

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

Department of Theoretical and Computational Molecular Science
Division of Theoretical Molecular Science II



ISHIZAKI, Akihito
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

2016 Professor, Institute for Molecular Science

Professor, The Graduate University for Advanced Studies

Visiting professor, Nagoya University

Awards

2015 10th Condensed-Matter Science Prize, Japan

2016 10th Young Scientist Award of the Physical Society of Japan

2016 18th Sir Martin Wood Prize

2017 Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology
The Young Scientists' Prize

Member

Assistant Professor
NGUYEN, Thanh Phuc

Post-Doctoral Fellow
KATO, Akihito
FUJIHASHI, Yuta

Secretary
AKABA, Atsuko

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Essentially, any quantum systems can never be regarded as “isolated systems.” Quantum systems are always in contact with “the outside world,” and hence their quantum natures are sometimes sustained and sometimes destroyed. In condensed phase molecular systems, especially, quantum systems are affected by the huge amount of dynamic degrees of freedom such as solvent molecules, amino acid residues in proteins, and so forth. Balance between robustness and fragility of the quantum natures may dramatically alter behaviors of chemical dynamics and spectroscopic signals. Quantum dynamics of energy/charge transfer dynamics in condensed phase molecular systems such as protein environments are remarkable examples of such phenomena.

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 excita-

tion 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.

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).
- 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]
- G. D. Scholes *et al.*, “Using Coherence to Enhance Function in Chemical and Biophysical Systems,” *Nature* **543**, 647–656 (2017).

1. Control of Excitation Energy Transfer in Condensed Phase Molecular Systems by Floquet Engineering

Excitation energy transfer (EET) is one of the most important processes in both natural and artificial chemical systems including, for example, photosynthetic complexes and organic solar cells. The EET rate, however, is strongly suppressed when there is a large difference in the excitation energy between the donor and acceptor molecules. We have demonstrated both analytically and numerically that the EET rate can be greatly enhanced by periodically modulating the excitation energy difference. The enhancement of EET by using this Floquet engineering, in which the system's Hamiltonian is made periodically time-dependent, is found to be efficient even in the presence of strong fluctuations and dissipations induced by the coupling with a huge number of dynamic degrees of freedom in the surrounding molecular environments. The shift of the optimal driving frequency as moving from the homogeneous to the inhomogeneous broadening limits can be used to probe the nuclear motion dynamics of the environment.¹⁾

2. Control of Quantum Dynamics of Electronic Excitation Transfer in Molecular Loop Structures: Spontaneous Breaking of Chiral Symmetry

Manipulation of quantum systems is the basis for many promising quantum technologies. How quantum mechanical principles can be used to manipulate dynamics of quantum dissipative systems is, however, still elusive because of strong decoherence effects arising from the interaction with the surrounding environment. We have demonstrated that electronic excitation transfer dynamics in molecular loop structures can be manipulated with the use of the Floquet engineering, in which the Franck-Condon transition frequency is temporally modulated in a periodic manner. Despite strong dephasing, the system's dynamics spontaneously breaks the chiral symmetry of the loop in a controllable fashion, followed by the generation of a steady-state current of electronic excitation. The breaking of chiral symmetry and the consequent controllable unidirectional flow of electronic excitations could be employed to construct functional molecular circuits for energy transport.²⁾

3. Non-Markovian Quantum-Classical Ratchet for Ultrafast Long-Range Electron-Hole Separation in Condensed Phases

In organic photovoltaic systems, a photogenerated molecular exciton in the donor domain dissociates into a hole and an electron at the donor-acceptor heterojunction, and subsequently separates into free charge carriers that can be extracted as photocurrents. The recombination of the once-separated electron and hole is a major loss mechanism in photovoltaic systems, which controls their performance. Hence, efficient photovoltaic systems need built-in ratchet mechanisms, namely,

ultrafast charge separation and retarded charge recombination. In order to obtain insight into the internal working of the experimentally observed ultrafast long-range charge separation and protection against charge recombination, we theoretically investigate a potential ratchet mechanism arising from the combination of quantum delocalization and its destruction by performing numerically accurate quantum-dynamics calculations on a model system. We demonstrate that the non-Markovian effect originating from the slow polaron formation strongly suppresses the electron-transfer reaction back to the interfacial charge-transfer state stabilized at the donor-acceptor interface and that it plays a critical role in maintaining the long-range electron-hole separation.³⁾

4. Intramolecular Vibrations Complement the Robustness of Primary Charge Separation in the Photosystem II Reaction Center

The energy conversion of oxygenic photosynthesis is triggered by primary charge separation in proteins at the photosystem II (PSII) reaction center (RC). Several time-resolved spectroscopic studies have reported that the primary charge separation in the PSII RC take place on subpicosecond time scale. However, it is one order of magnitude faster than the time constant of the charge separation starting from the special pair in the well-investigated purple bacterial RC, despite similarities in their arrangement of the pigments. As the coupling strengths between electron donors and acceptors are usually thought to be on the order of tens of wavenumbers, the precise mechanisms that enable subpicosecond charge separation in the PSII RC are to a large extent unknown.

To address the above question, we investigated the impacts of the protein environment and intramolecular vibrations on primary charge separation at the PSII RC. This was accomplished by combining the quantum dynamic theories of condensed phase electron transfer with quantum chemical calculations to evaluate the vibrational Huang-Rhys factors of chlorophyll and pheophytin molecules. We reported that individual vibrational modes play a minor role in promoting charge separation, contrary to the discussion in recent publications. Nevertheless, these small contributions accumulate to considerably influence the charge separation rate, resulting in subpicosecond charge separation almost independent of the driving force and temperature. We suggested that the intramolecular vibrations may complement the robustness of the charge separation in the PSII RC against the inherently large static disorder of the involved electronic energies.⁴⁾

References

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- 3) A. Kato and A. Ishizaki, *Phys. Rev. Lett.* **121**, 026001 (2018).
- 4) Y. Fujihashi, M. Higashi and A. Ishizaki, *J. Phys. Chem. Lett.* **9**, 4921–4929 (2018).