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SOLID-STATE PHENOMENA AND THE PRIMARY QUANTUM CONVERSION
PROCESS OF PHOTOSYNTHESIS

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ABSTRACT

June 16, 1958

The electronic properties of aggregates of highly conjugated organic molecules and the possible relationships between the phenomena associated with these properties and the role of chlorophyll in the primary quantum conversion process of photosynthesis are briefly discussed. Experimental evidence is presented which suggests that chlorophyll is functioning as a semiconductor in vivo. It is shown that such a function is compatible with both theory and experiment.

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Electron microscope studies of chloroplast material have revealed the existence of a remarkably complex lamellar structure which presumably constitutes the photosynthetic apparatus. It has therefore seemed reasonable to assume that the primary pigment involved in photosynthesis, chlorophyll a, is also present in some more or less ordered arrangement within the chloroplast. Such a concept is supported by other, more indirect, types of evidence (e.g. spectra and polarization of fluorescence). From this point of view it becomes of importance to inquire into the electronic properties of aggregated dye molecules in the hope that a greater understanding of the role of chlorophyll in the primary quantum conversion process may thereby be achieved.

Quantum mechanics tells us that when highly polarizable molecules are brought into close proximity, as in a crystal or a monolayer, their electronic states will be perturbed to an extent which is inversely proportional to the cube of the intermolecular distance and directly proportional to the square of the transition moment integral for the ground state to excited state transition. (1) These interactions lead to a band of state energies for the aggregate whose width is a function of the above parameters. As a consequence of this band structure, a quantum of energy absorbed by any one molecule will have a definite probability of being found in any other molecule of the aggregate, this probability being a direct function of the strength of the interactions. Thus, the extent to which energy migration will occur in the aggregate will be determined by the electronic band width, by the lifetime of the excited state and by the Uncertainty Principle. It is evidently possible to observe a continuous gradation of transfer efficiencies, depending upon the individual system under consideration. One may consider this mobile excited state of the aggregate (exciton) to consist of the excited electron and its associated positive hole moving together throughout the array. If, at some point in its path, the exciton

encounters a lattice imperfection (see below for qualifying remarks), an ionization may take place, that is, the electron and hole may become free to move independently of one another. This confers upon the aggregate the property of electrical conductivity (photoconductivity).

Although it is in principle possible to have an infinite spectrum of coupling strengths in dye aggregates, it has become increasingly apparent in recent years that the interactions giving rise to conduction bands and photoconductivity need not be very strong. (2) This is amply demonstrated by the case of tetraphenyl porphine. It has been found (3) that although the long wavelength absorption bands of this compound are essentially unaffected by solid-state interactions, carriers can be excited as efficiently by these transitions as by the Soret transitions which are appreciably changed in the solid. Inasmuch as the lowest singlet state excitons will be essentially immobile, these results also suggest that the excitation energy may not need to be funneled to special ionization sites in the crystal lattice. It is thus evident that the shape of the absorption spectrum of an ordered array is not an adequate criterion of the presence or absence of photoconductive properties.

It is apparent from the above considerations that the phenomena of energy transfer and photoconductivity are intrinsic properties of dye aggregates and will occur to a greater or lesser extent in all such systems. The problem before us therefore is to assess, from both a theoretical and an experimental and point of view, what role, if any, these properties play in the primary quantum conversion.

In principle, the shape of the absorption spectrum of an ordered array of molecules furnishes direct information as to the strength of the interactions involved and hence as to the extent of energy migration. Thus, on the basis of spectroscopic evidence, Jacobs et al. (4) have estimated that the number of excitation energy transfers between chlorophyll molecules in vivo during the

