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? Why does not energy get lost? 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. Particularly, recent observations of long-lived beating phenomena in two-dimensional electronic spectra of photosynthetic pigment-protein complexes stimulated a huge burst of activity in an interdisciplinary community of molecular science and quantum physics.[1)]

Selected Publications

- A. Ishizaki and Y. Tanimura, "Quantum Dynamics of System Strongly Coupled to Low-Temperature Colored Noise Bath: Reduced Hierarchy Equations Approach," *J. Phys. Soc. Jpn.* **74**, 3131–3134 (2005).
- A. Ishizaki and G. R. Fleming, "Unified Treatment of Quantum Coherent and Incoherent Hopping Dynamics in Electronic Energy Transfer: Reduced Hierarchy Equation Approach," *J. Chem. Phys.* **130**, 234111 (10 pages) (2009).
- A. Ishizaki and G. R. Fleming, "Theoretical Examination of Quantum Coherence in a Photosynthetic System at Physiological Temperature," *Proc. Natl. Acad. Sci. U.S.A.* **106**, 17255–17260 (2009).
- G. S. Schlau-Cohen, A. Ishizaki, T. R. Calhoun, N. S. Ginsberg, M. Ballottari, R. Bassi and G. R. Fleming, "Elucidation of the Timescales and Origins of Quantum Electronic Coherence in LHCII," *Nat. Chem.* **4**, 389–395 (2012).
- A. Ishizaki, T. R. Calhoun, G. S. Schlau-Cohen and G. R. Fleming, "Quantum Coherence and Its Interplay with Protein Environments in Photosynthetic Energy Transfer," *Phys. Chem. Chem. Phys.* **12**, 7319 (2010). [Invited perspective article]
- A. Ishizaki and G. R. Fleming, "Quantum Coherence in Photosynthetic Light Harvesting," *Annu. Rev. Condens. Matter Phys.* **3**, 333–361 (2012). [Invited review article]

1. Impacts of Protein-Induced Fluctuations upon Quantum Mechanically Mixed Electronic and Vibrational States in Photosynthetic Energy Transfer and 2D Electronic Spectra

Initially, 2D electronic spectroscopic experiments were conducted for the Fenna-Mathews-Olson (FMO) complexes isolated from green sulfur bacteria at a cryogenic temperature, 77 K and revealed the presence of quantum beats lasting for 660 fs. [Engel, *et al. Nature* **446**, 782–786 (2007).] However, it is generally thought that the coherence at physiological temperatures is fragile compared to that at cryogenic temperatures because amplitudes of environmental fluctuations increase with increasing temperature. To clarify this issue, a theoretical examination on lifetimes of electronic coherence in the FMO complex. Consequently, it was predicted that electronic coherence in the FMO complex might persist for 700 fs and 300 fs at 77 K and 300 K, respectively.2) These theoretical predictions were consistent with the initial experimental observation at a cryogenic temperature and newer experimental results at physiological temperatures of the FMO complex. However, Panitchayangkoon *et al.* [*Proc. Natl. Acad. Sci. U.S.A.* **107**, 12766–12770 (2009).] showed that quantum beats in the FMO complex persist for at least 1.5 ps at a cryogenic temperature, while the theoretical model did not produce electronic coherence with lifetime of 1.5 ps. Hence, signatures of nuclear vibrational contributions in 2D spectroscopy have attracted great interest of late, in particular to interpret the oscillatory transients observed for light-harvesting complexes that persist much longer than predicted electronic dephasing times. Several independent publications have alluded to nuclear vibrational effects as an explanation for the long-lived beatings.

In photosynthetic pigment-protein complexes, the Huang-Rhys factors of chlorophyll/bacteriochlorophyll molecules are generally thought small, suggesting that the photophysics therein is primarily electronic in nature, rather than vibrational. Indeed, the recent 2D electronic experiments on BChl molecules in solution did not find significant vibrational coherences. Concerning this point, Christensson *et al.* [*J. Phys. Chem. B* **116**, 7449–7454 (2012).] proposed that resonance between electronic and Franck-Condon active vibrational states serves to create vibronic excitons, *i.e.* quantum mechanically mixed electronic and vibrational states. Such states have vibrational characters and have enhanced transition dipole moments owing to intensity borrowing from the strong electronic transitions. Along this line it was discussed that coherent excitation of the vibronic excitons produces oscillations in 2D signal that exhibit picosecond dephasing time. Tiwari, Peters, and Jonas pointed out that the excitonically mixed electronic and vibrational states lead to an enhancement of the excitation of vibrational coherences in the electronic ground state as well. [*Proc. Natl. Aca. Sci. U.S.A.* **110**, 1203–1208 (2013).] It was also argued that this effect could explain the long-lived oscillations in the FMO complex.

The quantum mechanically mixed electronic and vibrational states or the vibronic excitons are plausible as an explanation for long-lived spectral beatings in 2D electronic spectra. However, a question naturally arises concerning the interplay between the vibronic resonance and fluctuations in electronic energies induced by the environmental dynamics. In general, energy eigenstates due to quantum mixing of the electronic and vibrational excitations are obtained via diagonalization of the Hamiltonian comprising the Franck-Condon transition energies and electronic interactions. It should be noticed that these are independent of any information on the environment such as temperature, reorganization energy, and fluctuations. Concerning this point, Ishizaki and Fleming3) characterized the impact of the surrounding environments upon the quantum delocalization with the use of the concurrence. They visually demonstrated that smaller electronic coupling, larger reorganization energy, and higher temperature cause the dynamic localization, even in the case that two electronic states resonate in a coupled homo-dimer. Recently, Ishizaki4) explored the influence of timescales of the environment-induced fluctuations upon the quantum mixing between electron donor and acceptor molecules in photo-induced electron transfer reaction. It was demonstrated that fast fluctuation and correspondingly fast solvation destroys the quantum mixing between the donor and acceptor in the vicinity of the crossing point of the diabatic free energy surfaces, leading to a diabatic reaction, whereas slow fluctuation sustains the quantum mixing and prompts the electron transfer reaction in an adiabatic fashion. Therefore, it is natural to raise a question of whether dynamic interaction with the electronic and vibrational states and the environment will change the nature of the quantum mechanically mixed electronic and vibrational states.

The main purpose of this project is to explore impacts of environment-induced fluctuations upon the quantum mechanically mixed electronic and vibrational states through calculations of electronic energy transfer dynamics and 2D electronic spectra. Further, we investigated to what extent vibrational modes play a role in electronic energy transfer dynamics under the influence of the environment-induced fluctuations. We found that the quantum mechanically mixed electronic and vibrational states does not paly an important role in photosynthetic energy transfer dynamics contrary to the prediction by the community although they induced longer-lived quantum beats in 2D electronic spectra of photosynthetic light harvesting pigment-protein complexes.

References

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