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Light Energy Conversion By Photosynthesis

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WITH the increasing human population and dwindling natural resources, a basic understanding of photosynthesis is necessary, as it is the only process on earth that not only provides us with oxygen to breathe and food to eat but is also the origin of the fossil fuels which satisfy our energy needs. A complete knowledge of this process may allow us to duplicate the important steps of this process outside the living plant and help us in utilizing the solar energy more effectively. This potential has only begun to be tapped in ways which allow for the development of more efficient agricultural techniques[1].

Two approaches are currently being taken by researchers in photosynthesis with the hope of relieving the ever-increasing demand on the earth's energy resources. One approach deals with the production of fuel by combining the ability of chloroplasts to produce energy-rich compounds with the capacity of certain bacteria to generate hydrogenase enzyme which helps strip off molecular hydrogen from the energy-rich compounds[2–5]. The second approach deals with the conversion of light energy into electrical energy[6,7]. Other approaches are also being considered at the moment. In order to achieve this conversion of energy, we must fully understand the path of solar energy conversion to chemical energy in photosynthesis, the focus of this present article.

Photosynthesis starts with efficient light absorption by several types of pigments—absorbing in different regions of the visible spectrum[8] — embedded in, or located on, special chloroplast membranes called thylakoids[9]. Light energy is absorbed by a collection of several hundred light harvesting molecules (chlorophyll and other accessory pigments) which are often referred to as bulk pigments or antenna molecules. The energy, thus absorbed, is ultimately transferred to certain unique chlorophyll molecules that are in a specialized environment and/or state of aggregation[10] and act as the "energy traps" or reaction centre molecules[11–13]. Here, the conversion of light energy into chemical oxidation-reduction potential energy occurs. An assembly of several hundred pigment molecules along with one reaction centre is referred to as a photosynthetic unit. The original concept of the photosynthetic unit arose from the experiments of Robert Emerson and William Arnold[14], who, in 1932, using short, bright and saturating flashes of light separated by an optimum dark period, showed that a maximum of one O_2 molecule could be evolved per 2400 chlorophyll molecules. Since in order to evolve one O_2 molecule four electrons (or H atoms) must be transferred from H_2O to $NADP^+$ in two photochemical steps (*see* below) involving eight individual transfers, 300 chlorophyll molecules are required for one H atom transfer. This then is a modified concept of the photosynthetic unit and represents the smallest unit capable of photochemical reactions (Fig. 1).

*References are cited only as a guide to literature; no attempt has been made to provide an exhaustive reference list. The interested reader may also consult *Annual Reviews of Plant Physiology* and the Bioenergetics section of *Biochimica Biophysica Acta* for further references and details.

Photosynthesis as a Redox Reaction: Electron Transfer

Data from various laboratories[15–18], but originating first from the laboratory of the late Robert Emerson at the University of Illinois[19–22], have led to the concept that electron transfer from H_2O to CO_2 occurs in two photochemical steps and is sensitized by two separate populations of pigment molecules, designated as photo or pigment systems I and II (Fig. 2). The hydrogen transport from H_2O to CO_2 is energetically an uphill process, the H_2O/O_2 couple having a redox potential (at *p*H 7·0) of +0·8V and $CO_2/[CH_2O]$ of –0·4V. The necessary energy gap of 1·2V is provided by light.

The primary act resulting from light absorption in pigment system II (PS II) produces an oxidant[23–26] $P680^+$ and a weak reductant[27–30] Q^-. $P680^+$, in turn, accepts an electron from another electron donor Z, which, in turn, accepts an electron from the positive charge accumulator M. The M^+, after its oxidation to M^{4+} (i.e. after four such steps), extracts four electrons from two molecules of water, evolving one molecule of O_2[31–33]: $M^{4+} + 2H_2O \rightarrow M + O_2 + 4H^+$. Light absorption in pigment system I produces a strong reductant (X^-) and a weak oxidant (oxidized P700), the latter in its reduced state being the energy trap of PS I[34,35]. Once, the light energy is converted into chemical potential energy, the central problem becomes one of transfer of hydrogen atoms (or electrons) from one carrier to the other carrier (Fig. 3).

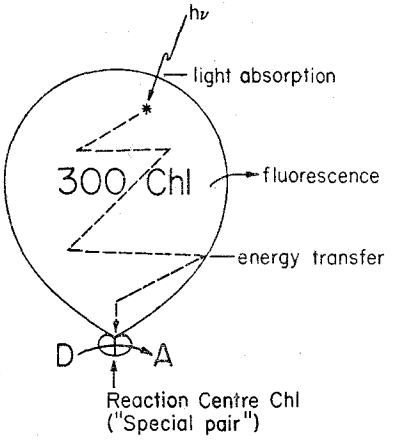

Fig. 1—Schematic diagram of a photosynthetic unit [It consists of a collection of about 300 pigment molecules (mainly chlorophylls; carotenoids may also be present) and a reaction centre chlorophyll made up of two chlorophyll *a* molecules. The term "special pair" is used here, because the two molecules are not just a dimer but are connected to each other by other ligands. As one possibility, it has been suggested that the C=O group of one Chl *a* molecule is connected to Mg of another molecule and vice versa by two water molecules. In blue-green and red algae, the photosynthetic unit of pigment system II also contains phycobilins (phycoerythrin, phycocyanin and allophycocyanin).]

