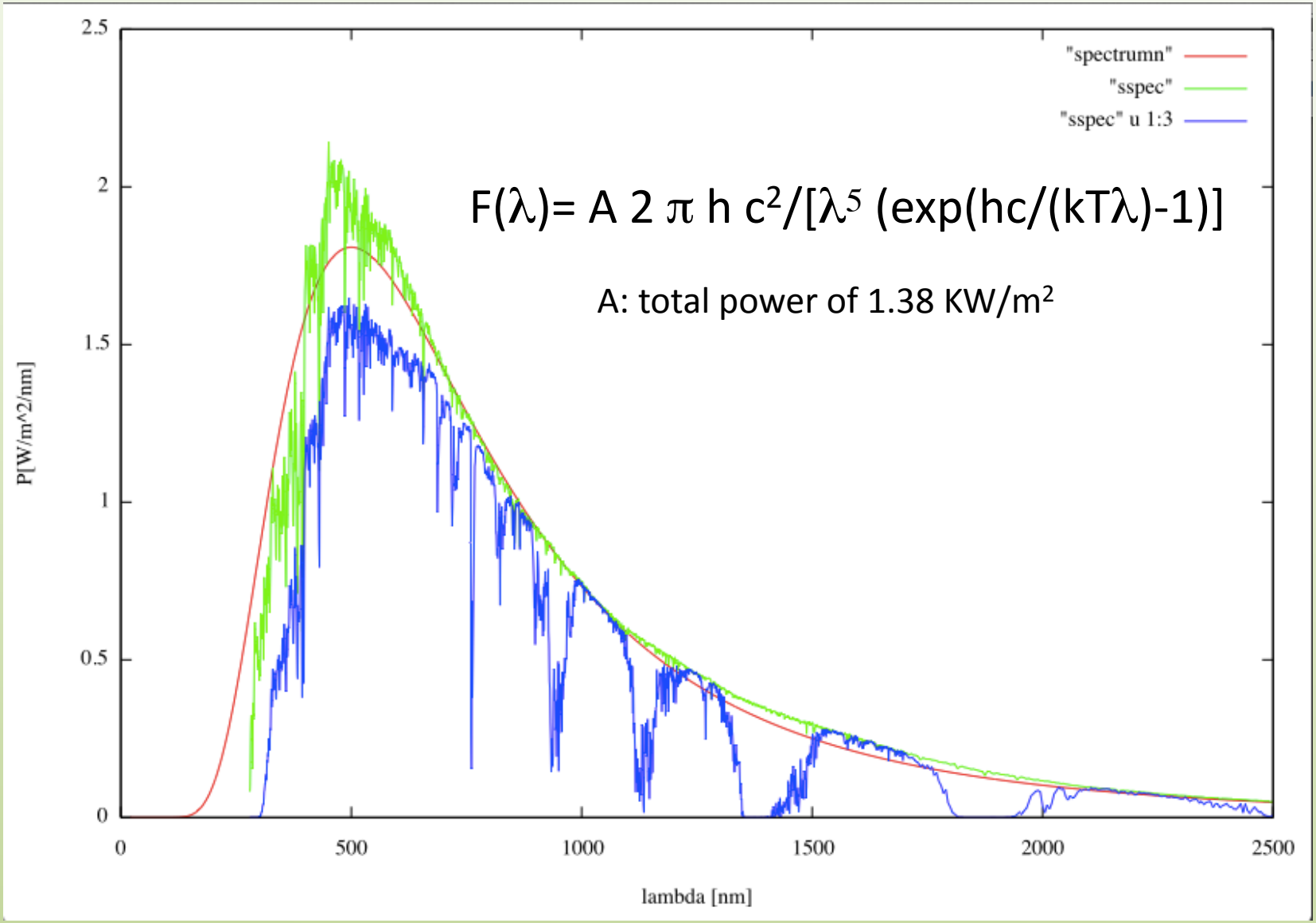
Solar Spectrum

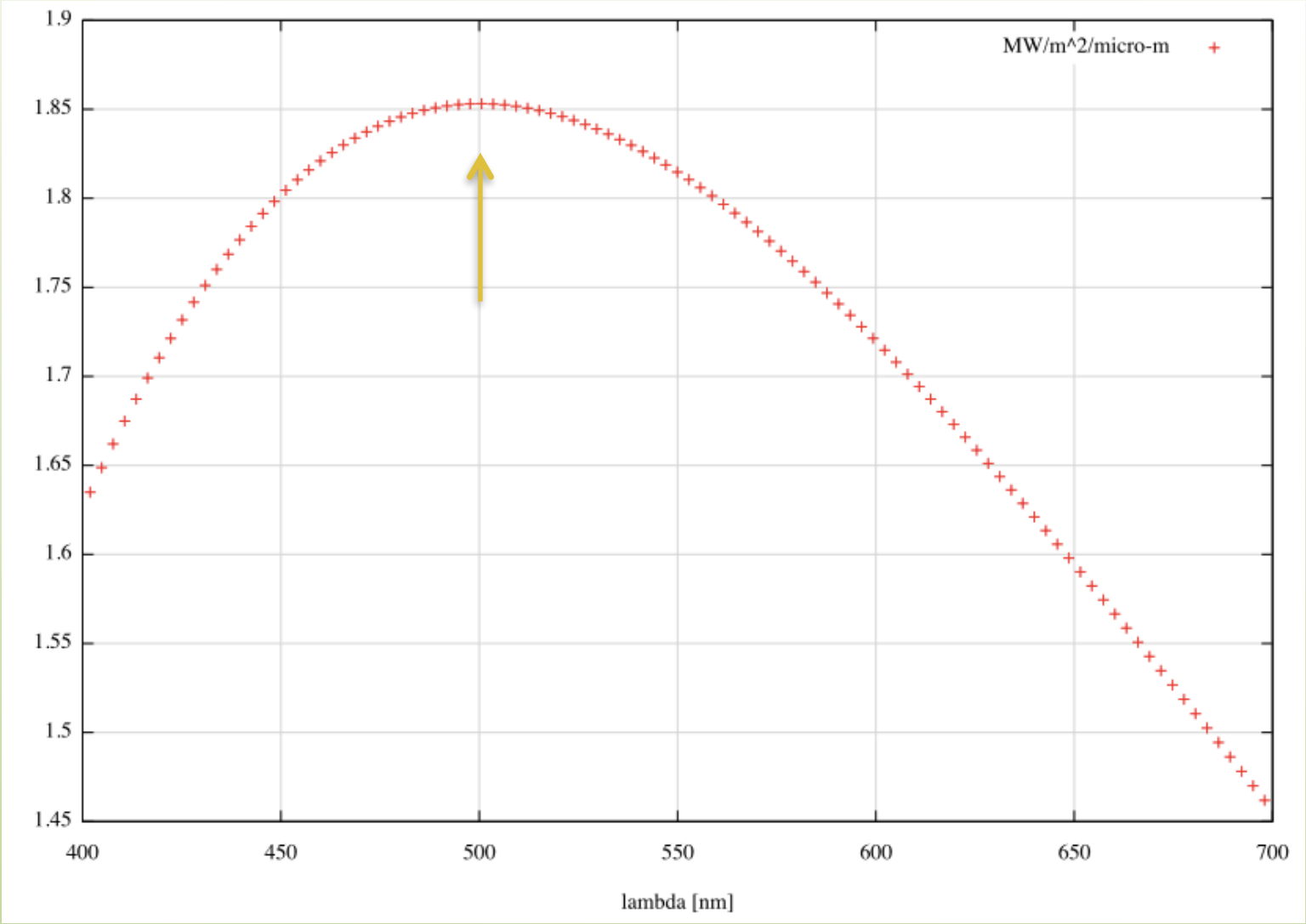
Black body Radiation at 5800 C



$F(\lambda) = A\ 2\ \pi\ h\ c^2/[\lambda^5\ (\exp(hc/(kT\lambda)-1)]$

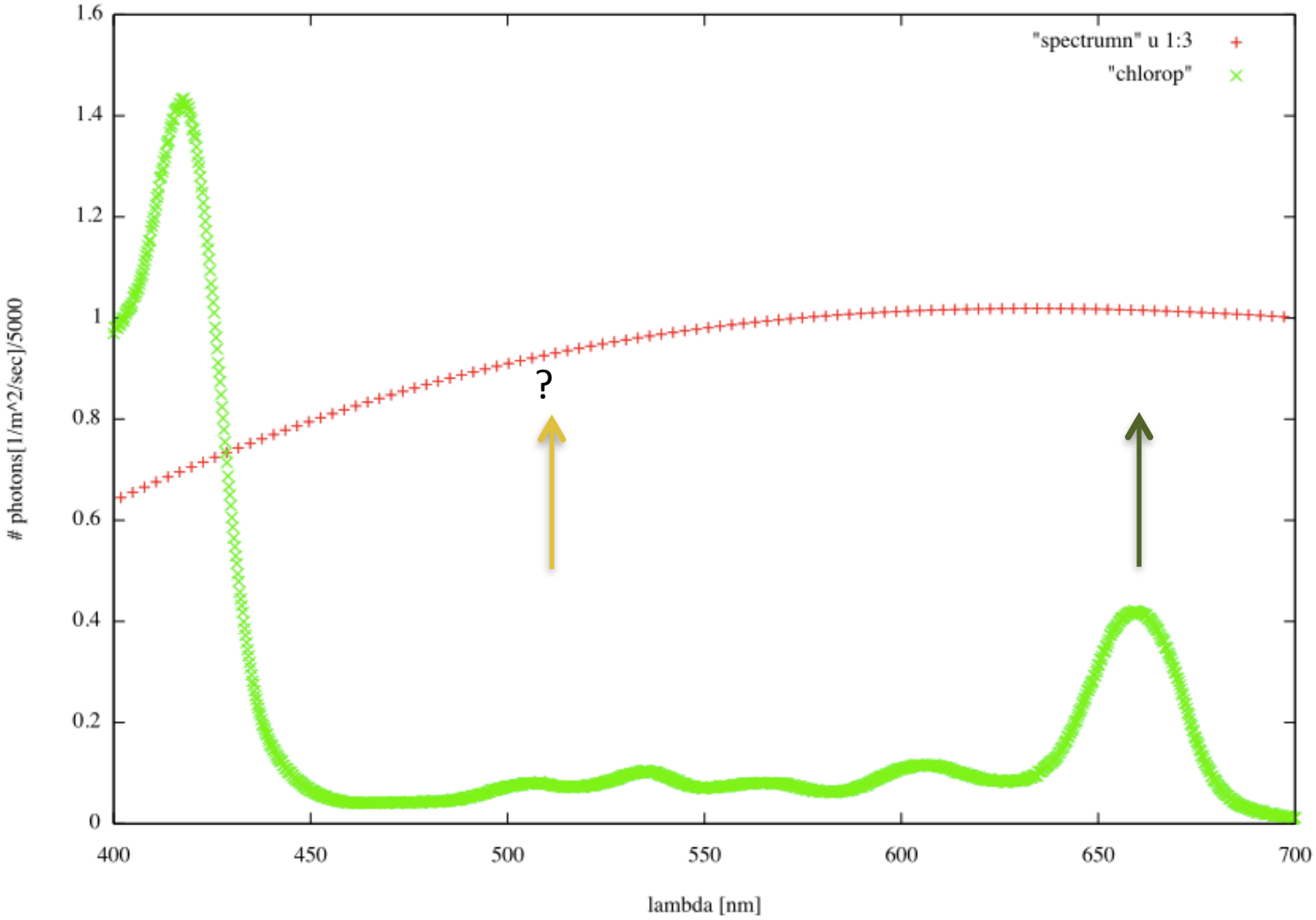
A: total power of 1.38 KW/m^2

Solar Spectrum: Maximum Intensity



Solar Spectrum: Maximum Photon Flux

Comparison to [Spectrum of Chlorophyll a]



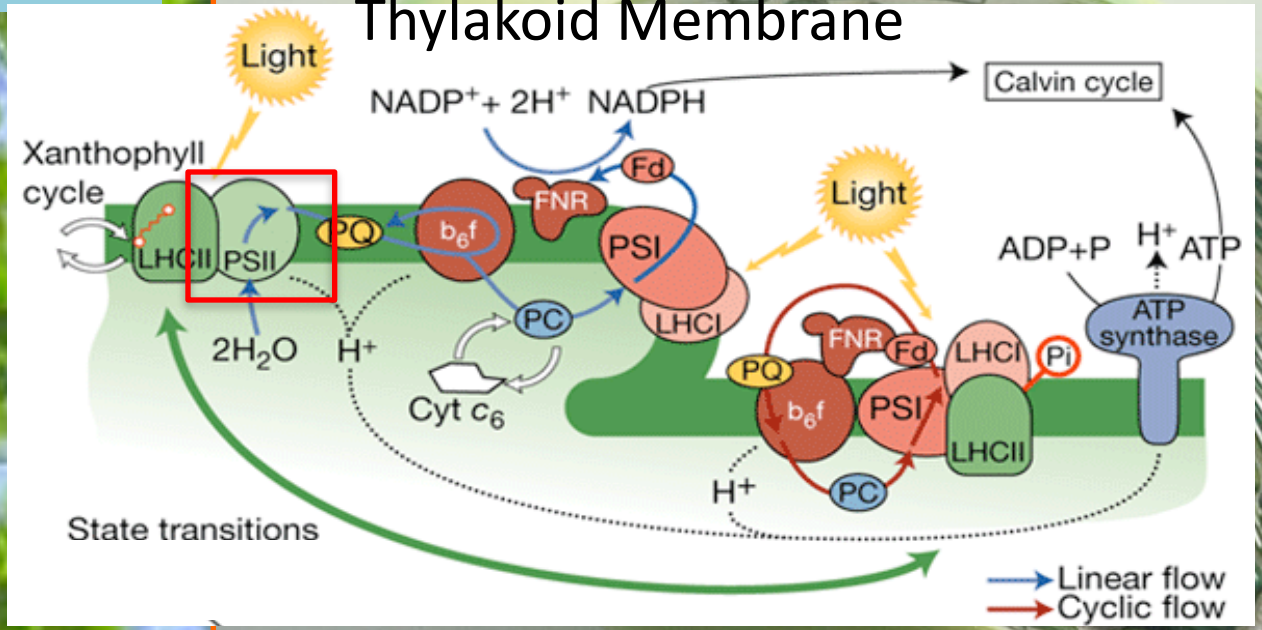
Flux of Solar Photons: Solution

```
      PROGRAM main
      IMPLICIT NONE
      DOUBLE PRECISION rd,rtot,F,rlmax,rlmin,dlambda
      DOUBLE PRECISION R,T,rc,rh,pie,rk,rl,rn,SB
      INTEGER i,J,npt
      npt=1000
      rlmax=3000.0E-9
      rlmin=20.00E-9
      dlambda=(rlmax-rlmin)/(npt-1.)
      rc=3.0E+08                ! Speed of light, m/sec
      rh=6.626E-34              ! Planck's constant, J sec
      pie=acos(-1.0)            ! pi
      rk=1.38E-23               ! Boltzmann constant, J K^{-1}
      T=5800.                   ! Sun Blackbody Temp, K
      SB=5.67E-8                ! Stefan-Boltzmann constant, W/m^2/K^4
      OPEN(1,FILE="spectrumn")
      DO i=1,npt
         rl=rlmin+(i-1)*dlambda
         rd=rl**5*(exp(rh*rc/(rk*rl*T))-1.)
         F=2.0*pie*rh*rc*rc/rd *1380./(SB*T**4) ! W/m^2/m  Blackbody radiation
         rtot=rtot+F*dlambda    ! W/m^2
         WRITE(1,22) rl*(1.0E+9),F*1.0E-9,F*1.0E-24/(rh*rc/rl)/5000. ! KW/m^2/micro-m, #phot/sec/nm^2/nm
      END DO
22    FORMAT(6(e13.6,2x))
      END
```

