

Catalytic Features of the [FeFe] Hydrogenase H-Cluster from *C. pasteurianum*

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To identify distinguishing features of the canonical $[2\text{Fe}]_{\text{H}}$ H-cluster that could be potentially relevant to [FeFe] hydrogenase catalysis, the electronic structure of several configurational isomers and analogues was analyzed. Movement of the bridging carbonyl and anticorrelation of the proximal and distal Fe–C_{terminal} bonds are key explanatory factors for variance over the considered models. Charge and bond order analysis suggest that cluster reduction leads to more ionic bonding between the bridging carbonyl and the distal iron, raising the possibility of simple electrostatic stabilization as a factor in charge accumulation prior to ultimate H₂ creation and release. The *cis*- and *trans*-cyano configurations possess similar properties, which may enhance catalytic robustness. Some initial data on electron transfer between the proximal auxiliary $[4\text{Fe}-4\text{S}]$ and the $[6\text{Fe}-4\text{S}]_{\text{H}}$ cluster will also be presented.