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ENERGY MIGRATION IN AGGREGATED PIGMENT SYSTEMS AND BIOLOGICAL ENERGY CONVERSION

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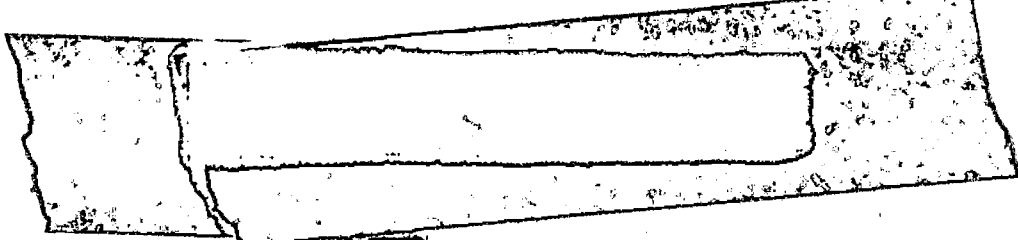
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AND BIOLOGICAL ENERGY CONVERSION

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ENERGY MIGRATION IN AGGREGATED PIGMENT SYSTEMS AND BIOLOGICAL ENERGY CONVERSION<sup>1</sup>

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ABSTRACT

In view of the importance of energy migration phenomena in biological energy conversion systems, a qualitative review is presented of exciton transfer and charge carrier migration in aggregated organic pigments. The application of these phenomena to photosynthesis is discussed.

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# ENERGY MIGRATION IN AGGREGATED PIGMENT SYSTEMS AND BIOLOGICAL ENERGY CONVERSION<sup>1</sup>

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## (1) Introduction

A characteristic feature of many biological energy conversion systems is the occurrence of highly conjugated organic molecules functioning either as light absorbers (chlorophylls, carotenoids etc.) or as components of oxidation-reduction couples (cytochromes). Morphological studies reveal the presence of apparently highly ordered lamellar structures consisting of pigments along with protein and lipid constituents. A further property of these systems is the ability to transfer energy from one component to another. For example, in photosynthesis it is known that electromagnetic energy can migrate from the so-called accessory pigments (phycocyanins, phycoerythrins, carotenoids etc.) to the chlorophylls (1,2,3,4). In addition, there is evidence for the existence of a functional photosynthetic unit consisting of several hundred chlorophyll molecules (5,6) which suggests that energy may migrate among the chlorophylls themselves. In the respiratory system, energy migration proceeds by the transfer of electrons from substrate through the cytochrome pigments to molecular oxygen (7).

Two types of energy migration are known to occur in pure organic molecular crystals. These are exciton transfer, which involves the migration of electromagnetic energy throughout the aggregate, and charge carrier migration, which involves the motion of free electrons and/or free positive holes. Thus, it has seemed natural to attempt to use these

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properties of the pure materials as models for the biological systems. It is of interest, therefore, to review some of the theoretical aspects of energy migration in aggregated pigments and to present some of the possible implications for biology, particularly for the photosynthetic system.

## (2) Energy Migration by Exciton Transfer

The principle experimental evidence for electromagnetic energy migration in organic molecular crystals is provided by studies of sensitized fluorescence, that is, fluorescence by molecules of one species excited by absorption in molecules of a different species. For example, the presence of traces of naphthacene (tetracene) dissolved in crystalline anthracene leads to fluorescence emission from both substances (8). When the naphthacene concentration is approximately 0.1 per cent, the anthracene fluorescence is almost completely replaced by the naphthacene emission. Similarly, traces of anthracene in crystalline naphthalene replace the ultraviolet fluorescence of the naphthalene with the blue-violet anthracene emission (8).

There are two mechanisms which have been invoked to explain these energy migration phenomena. One of these is the exciton theory which was first developed by Frenkel (9) and Peierls (10) and later applied to organic molecular crystals by Davydov (11), Craig and Hobbins (12) and Fox and Schnepf (13). Semiquantitative discussions of this theory have been given by Franck and Teller (14) and by Kasha (15). The other process is the resonance transfer of energy between molecules separated by large distances. This has been developed theoretically by Förster (16) and by Dexter (17). Inasmuch as most of the recent interpretations of the

electronic properties of molecular crystals have been in terms of the exciton theory, we will confine the present discussion to this theory. An excellent review of the current state of knowledge with respect to the theoretical and experimental aspects of organic crystal spectra has been given by McClure (18).

The basic assumption involved in the exciton theory is that the interaction energy between molecules in the crystal is small compared with the intramolecular energies so that the electronic structure of the molecules is essentially undisturbed by crystal formation. Such an assumption is consistent with the fact that the absorption spectra of most organic crystals are not much different from the spectra observed in the gas phase or in solution. This allows a wave function for the ground state of the crystal,  $\Phi_G$ , to be written to a first approximation as a simple product of molecular wave functions,  $\phi_k$  :

$$\Phi_G = \phi_1 \phi_2 \phi_3 \dots \phi_N = \prod_k \phi_k \quad (1)$$

If, now, we permit one of the molecules of the crystal or aggregate to be in an excited electronic state, we may write an excited state wave function,  $\Phi_i^*$ , in which the  $i$ th molecule is excited, as follows:

$$\Phi_i^* = \phi_1 \phi_2 \phi_3 \dots \phi_i^* \dots \phi_N = \phi_i^* \prod_{k \neq i} \phi_k \quad (2)$$

It is apparent that, if all of the molecules in the crystal are identical, all of the wave functions  $\Phi_i^*$  will be energetically equivalent. Therefore, if a mechanism exists by which excitation energy may be exchanged between molecules  $i$  and  $j$  in the aggregate, the wave functions for the excited state of the aggregate could be written as a sum, over all of the molecules, of the functions  $\Phi_i^*$ . This is equivalent to saying that a single excitation in an aggregate of molecules belongs to all of the molecules in the aggregate. Such a mechanism for energy exchange is introduced



into the theory in the form of a perturbation caused by dipole-dipole interaction between the transition dipole for the electronic transition<sup>3</sup> and an induced dipole in a neighboring molecule. The magnitude of this interaction will be proportional to  $\frac{1}{r^3}$ , where  $r$  is the intermolecular separation, and to the square of the transition moment integral for the ground state to excited state transition (18,19). Thus, the wave function for the excited state of the aggregate,  $\Psi^*$ , may be written as:

$$\Psi^* = \sum_{i=1}^N \Phi_i^* \quad (3)$$

and excitation energy may be said to migrate throughout the aggregate.

