

# Tripartite model for the photochemical apparatus of green plant photosynthesis

(energy coupling/energy transfer/energy distribution)

WARREN L. BUTLER AND RETO J. STRASSER

Department of Biology, University of California, San Diego, La Jolla, California 92093

Contributed by Warren L. Butler, June 9, 1977

**ABSTRACT** Equations for fluorescence and the rates of photochemistry of photosystem I and photosystem II are derived from a photochemical model for the photosynthetic apparatus that includes the various interactions of the light-harvesting chlorophyll *a/b* complex with photosystem I and photosystem II as specific photochemical rate constants. The degree of coupling between photosystem II and the chlorophyll *a/b* complex which is expressed as a product of two probability terms plays a central role in this three-pigment system. The cycling of excitation energy back and forth between photosystem II and the chlorophyll *a/b* complex increases the exciton density in both arrays of chlorophyll according to a simple analytical expression in the equations. These equations of the tripartite model provide new and credible insights into the photochemical apparatus of photosynthesis.

The tripartite model of the photochemical apparatus of photosynthesis presented previously by Butler and Kitajima (1, 2) was based on earlier chloroplast fractionation studies (3, 4) that identified three major types of chlorophyll assemblages. Two of these were the photochemically active pigment systems, photosystem I (PSI) and photosystem II (PSII), which were represented as units containing antenna chlorophyll *a*, Chl<sub>aI</sub>, or Chl<sub>aII</sub>, and a reaction center, P<sub>I</sub>·A<sub>I</sub> or P<sub>II</sub>·A<sub>II</sub>, whereas the third was the photochemically inactive light-harvesting chlorophyll *a/b* complex, denoted Chl LH, which contained all of the chlorophyll *b* and approximately half of the total chlorophyll. It was assumed that excitation energy flowed freely back and forth between Chl LH and PSII but that energy transfer from PSII to PSI or from Chl LH to PSI occurred only in a unidirectional manner.

The model was expressed in terms of photochemical rate constants representing the various pathways by which excitons in the photochemical apparatus were utilized or dissipated and equations for the yields of fluorescence and photochemistry were expressed in terms of those rate constants and the state of the reaction centers. It was assumed that the fluorescence measured at 692 nm at -196° was representative of the fluorescence from PSII whereas that measured at 730 nm at -196° was representative of the fluorescence from PSI. The low-temperature emission band at 685 nm was attributed to Chl LH but it was assumed that the energy coupling between Chl LH and PSII was sufficiently tight that, to a first approximation, Chl LH could be considered to be antenna chlorophyll for PSII. Thus, in essence, the tripartite model was reduced to a bipartite model which simplified the derivation of the analytical expressions.

The bipartite formulation has been very useful for the ex-

amination of energy distribution in the photochemical apparatus including energy transfer from PSII to PSI but a certain lack of rigor was introduced into the model by the simplifying assumptions which precluded precise definitions of the interactions of Chl LH. The purpose of the present study is to derive the equations for fluorescence and photochemistry for a truly tripartite model in which the interactions of Chl LH with the rest of the photochemical apparatus have been included as specific photochemical rate constants. It will be seen that the tripartite formulation of the model, while more complex, does provide insights into the distribution and flux of energy within the photochemical apparatus that were not apparent in the bipartite model.

## THE TRIPARTITE MODEL

The photochemical rate-constant diagram that was used previously for the bipartite model (2) is expanded here (Fig. 1) to include rate-constant terms for fluorescence from Chl LH ( $k_{FIII}$ ), energy transfer from Chl LH to Chl<sub>aII</sub> and to Chl<sub>aI</sub> ( $k_{T(32)}$  and  $k_{T(31)}$ , respectively), and energy transfer from Chl<sub>aII</sub> to Chl LH and to Chl<sub>aI</sub> ( $k_{T(23)}$  and  $k_{T(21)}$ , respectively). The fractions of the quantum flux absorbed by Chl<sub>aI</sub>, Chl<sub>aII</sub>, and Chl LH are represented by  $\alpha$ ,  $\beta$ , and  $\gamma$ , respectively, such that  $\alpha + \beta + \gamma = 1$ . As noted previously (1, 2), all variable fluorescence originates at closed PSII reaction centers (P<sub>II</sub>·A<sub>II</sub><sup>-</sup>) which return trapped excitation energy back to Chl<sub>aII</sub> via the  $k_{III}$  process.

