Mechanism of Electrocatalytic Hydrogen Production by a Di-Iron Model of Iron-Iron Hydrogenase: A Density Functional Theory Study of Proton Dissociation Constants and Electrode Reduction Potentials

Panida Surawatanawong, Jesse W. Tye, Marcetta Y. Darensbourg, and Michael B. Hall*

Department of Chemistry, Texas A&M University, College Station, TX 77843-3255

Supporting Information

Standard state conversion[i]

To convert free energy from gas phase at 1 atm to solution phase at 1 M, we used the equation:

$$\Delta G^{o'} = \Delta G^{o} + RT\ln(\frac{Q^{o'}}{Q^{o}})$$

where Q is the reaction quotient, the ratio of concentrations that appear in the equilibrium constant. $\Delta G^{o'}$ and $Q^{o'}$ are defined for all species at 1 M and ΔG^{o} and Q^{o} are defined for all species at 1 atm. From ideal gas law, at 298.15 K and 1 atm the molar volume of a perfect gas is 22.47 L mol^{-1}. Assuming A, B, and C are ideal gases, their concentration at 1 atm are 1/22.47 M. For example: A + B → C, the reaction quotient Q is [C]/[A][B].

$$\Delta G^{o'} = \Delta G^{o} + RT\ln\left(\frac{\frac{1}{1\cdot 1}}{\frac{24.47\cdot 24.47}{24.47}}\right)$$

$$\Delta G^{o'} = \Delta G^{o} - RT\ln(24.47)$$

$$\Delta G^{o'} = \Delta G^{o} - 1.89 \qquad \text{kcal/mol at 298.15 K}$$

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[i] Cramer, C. J. *Essentials of Computational Chemistry: Theories and Models*; 2nd ed.; Wiley 2004.

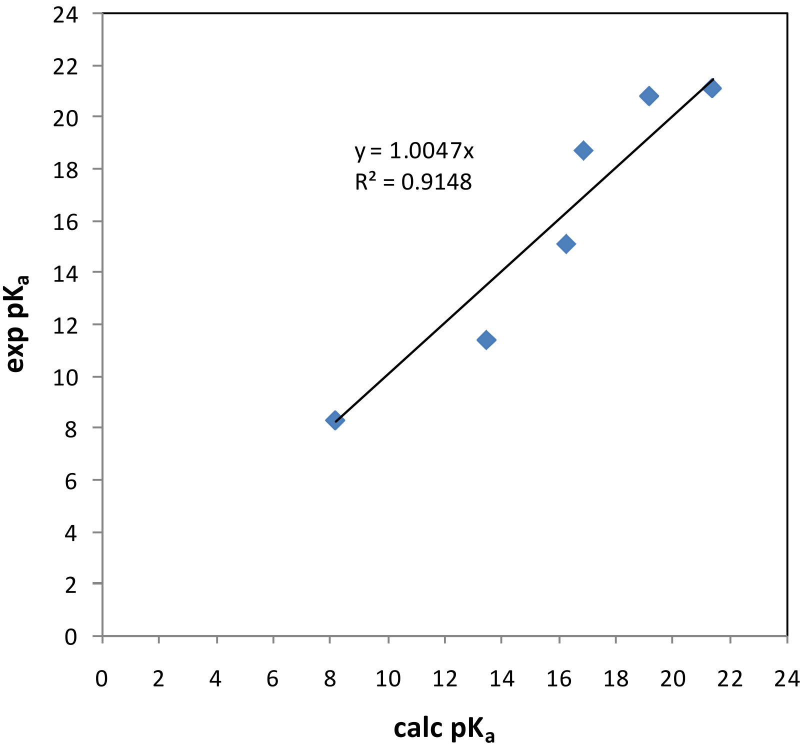


Figure S1. The plot of experimental pK_a of metal carbonyl hydride complexes, $Co(CO)_4H$ (8.3), $Fe(CO)_4H_2$ (11.4), $Mn(CO)_5H$ (15.1), $Ru(CO)_4H_2$ (18.7), $Os(CO)_4H_2$ (20.8), and $Re(CO)_5H$ (21.1), against the pK_a calculated by B3LYP/BS2//B3LYP/BS1. The proton solvation free energy used for the calculation of pK_a is -252 kcal/mol.

