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CHARGE SEPARATION IN THE LIGHT REACTIONS OF PHOTOSYNTHESIS

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Abstract: The initial events of the photosynthetic light reactions are
described in terms of light absorption, excitation transfer, trapping,
and electron transfer by radical-pair charge separation.

Our growing understanding of the light reactions of photosythesis now
makes it possible to formulate a general scheme that applies to photo-
synthetic bacteria and to Photosystems 1 and 2 of higher plants and
algae [1,2]. Certainly there are differences in the chemical nature of
the pigments involved, in the arrangement of the molecules in their mem-
brane bound complexes and in the specific electron carriers involved.
Nevertheless, the similarities in the mechanism of excitation transfer
and trapping and in the kinetics of the initial charge separation are
striking.

1) Light absorption occurs in a collection or antenna of chlorophyll
(Chl) and other pigments in protein complexes. These complexes are con-
strained to defined geometries and separations that are important
aspects of their function.

2) Excitation transfer occurs by exciton coupling among the molecules
within a single BChl- or Chl-protein complex and then by resonance or
Förster transfer to neighboring complexes [3]. Excitation transfer
typically involves 100 or more such steps, and yet the excitation
reaches the reaction center within a few hundred picoseconds.

3) Excitation trapping in the reaction centers occurs because,
typically, the excited singlet state of the reaction center Chl lies
somewhat lower in energy than that of the antenna pigments, and because
it contains several coupled molecules, a configuration that helps to
delocalize the excitation.

4) Electron transfer in the reaction centers occurs from an electron
donor, P, to a primary electron acceptor or intermediate carrier, A_1 or

I, typically within 5 psec {4}. The reaction center contains electron donors and acceptors in a well-defined complex of chlorophylls, protein, lipid and other redox components, which can be formulated in a simple linear association, ... D_2 D_1 P A_1 A_2... The initial charge separation, $P^*A_1 \rightarrow P^+A_1^-$, produces a radical pair in which the electron spins are initially antiparallel, as in their singlet precursor.

5) Electron transfer from the primary to a secondary acceptor, $P^+A_1^-A_2 \rightarrow P^+A_1A_2^-$, helps to stabilize the charge separation by decreasing the electrostatic interaction between the oppositely charged species and by otherwise decreasing the overall energy. This transfer occurs in about 200 psec [5]. Back reactions, which may result in delayed fluorescence, become less likely, as a consequence. During the lifetimes of these two charge-separated states, singlet-triplet mixing occurs in the radical pairs leading to electron spin polarization that can be seen using rapid-kinetic EPR methods [6]. Recombination of the radical pairs can also lead to triplet states of the reaction center pigments having characteristic magnetic field interactions and EPR polarization patterns [7,8].

6) Secondary donors and acceptors complete the charge separation to produce a state $D_m^+...D_2D_1PA_1$ $A_2...A_n^-$ in which the light energy has been stabilized as stored chemical potential.

Light Absorption and Electronic Excitation Transfer

Upon the absorption of photons of visible light, pigment molecules such as chlorophylls, carotenoids or phycobilins undergo a transition to an excited singlet state. The overall state of the excited molecule is such that all of the spins are still paired; i,e., the overall spin angular momentum of a singlet excited state is zero, even though its energy is greater than that of the ground state.

