1. (22 pts)

1a. (8 pts) Using a group theoretical approach, construct a MO energy level diagram for trigonal planar BH$_3$. Include appropriate symmetry labels and discuss the logic used as well as any assumptions made in the construction of the MO diagram.

As always, we first draw a picture of the molecule we are considering (including axes):

What is the point group of this molecule? D$_{3h}$

First, we figure out what orbitals are involved. The valence orbitals of the boron atom are the 2s, 2px, 2py, and 2pz orbitals. The hydrogen atoms contribute three 1s orbitals.

Next, we figure out the symmetry of the orbitals involved. We make SALC’s of the hydrogen 1s orbitals.

\[
\begin{array}{ccccccc}
\Gamma & 1s & 2C_3 & 3C_2 & \sigma_h & 2S_3 & 3\sigma_v \\
\hline
D_3h & 3 & 0 & 1 & 3 & 0 & 1 \\
\end{array}
\]

which reduces to $A_1’ + E’$

Let's look at what these look like:

Looking in the character table, we see that: 2s has $a_1’$ symmetry; 2px and 2py have $e’$ symmetry; 2pz has $a_2”$ symmetry
Recognizing that hydrogen is more electronegative than boron, we can suspect that the hydrogen $a_1$ SALC will have the lowest energy and slightly lower than the $e''$ SALC's because of the nodal surfaces that exist although the atoms are not formally bonded. Thus, we get:

\[
\begin{align*}
B & \quad BH_3 & \quad H_3 \\
2e' & \quad 3a_1' & \quad 1a_2'' \\
a_2'' & \quad e' & \quad 1a_1' \\
a_1' & \quad 1e' & \quad e' \\
2a_1' & \quad a_1' & \quad H_3 \\
1s & \quad 1a_1' & 
\end{align*}
\]
**1b.** (10 pts) Draw an orbital correlation (Walsh) diagram that illustrates what happens to each of the bonding molecular orbitals of BH$_3$ upon distortion to a trigonal pyramidal geometry. Explain your reasoning. **Hint:** first construct a MO energy level diagram for “trigonal pyramidal” BH$_3$.

“trigonal pyramidal” BH$_3$ has C$_{3v}$ symmetry. Thus, our salc’s are:

<table>
<thead>
<tr>
<th>C$_{3v}$</th>
<th>E</th>
<th>2C$_3$</th>
<th>30v</th>
</tr>
</thead>
<tbody>
<tr>
<td>Γ$_{1s}$</td>
<td>3</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

which reduces to A$_1$ + E

From the character table, Boron 2s has a$_1$ symmetry; 2p$_x$ and 2p$_y$ have e symmetry; 2p$_z$ has a$_1$ symmetry. Thus, we get:

```
1s (a$_1$) ------------------- 1a$_1$
```

```
B

BH$_3$

H$_3$
```

```
\[ \begin{align*}
&4a_1 \\
&2e \\
&e + a_1 \\
&a_1 \\
&3a_1 \\
&1e \\
&2a_1 \\
\end{align*} \]
```

```
\[ \begin{align*}
&e \\
&a_1 \\
\end{align*} \]
```

```
\[ \begin{align*}
&\text{+} \\
&\text{+} \\
&\text{+} \\
&\text{+} \\
&\text{+} \\
\end{align*} \]
```

```
\[ \begin{align*}
&\text{+} \\
&\text{+} \\
&\text{+} \\
\end{align*} \]
```
Since the $1a_2''$ orbital is essentially $p_z$ orbital in $D_{3h}$ symmetry, overlap with hydrogen $1s$ orbitals increase as they move off the nodal plane. Thus, bending the molecule results in a sharp drop in the energy of $1a_2''$, it drops much faster than the two $1e$ orbitals which rise beneath it.

**1c. (4 pts)** Using your Walsh (orbital correlation) diagram, predict the structure of $\text{H}_3\text{O}^+$. Explain!

$\text{H}_3\text{O}^+$ has eight valence electrons; it is isoelectronic with $\text{NH}_3$. The overall energy of the molecule will be lower upon adopting trigonal pyramidal geometry as the Walsh diagram indicates!
2. (14 pts) Rationalize the trend in each of the following sets of IR-active CO stretching frequencies (cm$^{-1}$):

(a) 

<table>
<thead>
<tr>
<th>Complex</th>
<th>Frequency (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(CO)$_4$</td>
<td>2040</td>
</tr>
<tr>
<td>[Co(CO)$_4$]$^-$</td>
<td>1890</td>
</tr>
<tr>
<td>[Fe(CO)$_4$]$^{2-}$</td>
<td>1730</td>
</tr>
<tr>
<td>[Mn(CO)$_4$]$^{3-}$</td>
<td>1670</td>
</tr>
</tbody>
</table>

These isoelectronic complexes have increasing negative charges to delocalize in the order Ni(CO)$_4$ $< [Co(CO)$_4$]$^-$ $< [Fe(CO)$_4$]$^{2-}$ $< [Mn(CO)$_4$]$^{3-}$. Delocalization via back donation into the $\pi^*$ orbitals of the CO ligands causes a decrease in the CO bond order and thus a shift of the CO stretching frequencies ($\nu$CO) to progressively lower energies in the order given.

