

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

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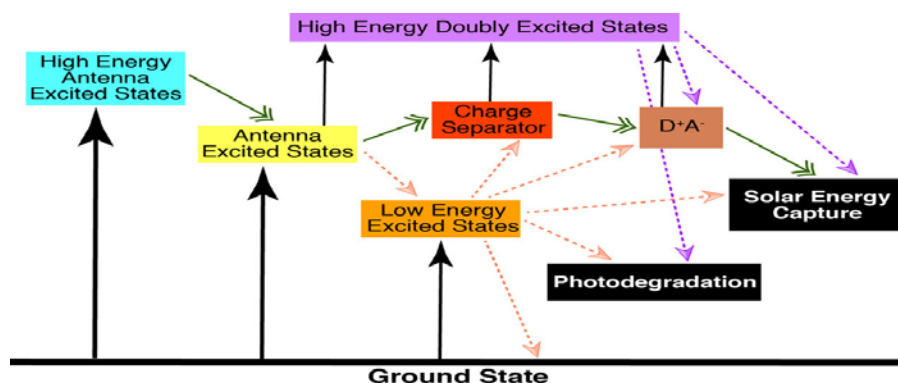
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ABSTRACT: While the majority of the photochemical states and pathways related to the biological capture of solar energy are now well understood and provide paradigms for artificial device design, additional low-energy states have been discovered in 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.

GRAPHICAL ABSTRACT:



HIGHLIGHTS

- Unexpected low-energy states have been uncovered in many photosynthetic systems.
- In many cases, their nature and significance largely remain unknown.
- Their presence can challenge established ideas concerning photosynthetic function.
- Concerted new experimental and computational strategies are required.
- Similar states may be critical in artificial solar-energy capture devices.

KEYWORDS: photosynthesis, excited states, exciton coupling, charge transfer, non-photochemical quenching, primary charge separation

ABBREVIATIONS:

PPC:	pigment-protein complex
PSIcc:	Photosystem I core complex
PSIIcc:	Photosystem II core complex
PSII-RC:	Photosystem II reaction center
LHC-I:	plant light-harvesting complex I
LHC-II:	plant light-harvesting complex II
LH1:	bacterial light-harvesting complex 1
LH2:	bacterial light-harvesting complex 2
FMO:	Fenna–Matthews–Olson
C-PCC:	C-phycoyanin
C-APC:	C-allophycocyanin
OEC:	oxygen evolving complex
CT:	charge transfer
Chl:	chlorophyll
HOMO:	highest-occupied molecular orbital
LUMO:	lowest-unoccupied molecular orbital
CD:	circular dichroism
MCD:	magnetic circular dichroism
HB:	hole-burning
2DES:	two-dimensional electronic spectroscopy
Δ FLN:	change in fluorescence line narrowing

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 (LH1) and II (LH2), the Fenna–Matthews–Olson (FMO) protein, as well as in carotenoid systems and in phycobilisomes such as C-phycoyanin (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 1d).
- 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 Figs. 2b and 2c show the excitation of cations and anions, respectively. For radical ions, low-energy tripdouplet bands are possible.

Tripdouplets 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). Tripdouplets 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, tripdouplets 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].

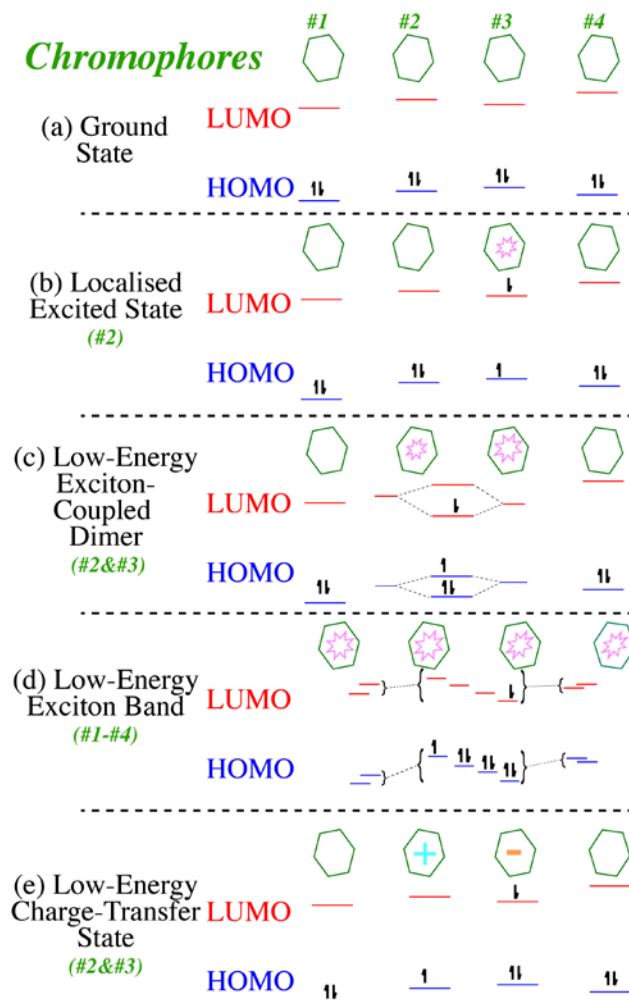


Figure 1. Schematics of an assembly of 4 *non-identical* chromophores. Even if they are of the same type, site heterogeneity

dictates that they differ in HOMO and LUMO orbital energies. Section (a) displays the ground states. Sections (b) to (e) display various possibilities for low-energy excited-states, either localized on one chromophore, associated with exciton coupled dimers or bands, or arising through charge transfer. While chromophores often have near-degenerate HOMO and LUMO levels, complicating the nature of the localized excitations, the depicted scenarios generally apply.