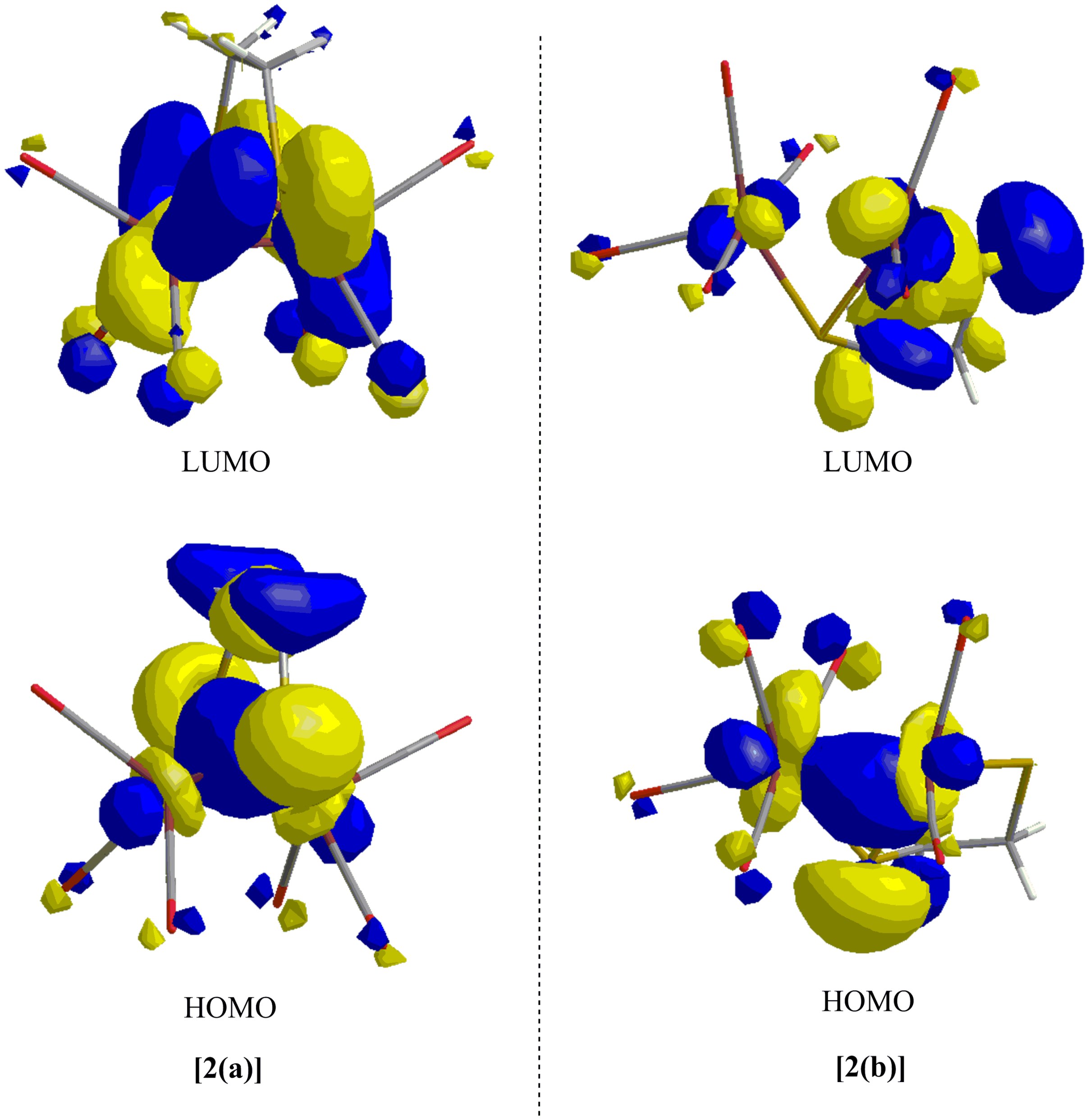
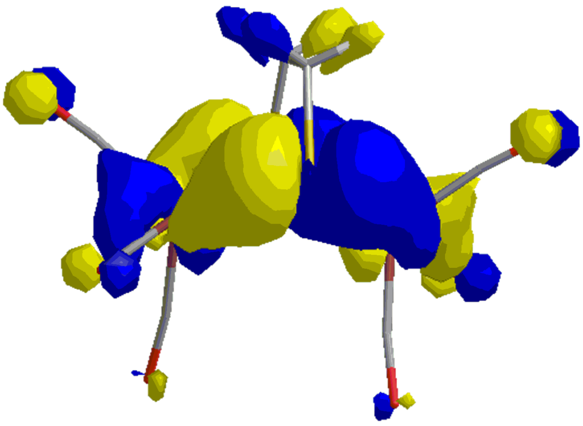


