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Relation between Exciton Bands and Conduction Bands in Molecular Lamellar Systems*

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1. INTRODUCTION

BIOPHYSICAL investigations on a molecular level turn naturally to the phenomena of energy transfer and electron transfer for the interpretation of the behavior of the ordered structures found in biological systems. The famous Korányi lecture[1,2] of Szent-Györgyi has done much to stimulate interest in these phenomena, although earlier recognition of their importance, e.g., in the photosynthetic system, had been made.

The general tendency in this field at present seems to be the adoption without caution of the ideas and terminology of the solid-state physics of atomic and ionic semiconductors, to the interpretation of biological systems. Since the latter are usually molecular aggregates bound weakly by van der Waals forces (molecular lamellae) or very strongly by overlap forces (intramolecular forces in proteins), it is worthwhile to examine critically the differences between the atomic and molecular array problems, to see how valid is the application of the ideas of solid-state physics to biological mechanisms.

Since most of the treatments of the exciton theory are presented in fairly intricate mathematical terms, an attempt is made here to give a simple but accurate account of excitation-energy transfer as well as of electronic conduction in atomic and molecular aggregates.

2. EXCITONS

The theory of excitons in atomic lattices was developed by Frenkel,[3,4] and elaborated later by other physicists.[5–10] The application of exciton theory to molecular crystals was first made by Davydov.[11,12] A semiclassical treatment of excitons in van der Waals pigment polymers was given by Förster.[13] Qualitatively the same idea was also used by Förster to interpret the spectra of pigment dimers, and has been treated quantum mechanically by Simpson's group.[14] The extension to excitons in pigment aggregates of various geometries has been made by McRae and Kasha.[15] The problem of energy transfer between pairs of randomly oriented molecules was treated quantum mechanically by Förster.[16] All of the foregoing studies make use of the same physical basis, which is described in the following. Several papers of a descriptive nature on the topic of energy transfer have been published,[17–20] mainly from the phenomenological viewpoint.

Three different definitions of the *exciton* have been given, illustrating different aspects of the idea, but not all of which seem equally suitable for a critical understanding:

(1) Exciton states involve excitation of an assembly of atoms (or molecules) in concert, instead of localized excitation of individual species of the assembly.

(2) An exciton can be described by a wave packet traveling through an assembly of atoms (or molecules), and arising from a superposition of exciton states (defined in the foregoing).

(3) An exciton is a neutral excitation "particle," consisting of an electron and a positive hole, traveling together through the lattice.

Each of these definitions is next considered in order to clarify the picture of an exciton.

For a discussion of the first definition of an exciton, consider a simple two-dimensional model of an atomic and a molecular lattice [Figs. 1(a) and 1(b)]. The atomic lattice is assumed to be an ionic one held together by Coulombic forces (for simplicity, the positive and negative ions are not distinguished, the ions are assumed to be isoenergetic in their electronic states throughout, and overlap is assumed to be negligible in the ground state of the lattice). All but one of the ions are shown to be in their ground state, indicated schematically by circles representing spherically symmetrical orbitals.† The ion (2,2),‡ however, is shown with an electron excited to a p-type orbital. This model of the excited lattice forms the basis of what is designated as a *zeroth-order* description, because it is not possible to localize excitation to one atom in such a system. Thus, atom (3,2) might equally well be excited, etc. Abstracting the second row of atoms for simplicity, the following zeroth-order descriptions could be given of singly excited states (where asterisk denotes excitation of atom A_n)

$$(\text{i}) = A_1{}^*A_2A_3A_4,$$
$$(\text{ii}) = A_1A_2{}^*A_3A_4,$$
$$(\text{iii}) = A_1A_2A_3{}^*A_4,$$
$$(\text{iv}) = A_1A_2A_3A_4{}^*.$$

