A MOLECULAR DYNAMICS STUDY OF LYS-TRP-LYS: STRUCTURE AND DYNAMICS IN SOLUTION FOLLOWING PHOTOEXCITATION

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We report studies of the structure and dynamics of a tripeptide Lys-Trp-Lys (KWK) in aqueous solution following photoexcitation by molecular dynamics simulations. Each conformer is stabilized by a π-cation interaction between one of three protonated amino groups and the indole moiety. For the excited state of tryptophan in KWK, the simulated molecular dynamics of the three isomers are similar, all in good agreement with recent femtosecond experiments. Specifically, we observe (1) the fluorescence anisotropy is dominated by a single exponential component and decays in $\sim 130ps$; (2) the total dynamic Stokes shift reaches $\sim 2700cm^{-1}$; and (3) the excited state relaxation dynamics occurs on several time scales ranging from femtoseconds to tens of picoseconds. The water and protein dynamics are strongly correlated. On a still longer time scale, we observe isomerization of two excited state conformers to the other most stable one, an analog for evolution of trajectories along the funnel on the rugged free energy landscape to the final "native" state. Our studies suggest new experiments to detect this unique dynamics.