If one calculates an excitation energy for the crystal, using equations (1) and (3), one obtains (11):

$$\Delta E = \Delta E_m + D + E \quad (4)$$

where  $\Delta E_m$  is the energy of excitation for an isolated molecule,  $D$  represents a shift in transition energy due to the energy of interaction of the charge distribution of an excited molecule with its ground state neighbor and to the binding energy of the crystal in its ground state (heat of sublimation) and  $E$  arises from the exchange of energy among the molecules in the aggregate. From the form of the  $E$  term (11), one can conclude that to each discrete allowed electron energy level in the isolated molecule, there corresponds in the crystal a band of densely distributed allowed electron energies. That is, the excited states of the isolated molecules are split into a band of energies in the crystal. The number of energy levels in the band is equal to the number of molecules in the aggregate and the width of the band is determined by the magnitude of the interactions between excited state and ground state. This band of energy levels is called the exciton band and the exchange of excitation energy between molecules is designated as exciton migration. It is worth

noting that, in molecular crystals, the ground states are not split, although they will, in general, be slightly lowered in energy with respect to the isolated molecule due to van der Waals interaction.

The relationship between the energy levels in the isolated molecule and those in the molecular crystal is shown in Figure 1. The diagram also depicts the convergence of the energy levels in the isolated molecule to an ionization limit. The ionization limit in the crystal represents the energy level at which the electron is within the crystal but not specifically attached to any one molecule. The addition of a further amount of energy equal to the work function for the crystal would lead to photoemission of electrons (photoelectric effect).

It is apparent from the above analysis that the extent of energy migration in molecular crystals will be determined by the intensity of the ground state to excited state transition and by the strength of the interactions between the molecules. However, interaction energies too small to exert a measurable effect on the absorption spectrum may still allow significant exciton migration to take place. For example, a splitting or broadening of as little as  $1 \text{ cm}^{-1}$  ( $0.3 \text{ \AA}$  at  $5000 \text{ \AA}$ ) can lead to as many as 1000 energy transfer processes between molecules during the lifetime of the exciton. (18) In anthracene, it has been estimated (20) from experiments on sensitized fluorescence that approximately one million unit cells are visited by the exciton during its lifetime (ca.  $10^{-8}$  seconds). The distances over which excitations may diffuse have been estimated (21) as 0.1 microns in anthracene and 0.2 microns in naphthalene.

In a given case, not all of the transitions from the ground state to the various levels of the exciton band will be allowed. This is due to the fact that the way in which the functions,  $\Phi_i^*$ , are combined to form the wave function will be determined by the symmetry of the aggregate. For example, in the linear polymers of the cyanine dyes, only the transition

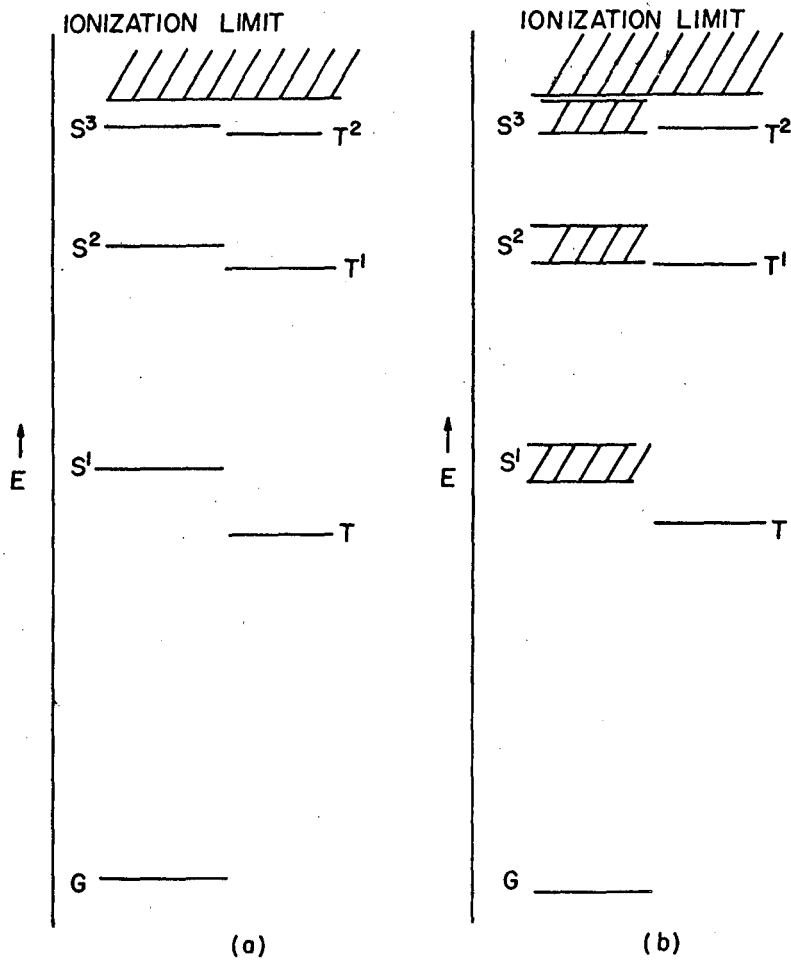


Figure 1.

between the ground state and the lowest level of the exciton band is allowed. This gives rise to an extremely sharp transition on the long wave length side of the isolated molecule absorption and to resonance fluorescence. On the other hand, in anthracene, which has two molecules with different orientation per unit cell, transitions to both the top and bottom of the exciton band are allowed, and one can observe a splitting of the isolated molecule absorption into two closely-spaced components in the crystal.

