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Kinetics of Luminescence and of Electron Transport in Photosystem II. When Electron Transport on Acceptor Side of this System is Blocked

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Introduction

This paper is a theoretical consideration of kinetics of chlorophyll *a* prompt and delayed fluorescence and of electron transport in reactive centers of photosystem II (PSII) during and after illumination with light of different intensity when the electron transport from a primary acceptor of PS II to the pool of intermediate carriers is blocked. The following is shown:

(1) Depending on excitation irradiances, the curves of primary acceptor reduction may be of two different shapes. At sufficiently high excitation irradiances they consist of fast and slow phases. At low irradiances there are only one-phase curves.

(2) Induction curves of prompt fluorescence are of two shapes. At low and high excitation irradiances there is only one phase and at some intermediate irradiances the curves may illustrate fast and slow phases.

(3) A change of delayed fluorescence with time may be of three shapes: monotonously increasing (one-phase) in weak light, having a maximum at high irradiances, consisting of many phases at intermediate values of irradiances.

(4) The nature of a change of prompt and delayed fluorescence after turning off the light depends on whether a steady state was attained during illumination or not. After a short single pulse of saturating power

a fast transition of a part of the reactive centers into an open state must always take place, causing a sharp decrease of prompt and delayed fluorescence.

(5) There is a range of excitation irradiances over which reillumination of a sample partly adapted to dark may increase the rate of fluorescence yield change several times as compared to that of a completely adapted sample.

(6) A change in concentration of a reduced form of primary donor always follows the curves having a maximum.

(7) In case of a multicentral model of PSU, the curve of the primary acceptor reduction changes during illumination faster than the induction curve of fluorescence. The reverse relationship between these curves is observed after turning off the light.

(8) It has been shown in an explicit form which factor caused one or another kinetic pattern for any of the parameters in question.

A great body of experimental data on kinetics of processes in photosystem II (PS II) has brought to the forefront the development of a mathematical model of these processes, including prompt and delayed chlorophyll *a* fluorescence with $\lambda_{max} = 685$ nm, a change in concentration of oxidized (reduced) form of primary donor and acceptor of electrons, the value of total electron flow through the reactive centers. The model must explain the experimental data available and systematize them, thus promoting further investigations into mechanisms of the above processes and structural arrangement of the systems in which they proceed.

An attempt to construct such a model was made by us in [1]. It is based on the following principles (Fig. 1).

1. The concept of a certain type of photosynthetic unit (PSU) model [2–11] was used.

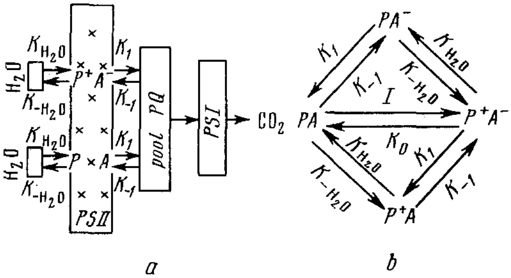

Figure 1. Scheme of PS II reactive centers participation in noncyclic electron transport (a) and different states of a reactive center (b). k_0 is the effective value of the constant of reverse electron transfer in double-charged centers. k_{H_2O}, k_{-H_2O}, k_1 and k_{-1} are the values with a dimensionality of sec^{-1} describing direct (k_{H_2O}, k_{-H_2O}) and reverse (k_{-H_2O}, k_{-1}) processes of electron transfer on donor (k_{H_2O}, k_{-H_2O}) and acceptor (k_1, k_{-1}) sides of photosystem II.

2. Consumption of energy from singlet-excited states of the molecules of PSU pigment matrix by the reactive centers is limited not by the migration rate of excitation along the PSU but by the efficiency of its capture with centers [12] and without any noticeable localization of excitation in the vicinity of the reactive center.

3. The basic elements of the reactive center (a primary donor si,P *and* a primary acceptor of electrons A) are "assembled" once and for all as a complex in which electron transfer from P to A ($PA \rightarrow P^+A^-$) takes place at the expense of excitation quantum, P is considered to be identical to P 680 [13]. There are only one acceptor and one donor in each center.

4. Dark redox reactions on donor and acceptor sides of the reactive center proceed completely and independently of one another. There is no cyclic electron flow from A^- to P^+, except for their reverse transfer in the centers. This results in four differently charged forms of the center: neutral PA ("open" center), single P^+A and PA^- and double-charged P^+A^-. The last three forms determine the "closed" state of the center [14].

5. The rate constants of direct (k_{H_2O}) and reverse (k_{-H_2O}) electron transfer on the donor side of PS II are commensurable. As a result, in an equilibrium state (i.e., upon complete dark adaptation) a portion $(p^+)_{eq}$ of the primary donor P is oxidized and the same portion α_1 of the reactive centers is closed owing to the presence of P^+A form.

$$[\alpha_1 = (p^+a)_{eq} = (p^+)_{eq} = k_{-H_2O}/\Sigma_{H_2O}, \text{ where } \Sigma_{H_2O} = k_{H_2O} + k_{-H_2O}].$$

6. Delayed fluorescence is excited by the reverse electron transfer in double-charged centers P^+A^- from reduced acceptor A^- to an oxidized donor P^+ [15, 16]. Emission of fluorescence quanta occurs during energy migration along the PSU pigment matrix.

Later [17–19] it was shown that various steady-state patterns of the processes in PS II based on the above concepts and on the multicentral type of PSU model (i.e., a model where several reactive centers are assembled in a single functional system on the level of excitation energy migration) agree fairly well with experiment. Therefore we decided to consider some problems of non-steady-state kinetics in terms of previous concepts. In this paper the case is investigated when electron transfer from a reduced primary acceptor of PS II to the next electron carrier in the chain of non-cyclic transport towards PS I (plastoquinone) is blocked.

To completely explain the factors causing the most general properties of non-steady-state kinetics, it is advisable to consider at first the problem in terms of a unicentral PSU model (i.e., a model where each reactive center has its own set of light-collecting molecules). In this case the problem will be solved only qualitatively, but, unlike the multicentral model, the solution is an analytical one up to the end. This makes possible a deeper insight into the physical meaning of the processes taking place. Next, using the results obtained, we solve approximately some particular cases in terms of a multicentral model, and the most interesting ones solve numerically on the computer.

Unicentral Model

Initial System of Equations and its Solution

The equations describing the processes in PS II in terms of a unicentral PSU model were derived by us earlier [1]. For the problem in question we may use the system of equations derived in [17], putting $c = k_1 = 0$. After this the system simplifies and becomes:

$$\begin{aligned}
(\dot{p}^+) &= -(I\epsilon L + \Sigma_{\mathrm{H_2O}} - \tilde{k}_0)(p^+) - I\epsilon L(a^-) + (I\epsilon L - \tilde{k}_0)(p^+a^-) \\
&\quad + I\epsilon L + k_{-\mathrm{H_2O}} \\
(\dot{a}^-) &= -I\epsilon L(p^+) - I\epsilon L(a^-) - (I\epsilon L - \tilde{k}_0)(p^+a^-) + I\epsilon L \qquad (1) \\
(\dot{p}^+a^-) &= -I\epsilon L(p^+) - (I\epsilon L - k_{-\mathrm{H_2O}})(a^-) + (I\epsilon L - \tilde{k}_0 - \Sigma_{\mathrm{H_2O}})(p^+a^-) + I\epsilon L
\end{aligned}$$

The condition $k_1 = 0$ means that there is no electron transport from A^- to plastoquinone.

