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Computational Studies of Face-To-Face Porphyrin Catalyzed Oxygen Reduction

Rick Muller (rmuller@sandia.gov)

Sandia National Laboratories, Albuquerque, NM

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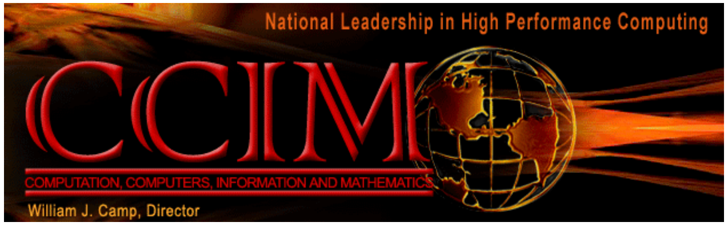
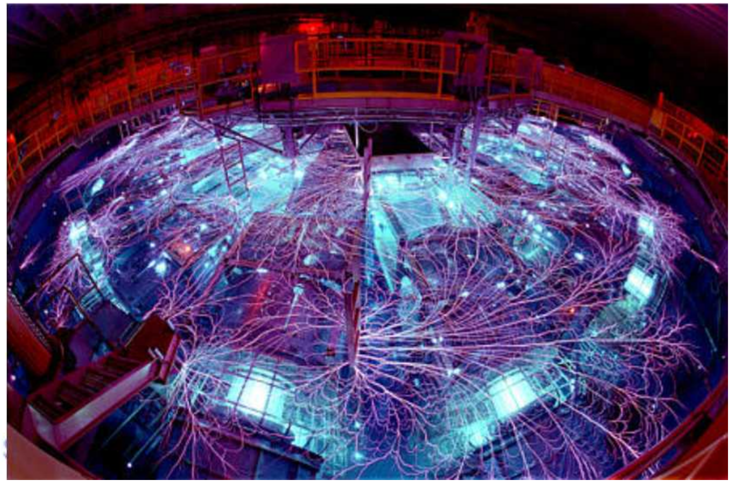
Abstract

We are investigating the use of face-to-face porphyrin (FTF) materials as potential oxygen reduction catalysts in fuel cells. The FTF materials were popularized by Anson and Collman , and have the interesting property that varying the spacing between the porphyrin rings changes the chemistry they catalyze from a two-electron reduction of oxygen to a four-electron reduction of oxygen. Our goal is to understand how changes in the structure of the FTF materials lead to either two-electron or four-electron reductions. This understand of the FTF catalysis is important because of the potential use of these materials as fuel cell electrocatalysts. Furthermore, the laccase family of enzymes, which has been proposed as an electrocatalytic enzyme in biofuel cell applications, also has family members that display either two-electron or four electron reduction of oxygen, and we believe that an understanding of the structure-function relationships in the FTF materials may lead to an understanding of the behavior of laccase and other enzymes. We will report the results of B3LYP density functional theory studies with implicit solvent models of the reduction of oxygen in several members of the cobalt FTF family.

