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**UNIT – IV**

**Application of Group Theory to Spectroscopy**

Symmetry of Normal modes of vibrations, application of Group theory to normal modes of vibrations and to normal mode analysis – symmetry properties of integrals – application for spectral selection rules of vibration spectra – IR and Raman active fundamentals symmetry of molecular orbitals and symmetry selection rule for electronic transitions in simple molecules like water, ammonia and ethylene.

## APPLICATIONS OF GROUP THEORY TO SPECTROSCOPY

Group theory helps in two aspects of vibrational spectroscopy.

- (i) Firstly helps in the classification of the normal modes of vibrations according to the irreducible representations of the point group of the molecule.
- (ii) Secondly, it helps in qualitatively finding out Raman and IR spectral activity of the fundamentals as well as overtone and combination bands.

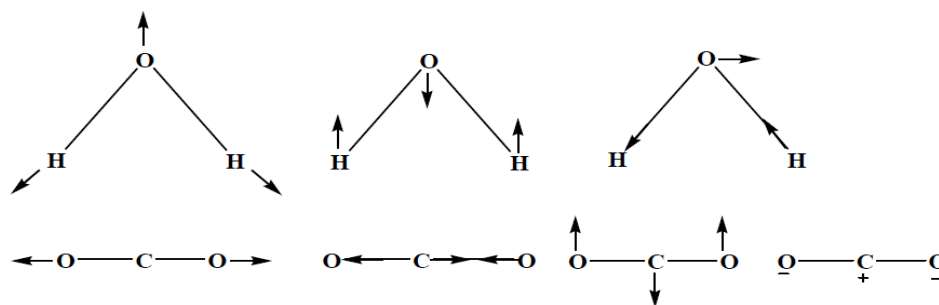
Molecular motion includes translations, rotations and vibrations. The total number of degrees of freedom (types of molecular motion) is equal to  $3N$ , where  $N$  is the number of atoms in the molecule. Of the  $3N$  types of motion, three represent molecular translations in the  $x$ ,  $y$  or  $z$  directions. Linear molecules have two rotational degrees of freedom, and non-linear molecules have three rotational degrees of freedom.

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

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

Motion	Degrees of freedom to describe the motion	
	Linear	Non linear
Translation	3	3
Rotation	2	3
Vibration	$3N-5$	$3N-6$

These degrees of freedom for vibrational motion are called the normal or fundamental modes of vibration. Depending on the type of molecule, these normal modes may be active either in IR or Raman or both. Example, the normal modes of vibration in  $H_2O$  and  $CO_2$  molecules.



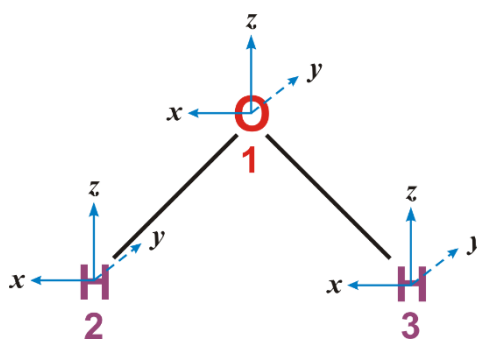
A knowledge of the symmetry of vibrational modes in molecules will be helpful in predicting whether these modes of vibrations will give rise to infrared or Raman spectrum or both these spectra.

To obtain total reducible representations  $\Gamma_{\text{red}}$  for all molecular motion, we must consider the symmetry properties of the three cartesian coordinates on all atoms of the molecule.

If a symmetry operation changes the position of an atom, all three cartesian coordinates contribute a value of 0.

For operations that leave an atom in place, the character is +1 for an axis that remains in position, -1 for an axis that is reversed, and 0 for an axis that has been moved.

### The Representations of Vibrational modes in H<sub>2</sub>O



**E** : Identity leaves all 3 atoms in position, so the character will be 9.

**C<sub>2</sub>**: The C<sub>2</sub> axis goes through the oxygen atom, and exchanges the hydrogen atoms. The z axis on oxygen stays in position. This axis contributes +1 towards the character for C<sub>2</sub>.

The y axis on oxygen is rotated by 180°. This reverses the axis, and contributes -1 to the character for C<sub>2</sub>. The x axis on oxygen is also rotated by 180°. This reverses the axis, and contributes -1 to the character for C<sub>2</sub>.