In the derivations that follow, we will distinguish  $\psi$  terms that are constants from  $\varphi$  terms that are variables and depend on the state of the PSII reaction centers. The probability that an exciton in Chl LH or Chl<sub>aI</sub> will be dissipated via a particular pathway is a constant—e.g.,  $\psi_{T(32)} = k_{T(32)}[k_{FIII} + k_{T(32)} + k_{T(31)}]^{-1}$ . The energy flux in Chl<sub>aII</sub>, however, depends on the state of the PSII reaction centers. An exciton in Chl<sub>aII</sub> has a choice of de-excitation via  $k_{FII}$ ,  $k_{DII}$ ,  $k_{T(23)}$ ,  $k_{T(21)}$ , or  $k_{TII}$  (i.e., trapping by the PSII reaction center chlorophyll). If the exciton is trapped in a reaction center that is open (P<sub>II</sub>·A<sub>II</sub>), photochemical charge separation is accomplished. However, if the exciton is trapped in a reaction center that is closed (P<sub>II</sub>·A<sub>II</sub><sup>-</sup>), the energy cannot be used ( $k_{PII} = 0$ ) but may be transferred back to the antenna chlorophyll of PSII (via  $k_{III}$ ) where the various de-excitation pathways again compete. The transfer of energy from the closed PSII reaction centers back to Chl<sub>aII</sub> increases the exciton density to Chl<sub>aII</sub> and thereby increases the flux through the PSII dissipative pathways.

It was shown previously (1, 5) that if we assume that there is no energy transfer between PSII units—i.e., a “separate

The costs of publication of this article were defrayed in part by the payment of page charges from funds made available to support the research which is the subject of the article. This article must therefore be hereby marked “advertisement” in accordance with 18 U. S. C. §1734 solely to indicate this fact.

Abbreviations: PSI, photosystem I; PSII, photosystem II; Chl<sub>a</sub>, chlorophyll *a*; Chl LH, chlorophyll *a/b* complex.

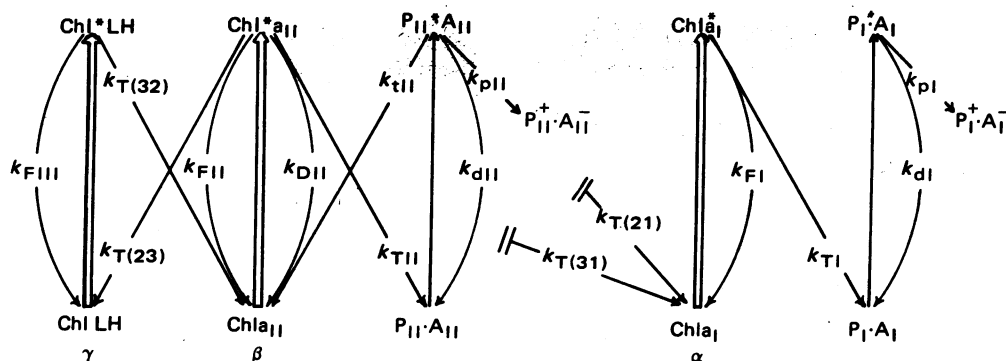


FIG. 1. Photochemical rate-constant diagram from tripartite model. See text for definitions. \*, Excited chlorophyll molecules.

package" model for PSII—we can express the  $\varphi$  terms as:

$$\begin{aligned} \varphi_{FII} &= \psi_{FII} \left( A_{II} + \frac{1 - A_{II}}{1 - \psi_{TII}\psi_{tII}} \right) \\ \varphi_{T(23)} &= \psi_{T(23)} \left( A_{II} + \frac{1 - A_{II}}{1 - \psi_{TII}\psi_{tII}} \right) \\ \varphi_{T(21)} &= \psi_{T(21)} \left( A_{II} + \frac{1 - A_{II}}{1 - \psi_{TII}\psi_{tII}} \right) \end{aligned} \quad [1]$$