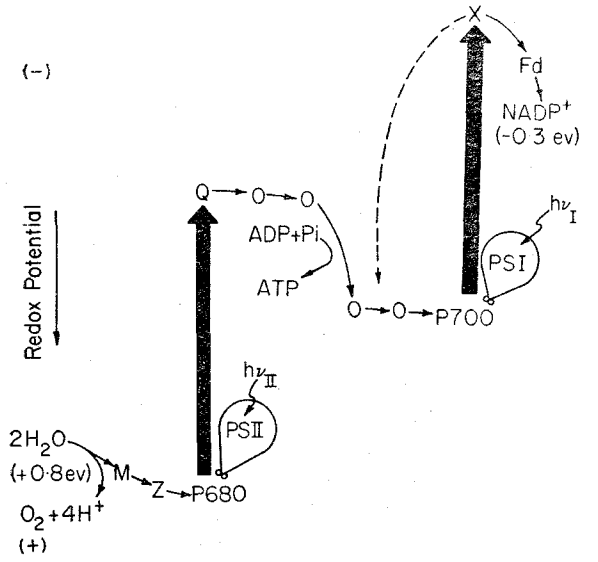

Fig. 2 — Two-pigment system and two-light reaction scheme [Excitation ($h\nu$ II) in pigment system II (PS II) oxidizes reaction centre chlorophyll *a* P680 to its cation $P680^+$ and reduces a quinone-type electron acceptor (Q) to a semiquinone anion. $P680^+$ oxidizes another component *Z*, which then oxidizes M. M must accumulate four positive equivalents, i.e. PS II must operate 4 times before enough oxidizing power accumulates on M to extract 4 electrons from water and evolve one O_2 molecule (*see* Fig. 3). M and Z are, perhaps, Mn-containing complexes. Electrons on Q^- flow downhill energywise through various intermediates (*see* Fig. 3); during this electron flow, enough energy is available to produce adenosine triphosphate (ATP) from inorganic phosphate (Pi) and adenosine diphosphate (ADP). Excitation ($h\nu_I$) in pigment system I (PS I) oxidizes reaction centre chlorophyll *a* P700 to its cation $P700^+$ and reduces an iron-containing complex (X). (Both $P700^+$ and X^- have unpaired electrons and are, therefore, measurable by Electron Spin Resonance technique.) $P700^+$ recovers electrons which come down from reduced Q. X^- reduces ferredoxin (Fd) which then reduces nicotinamide adenine dinucleotide phosphate ($NADP^+$) with the aid of Fd-$NADP^+$ reductase. The dotted arrow from X shows one of the ways of cyclic electron flow around PS I. A cyclic flow could also involve phosphorylation. Cytochrome b_6 has been suggested as an intermediate in this cyclic flow. The numbers in parentheses indicate the redox potential of H_2O/O_2 and $NADP^+$/NADPH couples at *p*H 7·0.]

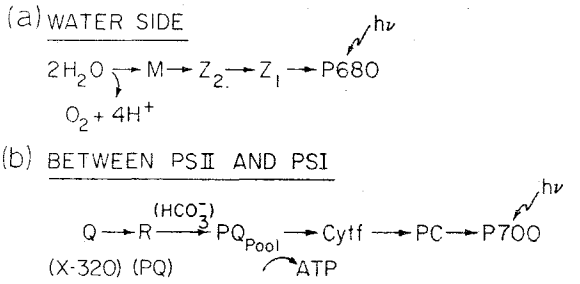

Fig. 3 — (a) top portion labelled 'water side' shows the intermediates between water and the reaction centre P680 (bottom left portion of Fig. 2) [No further details are shown here except to suggest that there may be two intermediates Z_1 and Z_2 between P680 and *M*. Kinetic measurements for the recovery of $P680^+$ to P680 show several components suggesting these intermediates. It is likely that oxidation of Z_2 to Z_2^+ by Z_1^+, after excitation of P680 by light, is monitored by an electron spin resonance signal labelled II_{vf}. The four steps involved in the oxidation of M to M^{4+} may also be written in terms of manganese complexes ($M=Mn^{2+}/Mn^{2+}$; $M^+=Mn^{2+}/Mn^{3+}$; $M^{2+}=Mn^{3+}/Mn^{3+}$; $M^{3+}=Mn^{4+}/Mn^{3+}$; $M^{4+}=Mn^{4+}/Mn^{4+}$; *see* text); O_2 is evolved by a reaction of M^{4+} with $2H_2O$ yielding M, O_2 and $4H^+$.]

(b) — Bottom portion labelled "between PS II and PS I" shows the intermediates between Q and P700. [Q is a quinone type compound and when reduced forms a semiquinone anion measured as an absorbance change lebelled X-320; reduction of Q is also measured by a rise in chlorophyll *a* fluorescence yield or by an absorbance change labelled C550. R is, in all likelihood, also a plastoquinone (PQ) molecule. It is suggested that R accepts electrons from Q one by one, but delivers them to the PQ pool as a pair in one step. (HCO_3^-) above the arrow between the R and PQ pools means that its presence is necessary for this electron flow. Enough energy is available during electron flow from PQ pool to cytochrome *f* (cyt *f*) that can be used for making ATP. (In the present day picture of phosphorylation, this statement must be modified.) Plastocyanin (PC) is the electron donor to $P700^+$. There is a suggestion that there may be another parallel pathway between PQ pool and P700.]

