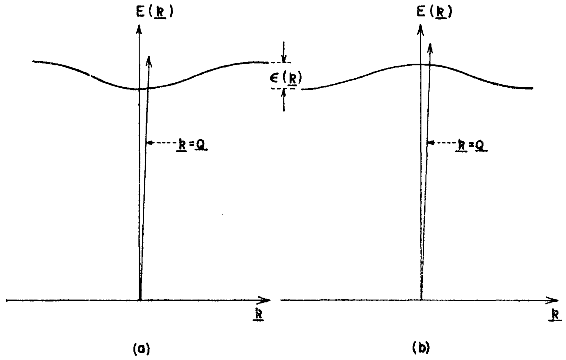

FIG. 1. First Brillouin zones for excitons. (a) Exciton velocity increases with increasing wave vector, (b) exciton velocity decreases with increasing wave vector.

The region $\mathbf{k} \sim 0$ lies near the center of the Brillouin zone (see Fig. 1) which, owing to the periodicity of $\epsilon(\mathbf{k})$, is always a stationary point on the $\epsilon(\mathbf{k})$ vs $\mathbf{k}$ curve. An exact calculation of the exciton zones of crystals of organic molecules is not yet available, but in general the point $\mathbf{k} \sim 0$ may be a minimum, a maximum, or a saddle point. Emission spectra will depend critically on the Brillouin zone structure.

A question arises concerning the stationary state character of the crystal excited states. Experiments with relatively thick crystals ($> 1\mu$) clearly indicate that the excitation energy is absorbed into a very small region of the crystal, and is not initially spread over the entire crystal as prescribed by $\Psi(\mathbf{k})$. However, within the regions of absorption, the resonance interaction causes a delocalization of the excitation. The good agreement between the theoretical and experimental Davydov splittings for most crystals of aromatic molecules is relatively unaffected by extending the calculations to include interactions between molecules separated by distances of greater than 20 Å. So, on this basis, experiment cannot decide on the extent of the initial delocalization of the excitation energy. A state for which the excitation is spread over only a few molecules is not a true stationary state of the system. Such *regional excited states* should be described as a superposition of crystal stationary states $\Psi(\mathbf{k})$, with time-dependent coefficients. The time-dependence of the coefficients then describes the spread of excitation away from the regions. This description represents the expansion, with time, of an exciton wave packet. Thus, subsequent to the formation of regional excitation, the energy tends to become delocalized over the entire system.

It may be useful to describe the delocalization of excitation within a region in terms of stationary states of that region. The perturbation on these molecules by the remainder of the molecules in the crystal would lead to the spreading of the wave packet, as described above.

4. The Participation of Phonons

The momentum of a phonon is $\hbar\mathbf{p}$ where $\mathbf{p}$ is the wave vector of the phonon. The selection rule for optical transitions can again be expressed[9] in terms of the conservation of momentum as $\mathbf{k} + \mathbf{p} = \mathbf{Q}$ or $\mathbf{k} + \mathbf{p} \sim 0$. Thus exciton-phonon interaction causes the exciton to move to a region of $\mathbf{k}$ space where $\mathbf{k} \neq 0$. Emission could then occur with the production of a photon $\mathbf{Q}$, but only if simultaneously the phonons $\mathbf{p}$ are absorbed.

It follows that the theoretical treatment of emission spectra must involve a calculation of the zone structure for particular cases. The exciton momentum (or effective mass) is sensitive to movements in $\mathbf{k}$ space, so such processes as nonradiative dissipation of excitation energy, luminescence lifetime, and energy transfer efficiency will be governed by the dependence of $\epsilon(\mathbf{k})$ on $\mathbf{k}$.

5. Influence of Zone Structure on Emission

Figure 1(a) illustrates the case where the momentum of the exciton increases with increasing energy. The effective mass of the exciton is obtained from the slope of the $\epsilon(\mathbf{k})$ vs $\mathbf{k}$ curve. After excitation at $\mathbf{k} = \mathbf{Q}$, the exciton wave can be propagated through the crystal within the narrow band of frequencies $\epsilon(\mathbf{k})$. At low temperatures the exciton should annihilate radi-

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[9] F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 326.

atively within a short time (10^{-9} sec) and the Stokes shift ΔS is expected to be very small:

$$\Delta S = \epsilon(\mathbf{Q}) - \epsilon(0) \backsim 0 \, .$$

If $\mathbf{k} = 0$ is not the bottom of the exciton band, as in Fig. 1(b), the exciton will thermalize (emit phonons) to the bottom of the band $\mathbf{k}_p$ in a very short time (10^{-12} sec). This exciton may only emit radiation under the influence of phonons so the fluorescence efficiency in this case should be temperature dependent with the Boltzmann factor

$$\exp - [\epsilon(\mathbf{Q}) - \epsilon(\mathbf{k}_p)]/kT \, .$$

The half-life for fluorescence of quanta Q_p is probably very long ($\sim 10^{-6}$ sec) so energy transfer to impurities should be very efficient at low temperatures, and should decrease with increasing temperature. Further, the influence of defects should be most marked in this case. In the first case [Fig. 1(a)] the energy transfer efficiency should decrease with decreasing temperature due to the slower propagation of exciton waves in the region of $\mathbf{k} = 0$ [the group velocity of excitons is given by $(1/\hbar)$ $\text{grad}_{\mathbf{k}}\, E(\mathbf{k})$].

6. Two Types of Excitation Wave

The basic theory of excitons predicts two types of excitation wave. The first is the free exciton which is qualitatively discussed above. If the optically produced exciton is caused to propagate at a rate comparable to the intramolecular vibration frequencies, its progress will be impaired due to the local disturbances of the lattice. The resulting excitation moves through the crystal very slowly and was called by Davydov a localized exciton[10] (these waves were also discussed by Frenkel[11] and Peierls[4] although in a more restricted sense).

The excitation energy of free excitons characterized by a wave vector $\mathbf{k}$ in the μth excitation zone corresponding to the fth molecular electronic state, is

$$\Delta E^f_\mu(\mathbf{k}) = \Delta E^f_{m\beta} + D^f_{m\beta}(0) + \epsilon^f_\mu(\mathbf{k}) \, . \tag{3}$$

These equations characterize the energies of μ bands of excitation ($\mu = 1,2 \cdots$; is the number of molecules in the unit cell) corresponding to the spread of excitation over the βth molecule belonging to the mth unit cell.[12] As before [Eq. (2)], $D^f_{m\beta}(0)$ represents the difference in stabilization energy of an unexcited compared with an excited molecule, in the zeroth approximation, i.e., when the lattice is assumed rigid. The energy difference $D^f_{m\beta}$ is obtained by summing the matrix elements (4) over all molecules in the crystal:

$$\int (\overset{0}{\varphi}_{n\alpha})^2 V_{n\alpha,m\beta}(\overset{f}{\varphi}_{m\beta})d\tau - \int (\overset{0}{\varphi}_{n\alpha})^2 V_{n\alpha,m\beta}(\overset{0}{\varphi}_{m\beta})^2 d\tau \, . \tag{4}$$

The $\epsilon^f_\mu(\mathbf{k})$ are given by (5) where $\mathbf{m}$ and $\mathbf{n}$ are the position vectors of the mth and nth molecules and $M^f_{n\alpha,m\beta}$ determines the exchange of excitation between the $n\alpha$th and $m\beta$th molecules:

$$\epsilon^f_\mu(\mathbf{k}) = \sum{}' M^f_{n\alpha,m\beta}\, e^{i\mathbf{k}\cdot(\mathbf{m}-\mathbf{n})} \tag{5}$$

$$M^f_{n\alpha,m\beta} = \int \overset{0}{\varphi}_{n\alpha} \overset{f}{\varphi}_{m\beta} V_{n\alpha,m\beta} \overset{f}{\varphi}_{n\alpha} \overset{0}{\varphi}_{m\beta} d\tau \, . \tag{6}$$

The excitation exchange interaction operator $V_{n\alpha,m\beta}$ may be written as a multipole expansion. Only the dipolar term is important in determining $M^f_{n\alpha,m\beta}$ when the electronic transition in the free molecule is allowed for electric dipole radiation and the dipole length of the transition is small in comparison to the distance between molecules in the crystal. Within this approximation (zeroth order, neglecting the exchange terms in $D^f_{m\beta}$) the magnitudes of $D_{m\beta}$ and $\epsilon^f_\mu(0)$ are usually between 100 and 10 000 cm^{-1} for oscillator strengths ranging from 0.01 to 1.0.

The dipole approximation works extremely well for most organic crystal excited states as well as for some large composite molecules and dimeric systems. As a consequence, calculations are very much simplified. However, and what is probably most important to the chemist, the validity of the approximation permits the replacement of the complete Coulomb interaction potential for complex molecular systems by a potential due to the classical interactions of transition moment dipoles. Thus, the physical description of the excited states of aggregates of molecules is reduced to a classical problem. Consequently, without recourse to quantum mechanics or group theory, the chemist may predict the relative energies, polarizations, and relative intensities of such electronic transitions.

Localized excitons may arise if the conditions mentioned at the beginning of this section are extant. The wave function describing the spread of excitons associated with local distortions is necessarily contracted because of the rapid attenuation of the lattice vibrational function with increasing distance from the distorted region. Thus the matrix elements for excitation transfer $\epsilon^f_\mu(\mathbf{k})_{\text{loc}}$ are of the form (7).

$$A^f_{n\alpha,m\beta} M^f_{n\alpha,m\beta}\, e^{i\mathbf{k}\cdot(\mathbf{m}-\mathbf{n})} \, . \tag{7}$$

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[10] A. S. Davydov and A. F. Lubchenko, Ukrain. Fiz. Zhur. 1, 5 (1956).

[11] J. Frenkel, Physik. Z. Sowjetunion. 9, 158 (1936).

