



Emerging techniques

Efficient light harvesting through carotenoids

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Abstract

We review the factors that control the efficiency of carotenoid-chlorophyll excitation transfer in photosynthetic light harvesting. For this we summarize first the recently developed theory that describes electronic couplings between carotenoids and chlorophylls and we outline in particular the influence of length of conjugated system and of symmetry breaking on the couplings. We focus hereby on the structurally solved lycopene-BChl system of LH 2 from *Rhodospirillum rubrum* and the peridinin-Chl *a* system of PCP from *Amphidinium carterae*. In addition, we review recent spectroscopic data for neurosporene, spheroidene and lycopene, three carotenoids with different lengths of conjugated systems. On the basis of the measured energies, emission lineshapes, solution and protein environment lifetimes for their $2A_g^-$ and $1B_u^+$ states as well as of the theoretically determined couplings, we conclude that the transfer efficiencies from the $2A_g^-$ state are controlled by the Car($2A_g^-$)–BChl(Q_g) electronic couplings and the $2A_g^- \rightarrow 1A_g^-$ internal conversion rates. We suggest that symmetry breaking and geometry rather than length of conjugated system dominate couplings involving the $2A_g^-$ state. Differences in transfer efficiencies from the $1B_u^+$ state in LH 2 and PCP are found to be dominated by the differences in spectral overlap. The role of the $1B_u^+$ state is likely to be influenced by a lower-lying (in longer polyenes), optically forbidden $1B_u^-$ state.

Introduction

In photosynthetic light harvesting, light absorption through chlorophylls (Chl) is accompanied by light absorption through a second class of chromophores, the carotenoids (Car). The absorbed light energy is then transferred, in the form of electronic singlet excitations, from the carotenoids to the chlorophylls in the light-harvesting complexes which, in turn, transfer it to the photosynthetic reaction center. A second function of carotenoids is photoprotection by quenching chlorophyll triplet states to prevent generation of highly reactive singlet oxygen. The influence of the length and geometry of carotenoids on their photoprotection efficiency has been addressed in several articles, e.g. in Farshoosh et al. (1994), Angerhofer et al. (1995), Young and Frank (1996) and Farshoosh et al. (1997). In the present article, we focus on recent

studies of singlet excitation transfer and the light-harvesting function (Koyama et al. 1996; Frank et al. 1997) of carotenoids.

Carotenoids, along with polyenes, have an unusual structure of electronic excitations, a high-lying, absorbing state, which is often labeled according to its symmetry in pure polyenes as $1B_u^+$, and a low-lying, optically forbidden S_1 or $2A_g^-$ state. The discovery of the latter state dates back nearly 30 years (Schulten and Karplus 1972; Hudson and Kohler 1972). The $1B_u^+$ state decays within hundreds of fs into the $2A_g^-$ state. Theory had suggested that there exists another optically forbidden $1B_u^-$ state between the $1B_u^+$ and $2A_g^-$ state for carotenoids (polyenes) with six or more conjugated double bonds (Tavan and Schulten 1987), which has recently been observed in experiments (Sashima et al. 1999, 2000). The discovery of this new state requires a relabeling of the states. The

$1B_u^+$ state, which had been denoted as the S_1 state before 1972, then the S_2 state, is now realized to be often the third excited, i.e. S_3 , state, while a $1B_u^-$ is the S_2 state. We will adopt this new notation throughout our article. Since this notation is unfamiliar, we will in addition frequently refer to the polyene labels to avoid confusion.

The overall transfer efficiencies for $\text{Car} \rightarrow \text{Chl}$ transfer have been measured by fluorescence excitation spectroscopy, showing a variability between different species and light-harvesting complexes. The overall transfer efficiency is close to 100% in *Rhodobacter (Rb.) sphaeroides* (Cogdell et al. 1981; Van Grondelle et al. 1982; Kramer et al. 1984; Trautmann et al. 1990), between 38–75% in *Rhodospseudomonas (Rps.) acidophila* (Augerhofer et al. 1986; Chadwich et al. 1987; Cogdell et al. 1992), and as low as 30% in LH-1 of *Rhodospirillum (Rs.) rubrum* (Frank 1993). The differences in efficiencies have not yet found a satisfactory explanation.