A further point of interest is that triplet states will in general not be affected by aggregation (see Figure 1), inasmuch as transition probabilities for singlet-triplet transitions are small. However, McRae and Kasha (22) have pointed out that aggregation should enhance the probability of the population of the lowest triplet state. This is due to two effects: (a) the broadening of the first excited singlet state should increase the energy overlap between this state and the lowest triplet state and (b) if the geometry of the aggregate is such as to lead to a lowered probability of transition from the ground state to the lowest level of the exciton band (and vice-versa), a large enhancement in triplet state population should result (this effect is maximum for a card-pack type of structure).

### (3) Energy Migration by Charge Carrier Motion.

The principle experimental evidences for the occurrence of charge carrier migration in organic crystals are the phenomena of semiconductivity and photoconductivity. (23) These experiments involve the measurement of increases in electrical conductivity as a result of illumination in the molecular absorption bands (photoconductivity) or as a result of heating (semiconductivity). In these systems, conductivity is found to increase

exponentially with temperature (this property can be used to define a semiconductor). Activation energies are invariably smaller than the energy difference between the ground state and the first excited singlet state (see below for further discussion). Pure organic crystals are normally quite poor conductors, with room temperature specific resistivities ranging from  $10^7$ - $10^{24}$  ohm cm, as compared with approximately  $10^2$  ohm cm in pure germanium crystals. Such a large difference in resistivities between the two types of systems is consistent with the large difference in interaction energies in atomic or ionic crystals as opposed to organic molecular crystals. For example, heats of sublimation are 2-3 ev. in the inorganic systems and approximately 0.01 ev. in many organic molecular crystals.

It is apparent that the thermal or photo-production of excitons cannot impart electrical conductivity to molecular crystals. This is because excitons represent bound states of the electron, that is, states in which the excited electron is bound by Coulombic forces to the molecule with which it is associated. It is useful in the present context to consider an exciton as consisting of an electron-positive hole pair, the positive hole representing the vacancy in the electronic structure of the molecule produced by the excitation of an electron from the highest filled orbital to the lowest unfilled orbital. Thus, conductivity can only occur if the electron and the hole are ionized. Such ionization may be said to have occurred when the electron and the hole are sufficiently far apart so as to be able to move independently of one another.

Before we discuss in detail the mechanism of formation of charge carriers in organic crystals, it is useful to consider the inorganic semiconductors. These systems have been widely studied and a great deal is known about their properties (24,25). In an atomic or ionic lattice

the interactions are such that the ground electronic states of the atoms or ions are split into a band of energy levels (valence band). Thus, in these systems, even in the ground state it is not possible to associate a given electron with a given atom or ion. The excited states also interact strongly and are split into a band (conduction band). Thus, an increase in temperature or absorption of light raises an electron from the valence band to the conduction band, resulting directly in electrical conductivity, due both to the excited electron and to the positive hole.

We see, therefore, that in the inorganic case, the interactions are of sufficient magnitude to require electron delocalization resulting in excited states which are also conducting states. In organic crystals, on the other hand, interactions are very much smaller, ground states are not split and excited states are non-conducting exciton states.

How, then, are charge carriers produced in organic molecular crystals? It is apparent from Figure 1 that if sufficient energy is imparted to the crystal, the electron will be raised to the ionization limit and electrical conductivity will result. Lyons (26) has estimated that for anthracene this energy should be  $5.2 \pm 0.6$  ev. and for naphthalene  $6.5 \pm 0.6$  ev. However, the activation energies for semiconductivity in these systems are known to be 1.9 ev. and 3.9 ev., respectively, and photoconductivity is known to result from absorption in the first excited singlet states (3.2 ev. and 4.1 ev., respectively). Evidently, at least for these molecules, conductivity cannot be the result of excitation to the ionization limit.

As Lyons (26) has pointed out, anthracene and the higher aromatics have been shown to have a positive electron affinity (27). Thus, the process of ionization of an exciton will be made easier by the interaction of the electron and a neighboring molecule. Furthermore, these highly

conjugated molecules have large polarizabilities and therefore ionization will be further aided by the polarization of the environment by the electron. This point of view has been adopted by a number of authors (26,28,29). For example, Lyons (26) has estimated the energy necessary to ionize a number of organic molecules in the crystalline state, with the electron being trapped by a neighboring molecule (formation of nearest-neighbor ion-pairs). For anthracene and naphthalene values of 2.2 ev. and 3.9 ev., respectively, were calculated. From these values and from the values for the energy levels of the lowest excited states of anthracene and naphthalene, Lyons estimated that additional energy amounting to  $0.5 \pm 0.6$  ev. and  $0.8 \pm 0.6$  ev. for anthracene and naphthalene, respectively, are necessary to completely ionize the exciton. This extra energy could be derived from (a) a discontinuity in the lattice, (b) thermal energy or (c) a sufficiently strong electric field. Thus, this mechanism seems within the realm of possibility, although it should be kept in mind that the calculations are approximate and are susceptible to appreciable errors. It is worth noting, at this point, that the amount of energy required to form ionized electrons and holes (charge carriers) in an organic crystal does not bear any a priori relationship to the amount of energy required to excite a molecule to its lowest excited state (see reference 23, p. 666).

