The μ_4-Sulfide Bridged Tetranuclear Cu_Z Cluster of Nitrous Oxide Reductase : Electronic Structure and role in N_2O Reduction

Somdatta Ghosh, Serge I. Gorelsky, Peng Chen, Edward I. Solomon.

Department of Chemistry, Stanford University, Stanford, California 94305, U.S.A.

Nitrous oxide (N_2O) reduction is a chemical challenge both for selective oxidation of organic substrates and its removal as a green house gas. The reduction of N_2O is thermodynamically favorable but kinetically inert, and requires activating transition metal centers. In biological systems, N_2O reduction is the last step in the denitrification process of the bacterial nitrogen cycle and is accomplished by the enzyme nitrous oxide reductase, whose active site consists of a unique μ_4-sulfide bridged tetranuclear Cu_Z cluster which has many unusual spectroscopic features.

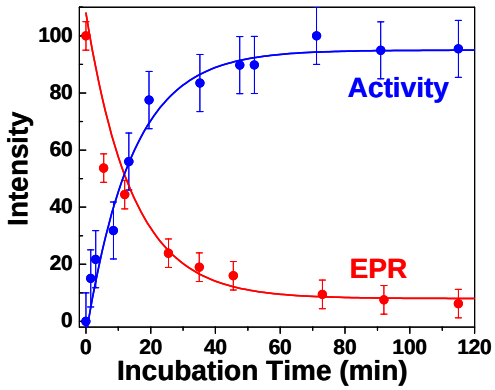
Recent studies have developed a detailed electronic structure description of the resting Cu_Z cluster by using low temperature UV-Vis, variable temperature variable field MCD, EPR, resonance Raman, and XAS techniques. The catalytically relevant form, involved in N_2O reduction, has been determined to be the all reduced $4Cu^I$ cluster, using EPR-enzyme activity correlation. DFT calculations provide insight into the role of this reduced tetranuclear Cu_Z cluster in the activation of N_2O for 2-electron reduction and the possible steps involved in the mechanism of N_2O reduction.

Acknowledgement: This research is supported by NIH DK- 31450. We acknowledge our collaborators Prof. I. Moura, Prof. J.J.G. Moura, and Prof. D. M. Dooley.

References:

1. Somdatta Ghosh, Serge I. Gorelsky, Peng Chen, Ines Cabrito, Jose J.G. Moura, Isabel Moura, and Edward I. Solomon. "Activation of N_2O Reduction by the Fully Reduced μ_4-Sulfide Bridged Tetranuclear Cu_z Cluster in Nitrous Oxide Reductase" J.Am. Chem. Soc. 125(2003):15708.
2. Peng Chen, Serge I. Gorelsky, Somdatta Ghosh and Edward I. Solomon. "N_2O Reduction by the μ_4-Sulfide Bridged Tetranuclear Cu_z Cluster Active Site" Angew. Chem. Int. Ed. 43(2004): 4132.

EPR-Activity Correlation



Geometry optimized DFT