[12] A. S. Davydov, *Theory of Molecular Excitons*, translated by M. Kasha and M. Oppenheimer, Jr. (McGraw-Hill Book Company, Inc., New York, 1962), Chap. VII.

$A^f_{n\alpha,m\beta}$ is a vibrational overlap integral which expresses the probability that the same local deformation is to be found at the initial ($n\alpha$) and final ($m\beta$) sites in the crystal. The value of the integral is extremely small and, consequently, the region of energy transfer will remain in the immediate neighborhood of a slowly moving distortion. Further, the energy zones for localized excitons will be virtually independent of wave vector [$\epsilon^f_\mu(\mathbf{k})_{\text{loc}} \sim 0$] and lie very close together. The excitation energy of localized excitons is therefore given by (8).

$$(\Delta E^f_\mu)_{\text{loc}} = \Delta E^f_{m\beta} + (\mathcal{E}^f - \mathcal{E}^0) . \qquad (8)$$

The energy difference $(\mathcal{E}^f_e - \mathcal{E}^o) = \Delta\mathcal{E}_{f-0}$ represents the difference in binding energy for the excited and unexcited distorted configuration. The inequality (9) is a necessary consequence of the excited molecule spontaneously changing its equilibrium location in the lattice:

$$D^f_{m\beta}(0) \geqslant \Delta\mathcal{E}_{f\cdot 0} . \qquad (9)$$

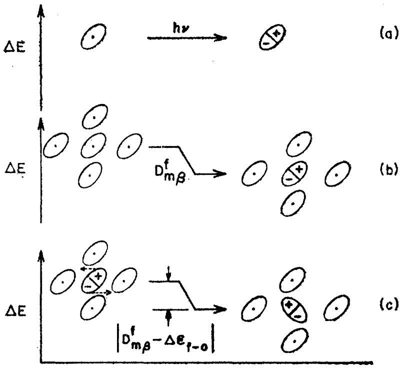

FIG. 2. Energy terms for excitons in a molecular crystal. (a) Excitation of free molecule ($\Delta E = 0$), (b) excitation of molecule in a lattice; $D^f_m\beta$ is usually, but not necessarily, negative, (c) localization of the excitation, $|D^f_m\beta - \Delta\mathcal{E}_{f-0}|$ is always negative.

This is graphically represented in Fig. 2(c). The difference in energy between the two types of exciton for a given zone μ is

$$\Delta E_{\text{free}} - \Delta E_{\text{loc}} = D^f_{m\beta}(0) - \Delta\mathcal{E}_{f-0} + \epsilon^f_\mu(\mathbf{k}) . \quad (10)$$

Utilizing Eq. (10), and the inequality (9) [and assuming that $\epsilon^f_\mu(\mathbf{k})_{\text{loc}} = 0$] the following two situations arise: (i) $\Delta E_{\text{free}} > \Delta E_{\text{loc}}$; this is represented in Fig. 3(a). The necessary condition is that $\epsilon^f_\mu(\mathbf{k})$ has only positive values in the zone μ. The exciton is self-trapped only in the region $\mathbf{k} = 0$ where the velocity of propagation is small. (ii) $\Delta E_{\text{free}} < E_{\text{loc}}$; the value of $\epsilon^f_\mu(\mathbf{k})$ should be negative and of large enough magnitude. The resulting zone structure is shown in Fig. 3(b).

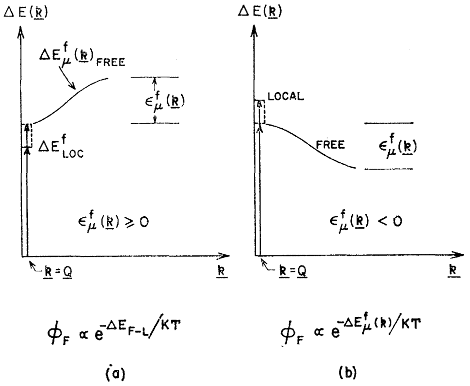

FIG. 3. Two types of localized exciton. (a) Energy of localized exciton is less than that of a free exciton, (b) Energy of localized exciton is greater than that of a free exciton.

Prior to the formation of localized excitons it is necessary that the energy transfer time is of comparable or of longer duration than the vibrational half-periods (τ_L) for the free molecule. The lowest frequency modes of aromatic hydrocarbons are of the order of 100 cm^{-1} corresponding to a half-period of about 10^{-13} sec.

The half-life of energy transfer τ_t is determined by the strength of the interaction between molecules, specifically

$$\tau_t = (h/2\pi)|\epsilon^f_\mu(\mathbf{k})|^{-1}$$

for values of $\epsilon^f_\mu(\mathbf{k})$ of 50 cm^{-1} we have $\tau_t = \tau_L$. Thus, although local excitons will be most important for the weakly coupled situations, e.g., crystals of benzens, naphthalene, stilbene, the ratio $\tau_L/(\tau_t + \tau_L)$ seldom exceeds 0.9 except for very strongly coupled systems such as perylene (see Sec. II.5) for which $\tau_t \sim 10^{-15}$ sec.

The localization of excitons is further illustrated in Fig. 4. The levels S_0 and S_0' represent the ground and excited states of the crystal for $\mathbf{k} = 0$. When $\mathbf{k}$ is very small, the group velocity is small and the above inequality ($\tau_L < \tau_t$) is satisfied, so the lattice can distort. The molecular levels corresponding to the new equilibrium position are now given by S and S'. The ground state energy is raised and the excited state is stabilized. In the absence of a distortion a resonance transfer of energy may occur between molecules S_0' and P_0 which corresponds to the simultaneous transitions $S_0' \rightarrow S_0$; $P_0' \leftarrow P_0$. However, the distorted excited state is now S' and resonance transfer can occur between the two molecules with a like-

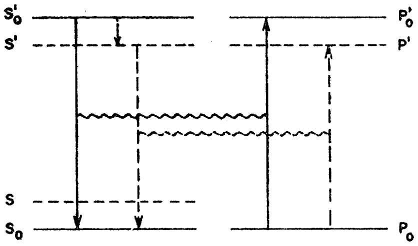

FIG. 4. Inhibition of energy transfer at low temperature due to localization of excitation energy.

lihood determined by the probability of the two simultaneous transitions: $S' \rightarrow S_0$; $P' \leftarrow P_0$. Each of these is strongly Franck-Condon forbidden, especially at very low temperatures.

The transition $S' \rightarrow S$ corresponds to localized exciton emission which, according to the description of Fig. 4, should be observed only when the conditions of Fig. 3(b) are satisfied, i.e., when $\epsilon_\mu^f(\mathbf{k})$ is greater than zero. The sign of ϵ_μ^f is determined by the disposition of the molecules in the crystal, i.e., by the sign of $M^f_{n\alpha,m\beta}$. Within the dipole approximation, $\epsilon_\mu^f(\mathbf{k})$ has the form

$$\epsilon_\mu^f(\mathbf{k}) = e\mathbf{M}_f^2 \sum_{i<j} \mathbf{r}_{ij}^{-3}(3\cos\theta_i\cos\theta_j - \cos\theta_{ij})e^{i\mathbf{k}\cdot(\mathbf{r}_i-\mathbf{r}_j)},$$

where $\mathbf{M}_f$ is the transition moment to the fth molecular level; θ_i and θ_j are the angles made by the transition moment dipole in the ith and jth molecules with the line joining their centers; θ_{ij} is the angle between the transition moments located in the ith and jth molecules; and $\mathbf{r}_i$ and $\mathbf{r}_j$ are the vector positions of these molecules separated by the distance $\mathbf{r}_{ij}$. Within this approximation it should be possible to make some meaningful band calculations for certain directions in a few simple organic crystals.

7. Molecular Vibrations

For most aromatic organic molecules, other than dyestuffs and some polymers, the lowest excited electronic states have oscillator strengths of about 10^{-1} to 10^{-3}. This results in (dipole-dipole) interaction terms between such molecules, of the order of 10^{-1} to 10^{-3} times the diffuse molecular vibrational band widths. Under such circumstances, the coupling occurs between the various vibronic levels of the molecules in the crystal. This conclusion was reached theoretically by Simpson and Peterson[13] and has been experimentally verified.

Phenomenologically, the magnitude of the molecular vibrational periods determines the nature of coupling between molecules in aggregates. Two extreme coupling situations are recognized [13–15]:

(a) *Weak coupling.* As described above, the interaction energy is very much less than the electronic band width. Consequently, only individual vibronic states may interact to any extent; i.e., the interaction does not admit a broad range of resonance coincidences. The vibrational deactivation of a molecule can occur much faster than the transfer of energy between molecules. The "exciton" is therefore thermally equilibrated more rapidly than the rate of propagation of an electronic wave packet from the excited region. During the period of thermal equilibration the transfer probability is related to the exchange of energy between two continua [i.e., $\propto \epsilon(\mathbf{k})^{-2}$].[14] Eventually individual molecules in the lattice will be in excited states executing only zero-point motions and the relative transfer probability now depends on extent of the interaction with phonons and the rate of fluorescence. Thus energy transfer may still be efficient in the limit of weak coupling. Crystals for which the Davydov splitting is less than a few hundred wave numbers should satisfy the above criteria.

(b) *Strong coupling.* The transfer time is comparable with, or less than, the molecular vibrational period. In this event, the interaction energy is large compared to the vibronic band widths; i.e., the interaction admits a broad range of resonance coincidences. In this case the exciton is never localized over one molecule, consequently well-developed molecular vibrational structure is not expected in the spectra of such crystals.

Normally the force constants describing the nuclear motion of free molecules are very slightly changed during electronic excitation. The bonding energy of carbon atoms usually decreases in an excited state ($\pi\pi^*$) causing the force constant to drop by about 1 to 10%. The decrease is small because the effect of electronic excitation is spread over the whole π-molecular framework. One would therefore predict even less change in vibration frequency for molecules in a crystal, where the excitation is spread over many molecules (see Sec. II-5).

