# Vibrational Spectroscopy

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- ✓ What are the different types of symmetry elements present in the molecules?
- ✓ How many symmetry operations are generated?
- ✓ It is the symmetry operations that constitute a group.
- ✓ How to represent a group using various functions as the basis?
- ✓ What is reducible representation and how it can be reduced to irreducible representations?
- ✓ We have also learnt about character table of a point group and why these are important to a chemist?

- ✓ Now we will make use of all the knowledge about symmetry and group theory in dealing with the chemical applications of bonding, MO formation vibrational spectra of transitional metal complexes etc.
- ✓ In this discussion, we will discuss vibrational spectroscopy in light of symmetry of the molecule. The Symmetry of the molecules and solids is very important and is very powerful tool in the hand of chemists for understanding of bonding and physical properties.
- ✓ Infrared spectroscopy is one of the most important analytical techniques available to scientists. One of the great advantages of infrared spectroscopy is that any sample in any state may be investigated .Liquids, solutions, pastes, powders, films, fibres, gases and surfaces can all be investigated properly and with accuracy.

- ✓ Infrared spectroscopy is a technique based on the vibrations of the atoms of a molecule.
- ✓ An infrared spectrum is commonly obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed at a particular energy.
- ✓ The energy at which any peak in an absorption spectrum appears corresponds to the frequency of a vibration of a part of a sample molecule. The point group theory of molecular symmetry will now be used for interpreting the vibrational spectra of the molecules.
- ✓ The presence of certain symmetry in molecules greatly reduces the efforts in predicting the molecular properties of molecules.
- ✓ In earlier chapters we have seen that how Γ3N can be obtained and reduced to irreducible representations of the point group to which the molecule belongs. In this chapter we will make use of these principles to have good deal of information's about IR and Raman spectra of the molecules.

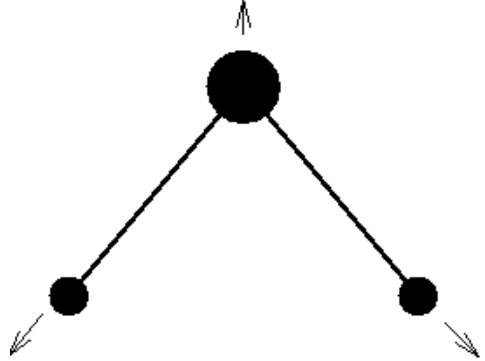
- ✓ A vibrational spectroscopy - IR and Raman are the most common vibrational spectroscopies for assessing molecular motion and fingerprinting species.
- ✓ Routine energy range of IR/Raman is 200 - 4000 $cm^{-1}$ .
- ✓ One of the practical uses of point groups and group theory for the inorganic chemist in is predicting the number of infrared and Raman bands that may be expected from a molecule.
- ✓ Spectroscopic techniques all work on the principle of that, under certain conditions, materials absorb or emit energy. Different spectroscopic techniques operate over different, limited frequency ranges within this broad spectrum, depending on the processes and magnitudes of the energy changes.
- ✓ he infrared region of the spectrum encompasses radiation with wave numbers ranging from about 12,800 to 10 cm-1 or wavelengths from 0.78 to 1000 µm. The infrared spectrum is divided into near-, mid-, and far-infrared radiation. Table -1 gives energy ranges for these regions.

| | | |
|---|---|---|
| Near IR | 15000 $cm^{-1}$ to 3000 $cm^{-1}$ | 0.67 µm – 3.33 µm |
| Mid IR | 4000 $cm^{-1}$ to 400 $cm^{-1}$ | 2.5 µm – 25 µm |
| Far IR | 200 $cm^{-1}$ to 10 $cm^{-1}$ | 50 µm – 1000 µm |
| Most used | 4000 $cm^{-1}$ to 670 $cm^{-1}$ | 2.5 µm – 15 µm |

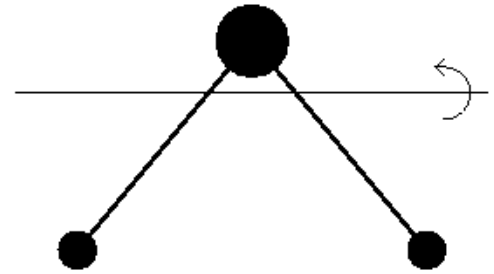
Normal Modes of Vibration

- ✓ The complex vibrations of a molecule are the superposition of relatively simple vibrations called the normal modes of vibration. Each of these vibrational motions involve displacement of the atoms or deformation of angles .These independent displacements/deformations are called normal modes of vibrations of the molecules. These are generally divided in bond stretchings and angle deformations. Each of these vibrational modes occur at characteristics energy/ frequency which is dependent on the strength of restoring force, called as restoring force constant. Each normal mode of vibration has a fixed frequency. It is easy to calculate the expected number of normal modes for a molecule made up of N atoms. For N atomic molecule the degrees of freedom are 3N.

