The mechanism of energy transfer and trapping in Photosystem I

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1. INTRODUCTION

The collection and transfer of excitation energy to the reaction centers of the photosynthetic unit of bacteria, cyanobacteria, and higher plants, known as light harvesting, is one of the most exquisitely effective processes in nature, with efficiencies approaching 100%. Discovering the design principles at work in these photosynthetic antenna and reaction center complexes has been a preoccupation of ultrafast spectroscopy for many years. Indeed George Porter, writing in 1986, stated that 'The study of photosynthesis is, and probably always will be, the greatest odyssey of the photochemist' [1]. A full molecular-level understanding of the principles underlying plant and bacterial light harvesting has required the availability of atomic resolution structures for the (bacterio)chlorophyll-protein complexes that comprise the antenna system [2-14]. In parallel, the need to characterize the systems experimentally at a much deeper level than that of a single ensemble averaged rate constant has stimulated the development of new spectroscopic techniques, such as the one- and two-color photon echo peak shift methods [15-18].

The first system to be studied and characterized at a truly microscopic level was the purple bacterial light harvesting complex LH2 [2,13,19-35]. The beautifully 9-or 8-fold symmetric complexes revealed a mixture of weak and moderately strong electronic coupling, and showed that in many cases the principle of maximum overlap of donor emission and acceptor absorption spectra was ignored by the natural system. Indeed the conclusion from this system and from the purple bacterial reaction center is that optical spectroscopy is intrinsically incapable of revealing the way in which the individual molecules 'see' each other. This means that, at the present time, the general design principles of light harvesting structures can only be revealed by a combination of experiment and theory.

One striking aspect of LH2 and the structurally similar LH1 complex is the high symmetry and structural regularity of their quasi-one dimensional ring structures [2,9,13]. This regular structure leads, amongst other things, to a clear energy funnel in the purple bacterial photosynthetic unit with LH2 containing 800 and 850 nm absorbers and the reaction center-encircling LH1 complex containing 870 or 875 nm absorbers. These energy shifts are achieved through a combination of bacteriochlorophyll (BChl)-protein interaction and BChl-BChl excitonic interactions.

The structure of the core antenna of Photosystem I (PSI) stands in striking contrast to the bacterial system. The 96 non-equivalent chlorophyll (Chl) molecules are very densely
packed in a three dimensional arrangement with little apparent symmetry or regularity [5].
This immediately raises the question of whether there are new design principles at work in
PSI as compared to the bacterial system. In particular, no obvious energy funnel is apparent;
indeed there are antenna Chls which absorb to the red of the primary electron donor, P700
[36,37]. In this article we summarize the experimental timescales for energy transfer in PSI
[38-41] and compare them with results from a detailed quantum dynamical calculation
[42,43]. The remarkable success of the calculations in reproducing the experimental
timescales encourages exploration of the design principles at work in PSI and enables us to
present snapshots of the way in which energy flows through this spatially and energetically
disordered system.

2. PHOTOSYSTEM I

Figure 1 shows three views of the structure of Photosystem I of the cyanobacterium
Synnechococcus elongatus. The left hand column shows the space filling representation (van
der Waals radius) for the chlorophyll molecules only, the central column shows the space
filling representation of the entire complex (Chls, carotenoids, protein), while the right hand
column shows the licorice representation. The primary electron donor, P700 is shown (in the
center of the structure) in black. Looking down from above the membrane plane (top row) one
sees the central reaction center (RC) region of 6 Chls, plus the two ‘linker’ Chls [5], spatially
segregated from the bulk of the antenna. This spatial segregation is similar to that achieved
by the reaction center/LH1 combination of purple bacteria [44,45], and is presumably
necessary to ensure the correct flow of electrons in the RC. All RC/antenna systems appear to
exploit the stronger distance dependence of electron transfer vs. energy transfer to isolate the
electron transfer components from the bulk of the antenna system.

The 88 antenna Chls are roughly segregated to the upper and lower membrane planes
(Fig. 1, third row), but aside from this little spatial order is evident. What is particularly
striking in the space filling views is that, aside from the region immediately surrounding the
RC, the Chls fill almost the entire volume of the protein.

Given the density of Chl in PSI, it is immediately obvious that any detailed description
of energy transfer in this system will need to handle both weakly coupled (Forster-type) and
strongly coupled (excitonic) systems self consistently. It is also evident that discerning rate
limiting steps and optimizing principles may not be straightforward.

Fig. 1. Space filling in Photosystem I illustrated from three points of view: above the membrane plane
(top), side view (bottom) and in between (middle). The left hand column shows the Chls in PSI with
the special pair highlighted in black. The middle column contains all of the atoms in the structure with
the Chls in black. The right hand column depicts the Chls in the licorice representation.
Fig. 2. Calculated $Q_y$ excitation energies of Chls in PSI and its relation to the distance of the Chl from Chl EC-A1, one of the two Chls in the special pair, P700.