The strong reductant (X^-) reduces an iron-sulphur protein, ferredoxin, which, in turn reduces nicotinamide adenine dinucleotide phosphate ($NADP^+$) to NADPH with the aid of the enzyme ferredoxin-$NADP^+$ reductase. Another compound, labelled ferredoxin-reducing substance, may play some important role in the reduction of ferredoxin by X^-, but this has not yet been established at all.

The weak oxidant produced by PS I oxidizes Q^- through a chain of electron carriers involving an unknown compound labelled R[36–38], a plastoquinone[39], cytochrome *f*[40] and plastocyanin[41]. Energetically, the oxidation of Q^- is a downhill process and is coupled with the production of ATP[42] from ADP and inorganic phosphate (Pi). The existence of a cyclic flow of electrons around photosystem I has also been documented[43]. A cytochrome (cyt b_6) may be involved in this reaction as an intermediate[44]. The cycle starts at X^- and ends in $P700^+$. When the cycle includes plastoquinone, there is a coupling of this cyclic electron flow with ATP production. There may be several routes through which the electron flows from X^- to $P700^+$. If there were a direct large scale back reaction ($P700^+$. $X^- \rightarrow P700 \cdot X$), there would not be any useful utilization of the energy, but simply a loss in the form of heat or light.

The identity of the unknown donors and acceptors is currently under active investigation in various laboratories. X is perhaps an Fe-S protein, as evidenced by its electron spin resonance signal[45]. A component with an absorption band at 430 nm (labelled P430) has also been suggested to be X[46]. Whether these two entities are one and the same compound is not yet fully certain. Plastocyanin plays the key role of donating electrons to $P700^+$[47]. The identity of Q has

been debated; it seems to be a type of plastoquinone[30a], a quinone type compound with an absorption band around 320 nm (labelled X-320)[29]. The identity of M is least known, although suggestions are that it is a Mn-containing protein; Z may contain tightly bound manganese.

The evolution of oxygen from water is the most mysterious of all processes in photosynthesis. Research from the laboratories of Pierre Joliot[49] and Bessel Kok[50] has shown that four positive charges must accumulate on M before an O_2 molecule may be evolved. These researchers have used the terminology of S for M; S is not used here because it reflects the entire complex MZP680Q. In a simplified form, the state of S may be represented by the letter M; the four steps operate as follows :

$$M \xrightarrow{h\nu} M^{+} \xrightarrow{h\nu} M^{2+} \xrightarrow{h\nu} M^{3+} \xrightarrow{h\nu} M^{4+} \xrightarrow{2H_2O \rightarrow O_2 + 4H^+} M,$$

where the superscripts indicate the number of + charges on M, O_2 being evolved only in the last step. This model is supported by various kinetic data. It is likely that Mn, which can exist in various oxidation states, is the charge accumulating element, but no direct experimental data are available yet. Recent experiments, using NMR techniques, have given the first indication that manganese may indeed be involved in these steps[51,52].

It is now firmly established that if isolated chloroplast fragments (incapable of CO_2 fixation) are depleted of HCO_3^- ion, they become incapable of performing Hill reaction (i.e. evolution of O_2 and reduction of an artificial dye)[53–55]. Addition of HCO_3^- restores Hill reaction. Stemler *et al.*[56] have shown that bicarbonate (HCO_3^-) ions are essential for the relaxation of the various S states (e.g. Z $P680^+$ Q^- to Z^+ P680Q). The roles of Mn-containing protein (not yet isolated), HCO_3^- and the chloride ions need to be further investigated before a complete picture of O_2 evolution will be available. In recent years, however, it has become clear that the major role of HCO_3^- is in the electron flow from Q to plastoquinone (PQ) pool[57], and this effect is located between R and PQ pools[38,58,58a].

NADPH and ATP, the end products of the above set of reactions, are then utilized in the conversion of CO_2 into carbohydrates. The details of CO_2 fixation into carbohydrates, the path of electrons from H_2O to CO_2, the role of chlorophyll, and the primary events of photosynthesis have been discussed by Bassham[59], Levine[60], Rabinowitch and Govindjee[61], and Govindjee and Govindjee[11], respectively.

In photosynthetic bacteria, the O_2 evolution mechanism is absent, and the end products of electron flow are NADH and ATP; other details of the process are quite different; this will not be discussed further.

To appreciate the process of photosynthesis, we must understand the fate of the energy absorbed by a chlorophyll molecule, and the reasons why the oxidized donors and the reduced acceptors, produced by light, do not recombine immediately (thermodynamically, the most favoured reaction), to dissipate the stored energy.

Excitation Process

Type of pigments — Absorption of light in higher plants is due to green chlorophylls of types *a* and *b* and many types of yellow and orange carotenoids, belonging to either the carotene group or the carotenol group (the xanthophylls). Several classes of algae (e.g. blue-green and red aglae) contain, instead of chlorophyll *b*, water-soluble blue (phycocyanins) and red (phycoerythrins) pigments. Brown algae and diatoms contain a carotenoid called fucoxanthol. Photosynthetic bacteria contain bacteriochlorophyll instead of chlorophyll as their major pigment. Absorption spectra of some of these pigments are shown in Fig. 4.

