

INFRARED SPECTROSCOPY

SC

It is a powerful technique for chemical identification. It gives important information about the structure of compounds.

IR spectra originate from the absorption of energy by a molecule in IR region and the transition occurs between two vibrational levels.

IR region extends from the end of visible spectrum to microwave region. It is divided into three regions.

U.V	VISIBLE	R	IR	MICROWAVE
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IR

↓
Near IR
(Covetone
region)
 $0.8 - 2.5 \mu\text{m}$.

↓
Middle IR
(Vib & Rot
region)
 $2.5 - 15 \mu\text{m}$.

↓
Far IR
(ROT. region),
 $150 - 2000 \mu\text{m}$.

$2.5 - 45 \mu\text{m}$

↓
Group frequency
region.
 $2.5 - 8 \mu\text{m}$.

↓
Finger Print
region
 $8 - 15.4 \mu\text{m}$.

Group frequency region - Stretching vibrations of heteronuclear diatomic molecules.

Finger Print region - Stretching and bending vibrations of polyatomic molecules. As this absorption region is very useful in the identification of functional groups, this region is called as finger print region.

Theory :-

1) Correct λ of radiation :-

The molecule will absorb IR radiation only when the energy difference between the two vibrational levels matches with the frequency of incident radiation. After absorbing the radiation, the molecule will vibrate at an increased amplitude.

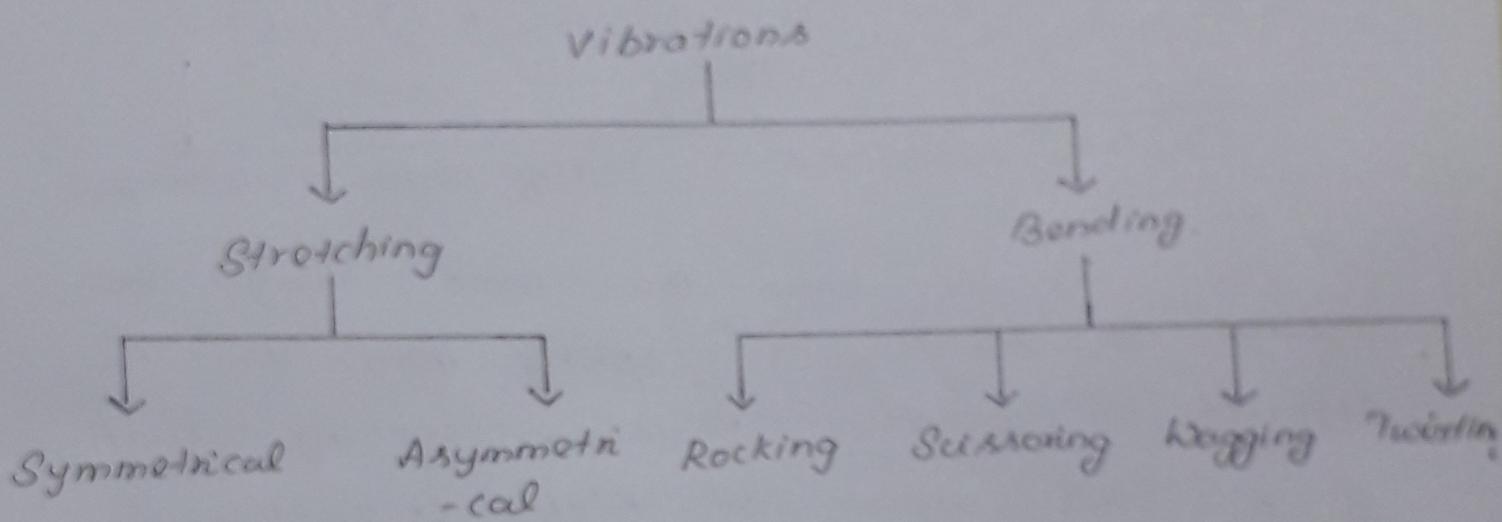
2) Electric Dipole :-

Some molecules have dipole moment by nature i.e. they possess permanent dipole moment. But for some molecules dipole moment will be produced after absorption of IR radiation.

Hence change in dipole moment in a molecule by the absorption of IR radiation is a basic requirement for a compound to be IR active.

O_2 and N_2 do not possess electric dipole. Hence they can not be excited by IR radiation and thus they do not give rise to IR absorption spectra. However H_2O & CO_2 absorb IR radiation because they possess dipole moment.

