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Novel Materials for Efficient Stationary Sources via Oxyfuel Combustion

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U.S. DEPARTMENT OF ENERGY | NNSA

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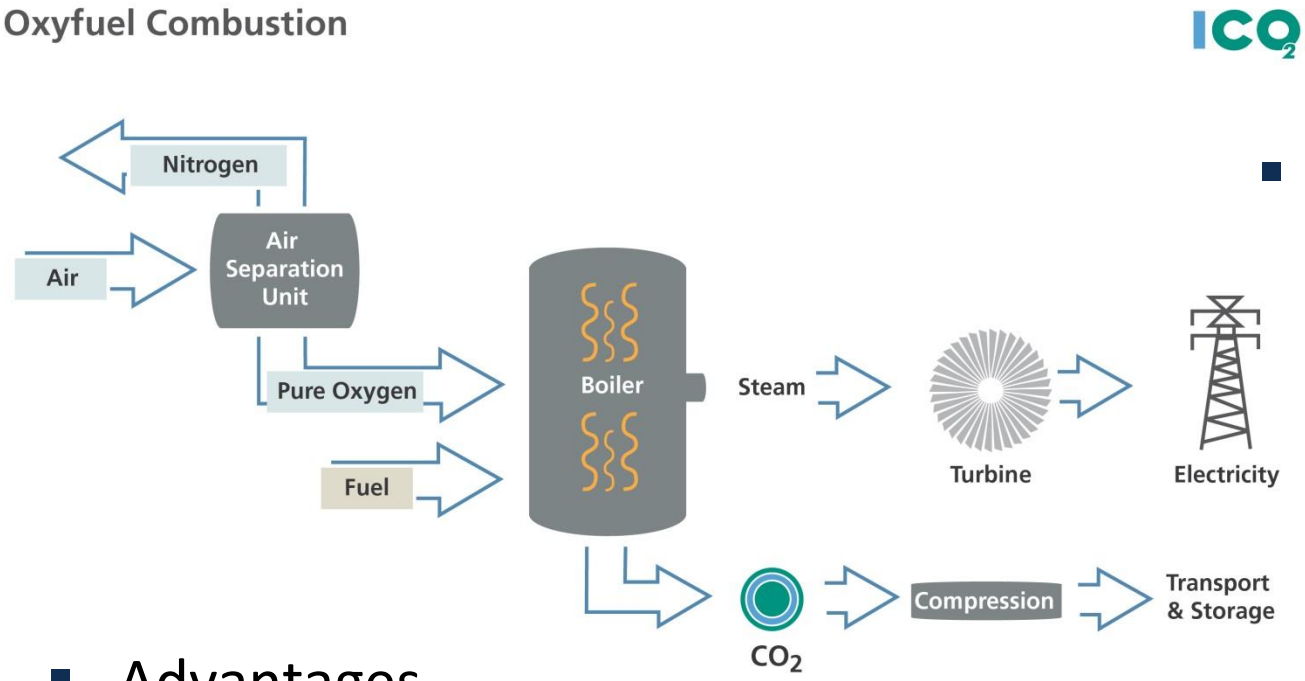
Oxyfuel Combustion

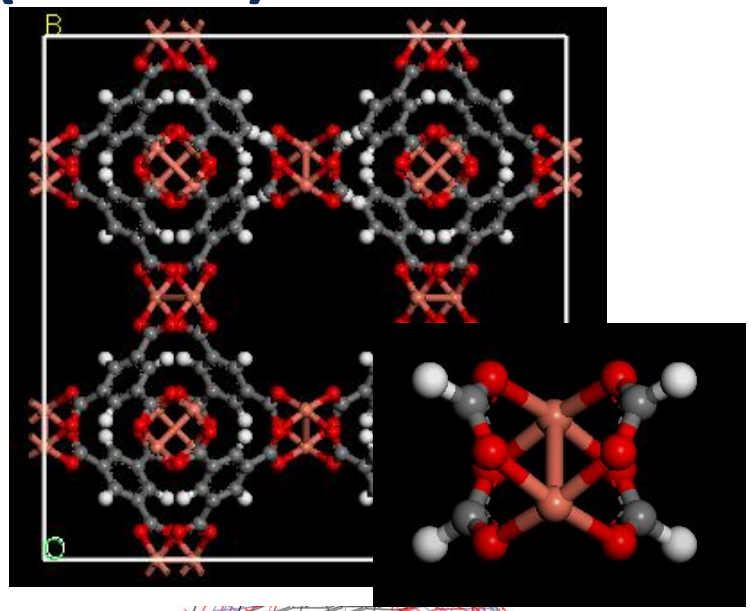


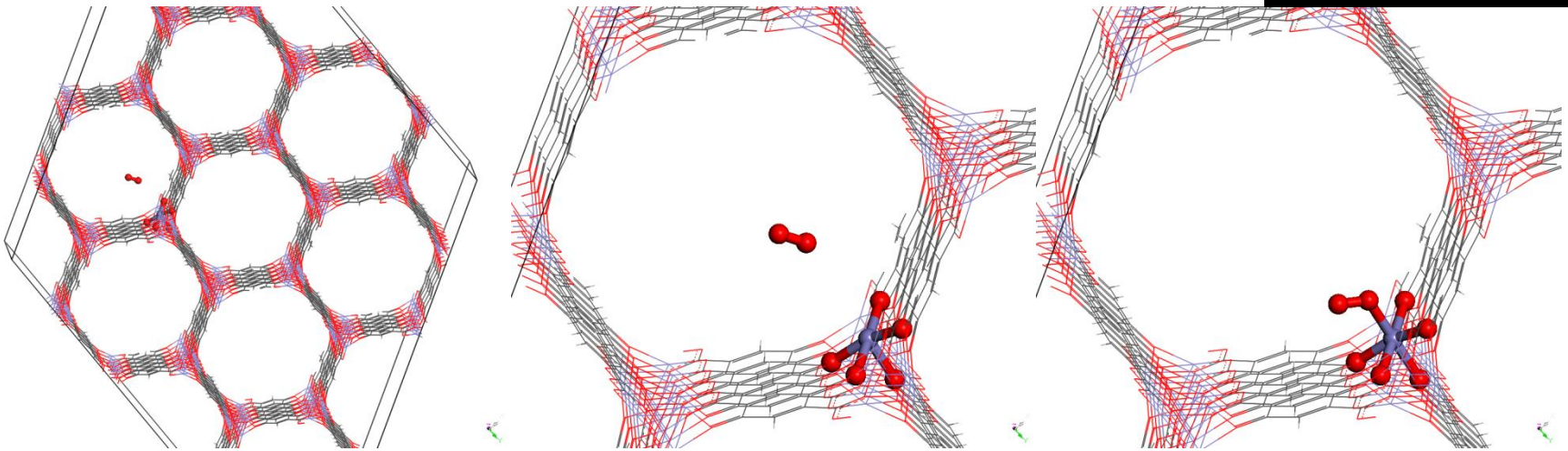
- Advantages
  - Reduction of fuel needed
  - Higher production capacity
    - High temp and high heat transfer
  - Can improve efficiency 20-60%
  - Reduces NOx emissions
  - CO_2 capture/use