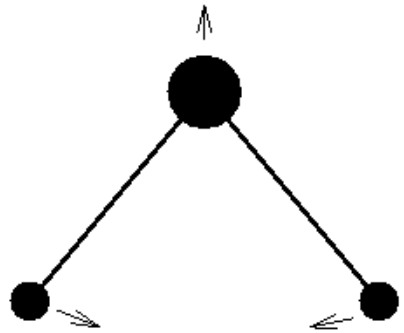
- ✓ Out of these we have to take care of three translational motions along x-,y-,z- axes and three rotational degrees of freedom, Rx, Ry, Rz rotations about x, y, z axes respectively.
- ✓ A mode in which all atoms are moving in the same direction is equivalent to moving the molecule in that direction.
- ✓ A mode in which atoms move to rotate (change the orientation of) the molecule.
- ✓ There are 3 rotational modes for nonlinear molecules, and 2 rotational modes for linear molecules.
- ✓ These motions also occur when molecule absorbs IR radiations.



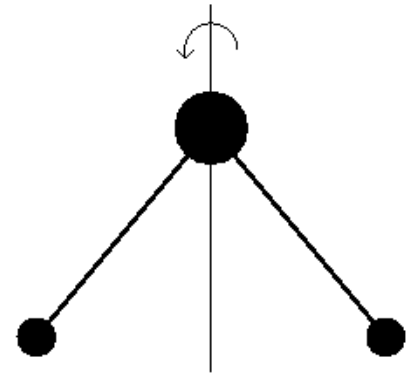
Symmetric stretch, $\nu_1$



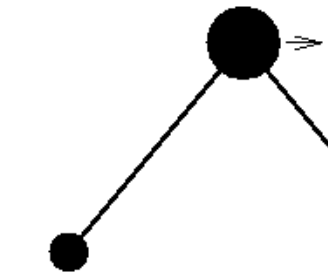
A rotational axis



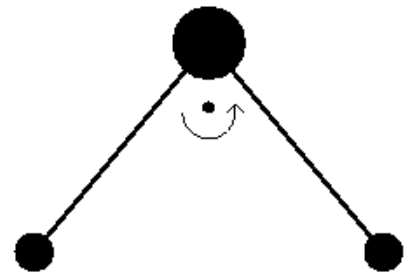
Bending, $\nu_2$



B rotational axis



Anti–symmetric stretch, $\nu_3$

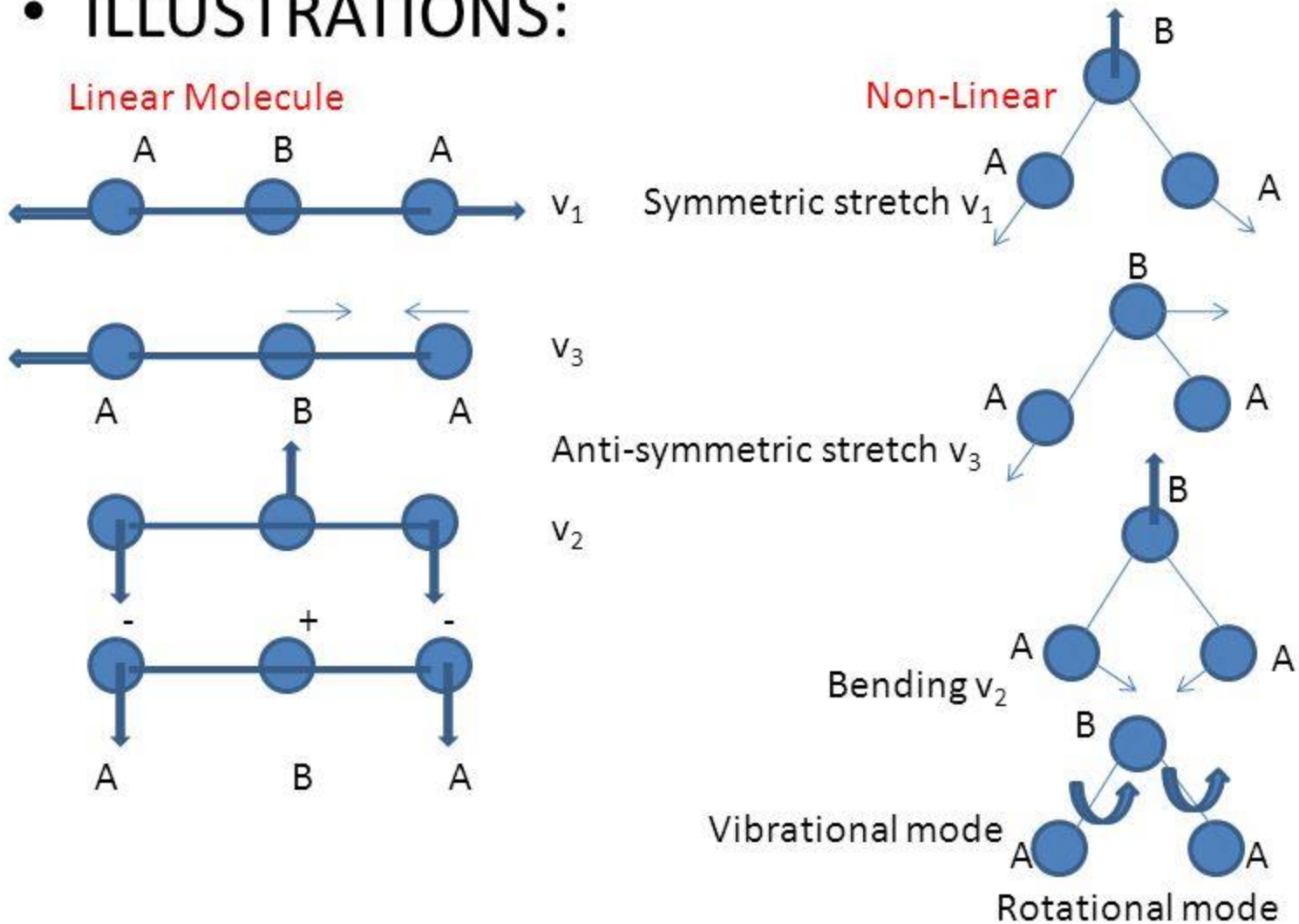


C rotational axis

- ✓ (i) Linear molecule of N atoms has normal modes = 3N – 5 as rotation about molecule is generally forbidden
- ✓ (ii) Nonlinear/bent molecule/ of N atoms has normal modes = 3N - 6
- ✓ The symmetries of the normal modes can be classified with the help of symmetry and group theory.

# DEGREES OF FREEDOM

- ILLUSTRATIONS:

