

# 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  
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#### Professional Employment

2006 JSPS Research Fellow, Kyoto University  
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2010 Postdoctoral Fellow, Lawrence Berkeley National Laboratory  
2012 Research Associate Professor, Institute for Molecular Science  
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2016 Professor, Institute for Molecular Science  
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#### Awards

2015 10<sup>th</sup> Condensed-Matter Science Prize, Japan  
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2016 18<sup>th</sup> Sir Martin Wood Prize  
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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. Probing Exciton Dynamics with Spectral Selectivity through the Use of Quantum Entangled Photons

Quantum light, such as entangled photons, are promising resources for the development of new spectroscopic techniques. For example, non-classical correlations between entangled photons can be potentially exploited to enhance the precision of optical measurements beyond classical techniques or to extract matter information with simpler optical systems compared to conventional schemes. In this respect, the entangled photons may open new avenues for unambiguously extracting information about dynamic processes in complex molecules such as photosynthetic light-harvesting systems, in which multiple electronic states are present within a narrow energy range, from the congested spectra. However, to date, only a few theoretical studies have been reported on the application of entangled photons to time-resolved spectroscopic measurements. Hence, there is no comprehensive understanding of what non-classical states of light are suitable for implementing real-time observation of dynamical processes in condensed phases.

Here, we propose a novel time-resolved spectroscopy technique that selectively enhances specific signal contributions by harnessing the non-classical correlations between entangled photons generated via parametric down-conversion (PDC) pumped with a monochromatic laser. The key feature in the proposed technique is that the entanglement time, which is the hallmark of the non-classical photon correlations, works as a spectral filter in signal processing to selectively resolve a specific region of spectra, while it simultaneously offers a knob for controlling the accessible time region of dynamics in molecules. For demonstration purposes, we apply the proposed spectroscopic scheme to the Fenna-Matthews-Olson (FMO) pigment-protein complex from the photosynthetic green sulfur bacterium. The results show that the phase-matching functions of the PDC in the nonlinear crystals such as periodically poled  $\text{KTiOPO}_4$  (PPKTP) crystal and  $\beta\text{-BaB}_2\text{O}_4$  (BBO) crystal allow one to separately measure specific peaks of spectra in the FMO complex by tuning the entanglement time and the central frequencies of the entangled photons. It is also found that the spectral filtering can be implemented in the range of currently available entangled photon sources. Moreover, the results indicate that the spectral filter effects can be easily adjusted by changing nonlinear crystals and/or their properties because the spectral distribution of the phase-matching function strongly depends on the properties of the nonlinear crystal. Since, in addition to the BBO and PPKTP crystals considered in this study, there is a wide range of nonlinear crystals that have been used for PDC in the near-infrared and visible regions, the proposed technique is expected to be applicable not only to the FMO complex but also to other light-harvesting systems by finding an appropriate nonlinear crystal corresponding to the spectral range of the molecular system of interest. We thus anticipate that the proposed technique can be a useful tool for monitoring step-by-step energy transfer pathway in the light-harvesting systems by selectively extracting desired signal contributions from the congested spectra.<sup>1)</sup>

## 2. Benefit of Coexistence of Chlorophyll *a* and *b* in Antenna of Photosystem II

Chlorophylls (Chls) in the photosystem II (PSII) play essential parts in the initial process of oxygenic photosynthesis, *i.e.*, the solar light is collected by Chls embedded in the light-harvesting complexes termed antenna, and then the excitation energy is transferred to Chls in the reaction center, where the charge separation takes place. The antenna includes two distinct types of Chls, Chl *a* and *b*, whereas the reaction center possesses a single type Chl *a*. As the transition energy of Chl *b* is higher than that of Chl *a*, the excitation energy flows from Chl *b* to Chl *a*. Hence, if all the pigments in the antenna are composed of Chl *b*, higher efficiency of the excitation energy transfer to the reaction center could be expected [H. Kim, *et al.*, *arXiv:2101.04848* (2021)]. Even though such an ‘all-*b*’ system would offer an advantage in photosynthesis, the naturally occurring antenna binds both Chls *a* and *b* throughout the green plants. The reason why the mixed Chl system is adopted in the antenna found in nature has yet to be understood clearly.

In this work, we investigated the role of Chl *a* existed in the antenna during the excitation energy transfer (EET). The rate constants of the EET within and between domains, each of which comprises strongly coupled Chls forming delocalized excited states, were calculated with the aid of the Redfield and generalized Förster theory. To discuss how the ratio  $\kappa$  of Chl *b* to *a* in the antenna affects the time evolution of the excitation energy distribution, we considered the hypothetical models of the PSII where  $\kappa$  was equal to or different from that in the natural PSII. The results show the quantum yield of the EET to the reaction center is improved with increasing  $\kappa$ , as expected. Moreover, it is found that in the case of the natural PSII, the excitation energy was localized at particular pigment-protein complexes in the antenna, termed CP26 and CP29, where the occurrence of non-photochemical quenching during the photoprotection was suggested in the previous study [T. K. Ahn, *et al.*, *Science* **320**, 794 (2008)]. The results indicate the natural PSII possesses the optimal structure not only for collecting the light energy into the reaction center but also for balancing the EET and the other processes, such as photoprotection.

## 3. Dynamics of the Coupled System Composed of Electrons and Anharmonic Lattice Vibrations in Solid

Anharmonicity of lattice vibrations is responsible for a large quantity of phenomena including thermal conductivity, structural phase transition, and so forth. Moreover, recent studies suggested lattice anharmonicity would have a dominant role in the carrier dynamics of some sort of soft semiconductors, *e.g.*, lead-based halide perovskites which exhibit novel optoelectronic properties. Here, we theoretically investigate the dynamics of the coupled systems composed of electrons and anharmonic lattice vibrations. We highlight the importance of the timescale difference between electron and lattice dynamics in determining the materials properties.

### Reference

1) Y. Fujihashi *et al.*, to be submitted.