Once the excited state is achieved several possible fates become available, as illustrated in Fig. 1. The molecule may simply return to the ground state by re-emitting the radiation as fluorescence or by an internal conversion process that dissipates the excess energy as heat. Alternatively, spin transition may occur by intersystem crossing to a triplet state where the electron spins are no longer all paired. In addition, in certain cases electron transfer processes to an electron acceptor or from an electron donor species may occur, as may photo-chemical reactions or electronic excitation transfer to other molecules in the vicinity. Each of these processes has its manifestation in the
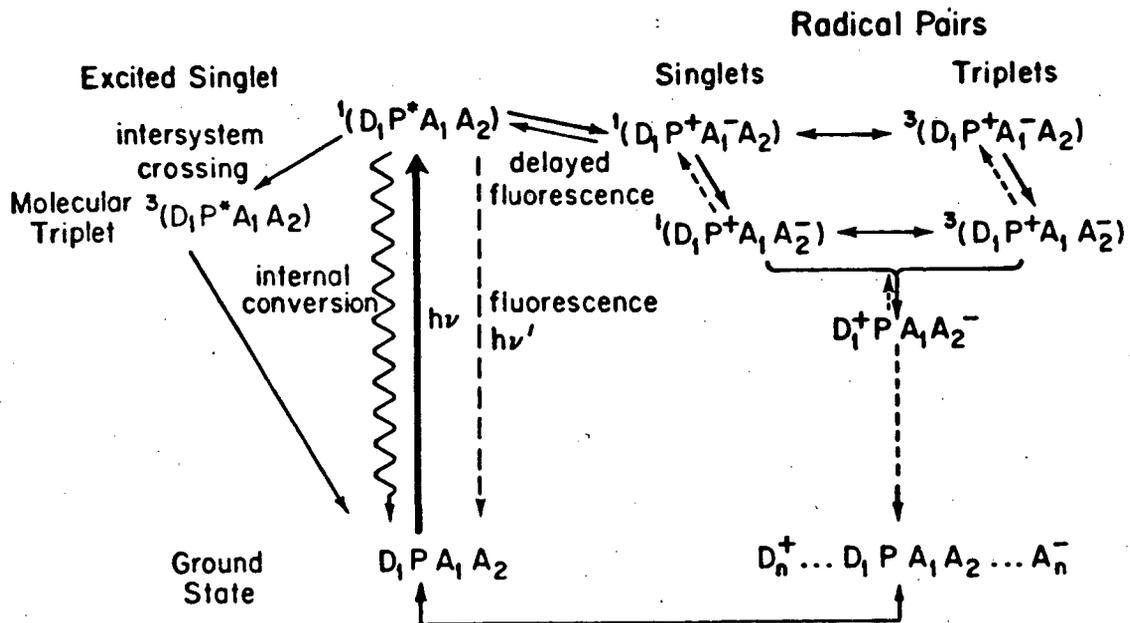
Radical Pairs

Excited Singlet   Singlets   Triplets

intersystem $^1(D_lP^*A_1A_2)$ ⇌ $^1(D_lP^+A_1^-A_2)$ ⟷ $^3(D_lP^+A_1^-A_2)$
crossing   delayed
Molecular $^3(D_lP^*A_1A_2)$ fluorescence
Triplet
                                            $^1(D_lP^+A_1A_2^-)$ ⟷ $^3(D_lP^+A_1A_2^-)$
internal
conversion $h\nu$ fluorescence
                      $h\nu'$ $D_l^+P A_1 A_2^-$

Ground $D_lP A_1 A_2$ $D_n^+ \ldots D_l P A_1 A_2 \ldots A_n^-$
State

Fig. 1. The primary light reactions of photosynthesis leading to
charge separation among electron donors (P, $D_1 \ldots D_n$) and
acceptors (A_1, $A_2 \ldots A_n$) by the radical pair mechanism. Double
headed arrows (⟷) indicate quantum mechanical mixing of
singlet and triplet radical pairs leading to electron spin
polarization (see text). Reactions that are known to be
reversible are indicated by double arrows (⇌). Some
alternate (competing) paths for deexcitation of the excited
singlet state are shown. Others, such as the reaction center
radical-pair triplet state (see text) are thought to occur
only when A_2 is reduced to A_2^- prior to photon excitation.

photosynthetic light reactions. The processes compete with one another
in contributing to the rate of decay of the excited states, and any one
of them (such as fluorescence) may be used to monitor the decay of the
excited state populations. Indirectly, such signals reflect the
competition from other paths (such as electron transfer).

Most, if not all, of the light-harvesting pigments are contained in
definite complexes with protein, with from 2 to 20 pigment molecules per
complex [9-11]. The chlorophylls, phycobilins, etc. within these com-
plexes are sufficiently close to one another that they undergo internal
interactions of an excitonic nature. A singlet excited state in such a
supermolecular array is rapidly delocalized (typically within 10^{-13} to

10^{-14} sec) over the entire set of coupled chromophores [12]. In a sense this constitutes the first stage in the migration of excitation toward the reaction center.