(b) 

<table>
<thead>
<tr>
<th>Complex</th>
<th>Frequencies (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[(\eta^6$-C$_6$H$_6)$Cr(CO)$_3$]</td>
<td>1980, 1908</td>
</tr>
<tr>
<td>[CpMn(CO)$_3$]</td>
<td>2027, 1942</td>
</tr>
</tbody>
</table>

Mn(I) has higher effective nuclear charge than Cr(0). Hence it attracts the electrons more strongly and less charge is back-donated into the $\pi^*$ orbitals of the CO ligands. The CO bond in the manganese compound is therefore weakened to a lesser extent and $\nu$CO is higher.
3. (14 pts)
3a. (8 pts) The molecular orbital (MO) energy level diagram for CO was discussed in class. Draw a MO energy level diagram for the CS molecule (use appropriate labels and explain the your reasoning).

The CO MO diagram is shown below as we derived it in class

On the Pauling scale, \( \chi \) of C = 2.544 and \( \chi \) of S = 2.589. Thus, the sulfur valence orbitals are slightly lower in energy. As in CO, we overlap orbitals with same symmetry and similar energies; the 3\( \sigma \) orbital derived from overlap of 2\( p_z \) and 3\( p_z \) orbitals is pushed up in energy due to mixing between s and \( p_z \) orbitals.

Note that the C 2\( p \) orbitals make a greater contribution to the 1\( \pi \) MO in CS than in CO since sulfur 3\( p \) orbitals are closer in energy to C 2\( p \) orbitals. However, the 1\( \pi \) MO in CS is less bonding in character because the S 3\( p \) orbitals are more diffuse than the C 2\( p \) orbitals and thus, overlap less efficiently with C 2\( p \) orbitals. Thus, the 1\( \pi \) MO in CS will rise in energy due to: (1) the reduced overlap; (2) the rise in energy of sulfur valence orbitals (versus oxygen valence orbitals); and (3) the increased participation from the C 2\( p \) orbitals.
On the other hand, the increase in energy and radial extent of the S 3p orbitals (versus O 2p orbitals) will cause the $1\pi^*\text{MO}$ in CS to be less antibonding (versus in CO) due to more contribution from S 3p orbitals and less from C 2p orbitals. Thus, the $1\pi^*\text{MO}$ in CS decreases in energy relative to the corresponding orbital in CO.

The $3\sigma_g$ is only weakly bonding and consists of contributions from C(2p$_z$), C(2s), and S(3p$_z$). The energy of the $3\sigma_g$ orbital is thus a sum of the energies of np, C(2p$_z$), and C(2s) orbitals: as the np rises in energy so does the $3\sigma_g$ orbital. Thus, the $3\sigma_g$ orbital is higher in energy in CS than in CO.


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**3b.** (6 pts) On the basis of MO energy level diagrams for CO and CS, and our discussions of transition metal-carbonyl (M-CO) bonding interactions, predict: (i) whether CS (thiocarbonyl) will be a better or poorer sigma ($\sigma$) donor than CO. And (ii) whether CS will be a better or poorer pi ($\pi$) acceptor than CO. Explain your reasoning!

(i) Based on the reasoning above, the $3\sigma_g$ orbital (HOMO) in CS is at higher energy hence CS will be a better sigma ($\sigma$) donor. (ii) The $1\pi^*$ MO (LUMO) in CS is lower in energy relative to the LUMO in CO hence CS will be a better pi ($\pi$) acceptor than CO.
4. (22 pts)
4a. (8 pts) Draw all possible geometrical isomers of \([\text{Co}(\text{en})_2(\text{NO}_2)_2]\). Indicate the handedness of any optical isomers.

\[ \text{Co} \quad \text{N} \quad \text{O}_2 \quad \text{N} \quad \text{N} \quad \text{en} \quad \text{en} \quad \text{N} \quad \text{O}_2 \quad \text{N} \]

\[ \text{A-isomer} \quad \text{A-isomer} \quad \text{A-isomer} \]