The following characteristic equation corresponds to system (1):

$$\begin{aligned}
\lambda^3 &+ (I\epsilon L + 2\Sigma_{\mathrm{H_2O}} + \tilde{k}_0)\lambda^2 + [I\epsilon L(2\Sigma_{\mathrm{H_2O}} - k_{-\mathrm{H_2O}}) + \Sigma^2_{\mathrm{H_2O}} \\
&+ \tilde{k}_0(\Sigma_{\mathrm{H_2O}} + k_{-\mathrm{H_2O}})]\,\lambda + I\epsilon L(\Sigma^2_{\mathrm{H_2O}} - k_{-\mathrm{H_2O}}\Sigma_{\mathrm{H_2O}}) \\
&+ \tilde{k}_0\Sigma_{\mathrm{H_2O}}k_{-\mathrm{H_2O}} = 0 \qquad (2)
\end{aligned}$$

This equation is satisfied with the roots

$$\begin{aligned}
\lambda_{1,2} &= -0.5\{(I\epsilon L + \Sigma_{\mathrm{H_2O}} + \tilde{k}_0) \mp [I\epsilon L + \Sigma_{\mathrm{H_2O}} + \tilde{k}_0)^2 \\
&\qquad - 4(I\epsilon L k_{\mathrm{H_2O}} + \tilde{k}_0 k_{-\mathrm{H_2O}})]^{1/2}\} \\
\lambda_3 &= -\Sigma_{\mathrm{H_2O}} \qquad (3)
\end{aligned}$$

Here, as before, I is the excitation irradiance expressed as a number of quanta per cm^2 per sec; ϵ is the effective cross section for a capture of light quantum by one PSU; L is the quantum efficiency of consumption of singlet-excited states of PSU pigment matrix molecules by electron transfer in centers at $\alpha_1 = 0$; (p^+), (a^-) are normalized concentrations of the corresponding forms of the donor and acceptor of electrons: (p^+a^-) and α are the normalized concentrations of double-charged and closed centers, respectively; $\tilde{k}_0 = k_0(1 - L)$, where k_0 is the effective value of the constant of electron reverse transfer in the centers; $(\dot{p}^+)$ and so on are the rates of corresponding value changes.

The fluorescence yield (ρ) of photon collecting molecules is the function of closed center fraction α[6, 7]:

$$\rho = \rho_0 + (\rho_\infty - \rho_0)\alpha \qquad (4)$$

where ρ_0 and ρ_∞ are the quantum yields of prompt fluorescence in photosynthetic units with open and closed centers, respectively. The relationship between α, (p^+), (a^-) and (p^+a^-) is given by a simple equation:

$$\alpha = (p^+) + (a^-) - (p^+a^-) \tag{5}$$

The delayed fluorescence intensity F_d depends on (p^+a^-) according to the law

$$F_d = k_0\rho_0 M(p^+a^-) \tag{6}$$

where M is the number of PSU per unit volume: ρ_d, the quantum yield, is equal to

$$\rho_d = k_0\rho_0 \frac{(p^+a^-)}{I\epsilon} \tag{7}$$

We shall solve system (1) for the case when a sample was at first completely adapted to dark [i.e., when $t = 0$, $(p^+a^-) = (a^-) = 0$ and $(p^+) = \alpha = \alpha_1$]; at instant $t = 0$ the illumination begins with a rectangular light pulse with duration t.

Having determined the functional relation between (p^+), (a^-), (p^+a^-), and t, we can easily obtain the time dependence of other values using formulas (4)–(7).

The solution of system (1) may have the following form:

$$\frac{(Y - Y_{\text{st}})}{-Y_{\text{st}}} = R_y^1\, e^{\lambda_1 t} + R_y^2\, e^{\lambda_2 t} + R_y^3\, e^{\lambda_3 t} \tag{8}$$

for (p^+) and

$$\frac{(Y - Y_{\text{st}})}{(Y_{t=0} - Y_{\text{st}})} = R_y^1\, e^{\lambda_1 t} + R_y^2\, e^{\lambda_2 t} + R_y^3\, e^{\lambda_3 t} \tag{9}$$

for the rest of the parameters, where y denotes any of them; y_{st} and $y_{t=0}$ are their values at steady state and at initial moment, respectively.

An explicit form of the factors from (8) and (9) is given in Tables I and II.

Properties of the System in Question

A. Light Stage. As seen from Table I, upon illumination of the sample adapted to dark the time dependence of the parameters under consideration is described by the sum of two exponents. Figure 2 illustrates a change of the indices of these exponents $-\lambda_1$, $-\lambda_2$, $-\lambda_3$; Fig. 3 shows a change of preexponential factors with excitation

TABLE I. Explicit expression for preexponential factors in equations (8) and (9), roots of characteristic equations, and steady-state values of the considered parameters with respect to their initial values, excitation irradiances, and internal parameters of the system for the case when a sample completely adapted to dark is illuminated[a]

$$\lambda_{1,2} = 0.5\{-(I\epsilon L + \Sigma_{H_2O} + \tilde{k}_0) \pm [(I\epsilon L + \Sigma_{H_2O} + \tilde{k}_0)^2 - 4(I\epsilon L k_{H_2O} + \tilde{k}_0 k_{-H_2O})^{1/2}\}$$

$$\lambda_3 = -\Sigma_{H_2O}$$

Y	$Y_{t=0}$	Y_{st}	R_y^1	R_y^2	R_y^3	$\tilde{I}\epsilon L$ $(R_y^1 = R_y^2)$
(p^+)	$\alpha_1 = \dfrac{k_{-H_2O}}{\Sigma_{H_2O}}$	α_1	$\dfrac{-I\epsilon L k_{H_2O}}{(\lambda_1 - \lambda_2) k_{-H_2O}}$	$\dfrac{I\epsilon L k_{H_2O}}{(\lambda_1 - \lambda_2) k_{-H_2O}}$	0	
(a^-)	0	$\dfrac{I\epsilon L(1 - \alpha_1)}{I\epsilon L(1 - \alpha_1) + \tilde{k}_0 \alpha_1}$	$\dfrac{-\lambda_2(\Sigma_{H_2O} + \lambda_1)}{(\lambda_1 - \lambda_2)\Sigma_{H_2O}}$	$\dfrac{\lambda_1(\Sigma_{H_2O} + \lambda_2)}{(\lambda_1 - \lambda_2)\Sigma_{H_2O}}$	0	$\dfrac{\Sigma_{H_2O}}{1 - 2\alpha_1} + \tilde{k}_0$
(p^+a^-)	0	$\dfrac{I\epsilon L \alpha_1(1 - \alpha_1)}{I\epsilon L(1 - \alpha_1) + \tilde{k}_0 \alpha_1}$	$\dfrac{-\lambda_2(k_{-H_2O} + \lambda_1)}{(\lambda_1 - \lambda_2) k_{-H_2O}}$	$\dfrac{\lambda_1(k_{-H_2O} + \lambda_2)}{(\lambda_1 - \lambda_2) k_{-H_2O}}$	0	$\dfrac{\alpha_1}{2 - 3\alpha_1}(\Sigma_{H_2O} - \tilde{k}_0)$