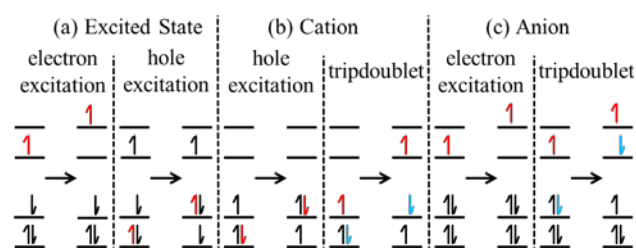


Figure 2. Possible low-energy hole excitations, electron excitations, and/or tripdoubt excitations of a photoactive species: being (a) an excited state, (b) a cation, or (c) an anion. Electrons directly affected by the transition are highlighted in red or blue; tripdoubt transitions are low-energy double excitations whilst the remainder are single excitations.

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, AB^+ .
- 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.

3. What is known and the current challenges

3.1 Photosystem-I core complex (PSIcc)

Although quite a large photosystem, this is perhaps one of the best understood. Detailed experimental data is available, including

full assignments of absorption and time-resolved fluorescence spectra [35-47]; one proposed assignment of its absorption spectrum is shown in Fig. 3 where the Chl molecules in each monomer of its trimeric unit are coloured to indicate its absorption range. High-resolution crystal structures are available for cyanobacterial PSIcc [48] and, more recently, also for plant PSIcc [49, 50].

Work has focused on the local excitation energies of the individual chromophores and on the exciton couplings between the local states [36, 38]. Unpublished simulations of the extensive emission spectral data have shown promising results but were based on dividing the system into “exciton domains”, allowing the nuclear dynamics to be approximated and the electronic motion solved. While such approaches qualitatively capture the essence of the physical situation (and have been shown to work well for PSIcc [51, 52]), there is no strict rule for the definition of exciton domains and, therefore, the results are not fully predictive. A significant amount of effort has already been spent in determining the electronic structure and its dependence on the nuclear coordinates of photosystem I [36, 38, 53]. Thus the data needed for full quantum simulation of the nuclear and electronic dynamics to be performed is available and thus *a priori* spectral predictions, in principle, can be made.

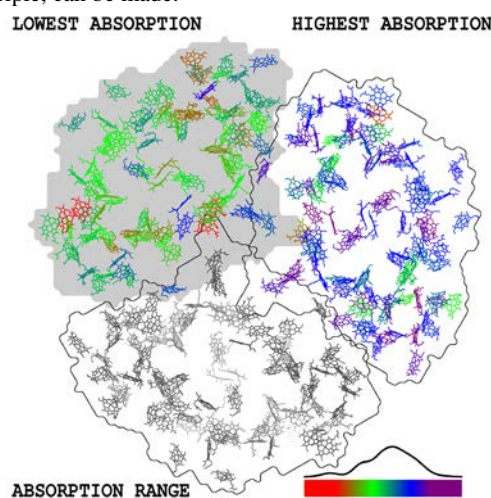


Fig. 3 A calculation of the lowest energy, highest energy, and energy range for absorption of exciton-coupled chlorophyll molecules in the PSI-cc trimer [36]. Reproduced from S. Yin, M.G. Dahlbom, P.J. Canfield, N.S. Hush, R. Kobayashi, J.R. Reimers, J. Phys. Chem. B, 111 (2007) 9923-9930, Copyright (2007) *American Chemical Society*.

With the exception of some low-energy states in the reaction centre [54], CT states have not generally been considered in previous modelling, interpretations of electrochromic Stark measurements, or interpretations of magnetic-circular-dichroism (MCD) data. These questions are worth pursuing as anything learned concerning the low-energy states in this system will doubtless be relevant to other photosynthetic systems. As the situation in PSIcc may actually be such that CT states are mostly hidden in traditional spectra, focused experiments designed based on calculated anticipated properties appear to be required. Note that there has been observed a low energy tail in PSIcc that is similar to a critical unexplained feature in PSII [13, 55], extending to 840 nm at both ambient and cryogenic temperatures [56]. This could be an immediate focus of attention.

In the case of PSIcc the interpretation of this surprisingly long-wavelength absorbance is perhaps more difficult than for PSIIcc due to its spectral overlap with chromophores of the antennae, which extend to ~730 nm. PSIcc absorbance beyond 800 nm was unambiguously assigned to the reaction center pigments by comparing the oxidation kinetics of the special pair (P700) in species with a different content of red antenna states. The very similar kinetics seen was thus interpreted as being due to direct excitation of a low-lying charge transfer (CT) state of the

reaction center. Since the photochemical yield of P700⁺ arising from excitation of this low-energy state was found to be poor it was concluded that this CT state was not part of the usual electron transfer chain but, if needed, could be tuned in energy such that the photochemical yield would increase. So far, only a qualitative illustration of the involved free energy surfaces was provided; a microscopic explanation is still missing [55, 56].

The better-known PSIIc red antenna absorptions at wavelengths < 730 nm are characterised by a large change in the dipole moment and electronic polarizability between electronic ground and excited states, a large exciton-vibrational Huang Rhys factor and large pressure shifts. These are all characteristic of significant mixing between exciton and CT states. This analysis was established using Stark spectroscopy [57] and by combining hole-burning, Stark and high pressure spectroscopies [39].

3.2 Bacterial Light-Harvesting Complex 2 (LH2)

This system is again particularly important, as a large amount of data is available [58-60]. Its basic structure is sketched in Fig. 4. Modelling has assisted with detailed interpretation of this data, as well as with the identification of specific site energies and excitonic coupling strengths [61, 62]. Much is known about shape, environment, and the mechanisms of its photophysical processes [63-67]. However, some issues remain to be solved that are significant in the broader context of forming a unified description of the low-energy states of all biological photosynthetic units. In particular, the availability of high-resolution spectroscopic data, depicting how vibrational motions couple to the excitation and de-excitation processes, will prove useful in future studies.