- Disadvantages
  - High cost to separate O_2 and N_2 using current method of cryogenics
  - Complex plants with low productivity

Metal-Organic Frameworks (MOF's)

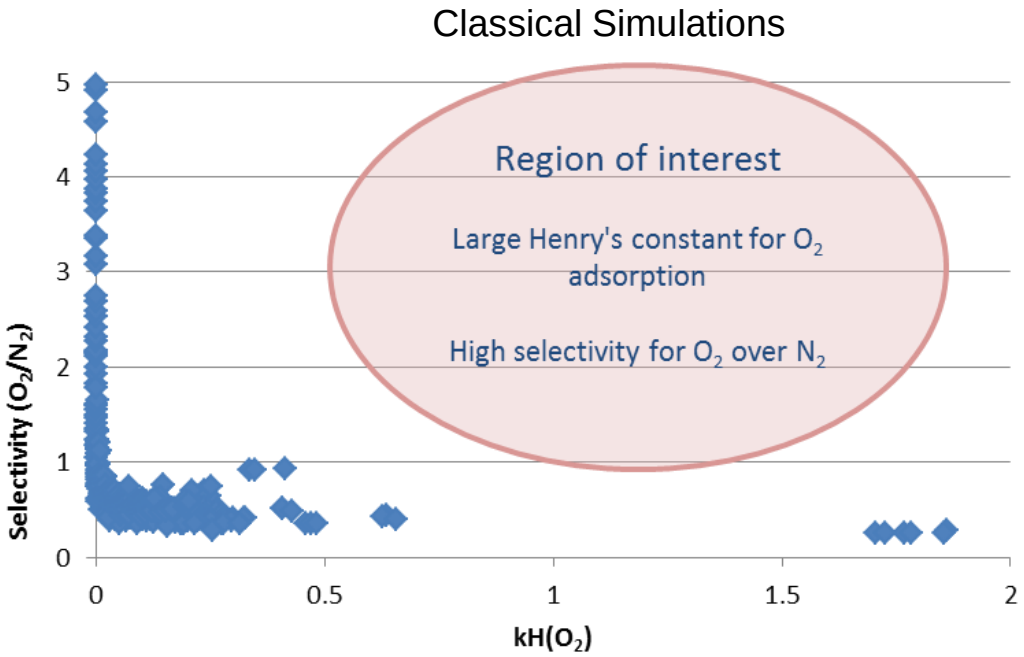
- Nanoporous materials
- High adsorption and separation capabilities
- Metal ions combined with rigid organic molecules





MOF's

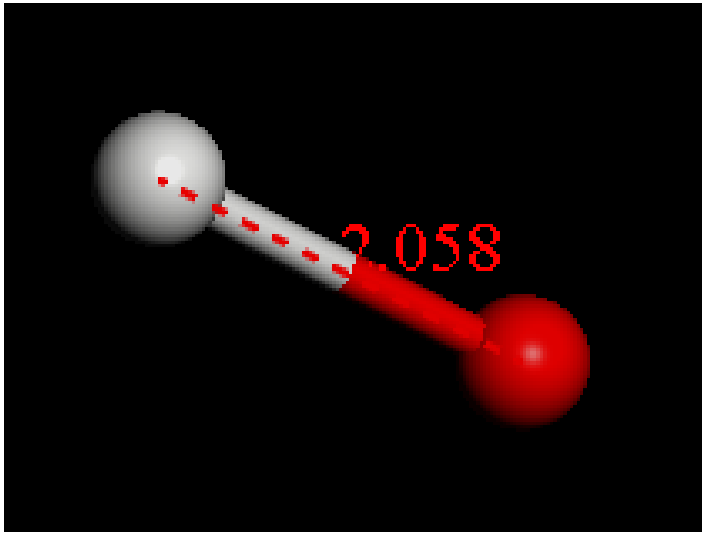
- Most MOF's studied show little or no preference for oxygen or nitrogen adsorption



- Compare MO/MN and MO_2/MN_2 binding energies
- $E_{binding} = E_{MOF+O_2} - E_{MOF} - E_{O_2}$