The character for the C<sub>2</sub> operation will be +1 (z axis on oxygen) -1 (y axis on oxygen) -1 (x axis on oxygen) = -1

**$\sigma_{\text{v}(xz)}$**  :The xz mirror plane is the molecular plane, and all three atoms remain in position. The z axis and the x axis both lie within the xz plane, and remain unchanged. Each unchanged axis contributes +1 to the character for the symmetry operation. For 3 atoms, the contribution to the character will be: 3(1+1) =6. The y axis will be reversed by the

mirror plane, contributing a value of -1 for each of the three atoms on the plane. The character for the xz mirror plane will be:  $6-3 = 3$

$\sigma_{v(yz)}$ : The yz mirror plane bisects the molecule. Only the oxygen atom lies in the plane. The y and z axis lie within the yz plane, and each contributes +1 to the character. The x axis on oxygen is reversed by the reflection, and contributes a -1 towards the character. The character for reflection in the yz plane is:  $1+1-1=1$

### Total representation of water molecule

$C_{2v}$	E	$C_2$	$\sigma_v(xz)$	$\sigma_v(yz)$
$\Gamma_T$	9	-1	3	1

A simpler method can be devised to obtain the reducible representation for any molecule. The character for the operation R in the reducible representation  $\chi_{xyz}(R)$  is given by the product of the number of unshifted atoms,  $U_R$ , and the character of the matrix for the operation R,  $\chi(R)$ .

Thus we can write

$$\chi_{xyz}(R) = U_R \chi(R)$$

The following table gives the characters of matrices for the various symmetry operations.

Symmetry Operation (R)	Character (X (R))
Identity	3
Rotation about $C_n$ axis	$2 \cos \theta + 1$
Improper rotation about $S_n$ axis	$2 \cos \theta - 1$
Reflection	1
Inversion	-3

Now for  $C_{2v}$  the total representation can also be obtained from above table:

The number of times that one of the irreducible representations occurs in a reducible representation (total representation for the water molecule) is given by the Reduction

formula:

$$a_i = \frac{1}{h} \sum_{\mathbf{R}} g \chi_{\mathbf{T}}(\mathbf{R}) \chi_i(\mathbf{R})$$

Where:  $a_i$  the no. of times the irreducible representation  $i$  occurs in the total representation T

$h$  the order of the group

$C_{2v}$	E	$C_2$	$\sigma_v(xz)$	$\sigma_v(yz)$
No. of unshifted atoms	3	1	3	1
Character per atom	3	-1	1	1
Total representation	9	-1	3	1

$\mathbf{R}$  the symmetry operations

$g$  the number of symmetry operations in a class

$\chi_i(\mathbf{R})$  the character associated  $i^{\text{th}}$  representation with the symmetry operation  $\mathbf{R}$

$\chi_{\mathbf{T}}(\mathbf{R})$  Total reducible representations with symmetry operation  $\mathbf{R}$

The character table of water with total representation is given as

$C_{2v}$	E	$C_2$	$\sigma_v(xz)$	$\sigma_v(yz)$
$A_1$	1	1	1	1
$A_2$	1	1	-1	-1
$B_1$	1	-1	1	-1
$B_2$	1	-1	-1	1
$\Gamma_{\mathbf{T}}$	9	-1	3	1

$$A_1 = \frac{1}{4} [(9)(1) + (-1)(1) + (3)(1) + (1)(1)] = \frac{1}{4}(12) = 3$$

$$A_2 = \frac{1}{4} [(9)(1) + (-1)(1) + (3)(-1) + (1)(-1)] = \frac{1}{4}(4) = 1$$

$$B_1 = \frac{1}{4} [(9)(1) + (-1)(-1) + (3)(1) + (1)(-1)] = \frac{1}{4}(12) = 3$$

$$B_2 = \frac{1}{4} [(9)(1) + (-1)(-1) + (3)(-1) + (1)(1)] = \frac{1}{4}(8) = 2$$

We find, therefore, that our total representation breaks down into 9 1-D irreducible representations:  $3A_1$ ,  $A_2$ ,  $3B_1$ , and  $2B_2$ . Therefore  $T_{3N}$  is written as

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

The sum of the irreducible representations of vibrational modes  $T_{vib}$  is related to  $T_{3N}$  by the relation

$$T_{vib} = T_{3N} - [T_x + T_y + T_z + R_x + R_y + R_z]$$

$C_{2v}$	$E$	$C_2$	$\sigma_v(xz)$	$\sigma'_v(yz)$		
$A_1$	1	1	1	1	$z$	$x^2, y^2, z^2$
$A_2$	1	1	-1	-1	$R_z$	$xy$
$B_1$	1	-1	1	-1	$x, R_y$	$xz$
$B_2$	1	-1	-1	1	$y, R_x$	$yz$