It is apparent from the above discussion that it is possible to give a reasonable semiquantitative interpretation of the formation of free charge carriers in organic crystals in terms of the ionization of an exciton facilitated by the polarizability and the electron affinity of the host molecules. However, this mechanism can hardly be said to be established. In the first place, more rigorous quantitative calculations are needed. Secondly, difficulties arise when one attempts to interpret semiconductivity in terms of this mechanism. For example, although

activation energies seem to correlate fairly well with estimates of the energy necessary to form nearest-neighbor ion-pairs, these states are not sufficiently dissociated to be conducting (see above). Lyons has suggested that perhaps this additional energy could be acquired from a large localized electric field associated with an imperfection in the crystal. It is interesting that, for a number of systems, activation energies for semi-conductivity also seem to correlate fairly well with the energy levels of the lowest triplet states. This has led Rosenberg (30) to propose a mechanism in which the triplet state is a necessary intermediate in the formation of charge carriers.

In the above discussion it has been assumed that the observed conductivity properties of organic crystals are intrinsic to the bulk material being investigated. While it seems reasonable to expect intrinsic semiconductivity and photoconductivity in highly conjugated systems, in many cases it has been shown (31,32,33,34) that small amounts of impurity materials can change the conductivity properties of these systems by many orders of magnitude. For this reason, it is necessary to use caution in attempting to interpret the results of measurements on these properties, particularly in view of the difficulties involved in purifying many organic compounds.

We must now inquire into what is known in organic systems about the probability of charge carrier formation from excitons and about the movement of charge carriers through the lattice. These are properties of great interest from the biological point of view. Lyons (26) has estimated transition probabilities for the direct optical excitation from the ground state to the ionized state. According to these calculations, such transitions would have oscillator strengths of about  $10^{-6}$ . Thus, direct excitation to the ionized state is very improbable, with about the same



order of improbability as transitions from the ground state to the lowest triplet state. This, however, does not necessarily mean that the formation of ionized states from singlet state excitons is also highly improbable. For example, in many systems it is possible to achieve quite high efficiencies of conversion of light energy into triplet states via the radiationless crossing-over from the first excited singlet state. Thus, radiationless processes can provide a mechanism for the population of states to which radiative transitions are highly forbidden.

Unfortunately, little more of a definitive nature can be said regarding either quantum yields or mobility of charge carriers. This is mainly due to the fact that one cannot directly measure charge carrier concentrations in organic systems. Experimentally, one is restricted to measurements of current, which is related to carrier concentration by the following equation:

$$i = \mu N e A E \quad (5)$$

where  $i$  = current

$e$  = electronic charge

$\mu$  = charge carrier mobility in  $\text{cm}^2/\text{volt second}$

$N$  = number of charge carriers

$E$  = electric field strength in volts/cm

$A$  = cross-sectional area of conductor

Thus, a current measurement does not separate mobility and concentration. In order to do this one must have an independent method of estimating one or the other of these variables. While such methods do exist, thus far they have proven inapplicable to organic semiconductors. The failure of these methods is usually interpreted as indicating low mobilities and low quantum yields for carrier formation, or both. However, it is known from experiments that, in some systems (anthracene (35), tetracene, chrysene, pyrene and anthranthrene (36)), holes are the more mobile current

carriers.

(4) Energy Conversion in Photosynthesis.

In the laboratory of Professor Calvin in Berkeley, we have been mainly concerned with the investigation of the primary quantum conversion process in photosynthesis in plant materials and with the study of model systems related to the naturally-occurring system. By quantum conversion in photosynthesis is meant the process whereby light absorbed by chlorophyll gives rise to oxidizing and reducing entities. The oxidizing entity results in the formation of molecular oxygen from water and the reducing entity is used ultimately to reduce  $\text{CO}_2$  to the level of carbohydrate. Electron microscopy (37) has revealed the existence of highly ordered structures in chloroplasts (the site of photosynthesis) and thus it has seemed natural to attempt to conceive of quantum conversion in terms of the properties of aggregates of organic molecules. A number of other lines of evidence have led to speculation in this same direction. Electron spin resonance (ESR) absorption due to unpaired electron spins, as a result of the absorption of light in chlorophyll absorption bands, has been detected in leaves, algae, photosynthetic bacteria and isolated chloroplasts (38,39,40,41). Some typical experiments with isolated spinach chloroplasts are shown in Figure 2. The fact that one can get effects at liquid  $\text{N}_2$  temperature with red light has suggested that a physical rather than an enzymatic process is responsible for the formation of at least some of the unpaired electrons. Similar indications of the photophysical nature of the early stages of photosynthesis comes from studies of the luminescence of plant materials (42,43,44,45). Some typical luminescence decay curves for spinach chloroplasts and for *Chlorella* are shown in Figure 3. These data were obtained by illumination

