Reminder: From the Notes

Determine the reducible representation for a molecule of ammonia and describe the spectrum.

- determine the atoms that remain at the same position under each symmetry operation (atoms)
- take the contribution for each symmetry atom from table \( \chi(\text{per atom}) \)
- to generate the reducible representation

\[
\begin{array}{c|ccc}
C_{3v} & E & 2C_3 & 3\sigma_v \\
A_1 & 1 & 1 & 1 \\
A_2 & 1 & 1 & -1 \\
E & 2 & -1 & 0 \\
\end{array}
\]

\[ \chi(NH_3) = 3A_1 + 1A_2 + 4E \]

- then apply the reduction formula using a reduction table
- show the full working for one irreducible representation or symmetry
- check that you have 3N components

\[ n_{IR} = \frac{1}{h} \sum k \cdot \chi^R(Q) \cdot \chi(Q) \]

\[
\begin{array}{c|ccc}
C_{3v} & E & 2C_3 & 3\sigma_v \\
\Gamma(NH_3) & 12 & 0 & 2 \\
A_1 & 1 & 1 & 1 \\
\end{array}
\]

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

\[ n_{A_2} = \frac{1}{6} \left[ 12 + 0 + 6 \right] = \frac{18}{6} = 3 \\
\]

\[ n_{E} = \frac{1}{6} \left[ (1 \cdot 12 \cdot 1) + (3 \cdot 2 \cdot -1) \right] = \frac{6}{6} = 1 \\
\]

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

\[ \Gamma(NH_3) = 3A_1 + 1A_2 + 4E \]

Figure 3 Reduction for ammonia

- N=4 for ammonia, 3N=12 and number of IR is 3+1+(4*2)=12 good!

Hunt / Workshop 1
• determine the irreducible representations for the translation and rotation of the whole molecule, subtract these from the reduced representation to remove the CoM motions

\[ \Gamma(T) = 1A_1 + 1E \]
\[ \Gamma(R) = 1A_2 + 1E \]
\[ \Gamma(T + R) = 1A_1 + 1A_2 + 2E \]
\[ \Gamma_{vib}(NH_3) = \Gamma(NH_3) - \Gamma(T + R) \]
\[ = (3A_1 + 1A_2 + 4E) - (1A_1 + 1A_2 + 2E) = 2A_1 + 2E \]

Figure 4 Remove CoM motion

• determine the IR and Raman activity of these modes
  o IR have the same symmetry as the translational motions \( \Gamma(T) = A_1 + E \)
  o Raman have the same symmetry as the binary functions \( \Gamma(f) = A_1 + E \)

• write out the \( \Gamma_{vib} \) in the manner identified in the lectures, ie identify if the vibration is IR active or Raman active and if the Raman mode is polarised or depolarised

\[ \Gamma_{vib}(NH_3) = 2A_1(IR, pol) + 2E(IR, depol) \]

Determine the Form of the NH\(_3\) Vibrational Modes (only one vector of any degenerate modes is required)

• do the stretches first
• complete the reduction table for the reducible representation of the stretch and then use the reduction formula to reduce the representation to its IR components

\[ C_{nv} \]
\[ \Gamma(s_{N-H}) \]
\[ E \]
\[ 2C_3 \]
\[ 3\sigma_v \]

\[ A_1 \]
\[ 1 \]
\[ 1 \]
\[ 1 \]
\[ \Rightarrow \frac{1}{6}[1 \cdot 3 \cdot 1 + 0 + (3 \cdot 1 \cdot 1)] = \frac{6}{6} = 1 \]

\[ \Gamma(s_{N-H}) = A_1 + E \]

Figure 5 Setup for determining the symmetry of the stretching modes

• use the projection operator to determine the form of the vibrations by completing the projection table for the N-H stretches of ammonia

\[ P_I[f] = \frac{1}{h} \sum Q \chi^{\text{irr}}(Q) \cdot Q[f] \]

\[ C_{3v} \]
\[ E \]
\[ C_1 \]
\[ C_2 \]
\[ \sigma_v (1) \]
\[ \sigma_v (2) \]
\[ \sigma_v (3) \]

\[ Q(s_1) \]
\[ s_1 \]
\[ s_2 \]
\[ s_3 \]
\[ s_1 \]
\[ s_3 \]
\[ s_2 \]