α	α_1	$\frac{I\epsilon L(1-\alpha_1)+\tilde{k}_0\alpha_1^2}{I\epsilon L(1-\alpha_1)+\tilde{k}_0\alpha_1}$	$\frac{-\lambda_2(k_{H_2O}+\lambda_1)}{(\lambda_1-\lambda_2)k_{H_2O}}$	$\frac{\lambda_1(k_{H_2O}+\lambda_2)}{(\lambda_1-\lambda_2)k_{H_2O}}$	0	$\Sigma_{H_2O}+\tilde{k}_0\frac{1-3\alpha_1}{1-\alpha_1}$
ρ	$\rho_1=\rho_0+(\rho_\infty-\rho_0)\alpha_1$	$\frac{\rho_\infty\{I\epsilon L(1-\alpha_1)+\tilde{k}_0\alpha_1[1-L(1-\alpha_1)]\}}{I\epsilon L(1-\alpha_1)+\tilde{k}_0\alpha_1}$	$\frac{-\lambda_2(k_{H_2O}+\lambda_1)}{(\lambda_1-\lambda_2)k_{H_2O}}$	$\frac{\lambda_1(k_{H_2O}+\lambda_2)}{(\lambda_1-\lambda_2)k_{H_2O}}$	0	$\Sigma_{H_2O}+\tilde{k}_0\frac{1-3\alpha_1}{1-\alpha_1}$
ρ_d	0	$\frac{\rho_0\tilde{k}_0L\alpha_1(1-\alpha_1)}{I\epsilon L(1-\alpha_1)+\tilde{k}_0\alpha_1}$	$\frac{-\lambda_2(k_{H_2O}+\lambda_1)}{(\lambda_1-\lambda_2)k_{-H_2O}}$	$\frac{\lambda_1(k_{H_2O}+\lambda_2)}{(\lambda_1-\lambda_2)k_{-H_2O}}$	0	$\frac{1}{2-3\alpha_1}(\Sigma_{H_2O}-\tilde{k}_0)$
ρ_Σ	ρ_1	ρ_∞	$\frac{-(\lambda_2+I\epsilon L+\tilde{k}_0)}{(\lambda_1-\lambda_2)}$	$\frac{(\lambda_1+I\epsilon L+\tilde{k}_0)}{(\lambda_1-\lambda_2)}$	0	$\Sigma_{H_2O}-\tilde{k}_0$

[a] I is the excitation light intensity expressed as a number of quanta per cm^2 per second: ϵ is the effective cross section for a capture of light quanta by a set of light-collecting chlorophyll molecules present in a reactive center; L is the quantum efficiency of consumption of singlet-excited states of PSU pigment matrix molecules by electron transfer incenteres; (p^+), (a^-), (p^+a^-), and α are the relative concentrations (fractions) of the oxidized form of the primary donor P^+, reduced primary aceptor A^-, double-charged P^+A^-, and closed $P^+A^- + PA^- + P^+A$ centers, respectively: ρ is the quantum yield of prompt fluorescence; ρ_0 and ρ_∞ are the quantum yields of prompt fluorescence in photosynthetic units with open and closed centers, respectively; ρ_d is the quantum yield of delayed fluorescence; $\rho_\Sigma = \rho + \rho_d$; $\tilde{k}_0 = k_0\ (1-L)$, where k_0 is the effective value of the constant of the reverse electron transfer in double-charged centers; $\Sigma_{H_2O} = k_{H_2O} + k_{-H_2O}$ where k_{H_2O} is the rate constant of P^+ reduction by the water decomposition system and k_{-H_2O} is the constant of the reverse reaction; $\tilde{I}$ is the values of excitation irradiances, where $R_y^1 = R_y^2$.

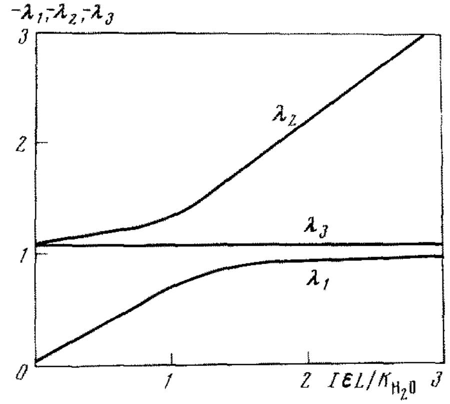

Figure 2. Roots of characteristic equations of system (1) as a function of relative excitation irradiance ($I\epsilon L/k_{H_2O}$). The values of $\lambda_{1,2,3}$ are given with respect to k_{H_2O}. Calculated at $k_0 = 0.01\ k_{H_2O}$; $L = 0.9$; $k_{-H_2O} = 0.1\ k_{H_2O}$.

irradiances. These figures, along with Table I, diaplay the main kinetic specific features of the system.

Since $(p^+)_{st} = (p^+)_{eq} = \mathrm{const}$, (p^+) deviation from an equilibrium value always follows the curves with a maximum. This case is described by the sum of exponents with equal amplitudes but different signs

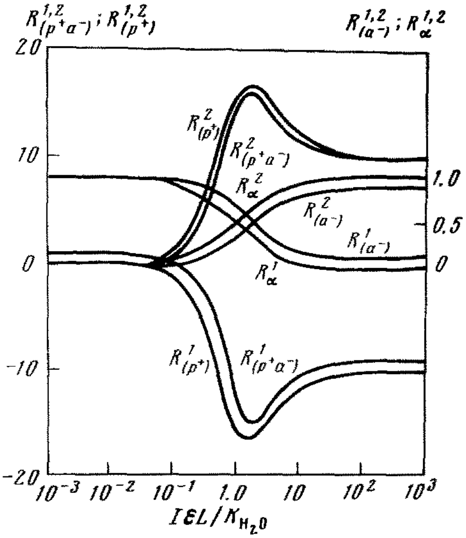

Figure 3. Preexponential factors (Table I) in formulas (8) and (9) as a function of relative irradiance $I\epsilon L/k_{H_2O}$.The rest is as in Fig. 2.

$(R^1_{(p^+)} + R^2_{(p^+)} = 0)$. The degree of deviation of (p^+) from $(p^+)_{eq}$ increases with excitation irradiance, tending to a limit equal to the ratio $(1 - \alpha_1)/\alpha_1$.

A change of double-charged centers (p^+a^-) with time accompanied by a proportional change of F_d and ρ_d may be of three different shapes. If $R^1_{(p^+a^-)} \ll R^2_{(p^+a^-)}$ or $R^2_{(p^+a^-)} = 1$ the dependence is exponential; for positive and approximately equal $R^1_{(p^+a^-)}$ and $R^2_{(p^+a^-)}$ it is a two-phase curve; when $R^2_{(p^+a^-)} > 1$ and $R^1_{(p^+a^-)} < 0$ there is a maximum on the curve.

A change in the rest parameters, namely $(a^-), \alpha, \rho, \rho_\Sigma = (\rho + \rho_d)$. follows either one-phase (exponential) curves or two-phase ones. The latter are observed over the range of excitation irradiances where R^1_y and R^2_y are commensurable. The values of excitation irradiances $I \epsilon L$ ensuring the equalities $R^1_y = R^2_y$ are also presented in Table I.

Kinetics of primary acceptor A reduction deserves special attention. From the corresponding formulas in Table I it is seen that for $I \to \infty, R^1_{(a^-)} \to \alpha_1$ and $R^2_{(a^-)} \to (1 - \alpha_1)$ (see also Fig. 3). Thus, for $I \gtrsim 0.1\, \tilde{I}_{(a^-)}$ the dependence of (a^-) on t is two-phase everywhere. Over the range $I \gtrsim 10\tilde{I}_{(a^-)}$ the kinetics of (a^-) change is characterized by the following basic features. Slow phase of (a^-) vs t curve has a constant amplitude equal to α_1 and constant extinction time $(1/k_{H_2O})$. Time constant of fast phase is inversely proportional to excitation irradiances at constant amplitude equal to $(1 - \alpha_1)$. Such a picture of primary acceptor reduction in intensive light can be observed only when the number of closed centers of P^+A type under the conditions of dark adaptation is measurable (their fraction is α_1). Indeed, if excitation irradiance is such that during time interval $T_1 \ll (1/k_{H_2O})$ each center of the PA type, whose fraction is $(1 - \alpha_1)$, absorb one light quantum, then on time interval T_2 satisfying the condition $T_1 < T_2 < (1/k_{H_2O})$ α will equal unity with a high degree of accuracy when there are two types of closed centers: P^+A^- and P^-A. Donor P^+ oxidized molecules are reduced with time by the water decomposition system (the rate constant is k_{H_2O}). As a result of the reduction the centers of the P^+A type transform at first into PA and then, having absorbed an excitation quantum, into P^+A^-. From here it follows that in those centers which in dark had the form P^+A, A will be reduced with a rate equal to that of an electron originating from the water decomposition system.