Sandia, Computation, and Chemistry





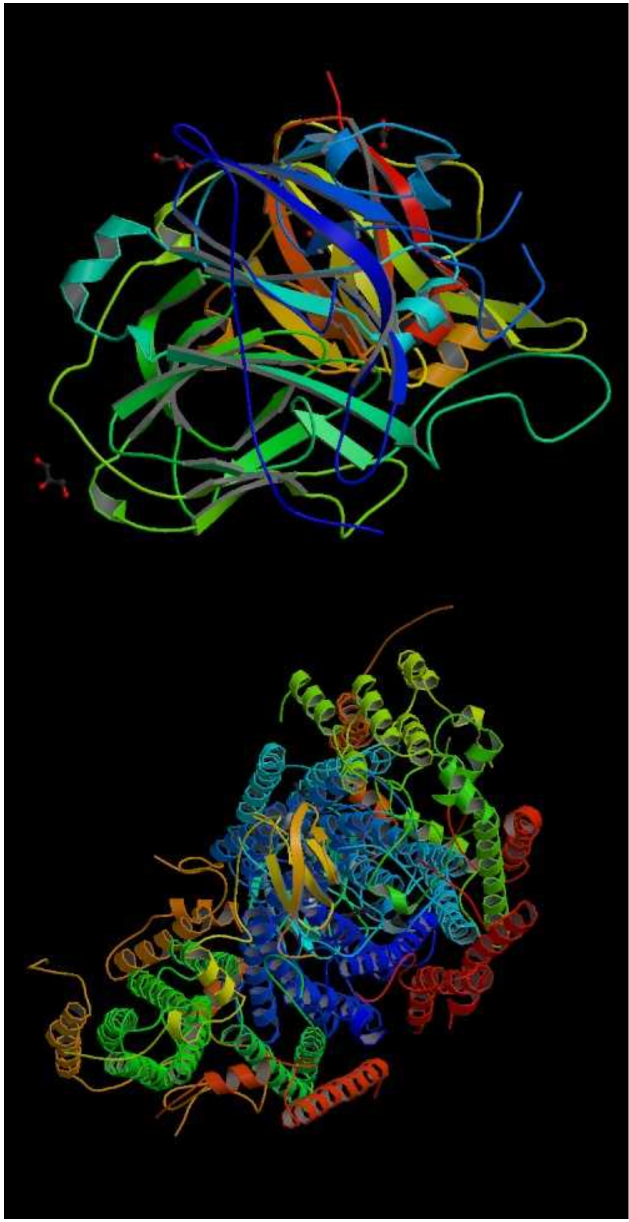
- Sandia National Laboratories, Computational Physics, Atomistic Simulation Techniques
- DFT Method Development
  - Make methods faster, more parallel
  - Make functionals more accurate
- Need difficult applications
  - What new methods do we need?
  - Organometallic chemistry
  - 50/50 split methods/apps

Sandia's Bio Micro Fuel Cell Program

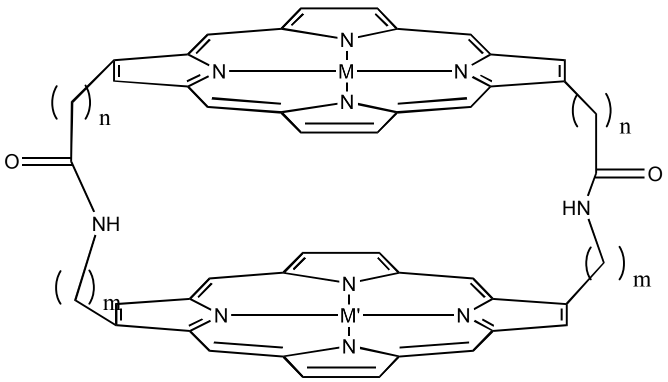
- Project at Sandia to use **glucose** instead of hydrogen or methanol to power PEM fuel cell.
- Harvest glucose from living plants.
- Use enzymes instead of Pt electrodes for catalysis
- *Bioinspired* catalysis: Can we extract a small portion of an enzyme and use this as an electrocatalyst?
- If so, how much/what to extract?

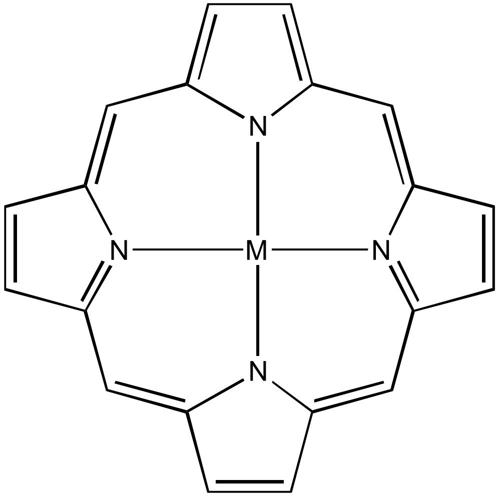
Laccase and Oxygen Reduction

- Goal: Improve the oxygen reduction catalyst in the biofuel cell.
  - Reduce amount of precious metals
  - Reduce overpotential and poisoning
- Laccase and Cyctochrome C Oxidase both reduce oxygen
  - 4 e-: $O_2 \rightarrow 2\ H_2O$ (fungal)
  - 2 e-: $O_2 \rightarrow H_2O_2$ (tree)
- Use modeling to understand how enzymes select between 2e and 4e pathways to build the preference for 4e processes into our catalysts