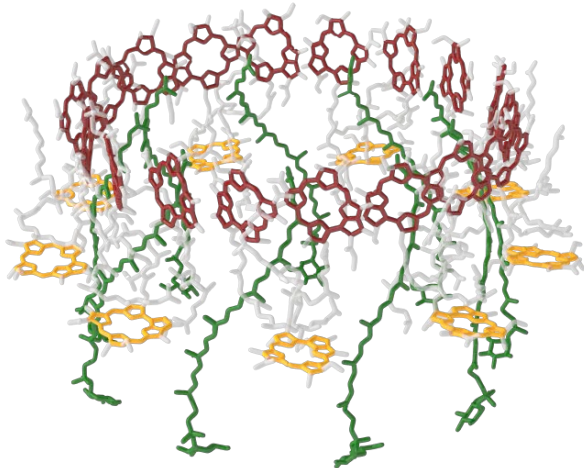


Fig. 4 The principle cofactors in the structure of LH2 from *Rps. acidophila* [68]. Reproduced from Z. Papiz, S.M. Prince, T. Howard, R.J. Cogdell, N. W. Isaacs, *J. Molec. Bio.*, 326 (2003) 1523-1538, with permission of *Elsevier*.

There is a significant yet unexplained feature found for the low-energy 850 nm band of the LH2 complex: this band has unexpectedly large electron-phonon coupling [69]. Analogous strong coupling is also present in LH1 complexes [70]. No simple explanation of this data currently exists. It was first explained by exciton self-trapping, a well-known phenomenon in physics of molecular crystals, referring to the fact that due to strong interaction with lattice phonons, the B850/B875 molecular arrangements might deform, trapping the exciton on a limited spatial region of the ring [69-73]. Referring to strong Stark absorption effect observed in LH2 and LH1 complexes [74-76], it was also suggested that this process might be promoted by mixing the low-energy exciton states with CT states between the adjacent chromophores in the weakly interacting B850 and B875 rings. A role for CT states in this process, which may also be called exciton polaron formation, has further been emphasised in a recent 2D

study [77] on the wild type LH2 as well a mutant which exhibits a 40 nm blue shifted low-energy absorbance band. A red-shifted state which quenches the fluorescence has been identified in the mutant and has been assigned to a CT state. There is indirect evidence for the presence of this CT state in the wild type at a similar energy as in the mutant. The molecular identity of this CT state is, however, still an open question. The authors suggest that it might be caused by the more weakly coupled B800 pigments, as the latter are much less affected by the mutation than the strongly coupled B850 pigments. In the context of LH2, possible CT states have been modelled theoretically [78-80]. More detailed and focused quantum dynamics modelling has yet to be done, and any predictions made needed to be tested, e.g., by MCD measurements.

3.3 Plant Light-Harvesting Complex II (LHC-II)

Many aspects of LHC-II, for which the major chromophores are shown in Fig. 5, remain controversial [81-83]. In laboratory experiments, biological samples including LHC-II are solubilised in detergent. The structure of LHC trimers have been shown to have been perturbed by the uses of surfactants [84]. It was demonstrated that the low-energy region around 685-710 nm changes its spectral features significantly when the detergent concentration is reduced. This effect is not associated simply with aggregation. Early observations established that spectral holes were not easily formed in this region [85]. Recently, however, spectral hole-burning has indeed been identified [86], suggesting that these states are associated neither with an underlying electronic state nor with very rapid intramolecular energy transfer. Such effects would be expected to lead to very broad and experimentally undetectable spectral holes, as is the case for the lowest energy (CT) state of PSII [87, 88].

Stark spectra have also been measured and interpreted in terms of composite CT/exciton character [89]. The observed change in dipole moment upon electronic excitation was actually determined to be low and therefore not clearly supportive of this conclusion. The possible role of CT states in the non-photochemical quenching process is of interest [90-92] and a recent detailed temperature-dependent fluorescence study [93] has brought the involvement of such states into focus.

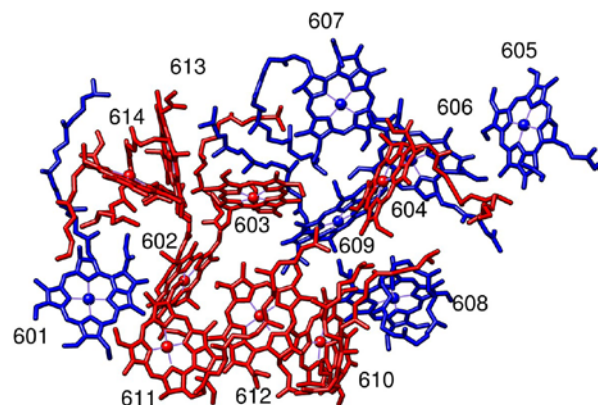


Fig. 5 The principle cofactors in the structure of LHC-II [94] from spinach, showing A-type (red) and B-type (blue) pigments.

Calculations of site energies and excitonic couplings have been performed for LHC-II [95, 96] as well as for the homologous minor antenna complex CP29 [97]. These were based on the known crystal structures [94, 98, 99] and refined to fit experimental spectra [97, 100]. Overall, the calculations confirmed earlier assignments of red-shifted chlorophylls [101, 102] and led to calculated energy transfer rates providing a structure-based interpretation of pump-probe spectra [96, 101, 103-105]. Also, information from mutagenesis experiments and difference spectra [106-108] helped to evaluate the site energies [95, 97].

An interesting problem is the inclusion of intramolecular vibrational modes into exciton modelling calculations. One

possibility is to explicitly include a few of those modes into the exciton Hamiltonian as effective intramolecular vibrational modes, and to describe the coupling of these modes to the remaining vibrational degrees of freedom using perturbation theory [109-111]. Because of the small Franck-Condon factors involved, the effective exciton coupling involving excited vibronic transitions is small and hence one may expect dynamic localization effects due to their coupling to protein vibrations. Such dynamic localization effects, however, are neglected in the “effective mode” models described above. An implicit treatment of these effects was suggested [103] by allowing exciton delocalization to occur only between 0-0 transitions. Full quantum dynamics simulations are required to judge the validity of such a treatment. Transfer rate predictions are very dependent on the model and level of kinetic theory utilised. Results can differ by an order of magnitude [103]. Excitation transfer rates from the Chl-b to Chl-a bands have been recently investigated using quantum dynamics for two different parameter sets of LHC-II, demonstrating the need for improved models to identify transient bottleneck states [112]. A sophisticated incorporation of CT bands is also required.

