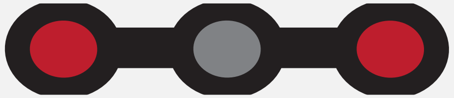
Molecular Symmetry - Vibrational Spectroscopy Identification of IR & Raman Active Modes

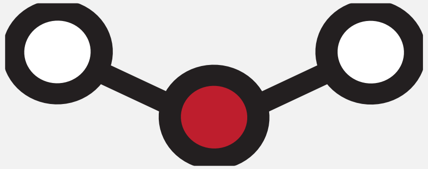
Kristen Aviles | CHEM 411W | Feb. 3rd, 2025

Symmetry analysis allows a method to predict vibrational modes.

We can predict the number of vibrational modes by:

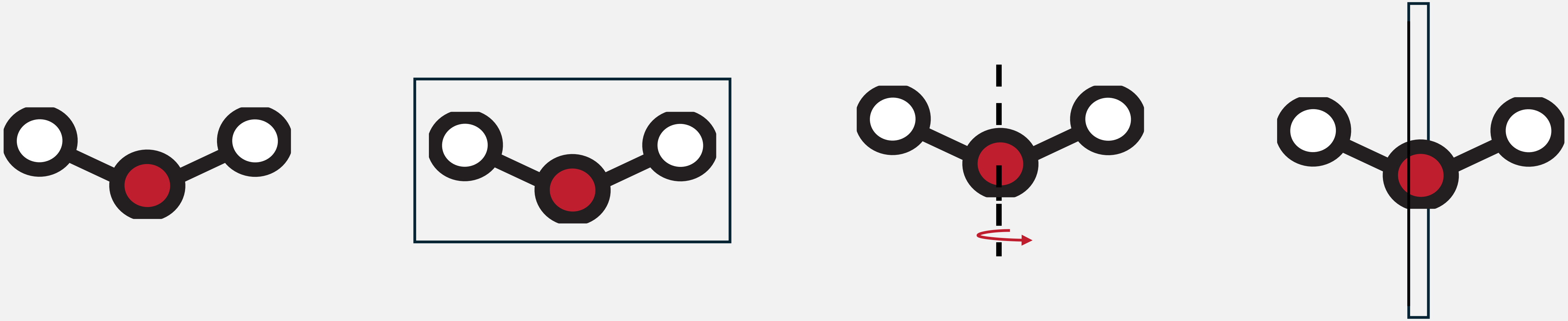
Linear	Nonlinear
3N – 5	3N – 6





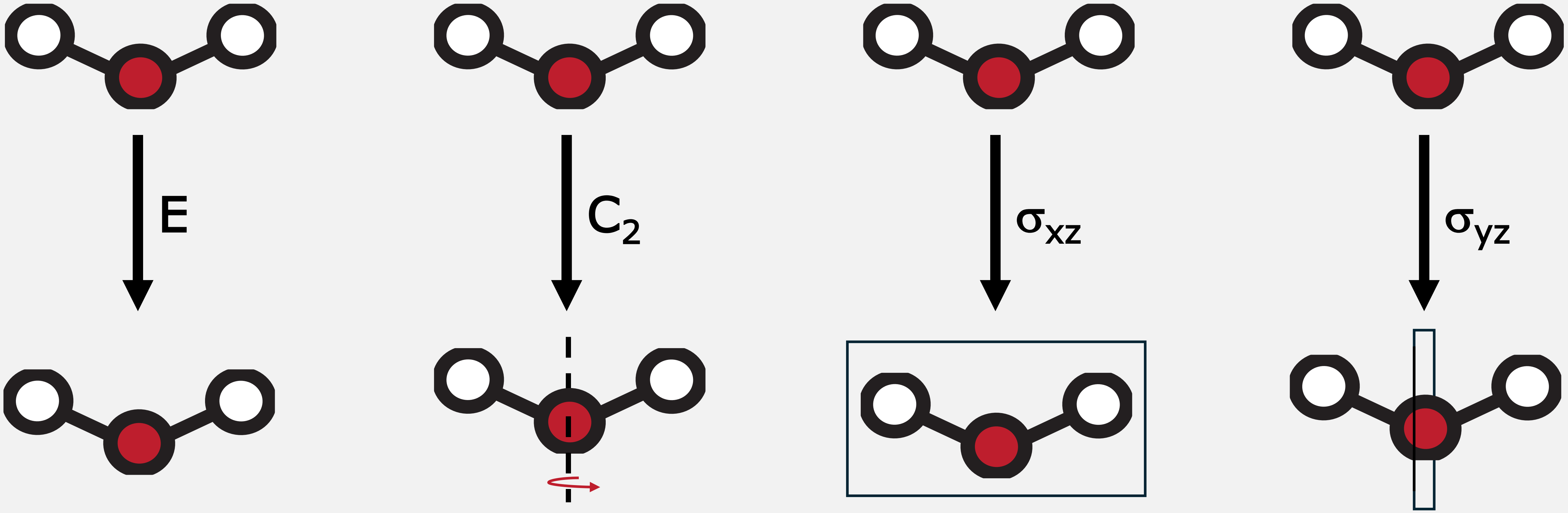
But how many are IR active? How many are Raman active?

