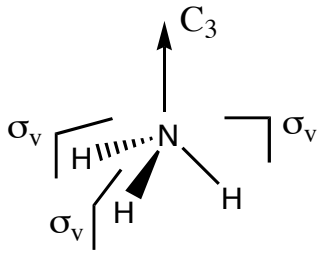
Reminder: From the Notes

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



C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	−1
E	2	−1	0

Figure 1 C_{3v} point group and symmetry elements

- determine the atoms that remain at the same position under each symmetry operation (*atoms*)
- take the contribution for each symmetry atom from table *χ(per atom)*
- to generate the reducible representation

Figure 1 C_{3v} point group and symmetry elements

C_{3v}	E	C_3	σ_v
atoms	4	1	2
$\chi(per\ atom)$	3	0	1
$\Gamma(NH_3)$	12	0	2

Figure 2 Representation table for ammonia

- 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

$$n_{IR} = \frac{1}{h}\sum_{Q} k \bullet \chi^{IR}(Q) \bullet \chi^{R}(Q)$$

C_{3v}	E	$2C_3$	$3\sigma_v$
$\Gamma(NH_3)$	12	0	2
A_1	1	1	1

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

$$n_{A_1} = \frac{1}{6}\left[12 + 0 + 6\right] = \frac{18}{6} = 3$$

$$n_{A_2} = \frac{1}{6}\left[(1 \bullet 12 \bullet 1) + (3 \bullet 2 \bullet -1)\right] = \frac{6}{6} = 1$$

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

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

Figure 3 Reduction for ammonia

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

- determine the irreducible representations for the translation and rotation of the whole molecule, subtract these from the reduced representation to remove the CoM motions

$$\Gamma(T) = 1A_1 + 1E$$
$$\Gamma(R) = 1A_2 + 1E$$
$$\Gamma(T+R) = 1A_1 + 1A_2 + 2E$$
$$\begin{aligned}\Gamma_{vib}(NH_3) &= \Gamma(NH_3) - \Gamma(T+R)\\ &= \left(3A_1 + 1A_2 + 4E\right) - \left(1A_1 + 1A_2 + 2E\right)\\ &= 2A_1 + 2E\end{aligned}$$

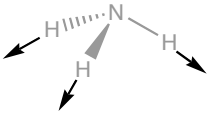
Figure 4 Remove CoM motion

- determine the IR and Raman activity of these modes
  - IR have the same symmetry as the translational motions $\Gamma(T) = A_1 + E$
  - Raman have the same symmetry as the binary functions $\Gamma(f) = A_1 + E$
- write out the Γ_{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 delpolarised

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

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



N-H stretches

C_{3v}	E	$2C_3$	$3\sigma_v$	
$\Gamma(s_{N-H})$	3	0	1	
A_1	1	1	1	$\Rightarrow \frac{1}{6}\left[(1\bullet 3\bullet 1) + 0 + (3\bullet 1\bullet 1)\right] = \frac{6}{6} = 1$
$\Gamma(s_{N-H}) - A_1$	2	−1	0	$\Rightarrow E$

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

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

$$P_\Gamma[f] = \frac{1}{h}\sum_Q \chi^{IR}(Q) \bullet Q[f]$$

C_{3v}	E	C_3^1	C_3^2	$\sigma_v(1)$	$\sigma_v(2)$	$\sigma_v(3)$
$Q[s_1]$	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

C_{3v}	E	C_3^1	C_3^2	$\sigma_v(1)$	$\sigma_v(2)$	$\sigma_v(3)$
$Q[s_1]$	s_1	s_2	s_3	s_1	s_3	s_2
A_1	1	1	1	1	1	1
$\chi^{A_1}(Q)\bullet Q[s_1]$	s_1	s_2	s_3	s_1	s_3	s_2

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

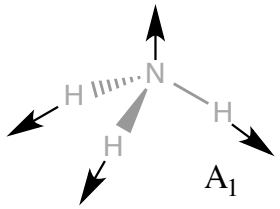


Figure 7 Finding the A_1 vibrational vector function

- 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

C_{3v}	E	C_3^1	C_3^2	$\sigma_v(1)$	$\sigma_v(2)$	$\sigma_v(3)$
$Q[s_1]$	s_1	s_2	s_3	s_1	s_3	s_2
E	2	−1	−1	0	0	0
$\chi^{A_1}(Q)\bullet Q[s_1]$	$2s_1$	$-s_2$	$-s_3$	0	0	0

