Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

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Education
2001 B.S. Kyoto University
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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
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2016 Professor, Institute for Molecular Science
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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 The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology
The Young Scientists' Prize
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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. 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 was 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.[1)]

2. Achieving Two-Dimensional Optical Spectroscopy with Temporal and Spectral Resolution Using Quantum Entangled Three Photons

Recent advances in techniques for generating quantum light have stimulated research on novel spectroscopic measurements using quantum entangled photons. One such spectroscopy technique utilizes non-classical correlations among entangled photons to enable measurements with enhanced sensitivity and selectivity. In this work, we investigated spectroscopic measurement utilizing entangled three photons generated through cascaded parametric down-conversion. In this measurement, time-resolved entangled photon spectroscopy with monochromatic pumping [A. Ishizaki, *J. Chem. Phys.* **153**, 051102 (2020)] is integrated with the frequency-dispersed two-photon counting technique, which suppresses undesired accidental photon counts in the detector and thus allows one to separate the weak desired signal. This time-resolved frequency-dispersed two-photon counting signal, which is a function of two frequencies, is shown to provide the same information as that of coherent two-dimensional optical spectra. The spectral distribution of the phase-matching function works as a frequency filter to selectively resolve a specific region of the two-dimensional spectra, whereas the excited-state dynamics under investigation are temporally resolved in the time region longer than the entanglement time. The signal is not subject to Fourier limitations on the joint temporal and spectral resolution, and therefore, it is expected to be useful for investigating complex molecular systems in which multiple electronic states are present within a narrow energy range.[2)]

3. Insights into Photosynthetic Energy Transfer Gained from Free-Energy Structure: Coherent Transport, Incoherent Hopping, and Vibrational Assistance Revisited

Giant strides in ultrashort laser pulse technology have enabled real-time observation of dynamical processes in complex molecular systems. Specifically, the discovery of oscillatory transients in the two-dimensional electronic spectra of photosynthetic systems [G. S. Engel, *et al.*, *Nature* **446**, 782 (2007)] stimulated a number of theoretical investigations exploring the possible physical mechanisms of the remarkable quantum efficiency of light harvesting processes. In this work, we revisited the elementary aspects of environment-induced fluctuations in the involved electronic energies and present a simple way to understand energy flow with the intuitive picture of relaxation in a funnel-type free-energy landscape. The presented free-energy description of energy transfer reveals that typical photosynthetic systems operate in an almost barrierless regime. The approach also provides insights into the distinction between coherent and incoherent energy transfer and the criteria by which the necessity of the vibrational assistance is considered.[3)]

4. Direct and Ultrafast Probing of Quantum Many-Body Interaction and Mott-Insulator Transition through Coherent Two-Dimensional Spectroscopy

Interactions between particles in quantum many-body systems play a crucial role in determining the electric, magnetic, optical, and thermal properties of the system. The recent progress in the laser-pulse technique has enabled the manipulations and measurements of physical properties on ultrafast timescales. In this work, we proposed a method for the direct and ultrafast probing of quantum many-body interaction through coherent two-dimensional (2D) spectroscopy. Up to a moderate interaction strength, the inter-particle interaction manifests itself in the emergence of off-diagonal peaks in the 2D spectrum before all the peaks coalesce into a single diagonal peak as the system approaches the Mott-insulating phase in the strongly interacting regime. The evolution of the 2D spectrum as a function of the time delay between the second and third laser pulses can provide important information on the ultrafast time variation of the interaction.[4)]

References

1) A. Ishizaki, *J. Chem. Phys.* **153**, 051102 (7 pages) (2020). [Editor's Pick]
2) F. Fujihashi and A. Ishizaki, *J. Chem. Phys.* **155**, 044101 (13 pages) (2021).
3) A. Ishizaki and G. R. Fleming, *J. Phys. Chem. B* **125**, 3286–3295 (2021).
4) T. P. Nguyen and Q. T. Pham, *arXiv:*2009.08598 (2021).

Awards

FUJIHASHI, Yuta; 15th Young Scientist Award of the Physical Society of Japan (2021).
ISHIZAKI, Akihito; Research Award of Quantum Life Science Society (2021).