Studies by Brown[62] and Gasanov and French[63] have confirmed the presence of different spectroscopic forms of chlorophyll *a in vivo*. They are indicated by their red absorption maxima (in nanometres) as Chl *a* 660, Chl *a* 670, Chl *a* 680, Chl *a* 685, Chl *a* 690 and Chl *a* 695-720, etc. In all probability, these different Chl *a* forms are Chl *a* molecules in different environments (different states of aggregation[64] or different Chl-protein complexes)[65] which have evolved so as to aid in the efficient utilization of light energy by plants.

What really happens during light absorption? — The chlorophyll *a* molecule has a conjugated single-double bond ring containing the so-called π electrons. As a result of interaction between light quanta (or photons) and the electrons, absorption of a photon leads to quantized "upward" transition of a π electron within 10^{-15} sec (Fig. 5). Light energy is thereby converted into electronic excitation energy, and the molecule is said to have gone into an excited state. The energy difference ($\triangle E$) between the ground and the excited state must equal the energy of the absorbed quantum. In chlorophyll *a*, there are two important excited states available. The one reached by absorption of red light (around 680 nm) is called the first singlet excited state S_1 (the lowest lying excited state), and the one reached by absorption of blue light (around 440 nm) is referred to as the third singlet excited state S_3. These two transitions are responsible for the main absorption bands of chlorophyll *a*[66].

In chlorophyll *a*, as in all polyatomic molecules, we have to concern ourselves with the vibrations, as well

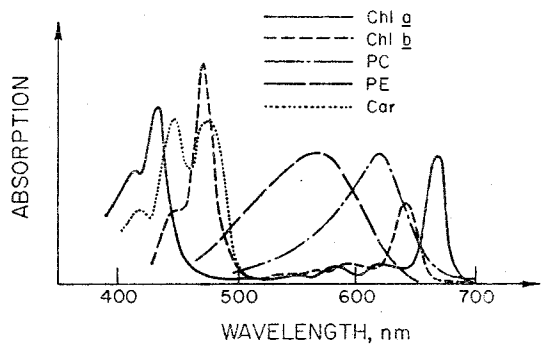

Fig. 4 — Estimated absorption spectra of various pigments *in vivo* [Chl *a*, chlorophyll *a*; Chl *b*, chlorophyll *b*; PC, phycocyanin; PE, phycoerythrin; and Car, carotenoids. Chlorophylls have absorption spectra in the blue and red regions. PC absorbs orange light, PE green light and Car, blue-green light.]

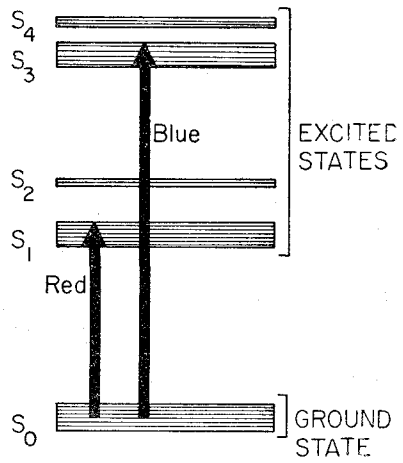

Fig. 5 — Diagrammatic sketch of the energy level diagram of chlorophylls [S_0, S_1, S_2, S_3 and S_4 are the ground, first, second, third and fourth excited states respectively. Main absorption bands in the red and blue regions are due to $S_0 \rightarrow S_1$ and $S_0 \rightarrow S_3$ transitions, respectively.]

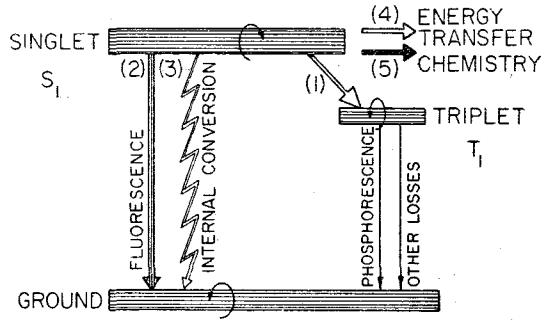

Fig. 6 — Fates of first singlet excited state [*see* text for explanation. Small curly arrows show the spins of electrons. In the triplet state, the electron has parallel spin to that in the ground state, but in the singlet state, it is antiparallel. (1) indicates intersystem crossing. Triplet state (T_1) has not yet been shown to be involved in the main path of chemistry, but its existence *in vivo* has been shown by various methods.]

as rotations of molecules. Thus, the ground state cannot be represented by a single energy level, but must be represented by several closely spaced vibrational energy levels. Similarly, the excited state(s) are also composed of multiple vibrational and rotational levels. In the first approximation, the difference in energy between ground and the excited electronic levels is 1-2 eV, while that between the various vibrational levels is 0·1 V; the rotational levels, superimposed on these levels, are separated by 0·01 eV.

Light absorption leading to an upward transition of an electron may occur from any of the various vibrational levels of the ground state to any of the vibrational levels of the excited singlet state(s). Thus, molecular absorption is represented by broad spectral bands corresponding to the frequencies of light that provide the necessary amounts of energy for these transitions.

