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Department of Chemistry

Special Seminar

3 p.m. Monday, Aug. 24 • Kate & Michael Barany Conference Room

Assistant Professor

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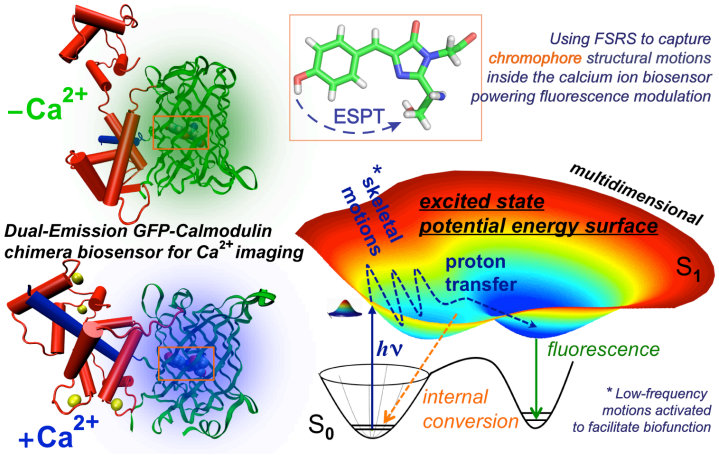
Capturing Molecular Structural Snapshots of Photoexcited Chromophores with Ultrafast Raman Spectroscopy

Research interests: investigating the structure-function relationships of biomolecules and novel materials, ranging from fluorescent proteins, which can light up subcellular entities for bioimaging, proteins and enzymes, which are potential targets for biomedicine, to nanoclusters and metal-organic complexes in solution.
Website: http://chemistry.oregonstate.edu/Fang

Abstract

Photochemical reactions power numerous biological and energe-related processes and their importance cannot be overstated. Photosynthesis, vision, and bioluminiscence all rely on structural dynamics of chromophores,[1,2] commonly a conjugated organic moiety in condensed phase from water to proteins, responsible for light absorption and emission. To capture atomic motions determining the fate of photoexcited chromophore in a range of microenvironements, we develop femtosecond stimulated Raman spectroscopy (FSRS)[3-5] with broadly tunable pulses aided by femtosecond transient absorption, cascaded four-wave mixing, vibrational normal mode calculation, and molecular dynamics simulation to dissect the multidimensional reaction coordinate of photoacid in solution and fluorescent protein Ca^{2+} biosensors in water. Following UV excitation, the photoacid pyranine undergoes characteristic motions to either facilitate excited-state proton transfer (ESPT) when proton acceptors are nearby,[3,6] or perform vibrational cooling in solvents lacking proton accepting capability.[7] In analogy, FSRS results on genetically encoded Ca^{2+} sensors for optical imaging (GECOs) with the three-residue chromophore reveal different structural evolution following photoexcitation in the Ca^{2+}-free vs. bound state.[8,9] The *gating* motions for green fluorescence in these biosensors are retrieved from Fourier transform of vibrational quantum beats, whereas blue fluorescence is due to inhibition of ESPT near the chromophore. Besides crucial design principles for molecular functionalization, FSRS is proven to be a powerful optical tool to elucidate hidden reaction cooridnate 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 in collecting anti-Stokes FSRS data for pyranine to differentiate protonated and depronated species in S_1 and time-resolved third harmonic generation to infer phonon dynamics[10] will be briefly discussed.



Dissecting reaction coordinate to understand fluorescence mechanisms of emerging fluorescent protein biosensors for calcium ion imaging.

References

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Host: Professor Renee Frontiera