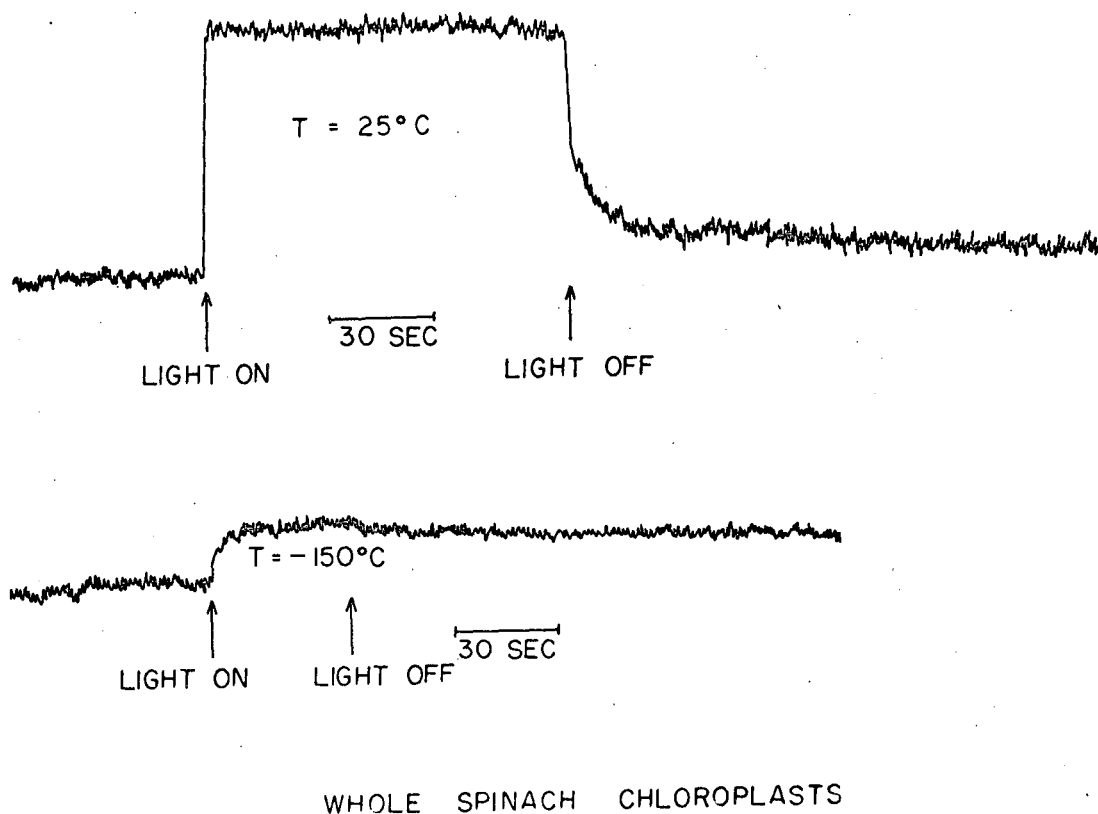


Figure 2.

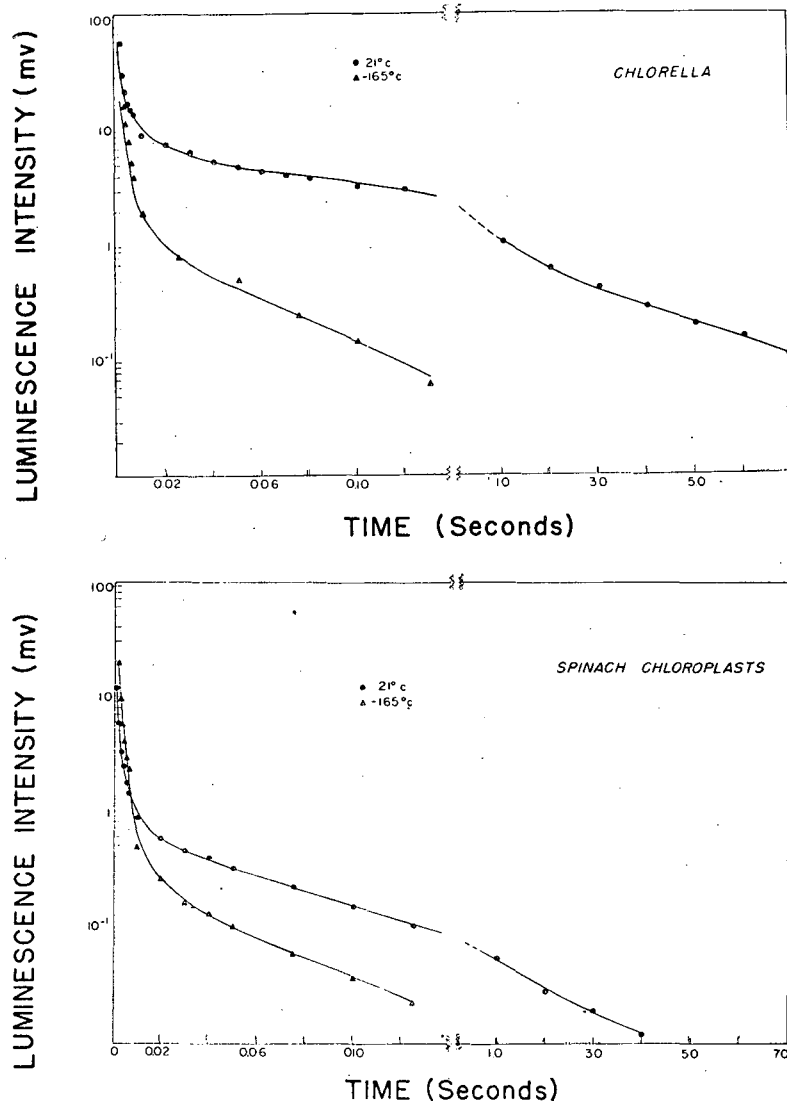


Figure 3.

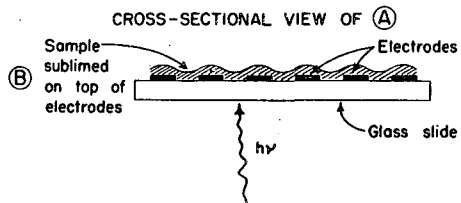
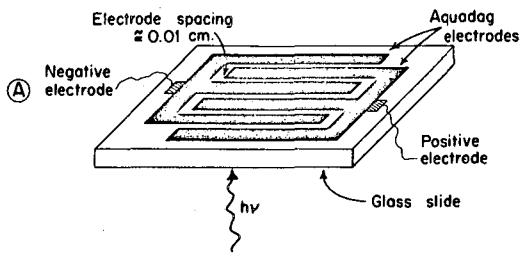
with a high-intensity short-duration flash. Cooling to liquid  $N_2$  temperature results in the disappearance of only the slower portions of the luminescence decay curve. At all temperatures, the luminescence is the result of the transition between the first excited singlet state and the ground state of chlorophyll. It is significant that similar millisecond time-constant singlet-singlet emissions have been observed at low temperatures in crystals of phenanthrene and naphthalene (46,47).

Arnold and Sherwood (48) and experiments in our own laboratory have demonstrated that dried chloroplasts are photoconductive and that thermoluminescence (light emission as the result of heating in the dark subsequent to a prior illumination) can be observed in these systems. This latter phenomenon is typical of photoconductors in which trapping of charge carriers occurs.

