

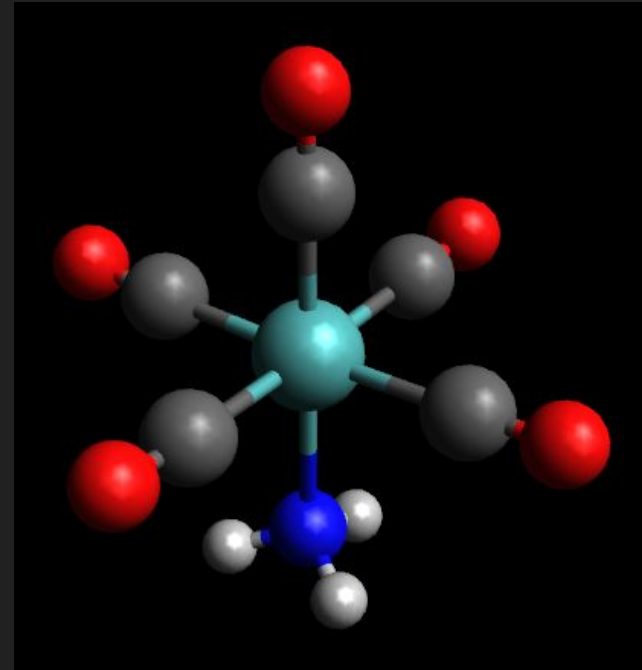
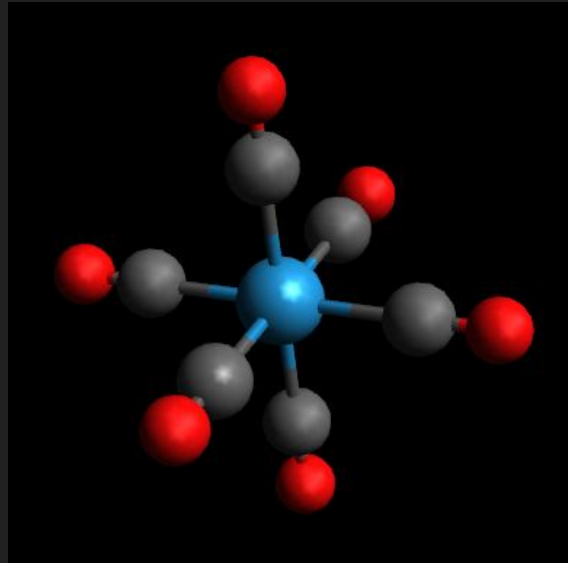
Trends in CO vibrational frequencies of 5d $M(CO)_6$ and $Mo(CO)_5L$

Jatin Kansal

Introduction

What are 5d $M(\text{CO})_6$ and $\text{Mo}(\text{CO})_5\text{L}$

- Transition Metals in 6th period of d group.
- Coordination compounds with CO as ligand
- Additional L replaces CO
- Octahedral Geometry



Computational Setup

Functional and Basis Sets

- Functional: B3LYP
- Pople style basis sets unavailable for bigger atoms
- Ahlrichs def2 family
- Double-zeta: def2-SVPD
- Triple-zeta: def2-TZVPD
- Need diffuse functions because a lot of the complexes are anions
- Wanted to try QZ but too much computational power needed

```
-----  
BASIS SET INFORMATION  
-----
```

```
There are 3 groups of distinct atoms
```

```
Group   1 Type W   : 8s8p6d1f contracted to 6s5p3d1f pattern {311111/41111/411/1}  
Group   2 Type C   : 12s6p3d1f contracted to 6s3p3d1f pattern {621111/411/111/1}  
Group   3 Type O   : 12s7p3d1f contracted to 6s4p3d1f pattern {621111/4111/111/1}
```

Choice of Complexes

Complex	Multiplicity	B3LYP/ def2-SVPD (cm ⁻¹)	B3LYP/ def2-TZVPD (cm ⁻¹)	Experimental (cm ⁻¹) ^[1]
[Hf(CO) ₆] ⁺	4			2075
[Hf(CO) ₆] ²⁻	1			
Hf(CO) ₆	1			
[Ta(CO) ₆] ⁻	1			
Ta(CO) ₆	2			
W(CO) ₆	1			2000
[W(CO) ₆] ⁻	2			
Os(CO) ₆	1			

Complex	Multiplicity	B3LYP/ def2-SVPD (cm ⁻¹)	B3LYP/ def2-TZVPD (cm ⁻¹)	Experimental (cm ⁻¹) ^[1]
Mo(CO) ₆	1			2003
[Mo(CO) ₅ F] ⁻	1			
[Mo(CO) ₅ Cl] ⁻	1			
[Mo(CO) ₅ CN] ⁻	1			
Mo(CO) ₅ NO	2			
[Mo(CO) ₅ NO] ⁺	1			
[Mo(CO) ₅ NO] ⁻	1			
Mo(CO) ₅ NH ₃	1			

Remark: Some of these are just theoretical complexes and others (ionic) are usually found in solutions, but we perform calculations on isolated molecules and ions.