After absorbing IR radiation, various types of vibrations can take place.



Stretching Vibrations :-

In this type, the bond length between the two atoms increases or decreases, but the axis remains same.

1) Symmetrical Stretching :-

The movement of atoms with respect to the central atom in a molecule takes place in the same direction.



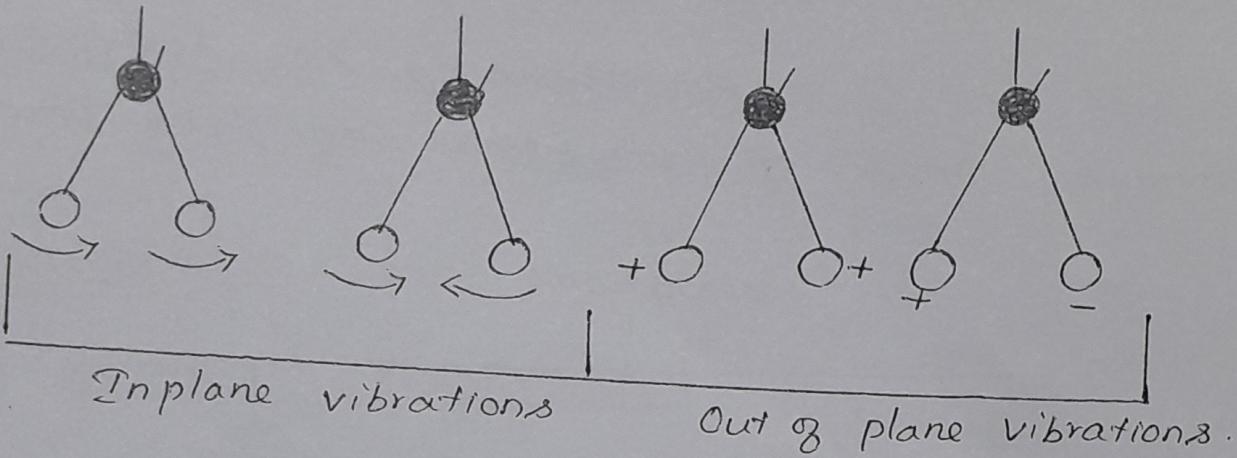
2) Asymmetrical Stretching :-

In this type one atom moves away while the other moves towards the central atom.



Bending Vibrations :-

In this type of vibrations, the position of the atom changes w.r.t. the original bond axis.



We know that more energy is required to stretch a spring than that is required to bend it. Thus, stretching vibrations of a bond appear at high frequencies when compared to bending vibrations.

a) Rocking :-

In this type, the two atoms move in the same direction.

b) Scissoring :-

In this type, the two atoms approach each other.

c) Wagging :-

In this type, the two atoms either move up or down w.r.t. the plane w.r.t. the

These transitions are spectroscopically forbidden.

For a molecule to absorb MW radiation, it should possess a permanent dipole moment.

Infra Red Spectroscopy :

Hooke's Law :

The value of stretching vibrational frequency of a bond can be calculated accurately by the application of Hooke's law which may be represented as

$$\frac{v}{c} = \bar{v} = \frac{1}{2\pi c} \left[\frac{\frac{k}{m_1 m_2}}{m_1 + m_2} \right]^{\frac{1}{2}}$$

$$= \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}.$$

where μ is the reduced mass.

m_1 & m_2 are the masses of atoms in a particular bond.

k - force constant of the bond and relates to

It is approximately 5×10^5 g/sec². It becomes double and triple for the double & triple bond respectively.

C = Velocity of radiation = 2.998×10^{10} cm/sec⁻¹.

∴ the value of vibrational frequency (ν) or wave number ($\bar{\nu}$) depends on

- i) Bond strength & ii) Reduced mass.

Clearly, if the bond strength increases or the reduced mass decreases, the value of the vibrational frequency increases.

Condition for IR active:

- 1) Correct λ of radiation:

The molecule will absorb IR radiation only when the energy difference between the two vibrational level matches with the frequency of incident radiation. After absorbing the radiation, the molecule will vibrate at an increased amplitude.

- 2) Electric Dipole:

Some molecules have dipole moment by nature i.e. they possess permanent dipole moment.

But for some molecules dipole moment will be produced after absorption of IR radiation.

Hence, a change in dipolemoment in a molecule by the absorption of IR radiation is a basic requirement for a compound to be IR active.

