(1) (a) BF$_4^-$ tetrahedral ($T_d$)

\[
\begin{array}{c|cccccc}
T_d & E & 8C_3 & 3C_2 & 6S_4 & 6\sigma_d \\
\hline
\Gamma_{xyz} & 3 & 0 & -1 & -1 & 1 \\
\Gamma_{\text{unmoved atoms}} & 5 & 2 & 1 & 1 & 3 \\
\Gamma_{\text{total}} & 15 & 0 & -1 & -1 & 3 \\
\end{array}
\]

If we reduce $\Gamma_{\text{total}}$ we find that:

$$\Gamma_{\text{total}} = A_1 + E + T_1 + 3T_2$$

Looking at the character table, we can see that:

$$\Gamma_{\text{rotational}} = T_1$$

and

$$\Gamma_{\text{translational}} = T_2$$

therefore,

$$\Gamma_{\text{vibrational}} = A_1 + E + 2T_2$$

By inspection of the character table, the $2T_2$ modes are IR active and $A_1$, $E$, and $2T_2$ modes are Raman active.

(b) ClNO bent ($C_s$)

\[
\begin{array}{c|cc}
C_s & E & \sigma_h \\
\hline
\Gamma_{xyz} & 3 & 1 \\
\Gamma_{\text{unmoved atoms}} & 3 & 3 \\
\Gamma_{\text{total}} & 9 & 3 \\
\end{array}
\]

\[ \Gamma_{\text{total}} = 6A' + 3A'' \]
\[ \Gamma_{\text{rotational}} = A' + 2A'' \]
\[ \Gamma_{\text{translational}} = 2A' + A'' \]

therefore,

\[ \Gamma_{\text{vibrational}} = 3A' \]

IR active: 3A'
Raman active: 3A'

(c) XeO₃ trigonal pyramid (C₃v)

\[
\begin{array}{c|ccc}
\text{C₃v} & E & 2C_3 & 3\sigma_v \\
\hline
\Gamma_{\text{xyz}} & 3 & 0 & 1 \\
\Gamma_{\text{unmoved atoms}} & 4 & 1 & 2 \\
\Gamma_{\text{total}} & 12 & 0 & 2 \\
\end{array}
\]

\[ \Gamma_{\text{total}} = 3A_1 + A_2 + 4E \]
\[ \Gamma_{\text{rotational}} = A_2 + E \]
\[ \Gamma_{\text{translational}} = A_2 + E \]

therefore,

\[ \Gamma_{\text{vibrational}} = 2A_1 + 2E \]

IR active: 2A₁ + 2E
Raman active: 2A₁ + 2E

(d) ClF₃ t-shaped (C₂v)
\[
\begin{array}{c|cccc}
C_{2v} & E & C_2(z) & \sigma_v(xz) & \sigma_v(yz) \\
\hline
\Gamma_{xyz} & 3 & -1 & 1 & 1 \\
\Gamma_{\text{unmoved atoms}} & 4 & 2 & 2 & 4 \\
\Gamma_{\text{total}} & 12 & -2 & 2 & 4 \\
\end{array}
\]

\( \Gamma_{\text{total}} = 4A_1 + A_2 + 3B_1 + 4B_2 \)

\( \Gamma_{\text{rotational}} = A_2 + B_1 + B_2 \)

\( \Gamma_{\text{translational}} = A_1 + B_1 + B_2 \)

therefore,

\( \Gamma_{\text{vibrational}} = 3A_1 + B_1 + 2B_2 \)

IR active: \( 3A_1 + B_1 + 2B_2 \)

Raman active: \( 3A_1 + B_1 + 2B_2 \)

(e) \( \text{SF}_4 \) see-saw (\( C_{2v} \))

