TRANSFER-TO-THE-TRAP LIMITED MODEL OF ENERGY TRANSFER IN PHOTOSYSTEM 1

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1.Introduction

The PS 1 core particle is a large pigment-protein complex that binds both antenna and reaction centre (RC) and contains approximately 100 chl *a* in total. The antenna chls can be excited by (sun)light and transfer the energy to the primary electron donor P700 from which a charge separation can take place.
It is presently unclear if the rate at which excitations are converted into a charge separation is limited by the intrinsic rate of charge separation (trap limited model) or if the rate at which excitations are transferred between antenna chlorophylls is limiting (diffusion limited model). The structure of PS1 from *Synechococcus* elongatus, recently obtained by X-ray crystallography [1], which we assume to be similar to PS 1 of *Synechocystis*, shows that the RC is positioned relatively isolated from the bulk antenna, and therefore two distinctly different distance scales are present in PS1: the interpigment distance within the antenna, which is small and the distance from the antenna to the RC, which is large. Therefore a third, transfer-to-the-trap, limited model was proposed which suggests that the rate of excitation transfer from the bulk antenna to the RC is limiting [2,3].
The PS1 absorption spectrum is spectrally highly heterogeneous due to differences in pigment-pigment and pigment-protein interactions. The most striking example of this is given by one or more pools of so-called “red” or “long wavelength” chls present in PS I that absorb at energies lower than P700. The number, size and absorption maxima of these pools are highly species-dependent [4,5]. In PS I from *Synechocystis* PCC 6803 one pool of red pigments is present, consisting of 2 chls, with an absorption maximum of 708 nm at 4 K [4]. In contrast to *Synechocystis*, PS 1 of *Synechococcus* elongatus has two pools of red pigments with absorption maxima that at 708 (C708) and 719 nm (C719) at 4K containing 4-5 chls and 5-6 chls, respectively[5].
Also at room temperature the red chlorophylls absorb at a considerably lower energy than the bulk antenna and the primary electron donor P700. Therefore they are expected to have a prominent effect on the kinetics of PS 1 at physiological temperatures.

The purpose of these red chl species is still unclear. It is possible that they help to guide excitations to P700 by providing a nearby trap; therefore it has been suggested that the "linker" chls (fig. 1) are the red chls. It is however also possible that the red pigments increase the cross-section for absorption of red light, or that they are involved in photoprotection.

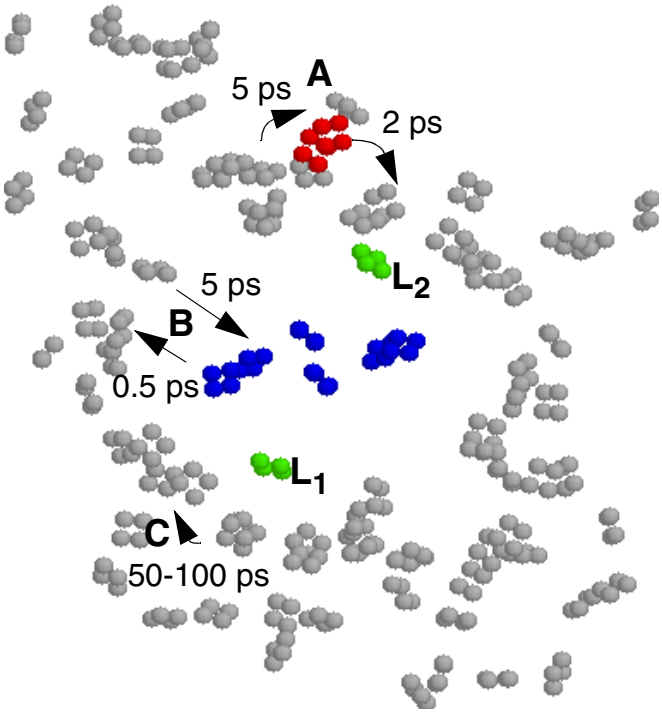

Figure 1. Top View of the positions of the chlorophylls in PS 1 according to [1]. Every 4 spheres represent the 4 nitrogen atom to which the central MG is ligated. Approximate rates are given for transfer between bulk antenna pigments and A: red pigments, B: the RC and C: other bulk antenna pigments. Notice the presence of two "linker" chls, L_1 and L_2 relatively close to the RC.