Figure S2. Frontier molecular orbitals of **[2(a)]** (left) and **[2(b)]** (right).



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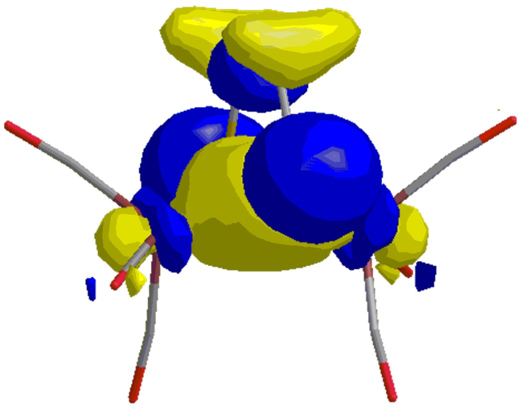

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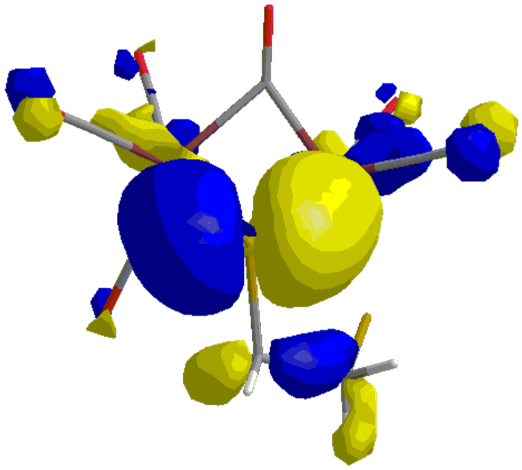
$[2(a)]^{2-}$



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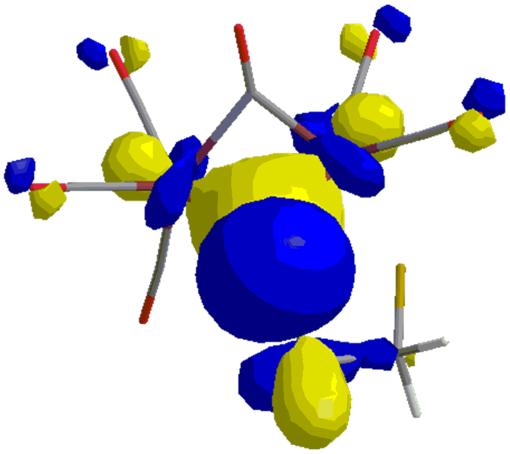

HOMO-1

$[2(b)]^{2-}$

Figure S3. Frontier molecular orbitals of **$[2(a)]^{2-}$** (left) and **$[2(b)]^{2-}$** (right).