1a. (8 pts) Select the most reasonable Lewis structure for the SCN\(^-\). Explain what makes each incorrect or unlikely structure less stable than the most reasonable structure.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Lewis Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{S} = \text{C} = \text{N}^- )</td>
</tr>
<tr>
<td>2</td>
<td>( \text{S} = \text{C} = \text{N}^- )</td>
</tr>
<tr>
<td>3</td>
<td>( \text{S} = \text{C} = \text{N}^- )</td>
</tr>
<tr>
<td>4</td>
<td>( \text{S} = \text{C} = \text{N}^- )</td>
</tr>
</tbody>
</table>

Structure 1 is unfavorable because the negative charge is on S and not the more electronegative N.
Structure 2 is very unfavorable because of -2 charge on S and +1 charge and only 6e on the more electronegative N.
Structure 3 is the best because the negative charge is on the more electronegative N.
Structure 4 is unfavorable because the charges are widely separated, N is (-2) and \( \pi \) bonding is less important to S than to N.
1b. (6 pts) Select the more stable (canonical) structure for the compound below. Explain what makes one structure more stable than the other.

Structure 1 has charge separation but with -1 charge on the more electronegative N. Structure 2 has favorable charge distribution (all atoms have zero formal charge) but \( \pi \) bonding is less important for third period elements. Nonetheless, Structure 2 makes a significant contribution to the overall structure since the six membered ring in \((\text{NPCl}_2)_3\) is nearly planar with 120° angles and all P-N distances equal but smaller than the sum of the single bond radii. However, in contrast to benzene, the 6 \( \pi \)-electrons are not completely delocalized but participate in three-center bonds that extend over the PNP units. It is estimated that each P-N bond has a \( \pi \)-bond order of 0.5 although this is still a matter of some debate. Thus structure 2 is somewhat more stable.

1c. (6 pts) Select the more stable (canonical) structure for the compound below. Explain what makes one structure more stable than the other.

Both B and N are neutral in Structure 1 but B has less than an octet of electrons. Structure 2 has unfavorable charge separation: B has a -1 charge while N has a +1 charge. However, there are more strong bonds in Structure 2 and the \( \pi \) bonding is delocalized around the ring. For example in \((\text{HB-NH})_3\), all the internuclear distances and angles (120°) are identical, and the ring is planar. MO calculations indicate that the \( p\pi \)-orbitals of the sp\(^2\)-boron atoms are each occupied by only 0.5 electrons (compared with 1.0 electrons in benzene). This means that structure 1 has considerable weight although structure 2 is more stable.
2a. (20 pts) Assign each of the following molecules to the appropriate point group.

(i) \( \text{B}_2\text{H}_6 \)

\[
\begin{array}{c}
\text{H} \\
\text{H} \\
\text{B} \\
\text{H} \\
\text{H} \\
\text{H} \\
\end{array}
\]

\( \text{D}_{2h} \)

(ii) \( \text{Be}_3(\text{CH}_3)_8 \)

\[
\begin{array}{c}
\text{H}_3\text{C} \\
\text{C} \\
\text{Be} \\
\text{C} \\
\text{Be} \\
\text{H}_3 \\
\text{CH}_3 \\
\end{array}
\]

\( \text{D}_{2d} \)

(iii) \( \text{trans-Mo(CO)}_4(\text{PPh}_3)_2 \)

\[
\begin{array}{c}
\text{L} \\
\text{OC} \\
\text{Mo} \\
\text{CO} \\
\text{OC} \\
\text{L} \\
\text{CO} \\
\end{array}
\]

\( \text{D}_{4h} \)

(iv) \( \text{cis-Mo(CO)}_4(\text{PPh}_3)_2 \)

\[
\begin{array}{c}
\text{L} \\
\text{OC} \\
\text{Mo} \\
\text{CO} \\
\text{OC} \\
\text{L} \\
\text{CO} \\
\end{array}
\]

