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Quantum mechanical studies of the depolymerization of lignin by the $ZnCl_2$:Ethylene Glycol Deep Eutectic Solvent

PRESENTED BY

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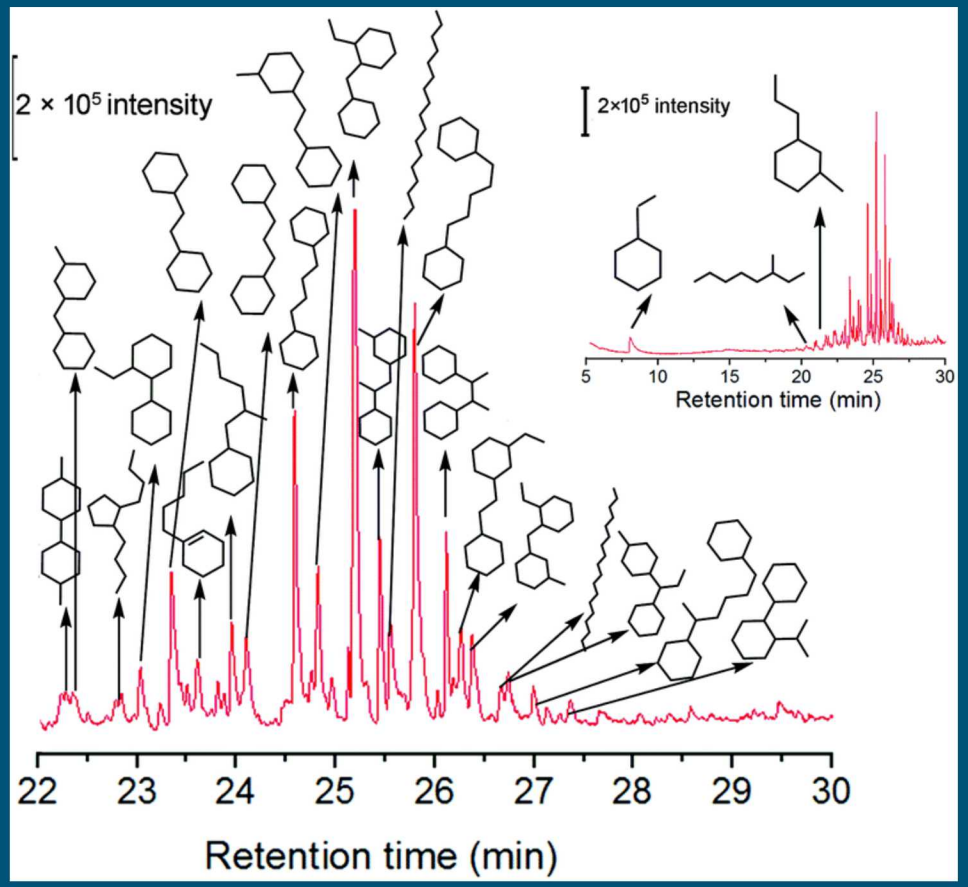
Depolylmerization of lignin: valuation of lignols

- Lignin makes up about 15 to 20% of all the worlds biomass
- Depolymerization => bio-renewable source for products
- Depolymerization of lignin is challenging
  - Technologically challenging
  - Expensive
- Ionic liquids can work, but starting materials are expensive
- Deep Eutectic Solvents => much cheaper
  - Can incorporate catalysts
  - May lead to cheaper depolymerization strategies

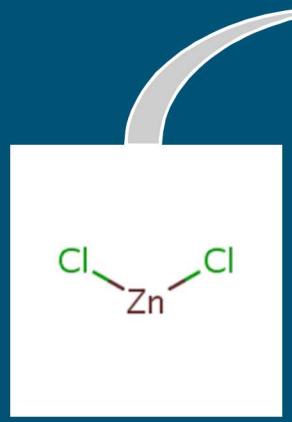


Green Chem., 2015, 17, 5131-5135

What is a Deep Eutectic Solvent (DES) ?

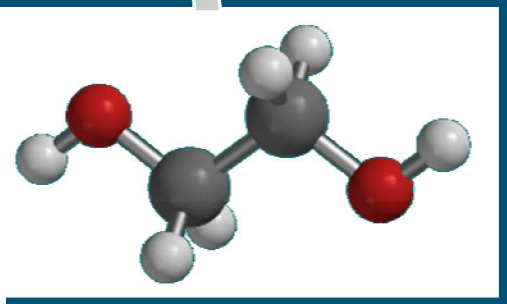
A eutectic is a solution which freezes at a temperature that is lower than the constituents which make up the solution

- Eutectics have many applications, including
  - Solubility
  - Extractions
- Solids which have high melting points can be dissolved => DES