lifetime of the first excited singlet state is probably of the order of several hundred. The assumption that one has to make in order to arrive at this figure is that the shape of the red absorption band (in particular, its broadness compared to the solution spectrum and the inability to resolve any structure) is a consequence of weak interactions leading to a coupling of the electronic excitation with molecular and lattice vibrations, thus requiring that the excitation energy remain in each molecule for a minimum of 10^{-13} seconds. However, it is known on theoretical grounds (1,5,6) that the shape of the absorption spectra of aggregates will be extremely sensitive to the structural arrangement of the molecules. For example, the polymers of isocyanine have a very narrow band on the long wave side of the monomer absorption in spite of the broadness of the first excited state of the aggregate. This is due to a selection rule imposed by the linearity of the polymer which allows transitions only to the lowest level of the excited state energy band. On the other hand, for hydrocarbons such as anthracene, two absorptions are found in the crystal spectrum with maxima at either side of the monomer maximum due to transitions to the top and bottom of the excited state energy band. This is a consequence of a structural arrangement in which two molecular orientations exist within a single plane of the crystal.

Although very little is known about the manner in which chlorophyll molecules are oriented in vivo, it is probably reasonable to assume that they are in the form of a monolayer and are quite likely not perfectly ordered. (4) Both of these conditions would tend to decrease the intermolecular interactions. On the other hand, the long wave absorption in chlorophyll is very intense and this would lead one to expect strong interactions for any reasonably small intermolecular separation. We may thus consider two possibilities. If the structure of the chlorophyll aggregate is such as to allow two transitions, the inability to resolve the spectrum is probably an indication of weak interactions and hence relatively limited energy migration, as proposed by Jacobs,

et al. (4) In this case, the red shift in the spectrum would have to be ascribed to other interactions, e.g. chlorophyll-protein associations. Alternatively, if the red shift is a consequence of only one allowed transition, then the width of the excited state is of the order of several hundred wave numbers indicating a moderately strong interaction. The broadness of the band in this case, as contrasted with the sharp polyisocyanine band, may be the result of the presence of regions of differently aligned chlorophyll molecules which would lead to slightly varying wavelength maxima for the different degrees of interaction which exist in the aggregate. Extensive energy migration may then occur within each region. Thus, one cannot completely rule out the possibility that the actual number of transfers in vivo may be significantly larger than several hundred.

Another point of interest is the role of the triplet state in vivo. McRae and Kasha (6) have considered dye aggregates from a theoretical point of view and conclude that the probability of the population of the lowest triplet state should be enhanced in these systems due to an increased overlap in energy between the first excited singlet state and the triplet state and, in some cases, to a selection rule forbidding the transition to the lowest level of the singlet manifold. Inasmuch as triplet states will be essentially unaffected by aggregation (because of the extremely small transition moment integrals involved) triplet state exciton migration should be a relatively inefficient process. Thus, if the low yield of fluorescence in vivo is a consequence of a highly probable crossing-over into the triplet state, any chemical utilization of the excitation energy would presumably have to take place in the immediate environment of the triplet state chlorophyll molecule involved. This would introduce a degree of randomness into the quantum conversion process which is not altogether desirable. However, experimental results obtained in our laboratory (7,8) indicate that perhaps the triplet state is not populated at all in vivo or only to a very small extent. We have observed that the delayed

light emission of green plant materials from one millisecond after excitation to 30 seconds after excitation always originates in the first excited singlet state of chlorophyll, even at temperatures as low as -170°C where emission from the triplet state should be greatly facilitated.

If the triplet state of chlorophyll is not populated to any great extent in vivo, a highly efficient process must exist which competes with the singlet-to-triplet conversion. It is conceivable that this process involves the ionization of the exciton with the formation of charge carriers in conduction bands which would then be free to migrate until they were trapped by suitable acceptors. Such a concept was first proposed by Katz in 1949. (9) There exists some experimental evidence which tends to support this point of view. Arnold and Sherwood (10) have demonstrated that dried films of chloroplasts exhibit semi-conductivity and thermoluminescence. Light-induced electron spin resonances (ESR) have been observed in wet chloroplast material (11) as well as long-lived luminescences (12) which are characteristic of semiconductors. In our own laboratory we have been studying both the light-induced ESR (13) and the delayed emission (5,8,14) of plant materials. Some of the results of these studies which bear on the present discussion are reproduced in Figures 1, 2 and 3. In Figure 1 we see that the production of unpaired spins ^{proceeds} at comparable rates at both 25°C and at -150°C . The smaller signal at the lower temperature suggests that more than one type of radical is produced at room temperature. This is confirmed by results at intermediate temperatures (not shown) where a complex growth curve is obtained, clearly demonstrating two separate radical-producing processes. The fact that the signal exhibits little or no decay at -150°C demonstrates that the unpaired spins are trapped at these temperatures. In Figure 2 are shown the luminescence decay curves for spinach chloroplasts at room temperature at -168°C . The predominant effect of cooling is to cause the disappearance of the slow components of the decay. The curves for the inter-