![Diagram of SF4]

\[
\begin{array}{c|cccc}
C_{2v} & E & C_2(z) & \sigma_v(xz) & \sigma_v(yz) \\
\hline
\Gamma_{xyz} & 3 & -1 & 1 & 1 \\
\Gamma_{\text{unmoved atoms}} & 5 & 1 & 3 & 3 \\
\Gamma_{\text{total}} & 15 & -1 & 3 & 3 \\
\end{array}
\]

\( \Gamma_{\text{total}} = 5A_1 + 2A_2 + 4B_1 + 4B_2 \)

\( \Gamma_{\text{rotational}} = A_2 + B_1 + B_2 \)

\( \Gamma_{\text{translational}} = A_1 + B_1 + B_2 \)

therefore,

\( \Gamma_{\text{vibrational}} = 4A_1 + A_2 + 2B_1 + 2B_2 \)

IR active: \( 4A_1 + 2B_1 + 2B_2 \)

Raman active: \( 4A_1 + A_2 + 2B_1 + 2B_2 \)
Axes oriented such that z-axis goes through O-Xe-O bond and x-axis is through Xe, perpendicular to the plane of the molecule.

\[
\begin{array}{|c|c|c|c|c|c|c|c|}
\hline
 & D_{2h} & E & C_2(z) & C_2(y) & C_2(x) & i & \sigma(xy) & \sigma(xz) & \sigma(yz) \\
\hline
\Gamma_{xyz} & 3 & -1 & -1 & -1 & -3 & 1 & 1 & 1 \\
\Gamma_{\text{unmoved atoms}} & 5 & 3 & 3 & 1 & 1 & 3 & 3 & 5 \\
\Gamma_{\text{total}} & 15 & -3 & -3 & -3 & 3 & 3 & 3 & 5 \\
\hline
\end{array}
\]

\[
\Gamma_{\text{total}} = 2A_g + B_{1g} + B_{2g} + 2B_{3g} + 3B_{1u} + 3B_{2u} + 3B_{3u}
\]

\[
\Gamma_{\text{rotational}} = B_{1g} + B_{2g} + B_{3g}
\]

\[
\Gamma_{\text{translational}} = B_{1u} + B_{2u} + B_{3u}
\]

Therefore,

\[
\Gamma_{\text{vibrational}} = 2A_g + B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u}
\]

(b) IR active: 2B_{1u} + 2B_{2u} + 2B_{3u}
Raman active: 2A_g + B_{3g}

(c) To solve this problem we need to look at what happens to A_1, E and T_2 when lowering the symmetry from T_d to C_{2v}:

\[
\begin{array}{c}
T_d \quad \rightarrow \\
A_1 \quad \rightarrow \\
E \quad \rightarrow \\
T_2 \quad \rightarrow \\
C_{2v}
\end{array}
\]

The normal modes for this molecule are: 4A_1 + A_2 + 2B_1 + 2B_2

(d) IR active: 4A_1 + 2B_1 + 2B_2
Raman active: 4A_1 + A_2 + 2B_1 + 2B_2

(e) There are several possible answers to this question:

(i) Neither structure is correct since neither has the correct number of IR bands.

(ii) Structure I, which gives 8 possible IR bands, is correct and one of the stretches is too weak to be seen or lies under another band.
Axes oriented such that z-axis goes through the two N-atoms, y-axis goes through the two S-atoms and x axis is perpendicular to the plane of the molecule.

\[ \Gamma_{xyz} = \Gamma_{\text{unmoved atoms}} = \Gamma_{\text{total}} = 12 \]

\[ \Gamma_{\text{total}} = 2A_g + B_{1g} + B_{2g} + 2B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u} \]

\[ \Gamma_{\text{rotational}} = B_{1g} + B_{2g} + B_{3g} \]

\[ \Gamma_{\text{translational}} = B_{1u} + B_{2u} + B_{3u} \]

therefore,

\[ \Gamma_{\text{vibrational}} = 2A_g + B_{3g} + B_{1u} + B_{2u} + B_{3u} \]