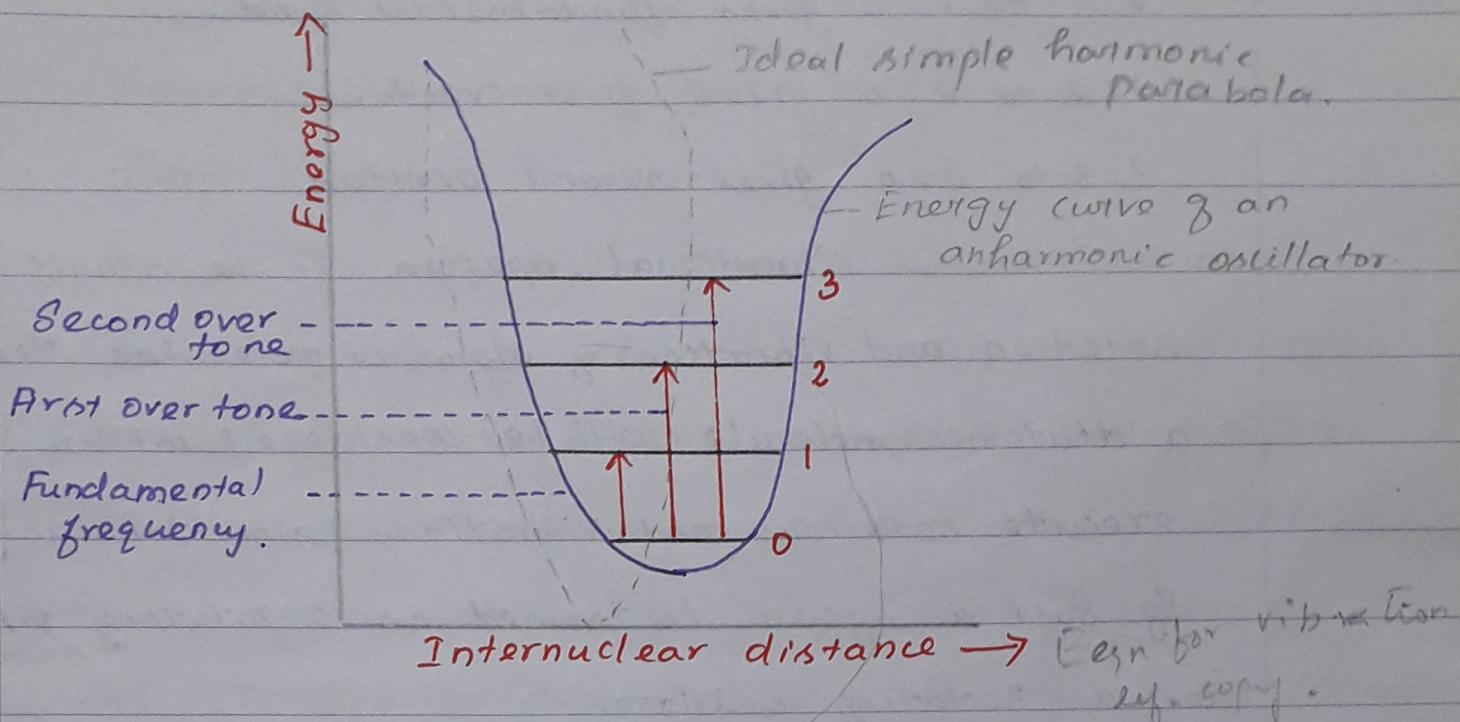
Symmetric diatomic molecules like O_2 & N_2 do not possess electric dipole. Hence, it can not be excited by IR radiation and thus they do not give rise to IR absorption spectra. However H_2O & CO_2 absorb IR radiation because they possess dipolemoment.

Selection Rule:

1. Molecules to absorb IR radiation, there must be a change in dipolemoment as it vibrates.
2. In the absorption of radiations, only transitions for which $\Delta v \pm 1$ can occur.

The transition from $v_0 \rightarrow v_1$ is allowed. The frequency corresponding to this vibration is called fundamental frequency. Transition from $v_0 \rightarrow v_2$ or v_3 are not theoretically possible. But due to anharmonicity, these transitions do occur.

Hence the transition from $v_0 \rightarrow v_2$ is called first overtone and $v_0 \rightarrow v_3$ is called second overtone.



Vibrational Spectra of diatomic molecules: (10)

Selection Rule :

Real molecules do not obey exactly the laws of simple harmonic motion. The bonds in real molecules are known as real bonds. Although, real bonds may be considered to be perfectly elastic, obeying Hooke's law, at larger distortions they deviate from the behaviour of Hooke's law.