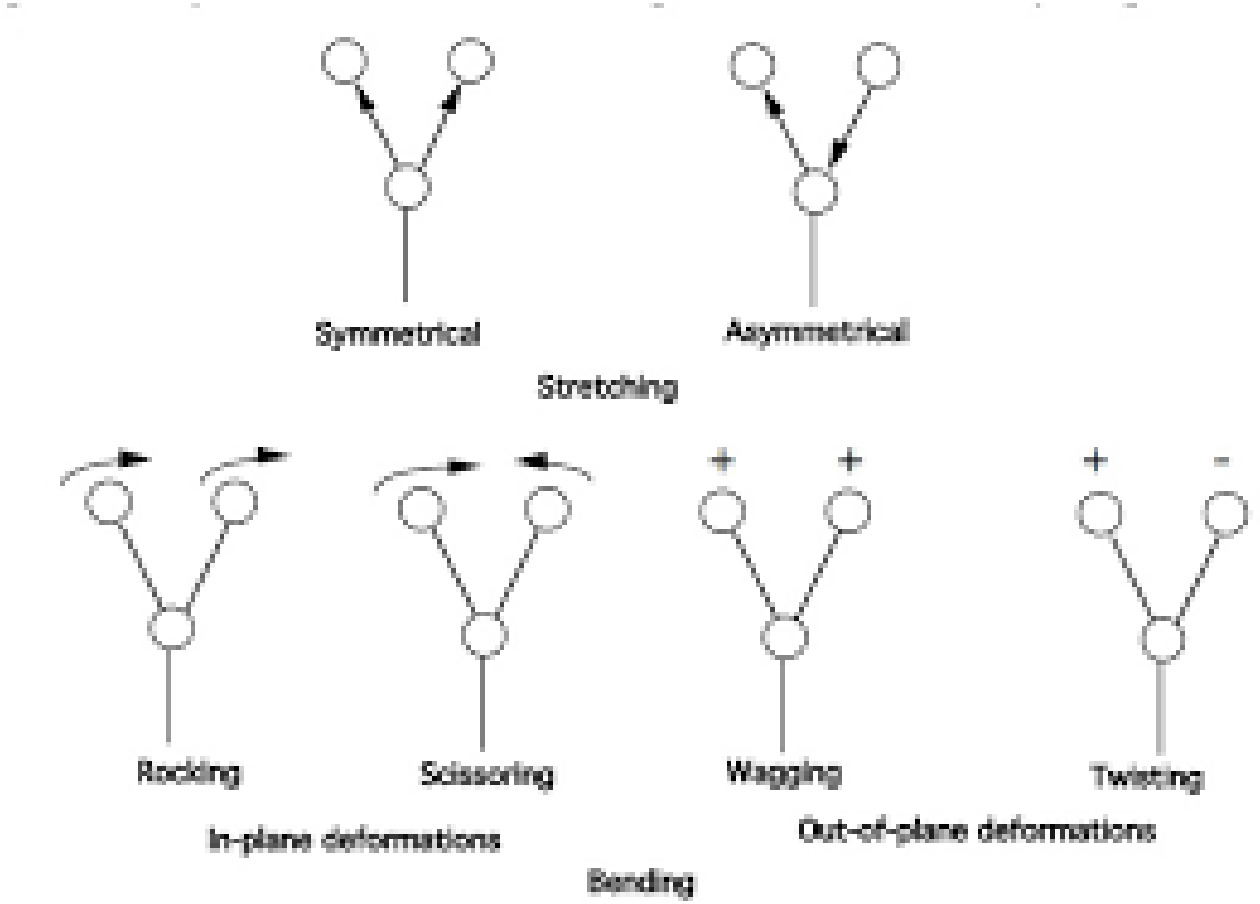


- ✓ All these modes vibrate with different frequency and thus require different energy to occur. How the values these characteristics energy/ frequency are obtained?

  There two complimentary techniques available for this

  (A)Infrared Spectroscopy (IR)

  (B)Raman spectroscopy (R)
- ✓ .Both these techniques when used together provide lot of information about molecular bonding.
- ✓ Let us mention the basic principles of these techniques. The fundamental difference between IR and Raman techniques is that in the former absorption of photons is studied in later case scattering of photons (elastic and non-elastic) is studied.


Symmetrical
Asymmetrical
Stretching
Rocking
Scissoring
Wagging
+
+
+
-
Twisting
In-plane deformations
Out-of-plane deformations
Bending

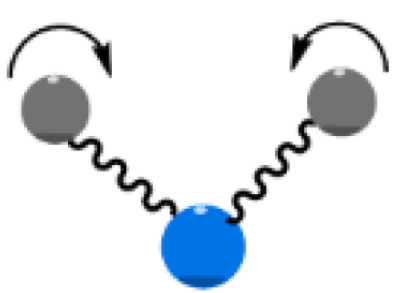
## Stretching Vibrations

Symmetrical



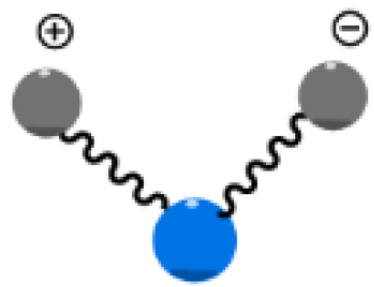
Asymmetrical

## Bending Vibrations

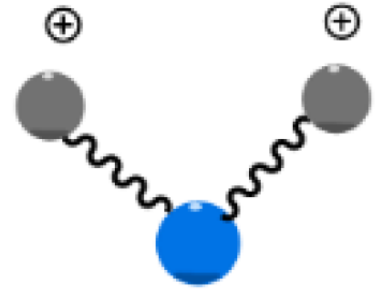


Scissoring

Rocking




Twisting




Wagging

*In plane*

*Out of plane*

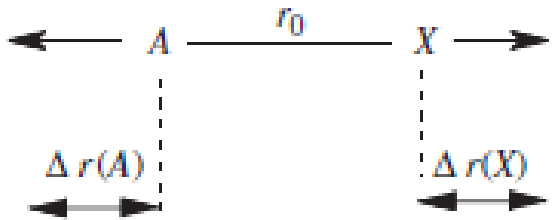
Infrared Spectroscopy (IR):