Fates of Excitation Energy

Photochemically, the first singlet excited state appears to be the most important state. Absorption leading to the production of higher excited states results in a rapid (wthin 10^{-13} to 10^{-14} sec) de-excitation by radiationless processes to the first excited state. Once the first excited singlet state of chlorophyll *a* is attained, the molecule has several options open to it (Fig. 6): (i) It can enter into a still different but lower-lying energy state called the triplet state. Such a fate is referred to as intersystem crossing. (ii) It can emit a quantum of light, while the electron returns to the ground state (fluorescence). The fluorescent quantum has a lower frequency (or longer wavelength) than that of the quantum absorbed; this occurs because some of the energy is lost via internal conversion when the molecule relaxes from the higher vibrational levels to the lowest vibrational level of the excited state before the quantum is emitted. (iii) It can lose its energy as heat by internal conversion. (iv) It can transfer its excitation energy to a neighbouring molecule having equivalent energy levels; this is the main fate of light absorbed in the antenna or bulk Chl *a* or other pigment molecules, and will be discussed later. (v) It can enter into a photochemical reaction of the type mentioned earlier; this, of course, is the primary fate of the energy reaching the reaction centre Chl *a* molecules.

A back reaction of the primary photochemical reaction also occurs to a limited extent. A recombination of the reduced electron acceptor (Q^-) and of the oxidized electron donor ($P680^+$ or Z^+) leads to the production of delayed light emission, which has the same spectral characteristics as chlorophyll fluorescence (*see* Lavorel[67] and Govindjee *et al.*[67a]).

The triplet state — In green plants, no convincing experiment exists to date that demonstrates directly the role of triplets[68] in the main pathway of photosynthesis, although a great deal of data are now available which indicate that triplets are indeed present *in vivo*. Dutton and Leigh[69] observed certain electron spin resonance signals, ascribed to absorption and emission among the three sublevels of the triplet state of bacteriochlorophyll in photosynthetic bacteria; however, this was possible only when the primary electron acceptor molecules were kept in the reduced state.

Analysis of delayed light emission in green plants in our laboratory[70], in terms of triplet-triplet annihilation theory, has led us to believe that triplets must be present in a concentration less than 10^{-7} of the total chlorophylls present to account for the results thus far obtained. Krasnovsky *et al.*[71] have discovered phosphorescence (*see* below) around 960 nm from green plants, and Hoff *et al.*[72] obtained evidence for the presence of triplets with slightly different energy levels from pigment systems I and II.

If a chlorophyll *a* molecule is in the triplet state, it will also have several options: (i) The electron can be kicked back up to the first excited state by thermal energy. From there it can return to the ground state by emitting a light quantum as fluorescence, but this fluorescence would be delayed from the time of absorption due to the longer lifetime of the triplet state, and

is thus called delayed fluorescence; it has the same frequency of emission as that of the fluorescence, because the energy gap between the excited state and the ground state is the same. It is not yet certain if any component of the delayed light emission observed in photosynthetic systems is due to this mechanism. (ii) The electron can be kicked up to a higher lying excited triplet state if the proper frequency of light is available[73]; this has been shown for chlorophyll *a* *in vitro* by using bright flashes of light. (iii) The electron can go down to the ground level directly accompanied by light emission called phosphorescence; the wavelength of emission is predicted to be longer than that for fluorescence, because the energy gap between the triplet and the ground states is smaller than that between the excited singlet and the ground state. Phosphorescence from Chl *a* has been demonstrated *in vitro* and *in vivo*[71]. (iv) The electron can fall back to the ground state accompanied by heat loss (internal conversion). (v) The energy in the triplet state may be transferred to triplet states of the neighbouring molecules; however, this path has not been demonstrated experimentally. (vi) Finally, the triplet state may be directly involved in photochemical reactions, although no experimental evidence exists.

Chlorophyll fluorescence — A green leaf, when excited with blue, green, yellow, orange or red light, emits red light[74-76]. This light emission (fluorescence) is very weak in plants. For example, for every 100 photons of light absorbed, only 3–6 photons are emitted; this is understandable, as most of the absorbed photons must be used for photochemical reactions. It is not easy to observe chlorophyll fluorescence with the naked eye due to its low intensity. However, fluorescence from chlorophyll solutions can be easily observed with the naked eye, by exciting with blue light, due to the higher yield of fluorescence in such samples. The efficiency of fluorescence of chlorophyll in solution is high, because the excitation energy is not utilized in photosynthesis and other modes of de-excitation are perhaps also decreased.

At room temperature, the spectral distribution of light emission in green plants consists of a major band at 685 nm, and a minor band around 740 nm (Fig. 7). Emission spectra measured at low temperatures (e.g.77° K) show bands at 685, 695 and 730 nm[77-79]. Pigment system II is mainly responsible for the 685 and 695 nm bands, while the 730 nm band originates mainly from pigment systems I[80-82] (Fig. 8).

Fluorescence transient — Chlorophyll *a* fluorescence intensity, *in vivo*, undergoes changes as a function of the time of illumination. This phenomenon, called the Kautsky effect, after its discoverer, can be broadly classified as fast or slow[83]. The fast change, involving a biphasic rise of fluorescence and subsequent decay, is completed in approximately 2 sec and the slow one, often involving a rise to a peak and then a slow decay to a terminal steady state, lasts for several minutes (Fig. 9).

