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Molecular Basis for the Photosynthetic Primary Process

(energy upconversion/excitonic interactions/photosynthesis)

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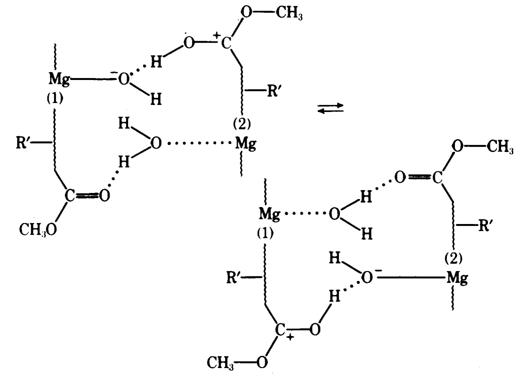
ABSTRACT In this paper, the molecular details for the primary reaction in photosynthesis are deduced from several recent critical experimental observations. A symmetrical structure is proposed for the basic unit of the reaction center in plant photosynthesis. A mathematical consequence of the symmetrical arrangement is the creation of an anomalously long-lived trap state, which makes possible the summation of a reaction-center triplet excitation and an antenna chlorophyll singlet excitation to bring the photoactive chlorophylls to a charge-transfer state prior to entering into a primary photochemical reaction.

It has long been recognized that certain chlorophyll (Chl)-a molecules in plants and photosynthetic bacteria are capable of performing highly efficient photochemical work under the illumination of relatively low-energy photons in the near infrared. No parallel situation exists in chemistry. Chlorophyll-a molecules by themselves are not photochemically activated by visible or infrared photons.

In existing theories (1–3), the possible involvement of the excited singlet and triplet eigenstates of the Chl-a molecule in the primary photochemical reactions has been considered. In a recent paper (4), I suggested a basic mechanism for the primary reaction in photosynthesis. Through interactions between the lowest-lying triplet state of the reaction-center chlorophylls and the first excited singlet state of the antenna chlorophylls, absorbed light quanta are upconverted to a higher-lying charge-transfer state. In this paper, the molecular details of the energy-upconversion reaction are described in terms of experimental observations and first principles.

Nature of the photoactive charge-transfer state

In seeking the most probable configuration for the reaction-center chlorophylls, we take into cognizance: (*i*) the recent finding (5–10) that the primary photooxidation product of *in vivo* photosynthesis contains a special pair of Chl molecules over which the spin density is equivalently distributed and (*ii*) *in vitro* mixtures of Chl and H_2O give rise to photoactive 1:1 Chl–H_2O adducts (10). We propose an interesting symmetrical (C_2) structure (see Fig. 1) in which the two parallel porphyrin rings of the Chl molecules are complementarily held in position by two H_2O molecules, each being involved in a hydrogen bond to the carbonyl of the ring V carbomethoxy group of one Chl molecule and an oxygen coordination bond to the magnesium atom of the second Chl molecule. This structure is a modification of the original Katz model (10) in which the two chlorophyll molecules are asymmetrically linked by a single H_2O molecule with one chlorophyll acting as an electron donor and the second an acceptor. The symmetry of the present model, which appears to be consistent with the observation of the equivalent spin distribution in the photooxidized special pair, suggests a number of theoretical possibilities. Upon light excitation, for example, two equivalent tautomeric forms of the postulated charge-transfer state are generated:



[A]

where (1) and (2) denote the porphyrin rings of the two reaction-center chlorophylls, R′ denotes the phytyl group, and

