



## Introduction

- Exposure to heavy metal compounds causes various detrimental health effects<sup>1</sup>
  - Effects of mercury exposure include:
    - Minamata Disease<sup>2</sup>
    - Impaired Neurological Development<sup>3,4</sup>
- Research involving a BODIPY crown ether (Kim et al., 2009) has demonstrated that substituting oxygen with sulfur atoms makes the crown more selective to 'soft' heavy metals such as mercury (II)<sup>5</sup>
- Crown ether**: a molecule known for its ability to capture cations
- BODIPY**: a fluorophore dye that emits fluorescence

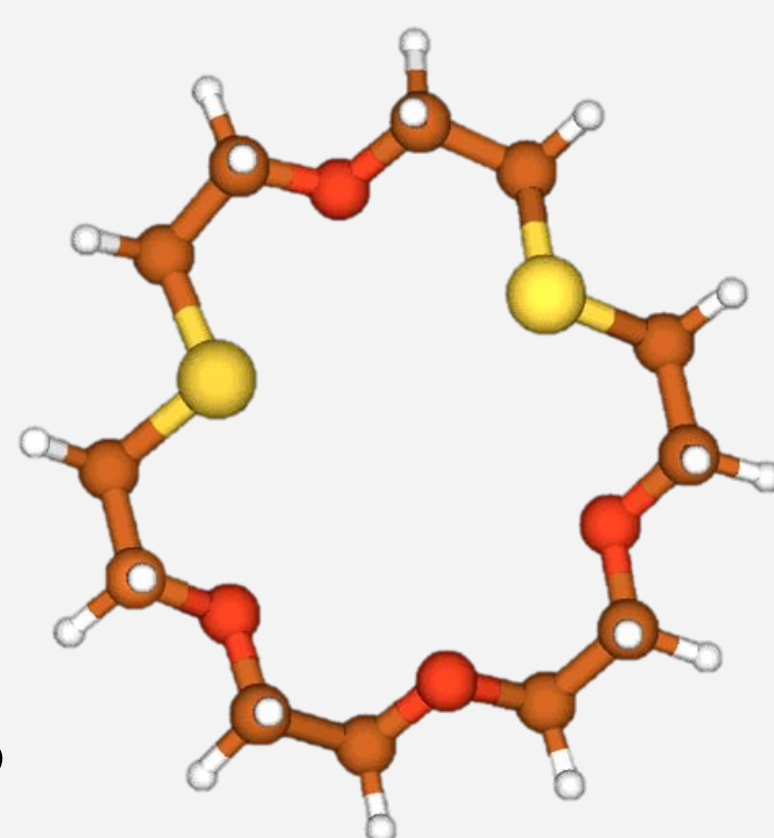


Figure 1: Optimized crown ether

## Purpose

- To find the optimal oxygen-sulfur substitution that would allow for the crown to have a higher affinity to mercury over other heavy metals.

## The Cost of Computational Research

- Calculations require memory, processors and time
- Programs: Gaussian<sup>6</sup> or GAMESS<sup>7</sup>
  - Gaussian is faster, but it is licensed.
- Methods: RHF(Restricted Hartree-Fock) or DFT(Density Functional Theory)
  - RHF is faster but DFT gives more accurate results