2.The nature of the red chlorophylls in photosystem 1

On the basis of energy selective fluorescence emission experiments we concluded that the Stoke's shift of the red chls is remarkably large [4, 5, *Spirulina* unpublished results]. Figure 2 shows a typical example of extreme red excitation in PS1 from *Synechocystis* measured at 5 K. The maximum of the phonon wing is located at about 160 cm^{-1} from the wavelength of excitation. For increasingly selective excitation a marked progression (at 25 cm^{-1} intervals) can be discerned superimposed on the smooth broad emission feature. Both the large Stoke's shift and this progression are unique for the red pigments in PS 1 and are not observed in other chl *a* containing photosynthetic systems, such as LHC II, Cyt b_6f and PS 2 RC's [6,7,8].
Preliminary modeling of these emission spectra indicates that the Huang Rhys factor, S for the phonons is 3 or larger, which should be compared to S =0.6 for LHC II [6]. The most simple interpretation for this remarkable difference is that in *Synechocystis* the emitting species strongly is a coupled dimer. For PS 1 from *Synechococcus* and *Spirulina* we find that these S-values are even larger and consequently we propose that also in these systems the red chls correspond to dimers or even larger aggregates of chl a.

3.Transfer-to-the-trap limited model

The transfer-to-the-trap limited model is based on the idea that there exist (at least) two distance scales and therefore (at least) two time scales for energy transfer in photosystem

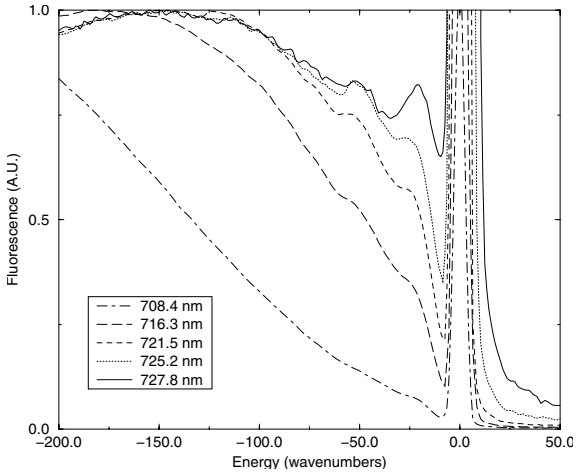

figure 2. Energy selective emission spectra of monomeric PS 1 of *Synechocystis* at 5K. The spectra are plotted relative to the wavenumber of excitation (sharp scatter peak)

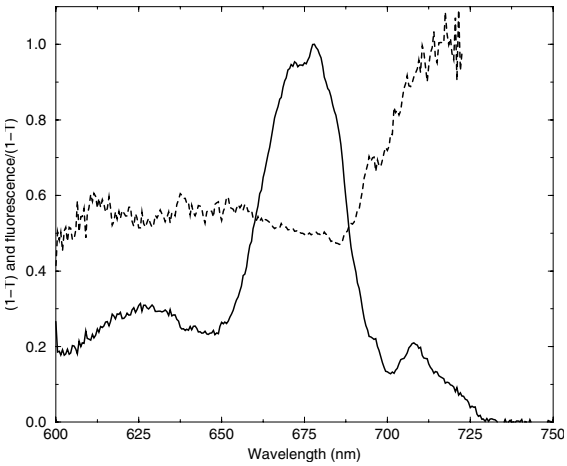

figure 3. Fluorescence excitation spectrum divided by 1-T of trimeric PS 1 of *Synechococcus*.

1 (see fig 1). The first, short, distance scale occurs in the antenna, and reflects the average distance between neighboring chls and results in ultrafast (<100 fs) energy transfer among antenna chls. The second, longer distance scale reflects the 'Förster' average distance between the antenna chls and the RC pigments and is responsible for 'slow' (~10 ps) energy transfer from the antenna to the RC. In such a model following excitation of the bulk antenna transfer to the RC and transfer to the red states present in the antenna will compete. This is elegantly demonstrated in a long-wavelength fluorescence excitation spectrum measured for PS 1 of *Synechococcus* at low temperature (fig 3)[9]. Excitation of the bulk antenna yields about 50% of the fluorescence as compared excitation of the red chls. We note the 'dips' in the excitation spectrum at 685 and 696-700 nm are in this view corresponding to RC absorption bands

4.Simulation of (sub) ps time resolved fluorescence measurements of *Synechococcus* elongatus

We have performed time resolved fluorescence experiments at different wavelengths of excitation using a synchroscan streakcamera. In order to understand the observed processes and the time scale on which they occur, we performed a simulation based upon the crystal structure [1]. We compare the results with the concept of the transfer-to-the-trap limited model.

