1. Assign the following molecules to their appropriate point groups.

- **HOOPO**
  - $C_{\infty}$: no
  - $C_n$: no
  - $\sigma$: yes
  - Point group: $C_s$

- **HOO**
  - $C_{\infty}$: no
  - $C_n$: yes $\rightarrow$ $C_2$
  - $S_n$: no
  - $\sigma$: no
  - $\sigma_v$: yes
  - Point group: $C_{2v}$

- **As drawn, not delocalized**
  - $C_{\infty}$: no
  - $C_n$: yes $\rightarrow$ $C_3$
  - $S_n$: no
  - $\sigma$: no
  - $\sigma_v$: yes
  - If delocalized: $D_{3h}$

- **SO**
  - $C_{\infty}$: no
  - $C_n$: no
  - $\sigma$: yes
  - Point group: $C_1$

- **F-Si-F**
  - $C_{\infty}$: no
  - $C_n$: yes $\rightarrow$ $C_3$ $\rightarrow$ $4C_3$
  - $S_n$: no
  - $6\sigma$: yes
  - Point group: $T_d$

- **F-P-F**
  - $C_{\infty}$: no
  - $C_n$: yes $\rightarrow$ $C_3$ $\rightarrow$ $4C_3$
  - $S_n$: no
  - $\sigma$: yes
  - Point group: $D_{3h}$
2. Find and draw all of the symmetry elements in an octahedron.  

Eliminate

Draw the symmetry elements. You can redraw the molecule a few times so that it easy to see your elements. Also give one example of each type of symmetry element.

3. What are the symmetries of the normal modes of vibration of these molecules?
Nonlinear

3N = 3(4) - 12 total degrees of freedom

Point group? C\textsubscript{3v}

C\textsubscript{3v}  
E  2C\textsubscript{3}  \sigma\textsubscript{v}

Unshifted atoms 4 1 2
Contributions 3 0 1

per atom
\( \Gamma_{\text{total}} \) 12 0 2

\( A_1 = \frac{1}{6} \left[ 12(1)(1) + 0 + 2(3)(1) \right] = \frac{1}{6}(18) = 3 \)

\( A_2 = \frac{1}{6} \left[ 12(4)(1) + 0 + 2(3)(1) \right] = \frac{6}{6} = 1 \)

\( E = \frac{1}{6} \left[ 12(3)(3) + 0 + 2(3)(0) \right] = \frac{24}{6} = 4 \)

\( \Gamma_{\text{total}} = 3A_1 + A_2 + 4E \rightarrow 12 \text{ degrees of freedom} \)

\( \Gamma_{\text{trans}} = A_1 + E \) (from \( x, y, z \) in character table)

\( \Gamma_{\text{rot}} = A_2 + E \) (from \( R_x, R_y, R_z \) in table)

\( \Gamma_{\text{vib}} = 2A_1 + 2E \) (3N - 6 = 6 degrees of freedom)

6 normal modes
$3N: 3(3) = 9$ degrees of freedom

\[
\begin{array}{c|c|c|c}
\text{U. A.} & \sqrt{2} & \sigma_v(xz) & \sigma_v'(yz) \\
\hline
3 & 1 & 1 & 3 \\
\text{cont. per atom.} & 3 & -1 & 1 & 1 \\
9 & -1 & 1 & 3 \\
\end{array}
\]

- $A_1: \frac{1}{4} \left[ 9(1)(1) + -1(1)(1) + 1(1)(1) + 3(1)(1) \right] = \frac{12}{4} = 3$

- $A_2: \frac{1}{4} \left[ 9(1)(1) + -1(1)(1) + 1(1)(-1) + 3(1)(-1) \right] = \frac{4}{4} = 1$

- $B_1: \frac{1}{4} \left[ 9(1)(1) + -1(1)(-1) + 1(1)(1) + 3(1)(1) \right] = \frac{8}{4} = 2$

- $B_2: \frac{1}{4} \left[ 9(1)(1) + -1(1)(-1) + 1(1)(1) + 3(1)(1) \right] = \frac{12}{4} = 3$

\[\Gamma_{\text{total}} = 3A_1 + 1A_2 + 2B_1 + 3B_2\]

\[\Gamma_{\text{trans}} = A_1 + B_1 + B_2\]

\[\Gamma_{\text{rot}} = A_2 + B_1 + B_2\]

\[\Gamma_{\text{vib}} = 2A_1 + B_2 \quad \text{(Three degrees of freedom)}\]

