Mill Designed Biobleaching Technologies

Dr. A. Ragauskas[1]

Dr. T. Elder[2]

Dr. C. Felby[3]

[1]Institute of Paper Science and Technology, Atlanta, GA

[2]School of Forestry, Auburn University, Auburn, AL

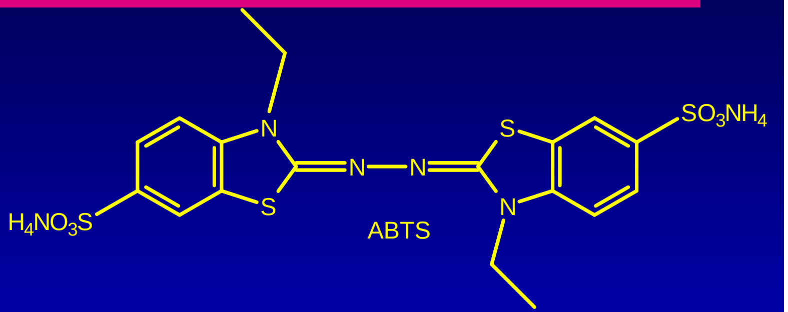
[3]Novo Nordisk A/S, 2880 Bagsvaerd, Denmark

PROJECT OBJECTIVES

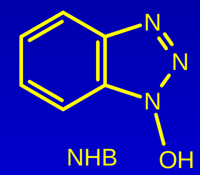
- Develop a Laccase-Mediator System (LMS) for closed-mill kraft bleaching operations.
- Optimize LMS delignification.
- Design and test cost effective
    - * Laccase mediators
    - * Mediators for laccase mimic systems.

Mediators

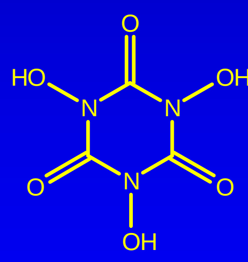
- Numerous compounds have been proposed
- First Generation
  - ABTS
- Second Generation
  - HBT
- Third Generation
  - VA
  - NHAA



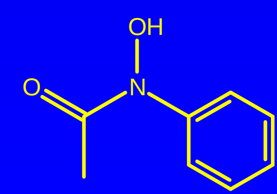
ABTS



NHB

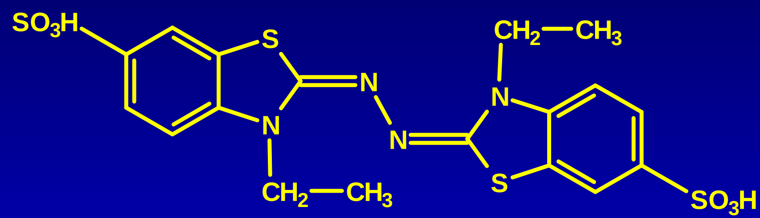


VA



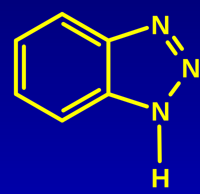
NHAA

Paice (ISWPC 97)

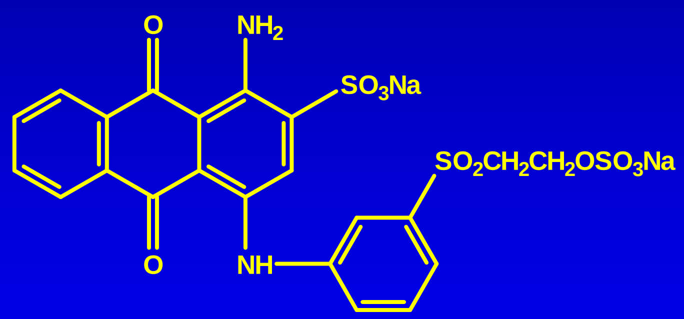


ABTS

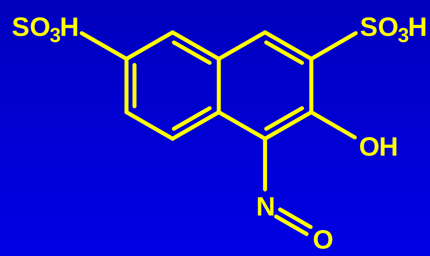
HBT



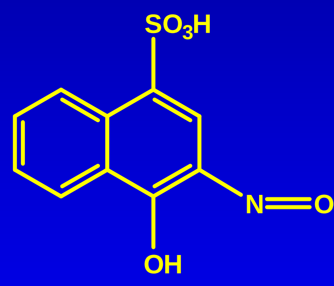
BZT



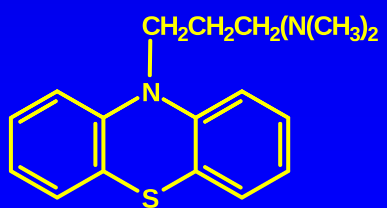
RBB



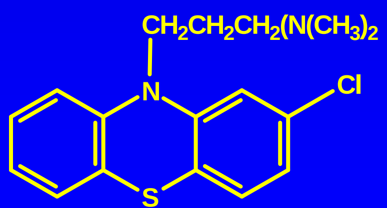
NNDS



HNNS



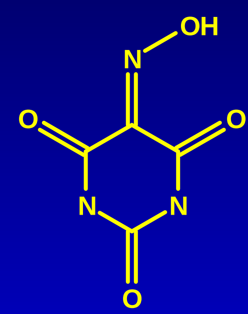
PZ



CPZ

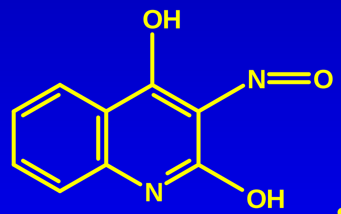
Amann (ISWPC 1997)