4.1 Förster calculation

We calculated Förster transfer rates using the locations of the 89 chls found in the crystal structure. Overlap integrals were calculated from the absorption and emission spectra of chl a in solution as a function of the energy difference between donor and acceptor. All

other factors (orientations, index of refraction) in the Förster formula were contained in one parameter of the simulation, determining the median hopping time, τ_{hop}.

4.2 Trapping
The trapping time τ_{trap} from P700 was a parameter that was varied.

4.3 Composition of the antenna
All main antenna pigments were taken to absorb at 680 nm, both chls representing P700 were taken at 700 nm. A number of red pigments could be selected and assigned a different wavelength.
We started out modeling measurements of PS 1 isolated from *Synechocystis* PCC 6803 which is more simple since it only contains a C708 pool containing 2 red chls (see for details Gobets et al., these proceedings). Since they are thought to form an excitonically coupled dimer [4] we tried different dimers absorbing at 708 nm.
To model our *Synechococcus* data we added one more dimer at 708 nm, and chose 4 chls to absorb at 715 nm, representing C719. The latter we put in the region where the different monomers in the trimer touch, since the far red chls are thought to play a role in trimerisation [10]

4.4 Parameters of the simulation
We found in *Synechocystis* PS 1 that to obtain a reasonable description of our data the red chls could not be located in the direct vicinity of the RC. The parameters used imply a median hopping time $\tau_{hop}$of 43 fs, and an intrinsic rate of charge separation τ_{trap} of 0.62 ps. We realize that this value of τ_{hop} is shorter than found in [11], but we note that the PS 1 particles used in those experiments only contained ~40 chl *a*/P700 whereas our preparation contains ~100 chl *a*/P700 and therefore likely has a shorter mean distance between chls in the antenna, and therefore faster Förster rates.

4.5 Results of the simulation
We used the same trapping rate and hopping rate of the simulation of the *Synechocystis* data to describe the *Synechococcus* results.Our model for *Synechococcus* yields 4 different time constants: 50 ps, 7.8 ps, 2.7 ps and ~ 1 ps. The latter is the sum of the 86 time constants faster than 1.8 ps which will be observed as one single time constant with the time resolution of our apparatus. This is the same number of times found experimentally. Figure 4a'-c' show the simulation of our data. We reconstructed DAS with estimated emission bands of the main antenna, the C708 and C719 chls.
For aselective excitation a 2.7 ps equilibration component fully dominates a much smaller ~1 ps equilibration. A smaller 7.8 ps component is also present and clearly represents transfer to a pool located more to the red.
This 7.8 ps component is also present for C708 selective excitation. However in that case the fast equilibration component is dominated by the ~1 ps component, which is negative on both sides of a positive region.
For C719 selective excitation the dynamics are dominated by the 2.7 ps component,

