S1-5

^{13}C and ^{57}Fe ENDOR of Nitrogenase: Can it Tell the Substrate-Binding Site in the Active Site?

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Nitrogenase, comprised of the MoFe and Fe proteins, catalyzes the reduction of dinitrogen to ammonia at ambient temperature and pressure. The MoFe protein contains two metal centers, the P-cluster (Fe8S7-8) and the FeMo-cofactor (Fe7S9:homocitrate), the substrate binding site. Despite the availability of the crystal structure of the MoFe protein, suprisingly little is known about the molecular details of catalysis at the active site, and no small-molecule substrate or inhibitor had ever been shown to directly interact with a protein-bound cluster of the functioning enzyme, until our electron-nuclear double resonance (ENDOR) study of CO-inhibited nitrogenase. Numerous models have been proposed for substrate binding to the FeMo-cofactor, but there is no direct evidence to support any of them, and the location and mechanism of substrate reduction remains one of the outstanding questions concerning nitrogenase function. One strategy employed to understand this mechanism is to study the interactions of nitrogenase with "nitrogen-like" molecules with C-C, C-S, C-N, and C-O multiple bonds. In this talk, the substrate-binding modes and sites at the FeMo-cofactor as studied by ENDOR of reaction intermediates of wild type and mutant nitrogenase that form under turnover conditions with C2H2, CS2, and CO are discussed.