Figure 6 Filling in the projection table
- we treat $A_1$ first, the equation is the sum along the row

$$
\begin{array}{c|ccccccc}
C_{3v} & E & C^1_3 & C^2_3 & \sigma_A(1) & \sigma_A(2) & \sigma_A(3) \\
Q[s_1] & s_1 & s_2 & s_3 & s_1 & s_3 & s_2 \\
A_1 & 1 & 1 & 1 & 1 & 1 & 1 \\
\end{array}
$$

$$
\chi_h^A(Q) \cdot Q[s_1] = s_1 \quad s_2 \quad s_3 \quad s_1 \quad s_3 \quad s_2
$$

$$
\nu_{N-H}(A_1) = \frac{1}{6} [s_1 + s_2 + s_3 + s_1 + s_2] = \frac{1}{6} [2s_1 + 2s_2 + 2s_3] = \frac{1}{3} [s_1 + s_2 + s_3]
$$

**Figure 7** Finding the $A_1$ vibrational vector function

- find the equation and draw the vibration for one degenerate E mode, finding the second requires generating an orthogonal function which is beyond the scope of this course

$$
\begin{array}{c|ccccccc}
C_{3v} & E & C^1_3 & C^2_3 & \sigma_A(1) & \sigma_A(2) & \sigma_A(3) \\
Q[s_1] & s_1 & s_2 & s_3 & s_1 & s_3 & s_2 \\
E & 2 & -1 & -1 & 0 & 0 & 0 \\
\chi_h^E(Q) \cdot Q[s_1] & 2s_1 & -s_2 & -s_3 & 0 & 0 & 0
\end{array}
$$

$$
\nu_{N-H}(E) = \frac{1}{6} [2s_1 - s_2 - s_3]
$$

**Figure 8** One of the E stretching modes

- do the breathing modes next, use double arrowheads
- determine the reducible representation, reduce it (using information already obtained above) and eliminate redundant modes
  - the $A_1$ mode is redundant, if the molecule was planar all of the H-N-H angles cannot close at once, this leaves only the E mode
  - sketch the vibration with single head arrows, removing CoM motion

**Figure 9** Setup for the breathing modes
• consider the out-of-plane motions
• determine the reducible representation, reduce it (using information already obtained above) and eliminate redundant modes
  o the E mode must be redundant, because we have already found all the allowed E modes
  o sketch the vibration with single head arrows, removing CoM motion

\[
\begin{array}{c}
\text{N-H out-of-plane bends} \\
\end{array}
\]

\[
\Gamma_{vib}(NH_3) = 2A_1 + 2E \\
= \Gamma_{\text{stretches}} + \Gamma_{\text{bends}} \\
\Gamma_{\text{stretches}} = A_1 + E \\
\therefore \Gamma_{\text{bends}} = A_1 + E \\
\Gamma_{\text{bends}} = \Gamma_{\text{breathing}} + \Gamma_{\text{umbrella}} \\
\Gamma_{\text{breathing}} = E \\
\therefore \Gamma_{\text{umbrella}} = A_1
\]

\[
\begin{array}{c|cc}
C_3v & E & 2C_3 \& 3\sigma_v \\
\hline
\Gamma(b_{X-N-H}) & 3 & 0 & 1 \\
\end{array}
\]

\[
\begin{array}{c}
\text{Figure 10 Setup for the umbrella modes} \\
\end{array}
\]

**Complete the Assignment and Describe the Spectrum**

• stretches occur at higher wavenumbers than bends
• asymmetric modes generally occur at higher energies than symmetric modes

<table>
<thead>
<tr>
<th>Infrared (matrix, cm(^{-1}))</th>
<th>Activity</th>
<th>Symmetry</th>
<th>Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>3378</td>
<td>IR, depol</td>
<td>E</td>
<td>v\text{3a} asym stretch</td>
</tr>
<tr>
<td>3223</td>
<td>IR, pol</td>
<td>A\text{1}</td>
<td>v\text{1} sym stretch</td>
</tr>
<tr>
<td>1646</td>
<td>IR, depol</td>
<td>E</td>
<td>v\text{4a} asym bend</td>
</tr>
<tr>
<td>1060</td>
<td>IR, pol</td>
<td>A\text{1}</td>
<td>v\text{2} sym bend</td>
</tr>
</tbody>
</table>

\[
\Gamma_{vib}(NH_3) = 2A_1(\text{IR, pol}) + 2E(\text{IR, depol})
\]