All of the above experiments are consistent with an hypothesis involving the formation of charge carriers by illumination of chlorophyll, the trapping of these carriers and their utilization in chemical or enzymatic reactions (49,50).

In view of the occurrence of quinones (Vitamin K, coenzyme Q) (51,52) in photosynthetic systems, we felt it would be of interest to investigate the effect of similar substances on the conductivity properties of pigments (52). A number of systems have been examined, including metal-free phthalocyanine, tetracene, coronene, decacyclene, and methyl pheophorbide a as the semiconductor (electron donor) moiety, and chloranil, ortho-chloranil and phenanthrenequinone as the oxidizing (electron acceptor) moiety. The type of sample holder used in the measurements is shown by the "surface" cell in Figure 4. The pigment material was either sublimed onto the graphite electrodes or introduced by solvent evaporation from pigment

"SURFACE" CELL SHOWING ARRANGEMENT OF ELECTRODES



EXPLODED VIEW OF SANDWICH CELL

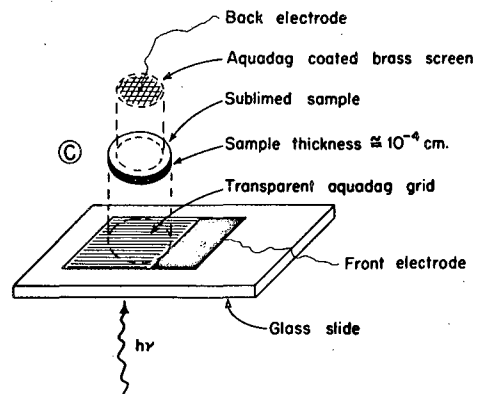


Figure 4.

solutions. A benzene solution of the oxidizing agent was then sprayed onto the back surface of the dye film. In this manner it was possible to measure the semiconductivity and photoconductivity of the pigment material before and after the introduction of oxidizing agent. In general, both the semiconductivity and the photoconductivity of the pigment materials was found to increase greatly upon the addition of the electron acceptor. The system which we have investigated in the greatest detail is the phthalocyanine-ortho-chloranil couple. Some of the results are shown in Figure 5. It is apparent that both the dark conductivity and the photoconductivity of the phthalocyanine increase quite spectacularly upon the addition of small amounts of ortho-chloranil. Saturation dark currents are about  $10^7$  times those of the pure material whereas saturation photocurrents are about  $10^5$  times those of the pure material. In addition to these changes, one can measure, using ESR "techniques," the formation of unpaired electrons in the dark upon the addition of ortho-chloranil to the phthalocyanine and also the generation of a potential difference between the phthalocyanine layer and the ortho-chloranil layer with the phthalocyanine becoming positive and the ortho-chloranil becoming negative. This suggests that the following reaction takes place in the dark:<sup>4</sup>



leading to the increase in conductivity due to  $PH^{\ominus}$ , the formation of unpaired spins and the generation of a potential difference across the layer.

Illumination of the phthalocyanine layer with wave lengths in the absorption maxima leads to an increase in conductivity, a decrease in unpaired spin concentration and an increase in the potential difference across the layer. A typical ESR experiment is shown in Figure 6. All of

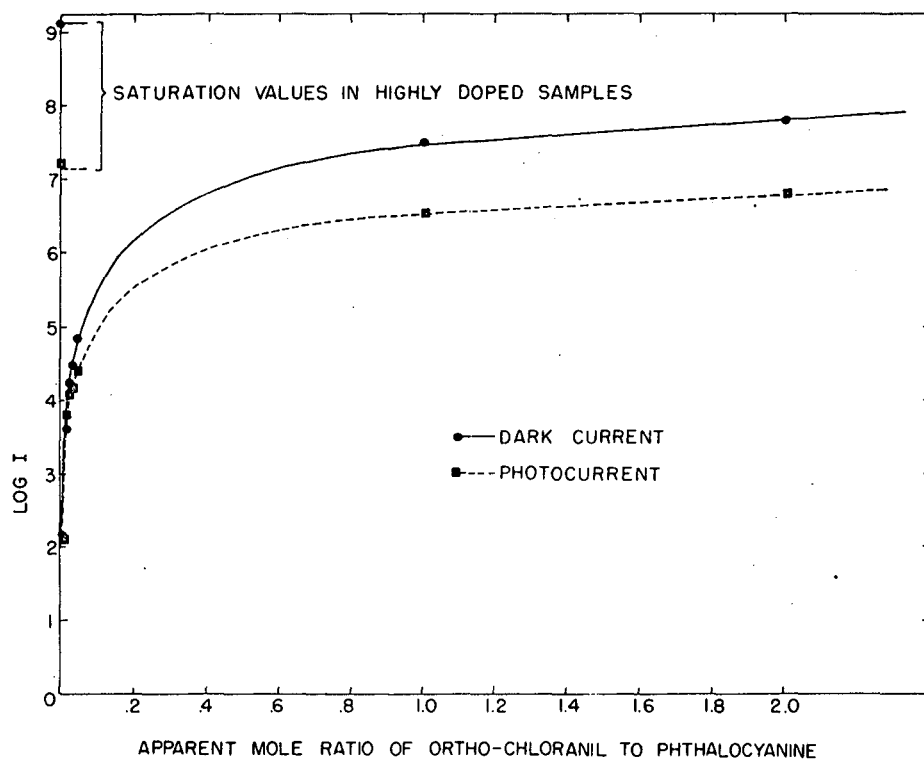


Figure 5.



