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高等植物光系统Ⅱ捕光复合体向反应中心能量传输的四能级理论

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摘要: 结合近年来对光系统Ⅱ中捕光复合体(LHC Ⅱ)的结构、光谱和动力学研究成果,提出一个四能级模型来模拟能量从 LHC Ⅱ向反应中心的传递过程,并根据这个模型建立了一组速率方程,从理论的角度分析了高等植物光系统Ⅱ LHC Ⅱ中的能量传递过程。根据计算结果从整体上描述了光系统Ⅱ外周天线向反应中心的传能机制,并发现此过程中分子间有较强的相互作用。针对 LHC Ⅱ 的光谱、动力学特性和生物体结构对解析解进行了进一步的近似。讨论了 LHC Ⅱ的能量传递的大致途径和耗散机制,认为分子间能量传递的主要方式是在能级相邻分子间的传递,损耗是和能量传递过程紧密相关,随能级的降低损耗增大。对光强过强时的光保护机制也进行了探讨。

关键词: LHC Ⅱ; 四能级模型; 速率方程; 传能; 耗散

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A Four-Level Theory on Energy Transfer of the Light-Harvesting Complex Ⅱ in PS Ⅱ in Higher Plants

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Abstract: With reference to the recent achivements about the structure, spectra and kinetics of light-harvesting complex (LHC Ⅱ) in PS Ⅱ of higher plants, a four-level model was provided to simulate the energy transfer process from LHC Ⅱ to the reaction center. On the basis of this model, a set of rate equation was established. Analysis of its algebra solution led to a general picture of energy transfer process in LHC Ⅱ of higher plants and the strong interaction among pigment molecules in this process. Based on the spectra, kinetics and biological structural data providing some information of energy transfer path and energy dissipation mechanism, it has been found that energy transfer mainly happened between the pigments whose energy level was most closely adjacent, the loss of energy had a close relation to the process of energy transfer and tended to increase with the decrease of energy level. The protective mechanism of antenna system was also discussed.

Key words: LHC Ⅱ; four-level model; rate equation; energy transfer; energy dissipation

In photosynthesis, the light-harvesting complex, LHC Ⅱ takes in the solar energy and transfers it to the PS Ⅱ reaction center, to transform the excitation energy into the energy of the charge separation. The light-harvesting complex is the most abundant membrane protein in plant and algae chloroplast and it binds more than 50% of the polypeptide and chlorophyll content of plant thylakoid. The efficiency of the photochemical energy used by chlorophyll surpasses 90%. Such high efficiency requires a very high quantum conversion efficiency of the energy transfer from LHC Ⅱ to the reaction center. So it is obvious that the biological function systems carry on a higher efficient energy transfer and transform using the highly optimized structure of the antenna and the reaction center.

The excitation energy transfer in the photosynthesis antenna system has always been a subject to our attention. Many studies of LHC Ⅱ structure, spectral organization

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and energy transfer rate have already been reported, never the less many doubts also exist in the structure-function relation. For example, inner pigment molecule direction and its space position, complex spectra, relation of time constant correspond to its pigment component, etc. The route of the excitation energy transfer in the antenna system depends on the distance between molecules, molecule direction, space structure of molecules, radiation loss and the competition mechanism between energy of pigment emitting fluorescence and energy of making up photosynthesis[1,2]. Three-dimensional structure of plant light-harvesting complex has been determined at 0.34 nm resolution by electron crystallography of two-dimensional crystals[3]. These results show that the biological protein crystal is a trimer that consists of three symmetrical arranged monomers. Every monomer includes the three membrane-spanning α-helices, ~7 chlorophyll a and 5 chlorophyll b molecules. All porphyrin-ring direction is perpendicular to two tiers near the position between upper and lower surface of the thylakoid membranes. The center distances between chlorophyll of the same plane and different plane are 0.9—1.4 nm, 1.3—1.4 nm respectively. These data show that all chlorophyll b molecules are closely in contact with chlorophyll a and the majority of chlorophyll a molecules are nearly adjacent to β-car. Therefore, we explain that the excitation energy transfer from chlorophyll b to chlorophyll a and the trime-state energy transfer from chlorophyll a to β-car are very rapid and highly efficient. In the light-harvesting complex LHC Ⅱ, the accumulation structure of pigment molecules is just a structure base of strong exciton coupling and rapid energy transfer, but at present the space resolution of structure analysis can not resolve the chlorophyll a and chlorophyll b in the LHC Ⅱ.

