

Coherent Dynamics and Dissipative Relaxation of Excitations in Molecular Aggregates

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To efficiently harvest solar light, photosynthetic organisms are equipped with pigment-protein antenna complexes. These complexes are responsible for the absorption of light energy, which is subsequently transferred to the reaction center (RC), where this energy is stabilized as a chemical potential. As a result of the structural arrangement and spectral composition of the pigment molecules, at low excitation intensities the efficiency of this process is close to unity. In addition to the light-harvesting function, the light-harvesting complexes have also another – regulation function, which is a physiologically significant strategy evolved by plants [1]. Rapid excitation density control in photosystem II (PSII), termed as non-photochemical quenching (NPQ), ensures high efficiency and robustness of plant photosynthesis under fluctuating light, even at very high intensities. For a reasonable effect to be achieved, the mechanism responsible for NPQ should be competitive with the excitation trapping by an open RC [2]. The NPQ phenomenon is usually attributed to some activated quenching species which allow the excitation to undergo a rapid non-radiative decay. The exact location of these quenching species within the antenna and its precise nature are a matter of on-going debate, with both chlorophylls (Chl) and carotenoids (Car) being put forward as essential components of the quenching mechanism, while the regulation function is usually attributed to the external conditions. For this purpose the exciton dynamics in a molecular heterodimer is studied as a function of differences in excitation and reorganization energies, asymmetry in transition dipole moments and excited state lifetimes. It is demonstrated that the system-bath interaction rather than the excitonic effect determines the excitation quenching ability of such a dimer. The dynamics are simulated using nonperturbative density matrix theory, which allows us to describe the spectral and temporal signatures of various system-bath coupling regimes [3]. Electronic excitations in molecular aggregates embedded in protein environment experience a complex multistep relaxation, which could be traced using various time-resolved spectroscopy techniques. To understand the regulation abilities a diffusion-controlled model describing the fluorescence blinking of single photosynthetic light-harvesting complexes (LHCII) is developed and discussed [4].

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