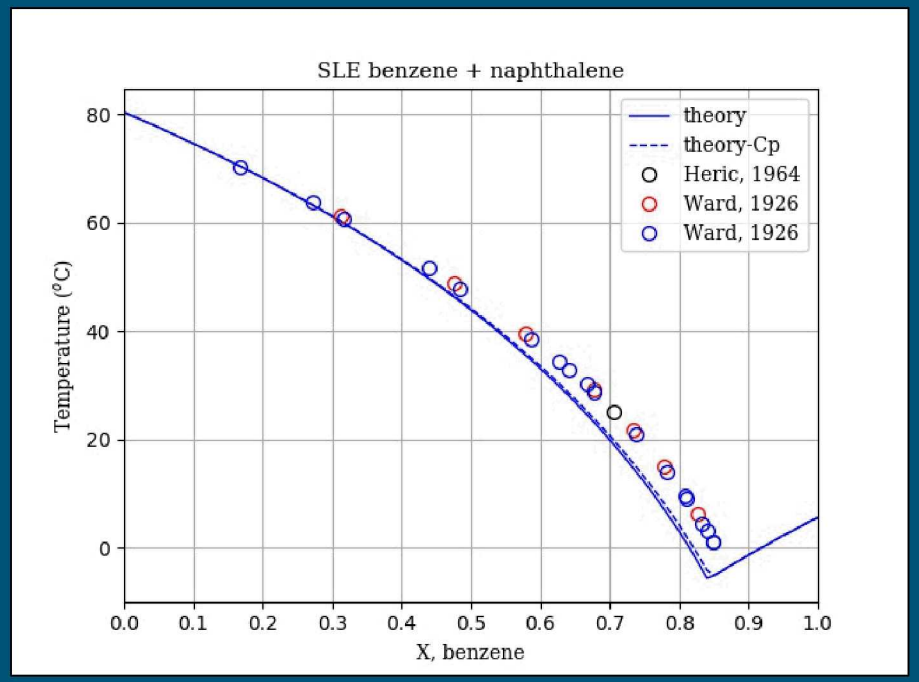


MP ~290°C

Liquid



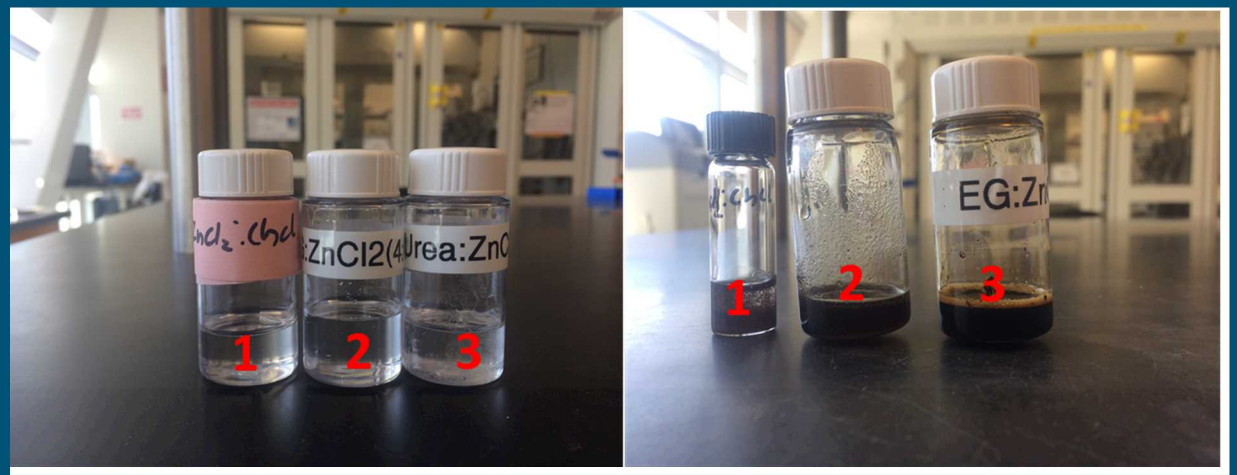
MP -12.9°C



EoS methods can provide reliable Solid-Liquid-Equilbrium curve estimates

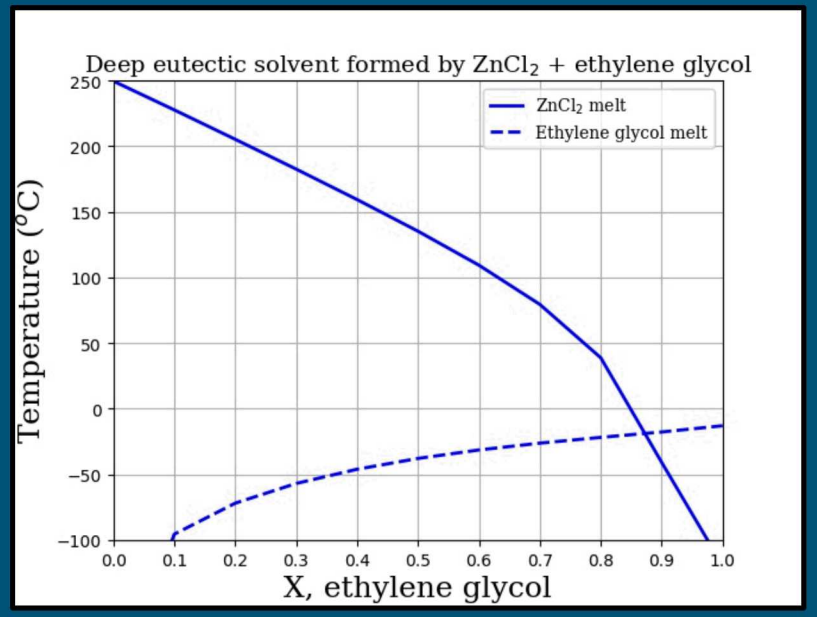
$ZnCl_2$ + ethylene glycol can form a DES

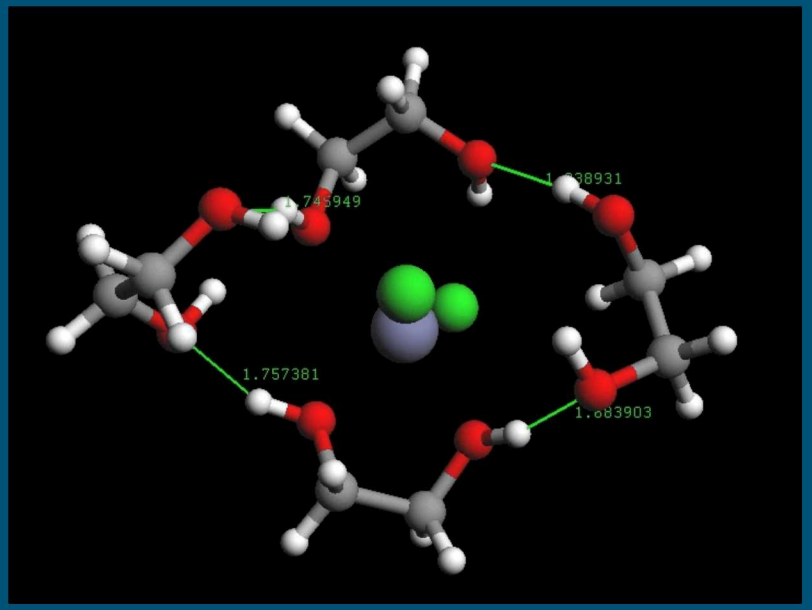
- The eutectic point occurs at 4:1 EG:$ZnCl_2$
- The eutectic solvent serves as a solvent for dissolving lignin
- $ZnCl_2$ => lignin dissociation



DES Synthesis (molar ratio)	Lignin solubility (120 °C)
1-> ZnCl2:ChCl (2:1) semi viscous	1-> ZnCl2:ChCl (2:1) ~10 wt %
2-> EG:ZnCl2 (4:1) not viscous	2-> Urea:ZnCl2 (3.5:1) 1 wt%
3-> Urea:ZnCl2 (3.5:1) very viscous	3-> EG:ZnCl2 (4:1) >10 wt%