As is seen from the formulas in Table I, the quantum yield of prompt and delayed fluorescence in steady state

$$\rho_{\Sigma,st} = \rho_{st} + \rho_{d,st} = \rho_\infty$$

is independent of I, whereas the contribution of ρ_{st} and $\rho_{d,st}$ to ρ_∞ does depend on I. Thus, for example, if $\alpha_1 = 0.1$, $L = 0.9$, and $I = 0$, then $\rho_{st} = 0.19\, \rho_\infty$, while $\rho_{d,st} = 0.81\, \rho_\infty$. When $I \epsilon L$ is equal to $10k_0$, $\rho_{st} = 0.99\, \rho_\infty$ and $\rho_{d,st} = 0.01\, \rho_\infty$ (Fig. 4). All the above is due to the fact that ρ_{st} is an increasing and $\rho_{d,st}$ a decreasing function of I and $\rho_{st} + \rho_{d,st} = \text{const}$.

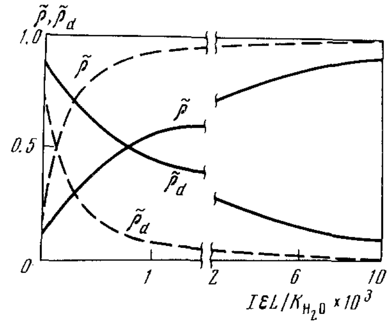

Figure 4. Theoretical dependences of steady-state values of quantum yields of prompt ρ and delayed ρ_d fluorescence on relative excitation irradiances $I\epsilon L/k_{H_2O}$ for unicentral (———) and multicentral (———) models of the photosynthetic unit. Calculated parameters are the same as in Fig. 2.

Using the expressions given in Table I, one can see that (a) the mean time t during which ρ_Σ changes from ρ_1 to ρ_∞ is determined by

$$\bar{t} \equiv \int_{\rho_1}^{\rho_\infty} t d\rho_\Sigma / \int_{\rho_1}^{\rho_\infty} d\rho_\Sigma = 1/[I\epsilon L(1-\alpha_1) + \tilde{k}_0\alpha_1]$$

(b) The area σ between ρ_∞ and the inductive curve ρ_Σ (t) equals

$$\sigma \equiv \int_0^\infty [\rho_\infty - \rho_\Sigma(t)]\, dt = (\rho_\infty - \rho_1)\,\bar{t}$$

(c) The number of quanta stored by the system is determined from the inductive curve $\rho_\Sigma(t)$

$$\bar{\sigma} \equiv I\epsilon M\sigma/\rho_\infty = MI\epsilon L(1-\alpha_1)\,\bar{t} = [A^-]_{\rm st}$$

and equals the stead-state concentration $[A^-]_{\rm st}$ of the primary acceptor reduced.

B. Dark Stage. The expressions for the factors in (8) and (9) corresponding to this stage are given in Table II.

Considering the kinetics after turning off the light, we shall restrict ourselves to the case close to the real one when $k_{H_2O} \gg \tilde{k}_0$. Under this condition $\lambda_1 = -\tilde{k}\alpha_1$ and $\lambda_2 = -(\Sigma_{H_2O} + \tilde{k}_0) \approx \lambda_3$, i.e., we are dealing here not with three but with two exponents (with a certain degree of approximation. The pre-exponential factor for the second exponent is $\tilde{R}_y^2 = R_y^2 + R_y^3$.

Next, the character of the kinetic curves in dark conditions will differ depending on whether (p^+) is in an equilibrium or near-equilibrium state at the instant of turning on the light. If $(p^+) = \alpha_1$, $(p^+a^-) = \alpha_1(a^-)$. As is seen from the formulas for R_y^2 and R_y^3 in Table II R_y^2 and R_y^3 and,

TABLE II. Explicit expression for preexponential factors in equations (8) and (9), roots of the characteristic equation, and steady-state values of the parameters considered with respect to their initial values and internal parameters of the system during dark relaxation[a]

$$\lambda_{1,2} = 0.5\{-(\Sigma_{H_2O} + \tilde{k}_0) \pm [\Sigma_{H_2O} + \tilde{k}_0)^2 - 4k_0 k_{-H_2O}]^{1/2}\}$$

$$\lambda_3 = -\Sigma_{H_2O}$$

Y	$Y_{t=0}$	Y_{st}	R_y^1	R_y^2	R_y^3
(p^+)	$(p^+)_T$	α_1	$\dfrac{-\lambda_1[(a^-)_T\lambda_2 + \tilde{k}_0(p^+a^-)_T]}{(\lambda_1-\lambda_2)(\Sigma_{H_2O}+\lambda_1)[(p^+)_T-\alpha_1]}$	$\dfrac{\lambda_2[(a^-)_T\lambda_1 + \tilde{k}_0(p^+a^-)_T]}{(\lambda_1-\lambda_2)(\Sigma_{H_2O}+\lambda_2)[(p^+)_T-\alpha_1]}$	$\dfrac{\alpha_1(a^-)_T - (p^+a^-)_T}{(1-\alpha_1)((p^+)_T-\alpha_1)} + 1$
(a^-)	$(a^-)_T$	0	$\dfrac{-[(a^-)_T\lambda_2 + \tilde{k}_0(p^+a^-)_T}{(\lambda_1-\lambda_2)(a^-)_T}$	$\dfrac{(a^-)_T\lambda_1 + \tilde{k}_0(p^+a^-)_T}{(\lambda_1-\lambda_2)(a^-)_T}$	0
(p^+a^-)	$(p^+a^-)_T$		$\dfrac{\lambda_1[(a^-)_T\lambda_2 + \tilde{k}_0(p^+a^-)_T]}{(\lambda_1-\lambda_2)\tilde{k}_0(p^+a^-)_T}$	$\dfrac{-\lambda_2[(a^-)_T\lambda_1 + \tilde{k}_0(p^+a^-)_T]}{(\lambda_1-\lambda_2)\tilde{k}_0(p^+a^-)_T}$	0
α	α_T	α_1	$\dfrac{-(k_{H_2O}+\lambda_1)[(a^-)_T\lambda_2 + \tilde{k}_0(p^+a^-)_T]}{(\lambda_1-\lambda_2)(\Sigma_{H_2O}+\lambda_1)(\alpha_T-\alpha_1)}$	$\dfrac{(k_{H_2O}+\lambda_2)[(a^-)_T\lambda_1 + \tilde{k}_0(p^+a^-)_T]}{(\lambda_1-\lambda_2)(\Sigma_{H_2O}+\lambda_2)(\alpha_T-\alpha_1)}$	$\dfrac{\alpha_1(a^-)_T - (p^+a^-)_T}{(1-\alpha_1)(\alpha_T-\alpha_1)} + \dfrac{(p^+)_T-\alpha_1}{(\alpha_T-\alpha_1)}$
ρ	ρ_T	ρ_1			
F_d	$F_{d,T}$	0	$\dfrac{\lambda_1[(a^-)_T\lambda_2 + \tilde{k}_0(p^+a^-)_T]}{(\lambda_1-\lambda_2)\tilde{k}_0(p^+a^-)_T}$	$\dfrac{-\lambda_2[(a^-)_T\lambda_1 + \tilde{k}_0(p^+a^-)_T]}{(\lambda_1-\lambda_2)\tilde{k}_0(p^+a^-)_T}$	0

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[a] Subscript T denotes the corresponding values at the instant of turning off the light. F_d is the intensity of delayed fluorescence. The rest is as in Table I.

consequently, $\tilde{R}_y^2$ are equal to zero when the above relationship takes place. Thus, when $(p^+) = \alpha_1$ the dark relaxation of (a^-), (p^+a^-), and of F_d follows the exponential law, the exponent being determined by the product $k_0(1-L)\alpha_1$.