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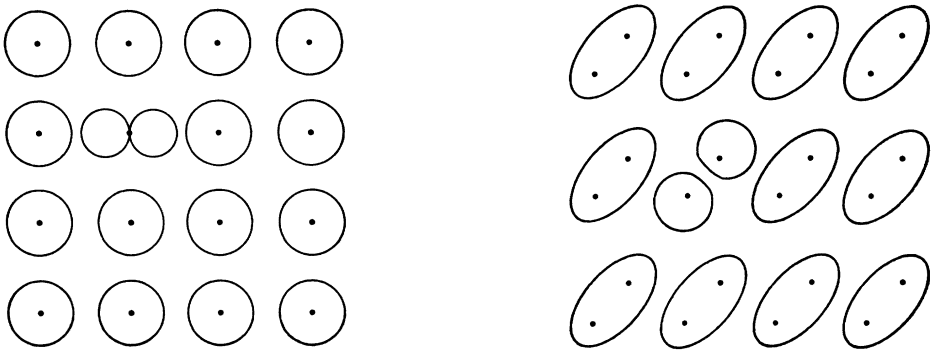
† The biologist unfamiliar with the characteristic three-dimension orbital wave functions of atoms and molecules will find it helpful to consult *The Chemical Aspects of Light* by E. J. Bowen [(Clarendon Press, Oxford, England, 1946), second edition], especially pages 68, 100–115, and 139.

‡ Row 2, column 2, from left upper corner.



(a) (b)

FIG. 1. (a) Zeroth-order description of a section of an atomic lattice having one atom with an electron in its lowest excited orbital, the remaining atoms with electrons in their ground orbitals. (b) Zeroth-order description of a section of a molecular lattice with one molecule with an electron excited to its next highest orbital, the remaining molecules with electrons in their ground orbitals.

None of these is by itself a suitable description of the excited array, since they could (according to the assumption) all have the same energy, and if they could *interact* with each other, new states which are true stationary states in the quantum-mechanical sense will arise. These new states are the *exciton states* of the first definition; if only the foregoing four atoms were considered, they would have the form

$$\mathrm{I}=\frac{1}{\sqrt{4}}[(\mathrm{i})+(\mathrm{ii})+(\mathrm{iii})+(\mathrm{iv})],$$

$$\mathrm{II}=\frac{1}{\sqrt{4}}[(\mathrm{i})+(\mathrm{ii})-(\mathrm{iii})-(\mathrm{iv})],$$

$$\mathrm{III}=\frac{1}{\sqrt{4}}[(\mathrm{i})-(\mathrm{ii})-(\mathrm{iii})+(\mathrm{iv})],$$

$$\mathrm{IV}=\frac{1}{\sqrt{4}}[(\mathrm{i})-(\mathrm{ii})+(\mathrm{iii})-(\mathrm{iv})],$$

where the signs (see later) result from the requirement (of orthogonality) that the stationary states (I) to (IV) be completely independent. This statement would be true only if it were appropriate to assign an equal weighting to each of the zeroth-order states, i.e., for an infinite array. The present argument is artificial in the sense that it attempts to simplify the picture by abstracting four molecular units from a very large aggregate. It should be noted that each of the stationary exciton states involves all of the zeroth-order descriptions; that is, *each of the stationary exciton states involves excitation of all of the atoms considered as locally excited.* Thus, in the exciton states the excitation is delocalized.

The second definition arises from the possibility, pointed out by Frenkel,[3,4] of construction of wave packets from the stationary exciton states. This is a useful aspect for discussions of electronic energy transfer in atomic and molecular systems. The properties of the wave packet can be calculated by quantum-mechanical methods.[7,9,10]

The third definition can be misleading, so its meaning is examined more fully. In Fig. 1(a), the atomic ion (2, 2) is schematically shown to have an electron in a *p*-type excited orbital. Both the excited atom and the ground-state atom are electrically neutral and electronically symmetrical. The excited atom is produced from a ground-state atom by the polarizing influence of the electric vector of the interacting light wave (the electric vector having been taken to be horizontal, and in plane). While the light wave impinges, a *transitory dipole moment* is induced in the atom, but no permanent charge separation, i.e., ionization, takes place. Thus, the definition of an exciton as an "electron-positive hole" combination can be meaningful largely in a figurative sense, since the exciton involves excited *bound-electron* states of the electron and its originating atom. To actually ionize the "pair" requires the additional energy between the exciton level and the ionization limit.