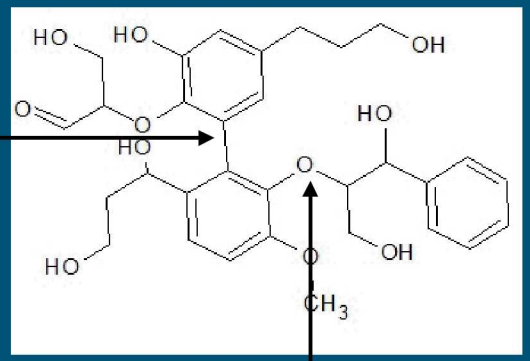
Lignin solubility is > 10 wt%



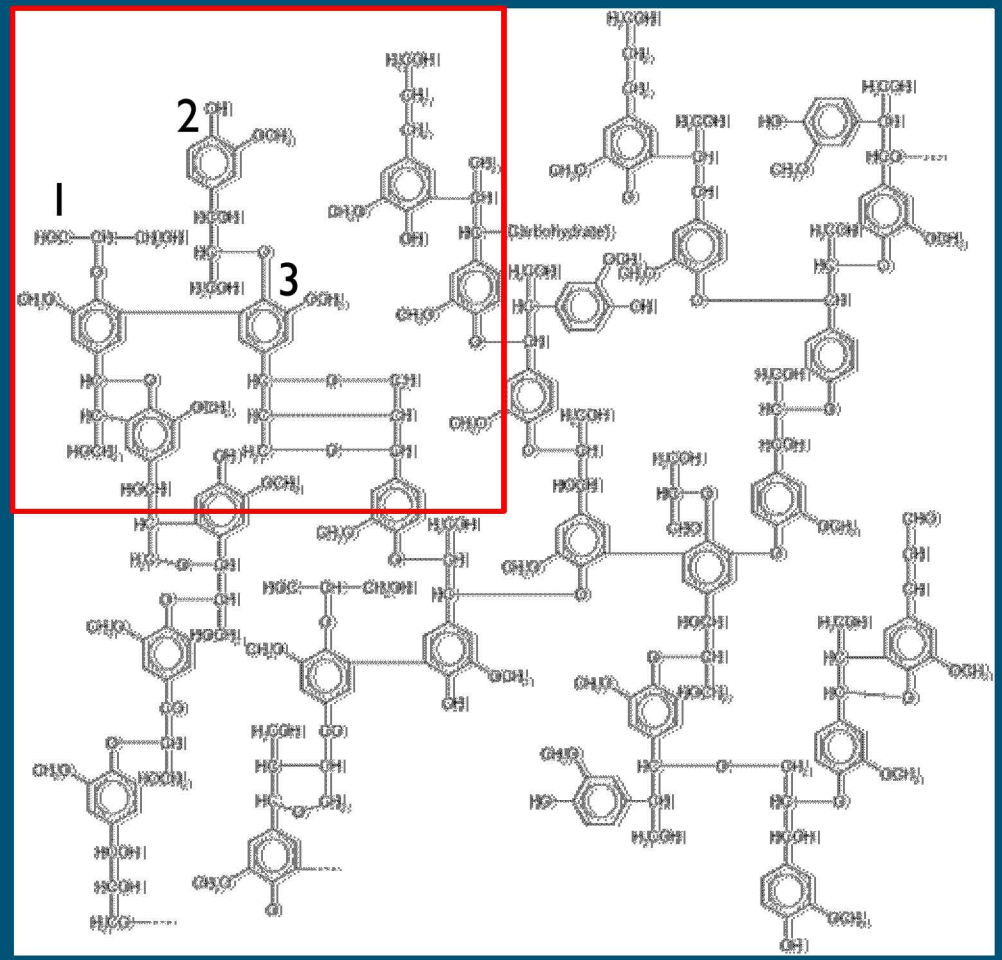


Lignin model

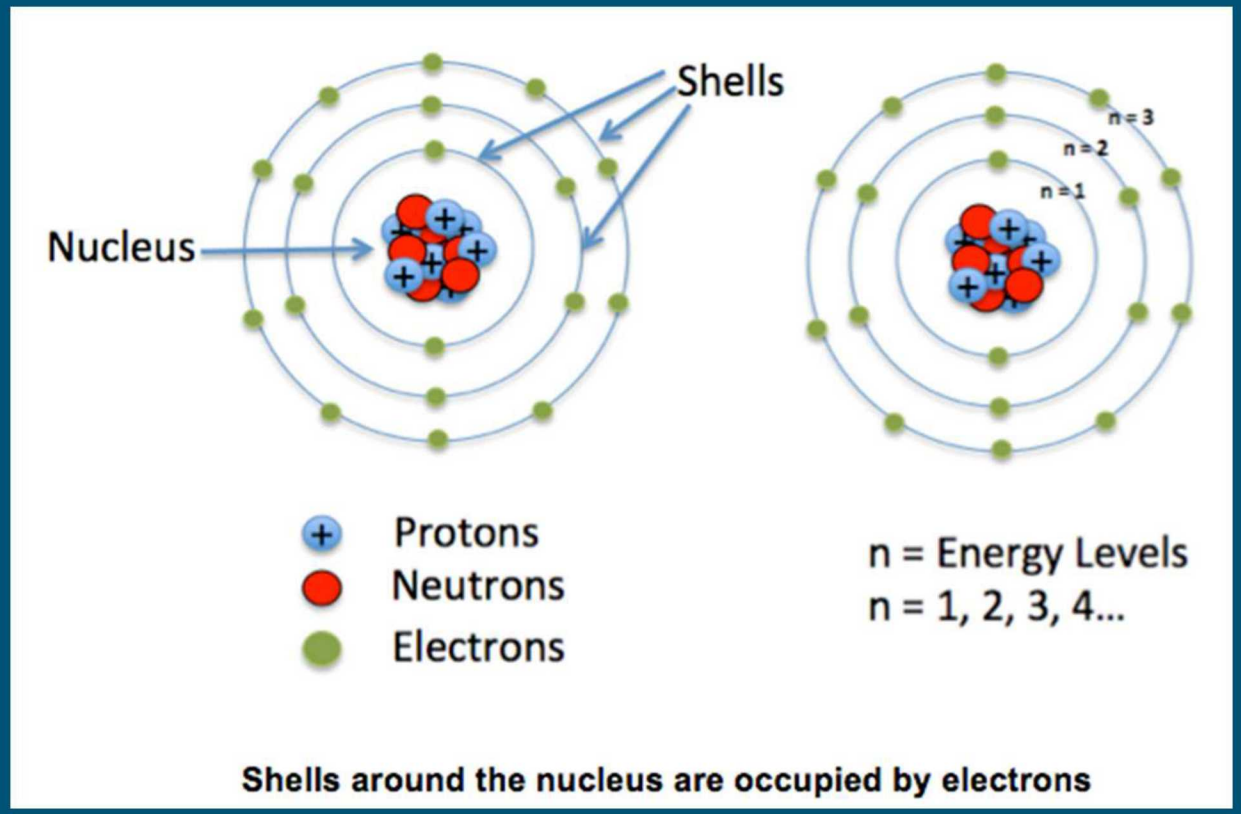
β-β-linkage



B-O4 linkage



Methodology



- Geometry optimizations (B3LYP/6-31+G*)
- Frequencies/ZPE using B3LYP/6-31+G*
- Solvation included using PCM (polarized continuum model) ethylene glycol
- Zn is modeled using LANL2DZ ECP
- Single point calculation using MP2/6-31+G*
- Accuracy of B3LYP is ~ 6 kcal mol^{-1}
- Accuracy of MP2 is ~ 4 kcal mol^{-1}