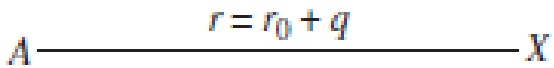
- ✓ In infrared spectroscopy if a sample is irradiated with infrared light, then those frequencies that match the corresponding frequencies of vibrational modes will be absorbed i.e., absorbed frequency can be measured.
- ✓ During infrared radiation on the molecule, rotational motions of the molecule , translational motions of the molecule, vibration of bonds in the molecule and angle deformations in the molecule do occur depending of the frequency range. Rotational and translation motions complicate the investigations. So we have to account for these motions.

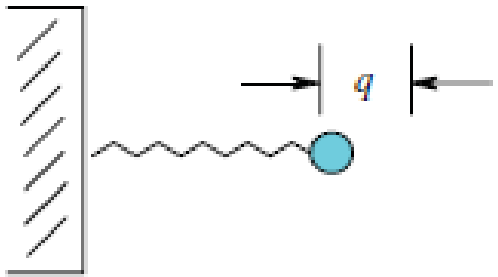
In order the absorption of IR radiations by the molecule occur following two conditions must be satisfied

(a) Dipole moment the molecule must change as a result of molecular vibration. The change in dipole moment allows the electric field component of electromagnet radiations to interact with the molecule's electric diploe moment. The symmetric molecules which do not have dipole moment during vibrations do not interact with the electromagnet radiations. And thus these are IR inactive.

