

13/4/2020

levels are given by selection rule between which transition can occur.

The simple selection rule for a harmonic oscillator undergoing vibrational changes as given by

$$\Delta v = \pm 1$$

For absorption is  $\Delta v = +1$  selection rule  $\Delta v = -1$  is not used in vibrational transition.

Transition from  $v=0$  to  $v=1$  or  $v=1$  to  $v=2$  — etc are only allowed and transition from  $v=0$  to  $v=2$  or  $v=2$  to  $v=4$  — etc are not permitted. Hence each mode of vibration would give one band or one ~~spiral~~ spectral line.

### Frequency of spectral band in vibrational spectra —

The equation for the quantised vibrational energy levels is given by,

$$G(v) = E_v = \frac{E_0}{hc} = \left(v + \frac{1}{2}\right) \omega_e \text{ cm}^{-1} \quad \text{--- (1)}$$

Suppose a transition occurs from level  $v$  to  $(v+1)$ , then for quantum number  $v$ ,

$$E_v = \left(v + \frac{1}{2}\right) \omega_e \text{ cm}^{-1} \quad \text{--- (2)}$$

and for quantum number  $v = v+1$  we have

$$E_{v+1} = \left(v+1 + \frac{1}{2}\right) \omega_e \text{ cm}^{-1} \quad \text{--- (3)}$$

using the selection rule ( $\Delta v = +1$ ) we get.

$$\begin{aligned} E_{v+1} \rightarrow v &= \left(v+1 + \frac{1}{2}\right) \omega_e - \left(v + \frac{1}{2}\right) \omega_e \\ &= \omega_e \text{ cm}^{-1} \end{aligned}$$

Because  $\frac{E_0}{hc} = \bar{\nu}_0$  is then

$$\bar{\nu}_{(v+1) \rightarrow v} = \omega_e \text{ cm}^{-1} \quad \text{--- (4)}$$

The frequency of absorption in terms of wave number between any two neighbouring energy levels is equal  $(\omega_e) \text{ cm}^{-1}$ , we directly get the wave number of spectral lines absorbed.

Force Constant -

The vibration of spring the particle attached to the spring also undergoes a periodic motion. Atoms in a molecule which are joined by bonds, are not at rest, but vibrate constantly.

For such a harmonic oscillator according to Hooke's law, restoring force is directly proportional to the displacement.

$$f \propto x \quad \text{or} \quad f = -kx \quad \text{--- (1)}$$

where  $x$  is the displacement of one atom, from its equilibrium position wrt. other atom. Negative sign shows that force  $f$  is restoring force and  $k$  is force constant.

Determination of force constant -

According to classical mechanics, the vibrational frequency of a particle of mass  $m$  connected by a spring of force constant  $k$  is given by -

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m}} \quad \text{--- (2)}$$

CGS unit - dynes/cm.

In case of diatomic molecule like AB the constituting atoms of masses  $m_1$  and  $m_2$  in the molecule vibrate back and forth relative to their centre of mass in opposite direction. Considering their motion to be simple harmonic, the vibrational frequency is given by eq (2) with  $m$  replaced by reduced mass  $\mu$  of the molecule

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \text{ sec}^{-1} \quad \text{--- (3)}$$

$$\mu = \frac{m_1 \times m_2}{m_1 + m_2}$$

Therefore, above frequency in eq (3) is divided by  $C$ , the velocity of light

$$\frac{\nu}{c} = \bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} \text{ cm}^{-1} \quad \text{--- (4)}$$

In calculations of force constant the reduced mass of the molecule  $\mu$  is divided by Avogadro's No.  $N$  Thus

$$\bar{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu N}}$$

$$(\bar{\nu})^2 = \frac{1}{4\pi^2 c^2} \cdot \frac{kN}{\mu}$$

$$\therefore (\bar{\nu})^2 = 17.0 \times \frac{k}{\mu}$$

Degree of Freedom -

One of the independent components of motion (translation, vibration and rotation) of an atom or molecule is called as degree of freedom. It is the number of variables required to describe the motion of a particle completely. A molecule can have three types of degrees of freedom and a total of  $3N$  degree of freedom where  $N$  equals the number of atoms in the molecule.

These degree of freedom can be broken down into 3 categories -

(1) Translational - These are the simplest of the degree of freedom. These entail the movement of the entire molecule's centre of mass. This movement can be ~~comple~~ completely described by three orthogonal vectors and thus contains 3 degree of freedom.

(2) Rotational - These are rotations around the centre of mass of the molecule and like the translational movement they can be completely described by three orthogonal vectors. It means contain only 3 degree of freedom. Linear molecule only two degree of freedom are present due to the rotation along the bonds in the molecule having a negligible inertia.