- B3LYP => some e^- correlation
- MP2 => 2nd order perturbation on HF
  - Includes more e^- correlation

e^- correlation is important in computational chemistry

Anatomy of a Basis set

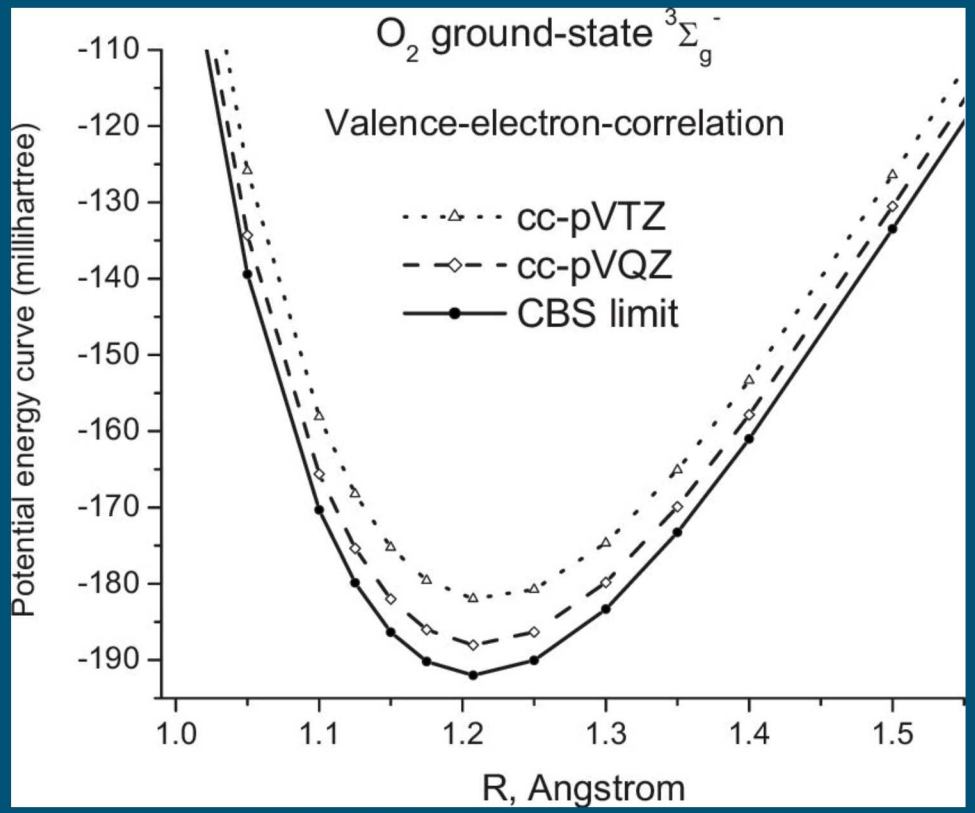
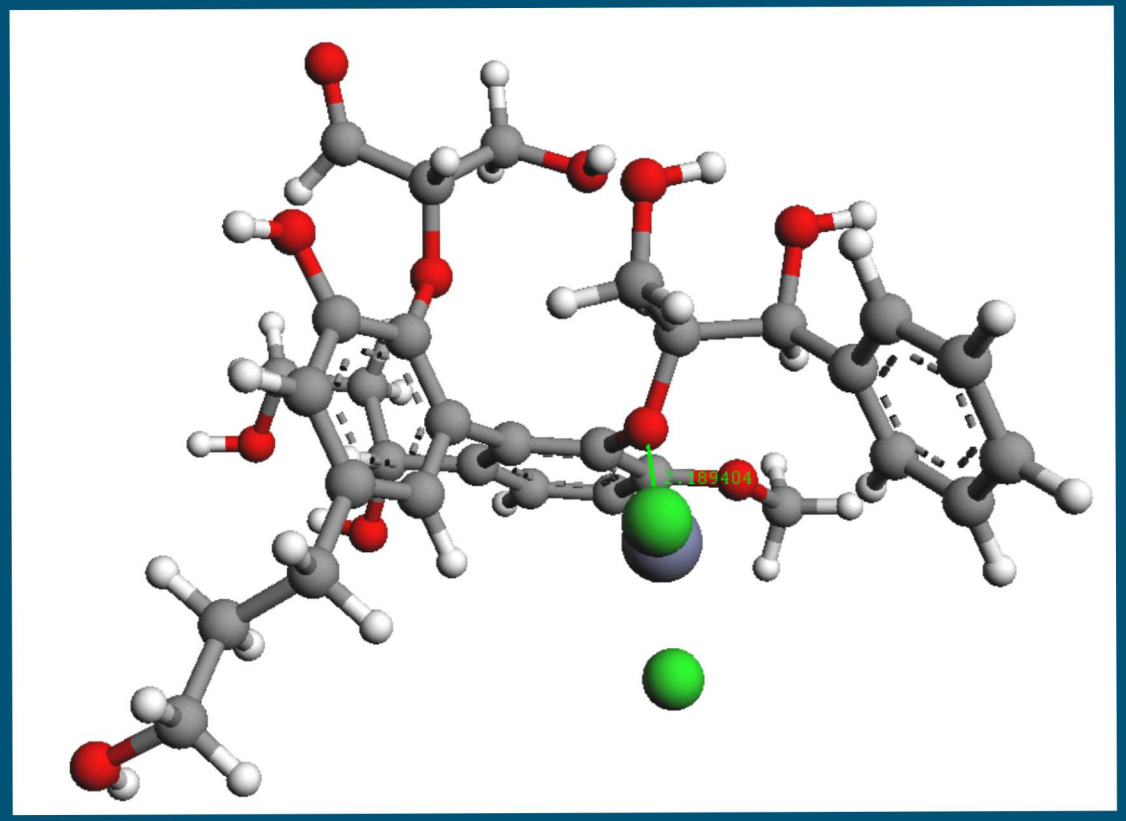


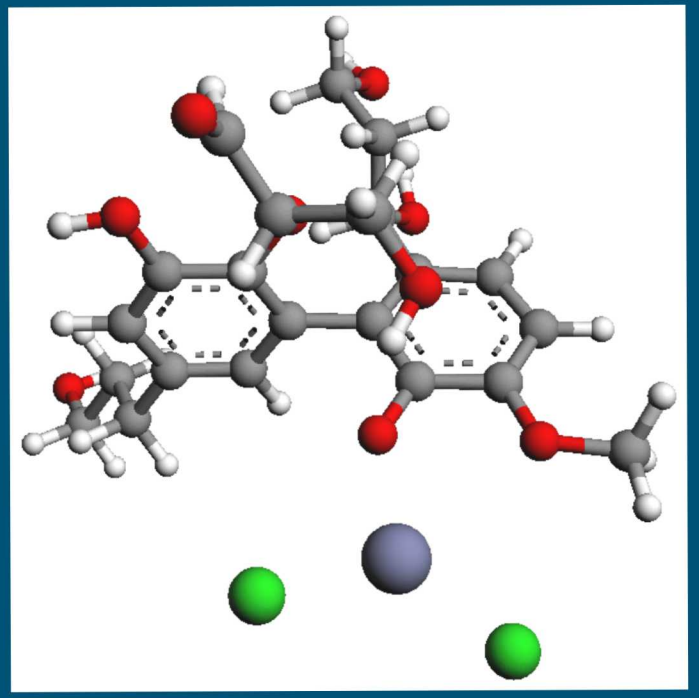
FIG. 1. Lower parts of the full valence-CI PECs [E(O2X Σ3g−)−2E(O P3)] obtained by CEEIS calculations using Dunning's correlation-consistent triple- and quadruple-zeta basis sets and the CBS limit.