HBT



VA

NHAA



NC

NNS

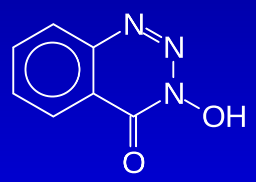
Sealy et al. (1999)

1

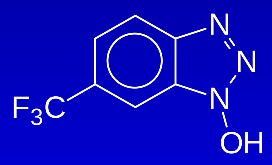
2

3

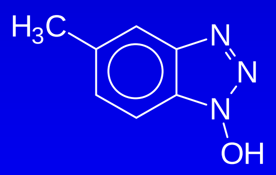
4



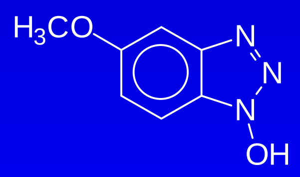
5



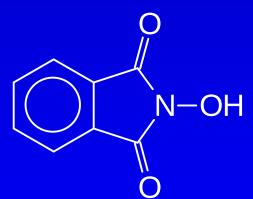
6



7

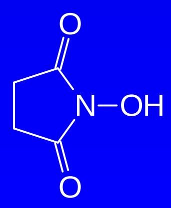


8

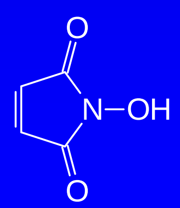


9

10



11



12

Experimental Results

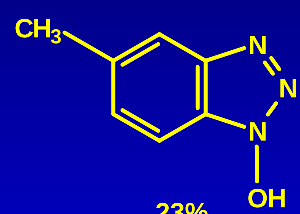
- Sealy et al. (1999) delignification results

41%

>

28%

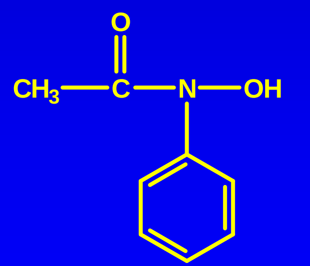
~



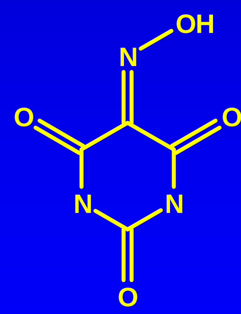
23%

- Amann (1997)

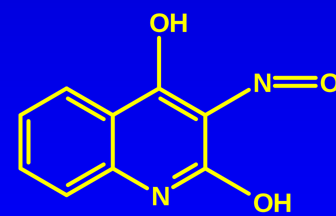
HBT
kappa=5.8
redox potential=1.13V



NHAA
kappa=5.7
redox potential=1.00/1.21V



VA
kappa=5.5
redox potential=0.97V



NC
redox potential=0.98

Objectives

- HBT has been found to be effective
- More recently the efficacy of VA and NHAA have been reported
- Properties that control the effectiveness of a mediator are not clear
  - e.g. No obvious optimum among redox potentials (Amann 1997)
- Current work
  - computational methods
    - examine extant mediators
    - determine any systematic changes as a function of substitution
    - use these data to guide mediator selections

Methods

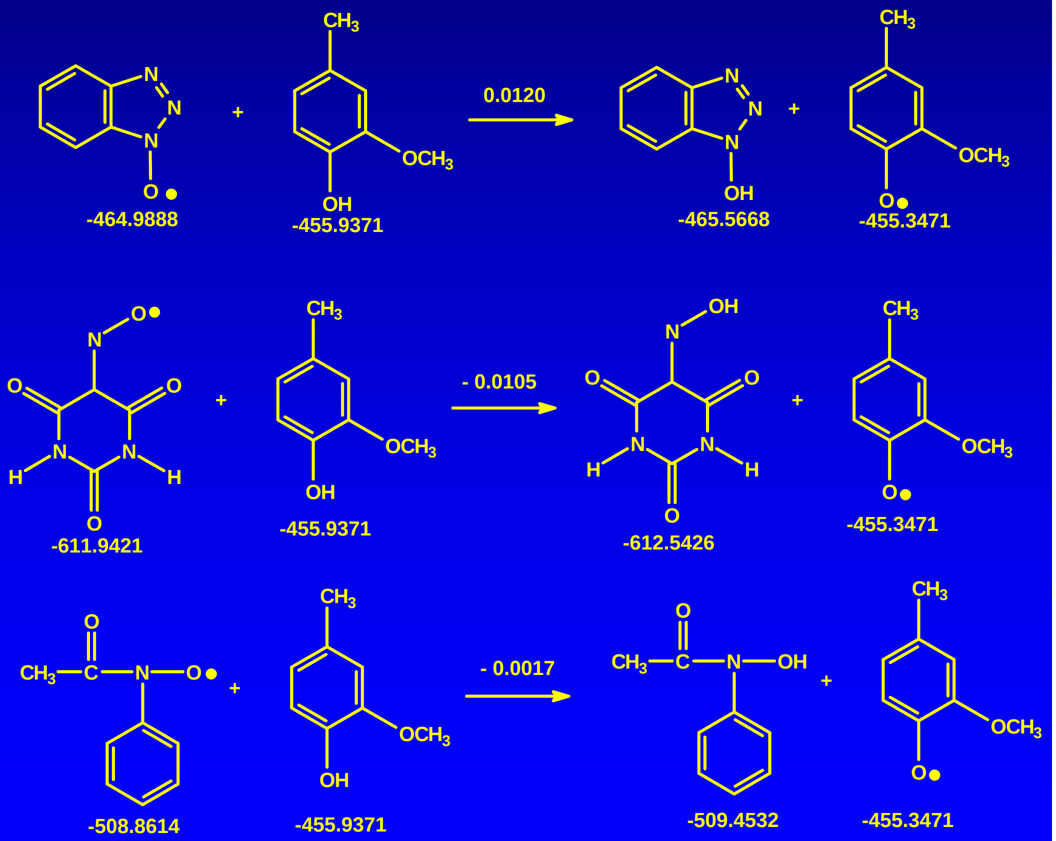
- Ab initio calculations
  - Gaussian
  - 3-21G* basis set
  - geometry optimization
- Cray C-90-Alabama Supercomputer Authority
- Unichem

