Sri Chandrasekharaendra Saraswathi Viswa Mahavidyalaya
(Deemed to be University)
Kanchipuram, Tamilnadu

ONLINE COURSE

Department of Chemistry

Normal Mode Analysis

V.Santhanam
Department of Chemistry
SCSVMV (Deemed to be University)
Kanchipuram
email: santhanam@kanchiuniv.ac.in
Mobile: 9003760205

What we are going to learn?

- **Degrees of freedom**
  - **Translational**
  - **Rotational**
  - **Vibrational**
- **When a rotational degree of freedom is considered?**
- **Symmetries of translations and rotations.**
- **Determining the reducible representation for a C_{2v} molecule with using 3N coordinates.**
- **Reduction of the reducible representation.**
- **Symmetries of vibrations.**

- Objective:
  - To understand the principles behind normal mode analysis.
  - To understand and appreciate the application of group theory to vibrational spectroscopy.
  - To assign symmetry labels to molecular vibrations and drawing conclusions for activity of vibrations in IR and Raman spectra.
- Outcome:

The students will be able to

  - Understand the significance of group theory in vibrational spectra.
  - Use the character tables for predicting the IR and Raman activities.
- Prerequisites:
  - Degrees of freedom
  - Basics of group theory
  - Mulliken Symbols
  - Theories of IR and Raman Spectra

Degrees of Freedom

- A molecule containing N atoms will have 3N degrees of freedom.
- If N atoms are assumed to be independent, each atom is associated with three degrees of translational freedom.
- For N atoms, there will be 3N degrees of translational freedom.
- The number of degrees of freedom remains conserved, even when the atoms join together to form the molecule.

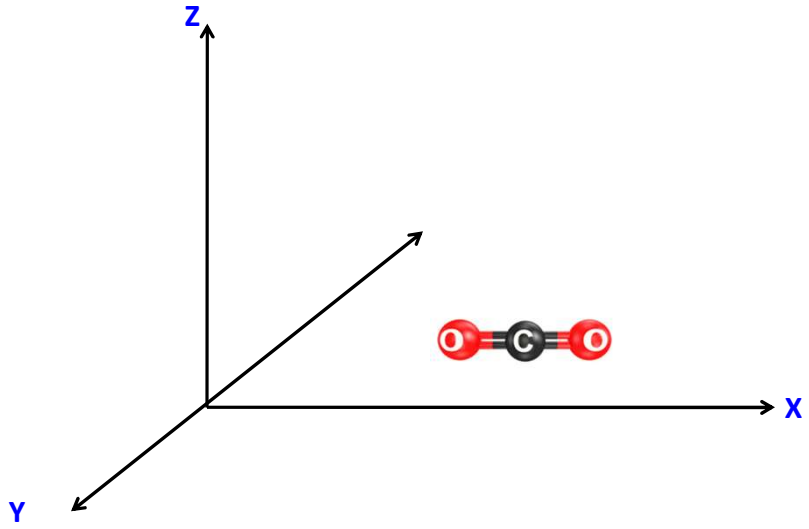
Degrees of Freedom

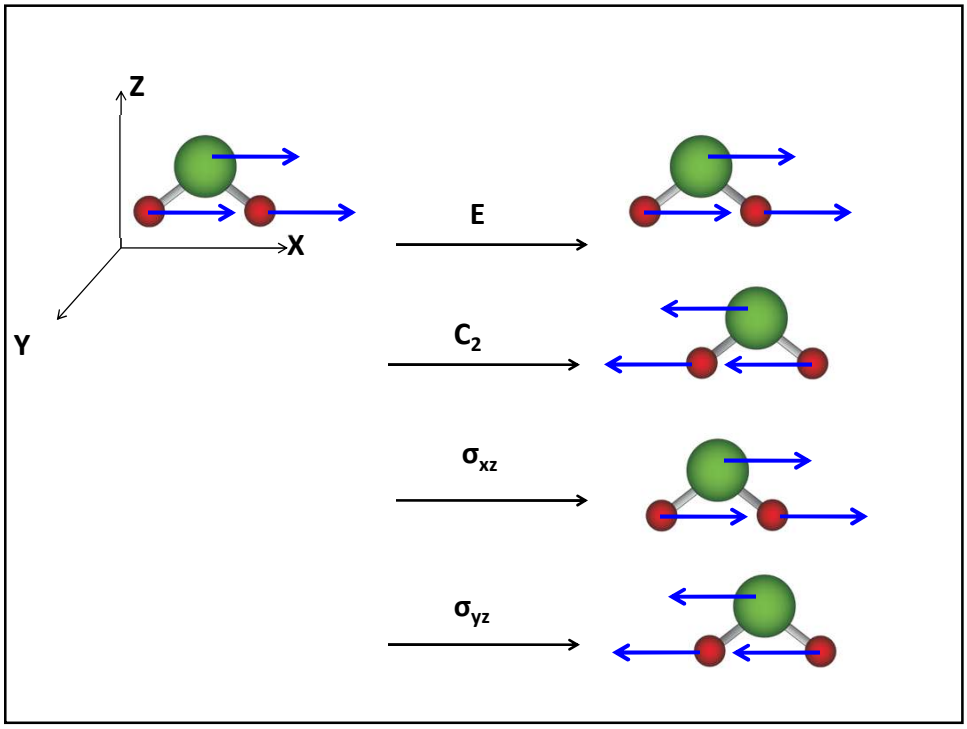
- Only three degrees of translational freedom for the molecule.
- Others will be rotational and vibrational degrees of freedom.
- These 3N vectors may be taken as basis for evaluating the total character associated with the 3N degrees of freedom.

