MODEL ANSWER

1) ***Determine the point group.***

BF_3 is in the D_{3h} point group.

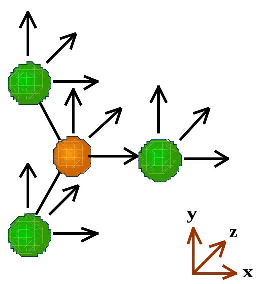
2) ***Degrees of freedom.***

BF3 is a non-linear molecule, with 4 atoms.

Using the equation 3N, we see that BF_3 has 12 degrees of freedom.
Using the equation 3N – 6, we see that BF_3 has (12 – 6 =) 6 vibrational degrees of freedom.

3) ***Determine irreducible representations of Γ_{tot}.***

Three axes put on each atom. $\Gamma_{4\ atoms}$ calculated by seeing the effect on the axes by all the symmetry operations.



	E	$2C_3$	$3C_2$	σ_h	2S3	$3\sigma_v$
$\Gamma_{4\ atoms}$	12	0	-2	4	-2	2

The contributions from each symmetry species are as follows.

A_1': **1/12 [(12x1x1) + (0x1x2) + (-2x1x3) + (4x1x1) + (-2x1x2) + (2x1x3)]**

= 1/12 [12 – 6 + 4 – 4 + 6] = 1

A_2': **1/12 [(12x1x1) + (0x1x2) + (-2x-1x3) + (4x1x1) + (-2x1x2) + (2x-1x3)]**

= 1/12 [12 + 6 + 4 - 4 - 6] = 1

E': **1/12 [(12x2x1) + (0x-1x2) + (-2x0x3) + (4x2x1) + (-2x-1x2) + (2x0x3)]**

= 1/12 [24 + 8 +4] = 3

A_1'': **1/12 [(12x1x1) + (0x1x2) + (-2x1x3) + (4x-1x1) + (-2x-1x2) + (2x-1x3)]**

= 1/12 [12 – 6 –4 +4 –6] = 0

A_2'': **1/12 [(12x1x1) + (0x1x2) + (-2x-1x3) + (4x-1x1) + (-2x-1x2) + (2x1x3)]**

= 1/12 [12 + 6 –4 +4 +6] = 2

E'': **1/12 [(12x2x1) + (0x-1x2) + (-2x0x3) + (4x-2x1) + (-2x1x2) + (2x0x3)]**

= 1/12 [24 – 8 – 4] = 1

Therefore $\Gamma_{tot} = A_1' + A_2' + 3E' + 2A_2'' + E''$

Γ_{tot} has twelve degrees of freedom. This agrees with our earlier answer.

3) Determine Γ_{vib}.

We know that $\Gamma_{tot} = \Gamma_{trans} + \Gamma_{rot} + \Gamma_{vib}$

From character table we see that…

$\Gamma_{trans} = E' + A_2''$
$\Gamma_{rot} = A_2' + E''$

Therefore using $\Gamma_{vib} = \Gamma_{tot} – \Gamma_{trans} - \Gamma_{rot}$

$\Gamma_{vib} = A_1' + 2E' + A_2''$

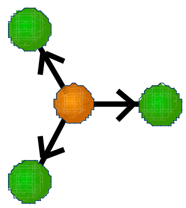
Γ_{vib} has six degrees of freedom. This agrees with our earlier answer.

4) Split into stretches and bends.

BF_3 has three bonds, so therefore has 3 stretches and 3 bends.

5) *Determine irreducible representations of $\Gamma_{stretch}$.*

One axis put on each bond. Bond calculated by seeing the effect on the axes by all the symmetry operations.



	E	$2C_3$	$3C_2$	σ_h	2S3	$3\sigma_v$
$\Gamma_{3\ bonds}$	3	0	1	3	0	1

The contributions from each symmetry species are as follows.

A₁': **1/12 [(3x1x1) + (0x1x2) + (1x1x3) + (3x1x1) + (0x1x2) + (1x1x3)]**

= 1/12 [3 + 3 + 3 +3] = 1

A₂': **1/12 [(3x1x1) + (0x1x2) + (1x-1x3) + (3x1x1) + (0x1x2) + (1x-1x3)]**

= 1/12 [3 – 3 +3 - 3] = 0

E': **1/12 [(3x2x1) + (0x-1x2) + (1x0x3) + (3x2x1) + (0x-1x2) + (1x0x3)]**

= 1/12 [6 + 6] = 1

A₁": **1/12 [(3x1x1) + (0x1x2) + (1x1x3) + (3x-1x1) + (0x-1x2) + (1x-1x3)]**

= 1/12 [3 + 3 – 3 –3] = 0

A₂": **1/12 [(3x1x1) + (0x1x2) + (1x-1x3) + (3x-1x1) + (0x-1x2) + (1x1x3)]**

= 1/12 [3 – 3 – 3 + 3] = 0

E": **1/12 [(3x2x1) + (0x-1x2) + (1x0x3) + (3x-2x1) + (0x1x2) + (1x0x3)]**

= 1/12 [6 - 6] = 0

Therefore $\Gamma_{stretch}$ = A$_1$' + E'

6) Determine Γ_{bend}.

We know that $\Gamma_{bend} = \Gamma_{vib} - \Gamma_{stretch}$

Therefore Γ_{bend} = E' + A$_2$"

7) Assign irreducible representations to spectra.

From character tables we see that only E' will be visible in both IR and Raman spectra.

E' stretch will be at higher energy (1505 cm^{-1})
E' bend will be at lower energy (482cm^{-1})

From character tables we see that A$_1$' will not be visible in the IR.

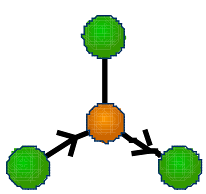
A$_1$' stretch will be at 888 cm^{-1}

From character tables we see that A2" will not be visible in Raman.

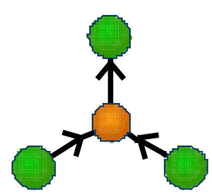
A2" bend will be at 718cm^{-1}

1505	**(R, IR)**	**E' stretches**
888	**(R)**	**A$_1$' stretch**
718	**(IR)**	**A$_2$" bend**
482	**(R, IR)**	**E' bends**

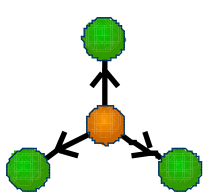
***8) Sketch these vibrations* (although not specifically asked for, this is a common question).**



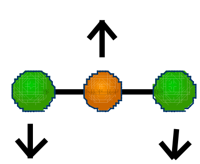
E' stretch



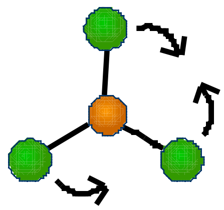
E' stretch



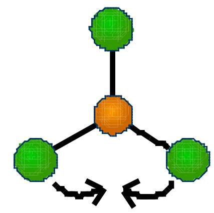
A$_1$' stretch



A$_2$" bend



E’ bend



E’ bend