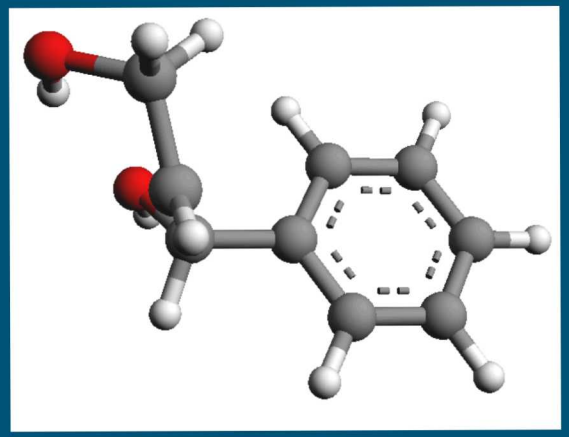
Published in: Laimutis Bytautas; Klaus Ruedenberg; *J. Chem. Phys.* **132,** 074109 (2010)
DOI: 10.1063/1.3298373

- 2 parts to a QM method
  - The physics behind the calculation
  - The way e- are described
- The physics was explained in the previous slide
- The e- description => basis set
- Basis set => # functions used to describe C, O, H
- Bigger basis sets => more accuracy (usually)
- Unsuitable basis sets => large errors
- 6-31+G* => small but relatively accurate
  - Includes diffusion functions
  - Includes polarization functions (imp. charged systems)

