**Problem Set 1**
**Ch153a – Winter 2024**
**Due: 8 January 2024**

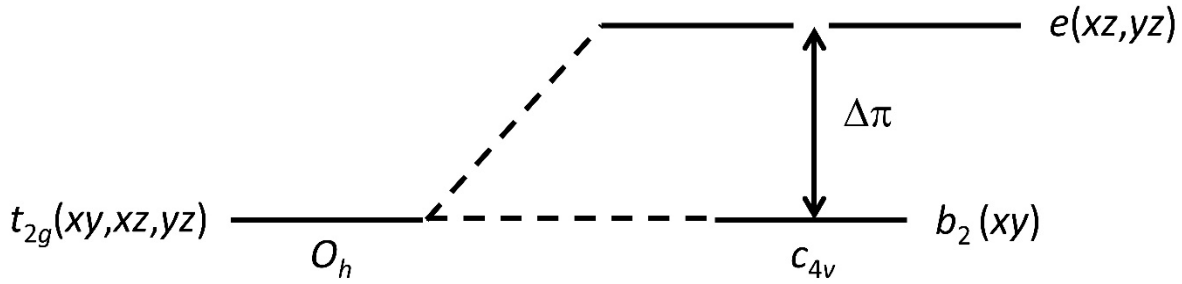
1a. Construct an MO diagram for $C_{4v}$ $[L_5MO]^{n+}$ (L is an uncharged ligand, for example, $H_2O$ or $NH_3$) using the following orbitals: five metal 3d orbitals, one set of five ligand $\sigma$ orbitals, and the oxo $\sigma + 2p\pi$ orbitals.

b. Predict the ground state electronic configuration and the metal-oxo bond order for each of the following:

| | | |
|---|---|---|
| $[L_5VO]^{2+}$ | $V^{IV}$ | $d^1$ |
| $[L_5CrO]^{3}+$ | $Cr^{V}$ | $d^1$ |
| $[L_5CrO]^{2+}$ | $Cr^{IV}$ | $d^2$ |
| $[L_5MnO]^{3+}$ | $Mn^{V}$ | $d^2$ |
| $[L_5MnO]^{2+}$ | $Mn^{IV}$ | $d^3$ |
| $[L_5FeO]^{2+}$ | $Fe^{IV}$ | $d^4$ |

c. Do you think that $[L_5CoO]^{2+}$ is a stable complex? Why or why not?

2. Electronic Structure and Spectra of Metal Oxo and Nitrido Complexes




The $d\pi$-orbital splitting for a tetragonal oxo- or nitrido-metal complex is shown above.

The following states arise from the $d^1$ and $d^2$ configurations in this scheme:

$d^1$:

| | |
|---|---|
| $^2E[(xz,yz)^1]$ | $E = \Delta_\pi$ |
| $^2B_2[(xy)^1]$ | $E = 0$ |

$d^2$:

| | |
|---|---|
| $^3A_2[(xz,yz)^2]$ | $E = 2\Delta_\pi + A - 5B$ |
| $^1A_1[(xz,yz)^2]$ | $E = 2\Delta_\pi + A + 7B + 4C$ |
| $^1B_1[(xz,yz)^2]$ | $E = 2\Delta_\pi + A + B + 2C$ |
| $^1B_2[(xz,yz)^2]$ | $E = 2\Delta_\pi + A + B + 2C$ |
| $^1E[(xy)^1(xz,yz)^1]$ | $E = \Delta_\pi + A + B + 2C$ |
| $^3E[(xy)^1(xz,yz)^1]$ | $E = \Delta_\pi + A - 5B$ |
| $^1A_1[(xy)^2]$ | $E = A + 4B + 3C$ |

The absorption spectra of $Cr^{V}(N)(CN)_5^{3-}$ and $Mn^{V}(N)(CN)_5^{3-}$ are shown below.

In $Cr^{V}(N)(CN)_5^{3-}$, the lowest energy spin-allowed absorption band is at 23,300 $cm^{-1}$.

In $Mn^{V}(N)(CN)_5^{3-}$, the lowest energy spin-allowed absorption band is at 19,400 $cm^{-1}$.

a. Provide an assignment for the lowest energy spin-allowed absorption band in each complex.
b. Use the foregoing orbital splitting diagram and the state energies to determine the values of $\Delta_\pi$ in the Cr and Mn complexes. Assume that $B$ = 500 $cm^{-1}$ and C/B = 4.