STRUCTURE DETERMINATION USING IR & RAMAN SPECTROSCOPY

IR SPECTRUM

- Transitions between the vibrational levels result in the IR spectra.
- For a mode of vibration to be IR active,the vibrational mode must give rise to a change in dipole moment.

Vibrations can be divided into two, depending on dipole moment change:

1. Parallel to the axis of rotational symmetry

2. Perpendicular to the axis of rotational symmetry

RAMAN SPECTRUM

. When a beam of monochromatic light is passed through a trasparent medium the scattered light contains other frequencies in addition to the incident frequency.

. The new lines on the original spectral lines is known as Raman spectra.

. The spectrum contains :

.STOKES LINES

.ANTI-STOKES LINES

For a molecule to be Raman active, there are three criteria:

. Molecular rotation or vibration must produce a change in the shape or size of the polarisability ellipsoid.

. Change in one of the six components of the polarisability tensor.

. It is also judged by the variation of polarisability as a function of some displacement coordinate.

MUTUAL EXCLUSION PRINCIPLE

If a molecule has centre of symmetry then Raman active vibrations are IR inactive and vice versa.

Determination of molecular structure is based on:

- Application of symmetry
- Vibrational selection rules
- State of polarisation of lines
- Observed frequencies

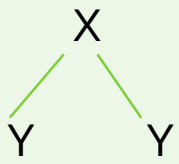
Molecules of type AB_2

Triatomic with possibilities :

- Linear symmetric- CO_2 , CS_2
- Bent symmetric – SO_2
- Linear asymetric- N_2O

* Linear symmetric molecule has to obey rule of mutual exclusion due to centre of symmetry.
* In bend and linear asymmetric three different modes are IR and Raman active.
* If molecule is linear P,R branches are present in IR spectrum while P,Q,R branches are present in non-linear molecules.

Fundamentals of AB_2 type molecule

Model	No.of fundamentals Allowed in IR	No. Permitted in Raman effect	No. Of IR & Raman coincidences	No.of polarized Raman lines
Linear Y—X—Y	2	1	0	1
Bent 	3	3	3	2
Linear Y—Y—X	3	3	3	2

Molecules of type AB_3

. Mainly 2 types

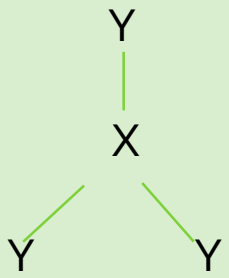
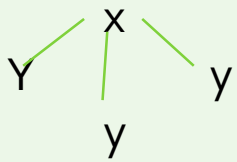
1. symmetric planar
2. symmetric pyramidal

. 3N-6= 6 fundamental vibrations.

. If molecular shape has symmetry this number of fundamental vibration will be reduced by degeneracy.

. In symmetrical planar and pyramidal shapes one stretching mode and one angle deformation mode are each doubly degenerate . So only 4 different fundamental frequencies.

Fundamentals of symmetric AB_3 molecule

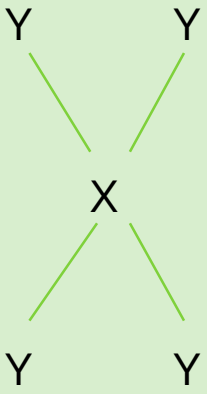
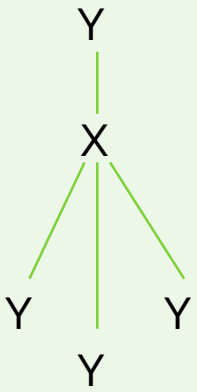
Model	No. Of distinct fundamentals	No. Of fundamentals active in IR	No. Of fundamentals active in Raman	No. Of IR & Raman coincidences	No.of polarized Raman lines
Planar 	4	3	3	2	1
Pyramidal 	4	4	4	4	2

Molecules of type AB_4

- Common models in this category are :

  . Square planar – 7 fundamental modes

  . Tetrahedral – 4 fundamental modes

Model	No. Of distinct fundamentals	No. Of fundamentals active in IR	No. Of fundamentals active in Raman	No. Of IR & Raman coincidences	No.of polarized Raman lines
Square planar 	7	3	3	0	1
Tetrahedral 	4	2	4	2	1

THANK YOU....