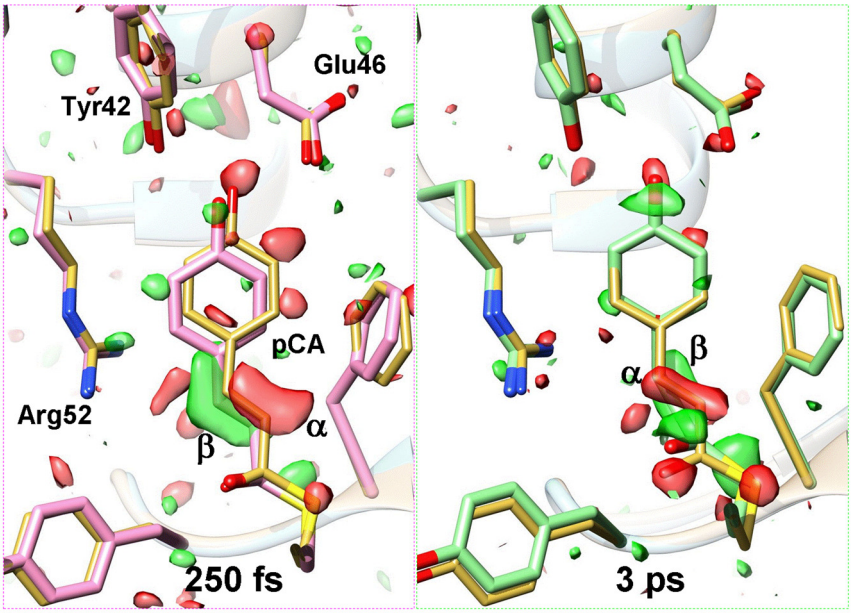
Ultrafast Structural Dynamics in Proteins

M. Schmidt[1]

[1] University of Wisconsin-Milwaukee, Milwaukee, Wi, U.S.A.



Fundamental events in chemical reactions such as bond braking, bond formation and isomerization happen on the femtosecond time scale. Isomerizations are of particular importance to both chemistry and biology. Cis-trans isomerizations lie at the base of light perception and numerous highly important reactions such as proton pumping and energy generation by light. These reactions sparked the interest of theorists and experimentalists alike. Although computational approaches to characterize these reactions “in-silico” as well as spectroscopic approaches to determine the dynamics were extremely successful, the three dimensional structures remained experimentally elusive.

We established that time-resolved serial femtosecond crystallography (TR-SFX) works at the LCLS [1] and followed the trans to cis isomerization of the central para-coumaric acid (pCA) chromophore in the photoactive yellow protein in real time [2]. Excited state (ES) structural dynamics of the pCA initiates the trans to cis isomerization. Relaxation from the ES potential energy surface (PES) to the ground state (GS) PES occurs at about 600 fs, after which the configuration of the chromophore is cis. By comparing X-ray structures on both the ES-PES and the GS-PES on time scales from 100 fs to 3 ps we structurally characterize the long sought after transition through a conical intersection for the first time.

1. Tenboer, J. et al. Time-resolved serial crystallography captures high-resolution intermediates of photoactive yellow protein. *Science* **346**, 1242-6 (2014).
2. Pande, K. et al. Femtosecond Structural Dynamics Drives the Trans/Cis Isomerization in Photoactive Yellow Protein. *Science* **352**, 725-729 (2016).