

PHOTODYNAMICS IN A PHOTOSYNTHETIC LIGHT HARVESTING COMPLEX

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Photosystem I (PSI) is a subunit of oxygenic photosynthetic system consisting of a few hundreds of chlorophyll (Chl) molecules as well as protein backbones supporting them in bacteria, algae, and higher plants. Chls in PSI absorb the sun light energy and the energies are transferred over the Chls and finally to the reaction center where chain reaction of the photosynthetic electron transfer initiates. The collection and transfer of excitation energy to the reaction centers, known as light harvesting, is one of the most exquisitely effective processes in nature, with efficiencies approaching 100%. Dynamics of energy transfer in PSI has been studied by theoretical methods. Crucial factors controlling energy transfer dynamics are electronic transition Hamiltonian of the Chls and fluctuation dynamics of nuclear degrees of freedom coupled to the electrons in the system. Since the electronic transition energy of a Chl is highly sensitive to the environment of the molecule affecting the electronic state via electrostatic and/or hydrogen bonding interactions, it is required to know the accurate structural information of the system as well as dynamical information of the nuclear fluctuation in order to model the energy transfer phenomena. Recently the X-ray crystal structure of PSI from cyanobacterium *Synechococcus elongatus* with 2.5 resolution was revealed. Based on the structure, Qy excitation energies of the 96 Chls in the PSI protein environment was calculated using a semi-empirical quantum mechanical method (Damjanovic et al., J. Phys. Chem. B 106, 10251). A model is developed based on experimentally determined spectral densities and Modified Redfield theory is used within a master equation approach to study the dynamics of Chl-Chl energy transfer (M. Yang et al., Biophys. J. 85, 140). The results agree well with that of time-resolved fluorescence measurements (Kennis et. al., J. Phys. Chem. B105, 4485). The design principles of PSI were investigated by randomly shuffling the Chl orientations and site energies. The trapping time is sensitive to the specific orientations and site energies of the linker Chls and the pigments in the reaction center (RC), but is largely independent of the exact configuration of excitation energies and orientations in the antenna. A kinetic domain model is

developed and applied to understand the rate limiting steps of energy trapping. The slowest steps are found to be excitation energy transfer from the antenna to the RC and to the trap from within the RC.