On the other hand, the transitory dipole induced by the light wave would be directly the cause of the interaction of the zeroth-order states, since all neighboring dipoles could interact with each other in a purely electrostatic way.§ Incidentally, the signs in the exciton states (I) to (IV) should not be taken to mean electron nodes (as in ordinary electronic wave functions), but nodes signifying the phase relation between the transitory dipole moments of the zeroth-order states (see Sec. 4).

The molecular lattice of Fig. 1(b) can be discussed analogously. It is assumed that here van der Waals forces bind the molecules into ordered layers (crystals, or lamellae), and that negligible electron overlap is present in the ground and lowest excited states. The molecular axis is shown inclined at 45° to the layer direction; for simplicity, a two-center molecular orbital is considered. The molecule shown excited (2, 2) has an electronic orbital node perpendicular to the molecular axis. The excited molecule is thus electrically neutral and symmetrical, and is produced from a ground-state molecule by a light wave of the right frequency with

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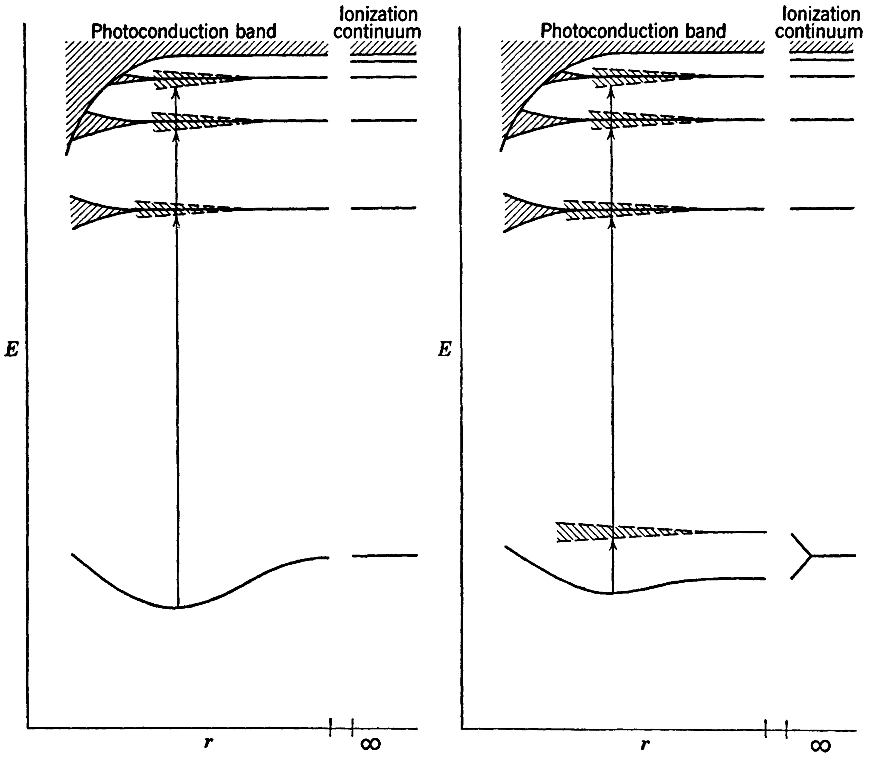
§ In the formal treatment of the theory, the expansion of the intermolecular interaction potential results in a series of terms, of which the dipole-dipole terms are the predominant ones for formally allowed electronic excitation.



(a) (b)

FIG. 2. Schematic energy *vs* interspecies-distance curves for a crystal or aggregate taken as a whole. (a) atomic lattice, (b) molecular lattice or lamellar structure, showing onset of exciton bands and conduction bands. Exciton-band splitting exaggerated, and overlap interaction shown independent of dipole-dipole interaction (cf. Fig. 3).

its electric vector oriented along the molecular axis. The identical symbolic description of the zeroth-order states and exciton states, used for the foregoing atomic lattice model, is applicable to this molecular model.

From the foregoing discussion, it should be clear that exciton states cannot impart electrical conductivity. It is found experimentally that excitation of atomic lattices to exciton states produces no photoconduction of electrons (see Sec. 4).

3. ORIGIN OF EXCITON BANDS AND CONDUCTION BANDS

The origin and relation of exciton bands and conduction bands may be clarified by a discussion of their dependence on interspecies distance. In Fig. 2 are given, schematically, energy *vs* interatomic (interionic) distance (a) and energy *vs* intermolecular distance (b) for the energy levels of a crystal or aggregate taken as a whole.