Figure 2: Large files are run on the Canada-wide supercomputer, Grex

## Background Information

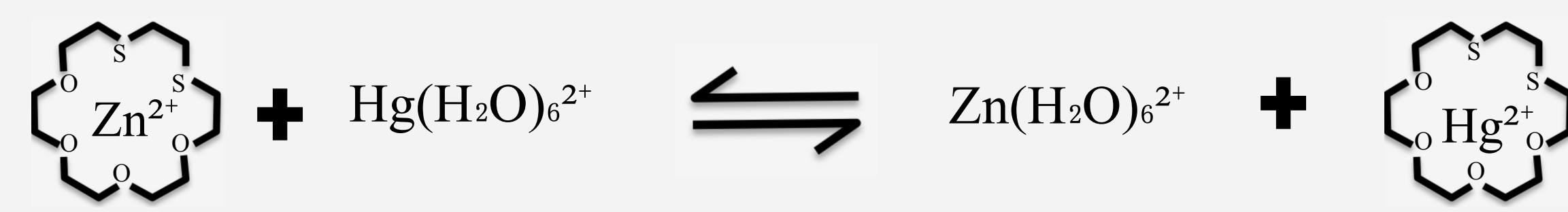
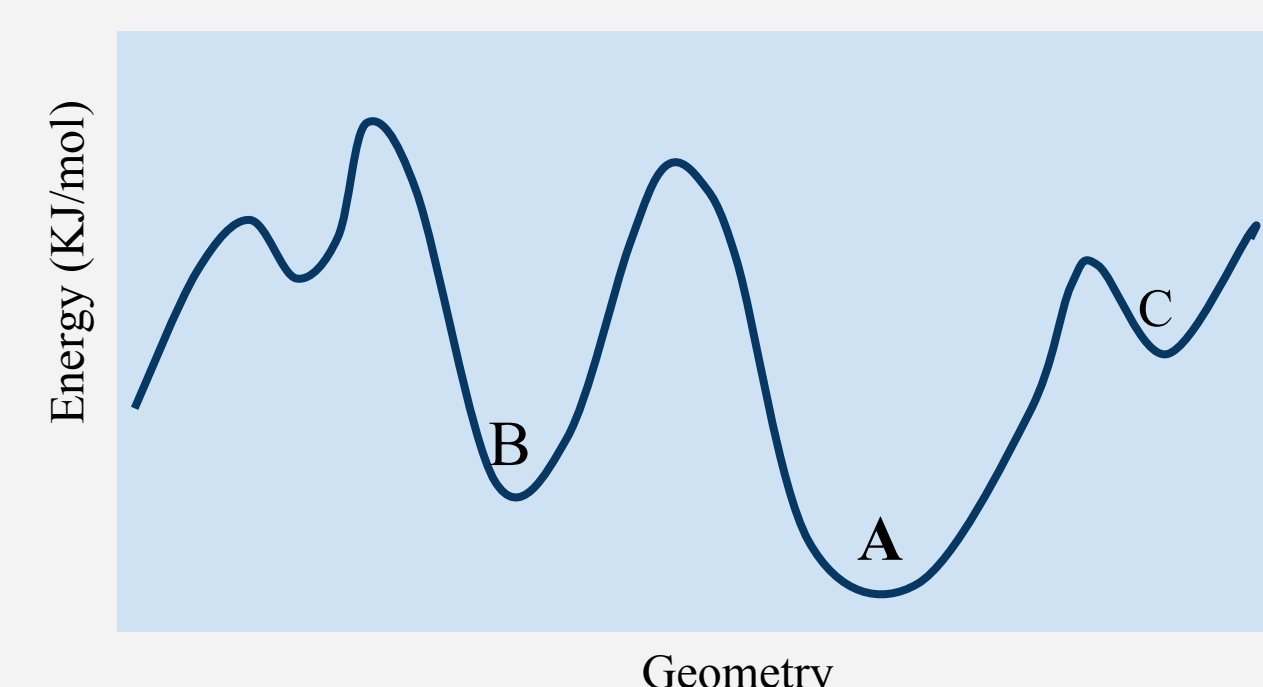


Figure 3: Exchange reaction which occurs during calculation. Each side of the equation is evaluated for lowest energy and affinity of metal to crown; which is used to determine the preferred side of the equation.

### Geometry Optimization:

- coordinates of the local minima; where the molecule has the lowest energy.

Figure 4: Energy of a molecule. While there may be multiple local minimas(A,B,C); geometry optimization finds the global minima(A).



## Methods

- Computational chemistry involves running theoretical calculations on molecules

### Create Input File

#### Input files specify:

- Computational requirements
- Type of calculation
- Method and basis sets
- Molecular Geometry
- Run calculations on file

```
%NProcShared=2
$mam=10GB
#p test RHF/gen 6d Pseudo=read opt=(calcAll, cartesian)
freq
SCF=Tight GFinpup Iop(6/7=3)

18-crown-2-S4-PBE1PBE/6-31G(d) ... Coord built from
18c2s4_para_rhf_631d_gx.xyzopt/2 isolated pairs of Sulfurs

2 1
Cd 0.000000 0.000000 0.000000
C -0.558867 -3.536197 -0.007998
C -3.416093 2.352157 -0.186902
C 2.179250 -3.106588 -0.273262
```