One particularly interesting feature of this system is that under strong-light conditions the protein PsbS, the crystal structure of which has recently been determined, binds to LHC-II so as to regulate state energies [113]. A CT state is believed to be lowered in energy, so as to become an energy sink and thus facilitate internal conversion into the ground state. This results in excited state quenching. Understanding the details of how this occurs is an important step towards understanding the general properties of low-energy states in photosynthesis.

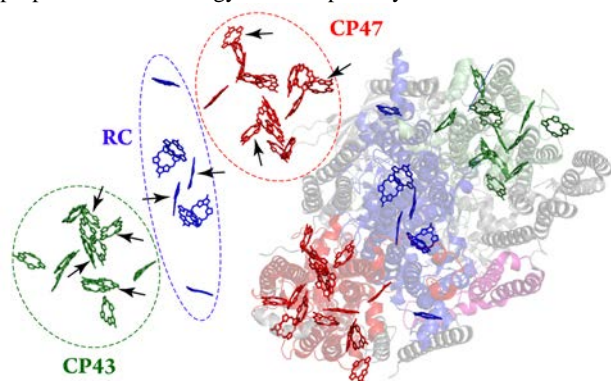


Fig. 6 The PSIIcc dimer as viewed from above the membrane. The protein components have been removed in lhs PSIIcc for clarity. Pigments thought associated with low-energy states are marked with arrows. Adapted from ref. [114].

3.4. Photosystem-II core complex (PSIIcc)

PSIIcc, for which principal components are shown in Fig. 6, is particularly important. It is only this enzyme which enables oxygen evolution [12] and is thus a major target for the development of an artificial biomimetic water splitting catalyst. A remarkable observation [87, 115] is that direct excitation of a broad band near 705 nm, extending to 730 nm at cryogenic temperatures, leads to primary charge separation despite the transition being at much lower energy than the lowest optical transition assigned to the reaction center (PSII-RC) believed to be the portal for solar energy conversion. This low energy state does not hole-burn [87, 88], meaning it is associated with a large density of vibrational states either from the presence of a dark underlying state (say a CT state) or perhaps because there is extremely fast intramolecular vibrational relaxation in the absorbing state.

Oxygen evolution from plant leaves has been seen [115] using CW laser excitation with wavelengths as long as 780 nm. This work was interpreted as arising from thermal activation of P680 via excitation of (unidentified) low energy antenna pigments. Long wavelength-induced charge separation was seen to occur

[116] at room temperature following high-powered pulsed laser excitation extending as far as 800 nm.

Broad, low temperature emission peaking at 780 nm has been seen to arise from direct, low-power CW excitation into the lowest-energy state in PSIIcc in both plants and cyanobacteria. This result appears to be initially at odds with the room temperature data, which points to absorption at wavelengths as long as 800 nm, as it would imply a significant negative Stokes shift [13]. Further work, preferably using low powered CW excitation, is called for. An unusual emission band near 760 nm has also been observed in PSII of lichens and desert algae but its origin is at present unknown [117-119].

There is no consensus yet about the kinetics and detailed mechanism of primary charge separation in PSII-RC. It seems to be clear now that electron transfer can start at the chlorophyll Chl_{D1} [9, 120-122] as well as from the special pair P_{D1}/P_{D2}, as is seen in bacterial RCs. Whereas from femtosecond VIS-pump/IR-probe experiments, a time constant of 600-800 fs was extracted for reduction of the pheophytin Pheo_{D1} by Chl_{D1}, VIS-pump/VIS-probe experiments revealed a 3 ps time constant for this process. Taking into account a 30 % equilibrium population of Chl_{D1} at $T = 300$ K [51], these time constants correspond to intrinsic time constants of 200-250 fs and 1 ps, respectively. It may be that multiple charge separation channels are active simultaneously [120, 123, 124].

An even faster intrinsic time constant of 100 fs was inferred from structure-based modelling of light-harvesting and trapping of excitation energy in PSIIcc [51]. These fast rates involved raise the question about the mechanism of primary charge separation. Most likely, the usual assumption of non-adiabatic electron transfer theory that vibrational relaxation is fast, is not valid and more advanced theories have to be applied [125].

There has also been a long-standing debate as to the rate of energy transfer from the antenna to the RC in PSIIcc [51, 126-128] and, thereby, about the kinetic bottleneck of the light-harvesting/charge transfer reactions. Structure-based modelling [51, 127] suggests that the bottleneck is the transfer from the CP43 and CP47 subunits to the RC, taking about 50 ps. There are, however, also different interpretations of kinetic data, that suggest that instead exciton equilibration in PSIIcc is ultrafast (1.5 ps) [121, 129] and that the dominant time constant of 40-60 ps observed in the fluorescence decay is due to reversible electron transfer reactions. Indeed, time-resolved fluorescence data of PSIIcc could be modelled by both approaches [130]. Experimentally, slow excitation transfer rates from CP43 and CP47 to the RC at low temperatures were first identified and measured [131, 132] using hole-burning techniques. Femtosecond techniques at room temperature were later applied [128] and direct evidence for the slow exciton transfer times was obtained recently from femtosecond VIS-pump/IR probe experiments on oriented single crystals of PSIIcc [133].

Another unexplained observation is that in liposomes the minor antenna is not required as a conduit for energy transfer from the major antenna to the core [134]. These systems exhibit a low-energy F730 band that could be related to bands observed in systems containing minor antennae. Experimental verification that the signal does not arise simply from the sample preparation procedure is required.