4b. (6 pts) Provide an example for each of the following types of isomerism:
(i) Ionization isomerism
   Examples include:
   (a) \([\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Br}_2\) and \([\text{Pt}(\text{NH}_3)_4\text{Br}_2]\text{Cl}_2\)
   (b) \([\text{Co}(\text{NH}_3)_5\text{Br}]\text{SO}_4\) and \([\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{Br}\)

(ii) Linkage isomerism
   Examples include:
   (a) \([\text{Ir}(\text{NCS})(\text{NH}_3)_5]^2+\) and \([\text{Ir}(\text{SCN})(\text{NH}_3)_5]^2+\)
   (b) \([\text{Co}(\text{NO}_2)(\text{NH}_3)_5]\text{Cl}_2\) (N-bonded) and \([\text{Co}(\text{ONO})(\text{NH}_3)_5]\text{Cl}_2\) (O-bonded)

(iii) Coordination isomerism
   Examples include:
   (a) \([\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]\) and \([\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]\)
   (b) \([\text{Pt}(\text{NH}_3)_4][\text{PdCl}_4]\) and \([\text{Pd}(\text{NH}_3)_4][\text{PtCl}_4]\)

4c. (8 pts) Name the following compounds according to IUPAC rules:
(i) \([\text{CrCl}_2(\text{NH}_3)_4]\text{Cl}\) - Tetraamminedichlorochromium(III) chloride
(ii) \(\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]\) - Potassium trichloro(ethylene)platinate(II)
(iii) \([\text{Co}(\text{NO}_2)_3(\text{NH}_3)_3]\) - Triamminetrinitrito-N-cobalt(III)
(iv) \([\text{Cr}(\text{OH})(\text{H}_2\text{O})_3(\text{NH}_3)_2](\text{NO}_3)_2\) - Diamminetriaquahydroxochromium(III) nitrate
5. (18 pt)

5a. (10 pts) Joe Greenhorn thinks that the structure of $[\text{Fe(PMe}_3)_3(\text{CO})_2]$ is most probably A or B. Using group theory, determine the number IR-active CO stretches A should possess. Would you expect B to show a greater or lesser number of CO stretches than A in its IR spectrum? Explain why.

![Diagram of structures A and B]

<table>
<thead>
<tr>
<th>C symmetry</th>
<th>E</th>
<th>$\alpha_h$</th>
<th>$\Gamma_{\text{CO}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs</td>
<td></td>
<td></td>
<td>2</td>
</tr>
</tbody>
</table>

which reduces to $2A'$. Thus, two resonances will be observed in the IR spectrum since $A'$ belongs to one of the cartesian axes.

B will show a lesser number of CO stretches than A in its IR spectrum because it has higher symmetry than A; the higher the symmetry, the lower the number of CO stretches expected!

5b. (8 pt) Explain how you would differentiate between A and B via $^1\text{H}$ and $^{31}\text{P}$ NMR data. Be specific!

A: two $^1\text{H}$ NMR resonances in 2:1 ratio for the PMe$_3$ methyls; the two equatorial PMe$_3$'s are exchangeable by reflection. The equatorial PMe$_3$ methyls will show as a doublet (coupling to axial PMe$_3$ will be very small). Similarly, the axial PMe$_3$ will show as a doublet.

B: one $^1\text{H}$ NMR doublet resonance since all are exchangeable by C$_3$ rotation

A: two $^{31}\text{P}$ resonances in 2:1 ratio for the PMe$_3$'s; the two equatorial PMe$_3$'s are exchangeable by reflection. The equatorial PMe$_3$'s will show as a doublet resonance while the axial PMe$_3$ will be a triplet due to P-P coupling.

B: one $^{31}\text{P}$ singlet resonance since all are exchangeable by C$_3$ rotation.
6. (8 pts) At -22 °C, PCl$_2$F$_3$ is fluxional, all fluorine atoms are indistinguishable by NMR spectroscopy. At -143 °C, $^{19}$F NMR spectroscopy clearly indicates the presence of two distinct types of fluorine atoms in a F$_{ax}$ to F$_{eq}$ ratio of 2:1. Explain these experimental observations.

PCl$_2$F$_3$ is a five coordinate complex hence trigonal bipyramidal and square pyramidal geometry are possible structures. Berry pseudorotations occur at -22 °C and equilibrate the axial and equatorial sites in a trigonal bipyramid while passing through square pyramidal geometry, hence all fluorine atoms are indistinguishable by NMR spectroscopy. At -143 °C, the fluxional process is slow on the NMR timescale and two distinct types of fluorine atoms, F$_{ax}$ and F$_{eq}$, are observed in 2:1 ratio. According to Bent’s rule, more electronegative substituents prefer hybrid orbitals with less s character. Therefore, two fluorine atoms will occupy the two axial sites and the third will occupy one of the equatorial sites, hence the 2:1 ratio.