The fast change (labelled OIDPS) is sensitive to the rate of electron flow, as shown by the effect of addition of certain electron acceptors and inhibitors of electron flow[84]. This change has been explained in terms of the primary photochemical reactions occurring at

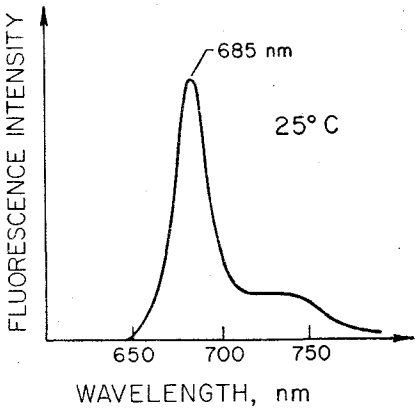

Fig. 7 — Fluorescence emission spectra of a chloroplast suspension at 25°C [The shoulder around the 730-740 nm region is due mainly to the "mirror image" of the vibrational band of chlorophyll *a* on the short wavelength side of the main red absorption band around 678 nm. Most of the emission is from pigment system II. However, a portion of emission around the 712-715 nm region originates in pigment system I.]

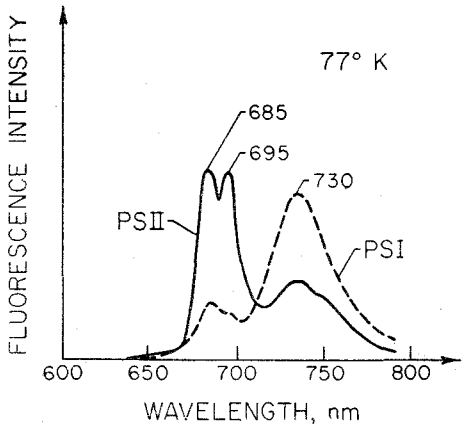

Fig. 8 — Fluorescence emission spectra of pigment system II (PS II) and I (PS I) at 77°K[Qualitatively, more of 685 and 695 nm emission bands belong to PS II and more of the 730 nm band to PS I.]

reaction centre II and the subsequential electron transport through the intersystem electron carrier (A) to the primary electron acceptor of photosystem I (X)[85].

Additionally, conformational changes in the thylakoid membrane are suggested to cause slow fluorescence changes[83]. One hypothesis is as follows. If the highly fluorescent pigment system II and the weaky fluorescent pigment system I are brought close together, energy absorbed in pigment system II could "spill over" to pigment system I, reducing the overall fluorescence yield. However, if the two systems move farther apart, the fluorescence yield is increased, as this spill over is no longer permitted. A conformational change of the thylakoid membrane is initiated by light, probably, via a series of events: ion movements, which lead to structural alterations of the membrane, resulting in the movement of pigment

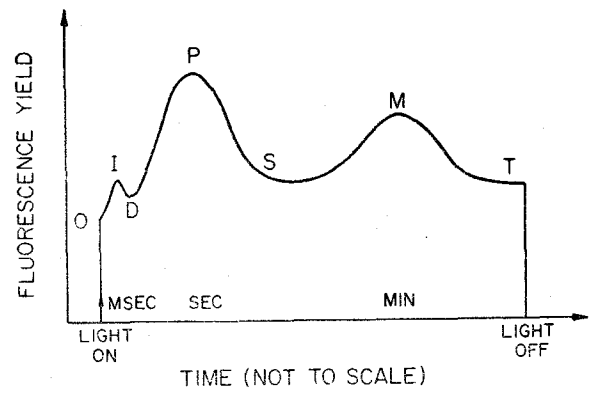

FIg. 9 — Fluorescence yield as a function of time of illumination with strong light (diagram) [0I phase is the photochemical phase (Q to Q⁻ reaction); ID decline indicates interaction with system I or possibly a fast "spill over" of energy from strongly fluorescent PS II to weakly fluorescent PS I; DP rise is due to accumulation of Q^- as the electron acceptor of PS I X accumulates as X^-. P to S decay is complex and may include conformational changes leading to changes in "spill over" of excitation energy from PS II to PS I. Conformational changes may arise due to efflux of Mg^{2+} and influx of H^+ into the thylakoid membranes. SMT phase is also related to such conformational changes due to ionic and other changes in the thylakoid membrane.]

systems closer or farther apart. Alternatively, movement of chlorophyll molecules closer to one another in pigment system II alone could lead to an increase in internal conversion and decrease in fluorescence yield[86].

The best indication of the relationship of the membrane changes to Chl *a* fluorescence comes from the effect of divalent cations (e.g. Mg^{2+}) on the Chl *a* fluorescence in isolated chloroplasts. In the presence of the herbicide 3(3,4-dichlorophenyl)-1,1-dimethylurea (DCMU), an inhibitor of the intersystem electron flow, Mg^{2+} causes an increase in fluorescence above the intensity reached with DCMU treatment alone, implying that it is an effect unrelated to electron transport[87,88]. Measurements of the fluorescence emission spectra in the presence and absence of Mg^{2+} show a relative increase in the height of pigment system II (PS II) emission peaks over the pigment system I (PS I) emission peak. This could imply that Mg^{2+} either decreases the spill over of energy from PS II to PS I[88] or increases the spill over of energy from PS I to PS II[89].

Mohanty *et al.*[84] and Jennings and Forti[90] showed that glutaraldehyde fixation of chloroplasts did not permit the above changes. Thus, some sort of structural changes must be involved in the above phenomenon. However, structural changes, as monitored by 90° light scattering changes, are not precisely related to fluorescence changes[91]. It is suggested that microconformational changes are responsible for fluorescence changes[92].

In cation depleted chloroplasts, Gross and Hess[93] have shown that low concentration of monovalent cations increases the spill over of energy from system II to system I, whereas further addition of divalent cations decreases this spill over. Wydrzynski *et al.*[94] have suggested that these effects involve interaction with antenna chlorophyll molecules. The concept of changes in spill over has recently been confirmed by D. Wong and Govindjee (unpublished) by measurements on polarization and lifetime of system II and system I fluorescence. The regulation of excitation energy transfer by cations has recently been reviewed by Barber[95].

