Predicting the Reactions of CS_2 with Group IV and Group VI Transition Metal Oxides

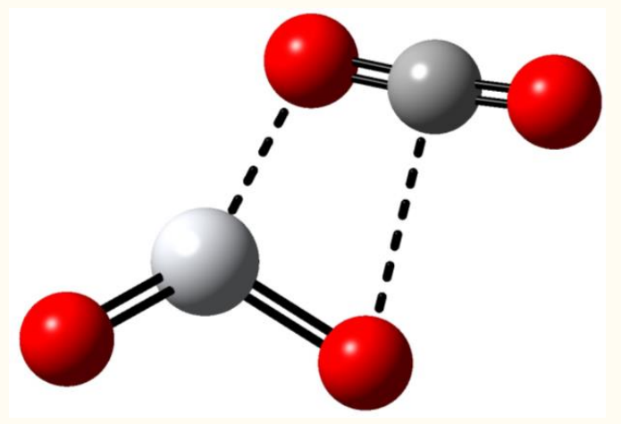
Marissa Blair[1], David A. Dixon[2], and Zachary R. Lee[1]*

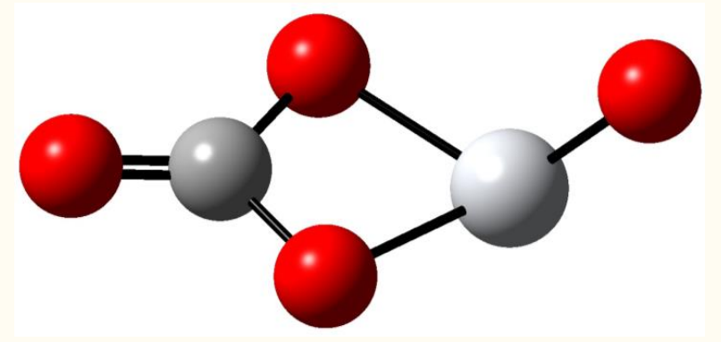
[1]*Department of Biology and Chemistry, Morehead State University*
[2]*Department of Chemistry and Biochemistry, The University of Alabama*

Overview

- Electronic structure methods are being used to study the addition of CS_2 to Group IV $(MO_2)_n$ and Group VI $(MO_3)_n$ (n = 1, 2, 3) nanoclusters, beginning with the MO_2 and MO_3 monomers according to a “bottom-up” approach.
- **Physisorption** is a process in which molecules bind through Van der Waals interactions. The enthalpies of these reactions are rather low, and these interactions are usually favored at lower temperatures.
- **Chemisorption** is adsorption in which chemical bonds are broken and/or formed therefore, an entirely new chemical species is formed.
- CS_2 absorbed clusters of TiO_2 and CrO_3 were first optimized with harmonic vibrational frequencies calculated at the B3LYP/DZVP2 level to quickly provide good starting structures for more accurate optimizations/frequencies at the B3LYP/aD level.
- The preliminary density functional theory (DFT) calculations in this study provide structures and vibrational frequency thermodynamic corrections for later expanding upon by way of single point correlated molecular-orbital theory (MO) calculations, mainly CCSD(T), to study the structures and energies which could arise from Lewis acid-base addition (physisorption) and formation of COS_2^{2-} (chemisorption) of CS_2 to these clusters will be predicted.
- All LBE Values reported in kcal/mol..