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

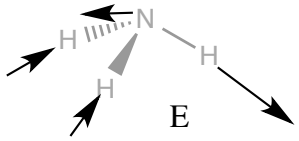
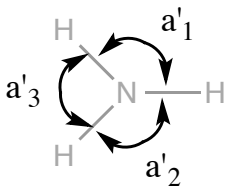


Figure 8 One of the E stretching modes

- 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



C_{3v}	E	$2C_3$	$3\sigma_v$
$\Gamma(a_{H-N-H})$	3	0	1

$$\nu_{N-N-H}(E)=\frac{1}{6}\left[2a_1-a_2-a_3\right]$$

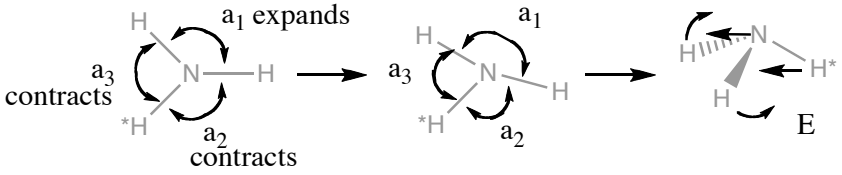
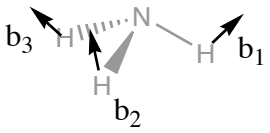


Figure 9 Setup for the breathing modes

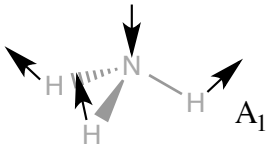
- consider the out-of-plane motions
- determine the reducible representation, reduce it (using information already obtained above) and eliminate redundant modes
  - the E mode must be redundant, because we have already found all the allowed E modes
  - sketch the vibration with single head arrows, removing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



N-H out-of-plane bends

C_{3v}	E	$2C_3$	$3\sigma_v$
$\Gamma(b_{X-N-H})$	3	0	1

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



$$\nu_{OOP-bend}(A_1) = \frac{1}{3}[b_1 + b_2 + b_3]$$

Figure 10 Setup for the umbrella modes

Complete the Assignment and Describe the Spectrum

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

Infrared (matrix, cm^{-1})	Activity	Symmetry	Mode
3378	IR, depol	E	ν_{3a} asym stretch
3223	IR, pol	A_1	ν_1 sym stretch
1646	IR, depol	E	ν_{4a} asym bend
1060	IR, pol	A_1	ν_2 sym bend

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

- 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 2 of which will be due to degenerate modes, and the Raman spectrum will also contain 4 peaks 2 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_1 and E symmetry, the A_1 mode will be Raman polarised
- the two lowest wavenumber modes will belong to bends. The umbrella motion is totally symmetric A_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 $Xe(O)F_4$[1]

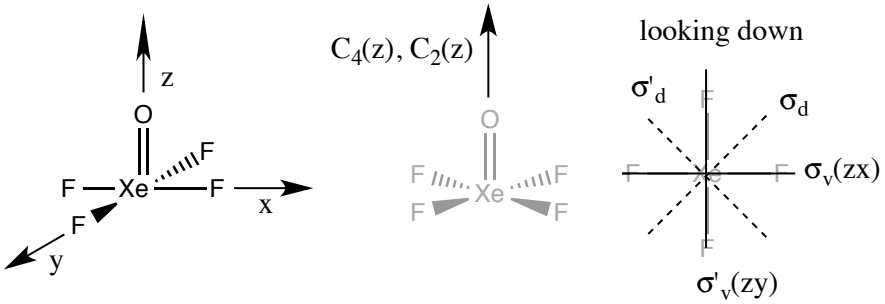
- determine $\Gamma_{vib}(Xe(O)F_4)$
- include diagrams of all the normal modes (bends and stretches)
- complete the table below
- show your working

Infrared (vapour, cm^{-1})	Raman (liquid, cm^{-1})	Symmetry	Normal Mode
926	920 (pol)	A_1	Xe=O sym stretch
609	605 (depol)		
576	567 (pol)		
	527 (depol)		
361	364 (depol)		
288	286 (pol)		
	232 (depol)		
	220 (depol)		
159	160 (depol)		