An analysis of the products arising the charge separation induced via excitation of low energy CT states is an alternative approach to addressing the nature of these states. In PSII membranes charge separation induced by 750 nm laser flashing at 5 K revealed complete preference of the Tyr_Z^{ox} formation and discrimination of the Cytb₅₅₉/Chl_Z/Car donating pathway if compared to the 532 nm flash excitation [135]. These results have been interpreted to suggest that the CT band, excited by far red light could ultimately involve the production of a Chl_{D1}-P_{D1} ion pair [135].

PSIIcc has been often studied computationally. These studies have been based on X-ray structures of varying precision and based on results from samples utilising varying workups. A

structure-based computation of chlorophyll site energies has so far only been performed for the CP43 core antenna subunit [136, 137] in the framework of a combined quantum chemical/electrostatic approach [138] using crystal structures of dimeric PSIIcc from *Thermosynechococcus vulcanus* [139, 140] and *Thermosynechococcus elongatus* [141] as well as for PSII-RC in a quantum chemical approach [142]. Work is in progress to extend these studies to CP47 and to also include information from the most recent refined crystal structure of *T. elongatus* [143]. Meanwhile, simulations of optical spectra and excitation energy transfer in PSIIcc have to rely on fitted site energies [9, 10, 51, 52, 144, 145]. In this context, circularly polarized luminescence (CPL) has emerged recently as a powerful tool to identify red-shifted chlorophyll states [146]. This assumes that isolated CP43 and CP47 sub-unit samples studied represent intact complexes, and not a mixture of intact/destabilized proteins. Experimentally measured spectral densities for each PPC would also greatly assist modelling as they affect fitted site energies [32].

Moreover, some analyses ignore CT states and also the possibility of strong coupling to vibrations, although such effects have been studied also in other contexts [147, 148]. Computational and experimental studies of mutagenesis of PSIIcc peripheral low-energy states have also been performed, focusing on their role in photo-protection [118, 119, 149]. What is required is a uniform high-level approach considering all system properties. In addition, often only isolated protein complexes are studied, species possibly far from their native environment inside membrane or cells.

The purity and/or 'intactness' of isolated complexes may be one reason that optical spectra of CP43, CP47 and PSIIcc reported in the literature have varied [150, 151]. This naturally leads to questions regarding the relevance of pigment site-energies etc. subsequently deduced via the modelling of data.

The CP47 peripheral antenna protein is indeed more difficult to separate from the parent PSIIcc than the CP43 antenna [152]. This fact most likely contributes to optical spectra of CP47 in particular having varied so significantly over the years. This in turn has led to disagreement as to which spectra represent CP47 complexes which more closely mimic CP47 as present in the parent PSIIcc [146, 150]. There has been little agreement regarding the important question as to which Chl's contribute (see Fig. 6) to the lowest energy exciton state(s) in CP47 [51, 52, 150]. Recent CPL data [114] address this question.

The differences between various CP47 samples, may be partly attributable to the presence or absence of the minor psbH protein. This protein subunit can indeed be lost during the isolation procedure. The parent PSIIcc is more likely to retain the psbH protein, but even in this case, one cannot assume that the psbH protein interacts with the (isolated) CP47 Chls in the same way as it does in PSIIcc's. The sharing of samples and protocols between labs and workers may be a way to resolve problems associated with the inherent variability, vulnerability and complexity of photosynthetic samples.

3.5 Bacterial Light-Harvesting Complex 1 (LH1)

While this system, whose structure and key function is highlighted in Fig. 7, is thought to be generally well understood, several purple bacteria display low-energy absorption at 909 nm [153, 154], 915 nm [155], and 963 nm [156] at room temperature. Stark spectra revealed a significant CT character of these states [157]. Among these, the LH1 Q_y (915 nm) from *Thermochromatium tepidum* has been demonstrated to be regulated by Ca^{2+} ions [158], and the first interpretations are just appearing [157]. Interestingly, these excitations lead to primary charge separation yet appear to demand unprecedented uphill energy transfer (the observed fluorescence lifetime is 5 ns at 4 K). It is possible that there is an alternate, as yet unknown mechanism that leads to charge separation. Sumi [159] suggested that charge separation in the RC can occur directly from the low energy LH1 states in a superexchange-type mechanism, where the low energy

special pair excited state acts as a bridge. This issue is important as a similar situation may exist in other systems and hence LH1 may prove to be a significant stepping-stone. A crystal structure for LH1 has been determined at 3.0 Å [160] and a much higher-resolution structure is now being developed. This will allow a complete spectroscopic analysis. Detailed exciton dynamics, determined as a function of concentration are known [161]. The role of strong exciton-phonon coupling like in LH2 is clearly critical [70, 162], as is the coupling of the LH1 states with the RC states [6, 163] that need further experimental characterization and computational modelling. An interesting model system for the study of exciton-vibrational motion is the B820 subunit of LH1, which contains just two alpha helices that each bind on bacteriochlorophyll a pigment. This system has been very useful in the development of lineshape theory [33] and in the extraction of an exciton-vibrational Hamiltonian from 2DES [164].

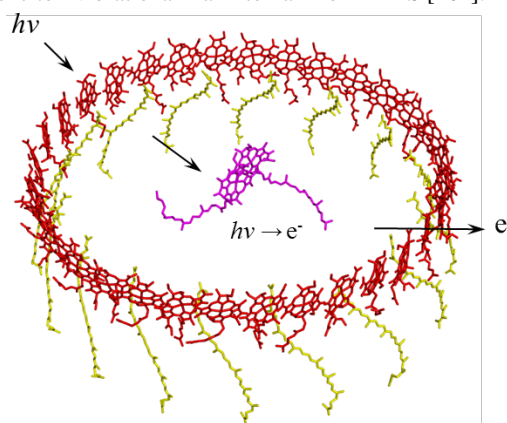


Fig. 7 The principle components and function of LH1, including the special-pair from its reaction centre from *Tch. tepidum* [160].