in which  $\psi_{tII} = k_{tII}(k_{tII} + k_{dII})^{-1}$ . The  $\psi$  terms in front of the parentheses in Eqs. 1 are the probabilities that an exciton will take that particular pathway and the terms inside the parentheses indicate the factor by which the exciton density in Chla<sub>II</sub> increases as the PSII reaction centers close. [We also could have assumed a "matrix" model for PSII in which all of the PSII reaction centers were available to all of the Chla<sub>II</sub> (1). In that case, the term inside each pair of the parentheses in Eqs. 1 would be  $[1 - \psi_{TII}\psi_{tII}(1 - A_{II})]^{-1}$ .] The  $\varphi$  terms vary from a minimum value—e.g.,  $\varphi_{T(23)(0)} = \psi_{T(23)}$  when  $A_{II} = 1$ —to a maximum value,  $\varphi_{T(23)(M)} = \psi_{T(23)}(1 - \psi_{TII}\psi_{tII})^{-1}$  when  $A = 0$ . Bear in mind that the  $\psi$  and  $\varphi$  terms refer to processes occurring in the different parts of the photochemical apparatus. The overall yield terms,  $\Phi$ , are measurable quantities defined as output versus input. For example, the overall yield of PSII fluorescence,  $\Phi_{FII}$ , is defined as the intensity of PSII fluorescence,  $F_{II}$ , divided by the quantum flux absorbed by the entire photochemical apparatus,  $I_a$ .

Let us first consider the fluorescence from Chl LH. The energy absorbed by Chl LH will be  $I_a\gamma$  and a part of that energy,  $I_a\gamma\psi_{FIII}$ , will be emitted immediately as fluorescence. However, another part of that energy,  $I_a\gamma\psi_{T(32)}$ , will be transferred to Chla<sub>II</sub> and a part of that,  $I_a\gamma\psi_{T(32)}\varphi_{T(23)}$ , will be returned to Chl LH where fluorescence can again occur. In fact, there will be a continual cycling of energy from Chl LH to Chla<sub>II</sub> and back to Chl LH until the energy is used, fluoresced, or dissipated. Thus, the fluorescence from Chl LH due to light absorbed by Chl LH can be expressed as an infinite series:

$$F_{III(\gamma)} = I_a\gamma[1 + \psi_{T(32)}\varphi_{T(23)} + (\psi_{T(32)}\varphi_{T(23)})^2 + \dots]\psi_{FIII}$$

In addition, light energy absorbed by Chla<sub>II</sub> can be transferred to Chl LH,  $I_a\beta\varphi_{T(23)}$ , and that energy will go through the same cycling process. Thus, the fluorescence from Chl LH due to light absorbed by Chla<sub>II</sub> will be:

$$F_{III(\beta)} = I_a\beta\varphi_{T(23)}[1 + \psi_{T(32)}\varphi_{T(23)} + (\psi_{T(32)}\varphi_{T(23)})^2 + \dots]\psi_{FIII}$$

The infinite series in these two equations converges to a simple expression  $[1 - \psi_{T(32)}\varphi_{T(23)}]^{-1}$  so that the equation for the total fluorescence from Chl LH can be written as:

$$F_{III} = \frac{\gamma + \beta\varphi_{T(23)}}{1 - \psi_{T(32)}\varphi_{T(23)}} I_a\psi_{FIII} \quad [2]$$

A similar expression can be derived for the fluorescence from Chla<sub>II</sub>. In that case, the energy absorbed by Chla<sub>II</sub> may be transferred to Chl LH and back to Chla<sub>II</sub> in a cycling process in which the fraction  $\varphi_{T(23)}\psi_{T(32)}$  is returned to Chla<sub>II</sub> on each cycle. The fluorescence from Chla<sub>II</sub> due to light absorbed by Chla<sub>II</sub> will be:

$$F_{II(\beta)} = I_a\beta[1 + \varphi_{T(23)}\psi_{T(32)} + (\varphi_{T(23)}\psi_{T(32)})^2 + \dots]\varphi_{FII}$$

whereas that due to light absorbed in Chl LH will be:

$$F_{II(\gamma)} = I_a\gamma\psi_{T(32)}[1 + \varphi_{T(23)}\psi_{T(32)} + (\varphi_{T(23)}\psi_{T(32)})^2 + \dots]\varphi_{FII}$$

for a total fluorescence from Chla<sub>II</sub> of:

$$F_{II} = \frac{\beta + \gamma\psi_{T(32)}}{1 - \psi_{T(32)}\varphi_{T(23)}} I_a\varphi_{FII} \quad [3]$$

