

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

Research Center of Integrative Molecular Systems Division of Trans-Hierarchical Molecular Systems



ISHIZAKI, Akihito
Research Associate Professor
[ishizaki@ims.ac.jp]

Education

2008 D.Sc. Kyoto University

Professional Employment

2006 JPSP Research Fellow, Kyoto University

2008 JPSP Postdoctoral Fellow for Research Abroad, University of California, Berkeley

2010 Postdoctoral Fellow, Lawrence Berkeley National Laboratory

2012 Research Associate Professor, Institute for Molecular Science

2013 Fellow 2012–2013, Wissenschaftskolleg zu Berlin

Member

Post-Doctoral Fellow
FUJIHASHI, Yuta

Secretary
YAMADA, Mariko

Keywords

Quantum Dynamics, Energy/Charge Transfer, Photosynthetic Light Harvesting

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 LHClI," *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. Impact of Environmentally Induced Fluctuations on Quantum Mechanically Mixed Electronic and Vibrational Pigment States in Photosynthetic Energy/Charge Transfer and 2D Electronic Spectra

Recently, nuclear vibrational contribution signatures in two-dimensional (2D) electronic spectroscopy have attracted considerable interest, in particular as regards interpretation of the oscillatory transients observed in light-harvesting complexes. These transients have dephasing times that persist for much longer than theoretically predicted electronic coherence lifetime. As a plausible explanation for this long-lived spectral beating in 2D electronic spectra, quantum-mechanically mixed electronic and vibrational states (vibronic excitons) were proposed by Christensson *et al.* [*J. Phys. Chem. B* **116**, 7449 (2012)] and have since been explored. In this work, we address a dimer that produces little beating of electronic origin in the absence of vibronic contributions, and examine the impact of protein-induced fluctuations upon electronic-vibrational quantum mixtures by calculating the electronic energy transfer dynamics and 2D electronic spectra in a numerically accurate manner. It was found that, at cryogenic temperatures, the electronic-vibrational quantum mixtures are rather robust, even under the influence of the fluctuations and despite the small Huang-Rhys factors of the Franck-Condon active vibrational modes. This results in long-lasting beating behavior of vibrational origin in the 2D electronic spectra. At physiological temperatures, however, the fluctuations eradicate the mixing, and hence, the beating in the 2D spectra disappears. Further, it was demonstrated that such electronic-vibrational quantum mixtures do not necessarily play a significant role in electronic energy transfer dynamics, despite contributing to the enhancement of long-lived quantum beating in 2D electronic spectra, contrary to speculations in recent publications.^{1,2)}

The most significant aspect of this work is, of course, clarification of the confusion concerning the long-lived quantum beats observed in 2D electronic spectra of photosynthetic light harvesting systems. However, I would like to emphasize another significance of the work from the viewpoint of fundamental physics. In general, energy eigenstates due to quantum mixing among multiple states are obtained via mathematical diagonalization of Hamiltonians of interest. It should be noted that these are usually independent of any environmental factors such as temperatures and fluctuations, even though one considers quantum systems in condensed phases. Thus, once quantum delocalizations are introduced “mathematically” (*i.e.* invariable coefficients in a linear combination), they are never destroyed by the environmental factors. However, the reality is not the case.²⁾ In order to capture subtle robustness and fragility of quantum mixing under the influence of the fluctuations, we employed the beating amplitudes of the ground state bleaching pathways in 2D nonrephasing spectra “as a measure

of the degrees of the quantum mixture between electronic and vibrational pigment states.” This successfully visualizes the degrees of the quantum mixture between electronic and vibrational pigment states under the influence of protein-induced fluctuations at different temperatures.

2. Influence of Weak Vibrational-Electronic Couplings on 2D Electronic Spectra and Inter-Site Coherence in Weakly Coupled Photosynthetic Complexes

Coherence oscillations measured in two-dimensional (2D) electronic spectra of pigment-protein complexes may have electronic, vibrational, or mixed-character vibronic origins, which depend on the degree of electronic-vibrational mixing. Oscillations from intra-pigment vibrations can obscure the inter-site coherence lifetime, of interest in elucidating the mechanisms of energy transfer in photosynthetic light-harvesting. Huang-Rhys factors (S) for low-frequency vibrations in Chlorophyll and Bacteriochlorophyll are quite small ($S \leq 0.05$), so it is often assumed that these vibrations influence neither 2D spectra nor inter-site coherence dynamics. In this work, we explore the influence of S within this range on the oscillatory signatures in simulated 2D spectra of a pigment heterodimer. To visualize the inter-site coherence dynamics underlying the 2D spectra, we introduce a formalism which we call the “site-probe response.” By comparing the calculated 2D spectra with the site-probe response, we show that an on-resonance vibration with Huang-Rhys factor as small as $S = 0.005$ and the most strongly coupled off-resonance vibrations ($S = 0.05$) give rise to long-lived, purely vibrational coherences at 77 K. We moreover calculate the correlation between optical pump interactions and subsequent entanglement between sites, as measured by the concurrence. Long-lived inter-site coherence and site entanglement increase with S at 77 K, and this dependence all but vanishes at physiological temperature, as environmentally-induced fluctuations destroy the vibronic mixing.^{4,5)}

References

- 1) Y. Fujihashi, G. R. Fleming and A. Ishizaki, *J. Chem. Phys.* **142**, 212403 (2015).
- 2) A. Ishizaki and G. R. Fleming, *New J. Phys.* **12**, 055004 (13 pages) (2010).
- 3) Y. Fujihashi, G. R. Fleming and A. Ishizaki, *J. Chin. Chem. Soc.* (2015), in press. DOI: 10.1002/jccs.201500100.
- 4) D. M. Monahan, L. Whaley-Mayda, A. Ishizaki and G. R. Fleming, *J. Chem. Phys.* **143**, 065101 (2015).
- 5) D. M. Monahan, L. Whaley-Mayda, A. Ishizaki and G. R. Fleming, *Ultrafast Phenomena XIX (Springer Proceedings in Physics)* **162**, 553 (2015).