(b) The frequency of IR radiations must match the natural frequency of vibrations of the molecule. If there is mismatch in frequencies there will be absorption of IR radiations.


$r_0$
A
X
$\Delta r(A)$
$\Delta r(X)$


$r = r_0 + q$
A
X

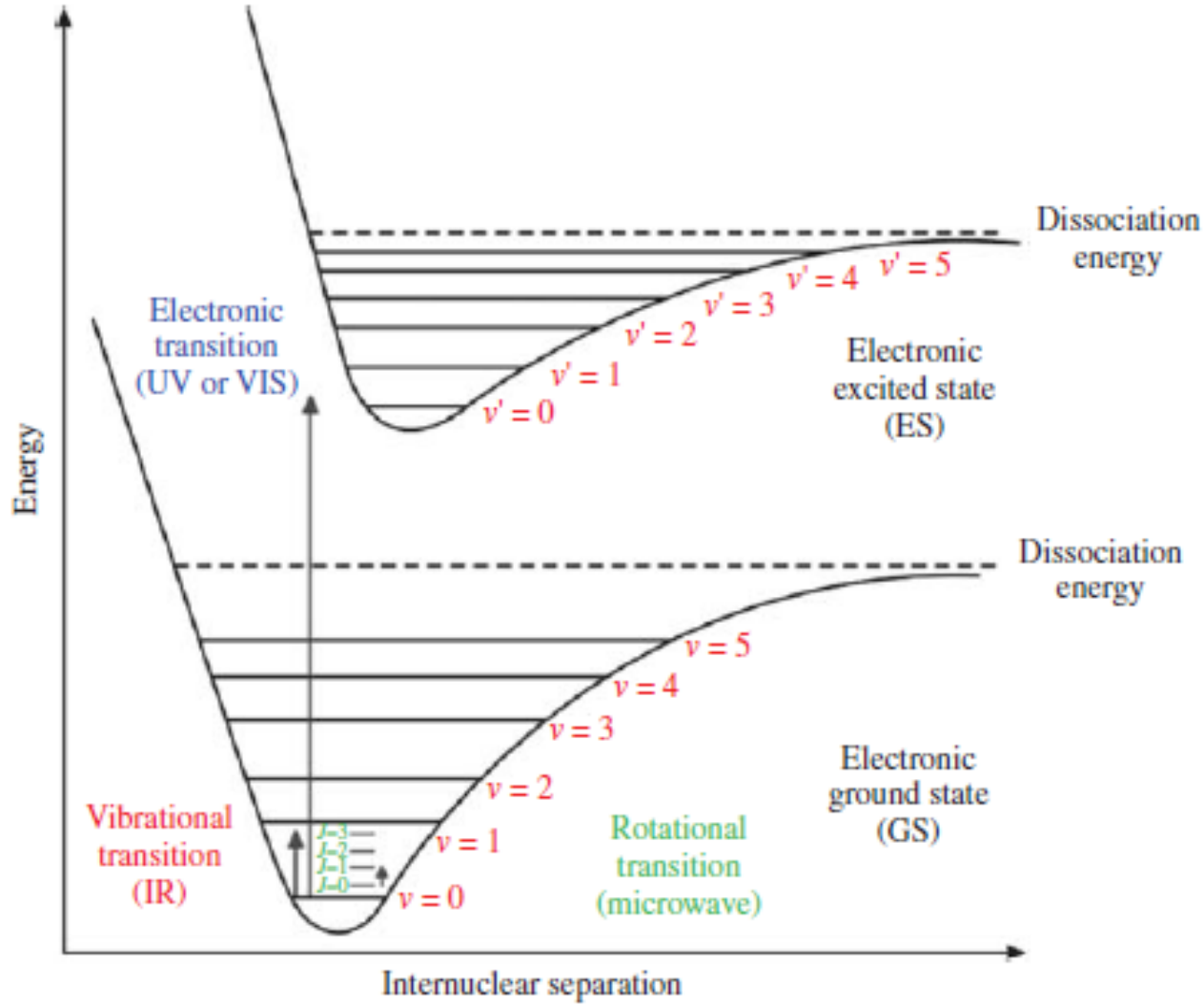

q

- ✓ The three types of molecular transitions may occur during IR radiations.
- ✓ (i)When a molecule rotates about its centre of mass about any one of the axes, the electric field component fluctuates. Due to these fluctuation interactions between external electric field and internal natural electric field absorption of IR radiations may be occur. The transition energy range is of the order $\upsilon$ <100 $cm^{-1}$. Due to this vibrational peak in IR spectrum is further divided and thus complicates the investigations
- ✓ (ii) Vibrational-rotational transitions. This type of transition may arise due to molecular electric dipole moment caused by the combination of bond vibration and molecular rotation.
- ✓ (iii) In mid-IR region most of the important vibrational transitions occur. This frequency range is of the order $\upsilon$ =13000 -675 $cm^{-1}$.