M-O Calculations

- Start by optimizing the geometry of Metal-Oxygen molecules



- Gaussian
- Material Studios

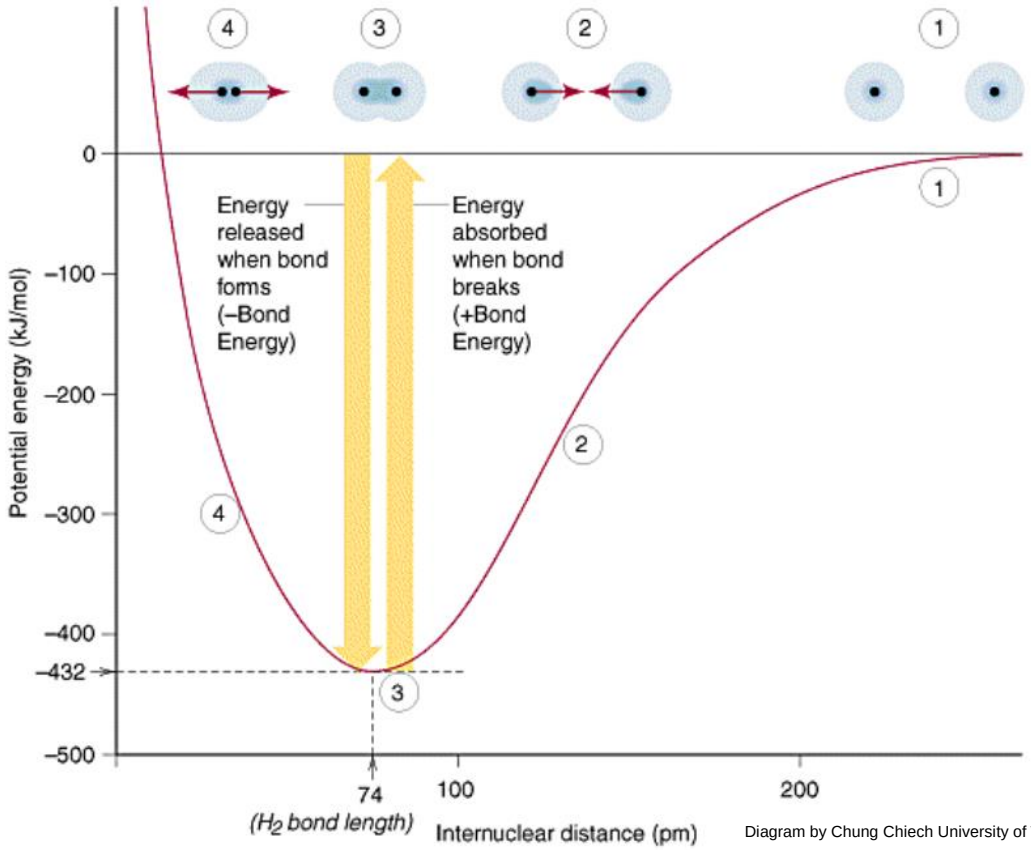


Diagram by Chung Chiech University of Waterloo

MO/MN Calculations: Multiplicities

- Multiplicity
  - Unpaired electron spins
  - Equals 2S+1
    - S = total spin

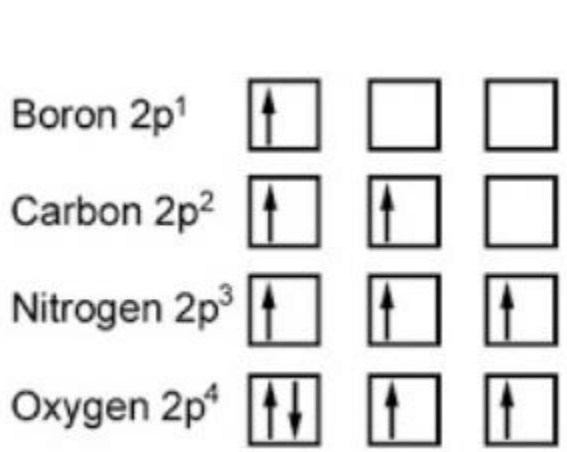


Diagram by Hari Prasad Chaudhary

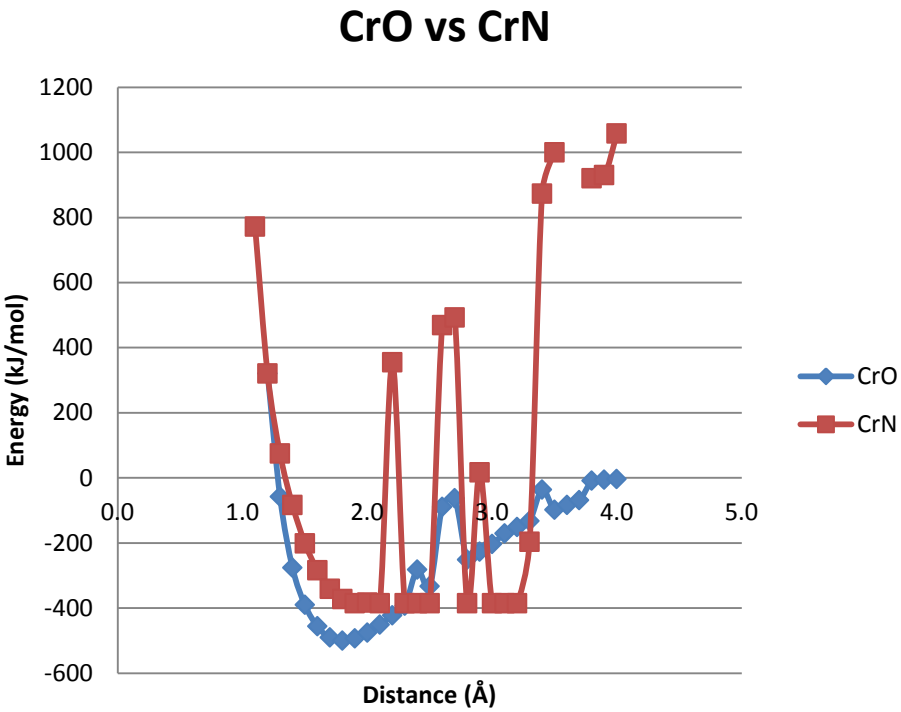
Element	Beginning Distance
Sc	3.3 Å

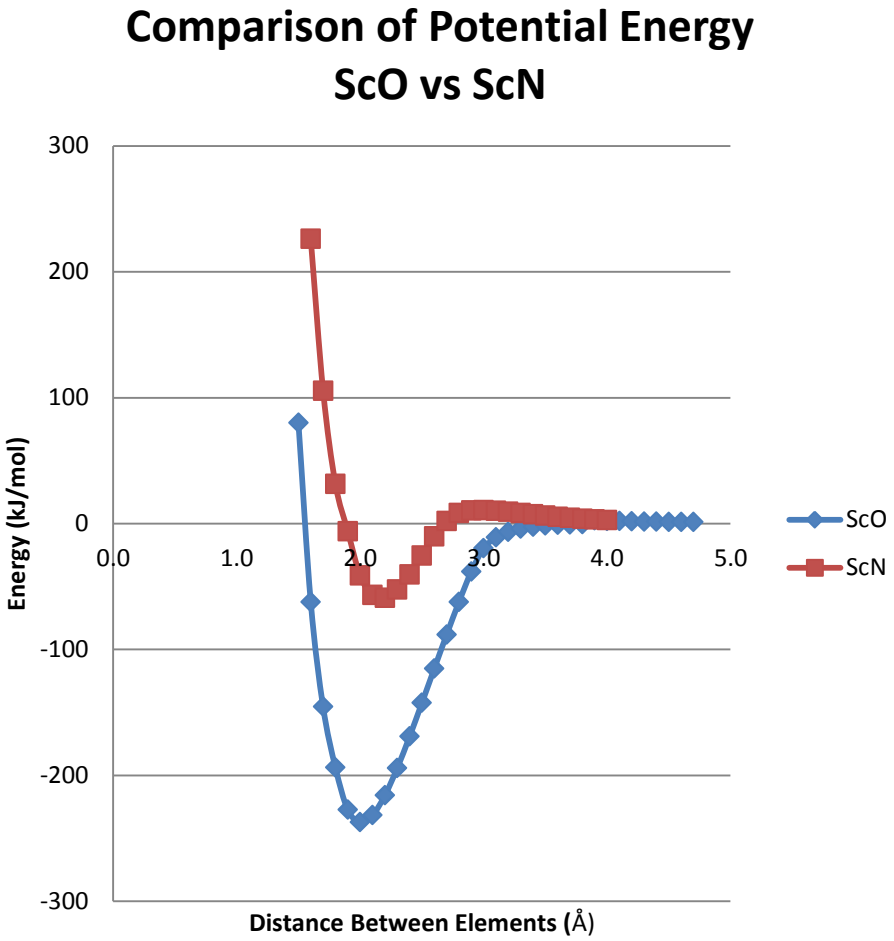
Operator			
B3LYP/6-31G*	Doublet	Quartet	
Energy	-835.6315119	-835.6710233	A.U.
Time	51.2	3.3	s