The atomic array is assumed, as before, to be made up of ions with isoenergetic electronic states, brought together into a Coulombic lattice (positive and negative ions not distinguished). Since the *Coulombic* potential varies as $1/r$, it would be effective at the greatest interatomic separations, and strong ground-state binding results [Fig. 2(a)]. Next in distance dependence would be the long-range $1/r^3$ *dipole-dipole* interaction between excited states. Depending upon the strength of the interaction, each state of the isolated ion would split into an N-fold exciton band (where N equals the number of ions in the assembly). The exciton-band width[15] is proportional to the intensity of the transition in the unit species, and depends upon the orientation of the transition dipole moments (besides the $1/r^3$ dependence, and a rather insensitive function of the number of unit species in the array). Finally, there is the extremely short-range electron *overlap* interaction. This short-range characteristic of overlap forces arises from the exponential fall of electron orbital wave functions in the exterior of atoms (and molecules). In Fig. 2(a), it is assumed that negligible overlap is present in the ground state of the atoms, but that, in the excited state, overlap may occur yielding a conduction band, because of orbital expansion upon high quantum-number excitation. If there is overlap in the ground state, a *valence band* is said to arise, analogous to the conduction band for the excited states.

The point to be noted from the above is that, because of the long-range nature of the dipole-dipole interaction, nonphotoconducting exciton bands can exist discrete from the photoconduction bands. Nevertheless, atomic exciton bands usually lie not far below the photoconduction band of atomic lattices.

The molecular case has some qualitatively different features. However, it is well known that gaseous molecules exhibit converging series absorption in the vacuum ultraviolet (molecular Rydberg series) whose convergence limits represent the ionization potentials for various electrons in the molecule. One could antici-

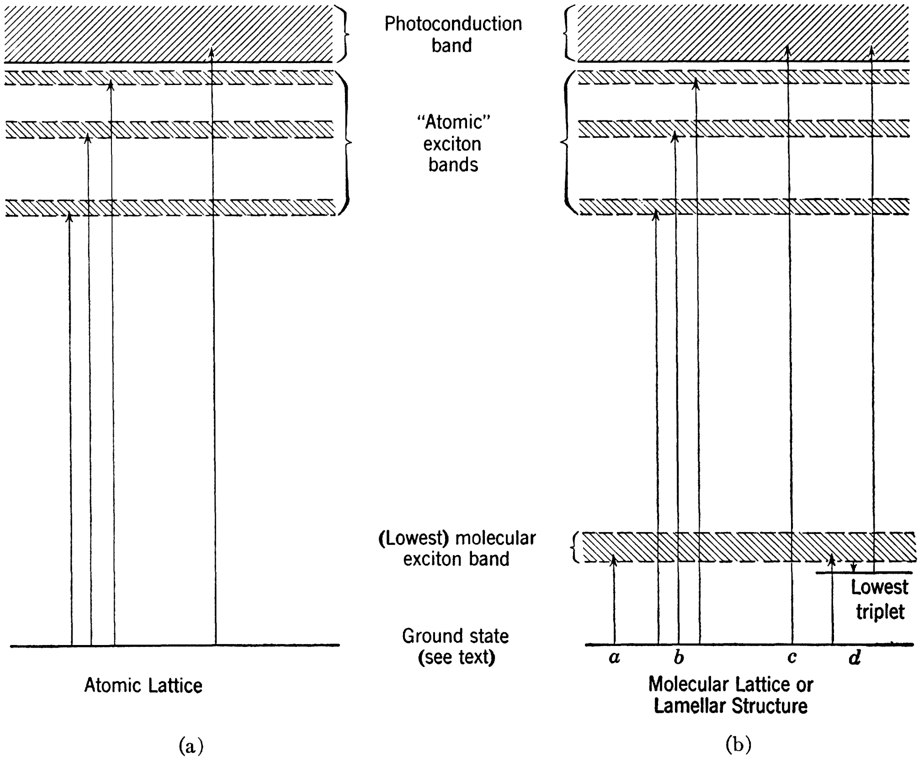


FIG. 3. Energy-band diagram at equilibrium separation for a crystal or aggregate taken as a whole. (a) atomic lattice, (b) molecular lattice or lamellar structure.

pate that dipole-dipole interactions between the electrons in Rydberg levels would give rise to "atomic" exciton bands. These are indicated in the upper part of Fig. 2(b), analogous to the exciton bands of Fig. 2(a).