The fluorescence from Chla<sub>I</sub> will have three possible sources of excitation: one due to the direct absorption by Chla<sub>I</sub>,  $I_a\alpha$ , one due to the excitation energy in Chla<sub>II</sub> that is transferred to Chla<sub>I</sub>, and the third due to the excitation energy in Chl LH that is transferred to Chla<sub>I</sub>.

$$F_I = \left[ \alpha + \frac{(\beta + \gamma\psi_{T(32)})\varphi_{T(21)} + (\gamma + \beta\varphi_{T(23)})\psi_{T(31)}}{1 - \psi_{T(32)}\varphi_{T(23)}} \right] \times I_a\psi_{FI} \quad [4]$$

Equations can also be written for the rates of photochemistry by PSI and PSII. We assume that energy trapped by a PSII reaction center is used for photochemistry if the reaction center is open (i.e.,  $k_{pII} \gg k_{tII}$  or  $k_{dII}$ ). The rate of photochemistry will be determined by the excitation energy in Chla<sub>II</sub>, the probability of trapping excitons by the reaction centers,  $\psi_{TII}$ , and the fraction of the reaction centers that are open:

$$P_{II} = \frac{\beta + \gamma\psi_{T(32)}}{1 - \psi_{T(32)}\varphi_{T(23)}} I_a\psi_{TII}A_{II} \quad [5]$$

and for PSI:

$$P_I = \left[ \alpha + \frac{(\beta + \gamma\psi_{T(32)})\varphi_{T(21)} + (\gamma + \beta\varphi_{T(23)})\psi_{T(31)}}{1 - \psi_{T(32)}\varphi_{T(23)}} \right] \times I_a\psi_{TIA_I} \quad [6]$$

Eqs. 2–6 represent a complete description of the tripartite model of the photochemical apparatus of photosynthesis in green plants. The term  $[1 - \psi_{T(32)}\varphi_{T(23)}]^{-1}$ , which appears in each of these equations, represents the increase in exciton density in Chl LH and Chla<sub>II</sub> due to the cycling of excitation energy back and forth between these two arrays of chlorophyll just as the cycling of excitation energy between Chla<sub>II</sub> and the closed PSII reaction centers causes the exciton density in Chla<sub>II</sub> to increase by a factor of  $(1 - \psi_{TII}\psi_{tII})^{-1}$ .

Significant differences are apparent between these equations derived for the tripartite model and the previous equations that represented a bipartite model. In the previous equations, derived on the assumption that there was no energy transfer between PSII units, fluorescence increased from a minimum,  $F_0$ , level to a maximum,  $F_M$ , level as a linear function of  $A_{II}$ . The expressions derived for the tripartite model also on the assumption of no energy transfer between PSII units are no longer linear functions of  $A_{II}$ . Even though the  $\varphi$  terms shown in Eqs. 1 are linear functions of  $A_{II}$ , the appearance of  $\varphi_{T(23)}$  in the denominator of the equations introduces a nonlinearity which will be examined in more detail in the *Discussion*.

An important experimental observation in our previous work was that X-Y plots of the fluorescence at 730 nm versus that at 692 nm (or, in fact, between any pair of emission wavelengths) measured between the  $F_0$  and  $F_M$  levels as the fluorescence excitation light closed the PSII reaction centers of  $-196^\circ$  gave perfectly straight lines that could be extrapolated back to the  $F_{730}$  axis (6). Such results were predicted from the previous bipartite set of equations because both  $F_I$  and  $F_{II}$  were linear functions of  $A_{II}$ . However, the present nonlinear equations should be examined to determine if they predict the linear X-Y plots as well.

The nonlinearity of  $F_I$ ,  $F_{II}$ , and  $F_{III}$  can be expressed by differentiating Eqs. 2, 3, and 4 with respect to  $A_{II}$ .

$$\frac{dF_I}{dA_{II}} = - \frac{(\beta + \gamma\psi_{T(32)})}{(1 - \psi_{T(32)}\varphi_{T(23)})^2} (\varphi_{T(21)(M)} + \psi_{T(31)}\varphi_{T(23)(M)}) I_a \psi_{FI} \quad [7]$$

$$\frac{dF_{II}}{dA_{II}} = - \frac{(\beta + \gamma\psi_{T(32)})}{(1 - \psi_{T(32)}\varphi_{T(23)})^2} I_a \varphi_{FII(M)} \quad [8]$$

$$\frac{dF_{III}}{dA_{II}} = - \frac{(\beta + \gamma\psi_{T(32)})}{(1 - \psi_{T(32)}\varphi_{T(23)})^2} \varphi_{T(23)(M)} I_a \psi_{FIII} \quad [9]$$