8. Polarization Phenomena

In the rigid lattice theory the polarization ratio is simply the ratio of the squares of the projections of

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[13] W. T. Simpson and D. L. Peterson, J. Chem. Phys. **26**, 588 (1957).

[14] Th. Förster, in *Comparative Effects of Radiation,* edited by M. Burton, J. J. Kirby Smith, and J. L. Myers (John Wiley & Sons, Inc., New York, 1960), p. 300.

[15] E. G. McRae, Australian J. Chem. **14**, 329, 344, 354 (1961).

the electronically active molecular axis onto the two crystal axes. Experimentally this is determined by an intensity ratio at one wavelength, if the coupling is very weak; and by the ratio of areas under the two oppositely polarized absorption curves, if the coupling is strong. In some cases the experimentally observed ratio differs considerably from the oriented gas picture and the deviations may be accounted for by mixing in higher energy crystal states.[2]

The polarization of emission spectra is not so clearly defined. In most polarized fluorescence spectra the intensity ratio is either close to that predicted for an oriented gas model, or to the value observed in the absorption spectrum if these are different. At first sight, this appears a strange result in view of the fact that the emission involves a transition from an electronic level that belongs to one irreducible representation of the factor group, to a totally symmetric ground state. Consider a monoclinic crystal, space group C_{2h}^5, with two molecules per unit cell (e.g., naphthalene, anthracene). The factor group is C_{2h} and dipole allowed transitions are either B_u(*ac*-plane polarized) or A_u(*b* polarized). The allowed electronic levels of the isolated molecule are split into two states in the crystal, namely, the A_u and B_u states. Suppose that the lowest energy excited state is A_u and the ground electronic state is A_g. Therefore, on the rigid lattice model the emission spectrum should be entirely *b* polarized. However, it is easily seen that this is not so when molecular vibrations are considered. For electric dipole allowed electronic transitions of organic molecules (i.e., those transitions not made allowed by vibrational-electronic coupling) only the totally symmetric quanta are excited. These vibrational wave functions for D_{2h} molecules (e.g., naphthalene and anthracene) transform like the a_{1g} representation of the group. In a crystal of the abovementioned class, each a_{1g} vibration may correspond to either the a_g or b_g representation of the factor group. These vibrational states will split under an interaction potential although in actual cases this splitting may be extremely slight ($< 1\ \mathrm{cm}^{-1}$). Thus fluorescence involving the excitation of ground state vibrations will not be uniquely polarized. Figure 5 shows an energy level diagram for the crystal with an A_u emitting level. The vibrationless transition, $A_u[v' = 0] \rightarrow A_g[v = 0]$, is entirely *b* polarized. The vibronic transition, $A_u[v' = 0] \rightarrow (A_g \times a_g + A_g \times b_g)[v = 1]$ has components along the *b* axis and in the *ac* plane; i.e., $A_u \times (A_u) \times a_g = A_u \times (B_u) \times b_g = A_g$. The ratio of *b* to *a* polarized intensity in a vibronic transition is simply the oriented gas ratio or the polarization ratio in absorption.

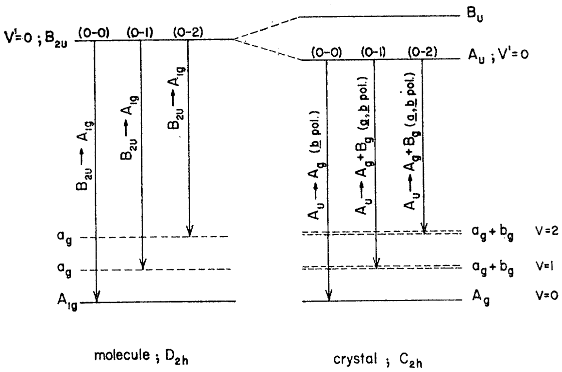

FIG. 5. Vibronic terms in a molecular crystal.

The above group-theoretical argument does not admit a temperature dependence of the polarization of vibronic fluorescence bands although the polarization in the region of the 0-0 band should lose uniqueness at higher vibrational temperatures.

McRae has described a general theory of vibronic transitions in aggregates and dimers,[15] and for the particular case of two weakly-coupled molecules per unit cell[16] which encompasses the same general conclusions as the simpler argument given above.

9. The Influence of Defects and Imperfections

The motion of excitation waves in the periodic lattice clearly is extremely sensitive to disturbances of the crystalline order. In imperfect regions the excitation is no longer spread over the whole crystal in a manner described by the pure crystal wave function. The extent to which the defect region perturbs the excitation wave will depend on the following:

(a) the region of **k** space through which the wave is propogating; i.e., the phase relationships among excited unit cells.
(b) the extent of exciton-phonon coupling,
(c) the absolute temperature,
(d) the "pure" intermolecular coupling compared to the coupling of molecules at the defect.

The first three effects take into account the changes of exciton momentum (velocity) which will ultimately determine the probability of localization at such sites. The fourth necessitates some discussion regarding the types of defect to be expected in molecular crystals of large molecules. At 300°K thermal fluctuations may amount to considerable deviations from the average (measured) lattice constants. Thermal motions *per se* are not considered as defect perturbations but are treated as ideal lattice parameters. The molecules in the region of a defect are con-

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[16] E. G. McRae, J. Chem. Phys. **33**, 932 (1960).

strained to take up relative orientations which are different from the orientation of molecules in the pure crystal. The defect can have electronic states which are not degenerate with the crystal states. They may, conceivably, be either above or below the crystal states.

Vacancies in the lattice constitute a special case of (d) where the extra space may permit molecules to rotate considerably under the influence of dipole-dipole attractive forces until the excitation energy becomes completely localized on, say, a pair of very strongly interacting molecules.

Should certain rearrangements of the ideal crystalline order be present in the crystal ground state, then it is possible to observe absorption to such levels. Only the unexcited crystal has a minimum of potential energy with properly oriented molecules. At a locally excited region the van der Waals forces are likely to be dominated by resonance force interactions.

Although it is not yet possible to detail the nature of defects, there is little difficulty involved in visualizing a variety of appropriate rearrangements of molecules. For this reason it would be surprising if they did not play an important role in the emission spectra of organic crystals.

In the event that a large number of states associated with defects in the lattice lie below the pure crystal levels, then the distribution over these (quasi-continuous) levels will be temperature dependent. The fraction of the total emission which is associated with defects will increase with decreasing temperature giving rise to the following phenomena:

(a) The whole spectrum will red-shift due to the changing spectral origins,
(b) The polarization ratio will change, although it may either increase or decrease,
(c) The free exciton emission will decrease with increased population of defect levels,
(d) The efficiency of energy transfer will decrease.

10. Nonradiative Conversion of Excitation Energy into Heat

The majority of organic molecules in condensed media have unique emission spectra which are independent of the energy of excitation. The fluorescence originates from the lowest excited singlet state of the molecule. Thus it arises that no emission is observed from higher electronic states even though the natural lifetime for such emission can be extremely short (e.g., 10^{-10} to 10^{-11} sec). It is therefore assumed that excited molecules transfer vibrational energy to the surrounding quasi-continuous medium with a half-life of the order 10^{-12} to 10^{-13} sec. The radiative lifetime of the upper states is therefore shortened and their quantum yields of emission are less than 10^{-2} to 10^{-3}. Phonon frequencies in aromatic crystals are usually between 10 and 100 cm^{-1} so the period of a crystal vibration (10^{-12} to 10^{-13} sec.) is longer than that of a molecular vibration (10^{-14} to 10^{-15}). Consequently any excess energy in individual molecular vibrations, after excitation of a crystal, will be rapidly transferred to the phonon states of the lattice. Under steady illumination the crystal will be in a quasi-equilibrium state with excitons, undergoing the various processes already described, populating the Brillouin zone in accordance with Boltzmann statistics. The necessary conditions for quasi-equilibrium were discussed in a recent review.[17] Thus, with crystals as for molecules, we expect unique emissions which originate only from levels having appreciable Boltzmann factors at the temperature of the experiment.

In view of the selection rule $\mathbf{k} = \mathbf{Q}$ for optical transitions, those excitons which go into levels of the band for which $\mathbf{k} \neq \mathbf{Q}$ cannot emit without the participation of phonons. The fluorescence yield will either increase [Fig. 1(a)] or decrease [Fig. 1(b)] with decreasing temperature. The extent of the temperature variation will depend on the value of $\exp[\epsilon(\mathbf{k})/kT]$. Thus the process of internal conversion of excitation energy in pure crystals can be understood in terms of the high probability of conversion of excitons into phonons in regions of the zone where $\mathbf{k} \neq \mathbf{Q}$.[18,19]

If the crystal contains a significant concentration of defects, there should be other internal conversion mechanisms. The phenomenon of concentration quenching of fluorescence is well known for aromatic molecules though only slight concentration quenching occurs in rigid media wherein the low-frequency rotational motions of the molecules are damped. This emphasizes that emission can occur from defect and impurity states in the crystal because the system is rigid. If these centers behave like free molecule states, the fluorescence efficiency will not be unity. Instead, a portion of the electronic excitation energy is used to populate the triplet levels of the molecules and another portion is possibly transformed directly into ground state vibrations. The over-all fluorescence efficiency of the "impure" states can therefore be

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[17] V. L. Broude, A. F. Prikhotk'o, and E. I. Rashba, Uspekhi Fiz. Nauk. **67**, 99 (1959).

[18] A. S. Davydov, Bull. Acad. Sci. U.S.S.R. Phys. Ser. **15** 605 (1951).

[19] J. Franck and E. Teller, J. Chem. Phys. **6**, 861 (1938).

temperature dependent but the fluorescence yield will decrease with increasing temperature.