Degrees of Freedom

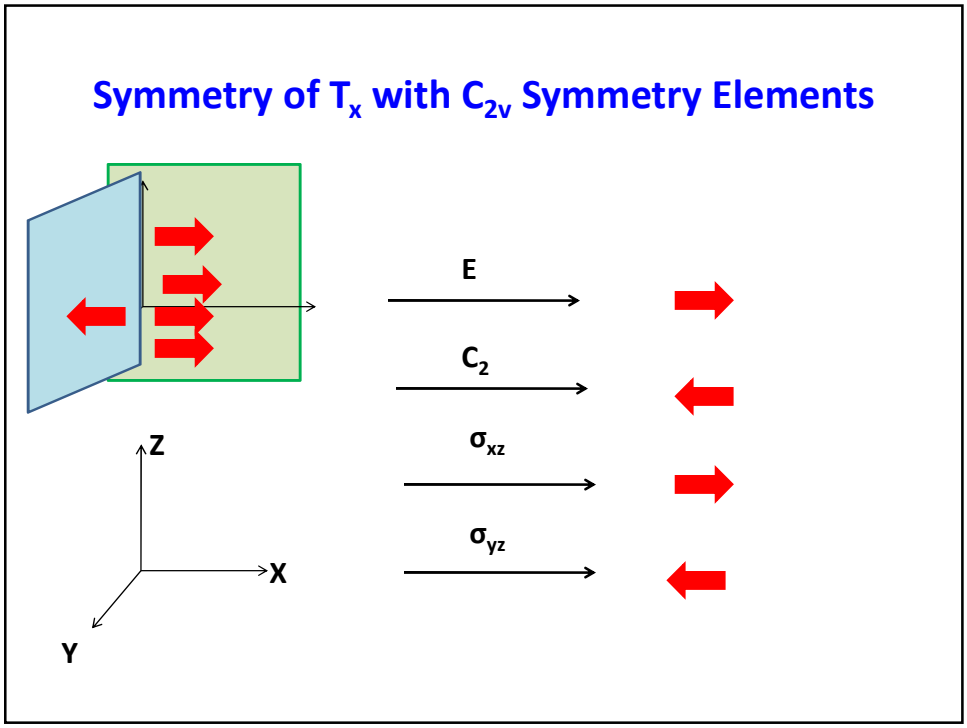
- subtracting the characters relating to the translational and rotational degrees of freedom from the above total character to get the character relating to vibrational degrees of freedom.
- In the 3N types of motion, three represent molecular translations in the x, y or z directions.
- Linear molecules have two rotational degrees of freedom, and non-linear molecules have three rotational degrees of freedom.

Translational Degrees of Freedom

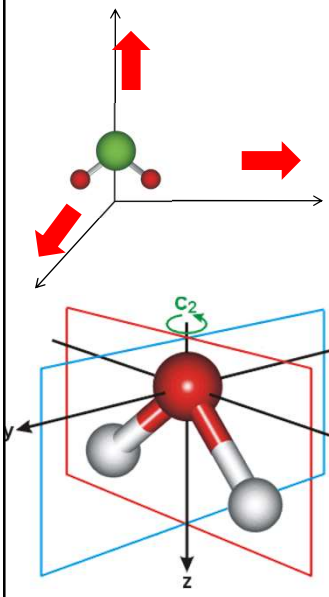




Symmetry of T_x with C_{2v} Symmetry Elements

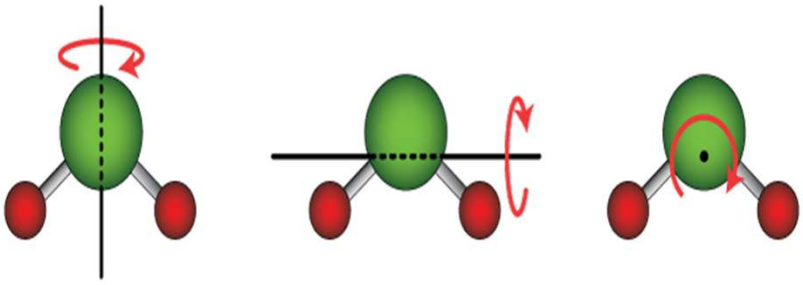


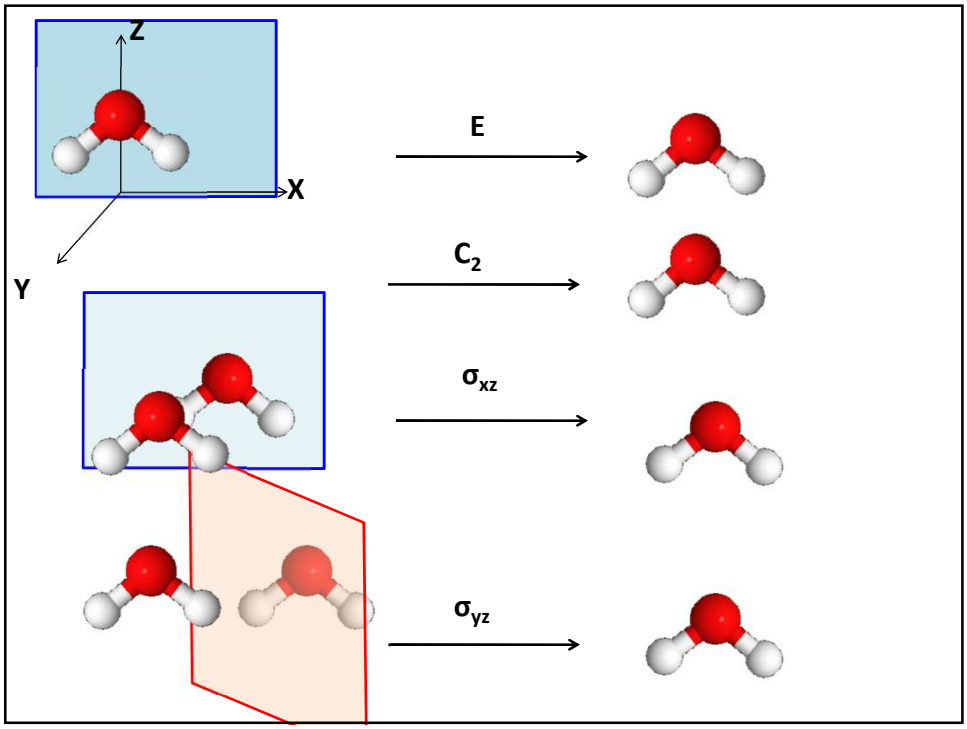
Symmetries of translations in Water molecule