CELLS

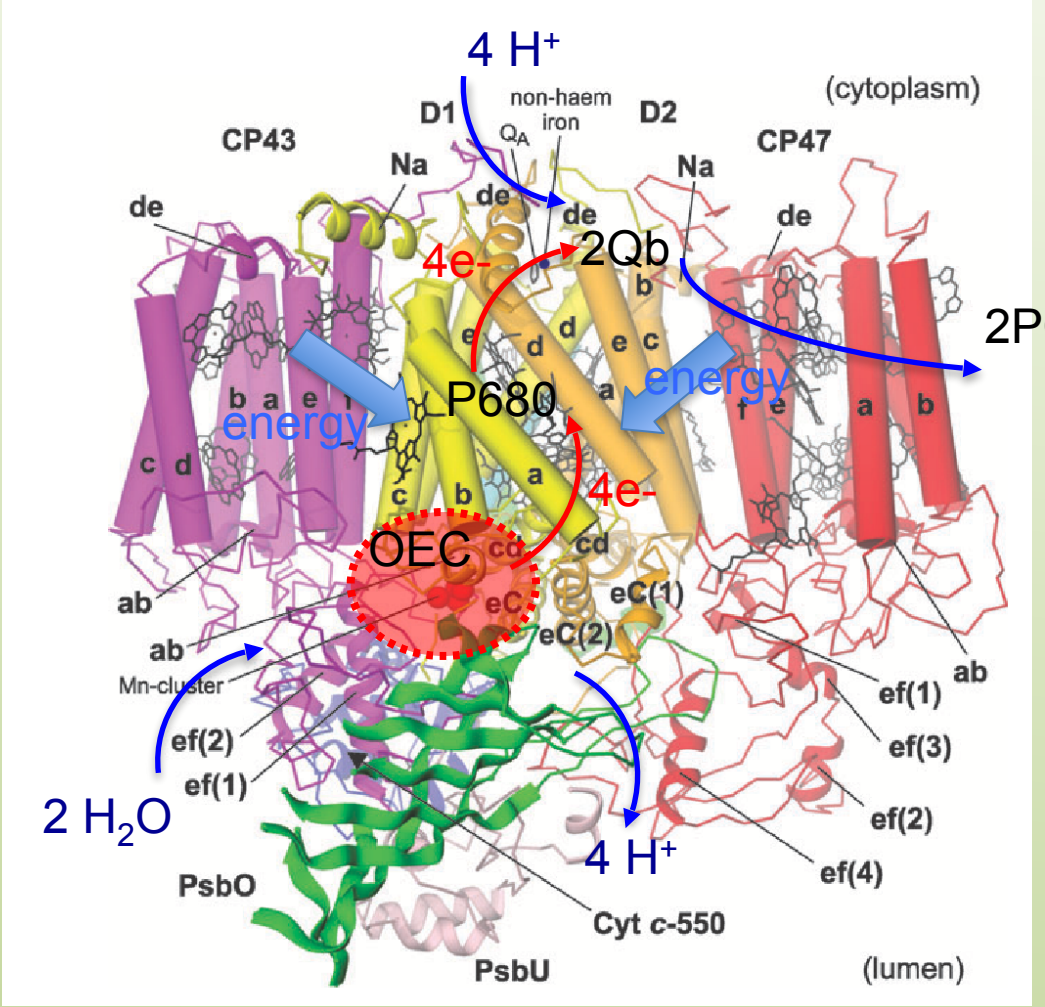
Chloroplast

Thylakoid Membrane

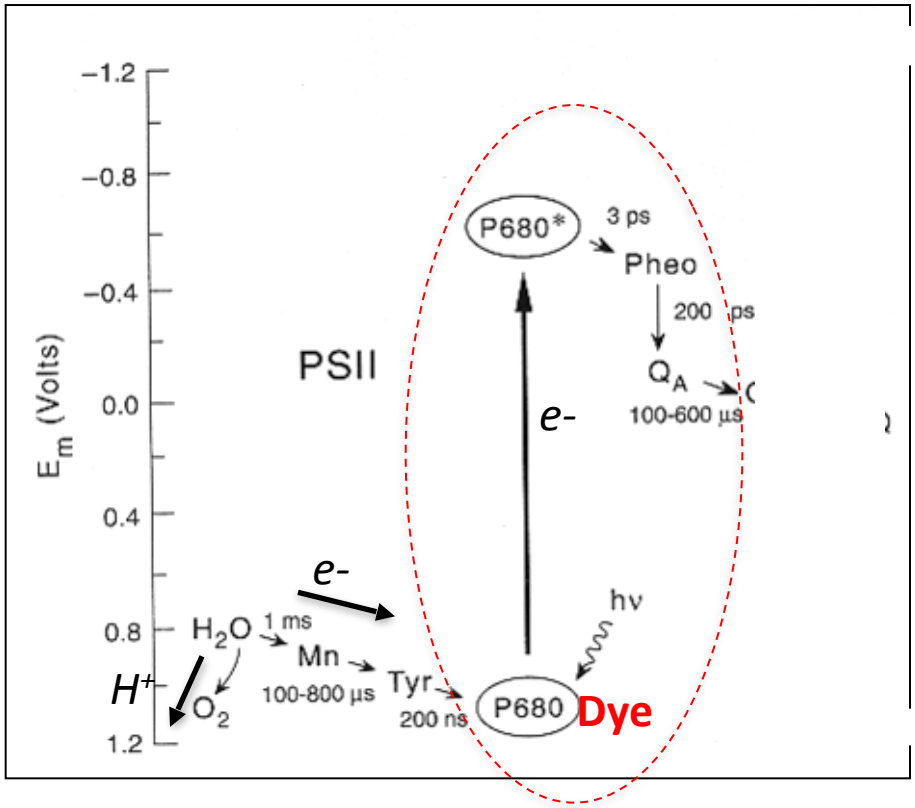


Breakthroughs in X-ray Diffraction Models of Photosystem II

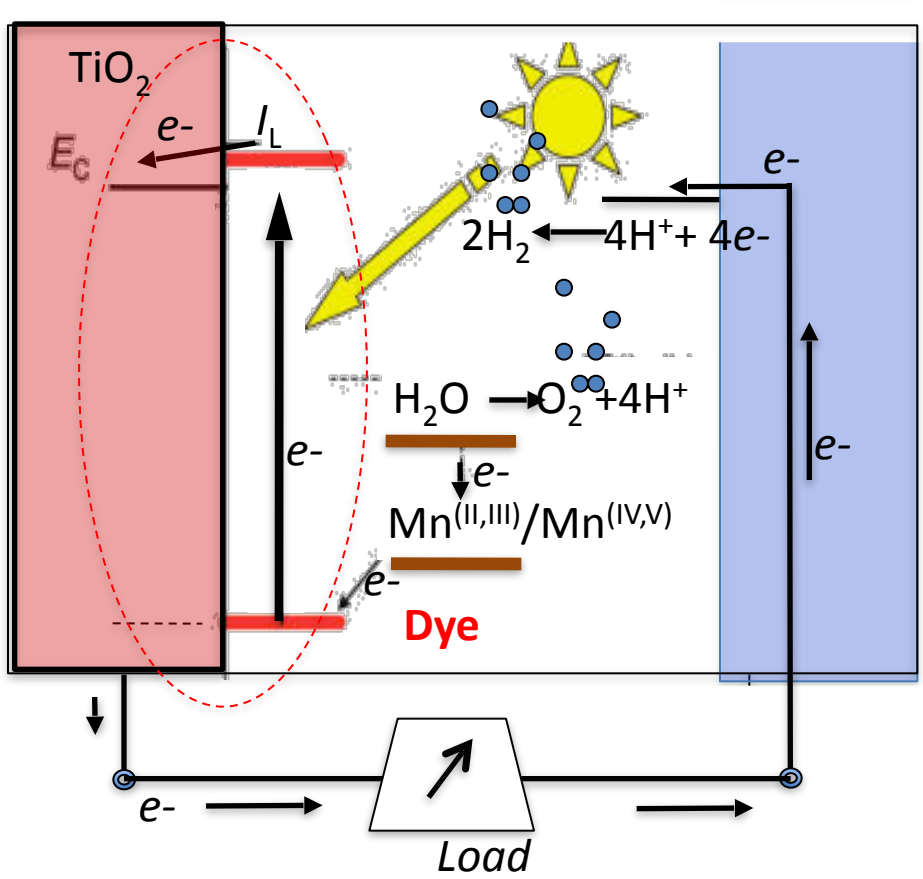
Ferreira, K. N. et al *Science* **2004**, *303*, 1831-1838. [3.5 Å resolution]
Biesiadka, J. et al *Phys. Chem. Chem. Phys.* **2004**, *6*, 4733-4736. [3.2 Å resolution]
Loll, B. et al *Nature* **2005**, *438*, 1040-1044 [3.0 Å resolution]
Guskov A, Kern J, Gabdulkhakov A, et al. *Nature Struct. & Mol. Biol.* **2009**, *16*, 334-342 [2.9 Å resolution]
Umena, Y., Kawakami, K., Shen, J.-R., and Kamiya, N. (2011) *Nature*, 473, 55-60 [1.9 Å resolution]



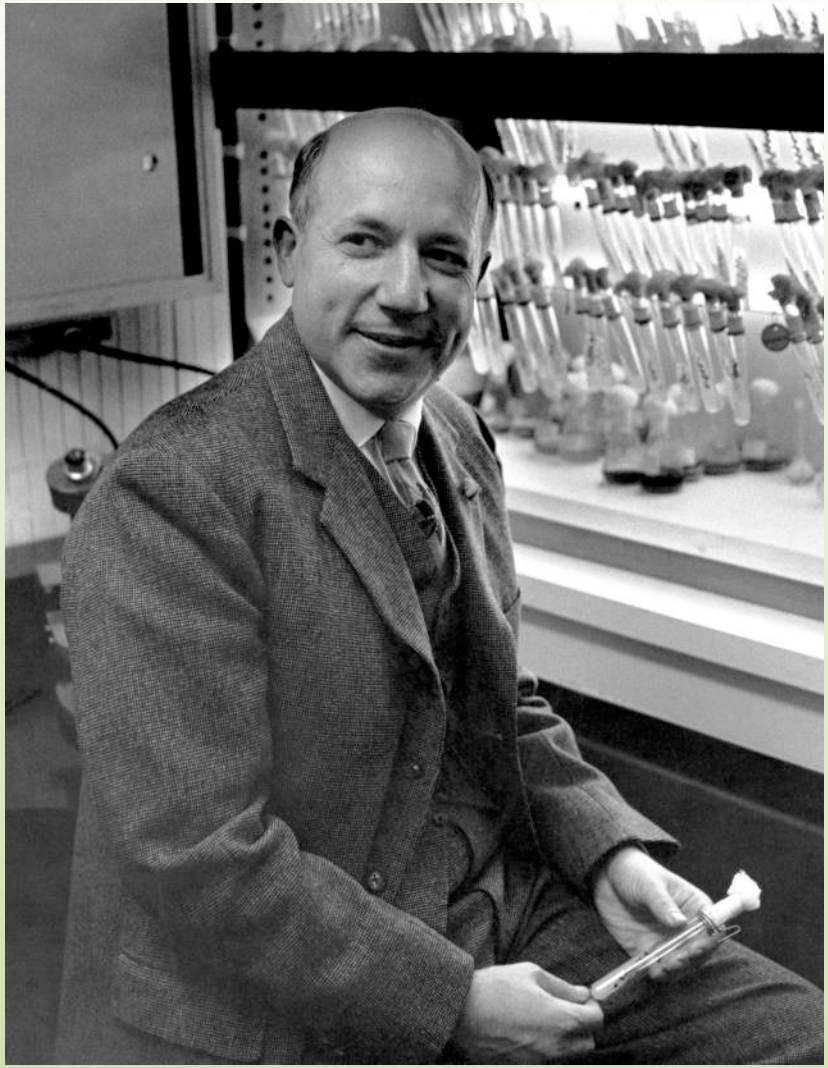
Natural Photosynthesis
PSII Energy Diagram



