LIGHT-HARVESTING AND PHOTOPROTECTION BY CAROTENOIDS: STRUCTURE-BASED CALCULATIONS FOR PHOTOSYNTHETIC ANTENNA SYSTEMS

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1. Introduction

Carotenoids play a key role in photosynthetic antenna complexes. In LH2 of purple bacteria, carotenoids act as light-absorbers in the blue-green region of the spectrum. Absorption of a photon is followed by rapid singlet excitation energy transfer to bacteriochlorophyll (BChl). In addition to their light-harvesting role, carotenoids photoprotect antenna complexes, i.e., they prevent the formation of photo-oxidizing singlet oxygen by quenching BChl triplet states through triplet excitation transfer. The energy levels of carotenoids and BChls depicted in Fig. 1 suggest four possible channels for singlet excitation transfer from carotenoids, namely, transfer from the strongly absorbing $1B_u^+$ state of carotenoid to the B850 BChl Q_x state (channel I) and transfer from the optically forbidden carotenoid $2A_g^-$ state to the Q_y state of B850 BChl (channel III). Transfer from carotenoid can also occur to B800 BChl, either through $1B_u^+ \rightarrow$ B800 Q_x (channel II) or $2A_g^- \rightarrow$ B800 Q_y (channel IV) transfer. B800 BChl then transfers excitation to the B850 BChl ring.
Lifetime measurements of the carotenoid states in solvent and in the LH2 complex of *Rhodobacter sphaeroides* 2.4.1 provide information on transfer rates and efficiencies for the different channels [3]. The 1 B_u^+ state lifetime of 150 fs in solvent and 80 fs in LH2 [2] suggests a rate $k_I + k_{II}$ of 1/(170 fs) for transfer along channels I and II with an efficiency of 47 %. The $2A_g^-$ lifetime of 10 ps in solvent and 2 ps in LH2 leads to a rate $k_{III} + k_{IV}$ of 1/(2.5 ps) for channels III and IV with an efficiency of 42 %.
An explanation of the observed transfer rates requires a description of the Coulombic interaction between carotenoids and chlorophylls. The widely known Förster mechanism of excitation transfer [1] accounts solely for the leading (dipole-dipole) term in the multipole expansion of the Coulomb interaction and requires that the participating states are optically allowed. This approximation becomes invalid for the closely spaced chromophores in LH2 with separations smaller than the chromophore sizes [4, 5, 6]. A theoretical treatment of excitation transfer then requires an account of the full Coulomb interaction (Coulomb mechanism). Alternatively,

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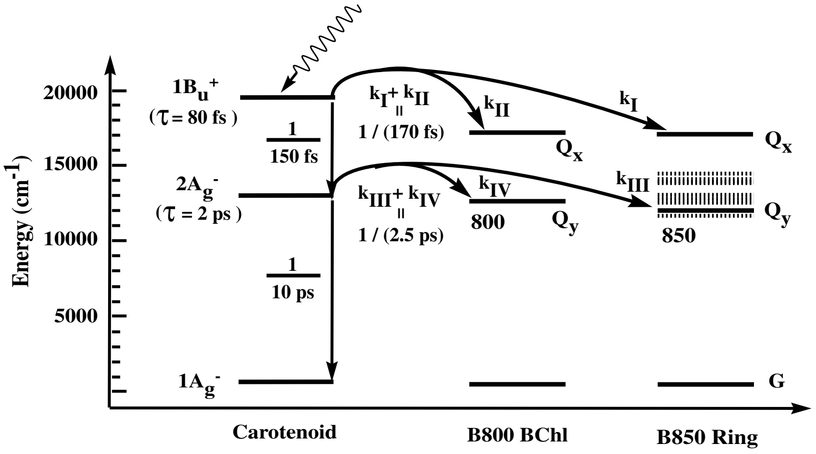

Figure 1: Energy levels of carotenoid and BChl states in LH2. States of individual chromophores are indicated as full lines, the dotted lines depict exciton states of the B850 BChl ring. Four channels of excitation transfer from carotenoid to BChl compete with internal conversion of the carotenoid states as indicated by the arrows. The rates shown for the different channels are inferred from lifetime measurements as described in the text.

singlet excitation transfer can proceed through electron exchange (Dexter mechanism) [7]. Transfer of triplet excitations, which involves a spin change, relies solely on electron exchange.
Recently, the crystal structures of LH2 from *Rhodopseudomonas acidophila* [8] and *Rhodospirillum molischianum* [9] have been elucidated. These complexes form rings of eight, respectively, nine identical monomeric subunits. Each unit contains one carotenoid, one BChl absorbing at 800 nm (B800) and two BChls absorbing at 850 nm (B850). We present here the results of calculations of electronic couplings and transfer rates for singlet and triplet excitation transfer based on the structure of LH2 from *Rs. molischianum*.