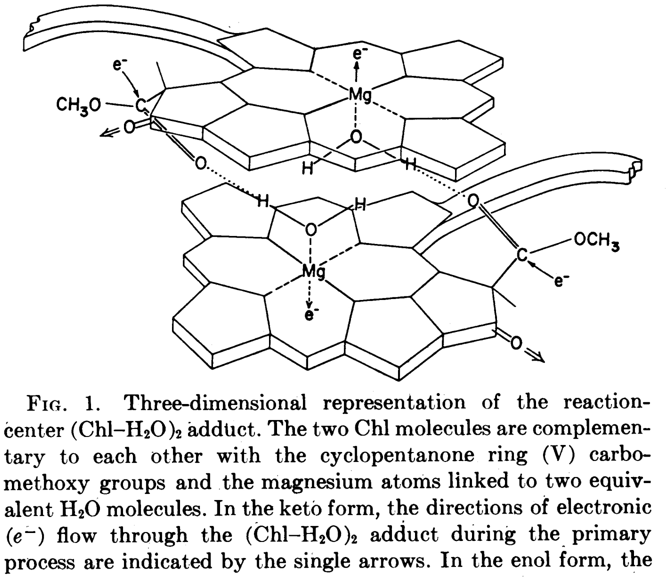


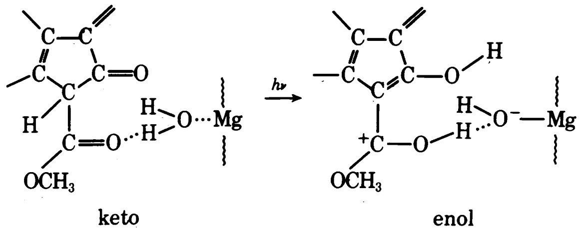
FIG. 1. Three-dimensional representation of the reaction-center (Chl–H_2O)$_2$ adduct. The two Chl molecules are complementary to each other with the cyclopentanone ring (V) carbomethoxy groups and the magnesium atoms linked to two equivalent H_2O molecules. In the keto form, the directions of electronic (e^-) flow through the (Chl–H_2O)$_2$ adduct during the primary process are indicated by the single arrows. In the enol form, the electronic influx will be delocalized. The two ring V keto groups are probably engaged in endogamous interactions (indicated by the double arrows) with antenna Chl molecules. The two magnesium atoms may be engaged in exogamous interactions with charge-carrying agents.

Abbreviation: Chl, chlorophyll.

—$COOCH_3$ is the ring V ester group. From [**A**], the (Chl–$H_2O)_2$ reaction-center adduct enters into a primary photochemical reaction, producing the cation radical $(Chl\text{–}H_2O)_2^+$ which presumably yields the observed equal spin delocalization effect (5–9).

The postulated symmetrical tautomeric structures [**A**] for the charge-transfer state invoke the transfer of a water *proton* to a dipolar molecule under light excitation. The excitation energy for bringing about the postulated charge-transfer state [**A**] is expected to be at least commensurate with the photons (in the wavelength region 350–400 nm) which activate the known photochemical hydride abstraction reactions (11–14) in which only C—H bonds (and not the —OH group) have been found to react with the carbonyl compounds. It appears likely that the tautomerism involving the symmetrical adduct structures [**A**] contributes at least partially to the lowering of the energy of the postulated charge-transfer state, such that the primary photochemical reaction can be triggered by a red-to-blue photon upconversion process (4). This upconversion process is related to the well-established upconversion phenomena observed in solid-state materials (15, 16).

In further examination of the postulated photoactivity of the charge-transfer state [**A**], an intriguing possibility suggests itself. If, in the charge-transfer state, the ring V β-keto-ester group exists in the enol form, we readily observe that



the positive charge on the carbonium ion in structure [**A**] becomes in resonance with the π-electron system of the macrocycle. The postulated photoenolization process belongs to the general class of photoisomerization reactions discussed by Gelbart *et al.* (17). A visual inspection of the molecular models reveals that while the angle θ subtended by the molecular orientations of the two partner chlorophylls can be acute for strain-free keto configurations, only enol configurations with $\theta > 90°$ are allowed due to the coplanarity of ring V with the macrocycle in the enol form of Chl. The charge delocalization process thus results in an adiabatic potential surface for the charge-transfer state which is horizontally displaced from the adiabatic surfaces of the keto states. In terms of the theory of molecular relaxation (17–20), this displacement rigorously results in an energy barrier for transitions between the enol state and the keto states. This effect is expected to lengthen the intrinsic lifetime of the postulated charge-transfer state.

Optical activity, symmetry, and energy trap of the photoactive dimer

The absolute configuration for the chlorophyll-a molecule (21) corresponds to a levo-rotatory isomer found in nature. This configuration leads to the C_2 special pair illustrated in Fig. 1. An $S_2(Chl\text{–}H_2O)_2$ adduct with an angle $\theta \sim 180°$ would have resulted had a racemic pair of Chl molecules been involved.

The pure spin states S_0 and S_1 in the Chl molecule may be respectively denoted by $|^1\phi_0 00\rangle$ and $|^1\phi_1 00\rangle$, where the spin quantum numbers $s = 0$ and $m_s = 0$ are explicitly given. Likewise, we denote the three degenerate components of the pure triplet T_1 by $|^3\phi_1 11\rangle$, $|^3\phi_1 10\rangle$, and $|^3\phi_1 1\bar{1}\rangle$, where again the spin quantum numbers $s = 1$ and $m_s = 1$, 0, and -1 are explicitly given. Since S_1 amd T_1 are relatively close by on the energy scale, singlet-triplet admixtures may occur via spin-orbit ($\mathbf{s}\cdot\mathbf{l}$) coupling through the non-diagonal matrix elements (22).