Using the values of  $T_x$ ,  $T_y$ ,  $T_z$ ,  $R_x$ ,  $R_y$  and  $R_z$  in the character table for this groups, we get

$$T_{vib} = (3A_1 + A_2 + 2B_1 + 3B_2) - (B_1 + B_2 + A_1 + B_2 + B_1 + A_1)$$

$$T_{vib} = 2A_1 + B_2$$

Thus the three normal modes of vibration of water molecule belong to  $A_1$  and  $B_2$  representations. Of these, those vibrations which belong to  $A_1$  symmetry are called totally symmetric vibrations.

### Infrared selection rules

Consider our total vibrational wavefunction  $\Psi_v$ , which is equal to the product of the  $k$  normal mode wavefunctions,  $\phi(n_i)$ :

$$\Psi_v = \phi(n_1) \phi(n_2) \phi(n_3) \phi(n_4) \dots \phi(n_k)$$

If we denote the ground state wavefunction by  $\Psi_v^\circ$  and the excited state by  $\Psi_v^j$  (indicating a transition to the  $j^{\text{th}}$  normal mode), then for a fundamental transition to occur by absorption of IR dipole radiation it is necessary that one or more of the following integrals be non-zero:

$$\int \Psi_v^\circ \mathbf{x} \Psi_v^j d\tau \neq 0$$

$$\int \Psi_v^\circ \mathbf{y} \Psi_v^j d\tau \neq 0$$

$$\int \Psi_v^\circ \mathbf{z} \Psi_v^j d\tau \neq 0$$

$x$ ,  $y$  and  $z$  in the integrals refer to the orientation of the oscillating electric vector of the radiation field relative to a Cartesian coordinate system fixed on the molecule.

In order for one (or more) of these integrals to be non-zero, the normal mode vibrational wavefunction,  $\Psi_v^j$ , must belong to the same representation as  $x$ ,  $y$ , or  $z$ .

Therefore:

A fundamental will be infrared active if the normal mode that is being excited belongs to the same representation as any one (or several) of the Cartesian coordinates.

$C_{2v}$	$E$	$C_2$	$\sigma_v(xz)$	$\sigma'_v(yz)$		
$A_1$	1	1	1	1	$z$	$x^2, y^2, z^2$
$A_2$	1	1	-1	-1	$R_z$	$xy$
$B_1$	1	-1	1	-1	$x, R_y$	$xz$
$B_2$	1	-1	-1	1	$y, R_x$	$yz$

For Raman scattering it is necessary that at least one integral of the type below be non-zero:

$$\int \psi_v^o \mathbf{P} \psi_v^j d\tau \neq 0$$

$P$  represents the polarizability tensor of the molecule and is equal to one of the quadratic (square) or binary functions of the Cartesian coordinates:

$$P = x^2, y^2, z^2, \underbrace{xy, xz, yz}_{\text{and combinations of (e.g., } x^2-y^2)}$$

A fundamental will be Raman active if the normal mode that is being excited belongs to the same representation as any one (or several) of the components of the polarizability tensor of the molecule.

$C_{2v}$	$E$	$C_2$	$\sigma_v(xz)$	$\sigma'_v(yz)$		
$A_1$	1	1	1	1	$z$	$x^2, y^2, z^2$
$A_2$	1	1	-1	-1	$R_z$	$xy$
$B_1$	1	-1	1	-1	$x, R_y$	$xz$
$B_2$	1	-1	-1	1	$y, R_x$	$yz$

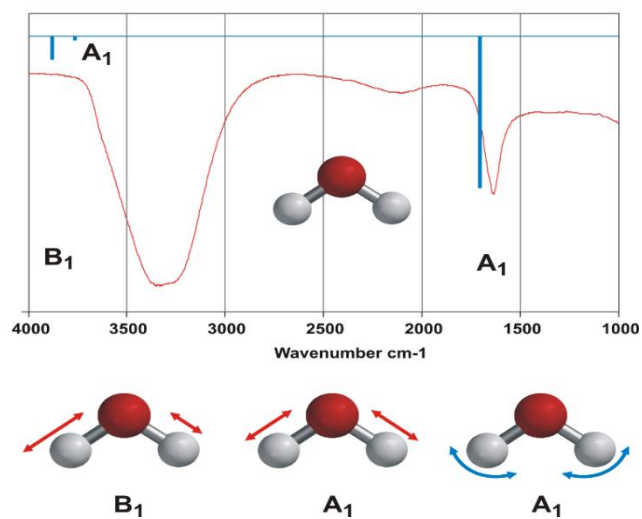
In general, for any molecule that has an inversion center of symmetry ( $i$ ), there will NOT be any fundamental normal modes in common between IR and Raman spectra.