Computational Observables

- Energetics
  - heats of reaction with specified lignin model
  - molecular orbital energies as an indicator of oxidation potential
- Kinetics
  - molecular orbital occupancy
  - spin density of radicals
  - dipole moment

Energetics
Heats of Reaction

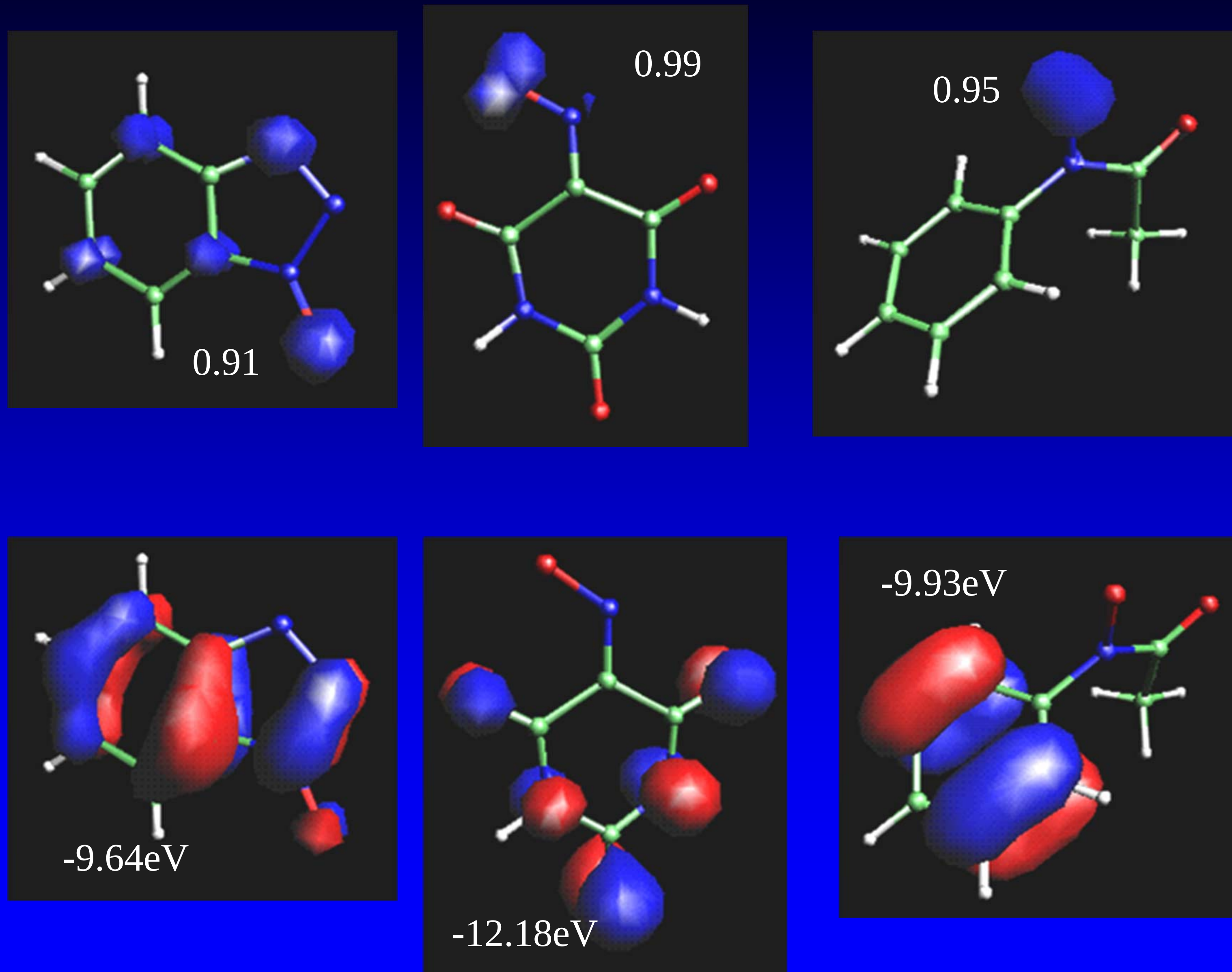
- HBT is slightly endothermic
- VA is most exothermic