$$L\langle s,m_s|\mathbf{s}|s+1,m_s \pm 1\rangle = \mp L\langle s||\mathbf{s}||s+1\rangle[(s \pm m_s + 1) \times (s \pm m_s + 2)]^{1/2} \quad [1]$$

$$L\langle s,m_s|\mathbf{s}|s+1,m_s\rangle = L\langle s||\mathbf{s}||s+1\rangle[(s+1)^2 - m_s{}^2]^{1/2} \quad [2]$$

where L is a constant arising from the orbital angular momentum coupling, and $\langle s||\mathbf{s}||s+1\rangle \equiv \Delta/L$ is a proportionality constant known as a reduced spin matrix element (22). Upon diagonalization in the usual manner, we obtain the approximate spin-corrected wavefunctions for the lowest excited singlet

$$|^1\Phi_1\rangle = |^1\phi_1 00\rangle + \frac{\delta}{5\Delta}\left(|^3\phi_1 10\rangle - \sqrt{2}|^3\phi_1 11\rangle + \sqrt{2}|^3\phi_1 1\bar{1}\rangle\right) \quad [3]$$

$$|^3\Phi_1\rangle_\alpha = \frac{1}{\sqrt{5}}\left[\left(|^3\phi_1 10\rangle - \sqrt{2}|^3\phi_1 11\rangle + \sqrt{2}|^3\phi_1 1\bar{1}\rangle\right) - \frac{\delta}{\Delta}|^1\phi_1 00\rangle\right] \quad [4]$$

$$|^3\Phi_1\rangle_\beta = \frac{1}{\sqrt{2}}\left(|^3\phi_1 11\rangle + |^3\phi_1 1\bar{1}\rangle\right) \quad [5]$$

$$|^3\Phi_1\rangle_\gamma = \frac{1}{\sqrt{5}}\left(\frac{1}{\sqrt{2}}|^3\phi_1 11\rangle + 2|^3\phi_1 10\rangle - \frac{1}{\sqrt{2}}|^3\phi_1 1\bar{1}\rangle\right) \quad [6]$$

where

$$\delta = 5\Delta^2[E(^1\phi_1) - E(^3\phi_1)]^{-1} \quad [7]$$

$E(^1\phi_1)$ and $E(^3\phi_1)$ being the energies of the pure-spin states $|^1\phi_1\rangle$ and $|^3\phi_1\rangle$, respectively. In the above calculation, we have neglected the interactions of $|^1\phi_1 00\rangle$, $|^3\phi_1 11\rangle$, $|^3\phi_1 10\rangle$, and $|^3\phi_1 1\bar{1}\rangle$ with the ground state singlet $|^1\phi_0 00\rangle$ which we now write as $|^1\Phi_0\rangle$ in keeping with the notations of Eqs. **3–7**. We have also overlooked matrix elements containing the reduced matrix element $\langle s||\mathbf{s}||s\rangle$.

In the C_2 $(Chl\text{–}H_2O)_2$ adduct, the ground state singlet for Chl(1) and Chl(2) can be written as the symmetric product state

$$^1\psi_0(A) = |^1\Phi_0(1)\rangle|^1\Phi_0(2)\rangle \quad [8]$$

where $^1\psi_0(A)$ transforms as the identity irreducible representation A of the C_2 point group. The excited singlet of the special-pair chlorophylls is doubly degenerate in the zeroth-order since the product states $|^1\Phi_1(1)\rangle|^1\Phi_0(2)\rangle$ and $|^1\Phi_0(1)\rangle|^1\Phi_1(2)\rangle$, corresponding respectively to the singlet excitation residing either on Chl(1) or Chl(2), are indistinguishable from each other by virtue of the exact equivalence of the two Chl molecules. Due to Coulomb interactions of the outer electrons of the Chl molecules, however, a given initial excitation will become delocalized over the two Chl molecules. The transmittance of the excitation from one molecule to the other causes a splitting of the 2-fold degeneracy (23). The resulting