The equality $(p^+a^-) = \alpha_1(a^-)$ or $(p^+) = \alpha_1$ is realized in two cases: in the strict sense, when a steady state is attained in light, and, approximately, during the transition period at low irradiances. The latter is confirmed by the plot $R^2_{(p^+)}$ vs $I\epsilon L$ presented in Fig. 3. When $I\epsilon L \ll k_{H_2O}$, $R^2_{(p^+)} \approx 0$, i.e. over this range of $I\epsilon L$ values, (p^+) practically does not deviate from its equilibrium value.

Consider now another limiting case when the deviation of (p^+) from its equilibrium value is maximum at the moment of turning off the light. This can take place at high I $(I\epsilon L \gg 10k_{H_2O})$ and small T $[T \ll (1/k_{H_2O})]$. After such a pulse the following equations are approximately valid: $(p^+a^-) = (a^-) = (1-\alpha_1)$ and $(p^+) = \alpha = 1$. Using the formulas from Table II, we see that $R^1_{(p^+)} = R^2_{(a^-)} = 0$; $R^2_{(p^+)} = R^1_{(a^-)} = 1$; $R^1_{(p^+a^-)} = R^1_{F_d} = R^2_\alpha = \alpha_1$; $R^2_{(p^+a^-)} = R^2_{F_d} = R^1_\alpha = (1-\alpha_1)$. Thus, in this case, as before, (a^-) relaxation follows only the one-phase law, and that of (p^+) only the fast law. The rest of the values, (p^+a^-), F_d, α (and, consequently, ρ) change according to two-phase curves. The fast phase $R^2_{(p^+a^-)} = R^2_{F_d} = (1-\alpha_1)$ predominates for (p^+a^-) and F_d and the slow one $R^1_\alpha = R^1_\rho = (1-\alpha_1)$ for α or ρ. Repeating in part the considerations given in the previous section of the kinetics of A reduction, we may explain the above in the following way. Since under the conditions of dark adaptation the reactive centers are in two forms P^+A (fraction α_1) and PA (fraction $1-\alpha_1$), at the end of a light pulse with a duration $T \ll (1/k_{H_2O})$ and at high excitation irradiance all PA convert into P^+A^- and P^+A remain in the initial state. Thus, at instant T after the beginning of illumination all centers are closed, i.e., $\alpha = 1$, but have two forms P^+A^- and P^+A. After illumination almost all P^+A convert into open centers PA in time comparable with $(1/k_{H_2O})$. This transition causes a fast phase of change in α and, consequently, in ρ. Simultaneously, the main part $(1-\alpha_1)$ of the centers of the P^+A^- type convert into PA^-. After this period of time, when kinetics is mainly determined by the electron transport on the donor side of PS II, the concentration of P^+ attains practically the equilibrium value. Then the system relaxation proceeds only due to reverse electron transport in the centers.

C. Reillumination. Consider now the relationship between the rates of a change in the total fluorescence quantum yield $[\rho_\Sigma\ (t)]$ for the same $\rho_\Sigma\ (t') \neq \rho_1$ after complete and partial adaptation of a sample to dark. The problem is presented graphically in Fig. 5.

Let the system, being in the process of dark relaxation after a steady state has been attained in light, be reilluminated withn the same excitation irradiance. In this case the initial values (a^-) and (p^+a^-) are

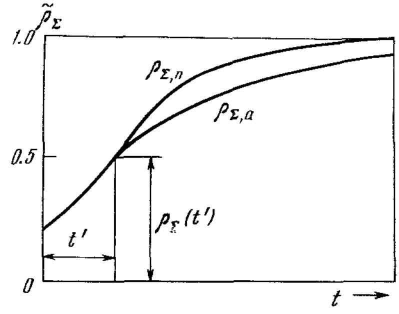

Figure 5. Schematic curves of a change in quantum yield of total fluorescence $\rho_\Sigma(t) = \rho(t) + \rho_d(t)$ in samples completely $\rho_{\Sigma,a}(t)$ and partially $\rho_{\Sigma,n}(t)$ adapted to dark.

not equal to zero, $\alpha \neq \alpha_1$ and, correspondingly, $\rho \neq \rho_1$. The equation describing the kinetics has the same form as before:

$$[\rho_\Sigma(t-t') - \rho_\infty]/[\rho_\infty(t') - \rho_\infty] = R^1_{\rho_\Sigma}\, e^{\lambda_1 t} + R^2_{\rho_\Sigma}\, e^{\lambda_2 t} \qquad (9')$$

where $t \gg t'$ and $R^{1.2}_{\rho_\Sigma}$ are the same as in Table I. From here the rate of change in $\rho_\Sigma(t)$, i.e. $\dot{\rho}_\Sigma(t)$ for a nonadapted sample at the moment of turning on the light is equal:

$$\dot{\rho}_{\Sigma,n} = [\rho_\Sigma(t) - \rho_\infty]\,[R^1_{\rho_\Sigma}\lambda_1 + R^2_{\rho_\Sigma}\lambda_2] \qquad (10)$$

The similar value for an adapted sample at the instant $t = t'$ is described by the expression

$$\dot{\rho}_{\Sigma,a} = (\rho_1 - \rho_\infty)(R^1_{\rho_\Sigma}\lambda_1 e^{\lambda_1 t'} + R^2_{\rho_\Sigma}\lambda_2 e^{\lambda_2 t'}) \qquad (11)$$

Using (10), (11), and (9) for $\rho_\Sigma(t)$ we may show that

$$\frac{\dot{\rho}_{\Sigma,n} - \dot{\rho}_{\Sigma,a}}{\dot{\rho}_{\Sigma,a}} = \frac{(\lambda_1 - \lambda_2)R^1_{\rho_\Sigma}R^2_{\rho_\Sigma}(-e^{\lambda_1 t'} + e^{\lambda_2 t'})}{\lambda_1 R^1_{\rho_\Sigma} e^{\lambda_1 t'} + \lambda_2 R^2_{\rho_\Sigma} e^{\lambda_2 t'}} \geqslant 0 \qquad (12)$$

since the product $(\lambda_1 - \lambda_2)R^1R^2$ is positive and $(-e^{\lambda_1 t'} + e^{\lambda_2 t'})$ as well as the denominator in the right-hand side of (12) are always negative.

Thus, we see that for $\rho_\Sigma(t') \neq \rho_1$ the rate of change of $\rho_\Sigma(t)$ in an adapted sample is always less than in a nonadapted one. A simple calculation shows that at $\alpha_1 = 0.1$, $L = 0.9$, $I\epsilon L/k_{H_2O} = 1.1$ and $t' = (1/k_{H_2O})$ the left-hand side of (12), is, approximately, 10% whereas at $\alpha_1 = 0.5$ it is as high as 120%.

