

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

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Photosynthesis provides the energy source for essentially all living things on Earth, and its functionality has been one of the most fascinating mysteries of life. Photosynthetic conversion of the energy of sunlight into its chemical form suitable for cellular processes involves a variety of physicochemical mechanisms. The conversion starts with the absorption of a photon of sunlight by one of the light-harvesting pigments, followed by transfer of electronic excitation energy to the reaction center, where charge separation is initiated. At low light intensities, surprisingly, the quantum efficiency of the transfer is near unity. A longstanding question in photosynthesis has been the following: *How does light harvesting deliver such high efficiency in the presence of disordered and fluctuating dissipative environments?* At high light intensities, on the other hand, the reaction center is protected by regulation mechanisms that lead to quenching of excess excitation energy in light harvesting proteins. The precise mechanisms of these initial steps of photosynthesis are not yet fully elucidated from the standpoint of molecular science.

1. An Analytical Continuation Approach for Evaluating Emission Lineshapes of Molecular Aggregates and the Adequacy of Multichromophoric Förster Theory

In large photosynthetic chromophore-protein complexes not all chromophores are coupled strongly, and thus the

situation is well described by formation of delocalized states in certain domains of strongly coupled chromophores. In order to describe excitation energy transfer among different domains without performing extensive numerical calculations, one of the most popular techniques is a generalization of Förster theory to multichromophoric aggregates (generalized Förster theory) proposed by Sumi [*J. Phys. Chem. B* **103**, 252 (1999)] and Scholes and Fleming [*J. Phys. Chem. B* **104**, 1854 (2000)].

The aim of this project is twofold. In the first place, by means of analytic continuation and a time convolutionless quantum master equation approach, a theory of emission lineshape of multichromophoric systems or molecular aggregates was proposed.¹⁾ In the second place, a comprehensive framework that allows for a clear, compact and effective study of the multichromophoric approach in the full general version proposed by Jang, Newton and Silbey [*Phys. Rev. Lett.* **92**, 218301 (2004)] was developed.¹⁾

We applied the present theory to simple paradigmatic systems and we showed on one hand the effectiveness of time-convolutionless techniques in deriving lineshape operators and on the other hand we showed how the multichromophoric approach can give significant improvements in the determination of energy transfer rates in particular when the systems under study are not the purely Förster regime. The presented scheme allows for an effective implementation of the multichromophoric Förster approach which may be of use for simulating energy transfer dynamics in large photosynthetic aggregates, for which massive computational resources are

usually required. Furthermore, our method allows for a systematic comparison of multichromophoric Förster and generalized Förster theories and for a clear understanding of their respective limits of validity.

2. Interactions between Quantum Mixing and the Environmental Dynamics Controlling Ultrafast Photoinduced Electron Transfer Reaction

All the photosynthetic reaction centers (RCs) share considerable similarities in the nature and arrangement of the redox cofactors. The primary charge separation in photosystem II (PSII) of green plants was assumed to be similar to purple bacteria. In the mid-1990s, the charge separation in the PSII RC was shown to follow a different mechanism than bacterial RCs. In the 2000s, the primary charge separation in the PSII RC was investigated by independent studies using femtosecond pump-probe spectra of the D1/D2/cytb559 complex isolated from PSII in the visible/mid-IR [Groot, *et al.*, *Proc. Natl. Acad. Sci. USA* **102**, 13087 (2005).] and visible [Holzwarth, *et al.*, *Proc. Natl. Acad. Sci. USA* **132**, 6895 (2006).] spectral regions. Both reports identified the accessory chlorophyll as the primary electron donor and pheophytin as the primary electron acceptor. Time constants of 600–800 fs and 3 ps were extracted for the pheophytin reduction, which yielded values of 200–300 fs and 1 ps as the intrinsic time constant of the primary charge separation. Theoretical analyses of time-dependent emissions from the PSII core complex yielded 100 fs as the intrinsic time constant. [Raszewski and Renger, *J. Am. Chem. Soc.* **130**, 4431 (2008).] Regardless of the controversial differences, all the values for the PSII RC are faster than the time constant of 3 ps measured for the primary electron transfer (ET) starting from the special pair in purple

bacterial RCs. An ultrafast primary charge separation pathway was also revealed in a purple bacterial RC (approximately 400 fs), which starts from the accessory bacteriochlorophyll. [van Brederode, *et al.*, *Biochemistry* **36**, 6855 (1997).] The coupling strengths between electron donors and acceptors are usually thought to be tens of cm^{-1} , and the precise mechanisms enabling the subpicosecond charge separation are mostly unknown.

The timescales of most environmental dynamics, such as solvation or protein reorganization involved in photoinduced ET, occur in the subpicosecond and picosecond range. Thus, the reported subpicosecond timescales imply that the ET reaction may take place beyond the nonadiabatic limit; an adiabatic fashion in which the reaction is dominated by vibrational/environmental motions in an adiabatic (free) energy surface that reflects quantum mixing between the initial and final states.

In this project, to explore the potential causes for subpicosecond timescales of the primary charge separation in photosynthetic RCs, we investigated the interactions between environmental dynamics and quantum mixing that affects the ultrafast photoinduced ET dynamics using quantum dynamics simulation. It was shown that the timescales of environmental dynamics change the nature of the ET reaction (*i.e.*, adiabatic or nonadiabatic), dramatically affect the rates and temperature dependences, and enable subpicosecond reactions despite small donor–acceptor coupling.²⁾

References

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- 2) A. Ishizaki, *Chem. Lett.* **42**, 1406–1408 (2013).