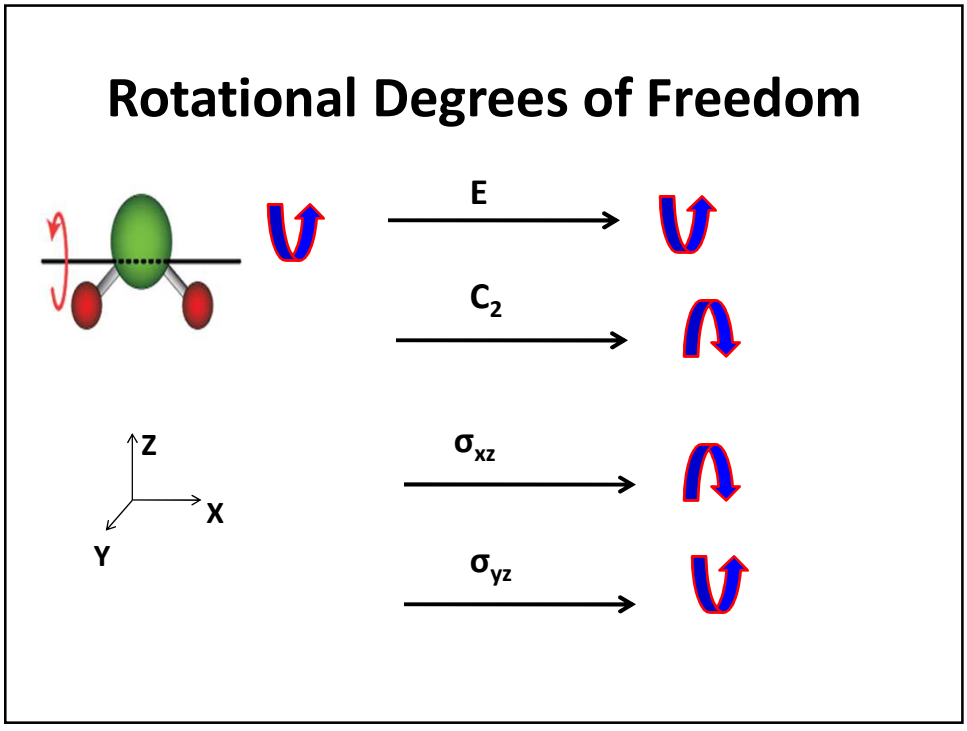
	E	C_2	σ_{xz}	σ_{yz}	
T_x	→	←	→	←	
	+1	-1	+1	-1	B_1
T_y	↙	↗	↗	↙	
	+1	-1	-1	+1	B_2
T_z	↑	↑	↑	↑	
	+1	+1	+1	+1	A_1

Rotation of H_2O Molecule Along Different Axes

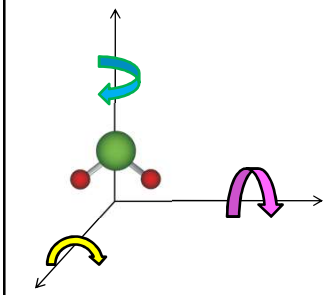


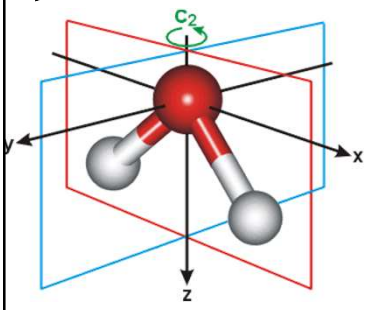


Rotational Degrees of Freedom



Symmetries of rotations in Water molecule



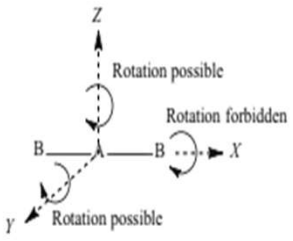


	E	C_2	σ_{xz}	σ_{yz}	
R_x					B_2
R_y					B_1
R_z					A_2

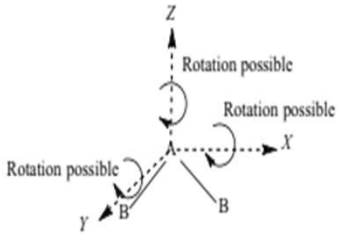
Molecular Vibrations

For linear molecules, the number of molecular vibrations = 3N-3-2 = 3N-5.