Artificial Photosynthesis
Dye Sensitized Solar Cell



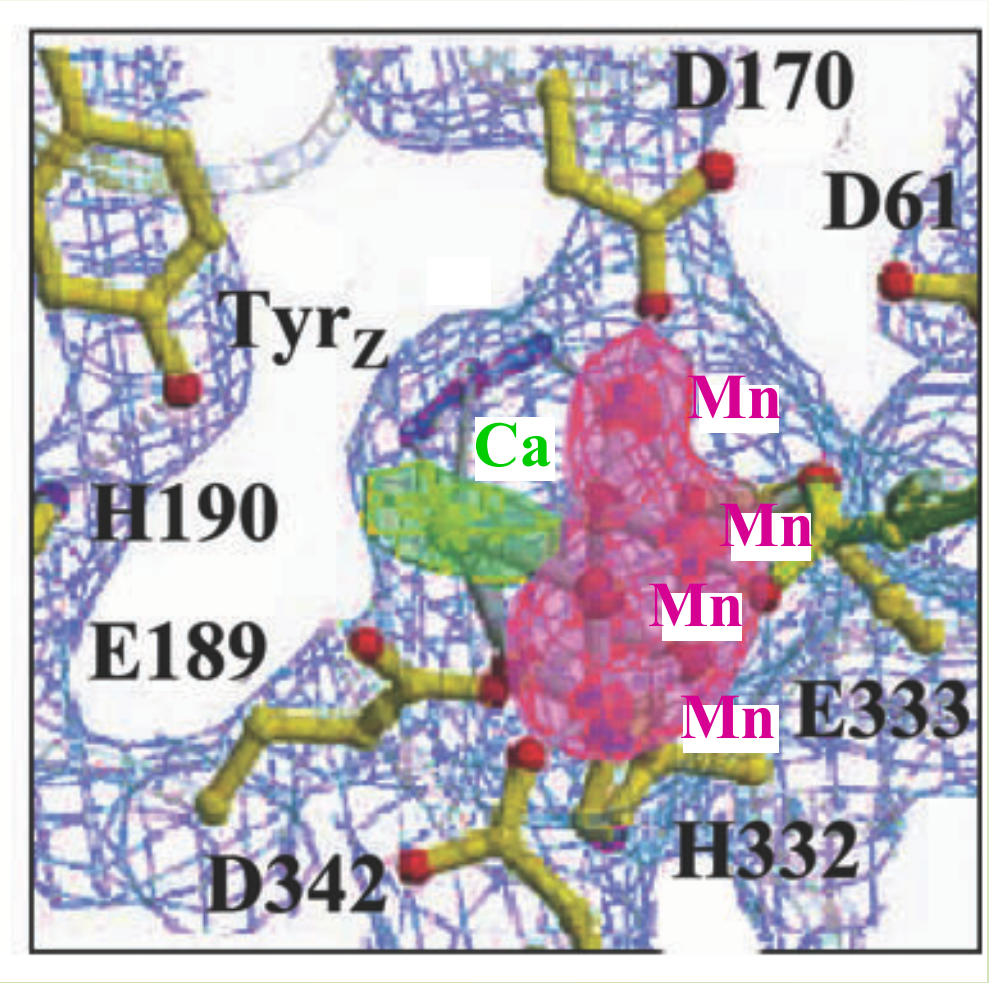
$$2H_2O(l) \xrightarrow{Cat.} O_2(g) + 4H^+(aq) + 4e^-$$



It is time to build an actual *artificial photosynthetic* system, to learn what works and what doesn't work, and thereby set the stage for making it.
Melvin Calvin

Jim Barber's Model

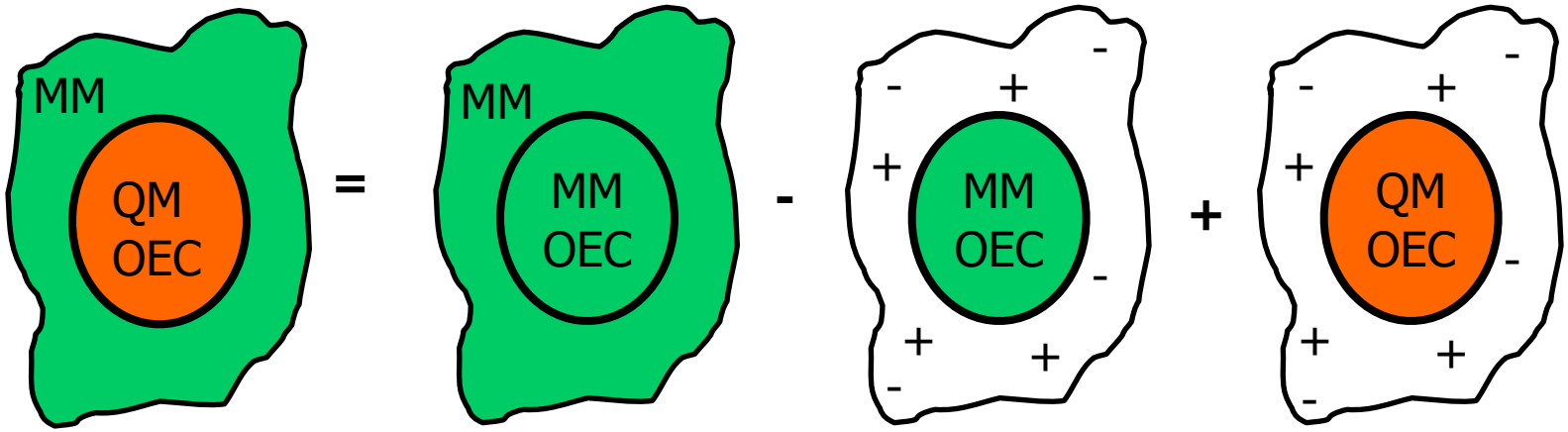
Ferreira et al. *Science* (2004) **303**:1831-1838



The coordinates of the Mn atoms were chosen consistently with the observed dual-lobe electronic density to have Mn-Mn distances of about 2.7 Å and 3.3 Å length as reported by XAS studies [see, e.g., George, G.N.; Prince, R.C. and Cramer, S.P. Science (1989) **243**:789-791] and the cuboidal structure with a dangling Mn suggested by EPR and ENDOR data [Peloquin, J.M.; Campbell, K.A.;Eandall, D.W.;Evanchik, M.A.;Pecoraro, V.L.;Amstrong, W.A.;Britt, R.D. J. Am. Chem. Soc. (2000) **122**:10926-10942].

Quantum Mechanics / Molecular Mechanics (QM/MM) Hybrid Methodology (Warshel, 1976)

Two-layer ONIOM-Electronic Embedding (EE) (Morokuma), G03.



QM = DFT B3LYP/lacvp*
MM = Amber Force Field

UB3LYP ONIOM-EE optimizations

DFT QM/MM:

J.A. Gascon and V.S. Batista, *Biophys. J.* **87**, 2931-2941 (2004)

J.A. Gascon, E.M. Sproviero and V.S. Batista, *J. Chem. Theor. Comput.* **2**, 11-20 (2005)

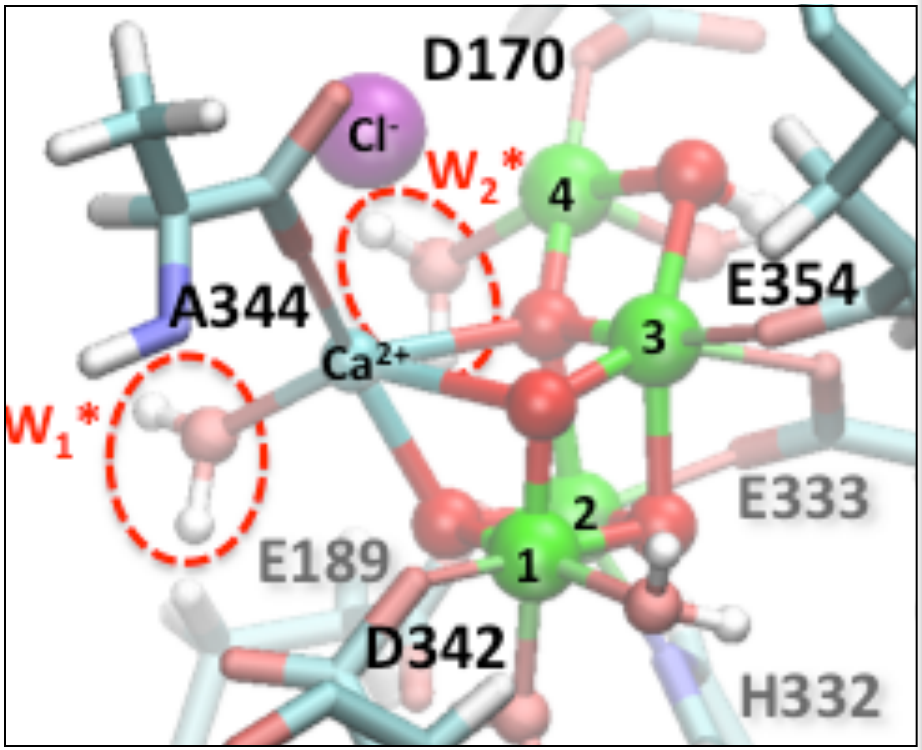
DFT QM/MM Self-Consistent Protein Polarization:

J.A. Gascon, S.S.F. Leung, E.R. Batista and V.S. Batista, *J. Chem. Theor. Comput.* **2**, 175-186 (2006)

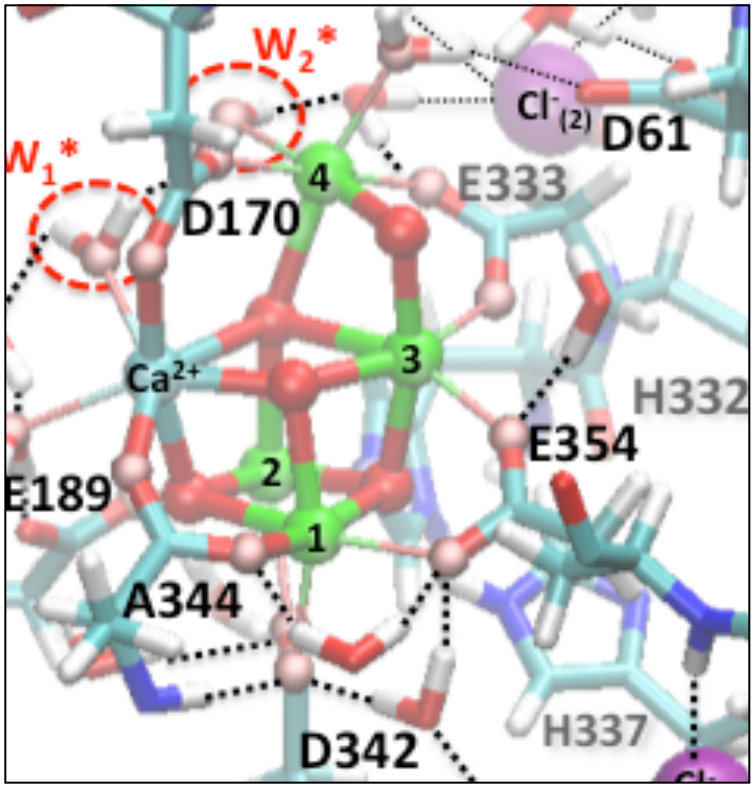
DFT-QM/MM Model

Sproviero, E.M; Gascon, J.A. et. al. *J. Chem. Theor. Comput.*, (2006) **4:**1119-1134; *Curr. Op. Struct. Biol.,* (2007) **17:**173-180; *Phil. Trans. Royal Soc. London B* **363**:1149-1156 (2008); *Coord. Chem. Rev.* **252**:395-415 (2008) ; *J. Am. Chem. Soc.* **130**:3428-3442 (2008); *J. Am. Chem. Soc.* **130**:6427-6430 (2008); *Biochemistry* **50**, 6308-6311 (2011); *Biochemistry* **50**, 6308-6311 (2011); *Biochemistry* **50**, 6312-6315 (2011); *Biochemistry* in press (2013).