3. THE ENERGY LANDSCAPE OF PHOTOSYSTEM I

Photosystem I represents a classic example of a system where high quality structural information, though essential, is inadequate to understand the dynamical behavior of a biological system. The absorption spectrum of PSI is very broad compared to the spectrum of Chl in solution. The dense packing revealed in Figure 1 can be expected to produce a broad range of spectral shifts through intermolecular interactions. In addition, the Chls are bound in 96 non-equivalent sites each with their own unique set of polar, hydrogen bonding, and macrocycle distortion interactions. Our solution to this problem was to calculate the electronic excitation energies of all 96 Chls, including their neighboring protein residues and use these results to construct a 96 x 96 Hamiltonian for the complex. This is then used to calculate the low temperature spectrum of the entire complex, and then coupled with a spectral density taken from experiment [46-48], to calculate the ambient temperature spectrum[49-51]. The calculated excitation energies are summarized in Figure 2 in which excitation energies are plotted as a function of distance from Chl EC-A1, one of the two Chls that constitute the primary electron donor, P700. A very broad distribution of energies is evident, but there is clearly no evidence for a downhill (funnel) energy landscape in the bulk antenna.

4. ENERGY FLOW IN PHOTOSYSTEM I

A recent combined fluorescence up-conversion and streak camera study of PSI by the van Grondelle and Fleming groups resulted in a global fit to the wavelength resolved fluorescence decay that involved four exponential components [38]. These were: 38 ps, assigned to the overall trapping time for excitation; 3.6 ps, assigned to energy equilibration between the bulk Chls and the red shifted Chls; 360 fs, assigned to energy equilibration among the bulk Chls of the antenna; and a 9.8 ps component, suggested to be related to energy flow between individual monomeric PSI units in the overall trimeric assembly of PSI found in cyanobacteria. Of course, in making such a global fit to the fluorescence data, one has no idea whether these timescales can be ascribed simple physical meanings of the type suggested above, or result from complex averages of microscopic timescales. In order to gain microscopic insight into the mechanism of energy transfer and trapping in PSI, we carried out a detailed quantum dynamical calculation of the entire process.
5. CALCULATION OF ENERGY TRANSFER IN PHOTOSYSTEM I

The ingredients of our calculation of energy transfer and trapping in PSI are shown schematically in Figure 3. These calculations are challenging because of the presence of groups of moderately or strongly interacting pigments, along with pigments spaced at distances that make a weak coupling picture inappropriate. Our calculation is based on a modified version of Redfield theory developed by Mukamel and coworkers [52] and extended by Yang and Fleming [53], and is described in detail in ref [43]. This formulation reduces to Forster theory when the excitation is localized on individual molecules, and is practically applied by using a cutoff value of $J_{\text{cutoff}} = 120$ cm$^{-1}$ for the Coulomb coupling to partition $H_{\text{Coul}}$ into $H_{\text{Coul},S} + H_{\text{Coul},W}$. Couplings for which $H_{nm} > J_{\text{cutoff}}$ (n and m label individual Chls) enter into $H_{\text{Coul},S}$, couplings weaker than $J_{\text{cutoff}}$ enter into $H_{\text{Coul},W}$. We express the total Hamiltonian in the exciton basis set $|\mu\rangle,|\mu'\rangle$, which is obtained by diagonalization of $H_{\text{el}}^{\mu} + H_{\text{Coul},S}^{\mu}$. The rate of energy transfer is controlled by the off-diagonal Hamiltonian for the two states $|\mu\rangle$ and $|\mu'\rangle$:

$$H_{\mu\mu'} = \langle \mu | (H_{\text{el-phon}} + H_{\text{Coul},W}) |\mu'\rangle$$

If $H_{nm} > J_{\text{cutoff}}$, the Coulomb interaction $H_{\text{Coul},S}$ is included in the Hamiltonian of the exciton basis states and $H_{\text{Coul},W} = 0$. In this case energy transfer is brought about by electron-phonon coupling. If $H_{nm} < J_{\text{cutoff}}$, the Coulomb contribution to the exciton states is negligible ($H_{\text{Coul},S} = 0, H_{\text{Coul},W} = J_{nm}$) and is, in fact, the perturbation responsible for energy transfer.

The magnitude of the off-diagonal Hamiltonian (i.e. the energy transfer rate) thus depends on the strengths of the electron-phonon and Coulombic couplings and also the overlap of the two exciton wavefunctions[53]. Energy transfer rates from state $\mu'$ to state $\mu$, are calculated via the golden rule [54] and used as inputs to a master equation calculation of the excitation transfer kinetics in PSI, in which the dynamical information is included in the matrix $K$. 