Electronic State with Lowest Energy	Quartet

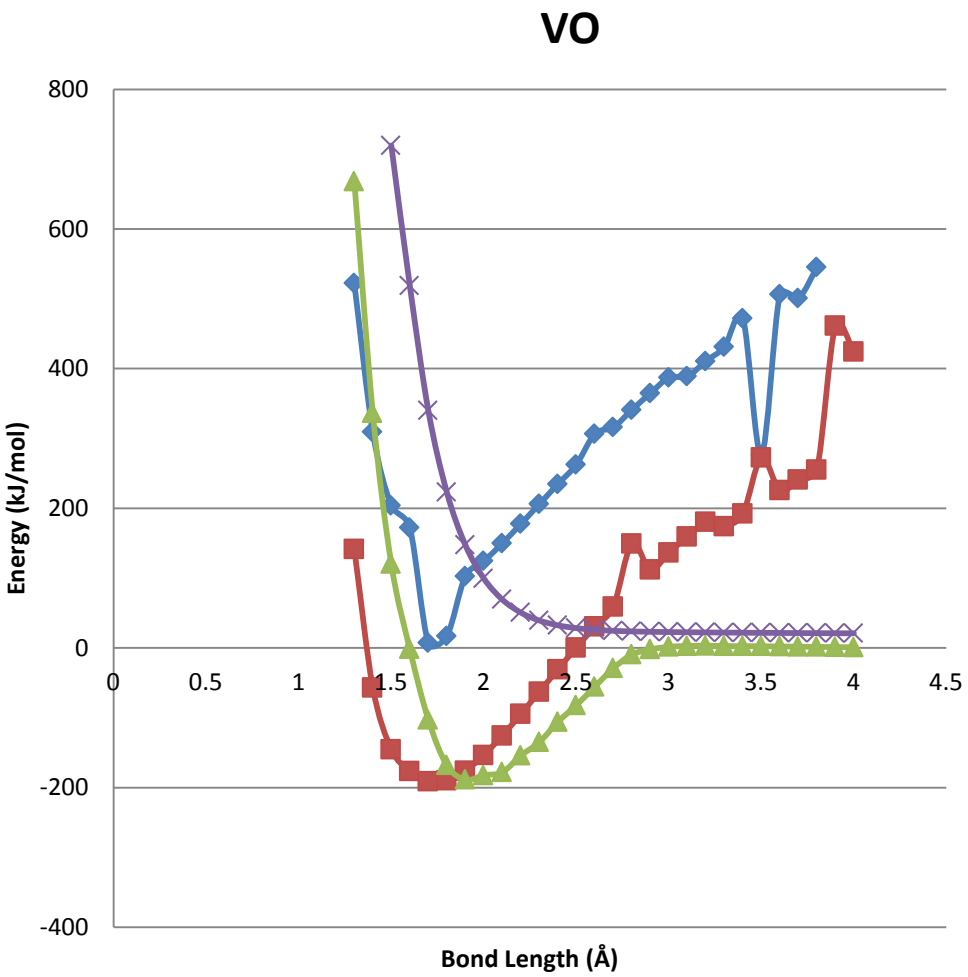
Potential Energy Graphs for MO/MN for Lowest Multiplicity at the Optimized Bond Length