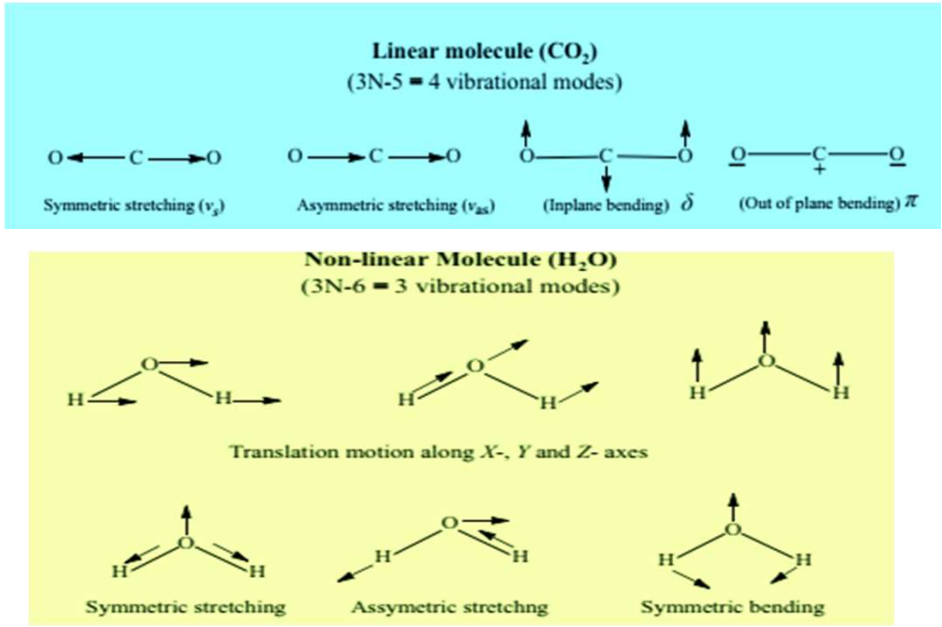
For non-linear molecules, the number of molecular vibrations = 3N-3-3= 3N-6.



Linear molecule (a)



Non linear molecule (b)



Molecular Vibrations

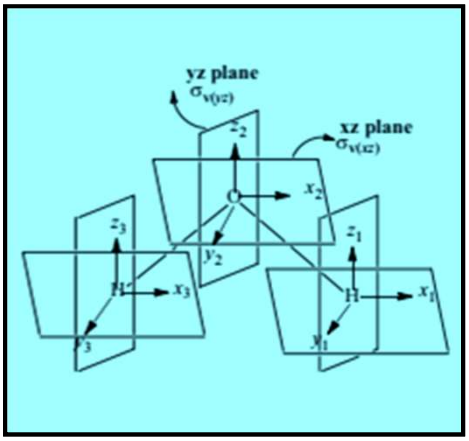
- **The complex vibrations of the molecules are due to the superimposition of relatively simple vibrations.**
- **Each of these vibrational motions involves displacement of atoms or deformation of angles.**
- ***These independent displacements/ deformations are called normal modes of vibrations of the molecules.***

Molecular Vibrations

- These are generally divided in bond stretchings and angle of deformations.
- Each of these vibrational modes occurs at a characteristic energy/frequency that is dependent on the strength of the restoring force called restoring force constant.

Basis vectors for H_2O molecule

- Let us consider the H_2O molecule belonging to C_{2v} point group with symmetry operations E, C_2, $\sigma_{v(xz)}$ and $\sigma_{v(yz)}$.
- The basis vectors of the atoms representing the degrees of freedom may be denoted as x_1, y_1, z_1, x_2, y_2, z_2 and x_3, y_3, z_3.



Basis vectors for H_2O molecule

- From the transformations of these vectors during each of the above point group symmetry operations, one can set up nine dimensional matrices from which the corresponding characters can be worked out.
- The matrix product indicating the transformations will appear as

$$\begin{bmatrix} & & \\ & \text{Transformation matrix} & \\ & & \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \\ \vdots \\ z_3 \end{bmatrix} = \begin{bmatrix} x_1' \\ y_1' \\ z_1' \\ \vdots \\ z_3' \end{bmatrix}$$

Operation E

On applying E operation, all the vectors are retained as such, and hence $x_1' = x_1$, $y_1' = y_1$, $z_1' = z_1$, etc.

$$E\begin{bmatrix}x_1\\y_1\\z_1\\x_2\\y_2\\z_2\\x_3\\y_3\\z_3\end{bmatrix} = \begin{bmatrix}x_1'\\y_1'\\z_1'\\x_2'\\y_2'\\z_2'\\x_3'\\y_3'\\z_3'\end{bmatrix} \begin{matrix}x_1' = x_1+0+0+0+0+0+0+0+0\\ y_1' = 0+y_1+0+0+0+0+0+0+0\\ z_1' = 0+0+z_1+0+0+0+0+0+0\\ x_2' = 0+0+0+x_2+0+0+0+0+0\\ y_2' = 0+0+0+0+y_2+0+0+0+0\\ z_2' = 0+0+0+0+0+z_2+0+0+0\\ x_3' = 0+0+0+0+0+0+x_3+0+0\\ y_3' = 0+0+0+0+0+0+0+y_3+0\\ z_3' = 0+0+0+0+0+0+0+0+z_3\end{matrix} \begin{bmatrix}1&0&0&0&0&0&0&0&0\\0&1&0&0&0&0&0&0&0\\0&0&1&0&0&0&0&0&0\\0&0&0&1&0&0&0&0&0\\0&0&0&0&1&0&0&0&0\\0&0&0&0&0&1&0&0&0\\0&0&0&0&0&0&1&0&0\\0&0&0&0&0&0&0&1&0\\0&0&0&0&0&0&0&0&1\end{bmatrix}\begin{bmatrix}x_1\\y_1\\z_1\\x_2\\y_2\\z_2\\x_3\\y_3\\z_3\end{bmatrix}$$