Multicentral Model

Initial Equations

The system of equations corresponding to this model is of the form [17]

$$(\dot{p}^+) = [I\epsilon L(1-\alpha) - \tilde{k}_0(p^+a^-)]/(1-L\alpha) - \Sigma_{H_2O}(p^+) + k_{H_2O} \quad (13.1)$$

$$(\dot{a}^-) = [I\epsilon L(1-\alpha) - \tilde{k}_0(p^+a^-)]/[1-L\alpha] \quad (13.2)$$

$$(\dot{p}^+a^-) = [I\epsilon L(1-\alpha) - \tilde{k}_0(p^+a^-)]/(1-L\alpha) - \Sigma_{H_2O}(p^+a^-) + k_{-H_2O}(a^-) \quad (13.3)$$

$$\alpha = (p^+) + (a^-) - (p^+a^-) \quad (13.4)$$

The dependence of fluorescence yield on α is nonlinear [6, 7]:

$$\rho = \rho_0/(1-L\alpha) \quad (14)$$

Delayed fluorescence intensity is expressed as

$$F_d = MQ\rho k_0(p^+a^-) \quad (15)$$

and, correspondingly, its quantum yield

$$\rho_d = \rho\, k_0(p^+a^-)/I\epsilon \quad (16)$$

where M is the number of PSU of the multicentral type in a volume unit and Q is the number of the reactive center in one PSU.

Properties of the System under Consideration

A. Light Stage. Using (13), we see that the dependence of steady-state values of (p^+), (a^-), (p^+a^-), and α on excitation irradiance (I) is the same as for unicentral model (see Table I). The sum of prompt and delayed fluorescence quantum yields in a steady state is equal to ρ_∞ as before. The character of ρ_{st} and ρ_d change depending on I as shown in Fig. 4.

At low excitation irradiances when (p^+) does not deviate from its equilibrium value ($I\epsilon L/k_{H_2O} \leqslant 0.01$) during the transition period, i.e., when the expressions $(p^+) = \alpha_1$, $(p^+a^-) = \alpha_1\,(a^-)$, and $\alpha = \alpha_1 + (1-\alpha_1)(a^-)$ are valid, ρ and ρ_d increase only owing to the rise in concentration of the reduced acceptor. In this case equation (13.2) transforms into

$$(\dot{a}^-) = \frac{I\epsilon L(1-\alpha_1)[1-(a^-)] - \tilde{k}_0\alpha_1(a^-)}{1-L\alpha_1 - L(1-\alpha_1)(a^-)} \quad (17)$$

From here the relationship between (a^-) and t follows:

$$(a^-)_{st}\left\{(a^-) + (a^-_{st}) - \frac{1-L\alpha_1}{L(1-\alpha_1)} \ln \frac{(a^-_{st})-(a^-)}{(a^-_{st})}\right\} = I\epsilon t \quad (18)$$

The curves $\rho(t)$ and $F_d(t)$ corresponding to this case are shown in Fig. 6.

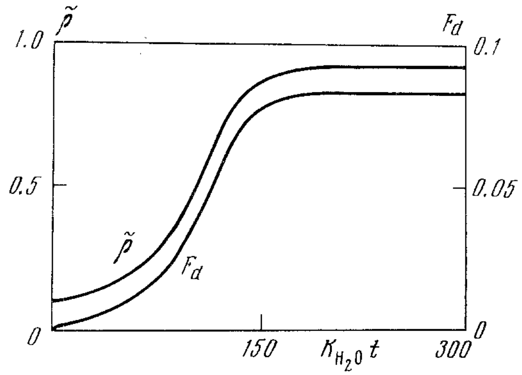

Figure 6. Theoretical curves of a change in quantum yield of prompt and in intensity of delayed F_d fluorescence in weak light. $(I\epsilon L/k_{H_2O}) = 0.01$. The rest of the calculated parameters are the same as in Fig. 2.

If the excitation irradiance is sufficiently high $(I\epsilon L/k_{H_2O} \gg 10)$, the equalities $[(p^+) - \alpha_1] = (a^-) = (p^+a^-) = \alpha - \alpha_1$ are valid on time interval $T \leqslant (0.1/k_{H_2O})$ after the onset of illumination, i.e., nonequilibrium values of these parameters change proportionally. Then, for example, for (a^-) equation (13.2.) becomes

$$(\dot{a}^-) = \{I\epsilon L[1 - \alpha_1 - (a^-)]\} / [1 - L\alpha_1 - L(a^-)] \tag{19}$$

with corresponding solution

$$(a^-) - \frac{1-L}{L} \ln \frac{1 - \alpha_1 - (a^-)}{1 - \alpha_1} = I\epsilon t \tag{20}$$

where (a^-) acquires the values between zero and $(1 - \alpha_1)$.

Over the range of excitation irradiances from 0.01 to $10 I\epsilon L/k_{H_2O}$ the kinetic behavior of ρ and F_d can be more complicated. Thus, over the range $I\epsilon L \approx k_{H_2O}$ the end stage of the $\rho(t)$ curve may have the "tail" (Figs. 8, 9, and 12); when $(I\epsilon L/k_{H_2O}) \approx (0.01\text{–}0.05)$ the curves $F_d\ (t)$ are multiphase (Fig. 7).

B. Dark Stage. Under dark condition system (13) becomes

$$(\dot{p}^+) = -\tilde{k}_0(p^+a^-)/(1 - L\alpha) - \Sigma_{H_2O}(p^+) + k_{-H_2O} \tag{21.1}$$

$$(\dot{a}^-) = -k_0(p^+a^-)/(1 - L\alpha) \tag{21.2}$$

$$(\dot{p}^+a^-) = -\tilde{k}_0(p^+a^-)/(1 - L\alpha) - \Sigma_{H_2O}(p^+a^-) + k_{-H_2O}(a^-) \tag{21.3}$$

$$\alpha = (p^+) + (a^-) - (p^+a^-) \tag{21.4}$$

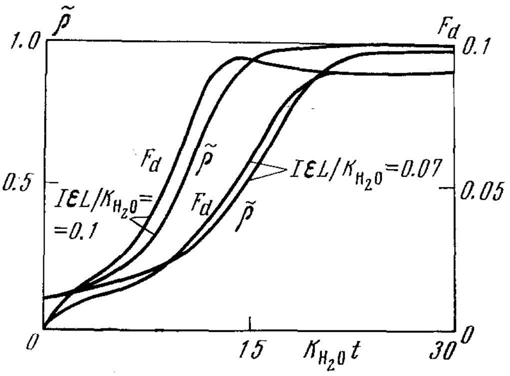

Figure 7. The same as in Fig. 6 at $(I\epsilon L/k_{H_2O}) = 0.07$ and 0.1.

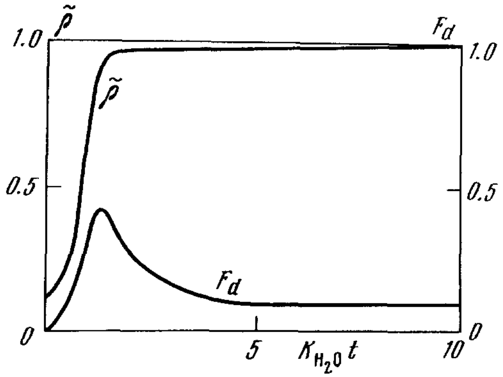

Figure 8. The same as in Figs. 6 and 7 at $(I\epsilon L/k_{H_2O}) = 1.1$.

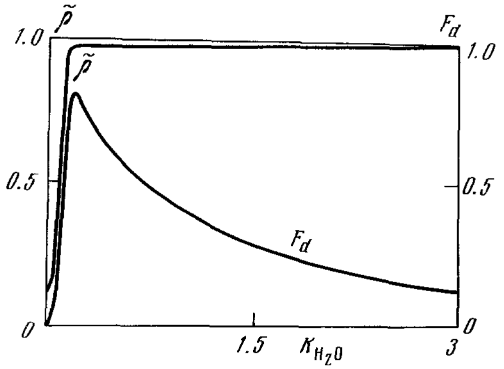

Figure 9. The same as in Figs. 6, 7, 8 at $(I\epsilon L/k_{H_2O}) = 10$.