## Methods

Calculations:

Geometry Optimization

Frequencies

Output File

\*\*\*\*\* EQUILIBRIUM GEOMETRY LOCATED \*\*\*\*\*

TOTAL ENERGY = -2255.9482633776

COORDINATES OF ALL ATOMS ARE (ANGS)

ATOM	CHARGE	X	Y	Z
HG	80.0	0.0012627227	-0.0286989352	0.0026295802
C	6.0	0.7186587702	-3.6113830812	-0.2406186463
C	6.0	-4.0421696694	1.1107662966	-0.3180589728
C	6.0	3.0807844719	-2.2385754298	-0.7211853317
C	6.0	-4.0694176638	-1.1829128151	0.2876247438

Calculation:

Creates an output file containing:

☐ Optimized geometry
 ☐ Frequencies
 ☐ Thermochemistry (energy)

### Visualize Molecule

- Changes to the crown can be seen through visualization programs

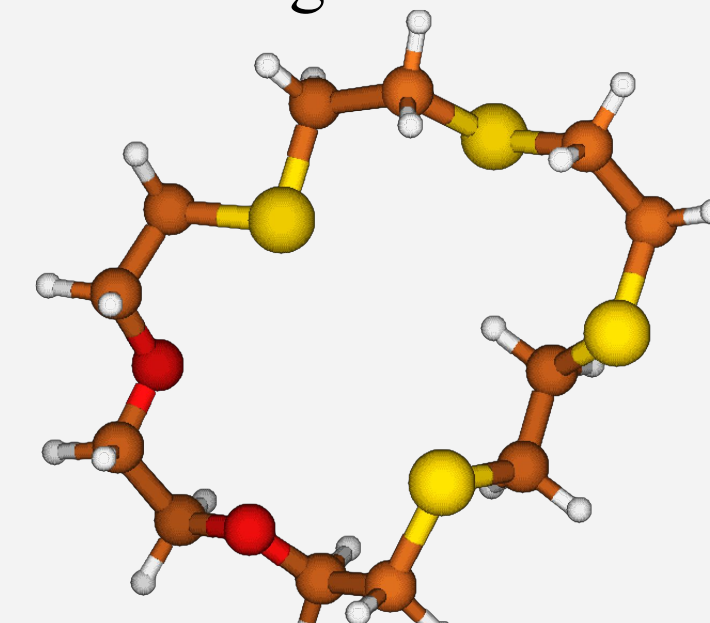


Figure 5.1

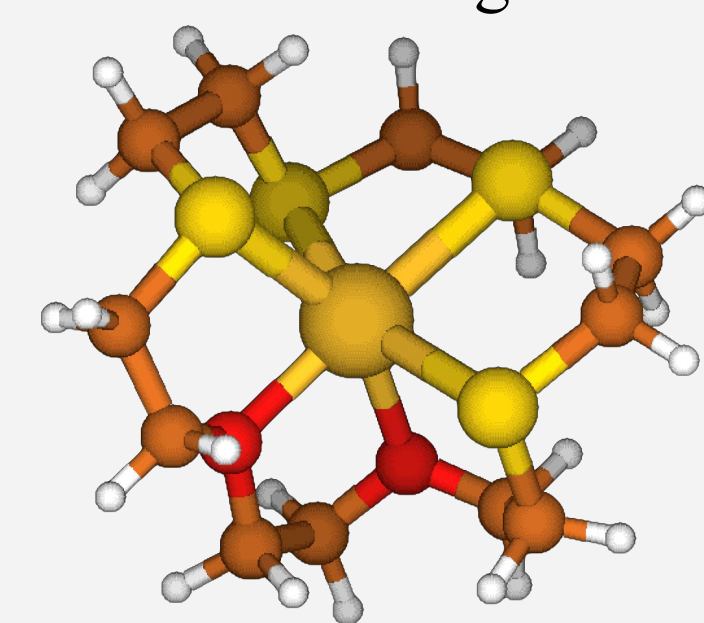


Figure 5.2

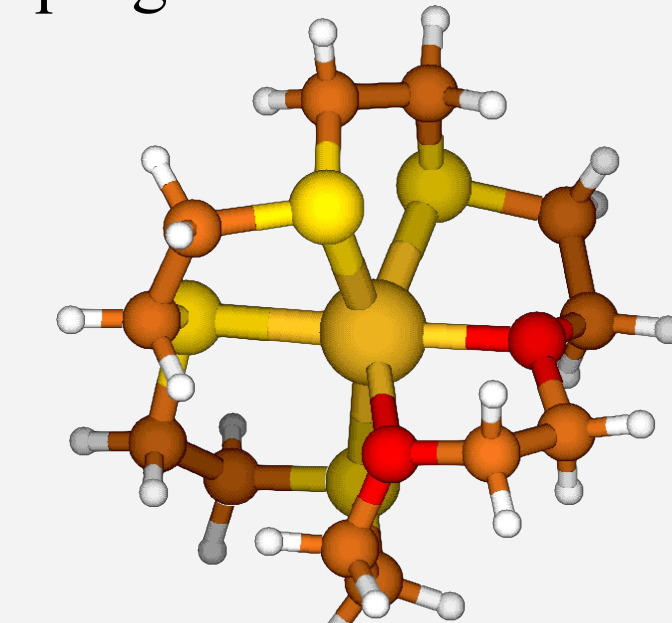


Figure 5.3

Figure 5: Visualization of 3 molecules using Molden<sup>8</sup>. **Figure 5.1:** Crown ether in gas phase **Figure 5.2:** crown ether with added metal (Zn<sup>2+</sup>) in gas phase **Figure 5.3:** crown ether with Zn<sup>2+</sup> in acetonitrile solvent

## Results

Figure 6:

Negative values indicate Hg is the preferred metal in the crown during exchange reaction.