In IR spectroscopy quanta of radiation in IR region have energy comparable to those required for vibrational transitions in molecules. The energy of a molecule is the sum of energies of types

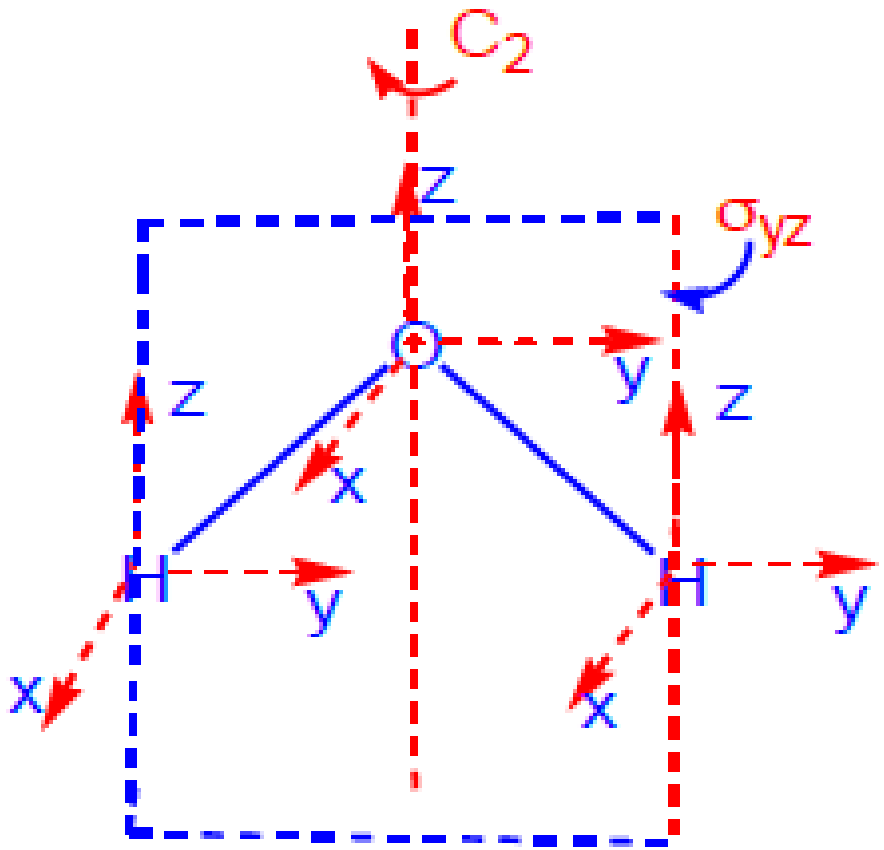
$$E = E_{ele} + E_{vib} + E_{rot} + E_{tra} + E_{nuc}$$

- ✓ $E_{ele}$: is the electronic energy of all the electrons of the molecule
- ✓ $E_{vib}$: is the vibrational energy of the molecule, i.e., the sum of the vibrations of the atoms in the molecule
- ✓ $E_{rot}$: is the rotational energy of the molecule, which can rotate about the three axes, x,y,z
- ✓ $E_{tra}$: is the translational energy of the molecule, which is due to the movement of the molecule as a whole along the three cartesian axes, x, y, z
- ✓ $E_{nuc}$: is the nuclear energy.


Energy
Internuclear separation
Dissociation energy
Electronic excited state (ES)
Electronic transition (UV or VIS)
v' = 0
v' = 1
v' = 2
v' = 3
v' = 4
v' = 5
Dissociation energy
Electronic ground state (GS)
Vibrational transition (IR)
Rotational transition (microwave)
v = 0
v = 1
v = 2
v = 3
v = 4
v = 5
J=3
J=2
J=1
J=0

Generating of reducible representation taking 3N vectors (x,y,z axes)as basis:

- ✓ In this section we will recollect some facts about reducible representations and irreducible representations by taking few examples.
- ✓ Let us take $H_2O$ molecule and make use of 3N Cartesian coordinates on each and every atom as basis for representation. The x,y,z vectors on each atom of $H_2O$ together with various symmetry elements in it are shown in figure


