

# Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

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#### Education

2001 B.S. Kyoto University  
2005 M.S. Kyoto University  
2008 D.S. Kyoto University

#### Professional Employment

2006 JSPS Research Fellow, Kyoto University  
2008 JSPS 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 10<sup>th</sup> Condensed-Matter Science Prize, Japan  
2016 10<sup>th</sup> Young Scientist Award of the Physical Society of Japan  
2016 18<sup>th</sup> Sir Martin Wood Prize  
2017 The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology  
The Young Scientists' Prize  
2020 JSPS Prize  
2020 Japan Academy Medal

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#### Keywords

Quantum Dissipative Systems in Complex Molecular Systems, Quantum Optics, Light-Matter Interaction

Quantum dynamic phenomena are ubiquitous in molecular processes, and yet remain a challenge for experimental and theoretical investigations. On the experimental side, it has become possible to explore molecules on a time scale down to a few femtoseconds. This progress in ultrafast spectroscopy has opened up real-time observation of dynamic processes in complex chemical and biological systems and has provided a strong impetus to theoretical studies of condensed phase quantum dynamics.

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 spec-

troscopic signals. Therefore, theoretical tools to adequately describe (1) dynamical behaviors of quantum systems affected by the huge amount of dynamic degrees of freedom and (2) the interaction with radiation fields should be developed.

For this purpose, our research group has been tackling the following subjects:

- (1) Developments of condensed phase quantum dynamic theories
- (2) Quantum theories to describe dynamical and transport processes in materials and biological systems
- (3) Theoretical investigations on measurement and control with the use of atomic-molecular-optical (AMO) physics approaches.

In recent years, specifically, special attention is devoted to the subject (3). We have been examining whether ideas and concepts in the field of quantum science and technology would provide novel control knobs that supplement classical parameters in conventional spectroscopic tools such as frequencies and time delays.

#### Selected Publications

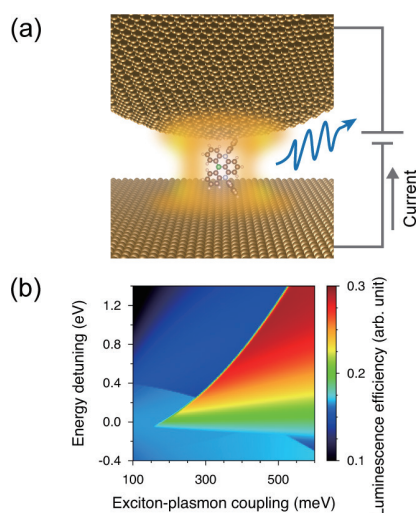
- A. Ishizaki and G. R. Fleming, “Quantum Coherence in Photosynthetic Light Harvesting,” *Annu. Rev. Condens. Matter Phys.* **3**, 333–361 (2012). [Invited review article]
- G. D. Scholes *et al.*, “Using Coherence to Enhance Function in Chemical and Biophysical Systems,” *Nature* **543**, 647–656 (2017).
- T. P. Nguyen and A. Ishizaki, “Control of Excitation Energy Transfer in Condensed Phase Molecular Systems by Floquet Engineering,” *J. Phys. Chem. Lett.* **9**, 1243 (2018).
- A. Kato and A. Ishizaki, “Non-Markovian Quantum-Classical

Ratchet for Ultrafast Long-Range Electron–Hole Separation in Condensed Phases,” *Phys. Rev. Lett.* **121**, 647 (2018).

- Y. Fujihashi, R. Shimizu and A. Ishizaki, “Generation of Pseudo-Sunlight via Quantum Entangled Photons and the Interaction with Molecules,” *Phys. Rev. Res.* **2**, 023256 (2020).
- A. Ishizaki, “Probing Excited-State Dynamics with Quantum Entangled Photons: Correspondence to Coherent Multidimensional Spectroscopy,” *J. Chem. Phys.* **153**, 051102 (2020). [Editor’s Pick]

