Modeling Studies of Electron Transfer Processes in Photosynthesis

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PSII, Cyt b_6f, PSI

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FNR docking site

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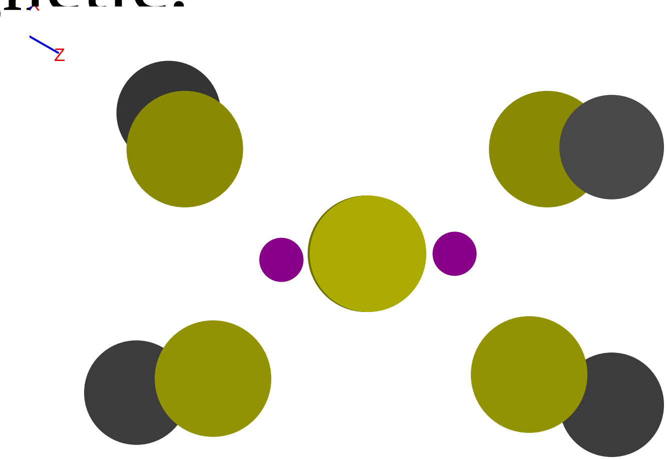
Ferredoxin as an electron shuttle

- $Fe_2S_2(SH)_4$ symmetric (D_{2h}) theoretical model.
- Oxidized form is $3d^5$ plus $3d^5$ anti - ferromagnetic.

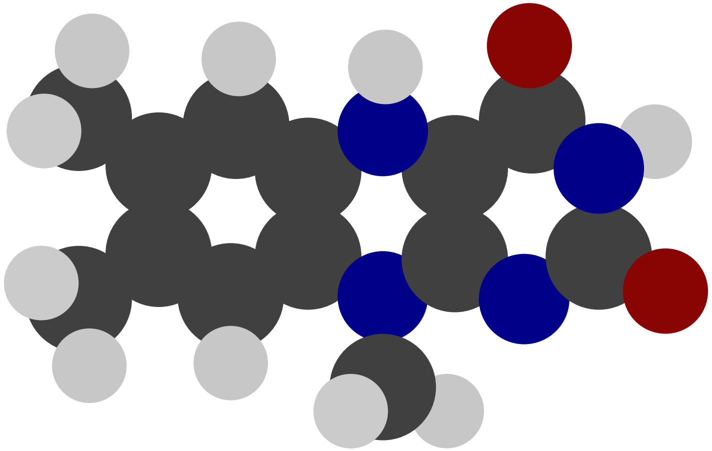


Energetic properties of ferredoxin

- Heisenberg Hamiltonian $E(S) = -J\ S(S+1)$
- J is -61 and -91 cm^{-1} for CASSCF and CI wavefunctions, respectively.
- EA 4.85 eV or -.25 eV with respect to SHE.
- Experimental EA -0.4 eV with respect to SHE.

FAD(flavin adenine dinucleotide)

- The receptor site for Fd-NADP$^+$ Reductase
- Reduction potentials: First 6.3 eV, Second 5.6 eV.



Electron Transfer Rate

- $K_{el} = \upsilon_{eff}\kappa_{el}\Gamma_n \exp(-E\dagger/k_B T)$
- $\kappa_{el} = 2P_0/(1 + P_0)$
- $P_0 = 1 - \exp(-2\pi\gamma)$
- $2\pi\gamma = H_{if}^2\pi^{3/2}/h\upsilon_{eff}[k_B T E_\lambda]^{1/2}$
- If $2\pi\gamma >> 1$ $k_{el} = 1$ (adiabatic)
- If $2\pi\gamma << 1$ k_{el} proportional to H_{if}^2 (diabatic) (present case)

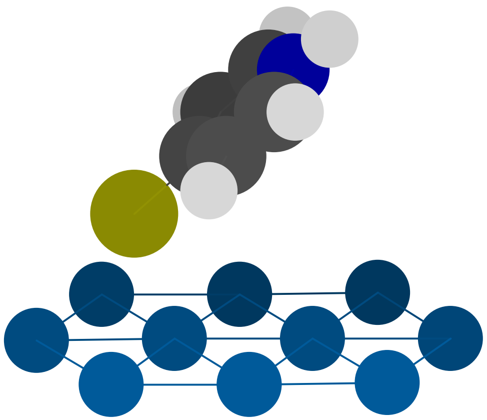
Methods

- TM atoms LANL2DZ + f, other atoms CC-pVDZ
- DFT for most calculations
- H_{ab} calculations use UHF based CIS method
- Assuming a 2X2 CI problem
- $H_{if} = 1/2\,[(\lambda_1 - \lambda_2)^2 - (H_{ii} - H_{ff})^2]^{1/2}$
- Fer-FAD has -1 charge on Fer and +1 charge on FAD. Need to correct for 1/R term.
- Similarly +1 charge is added 2 Angstrom behind Au cluster to increase Au cluster EA.

Comparison of H_{if}^2

- For Fer-FAD at 6 Angstrom (experiment) H_{if} is 0.6 eV
- For Fer-Au_{10} at 7 Angstrom (computed minimum) H_{if} is ~0.2 eV
- Expect lower H_{if} for larger Au cluster
- FNR > 9 X more efficient electron acceptor
- Orientation effects may also favor FNR

Au_{10}-S-$C_5H_4NH^+$



- Binding energy Au_{10}-S 1.3 eV
- EA 4.9 eV
- H_{if}^2 comparable to FAD
- Plus charged NH^+ group should orient $Fe_2S_2^-$ moiety.

Conclusions

- Au electrode is poorer electron acceptor than FNR
- $S\text{-}C_5H_4NH^+$ SAM has similar Electron acceptor properties to FAD

Diffusion Rates

- We use namd2 for MD simulations using CHARMM force field.
- We developed parameters for Fe_2S_2 and Cu of metal containing proteins and for plastoquinone.
- Steered Molecular Dynamics (SMD) method is used to calculate mobility.

Plastocyanin

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Plastoquinone

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Mobilities, $cm^2\ s^{-1}/kcal\ mol^{-1}$

Plastoquinone in lipid bilayer (POPC)	13.4×10^{-6}
Plastocyanin in water	0.68×10^{-6}
Ferredoxin in water	0.57×10^{-6}
O_2 in lipid/water	$340 \times 10^{-6}/140 \times 10^{-6}$