HBT VA NHAA

Spin density

SOMO

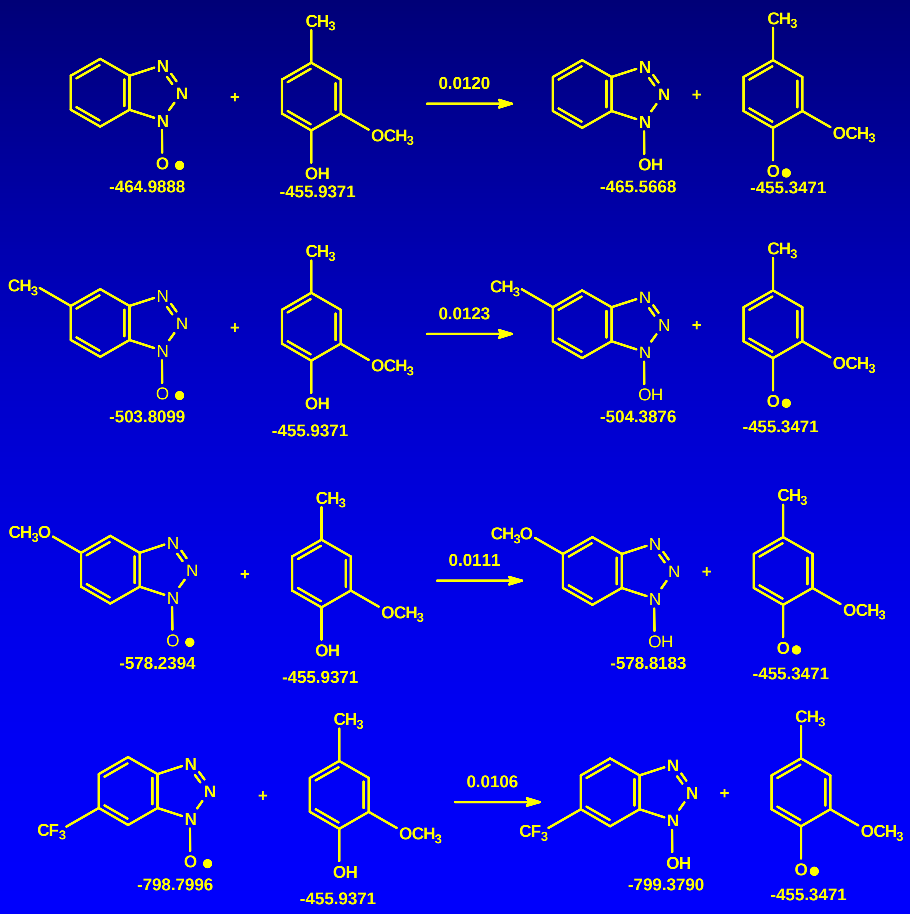


Results

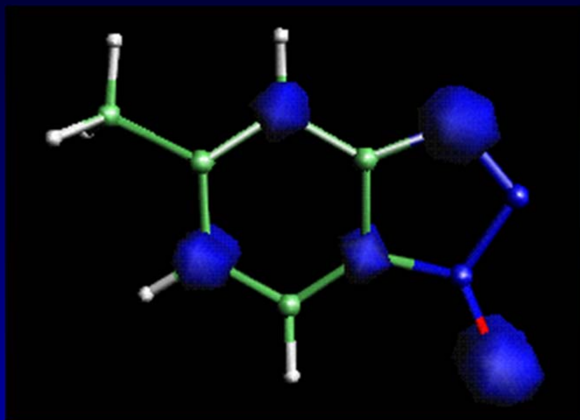
- Experimentally
  - VA gives lowest kappa, NHAA intermediate, HBT highest
- Computationally
  - VA lowest heat of reaction, followed by NHAA, and HBT
  - spin density VA>NHAA>HBT
  - E(SOMO) HBT>NHAA>VA
  - No (or very low) SOMO density on VA and NHAA

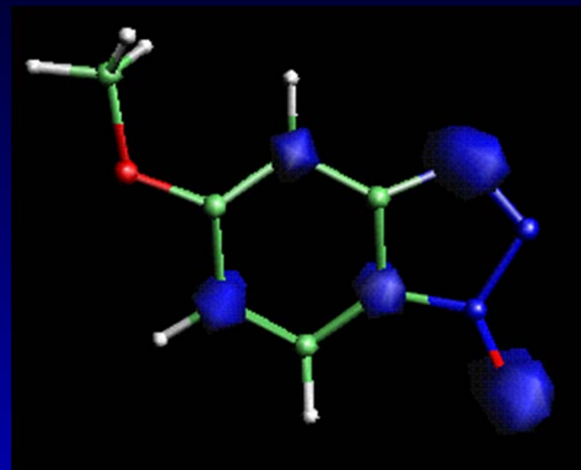
Effect of Substitution on HBT

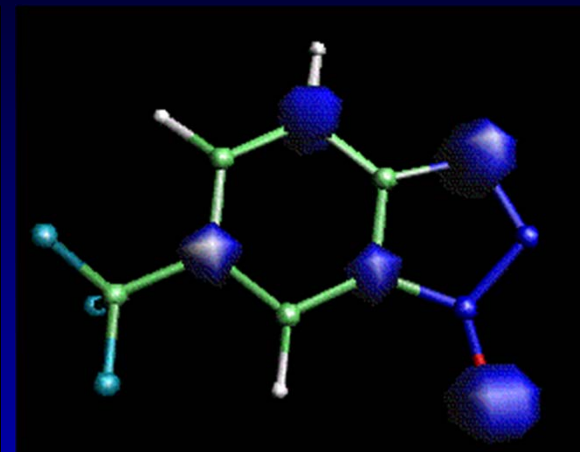
- All reactions are slightly endothermic
- Methoxyl and CF_3 substitution are energetically more favorable than HBT
- Substitution has little effect on spin density or SOMO