1 Materials and Experiment Base

1.1 Materials

The LHC Ⅱ samples were purified by the Photosynthesis Research Center, Institute of Botany, The Chinese Academy of Sciences.

1.2 Experiment base

Energy transfer kinetics and fluorescence spectroscopy of LHC Ⅱ have been measured in picosecond and femtosecond laser pump-probe experiments respectively. Steady state and ultrafast spectral technology were used to study the structure of antenna complex, in order to uncover the biological structure-function relation. Low temperature absorption, fluorescence, circular dichroism (CD), linear dichroism (LD) spectroscopy were performed on spectrum components in the LHC Ⅱ monomer and above six components were discovered. Also many kinetic studies were focused on the time range and route of energy transfer.

Hemelrijk *et al*[4] have studied the LHC Ⅱ trimer using CD, LD and fluorescence spectroscopy, and obtained the 6—9 spectrum components, i.e. 676 nm, 671—668 nm, 662 nm, 657 nm, 652—648 nm and 645—640 nm. The 676 nm component includes 40%—50% chlorophyll a band resonance intensity. That is to say that the origin of 676 nm spectrum is four chlorophyll a in LHC Ⅱ monomer. The analysis of LD, CD spectra indicated that there were exciton coupling between these chlorophyll molecules and other chlorophyll a/b. From the CD spectrum it can also be deduced the existence of strong exciton interaction of chlorophyll a/b. Studying the steady state and ultrafast spectra of the LHC Ⅱ, Kwa *et al*[5,6] also obtained similar conclusion and discovered three lifetime components, e.g. 2—6 ps, 13—36 ps and several hundreds ns respectively. They also deduced that the first component was produced by the excitation transfer in the pigments between different layers of the monomer, the 2nd component was among the different monomer pigment molecules, but longer lifetime component origination was unclear. Trinkunas *et al*[7] had studied the structure of LHC Ⅱ and photophysical processes and photochemical characteristic, and obtained the absorption spectra from 645.3 nm to 683.3 nm including 12 spectrum components. They have experimentally measured 6 spectrum components, i.e. 648 nm, 653 nm, 656 nm, 675 nm, 679 nm and 683 nm, respectively. Four lifetime components have been resolved, which were 180 fs, 480 fs, 6 ps and 3.6 ns, respectively. Many researchers also reported the studies on the structure and spectrum of LHC Ⅱ[9—14].

On the basis of these results we established a four-level model of LHC Ⅱ. It was most accurate that every spectrum component of the 12 chlorophyll a/b was best cut in single level, but 12 equations were required to resolve the 12 components, but was very difficult to resolve the 12 equations. Fortunately some chlorophyll has very similar level of structure, for example, some of the spectra only had 0.7 nm in difference, so we summed up the nearby spectrum components as a useful level and established a four-level model. Every level was a merge of several spectral characteristics and time constant could not be separated or molecule level difference was very small. Such a model can adequately explain the conclusion of majority of experiments to obtain 6 — 9 spectrum

components and 3—4 time constants. Oscar *et al*[15] also used a similar method to study the energy transfer and trapping of light-harvesting antenna (LHA) in violet bacteria.

2 Energy Transfer Theory in LHC Ⅱ

2.1 Rate equation and solution

This model is similar to most models, only to consider the energy transfer between chlorophyll a/b. Our studies have not involved the energy transfer processes between carotenoid and xannthophyll and those between other pigment molecules and chlorophylls. Every LHC Ⅱ monomer includes 2 — 3 carotenoid molecules. These molecules exert a light protection on photosynthesis to prevent the formation of destructibility single state oxygen, which is important for the formation of LHC Ⅱ structure[16]. At the same time it can also absorb blue-green light, and transfer single state excitation energy to the chlorophyll molecule[16].

In order to discuss the energy transfer from LHC Ⅱ to the reaction center, we have not involved the energy transfer processes of inner antenna CP43 and CP47.

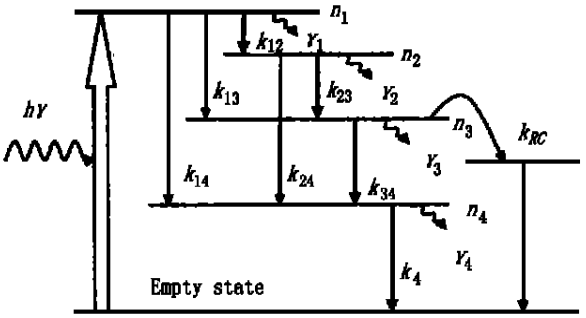

Fig.1. Four-level model on energy transfer of the light-harvesting complex Ⅱ from higher plants.