C2
z
σyz
z
y
z
x
H
y
H
y
x
x

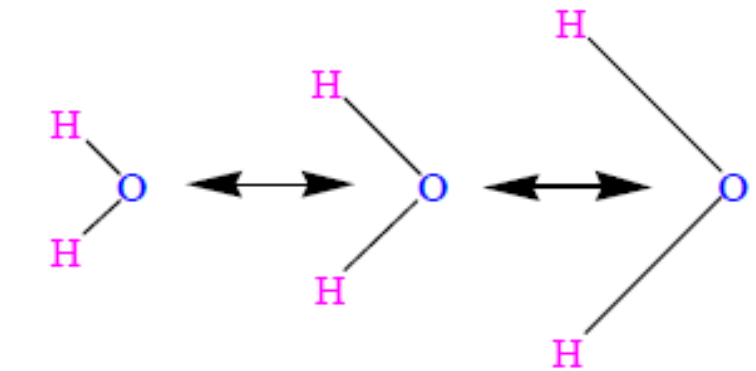
- ✓ Γ3N can be reduced by following standard method and the results are given as;
- ✓ Let us now find how many times A1,A2,B1,B2 irreducible representations are there in Γ3N
- ✓ (A1)=1/4[1x9x1+1x-1x1+1x1x1+1x3x1]=1/4[12]=3 ie 3A1
- ✓ (A2)=1/4[1x9x1+1x-1x1+1x1x-1+1x3x-1]=1/4[4]=1 ie A2
- ✓ (B1)=1/4[1x9x1+1x-1x-1+1x1x1+1x3x-1]=1/4[8]=2 ie 2B1
- ✓ (B2)=1/4[1x9x1+1x-1x-1+1x1x-1+1x3x+1]=1/4[12]=3 ie 3B1
- ✓ Therefore, Γ3N = 3A1+A2+2B1+3B2
- ✓ Since A1, A2, B1, B2 are one dimensional, the sum of their characters for E in Γ3N ie 3+1+2+3 equals to 9 . This gives a cross check of your result.
- ✓ These are the results obtained by taking 3N Cartesian coordinates as the basis. We can get similar results by taking bond vectors as basis for representations.

- ✓ Character tables
- ✓ Associated with each point group is a ‘character table’ which contains information needed to work out all of the properties that depend on the molecular symmetry. These are so important that you will find collections of them in most Inorganic and Physical Chemistry textbooks as well as specialist texts on group theory. The table below is for the C2v point group.

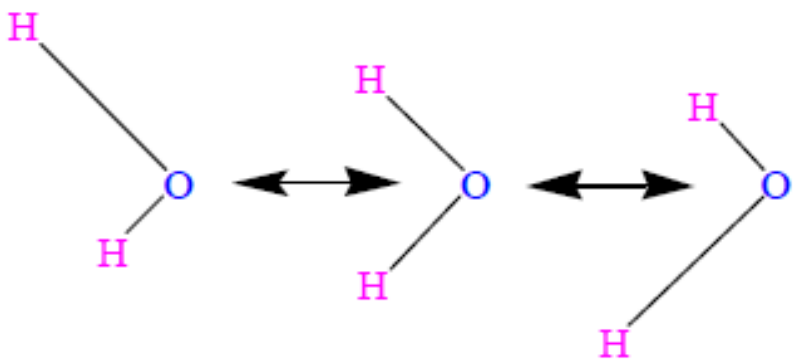
| $C_{2v}$ | E | $C_2$ | $s_v(xz)$ | $s_v(yz)$ | | |
|---|---|---|---|---|---|---|
| $A_1$ | 1 | 1 | 1 | 1 | z | $x^2, y^2, z^2$ |
| $A_2$ | 1 | 1 | -1 | -1 | $R_z$ | xy |
| $B_1$ | 1 | -1 | 1 | -1 | $x, R_y$ | xz |
| $B_2$ | 1 | -1 | -1 | 1 | $y, R_x$ | yz |

- The name of the point group is given in the top, left -hand corner
- The symmetry elements for the group are given on the top row
- The left hand column gives symmetry labels used to label properties such as molecular orbitals and vibrations according to their symmetry
- The numbers in the middle are called ‘characters’ (symbol ? – Greek letter ‘chi’) and represent the effect of the symmetry opera tions on these properties