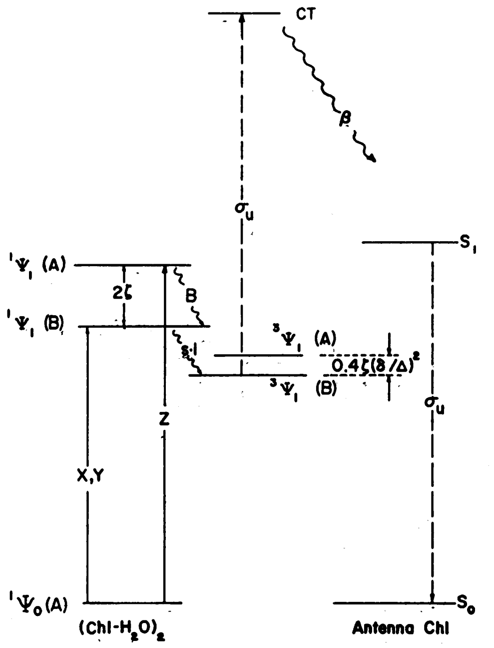


FIG. 2. Energy upconversion in the C_2 $(Chl\text{-}H_2O)_2$ adduct. A and B are the C_2 irreducible symmetry representations. Radiationless coupling between $^1\psi_1(A)$ and $^1\psi_1(B)$ through a B vibration of the C_2 adduct is expected to be unimportant. Intersystem crossing between $^1\psi_1(B)$ and $^3\psi_1(B)$ can occur via spin admixtures in Eqs. **3** and **4**. Electric dipole transitions from the ground state $^1\psi_0(A)$ to $^1\psi_1(A)$ and $^1\psi_1(B)$ occur respectively via the Z and the X and Y transition moments, as indicated.

singlet state functions can be written in the symmetric form

$$^1\psi_1(A) = \frac{1}{\sqrt{2}}\left(|^1\Phi_1(1)\rangle|^1\Phi_0(2)\rangle + |^1\Phi_0(1)\rangle|^1\Phi_1(2)\rangle\right) \quad [9]$$

and in the antisymmetric form

$$^1\psi_1(B) = \frac{1}{\sqrt{2}}\left(|^1\Phi_1(1)\rangle|^1\Phi_0(2)\rangle - |^1\Phi_0(1)\rangle|^1\Phi_1(2)\rangle\right) \quad [10]$$

where the transformation properties of the state functions **9** and **10** are prescribed according to the two C_2 irreducible representations A and B. If we consider only the dipole–dipole interaction and neglect effects arising from the small horizontal displacement between the two magnesium atoms in the keto form of the $(Chl\text{-}H_2O)_2$ adduct, we find that $^1\psi_1(A)$ and $^1\psi_1(B)$ will be split by an energy equal to two times the dipole–dipole coupling parameter

$$\xi = \frac{e^2}{R_{12}^3}\,|\langle ^1\phi_0 00|\mathbf{r}|^1\phi_1 00\rangle|^2 \cos\theta \quad [11]$$

where $e\langle ^1\phi_0 00|\mathbf{r}|^1\phi_1 00\rangle$ is the transition moment between the two pure singlet states $|^1\phi_0 00\rangle$ and $|^1\phi_1 00\rangle$, θ is the angle subtended by the molecular orientations of Chl(1) and Chl(2), and R_{12} is the vertical distance between the two parallel porphyrin rings.

Analogous results can be obtained for the triplet excitation of the special-pair structure. The wavefunctions in this case are given by the symmetric state

$$^3\psi_1(A) = \frac{1}{\sqrt{2}}\left(|^3\Phi_1(1)\rangle|^1\Phi_0(2)\rangle + |^1\Phi_0(1)\rangle|^3\Phi_1(2)\rangle\right) \quad [12]$$

and the antisymmetric state

$$^3\psi_1(B) = \frac{1}{\sqrt{2}}\left(|^3\Phi_1(1)\rangle|^1\Phi_0(2)\rangle - |^1\Phi_0(1)\rangle|^3\Phi_1(2)\rangle\right) \quad [13]$$

Since dipole coupling between $|^1\Phi_0\rangle$ and $|^3\Phi_1\rangle$ occurs only through the singlet admixture in $|^3\Phi_1\rangle_\alpha$ (see Eq. **4**), the energy of the splitting between $^3\psi_1(A)$ and $^3\psi_1(B)$ is found to be $0.4\,\xi(\delta/\Delta)^2$, which is considerably smaller than that $2\,\xi$ between $^1\psi(A)$ and $^1\psi(B)$.

It is easy to see that when $\theta < 90°$, the coupling parameter ξ is positive (see Eq. **11**), and the antisymmetric states $^1\psi_1(B)$ and $^3\psi_1(B)$ are lower in energy than the corresponding symmetric states $^1\psi_1(A)$ and $^3\psi_1(A)$. This is a most significant result, for, since the keto form of $(Chl\text{-}H_2O)_2$ is perfectly strain-free at values of θ less than 90°, it appears reasonable to suppose that *nature elects to synthesize the C_2 $(Chl\text{-}H_2O)_2$ adduct in order to furnish photosynthetic organisms with an effective trap for the harvested excitation.* We observe that the antisymmetric triplet state $^3\psi_1(B)$ is not only spin forbidden but also symmetry forbidden with respect to the symmetric ground state singlet $^1\psi_0(A)$. The radiationless transition between A and B states via a B vibration of the $(Chl\text{-}H_2O)_2$ adduct is expected to be unimportant due to the large masses of the Chl molecules (20). Under optimum conditions for photosynthesis, therefore, the trapped excitation will live until it is "upconverted" to the photoactive charge-transfer state CT through energy-transfer interaction with an antenna S_1 excitation. The details given above are summarized in Fig. 2.

