## Scientific Challenges

## Enzymatic Reactions

- •CO photolysis in [FeFe]
- • $H_2$  oxidation in [NiFe]



Sterochemically simple but energetically difficul





## **Towards Biofuel Cells Design**



dley, Stewart, Ghosh, Kerkeni, Guo and co-workers Inorg Chem **47** 4753 (2008)

Molecules not undergoing photolysis relax more slowly to the ground state of the parent complex possibly because of the need to shed excess energy through vibrational cooling.



**3 proposed photoproducts** 

Ridley, Stewart, Ghosh, Kerkeni, Guo and co-workers Inorg Chem **47** 4753 (2008)

## Diagram of Reaction Scheme

•DFT: GGA-BP86/TZVP in vacuo and in heptane solution of global structure optimization and IR frequencies



dley, Stewart, Ghosh, Kerkeni, Guo and co-workers Inorg Chem **47** 4753 (2008)

•The IR studies provide insight into small cluster rearrangements that accompany oxidation state changes and CO inhibition.

•All fragments were only vibrationnally excited, and then rapid relaxation to the parent and photoproduct ground states.

•The computed spectra are in good agreement with the observed photoproducts and correspond to an axial-equatorial, equatorial-equatorial, and solvent adduct rearrangements, following carbonyl photolysis.

•The evidence of the 16 valence electrons photoproducts lay the groundwork for future studies of the reactivity of these active site models of the H2ase system.