Supporting Information for:

Orbital Contributions to CO oxidation in Mo-Cu Carbon Monoxide Dehydrogenase.

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Computational Details.

All calculations were performed with ADF2013.01[1] using the PBE functional[2, 3] and a triple-ζ basis set (TZP, small frozen core). Unless otherwise noted, all reported energies are Gibbs free energies and no atoms were held fixed. Nonpolar protein environment effects were modelled using the COSMO solvation model[4] (solvent: hexane). Reaction paths were mapped with the following procedure: an initial guess for the TS was located using linear transit calculations. The LT maximum was subjected to a frequency calculation followed by a TS search and subsequent frequency calculations to verify a saddle point. Finally, IRC calculations were used to ensure that the reaction minima connected appropriate reactants and products. NBO calculations were performed with the NBO 6.0 package[5] as integrated into ADF2013.01.

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2. M. Ernzerhof and G. E. Scuseria, *The Journal of Chemical Physics*, 1999, **110**, 5029-5036.
3. J. P. Perdew, K. Burke and M. Ernzerhof, *Physical review letters*, 1996, **77**, 3865-3868.
4. A. Klamt and G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2*, 1993, 799-805.
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Computational Energies.

Ethalpies

1-OH	-3900.9 kcal/mol
[1-OH]‡	-3890.1 kcal/mol
1-P	-3905.1 kcal/mol

$\Delta G^{\ddagger}$ (1-OH to 1-P) 12 kcal/mol

Ethalpies

1-OH_2	-4013.0 kcal/mol
[1-OH_2]‡	-3991.7 kcal/mol
1-P	-4020.1 kcal/mol