Developing Femtosecond Raman Spectroscopy to Elucidate Reaction Mechanisms of Biomolecules and Materials in Solution

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Abstract
Photochemical reactions power numerous biological and energy-related processes and their importance cannot be overstated. Photosynthesis, vision, and bioluminescence all rely on structural dynamics of chromophores, commonly a conjugated organic moiety in condensed phase from water to protein pocket, which are responsible for light absorption and emission. To reveal atomic choreography determining the fate of photoexcited chromophore in a range of local environments particularly involving water, we develop an emerging structural dynamics tool called femtosecond stimulated Raman spectroscopy (FSRS) with broadly tunable pulses in conjunction with femtosecond transient absorption, cascaded four-wave mixing, time-resolved third-harmonic generation, vibrational normal mode calculations, and molecular dynamics simulation to dissect the multidimensional reaction coordinate of photoacid in solution and fluorescent protein Ca2+ biosensors in water. Following 400 nm electronic excitation, the photoacid pyranine (HPTS) undergoes characteristic nuclear motions to either facilitate excited-state proton transfer (ESPT) when proton acceptors are nearby, or perform vibrational cooling in solvents lacking proton accepting capability such as methanol. In analogy, FSRS results on genetically encoded Ca2+ sensors for optical imaging (GECOs) with the three-residue SYG or TYG chromophore reveal dramatically different structural evolution pathways following photoexcitation in the Ca2+-free vs. bound state. The gating motions for green fluorescence in these biosensors are retrieved from Fourier transform analysis of vibrational quantum beats, whereas blue fluorescence is correlated with inhibition of ESPT by location change of key residues. Besides crucial design principles for molecular device functionalization from structural dynamics insights, FSRS is proven to be a powerful optical tool to elucidate hidden reaction coordinate during photochemical reactions in action, with simultaneously high spectral and temporal resolutions to effectively map excited-state potential energy surface of a wide range of functional materials and biomolecules. Recent advances using broadband up-converted multicolor array to generate laser sidebands and time-resolved third harmonic generation to reveal phonon dynamics will also be discussed.

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