Approach

- identify the point group
- locate all of the symmetry elements/operations
- find the reducible representation Γ_{3N} and reduce it
- determine Γ_{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 Γ_{3N} and reduce it

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
atoms	6	2	2	4	2
$\chi(per\ atom)$	3	1	−1	1	1
$\Gamma(Xe(O)F_4)$	18	2	−2	4	2

$$\Gamma_{3N}(Xe(O)F_4) = 4A_1 + A_2 + 2B_1 + B_2 + 5E$$

- determine Γ_{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 $\Gamma(R) = A_2 + E$

$$\begin{aligned}\Gamma_{vib}(Xe(O)F_4) &= \Gamma_{3N}(Xe(O)F_4) - \Gamma(T+R)\\ &= \left[4A_1 + A_2 + 2B_1 + B_2 + 5E\right] - \left[A_1 + A_2 + 2E\right]\\ &= 3A_1 + 2B_1 + B_2 + 3E\end{aligned}$$

  - 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 $\Gamma(IR) \Rightarrow \{A_1, E\}$
  - the Raman modes have the same symmetry as the binary functions, thus $\Gamma(Raman) \Rightarrow \{A_1, B_1, B_2, E\}$
- describe and *partly* assign the spectrum

$$\Gamma_{vib}(Xe(O)F_4) = 3A_1(IR,pol) + 2B_1(depol) + B_2(depol) + 3E(IR,depol)$$

  - 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

Infrared (vapour, cm^{-1})	Raman (liquid, cm^{-1})	Symmetry
926	920 (pol)	A_1
609	605 (depol)	E
576	567 (pol)	A_1
	527 (depol)	B_1 or B_2
361	364 (depol)	E
288	286 (pol)	A_1
	232 (depol)	B_1 or B_2
	220 (depol)	B_1 or B_2
159	160 (depol)	E

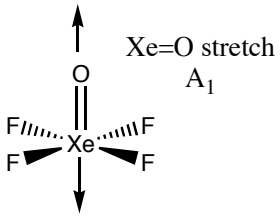
Generate the stretching modes

- there are two sets of stretching modes, those for Xe=O and those for Xe-F

- determine the reducible representation of each individually:

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
$\Gamma(Xe=O)$	1	1	1	1	1
$\Gamma(Xe-F)$	4	0	0	2	0

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

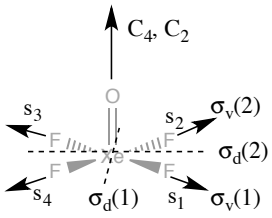


- reduce Γ(Xe-F)

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$	
$\Gamma(Xe-F)$	4	0	0	2	0	
A_1	1	1	1	1	1	$\Rightarrow \frac{1}{8}\left[(1\bullet 4\bullet 1)+0+(2\bullet 2\bullet 1)+0\right]=\frac{8}{8}=1$
E	2	0	−2	0	0	$\Rightarrow \frac{1}{8}\left[(2\bullet 4\bullet 1)+0+(1\bullet -2\bullet 1)+0\right]=\frac{8}{8}=1$
$\Gamma - A_1 - E$	1	−1	1	1	−1	$\Rightarrow B_1$

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.

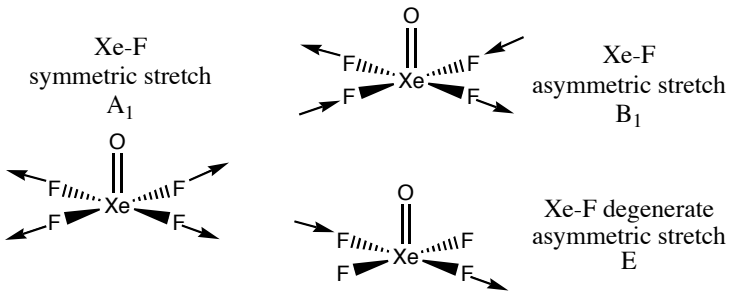


C_{4v}	E	C_4^1	C_4^3	C_2	$\sigma_v(1)$	$\sigma_v(2)$	$\sigma_d(1)$	$\sigma_d(2)$
$Q(s_1)$	s_1	s_2	s_4	s_3	s_1	s_3	s_4	s_2
A_1	1	1	1	1	1	1	1	1
B_1	1	−1	−1	1	1	1	−1	−1
E	2	0	0	−2	0	0	0	0