$3N - 6 = 3$

Point group: $D_4h$ or $D_{4h}$, 2 points

$3N - 6 = 15 - 6 = 9$
Because it has five atoms, we expect 9 vibrational modes, four of which will be stretching modes (because there are 4 bonds) and five of which will be bending modes.

\[ 3(5) = 15 \text{ degrees of freedom} \]

<table>
<thead>
<tr>
<th>E</th>
<th>2C(_4)</th>
<th>C(_2)</th>
<th>2C(_1)</th>
<th>2C(_2)</th>
<th>i</th>
<th>2(\sigma_4)</th>
<th>(\sigma_h)</th>
<th>2(\sigma_v)</th>
<th>2(\sigma_d)</th>
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<tbody>
<tr>
<td>U.A.</td>
<td>5</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>5</td>
<td>3</td>
</tr>
<tr>
<td>C/A</td>
<td>3</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-3</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

\[ A_{1g}: \frac{16}{16} = 1 \quad \text{A}_{2u} = 2 \]

\[ A_{2g}: \frac{16}{16} = 1 \quad B_{1u} = 0 \]

\[ B_{1g}: \frac{16}{16} = 1 \quad B_{2u} = 1 \quad E_{u} = 3 \]

\[ B_{2g}: \frac{16}{16} = 1 \]

\[ E_{g}: \frac{16}{16} = 1 \quad A_{1u} = 0 \]
\[ \Gamma_{\text{tot}} = 1A_{1g} + 1A_{2g} + 1B_{1g} + 1B_{2g} + 1E_g + 2A_{2u} + 1B_{2u} + 3E_u \]

- \( \Gamma_{\text{trans}} = A_{2u} \)
- \( \Gamma_{\text{rot}} = \)
- \( \Gamma_{\text{vib}} = 1A_{1g} + 1B_{1g} + 1B_{2g} + 1E_g + 2A_{2u} + 1B_{2u} + 2E_u \)

9 vibrations

\( A_{2u} + E_u \): IR active; transforms like \( x, y, z \)

\( A_{1g}, B_{1g} + B_{2g} \): Raman active; transforms like quadratic functions of \( x, y, z \) + linear combinations of them

\( B_{2u} \): Neither IR nor Raman

Since this molecule has \( n = 3 \), the IR + Raman active modes would be different.

5. \( P: 1s^2 2s^2 2p^6 3s^2 3p^3 \)

Point group: \( D_{3h} \)

\[ \Gamma_{\text{total}} = 5 \quad 2 \quad 1 \quad 3 \quad 0 \quad 3 \]

\( n = 3 \) has d-orbitals
\[ A_1' = 2 \]
\[ A_2' = 0 \]
\[ E' = 1 \]
\[ A_1'' = 0 \]
\[ A_2'' = 1 \]
\[ E'' = 0 \]

\[ \Gamma_{red} = 2A_1' + E' + A_2'' \]

A\textsuperscript{'}\textsubscript{1} orbitals: \( S, d_z^2 \)
E\textsuperscript{'} orbitals: \( p_x, p_y, d_{x^2-y^2}, d_{xy} \)
A\textsuperscript{''}\textsubscript{2}: \( p_z \)

Possible combinations:
\[ S, d_z^2, p_x, p_y, p_z \]
\[ d_{x^2-y^2}, d_{xy}, p_z \]
\[ d_{3p} \]

5 atomic orbitals \( \rightarrow \) 5 hybrid orbitals

\( F \)

5" [Ne]3s\textsuperscript{2}3p\textsuperscript{4} has d-orbitals

Point group: \( O_h \)
\[ \Gamma_7 \quad 6 \quad 0 \quad 0 \quad 2 \quad 2 \quad 0 \quad 0 \quad 0 \quad 4 \quad 2 \]

\[ A_{1g} = 1 \quad E_u = 0 \quad \Gamma_{\text{red}} = A_{1g} + E_g + T_{1u} \]

\[ A_{2g} = 0 \quad T_{1u} = 1 \quad A_{1g} \text{orbitals: } S \]

\[ E_g = 1 \quad T_{2u} = 0 \quad E_g \text{ n: } d_{z^2}, d_{x^2-y^2} \text{ only possible combination} \]

\[ T_{1g} = 0 \quad T_{1u} \text{ n: } p_x, p_y, p_z \]

\[ T_{2g} = 0 \]

\[ A_{1u} = 0 \]

\[ A_{2u} = 0 \]