The selection rules for all the transitions in anharmonic oscillator may be given as:

$$\Delta v = \pm 1, \pm 2, \pm 3 \dots$$

for these transitions in which

$v=1$ to $v=0$ gives fundamental band.

$v=2$ to $v=0$ gives first overtone.

$v=3$ to $v=0$ gives second overtone.

Vibrational spectra is the result of rotation and vibration of atoms or molecules. Hence, a diatomic molecule will be considered which can execute rotations and vibrations simultaneously. Such a system is termed as a rotating vibrator (or) a rotating oscillator.

Application of Vib-Rot spectra of diatomic molecules.

Selection Rule for heteronuclear diatomic molecule - CO :

The IR spectrum of a simple heteronuclear diatomic molecule reveals a series of regularly spaced peaks.

The vibration of C-O bond is described by the harmonic oscillator model. The energy levels of a harmonic oscillator is given by

$$E_V = \omega (V + \frac{1}{2})$$

V - vibrational quantum no. ($V=0, 1, 2, \dots$)

ω - harmonic frequency.

$$\omega = \sqrt{\frac{k}{\mu}}$$

k - spring constant

μ - reduced mass of the diatomic molecule.

$$\left[\because \mu = \frac{m_C m_O}{m_C + m_O} \right]$$

m_C - mass of carbon atom

m_O - " " oxygen atom.

The rotational levels of CO can be described as rigid rotor model is hence

$$E_J = B J (J+1)$$

J - Rotational quantum no. B - Rotation constant.
($0, 1, 2, 3, \dots$)

$$\therefore B = \frac{\hbar}{8\pi^2 I C}$$

∴ The combined rotational-vibrational energy can be obtained by

$$E_{v,J} = \omega(v+\frac{1}{2}) + BJ(J+1)$$

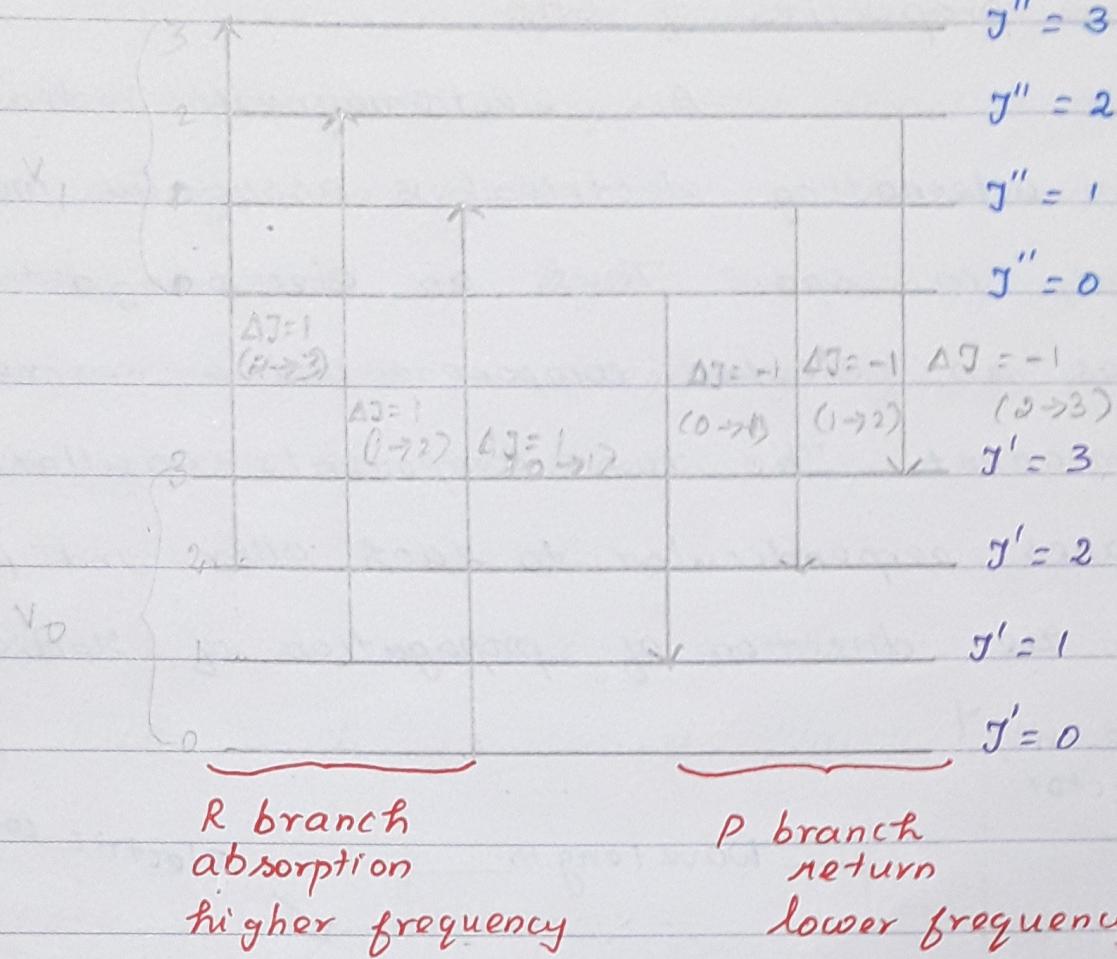
When CO absorbs a photon of IR light there can be change in vibrational & rotational quantum no.