## 1. Control and Enhancement of Single-Molecule Electroluminescence through Strong Light-Matter Coupling

The energetic positions of molecular electronic states at molecule/electrode interfaces are crucial factors for determining the transport and optoelectronic properties of molecular junctions. Strong light-matter coupling offers a potential for manipulating these factors, enabling to boost in the efficiency and versatility of these junctions. Here, we investigated electroluminescence from single-molecule junctions in which the molecule is strongly coupled with the vacuum electromagnetic field in a plasmonic nanocavity. We demonstrated an improvement in the electroluminescence efficiency by employing the strong light-matter coupling in conjunction with the characteristic feature of single-molecule junctions to selectively control the formation of the lowest-energy excited state. The mechanism of efficiency improvement was discussed based on the energetic position and composition of the formed polaritonic states. Our findings indicated the possibility to manipulate optoelectronic conversion in molecular junctions by strong light-matter coupling.<sup>1)</sup>



**Figure 1.** (a) Schematic illustration of electroluminescence from a dye molecule in a plasmonic nanocavity. (b) Two-dimensional plot of the electroluminescence efficiency as a function of the exciton-plasmon coupling strength and energy detuning.

## 2. Probing Exciton Dynamics with Spectral Selectivity through the Use of Quantum Entangled Photons

Quantum light is increasingly recognized as a promising resource for developing optical measurement techniques. Particular attention has been paid to enhancing the precision of the measurements beyond classical techniques by using nonclassical correlations between quantum entangled photons. Recent advances in quantum optics technology have made it possible to manipulate the spectral and temporal properties of

entangled photons, and the photon correlations can facilitate the extraction of matter information with relatively simple optical systems compared to conventional schemes. In these respects, the applications of entangled photons to time-resolved spectroscopy can open new avenues for unambiguously extracting information on dynamical processes in complex molecular and materials systems. Here, we proposed time-resolved spectroscopy in which specific signal contributions are selectively enhanced by harnessing the nonclassical correlations of entangled photons. The entanglement time characterizes the mutual delay between an entangled twin and determines the spectral distribution of the photon correlations. This characteristic allows us to filter out specific frequency regions of spectra while temporally resolving the state-to-state dynamics in the time region longer than half of the entanglement time. Therefore, the entanglement time plays a dual role as the knob for controlling the accessible time region of dynamical processes and the degrees of spectral selectivity. The results demonstrated that the application of quantum entangled photons to time-resolved spectroscopy leads to monitoring dynamical processes in complex molecular and materials systems by selectively extracting desired signal contributions from congested spectra. We anticipated that more elaborately engineered photon states would broaden the availability of quantum light spectroscopy.<sup>2)</sup>

## 3. Network Analysis with Quantum Dynamics Clarifies Why Photosystem II Exploits both Chlorophyll *a* and *b*

In land plants, chlorophyll-*a* and chlorophyll-*b* in light-harvesting proteins are responsible for absorbing solar energy. While the individual characteristics of these pigments are well-understood, the advantages of their coexistence have not been fully elucidated. Here, we presented a principled framework based on complex network analysis and quantum dynamics to investigate and quantify the features of this coexistence during excitation energy transfer in a photosystem II supercomplex. By using model networks with diverse chlorophyll compositions, our analysis revealed that the excited energy preferentially flows through specific domains, where excessive energy can be controlled, solely in those supercomplexes with a natural chlorophyll-*a/b* ratio, resulting in a moderate charge separation yield. Our findings suggested that light-harvesting proteins with the natural chlorophyll-*a/b* ratio are optimized to safely and efficiently capture light energy across various light intensities. By leveraging our framework, we could gain valuable insights into the mechanisms by which light-harvesting proteins harvest light energy and adapt to changing environmental conditions.<sup>3)</sup>

### References

- 1) K. Miwa, S. Sakamoto and A. Ishizaki, *Nano Lett.* **23**, 3231 (2023).
- 2) Y. Fujihashi, K. Miwa, M. Higashi and A. Ishizaki, *J. Chem. Phys.* **159**, 114201 (2023).
- 3) E. Kim, D. Lee, S. Sakamoto, J.-Y. Jo, M. Vargas, A. Ishizaki, J. Minagawa and H. Kim, submitted.