

SOLVENT DRIVEN COHERENT POPULATION TRANSFER IN TRYPTOPHAN

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The environment has a profound effect on the ultrafast photophysics of tryptophan due to radically different electronic nature of the lowest two singlets (La/Lb) which make up the first absorption band. In aqueous environment the polar La state becomes fluorescent. Therefore previous works have attributed the ultrafast dynamics to a sub-50fs Lb→La internal conversion followed by picosecond relaxation of solvent around the La-state.

We have investigated the primary photoinduced processes in solvated tryptophan by combining UV transient absorption spectroscopy with sub-30 fs temporal resolution and CASPT2/MM calculations and unveil a richer mechanism comprising of two population transfer events involving the La and Lb electronic state.

Our results reveal two consecutive coherent population transfer events involving the lowest two singlet states: a sub-50-fs nonadiabatic La →Lb through a conical intersection and a subsequent 220 fs reverse Lb→La due to solvent assisted adiabatic stabilization of La state. Vibrational fingerprints present in the transient spectra show compelling evidence of the vibronic coherence established between the two states from the earliest times after excitation and lasting till the back-transfer to La is complete.

I will present how the delayed response of solvent causes a dynamic inversion of the energetic order of the vibronically coupled states, which determines the direction of the population transfer.