It is apparent from Eqs. 7, 8, and 9 that the nonlinearities in the expressions for  $F_I$ ,  $F_{II}$ , and  $F_{III}$  are identical and will cancel out if one emission is plotted as a function of either of the other two. X-Y plots between any pair, as  $A_{II}$  goes from 1 to 0, will be a straight line that can be extrapolated back to the Y axis to give an intercept value. Table 1 gives the expressions for the slope and intercept values for various pairs of emissions. Much information was obtained in the bipartite model from measurements of the slope and intercept values of X-Y plots of  $F_I$  versus  $F_{II}$ . It is anticipated that similar information will be obtained from X-Y plots involving  $F_I$ ,  $F_{II}$ , and  $F_{III}$  within the context of the tripartite model.

Eqs. 7, 8, and 9 were obtained by using Eqs. 1 to define the  $\varphi$  terms as functions of  $A_{II}$ . The equations could also have been derived by using the "matrix" model equations for the  $\varphi$  terms. In that case, the nonlinearities would have been greater but they would also have cancelled out in the X-Y plots of fluorescence and the expressions shown in Table 1 would be unchanged.

## DISCUSSION

Joliot and coworkers (7, 8) first proposed that energy transfer between PSII units is responsible for the initial lag in the fluorescence induction curve measured in the presence of DCMU. The phenomenon is also manifested as a nonlinear dependence of fluorescence yield on the fraction of the PSII reaction centers that are closed. It was shown in our photochemical model for PSII (5) that, if we assumed a "separate package" model in which there is no energy transfer between PSII units, the nor-

Table 1. Expressions for slopes and intercept values for various pairs of emissions

Emission pairs	Slope	Intercept
$F_I$ vs $F_{II}$	$\frac{k_{T(21)} + k_{T(23)}\psi_{T(31)}}{k_{FII}} \psi_{FI}$	$I_a[\alpha + \gamma\psi_{T(31)}]\psi_{FI}$
$F_I$ vs $F_{III}$	$\frac{k_{T(21)} + k_{T(23)}\psi_{T(31)}}{k_{T(23)}} \frac{\psi_{FI}}{\psi_{FIII}}$	$I_a \left[ \alpha - \frac{k_{T(21)}}{k_{T(23)}} \gamma \right] \psi_{FI}$
$F_{III}$ vs $F_{II}$	$\frac{k_{T(23)}}{k_{FII}} \psi_{FIII}$	$I_a \gamma \psi_{FIII}$

malized fluorescence increase is a linear function of the fraction of PSII reaction centers that are closed at any time t.

$$\frac{F_t - F_0}{F_M - F_0} = 1 - A_{II} \quad [10]$$

in which  $F_t$  is the intensity of fluorescence at time t. On the other hand, if we assumed a "matrix" model in which all PSII reaction centers are available to all of the PSII antenna chlorophyll, that relationship is nonlinear (5):

$$\frac{F_t - F_0}{F_M - F_0} = \frac{1 - A_{II}}{1 + \frac{F_{II(V)}}{F_{II(0)}} A_{II}} \quad [11]$$

and the degree of nonlinearity depends on the relative extent of  $F_V$  for PSII ( $F_{II(V)} = F_{II(M)} - F_{II(0)}$ ). It was pointed out in the bipartite formulation (1, 2, 6) that the fluorescence of variable yield of PSI and PSII should have the same kinetic behavior and, indeed, it can be shown from the equations of the bipartite model that Eqs. 10 and 11 apply for PSI fluorescence as well as for PSII fluorescence. Eqs. 10 and 11 represent the extreme cases for energy transfer between PSII units. It is generally assumed that the photosynthetic apparatus functions somewhere between these two extremes and that the fluorescence, as a function of  $A_{II}$ , follows a relationship that is intermediate between Eqs. 10 and 11.