7. (17pts)  
7a. (5 pts) Draw a MO energy level diagram for NO (use appropriate labels and explain the your reasoning).

![NO MO Energy Level Diagram](image-url)

N

NO

O

Energy

2s

2p

2s

2p

1s

1s

2σ$_g$

2σ$_u$

1σ$_g$

1σ$_u$

3σ$_g$

3σ$_u$

1π$_g$

1π$_u$

3ο$_g$

3ο$_u$

1ο$_g$

1ο$_u$
We overlap orbitals with same symmetry and similar energies. However, due to increase in effective nuclear charge, the 2s and 2p orbitals are sufficiently different in energy to permit significant mixing. Thus, we get the diagram above. [You may run across some books in which mixing of 2s and 2p orbitals is invoked but this is not as significant as in CO. See Burtzoff, M.D.; Peter, L.; Zhang, D.Y. J. Mol. Struct. (Theochem), 2000, 532, 269-278.]

7b. (6 pts) Explain the differences in dissociation energies and bond lengths on addition and removal of an electron from NO.

<table>
<thead>
<tr>
<th>NO^+</th>
<th>NO</th>
<th>NO^-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond energy (kJ/mol)</td>
<td>1046.9</td>
<td>626.9</td>
</tr>
<tr>
<td>Bond length (pm)</td>
<td>106.3</td>
<td>115.1</td>
</tr>
</tbody>
</table>

NO a total of 15 valence electrons. Its electron configuration is: \( 1\sigma_g^21\sigma_u^*2\sigma_g^22\sigma_u^*23\sigma_g^21\pi_u^41\pi_g^*2 \) and its bond order = \( 1/2(10-5) = 2.5 \). The HOMO and LUMO are identical: the \( 1\pi_g^* \) orbitals. Addition of an electron to an antibonding orbital results in the following configuration: \( 1\sigma_g^21\sigma_u^*2\sigma_g^22\sigma_u^*23\sigma_g^21\pi_u^41\pi_g^*2 \) and a bond order = \( 1/2(10-6) = 2 \). This explains the reduced bond energy and increased bond length of NO^-.

Removal of an electron from an antibonding orbital results in the following configuration for NO^+: \( 1\sigma_g^21\sigma_u^*2\sigma_g^22\sigma_u^*23\sigma_g^21\pi_u^4 \) and a bond order = \( 1/2(10-4) = 3 \), consistent with the above data.

7c. (6 pts) The photoelectron spectrum of NO can be described as follows:

There is a single strong peak at 16.2 eV, a long series of lines from 15.65 eV to 19.01 eV and a shorter series of 6 lines from 9.21 eV to 10.51 eV. Using your MO diagram, account for this spectrum.

The ionization at 9.21 eV obviously comes from the HOMO since it is the electron that takes the least energy to remove. We can say offhand that it affects the bond length to some degree since it has moderate fine structure.

The longer series of lines display a lot of fine structure. We suspect that this is important in controlling the N-O bond length (and is quite possibly a \( \pi \)-type orbital). The peak at 16.2 eV shows no fine structure and is less likely to involve a \( \pi \)-orbital. We can suspect that it is \( \sigma \) in character.

The set with the strong fine structure runs from 15.65 eV to 19.01 eV; do we count it as lower or higher in energy than a single band at 16.2 eV?

This takes a little thought. If we have vibrationally excited states, then we have to put in a little extra photon energy because some of that energy is used up during the excitation of the vibrational state.
That means if an orbital lies at an energy of 15.65 eV, we might expect to add a few eV to excite the various vibrational states. So energies greater than 15.65 would appear, but not less.

This logic lets us conclude that the fine structure band from 15.65 eV to 19.01 eV represents an MO that is higher in energy than the 16.2 eV band. Therefore, based on everything we have concluded, the results are more consistent with a MO that does not involve mixing of 2s and 2p orbitals than one that does. Our assignments are then:

\[
\begin{align*}
9.21\text{ eV} & \rightarrow \pi^* \\
15.65\text{ eV} & \rightarrow \pi \\
16.2\text{ eV} & \rightarrow \sigma_2
\end{align*}
\]

Notice how close in energy the \(\pi\) and \(\sigma\) levels are! In general, you can associate \(\pi\)-bonds with fine structure.

**Bonus (10 pts)** Fill in the entire periodic table

![Periodic Table](image-url)