In addition, a molecule during its formation from atoms [at $r=\infty$ for molecular lattice; lower right corner of Fig. 2(b)] gives rise to excited (unfilled) molecular orbitals. For simplicity, only one filled and one excited orbital are indicated. In the formation of the molecular lattice, therefore, while the ground state becomes slightly lowered in energy through a weak van der Waals interaction, the molecular excited states of the assembly spread by dipole-dipole interaction into an N-fold exciton band (N equals the number of molecules in the assembly). Since molecular transitions are frequently very intense (oscillator strength $f \sim 1$), a large band splitting is to be expected (see later). Moreover, since highly conjugated molecules (i.e., pigment or dye molecules) have rather low-energy excited states, exciton bands far from the conduction band should be observed.

4. PROPERTIES OF EXCITON BANDS

The electrically nonconducting characteristic of exciton bands has been referred to above, and the physical basis for this property has been discussed. Some additional characteristics of atomic exciton bands are now mentioned. It is typical of atomic lattices that exciton bands are usually observed just below the conduction band. The optical properties of, e.g., the alkali halide crystals conform roughly to a behavior described by Fig. 2(a), which for the equilibrium interatomic separation yields an energy-level diagram such as Fig. 3(a). The pure alkali halide crystals are properly described as electrical *insulators* rather than as semiconductors, as far as their electronic behavior is concerned. For example, the KCl crystal[8,10] exhibits its first exciton band as a broadened line at 7.6 ev ($\bar{\nu} \sim 61\,000$ cm^{-1}, $\lambda \sim 1620$ A). Excitation of this band produces no photoconductivity. At 9.44 ev ($\bar{\nu} \sim 76\,000$ cm^{-1}, $\lambda \sim 1300$ A) photoconduction is observed. Thus, both types of bands are observed in the vacuum ultraviolet not far from each other. No contribution to dark conductivity would be expected at ordinary temperatures from this high-energy conduction band.

Another characteristic of atomic exciton bands is their occurrence in sets which fall into a converging series.[10] This behavior could be anticipated from their atomic character; i.e., the orbitals which would be used in the zeroth-order description of an atomic-lattice exciton are essentially hydrogenic in character, although extending over many lattice points. The series formulas are, of course, modified by the dielectric constant of the lattice, lattice interactions, etc.[10]

The band width for molecular exciton cases has been calculated[15] to be approximately 0.2 ev ($\Delta\bar{\nu} \sim 1600$ cm^{-1}) in linear pigment assemblies for an oscillator strength of 1 for the isolated molecule transition, at intermolecular distances of 10 A, and in a suitable geometry. Experimental studies indicate that this is the order of

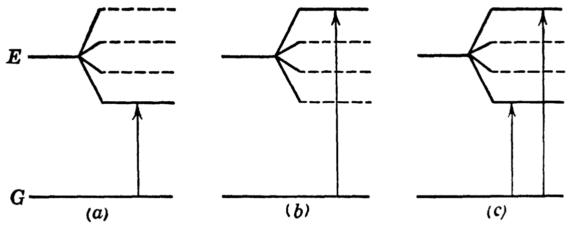


FIG. 4. Selection rules for exciton levels in linear arrays (cf. reference 15), for a hypothetical 4-unit molecular array. (*a*) head-to-tail, (*b*) card-pack, (*c*) alternate-translational-arrays of transition dipoles. Dashed line: forbidden exciton level; solid line: allowed exciton level. Diagram shows dipole-dipole splitting of zeroth-order excited states.

magnitude observed. For weaker optical transitions, or for greater intermolecular separations, smaller exciton-band widths can be expected.