To be productive the excitation must be transferred from one complex to the next until the reaction center is reached. This occurs by a mechanism akin to that of resonance transfer described by Förster [13] and in the time range 10^{-10} to 10^{-13} sec, depending on such factors as spectral overlap, chromophore orientation and spatial separation. We have developed a model, the Pebble Mosaic Model, of the photosynthetic membranes that incorporates some of the necessary features [3,11]. Others, in particular Seely, have considered additional aspects of energy funneling in designing models of efficient light-harvesting antennas [14]. Knox has given consideration to the consequences of grouping molecules in closely coupled ensembles [12]. Nevertheless, there is still much experimental and theoretical work needed to understand this process in photosynthetic membranes.

Excitation Trapping in a Reaction Center

As excitation migrates within the light-harvesting pigment-protein complexes, there normally arises an increasing probability that it will have reached a reaction center. From the point of view of the singlet excitation there are two distinct states of the reaction center that we may characterize as quenching and nonquenching. Excitation reaching a quenching reaction center is quickly abstracted from the antenna pigment system. Because there are mechanisms (see next section) for the subsequent regeneration of the excitation, we use the operational definition that a quenching reaction center is one that removes the singlet excitation for a time that is long compared with the jump time between adjacent light-harvesting pigment proteins. In a non-quenching state, the singlet excitation is not removed from the antenna--at least, not for significantly longer than the jump time. The excitation may pass through or reflect from a non-quenching reaction center and continue to migrate in the antenna pigment system [12].

There is an alternative designation of the reaction centers as open or closed, which is how they may be viewed from the photochemical perspective of their ability to carry out primary electron transfer (see next section). Butler, in particular, has cautioned that one should not equate an open reaction center with a quenching one and a closed reaction center with a non-quenching state [15].

The occurrence of reaction center quenching is reflected by changes in efficiency and lifetime of all competing processes, including fluorescence [16]. The quenching states, therefore, should correlate with a relatively low fluorescence yield and a short fluorescence lifetime, and the non-quenching state should be associated with a high fluorescence yield and a long lifetime. A simple two-state picture like this is attractive, but it is an inadequate representation of the actual situation in the photosynthetic membranes for two reasons.

First, excitation migrating in the light-harvesting antenna and encountering a non-quenching reaction center may continue to migrate until it encounters a quenching one [17]. This possibility of communication between reaction centers has been modeled by Robinson [18]. The continued migration may be extensive, as in the lake model, or it may be limited to visits to only a few reaction centers. The alternative, the puddle model, pictures each photosynthetic unit as containing a reaction center and its antenna which are isolated from communication via excitation transfer with any other photosynthetic unit. To complicate matters further, the extent to which excitation can transfer from one unit to another appears to be a parameter that is variable, depending on factors such as ion concentration, prior illumination and whether membranes are stacked or unstacked.

Second, the light harvesting pigments are not distributed homogeneously in the photosynthetic membranes. This is evident from the different classes of (B)Chl-proteins that can be isolated from plants and bacteria [9], as well as from the various spectroscopic forms present [19]. The inhomogeneity has been formulated for higher plants plants in terms of a tripartite model by Butler and Kitajima [20]. An analogous bipartite or tripartite model appears to apply to most photosynthetic bacteria. Some of these components provide better sinks than others for the excitation.