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

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

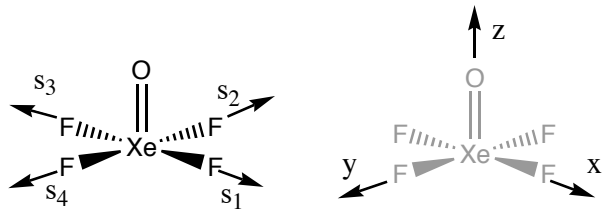
$$E \Rightarrow \frac{1}{8}\left[2s_1-2s_2\right]=\frac{1}{4}\left[s_1-s_3\right]$$



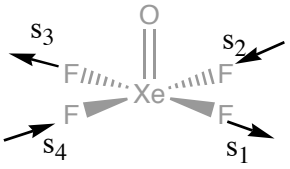
  - NOTE the determination of these as B_1 or B_2 depends on the position of the axes. If the axes lie along the bonds then the σ_v planes and σ_d planes are clearly determined. However if the bonds lie between the axes, the location of the σ_v planes and σ_d planes becomes less clear. In this case you could align the σ_v planes on the axes (between the bonds) and the σ_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 B_1 and B_2 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!)

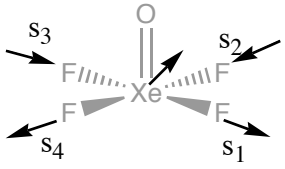


- for example the x^2-y^2 function spans the B_1 IR, then the vector form of the vibration must be similar, those vectors lying along the x-axis must remain unchanged (ie +x) and those lying along the y axis are inverted (ie –y)



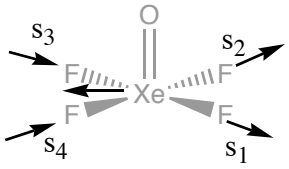
$$B_1 \Rightarrow \frac{1}{4}\left[s_1 + s_3 - s_2 - s_4\right]$$

- in addition (T_x, T_y) 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.



$$E_a \Rightarrow \frac{1}{\sqrt{2}}\left[s_1 - s_3\right]$$

$$E_b \Rightarrow \frac{1}{\sqrt{2}}\left[-s_2 + s_4\right]$$



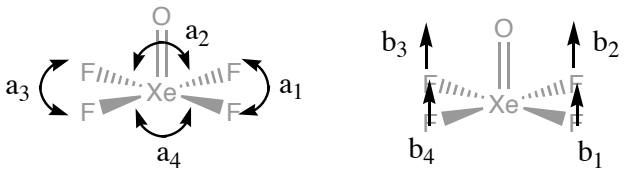
$$E_a + E_b \Rightarrow \frac{1}{2}\left[s_1 - s_3 - s_2 + s_4\right] = \frac{1}{2}\left[s_1 - s_2 - s_3 + s_4\right]$$

$$E_a - E_b \Rightarrow \frac{1}{2}\left[s_1 - s_3 + s_2 - s_4\right] = \frac{1}{2}\left[s_1 + s_2 - s_3 - s_4\right]$$

- 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



in-plane out-of-plane

C_{4v}	E	$2C_4$	C_2	$2\sigma_v$	$2\sigma_d$
$\Gamma(oop)$	4	0	0	2	0
$\Gamma(ip)$	4	0	0	0	2

- reduce to obtain

$$\Gamma(oop) = A_1 + B_1 + E$$
$$\Gamma(ip) = A_1 + B_2 + E$$
$$\Gamma_{bends} = 2A_1 + B_1 + B_2 + 2E$$

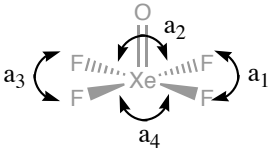
- identify redundant modes

$$\Gamma_{vib}(Xe(O)F_4) = 3A_1 + 2B_1 + B_2 + 3E$$
$$\Gamma_{bends} = \Gamma_{vib} - \Gamma_{stretches}$$
$$= \left[3A_1 + 2B_1 + B_2 + 3E\right] - \left[2A_1 + B_1 + E\right]$$
$$= A_1 + B_1 + B_2 + 2E$$