The foregoing comments on exciton-band width are not meant to imply that optical transitions of isolated molecules are necessarily to be broadened in the lamellar aggregates. On the contrary, one of the characteristics[3,4,11,15] of exciton bands is the restriction of optical transitions to only certain components of an exciton band. For example, once more consider the abstracted linear array of four atoms of Fig. 1(a). The exciton states (I) to (IV) can be depicted by vector models representing the dipole moments induced by the light wave with electric vector in the direction of the array,

$$\begin{aligned}&\mathrm{I}\rightarrow\rightarrow\rightarrow\rightarrow,\\&\mathrm{II}\rightarrow\rightarrow\leftarrow\leftarrow,\\&\mathrm{III}\rightarrow\leftarrow\leftarrow\rightarrow,\\&\mathrm{IV}\rightarrow\leftarrow\rightarrow\leftarrow.\end{aligned}$$

The dipole-dipole interaction would give (I) the lowest energy and (IV) the highest. Also, the resultant transition moment (vector sum of the individual moments) is finite in the case of (I), but zero for the remaining three states. Thus, the exciton band for this case would be observed to have the structure shown in Fig. 4(a), with only the lowest exciton state permitted in optical absorption. Thus, for this example, a long wavelength or red shift would be observed in the linear aggregate compared with the isolated atomic species, rather than a band broadening. Cases 4(b) and 4(c) correspond to other geometries for a linear array, the former for a card-pack orientation of dipoles, and the latter for an alternate translational orientation. The staggered arrangement of naphthalene molecules in the crystalline state also leads to this last result.[11] For an N-fold linear array, even though the exciton band will now have N components, analogous selection rules to those illustrated in Fig. 4 still apply.[15] Obviously, the ground state is not affected by the exciton process.

Finally, in the special case of dye-molecule aggregates, one additional result of exciton-band formation is to be noted. This is the enhancement of triplet excitation accompanying molecular aggregation.[14,15] Referring to Fig. 3(b), four separate electronic processes in molecular aggregates can be delineated: (a) molecular exciton-band excitation, (b) "atomic" exciton-band excitation, (c) photoconduction excitation, and (d) triplet excitation following exciton-band excitation.[14,15] The recently reported, dramatic experiments by Albert Szent-Györgyi, demonstrating[21] great enhancement of phosphorescence in dyes frozen in water solutions, seem to be due to the foregoing phenomenon.[15]

Furthermore, since triplet states of molecules have lifetimes of a millisecond or longer, double quantum processes such as the triplet to conduction-band process shown in Fig. 3(b) may be expected, following exciton-band, then triplet excitation. The exciton-band-to-triplet process is radiationless. In most dyes, the radiationless excitation of triplets is very weak in isolated molecules.

The Förster theory,[16] with its phenomenological aspect, permits useful calculations to be made on distance of dipole-dipole transfer of excitation energy. Karreman and Steele[22] have shown that excitation energy transfer in proteins by dipole-dipole interaction through the aromatic residues is plausible according to the Förster formula.

In this section, the complications[23] of intramolecular vibrational-electronic coupling in exciton interactions have been omitted for simplicity.

5. MOLECULAR SYSTEMS AS PHOTOCONDUCTORS AND SEMICONDUCTORS

If the energy gap between the ground state (or valence band) and the conduction band of an atomic lattice is small, intrinsic electrical conductivity is observed. For example, in pure germanium and pure silicon, the energy gaps are 0.7 and 1.10 ev ($\bar{\nu}\sim 5600$ and 9000 cm^{-1}), respectively.[10] In these solids, enough electrons can be thermally excited at room temperature so that dark electrical conductivity can be observed. The term semiconductor is applied,[10] arbitrarily, to solid materials which have a resistivity in the range 10^{-2} to 10^{9} ohm cm. For pure diamond, with an energy gap of 6 ev ($\bar{\nu}\sim 49\,000$), light of $\lambda\sim 2100$ A would be required to raise an electron to a conduction band. Materials which exhibit only photoconductivity are properly classified as insulators. Since molecular ionization potentials (gas phase) are in the range[24] 8 to 10 ev, one would expect pure molecular crystals and aggregates to act as insulators, having photoconductivity perhaps for 6 to 8 ev quanta, not intrinsic electrical semiconductivity. Observations of a weak photoconductivity have been made in organic crystals absorbing near-ultraviolet light, but evidence has accumulated that, in pure single crystals, even this weak photoconductivity becomes vanishingly small as surface effects, impurities, etc., are eliminated.[25]