2006 DFT QM/MM S_0 model



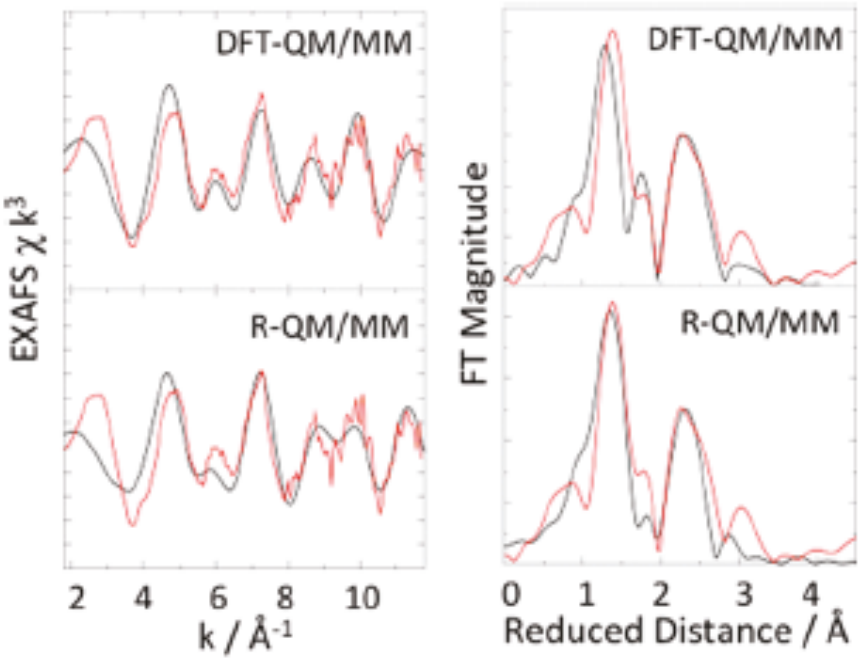
2011 Shen's X-ray model



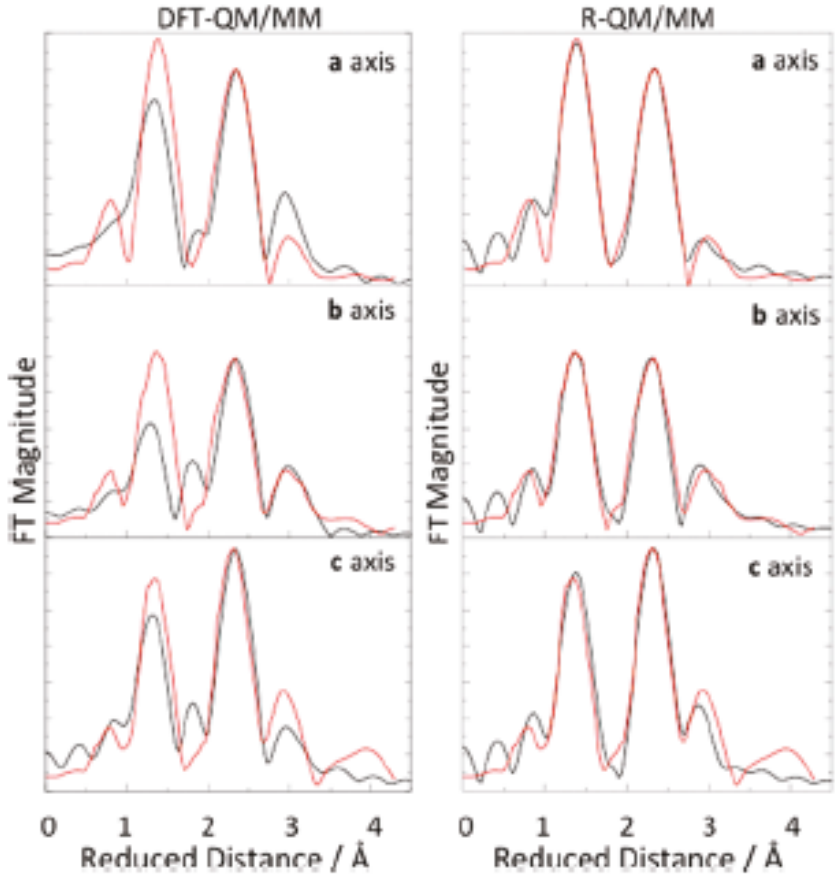
2011 DFT QM/MM Model: Validation by EXAFS Analysis

Biochemistry **50**, 6308-6311 (2011) Sandra Luber, Ivan Rivalta, Y. Umena, K. Kawakami, Jian-R. Shen, N. Kamiya, Gary Brudvig, and Victor S. Batista

Isotropic



Polarized



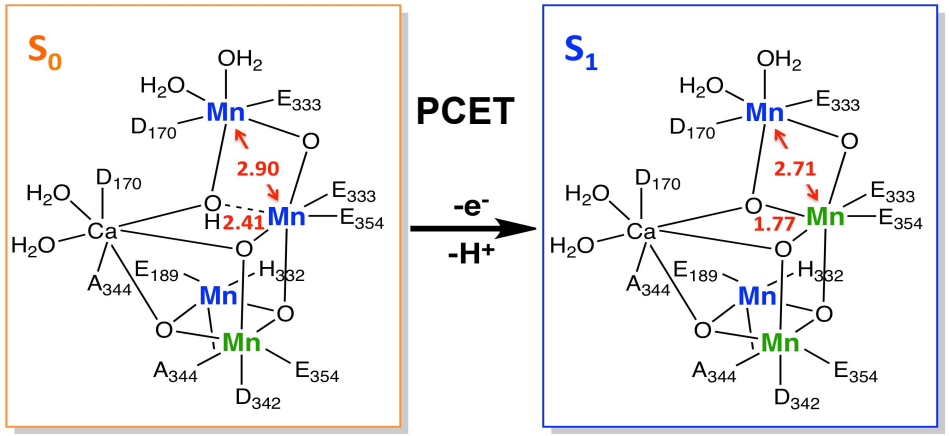
Experimental EXAFS Data:

Haumann, M.; Muller, C.; Liebisch, P.; Iuzzolino, L.; Dittmer, J.; Grabolle, M.; Neisius, T.; Meyer-Klaucke, W.; Dau, H. Biochemistry 2005, 44, 1894–1908.

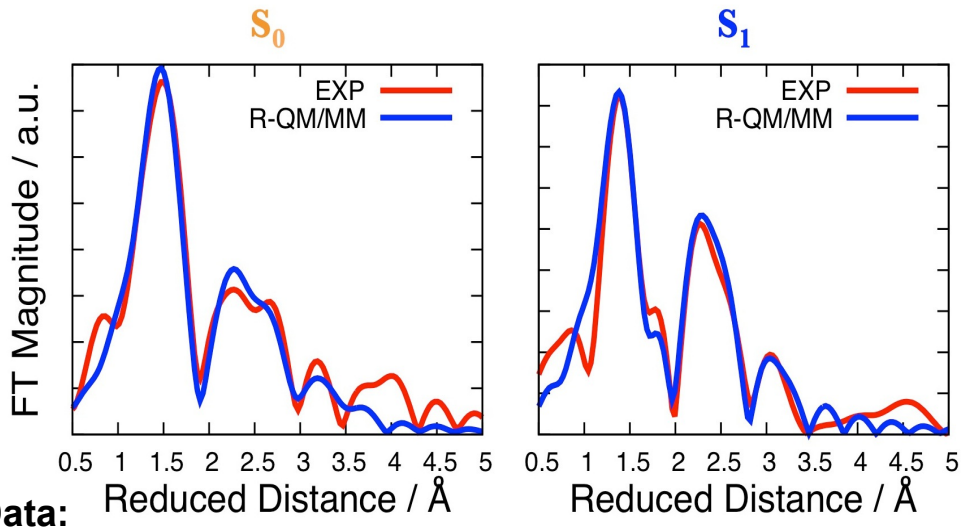
Yano, J.; Kern, J.; Irrgang, K. D.; Latimer, M. J.; Bergmann, U.; Glatzel, P.; Pushkar, Y.; Biesiadka, J.; Loll, B.; Sauer, K.; Messinger, J.; Zouni, A.; Yachandra, V. K. Proc. Natl. Acad. Sci. U.S.A. 2005, 102, 12047–12052.

S_0 -State Model of the OEC of Photosystem II

Biochemistry **52**: 7703-7706 (2013) Rhitankar Pal, Christian F. A. Negre, Leslie Vogt, Ravi Pokhrel, Mehmed Z. Ertem, Gary W. Brudvig, and Victor S. Batista

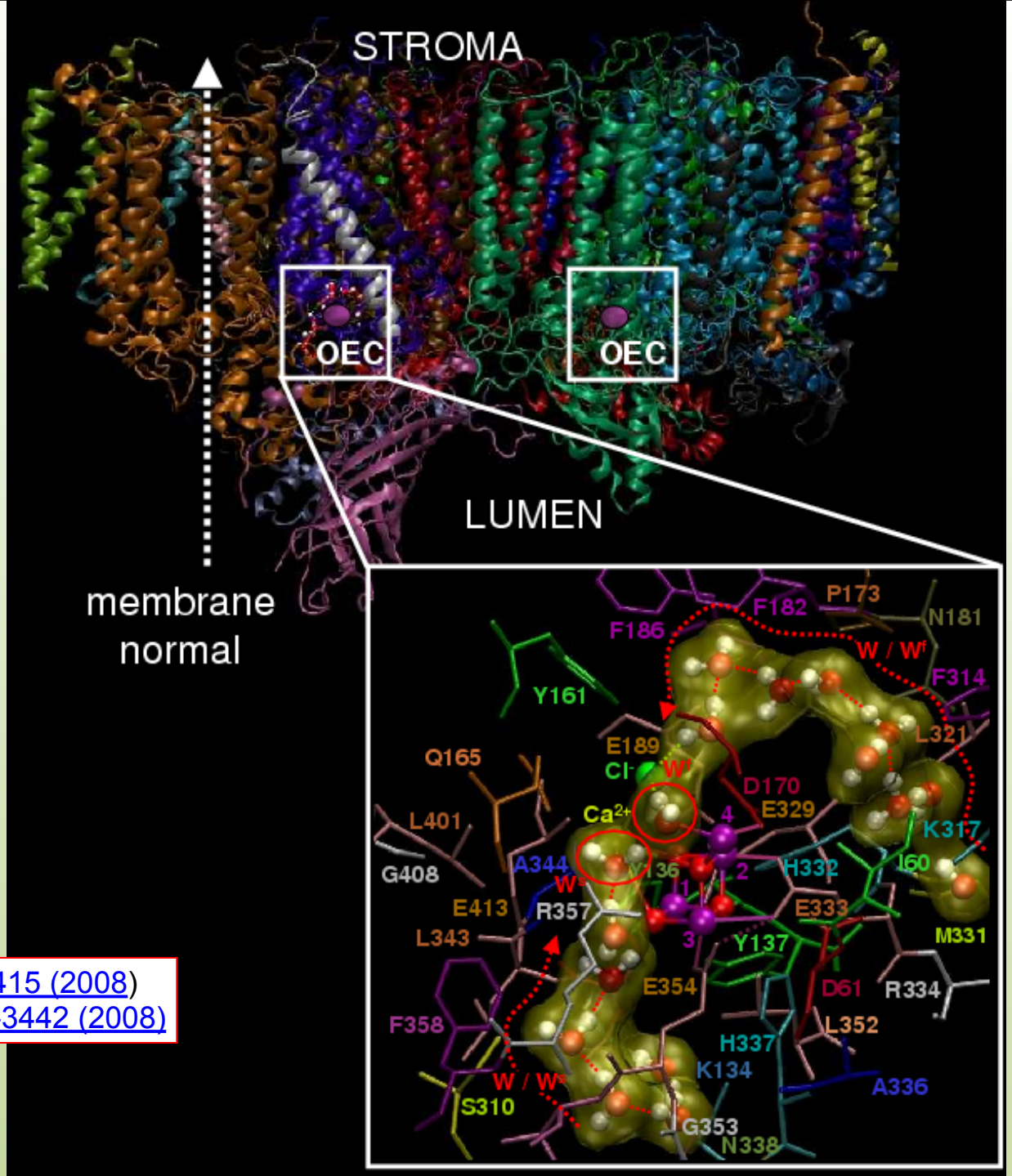


Dr. Rhitankar Pal
Dr. Christian Negre

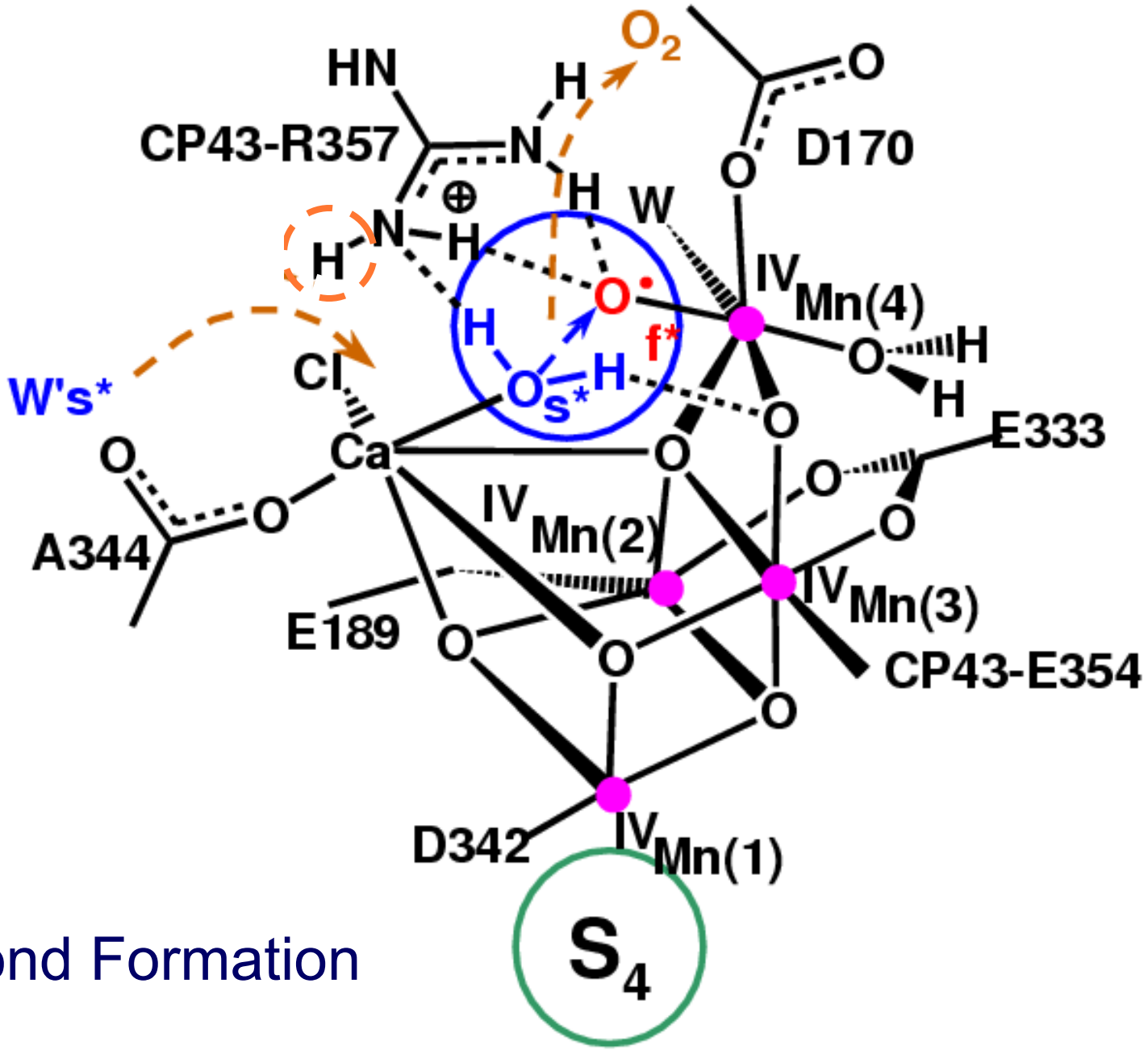


Experimental EXAFS Data:
Haumann, M.; Muller, C.; Liebisch, P.; Iuzzolino, L.; Dittmer, J.; Grabolle, M.; Neisius, T.; Meyer-Klaucke, W.; Dau, H. Biochemistry 2005, 44, 1894–1908.