All of this means that the fluorescence decay is usually not a simple exponential process, or even the sum of two exponentials representing quenching and non-quenching reaction centers, respectively [21]. An example is shown in Fig. 2 for spinach chloroplasts with Photosystem 2 reaction centers open (F_o) or closed by inhibitors and higher light intensity (F_{max}). In each case the fluorescence decay is resolved into three exponential components. The relative contribution of the slowest decay component (0.8-1.5 ns) is increased dramatically upon closing the
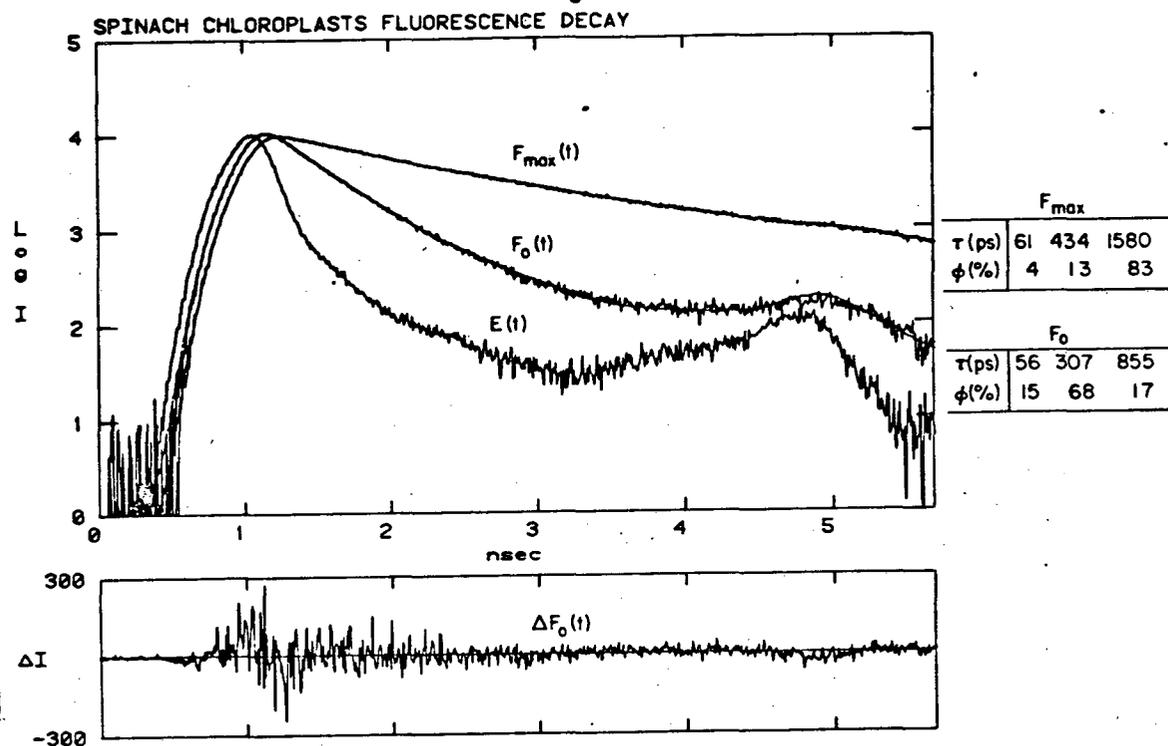
SPINACH CHLOROPLASTS FLUORESCENCE DECAY

F_{max}		
τ(ps) 61	434	1580
ϕ(%) 4	13	83

F_o		
τ(ps) 56	307	855
ϕ(%) 15	68	17

Fig. 2. Fluorescence decay curves for broken spinach chloroplasts; in sucrose, 0.1M; HEPES buffer, 10 mM, pH 7.5; $MgCl_2$, 5 mM; NaCl, 5 mM; contains 18 μg Chl/ml. Curve labeled F_{max}(t) obtained, from a sample containing, in addition, DCMU, 12.5 μM and hydroxylamine, 2 mM. Curve labeled F_o(t) obtained at very low laser intensity from a sample containing ferricyanide/ferro-cyanide, each 1.25 mM and gramicidin D, 1.67 μM. Measurement made on a sample in 1 cm square cuvette using single photon counting; excitation at 600 nm by a synchronously-pumped mode-locked dye laser (rhodamine 6G) at 88 MHz repetition frequency. Excitation pulse, curve E(t), width is determined by the photo-multiplier (RCA-C31034A) transit-time spread. Decay components extracted by method of least squares. Lifetime τ is the 1/e time, and yield ϕ is the product of the decay component initial amplitude times its lifetime. Deviation of calculated and ex-perimental results for F_o deconvolution is shown at the bottom; the fit for F_{max} was comparable. Fits with only two components were distinctly less satisfactory. Experiments performed by John A. Nairn and Dr. Wolfgang Haehnel (Ruhr Universität Bochum) in the author's laboratory.

reaction centers, especially if one also takes into account the increase (about 3-fold) in the overall fluorescence yield. The short lifetime and intermediate lifetime components show little or no absolute yield change (after correction for the overall fluorescence yield increase) upon closing the reaction centers. From other studies we know that the decay kinetics as a function of the state of the reaction centers reflects interactions among photosynthetic units, providing us with valuable insights into the structural arrangement and function of these membrane-associated components.