11. The Population of Triplet Levels in Crystals

To observe pure crystal phosphorescence from crystals with defect levels (which can trap free singlet excitons), it is not necessary for pure singlet exciton states to intersect with crystal triplet states. If the probability of trapping a free exciton at a defect is p_d, the probability of intersystem crossing at the defect is p_i (probably close to the value for the free molecule), and the probability of ultimate emission of triplet states is p_t, then the finite quantum yield of triplet exciton emission is $p_d \cdot p_i \cdot p_t$ assuming that all the excitons which are formed eventually emit.

There is experimental evidence which indicates that p_i for the free molecule is much greater than that for the crystal. The fluorescence lifetimes for crystals and for isolated molecules are of the same order of magnitude, dependent on the oscillator strength of the transition. Thus the increased ratio of fluorescence to phosphorescence intensity in the crystals compared to rigid solutions cannot be accounted for by changes in the fluorescence lifetime. It may then be concluded that p_i in the crystal is less than 0.01 of the solution value for most aromatic hydrocarbons if, as is often the case, the crystal phosphorescence lifetime corresponds closely to the value for solutions.

As already mentioned, the force constants for the nuclear motion of electronically excited molecules in crystals are usually closer to the ground state values than are those for electronically excited individual molecules (Sec. I-7). Thus the restoring forces acting on the nuclei of an electronically excited molecule are increased when the molecule is part of an aggregate, and the resulting amplitudes of zero point motion are decreased. The intersystem crossing probability in a molecule may depend on the extent to which the excited molecule can adjust to regions of the potential surface of the singlet state where intersections with the triplet states occur. This process therefore demands the attainment of a particular set of excited state nuclear configurations. However, in the crystal the normal vibrational amplitudes are restricted due to the rapid transfer of energy between molecules.

This discussion indicates that the probability of intersystem crossing in pure crystals is related to the degree of the intermolecular coupling which determines the transfer time, thus $p_i \propto \epsilon(\mathbf{k})^{-1}$.

Therefore the appearance of phosphorescence in organic crystals would depend not only on the strength of the (singlet) electronic transition in the free molecule, but also on the geometrical arrangement of molecules in the crystal and on the *wave vector of the singlet exciton.*

A further aspect of crystal triplet excitons concerns the very long lifetime of these levels which implies extreme sensitivity to impurities, defects and surface effects.

The nature of the intermolecular potential which perturbs the individual triplet levels and produces a band in the aggregate is not known. Terenin and Ermolaev[20] have shown that dipole-dipole forces are probably not involved in triplet-triplet energy transfer in solutions and they have suggested an electron exchange mechanism. All electron exchange integrals are neglected in the theories of molecular crystals referred to in this work. Although the dipole strengths of multiplicity forbidden transitions are about 10^{-5} to 10^{-6} of the corresponding allowed transitions, the probability of energy transfer under a dipole potential may still be high because of the much longer lifetimes of the triplet states.

Figure 6 shows the total emission (fluorescence and phosphorescence) of crystals of triphenylene at 77°K. The total emission of the free molecule (i.e., rigid glass spectrum) is shown for comparison. The ratio of phosphorescence to fluorescence yield is less for the crystal by a factor of 0.017. The lifetime of the phosphorescence is about 15 sec for the molecule; the decay of luminescence from the crystal is nonexponential with a half-lifetime of about one second.[21] The change in lifetime, and in the decay mechanism, might reflect the importance of imperfections and that triplet energy is nonradiatively transferred between molecules. The spectrum of triphenylene crystals is quoted here because it represents a rare type of organic crystal from which both fluorescence and phosphorescence are obtained with comparable intensities. Although triphenylene crystals have only one stable modification, the phosphorescence-fluorescence yield ratio can be caused to vary between 0.8 to 0.05 by changing the previous history of the luminescing crystal; e.g., by annealing, method or rate of crystallization, etc. Evidence of this nature strongly suggests that imperfections are responsible for the luminescent behavior of triphenylene.

Certain aromatic molecules containing oxygen or nitrogen atoms in conjugation; e.g., ketones, quinones, *N*-heteroaromatic molecules, show little or no

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[20] V. L. Ermolaev and A. N. Terenin, J. chim. phys. **55**, 698 (1958).

[21] R. M. Hochstrasser (unpublished).

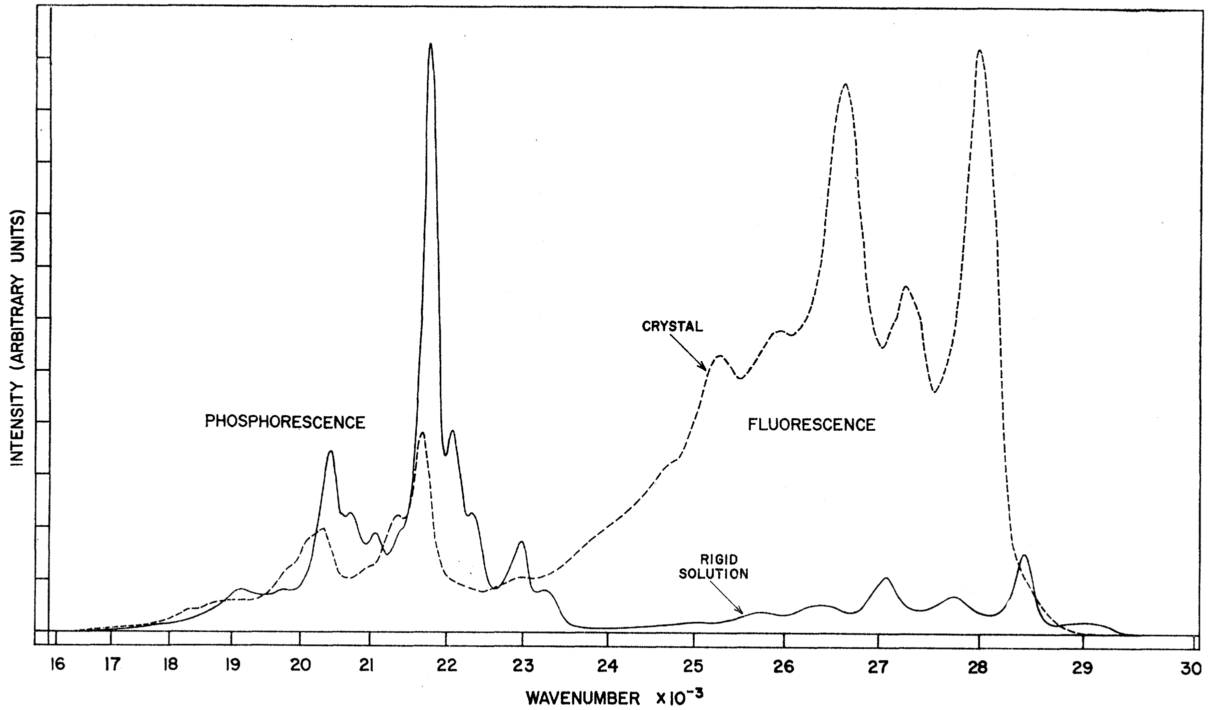

Fig. 6. The total emission spectrum of the triphenylene cystal (a) and molecule (b).

fluorescence but phosphoresce with high efficiency. Rigid solutions or crystals of benzophenone have a strong phosphorescence at low temperatures whereas the fluorescence is not detectable. When aromatic hydrocarbon impurities are included in benzophenone crystals to the extent of 10^{-4} mole hydrocarbon per mole benzophenone about 0.5 of the emission corresponds to phosphorescence of the hydrocarbon when the lowest triplet state of the guest lies at lower energy than the lowest triplet emitting level of benzophenone.[21] Naphthalene, triphenylene, chrysene, phenanthrene, anthracene, and pyrene can each efficiently trap the triplet excitation energy of the host crystal. The first four guest molecules do not have singlet states lower than the singlet state of the benzophenone crystal, thus the energy must be transferred nonradiatively between *a triplet state of the crystal* and a *triplet state of the guest molecule.* However, these experiments alone do not prove that the triplet excitation of the crystal is transported over the large distances indicated. The remaining guest molecules have lowest singlet states at energies intermediate between the lowest singlet and the lowest triplet state of the crystal. For these two cases virtually no *fluorescence* of the guest molecule is observed from which it may be concluded that energy transfer *via* the singlet exciton band is much less efficient than transfer *via* the triplet states of benzophenone molecules in the crystal. The last two experiments rule out the trivial transfer mechanism involving singlet exciton trapping at the neighborhood of a guest molecule followed by intersystem crossing and finally triplet-triplet energy transfer between nearby host and guest molecules. The calculated values of $\epsilon_\mu(\mathbf{k})$ for benzophenone crystals are extremely small within a dipole approximation, due to the forbidden character of the electronic transition involved.

II. GENERAL OBSERVATIONS OF CRYSTAL FLUORESCENCE[22]

1. Introduction and Classification

The fluorescence of organic crystals is studied by a variety of experimental techniques. To measure quantum yields the total, nonspectrally analyzed, fluorescence band usually is isolated with filters. Such measurements are fraught with difficulties owing to reabsorption phenomena, especially if values at various temperatures are required. Photographic tech-

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[22] Excellent reproductions of the electronic absorption spectra of aromatic hydrocarbons in rigid glass solution at 77°K are provided by E. Clar [*Aromatische Kohlenwasserstoffe* (Springer-Verlag, Berlin, 1952)], while the spectra of some other types of organic molecules at 300°K have been compiled by R. A. Friedel and M. Orchin [*Ultraviolet Spectra of Aromatic Compounds* (John Wiley & Sons, Inc., New York, 1951)]. The absorption spectra of aromatic crystals can be traced through the review references 5–7.

niques are used to examine fine structure and band shapes although it is difficult to measure relative intensities in this fashion. Photomultiplier recording spectrophotometers can be used to examine gross spectral effects such as relative yields and temperature fluctuations of intensity; this method usually does not allow for a study of the fine structure.