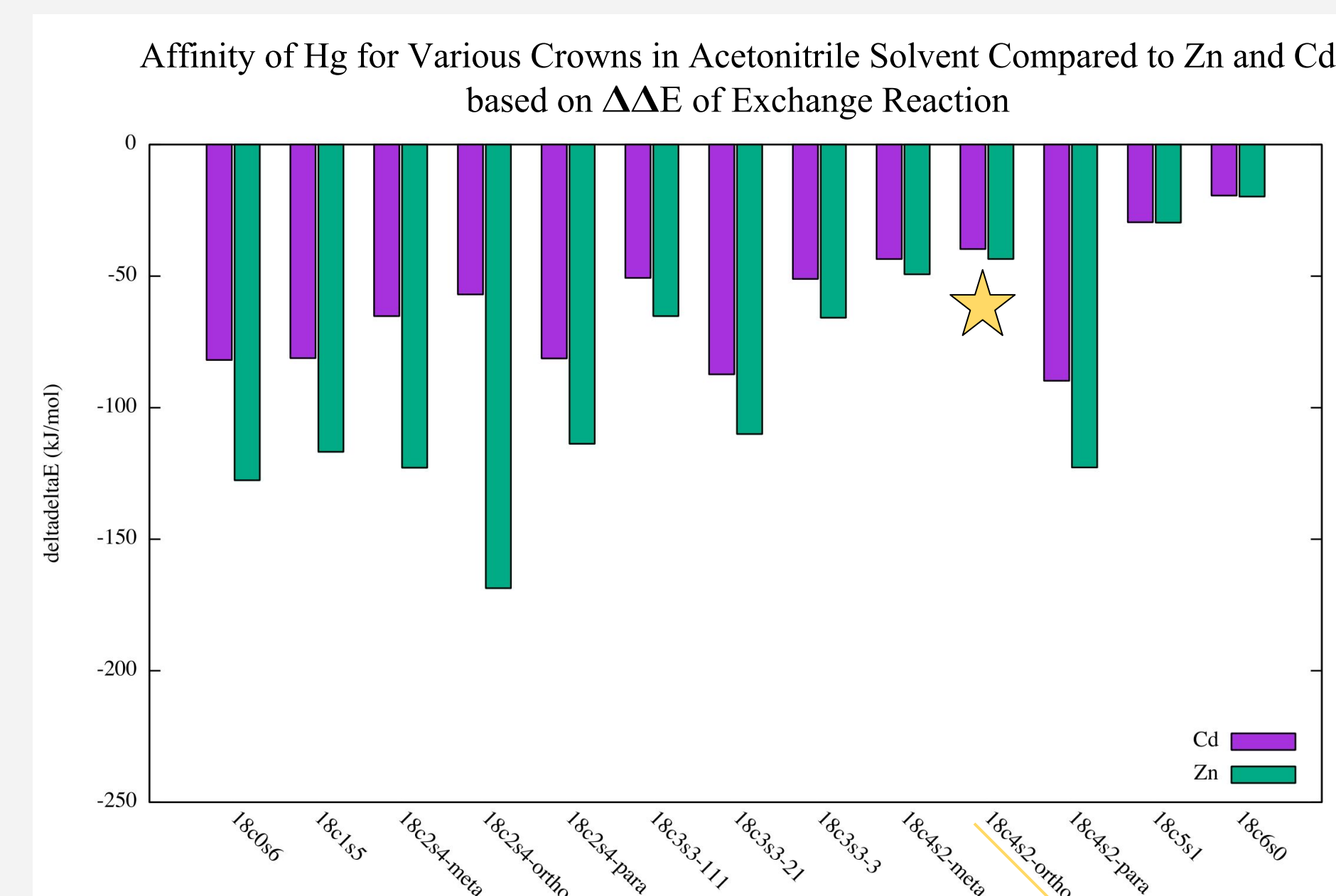