Charge Separation in the Reaction Centers

The primary electron donors and acceptors of the reaction center complexes are collections of (B)Chl molecules and, in some cases, their corresponding pheophytins. The similarity between the reaction center molecules and the pigments of the neighboring antenna assures good spectral overlap required for efficient transfer and trapping of singlet radiation in the reaction center [12,13]. The fact that the Chl or BChl donor species, particularly P700 and P870, are aggregates of two or more molecules leads to excitonic interactions that provide relatively low energy excited singlet states, which is an aid to efficient trapping [3]. The subsequent electron transfer between the primary electron donor (B)Chl aggregate, P, and the primary electron acceptor, designated A_1 or I, is subject to a strict energy requirement. There must be sufficient energy in the excited singlet state to provide for charge separation into a radical pair $P^+ A_1^-$ (Fig. 1). A wasteful back reaction of this charge separation is prevented by (1) dissipating a fraction of the singlet energy as heat, (2) delocalizing the hole and the electron over more than one molecule, (3) dephasing the electron spin so that triplet character is introduced into the radical pair, and (4) transferring the electron quickly from primary to secondary acceptors.

A meaningful way to consider the energy stored in the radical pair, $P^+ A_1^-$, is in terms of the redox couples $P \rightarrow P^+ + e^-$ and $A_1 + e^- \rightarrow A_1^-$. Photosystem 1 reduces a very low-potential electron acceptor at the expense of a moderate-potential electron donor. For this purpose, the donor P700 contains Chl in a "special pair" [22], which decreases its electrochemical (reduction) potential relative to that of monomeric Chl. The primary acceptor is probably also Chl [6], although there is uncertainty at present whether it is monomeric [23] or dimeric [24].

Photosystem 2, on the other hand, reduces a moderate potential electron acceptor by transferring an electron from a very high-potential donor. It has been proposed that the donor, P680, is a ligated monomeric Chl [25], thus making its electrochemical potential more positive than it would be if it were aggregated. The primary acceptor is a pheophytin (Pheo) molecule [26], which is reduced more easily than is Chl [27].

These underlying principles appear to extend to purple photosynthetic bacteria as well. The excited singlet state of bacterial reaction centers lies lower in energy than is the case with green plants; charge separation in bacterial reaction centers produces a moderate-potential electron donor and a moderate-potential primary acceptor. It is not surprising, then, that the donor P870 is a BChl dimer or special pair [28] and that the intermediate carrier I is BPheo [29]. Although influences from the immediate environment doubtless modulate these potentials, the state of aggregation and the presence or absence of Mg in the porphyrin are certainly important.

The kinetics and mechanism of charge separation in the reaction centers have been widely investigated using optical and magnetic resonance techniques [2,8]. Through the use of rapid kinetic (pico-second) absorption change measurements, charge transfer from the primary donor P870 in bacteria to the intermediate acceptor I (BPheo) is seen to occur in about 5 psec [4]. There is some question about whether the electron first resides on another BChl in the reaction center [30], pro-ducing a species $BChl_2^+ BChl^-$; but within about 30 psec the BPheo appears to become reduced. The lifetime of the state P^+I^- ($BChl_2^+$ $BPheo^-$) is about 200 psec at room temperature [5,30], whereupon the electron is transferred to a secondary acceptor (ubiquinone or menaquinone). The kinetics appears to be similar in Photosystem 1, although the the fast phase of P700 oxidation is not yet time resolved. The initial acceptor in this case appears to be Chl, as mentioned above.

These charge separation reactions occur even at a temperature of 4K; and when transfer to subsequent electron acceptors is blocked, the initial charge separation is reversible [31,32]. The back reactions of the different light reactions have different Arrhenius activation ener-gies at high temperatures, but in each of the three light reactions studied (PS1, PS2 and bacteria) the back reaction at sufficiently low temperature becomes temperature-independent with a time constant of about 1 msec. The interpretation of this behavior is that electron

tunneling through a potential barrier occurs in the initial charge separation and recombination. The detailed structure of the potential barrier and the distance of separation of the electron donors and acceptors involved are objectives of the analysis of this thermally-activated tunneling process [33].

The product of charge separation in the reaction center is best described as a radical pair that is born in a singlet state, $^1(P^+A^-)$. What this means is that the separated electrons on P^+ and A_1^- do not undergo an immediate loss of the spin correlation that they had in the excited singlet state $^1(P^*A_1)$ preceding the electron transfer. Because the odd electrons on P^+ and on A_1^- are now in different environments (particularly the magnetic environments owing to electron-nuclear hyperfine interactions), the electron spins gradually dephase, and within a nanosecond the radical pair develops triplet character, $^3(P^+A^-)$. The time evolution of this process is somewhat complicated; the basic pattern has been worked out, but it need not concern us here [6].