Water Channels



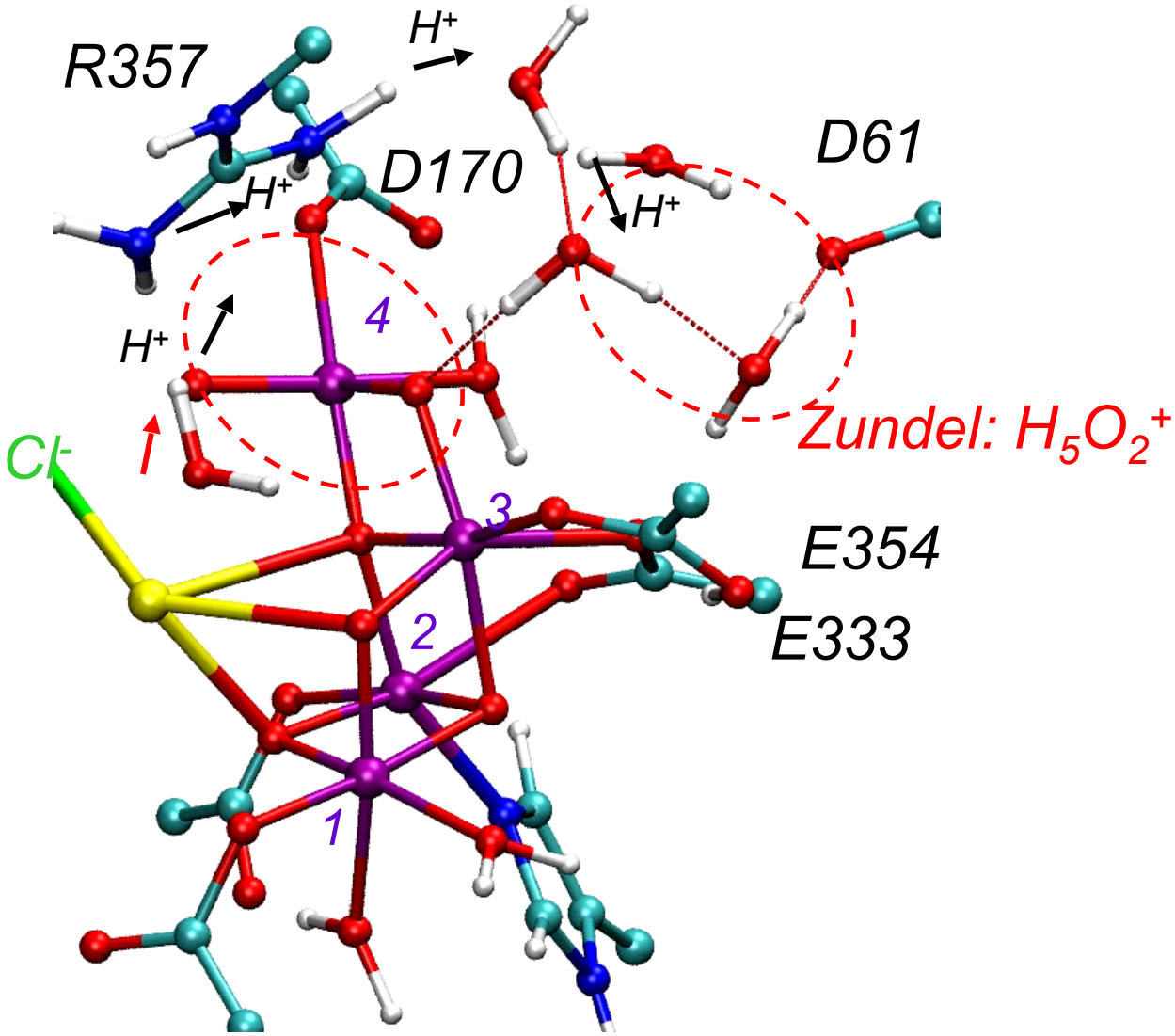
Coord. Chem. Rev. **252**:395-415 (2008)
J. Am. Chem. Soc. **130**:3428-3442 (2008)



O–O Bond Formation

O-O Bond Formation

Zundel/HOO-Mn(4) State Formation



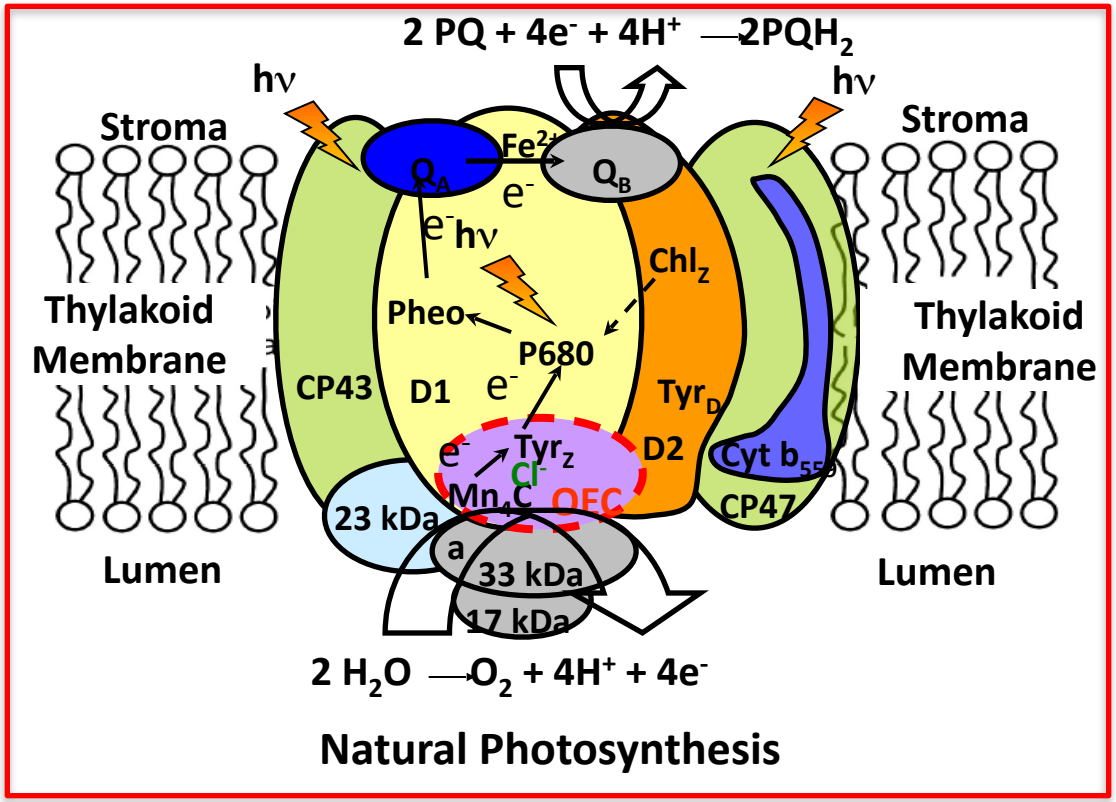
CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Biomimetic Water Oxidation

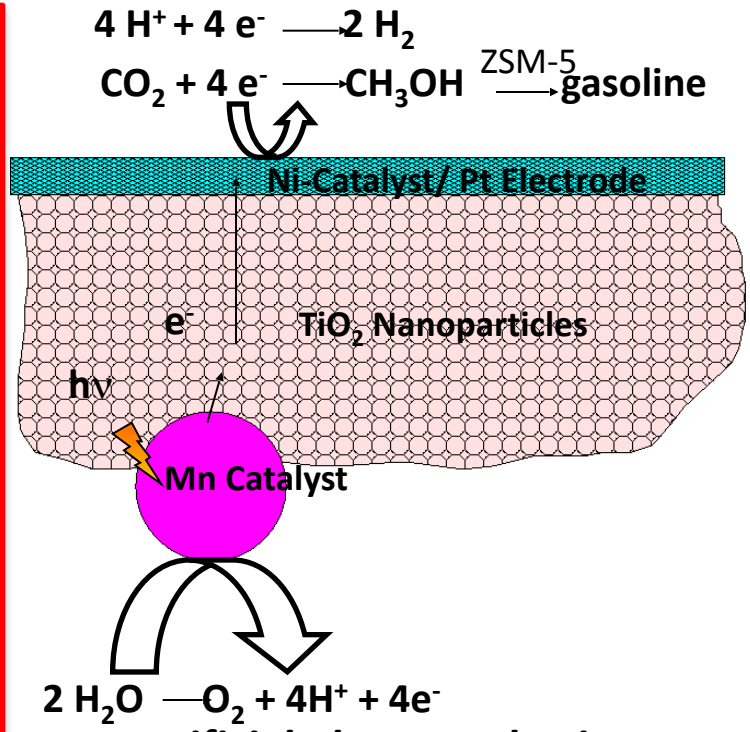
Catalytic Mn Complex Activated by Oxone

Thylakoid Membrane in Chloroplasts



Natural Photosynthesis

Photocatalytic Thin Film



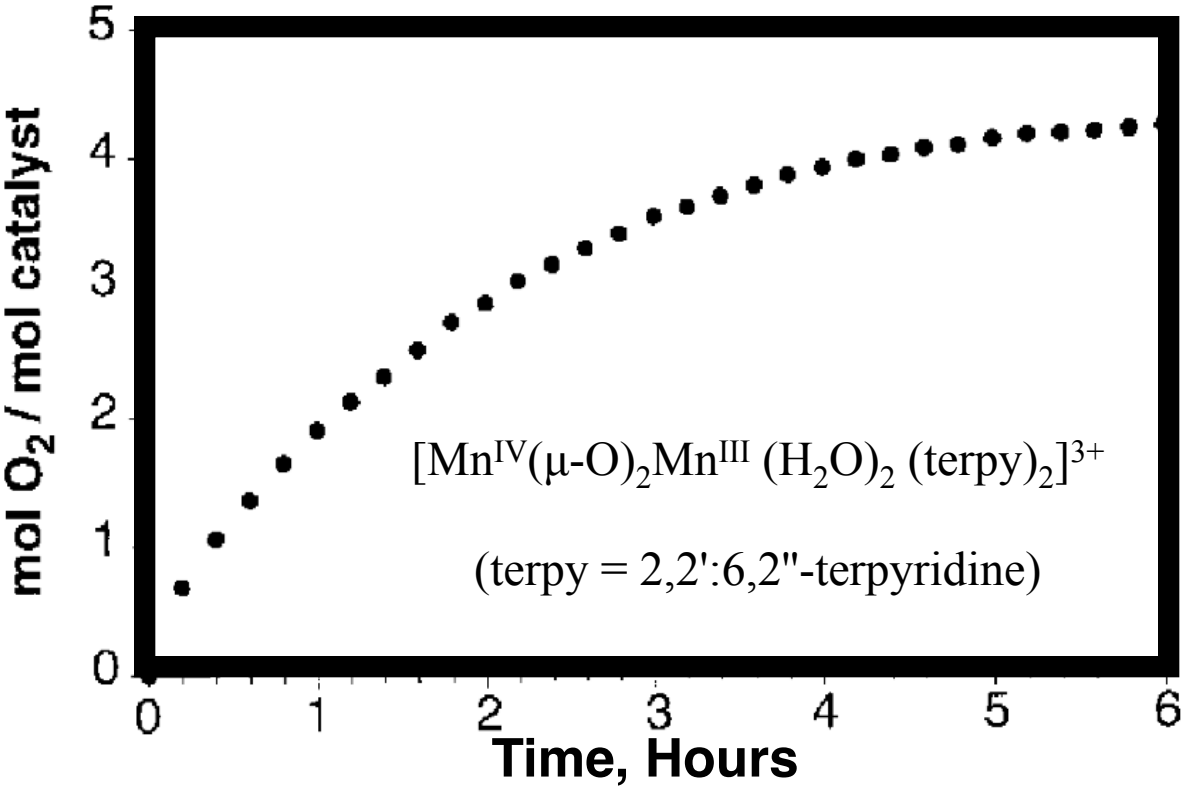
Artificial Photosynthesis

CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Biomimetic Oxygen Evolution

Catalytic Mn Complex Activated by Oxone

Crabtree, Brudvig and co-workers *Science* **283**, 1524-1527 (1999); *J. Chem. Edu.* 791-794 (2005).