Thus, for a complete understanding of crystal emission, it is necessary to combine these three approaches. The observed luminescence spectra are sensitive to the penetration depth of the exciting light and to the geometry of the optical system. Reabsorption effects may be minimized if the exciting light is strongly absorbed (minimum penetration depth) and the front surface of the crystal is illuminated and emission observed from the same surface.

For clarity it is worthwhile to subdivide the low-temperature emission spectra of organic crystals into classes depending on gross spectral features; the three main classes are given below:

Class (I)—Sharp (S)
Class (II)—Broad (B)
Class (III)—Diffuse (D)

Most crystals of large molecules have spectral regions belonging to both (I) and (II); such spectra are named SB. S-type fluorescence spectra may consist of many hundreds of lines varying in width from 25 to 1 cm^{-1}; B type consists of broad (500 to 1000 cm^{-1}) vibrational envelopes which usually resemble the fluorescence spectra of molecules in solution at higher temperatures; the SB type have fine structure superimposed on a B-type Franck-Condon envelope; D-fluorescence spectra consist of one extremely broad band ($\sim$ 3000 to 4000 cm^{-1}) which exhibits an apparent Stokes shift of about 4000 cm^{-1} relative to the allowed exciton band origin. Examples of each are discussed below.

2. S-Type Crystal Emission

For this group, the crystal spectra are considerably sharper than the low temperature solution spectra and grossly resemble the emission spectra of the vapors at low pressure. Benzene, its homologs, and naphthalene are in this category but only naphthalene will be discussed in any detail.

The fluorescence origin does not coincide with either of the free exciton absorption components.[23] Unfortunately the spectrum in this region is complicated by the presence of the impurity β-methylnaphthalene[24] and much of the emission from even highly "purified" naphthalene originates from the 31 062 cm^{-1} level of the impurity. The true fluorescence origin probably is at 30 950 cm^{-1} and is quite strong at 4.2°K at which temperature the energy transfer to the impurity becomes inhibited.[25] The free exciton components of the 0-0 band are observed in absorption[26] at 31 476 cm^{-1} (a polarized) and 31 636 cm^{-1} (b polarized), so there is a considerable gap between absorption and emission at 4.2°K. It is possible that this is a vibronic transition from 31 476 cm^{-1} involving the simultaneous excitation of a ground state vibration (520 cm^{-1}).

The fluorescence yield of naphthalene crystals (presumably containing traces of β-methylnaphthalene) is about 0.6 and is increased very slightly at 77°K.[27] As yet, no accurate intensity data are available for temperatures below 77°K. The fluorescence spectrum is polarized about twice as strongly along the b axis as along the a axis of 001,[26] which is about the same degree of polarization observed in the absorption spectrum to the lowest electronic state. From this, one may conclude that the emission does not originate from the lowest energy free exciton level (31 476 cm^{-1}), which is entirely a polarized. Alternatively, the emission spectrum could be ascribed to a sequence of transitions between vibrational exciton states as described in Sec. I-8. The remainder of the fluorescence spectrum can be analyzed in terms of known totally symmetric ground state vibrational frequencies. There is therefore indication that the excitation is, at the moment of emission, localized on individual molecules. Thus, no emission bands have yet been assigned to free exciton (0-0) transitions. Before this can be done it will be necessary to have confidence in the ultra-purity of the crystal. Defect centers may play a considerable role in the localization of the excitation energy.

A small fraction of the naphthalene fluorescence spectrum appears with a half-life of 10^{-2} to 10^{-3} sec instead of the usual 10^{-6} to 10^{-7} sec lifetime.[28,29] The spectral details of the slow fluorescence are not significantly different from the normal component and the lifetime decreases with increasing temperature. The occurrence of slow fluorescence must be con-

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[23] W. Obreimov and K. Shabaldas, J. Phys. U.S.S.R. **7**, 1668 (1943).

[24] A. F. Prikhot'ko and M. T. Shpak, Optics and Spectroscopy **6**, 119 (1959).

[25] H. C. Wolf, Naturwissenschaften **48**, 43 (1961).

[26] D. S. McClure and O. Schnepp, J. Chem. Phys. **23**, 1575 (1955).

[27] G. T. Wright, Proc. Phys. Soc. (London) **A68**, 701 (1955).

[28] H. Sponer, Y. Kanda, and L. A. Blackwell, J. Chem. Phys. **29**, 721 (1958).

[29] N. W. Blake and D. S. McClure, J. Chem. Phys. **29**, 722 (1958).

cerned with long-lived energy traps in the crystal. A brief discussion of possible mechanisms is given in Sec. III-8.

3. SB-Type Crystal Emission

Phenanthrene and stilbene are examples of SB emission. There is no evidence of vibration induced electronic transitions for the lowest levels of these molecules, so the question of mixing of electronic states probably does not arise.

High dispersion spectra of the fluorescence of these molecules have been examined by Prikhot'ko *et al.*[30,31] The absorption and fluorescence of phenanthrene was studied by McClure.[32] Both crystals show well-resolved sets of vibrational progressions which are related to the Raman frequencies of the free molecules. This fine structure is superimposed on broad envelopes which are spaced apart by approximately 1500 cm^{-1} and have an intensity distribution which corresponds closely to the Franck-Condon sequence in the free molecule fluorescence. The fine structure is not only apparent at 20°K (the temperature of the above experiments) but sometimes appears on the 77°K spectra. Both phenanthrene and stilbene show weak emission lines near the intrinsic absorption region. It was shown[30,31] that considerable changes occur in the weak line luminescence (and absorption) spectra upon annealing the crystals. Some of these lines are uniquely polarized and some are not polarized. These results were interpreted in terms of energy levels, near the levels of the perfect lattice, related to structural defects of the lattice. The low dispersion spectra of stilbene fluorescence exhibit properties which are entirely consistent with this viewpoint.[33] Figure 7 shows fluorescence spectra of stilbene at 300 and 77°K and each of the effects noted in Sec. I-8. are apparent (the energy transfer data are presented in Sec. III). The increased polarization ratio near the edge of the spectrum at 300°K was interpreted as due to free exciton emission[33] which is absent at 77°K because of the Boltzmann factor of the exciton band in relation to defect levels. Note that the high energy emission (29 500 cm^{-1}) is more intense at 300°K notwithstanding the increased reabsorption at this temperature. The continuous variation of the edge emission with temperature indicates, subject to the present interpretation, that the defect levels extend to nearly 200 cm^{-1} below the exciton band (the red-shift is also of this magnitude).[33] Figure 7 also shows the small change in quantum yield with temperature of stilbene luminescence.

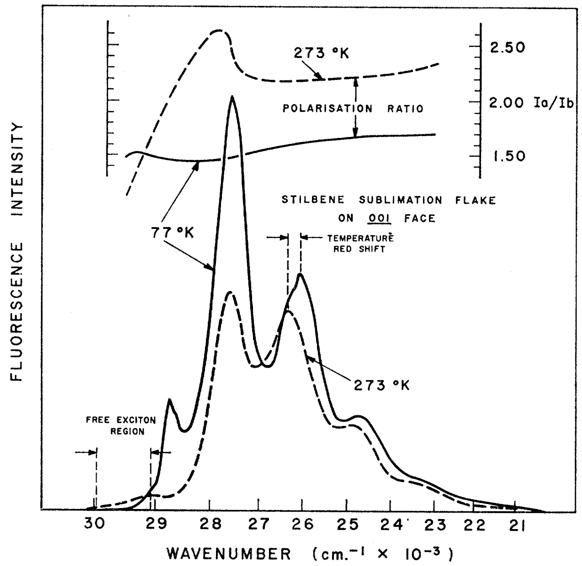

FIG. 7. The polarized fluorescence spectrum of the trans-stilbene crystal at 300 and 77°K.

The Davydov splittings for stilbene and phenanthrene are comparable with or less than kT down to below 20°K. On the basis of a pure crystal model the polarization ratio should decrease with increasing temperature as the Boltzmann factor for the upper factor group component (oppositely polarized) increases. Exactly the opposite is observed.

Each of these crystals is monoclinic (C_{2h}^5) with two (phenanthrene) and four (stilbene) molecules in the unit cell. The stilbene lattice is complicated by the presence of two asymmetric sets of two molecules per unit cell.[34] Thus there should be four crystal levels very closely spaced but only two of these have been observed.[30]

Phenanthrene has a slow fluorescence component which decays about ten times slower than the corresponding naphthalene emission. The long-lived fluorescence is indistinguishable from the normal crystal fluorescence.[28,29] The decay curve is nonexponential but the approximate half-duration is around 7 msec at 80°K and decreases to about 0.5 msec at 290°K.

4. SB-Type Anthracene

A special place is given to anthracene in view of the extensive literature dealing with the spectral properties of this hydrocarbon.

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[30] A. F. Prikhot'ko and I. Y. Fugol, Optics and Spectroscopy 7, 19 (1959).

[31] A. F. Prikhot'ko and I. Y. Fugol, Optika i Spectroskopiya 5, 582 (1958).

[32] D. S. McClure, J. Chem. Phys. 25, 481 (1956).

[33] R. M. Hochstrasser, J. Mol. Spectroscopy (to be published).

[34] J. M. Robertson and I. Woodward, Proc. Roy. Soc. (London) A162, 568 (1937).