As a consequence of singlet-triplet mixing of the radical pair species, electron spin polarization develops. This means that the population of the various spin sublevels in a magnetic field are not in thermal (Boltzmann) equilibrium. As a consequence, there is a transient signal that can be detected using rapid EPR instrumentation [34]. An example of this transient CIDEP (Chemically Induced Dynamic Electron Polarization) signal is shown in Fig. 3 (insert) for chloroplasts where the iron sulfur centers A and B were reduced in the dark by dithionite prior to cooling to 10 K. A brief (0.5 μs) flash of light from a dye laser produces a rapid CIDEP transient that relaxes with a time constant of about 50 μs to an absorptive (thermally relaxed) EPR signal of opposite sign. An analysis of the field-dependence (lineshape) of the rapid transient component of the microwave power (Fig. 3a) shows that it has emissive as well as absorptive components [34,35]. The pattern of the lineshape is diagnostic of a radical-pair origin (rather than a triplet origin, for example) for the signal arising from the reaction centers [6]. Furthermore, studies of the dependence on redox conditions and of the orientation dependence led to the proposal that electron spin polarization develops in two stages [6]. The first stage (seen in Fig. 3b, where the sample was cooled under illumination to reduce X) is represented by the radical-pair $P^+A_1^-$, where A_1^- is attributed to Chl^- with an isotropic electron spin tensor and a g-value very close to that of

Spinach Chloroplasts at 10° K
Dithionite, pH 10

Time (msec)
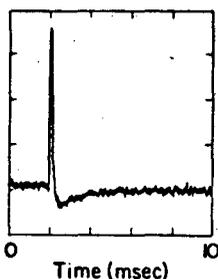
Amplitude of μsec transient

a) Cooled in dark
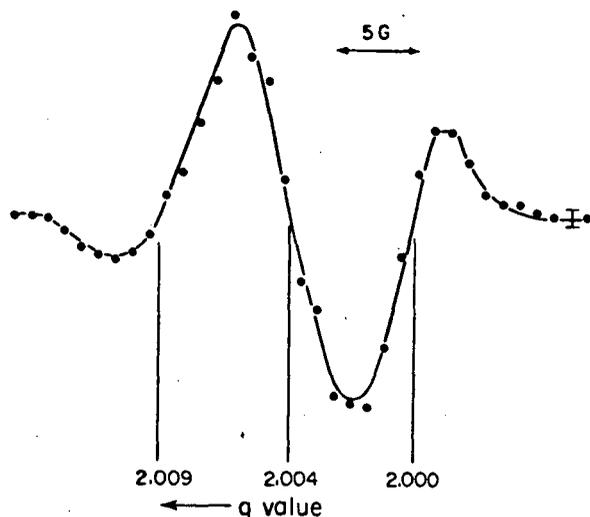
b) Illumination while cooling

5 G

2.009   2.004   2.000
⟵ g value
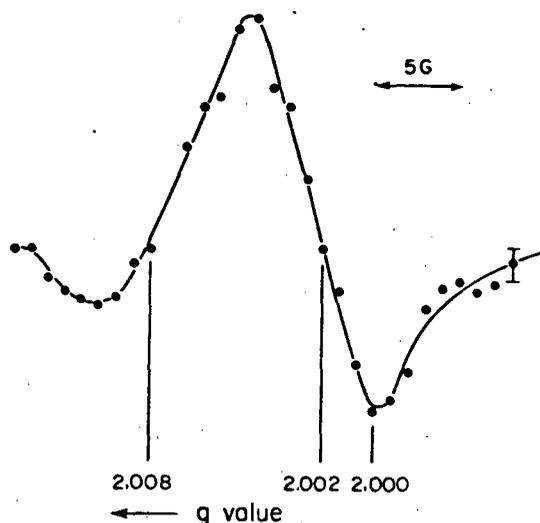
5 G

2.008   2.002 2.000
⟵ g value

Fig. 3. EPR transient signal generated by flash illumination of a
chloroplast sample in presence of dithionite, pH 10, cooled to
10K. Dye laser excitation, rhodamine 6G (ca 600 nm, 0.5 µs
FWHM, 130 mj/pulse. EPR field, 3273G; modulation frequency,
1 MHz; modulation amplitude, 4G; microwave power, 50 µW; Chl
content of sample, 0.35 mg ml^{-1}. Insert: Time transient,
sample cooled in dark, trace is average of 400 transients.