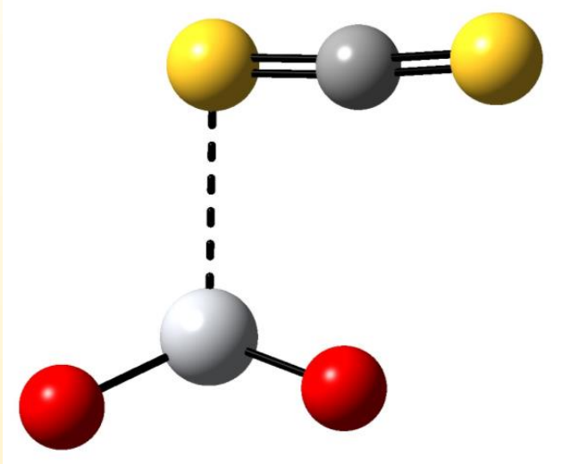
CO_2 + Group IV MO_2 Monomers

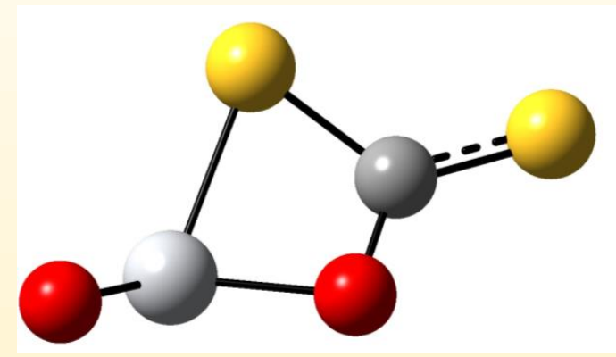

1-4P


1-4T

Cluster	B3LYP ΔH$_{298K}$	CCSD(T) ΔH$_{298K}$				CCSD(T) ΔG$_{298K}$
	aD	aD	aT	aQ	CBS	CBS
1-4P						
TiO_2	-14.2	-17.3	-16.4	-16.0	-15.8	-7.4
ZrO_2	-13.2	-15.9	-15.0	-14.5	-14.2	-6.1
1-4T						
TiO_2	-28.5	-30.9	-31.6	-31.3	-31.1	-20.0
ZrO_2	-32.1	-34.7	-34.6	-34.3	-34.1	-23.4
HfO_2	-39.6	-42.2	-43.3	-43.2	-43.0	-32.2