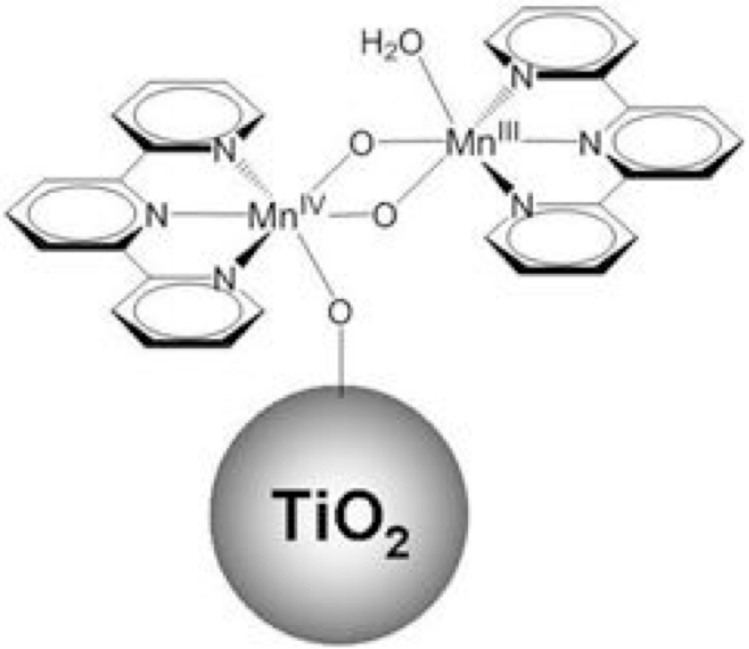


O_2-Evolution by Water Splitting: The Yale Mn-Terpy Dimer in Action

CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

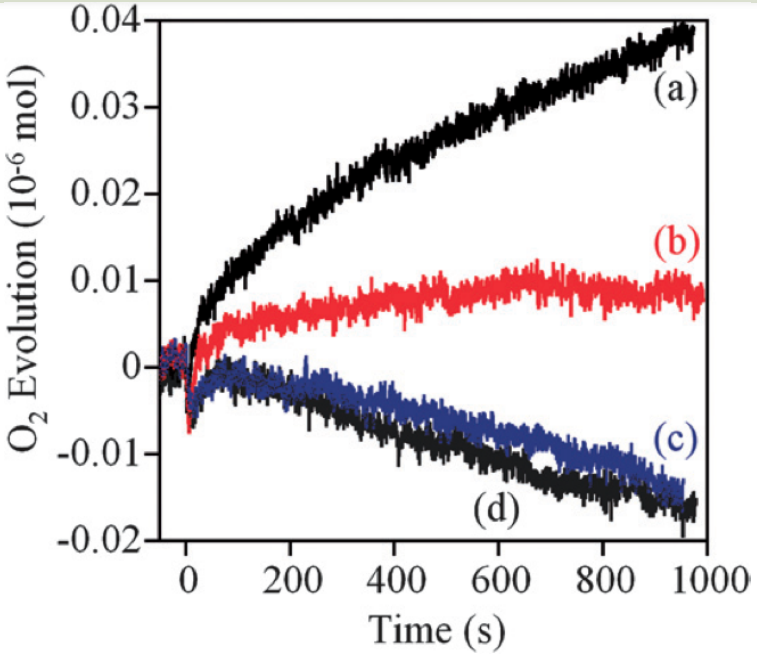
Modeling Biomimetic Oxygen Evolution

Water Oxidation by a Mn-Dimer Adsorbate



Mn Dimer **1** attached to TiO_2

[Li, G. *et al.* Energy Environ. Sci. (2008) 2:230-238]



O_2 evolution using Ce^{4+} as a single-electron primary oxidant. **1** was loaded on TiO_2 (50 mg) samples: (a) P25, (b) D450, and (c) D70. A control test was also done using (d) bare P25 NP's as the catalyst.

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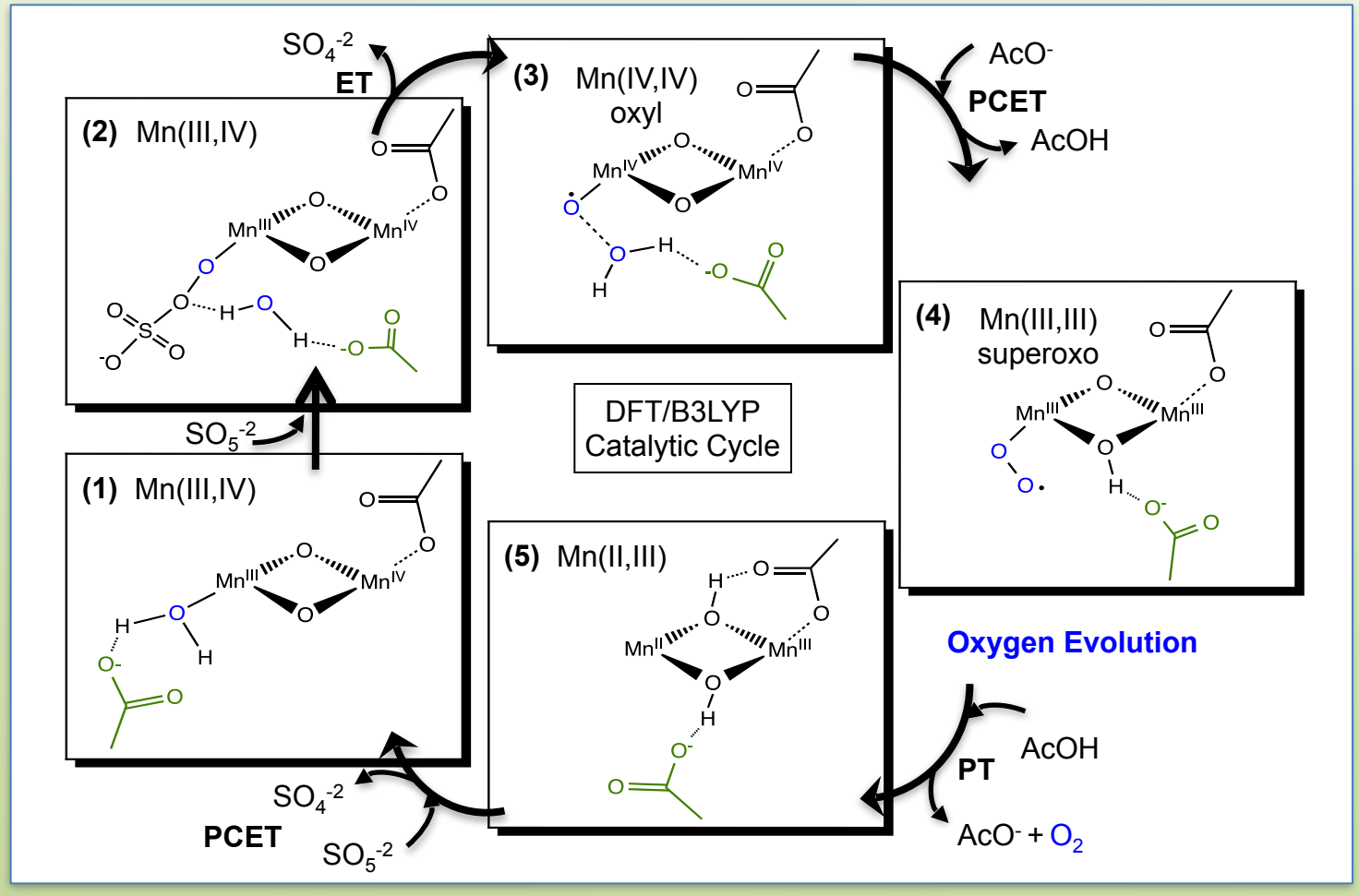
Department of Chemistry – Yale University

Modeling Biomimetic Oxygen Evolution

Water Splitting Catalyzed by a Mn-Dimer



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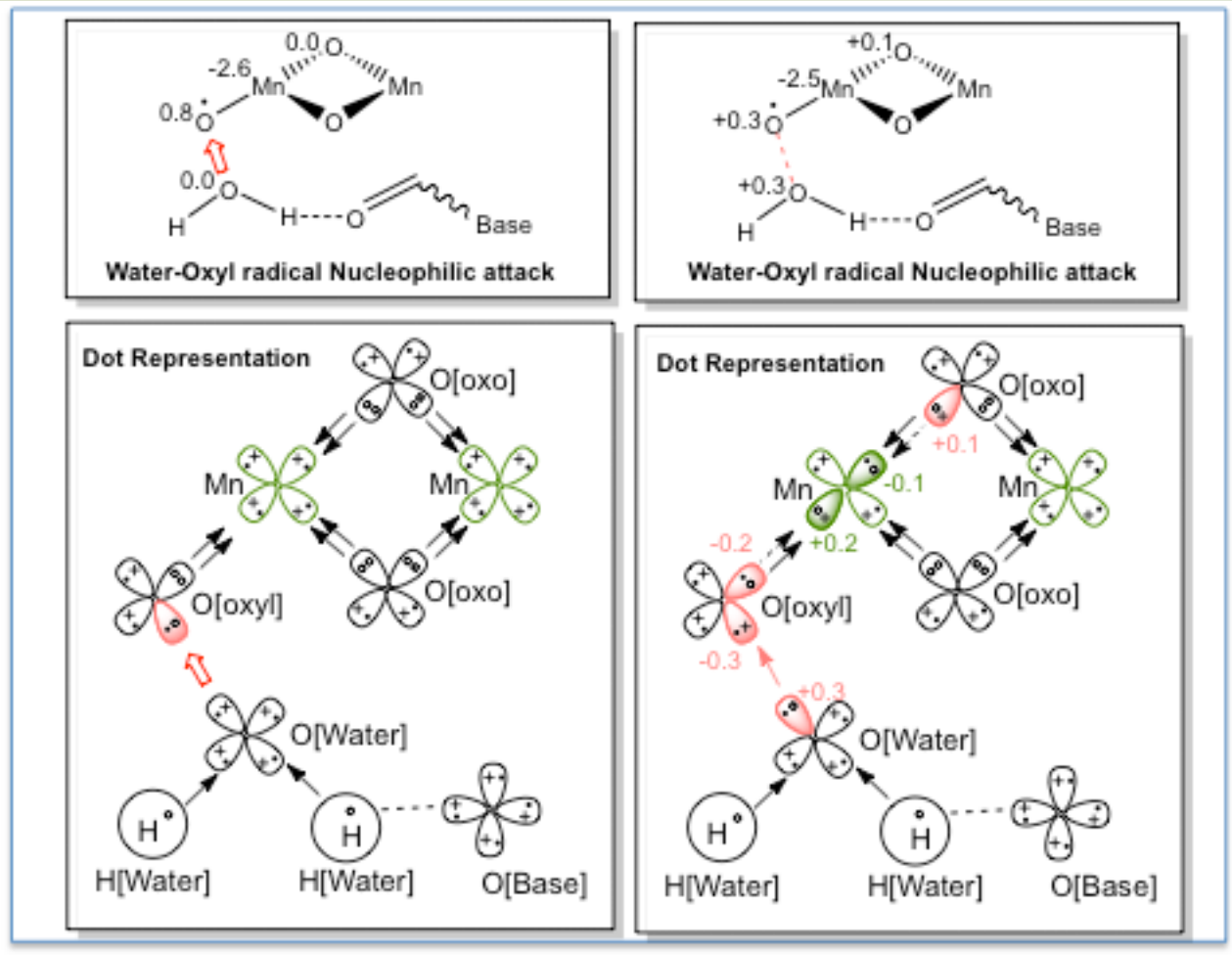
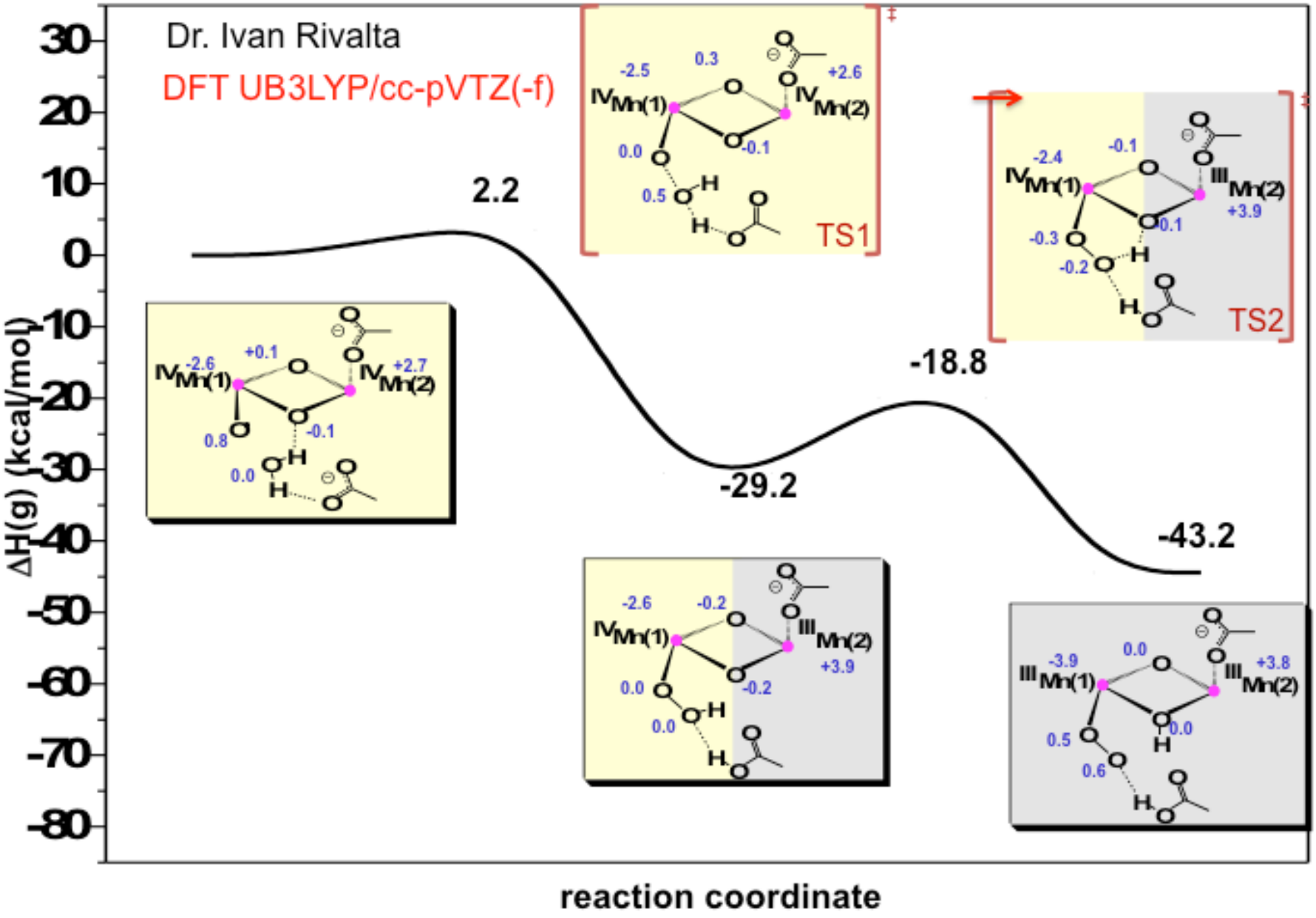
Department of Chemistry – Yale University