We can use **SYMMETRY** to answer this



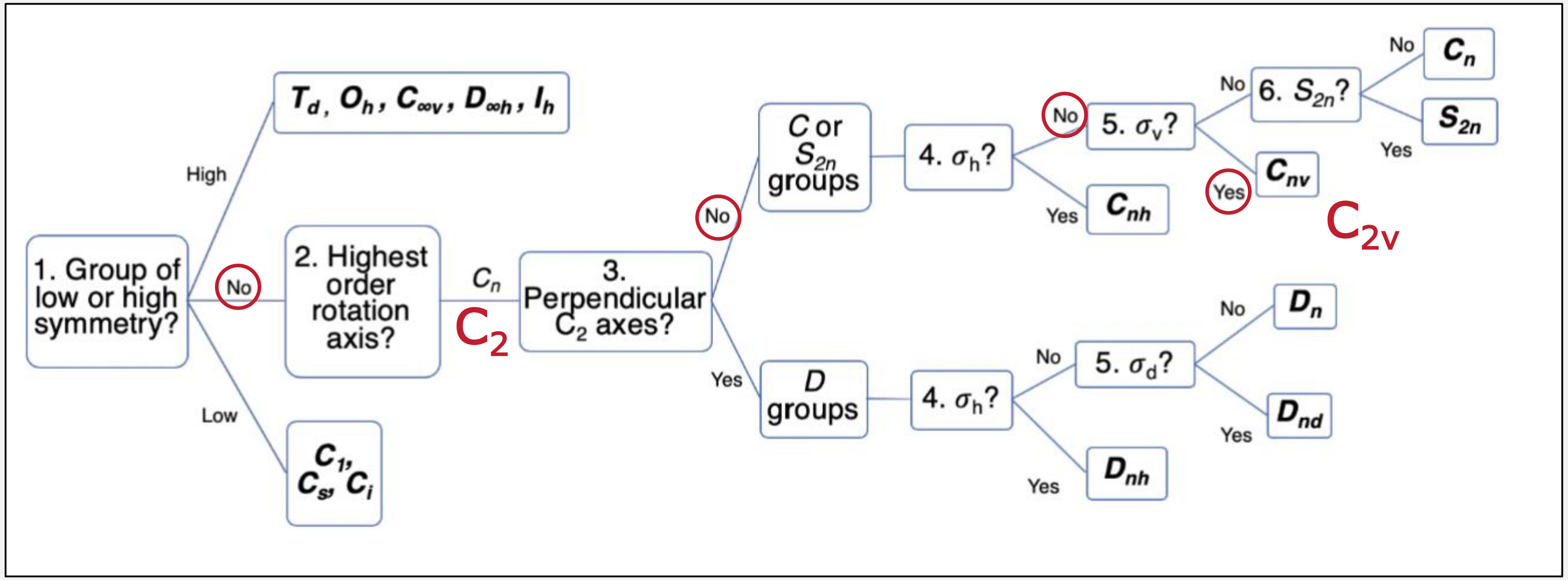
First, we need to evaluate the symmetry operations

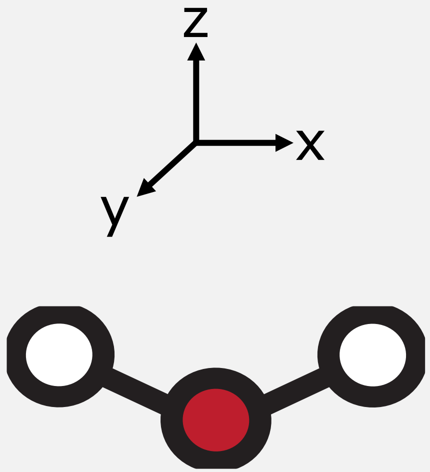
For example, lets use water:



Second, we need to identify the point group

For example, lets use water:



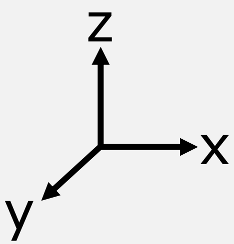
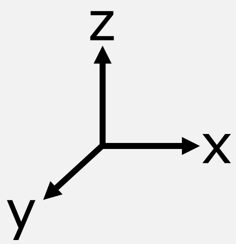
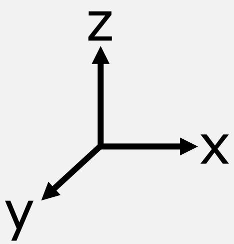
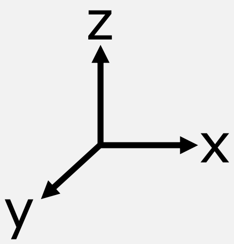