\( \text{C}_{2v} \)

\( \text{L} = \text{PPh}_3; \text{ignore Ph groups on P} \)
(v) TaF$^{3-}$ (square antiprism)

\[
\begin{array}{c}
\text{D}_{4d}
\end{array}
\]

(vi)

\[
\begin{array}{c}
\text{C}_s
\end{array}
\]

(vii)

\[
\begin{array}{c}
\text{C}_i
\end{array}
\]

(viii) NaCp

\[
\begin{array}{c}
\text{C}_{5v}
\end{array}
\]
2b. (5 pts) Which of the above molecules (in question #1) can have a permanent dipole moment? Explain your reasoning.

This question was meant to refer to question 2a. If your answered is based on question 1, it will be graded on that basis.

These molecules do not have any of the following: an inversion center (i), more than one C_n axes (n≠1), or a perpendicular mirror plane (σ_h)
3. (12 pts) Indicate whether each of the following statements is true or false. Explain your reasoning using an appropriate example.

(a, 3 pts) The $S_2$ operation is identical to a $\sigma$ operation: true or false? Explain why.

**False.** The $S_2$ operation is equal to inversion: $S_2 = C_2\sigma_h = i$

(b, 3 pts) The presence of a $\sigma$ in a molecule will rule out a dipole moment in the molecule: true or false? Explain why.

**False.** Only a horizontal mirror plane ($\sigma_h$) in a molecule will rule out a dipole moment in the molecule. Having a $\sigma_v$ does not prohibit a dipole moment in the molecule. For example, dichloromethane has a dipole moment even though a $\sigma_v$ is present in the molecule.
(c, 3 pts) Elements with high ionization energies tend to have large electron affinities as well: true or false? Explain why.

**True.** Both ionization energies and electron affinities depend on effective nuclear charge. High $Z_{\text{eff}}$ results in high ionization energy since the electron is strongly attracted to the nucleus. Similarly, an element has high electron affinity if the electron can enter a shell where it experiences a high $Z_{\text{eff}}$.

(d, 3 pts) The size of the transition metals decreases slightly going from left to right across the period: true or false? Explain why.

**True.** The slight decrease in size of the transition metals going from left to right across the period is due primarily to shielding effects. Going from left to right across the period, d orbitals are being filled. Since d electrons do not completely shield the outermost valence electrons from the accompanying increase in the nuclear charge, atomic size decreases slightly.

4. (18 pts)
   (a) (9 pts) Which of each of the following pairs of molecules has the larger bond angle? Explain your reasoning.

   (i) CH$_4$ and NH$_3$:
   CH$_4$ will have the larger bond angle. Both CH$_4$ and NH$_3$ have four steric pairs and will be based on tetrahedron geometry. However, repulsion between the lone pair on nitrogen and the bonding pairs will reduce the H-N-H angle from the 109.5° of a tetrahedron. In fact, the H-N-H angle is 107°.

   (ii) OF$_2$ and OCl$_2$
   OCl$_2$ has the larger angle. In OF$_2$, the electron density is displaced toward the more electronegative F atoms, reducing bonding pair-bonding pair repulsion. This allows the two lone pairs on the central oxygen atom to get further away from each other. Oxygen is more electronegative than chlorine hence the O-Cl bonding electron pairs spend more time around oxygen. This reduces contraction of the Cl-O-Cl angle.
(iii) PH$_3$ and NH$_3$

NH$_3$ has the larger angle. The P-H bonds are longer and the reduced electronegativity of P (compared to N) permits electron density to be displaced towards H to a greater extent than in the case of NH$_3$. Both these effects diminish bonding pair-bonding pair repulsion and thereby the H-P-H angle.

(b) (9 pts) Use VSEPR theory to predict the shapes of the following molecules and indicate approximate bond angles around the central atom (Explain your reasoning):

(i) SnCl$_2$ has two $\sigma$ bonds and a lone pair leading to an angular molecule with the bond angle less than 120° because of lone pair-bonding pair repulsion.