An obvious suggestion is that species with high transfer efficiencies can utilize transfer through the optically forbidden S_1 state, while those with lower efficiencies cannot. There are three factors that can in principle account for the differences in transfer efficiencies for different carotenoid-chlorophyll systems: The electronic coupling between the donor carotenoid and acceptor Chl state, the spectral overlap of donor emission and acceptor absorption spectra, and the lifetime of the donor state in the absence of energy transfer. The first two factors determine the energy transfer rate, which depends quadratically on the electronic coupling and linearly on the spectral overlap. The third factor determines the transfer efficiency because energy transfer has to compete with internal conversion in the donor.

The carotenoid S_3 and S_1 excited states are in resonance with Chl Q_x and Q_y excitations, thus allowing two different transfer pathways, $S_3 \rightarrow Q_x$ transfer, and $S_1 \rightarrow Q_y$ transfer. The transfer time for $\text{Car} \rightarrow \text{Chl}$ transfer has been measured or estimated to be in the range of 100–250 fs, which is on the order of the S_3 ($1B_u^+$) state lifetime. This means that the overall efficiency should be in the range of 30–70% if it were solely based on $S_3(1B_u^+) \rightarrow Q_x$ transfer. Species with near unit transfer efficiencies have to utilize the $S_1 \rightarrow Q_y$ pathway in addition. The question we seek to answer in the present publication is why $S_1 \rightarrow Q_y$ transfer is efficient in some species but not in others.

Our understanding of the mechanism of energy transfer between carotenoids and chlorophylls has

been greatly advanced by the recent high-resolution crystal structures of LH 2 from two species of purple bacteria, *Rps. acidophila* and *Rs. molischianum* (McDermott et al. 1995; Freer et al. 1996; Koepke et al. 1996). In addition, a high-resolution structure of the light-harvesting system peridinin–chlorophyll–protein (PCP) from the dinoflagellate *Amphidinium (A.) carterae*, in which carotenoids are the more abundant light absorbers, has been solved (Hofmann et al. 1996). The crystal structures provide information on the geometrical details of the arrangement of carotenoids and chlorophylls. This information would be of little value without a theory that allows one to evaluate the electronic couplings mediating excitation transfer on the basis of the geometry of the molecules involved.

The well-known Förster theory (Förster 1948, 1965) determines the geometry dependence of excitation transfer under the assumption that the relevant interaction between donor and acceptor can be approximated by the leading dipole–dipole term. This approximation is valid when the extension of the molecules involved is small compared to the distance between the molecules. In the case of $\text{Car} \rightarrow \text{Chl}$ transfer, the extension of the molecules (about 20 Å for carotenoids) is about as large as the distance between the molecule centers (about 15 Å) and larger than the distance between closest atoms (between 3 Å and 6 Å depending on the species and the Car–Chl pair) and one needs to account for the full Coulomb coupling without invoking a multipole approximation.

The necessary calculations are computationally challenging since they require knowledge of the wavefunctions of the highly correlated electron system of carotenoids and chlorophylls. Several groups have developed methods to calculate the full Coulomb coupling; e.g. in Nagae et al. (1993). The transition density cube method of the Fleming group (Krueger et al. 1998a, b; Scholes et al. 1999) and the evaluation of transition density matrix elements developed independently by the Schulten group (Ritz et al. 1998a; Damjanović et al. 1999) are both recent methods that follow the spirit of the work of Nagae et al. (1993). With these methods, it is now possible to evaluate the geometry dependence of the electronic coupling without the approximations inherent in Förster theory.

The full Coulomb coupling theory is less intuitive than the Förster theory since one has to take into account many different transition matrix elements that cancel each other partly. Even in the case of transfer between optically allowed states, the orientation