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Intramolecular Vibrational Preparation of the Unfolding Transition State of Zn$^{\mathrm{II}}$-substituted Cytochrome *c*: Picosecond Time-Resolved Fluorescence and Dynamic Stokes Shift Studies[1] WARREN F. BECK, SANELA LAMPA-PASTIRK, Department of Chemistry, Michigan State University

— We show that an intramolecular vibrational excitation provided by the radiationless decay of a covalently bound electronic chromophore can be exploited to drive a protein from its native folded state to the transition state for unfolding. Using this approach, we examine the effect of the polarity and viscosity of the solvent medium on the unfolding and refolding reactions of Zn$^{\mathrm{II}}$-substituted cytochrome *c* at room temperature. The dynamic Stokes shift of the S$_1$-state Zn$^{\mathrm{II}}$–porphyrin is monitored using picosecond time-resolved fluorescence spectroscopy as a probe of the protein and solvent dynamics that are associated with the crossing of the unfolding transition state and with the subsequent unfolding and refolding trajectories. The results show that the solvent polarity controls the activation energy for the unfolding and refolding reactions; the solvent viscosity further controls the rate by frictionally hindering the moving polypeptide. These findings suggest an important role for the solvent in the kinetic control of protein-folding trajectories on the energy landscape.

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