We note that the circular dichroism (CD) spectrum of LH1 from *Thermochromatium tepidum* is unusual [157, 165]. This has been interpreted as involving (unidentified) low-energy states [166, 167]. Q_y is non-conservative, displaying a single dominant negative CD band. The shape of the CD spectrum of this antenna is different to the CD spectra from several other LH1/LH2 antennae [168, 169] as these show almost conservative Q_y CD bands. A significant experimental program is required to investigate this further. We note that using the appropriate sample technologies, it is possible to measure very reliable, well-resolved CD spectra at low temperatures, avoiding artefacts associated with the birefringence of frozen samples [170]. Theoretical calculations of CT states, and their implications for CD spectroscopy, are challenging questions for future work. Carotenoid states could be involved as well as bacteriochlorophyll states and these should also be considered. A recent paper [171] has investigated remarkable uphill energy transfer from LH1 to the RC in *Thermochromatium tepidum* and *Rhodobacter sphaeroides*.

3.6 Carotenoids and phycobilisomes

Besides chlorophyllides, a number of other chromophores are important in photosynthesis and provide an alternative means of addressing the same fundamental issues concerning the nature of low-energy excited states. Considering such systems is also important as it enhances the bridge to artificial photosynthetic devices. The ultrafast spectroscopy of carotenoids, like the examples shown in Fig. 8 has been recently reviewed [172]. In particular, detailed fs dynamics has been measured for energy transfer between intramolecular CT states in carotenoids, as well as the rates of excitation transfer from these species to Chl-a Q_x and Q_y bands [173-182].

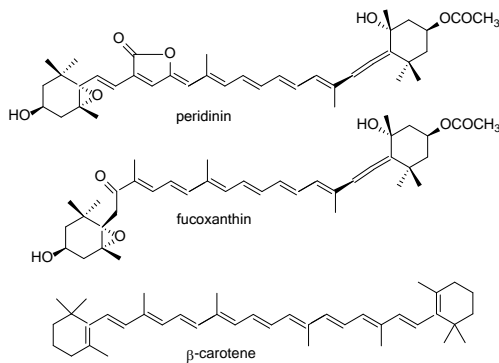


Fig. 8 Examples of carotenoids.

Also of interest is data from unusual organisms such as brown algae and diatoms. A significant advantage in studying processes in carotenoids is that their chemistry can be readily modified and the effects of such changes on spectra measured [7, 183-189], providing a range of detailed data to compare with theoretical predictions. By contrast to macrocyclic ring systems such as chlorophylls where conformational changes have at most only a minor effect, the chromophores often used in artificial devices have additional (classical) nuclear degrees of freedom that can control spectroscopy and kinetics. The carotenoids display such a property, exhibiting excited-state isomerization [190-193]. This type of process has been extensively studied computationally and much is known about how to do the calculations to get accurate answers and experimental interpretations [194, 195].

In addition to excited state isomerization [190-193], carotenoid ground state isomers have recently gained renewed attention [196-198]. The relationship between low-lying excited states and ground state isomers is straight forward: S^* , an excited state species found in longer chain carotenoids, was suggested to serve as a precursor for triplet states for carotenoids in light harvesting systems [199], even though this relation was challenged recently [200]. Within the so-called inhomogeneous ground state model, first discussed by van Grondelle and co-workers [201], S^* is interpreted as the lowest lying excited state of a local minimum in the ground state surface, S_0^* . The main excited state absorptive feature is associated with S_1 , the lowest lying excited state of the ground state's global minimum geometry, S_0 .

The inhomogeneous ground state model readily explains temperature dependent measurements, in which the relative ratio S_1/S^* increases at lower temperatures, i.e. S_0^* is frozen out and S_0 gain population, following Boltzmann's statistics [202, 203]. Besides these indications, it is a challenging experimental and theoretical task for the future to prove or disprove the inhomogeneous ground state model, given the practically identical absorption spectra of conformers S_0 and S_0^* .

Conformational change is important for the simplest light-harvesting systems, the phycobilisomes, making these significant targets for research on low-energy excited states. Fig. 9 shows a crystal structure that has been recently determined [204], inspired by reports that many aspects of plant photomorphogenesis are controlled by the phytochrome family of bilin-containing photoreceptors that detect red and far-red light by photointerconversion between a dark-adapted state and a photoactivated state via a photo-induced isomerization ("D-ring" rotation) [204]. Low-energy states are associated with these chemical processes, and their nature and influence needs to be determined.

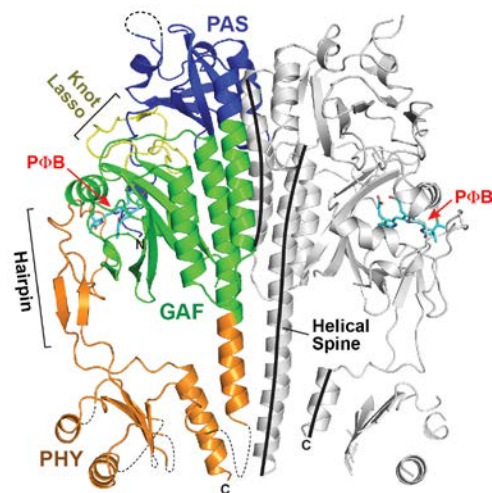


Fig. 9 The principle components in the structure of the phytochrome-B photosensory module from *Arabidopsis thaliana* [204]. Reproduced from E.S. Burgie, A.N. Bussell, J.M. Walker, K. Dubiel, R.D. Vierstra, Proc. Natl. Acad. Sci. U. S. A., 111 (2014) 10179-10184, with permission of the *National Academy of Sciences*.

