Abstract Submitted
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The Influence of Environment on the Reactivity, Dynamics and Spectroscopy of B12 Coenzymes.[1] ROSEANNE SENSION, University of Michigan, D. AHMASI HARRIS, ELIZABETH CARROLL, ANDREW STICKRATH — Adenosylcobalamin (AdoCbl) dependent enzymes catalyze a variety of chemically difficult reactions that proceed by mechanisms involving organic radicals. In these enzymes radicals are initially generated by homolysis of the cobalt-carbon bond to produce an adenosyl radical and a cob(II)alamin radical. This radical pair may also be generated by optical excitation of the AdoCbl cofactor with visible light. In the work presented here, time-resolved spectroscopic measurements spanning the time range from 10 fs to 10 ns are used to investigate the energetics and dynamics of AdoCbl and other cobalamins as a function of environment. These studies probe the influence of environment on the energy of the low-lying charge transfer states of the cobalamin and on the barriers for dissociation and for recombination of the geminate radical pair. When the AdoCbl coenzyme is bound to the enzyme glutamate mutase, the protein environment is found to stabilize the charge transfer state of AdoCbl relative to observations in water and ethylene glycol. However, the intrinsic rate constant for recombination is only slightly smaller than the rate constant measured in free solution, suggesting the protein does not greatly perturb the ground state stability of the cobalt-carbon bond.

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