On the other hand, there are several reports of semiconductivity in certain organic substances in the class of molecular crystals, especially those of Eley *et al.*[26–28]

The general observation seems to be that, if a molecule has an optical transition at around 1 ev ($\bar{\nu}\sim 8067$ cm^{-1}, $\lambda\sim 12\,500$ A), semiconductive behavior may be observed. This seems to be a necessary condition for semiconductivity, but not a sufficient one (see the following). For example, metal-free phthalocyanine exhibits semiconductivity (temperatures up to 400° C are used), with an indicated energy gap of ~ 1.2 ev ($\bar{\nu}\sim 9900$ cm^{-1}, $\lambda\sim 10\,200$ A). However, the lowest allowed optical transition in phthalocyanine is near the infrared, but not in the infrared. The side question that arises is whether the energy gap determined by the temperature dependence of the semiconductivity is in error, or whether the lowest triplet state (which seems to be in the region of $\lambda\sim 10\,000$ A[29]) is involved. Contrariwise, those substances which absorb only in or near the ultraviolet, such as diphenylbutadiene and diphenyloctatetraene, exhibit no dark semiconductivity,[26–28] indicating an energy gap of greater than 2.2 ev (~ 50 kcal/mole, $\bar{\nu}\sim 17\,000$ cm^{-1}, $\lambda\sim 5800$ A).

For intrinsic semiconductivity, not only must there exist a small gap between the filled levels and the unfilled levels, but there must exist sufficient intermolecular orbital overlap for a true conduction band to develop. Apparently, in the case of near ultraviolet-absorbing hydrocarbons, only a nonconducting exciton band may exist in the crystal. The stronger the van der Waals forces become, the greater is the chance that overlap interaction resulting in a conduction band will arise. Especially in the case of such dye-like molecules as pure phthalocyanines, chlorophylls, and cyanine dyes, one might anticipate significant development of a conduction band from overlap of the lowest excited-state orbitals. However, since resistivity measurements cover a wider decadic range[10] than almost any other physical property, and since conductivity measurements using powder samples are so subject to experimental artifacts, one cannot accept the observed results without caution as indicating that molecular crystals are good semiconductors at room temperature.

The semiconductivity reported[26–28] for proteins occupies a strange position. It is well known that proteins absorb in the ultraviolet, which would indicate that only photoconductivity could result, again if there were sufficient orbital overlap. Evans and Gergely,[30] in a widely misinterpreted paper, proposed that π-electron overlap *across* hydrogen bonds could give rise to sufficient overlap interaction to yield a "conduction" band. Using three different models, they obtained choices for the energy gap between the valence band (ground state) and conduction band of 3.5, 4.8, and 3.2 ev ($\lambda\sim 3500$, 2600, and 3800 A), respectively. [Eley *et al.*[26–28] quote an energy gap as given by Evans and Gergely to be ~ 2 ev ($\lambda\sim 6200$ A), but this is their value for the gap between two *filled* valence bands.] Thus, according to this discussion, and according to the pattern of results of Eley *et al.*,[26–28] *Evans and Gergely proved* (within the severe limits of their calculation) *that a pure protein should be an electrical insulator, exhibiting only photoconductivity and not semiconductivity.*

The semiconductivity observed[26–28] in proteins cannot be *intrinsic*, but if it is truly electronic, it may be *extrinsic*.[10] Extrinsic semiconductivity arises generally from the presence of lattice imperfections or impurity centers, which introduce new energy levels into the term scheme for a lattice structure. In biological systems, such perturbations of the perfect lattice probably play a very important role, and all of these discussions of the pure or perfect molecular lamellar structures are modified by their consideration. New energy levels appear in such systems, often greatly lowering the energy required for conductivity phenomena.[10]

The experiments of Arnold and Sherwood[31] demonstrate that, in the complex, heterogeneous structure of chloroplast, electron traps exist and are involved in luminescence and conductivity properties of the chloroplast. This type of investigation probably has valuable extension to other complex biological systems, and much valuable correlation with solid-state physics might be made in this connection. On the other hand, in the extremely small conductivity of weak semiconductors and insulators, it is difficult to unravel[8] ionic from electronic semiconductivity. Probably in proteins and chloroplasts, there is an appreciable ionic component of electrical conductivity.

