## FEMTOSECOND CONICAL INTERSECTION DYNAMICS OF TRYPTOPHAN IN PROTEINS AND VALIDATION OF SLOWDOWN OF HYDRATION LAYER DYNAMICS

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Water motion probed by intrinsic tryptophan shows the significant slowdown around protein surfaces but it is unknown how the ultrafast internal conversion of two nearly degenerate states of Trp ( ${}^{1}L_{a}$  and  ${}^{1}L_{b}$ ) affects the initial hydration in proteins. Here, we used a mini-protein with ten different tryptophan locations one at a time through site-directed mutagenesis and extensively characterized the conversion dynamics of the two states. We observed all the conversion time scales in 40-80 fs by measurement of their anisotropy dynamics. This result is significant and shows no noticeable effect on the initial observed hydration dynamics and unambiguously validates the slowdown of hydration layer dynamics as shown here again in two mutant proteins.