Modeling Biomimetic Oxygen Evolution

O-O Bond Formation: PCET



O-O BOND FORMATION: SUPEROXO INTERMEDIATE



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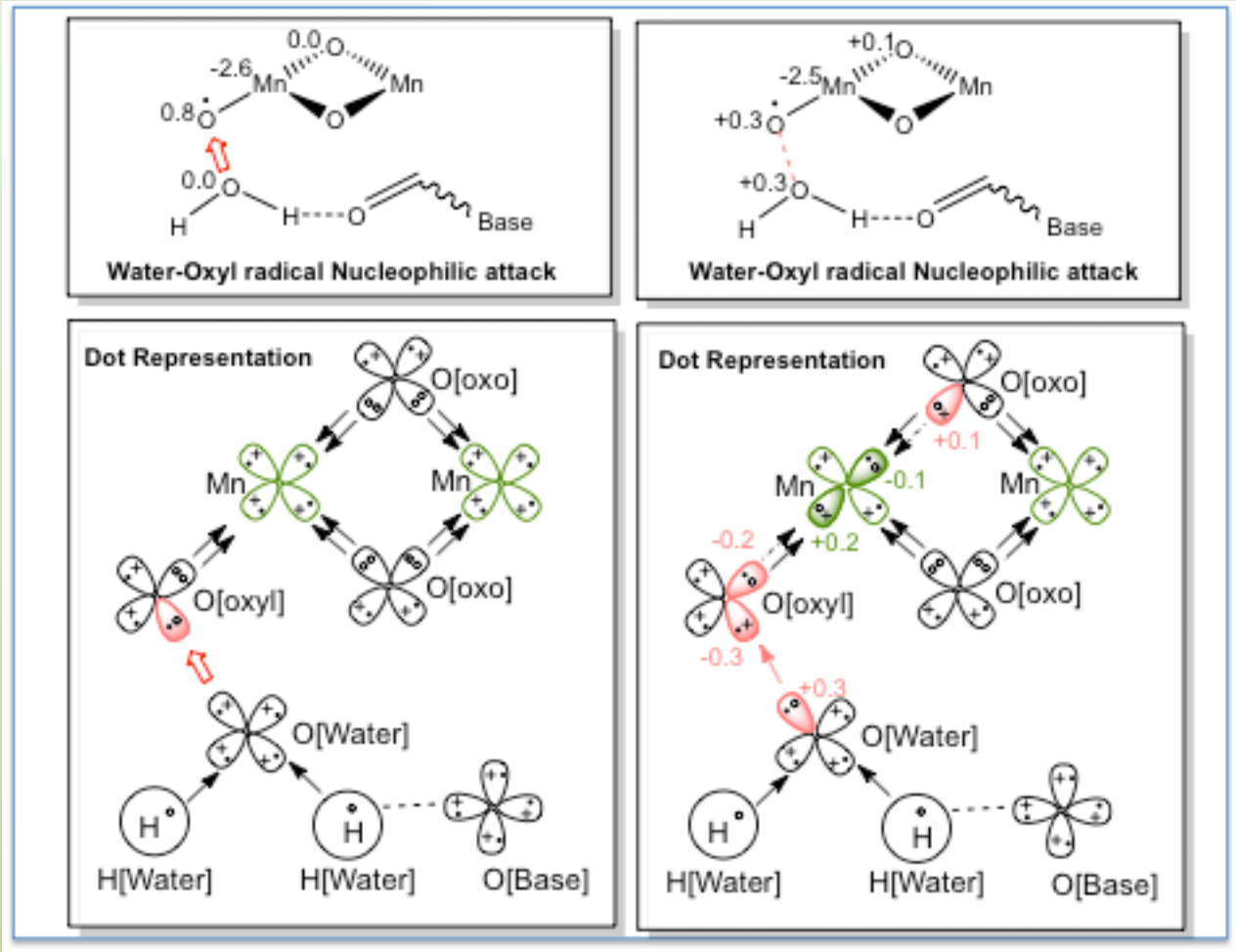
Department of Chemistry – Yale University

Biomimetic water Oxidation

O-O Bond Formation: Spin Injection

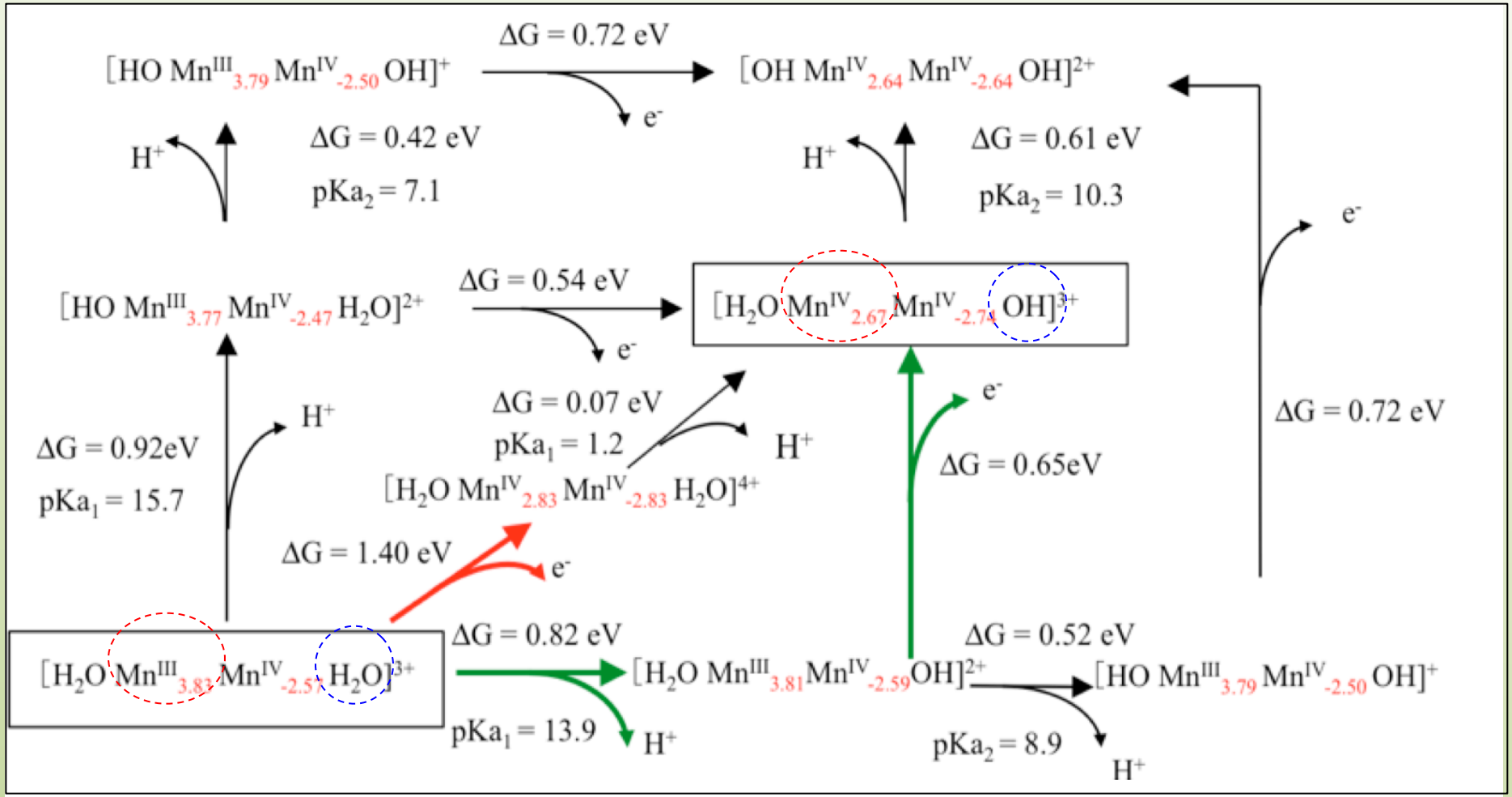


[Wang, T. *et al.* JCTC (2010) 6:755-760]

PCET: Activation Mechanism

Dr. Ting Wang

DFT UB3LYP/cc-pVTZ(-f) Free Energy Calculations: (III,IV) → (IV,IV) Transition



$$[H_2O\ Mn^{III}\ (\mu\text{-}O)_2\ Mn^{IV}\ OH_2]^{3+} \xrightarrow{pH=4.5} [H_2O\ Mn^{IV}\ (\mu\text{-}O)_2\ Mn^{IV}\ OH]^{3+} + H^+ + e^-$$

Pourbaix Diagrams: Theory vs. Experiments

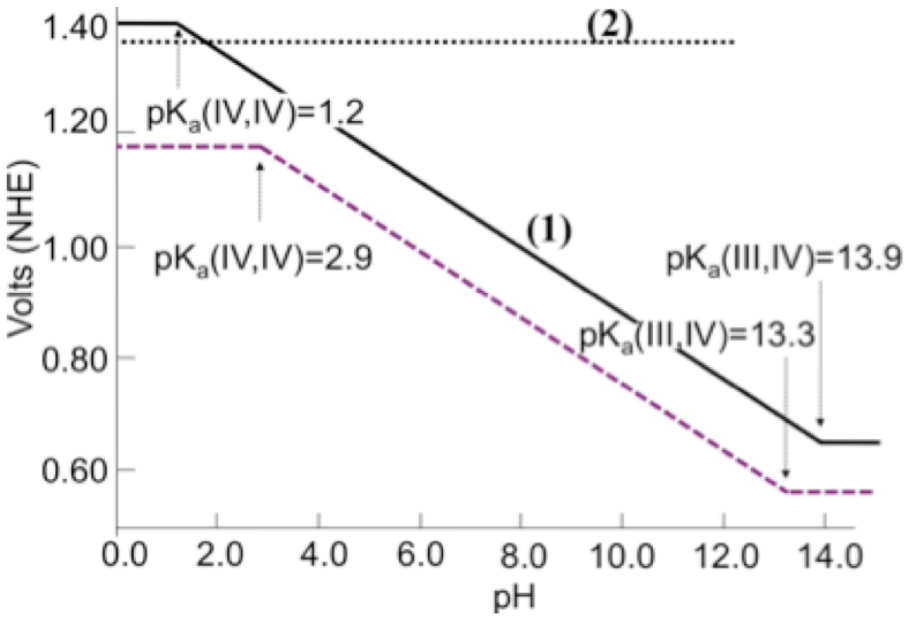
DFT UB3LYP/cc-pVTZ(-f) Free Energy Calculations

Regulation of PCET by Lewis Base (Carboxylate) Binding

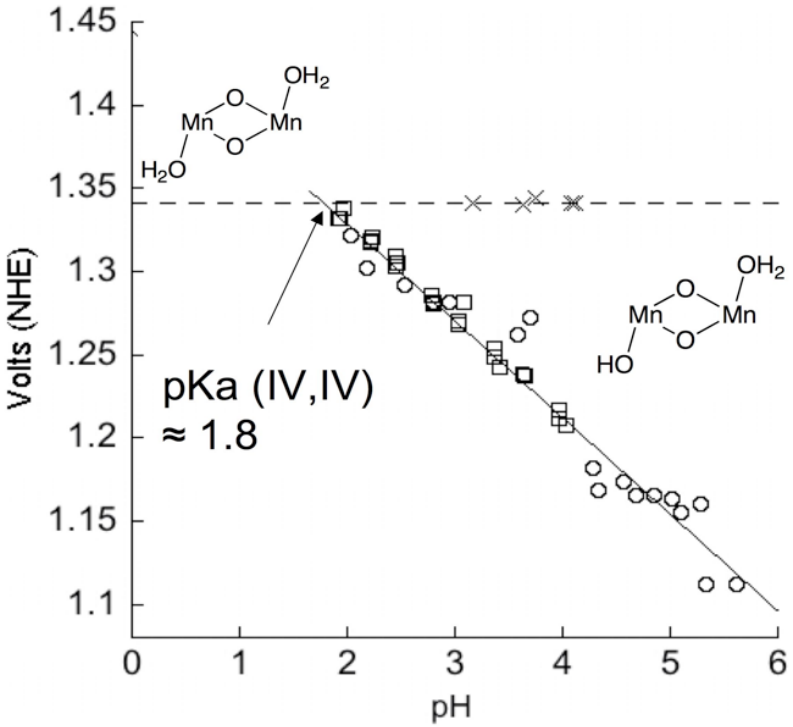
Dr. Ting Wang

[Wang, T. *et al.* JCTC (2010) 6:755-760]

Theory (Batista)



Experiments (Brudvig)



$[H_2O(terpy)Mn^{III}(\mu\text{-}O)_2Mn^{IV}(terpy)CH_3COO]^{2+}$ ⟶

$[HO\ (terpy)\ Mn^{IV}\ (\mu\text{-}O)_2\ Mn^{IV}\ (terpy)\ CH_3COO]^{+}+H^{+}+e^{-}$

