Femtosecond Two-Photon Absorption Spectroscopy
Probes Molecular Electron Charge Transfer

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Two-photon absorption (2PA) is an instantaneous nonlinear-optical process, where two simultaneously incident photons induce a transition from ground state to a higher-energy, excited electronic state. Even though the probability of such transitions under ambient illumination conditions is notoriously low, recent proliferation of high peak intensity, wavelength-tuneable femtosecond lasers, in conjunction with critical improvements achieved in the experimental techniques [1], have transformed the 2PA into a precision spectroscopic tool.

According to well-known Laporte spectroscopic selection rule, in molecular systems that maintain inversion symmetry, all permanent electric dipole moments vanish, and 2PA transitions between opposite parity states are forbidden. In reality, actual symmetry of molecules, especially those placed within complex environments, may appear lower than expected based on their nominal structure. Numerous experimental observations suggest that if the lowest-energy electronic transition is one-photon allowed, then the corresponding non-vanishing 2PA cross section is proportional to the square of the permanent electric dipole moment change in the same transition. Consequently, comparison between 1-photon absorption and experimentally measured 2PA spectrum reflects the degree of spontaneous symmetry breaking in nominally forbidden 2-photon transitions, as well as provides quantitative information about the transfer of electron charge upon transition from ground state to the excited state.

In this talk, we will describe our recent experiments, where we applied wavelength-tuneable femtosecond laser to measure the 2-photon absorption spectra with high accuracy in a broad range of wavelengths of a variety of molecular systems, including organometallic charge transfer complexes [2-4], fluorescent proteins [5], and DNA nucleotides [6], and then utilize the above data to determine how much the molecular permanent electric dipole moment changes upon transition from ground- to the excited state. Comparison with quantum-chemical theoretical calculations will be also discussed [4,5,7].

References