mediate temperatures (not shown) demonstrate a very complex temperature-dependence (see, for example, Figure 3). At no temperature can the decay curves be represented by a simple kinetic expression. These results indicate a mechanism consisting of more than one rate-limiting step.

If the phenomena of electron spin resonance and delayed light emission in plant material are indeed related to the early stages of photosynthesis, one would expect to find a high quantum yield for the former process and a much lower yield for the latter. Although it has not been possible to obtain an accurate quantum yield for the ESR signals, crude measurements indicate a value not less than 0.1 and probably higher. On the other hand, fairly accurate measurements of the luminescence quantum yield give values of the order of 10^{-6} for Chlorella and Scenedesmus and 10^{-7} for spinach chloroplasts. Thus the results are in accord with expectations. The lower yield for the chloroplast materials is mainly a reflection of a smaller proportion of slowly decaying light in this material as compared with the algae. This is probably a consequence of the partial removal of enzymes and smaller molecules in the preparation procedure. Similarly, if one disrupts algae by ultrasonication or subjects them to lyophilization, the luminescence of the material obtained in this way resembles that obtained at -170°C from whole cells in that it consists only of rapidly decaying light emission.

The presence of both a substantial luminescence decay and a substantial build-up of unpaired spins at temperatures approaching that of liquid nitrogen strongly suggests that the stages of the primary quantum conversion process immediately following exciton production do not involve the migration of atomic nuclei and thus are purely physical in nature. This is, of course, quite compatible with the semiconductor theory. In these terms, the unpaired spins formed at the low temperatures would be associated with electrons and holes trapped at suitable points in the chlorophyll lattice. The luminescence decay

At this temperature would be a reflection of a charge carrier lifetime prior to recombination and, if the decay curve can be decomposed into two components, perhaps the depopulation of a shallow trapping level as well. At room temperature, the trapped carriers can be enzymatically converted into radicals and even-electron molecules and the reversibility of these processes gives rise to the slow highly temperature-dependent components of the decay curves.

It is apparent that as yet there has been no unequivocal demonstration of the presence of charge carriers in vivo. It will be necessary to prove that such carriers are indeed produced with a high quantum yield before the semiconductor mechanism may be said to be on a secure footing. However, such measurements are extremely difficult to carry out and thus for the present we are forced to be content with indirect experiments of the type outlined above. It is certainly significant in this regard, although by no means conclusive, that Nelson (2) has shown that films of chlorophyll are photoconductive and that they are able to sensitize photoconductivity in inorganic phosphors. In addition, the experiments discussed in this symposium by Dr. Arnold (15) have certainly strengthened the experimental basis upon which the semiconductor hypothesis rests as well as pointed the way towards a possible understanding of the function of carotenoids.

In conclusion, we may say that if chlorophyll is indeed present in an aggregated state in vivo, both from a theoretical point of view and in terms of the experimental results which have been obtained to date, the semiconductor hypothesis can be said to be a reasonable interpretation of the primary quantum conversion process of photosynthesis. At the very least, it provides an excellent working hypothesis upon which to base further experimentation.