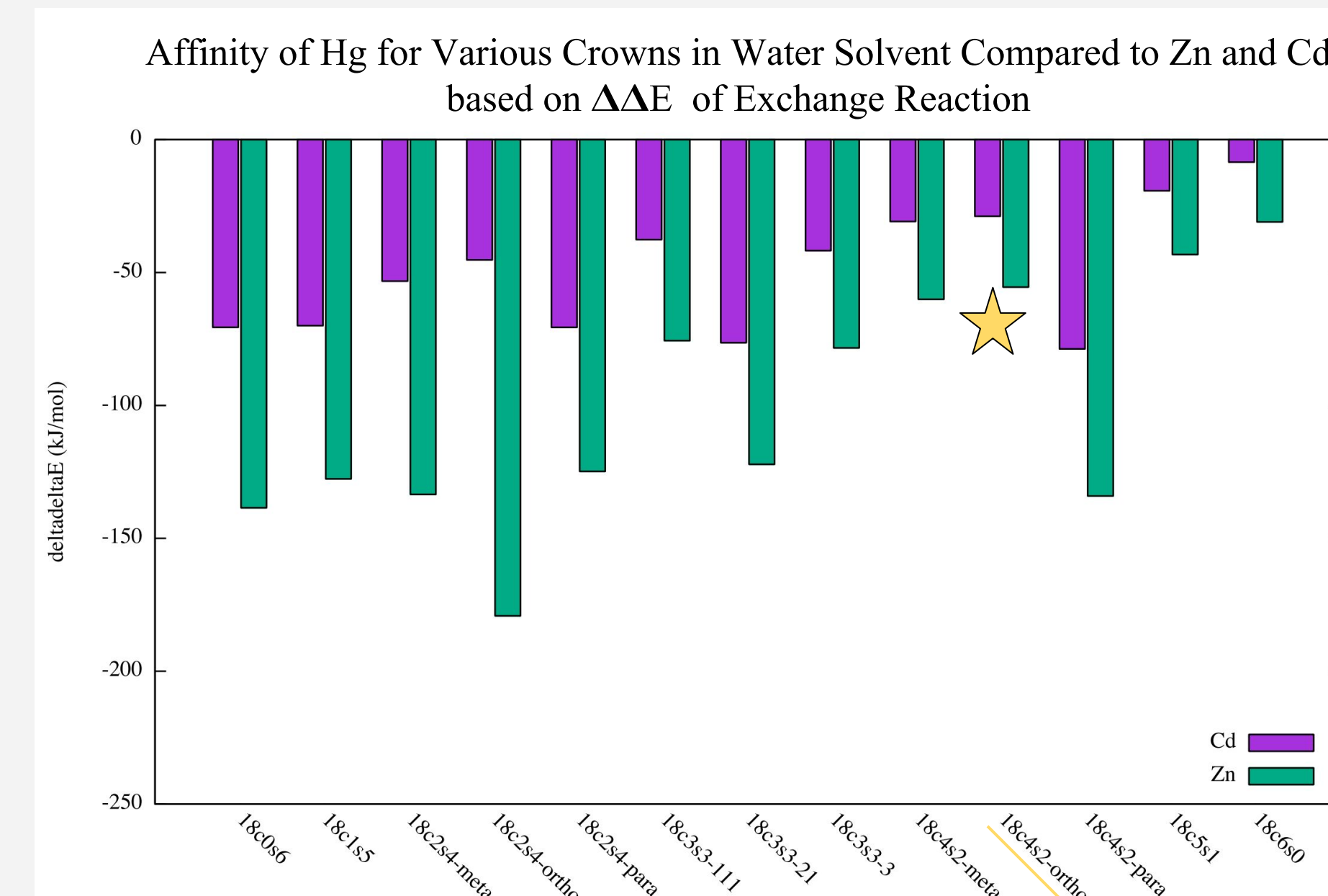