Discussion

The central features of the present model can be summarized as follows: (*a*) While the onset of the primary reaction requires the summation of two photons, the steady-state operation of the upconversion scheme observes a one-quantum-per-electron requirement (4) under normal light conditions. The steady-state scheme rigorously becomes a two-photon-per-electron process in the low-light limit (4). The steady-state one-quantum-per-electron operation allows for the highest possible quantum efficiency in the utilization of solar radiation by plant photosynthesis: Under optimum conditions, every photon above 700 nm in energy can in principle be converted to a one-electron chemical equivalent. *If* we accept the postulated "blue" energy requirement (about 350–400 nm) for attaining the charge-transfer state [**A**] [see above discussion on hydride abstraction reactions (11–14)], we can then appreciate how nature *must* have exploited the rather unique physico-chemical properties of Chl and H_2O in order to perform efficient *red* photochemistry even though the primary light reaction can only be triggered in the *blue*.

(*b*) The geometrical restrictions of the symmetrical H_2O linkages in the photoactive dimer $(Chl\text{-}H_2O)_2$ require hydrogen bonding to the ring V carbomethoxy carbonyls, leaving the two ring V keto groups available for endogamous bonding to the antenna Chl molecules. This requirement appears, at first sight, to contradict the *in vitro* observations by Katz and co-workers (10), who obtained a $(Chl\text{-}H_2O)_n$ ($n \gg 2$) adduct in which both the ring V keto group and the carbomethoxy carbonyl are hydrogen-bonded to a single water molecule. However, it is well established that the configurations of intermolecular interactions are strongly dependent on the host medium. The proposed *in vivo* (Chl–

$H_2O)_2$ adduct can conceivably be stabilized by the geometrical packing of the surrounding pigment molecules, and by additional hydrogen bonding involving the two ester carbonyls preceding the phytyl tails which presumably serve as anchors, lodged in the hydrocarbon milieu of the $(Chl-H_2O)_2$ adduct. The involvement of the carbomethoxy carbonyl and not the keto group in hydrogen bonding appears to be reasonable in view of the finding that the ester carbonyl forms a much stronger hydrogen bond than a keto group in conjugation with an aromatic system (24). The ring V keto group is in conjugation with the π-electron system of the Chl macrocycle.

(*c*) The Mg^{++} cation and the ring V β-ketoester group in Chl provide the necessary constituents for intermolecular bonding to the H_2O molecules. The β-ketoester group is the site of photoactivity. The presence of the lightest divalent cation, $Mg,^{++}$ in Chl suggests the minimization of the so-called "heavy atom" effect which tends to shorten the lifetime of the intermediate triplet state via spin-orbit coupling. In a generalization* of the present treatment, we have accounted for the photoactivity (10) of the $(Chl-H_2O)_n$ adduct in terms of the general properties of translational symmetry under cyclical boundary conditions. The significance of the short-lived (about 10^{-6} sec) triplet observed (25) in photosynthetic bacterial chlorophylls has also been discussed* in terms of symmetry selection rules within the framework of the upconversion proposal.

In conclusion, two concepts have been introduced here: (*i*) a specific molecular structure for the reaction center chlorophylls and (*ii*) the necessity of energy upconversion in reaching the photochemical state in photosynthesis. While the correctness of (*i*) is not dependent upon the correctness of (*ii*) and *vice versa*, the fact that the assumption of (*i*) appears to result in the prediction of (*ii*) on rigorous theoretical grounds (via the formation of the antisymmetric trap state) seems to strengthen the case for both concepts. Indeed, the significance of the upconversion theory may well extend beyond the question of plant photosynthesis. Since the principles that underlie the upconversion theory are fundamental, it is reasonable to suppose that *when the appropriate energy level schemes are available, upconversion reactions are generally expected for any molecular adduct consisting of repetitive components whose transition moments subtend acute angles.* Experimental effort in this direction should generate a class of high-quantum-yield photochemical reactions activated by visible and near-infrared photons.

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* Wassam, W. A. & Fong, F. K., "Exciton interactions in photoactive chlorophyll–water adducts," to be published.