3.7 The Fenna–Matthews–Olson (FMO) protein

The FMO protein is a small trimeric PPC that mediates excitation energy transfer between the outer antenna system (chlorosome) and the RC complex in green sulfur bacteria. It has a relatively simple structure (Fig. 10) in that it only binds up to eight bacteriochlorophyll (BChl) *a* chromophores per monomer [205, 206] and, therefore, is a suitable model system for experimental and theoretical research on PPCs. Accordingly, it is one of the best studied PPCs [2, 3, 7, 8, 32, 86, 207-229].

Despite its apparent simplicity, it took a long time to arrive at a suitable set of site energies and excitonic couplings to describe the optical spectra of the FMO protein. A critical aspect was to find reasonable values for the excitonic couplings by taking into account dielectric screening of pigment-pigment interactions by the protein [207, 208, 230, 231]. Louwe et al. [207] treated, in addition to the site energies, the effective dipole strength, used to calculate excitonic couplings, as a fit parameter and arrived at a value of $29 D^2$, a value that is significantly smaller than earlier estimates of $50-70 D^2$ [207] (for details, see the references given in [207]).

The lower dipole strength allowed them to find optimal site energies that resulted in a much-improved fit of optical spectra (linear and CD, triplet-minus-singlet difference spectra, and linear dichroism). A microscopic explanation for the small dipole strength was given by Adolphs and Renger [208] who developed a method, which is termed now Poisson-TrEsp, for the quantitative calculation of excitonic couplings. Whereas Louwe et al. [207] just dressed the exciton stick spectra with a Gaussian lineshape, Adolphs and Renger used a non-Markovian lineshape theory for the homogeneous spectrum and took into account static disorder in site energies by a Monte Carlo method. Despite the different lineshape theories used, both fit approaches resulted in similar site energies, resulting in prediction of the orientation of the FMO protein relative to the photosynthetic membrane containing the RC complex [208]. This prediction was verified three years later by Blankenship and coworkers using chemical labeling and mass spectrometry [209].

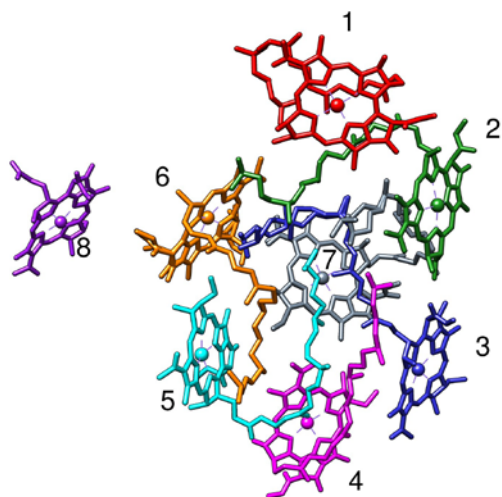


Fig. 10 The relative positions of BChl *a* 1-8 in the FMO complex [205] from *Chlorobaculum tepidum* (3ENI).

Nevertheless, not all details are known authoritatively, and a remaining challenge is the determination of accurate reorganization energies λ of the optical transitions of individual pigments. So far, because of simplicity and lack of detailed information, it has been assumed that all pigments exhibit the same local reorganization energy. From a fit of the temperature dependence of linear absorption [230, 231], Adolphs and Renger [208] estimated an average Huang Rhys factor of 0.5 for the local pigment excitations, which for their spectral density results in a reorganization energy of about 40 cm^{-1} . Reorganization energies in this range have been used in many theoretical treatments [210-213]. Recent experimental [214, 232] and modeling data [32, 215, 216] of the change in fluorescence line narrowing (ΔFLN), Stokes shift, and low energy bleach in the nonresonant hole burned spectra provided evidence that the reorganization energies of the low energy pigments (most likely BChl *a* 3 and 4; *vide supra*) are significantly smaller (about 15 cm^{-1}) than the average. This result indicates that not only the local transition energies (site energies) but also the local exciton-vibrational coupling is site dependent. It is a challenging task to unravel the differences and how they influence exciton relaxation. As a result, published site energies [207, 208, 230, 231] may also need further refinement [233]. Similar results are likely to apply also to other photosystems as well, indicating quite complex scenarios in which the treatment of subtle effects such as dielectric screening and detailed lineshape analysis can significantly affect outcomes.

The FMO protein of *Prosthecochloris aestuarii* has also served as a test-bed for the development of combined quantum chemical/electrostatic methods for the structure-based computation of site energies [217-219]. It was shown that besides amino acid side chains, the backbone architecture of a PPC can have a crucial influence on site energies due to the dipoles of the peptide bonds. In the FMO protein of *P. aestuarii*, two α -helices were found to determine the lowest energy state at BChl *a* 3 [217]. There seems to be a consensus now in the literature that indeed BChl *a* 3 has the lowest site energy (around 820 nm, see Table 2 in [8]).

However, controversy remains concerning the site energy of the more recently discovered BChl *a* 8, which is located at the side opposite to BChl *a* 3 [205]. Calculations based on the *P. aestuarii* structure found this pigment to have the highest site energy (around 790 nm) [219]. The origin of the blue shift is a conglomerate of negatively charged amino acid side chains. These results suggest that the direction of excitation energy flow in the FMO protein is defined by an energy funnel conforming to a well-established paradigm. The assignment of a site energy of 790 nm to the eighth pigment was challenged by an analysis that combines chemical oxidation with the effects of different isolation

procedures, suggesting that the site energy is around 805 nm [220, 233].

However, these studies were performed on the FMO protein of *Chlorobaculum tepidum*, which is known to have a different absorption spectrum [205]. The chemical environment of the eighth pigment has been suggested to be responsible for the spectral changes [205]. Structure-based computations have not yet addressed the differences between species. This remains a challenging task for the near future. Placing the site energy of BChl *a* 8 lower, as suggested for *C. tepidum*, has interesting implications for energy transfer. On one hand the lower site energy brings this pigment closer to resonance with the baseplate fluorescence. Hence energy transfer from the baseplate to the FMO protein should be enhanced. On the other hand, local barriers in the FMO excitation energy landscape between BChl *a* 8 and BChl *a* 3 could slow down exciton relaxation in FMO. A resolution of this issue is therefore important to the understanding of function of the low energy states in the FMO protein.