Since $k_0 \ll k_{H_2O}$ the terms containing k_0 in (21.1) and (21.3) may be neglected on time interval $0 \div (10k_{H_2O})$ after turning off the light. In this case the solution of system (21) is determined by the equations

$$
\begin{aligned}
(p^+) &= [(p_T^+) - \alpha_1]\, e^{-\Sigma_{H_2O} t} + \alpha_1 \\
(a^-) &= (a^-)_T \\
(p^+a^-) &= [(p^+a^-)_T - \alpha_1 (a^-)_T]\, e^{-\Sigma_{H_2O} t} + \alpha_1 (a^-)_T \\
\alpha &= [\alpha_T - \alpha_1 - (1-\alpha_1)(a^-)_T]\, e^{-\Sigma_{H_2O} t} + (1-\alpha_1)(a^-)_T + \alpha_1
\end{aligned}
\tag{22}
$$

where subscript T denotes the values of corresponding parameters at the moment of turning off the light. If we substitute the expressions for α and (p^+a^-) from (22) into (14) and (15), the following time dependences of ρ and F_d are obtained:

$$
\rho = \frac{\rho_0}{1 - L\alpha_1 - L\{[\alpha_T - \alpha_1 - (1-\alpha_1)(a^-)_T]\, e^{-\Sigma_{H_2O} t} + (1-\alpha_1)(a^-)_T\}}
\tag{23}
$$

$$
F_d = MQ\rho_0 k_0 \frac{[(p^+a^-)_T - \alpha_1 (a^-)_T]\, e^{-\Sigma_{H_2O} t} + \alpha_1 (a^-)_T}{1 - L\alpha_1 - L\{[\alpha_T - \alpha_1 - (1-\alpha_1)(a^-)_T]\, e^{-\Sigma_{H_2O} t} + (1-\alpha_1)(a^-)_T\}}
\tag{24}
$$

After $e^{-\Sigma_{H_2O} t}$ becomes zero, system (22) takes the form

$$
\begin{aligned}
(p^+) &= \alpha_1 \\
(a^-) &= (a^-)_T \\
(p^+a^-) &= \alpha_1 (a^-)_T \\
\alpha &= \alpha_1 + (1-\alpha_1)(a^-)_T
\end{aligned}
\tag{25}
$$

where further relaxation of (a^-) and, consequently, of (p^+a^-) and α proceeds in conformity with the equation

$$
(\dot{a}) = \tilde{k}_0 \alpha_1 (a^-)/[1 - L\alpha_1 - L(1-\alpha_1)(a^-)]
\tag{26}
$$

having the following solution:

$$
L(1-\alpha_1)[(a^-)_T - (a^-)] + (1 - L\alpha_1)\ \ln\, [(a^-)/(a^-)_T] = \tilde{k}_0 \alpha_1 t
\tag{27}
$$

In the same way the values (a^-), (p^+a^-), and α change after the steady state is attained in light. Figures 10 and 11 present the corresponding plots of ρ and F_d after turning off the light.

Thus, after non-steady-state conditions of excitation, a change of ρ (or, to be more exact, of α) and F_d with t follows two-phase curves. The fast phase of the curve F_d is caused by a sharp decrease in concentration of double-charged centers in the process of P^+ reduction by the water decomposition system. On the curve $\rho(t)$ this is caused by the transition

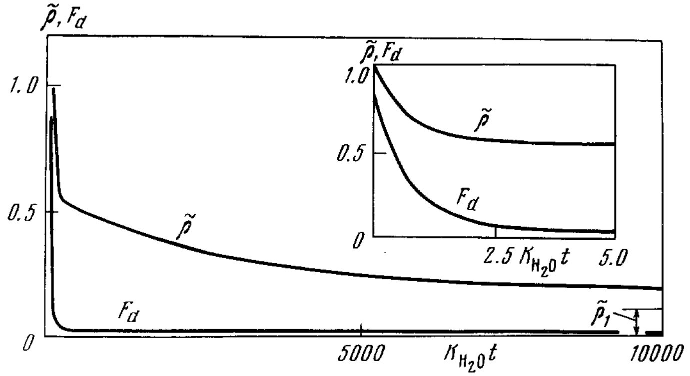

Figure 10. Change of ρ and F_d in dark after non-steady-state excitation conditions $(I\epsilon L/k_{H_2O}) = 50$ $T = (0.03/k_{H_2O})$. The inset shows the initial stages of ρ and F_d changes. The rest is the same as in Fig. 2.

of the P^+A centers to an open form (for details see the discussion of kinetics in terms of the unicentral model). After the attainment of near-equilibrium concentration of P^+ the further relaxation in the system takes place owing to reverse electron transfer in double-charged centers, whose concentration is expressed as $(p^+a^-) = \alpha_1(a^-)$, with subsequent expenditure of energy through delayed fluorescence and its consumption in chlorophyll a molecules on heating. An extremely long relaxation of (a^-) towards the initial (dark) state is in many respects connected with the fact that the energy of singlet-excited molecules of PSU pigment matrix is repeatedly using in open reactive centers for electron transfer.

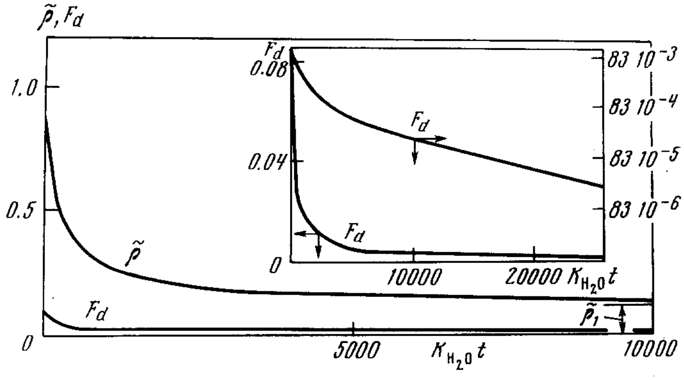

Figure 11. The same as in Fig. 10 after steady-state excitation conditions. $I\epsilon L/k_{H_2O} = 0.01$. The inset shows a change of F_d in a larger scale and in semilogarithmic coordinates.

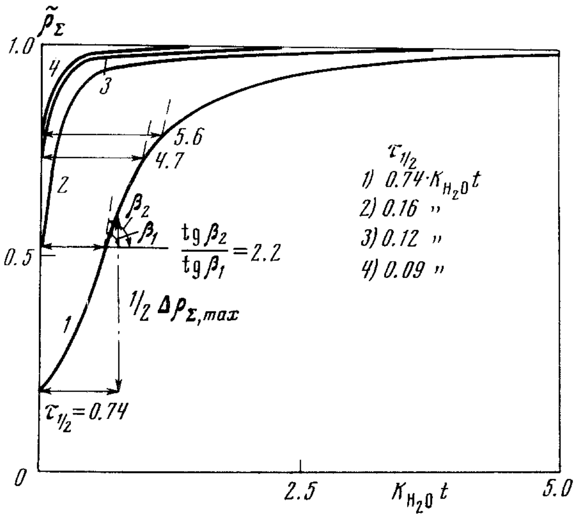

Figure 12. Theoretical curves of a change in $\rho_\Sigma(t)$ after complete (1) and partial (2, 3, 4) adaptation to dark. The dashed line near curve (1) shows the initial stages of $\rho_\Sigma(t)$ change in partly adapted samples (parallel transfer of the initial sections of curves 2, 3 and 4 along the absciss axis). $\tau_{1/2}$ is time during which $\rho_\Sigma(t)$ changes by 1/2 of $\Delta\rho_{\Sigma,\max}$. Calculated at $k_{-H_2O} = k_{H_2O}$; $I\epsilon(L/k_{H_2O}) = 1.2$; $L = 0.9$; $k_0 = 0.01$ k_{H_2O}.