(ii) PCl$_3$

Four steric pairs, 3 $\sigma$ bonds and a lone pair leading to trigonal pyramidal molecule with the Cl-P-Cl bond angle is less than 109.5° because of lone pair-bonding pair repulsion (Cl-P-Cl actually equal 100.3°).

(iii) (Me$_3$P)SbCl$_3$

There are 5 electron pairs around Sb, four bonding pairs and one lone pair. The lone pair requires more space and less electronegative donors prefer the equatorial axis. The Cl$_{eq}$-Sb-P angle will be less than 120° due to the lone pair. The Cl$_{ax}$-Sb-Cl$_{ax}$ angle will also be less than 180° due to the lone pair-bonding pair interactions.
5. (10 pts) Carbon monoxide has a larger bond dissociation energy (1072 kJ/mol) than molecular nitrogen (N₂, 945 kJ/mol). Suggest an explanation.

CO has about 76 kcal/mol contribution to its bond energy because of electronegativity difference between C and O; attraction between the slightly positive and negative ends strengthens the bonding. In other words, there is an ionic contribution to the bonding in CO that is not present in N₂. (While this is not the complete explanation, it covers most of the difference between CO and N₂. In spite of its high bond energy, it has been suggested that N₂ has some repulsion in its sigma bonding because of the short bond distance.)
4. (15 pts)
(a) (12 pts) What are the symmetries of the vibrational modes of \( \text{N}_2\text{F}_2 \)? Show your work (Hint: use the whole molecule method).

First, we assign the point group symmetry of \( \text{N}_2\text{F}_2 \) as \( C_{2h} \) and then draw a picture of what we are transforming including our axes. We place our \( x, y, \) and \( z \) vectors on each of the 4 atoms. Next, we transform the molecule under \( C_{2h} \) symmetry, seeing which of the 12 vectors go into themselves (+1 each), opposite themselves (-1 each) or somewhere else (0 each):

\[
\begin{align*}
\text{N} & \quad \text{N} \\
\text{F} & \quad \text{F} \\
\end{align*}
\]

\[
\begin{array}{c}
\text{C}_{2h} \\
\end{array}
\]

\[
\begin{array}{c}
\text{C}_{2h} \\
\end{array}
\]

\[
\begin{array}{c}
\text{C}_{2h} \\
\end{array}
\]

For \( \sigma_h \), 8 vectors (in the xy plane) stay where they are while 4 vectors directed along the z axis invert (go opposite) themselves. Thus, \( 8 - 4 = 4 \)

Apply our reduction formula and we get: \( 4A_g + 2B_g + 2A_u + 4B_u \); dimensionality = 12

Consulting the \( C_{2h} \) character table, we see that the translational vectors \( x, y, z \) transform as \( A_u \) and \( 2B_u \) representations and that the rotational vectors \( R_x, R_y, R_z \) transform as \( A_g \) and \( 2B_g \) representations. We subtract out these and get:

\[
\Gamma_{\text{vib}} = \Gamma_{12} - A_g - A_u - 2B_g - 2B_u = 3A_g + A_u + 2B_u \ (3N - 6 \text{ vibrations!})
\]

(b, 3 pts) How many different bands would be observed in the IR and Raman spectra of \( \text{N}_2\text{F}_2 \)? Which of the bands are both IR and Raman active? If none, explain your reasoning!
Consulting the $C_{2h}$ character table, 3 bands would be observed in the IR spectrum ($A_u$ and $2B_u$). Similarly, 3 bands would be observed in the Raman spectrum ($3A_g$). None are both IR and Raman active because there’s an exclusion rule for molecules with a center of symmetry: if a vibration is IR active then it can't be Raman active and vice versa.

**Bonus** (10 pts). Fill in the spots marked with an asterisk (*).