At room temperature, nearly all CO molecules will be present in ground state of vibrational energy level ($v=0$) and hence the possible transition is $v_0 \rightarrow v_1$ only.

But a wide range of rotational states are there in one vibrational level & hence the molecule occupy almost all the rotational energy levels & hence several rotational transitions ($\Delta J = \pm 1$) are possible for a single $v_0 \rightarrow v_1$ jump.

The rotational-vibrational transitions for CO molecule is shown in the figure. The ground state is assigned with single prime ('') and excited state as double prime ("').

For a single jump of $v_0 \rightarrow v_1$, it involves both increase & decrease of rotational



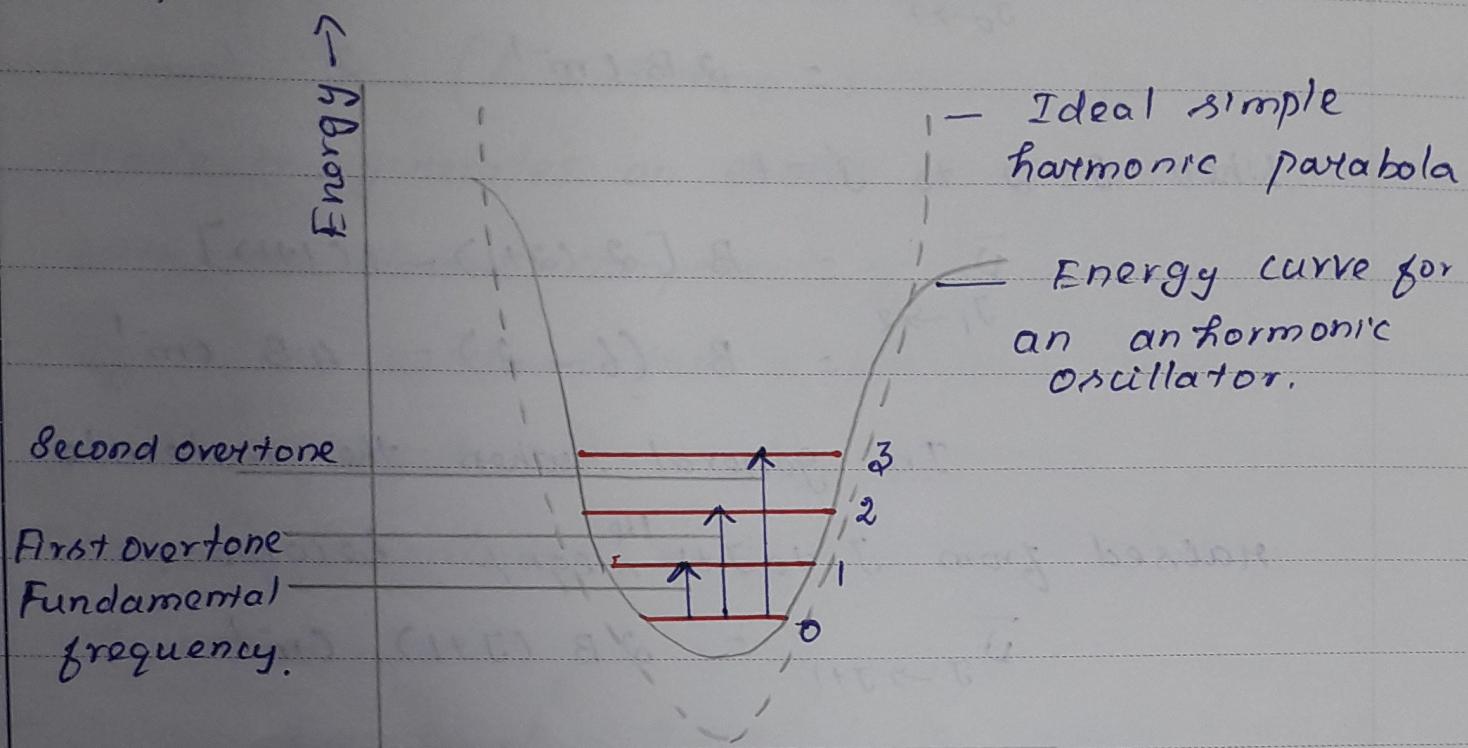
quantum nos/.

