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Incoherent light-induced excitation harvesting in molecular energy-conversion systems

There is a remarkable similarity between physical processes at play in (organic) photovoltaic cells and photosynthetic complexes [1,2]. In both types of systems, ultrafast time-resolved studies suggest that quantum coherences may enhance the excitation-harvesting efficiency by favoring non-equilibrated, "hot", and fast pathways involving delocalized states over equilibrated, "cold", and slow pathways involving localized trap states. Here, we present our recent contributions to the on-going debate on the relevance of these findings for excitation harvesting under incoherent light [3-6]. We develop a (numerically) exact description of excitonic dynamics in a molecular aggregate driven by weak-intensity radiation of arbitrary properties [3]. While the interaction with light is included up to the second order, the excitation-environment coupling is treated up to all orders. The resulting exact expression for the reduced density matrix is then recast as the hierarchy of equations of motion (HEOM) that explicitly and consistently includes the photoexcitation step. We then focus on a model photosynthetic dimer and examine its non-equilibrium steady state arising from the interplay between excitation generation, excitation relaxation, dephasing, trapping at the load, and recombination [4]. While the steady-state coherences in the slow-trapping limit are demonstrated to originate from the excitation-environment entanglement, we unveil an interesting relation between the dynamic coherences observed in ultrafast experiments on unloaded aggregates and the steady-state coherences in the fast-trapping limit. We apply a similar formalism to a microscopic effective Hamiltonian of an organic donor/acceptor heterojunction, where we elucidate the energy- and time-resolved dynamics of charge pairs all the way from their photogeneration to their extraction or recombination. The results indicate that charge separation proceeds via the "cold" pathway on which donor excitons first convert to relaxed charge-transfer excitons and then transform to separated charges [5]. We also analyze these results from the perspective of non-equilibrium thermodynamics. We quantify the difference between the equilibrium and non-equilibrium dependence of the charge-pair free energy on the intrapair separation. Our results reveal that this difference is largest when charge separation efficiency is large, which leads us to conclude that charge separation in efficient organic solar cells proceeds via a "cold" but non-equilibrated pathway [6].

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