CH_3 | CH_3O | CF_3



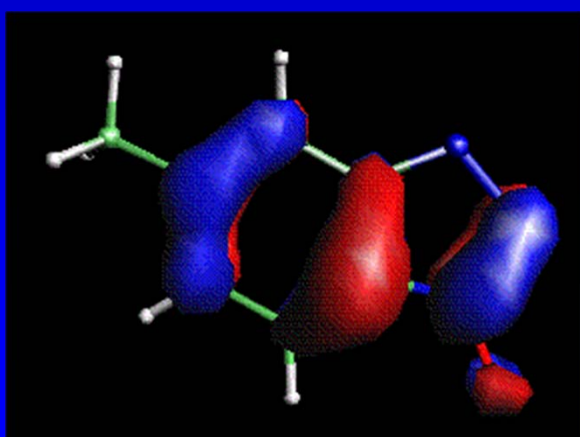


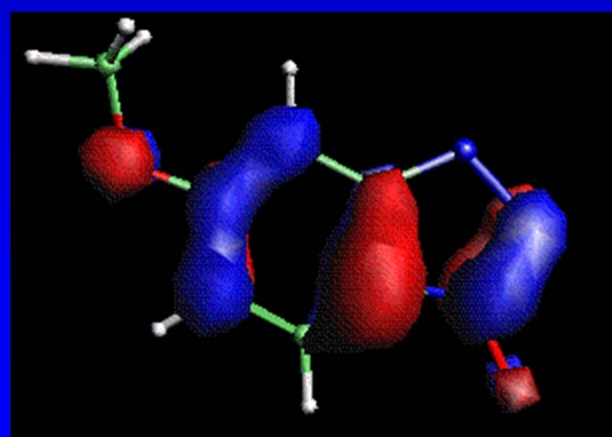


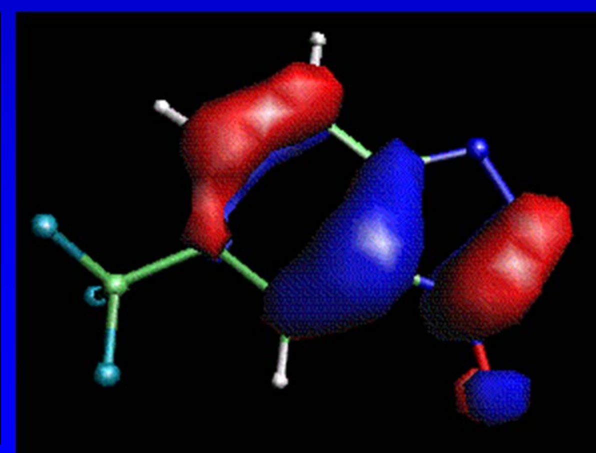
Spin density=0.91

Spin density=0.91

Spin density=0.92







E-SOMO=-9.4615eV

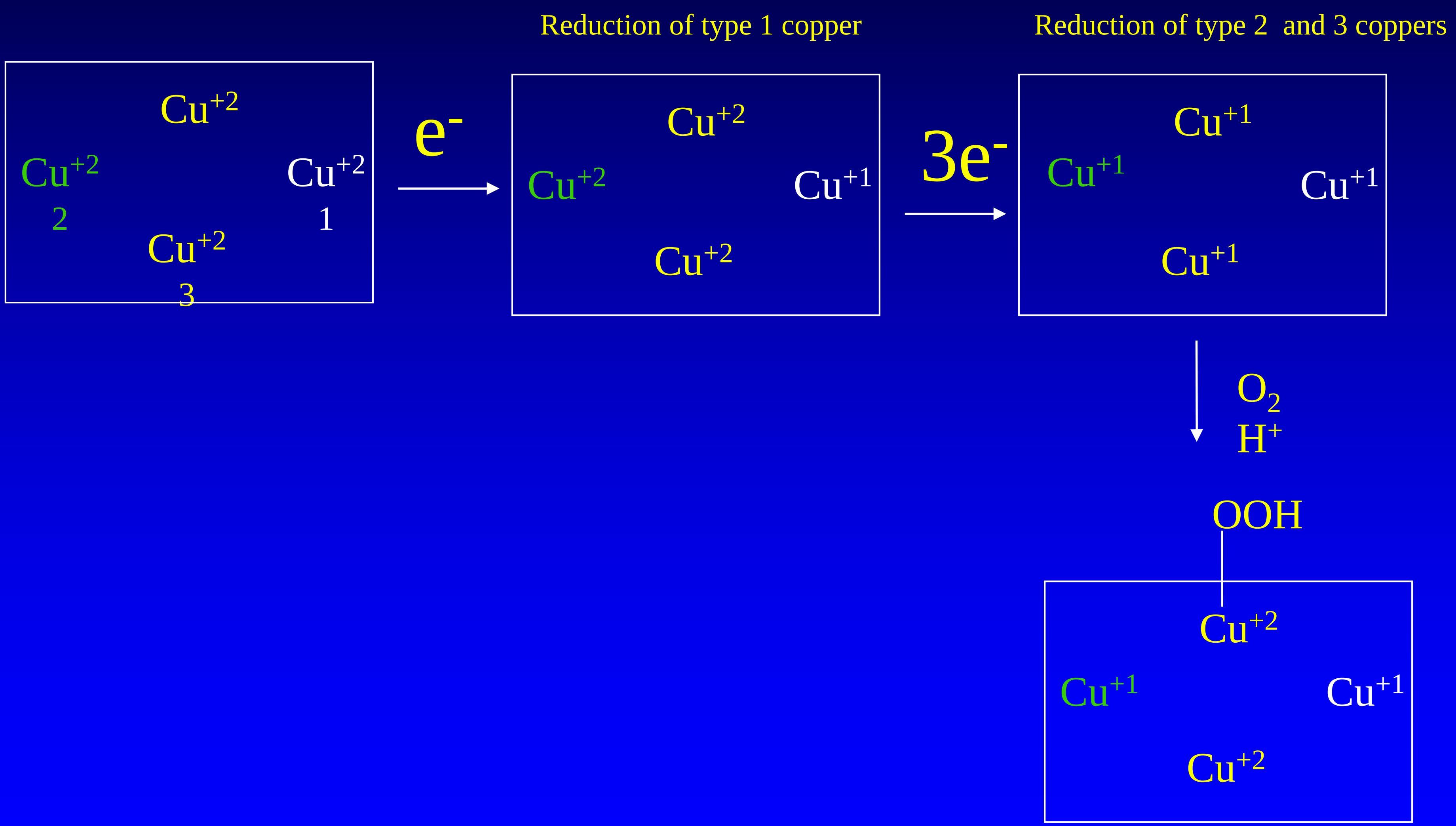
E-SOMO=-9.2873eV

E-SOMO=-10.2316eV

Calculations on Laccase

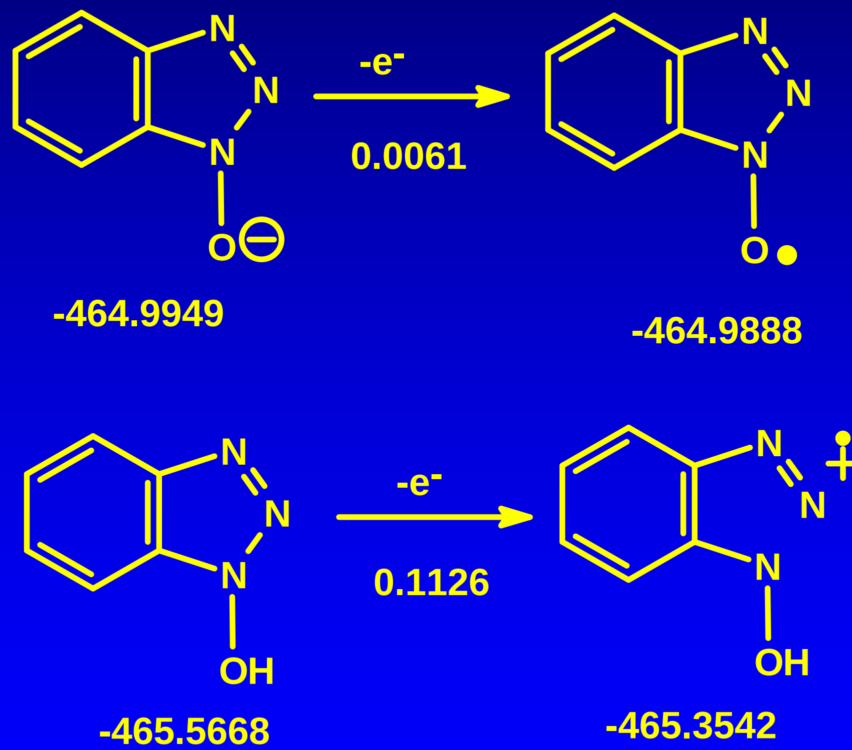
- Initial reduction from Cu^{+2} occurs at type 1 copper via a single-electron transfer
- hydrogen adds to the peroxide form, in a subsequent step

Catalytic cycle (Messerschmidt et al. 1993)



Calculations on Active Site

- Where does the initial single electron come from?
  - Dissociated form of substrate (or mediator)
  - Single electron transfer from substrate (or mediator)
  - removal of single electron from anion is much less energetic