Anson-Collman Face-to-Face Porphyrins





- Cofacial porphyrins with varying spacing
- Spacing changed preference for 2e vs 4e oxygen reduction
  - Co_2FTF_4 (n=m=1, M=M'=Co) best for 4e reduction
  - Co_2FTF_3 (0,1), Co2FTF5 (1,2) show only 2e reductions
  - Monoporphyrin had high activity for 2e process, but low lifetime
- Can we use DFT to understand this chemistry?
- If we understand it, can we generalize to enzymes?

Methods

- Use high quality computational modeling to understand difference between 4e and 2e reductions in FTF4
- Quantum chemistry - Density functional theory
  - Hybrid gradient-corrected functional (B3LYP)
  - Gaussian basis set (6-31G**, LACVP on Co)
- Poisson-Boltzmann solvation method to represent water
- Jaguar program suite

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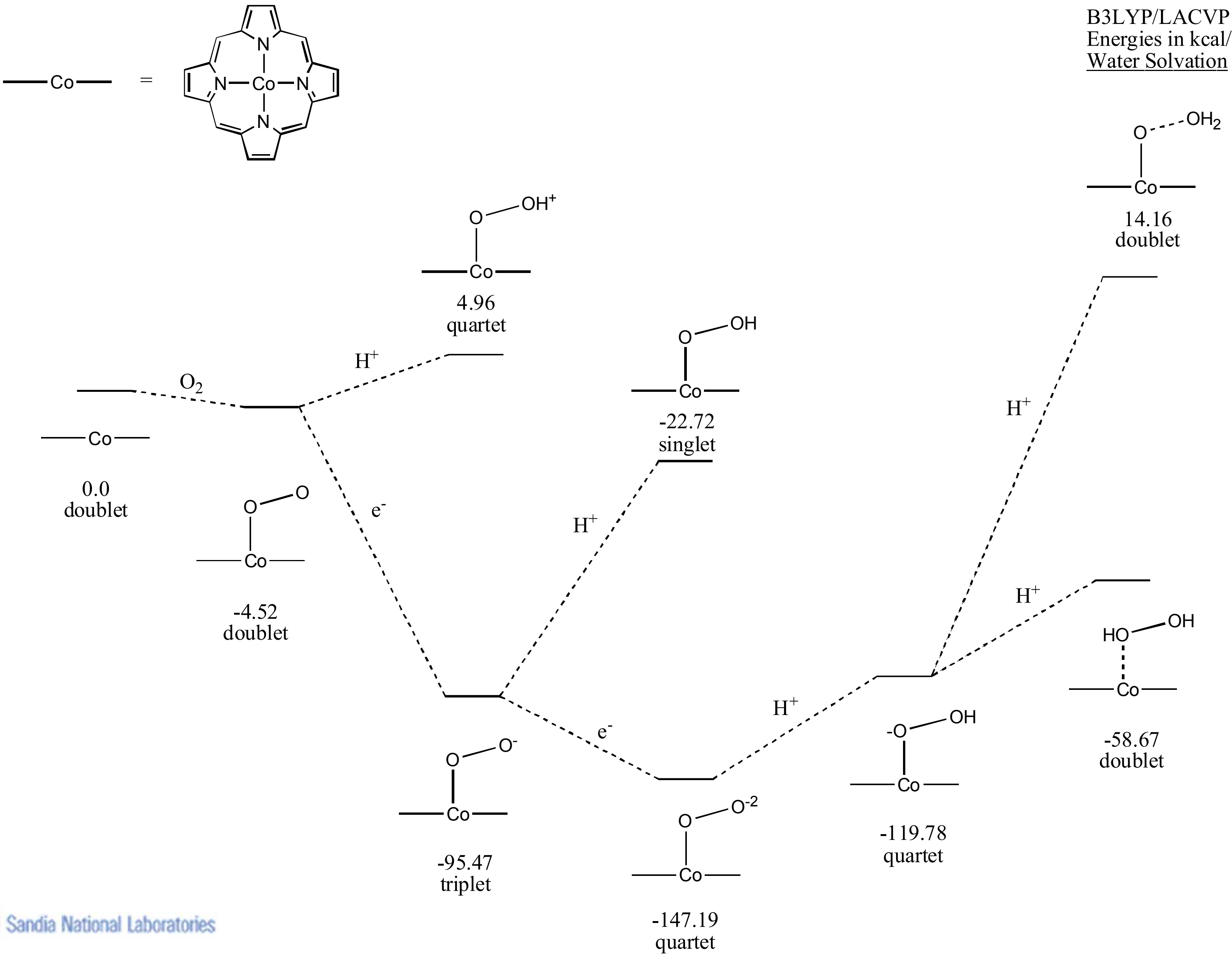
Monoporphyrin Chemistry (Solution)