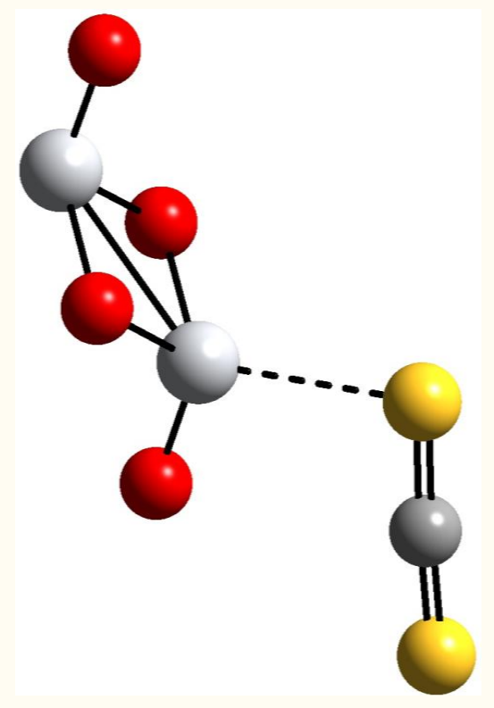
CS_2 + Group IV MO_2 Monomers

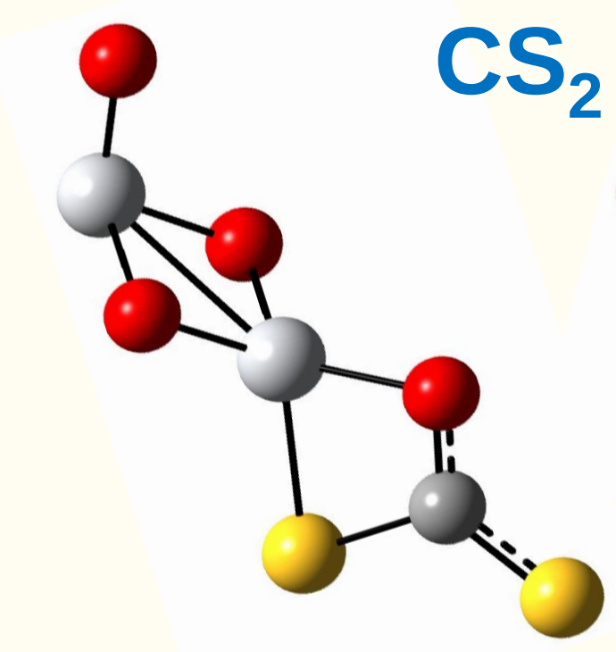

1-4P

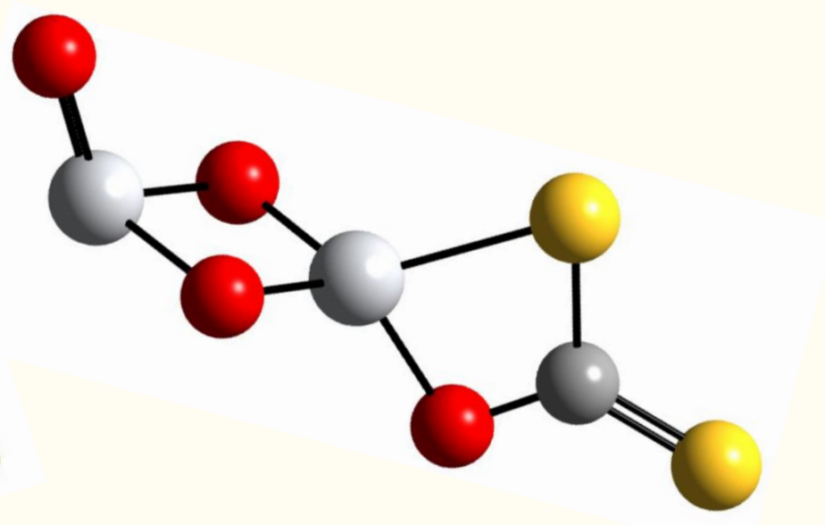

1-4T

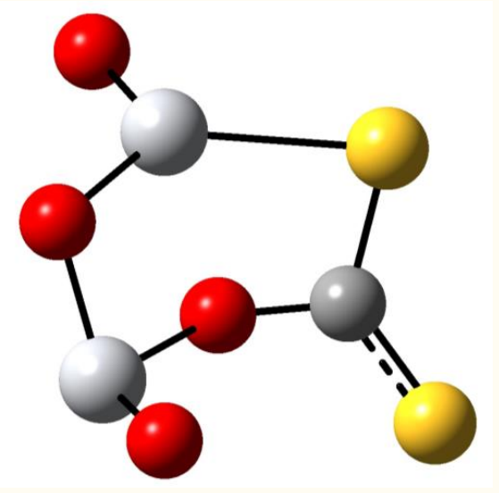
Cluster	B3LYP ΔH$_{298K}$	CCSD(T) ΔH$_{298K}$				CCSD(T) ΔG$_{298K}$
	aD	aD	aT	aQ	CBS	CBS
1-4P						
TiO_2	-12.6	-19.3	-19.0	-18.7	-18.6	-10.9
ZrO_2	-11.3	-22.0	-24.2	-24.6	-24.8	-17.1
HfO_2	-15.2	-26.6	-28.5	-29.0	-29.3	-21.2
1-4T						
TiO_2	-33.0	-40.8	-41.5	-41.9	-42.1	-31.8
ZrO_2	-36.4	-42.2	-42.1	-42.4	-42.5	-32.2
HfO_2	-44.0	-54.7	-57.5	-58.7	-59.3	-48.9