EFFECT OF ILLUMINATION ON THE ELECTRON SPIN RESONANCE SIGNAL OF  
O-CHLORANIL "DOPED" METAL FREE PHTHALOCYANINE

CURVE REPRESENTS UNPAIRED SPIN CONCENTRATION VS. TIME

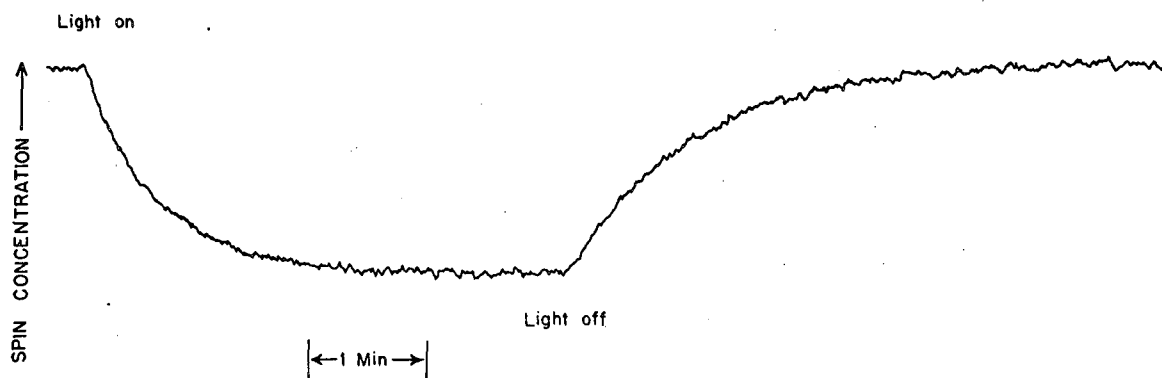


Figure 6.

these processes obey unimolecular kinetics with a time constant of about 40 seconds. These effects are probably due to the following reaction:



Inasmuch as illumination leads to a decrease in ESR signal, it is necessary to assume that  $\text{PH}^{\ominus}$ , although paramagnetic, is not detectable in our experiments, perhaps due to broadening of the resonance line. The decrease in ESR absorption, then, would be the result of the transformation of  $\text{CH}^{\bullet}$  (paramagnetic) into  $\text{CH}^{\ominus}$  (diamagnetic).

According to equation (6), the number of unpaired spins in the dark should be a measure of the charge carrier ( $\text{PH}^{\bullet}$ ) concentration. Thus, by measuring the conductivity one can calculate a mobility by means of Equation (5). This leads to a value of  $10^{-4}$  cm<sup>2</sup>/volt second for the mobility of holes in the phthalocyanine layer. This value should be compared with values of 1-1000 cm<sup>2</sup>/volt second for inorganic semiconductors. Furthermore, knowing carrier mobility one can measure a quantum yield for carrier production. Such measurements lead to a value of approximately unity for the quantum yield of charge carrier formation in the phthalocyanine-ortho-chloranil system. By comparing the properties of the pure phthalocyanine with those of the mixed system, it is possible to conclude that the quantum yield for carrier production in the pure material is probably less than  $10^{-1}$ . A further difference between the pure and the mixed systems is that the charge carrier lifetime in the latter is considerably longer than in the former. In fact, this is the principle reason for the large increase in steady-state photoconductivity in phthalocyanine upon the addition of ortho-chloranil. The reason for this increase in lifetime appears to be that the ortho-chloranil negative ions act as efficient electron trapping centers, thus making charge carrier recombination less probable.

From the above discussion, it seems possible to conclude that the presence of a layer of strong electron acceptor on a film of an organic dye will (a) increase the quantum yield for the production of charge carriers and (b) increase the lifetime of the charge carriers. Both of these effects would tend to increase the extent to which charge carriers are available to do chemical or biological work. On the basis of this picture, one can construct a model for the primary process in photosynthesis. Such a speculation is shown in Figure 7. Light absorbed by the chlorophyll layer (process "a") would lead to excitons (\*) which could migrate (process "b") until they came into the vicinity of the electron acceptor, A (perhaps a quinone, such as coenzyme Q). When this occurred, an electron would be transferred (process "c") from the chlorophyll exciton to the acceptor. The electrons could then be utilized in the  $\text{CO}_2$  reduction system via pyridine nucleotides. The hole in the chlorophyll layer would be free to migrate (process "d") until it came into contact with water or some hydroxylated compound. An electron would then be transferred to the chlorophyll positive species (process "e") resulting in the formation of ground-state chlorophyll and radicals which would ultimately lead to molecular oxygen. It is, of course, also possible to have a simultaneous double transfer of electrons (not shown), one from a chlorophyll exciton to A and the other from the hydroxylated species to chlorophyll positive ion.

Such a scheme, then, would provide a mechanism for the formation of oxidizing and reducing entities from light energy, for their utilization to do photosynthesis and for the prevention of their recombination. In addition, it would be consistent with the ESR and luminescence results with plant materials, with the morphology of the chloroplast and with what is known about similar processes in model systems. In this connection, it