Finally time dependent fluorescence spectra and kinetics can be obtained from the rate matrix and the spectrum of each eigenstate, $\mu$. The time dependent fluorescence, $F(t)$, can be written in terms of the eigenvalues and eigenvectors of the rate matrix $K$:

$$F(t) = \sum_{m=1}^{N} a_m \exp\left(-t/\tau_m\right)$$

where $-\tau_m^{-1}$ is the $m^{th}$ eigenvalue of $K$, and the amplitudes, $a_m$, are determined by the weighting factor for each eigenstate at the excitation and emission wavelengths as well as by the rate matrix. Thus the 96 time constants present in the rate matrix can be investigated for any desired combination of excitation and detection wavelength. When plots of $a_m$ vs. $\tau_m$ are examined, the time constants with substantial amplitudes can be clustered into four groups: sub 100 fs, 0.3 ps, 2-3 ps and 35-40 ps [43]. Global fitting of up-conversion data leads to time constants of 360 fs, 3.6 ps, 9.6 ps and 38 ps [38,39]. The experiments did not have sufficient time resolution to determine sub 100 fs time constants. Aside from this, our calculated times are in remarkable agreement with the experimental values, with the exception of the 9.6 ps component, which does not appear with significant amplitude in the calculations. Holzwarth et al. have suggested that this component arises at the interface of two monomeric PSI complexes[55], and since our calculation relates to a single PSI complex, it should not be expected to be present. Given the remarkable similarity of the remaining time constants between experiment and calculation, it seems reasonable to explore some of the details of the energy flow revealed by the calculation.

One interesting set of questions relates to the energy landscape. Is the energy landscape optimized to minimize the trapping time, or would some other arrangement be superior? How sensitive is the pathway for energy flow to the location/energy of the initially excited chlorophyll? In Figure 4a, snapshots of the excitation distribution for Chls B12 and B27 are shown (Chl labeling as in ref. [5]). Both molecules are in the peripheral PsAl antenna: Chl B12 is on the luminal side, 60 Å from Chl EC-A1, whereas Chl B27 is on the stromal side 43 Å from Chl EC-A1. Both examples illustrate the high connectivity of the PSI network and are rather similar after 5 ps with excitation visiting much of the antenna before final trapping. However, the two initial conditions evolve quite differently on short timescales and the snapshots show that the initial pathway away from Chl B12 involves only a small number of neighbors (~3). By contrast, for Chl B27, even at 100 fs substantial amplitude exists on at least ten sites. After a few picoseconds, once amplitude has leaked out of the initial position, the high connectivity of PSI results in very similar distributions.

Significant amplitude builds up on similar Chls in both series. One way to address whether this arises from spatial or energetic (or both) considerations is to examine snapshots where the antenna energy landscape is artificially set flat (Figure 4b). The initial trapping on Chl B12 is clearly a result of spatial isolation, however by 500 fs, energetics is clearly playing a role—compare the views at 500 fs—the homogeneous system has visited significantly more sites than in the calculated energy landscape model. The influence of the energy landscape is particularly striking for initial excitation of Chl B27, though again by 5 ps the distributions for Chl B27 and Chl B12 are very similar. Overall, the excitation is distributed considerably more evenly in the flat-landscape model, as would be expected, and the significance of specific sites to the energy flow to P700 is diminished.
Fig. 4. (a) Snapshots of the energy distribution after initial excitation of Chls B12 (left) and B27 (right). All Chls are illustrated by dots at 0 fs for clarity, after 0 fs, only Chls with substantial excitation are illustrated. (b) Same as (a) except in an artificially flat energy landscape.

The total trapping time (ensemble averaged) is 38 ps for the rough landscape model (in agreement with experiment) and 25 ps for the flat landscape model. It is evident from all the snapshots in Figure 4 that energy flow through the antenna is a major contributor to the overall trapping time. Detailed analysis shows that there are three major contributions to the overall trapping timescale [43,56] and that energy transfer around the reaction center is dominated by entropic rather than enthalpic (i.e., energy funnel) considerations. Diffusion to the region surrounding the reaction is very rapid and appears to be complete in around 5 ps as Fig. 4 clearly shows. Less evident from the snapshots is that back transfer, including transfer back from the reaction center Chls, makes a very substantial contribution to the overall trapping time. A kinetic domain model was developed to analyze the energy flow in spatially and energetically disordered energy transfer systems and can be used to systematically expose the major contributions to the trapping time [56].

6. CONCLUDING COMMENTS

An accurate microscopic model for energy transfer and trapping in Photosystem I has been developed. The model reveals two rate determining processes—energy diffusion through the antenna, and processes leading to excitation of P700, once excitation has reached the RC Chls. Note that in Figure 4 the amplitude on the RC Chls (aside from P700) is small at all times. Given the short trapping time for the flat energy landscape, one might wonder if the
rough energy landscape is advantageous. It would not be possible to pack Chls at the density of PSI without significant coupling and consequent energy shifting of the origin site energies. However, because of the high spatial connectivity of the antenna, it is very difficult for energy to become trapped for times longer than a few ps, obviating the need for an energy funnel. Thus the gain in cross-section and spectral coverage more than compensates for the very small decrease in charge separation quantum yield. Elsewhere, we have shown that the energy landscape of the bulk antenna does not strongly influence the overall trapping time, but that the energy configuration of the six reaction center Chls and the two linker Chls does appear to be highly optimized.

7. ACKNOWLEDGEMENTS

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098 and used resources provided by the National Energy Research Scientific Computing Center (contract number DE-AC03-76SF00098). Figures 1, 4 and 5 were produced in VMD [57].

REFERENCES