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Revealing Chemical Reaction Dynamics using Vibrational and Electronic Coherences

Elucidating reaction dynamics and mechanism of chemical reactions is a key role of physical chemistry. Gas-phase spectroscopy has realized describing molecular dynamics and single molecular chemical reactions in quantum mechanical point of view. However, there are significant discrepancies between the quantum mechanical intuitions interpreted by the gas-phase spectroscopy from the behavior of molecules in solution, which is the majority of chemical reactions closely related to human life. The discrepancies are attributed to strong intermolecular interaction, low regularity, high particle density, and high temperature, in general. Nonlinear spectroscopy, which measures the nonlinear optical response of materials, has a capability of investigating chemical reaction dynamics in solution by measuring the complicated optical response on multidimensional spaces. Such feature of nonlinear spectroscopy can dramatically reduce the redundant information from the complexity of solution.

The diffraction limit of optical electromagnetic field remarkably exceeds the size of molecules, so that the spectroscopic observation of single molecules inside a solution is almost impossible in principle. However, a molecular ensemble whose molecules are within a specific boundary condition can be selectively monitored using nonlinear spectroscopy. Two-dimensional electronic spectroscopy (2DES) is a third-order nonlinear spectroscopy technique that represents the spectral response of materials on a 3D space consisting of excitation frequency, time, and detection frequency. Excitation frequency informs the initial nuclear configuration and target electronic states. The spectroscopic property of a group of molecules indicated by an excitation frequency is projected on the detection frequency axis as a function of time. The contribution of chemical events of no interest (*e.g.*, solvation, intramolecular vibrational redistribution, vibrational relaxation) can be eliminated by examining the correlation between detection frequency and time. [1]

In the presentation, reaction dynamics (ultrafast intersystem crossing [2] and photosynthetic energy transfer [3,4]) studies investigated by multidimensional

spectroscopy techniques with sub-10-fs time resolution will be introduced. Time-resolved fluorescence, pump-probe spectroscopy, and 2DES are complementarily employed according to the spectroscopic properties of the molecular systems. Since the time resolution enables the direct observation of coherent vibrational motion, the correlation between the nuclear motion and a photoinitiated process is represented on the multidimensional space. Then, the reaction mechanisms can be deduced by analyzing the correlation based on quantum chemical calculations.

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[3] JW. Kim, et al., *J. Phys. Chem. Lett.* **2021**, 12 (27), 6292-6298

[4] JW. Kim, et al., *J. Phys. Chem. Lett.* **2022**, 13 (4), 1099-1106

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