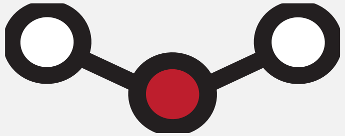
Locate the corresponding character table:

C_{2v}	E	C_2 (z)	$\sigma_v(xz)$	$\sigma_v(yz)$	linear functions, rotations	quadratic functions	cubic functions
A_1	+1	+1	+1	+1	z	x^2, y^2, z^2	z^3, x^2z, y^2z
A_2	+1	+1	-1	-1	R_z	xy	xyz
B_1	+1	-1	+1	-1	x, R_y	xz	xz^2, x^3, xy^2
B_2	+1	-1	-1	+1	y, R_x	yz	yz^2, y^3, x^2y

Third, we need to calculate the reducible representation

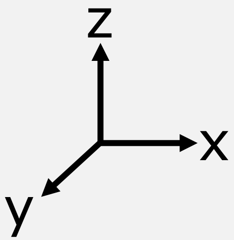
We must identify the contributions of each axis during each symmetry operation.
If the axis stays pointed in the same direction: +1 contribution
If the axis points in a different direction: -1 contribution

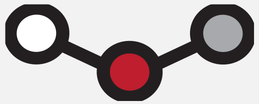
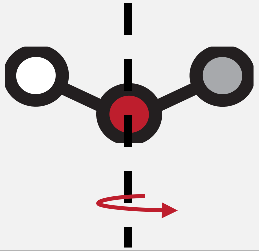
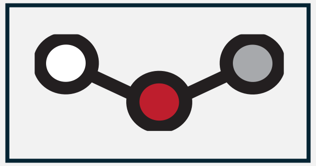
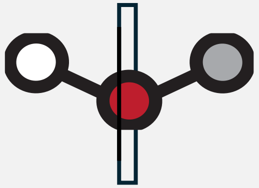
	E	C_2	σ_{xz}	σ_{yz}
Original				
Transformed				
Contribution				

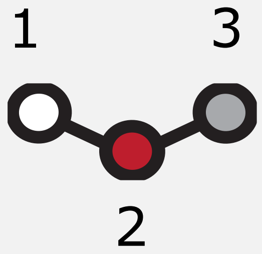


Third, we need to calculate the reducible representation

We must identify the number of stationary atoms following each symmetry operation.
If the atom stays in the same position : +1 contribution
If the atom changes position: 0 contribution

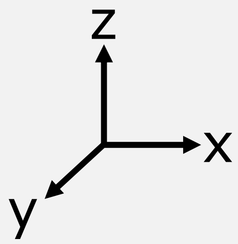


	E	C_2	σ_{xz}	σ_{yz}
Original				
Transformed				
Contribution				



White and grey still represent H atoms; slightly different colors to illustrate movement

Third, we need to calculate the reducible representation



Now we take each contribution and multiply them.
This affords us the reducible representation (Γ_{red})

	E	C_2	σ_{xz}	σ_{yz}
Axis Contribution	3	-1	1	1
Atom Contribution	3	1	3	1
Reducible Representation Γ_{red}				

Fourth, we need to calculate the irreducible representation

To calculate the irreducible representation, we use the formula:

$$a_i = \frac{1}{h}\sum_R [N * \Gamma_R \chi_i(R)]$$

C_{2v}	E	C_2 (z)	$\sigma_v(xz)$	$\sigma_v(yz)$	linear functions, rotations	quadratic functions	cubic functions
A_1	+1	+1	+1	+1	z	x^2, y^2, z^2	z^3, x^2z, y^2z
A_2	+1	+1	-1	-1	R_z	xy	xyz
B_1	+1	-1	+1	-1	x, R_y	xz	xz^2, x^3, xy^2
B_2	+1	-1	-1	+1	y, R_x	yz	yz^2, y^3, x^2y

a_i is the # of irreducible reps of a given type
h is the order of the group
N is the number of operations in the class
Γ_R is the character of reducible representation
$\chi_i(R)$ is the character of irreducible representations

$h = 4$

	E	C_2	σ_{xz}	σ_{yz}
Γ_{red}	9	-1	3	1

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A_1	+1	+1	+1	+1	z	x^2, y^2, z^2	z^3, x^2z, y^2z

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A_1 = ¼ ((1*9*1) + (1*-1*1) + (1*3*1) + (1*1*1)) = 12/4 = 3

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A_2	+1	+1	-1	-1	R_z	xy	xyz

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B_1	+1	-1	+1	-1	x, R_y	xz	xz^2, x^3, xy^2