(a) Spectra of EPR kinetic transient taken from peak-to-trough
amplitudes of initial transient, as seen in insert. Sample
cooled in darkness.

(b) Sample conditions as in part (a) except sample cooled to
10K under illumination by white light from a quartz-iodine
tungsten lamp. Data taken from K. Sauer, H.A. Frank and J.L.
McCracken, paper presented at this meeting.

P^+. The second stage (Fig. 3a) is represented by the subsequently-formed
radical pair $P^+A_1 X^-$ where X^- has an anisotropic spin tensor, is

oriented in a particular way in the chloroplast membranes [36] and had been detected previously as an early electron acceptor [37].

At this point it is useful to return to the question of the quenching character of reaction centers in relation to their openness to do photochemistry. Four distinct conditions of the reaction centers can be characterized. (1) With all potential donors in the reduced state and all acceptors in the oxidized state (i.e., $D P A_1 A_2...$) the reaction centers are open and, presumably, quenching [38]. (2) Under oxidizing conditions the state $D^+P^+A_1A_2$ can be produced. This closes the reaction centers to photochemistry but produces a low fluorescence yield, which is attributed to special quenching properties of the paramagnetic P^+ species [15]. (3) Under strongly reducing conditions, $DPA_1^-A_2^-$ may be produced. This should be a nonquenching state (high fluorescence) associated with closed reaction centers, unless A_1^- is a quencher [26]. (4) Under moderately reducing conditions, $DPA_1A_2^-$ is still open to initial charge separation. However, a rapid recombination will occur, $DP^+A_1^-A_2^- \rightarrow DP^*A_1A_2^-$, and this may result in an excited reaction center in either a singlet (hence, potentially fluorescent) state or in a triplet state. Evidence for both products is abundant [16,39]. This charge recombination leads to delayed singlet state fluorescence whose lifetime is extended by the charge recombination time. Triplet optical absorption [2,40] and EPR signals [8,41,42] are also seen, and the latter show polarization patterns clearly indicating a radical pair origin. An example is shown in Fig. 4 for a Photosystem 1 reaction center-enriched sample prepared as in Fig. 3b, where the sample was cooled under illumination to reduce X. The light-induced charge separation then produces the state $P700^+A_1^-$, which leads to the radical-pair triplet upon charge recombination (Fig. 4) and a different lineshape for the rapid transient EPR (Fig. 3b) arising from spin polarization in the radical pair $P^+A_1^-$. In photosynthetic bacteria, an analysis of the effect of a magnetic field on the analogous charge recombination [7] indicates that the electron on BPheo$^-$ proceeds through an intermediate carrier [43], perhaps a BChl of the reaction center complex [30], on its way to recombination with $P870^+$.