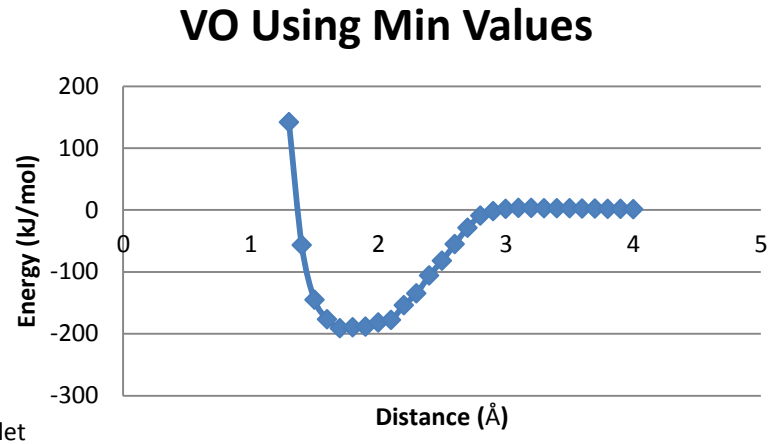
- Not all graphs came out as expected

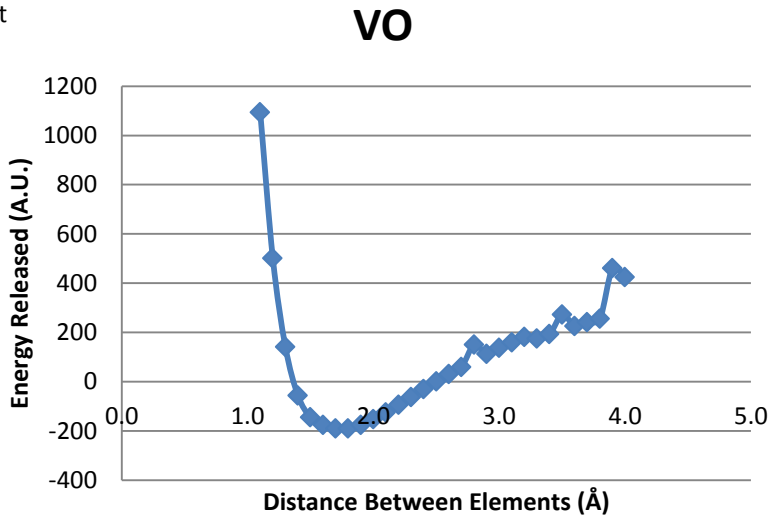




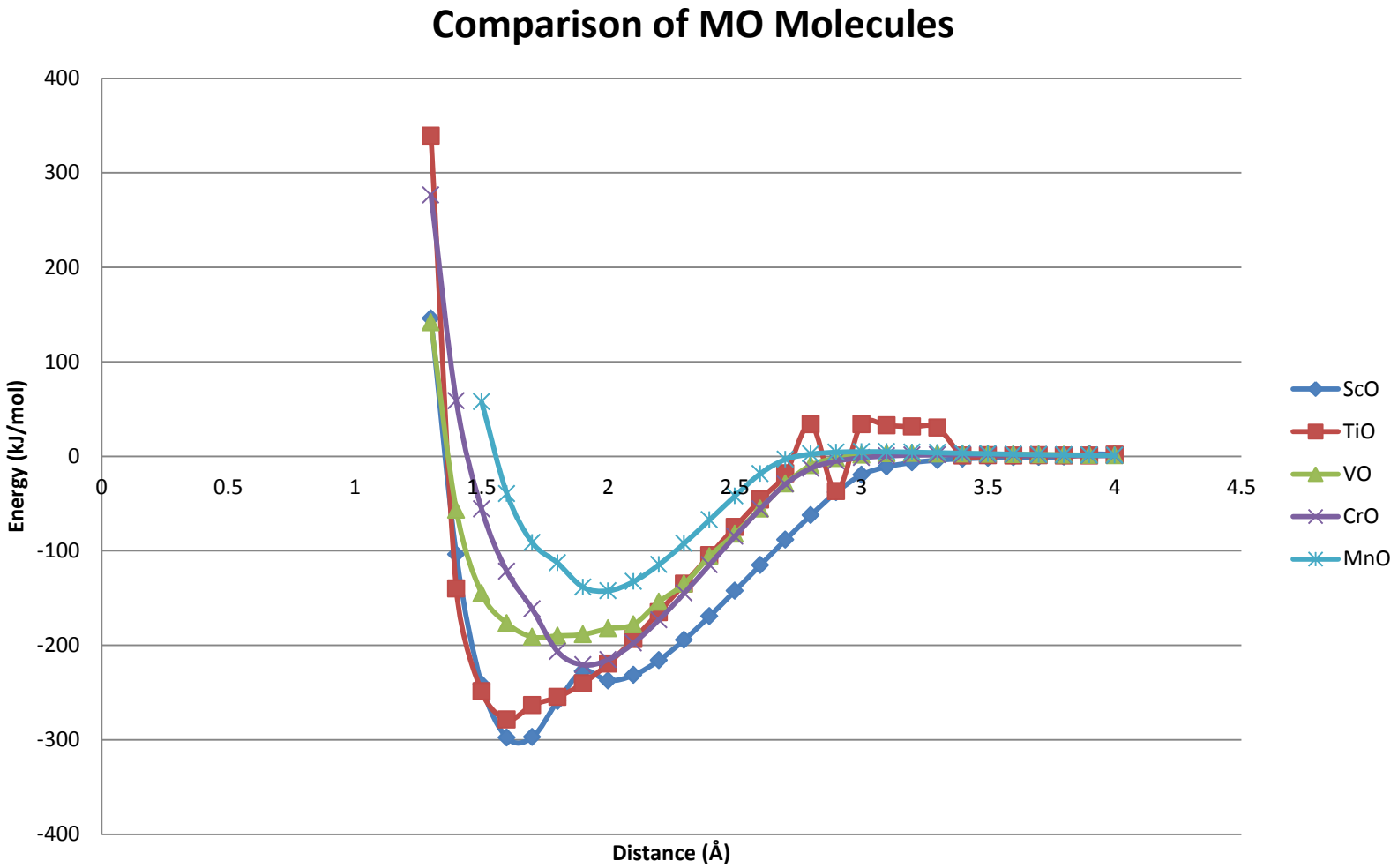
Multiple Multiplicities



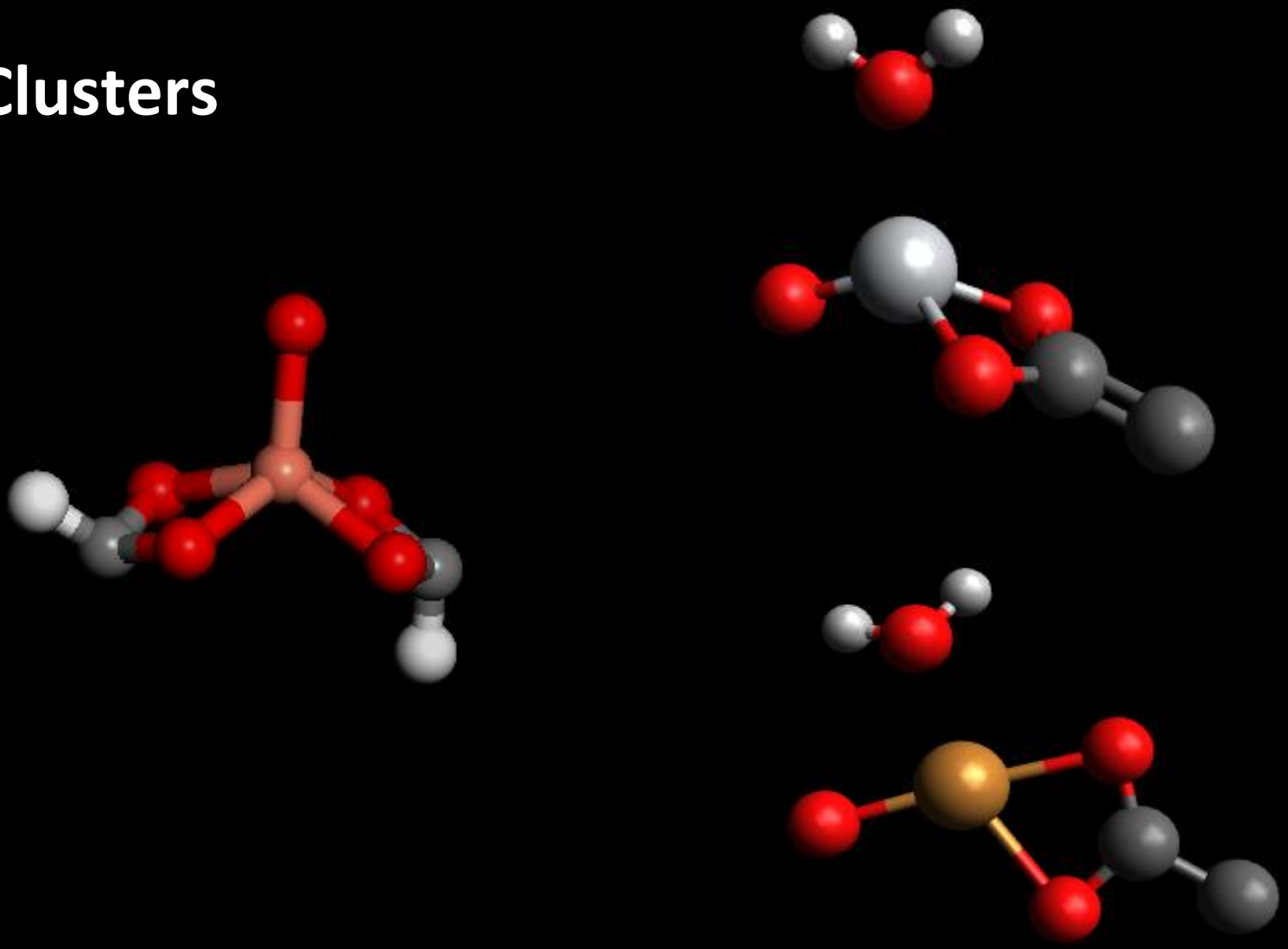




Multiple Multiplicities