Lifetime of excited states — The lifetime of excited state of a fluorescent molecule is the time necessary for fluorescence intensity to decay to $1/e$ of its maximum value. The elucidation of the exact mechanism of the primary reaction requires a knowledge of the kinetics of fluorescence emission, and such studies involve lifetime measurements. The lifetime of the higher singlet excited states is extremely short (of the order of 10^{-13}-10^{-14} sec). Fluorescence from the transition of the second or higher singlet to the first singlet state has never been observed in the living cell. There is no evidence that second or higher singlet excited states of chlorophyll *a* are directly involved in any photochemical reaction.

The lifetime of the first excited state (τ, first measured by Brody and Rabinowitch[96]; Terenin and coworkers[97]) is related to the quantum yield of fluorescence (ϕ) [$\tau = \phi \cdot \tau_0$, where τ_0, the intrinsic lifetime, is the lifetime of a molecule when the only mode of de-excitation is fluorescence]. The value of τ_0 can be calculated from the absorption spectrum. It is interesting to note that ϕ for Chl *a* in solution, calculated from $\tau = \phi . \tau_0$, was 0·33 (or 33%), exactly as much as measured directly. However, in living cells, the value of ϕ calculated from lifetime measurements is much higher than that measured by direct methods. Thus, it was suggested that the discrepancy must be due to the presence of some non- (or weakly-) fluorescent Chl *a* form which was not involved in τ measurements, but which absorbs light; this must have been the weakly fluorescent chlorophyll *a* of system I. Measurements of the lifetime of the excited state of Chl *a in vivo*, either when photosynthesis is stopped by added inhibitor[98] or by low temperature[99] (or is saturated with bright light), show only one component, with a value of the order of 2 nsec.

Seibert and Alfano[100], using a frequency-doubled mode locked Nd: glass laser and an instrument capable of measuring on picosecond time scale, discovered two fluorescing species in chloroplasts: one with a lifetime of $\leqslant$10 psec and the other with a lifetime around 300 psec. Based on differences in emission spectra, they suggested that the two lifetimes represent different Chl *a* molecules—the fast one arising from Chl *a* of pigment system I and the slower one from Chl *a* in pigment system II. However, these and many other early measurements are questionable in the light of the extremely high intensities used in their experiments. Such intensities cause annihilation of singlet states[101]. Recent data with low intensity single picosecond pulses give τ values similar to those obtained earlier by the phase method (0.4-2 nsec)[101a].

Excitation Energy Transfer

The excitation energy transfer from an accessory pigment (energy donor) to chlorophyll *a* (energy acceptor) has been demonstrated by exciting chlorophyll *b* and observing the fluorescence of chlorophyll *a*[102]. This sensitized fluorescence is due to the transfer of excitation energy from donor to acceptor molecules. From such studies, the excitation energy has been demonstrated to follow the path: phycoerythrin→ phycocyanin→ allophycocyanin→ chlorophyll (*see* ref. 103). Each transfer involves some loss of energy. It is believed that if light energy is absorbed by carotenoids, it can be directly transferred to Chl *a*, since green algae do not contain the phycobilins. However, chlorophyll *b* may be on this path in green algae and higher plants. All the photosynthetic pigments (except carotenoids) are known to fluoresce in solution. *In vivo*, however, Chl *a* fluorescence dominates due to the rest of the pigments transferring their absorbed energy to Chl *a* with relatively high efficiency. After reaching Chl *a*, the energy migrates among Chl *a* molecules until it finally reaches the reaction centre; this migration can be demonstrated by observing the depolarization of Chl *a* fluorescence when it is excited with polarized light[104,105]. The chlorophyll *a* molecules are presumably randomly oriented in the plane of the thylakoid membrane. Upon excitation with polarized light, the observed fluorescence is almost completely depolarized, as first shown by Arnold and Meek[104], thereby suggesting extensive energy migration. Decrease in polarization of fluorescence, when the energy trap of system II is closed[105], may be taken as evidence of Förster's slow energy transfer (*see* below).

Excitation energy transfer in photosynthetic systems is suggested to follow the so-called Förster's resonance theory[106]. According to this theory, the donor molecule undergoes relaxation to the lowest vibrational state prior to energy transfer. In Förster's slow transfer model, the energy transfer efficiency is dependent on three main factors: (i) $1/R^6$, where R is the distance between the donor and the acceptor molecule; (ii) the square of orientation factor (κ) depending on the mutual orientation of the dipole moments of the donor and acceptor molecules (in a random sample, κ is estimated to be 2/3); and (iii) the overlap integral, i.e. the overlap area between the absorption spectrum of the acceptor molecule and the fluorescence spectrum of the donor molecule. Apparently, the state of the photosynthetic pigments *in vivo* is such that Förster's slow resonance mechanism remains a reasonable hypothesis. Temperature dependence of energy transfer from one spectral form of chlorophyll *a* to another[107] and from phycocyanin to Chl *a*[108] supports Förster's slow resonance mechanism. Faster mechanism in which energy transfer occurs prior to relaxation to lowest vibrational state cannot be excluded yet. However, calculations of energy transfer, based on lifetime measurements, also support Förster's resonance mechanism.