When the O-H bonds in water vibrate, their motions are coupled together in two ways resulting :




symmetric or in-phase
$?_{sym}$
occurs at 3652 $cm^{-1}$

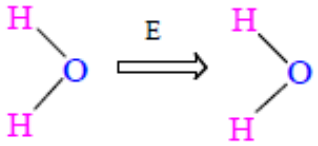
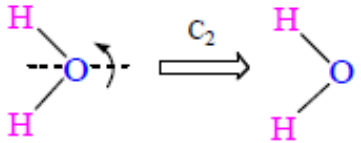
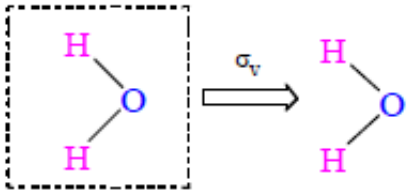
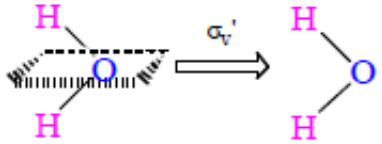



asymmetric or in-phase
$?_{asym}$
occurs at 3756 $cm^{-1}$

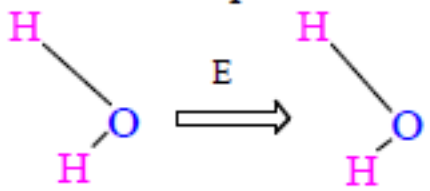
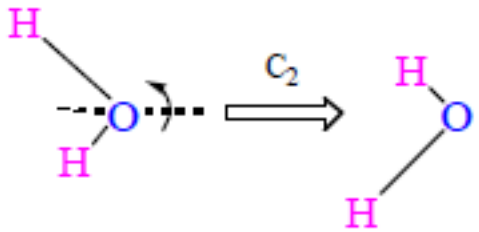
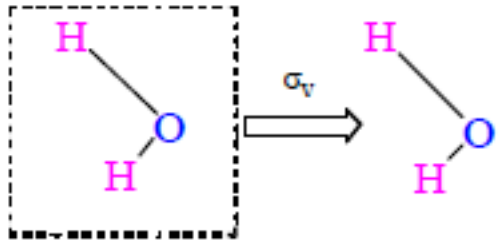
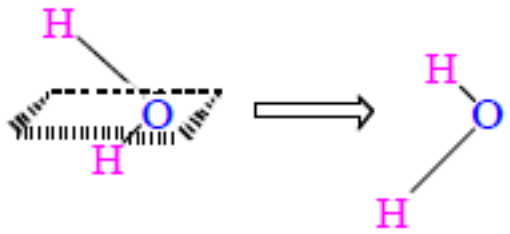
- ✓ Now the effect of each of the C2v symmetry operations on these vibrations is considered. To do this, · imagine the molecule to be frozen at some point in the vibration (but not at the mid-point)
- ✓ · perform each of the symmetry operations on this frozen molecule in turn
- ✓ · the effect of the operation is represented by a +1 if the molecule is completely unchanged
- ✓ · the effect of the operation is represented by a -1 if the molecule is reversed
- ✓ · this collection of numbers or ‘characters’ is then compared to those in the character table to obtain the symmetry label for the vibration.

Symmetric stretch:

Symmetric stretch:

| | effect of operation | character, ? |
|---|---|---|
| E |  | molecule unchanged: +1 |
| $C_2$ |  | molecule unchanged: +1 |
| $s_v$ |  | molecule unchanged: +1 |
| $s_v'$ |  | molecule unchanged: +1 |

Asymmetric stretch:

| | effect of operation | character, ? |
|---|---|---|
| E |  | molecule unchanged: +1 |
| $C_2$ |  | molecule reversed: -1 |
| $s_v$ |  | molecule unchanged: +1 |
| $s_v'$ |  | molecule reversed: -1 |

For the two individual bonds, the characters are then

| | E | $C_2$ | $s_v$ | $s_v'$ |
|---|---|---|---|---|
| two O-H bonds | 2 | 0 | 2 | 0 |

There is no row of the $C_{2v}$ table with these numbers. However, you may have spotted that these numbers are just those that are obtained by adding together the characters obtained for the symmetric and asymmetric stretches.

| | E | $C_2$ | $s_v$ | $s_v'$ |
|---|---|---|---|---|
| symmetric | 1 | 1 | 1 | 1 |
| asymmetric | 1 | -1 | 1 | -1 |
| two O-H bonds | 2 | 0 | 2 | 0 |

+

- ✓ Addition of any other rows together would not lead to the same set of numbers. Thus, if the procedure is carried out in reverse then the symmetry of the vibrations can be worked out by
  - · calculating the number of bonds that are unshifted by the symmetry operations
  - · looking to see which rows add together to give these numbers
- ✓ When the characters generated by a set of objects correspond to a row in the character table, the objects are said to span an ‘irreducible representation’ (or ‘irrep’ or even ‘IR’) of the point group:
- ✓ The symmetric stretch spans the a1 irreducible representation.
- ✓ The asymmetric stretch spans the b1 irreducible representation.
- ✓ When the characters generated by a set of objects correspond to a sum of rows in the character table, the objects are said to span a ‘reducible representation’
- ✓ The two O-H bonds span a reducible representation.