• there are 6 possible vibrations for NH\(_3\), all vibrations are present in both the Raman and Infrared spectra. The IR spectrum will contain 4 peaks of which will be due to degenerate modes, and the Raman spectrum will also contain 4 peaks of which will be polarised and the other two due to degenerate modes:
• the two highest wavenumber modes belong to the N-H stretches and will have A\text{1} and E symmetry, the A\text{1} mode will be Raman polarised
• the two lowest wavenumber modes will belong to bends. The umbrella motion is totally symmetric A\text{1} and thus will be polarised in the Raman spectrum. The breathing motion is a degenerate asymmetric bend of E symmetry.
Tutorial: The vibrational spectrum of Xe(O)F$_4$

Assign the vibrational spectrum of Xe(O)F$_4$

- determine $\Gamma_{\text{vib}}$(Xe(O)F$_4$)
- include diagrams of all the normal modes (bends and stretches)
- complete the table below
- show your working

<table>
<thead>
<tr>
<th>Infrared (vapour, cm$^{-1}$)</th>
<th>Raman (liquid, cm$^{-1}$)</th>
<th>Symmetry</th>
<th>Normal Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>926</td>
<td>920 (pol)</td>
<td>$A_1$</td>
<td>Xe=O sym stretch</td>
</tr>
<tr>
<td>609</td>
<td>605 (depol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>576</td>
<td>567 (pol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>361</td>
<td>364 (depol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>288</td>
<td>286 (pol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>159</td>
<td>160 (depol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>527</td>
<td>527 (depol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>232</td>
<td>232 (depol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>220</td>
<td>220 (depol)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>160</td>
<td>160 (depol)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Approach

- identify the point group
- locate all of the symmetry elements/operations
- find the reducible representation $\Gamma_{3N}$ and reduce it
- determine $\Gamma_{\text{vib}}$ by eliminating the CoM translations and rotations
- identify the infrared and Raman active modes
- describe and partly assign the spectrum
- generate the stretching modes
- generate the bending modes
- fully assign the spectrum

- Xe is a noble element and will have a full octet in the outer shell, thus the pseudo-structure is octahedral. The four fluorine ligands will form bonds with 4 electrons, and the oxygen will form a double bond sharing 2 more electrons, leaving two as a lone pair. The molecule will form a square pyramid with the fluorine ligands arranged on the square base and the oxygen taking the apical position.

- the molecule will belong to the C$_{4v}$ point group, and all of the symmetry elements have been located (check against the character table).

---

1 Group Theory for Chemists, Kieran Molloy, 2nd Ed, 2011, p52
Determine the vibrational spectrum

- find the reducible representation \( \Gamma_{3N} \) and reduce it

\[
\begin{array}{c|cccc}
C_{4v} & E & 2C_4 & C_2 & 2\sigma_v & 2\sigma_d \\
\hline
\text{atoms} & 6 & 2 & 2 & 4 & 2 \\
\chi \text{(per atom)} & 3 & 1 & -1 & 1 & 1 \\
\Gamma(Xe(O)F_4) & 18 & 2 & -2 & 4 & 2 \\
\end{array}
\]

\[
\Gamma_{3N}(Xe(O)F_4) = 4A_1 + 2B_1 + B_2 + 5E
\]

- determine \( \Gamma_{\text{vib}} \) by eliminating the CoM translations and rotations
  - translation are \( T_x, T_y, T_z \) listed in the character table \( \Gamma(T) = A_1 + E \)
  - rotation are \( R_x, R_y, R_z \) listed in the character table \( \Gamma(R) = A_2 + E \)
  
  \[
  \Gamma_{\text{vib}}(Xe(O)F_4) = \Gamma_{3N}(Xe(O)F_4) - \Gamma(T + R) \\
  = [4A_1 + A_2 + 2B_1 + B_2 + 5E] - [A_1 + A_2 + 2E] \\
  = 3A_1 + 2B_1 + B_2 + 3E
  \]
  - confirm using 3N-6 rule that you have the right number, \( N=6 \), 3N-6=12 and the number of modes is 3+2+1+6=12