	E	C_2	σ_{xz}	σ_{yz}
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A_1 = ¼ ((1*9*1) + (1*-1*1) + (1*3*1) + (1*1*1)) = 12/4 = 3

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B_1 = ¼ ((1*9*1) + (1*-1*-1) + (1*3*1) + (1*1*-1)) = 12/4 = 3

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B_2	+1	-1	-1	+1	y, R_x	yz	yz^2, y^3, x^2y

a_i is the # of irreducible reps of a given type
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A_2 = ¼ ((1*9*1) + (1*-1*1) + (1*3*-1) + (1*1*-1)) = 4/4 = 1

B_1 = ¼ ((1*9*1) + (1*-1*-1) + (1*3*1) + (1*1*-1)) = 12/4 = 3

B_2 = ¼ ((1*9*1) + (1*-1*-1) + (1*3*-1) + (1*1*1)) = 8/4 = 2

Fourth, we need to calculate the irreducible representation

To calculate the irreducible representation, we use the formula:

$$a_i = \frac{1}{h}\sum_R [N * \Gamma_R \chi_i(R)]$$

C_{2v}	E	C_2 (z)	$\sigma_v(xz)$	$\sigma_v(yz)$	linear functions, rotations	quadratic functions	cubic functions
B_2	+1	-1	-1	+1	y, R_x	yz	yz^2, y^3, x^2y

a_i is the # of irreducible reps of a given type

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Γ_R is the character of reducible representation

$\chi_i(R)$ is the character of irreducible representations

	E	C_2	σ_{xz}	σ_{yz}
Γ_{red}	9	-1	3	1

$$\boxed{\Gamma_{irred} = 3A_1 + 1A_2 + 3B_1 + 2B_2}$$

Should equal 3 * atoms (3N = 9)

3+1+3+2 = 9

h = 4

A_1 = ¼ ((1*9*1) + (1*-1*1) + (1*3*1) + (1*1*1)) = 12/4 = **3**

A_2 = ¼ ((1*9*1) + (1*-1*1) + (1*3*-1) + (1*1*-1)) = 4/4 = **1**

B_1 = ¼ ((1*9*1) + (1*-1*-1) + (1*3*1) + (1*1*-1)) = 12/4 = **3**

B_2 = ¼ ((1*9*1) + (1*-1*-1) + (1*3*-1) + (1*1*1)) = 8/4 = **2**

Fifth, we need to calculate the vibrational modes

To calculate the vibrational modes, we need to subtract the translations and rotations:

To find these locate the **linear functions and rotations.**

Translations are denoted as x, y, or z

Rotations are denoted as R_x, R_y, or R_z

C_{2v}	E	C_2 (z)	$\sigma_v(xz)$	$\sigma_v(yz)$	linear functions, rotations	quadratic functions	cubic functions
A_1	+1	+1	+1	+1	z	x^2, y^2, z^2	z^3, x^2z, y^2z
A_2	+1	+1	-1	-1	R_z	xy	xyz
B_1	+1	-1	+1	-1	x, R_y	xz	xz^2, x^3, xy^2
B_2	+1	-1	-1	+1	y, R_x	yz	yz^2, y^3, x^2y

$$\Gamma_{irred} = 3A_1 + 1A_2 + 3B_1 + 2B_2$$

$$\Gamma_{trans} \quad -1A_1 \qquad -1B_1 \quad -1B_2$$

$$\Gamma_{rot} \qquad -1A_2 \quad -1B_1 \quad -1B_2$$

$$\Gamma_{vib} = 2A_1 \qquad + 1B_1$$

$$\boxed{\Gamma_{vib} = 2A_1 + 1B_1}$$

Should equal 3N-6 (3N-6 = 3)
2+1 = 3

Lastly, we need to classify how many IR and Raman active vibrations occur

To find the IR and Raman active vibrations we need to locate the appropriate modes:

IR vibrations are denoted as **x, y, and z** in the linear functions column

Raman vibrations are binary products denoted as **xy, yz, xz, x^2, y^2, and z^2** in the quadratic functions column

C_{2v}	E	C_2 (z)	σ_v(xz)	σ_v(yz)	linear functions, rotations	quadratic functions	cubic functions
A_1	+1	+1	+1	+1	z	x^2, y^2, z^2	z^3, x^2z, y^2z
A_2	+1	+1	-1	-1	R_z	xy	xyz
B_1	+1	-1	+1	-1	x, R_y	xz	xz^2, x^3, xy^2
B_2	+1	-1	-1	+1	y, R_x	yz	yz^2, y^3, x^2y

$$\boxed{\Gamma_{vib} = 2A_1 + 1B_1}$$

$$\boxed{\Gamma_{IR} = 2A_1 + 1B_1}$$

3 possible active vibrations

$$\boxed{\Gamma_{Raman} = 2A_1 + 1B_1}$$

3 possible active vibrations