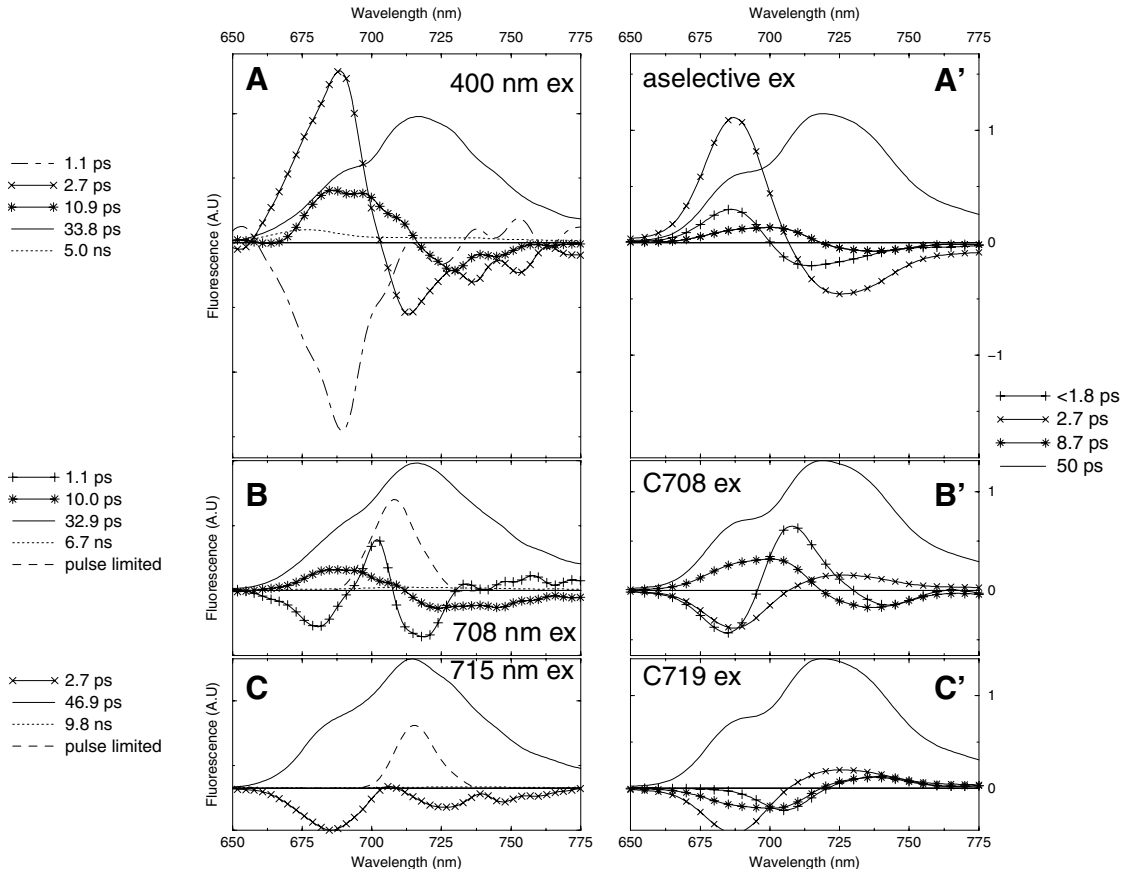

figure 4. Left, A-C: decay assocated spectra of time resolved fluorescence measurements of trimeric PS 1 from *Synechococcus* for excitation at 400 nm (aselective), 708 nm (first red pool) and 715 nm (second red pool). Right: A'-C'Simulation of these spectra.

which mainly reflects transfer to the main antenna pool.
For all wavelengths of excitation a spectrally identical all-positive 50 ps component was found. We do note that the absolute amplitude of this component increases as the excitation is more towards longer wavelengths (see absolute scaling on the right in fig 4a'-c') indicating that less "fast" trapping occurs upon selective excitation of the red chls.
All these features are qualitatively remarkably similar to our experimental data. Of course absolute amplitudes are not correct and also the time-constants could be better. We wish to emphasize that we have far from fully explored the model, and that the simulation presented here is the best of only 4 configurations tried. We therefore do not claim that this is the real configuration, but only that our results can qualitatively be described by our model.

5.Conclusions

The presented model qualitatively and to some extent quantitatively describes the observed spectral equilibration and trapping dynamics in *Synechococcus* and *Synechocystis* PS 1. If for *Synechocystis* using the parameters given above we increase the intrinsic rate of charge separation to infinite, the effective trapping time typically decreases from 25 to 15 ps; a clear demonstration of the transfer-to-the-trap limited model. Note however that the decrease of the trapping time is due to the competition between back transfer to the antenna (effective rate about 0.5 ps, see fig 1) and charge separation, indicating that in reality we are not far from regime of the trap limited case.
We finally remark that it was impossible within our model to obtain a good description of the equilibration and trapping kinetics in *Synechocystis* placing the two red chls at the position of the "linker" chls (see Gobets et al., these proceedings).

6.Acknowledgement

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7.References

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