The absorption edge of anthracene crystals exhibits a weak *b*-polarized shoulder which, under high resolution at low temperature, consists of a series of lines. They can be observed in emission[35,36] as well as in absorption.[37–39] The principal lines in this region were recently proved due to impurities (notably anthraquinone).[40] The anthracene emission spectrum closely resembles the stilbene and phenanthrene spectra in consisting of a "solution-type" Franck-Condon envelope on which is superimposed some sharp bands. As before, the region near the absorption edge contains many lines not associable with a normal vibrational analysis, and which vary in intensity and polarization according to the previous history of the crystal. An apparent free exciton emission is observed at 4.2°K, although it is extremely weak.[40]

The low dispersion spectra of anthracene show the identical general features discussed in Secs. II-3 and I-8. Other notable features are the irreproducibility of the Franck-Condon envelope with different crystals[41] or even with the same crystals at different temperatures.[42] This effect could be due to the presence of impurity levels as discussed above. The quantum yield of anthracene fluorescence is near unity[27] and does not change significantly with temperature. The continuous variation with temperature of many of the vibronic bands was studied in the range 300 to 4.2°K.[43] Changes occurred most markedly over certain ranges below 150°K; some bands increased and others decreased in intensity. It was concluded that a Boltzman distribution over the existing origins and a Franck-Condon effect are both important in determining the intensity distribution at a given temperature. Surprisingly, neither phenanthrene nor stilbene show this type of redistribution between 300 and 20°K,[31,32] (phenanthrene) and 300 and 4.2°K (stilbene).[33]

Recently Avakian and Wolf[44] have determined the form of the luminescence-temperature curve for anthracene crystals containing tetracene. They studied crystals containing 10^{-2} to 3×10^{-6} moles/mole of tetracene, between 60 and 4°K. In all cases, the maximum rate of change of the fluorescence yield ratio occurred at 35 ± 2°K, corresponding to an Arrhenius energy ($2kT$) of 47 cm^{-1}. The greatest changes in energy transfer efficiency occurred for concentrations between 10^{-3} and 10^{-5} moles/mole. At higher or lower concentrations than this the changes were only slight. Many more experiments of this detailed nature are required before the mechanism can be elucidated. However, these experiments and similar experiments on stilbene (see Sec. III-4) do indicate that the average transfer distance of the excitation energy depends on the temperature of the crystal.

In all the cases so far discussed there is a considerable apparent Stokes shift of the luminescence spectrum of some 200 to 300 cm^{-1} at low temperatures. This is not, however, a "gap" between the absorption and emission origins.

The polarization ratio of anthracene fluorescence is not constant and increases with increasing energy.[42] As for stilbene, the polarization ratio is largest close to the absorption edge; however, in this case the polarization ratio increases slightly with decreasing temperature. Anthracene forms monoclinic crystals (C_{2h}^5) with two molecules per unit cell. The Davydov splitting is 195 cm^{-1},[45,46] with the *b* component at lowest energy. Thus the free exciton emission spectrum at low temperatures should be uniquely *b* polarized and this uniqueness should be removed when the Boltzmann factor of the upper component is appreciable. At low temperatures (4.2°K) the polarization ratio is about $7{:}1(I_b/I_a)$,[42] which very nearly corresponds to an oriented gas ratio. If the crystal emission is not mainly exciton emission (*b* polarized), then the impurity or defect trapping centers must contain molecules which are properly oriented to the symmetry axes of the crystal; otherwise the oriented gas ratio would not be observed. It is probable from the work cited[43] that the actual emitting levels range from 0 to 47 cm^{-1} below the mobile exciton levels. The above-mentioned increase in polarization ratio in the onset of the fluorescence spectra of anthracene, stilbene and phenanthrene can be partly explained on the basis of the theory[16] which was discussed in Sec. I-8.

5. D-Type Crystals

This group is typified by pyrene and perylene. The structures are monoclinic (C_{2h}^5) with four molecules in

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[35] A. F. Prikhot'ko and I. Y. Fugol, Optika i Spektroskopiya **4**, 335 (1958).

[36] J. W. Sidman, Phys. Rev. **102**, 96 (1956).

[37] I. W. Obreimow and A. Prikhot'ko, Physik. Z. Sowjetunion **9**, 48 (1936).

[38] D. P. Craig and P. C. Hobbins, J. Chem. Soc. **1955**, 2309 (1955).

[39] J. Ferguson and W. G. Schneider, J. Chem. Phys. **28**, 761 (1958).

[40] P. W. Alexander, A. R. Lacey, and L. E. Lyons, J. Chem. Phys. **34**, 2200 (1961).

[41] P. Pesteil and L. Barbaron, J. phys. radium **15**, 92 (1954).

[42] J. Ferguson and W. G. Schneider, Can. J. Chem. **36**, 1070 (1958).

[43] L. E. Lyons and J. W. White, J. Chem. Soc. **1960**, 5213 (1960).

[44] P. Avakian and H. C. Wolf, Z. Physik **162**, 439 (1961).

[45] H. C. Wolf, Z. Naturforsch. **13A**, 414 (1958).

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the cell; four crystal states arise from each nondegenerate molecular level. Electronic transitions to only two of these states are allowed by symmetry. The forbidden crystal states lie at lower energy than the allowed levels.

Figure 8 shows the absorption and fluorescence spectrum of perylene at 77°K.[47] The calculated positions of the allowed factor group components (A_u and B_u) and the lowest forbidden component (B_g) are shown on the figure. Pyrene has a similar fluorescence spectrum which is considerably shifted from the absorption edge[48] Perylene and pyrene[49] are examples of a stronger type of coupling and as is shown in Sec. III this is consistent with the energy transfer features of these crystals.

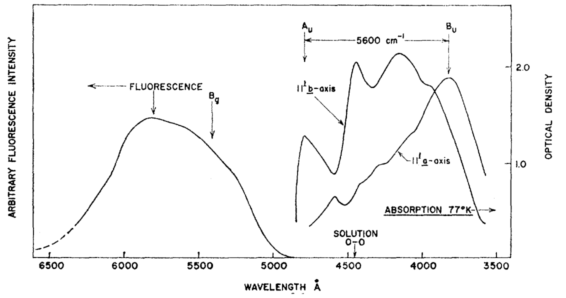

FIG. 8. The polarized absorption and emission spectrum of a perylene single crystal at 77°K [(001) face of sublimation flake].

Their fluorescence spectra cannot be due to allowed exciton emission for the following reasons:

(a) The spectra are unpolarized,

(b) There is no coincidence of absorption and fluorescence.

Similar broad emission spectra are obtained from dimers of these molecules[50] so it is best to regard the crystalline unit cell as containing two weakly coupled units of a strongly-coupled dimer. The emission may be interpreted as originating from *a symmetry-forbidden exciton band.* Such an emission only can occur be interpreted as originating from a symmetry-forbidden exciton band. Such an emission only can occur simultaneously with the excitation of an antisymmetric molecular vibration, which will permit mixing with an allowed crystal (or dimer) component. This interpretation will allow for the diffuse nature and spectral location of the spectra. Quantum yields or temperature coefficients are not yet known for these crystals. It is understandable why no defect line spectra are observed if the production of a defect necessitates the disruption of the dimeric structure. No delayed (slow component) of fluorescence is observed with these crystals. Other examples of D-type include benzpyrene and ovalene[51] as well as some hydrogen-bonded crystals, e.g., the naphthoic acids.[52] Other influences on the diffuse emission spectra concern charge resonance states which lie below the allowed crystal states.[53]

6. B-Type Emission

Although no high resolution studies are available for tetracene, the lower dispersion spectra show no indication of sharpness. The band, apart from a red shift, is very similar to the solution fluorescence.[21] Tetracene crystals are triclinic although the general arrangement of molecules in the crystal is similar to anthracene.

It is notable that tetracene crystals do not fluoresce appreciably at 300°K; yet the fluorescence is strong at 77°K. The fluorescence yield has an exponential temperature dependence with an Arrhenius energy of 53 cm^{-1} between 160 and 100°K, and 175 cm^{-1} above 160°K.[54] These energies are comparable with the values for the temperature dependent parameters of other crystals and are to be compared with the lattice vibrational frequencies. Chrysene has a B-type fluorescence, exhibits a strong slow component of fluorescence, and a phosphorescence in the crystalline state.[55] The slow fluorescence and the phosphorescence are of comparable intensity.

III. THE RELATIONSHIP BETWEEN THEORY AND EXPERIMENT

1. Introduction

The physical interpretative aspects of the theory of excitons in molecular crystals (Sec. I) and some

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[47] R. M. Hochstrasser (to be published).

[48] J. Ferguson, J. Chem. Phys. 28, 765 (1958).

[49] The lowest electronic state of pyrene has a very low intensity. However the calculated energies of the crystal states ($\mathbf{k} = 0$), of which there are four for each molecular state, suggest that the lowest crystal states may correspond to the forbidden components (B_g and A_g) of the *second lowest* free molecule state. Thus there is considerable overlapping of the crystal band structure for the lowest (weak) and second lowest (*very strong*) electronic states of the pyrene molecule. In emission spectroscopy it is only the nature of the coupling for the *lowest* crystal state (or states within the range comparable to kT) that is of consequence.

[50] Th. Förster and K. Kasper, Z. Elektrochem. 59, 976 (1955).

[51] B. Stevens, "Excitation Formation, Exciton Capture and the Crystal Structure of Aromatic Hydrocarbons," paper presented at the Fifth European Symposium on Molecular Spectroscopy, Amsterdam, 1961 (unpublished).

[52] R. M. Hochstrasser, Can. J. Chem. **39**, 1853 (1961).

[53] R. M. Hochstrasser, J. Chem. Phys. **36**, 1099 (1962).

[54] J. Ferguson, J. Mol. Spectroscopy **3**, 177 (1959).

[55] H. Sponer, *Delayed Fluorescence and Phosphorescence of Aromatic Molecules at 4.2°K* (to be published).

important experimental details (Sec. II) having been discussed, this section deals with specific experimental answers to theoretical predictions. Experimental results regarding energy transfer in mixed crystals are introduced and utilized in the discussion.