Fig.1 shows the four-level model on energy transfer from LHC Ⅱ to the reaction center. Each level represents a possible excited state of a group of pigments. On this level, only the transition from upper level to lower level takes place. Level 1 represents pigment molecules absorbing the shorter wavelength. The lower the level, the longer it represents the absorption wavelength of the pigments. Level 4 molecules absorb the longest wavelength. When the temperature is far lower than the temperature for the spectral width becoming inhomogeneously broaded, the energy transfer only takes place from top level to low level. Therefore, we only considered the energy transfer from upper level to lower level and neglected the energy transfer balance process between levels. This approximation has been pointed out in Oscar's model. Kwa *et al*[5] also pointed out that opposite direction energy transfer rate is less than positive direction in about 17 factors in the normal temperature. Therefore, the low temperature approximation is rational. n_i is the population in the ith energy level, k_i the total transition rate from the ith energy level down to each lower level, k_{ij} the transition rate from the ith level to the jth level, r_i the total loss of the ith level including all loss mechanism except going down to energy transition, such as radiation-free thermal loss and radiant fluorescence loss, etc.

In the model, the state number of each level satisfies the equation group:

$$\frac{dn_1}{dt} = k_1 n_1 - y_1 \tag{1}$$

$$\frac{dn_2}{dt} = k_2 n_2 - y_2 + k_1 n_1 \tag{2}$$

$$\frac{dn_3}{dt} = k_3 n_3 - y_3 + k_2 n_2 \tag{3}$$

$$\frac{dn_4}{dt} = k_4 n_4 - y_4 + k_3 n_3 \tag{4}$$

These kinetic parameters satisfy the relation:

$$k_1 = k_{12} + k_{13} + k_{14}$$

$$k_2 = k_{23} k_{24}$$

$$k_3 = k_{34} k_{Rc}$$

The primary condition is that: $n_1(0) = n_0$, $n_2(0) = n_3(0) = n_4(0) = 0$, i.e. the shortest chlorophyll b molecules of wavelength first take in solar energy. Then the energy absorbed by chlorophyll b is transferred to longer chlorophyll a/b molecules of wavelength. At last, chlorophyll a molecules in the proximate distance to the reaction center transfer excitation energy to the reaction center where energy is used to drive the primary charge separation photochemical reaction. The solution coefficient can be written as a matrix form:

$$n_1 = A_1 e^{-k_1 t} + B_1 e^{-k_2 t} + C_1 e^{-k_3 t} + D_1 e^{-k_4 t} + E_1 \tag{5}$$

$$n_2 = A_2 e^{-k_1 t} + B_2 e^{-k_2 t} + C_2 e^{-k_3 t} + D_2 e^{-k_4 t} + E_2 \tag{6}$$

$$n_3 = A_3 e^{-k_1 t} + B_3 e^{-k_2 t} + C_3 e^{-k_3 t} + D_3 e^{-k_4 t} + E_3 \tag{7}$$

$$n_4 = A_4 e^{-k_1 t} + B_4 e^{-k_2 t} + C_4 e^{-k_3 t} + D_4 e^{-k_4 t} + E_4 \tag{8}$$

The coefficient matrix can be re-written as

$$\lambda = \begin{vmatrix} A_1 & B_1 & C_1 & D_1 & E_1 \\ A_2 & B_2 & C_2 & D_2 & E_2 \\ A_3 & B_3 & C_3 & D_3 & E_3 \\ A_4 & B_4 & C_4 & D_4 & E_4 \end{vmatrix} = \begin{vmatrix} n_0 - \beta_1 & 0 & 0 & 0 & -\beta_1 \\ \frac{k_1}{k_2 - k_1} A_1 & -(A_2 + E_2) & 0 & 0 & \frac{k_1}{k_2} E_1 - \beta_2 \\ \frac{k_2}{k_3 - k_1} A_2 & \frac{k_2}{k_3 - k_2} B_2 & -(A_3 + B_3 + E_3) & 0 & \frac{k_2}{k_3} E_2 - \beta_3 \\ \frac{k_3}{k_4 - k_1} A_3 & \frac{k_3}{k_4 - k_2} B_3 & \frac{k_3}{k_4 - k_3} C_3 & -(A_4 + B_4 + C_4 + E_4) & \frac{k_3}{k_4} E_3 - \beta_4 \end{vmatrix} \tag{9}$$