The nonlinearity that appears in the tripartite equations for fluorescence merits examination because we assumed in Eqs. 1 that there was no energy transfer between PSII units. If the  $\varphi$  terms shown in Eqs. 1 are substituted into Eq. 2, 3, or 4, we can show in each case that:

$$\frac{F_t - F_0}{F_M - F_0} = \frac{1 - A_{II}}{1 + \frac{F_{II(V)}}{F_{II(0)}} \psi_{T(32)}\psi_{T(23)} A_{II}} \quad [12]$$

As expected, the kinetic behavior is identical for  $F_{III}$ ,  $F_{II}$ , and  $F_I$  but these fluorescences are nonlinear functions of  $A_{II}$  even though we assumed that there was no energy transfer between PSII units. The degree of nonlinearity depends on the coupling term  $\psi_{T(32)}\psi_{T(23)}$  which is always less than unity so that Eq. 12 is intermediate between Eqs. 10 and 11. The question remains, however, why the nonlinearity if there is no energy transfer between PSII units?

The tripartite equations would be equally valid if we had chosen a matrix model for the PSII units. In that case, the  $\varphi$  terms in Eqs. 1 would have been written in the form  $\varphi_{FII} = \psi_{FII} \times [1 - \psi_{TII}\psi_{II}(1 - A_{II})]^{-1}$  (1). Substitution of those  $\varphi$  terms into Eq. 2, 3, or 4 will give Eq. 11. We could also have formulated the tripartite system as a strictly separate package model in which each package consisted of one PSI unit, one PSII unit

with either an open or a closed reaction center, and the associated Chl LH. The  $\varphi$  terms for each of the individual packages would be assigned either the minimum or the maximum values depending on whether the PSII reaction center of that particular package was open or closed. The intensity of fluorescence from the sample at any given photochemical state would be the sum of the emissions from all of the individual packages, the fraction  $A_{II}$  having open PSII reaction centers and minimum  $\varphi$  values and the fraction  $1 - A_{II}$  having closed PSII reaction centers and maximum  $\varphi$  values. For such a model, Eq. 10 describes the relationship between fluorescence and the state of the PSII reaction centers. In the formulation that was used, the  $\varphi$  terms were written in the form that assumes no direct energy transfer between PSII units but energy coupling between Chl LH and Chla<sub>II</sub> was described with intermediate values of  $\varphi_{T(23)}$  even though any particular PSII unit should be either open or closed. In essence, energy coupling between Chl LH and Chla<sub>II</sub> was averaged over the entire sample. This averaging, in effect, simulates energy transfer between PSII units via Chl LH. This latter tripartite model of the photochemical apparatus can be represented schematically (Fig. 2) as individual PSII units embedded in a matrix of the light-harvesting chlorophyll *a/b* complex (Chl LH) with each PSII unit connected to a PSI unit.

Excitation energy can be transferred between PSII units by passing through Chl LH and the extent of such energy transfer depends on the coupling between Chl LH and Chla<sub>II</sub>—i.e., on the coupling term  $\psi_{T(32)}\psi_{T(23)}$ . The tighter the coupling, the greater the energy transfer between PSII units and the greater the nonlinearity of fluorescence as a function of  $A_{II}$ .

Energy coupling between Chl LH and Chla<sub>II</sub> takes on a central role in the tripartite model. The cycling of excitation energy back and forth between Chl LH and Chla<sub>II</sub> increases the exciton density in both arrays of chlorophyll by the factor  $[1 - \psi_{T(32)}\varphi_{T(23)}]^{-1}$ . In Eq. 3, for instance,  $F_{II}$  increases as the PSII reaction centers close because  $\varphi_{FII}$  increases and because  $\varphi_{T(23)}$  in the denominator term increases and the increase of  $[1 - \psi_{T(32)}\varphi_{T(23)}]^{-1}$  may contribute more to the fluorescence increase than the increase of  $\varphi_{FII}$ . The influence of energy coupling between Chl LH and Chla<sub>II</sub> on the fluorescence of variable yield can also be inferred from developmental studies with dark-grown bean leaves that have been partially greened by a series of brief flashes. These leaves, which have active PSI and PSII units but none of the light-harvesting chlorophyll *a/b* complex, show a ratio of  $F_V/F_0$  of PSII fluorescence at  $-196^\circ$  of about 1.2 (9). If the flashed leaves are greened further in continuous light, they accumulate the chlorophyll *a/b* complex and the ratio of  $F_V/F_0$  at 694 nm increases to values as high as 4.0–5.0. It can be shown from Eq. 3 that:

$$\frac{F_{II(V)}}{F_{II(0)}} = \frac{\psi_{TII}\psi_{tII}}{1 - \psi_{TII}\psi_{tII} - \psi_{T(32)}\psi_{T(23)}} \quad [13]$$