IR active: \( B_{1u} + B_{2u} + B_{3u} \)

Raman active: 2\( A_g + B_{3g} \)

\[ \Gamma_{C_{2v}} = \Gamma_{\text{unmoved atoms}} = \Gamma_{\text{total}} = 12 \]

\[ \Gamma_{\text{total}} = 4A_1 + 2A_2 + 3B_1 + 3B_2 \]

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

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

therefore,

\[ \Gamma_{\text{vibrational}} = 3A_1 + A_2 + B_1 + B_2 \]
IR active: $3A_1 + B_1 + B_2$
Raman active: $3A_1 + A_2 + B_1 + B_2$

If structure A is correct, the IR and Raman spectra should each have only three bands. If either, or both of the spectra contain more than three bands, this would indicate Structure B is correct.

(4) Assume the molecule lies in the yz plane, with the z-axis going through the C-C bond, the x-axis perpendicular to the plane of the molecule and the y-axis pointing down.

(a)

<table>
<thead>
<tr>
<th>$D_{2h}$</th>
<th>E</th>
<th>$C_2(z)$</th>
<th>$C_2(y)$</th>
<th>$C_2(x)$</th>
<th>i</th>
<th>$\sigma(xy)$</th>
<th>$\sigma(xz)$</th>
<th>$\sigma(yz)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{xyz}$</td>
<td>3</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-3</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma_{unmoved \ atoms}$</td>
<td>6</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>$\Gamma_{total}$</td>
<td>18</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>6</td>
</tr>
</tbody>
</table>

$\Gamma_{total} = 3A_g + B_{1g} + 2B_{2g} + 3B_{3g} + A_u + 3B_{1u} + 3B_{2u} + 2B_{3u}$

$\Gamma_{rotational} = B_{1g} + B_{2g} + B_{3g}$

$\Gamma_{translational} = B_{1u} + B_{2u} + B_{3u}$

therefore,

$\Gamma_{vibrational} = 3A_g + B_{2g} + 2B_{3g} + A_u + 2B_{1u} + 2B_{2u} + B_{3u}$

(b) We can separate the bond internal coordinates into one C-C bond and 4 C-H bonds.

<table>
<thead>
<tr>
<th>$D_{2h}$</th>
<th>E</th>
<th>$C_2(z)$</th>
<th>$C_2(y)$</th>
<th>$C_2(x)$</th>
<th>i</th>
<th>$\sigma(xy)$</th>
<th>$\sigma(xz)$</th>
<th>$\sigma(yz)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{CH}$</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>$\Gamma_{CC}$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
</tbody>
</table>

$\Gamma_{CC} = A_g$

$\Gamma_{CH} = A_g + B_{3g} + B_{1u} + B_{2u}$
(c) We can use the four C-C-H angles as internal coordinates for in-plane bending modes:

Each of these four angles can be varied independently of the others; we therefore expect no spurious modes.
\[ \Gamma_{01-04} = \Gamma_{CH} = A_g^* + B_{3g} + B_{1u} + B_{2u} \]

(e) We can use the results from Part C to write the SALS's easily:

\[ \beta^A_g (\Delta \theta_1) \propto \Delta \theta_1 + \Delta \theta_2 + \Delta \theta_3 + \Delta \theta_4 \]

\[ \beta^{B_{3g}} (\Delta \theta_1) \propto \Delta \theta_1 - \Delta \theta_2 + \Delta \theta_3 - \Delta \theta_4 \]

\[ \beta^{B_{1u}} (\Delta \theta_1) \propto \Delta \theta_1 + \Delta \theta_2 - \Delta \theta_3 - \Delta \theta_4 \]

\[ \beta^{B_{2u}} (\Delta \theta_1) \propto \Delta \theta_1 - \Delta \theta_2 - \Delta \theta_3 + \Delta \theta_4 \]

There are no spurious modes from this choice of in-plane internal coordinates.