6. PHOTOPHYSICAL STEPS IN THE PRIMARY PROCESS OF PHOTOSYNTHESIS

Since the work of Emerson and Arnold[32,33] and of Gaffron and Wohl,[34] it has been evident that absorption of energy by chlorophyll in chloroplast involves exciton behavior (called "resonance energy migration" in most of the literature). The review by Rabinowitch[20] summarized the recent status of this topic. However, since newer investigations have revealed that in pigment lamellar aggregates triplet excitation is facilitated,[14,15] the detailed primary photophysical steps require re-examination.

The lowest triplet states of chlorophyll-*a* and chlorophyll-*b* have been established spectroscopically by Becker and Kasha[29] to be at approx 1.42 ev ($\bar{\nu}\sim 11\,500$ cm^{-1}, $\lambda\sim 8700$ A). The quantum yield of triplet excitation (via excited singlet state) is so small in monomeric chlorophyll as to suggest that the lowest triplet state could not participate in the efficient process of photosynthesis. However, the finding[14,15] that triplet excitation is greatly enhanced by aggregation of pigment molecules suggests strongly that this mechanism may play an important role in the chloroplast. The process would involve excitation to the chlorophyll exciton band, followed by triplet excitation [Fig. 3(b), first steps of process *d*]. As in other pigments,[14,15] the quantum yield of fluorescence of aggregated chlorophyll (in the leaf) is diminished many-fold over that of isolated molecules in solution,[35] as would be required if enhancement of triplet excitation occurred.

The detection of photoproduced radicals in chloroplast by electron paramagnetic-resonance studies made by Commoner *et al.*[36–38] and investigated further by Calvin *et al.* (p. 157 and references 39–41) poses the question of the relation of the primary photophysical process of exciton-band excitation to the secondary photochemical process of radical production. The picture presented by Calvin and co-workers[41] proposes ionization at the exciton stage. It is possible that in the heterogeneous chloroplast structure some low-energy ionization center could exist, which traps the exciton energy, leading to the direct production of the radicals detected. But the energy of this exciton band is small ($\sim$1.8 ev, or $\sim$41 kcal/mole), and the existence of such low-energy ionizations is unknown in molecules. Moreover, the lowest exciton state is very short-lived, somewhat shorter in life than the lowest excited singlet state of isolated chlorophyll, so that it may not be a very efficient state for a photochemical act.

The lowest triplet state of chlorophyll has been observed to have a mean lifetime of approximately 1 msec in solution,[42,43] and would be expected to have a somewhat longer lifetime in the compact chloroplast structure. It is natural to favor the triplet state for participation in the photochemical act, especially in view of the previously discussed enhancement possibility. Moreover, it is quite possible that these favorable properties of the triplet state would permit a two-quantum process to be important in the photosynthetic system. For example, as shown in Fig. 2(b), even triplet-to-conduction-band excitation might be considered. The two-quantum hypothesis of Franck[44,45] has now mainly the objection[46] that the upper state he proposed for the second quantum was a triplet state, which must have a mean lifetime of less than 10^{-12} sec.

If the lowest triplet state of chlorophyll is involved in the primary process in photosynthesis, its steady-state concentration could be too low to detect by electron paramagnetic-resonance absorption. Moreover, special orientation problems are involved which have been only recently solved.[47] It seems fairly certain that a triplet state of chlorophyll in chloroplast could not be detected by electron paramagnetic resonance.

The phenomena of solid-state physics have much to contribute to the understanding of the physical behavior of biological systems, but the richest development of experimental approaches and theoretical understanding requires that detailed attention be paid to the typically molecular behavior of the materials involved.

ADDENDUM

Since completing this manuscript, the writer has had the opportunity of studying the full text of Garrett's chapter[25] in *Semi-Conductor Chemistry*. His comprehensive review covers additional researches not included for consideration in the foregoing and emphasizes the difficulty of making significant semiconductivity measurements.

The quantitative treatment of excitons in molecular aggregates is in preparation by E. G. McRae and M. Kasha, and will be published shortly elsewhere. Reference to a preliminary communication on this work[15] has been made in the text.

ACKNOWLEDGMENTS

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