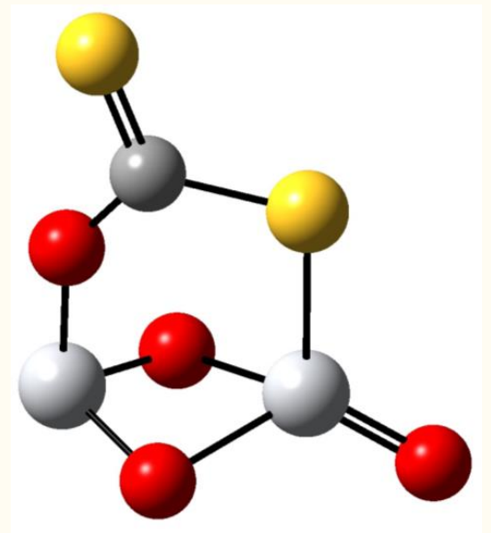
CS_2 + Group IV $(MO_2)_2$ Dimers


2-4P


2-4T-1

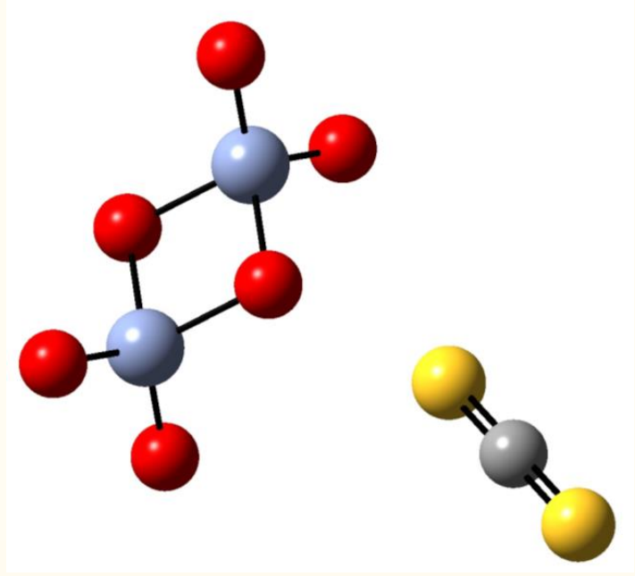

2-4T-2

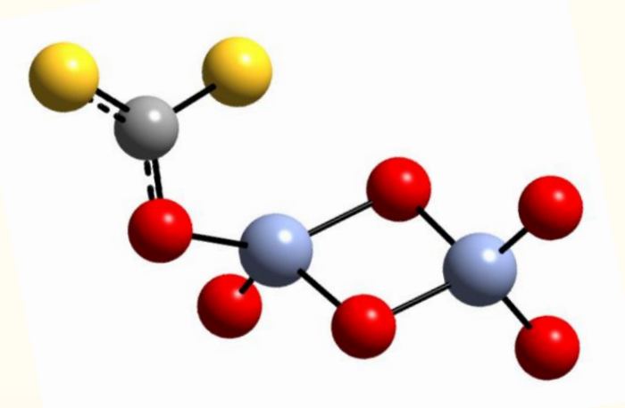

2-4B-1

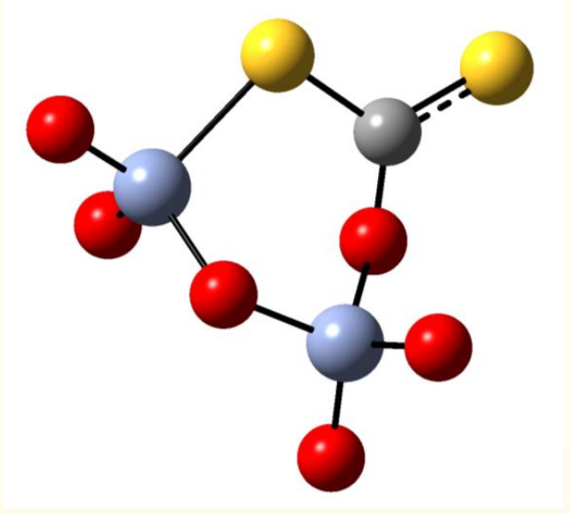

2-4B-2

Cluster	CS_2 LBEs		CO_2 LBEs	
	B3LYP ΔH$_{298K}$	B3LYP ΔG$_{298K}$	CCSD(T) ΔH$_{298K}$	CCSD(T) ΔG$_{298K}$
	aD	aD	aT	aT
2-4P				
Ti_2O_4	-12.5	-4.9	-17.2	-9.9
Zr_2O_4	-10.9	-3.5	-14.4	-6.5
Hf_2O_4	-13.8	-6.0	-16.3	-9.4
2-4T-1				
Ti_2O_4	-24.4	-14.2	-24.2	-13.7
Zr_2O_4	-31.3	-21.3	-30.5	-20.1
Hf_2O_4	-37.3	-27.2	-38.4	-28.0
2-4T-2				
Ti_2O_4	-24.1	-13.9	-24.2	-13.7
Zr_2O_4	-30.9	-20.9	-30.5	-20.1
Hf_2O_4	-37.0	-27.0	-38.4	-28.0
2-4B-1				
Ti_2O_4	-6.1	4.1	-15.7	-5.2
Zr_2O_4	-9.6	0.4	-17.6	-7.1
Hf_2O_4	-8.7	1.5	-17.8	-7.3
2-4B-2				
Ti_2O_4	-15.3	-4.3	-	-
Zr_2O_4	-21.5	-10.7	-	-
Hf_2O_4	-25.8	-14.9	-	-