$H_2O$  has fairly low  $C_{2v}$  symmetry (no inversion center) so there is extensive overlap of the IR and Raman active modes:

	IR	Raman
$2A_1$	$z$	$x^2, y^2, z^2$
$B_1$	$x$	$Xz$

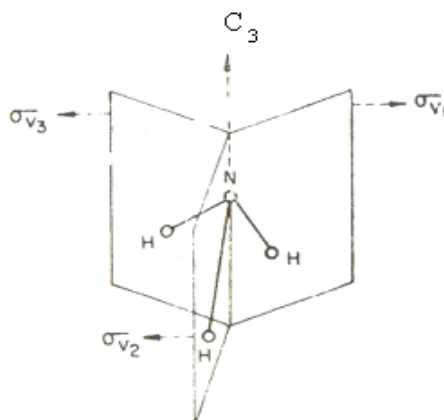
**IR spectra of water**





### The representations of vibrational modes in $\text{NH}_3$

1.  $\text{NH}_3$  molecule belongs to  $C_{3v}$  point group.
2. The various symmetry elements of this group are  $E, 2C_3, 3\sigma_v$
3. The reducible representation is obtained as follows



The symmetry elements in ammonia

$C_{3v}$	E	$2C_3$	$3\sigma_v$
No of unshifted atoms	4	1	2
Character per atom	3	0	1
Total character ( $T_R$ ) of the representation	12	0	2

This representation is split into the various irreducible representations by using the standard reduction formula

$$a_i = \frac{1}{h} \sum_R g \chi_T(R) \chi_i(R)$$

#### Character Table for $C_{3v}$

$C_{3v}$	E	$2C_3$	$3\sigma_v$		
$A_1$	1	1	1	$z$	$x^2 + y^2, z^2$
$A_2$	1	1	-1	$R_z$	
$E$	2	-1	0	$(x, y) (R_x, R_y)$	$(x^2 - y^2, xy) (xz, yz)$
$T_R$	12	0	2		

Using the standard reduction formula, we can deduce that

$$\begin{aligned} a_{A_1} &= \frac{1}{6} [1 \times 12 \times 1 + 2 \times 0 \times 1 + 3 \times 2 \times 1] \\ &= 3 \end{aligned}$$

$$\begin{aligned} a_{A_2} &= \frac{1}{6} [1 \times 12 \times 1 + 2 \times 0 \times 1 + 3 \times 2 \times (-1)] \\ &= 1 \end{aligned}$$

$$a_E = \frac{1}{6} [ 1 \times 12 \times 2 + 2 \times 0 \times (-1) + 3 \times 2 \times 0 ]$$

$$= 4$$

$T_{3N}$  is given by

$$T_{3N} = 3A_1 + A_2 + 4E$$

The irreducible representation  $T_{3N}$  thus obtained correspond to the translational, rotational and vibrational degrees of freedom.  $T_{3N}$  can be written as

$$T_{3N} = T_x + T_y + T_z + R_x + R_y + R_z + T_{vib}$$

$T_x, T_y, T_z$  and  $R_x, R_y, R_z$  can be obtained by using section III of the character table for the point group.

$$T_{vib} = T_{3N} - ( T_x + T_y + T_z + R_x + R_y + R_z )$$

$$T_x + T_y + T_z = A_1 + E$$

$$R_x + R_y + R_z = A_2 + E$$

$T_{vib}$  is given as

$$T_{vib} = 2 A_1 + 2 E$$

**The Raman activity of the vibrational modes of  $NH_3$  molecule.** The character table for  $C_{3v}$  group is used to obtain the following irreducible representations for the quadratic and binary Cartesian coordinates.

Quadratic and Binary Cartesian Coordinates	Representations.
$z^2$	$A_1$
$(x^2 - y^2, xy); (xz, yz)$	$E$

The representations obtained for the quadratic and binary coordinates ( $z^2; (x^2 - y^2, xy); (xz, yz)$ ) correspond to the symmetry species of the vibrational modes for  $NH_3$  molecule. Therefore, the vibrational modes of  $NH_3$  molecule are Raman active.