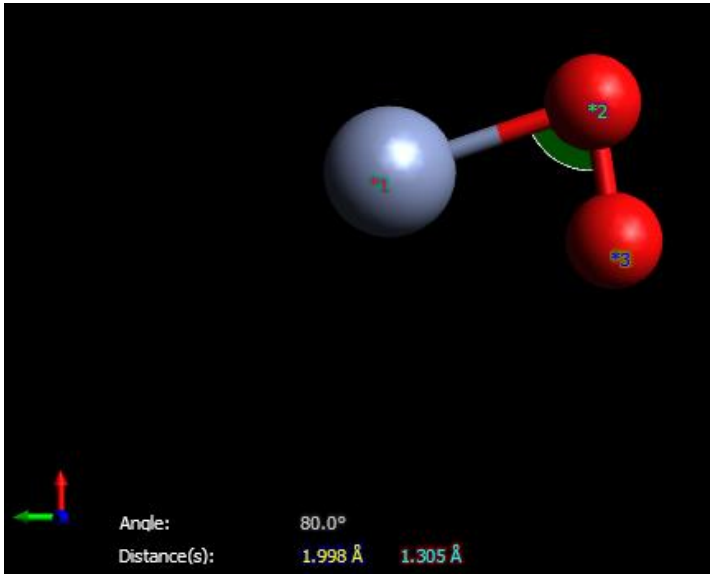


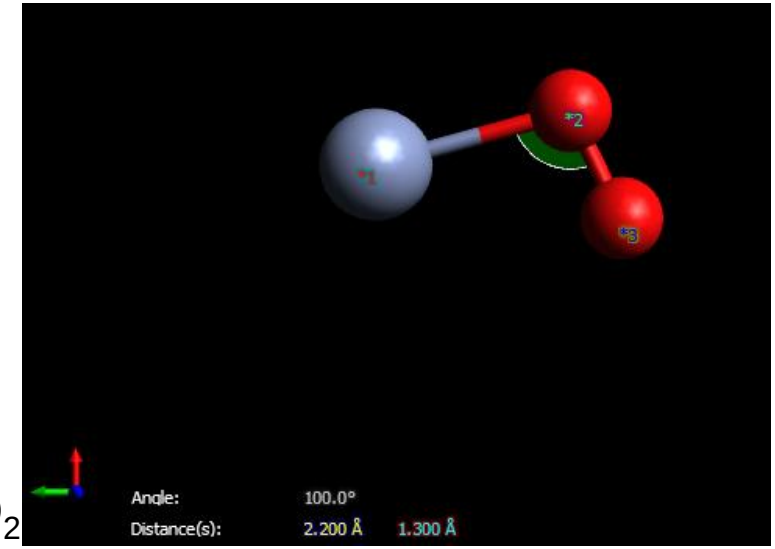
Clusters



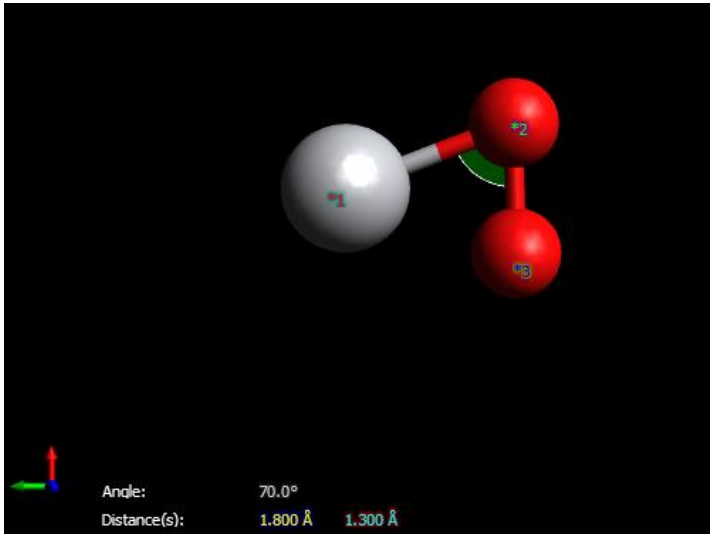
MO_2 vs MN_2

- 5 Metals
- 4 Multiplicities
- 14 Bond Angles
  - 50-70˚
- 25 Bond Distances
  - 1.1-3.5 Å
- = a lot of calculations