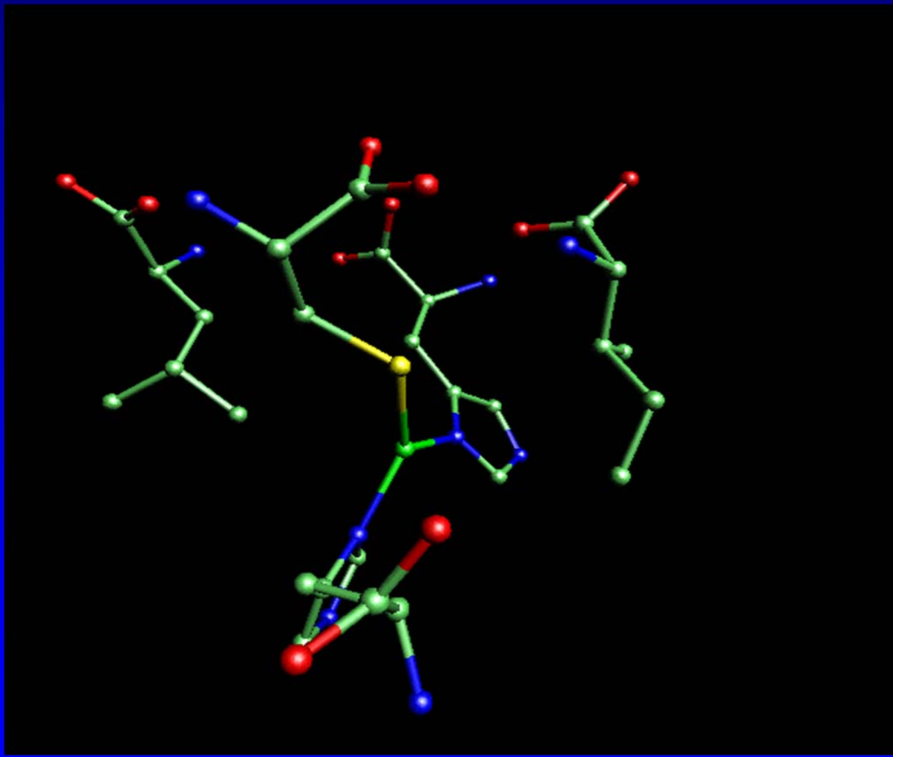


Calculations on Laccase

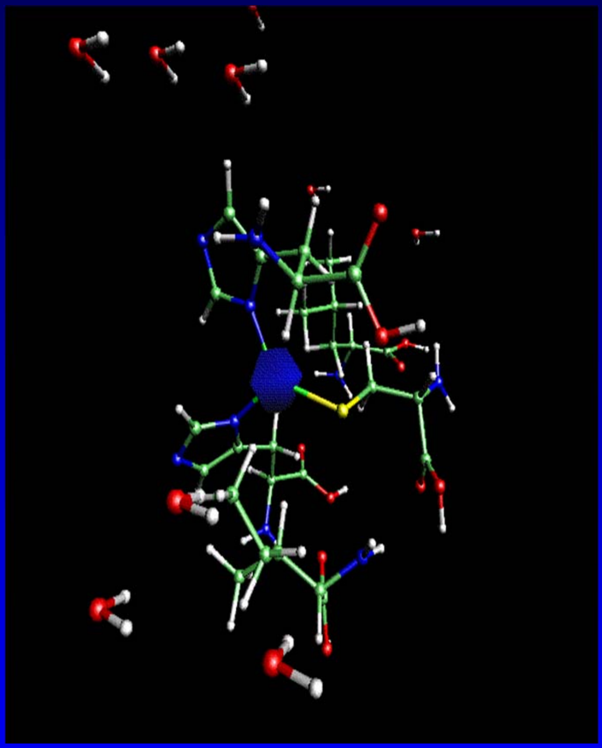
- Laccase structure has been recently released
  - 1A65 TYPE-2 CU DEPLETED LACCASE FROM COPRINUS CINEREUS
  - V. DUCROS, A.M. BRZOZOWSKI, K. WILSON, S. BROWN, P. OSTERGAARD, P SCHNEIDER, D.YAVER, A. PEDERSEN,G. DAVIES
  - Nat. Struct.Biol. 5:310 1998

Type 1-Active Site

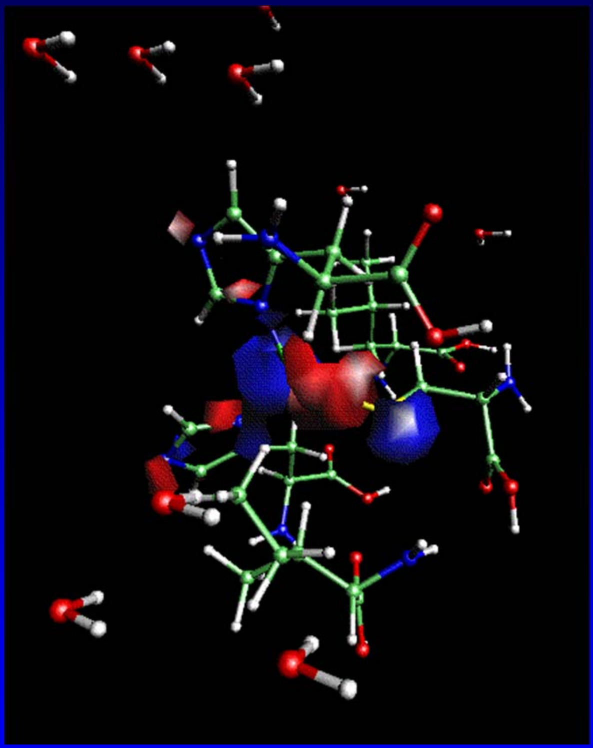
- Type 1-Copper (II) is bound to
  - 2 histidines
  - 1 cysteine
  - 1 leucine (variable)
  - small structural changes occur upon reduction