Using reaction centre preparations (i.e. preparations containing reaction centre bacteriochlorophyll molecules, but devoid of all antenna pigments) from photosynthetic bacteria and picosecond laser flashes, Netzel *et al.*[109] have been able to show that the excitation in bacteriopheophytin molecules (which constitute a part of the reaction centre complex in photosynthetic bacteria) causes changes in P890 (reaction centre bacteriochlorophyll) in approximately 6 ± 2 psec. This puts an upper time limit in which transfer of excitation energy occurs in this system.

The pigments of photosystems I and II may be arranged as if they formed a *lake*[110]. In this model, also referred to as the multicentral model[111], the reaction centres are dispersed randomly in a lake of bulk pigments, such that the excitation quanta arriving at a closed reaction centre can migrate to other open ones. However, there is another model called the isolated puddles or the unicentral model. In this model, each puddle has bulk pigments and one reaction centre molecule; the energy absorbed in one puddle is permitted to migrate only to its own reaction centre. The true situation, however, appears to be somewhere in between (the connected puddles model)[112]. We call it *pond* model. Experiments on chlorophyll *a* fluorescence induction in the presence of an electron transfer inhibitor suggest energy transfer among system II units[113]. Briantais *et al.*[114], on the basis of measurements of lifetime (τ) as a function of quantum yield of fluorescence, also suggested energy transfer among many units. No matter how the pigments are organized, energy transfer is known to be very efficient in photosynthesis, because the quantum yield of primary photochemical reactions (*see* below) is close to 1·0.

Primary photochemical reactions — The light energy absorbed by the photosynthetic pigment molecules is ultimately converted into chemical energy. As mentioned earlier, not all the pigment molecules are directly involved in photochemistry: only 1 out of every 300 chlorophyll molecules is directly associated with the photochemical reaction. Duysens[102] discovered a light-induced absorbance change at 890 nm in photosynthetic bacteria. This was later shown to be due to the reaction centre bacteriochlorophyll[115,116]. Kok[34] discovered a similar light-induced absorbance change at 700 nm in green plants; this was shown to be due to the trap for photosystem I labelled P700, which was shown to be photo-oxidized in light[35]. The photosystem II trap was discovered by Döring *et al.*[23] and was labelled P680 or P690; P680 is also involved in oxidation-reduction.

The primary photochemical reaction can be defined in different ways. It must be the first reaction to occur after a brief flash of light, it should be in the main pathway, and it must still occur at extremely low temperatures (77°K or lower). P700 is indeed oxidized at 77°K, but it cannot be fully reduced at that temperature; the P680 change is also observed at low temperature[117]. Experiments on the quantum yield of P700 oxidation, starting with the early measurements of B. Kok, have shown that it is a highly efficient reaction and, therefore, it must be in the main chain of events. The oxidation of P700 has been shown by Witt and coworkers[35] to occur within 20 nsec.

The two primary reactions in the green plants, as mentioned earlier, may be represented as :

(1) $P700 \cdot X \xrightarrow{h\nu} P700^{+} X^{-}$ and

(2) $P680 \cdot Q \xrightarrow{h\nu} P680^+ Q^-$

There are recent suggestions that Q may be preceded by another acceptor which may be very short-lived. The primary reaction in photosynthetic bacteria is:

$P890 \cdot X \xrightarrow{h\nu} P890^+ X^-$

The production of chlorophyll (or bacteriochlorophyll) cation radical has been demonstrated both by optical and electron spin resonance techniques. Recent data show that the unpaired electron left on P890 is shared between two molecules[116]. It has been suggested that the two chlorophyll (or bacteriochlorophyll) molecules in the reaction centre may be joined through H_2O-like bridges[118]. Recently, it has also been suggested that such a pair of Chl (BChl) is associated with a phaeophytin molecule; these are involved in the primary reactions such that one of the two BChl (Chl) molecules is oxidized and the phaeophytin reduced; the reduced molecule in a second, but very rapid reaction, reduces X. X^- has also been observed by both optical and electron spin resonance methods, and this may be a quinone type molecule in at least bacterial systems[119].

Summary and Concluding Remarks

The path of energy from the time it is absorbed by pigments to the time it is converted into oxidation-reduction energy is traced. Light absorbed in various pigments promotes these molecules to excited singlet states. The first excited singlet state, which has a lifetime of about 1 nsec, appears to be the state involved in photochemistry. Whether triplet states are involved in the main pathway is not yet certain. Excitation energy, in all likelihood, migrates by Förster's slow resonance mechanism, until it is trapped in special chlorophyll molecules called the reaction centre chlorophylls. In green plants, there are two types of separate (or partially connected) pigment assemblies for photosystems with their own reaction centres. These undergo oxidation-reduction, producing a chlorophyll cation and an anion. The chlorophyll cation in one assembly recovers electrons from H_2O, evolving O_2, and the anion transfers electrons to the second chlorophyll cation through a series of intermediates, producing ATP during the process. The second anion ultimately converts pyridine nucleotide ($NADP^+$) to NADPH. With the help of ATP and NADPH, CO_2 is then reduced to carbohydrates.

We must further learn the details of exactly how the excitation energy is transferred, how the cations and anions are produced, how molecular O_2 is produced in green plants, how the back-reactions of photosynthesis are prevented, and how electron flow is coupled to phosphorylation, before attempting to duplicate these steps outside the living cell.

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