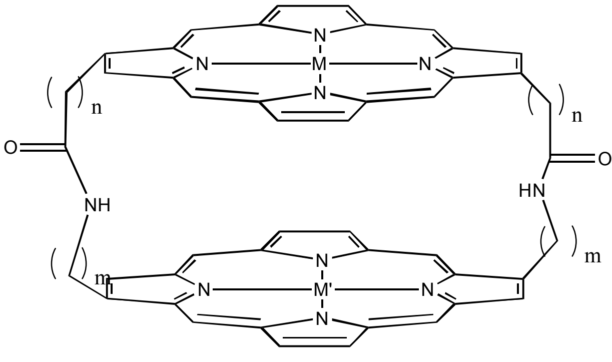
B3LYP/LACVP
Energies in kcal/mol
Water Solvation

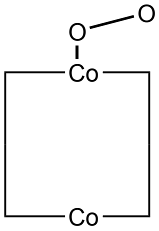
Monoporphyrin Results

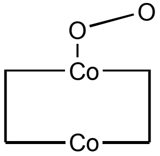
- Correctly conclude that 2e process results from monoporphyrin
- Experimental results shows that lifetime of monoporphyrin is very short
  - Can we look at a potentially caustic intermediate and show that it can dissociate?
  - Maybe HOOH is caustic enough…
- Don't currently know how to evaluate the cost of H^+/e^- in computing the enthalpy of formation
  - Currently approximate:
    - $\Delta H_f(e^-) = 0$ Open circuit voltage
    - $\Delta H_f(H_2) = 0$ Neutral pH
  - Need to use voltage, pH to adjust these values
    - Nice to be able to compute critical voltage, pH
    - $H_2 \rightarrow 2\ H^+ + 2\ e^-$

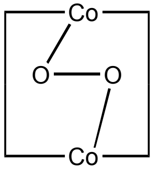
Ways to Bind O_2 to FTFs

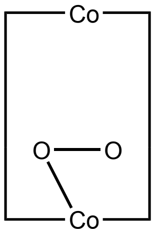
- *Outside* binding should lead to chemistry similar to the monoporphyrins
- *Inside* binding could lead to different chemistry
- The rings in *close FTFs* are too close to allow inside binding
- The rings in *far FTFs* are too far away to allow inside binding
- There may be an ideal spacing that allows good inside binding. The fact that FTF4 shows markedly different chemistry suggests that this may be that ideal distance