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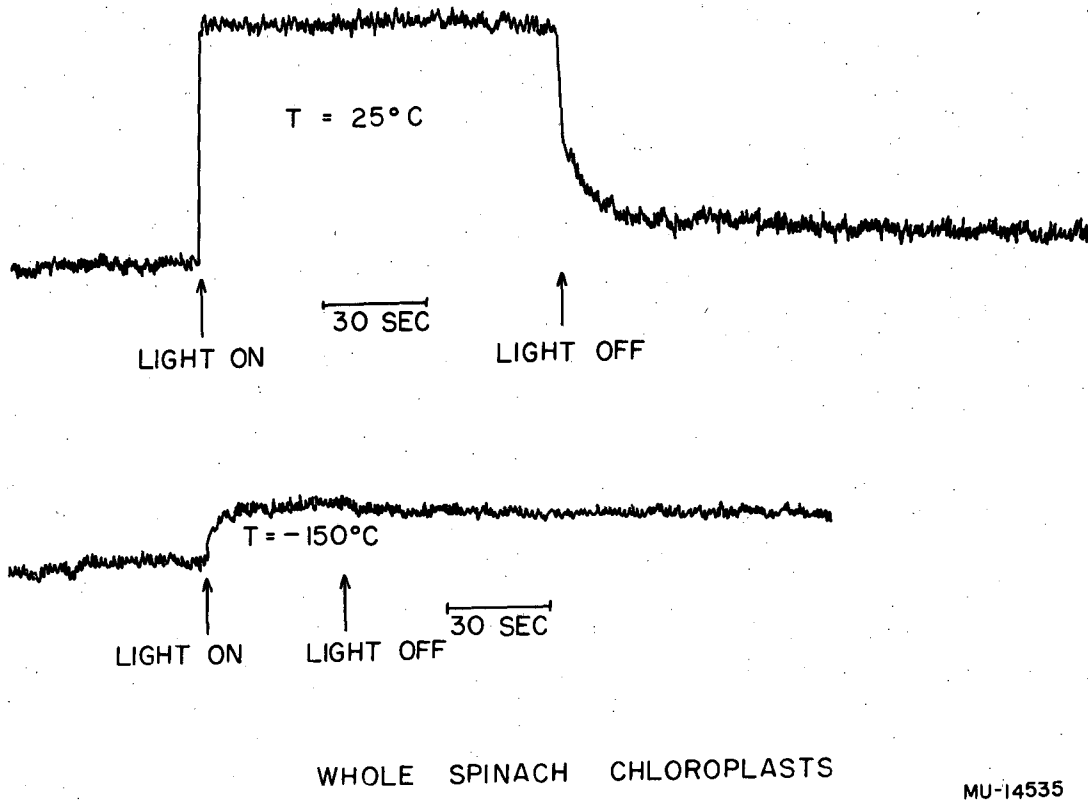
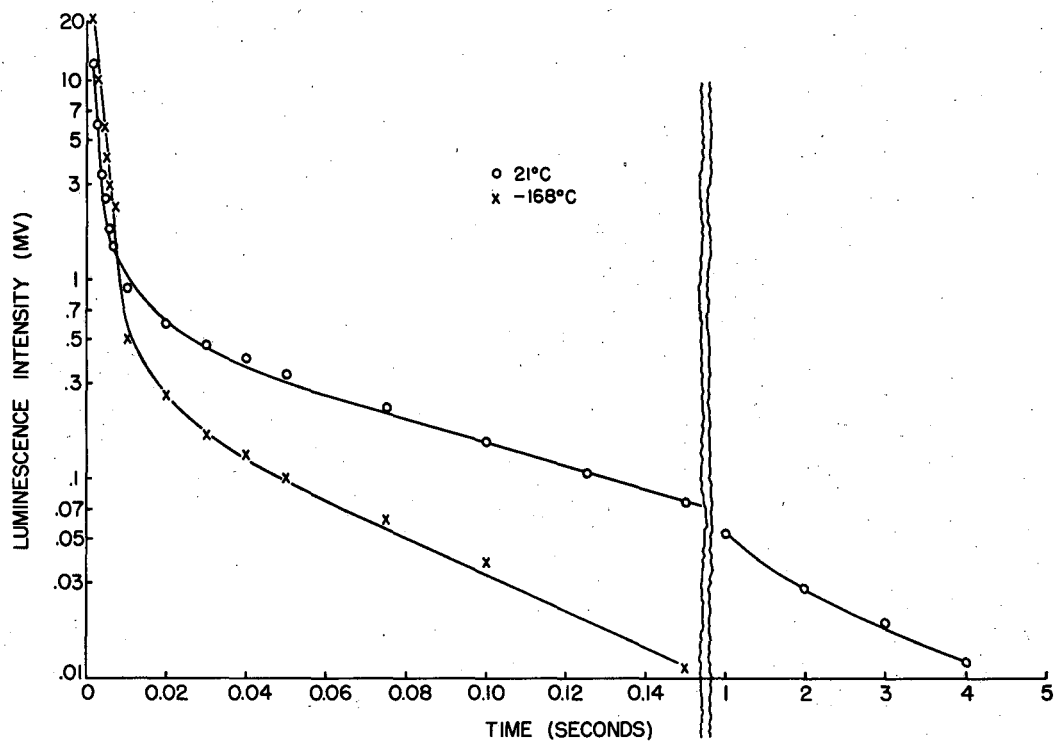