- 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

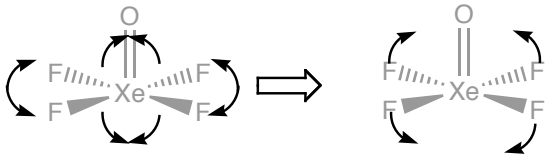


C_{4v}	E	C_4^1	C_4^3	C_2	$\sigma_v(1)$	$\sigma_v(2)$	$\sigma_d(1)$	$\sigma_d(2)$
$Q(a_1)$	a_1	a_2	a_4	a_3	a_4	a_2	a_3	a_1
B_2	1	−1	−1	1	−1	−1	1	1
E	2	0	0	−2	0	0	0	0

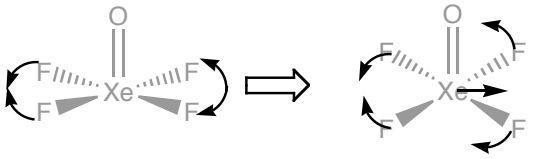
$$B_2 \Rightarrow \frac{1}{8}\left[a_1 - a_2 - a_4 + a_3 - a_4 - a_2 + a_3 + a_1\right] = \frac{1}{4}\left[a_1 - a_2 + a_3 - a_4\right]$$

$$E \Rightarrow \frac{1}{8}\left[2a_1 - 2s_3\right] = \frac{1}{4}\left[a_1 - a_3\right]$$

  - from these we can draw sketches of the vibrations, being sure to compensate for CoM motion.

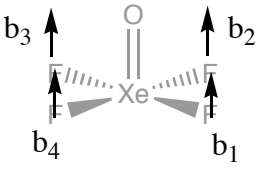


$$\frac{1}{4}\left[a_1 - a_2 + a_3 - a_4\right]$$



$$\frac{1}{4}\left[a_1 - a_3\right]$$

- then we need to project out the "out-of-plane" vibrations



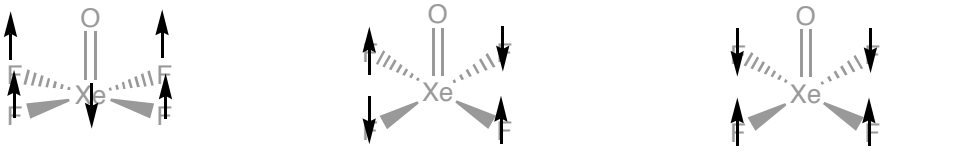
C_{4v}	E	C_4^1	C_4^3	C_2	$\sigma_v(1)$	$\sigma_v(2)$	$\sigma_d(1)$	$\sigma_d(2)$
$Q(b_1)$	b_1	b_2	b_4	b_3	b_1	b_3	b_4	b_2

- 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

$$A_1 \Rightarrow \frac{1}{4}\left[b_1 + b_2 + b_3 + b_4\right] \qquad B_1 \Rightarrow \frac{1}{4}\left[b_1 - b_2 + b_3 - b_4\right]$$

$$E_a \Rightarrow \frac{1}{2}\left[b_1 - b_2 - b_3 + b_4\right] \qquad E_b \Rightarrow \frac{1}{2}\left[b_1 + b_2 - b_3 - b_4\right]$$

- 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)



$$A_1 \Rightarrow \frac{1}{4}\left[b_1 + b_2 + b_3 + b_4\right] \quad B_1 \Rightarrow \frac{1}{4}\left[b_1 - b_2 + b_3 - b_4\right] \quad E_a \Rightarrow \frac{1}{2}\left[b_1 - b_2 - b_3 + b_4\right]$$

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

Infrared (vapour, cm^{-1})	Raman (liquid, cm^{-1})	Symmetry	Normal Mode
926	920 (pol)	A_1	Xe=O sym stretch
609	605 (depol)	E	Xe-F asym stretch
576	567 (pol)	A_1	Xe-F sym stretch
	527 (depol)	B_1	Xe-F asym stretch
361	364 (depol)	E	bend
288	286 (pol)	A_1	oop O-Xe-F bend
	232 (depol)	B_1 or B_2	bend
	220 (depol)	B_1 or B_2	bend
159	160 (depol)	E	bend

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