Abstract Submitted
for the MAR05 Meeting of
The American Physical Society

Picosecond Studies of Enzyme Mechanism in B12 Dependent Glutamase Mutase ROSEANNE SENSION, Departments of Chemistry and Physics, University of Michigan — Adenosylcobalamin-dependent (coenzyme B12, AdoCbl) enzymes catalyze a variety of chemically difficult reactions that proceed by mechanisms involving organic radicals. Radicals are initially generated by homolysis of the cobalt-carbon bond to generate an adenosyl radical and a cob(II)alamin radical. In the present study time-resolved spectroscopic measurements spanning the time range from 10 fs to 10 ns are used to investigate the kinetics of homolysis and recombination for adenosylcobalamin bound in the active site of glutamate mutase. These are the first such direct measurements on an adenosylcobalamin dependent enzyme. A short-lived intermediate is formed prior to formation of the cob(II)alamin radical. This intermediate was not observed upon photolysis of adenosylcobalamin in free solution. The intrinsic rate constant for geminate recombination for adenosylcobalamin bound to glutamate mutase is only slightly smaller than the rate constant measured in free solution, suggesting the protein does not greatly perturb the stability of the cobalt-carbon bond upon binding the coenzyme.

Roseanne Sension
Departments of Chemistry and Physics, University of Michigan

Date submitted: 01 Dec 2004 Electronic form version 1.4