

Condensed phase is a place where various photochemical reactions occur. Intraand inter-molecular relaxations and their interplay are the key processes that define the formation of a product state. Typically, these relaxations involve a vast amount of electronic and nuclear degrees of freedom. Ultrafast nonlinear spectroscopy has been contributed to study the excited state dynamics, whereas signal detection over a wide frequency range and in a multidimensional fashion is the key to disentangle complex processes. To this end, the applicant has been investigated the complex excited state dynamics by using following ultrafast nonlinear spectroscopy techniques.

### **(1) Broadband transient absorption spectroscopy**

Photosynthetic reaction is initiated by light-harvesting in the antenna complexes which is followed by electron transfer in the reaction center. These processes involve a huge number of pigment molecules (typically tens to thousands), making it challenging to unveil the overall reaction pathway. Broadband transient absorption (BBTA) spectroscopy can detect the electronic spectra over a wide frequency range (400-950 nm), which is crucial for disentangling the entire reaction. By using BBTA technique, complex reaction pathways in important natural/artificial photosynthetic systems were revealed [1-3].

Furthermore, by using ultrashort optical pulses, molecular vibrational signals can be observed in the time-domain, and the relationship between ultrafast electron transfer and vibrational coherence was clarified [4].

### **(2) Two-dimensional electronic vibrational spectroscopy**

In the past two-decades, the emerging technique two-dimensional electronic spectroscopy (2DES) has significantly advanced the field of ultrafast science. In contrast to the electronic spectroscopy, coherent two-dimensional electronic vibrational (2DEV) spectroscopy has an advantage in the simultaneous spectral resolution along both the visible excitation and the infrared detection frequencies, which allows the clear assignment of transient species.

Furthermore, line shape of the spectral features, which is related to a cross-correlation of vibrational and electronic dipoles, is sensitive to changes in electronic structure which reflects system-bath interaction. These advantages have made it possible to elucidate a nuanced picture of the complicated dynamics and synergistic motions involved in photoinduced proton-coupled electron transfer [5], and the character of mixed exciton-charge transfer state, previously proposed to be responsible for the far-red light operation of photosynthesis, in the photosystem II reaction center [6].

### **(3) Time-domain 2D Raman spectroscopy**

Recently emerged time-domain resonant 2D Raman spectroscopy has the potential to reveal the character of complex potential energy surfaces. However, the measurement requires stepping more than 10,000 delay points in total to obtain a sufficiently high frequency resolution and a broad frequency window, and thus the experimental implementation is extremely difficult. To overcome this challenge, the applicant developed a resonant 2D impulsive stimulated Raman spectroscopy (2D-ISRS) system based on rapid scanning of the time delay, which enables us to obtain a 2D Raman spectrum with unprecedented quality and to clearly reveal correlations among the vibrational manifolds of the excited state [7].

As listed above, the applicant has been consistently investigated the complex excited state dynamics in condensed phases by using ultrafast nonlinear spectroscopy and elucidated the key questions regarding the mechanism of important systems. In future, the applicant will continue the development of new spectroscopic methods, such as single-molecule level correlation spectroscopy, to elucidate the dynamics of chemical reactions even in statistical equilibrium systems that cannot be synchronized by optical excitation.

[1] *J. Am. Chem. Soc.*, **137** (2015) 13121.

[2] *J. Am. Chem. Soc.*, **138** (2016) 11599.

[3] *Phys. Chem. Chem. Phys.*, **24** (2022) 24714.

[4] *J. Am. Chem. Soc.*, **143** (2021) 14511.

[5] *J. Am. Chem. Soc.*, **143** (2021) 3104.

[6] *Nat. Commun.*, **13** (2022) 2275.

[7] *J. Phys. Chem. A*, **127** (2023) 5276