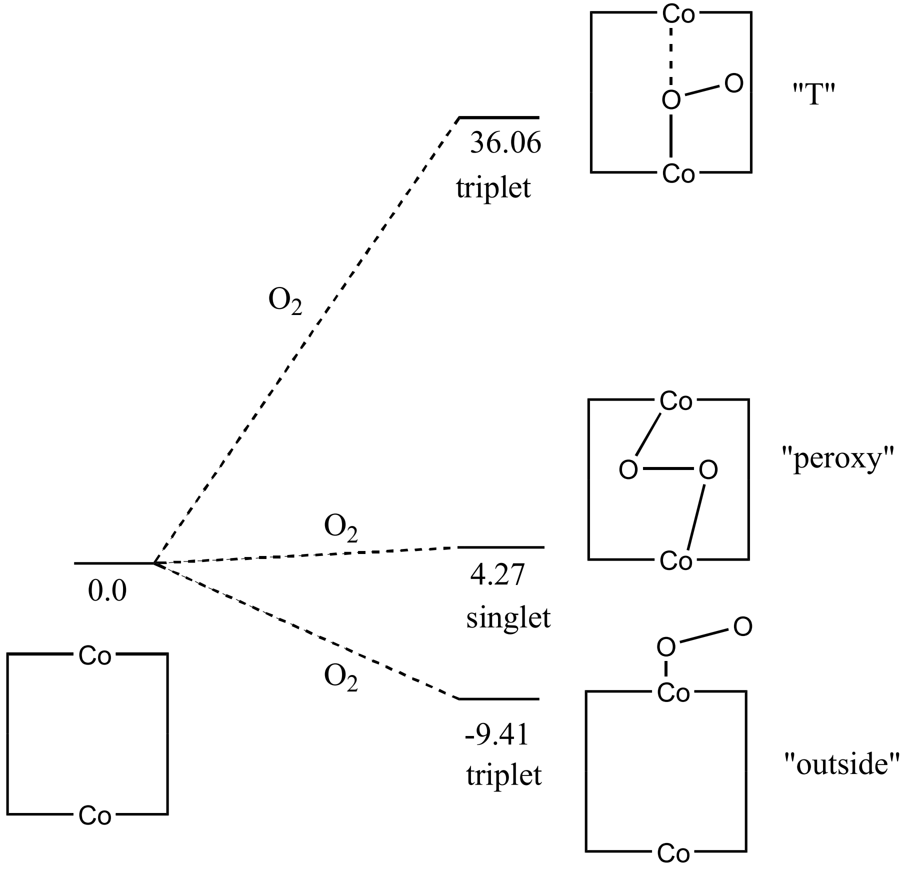






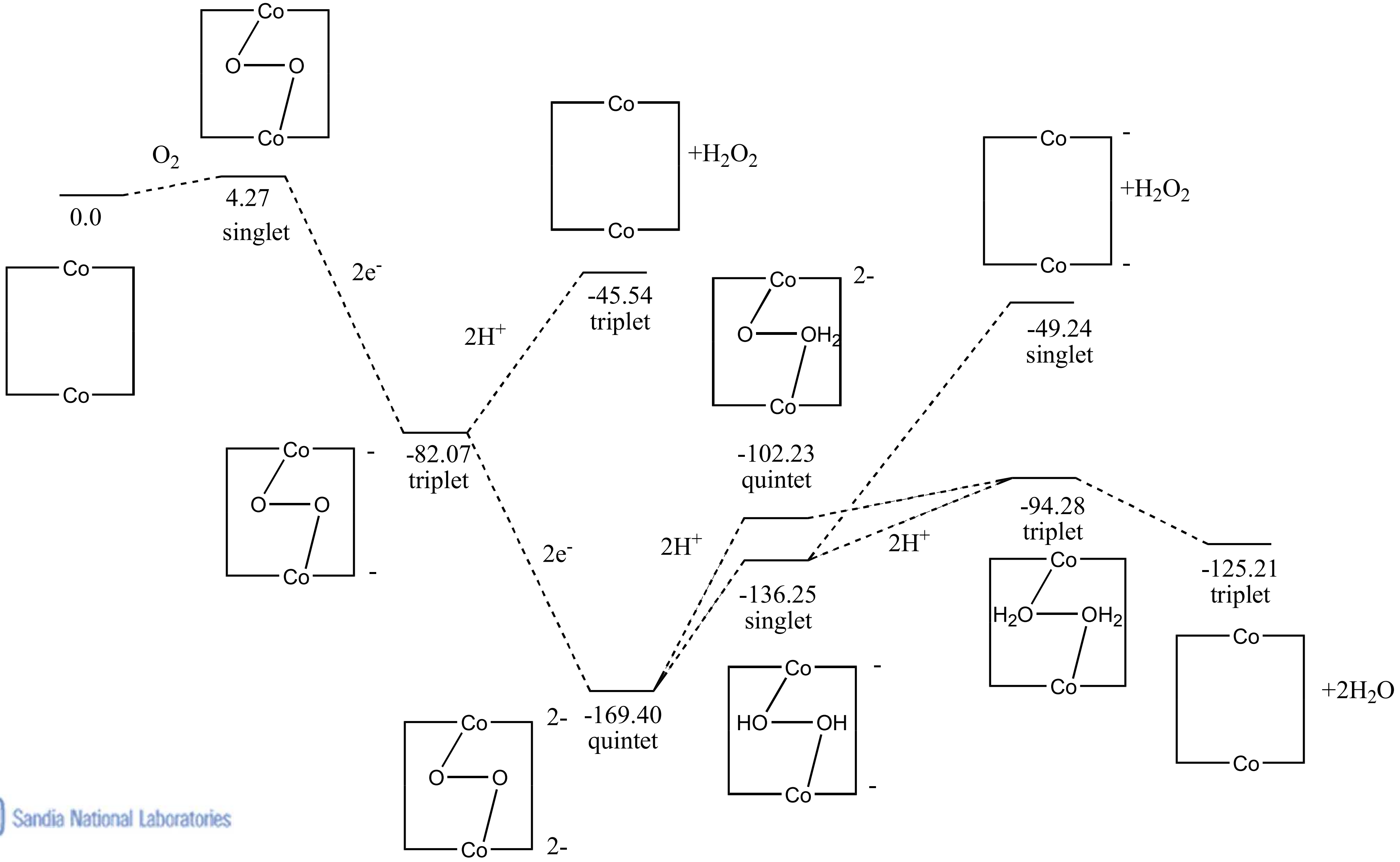
FTF4 O_2 Binding

B3LYP/LACVP
Water Solvent
Energy in kcal/mol



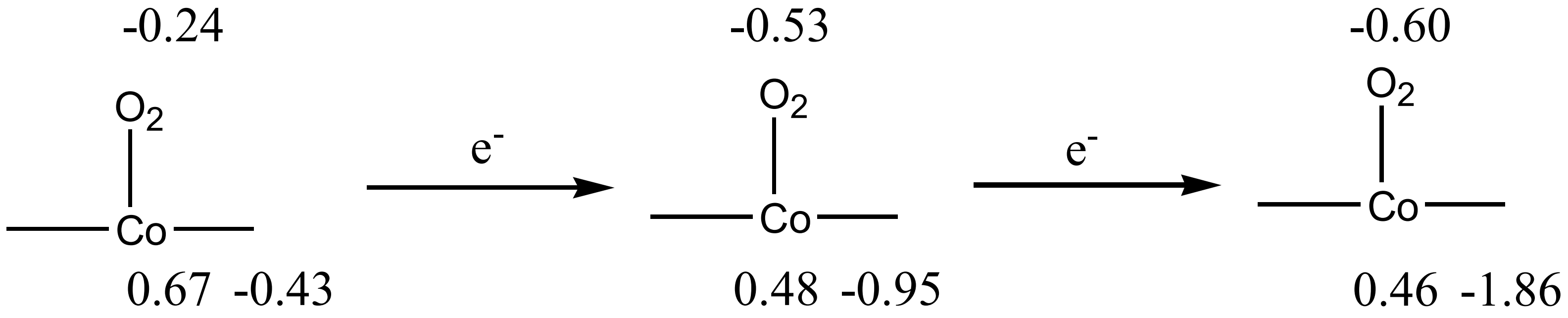
FTF4 O_2 Reductions

B3LYP/LACVP
Water Solvent
Energy in kcal/mol



Conclusions: Why Porphyrins Work

- Porphyrins can store charge without affecting substrate chemistry



- FTF4 can complex O_2 throughout reduction to keep H_2O_2 from dissociating after 2e reduction