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Optical Spectroscopy of Individual Photosynthetic Pigment Protein Complexes

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Photosynthesis is the process by which plants, algae and photosynthetic bacteria convert solar energy into a form that can be used to sustain the life process. The light reactions occur in closely coupled pigment systems. The energy is absorbed by a network of antenna pigment proteins and efficiently transferred to the photochemical reaction centre where a charge separation takes place providing the free energy for subsequent chemical reactions. The total conversion process, starting with the absorption of a photon and ending with a stable charge separated state occurs within less than 50 ps and has an overall quantum yield of more than 90%. The success of this natural process is based on both the highly efficient absorption of photons by the light-harvesting antenna system and the rapid and efficient transfer of excitation energy to the reaction centre.

It is known that most photosynthetic purple bacteria contain two types of antenna complexes, light-harvesting complex 1 (LH1) and light harvesting complex 2 (LH2) which both have a ring-like structure [1,2]. (Some bacterial species like *Rhodopseudomonas acidophila* contain a third light-harvesting complex termed B800-820.) The reaction centre (RC) presumably forms the core of the LH1 complex, while LH2 complexes are arranged around the perimeter of the LH1 ring in a two-dimensional structure. However the full three-dimensional structure of the whole photosynthetic unit is as yet unknown. The absorption of a photon (mainly) takes place in the LH2 pigments followed by a fast transfer of the excitation energy to the LH1 complex and subsequently to the reaction centre. It appears that the whole structure is highly optimized for capturing light energy and to funnel it to the reaction centre [3-7].

McDermott et al. [1] have elucidated the structure of the LH2 complex of the bacterium *Rhodopseudomonas acidophila* by X-ray crystallography in great detail. The light-absorbing pigments of LH2 comprise 27 bacteriochlorophyll *a* (BChl *a*) and 9 carotenoid molecules which are held in place by a protein framework. The BChl *a* molecules are non-covalently bound to these proteins. The special feature of the LH2 complex is that these molecules are arranged in two concentric rings slightly displaced with respect to each other along the common axis perpendicular to the plane of the rings, fig.1. One ring consists of a group of nine well-separated BChl *a* molecules (B800) with an absorption band around 800 nm. The other ring consists of eighteen closely interacting BChl *a* molecules (B850), in near van der Waals contact, absorbing at about 850 nm. Interestingly the LH2 complex is highly symmetric with a nine-fold symmetry axis which coincides with the cylindrical structure of the complex. The eighteen B850 molecules are oriented with the plane of the molecules parallel to the symmetry axis. In contrast, the B800 molecules have their plane aligned perpendicular to the symmetry axis (see fig.1).

Fig.1: Arrangement of the BChl *a* molecules, yellow (B800), red (B850), in the LH2 complex of *Rhodopseudomonas acidophila* as determined by McDermott et al. [1].

Excitation of an isolated BChl *a* molecule by absorption of light involves a transition from the ground state to the first excited singlet state. The latter has an intrinsic lifetime of a few nanoseconds. Remarkably the assembly of BChl *a* molecules is able to transfer the excitation energy to the reaction centre in a time much shorter than this [8,9]. Energy transfer within the LH2 complex occurs from the B800 to the B850 molecules in less than 1 ps, while among the B850 molecules it is an order of magnitude faster. This has been observed as an ultrafast depolarization of the fluorescence on a 100 fs time scale [10-12]. The transfer of energy from LH2 to LH1 and subsequently to the reaction centre occurs *in vivo* on a time scale of 5 – 10 ps, i.e., very fast compared to the decay of an isolated LH2 which has a fluorescence lifetime of 1.1 ns. As yet there is no consensus about the details of the

mechanisms of the energy transfer process. The great difficulty to determine the various parameters that play a role in the description of the electronic structure of light-harvesting complexes and the process of energy transfer is the fact that the optical absorption lines are inhomogeneously broadened as a result of heterogeneity in the ensemble of absorbing pigments (see for instance fig.2 upper trace).

In order to circumvent this problem we have applied single-molecule detection schemes to study the pigment protein complexes individually thereby avoiding ensemble averaging [13,14]. In fig.2, the fluorescence-excitation spectra of a single LH2 complex is compared with that of an ensemble of LH2 complexes. The two broad structureless bands at about 800 nm and 860 nm in the ensemble spectrum correspond to the absorptions of the B800 and B850 pigments respectively.

Fig.2: Comparison of an absorption spectrum from an ensemble of LH2 complexes (upper trace) and a fluorescence-excitation spectrum from an individual LH2 complex (lower trace). The vertical axis is valid for the lower spectrum, the ensemble spectrum is offset for clarity.

When observing the complexes individually, the ensemble averaging in these bands is removed and remarkable new spectral features become visible. The striking differences between the two absorption bands can be rationalized by considering the intermolecular interaction strength J between neighbouring BChl a molecules in a ring and the spread in transition energies Δ . J is mainly determined by the intermolecular distance and the relative orientation of the molecular dipole moments. Variations in site energies, Δ , can often be attributed to structural variations in the environment of the BChl a molecules, leading to changes in the electrostatic interaction with the surrounding protein. If the ratio J/Δ is small it is expected that the excitations are mainly localized on individual BChl a molecules. If the

coupling strength J between the BChl a molecules is much larger than Δ the description should be in terms of delocalized excited-state wavefunctions with relatively short energy relaxation times.

The analysis of our data yields that the first regime applies for the B800 pigments leading to excitations that are mainly localized on individual BChl a molecules [15]. In contrast the excitations of the B850 molecules have to be described as delocalized Frenkel excitons [16,17]. The presented model is in quantitative agreement with a theoretical study of the electronic excitations of such an aggregate [18].

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