$\chi = 9$

Operation C_2

The operation C_2 brings about the following changes: $x_1' = -x_3$, $y_1' = -y_3$, $z_1' = z_3$; $x_2' = -x_2$, $y_2' = -y_2$, $z_2' = z_2$; $x_3' = -x_1$, $y_3' = -y_1$, $z_3' = z_1$.

$$C_2\begin{bmatrix}x_1\\y_1\\z_1\\x_2\\y_2\\z_2\\x_3\\y_3\\z_3\end{bmatrix} = \begin{bmatrix}x_1'\\y_1'\\z_1'\\x_2'\\y_2'\\z_2'\\x_3'\\y_3'\\z_3'\end{bmatrix} \begin{matrix}x_1' = 0+0+0+0+0+0-x_3+0+0\\ y_1' = 0+0+0+0+0+0+0-y_3+0\\ z_1' = 0+0+0+0+0+0+0+0+z_3\\ x_2' = 0+0+0-x_2+0+0+0+0+0\\ y_2' = 0+0+0+0-y_2+0+0+0+0\\ z_2' = 0+0+0+0+0+z_2+0+0+0\\ x_3' = -x_1+0+0+0+0+0+0+0+0\\ y_3' = 0-y_1+0+0+0+0+0+0+0\\ z_3' = 0+0+z_1+0+0+0+0+0+0\end{matrix} \begin{bmatrix}0&0&0&0&0&0&-1&0&0\\0&0&0&0&0&0&0&-1&0\\0&0&0&0&0&0&0&0&1\\0&0&0&-1&0&0&0&0&0\\0&0&0&0&-1&0&0&0&0\\0&0&0&0&0&1&0&0&0\\-1&0&0&0&0&0&0&0&0\\0&-1&0&0&0&0&0&0&0\\0&0&1&0&0&0&0&0&0\end{bmatrix}\begin{bmatrix}x_1\\y_1\\z_1\\x_2\\y_2\\z_2\\x_3\\y_3\\z_3\end{bmatrix}$$

$\chi = -1$

(iii) The operation $\sigma_{v(xz)}$ brings about the following changes: $x_1' = x_3$, $y_1' = -y_3$, $z_1' = z_3$; $x_2' = x_2$, $y_2' = -y_2$, $z_2' = z_2$; $x_3' = x_1$, $y_3' = -y_1$, $z_3' = z_1$.

$$\sigma_{v(xz)}\begin{bmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{bmatrix} = \begin{bmatrix} x_1' \\ y_1' \\ z_1' \\ x_2' \\ y_2' \\ z_2' \\ x_3' \\ y_3' \\ z_3' \end{bmatrix} \begin{matrix} x_1' = 0+0+0+0+0+0+x_3+0+0 \\ y_1' = 0+0+0+0+0+0+0-y_3+0 \\ z_1' = 0+0+0+0+0+0+0+0+z_3 \\ x_2' = 0+0+0+x_2+0+0+0+0+0 \\ y_2' = 0+0+0+0-y_2+0+0+0+0; \\ z_2' = 0+0+0+0+0+z_2+0+0+0 \\ x_3' = x_1+0+0+0+0+0+0+0+0 \\ y_3' = 0-y_1+0+0+0+0+0+0+0 \\ z_3' = 0+0+z_1+0+0+0+0+0+0 \end{matrix} \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{bmatrix}$$

$\chi = 1$

(iv) The operation $\sigma_{v(yz)}$ brings about the following changes: $x_1' = -x_1$, $y_1' = y_1$, $z_1' = z_1$; $x_2' = -x_2$, $y_2' = y_2$, $z_2' = z_2$; $x_3' = -x_3$, $y_3' = y_3$, $z_3' = z_3$.

$$\sigma_{v(yz)}\begin{bmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{bmatrix} = \begin{bmatrix} x_1' \\ y_1' \\ z_1' \\ x_2' \\ y_2' \\ z_2' \\ x_3' \\ y_3' \\ z_3' \end{bmatrix} \begin{matrix} x_1' = -x_1 0+0+0+0+0+0+0+0 \\ y_1' = 0+y_1+0+0+0+0+0+0+0 \\ z_1' = 0+0+z_1+0+0+0+0+0+0 \\ x_2' = 0+0+0-x_2+0+0+0+0+0 \\ y_2' = 0+0+0+0+y_2+0+0+0+0; \\ z_2' = 0+0+0+0+0+z_2+0+0+0 \\ x_3' = 0+0+0+0+0+0-x_3+0+0 \\ y_3' = 0+0+0+0+0+0+0+y_3+0 \\ z_3' = 0+0+0+0+0+0+0+0+z_3 \end{matrix} \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x_1 \\ y_1 \\ z_1 \\ x_2 \\ y_2 \\ z_2 \\ x_3 \\ y_3 \\ z_3 \end{bmatrix}$$

$\chi = 3$

Reducible Representation of H_2O Molecule

C_{2V}	E	C_2	σ_{xz}	σ_{yz}
Γ_{3N}	**9**	**-1**	**1**	**1**

This reducible representation Γ_{3N} can be reduced into smaller irreducible representations to get the total degrees of freedom (vibrational, rotational and translational) of different symmetries.
This process/procedure of calculating total character of the reducible representation is very cumbersome and time consuming.