Even though  $\psi_{TII}$  should decrease as Chl LH accumulates, due to the increasing competition from  $\psi_{T(23)}$ , the increase in the coupling term  $\psi_{T(32)}\psi_{T(23)}$  will cause a marked increase in the  $F_V/F_0$  ratio. We would also expect from Eq. 12 that the fluorescence from a flashed leaf should be a linear function of  $A_{II}$  because the coupling term should be zero in the absence of Chl LH. However, the fluorescence should become an increasingly nonlinear function of  $A_{II}$  as Chl LH accumulates because both  $F_{II(V)}/F_{II(0)}$  and  $\psi_{T(32)}\psi_{T(23)}$  would be increasing.

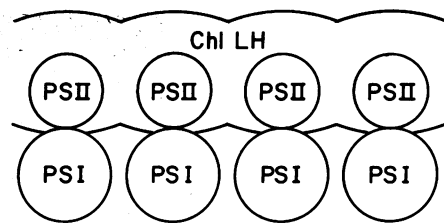


FIG. 2. Tripartite model represented as individual PSII units embedded in a matrix of light-harvesting chlorophyll *a/b* complex (Chl LH). Each PSII unit is connected to a PSI unit.

The effect of divalent cations on the distribution of excitation energy can also be examined in the context of the tripartite model. Homann (10) first reported that the addition of divalent cations to chloroplasts caused a marked increase of fluorescence, especially the fluorescence of variable yield, and Murata (11), who observed the same phenomenon, suggested that divalent cations caused a redistribution of excitation energy in favor of PSII. Butler and Kitajima (2) examined the effect of  $Mg^{2+}$  on energy distribution in the context of their bipartite formulation and confirmed that the yield of energy transfer from PSII to PSI was greater in the absence of divalent cations. The tripartite model now focuses the mechanism of energy distribution on the energy coupling between Chl LH and Chla<sub>II</sub>. We propose from Eq. 13 that the  $Mg^{2+}$ -induced increase in the fluorescence of variable yield from PSII is due to an increase in the coupling between Chl LH and Chla<sub>II</sub>. The increased coupling between Chl LH and Chla<sub>II</sub> may also compete with energy transfer to PSI. Arntzen and Ditto (12) recently reported from chloroplast fractionation experiments that  $Mg^{2+}$  induced a tighter association between the chlorophyll *a/b* complex and PSII. We expect to be able to estimate the value of  $\psi_{T(32)}\psi_{T(23)}$  from measurements of fluorescence at  $-196^\circ$  and to determine the extent to which that coupling term is affected by the presence of  $Mg^{2+}$ .

This work was supported by National Science Foundation Grant BMS 73-06884 and Swiss National Science Foundation Grant NR. 831.190.73.

- Butler, W. L. & Kitajima, M. (1974) in *Proceedings of the Third International Congress on Photosynthesis*, ed. Avron, M. (Elsevier Scientific Publishing Co., Amsterdam), pp. 13–24.
- Butler, W. L. & Kitajima, M. (1975) *Biochim. Biophys. Acta* **396**, 72–85.
- Wessels, J. S. C., San Alphen-Van Waveren, O. & Voorn, G. (1973) *Biochim. Biophys. Acta* **292**, 741–752.
- Thornber, J. P. & Highkin, H. R. (1974) *Eur. J. Biochem.* **41**, 109–116.
- Butler, W. L. & Kitajima, M. (1975) *Biochim. Biophys. Acta* **376**, 116–125.
- Kitajima, M. & Butler, W. L. (1975) *Biochim. Biophys. Acta* **408**, 297–305.
- Joliot, A. & Joliot P. (1964) *C. R. Hebd. Seance Acad. Sci.* **258**, 4617–4625.
- Joliot, P., Bennoun, P. & Joliot, A. (1973) *Biochim. Biophys. Acta* **305**, 317–328.
- Strasser, R. J. & Butler, W. L. (1977) *Biochim. Biophys. Acta*, in press.
- Homann, P. H. (1969) *Plant Physiol.* **44**, 932–936.
- Murata, N. (1969) *Biochim. Biophys. Acta* **189**, 171–181.
- Arntzen, C. J. & Ditto, C. L. (1976) *Biochim. Biophys. Acta* **449**, 259–274.