2. Free Exciton Emission

There is no unambiguous demonstration of free exciton emission from organic crystals. Anthracene has a weak band at 25 040 cm^{-1} which can be interpreted as free exciton emission owing to its coincidence with the phononless lowest factor group component. However, an impurity resonance line has not been ruled out. All of the crystals mentioned so far exhibit an increased emission intensity directly under the first absorption band when the temperature is raised (see, for example Fig. 7 in the region 29 500 cm^{-1}). Conceivably, this emission is free exciton emission, the increased yield at higher temperatures arising from *thermal depopulation of defect sites*. On the other hand this emission could manifest higher energy defect levels or even localized exciton levels at higher energy than the base of the free exciton band [see Fig. 3(b)].

According to a foregoing discussion, free excitons in thermal equilibrium with the lattice of an ideal crystal cannot luminesce without the help of phonons. It was shown theoretically that the collision time of an exciton with phonons (10^{-11} sec)[56] is much less than the lifetime of an exciton with simultaneous emission of a photon and a phonon (10^{-7} sec).[57] Therefore, the excitons are expected to reach thermal equilibrium with the lattice before emission. Accordingly free exciton emission can only be expected when $\mathbf{k} = 0$ is at the bottom of the exciton zone, and will decrease with increasing temperature. These theoretical results are presented in contradistinction to the present interpretation of the edge emission.

3. Two Types of Exciton

A few energy transfer experiments may be interpreted in terms of two types of exciton.[58] Nevertheless, it is extremely difficult to decide experimentally amongst the possible energy transfer mechanisms—for example, between one-stage and multi-stage processes. Figure 9 represents a crystal (0.3 mm thick) of pure stilbene. Deposited on the right-hand surface is a very thin layer ($\sim 0.1\mu$) of tetracene molecules in substitutional solid solution. When the left-hand surface is irradiated with light which is strongly absorbed, some tetracene emission is emitted from the opposite face of the crystal.[33] This is a clear demonstration of nonradiative energy transfer since the probability of tetracene absorbing either the exciting light or the fluorescence emission of stilbene is prohibitively low. However, the diffusion length of the exciton (more exactly 10^{-6} of the excitons) could not attain 0.3 mm. The successive emission and reabsorption of stilbene fluorescence produces excitons which are far removed from the incident surface; once they are close enough to the observed surface non-radiative transfer to tetracene may occur. This process should not be temperature dependent. In fact, at 10^{-7} moles/mole tetracene in stilbene there is no attenuation of energy transfer between 300 and 4.2°K. The fluorescence of a crystal has a very large extinction depth with respect to its own lattice.

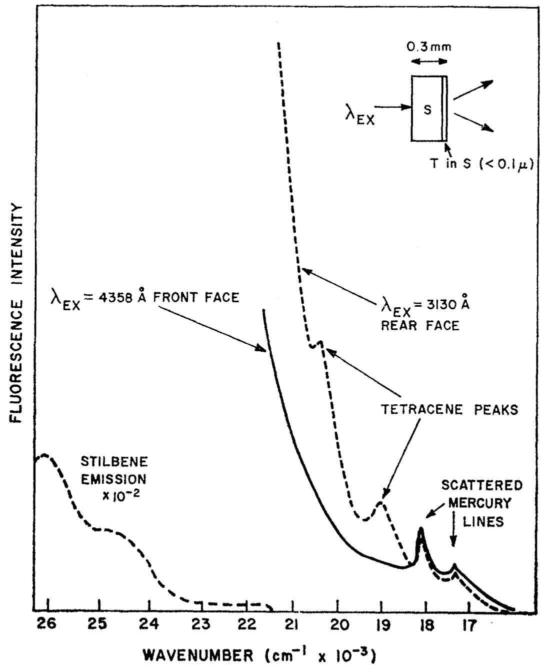

FIG. 9. Demonstration of nonradiative energy transfer of excitation energy in molecular crystals; a stilbene crystal containing a small amount of tetracene.

Possibly some of the emission bands near the absorption edge could be caused by trapped excitons. A study of the thermal kinetics and exact polarizations of these should aid the interpretation.

The distinction between localized excitons and defects represents a major experimental and theoretical problem especially since, at sufficiently low concentrations of defects, neither of these levels will be easily observed in absorption. Undoubtedly a model

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[56] V. M. Agranovich and Y. V. Konobeev, Optics and Spectroscopy **4**, 242 (1959).

[57] Y. M. Popov and A. S. Selivanenko, Optics and Spectroscopy **5**, 135 (1960).

[58] V. M. Agranovich and A. N. Faidysh, Optika i Spektroskopiya **1**, 983 (1956).

crystal is required for study which can become the organic analogue of germanium and silicon in the development of inorganic phosphors. In view of the current methods of purification of aromatic hydrocarbons and their ultimate susceptibility to oxidation and isomer inclusion, our ideal crystal is probably to be found elsewhere. Molecules containing certain functional groups can be more specifically purified by chemical methods.

4. Exciton Transfer and Its Dependence on Temperature

Experiment does not indicate that excitation energy is transferred via excitons *per se*, although many of the results are consistent with this model. In certain cases other descriptions of energy transport such as long range dipole-dipole coupling[59] or multi-stage processes (Sec. III-3) may be more appropriate. The diffusion length of free excitons has been calculated[60–63] and estimated from experiments.[64–66] There is fair agreement between the two approaches although the former are still very approximate.

The guest-host fluorescence yield ratio is attenuated at reduced temperatures. For the anthracene-tetracene system the attenuation occurs between 100 and 4.2°K.[42–44] The stilbene-tetracene system shows a change between 300 and 77°K which is unambiguously related to a change in energy transfer efficiency.[33] Figure 10 shows the tetracene fluorescence yield when (a) the host crystal is exclusively excited and (b) the tetracene is exclusively excited. The decrease in yield with increasing temperature in the latter case is due to the increased probability of nonradiative conversion of tetracene excitation energy into heat.

This type of evidence favors the exciton picture. The defect lattice model of Agranovich[67] predicts the type of temperature variations that are observed, but the theory does not suggest critical experiments. For a quasi-equilibrium distribution among defect levels, free excitons, and impurities, the observed temperature dependence of the quantum yield of impurity fluorescence ϕ_T can be obtained more simply from steady-state kinetics:

$$\phi_T = A \sum_i \exp\left[-\,h(\nu_0 - \nu_i)/kT\right] + B(1 + C_D/C_T)^{-1}\,,$$

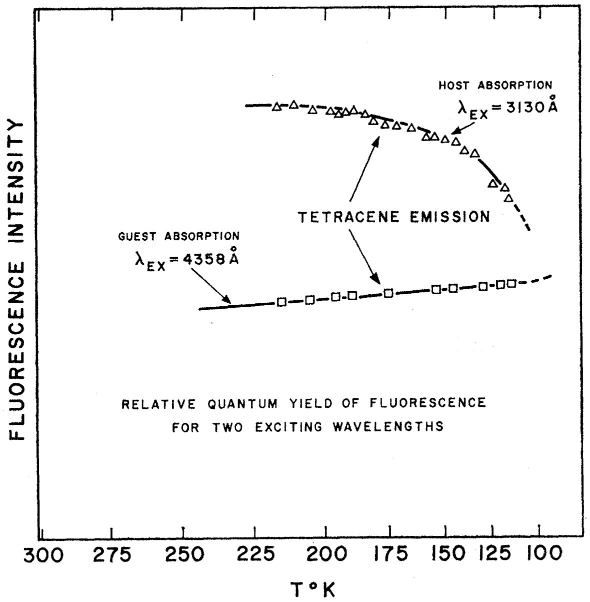

FIG. 10. Unambiguous demonstration of the variation of energy transfer efficiency with temperature; stilbene-tetracene systemÅ. 3130 light is uniquely absorbed by the host crystal; 4358 Å light is absorbed by the guest molecules. In each case the guest emission is observed.

where A and B are constants for a particular crystal; ν_0 is the energy of the free exciton band; ν_i is the energy of the ith defect site; and C_D and C_T are the concentrations of defect sites and impurity molecules, respectively. According to Fig. 10, which illustrates a near exponential increase of ϕ_T with increasing temperature, $\nu_0 - \nu_i$ is approximately 150 cm^{-1}. This is in good agreement with many of the line positions near the absorption edge.

The decrease of energy transfer efficiency at low temperature can also be interpreted in terms of the decreased overlap of emission (host) and absorption (guest) spectra. The rate of energy transfer between dissimilar molecules is proportional to the probability that an allowed emission transition in an excited molecule happens to coincide with a vibronic transition in a nearby unexcited molecule. This probability depends on the vibronic band width. In crystals the band width is affected by the extent of the interaction of electronic and/or vibrational states of molecules with the lattice vibrations. Thus the regions of resonance coincidence between donor-excited and acceptor-unexcited molecules should be reduced at very low temperatures. A pronounced sharpening of guest molecule absorption bands usually occurs between 77 and 20°K which coincides with the tem-

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[59] Th. Förster, Ann. Physik. (Liepzig) 2, 55 (1948).

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

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[64] J. Ferguson, Australian J. Chem. 9, 172 (1956).

[65] D. C. Northrup and O. Simpson, Proc. Roy. Soc. (London) **A234**, 136 (1956).

[66] H. C. Wolf, Z. Physik **139**, 318 (1954); **145**, 116 (1956).

[67] V. M. Agranovich, Uspekhi Fiz. Nauk. **71**, 141 (1960).

perature region for energy transfer attenuation in most crystals.