- **For complicated molecule, this procedure becomes further more difficult to be followed.**
- **For instance, if we want to find Γ_{3N} for benzene (C_6H_6), then we have to deal with 36X36 matrices.**
- **So, there is a need for simplified procedure for determining Γ_{3N}.**

Simplified Procedure for Determining Γ_{3N}

The simplified procedure involves in finding character of matrix corresponding to symmetry operation R [i.e. $\chi(R)$] without constructing 3N×3N matrices.

- By matrix multiplication rules, it is well clear that if an atom or its associated vector is shifted in space by/on applying any symmetry operation, then the atom/its associated vectors will not contribute to the character of the matrix or such vector will contribute zero to matrix character $\chi(R)$.
- Only unshifted atom or unshifted vector contributes $\chi(R) = +1$, and vector whose direction is reversed contributes $\chi(R) = -1$.

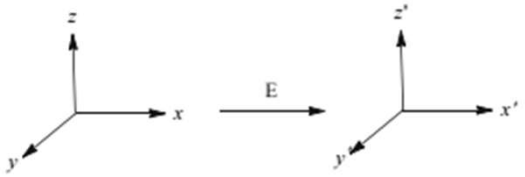
Steps Involved

Based on the above idea, the overall procedure for determining Γ_{3N} involves the following steps:

- ✓ Find the number of unshifted atoms during a particular symmetry operation taking one symmetry operation from each class.
- ✓ Workout the $\chi(R)$ for every unshifted atom for every symmetry operation taking one from each class.
- ✓ The contributions of these characters will be the same for the symmetry operation (R) in every point group when taken 3N vectors as the basis.
- ✓ Γ_{3N} can be written in the tabular form as shown earlier

Identity Operation

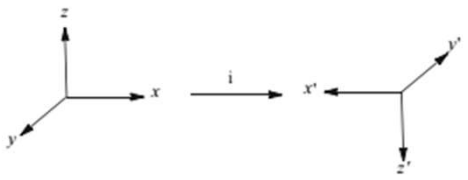
(i) **Identity operation, *E*** The effect of identity operation is shown below.



$$E\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} \quad \text{i.e.} \quad \begin{matrix} x' = x \\ y' = y \\ z' = z \end{matrix} \quad \text{or} \quad E = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \chi = +3$$

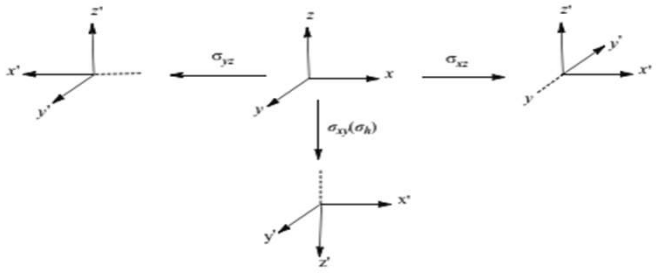
Inversion Operation

(ii) **Inversion operation, *i*** The effect of inversion operation is shown below.



$$i\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} \quad \text{i.e.} \quad \begin{matrix} x' = -x \\ y' = -y \\ z' = -z \end{matrix} \quad \text{or} \quad i = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \qquad \chi = -3$$

(iii) **Reflection operation, σ** The effects of reflection operations σ_{xz}, σ_{yz}, σ_{xy} (σ_h) are shown below.

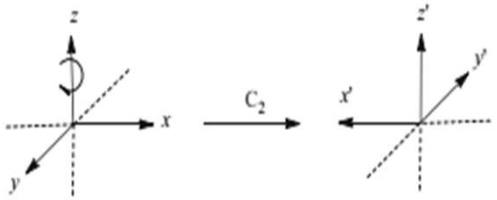


$$\sigma_{xz} = \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} \quad \text{i.e.} \quad \begin{matrix} x' = x \\ y' = -y \\ z' = z \end{matrix} \quad \text{or} \quad \sigma_{xz} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \chi = 1$$

$$\sigma_{yz} = \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} \quad \text{i.e.} \quad \begin{matrix} x' = -x \\ y' = y \\ z' = z \end{matrix} \quad \text{or} \quad \sigma_{xz} = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \chi = 1$$

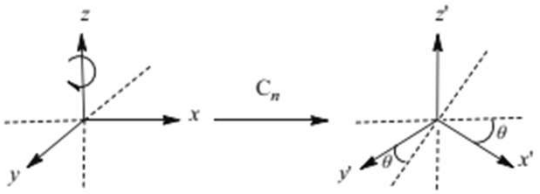
$$\sigma_{xy} = \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} \quad \text{i.e.} \quad \begin{matrix} x' = x \\ y' = y \\ z' = -z \end{matrix} \quad \text{or} \quad \sigma_{xz} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix} \qquad \chi = 1$$

(iv) **C_2 operation along z-axis** In this operation, molecule is rotated through 180°, and its effect is shown below.



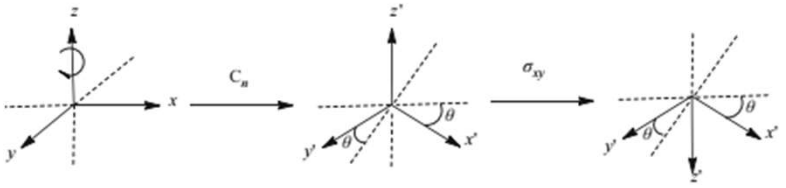
$$C_2 = \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} \quad \text{i.e.} \quad \begin{matrix} x' = -x \\ y' = -y \\ z' = z \end{matrix} \quad \text{or} \quad E = \begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \chi = -1$$

(v) **C_n operation along z-axis** In this operation, molecule is rotated through certain angle θ, and its effect is shown in the form of C_n matrix below.



$$\begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \quad \chi = 2\cos\theta + 1$$

(vi) **Improper rotation, S_n** This is equivalent to C_n operation through z-axis followed by reflection through a plane perpendicular to the rotation axis, that is, σ_{xy} (σ_h).