In the best documented examples (PS2, where $A_2 = Q$, and bacteria, where A_2 is ubiquinone) the state $DPA_1A_2^-$ is non-quenching [38,43]. It has been proposed that the high fluorescence yield comes predominantly from $P^+A_1^-$ charge recombination [44]. The origin of the variable fluor-
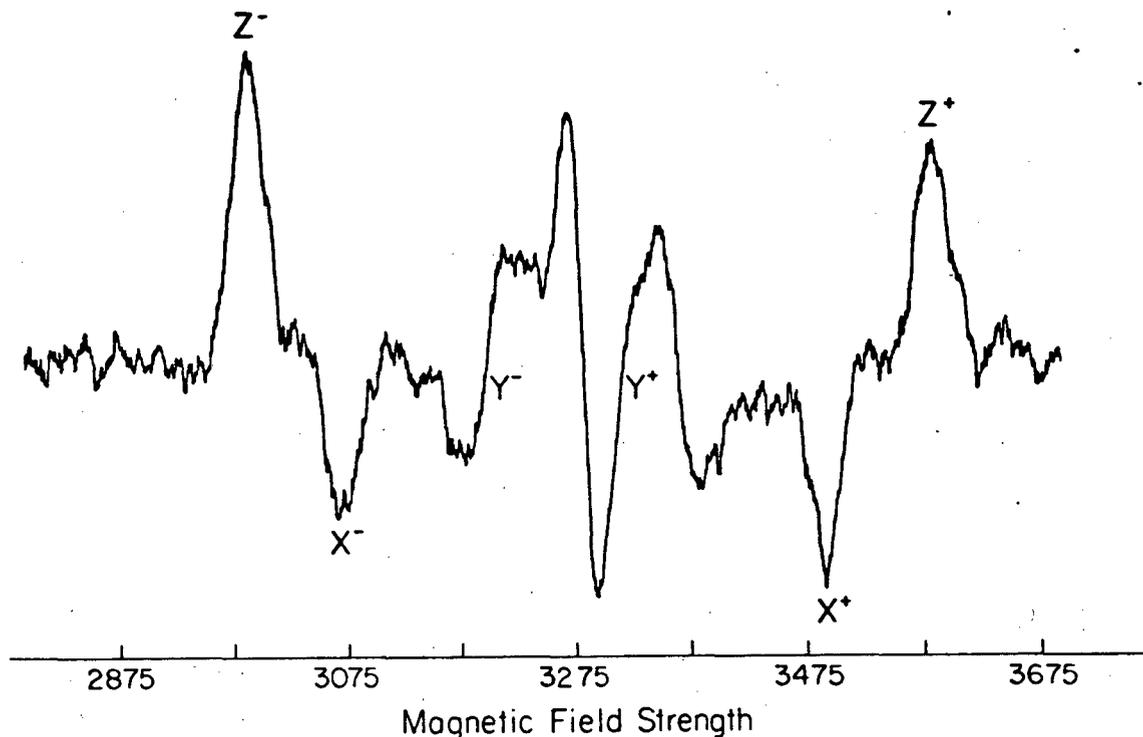
Fig. 4. Triplet EPR spectrum produced by illumination of Photosystem 1
particles at 77 K. Triton X-100 particles contain 80 Chl/P700
and Chl a/Chl b > 7; dithionite, 12 mM; phenazine
methosulfate, 1 mM; glycine buffer, 0.2 M, pH 10; Chl
concentration, 110 μg ml^{-1} in 50% ethylene glycol. Sample
illuminated 60 sec at 273K and during subsequent cooling to
77K. EPR spectrometer (Varian E-109) conditions: microwave
power, 1 mW; modulation amplitude, 40G; gain, 12.5; scan, 33G
min^{-1}. Light modulation and phase-sensitive detection at 33.5
Hz; time constant, 10 sec; illumination by xenon lamp
operating at 930 W. Experiment performed by Mary B. McLean in
the author's laboratory.

escence of PS2 and bacterial reaction centers is not yet clear. In any
case, one can see from this analysis that there is no simple correlation
between open and closed reaction centers, on the one hand, and quenching
or non-quenching states on the other.

Stabilization of Charge Separation by Secondary Donors and Acceptors

The spin-polarized primary radical pair of the reaction center relaxes (Fig. 3) by a complex pattern of processes. Spin-lattice relaxation removes the spin polarization in times of μsec or shorter. The radical pair loses energy as the electron moves to a secondary acceptor with a less electronegative potential and as the primary donor becomes reduced by less electropositive secondary donors. During this process an electric field is built up across the membrane [45], presumably in response to the spatial disposition of the various donor and acceptor species.

Conclusion

The storage of photon energy as chemical potential associated with separated positive and negative charge is the central fact of the photosynthetic light reactions. Absorption by an antenna of light harvesting pigments increases the light collecting efficiency of the reaction centers, but it puts severe demands on the design with respect to excitation transfer to the reaction centers. By a combination of excitonic and efficient resonance transfer between them, the extent of energy loss to competing processes is kept to a minimum.

The reaction center components are designed so as to convert the arriving electronic excitation energy into a charge-separated radical pair. The potentials associated with the electron donors and acceptors are precisely tailored to meet the demands of the reaction center products. Relaxation of the radical pair state stabilizes the charge separation and decreases the probability of wasteful back reactions. This relaxation involves some necessary energy losses, but there are also important entropic contributions to stabilization from spin-lattice interactions, spin dephasing and spatial delocalization of the electrons. A transmembrane electric field is generated that operates together with the oxidizing and reducing power of the electron transport component to drive the biochemical steps of photophosphorylation and carbon fixation.

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