<table>
<thead>
<tr>
<th>( D_{2h} )</th>
<th>E</th>
<th>( C_2(z) )</th>
<th>( C_2(y) )</th>
<th>( C_2(x) )</th>
<th>i</th>
<th>( \sigma(xy) )</th>
<th>( \sigma(xz) )</th>
<th>( \sigma(yz) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Gamma_{01-04} )</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4</td>
</tr>
</tbody>
</table>
(f) The choice of internal coordinates for out-of-plane bends is more difficult. Imagine lines through the two C atoms, perpendicular to the plane of the molecule. We can use the angles from these lines to the H atoms:

\[ \theta_5 \text{ “under” } \theta_5 \]
\[ \theta_6 \text{ “under” } \theta_6 \]
\[ \theta_7 \text{ “under” } \theta_7 \]
\[ \theta_8 \text{ “under” } \theta_8 \]

\[ \theta_5 + \theta_9 = 180^\circ; \theta_6 + \theta_{10} = 180^\circ; \theta_7 + \theta_{11} = 180^\circ; \theta_8 + \theta_{12} = 180^\circ; \]
we therefore expect 4 spurious modes.

Before we figure \( \Gamma_{\theta_5-\theta_{12}} \), let’s see what we expect. If we subtract the stretching and in-plane bending modes from \( \Gamma_{\text{vibrational}} \) we are left with

\[ \Gamma_{\text{out-of-plane}} = B_{2g} + A_u + B_{3u} \]

All of the operations except E move all of the angles. Reducing this rep gives us one irr. rep of each symmetry:

\[ \Gamma_{\theta_5-\theta_{12}} = A_g + B_{1g} + B_{2g} + B_{3g} + A_u + B_{1u} + B_{2u} + B_{3u} \]

We cannot increase both \( \theta_5 \) and \( \theta_9 \) at the same time, for this is physically impossible. Likewise, \( \theta_6 \) and \( \theta_{10} \), and so forth. Because the supplementary angles are related by \( \sigma(yz) \), any irr. rep for which \( \chi[\sigma(yz)] = \chi(E) \) will lead to a physically impossible mode. Thus, the spurious modes are \( A_g, B_{3g}, B_{1u}, \) and \( B_{2u} \). (*You should try using the projection operators of these irr. reps if you don’t follow the logic used above.*)

For the three remaining modes we expect:
\[ \hat{p}^{B_{2g}}(\Delta \theta_5) \propto \Delta \theta_5 + \Delta \theta_6 - \Delta \theta_7 - \Delta \theta_8 - \Delta \theta_9 + \Delta \theta_{10} + \Delta \theta_{11} + \Delta \theta_{12} \]

\[ \hat{p}^{A_{1u}}(\Delta \theta_5) \propto \Delta \theta_5 - \Delta \theta_6 + \Delta \theta_7 + \Delta \theta_8 - \Delta \theta_9 - \Delta \theta_{10} - \Delta \theta_{11} + \Delta \theta_{12} \]

This mode corresponds to twisting the two \( \text{CH}_2 \) fragments relative to one another.

\[ \hat{p}^{B_{3u}}(\Delta \theta_5) \propto \Delta \theta_5 + \Delta \theta_6 + \Delta \theta_7 + \Delta \theta_8 - \Delta \theta_9 - \Delta \theta_{10} - \Delta \theta_{11} - \Delta \theta_{12} \]

What about the \( B_{1g} \) mode, which has not yet been accounted for?

\[ \hat{p}^{B_{1g}}(\Delta \theta_5) \propto \Delta \theta_5 - \Delta \theta_6 - \Delta \theta_7 + \Delta \theta_8 - \Delta \theta_9 + \Delta \theta_{10} + \Delta \theta_{11} - \Delta \theta_{12} \]

This is not actually a vibrational mode; it corresponds to rotation about the C-C axis (\( R_2 \)).