- identify the infrared and Raman active modes
  - IR active modes have the same symmetry as the translational vectors, thus \( \Gamma(\text{IR}) \Rightarrow \{A_1, E\} \)
  - the Raman modes have the same symmetry as the binary functions, thus \( \Gamma(\text{Raman}) \Rightarrow \{A_1, B_1, B_2, E\} \)

- describe and partly assign the spectrum
  
  \[
  \Gamma_{\text{vib}}(Xe(O)F_4) = 3A_1(\text{IR, pol}) + 2B_1(\text{depol}) + B_2(\text{depol}) + 3E(\text{IR, depol})
  \]
  - from the 9 IR active modes, we expect to observe 6 peaks in the IR spectrum, 3 modes are degenerate. From the 12 Raman active modes, we expect to see 9 peaks in the Raman spectrum, 3 modes are degenerate (E) and these will also be coincident with the same modes active in the IR spectrum. A further 3 modes (A_1), will also be coincident with IR peaks, these will also be polarized (A_1). 3 depolarised modes not present in the IR spectrum will also be observed, however we cannot differentiate these as \( B_1 \) or \( B_2 \) modes on the evidence we have currently to hand

<table>
<thead>
<tr>
<th>Infrared (vapour, cm(^{-1}))</th>
<th>Raman (liquid, cm(^{-1}))</th>
<th>Symmetry</th>
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</tr>
<tr>
<td>609</td>
<td>605 (depol)</td>
<td>E</td>
</tr>
<tr>
<td>576</td>
<td>567 (pol)</td>
<td>A_1</td>
</tr>
<tr>
<td>527</td>
<td>527 (depol)</td>
<td>B_1 or B_2</td>
</tr>
<tr>
<td>361</td>
<td>364 (depol)</td>
<td>E</td>
</tr>
<tr>
<td>288</td>
<td>286 (pol)</td>
<td>A_1</td>
</tr>
<tr>
<td>232</td>
<td>232 (depol)</td>
<td>B_1 or B_2</td>
</tr>
<tr>
<td>220</td>
<td>220 (depol)</td>
<td>B_1 or B_2</td>
</tr>
<tr>
<td>159</td>
<td>160 (depol)</td>
<td>E</td>
</tr>
</tbody>
</table>

Generate the stretching modes

- there are two sets of stretching modes, those for Xe=O and those for Xe-F
• determine the reducible representation of each individually:

<table>
<thead>
<tr>
<th>$C_{4v}$</th>
<th>$E$</th>
<th>$2C_4$</th>
<th>$C_2$</th>
<th>$2\sigma_v$</th>
<th>$2\sigma_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma(Xe = O)$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$\Gamma(Xe - F)$</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
</tbody>
</table>

• obviously $\Gamma(Xe = O) = A_1$ and this mode will look like the following

![Xe=O stretch]

$A_1$

• reduce $\Gamma(Xe-F)$

<table>
<thead>
<tr>
<th>$C_{4v}$</th>
<th>$E$</th>
<th>$2C_4$</th>
<th>$C_2$</th>
<th>$2\sigma_v$</th>
<th>$2\sigma_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma(Xe - F)$</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>$E$</td>
<td>2</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\Gamma - A_1 - E$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>

and obtain $\Gamma(Xe - F) = A_1 + B_1 + E$

• now use the projection operator to determine the form of the vibrations
  - it is very important that all of the symmetry elements, and the individual vectors are clearly labelled.

![C4, C2]

$\sigma_{d(1)}$ $\sigma_{d(2)}$ $\sigma_{v(1)}$ $\sigma_{v(2)}$

$\sigma_{v(1)}$ $s_4$ $s_3$ $s_2$ $s_1$

$\sigma_{d(2)}$ $s_4$ $s_3$ $s_2$ $s_1$

$\sigma_{v(2)}$ $s_4$ $s_3$ $s_2$ $s_1$

$\sigma_{d(1)}$ $s_4$ $s_3$ $s_2$ $s_1$

$O(s_1)$ $s_1$ $s_2$ $s_3$ $s_4$ $s_1$ $s_2$ $s_3$ $s_4$

$A_1 \Rightarrow \frac{1}{8}[s_1 + s_2 + s_3 + s_4 + s_1 + s_2 + s_3 + s_4] = \frac{1}{4}[s_1 + s_2 + s_3 + s_4]$