Results: Simple dissociation



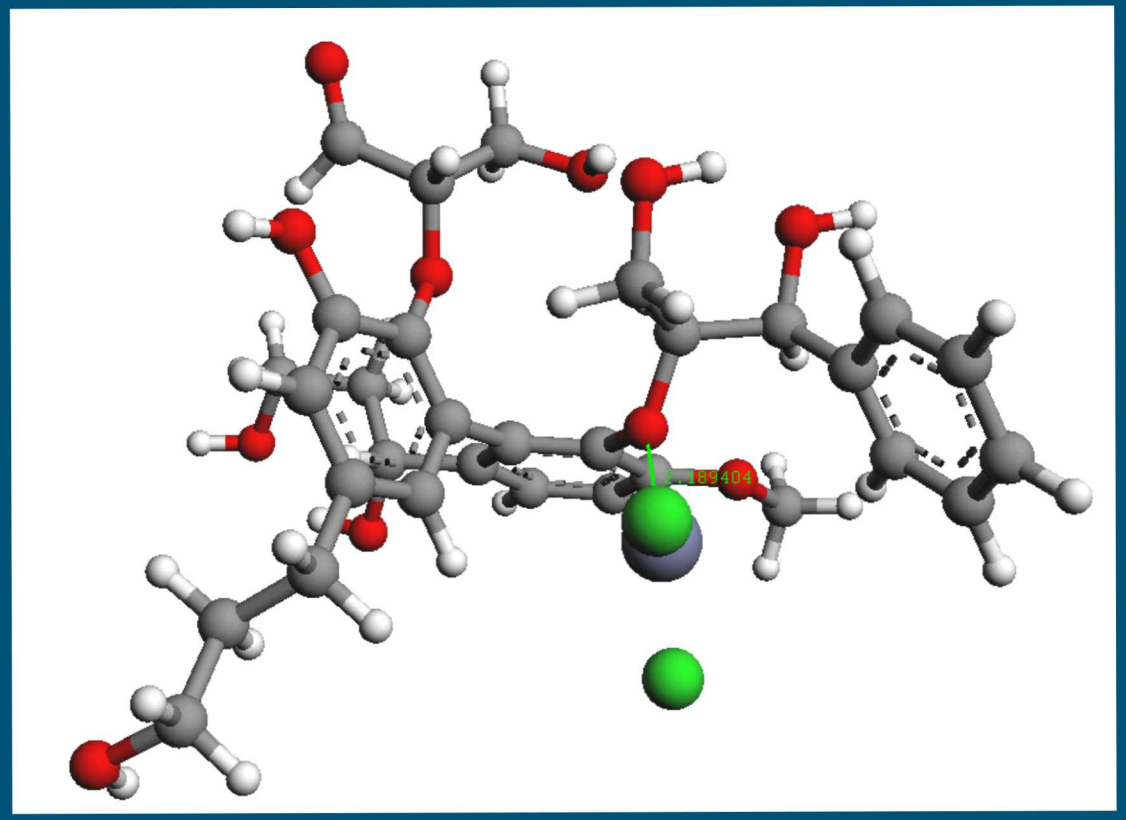


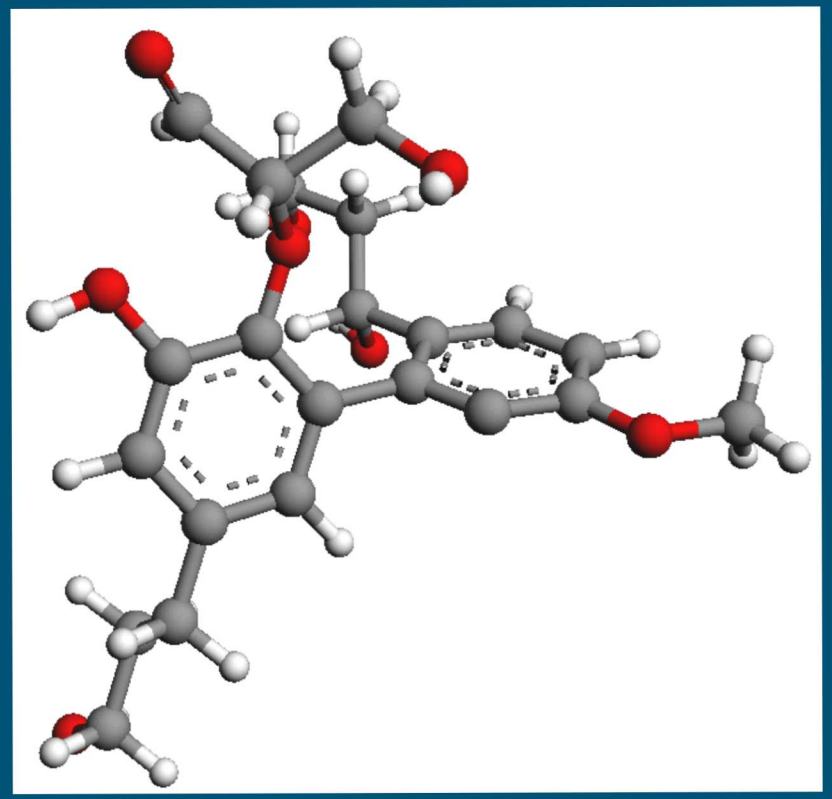


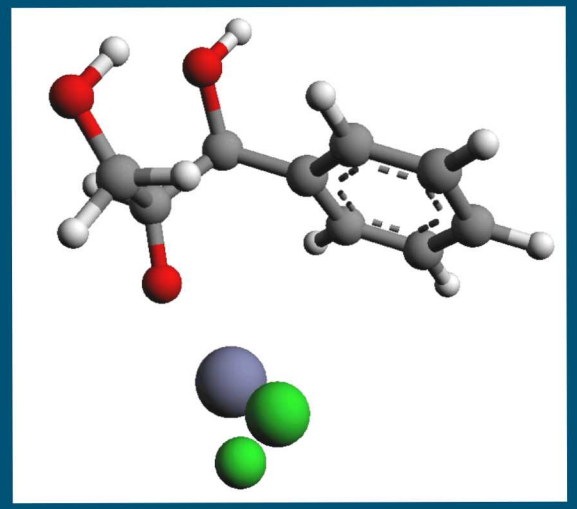
ΔE_{rxn} = 38.49 kcal mol^{-1}

ΔE_{rxn} (without $ZnCl_2$) = 76.53 kcal mol^{-1}

Results: Simple dissociation cont.