Decrease in rotational quantum no. $\Delta J = -1$ transitions are called P branch which appear in lower frequency.

Increase in rotational quantum no. $\Delta J = +1$ transitions are called R branch which appear in higher frequency.

For, CO there are 3 P branch and 3 R branch transitions.

Vibrational spectra of a diatomic molecule undergoing simple harmonic motion.



Inter nuclear distance \rightarrow .

Vibrations of a diatomic molecule may be considered as the vibrations of a simple harmonic oscillator. The vibrational energy of harmonic oscillator from wave mechanics is given by

$$EV = (v + \frac{1}{2}) \hbar \omega c$$

v - vibrational quantum no. which may takes on values 0, 1, 2 etc.

ω - fundamental frequency of vibration of the oscillator.

Light

It is evident from the above eqn/.. that when an oscillating molecule is in its rotational level i.e. when $v=0$, the energy becomes

$$E = \frac{1}{2} \hbar c \omega$$

This residual energy is usually known as zero point energy of the molecule.

Now, for a vibrational transition from any level v' to another of quantum no. v , the energy difference will be given by

$$\Delta E_v = E_v - E_{v'} = (v + \frac{1}{2}) \hbar c \omega - (v' + \frac{1}{2}) \hbar c \omega$$

$$\Delta E_v = (v - v') \hbar c \omega.$$

where $v - v'$ is the frequency of lines in the spectrum. This frequency has been expressed as wave number.

\therefore the above eqn. becomes

$$\bar{\nu} = \omega \pm \frac{\hbar}{8\pi^2 I C}$$

For vibrational rotational spectra of a diatomic molecule as a harmonic oscillator & a rigid rotator

$$E_{vr} = E_{TOTAL} = (v + \frac{1}{2}) \hbar c \bar{\omega} + \frac{\hbar^2}{8\pi^2 I C} J(J+1)$$

$$\bar{\nu} = \omega + \frac{\hbar}{8\pi^2 I C} \cdot J$$

P - Q - R bands.

The vibrational rotational spectrum of a substance does not occur in the form of a single line, but a number of lines appear on either side of the expected position.

Consider the eqn.

$$\tilde{V} = \omega \pm \frac{\hbar}{8\pi^2 I c} \cdot J$$

The first term ω in the eqn. gives the origin of centre of the fundamental band due to one step change in vibrational transition.

The second term $\pm \hbar/8\pi^2 I c$ gives the rotational fine structure because of rotational transition.

If J is positive, then the lines will appear on the higher frequency. These lines are known as R- branch of the vibration-rotation band. If J is negative, it corresponds to lower frequency. These lines are known as P branch of the vibration-rotation band. J may be close to zero. In this case vibrational transition is not accompanied by any significant rotational changes.

In general, a vibrational rotational band may display three branches corresponding to three cases

$\Delta J = +1$ R- branch

$\Delta J = 0$ Q- branch

$\Delta J = -1$ P- branch.

Significance of selection rules in spectroscopy:

The molecular spectra are generally governed by selection rules, which specify the changes in quantum numbers accompanying a particular transition. The selection rules are in fact, the basis of spectroscopy and have been obtained by making use of quantum theory of interaction of radiation with matter. In the absence of selection rules, the resulting spectrum would be very chaotic. For ex., the selection rule for a pure rotational transition for a diatomic molecule such as CO , H_2 , NO etc is $\Delta J = \pm 1$, where J represents the rotational quantum no. Similarly the selection rule for a pure vibrational transition is $\Delta v = \pm 1$ where v is the vibrational quantum no.