$B_1 \Rightarrow \frac{1}{8}[s_1 - s_2 - s_4 + s_3 + s_1 - s_4 + s_2 - s_3] = \frac{1}{4}[s_1 - s_2 - s_3 + s_4]$

$E \Rightarrow \frac{1}{8}[2s_1 - 2s_2] = \frac{1}{4}[s_1 - s_2]$

• NOTE the determination of these as $B_1$ or $B_2$ depends on the position of the axes. If the axes lie along the bonds then the $\sigma_v$ planes and $\sigma_d$ planes are clearly determined. However if the bonds lie between the axes, the location of the $\sigma_v$ planes and $\sigma_d$ planes becomes less clear. In this case you could align the $\sigma_v$ planes on the axes (between the bonds) and the $\sigma_d$
planes between the axes (along the bonds) or *vice versa*. As long as you are consistent with your labelling system the switch between the B₁ and B₂ is not important
- you can use the form of the binary functions to check you have the right mode (or even to derive the form of the mode very quickly!)

\[
B_1 \Rightarrow \frac{1}{4} [s_1 + s_3 - s_2 - s_4]
\]

- for example the \(x^2-y^2\) function spans the B₁ IR, then the vector form of the vibration must be similar, those vectors lying along the x-axis must remain unchanged (ie +x) and those lying along the y axis are inverted (ie –y)

\[
\begin{align*}
E_a &\Rightarrow \frac{1}{\sqrt{2}} [s_1 - s_3] \\
E_b &\Rightarrow \frac{1}{\sqrt{2}} [-s_2 + s_4]
\end{align*}
\]

\[
\begin{align*}
E_a + E_b &\Rightarrow \frac{1}{2} [s_1 - s_3 - s_2 + s_4] = \frac{1}{2} [s_1 - s_2 - s_3 + s_4] \\
E_a - E_b &\Rightarrow \frac{1}{2} [s_1 - s_3 + s_2 - s_4] = \frac{1}{2} [s_1 + s_2 - s_3 - s_4]
\end{align*}
\]

- in addition (Tₓ, Tᵧ) span the E IR, thus the vector combinations must resolve to a final vector (ignoring CoM corrections) that points either in the direction of the positive x-axis or positive y-axis.

\[
\begin{align*}
E_a - E_b &\Rightarrow \frac{1}{2} [s_1 - s_3 + s_2 - s_4] = \frac{1}{2} [s_1 + s_2 - s_3 - s_4]
\end{align*}
\]

- note that the projection operator method of determining the E stretch does not include the motion at \(s_3\) and \(s_4\), but is still correct, the vibration normally reported is the last one shown above
Generate the bending modes
- don't forget double headed arrows for in-plane, single headed arrows for out-of-plane motions

![Diagram of bending modes](image)

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$2C_4$</th>
<th>$C_2$</th>
<th>$2\sigma_v$</th>
<th>$2\sigma_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Gamma_{(oop)}$</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>$\Gamma_{(ip)}$</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2</td>
</tr>
</tbody>
</table>

- reduce to obtain
  \[
  \Gamma_{(oop)} = A_1 + B_1 + E
  \]
  \[
  \Gamma_{(ip)} = A_1 + B_2 + E
  \]
  \[
  \Gamma_{bends} = 2A_1 + B_1 + B_2 + 2E
  \]

- identify redundant modes
  \[
  \Gamma_{vib}(Xe(O)F_4) = 3A_1 + 2B_1 + B_2 + 3E
  \]
  \[
  \Gamma_{bends} = \Gamma_{vib} - \Gamma_{stretches}
  \]
  \[
  = [3A_1 + 2B_1 + B_2 + 3E] - [2A_1 + B_1 + E]
  \]
  \[
  = A_1 + B_1 + B_2 + 2E
  \]
  thus one $A_1$ mode must be redundant, this will be the in-plane angles, as it is impossible for all of these to expand or contract at the same time
  \[
  \Gamma_{(oop)} = A_1 + B_1 + E
  \]
  \[
  \Gamma_{(ip)} = B_2 + E
  \]
  \[
  \Gamma_{bends} = A_1 + B_1 + B_2 + 2E
  \]