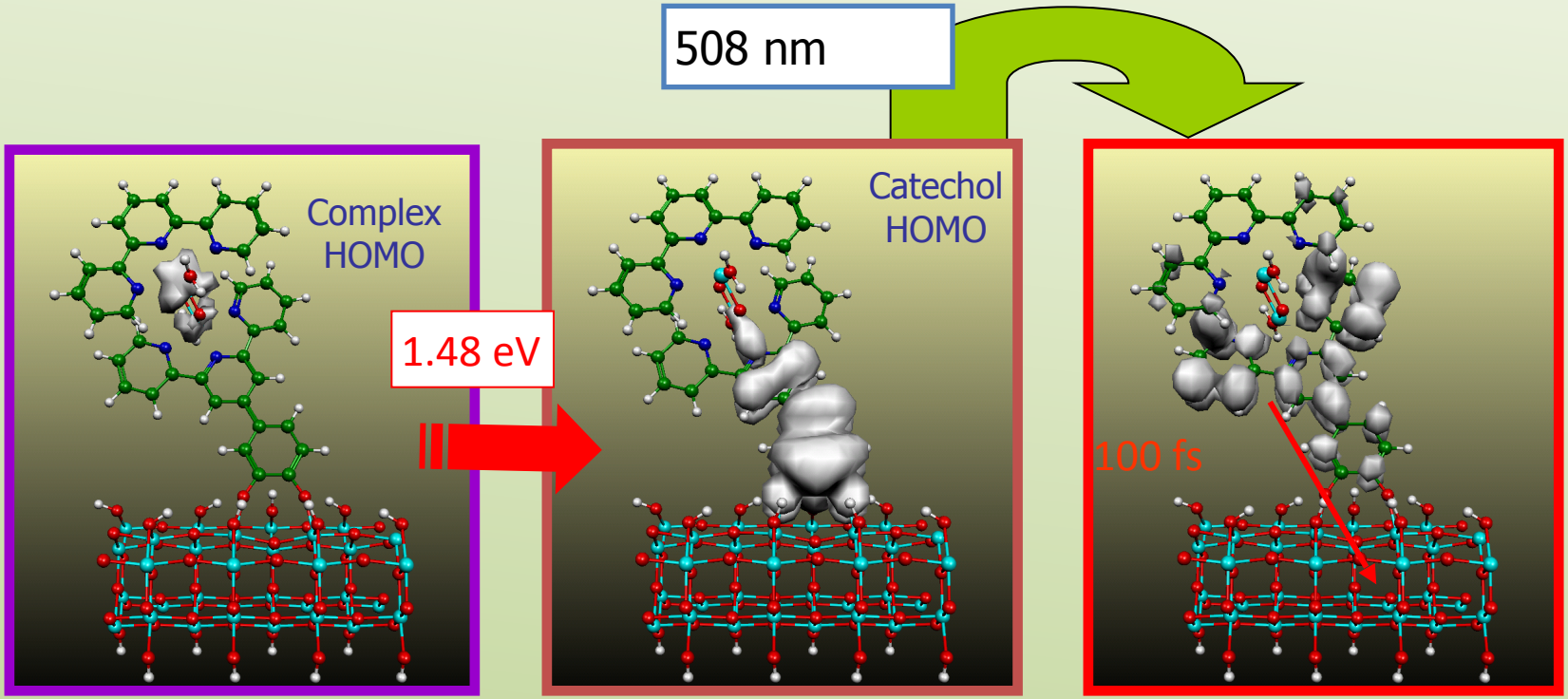
CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Visible-Light Photocatalysis

Photoactivation of a Mn-Adsorbate Complex

Sabas G. Abuabara, Clyde W. Cady, Jason B. Baxter, Charles A. Schmuttenmaer, Robert H. Crabtree, Gary W. Brudvig, and Victor S. Batista. J. Phys. Chem. C, 111:11982–11990 (2007).



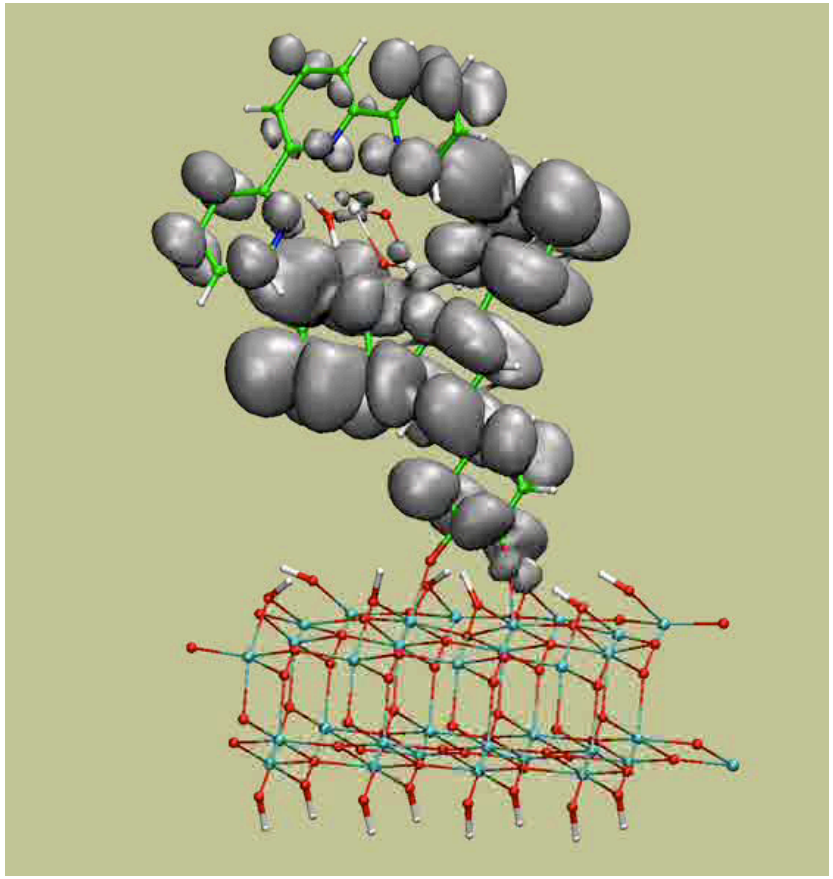
TiO_2 / $[Mn^{IV}(\mu\text{-}O)_2Mn^{III}(H_2O)_2(terpy)_2]^{3+}$

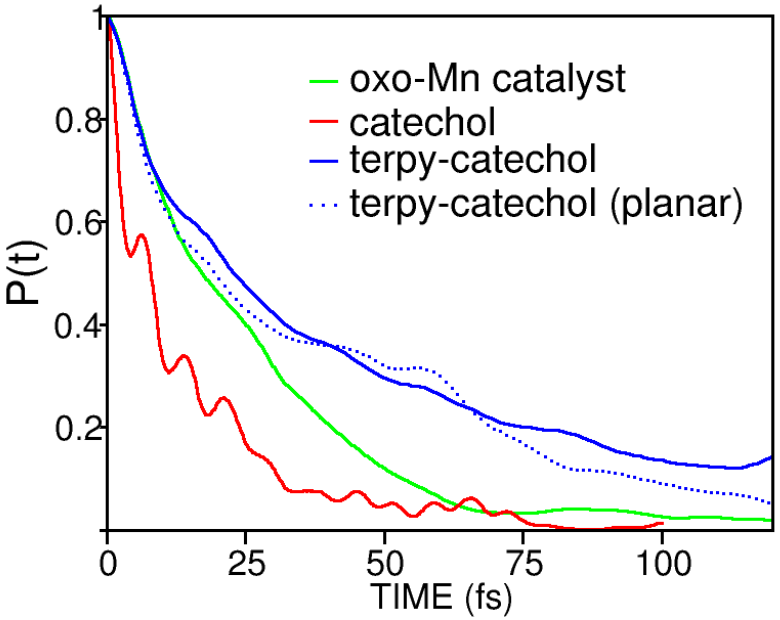
CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Biomimetic Oxygen Evolution

Simulations of IET from a Mn Adsorbate



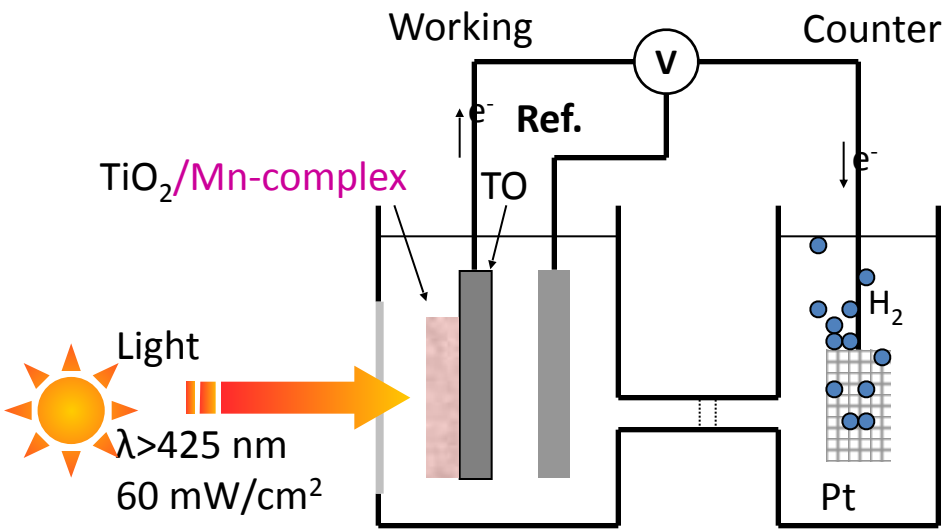


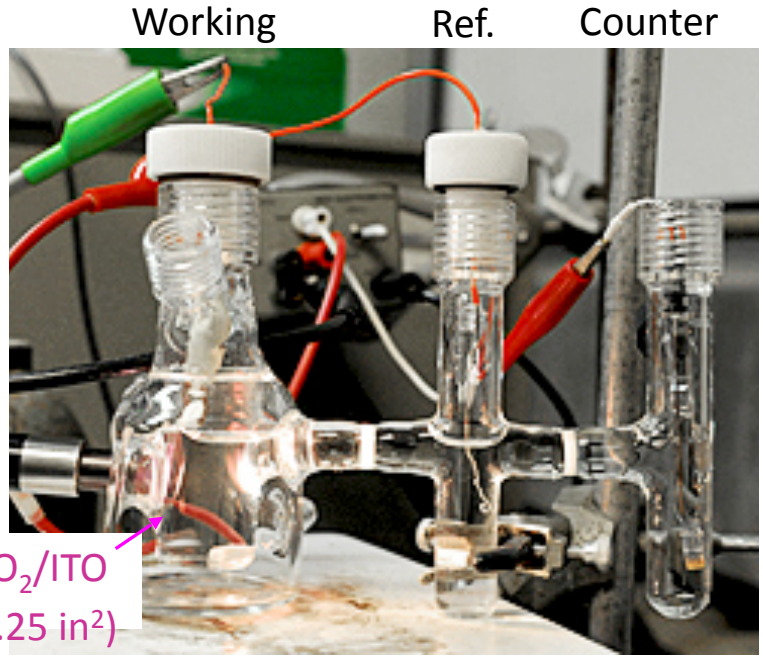
First 100 fs after photoexcitation of the Mn(III,IV) adsorbate

Sabas G. Abuabara

Photocatalysis with Visible Light

J. Catalysis **310**: 37-44 (2014) Photoelectrochemical Oxidation of a Turn-On Fluorescent Probe Mediated by a Surface Mn(II) Catalyst Covalently Attached to Ti_2 Nanoparticles, Alec C. Durrell, Gonghu Li, Matthieu Koepf, Karin J. Young, C.F. A. Negre, L. J. Allen, W. R. McNamara, H. Song, Victor S. Batista, Robert H. Crabtree and Gary W. Brudvig.





$(CH_3)_2CHOH \longrightarrow (CH_3)_2C=O + 2H^+ + 2e^-$ $\qquad 2H^+ + 2e^- \longrightarrow H_2$

Photocatalysis with Visible Light

Dr. Gonghu Li
Dr. Christiaan Richter

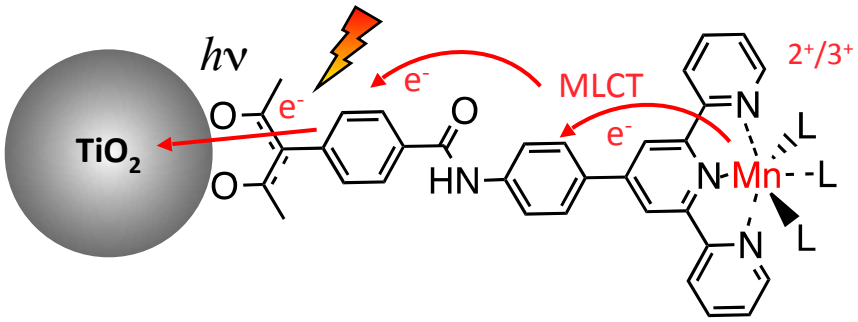
Photooxidation of isopropanol

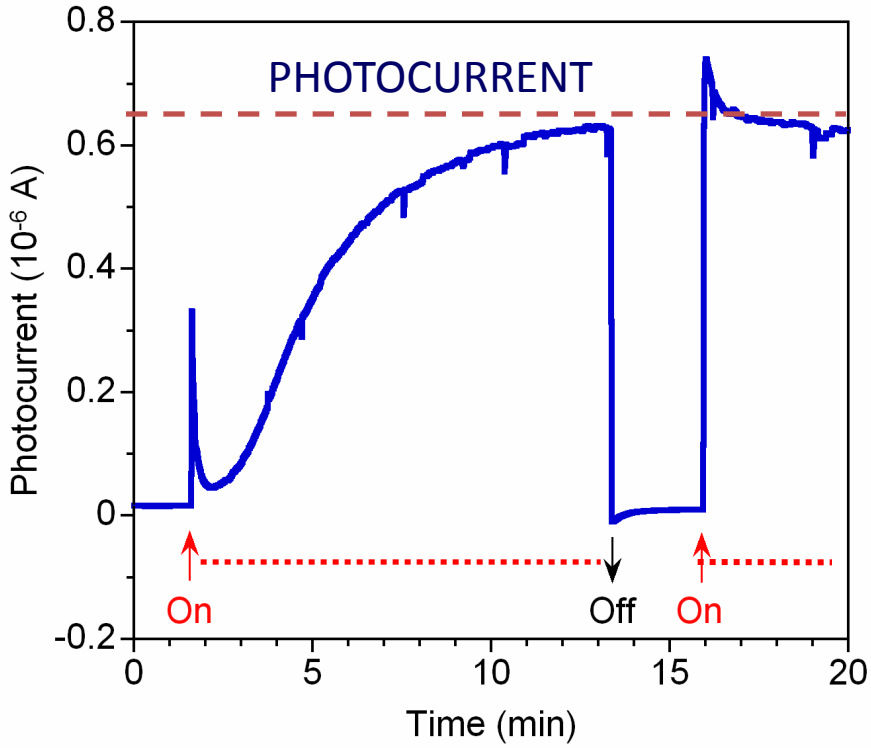
J. Catalysis **310**: 37-44 (2014)

Net redox reaction:

$$(CH_3)_2CHOH \xrightarrow[TiO_2/\text{Mn-cat.}]{h\nu} (CH_3)_2C{=}O + H_2$$

Photoactivation of the catalyst:





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