Figure 7:

Negative values indicate that Hg is the preferred metal in the crown during exchange reaction.

★ represents the crown used in Kim et al. paper.

## Conclusion

- Preliminary results indicate that having one sulfur and one oxygen atom connected to the linker makes the system more stable
- Crowns with best affinity for Hg:
  - 18c2s4-ortho, when competing with Cd [B]
  - 18c4s2-para, when competing with Zn [A]

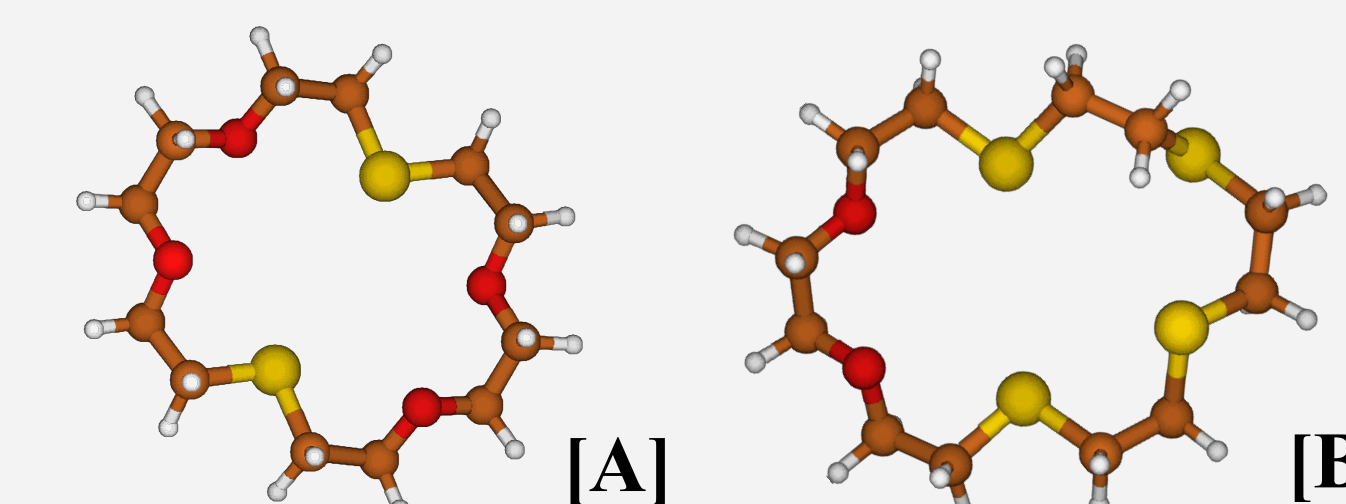
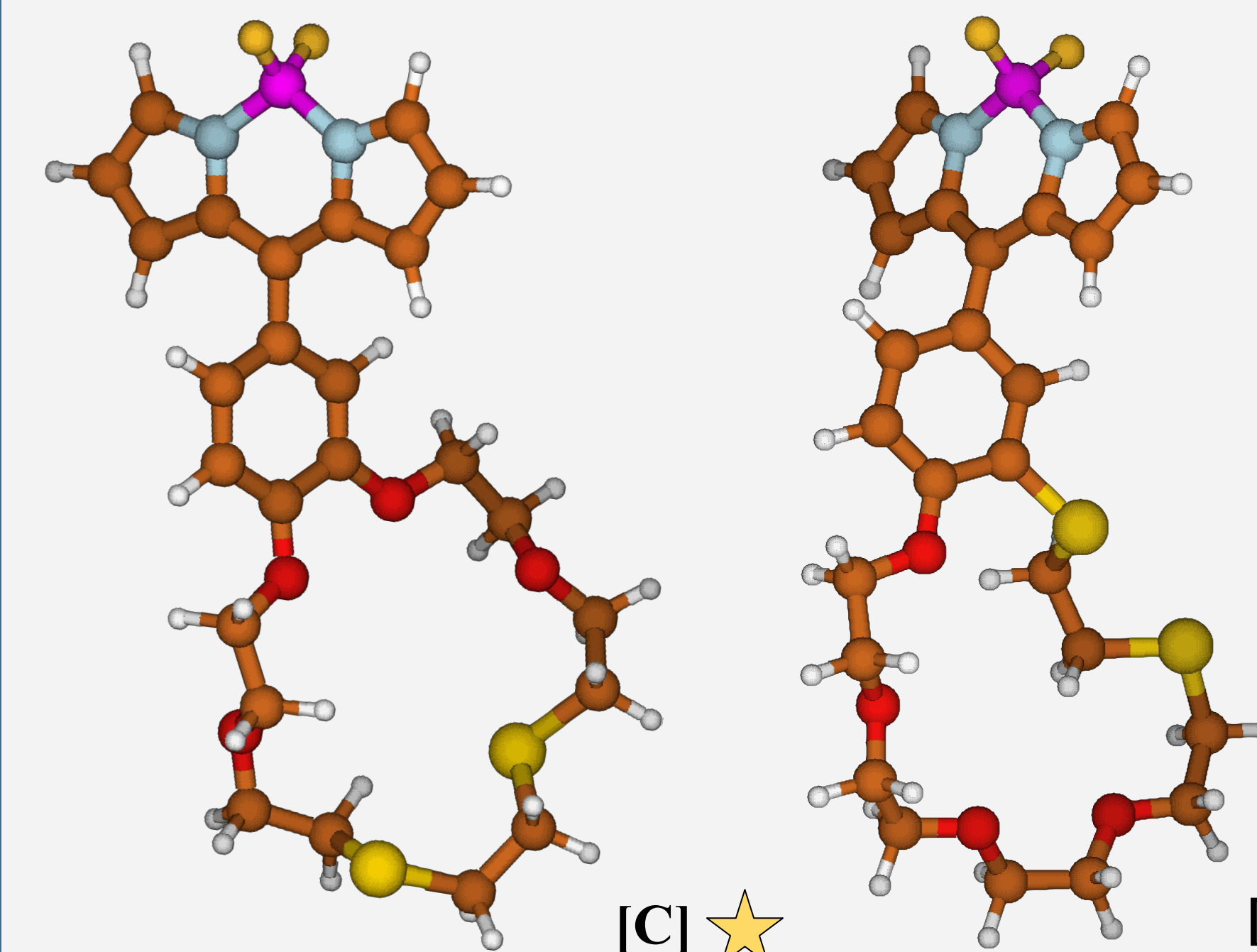


Figure 8: Optimal crowns for mercury detection



- Kim et al. model could be improved by attaching linker to different atoms, or by using a different crown

Figure 9: Detector systems, 18c4s2-ortho

[C] : Detector modeled by Kim et al. Total energy of -6276600.23 kJ/mol

[D] : Stabilized detector from our calculations Total energy of -6276623.30 kJ/mol

Energy difference between detectors = 23.06 kJ/mol

## Discussion and Future Steps

- Future calculations at higher levels of theory to ensure accurate trends in affinity of the crowns
- Experimental measurements could be done in addition to theoretical calculations
- Optimization was only calculated on the crown component. Further calculations could be performed with the BODIPY attached to the crown.
- The World Health Organization recognizes mercury as a chemical of major public health concern<sup>9</sup>
  - With a final system, mercury could be easily detected and steps could be taken for removal
- Other heavy metals such as Cadmium (Cd), Zinc (Zn), and Lead (Pb) are also known to cause harmful health effects<sup>10</sup>
  - Future studies could develop a crown selective for detecting other heavy metals (Cd, Pb, As)

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