(3) Vibrational - These are any other types of movement not assigned to rotational or translational and thus there are  $3N - 6$  degree of vibrational freedom for a nonlinear molecule and  $3N - 5$  for a linear molecule. These molecule vibration include bending, stretching, wiggling and many other.

Example - Find vibrational degree of freedom in  $O_2$  molecule.

Soln. -  $O_2$  is a linear molecule it has  $N = 2$   
∴ Degree of freedom =  $3N - 5 = 3 \times 2 - 5$   
 $= 1$

## Modes of Vibration

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In this model, the balls represent atoms of different masses and weightless springs of varying strengths correspond to the covalent bonds of different strengths of the molecule.

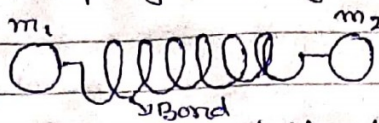


Fig - A covalent bond holding two balls

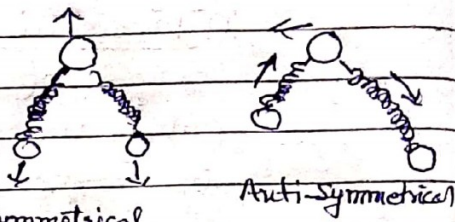
The covalent bonds are always in a state of continuous vibration. There are two types of fundamental vibrations in the molecules.

(1) Stretching - The stretching vibration are of two types - symmetrical and anti symmetrical. If all the bonds in a molecule stretch simultaneously,

the vibrations are called symmetrical vibrations. In anti symmetrical vibrations, all the bonds are not

stretched simultaneously, if

one bond is stretched, the other is compressed. These are in Fig. -



Symmetrical

Anti-Symmetrical

is compressed. These are in Fig. -

(2) Bending vibration - Vibrations in which any group vibrates perpendicular to the bond length is called bending vibrations. These may be classified as given below -

(a) Scissoring - In this the atoms vibrate similar to the blades of a scissor. Any two atoms come close to each other or move away from each other together.

(b) Wagging - Vibration perpendicular to the plane of the molecule and both atoms go one side once and other side second time together. When the vibration is called wagging vibration

(c) Twisting - Perpendicular vibration to the plane are called twisting vibration provided one atomic moves towards one side of the plane and the other towards other side of the plane. Atom with + sign goes away from the viewer and with - sign moves towards viewer together. After one vibration is reversed.

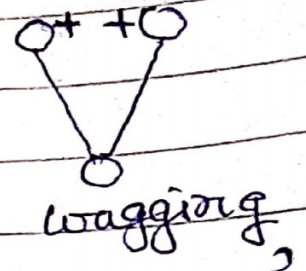
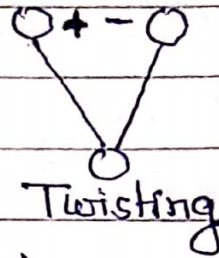
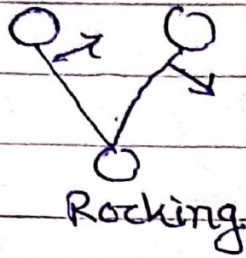
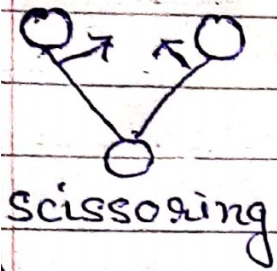
These shows in given fig -

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In plane Deformations

out of plane Deformations



In plane

out of plane

Fig - Different types of Bending vibrations

d) Rocking - When molecule vibrates in its own plane without deformation the vibration is called rocking. In these vibrations bonds are not changed. These are similar to rocking chairs.

Table 10.4. Characteristic Frequencies of some Functional Groups

Functional group	Vibrational Frequency ( $\text{cm}^{-1}$ )	Functional group	Vibrational frequency ( $\text{cm}^{-1}$ )
- OH	3600	$> \text{C} = \text{O}$	1750 - 1600
- NH <sub>2</sub>	3400	$> \text{C} = \text{C} <$	1650
$\equiv \text{CH}$	3300	$> \text{C} = \text{N} <$	1600
= CH <sub>2</sub>	3030	$\begin{array}{l} \rhd \text{C} - \text{C} \leftarrow \\ \rhd \text{C} - \text{N} < \\ \rhd \text{C} - \text{O} < \end{array}$ }	1200 - 1000
- CH <sub>3</sub>	2970 (asym. stretch) 2870 (sym. stretch) 1460 (asym. deform) 1375 (sym. deform)	$> \text{C} = \text{S}$	1100
- CH <sub>2</sub> -	2930 (asym. stretch) 2860 (sym. stretch) 1470 (deformation)	$\rhd \text{C} - \text{Cl}$ $\rhd \text{C} - \text{Br}$ $\rhd \text{C} - \text{I}$	725 650 550
- C $\equiv$ N	2250		
- C $\equiv$ C -	2220		

**Exercise**