ULTRAFAST PUMP-PROBE XANES ANALYZED WITH FDMNES SIMULATIONS REVEAL THE SEQUENTIAL STRUCTURAL EVOLUTION OF ADENOSYLCOBALAMIN AS A FUNCTION OF SOLVENT

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Adenosylcobalamin (AdoCbl) is a highly light-sensitive member of the cobalamin family. It features a central cobalt coordinated to a corrin ring, a 5'-deoxyadenosyl upper ligand, and a dimethylbenzimidazole lower ligand. The photochemistry of AdoCbl is important due to its central role as the chromophore in the CarH gene regulatory photoreceptor found in various bacterial species. Time-resolved X-ray absorption near-edge structure (XANES) examines the excited states of AdoCbl through the lens of atomic structural change from the central cobalt's perspective. The use of polarization selection deconvolves the changes into orthogonal molecule-defined directions, yielding more specific structural information instrumental in a thorough analysis with higher confidence. Extensive time-resolved XANES data have been collected on AdoCbl in both water and ethylene glycol solvent. To assign specific spectral features to structural changes in the AdoCbl, the XANES spectra are simulated and compared with the experimental difference spectra using the finite difference method near-edge structure (FDMNES) method. FDMNES allows for systematic investigation of the structural manipulations required to reproduce the experimental difference spectra. These simulations help to quantitatively uncover the sequential structural evolution of AdoCbl on an ultrafast timescale as a function of solvent, allowing for a better understanding of the fundamental relationship between this cofactor and its environment as well as the relationship between XANES spectral features and molecular structure in general.