Review

Challenges facing an understanding of the nature of low-energy excited states in photosynthesis

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ABSTRACT

While the majority of the photochemical states and pathways related to the biological capture of solar energy are now well understood and provide paradigms for artificial device design, additional low-energy states have been discovered in many systems with obscure origins and significance. However, as low-energy states are naively expected to be critical to function, these observations pose important challenges. A review of known properties of low energy states covering eight photochemical systems, and options for their interpretation, are presented. A concerted experimental and theoretical research strategy is suggested and outlined, this being aimed at providing a fully comprehensive understanding.

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1. Introduction

Photosynthesis provides virtually all the energy sustaining the biosphere [1]. The understanding of the process by which sunlight is converted into stored chemical energy presents an important and ongoing challenge to fundamental scientific research. The current worldwide effort to develop energy sources that do not add to the carbon dioxide burden of the atmosphere presents a clear focus to the purpose of this research. Many researchers are now striving to emulate in artificial devices the light harvesting, initial conversion of optical to electrical energy, and electrical to chemical energy conversion processes of natural photosynthesis [1,2].

Much of the basic science concerning light harvesting and energy transport leading up to primary charge separation is now considered to be well understood, though controversy remains as to the importance of quantum coherence and other non-classical effects to the process [2–8]. However, a variety of parallel discoveries concerning different photosynthetic apparati have challenged key established principles. These discoveries, considered in detail later in this review, concern observed low-energy absorption and/or emission from the Photosystem I core complex (PSIcc), the Photosystem II core complex (PSIIcc), plant light-harvesting complexes I (LHC-I), plant light-harvesting complex II (LHC-II), bacterial light-harvesters I (*LH*1) and II (*LH*2), the Fenna–Matthews–Olson (FMO) protein, as well as in carotenoid systems and in phycobilisomes such as C-phycocyanin (C-PC) and C-allophycocyanin (C-APC).

Low-energy states inherently act as sinks for energy, a property utilized, for example, in bacterial photosynthesis and in many artificial devices. For the photosystems we consider, established operation principles [9,10] do not embody the many low-energy states now known, and basic photosynthetic function is considered to proceed via states of *higher* energy. The presence of these low-energy states could therefore naively be expected to *prevent* or inhibit basic function by facilitating alternate pathways. However, in some cases, *direct* optical excitation of these unanticipated states has been shown to actually lead to *functional operation* of the photosynthetic unit, bypassing the established higher-energy mechanisms.

Thus, either the principles currently held are incomplete in that an over-riding factor remains to be discovered, or else some established principles may prove to be fundamentally incorrect. This issue has been flagged [11] as being one of the two most important challenges facing the photosynthesis community today. The other area of interest and controversy relates to the $CaMn_4O_5$ oxygen evolving complex (OEC) of PSIIcc [12]. The areas are somewhat related, in that the OEC also absorbs (albeit weakly) at low energies and such excitation(s) can lead to manganese photochemistry and/or photophysics [13].

Photoprotection and non-photochemical quenching [14] are induced by light but are not the emphasis of this review. They are important, but are secondary processes involving changes of photosystems on longer timescales and larger distances [15–23]. Emphasis instead is on possible direct functional roles such as that identified for peripheral light-harvesting complex Lhca4 associated with PSI: its low-energy states have recently been attributed to mixtures of charge-transfer (CT) and excitonic states that harvest low-energy light and make it available for function through uphill energy transfer [24,25].

We briefly review the properties of 8 photosynthetic systems, examining what is known and unknown about the low-energy absorptions in each system. No doubt, many different explanations will emerge to describe these phenomena. However, options and possibilities pertinent to one system may also be relevant to others. A comprehensive understanding of the properties of any system demands that alternative explanations are thoroughly examined. This review is thus intended to provide a conceptual basis for subsequent research in this field.

2. The issues faced in determining the natures of low-energy absorption

In general, low-energy absorptions in photosynthesis may arise from one of four processes, as illustrated in Figs. 1 and 2:

1) Individual chromophores having low-energy excited states due to interaction with the protein environment in their specific binding site (site energies) (Fig. 1b).
2) Arrangements involving excitonically coupled assemblies of chromophores, giving rise to low-energy excited states (Fig. 1c or d).
3) Low-energy excited states arising from CT transitions in which an electron is transferred from one chromophore to another, i.e. optically driven charge separation (Fig. 1e) [26].
4) Excitation of species arising from a previous absorption. This could happen in a number of ways. Fig. 2a shows the excitation of an excited state, while Fig. 2b and c show the excitation of cations and anions, respectively. For radical ions, low-energy tripdoublet bands are possible.

Tripdoublets are unusual in that they involve the parallel excitation of two electrons (see Fig. 2) and are consequently nominally "forbidden". They may however gain significant intensity through configuration-interaction with nearby "allowed" single electron excitation(s). Tripdoublets can have profound consequences on spectra of, for example, Chl cations and anions, leading to a relatively intense absorption at an energy where one would expect a triplet absorption [27]. However, tripdoublets can occur from the infrared at ~5000 nm (~2000 cm^{-1}) through to the visible region. They also can have profound spectral consequences in both absorption [28] and Stark spectroscopies [29,30].

Determining which process is dominant in any particular situation requires an assessment of:

- Site energies of individual chromophores and excitonic couplings of chromophore pairs, requiring information about the spatial structure of pigment-protein complexes (PPCs).
- Intermolecular and intramolecular geometries of excited states and their relationship to corresponding ground-state geometries.
- High-resolution absorption and emission spectra of the photosystems and their understanding in terms of both Franck-Condon allowed transitions associated with geometry changes and Herzberg-Teller allowed vibronic transitions associated with the geometry dependence of electronic wavefunctions [31].
- The shape of phonon spectral density [32,33], which will affect the interpretation of experimental data.
- Coupling of the electronic transitions with phonon modes of the medium, which could vary from pigment to pigment.
- The protein energy landscape [34].
- Excitonic coupling modification of excited-state equilibrium positions of nuclei.
- Energies of CT bands for chromophores in their protein environments.
- Configuration interaction coupling between CT states of form A^+B^- with those of conjugate polarity, A^-B^+.
- Configuration interaction coupling between CT states and neutral excitonic states and locally excited states.
- Geometry and intermolecular interaction changes upon the formation of CT states.
- Product analysis of the CT states excitation.
- Classical kinetics of excitation flow through photosystems.
- Quantum dynamics of exciton flow through photosystems.
- Properties of (metastable) chemical intermediates formed on the ps-ns timescale subsequent to excitation (e.g. a charge-separated state, an isomeric product, a photodegradation product, a triplet state).
- Determination of which excited-state species survive long enough to be excited by another photon under *natural light conditions*.
- Determination of triplet state energies of protein-bound chromophores.