

Spectroscopic and Computational Analysis of Nitrogenase's Homocitrate and NMF

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Although the first crystallographic structure of nitrogenase was published well over a decade ago, its mechanism of catalysis is still unclear. The active site of nitrogenase – FeMoco – is a $\text{MoFe}_7\text{S}_9\text{X}$ structure, which incorporates homocitrate as a bidentate ligand to the Mo (figure 1). Homocitrate's role is uncertain. Structural variations of the cofactors exist, with the molybdenum being replaced with vanadium or iron, yet the presence of homocitrate is apparently unaffected. Similarly replacement of the homocitrate with similar citrates in the NifV variant enzyme significantly reduces activity[1]. Removal of homocitrate hinders all nitrogen fixation[2].

To provide a better understanding of the role of homocitrate, we have been applying IR and resonance Raman from 100 to 1000 cm^{-1} to FeMoco extracted from the enzyme FeMoco into N-methyl formamide (NMF) and comparing these data with homocitrate and NMF measurements. With appropriate computational vibrational analysis these results are being integrated with referenced work to aid insight into nitrogenase's catalytic machinery.

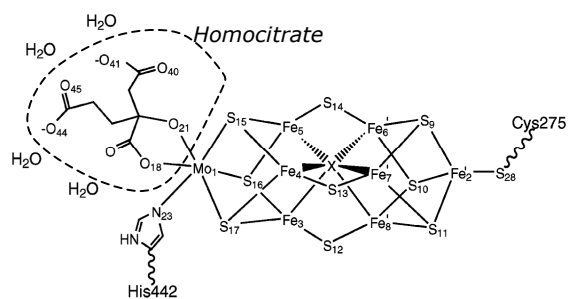


Figure 1 Structure of FeMoco ($\text{MoFe}_7\text{S}_9\text{Xhomocitrate}$)

[1] M. Madden, T. Paustian, P. Ludden, V Shah, Journal of Bacteriology, 173 (1991) 5403

[2] J. Kim, D. Wood, D. C. Rees, Biochemistry, 32 (1993) 7104.