- now we need to determine the form of the vibrations
- project out the "in-plane" vibrations

![Diagram of in-plane vibrations](image)

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>$C_{i}^1$</th>
<th>$C_{i}^2$</th>
<th>$C_4^1$</th>
<th>$C_4^2$</th>
<th>$\sigma_1(1)$</th>
<th>$\sigma_1(2)$</th>
<th>$\sigma_2(1)$</th>
<th>$\sigma_2(2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q(a_1)$</td>
<td>$a_1$</td>
<td>$a_2$</td>
<td>$a_4$</td>
<td>$a_3$</td>
<td>$a_4$</td>
<td>$a_2$</td>
<td>$a_3$</td>
<td>$a_4$</td>
<td>$a_1$</td>
</tr>
<tr>
<td>$B_2$</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>
<td>1</td>
</tr>
<tr>
<td>$E$</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

$B_2 \Rightarrow \frac{1}{8}[a_1 - a_2 - a_4 + a_3 - a_4 - a_2 + a_1] = \frac{1}{4}[a_1 - a_2 + a_3 - a_4]$

$E \Rightarrow \frac{1}{8}[2a_1 - 2a_3] = \frac{1}{4}[a_1 - a_3]$

- from these we can draw sketches of the vibrations, being sure to compensate for CoM motion.
• then we need to project out the "out-of-plane" vibrations

• it is clear that the modes will be of a form similar to the stretching Xe-F modes already determined. Thus we can immediately state the form of the equations

<table>
<thead>
<tr>
<th>$C_{4v}$</th>
<th>$E$</th>
<th>$C_4^1$</th>
<th>$C_4^3$</th>
<th>$C_2$</th>
<th>$\sigma_g(1)$</th>
<th>$\sigma_g(2)$</th>
<th>$\sigma_d(1)$</th>
<th>$\sigma_d(2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Q(b_1)$</td>
<td>$b_1$</td>
<td>$b_2$</td>
<td>$b_3$</td>
<td>$b_4$</td>
<td>$b_1$</td>
<td>$b_3$</td>
<td>$b_4$</td>
<td>$b_2$</td>
</tr>
</tbody>
</table>

• from these we can draw sketches of the vibrations, being sure to compensate for CoM motion (the binary functions are usually only used for stretches)
Fully assign the spectrum

- Stretches occur at higher energy than bends
- Double bonds are stronger than single bonds
- Asym vibrations are generally higher than sym vibrations of the same type
- The precise nature of some modes may not be able to be predicted

<table>
<thead>
<tr>
<th>Infrared (vapour, cm(^{-1}))</th>
<th>Raman (liquid, cm(^{-1}))</th>
<th>Symmetry</th>
<th>Normal Mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>926</td>
<td>920 (pol)</td>
<td>A(_1)</td>
<td>Xe=O sym stretch</td>
</tr>
<tr>
<td>609</td>
<td>605 (depol)</td>
<td>E</td>
<td>Xe-F asym stretch</td>
</tr>
<tr>
<td>576</td>
<td>567 (pol)</td>
<td>A(_1)</td>
<td>Xe-F sym stretch</td>
</tr>
<tr>
<td></td>
<td>527 (depol)</td>
<td>B(_1)</td>
<td>Xe-F asym stretch</td>
</tr>
<tr>
<td>361</td>
<td>364 (depol)</td>
<td>E</td>
<td>bend</td>
</tr>
<tr>
<td>288</td>
<td>286 (pol)</td>
<td>A(_1)</td>
<td>oop O-Xe-F bend</td>
</tr>
<tr>
<td></td>
<td>232 (depol)</td>
<td>B(_1) or B(_2)</td>
<td>bend</td>
</tr>
<tr>
<td></td>
<td>220 (depol)</td>
<td>B(_1) or B(_2)</td>
<td>bend</td>
</tr>
<tr>
<td>159</td>
<td>160 (depol)</td>
<td>E</td>
<td>bend</td>
</tr>
</tbody>
</table>

Where unspecified bends can be in-plane F-Xe-F or out-of-plane O-Xe-F bends.