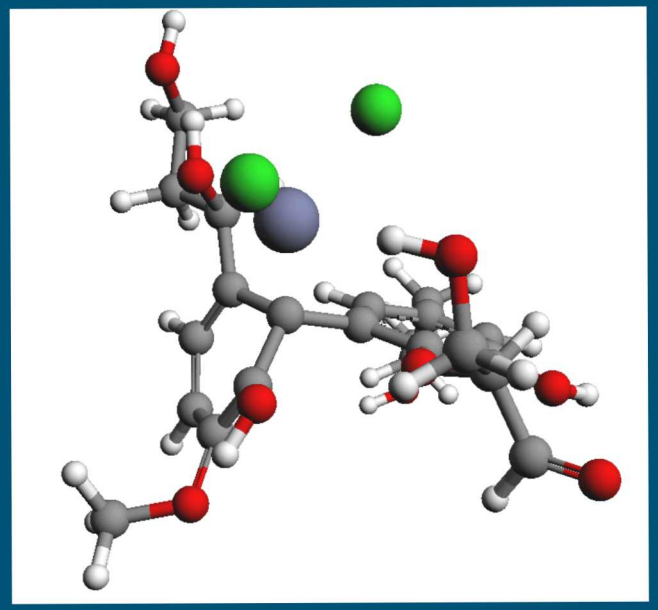


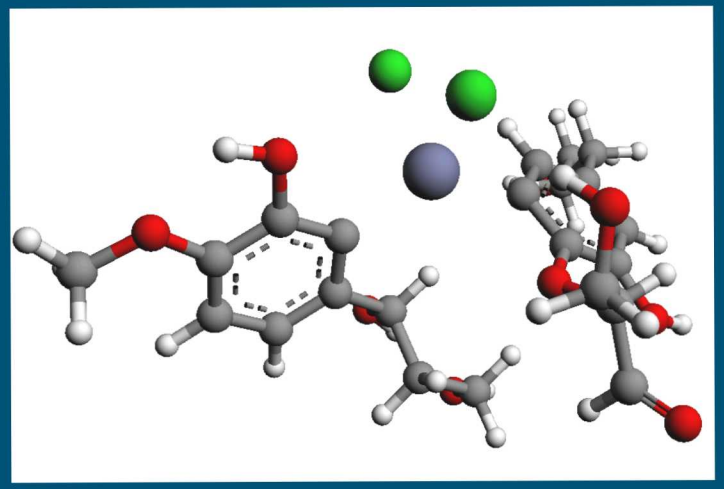


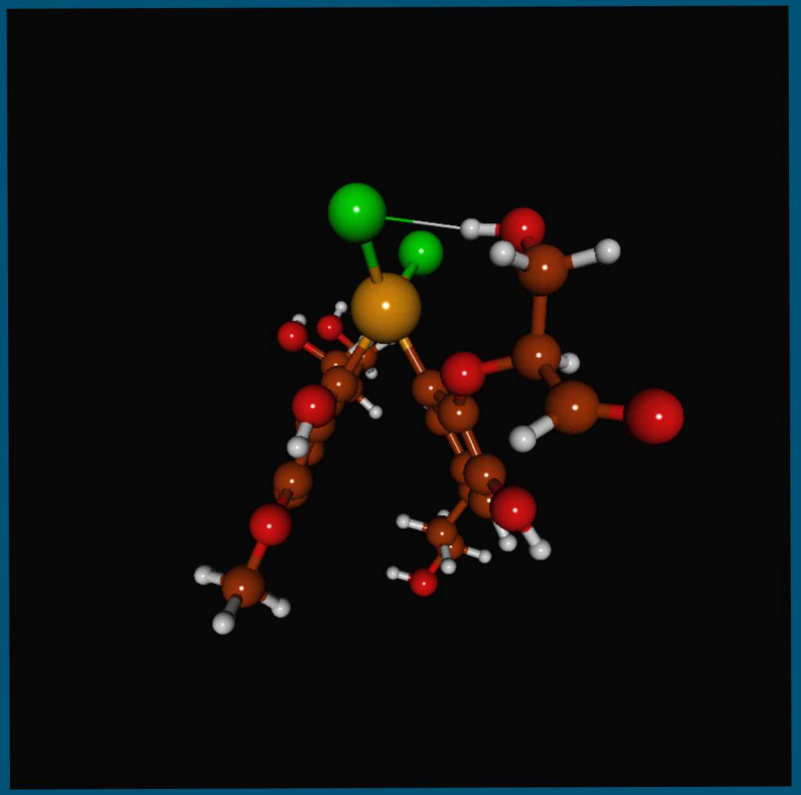
ΔE_{rxn} = 87.37 kcal mol^{-1}

ΔE_{rxn} (without $ZnCl_2$) = 85.10 kcal mol^{-1}

Results: Dissociation of di-lignol

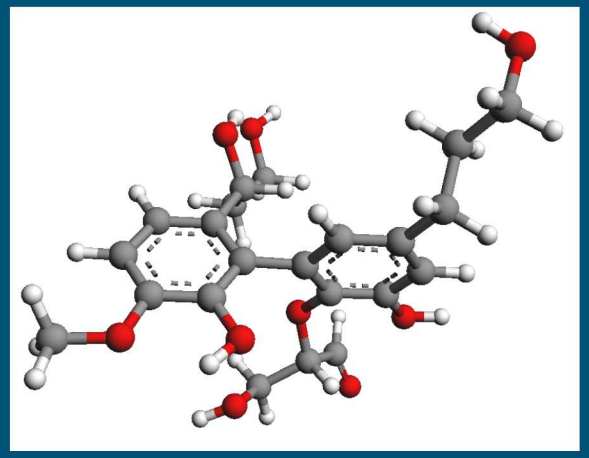


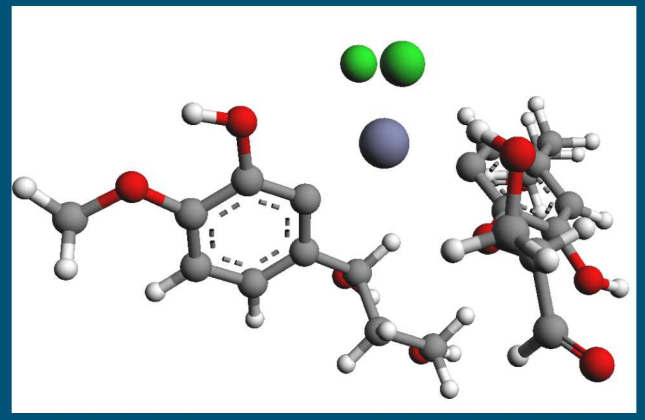


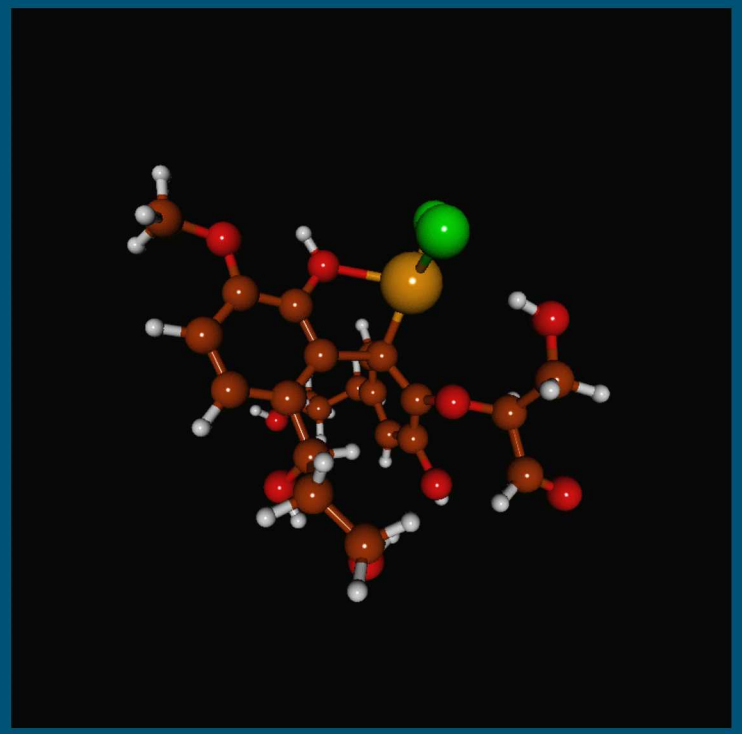


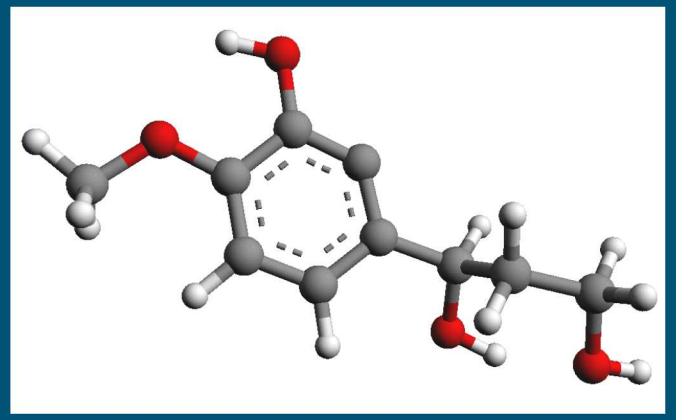
$ZnCl_2$ attacks the di-lignol by first attacking one of the aromatic rings. It then intercolates in between the two aromatic rings, before destroying the β-β-linkage

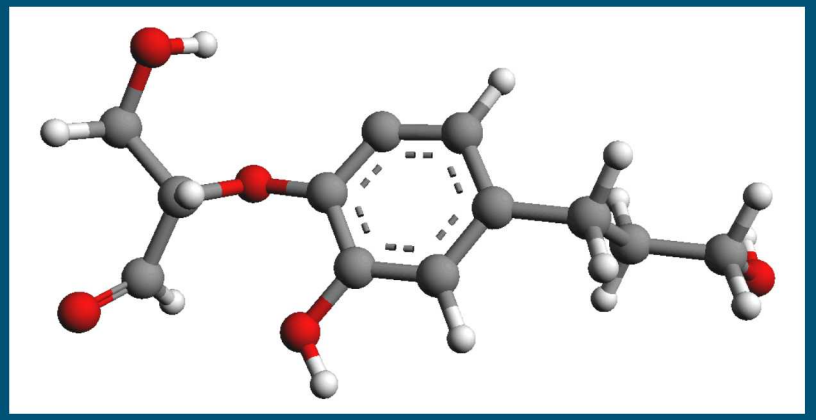
Results: Dissociation of di-lignol cont.







