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V-Nitrogenase reduction of carbon monoxide: A multiscale computational investigation

Nitrogenases are enzymes that reduce atmospheric nitrogen (N2) into bioavailable ammonia (NH3), thereby facilitaIng the nitrogen cycle and enabling life on Earth [1,2]. Nitrogenases can be divided into three main classes based on the idenIty of the heteroatom in the acIve site: molybdenum nitrogenase (Mo-nitrogenase), vanadium nitrogenase (V-nitrogenase), and iron- only nitrogenase (Fe-nitrogenase) [3,4]. Mo-nitrogenase, the most acIve and extensively studied among the three classes, has provided valuable insights into nitrogen fixaIon[5]. However, recent aWenIon has shiXed towards V-nitrogenase due to its remarkable ability to bind carbon monoxide (CO) in its resIng state and reduce CO predominantly to ethylene under turnover condiIons [6,7]. The availability of (recent) high-resoluIon (˜1Å) X-ray structures of V-nitrogenase provides an excellent starIng point for computaIonal invesIgaIons [8,9]. Here, we employ a hybrid quantum mechanical (QM)/molecular mechanical (MM) approach combined with the Broken Symmetry [10] method to invesIgate the electronic and magneIc properIes that facilitate CO binding to the resIng state of V- nitrogenase. Understanding enzymaIc CO capture and reducIon informs the design of new enzymes with great biotechnological potenIal. [1] Wilson, P. W.; Burris, R. H. The mechanism of biological nitrogen fixation. Bacteriological Reviews 1947, 11 (1), 41–73. [2] Burgess, B. K.; Lowe, D. J. Mechanism of Molybdenum Nitrogenase. Chem. Rev. 1996, 96 (7), 2983–3012. [3] HoVman, B. M.; Lukoyanov, D.; Yang, Z.-Y.; Dean, D. R.; Seefeldt, L. C. Mechanism of Nitrogen Fixation by Nitrogenase: The Next Stage. Chem. Rev. 2014, 114 (8), 4041–4062. [4] Jasniewski, A. J.; Lee, C. C.; Ribbe, M. W.; Hu, Y. Reactivity, Mechanism, and Assembly of the Alternative Nitrogenases. Chem. Rev. 2020, 120 (12), 5107–5157. [5] Burgess, B. K. The Iron-Molybdenum Cofactor of Nitrogenase. Chem. Rev. 1990, 90 (8), 1377–1406. [6] Lee, C. C.; Hu, Y.; Ribbe, M. W. Vanadium Nitrogenase Reduces CO. Science 2010, 329 (5992), 642–642. [7] Hu, Y.; Lee, C. C.; Ribbe, M. W. Extending the Carbon Chain: Hydrocarbon Formation Catalyzed by Vanadium/Molybdenum Nitrogenases. Science 2011, 333 (6043), 753–755. [8] Rohde, M.; Laun, K.; Zebger, I.; Stripp, S. T.; Einsle, O. Two Ligand-Binding Sites in CO-Reducing V Nitrogenase Reveal a General Mechanistic Principle. Science Advances 2021, 7 (22). [9] Rohde, M.; Grunau, K.; Einsle, O. CO Binding to the FeV Cofactor of CO-Reducing Vanadium Nitrogenase at Atomic Resolution. Angew. Chem. Int. Ed. 2020, 59 (52), 23626–23630. [10] Lovell, T.; Li, J.; Liu, T.; Case, D. A.; Noodleman, L. FeMo Cofactor of Nitrogenase: A Density Functional Study of States MN, MOX, MR, and MI. J. Am. Chem. Soc. 2001, 123 (49), 12392–12410.

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