CS_2 + Group VI $(MO_3)_2$ Dimers

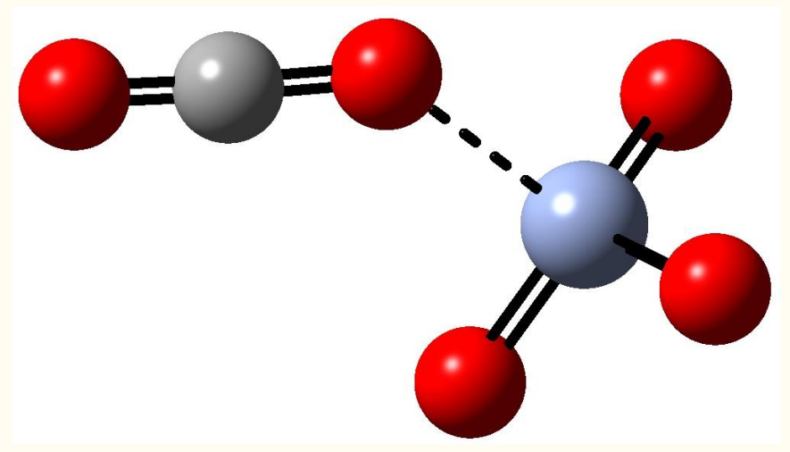

2-6P

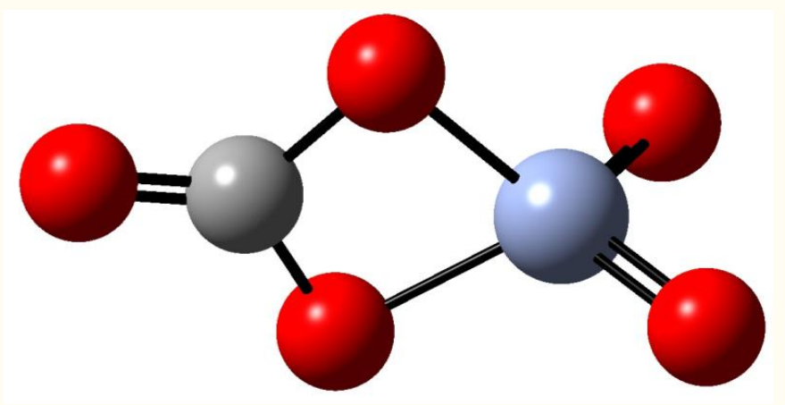

2-6T


2-6B

Cluster	CS_2 LBEs		CO_2 LBEs	
	B3LYP ΔH$_{298K}$	B3LYP ΔG$_{298K}$	CCSD(T) ΔH$_{298K}$	CCSD(T) ΔG$_{298K}$
	aD	aD	aT	aT
2-6P				
Cr_2O_6	0.7	2.7	-1.6	1.8
Mo_2O_6	0.1	5.2	-2.4	4.6
W_2O_6	-7.3	0.7	-9.3	-1.5
2-6T				
Cr_2O_6	14.4	24.3	24.8	35.1
Mo_2O_6	7.3	17.7	11.1	21.6
W_2O_6	1.1	11.5	1.4	11.8
2-6B				
Cr_2O_6	-1.1	8.2	5.4	14.9
Mo_2O_6	-0.6	8.6	0.1	9.0
W_2O_6	-4.7	4.8	-5.1	3.8