Where $\beta_i = r_i / k_i$ is the loss rate, reflecting the competition between photochemical reaction and all kinds of loss, for example, radiation-free loss, pigment emitting fluorescence. The greater the loss rate, the less the energy used for photochemical in this level. From the results of this calculation it was inferred that several dynamic

parameters expound the photosynthetic energy transfer mechanism within the LHC Ⅱ. Each level population decayed by law of multiexponential term and a loss constant term. The amplitude of multiexponential decay depended on the energy level transition rate and loss rate of this energy level and other level transition rate used for photosynthesis. Close coupling relation between energy levels indicated that there were strong interaction among different pigments. The strong interaction could be regarded as exciton coupling between pigments and dipole-dipole interaction. The energy transfer also received the action of the loss. The loss term E_i rose with the increasing level step. The change of population n_1 in level 1 depended on the loss term E_1 and rate β_1 of monoexponential energy transfer term. As illumination did not surpass the disruption threshold value, analyzing this term amplitude coefficient showed that the stronger the illumination, the greater the population n_0 from empty state pumped to energy level 1, the less the loss rate β, the more the energy transfer from level 1 going down to low level. Also the population n_2 of level 2 received the action of the loss and energy transfer. The amplitude of k_2 rate of energy transfer was a sum of the every loss term amplitude, thus the energy transfer ratio of this level was the largest according to k_2 rate. This law could also be seen from other energy level. Considering the practical biological process, high efficiency of energy transfer decided that the amplitude of energy transfer was far larger than the amplitude of loss term. The population change law of level 3 and level 4 also received the action of the loss and energy transfer. The loss term of level 3 included k_1 k_2, and E_3. The loss term of level 4 included k_1, k_2, k_3, and E_4.

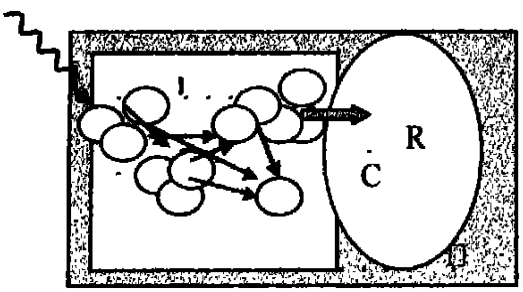

Fig. 2. Schematic map of energy transfer from LHC Ⅱ to reaction center.

The rate constant and the loss rate at last depended on the biont structure, for example, the distance among molecules, molecule direction, space structure of molecules, etc. If we understood the biont structure information of LHC Ⅱ, we could learn more about the mechanism of transfer energy and light energy loss, and we could know a general energy transfer mechanism within LHC Ⅱ.

2.2 First approximation

First, we think that energy transfer followed the principle of single step transfer among chlorophyll molecules, i.e. energy began to transfer from outer-ring excited molecule to the nearest level pigment molecules, without considering the energy transition in the cross over level. Thus, energy transferred step by step to Chl a in proximate distance to reaction center. At last, the Chl a transferred energy to the reaction center. k_{12}, k_{23} and k_{34} showed the energy transfer rate between every pigment component. This approximation basis was that energy level 4 was filled by a few of pigments. Since efficiency of energy transfer to the reaction center was so high, that a majority of energy was trapped by the reaction center. At last, only the least surplus energy decayed to energy level 4. Because level 3 pigments were responsible for excitation energy transfer from antenna system to the reaction center PS Ⅱ core complex, all excitation energy trapped by antenna could be transferred to the level 3. So level 3 possessed quite a few pigments. We further approximated that k_{14}, k_{13} and $k_{24}=0$. The solution of the above rate equation could be reduced as (10).

It could be seen from equation (10) that solution form has not been largely changed, except a very small change in coefficient value. Therefore, we obtained the conclusion that energy transfer process possibly existed in pigments which were not near. But the energy transfer was very faint, and produced no effect on the total form of energy transfer. The energy transfer mainly happened between the pigments whose energy level was the most adjacent. The loss of energy had a close relation to process of energy transfer and tended to increase with the decrease of energy level.