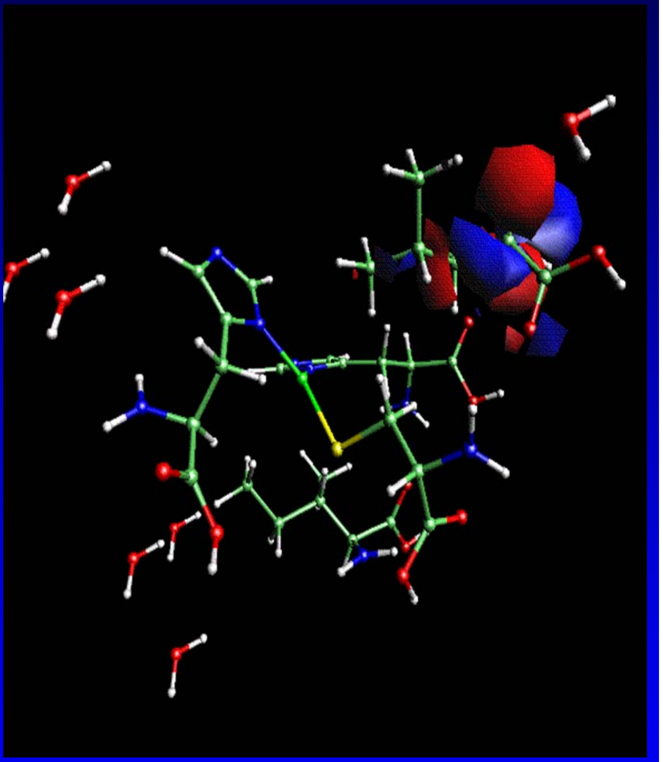
Type 1-Active Site-STO-3G



Spin density

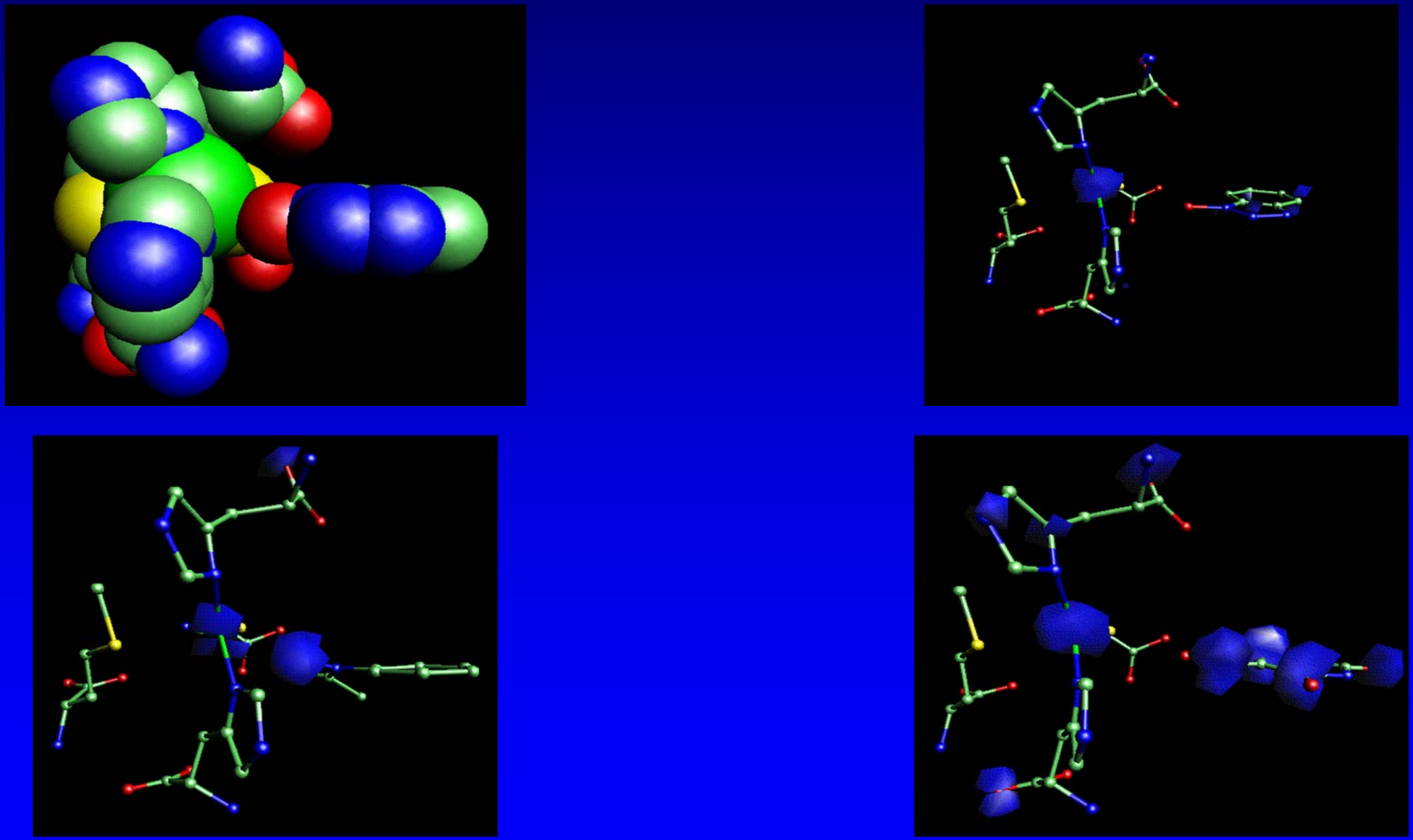


LUMO



HOMO

Interactions of Active Site with Mediators



Acknowledgements

- US Department of Energy
- Alabama Supercomputer Authority
- Auburn University Pulp and Paper Research and Education Center