5. Band Shapes in Absorption and Fluorescence

This aspect of organic crystal spectra has been neglected, both theoretically and experimentally. The same is not true for inorganic crystals.[68] In fact, the band shape may give valuable information regarding the structure of the Brillouin zone. The ideal cases are shown in Fig. 11. Due to the law of conservation of momentum, electronic transitions may occur to certain regions of the zone given by (see Sec. I-4)

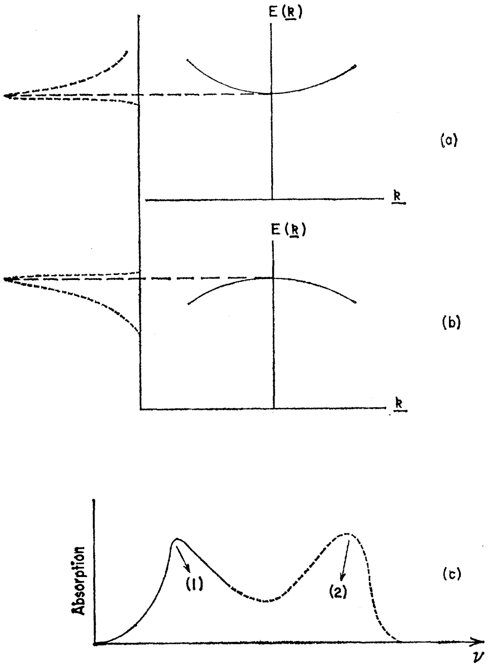

FIG. 11. Simplified band shapes for electronic spectra of molecular crystals, (a) blue shading, (b) red shading, (c) intensity distribution for overlapping bands.

$$\hbar\mathbf{k} + \hbar\mathbf{p} = \hbar\mathbf{Q} \, .$$

Since this selection rule is satisfied by a broad range of phonon momenta, a quasi-continuous range of photon energies are associated with a single electronic transition. Thus crystals will show absorption bands rather than the "lines" predicted in the zero approximation. The pure electronic states with wave functions $\Psi(\mathbf{r},\mathbf{R},O)$ are broadened by mixing with the nearby quasi-continuum of levels $\varphi(\mathbf{r},\mathbf{R},\mathbf{Q} - \mathbf{p})$ corresponding to states of wave vector $\mathbf{k} = \mathbf{Q} - \mathbf{p} \neq 0$. For Brillouin zones of the type shown in Fig. 11 (a) the crystal band will appear "blue shaded." Figure 11 (b) illustrates the other extreme. In actual cases this oversimplified picture will be complicated by overlapping bands in **k** space; however, the model may be applicable to certain absorption bands in a spectrum, e.g., the 0 − 0 band. In diffuse spectra effects of this nature should be manifested by unsymmetrical bands showing long-wavelength convexity and concavity of the shape of the band relative to the base of the spectrum [see Figure 11(c)].[68] It should be possible to observe "line" spectra in emission because the lattice vibrations will appear in separated transitions of exciton-phonon combinations.[69] A few bands in the absorption spectra of naphthalene[26] and phenanthrene[32] appear "blue shaded." There are numerous examples of electronic-lattice vibrational combinations in emission spectra.

6. Energy Transfer and Crystal Type

The transfer of energy from a host matrix to an impurity molecule can occur if the lowest electronic state of the impurity lies at lower energy than the lowest exciton state of the crystal. This offers no complications for SB- and B-type crystals where the lowest exciton state (calculated) corresponds to the first absorption band of the crystal. For D types, mentioned in Sec. II-5, the lowest energy crystal states are not observed in absorption (see, e.g., Fig. 8) but correspond to symmetry forbidden states in $\mathbf{k} = 0$. Thus tetracene does not quench the luminescence of pyrene[64] or perylene even though the lowest electronic level of tetracene lies at lower energy than the *first absorption bands* of either pyrene or perylene crystals. However, the pyrene luminescence is quenched by small amounts of perylene which proves that excitation energy is propagated over sufficiently large distances in D-type crystals. For the pyrene-perylene mixed crystal the emitting level is possibly an associated electronic level produced by specific interaction between the guest molecule and its nearest neighbor.[52]

In view of these energy transfer experiments there appears to be some indication that D-type excitons move through the lattice *during the process of thermal equilibration.* This conclusion is in substantial agreement with the strong coupling model (Sec. II-5). An empirical correlation between crystal structure and emission has been suggested.[50] There is an urgent need for detailed energy transfer experiments using D-type host crystals, particularly excitation spectra of energy transfer at low temperatures.

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[68] Y. Toyozawa, Suppl. Progr. Theor. Phys. (Kyoto) 12, 111 (1959).

[69] Reference 12, Chap. VI.

7. The Defect Lattice

The role of defects in the crystal is twofold: excitation energy traps; and exciton scatterers. The former type will quench the "pure" crystal emission while the latter will enhance the exciton emission and limit exciton mobility. To the present there is no direct evidence for these processes although most crystal emission spectra have properties which are consistent with the defect-trap model. Defect levels may profoundly influence other photo-properties of organic crystals, e.g., photoconductivity, slow-fluorescence, and lowest triplet state emission.

8. Slow Fluorescence

The simplest description of molecular crystals does not encompass energy storage states which could trap excitation energy for about 10^{-2} to 10^{-3} sec. At the present time there appear three possibilities for the mechanism of delayed fluorescence.

(*a*) *The utilization of molecular metastable states.* Under this heading are the following two possibilities: That the crystals contain an impurity with a metastable state (e.g., a lowest triplet level of a molecule with a singlet ground state or the ionized state of a donor or acceptor impurity) which lies in the region of the exciton band; that the lowest triplet levels of the crystal can be caused to regenerate singlet excitons through "two quantum" interactions of triplet excitons. The former explanation for very low temperatures requires a most improbable coincidence of excited levels. The latter is feasible, especially since it is just *those crystals with appreciable phosphorescence which exhibit slow fluorescence.* If this explanation is correct, the yield of slow fluorescence should increase as the square of the incident light intensity for certain intensity ranges.

(*b*) *Exciton dissociation and electron-hole recombination.* An important property of molecular excitons is the strong binding between the excited electron (e) and its positive hole (h). The binding energy is given approximately by

$$D_{e-h} = I_e - \Delta E(\mathbf{k}) - J_{eh} + A$$

where D_{e-h} is the binding energy, I_e is the ionization potential of a molecule in the crystal; $\Delta E(\mathbf{k})$ is the energy of the lowest exciton band; J_{eh} is the Coulomb attraction; and A the electron affinity of a molecule in the crystal. D_{e-h} will be around 2 to 3 eV for the complete separation of electrons and holes in crystals of aromatic hydrocarbons. The value of D_{e-h} for nonvertical values of I_e and $\Delta E(\mathbf{k}), \mathbf{k} \neq 0$, may be considerably less (see Fig. 12), in which event a small probability of spontaneous transitions to the ionization continuum might arise. The lifetime for slow fluorescence will then be determined by the rate of recombination of electrons and holes. Mechanisms of this general nature have been considered previously[55] although the obvious test experiments are not yet in the literature.

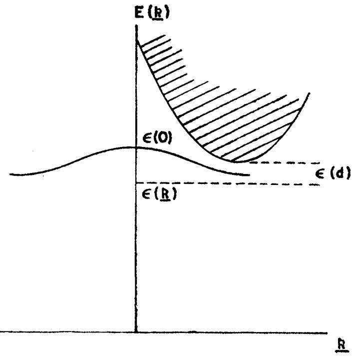

FIG. 12. Ionization states in a molecular crystal. The continuum is crosshatched.

(*c*) *Defect trapping sites.* Certain defect levels may provide a route to energy storage states although it is difficult so to envisage such long lifetimes in view of the relatively fast rate at which (singlet) excitation energy is transformed into heat. One method by means of which defects may store energy is illustrated in Fig. 13. If two molecules, adjacent in the crystal, have the appropriate relative orientations, the resulting electronic levels of the "dimer" defect may be as shown in Fig. 13. The transition from the lowest defect level is forbidden and the lifetime correspondingly increased. The exciton could be regenerated by the two quantum process described in (*a*), or by the excitation of certain lattice motions. The situation described in Fig. 13 is analogous to the energy storage

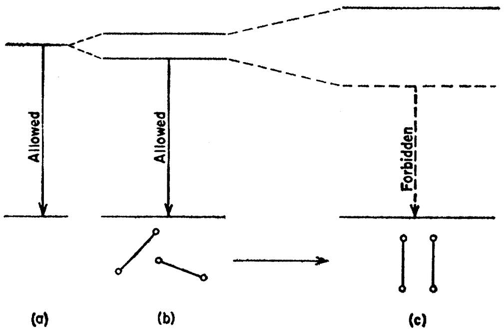

FIG. 13. A possible role of defects in the mechanism of delayed fluorescence in molecular crystals: (a) free molecule levels, (b) crystal levels, (c) a possible defect energy trap.

mechanism postulated by El-Bayoumi and Kasha[70] in studies of fluorescence quenching of dimers in solution.

9. Photoconductivity

The photoconduction of aromatic crystals appears to be related to the luminescence inasmuch as those crystals which luminesce with highest efficiency are often best photoconductors. Therefore, if photoconductivity is to be efficient, the lowest excited state of the crystal should not rapidly decay nonradiatively. This, in turn, suggests that photoconductive states are not populated "vertically," but involve the relaxation of exciton waves within the Brillouin zone. A probable zone structure is shown in Fig. 12. In this representation the initial kinetic energy of an exciton $[\epsilon(0)-\epsilon(\mathbf{k})]$ is larger than the binding energy $\epsilon(d)$ of the exciton, which is then able to dissociate into a free electron and a hole by emitting or absorbing phonons. In this example exciton absorption contributes directly to the photoconductivity which would necessitate that the photoelectric threshold and the exciton origin be reasonably close together. Such is apparently not the case for molecular crystals where there can be a gap of up to 2 to 3 eV. The presence of defects or impurities could provide other pathways for exciton dissociation if there were sufficient energy available at the active sites. Conjectures of this nature could readily be tested experimentally, by measurements of reflexion spectra, quantum yields, excitation spectra of slow fluorescence, photoconductive anisotropy, and the slow fluorescence of crystals in strong electric fields.

ACKNOWLEDGMENTS

It is a pleasure to thank Dr. Michael Kasha and Dr. William Rhodes for generous criticism and stimulating discussion.

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Polarization, Pyroelectricity, and Ferroelectricity of Ionic Crystals

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