2. Mechanism of Singlet Excitation Transfer

The rates for excitation transfer between donor D and acceptor A can be calculated using

$$k_{DA} \;=\; \frac{2\,\pi}{\hbar}\,|U_{DA}|^2 \int S_D(E)\;S_A(E)\;dE\;. \tag{1}$$

U_{DA} is the electronic coupling; $S_D(E)$ and $S_A(E)$ represent the normalized donor emission and acceptor absorption spectrum, both available from spectroscopic measurements. The electronic coupling U_{DA} in (1) can be expressed as a sum of two

Channel	U^{ex}_{DA}	$k(U^{ex}_{DA})$	U^{c}_{DA}	$k(U^{c}_{DA})$
I	2.7×10^{-6}	1.1×10^{5}	1.7×10^{-2}	$4.5 \times 10^{12} = 1/(220$ fs)
II	1.2×10^{-6}	2.2×10^{4}	1.6×10^{-2}	$4.1 \times 10^{12} = 1/(245$ fs)
III	4.1×10^{-6}	2.3×10^{5}	3.8×10^{-4}	$1.9 \times 10^{9} = 1/(530$ ps)
III (exciton)				$4.1 \times 10^{9} = 1/(240$ ps)
IV	3.8×10^{-8}	3.0×10^{1}	2.3×10^{-4}	$1.2 \times 10^{9} = 1/(870$ ps)

Table 1: Couplings (in eV) and transfer rates (in Hz) for the different singlet-singlet excitation transfer channels (c.f. Fig. 1) from lycopene to B850 BChl. The rates are calculated assuming that the coupling U_{DA} is either only due to exchange coupling $U_{DA} = U^{ex}_{DA}$ or only due to Coulomb coupling $U_{DA} = U^{C}_{DA}$. Because of the excitonic nature of the B850 Q_y band, the rates through Coulomb coupling are also calculated for transfer to the complete ring rather than to an individual B850 BChl.

contributions

$$U_{DA} \;=\; U^{c}_{DA} \;+\; U^{ex}_{DA} \;, \tag{2}$$

corresponding to Coulomb and electron exchange coupling between donor and acceptor states. The full Coulomb and exchange coupling are calculated as described in [5]. The calculation essentially involves evaluation of two-electron Coulomb and exchange integrals with wavefunctions obtained from a configuration interaction calculation with single and double excited configurations. In this calculation the chromophores were approximated with symmetric analogues which may induce significant errors especially when treating the asymmetrically shaped carotenoid.
In Table 1, the long-debated question of the mechanism of singlet excitation transfer between carotenoids and chlorophylls is addressed. The results identify the Coulomb mechanism as the dominant mechanism with the Coulomb coupling exceeding exchange coupling by several orders of magnitude for all channels.

3. Channels of Singlet Excitation Transfer

Neglecting the exchange contribution, the transfer rates for the different transfer channels can be determined from the rates for Coulomb coupling as shown in Table 1. The rates for channels I and II, $k_I = 1/(220$ fs) and $k_{II} = 1/(245$ fs), add up to a depopulation rate of the $1B_u^+$ state through excitation transfer of 1/(120 fs) which is in qualitative agreement with the experimentally predicted value of 1/(170 fs).
However, transfer from the $2A_g^-$ state is described less well by our calculations. The calculated rates for channels III and IV are $k_{III} = 1/(530$ ps) and $k_{IV} = 1/(870$ ps). The B850 BChls in LH2 form a ring of sixteen tightly coupled BChls which exhibit excitonic states [10]. Calculating the coupling to the excitonic states, assumed to be delocalized over the complete ring rather than to an individual BChl Q_y state, the transfer rate for channel III is enhanced to $k_{III} = 1/(240$ ps). This rate is still about two orders of magnitude too small compared to the experimental rate for transfer

from the $2A_g^-$ state of 1/(2.5 ps). A more accurate treatment of transfer from the $2A_g^-$ state needs to take two effects into account that will accelerate the transfer. First, a real carotenoid is not completely symmetric and can, thus, exhibit a small dipole moment. Second, vibrationally induced coupling can provide a further transfer channel which enhances the rates of excitation transfer.

4. Photoprotection

Photoprotection of LH2 requires that all BChl triplet states are quenched efficiently, i.e., that triplet excitation transfer from BChl to carotenoid has to be fast compared to the BChl triplet state lifetime of about 10 μs. In each monomeric subunit of LH2 the triplet states of two B850 BChls and one B800 BChl have to be quenched. For LH2 from *Rs. molischianum* we predict a transfer time of 770 ns for transfer from one of the B850 BChls to lycopene, thus, indicating efficient triplet quenching. Our calculations suggest an indirect quenching mechanism for the other B850 BChl. It is only coupled weakly to lycopene (transfer time $>$ 1 hour) but can transfer its triplet excitation within 4 ns to its closest and efficiently quenched B850 BChl. However, the calculated transfer time of 2.4 ms for B800 $\rightarrow$ lycopene transfer is too long for efficient triplet quenching. It has been suggested that a second set of eight lycopenes exists in LH2 of *Rs. molischianum* which are not resolved in the x-ray structure. This second set is likely to be involved in quenching of the B800 BChl.
A similar situation holds for LH2 of *Rps. acidophila*. Our calculations show that the resolved carotenoid quenches only the B800 BChl triplet state. The crystal structure of *Rps. acidophila* shows a second carotenoid per monomeric subunit resolved to about one third of its length. This partially resolved carotenoid quenches one of the B850 BChls in each subunit, the other B850 BChl being protected indirectly by B850 BChl - B850 BChl transfer. While the role of the second carotenoid could only be postulated for LH2 of *Rs. molischianum*, the efficient triplet quenching through the partially resolved carotenoid in *Rps. acidophila* adds further evidence to the assertion that two sets of carotenoids are necessary for an efficient quenching of all BChls and, thus, a successful photoprotection of LH2.

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