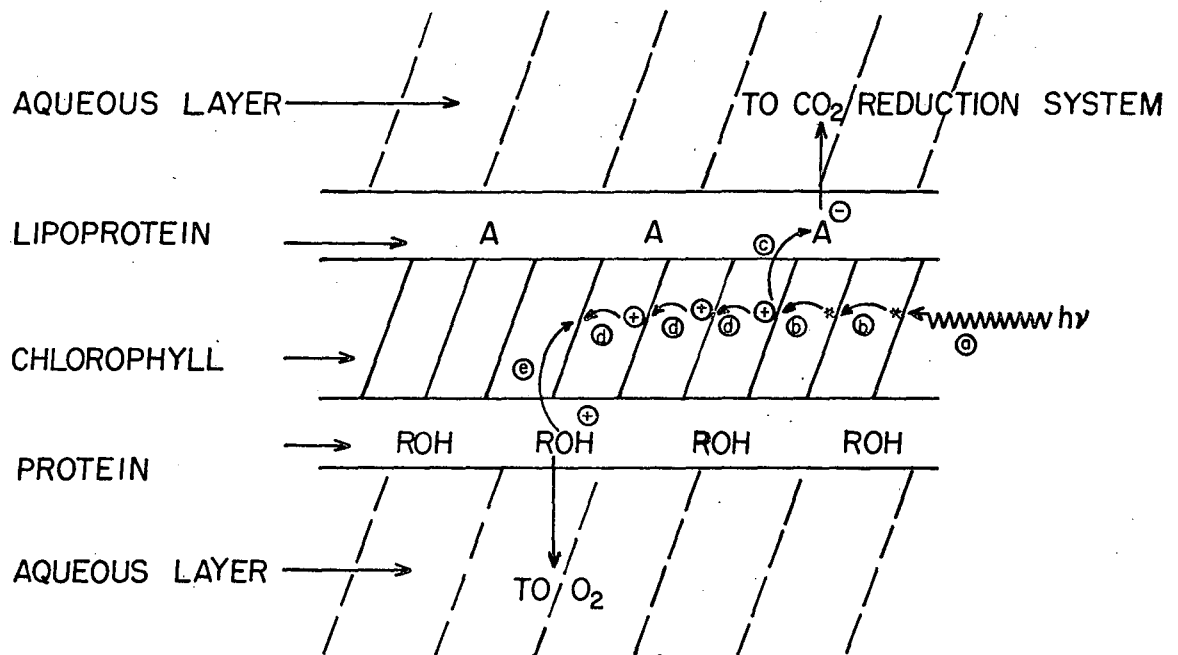


Figure 7.

is of interest that, using layered system of the type discussed above, it has been possible to construct cells from which current may be drawn as a result of illumination. While these experiments are still in the preliminary stages, they demonstrate that the electrons and holes formed upon illumination are indeed available to do chemical work.

#### (5) Problems for the Future

Although a considerable amount of information has been accumulated regarding the processes of energy migration in ordered organic systems, it is clear that many gaps in our knowledge exist, the filling in of which would undoubtedly aid in achieving a better understanding of biological energy conversion systems. For example, it would be quite helpful in many cases to be able to assess the range of exciton migration to be expected in biological systems. One could arrive at such estimates from in vitro studies of crystals of naturally-occurring pigment systems, either from theoretical calculations, from detailed spectroscopic investigations or from measurements of sensitized fluorescence. A related problem, which is just beginning to be investigated (54), stems from the possibility that pigment molecules in vivo are in the form of two-dimensional, rather than three-dimensional, aggregates. It is necessary to know whether or not there are significant qualitative or quantitative differences between the energy migration properties of these two types of aggregates.

With respect to charge carrier formation, it is evident that a good deal of theoretical and experimental work remains to be done before a complete understanding of the mechanisms involved in this process is achieved. Such an understanding is of importance with respect to an evaluation of the extent to which one can expect the occurrence of free charge

carriers in biological systems. Thus, it would be of value to investigate the manner in which excitons interact with lattice vibrations, lattice imperfections and external electric fields. In addition, one would like to have information concerning ionization potentials and electron affinities of naturally-occurring pigments in order to be able to estimate the energy required to form charge carriers. Finally, and perhaps most important of all, one would like to know quantum yields for carrier formation and the effect of environmental factors upon such yields.

A particularly important area of information, and one in which our knowledge is scanty, concerns the migration of charge carriers in molecular crystals. For example, we know very little about charge carrier mobilities in aggregates of biologically-important pigments and about the effect of structure and impurities upon such mobilities. New methods need to be developed to attack these problems. It is also of importance to evaluate charge carrier lifetimes and the effects of electron or hole traps upon such lifetimes as well as the availability of charge carriers in biological pigments for the performance of chemical work.

Most of the investigations outlined above deal with in vitro systems. However, the biologist will of course recognize the importance of simultaneous studies with in vivo systems. Of great importance are experiments designed to determine the extent to which electromagnetic energy migration and mobile charge carriers occur in these systems. These are difficult experiments, but they are essential before one can justify the application of solid-state theory to biological systems. Furthermore, the complexity of the biological systems will undoubtedly necessitate modifications of conclusions drawn from experiments upon in vitro systems.

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### Footnotes

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<sup>3</sup>If the electronic transition has no dipole moment, higher order terms must be used. For example, in the case of anthracene, the dipole-dipole term is important (see ref. 11 and 12), whereas for benzene, the first non-vanishing term is the octupole-octupole (see ref. 13). The latter term is proportional to  $1/r^7$ .

<sup>4</sup>The following abbreviations will be used in the discussion:

PH = metal-free phthalocyanine

PH\* = first excited singlet state of phthalocyanine

PH<sup>⊕</sup> = phthalocyanine positive ion

CH = ortho-chloranil

CH<sup>⊖</sup> = ortho-chloranil negative ion-radical

CH<sup>⊖⊖</sup> = ortho-chloranil double negative ion

## LEGENDS FOR FIGURES

- Fig. 1: Schematic representation of electronic energy levels in isolated molecules (a) and molecular crystals (b). G = ground state; S = excited singlet states; T = excited triplet states. The energy scale is distorted so as to show more clearly the phenomena of exciton band splitting and the occurrence of an ionization limit.
- Fig. 2: Rise and decay curves for light-induced ESR signals in spinach chloroplasts at 25°C and -150°C.
- Fig. 3: Decay curves of luminescence emission in Chlorella and spinach chloroplasts at 21°C and -165°C.
- Fig. 4: Schematic diagram of sample cells used in conductivity measurements.
- Fig. 5: Variation of dark conductivity and steady-state photoconductivity of metal-free phthalocyanine with amount of added ortho-chloranil.
- Fig. 6: Effect of illumination with white light on the ESR signal in ortho-chloranil-metal-free phthalocyanine junctions.
- Fig. 7: Schematic diagram of hypothetical photosynthetic quantum conversion process. A = electron acceptor, ROH = water or other hydroxylated species.

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