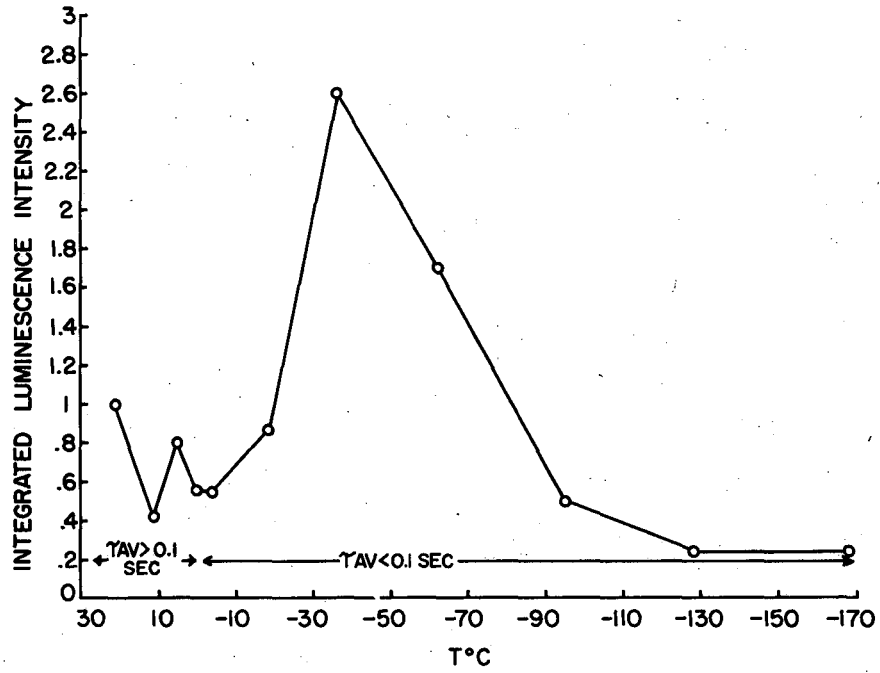
Fig. 1.



DECAY CURVE OF SPINACH CHLOROPLAST LUMINESCENCE AT TWO TEMPERATURES

MU-15140

Fig. 2.



INTEGRATED INTENSITY OF SPINACH CHLOROPLAST LUMINESCENCE
M 0.0015-5.0 SECONDS AFTER EXCITATION AS A FUNCTION OF TEMPERATURE

MU-15136

Fig. 3.

CAPTIONS FOR FIGURES

Figure 1. Growth and decay curves for light-induced electron spin resonance signals in whole spinach chloroplasts at 25° C and -150° C.

Figure 2. Decay curves for luminescence of whole spinach chloroplasts at 21° C and -168° C.

Figure 3. Integrated intensity of luminescence of whole spinach chloroplasts from 0.0015-5.0 seconds after excitation as a function of temperature.

τ_{av} = average lifetime of the luminescence.