Results

Validation Criteria

- First 6 vibrational modes must be 0
- No negative modes
- Generally between 1800-2200
- Geometry converged
- Orca terminated normally
- Visualize and check the modes in Avogadro

Complex	Multiplicity	B3LYP/ def2-SVPD (cm ⁻¹)	B3LYP/ def2-TZVPD (cm ⁻¹)	Experimental (cm ⁻¹) ^{[1][2]}
[Hf(CO) ₆] ⁺	4	2155	2136	2075
[Hf(CO) ₆] ²⁻	1	1832	1812/error	1759
Hf(CO) ₆	1	2056	2036/error	
[Ta(CO) ₆] ⁻	1	1953	1933	1847 - 1875
Ta(CO) ₆	2	2061	2040	
W(CO) ₆	1	2071	2052	2000
[W(CO) ₆] ⁻	2	1927, 1939, 1966	1904, 1922, 1945	
Os(CO) ₆	1	Didn't converge	Didn't converge	

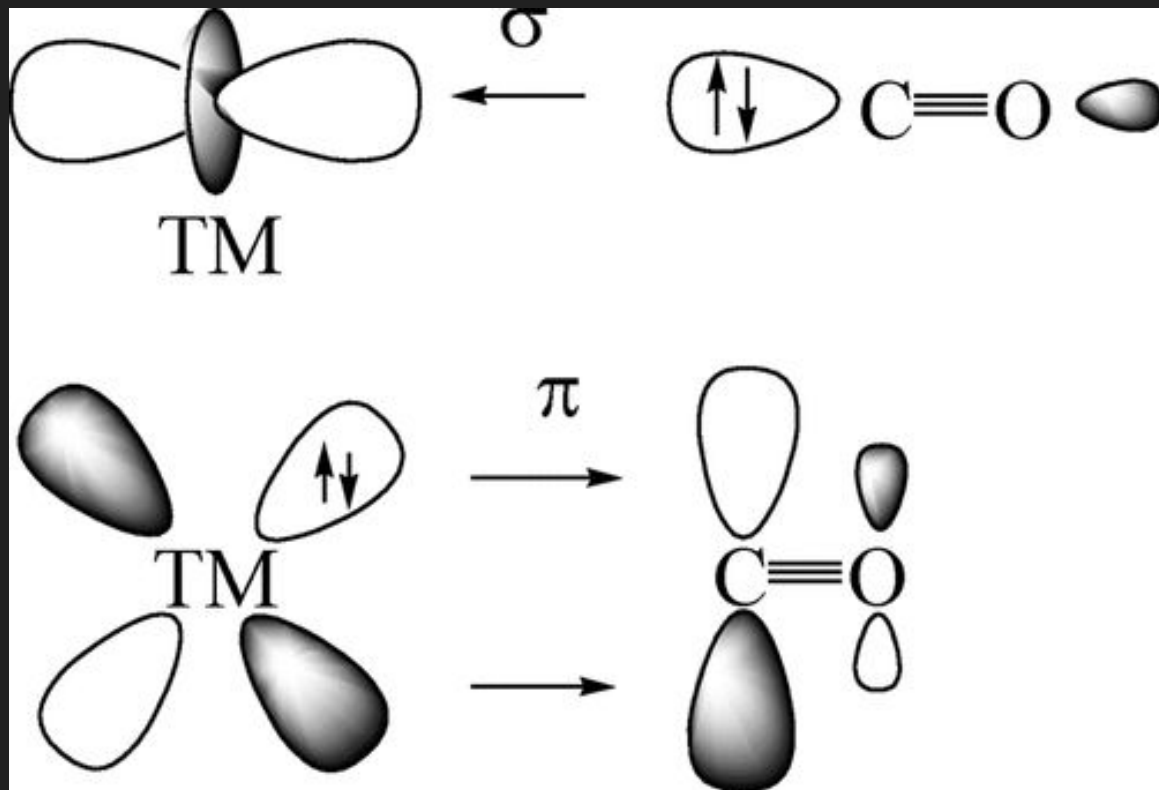
Complex	Multiplicity	B3LYP/ def2-TZVPD (cm ⁻¹)	Experimental (cm ⁻¹)
Mo(CO) ₆	1	2059	2003
[Mo(CO) ₅ F] ⁻	1	1898, 1972	
[Mo(CO) ₅ Cl] ⁻	1	1916, 1989	
[Mo(CO) ₅ CN] ⁻	1	1943, 1991	
Mo(CO) ₅ NO	2	2049, 2057, 2072	
[Mo(CO) ₅ NO] ⁺	1	1922, 2165, 2219, 2252	
[Mo(CO) ₅ NO] ⁻	1	1932, 1964, 1971	
Mo(CO) ₅ NH ₃	1	2005, 2018	

Results

- Pick 1-2 complexes to show the vibrations in Avogadro
- Trend: In general, the bigger the molecule (larger the CO bond length), lower the frequency (lower the wavenumber). Anions of the same complex will have lower vibrational frequency.
- Explanation by Dewar-Chatt-Ducanson (DCD) model of σ -donation and π -backdonation. π -backdonation weakens the CO bond and redshifts it into lower wavenumbers^[2]
- Free CO stretching frequency: 2143 cm^{-1} ^[3]

[2] Frenking et. al. (2021) Metal-CO Bonding in Mononuclear Transition Metal Carbonyl Complexes. ACS.
<https://pubs.acs.org/doi/10.1021/jacsau.1c00106>

[3] Rob Toreki's Organometallic Hybertextbook. <http://www.ilpi.com/organomet/carbonyl.html>



Schematic representation of the synergistic OC \rightarrow TM σ -donation and OC \leftarrow TM π -backdonation. Image from [2]

References

- [1] Assefa et. al. (2015) Vibrational Scaling Factors for Transition Metal Carbonyls. Elseiver.
<https://www.sciencedirect.com/science/article/pii/S0009261415007873>
- [2] Frenking et. al. (2021) Metal-CO Bonding in Mononuclear Transition Metal Carbonyl Complexes. ACS.
<https://pubs.acs.org/doi/10.1021/jacsau.1c00106>
- [3] Rob Toreki's Organnometallic Hybertextbook. <http://www.ilpi.com/organomet/carbonyl.html>

Thank You!