$$\lambda = \begin{vmatrix} A_1 & B_1 & C_1 & D_1 & E_1 \\ A_2 & B_2 & C_2 & D_2 & E_2 \\ A_3 & B_3 & C_3 & D_3 & E_3 \\ A_4 & B_4 & C_4 & D_4 & E_4 \end{vmatrix}$$

$$= \begin{vmatrix} n_0-\beta_1 & 0 & 0 & 0 & -\beta_1 \\ \frac{1}{k_{23}-k_{12}}k_{12}A_1 & -(A_2+E_2) & 0 & 0 & \frac{1}{k_{23}}k_{12}E_1-\beta_2 \\ \frac{1}{k_{34}-k_{12}}(k_{13}A_1+k_{23}A_2) & \frac{1}{k_{34}-k_{23}}k_{23}B_2 & -(A_3+B_3+E_3) & 0 & \frac{1}{k_{34}}(k_{23}E_2+k_{13}E_1)-\beta_3 \\ \frac{1}{k_4-k_{12}}(k_{14}A_1+k_{24}A_2+k_{34}A_3) & \frac{1}{k_4-k_{23}}(k_{24}B_2+k_{34}B_3) & \frac{1}{k_4-k_{34}}k_{34}C_3 & -(A_4+B_4+C_4+E_4) & \frac{1}{k_4}(k_{34}E_3+k_{24}E_2+k_{14}E_1)-\beta_4 \end{vmatrix} \quad (10)$$

$$\lambda = \begin{vmatrix} A_1 & B_1 & C_1 & D_1 & E_1 \\ A_2 & B_2 & C_2 & D_2 & E_2 \\ A_3 & B_3 & C_3 & D_3 & E_3 \\ A_4 & B_4 & C_4 & D_4 & E_4 \end{vmatrix}$$

$$= \begin{vmatrix} n_0 & 0 & 0 & 0 & 0 \\ \frac{1}{k_2 - k_1} k_{12} A_1 & -A_2 & 0 & 0 & 0 \\ \frac{1}{k_3 - k_1}(k_{13} A_1 + k_{23} A_2) & \frac{1}{k_3 - k_2} k_{23} B_2 & -(A_3 + B_3) & 0 & 0 \\ \frac{1}{k_4 - k_1}(k_{14} A_1 + k_{24} A_2 + k_{34} A_3) & \frac{1}{k_4 - k_2}(k_{24} B_2 + k_{34} B_3) & \frac{1}{k_4 - k_3} k_{34} C_3 & -(A_4 + B_4 + C_4) & 0 \end{vmatrix} \quad (11)$$

2.3 Second approximation

We know that energy transfer efficiency is very high within LHC Ⅱ. Thus the decays of the three anterior levels were only a very small part of total energy transfer rate. Only the lowest levels had larger distribution for total decay. This could also be seen from LHC Ⅱ fluorescence spectrum[6]. It could be seen from the above analysis that of loss term was increased progressively according to energy level. So, we defined the loss of all levels to loss term of energy level 4. The loss term for three anterior levels could be seen as zero. So equation (10) could be written as (11).

From the results it could be seen that level loss approximation resulted in value change of energy transfer and exponential decay, i.e. the amplitude of the energy transfer was decreased as that of the exponential decay was increased. This could also be seen from the decrease of diagonal linear element value and increase of exponential term coefficient. These conclusions indicated that there was a close relation between decay and energy transfer processes. We inferred that loss term in close relation with level 1 primary population exerted a decay action on the surplus light intensity in order to prevent light disruption within the antenna system, when the inherent decay in molecular level oneself was very small. The inferences needed to be further examined experimentally and theoretically.

3 Discussion

Using the kinetic method, we have studied the mechanism of outer antenna LHC Ⅱ transfer excitation energy to the reaction center within PS Ⅱ. Combining both the domestic studies and reports abroad, we established a four-level model to analyze energy transfer and transform in antenna system, and give the rate equation of energy transfer. At last, we discussed the analytical solution.

The above analysis indicated that energy transfer mainly occurred between the nearby level pigments. The short wavelength pigment molecule mainly absorbed the solar energy, then transferred energy to longer wavelength pigment molecules, ultimately the proximate energy level molecule got energy more than the farther molecules. In the process, part of the energy was lost by radiation-free thermal loss and fluorescence emission. The excited pigment then transferred energy to the longer wavelength pigment molecules untill energy was transferred to the longest wavelength Chl a molecule nearby the reaction center. Then the Chl a molecule transferred energy to the reaction center, where the photochemical reaction was driven. In the energy transfer process, there were strong interaction between molecules.

From the simplified discussion, we understood that energy transfer mainly happened between the pigments whose energy levels were most closely adjacent. The existence of the energy transfer of remote levels between molecules was relatively rare. The energy loss mechanism of antenna system might be summarized as follows:

(1) Loss term E_i value rose as level step was increased.

(2) There was a close the relationship between loss and energy transfer process.

(3) When the inherent loss term r in molecule level oneself was very small, in order to prevent disruption within the antenna system, super-intensity was decayed according to the exponential law.

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