Here, the symmetry operation C_n changes x to x' and y to y' only and σ_{xy} (σ_h) changes z to z', that is, di-reaction is reversed or sign is changed.

The effect of improper operation is thus the multiplication of C_n and σ_{xy} matrices as shown below.

$$\underset{C_n}{\begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & 1 \end{bmatrix}} \cdot \underset{\sigma_{xy}}{\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{bmatrix}} = \underset{S_n}{\begin{bmatrix} \cos\theta & \sin\theta & 0 \\ -\sin\theta & \cos\theta & 0 \\ 0 & 0 & -1 \end{bmatrix}} \quad \chi = 2\cos\theta - 1$$

Symmetry Operation (R)	$\chi(R)$ of matrices for operation R
E	+3
i	−3
$\sigma(\sigma_{xz}, \sigma_{yz}, \sigma_{xy})$	+1
C_2	−1
C_3^1 (θ= 120°), C_3^2 (θ= 240°)	0
C_4^1 (θ= 90°), C_4^3(θ= 270°)	+1
C_6^1 (θ= 60°), C_6^5(θ= 300°)	+2
S_3^1 (θ= 120°), S_3^5(θ= 240°)	−2
S_4^1 (θ= 90°), S_4^3(θ= 270°)	−1
S_6^1 (θ= 60°), S_6^5(θ= 300°)	0
In general, proper axis	$2\cos\theta + 1$
In general, improper axis	$2\cos\theta - 1$

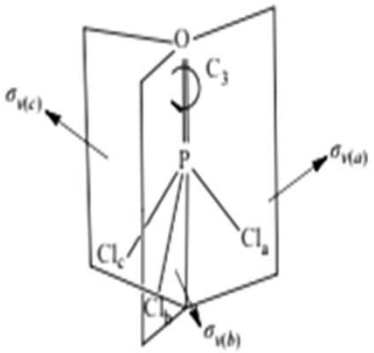
Let us take the H_2O molecule belonging to this point group having symmetry operations, E, C_2, $\sigma_{v(xz)}$ and $\sigma_{v(yz)}$.

1. **E does not shift any atom, so unshifted atoms are 3.**
2. **C_2 interchanges H_1 and H_2 but does not shift O. So unshifted atom is 1.**
3. **$\sigma_{v(xz)}$ does not shift any of the atoms as all lie in $\sigma_{v(xz)}$ (molecular plane) plane. So, unshifted atoms equal to 3.**
4. **$\sigma_{v(yz)}$ interchanges H_1 and H_2 but does not shift O. So unshifted atom is 1.**

C_{2V}	E	C_2	σ_{xz}	σ_{yz}
No. of Un-shifted Atoms	3	1	3	1
χ (R)	3	-1	1	1
Γ_{3N}	9	-1	3	1

C_3v point group (NH_3, $CHCl_3$ or $POCl_3$)

- Let us take the $POCl_3$ molecule belonging to C_{3v} point group having symmetry operations, E, $2C_3$ and $3\sigma v$.



- (i) Symmetry operation E does not shift any of the atoms. So, number of unshifted atoms are 5.
  (ii) C_3^1 along P = O bond shifts all the three Cl's but does not shift atoms P and O. So unshifted atoms are 2.
  (iii) σ_v containing P-O and one of the Cl's shifts only two Cl's. So unshifted atoms are 3.

C_{3v}	E	$2C_3$	$3\sigma_v$
No. of unshifted atoms (n)	5	2	3
$\chi(R)$ from Table 3.1	3	0	1
Γ_{3N} $[n \times \chi(R)]$	15	0	3

Symmetries of Vibrations in H_2O

C_{2V}	E	C_2	σ_{xz}	σ_{yz}
No. of Un-shifted Atoms	3	1	3	1
χ (R)	3	-1	1	1
Γ_{3N}	9	-1	3	1

Now we have to reduce the reducible representation in to irreducible representations by using reduction formula from GOT.

$$n = 1/h \sum N \chi_R \chi_I$$

Reduction Formula

$$n = 1/h \sum N \chi_R \chi_I$$

- χ_R and χ_I are the characters of the reducible and irreducible representations.

  The reducible representations you work out yourself and are the 'number of unchanged bonds'.
  The irreducible representations are found in the Character Table.

- **N** is the coefficient in front of each of the symmetry elements on the top row of the Character Table.
- **h** is the order of the group and is the sum of the coefficients of the symmetry element symbols (i.e. h = ΣN). The summation of the Reduction Formula is carried out over each of the columns in the Character Table for the irreducible representation under consideration.
- **n** is the number of times that the row representation will appear in the IR or Raman spectra.

C_{2V}	E	C_2	σ_{xz}	σ_{yz}
No. of Un-shifted Atoms	3	1	3	1
χ (R)	3	-1	1	1
Γ_{3N}	9	-1	3	1

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

$n(A_1) = ¼ . [(9.1.1) + (-1 .1 .1) + (3.1.1) + (1.1.1)]$
$= ¼ . [9 -1 +3 +1] = 3$
So the total representation contains $3A_1$ modes.

