EXPERIMENTAL STUDIES OF STRUCTURE, FUNCTION, AND COHERENT OSCILLATIONS IN BIOMOLEUCLES

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Femtosecond coherence spectroscopy (FCS) can be used to prepare and monitor coherent states of biological samples such as heme proteins. Following laser pulse induced ligand photolysis, the (initially planar) heme group is left far from its final product state equilibrium geometry. This leads to coherent oscillations of those modes composing the reaction coordinate for ligand binding and dissociation. Coherence studies, along with "white light" continuum measurements of the spectral dynamics, probe the dissociation, population decay, vibrational coherence and damping of this fundamental biochemical reaction. Investigations of the effect of temperature and sample condition on the coherent motions of the heme and on the ultrafast geminate rebinding of the diatomic (NO) ligand are also described and emphasized. The influence of the surrounding protein material is probed by utilizing heme model compounds and site directed mutants. These studies show that the spectrum of low frequency heme modes can be significantly altered by the coordination of the proximal axial ligand. The model compound investigations also allow the diatomic ligand rebinding barrier to be separated into "proximal" and "distal" contributions that can be separately determined. The NO rebinding studies reveal that NO decouples the rebinding reaction from the heme conformational substates and that the slower geminate phase of NO rebinding results from the return of the NO from a distal (Xe4) cavity.