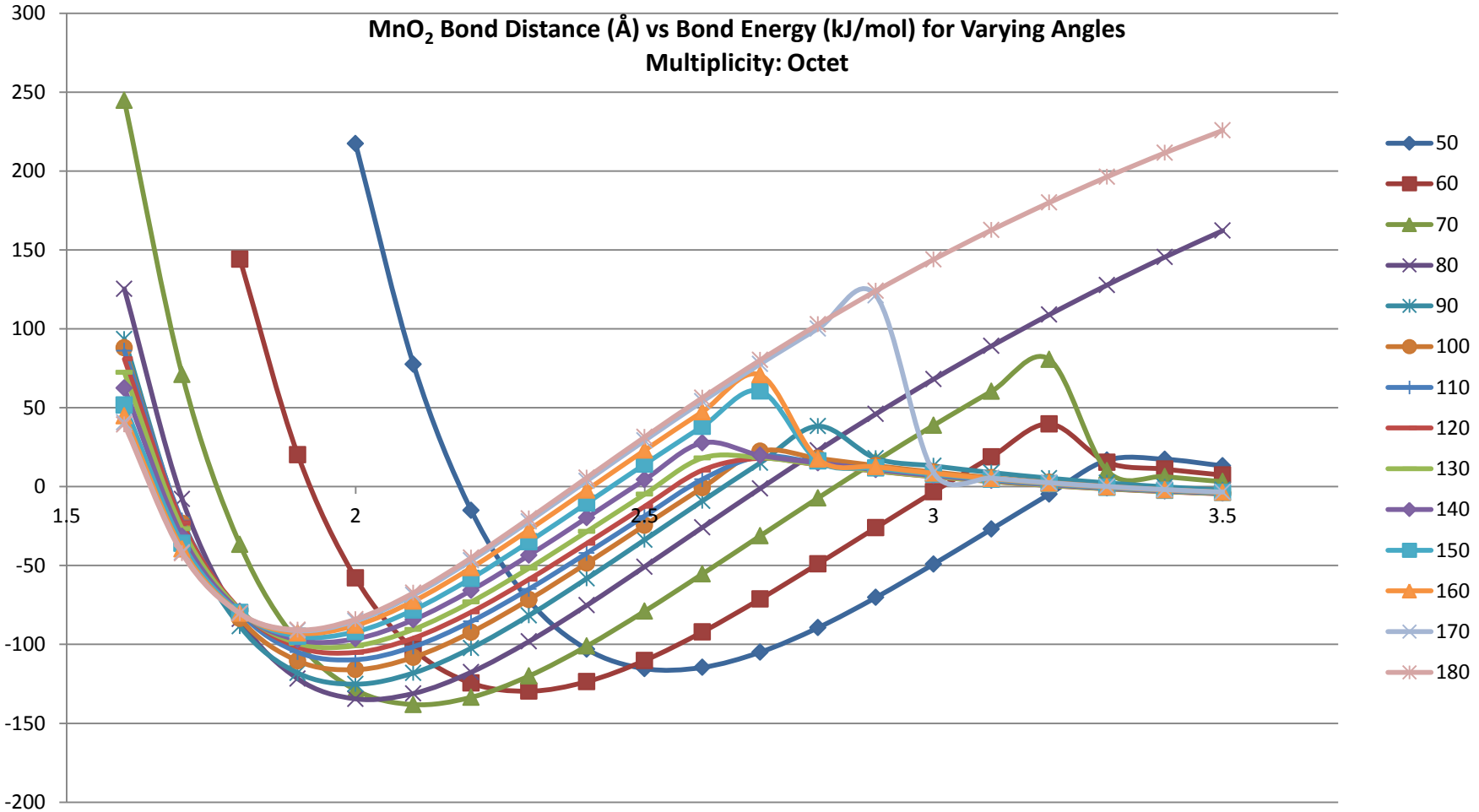


CrO_2

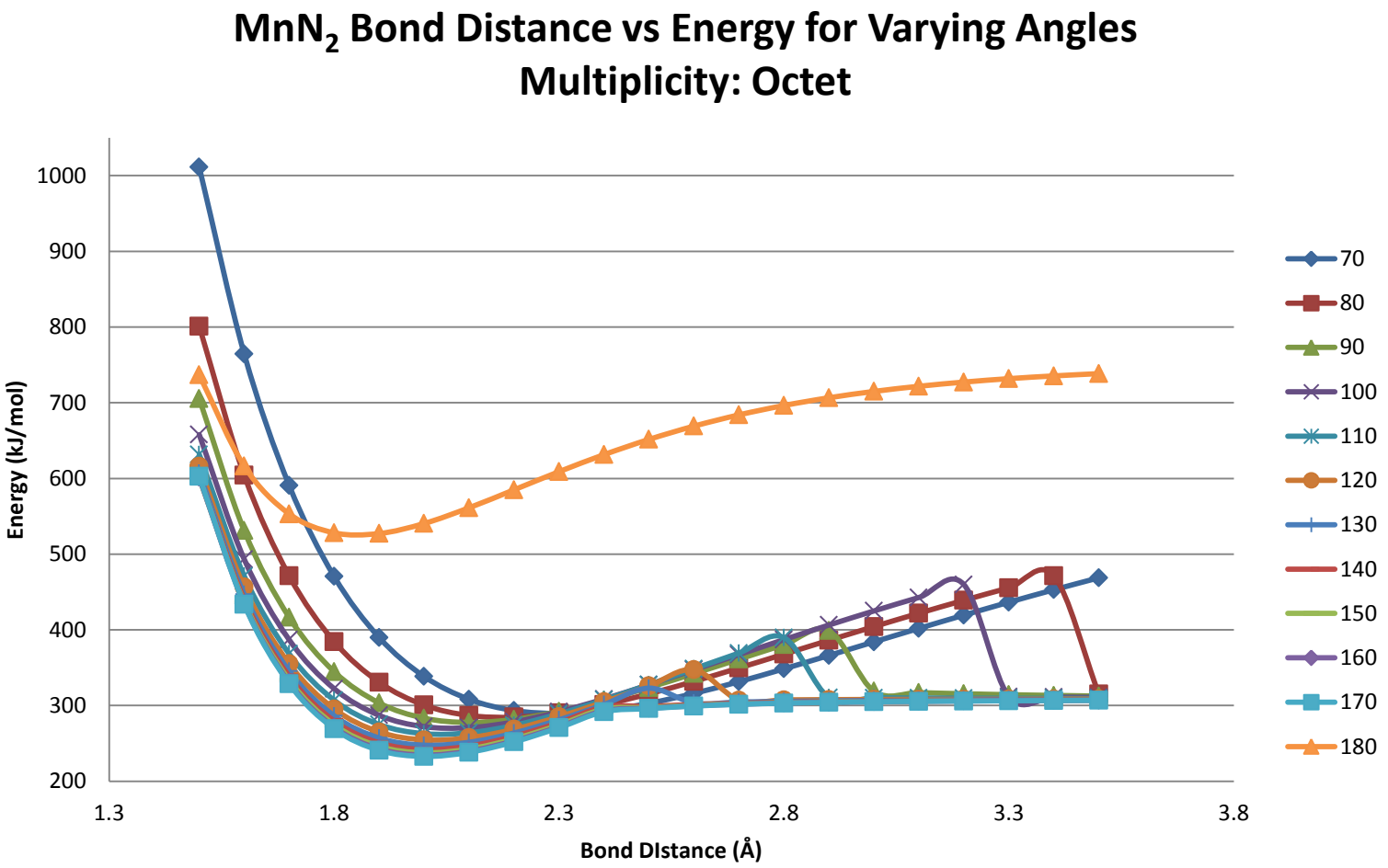


TiO_2

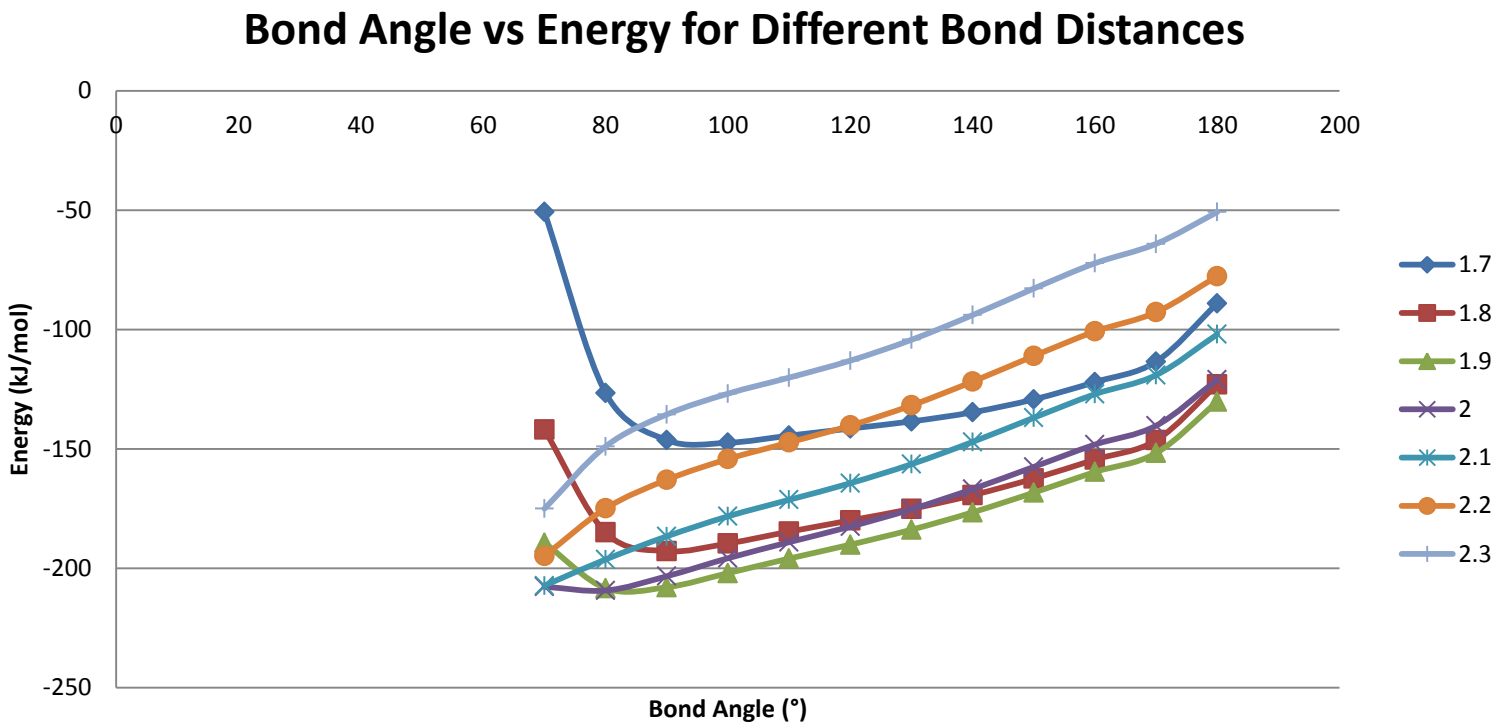
MO_2 vs MN_2


MnO2 Bond Distance (Å) vs Bond Energy (kJ/mol) for Varying Angles
Multiplicity: Octet
300
250
200
150
100
50
0
-50
-100
-150
-200
1.5
2
2.5
3
3.5
50
60
70
80
90
100
110
120
130
140
150
160
170
180

MO_2 vs MN_2


MnN2 Bond Distance vs Energy for Varying Angles
Multiplicity: Octet
Energy (kJ/mol)
1000
900
800
700
600
500
400
300
200
1.3
1.8
2.3
2.8
3.3
3.8
Bond DIstance (Å)
70
80
90
100
110
120
130
140
150
160
170
180

MO_2 vs MN_2


Bond Angle vs Energy for Different Bond Distances
Energy (kJ/mol)
0
-50
-100
-150
-200
-250
0
20
40
60
80
100
120
140
160
180
200
Bond Angle (°)
1.7
1.8
1.9
2
2.1
2.2
2.3

Conclusion

- Next Steps
  - Further refine simulations
  - Continue working with results to smooth graphs
  - MN_2 Calculations for all multiplicities
  - Continue moving towards larger clusters
- What I Learned
  - Quantum chemistry
  - Unix
    - Scripting
  - Life Skills