- **Similarly we can find the number of A_2,B_1 and B_2 modes also.**

$n(A_1) = ¼ . [(9.1.1) + (-1 .1 .1) + (3.1.1) + (1.1.1)] = 3$
$n(A_2) = ¼ . [(9.1.1) + (-1 .1 .1) + (3.-1.1) + (1.-1.1)] = 1$
$n(B_1) = ¼ . [(9.1.1) + (-1 .-1 .1) + (3.1.1) + (1.-1.1)] = 3$
$n(B_2) = ¼ . [(9.1.1) + (-1 .-1 .1) + (3.-1.1) + (1.1.1)] = 2$

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

$$\Gamma_{3N} = \Gamma_{trans} + \Gamma_{rot} + \Gamma_{vib}$$

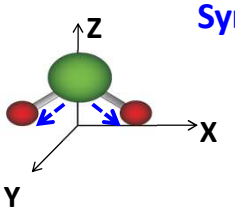
$$\Gamma_{vib} = \Gamma_{3N} - (\Gamma_{trans} + \Gamma_{rot})$$

$$\Gamma_{vib} = [\,(3A_1 + A_2 + 3B_1 + 2B_2) - (B_1 + B_2 + A_1) - (A_2 + B_1 + B_2)\,]$$

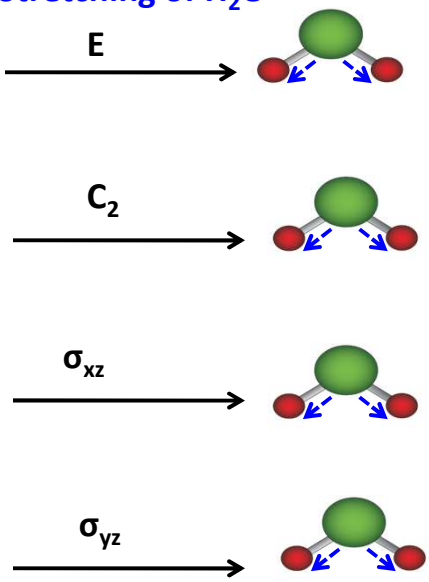
$$\Gamma_{vib} = 2A_1 + B_1$$

- So of the three vibrations possible for H_2O, two vibrations belong to A_1 and one to B_1 modes.

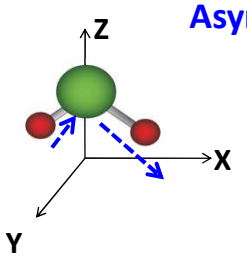
Symmetric Stretching of H_2O



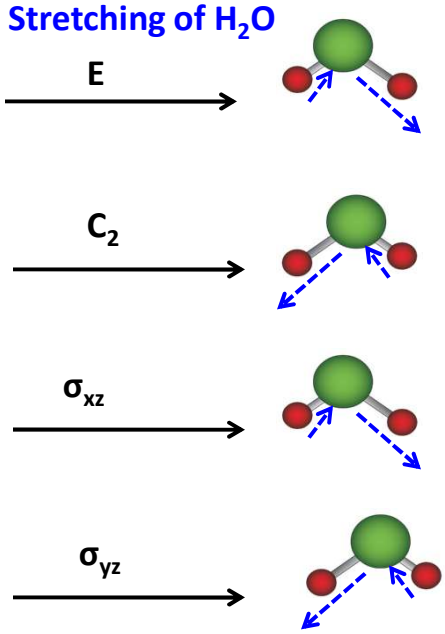
E	C_{2v}	σ_{xz}	σ_{yz}	
+1	+1	+1	+1	A_1



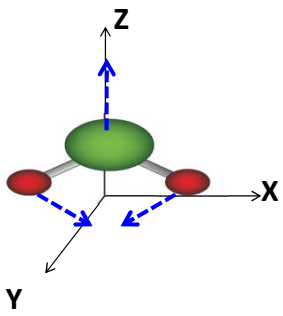
Asymmetric Stretching of H_2O



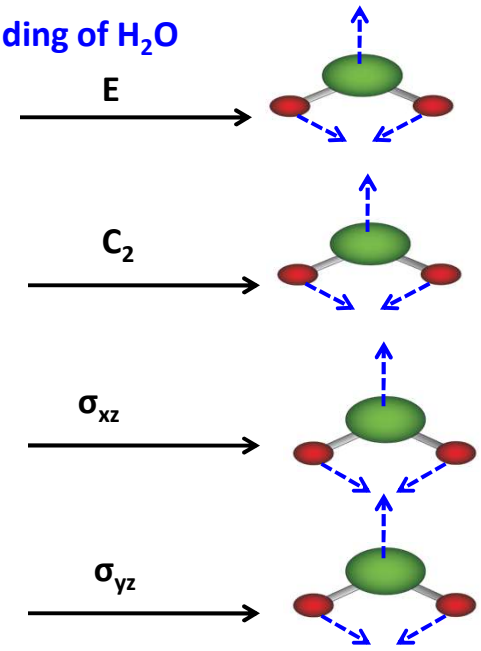
E	C_{2v}	σ_{xz}	σ_{yz}	
+1	-1	+1	-1	B_1



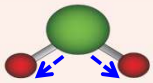
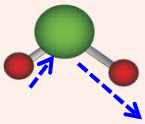
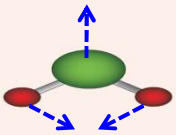
Bending of H_2O



E	C_{2v}	σ_{xz}	σ_{yz}	
+1	+1	+1	+1	A_1



Vibrations of H_2O

		
ν_1	ν_3	ν_2
A_1	B_1	A_1
3652 cm^{-1}	3756 cm^{-1}	1545 cm^{-1}

Thank You!!!