ULTRAFAST HYDRATION DYNAMICS AND COUPLED WATER-PROTEIN FLUCTUATIONS IN APOMYOGLOBIN

YI YANG, LUYUAN ZHANG, LIJUAN WANG, DONGPING ZHONG, *Departments of Physics, Chemistry, and Biochemistry, The Ohio State University, Columbus, OH 43210*.

Protein hydration dynamics are of fundamental importance to its structure and function. Here, we characterize the global solvation dynamics and anisotropy dynamics around the apomyoglobin surface in different conformational states (native and molten globule) by measuring the Stokes shift and anisotropy decay of tryptophan with femtosecond-resolved fluorescence upconversion. With site-directed mutagenesis, we designed sixteen mutants with one tryptophan in each, and placed the probe at a desirable position ranging from buried in the protein core to fully solvent-exposed on the protein surface. In all protein sites studied, two distinct solvation relaxations (1-8 ps and 20-200 ps) were observed, reflecting the initial collective water relaxation and subsequent hydrogen-bond network restructuring, respectively, and both are strongly correlated with protein's local structures and chemical properties. The hydration dynamics of the mutants in molten globule state are faster than those observed in native state, indicating that the protein becomes more flexible and less structured when its conformation is converted from fully-folded native state to partially-folded molten globule state. Complementary, fluorescence anisotropy dynamics of all mutants in native state show an increasing trend of wobbling times (40-260 ps) when the location of the probe is changed from a loop, to a lateral helix, and then, to the compact protein core. Such an increase in wobbling times is related to the local protein structural rigidity, which relates the interaction of water with side chains. The ultrafast hydration dynamics and related side-chain motion around the protein surface unravel the coupled water-protein fluctuations on the picosecond time scales and indicate that the local protein motions are slaved by hydrating water fluctuations.