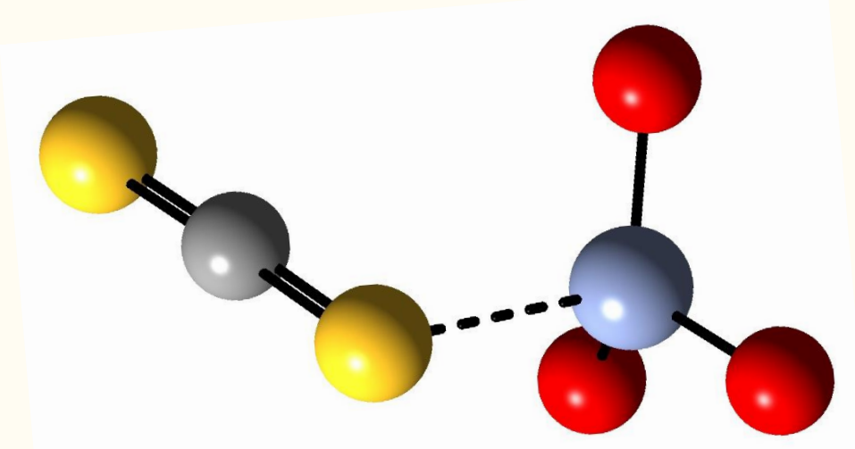
CO_2 + Group VI MO_3 Monomers

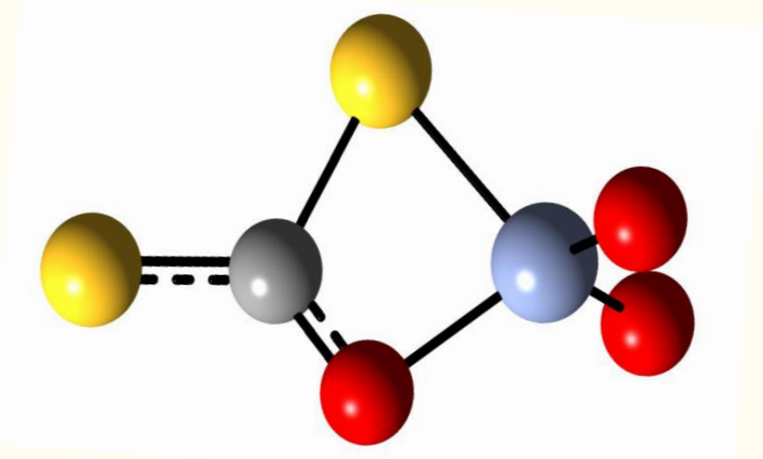

1-6P


1-6T

Cluster	B3LYP ΔH$_{298K}$	CCSD(T) ΔH$_{298K}$				CCSD(T) ΔG$_{298K}$
	aD	aD	aT	aQ	CBS	CBS
1-6P						
CrO_3	-19.3	-22.2	-22.2	-21.7	-21.4	-13.5
MoO_3	-18.9	-21.4	-20.9	-20.5	-20.3	-12.6
WO_3	-21.2	-24.6	-24.4	-24.0	-23.7	-15.9
1-6T						
CrO_3	-12.5	-9.8	-12.0	-11.7	-11.4	-0.6
MoO_3	-17.6	-17.8	-19.5	-19.3	-19.0	-7.4
WO_3	-21.5	-23.8	-25.5	-25.3	-25.1	-13.6

CS_2 + Group VI MO_3 Monomers


1-6P


1-6T

Cluster	B3LYP ΔH$_{298K}$	CCSD(T) ΔH$_{298K}$				CCSD(T) ΔG$_{298K}$
	aD	aD	aT	aQ	CBS	CBS
1-6P						
CrO_3	-23.5	-30.4	-16.2	-16.2	-16.7	-8.8
MoO_3	-23.6	-30.3	-29.3	-27.4	-26.2	-16.5
WO_3	-27.7	-35.1	-34.2	-33.6	-33.2	-23.5
1-6T						
CrO_3	-25.0	-30.3	-18.4	-19.4	-20.5	-10.2
MoO_3	-28.1	-33.5	-33.8	-34.0	-34.1	-23.9
WO_3	-32.8	-39.6	-39.9	-40.1	-40.2	-30.1

Conclusions and Future Work

- Both physisorption and chemisorption of CS_2 to Group IV and Group VI are heavily favorable, not likely indicative of adsorption to the bulk metal oxide surface.
- DFT results for the monomers only show reasonable agreement with CCSD(T), suggesting a need for correlated MO methods when using metal oxide clusters.
- The preliminary DFT results for CS_2 adsorption to Group IV and VI are consistent with previously published results for CO_2 in that chemisorption is heavily favored for the Group IV clusters whereas no mode of CS_2 adsorption is exhibiting thermodynamic favorability for the Group VI oxides.
- For future work, CS_2 dimer and trimer LBEs will be compared to established CO_2 and CS_2 bulk adsorption results in the literature and correlated against experimental and computational trends in the binding of acid gases to these metal oxides.