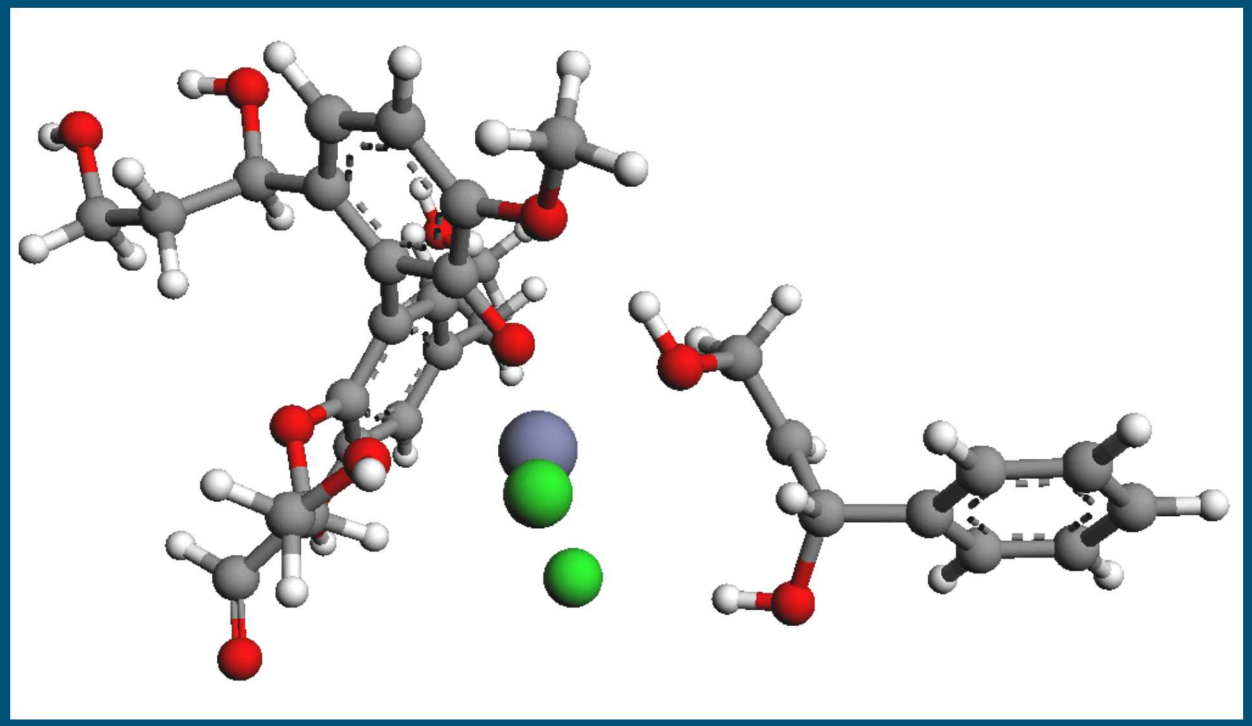


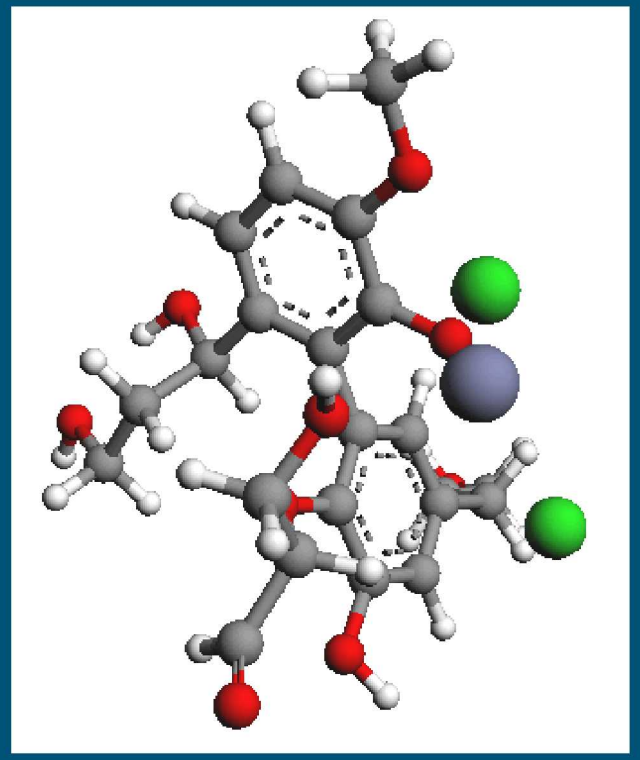


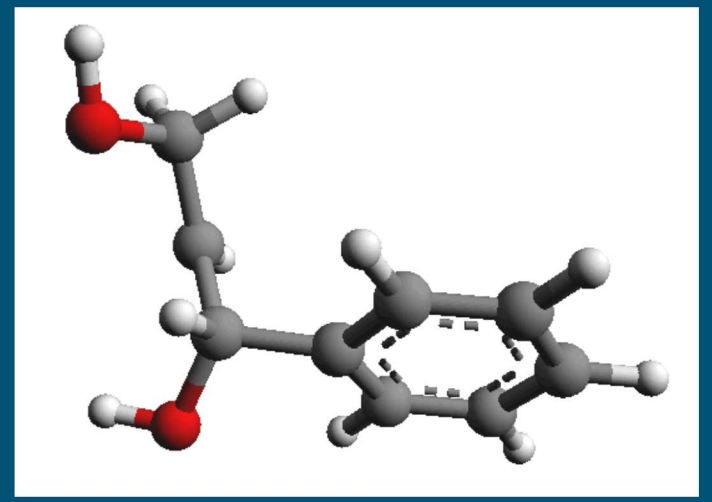
ΔE_{rxn} = -19.93 kcal mol^{-1}

ΔE_{rxn} (without $ZnCl_2$) = 103.58 kcal mol^{-1}

Results: anionic potential energy surface



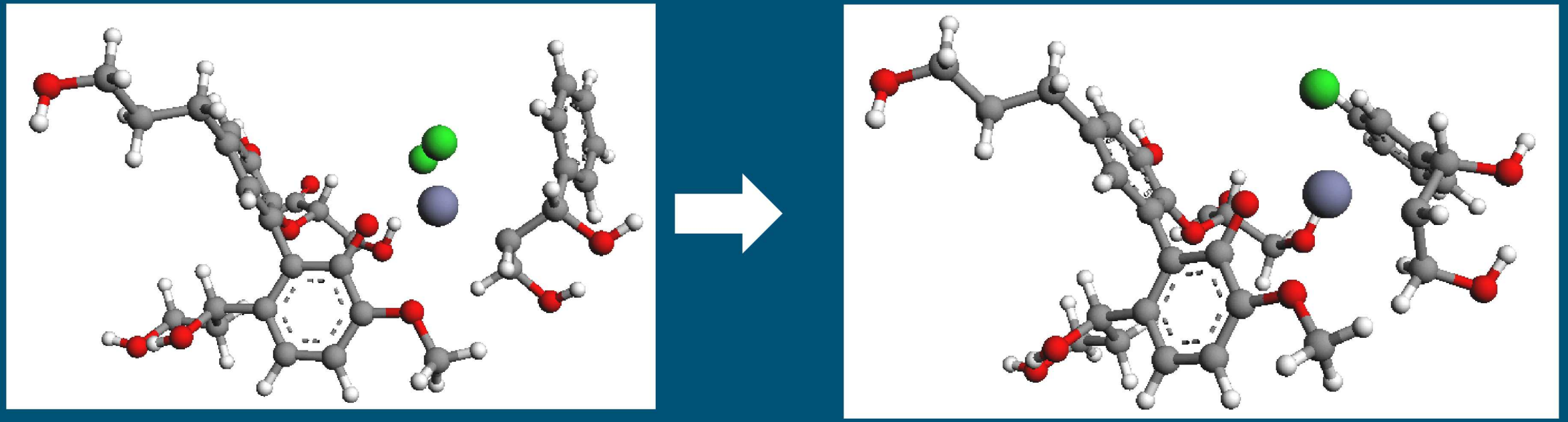




Oxygen donates an e^- to Zn => covalent bond
Leading to a negative charge on Zn
Configuration of Zn = [Ar] $3d^{10}4S^{2}5S^{1}$

ΔE_{rxn} = 15.33 kcal mol^{-1}
ΔE_{rxn} (without $ZnCl_2$) = 76.53 kcal mol^{-1}

Results: Anionic potential energy surface cont.



Summary

- $ZnCl_2$ can be used as a catalyst in the depolymerization of lignin
- Hydrogen bonding is potentially important to the depolymerization of lignin
- If hydrogen bonding changes (quantity, position, strength), then energetics and kinetics may change
- Other tri-lignol configurations need to be tested to understand the role hydrogen bonding plays
- The overall charge on Zn may also be important
- If Zn can take on a negative charge, the energetics and kinetics of lignin depolymerization changes
- Extension to quaternary and pentameric polymers of lignin may also be possible

Questions ?