Finally, we note that the FMO protein has also been used to test structure-based computational methods of calculating exciton-vibrational coupling [105, 109, 221, 222] and corresponding structural and spectral simulations [223-225].

The FMO protein was the first system studied by Fleming and coworkers in their pioneering work in 2D optical spectroscopy [210, 227]. This work greatly invigorated the field and attracted many scientists from other fields bringing to contribute their techniques and understandings. An example are non-perturbative methods for the treatment of the exciton-vibrational motion [7]. A detailed picture of excited state structure and energy transfer of PPCs can be provided by 2D spectroscopy. However, it is not always easy to extract the important information from the experimental data. An important feature to be investigated further is the potential of 2D spectroscopy in characterizing the exciton-vibrational Hamiltonian of PPCs. The first attempts have been reported for the FMO protein [210, 226, 227], with recent applications also to PSII-RC [110, 234] and LH2 [235].

From calculations of 2D spectra and comparison with experiments it has been suggested that the second strongest excitonic coupling in FMO (that between the 5th and 6th BChl *a*) should be reduced by 60 % compared to the value obtained in point-dipole approximation. This prediction could not be verified by Poisson-TrEsp calculations, which go beyond the point-dipole approximation and include screening effects and local field corrections [208]. Hayes and Engel [226] used calculations of 2D spectra of the FMO protein of *C. tepidum* to refine the site energies. A critical point in the Hayes and Engel approach is the assumption of an exponential screening law for the excitonic couplings that is not supported by Poisson-TrEsp calculations [208, 228]. It is at present not clear how much the inaccuracy of excitonic couplings and/or the shape of the spectral density [32] used in calculations influence the site energies inferred from 2D spectra.

The trimeric nature of FMO implies the presence of three equivalent emitters. It has been argued that the 825 nm absorption band of the FMO trimer cannot be attributed to a single electronic transition [86, 229]. More calculations on the full FMO trimer are needed, taking into account uncorrelated exciton energy transfer. Importantly the resultant calculations need to be able to describe the full set of frequency and time-domain data. It is also important that different sets of measurements are taken with the same samples, so as to avoid the difficulties associated with sample variability.

4. Conclusions

We have presented a brief summary of recent advances made in the understanding of low-energy states in photosynthesis, stressing that these advances often pose more questions than resolve issues. A concerted research effort is required to understand the properties of these states, both from the basic scientific perspective of the need to understand how natural

photosynthesis works, plus the commercial objectives of designing and understanding artificial photosynthetic, photovoltaic devices, and organic light-emitting diodes. Many new experimental methods are now available for this including modern Stark spectroscopies [10, 42, 74-76, 157, 236, 237], MCD [12, 13, 27], Δ FLN [238], hole burning (HB) [239], single-molecule spectroscopies [239, 240], two-dimensional time-resolved spectroscopies (2DES) [2-4], a new temperature dependent circularly polarized luminescence technique that has only been applied to CP43, CP47 and PSII [114, 146] and may be particularly applicable to FMO and other systems.

In addition, recent conceptual advances are available, such as the authoritative assignment of the visible absorption spectrum of chlorophyll-a, a subject of debate for 50 years, and indeed assignments for all the chlorophyllides [31]. Basic understanding has also been obtained of the nature of the lines seen in high-resolution chlorophyllide absorption and emission spectra [241]. Computational methods are available for improving X-ray structure coordinates [53, 242-245], simulating molecular and CT spectra in condensed phases [246-251] and taking into account the effects of exciton coupling [36, 138, 217, 218, 221]. Methods have also become available for using this data in both classical and quantum simulations of optical spectra, exciton dynamics and system function [7, 51, 52, 103, 188, 189, 252-257]. A more comprehensive relationship between HB/FLN single-molecule and 2DES methodologies should further the application of high-resolution frequency-domain spectroscopies in photosynthesis research [73, 238, 239, 258, 259].

In summary, what is needed is the application of a consistent set of both experimental and computational methods to all types of low-energy states in photosynthesis. This involves the communication of data and computational techniques as well as experimentalists having access to the same samples and experimental protocols. We feel that only this way will the general properties of all types of states be elucidated and their consequences identified.

Acknowledgments

J.R.R., A.F., and E.K. thank the Australian Research Council (Grant DP150103137) and Shanghai University for funding the research for this review. A.F. acknowledges the Estonian Research Council (grant IUT02-28) for partial support of this work. This work was partially supported by the Natural Science Foundation of China (Nos. 21572077, 21373094, 21172089, 31370275, 31570236). R.J. acknowledges the Division of Chemical Sciences, Geosciences, and Biosciences, Office of Basic Energy Sciences of the U.S. Department of Energy through Grant DE-SC0006678 for support. J. H. acknowledges funding by the Austrian Science Fund (FWF): START project Y 631-N27. T.K. acknowledges support by the DFG Heisenberg program and grant Kr 2889/7. This work was supported by a Scientific Research on Innovative Areas "All Nippon Artificial Photosynthesis Project for Living Earth (AnApple)" grant (No. 24107002) from the JSPS to HH. DFC acknowledges NSF grant No. CHE-1301157 for partial support for this work. F.M. and S.S. thank the Swedish Research Council for support of this work. T.R. acknowledges support from the Austrian Science Fund (FWF: P 24774-N27.)

Dedication

We would like to dedicate this review to Fabrice Rappaport. Fabrice had a long and distinguished career in photosynthesis research as well as serving as an Editor of this Journal. We hope that the broad vision he encompassed and the need to appeal to a wider photosynthesis community is reflected in this article. Vale Fabrice.

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