B. Reillumination. Figure 12 presents the calculated curves $\rho_\Sigma(t)$ corresponding to partial and complete adaptation of a sample to dark. Here we deliberately consider a somewhat unusual case, setting $\alpha_1 = 0.5$ for the calculation of these curves. This case vividly shows that the slope of the curves $\rho_\Sigma(t)$ obtained after repeated illumination may be several times that of the corresponding sections of the curve $\rho_\Sigma(t)$ observed after complete adaptation to dark. This is accompanied by a sharp reduction in time during which the value $\rho_\Sigma(t)$ changes by 1/2 of $\Delta\rho_{\Sigma,\max}$. All this, as we have already seen, is due to the fact that under the conditions of dark adaptation a part of the reactive centers has the P^+A form. At excitation irradiances $I\epsilon L \approx k_{H_2O}$ the values considered vary during a time interval commensurate with $(1/k_{H_2O})$. Therefore, at the instant of turning off the light two processes take place simultaneously: closing of the centers of the PA type due to electron transfer from P to A and opening of the centers of P^+A type due to motion of electrons toward P^+ from the water decomposition system. The contribution of the second process depends to a large extent on the degree of A^- reduction. Under the condition of complete dark adaptation, $(a^-)_{eq} = 0$, so that the concentration of centers in the P^+A form is a maximum. Therefore the "tail" in the curve $\rho_\Sigma(t)$ is also a maximum.

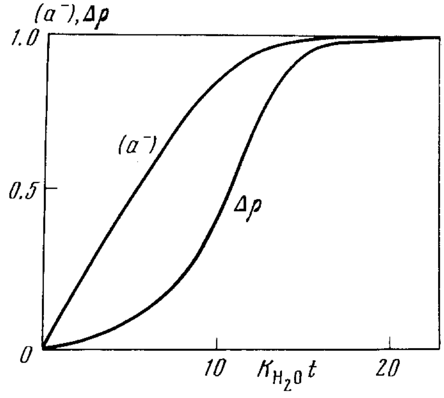

Figure 13. The normalized curves of a change in concentration of a primary acceptor (a^-) reduced form and of a variable part of fluorescence quantum yield $\Delta\rho$ at the instant of turning on the light. $I\epsilon L/k_{H_2O} = 0.1$. The rest is as in Fig. 2.

C. Relationship between Time Dependence of ρ and (a^-). Consider the relationship between changes in fluorescence quantum yield and the degree of reduction of the electron primary acceptor. Figures 13–15 are typical examples of the dependences in question. In Fig. 13 we see that at the instant of turning on the light (a^-) changes with time much faster than ρ. A deviation is observed at very intensive excitation irradiances at final stages of (a^-) and ρ variations (Fig. 14) when the rate of primary acceptor reduction is limited by the rate of electron arrival from the water decomposition system. On the contrary, after turning off the light ρ decreases faster than (a^-)(Fig. 15).

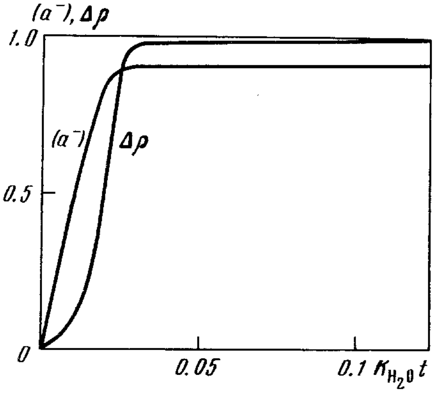

Figure 14. The same as in Fig. 13 at $I\epsilon L/k_{H_2O} = 50$.

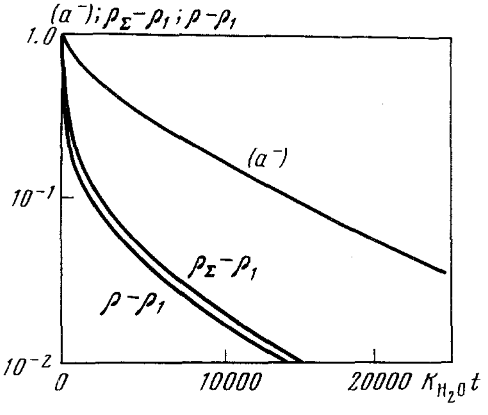

Figure 15. Kinetics of a change in semilogarithmic coordinates of primary accept (a^-) reduced form, of variables parts of prompt $(\rho - \rho_1)$ and total $(\rho_\Sigma - \rho_1)$ fluorescence in dark after the attainment of a steady state of the system in the light.

The above relationships between changes of ρ and (a^-) with time when light is turned on or turned off are due to the multicentral type of photosynthetic unit arrangement with nonlinear relationship between ρ and (a^-). In our calculations this follows from formula (14).

It should be noted that in a number of papers [20, 21] similar dependences between the curves of a change in fluorescence quantum yield and signal value C-550 assigned to the reduced form of a PS II primary acceptor are considered to be a proof of the fact that the oxidized form of an electron donor P^+ quenches fluorescence. If C-550 does belong to the primary acceptor of PS II, the relationship between the curves in question correlates qualitatively with those shown in Figs. 13 and 14 and, therefore, in no way testifies to the quenching effect of the oxidized form of a primary donor P^+. The conclusion drawn in [20, 21] on the quenching effect of P^+ is based on the assumption of linear dependence of fluorescence quantum yield on the fraction of closed centers.

Conclusions

The above analysis shows in what cases prompt and delayed fluorescence vary in accordance with a change in the degree of acceptor reduction and donor oxidation and when both these components of the reactive centers are equally important [22]. Thus, stationary values of ρ_{st}, $\rho_{d,st}$ or $F_{d,st}$ completely depend on the degree of primary acceptor reduction since $(p^+)_{st} = \text{const}$. A similar situation is observed at the instants of turning on and off the light with low excitation irradiances $I\epsilon L \leqslant 0.1\tilde{I}\epsilon L_{(p^+)}$ (see Fig. 2) as well as after illumination with light of any irradiance if a steady state was attained during illumination. A fast decrease of α and (p^+a^-) in dark after a short pulse of high power and a change of (p^+a^-) and ρ_d or F_d in light from maximum to steady-state value are caused only by a variation in the degree of donor oxidation whereas (a^-) is practically constant. When light of high power is turned on $[I\epsilon L \geqslant 10\tilde{I}\epsilon L_{(p^+a^-)}]$ the phase of an increase in $(p^+a^-)(F_d, \rho_d)$ as well as in α and ρ is observed with a simultaneous alteration of the degree of acceptor reduction and donor oxidation. The irradiance range from $0.1\,\tilde{I}\epsilon L$ to $10\tilde{I}\epsilon L\rho$, where the curves $\rho_\Sigma\,(t)$ and $\rho(t)$ are two-phased, is a transition range from the region where kinetics of $\rho_\Sigma\,(t)$ and $\rho(t)$ growth is determined by the degree of primary acceptor reduction only to the region where it becomes dependent on the degree of primary donor oxidation as well.

At the same time the analysis shows that two following trends in kinetics of chlorophyll *a* fluorescence with $\lambda_{max} = 685_{nm}$ in tissues of plants and green algae observed experimentally may be explained without additional assumptions: (1) the fact that it is impossible to convert all the centers into a closed state using a single saturation pulse with a microsecond duration [23]. (2) the fact that in the presence of DCMU or at temperature below 0° C the curves $\rho(t)$ or $\rho_\Sigma\,(t)$ for samples partly adapted to dark go up much faster than the corresponding sections of the curves in the samples completely adapted to dark [23, 24].

All this can be explained only by the existence of a measurable number of the reactive centers in the P^+A form under the condition of dark adaptation.

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