

# Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

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**Education**

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 spectroscopic 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. Precise Determination of Excitation Energies Based on Exciton-Polariton Measurements

The precise determination of the excitation energies in condensed-phase molecular systems is important for understanding system-environment interactions as well as for the prerequisite input data of theoretical models used to study the dynamics of the system. The excitation energies are usually determined by fitting of the measured optical spectra that contain broad and unresolved peaks as a result of the thermally random dynamics of the environment. Herein, we proposed a method for precise energy determination by strongly coupling the molecular system to an optical cavity and measuring the energy of the resulting polariton. The effect of thermal fluctuations induced by the environment on the polariton was also investigated, from which a power scaling law relating the polariton's linewidth to the number of molecules was obtained.<sup>1)</sup>

## 2. Controlling the Nonadiabatic Electron Transfer Reaction Rate through Molecular Vibration Polaritons

Recent experiments showed that the chemical reaction rate is modified by strongly coupling a nuclear vibration mode to the single mode of an optical cavity. Herein we investigated how the rate of an electron-transfer reaction depends on the molecule-cavity coupling. We found two main factors that determine the modification of the reaction rate: The relative shifts of the energy levels induced by the coupling and the mixing of the ground and excited states of molecular vibration in the ground state of the hybrid molecule-plus-cavity system through which the Franck-Condon factor between the initial and final states of the transition is altered. The effect of the mixing of molecular vibrational states on the reaction rate is, however, suppressed in a system containing a large number of molecules due to the collective nature of the resulting polariton, and thus should be observed in a system containing a small number of molecules. In contrast, the effect of the relative shifts of the energy levels should be essentially independent of the number of molecules coupled to the cavity.<sup>3)</sup>

## 3. Generation of Pseudo-Sunlight via Quantum Entangled Photons and the Interaction with Molecules

Light incident upon molecules triggers fundamental processes in diverse systems present in nature. However, under natural conditions such as sunlight illumination, it is impossible to assign known times for photon arrival due to continuous pumping, and therefore the photoinduced processes cannot be easily investigated. In this work, we demonstrated theoretically that the characteristics of sunlight photons, such as photon number statistics and spectral distribution, can be emulated through a quantum entangled photon pair generated with para-

metric down-conversion (PDC). We showed that the average photon number of sunlight in a specific frequency spectrum, e.g., the visible light, could be reconstructed by adjusting the PDC crystal length and pump frequency, and thereby the molecular dynamics induced by the pseudo-sunlight could be investigated. The entanglement time, which is the hallmark of quantum entangled photons, can serve as a control knob to resolve the photon arrival times, enabling investigations on real-time dynamics triggered by pseudo-sunlight photons.<sup>4)</sup>

## 4. Probing Excited-State Dynamics with Quantum Entangled Photons

Quantum light is a key resource for promoting quantum technology. One such class of technology aims to improve the precision of optical measurements using engineered quantum states of light. In this study, we investigate transmission measurement of frequency-entangled broadband photon pairs generated via parametric down-conversion with a monochromatic laser. It is observed that state-to-state dynamics in the system under study are temporally resolved by adjusting the path difference between the entangled twin beams when the entanglement time is sufficiently short. The non-classical photon correlation enables time-resolved spectroscopy with monochromatic pumping. It is further demonstrated that the signal corresponds to the spectral information along anti-diagonal lines of, for example, two-dimensional Fourier-transformed photon echo spectra. This correspondence inspires us to anticipate that more elaborately engineered photon states would broaden the availability of quantum light spectroscopy.<sup>5)</sup>

## 5. Prerequisites for Relevant Spectral Density and Convergence of Reduced Density Matrices at Low Temperatures

Hierarchical equations of motion approach with the Drude-Lorentz spectral density has been widely employed in investigating quantum dissipative phenomena. However, it is often computationally costly for low-temperature systems because a number of Matsubara frequencies are involved. In this work, we examined a prerequisite required for spectral density, and demonstrated that relevant spectral density significantly reduced the number of Matsubara terms to obtain convergent results for low temperatures.<sup>2)</sup>

## References

- 1) T. P. Nguyen and A. Ishizaki, *Phys. Rev. Res.* **1**, 033019 (2019).
- 2) T. P. Nguyen, Q. T. Pham and A. Ishizaki, *Sci. Rep.* **10**, 7318 (2020).
- 3) Y. Fujihashi, R. Shimizu and A. Ishizaki, *Phys. Rev. Res.* **2**, 023256 (2020).
- 4) A. Ishizaki, *J. Chem. Phys.* **153**, 051102 (2020). [Editor's Pick]
- 5) A. Ishizaki, *J. Phys. Soc. Jpn.* **89**, 015001 (2020).

## Awards

ISHIZAKI, Akihito; 16<sup>th</sup> JSPS Prize (2020).

ISHIZAKI, Akihito; 16<sup>th</sup> Japan Academy Medal (2020).