

## 2. ELECTROMAGNETIC RADIATION THEORY—NATURE OF ELECTROMAGNETIC RADIATIONS

### I. What is Electromagnetic Radiation ?

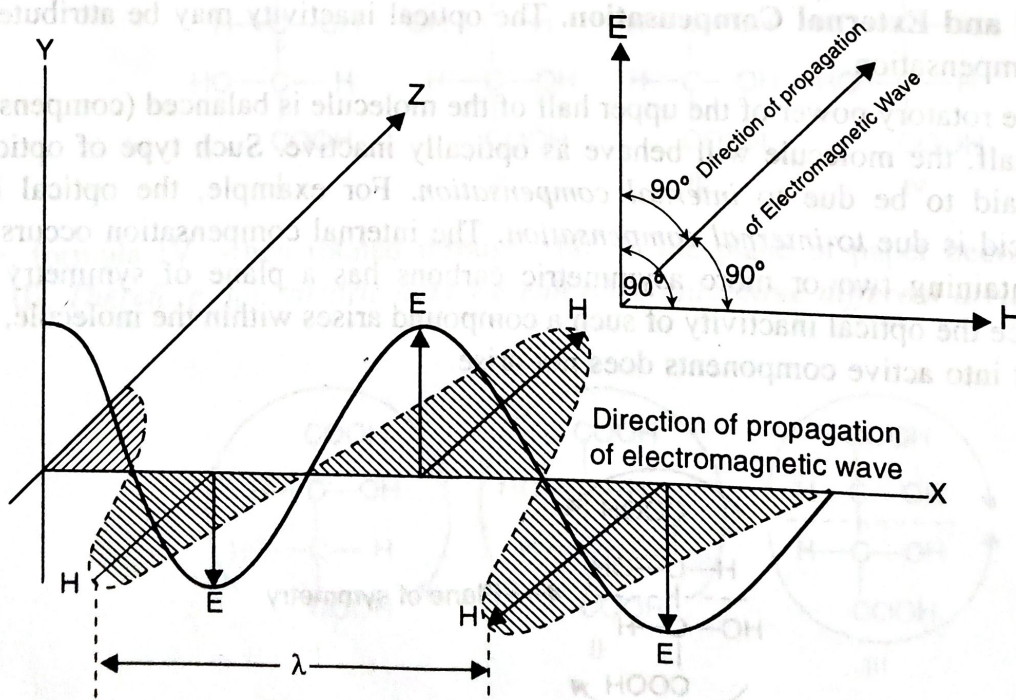
Maxwell suggested that an alternating current of high frequency is capable of radiating energy in the form of waves, which travel in space with the speed of light. He called these waves as *electromagnetic waves* or *electromagnetic radiations*. The electromagnetic radiations are so named because they consist of oscillating electric and magnetic fields (vectors) directed perpendicularly to each other and perpendicular to the direction of the propagation of the wave, as shown in Fig. 9.15.

Thus electromagnetic waves (or radiations) possess electrical and magnetic properties. The examples of electromagnetic radiations are radio waves, visible light (ordinary light), infrared light, ultraviolet light, X-rays and  $\gamma$ -rays.

*Difference between matter waves and electromagnetic waves.* 1. The matter waves are produced by the actual displacement of the particles of the medium, as in case of water or sound waves. But, the electromagnetic waves are produced by a periodic motion of charged particles. Hence vibratory motion of electrons would cause a wave train of oscillating electric and magnetic fields.

2. Matter waves require a medium for transmission or propagation. However, electromagnetic waves do not require any medium for their propagation, *i.e.*, they travel through empty space.

3. Electromagnetic waves travel with the velocity of light, whereas the velocity of matter wave is very-very low. In fact, the speed of matter wave is the speed of the particles themselves.



**Fig. 9.15.** An electromagnetic wave; *E* is the electrical vector; *H* is the magnetic vector. Both oscillate in perpendicular planes.



## II. Characteristics of Electromagnetic Radiations

General characteristics of electromagnetic radiations are :

- (i) All the electromagnetic radiations (waves) are associated with oscillating electrical and magnetic vectors at right angle to each other and also right angle to the direction of propagation.
- (ii) All the electromagnetic radiations have the same speed in vacuum. They travel in vacuum (space) with the speed of light. But their speeds are reduced in material media and to different extent. Thus mixture of electromagnetic radiations can be separated out into components.
- (iii) Energy can be transmitted through space by electromagnetic waves.
- (iv) Different types of electromagnetic radiations differ from one another in their wavelength (or frequency).
- (v) Since velocity of all types of electromagnetic radiations is constant, the greater the frequency of radiation, the shorter is its wavelength.

(vi) A radiation (electromagnetic) is characterised by the nature of its wave which are characterised by the following wave properties :

(a) *Wavelength* ( $\lambda$ ). It is the straight distance between two successive crests or troughs of the wave. It is denoted by  $\lambda$  and is expressed in terms of cm, metre, or angstrom ( $\text{\AA}$ ).

$$1 \text{ \AA} = 10^{-8} \text{ cm} = 10^{-10} \text{ metres}$$

(b) *Wave number* ( $\bar{\nu}$ ). It is defined as the number of wavelengths which can be accommodated in one cm length along the direction of propagation. It is denoted by ( $\bar{\nu}$ ). Hence

$$\bar{\nu} = \frac{1}{\lambda}$$

The wave number is generally expressed in the unit of  $\text{cm}^{-1}$ .

(c) *Frequency* ( $\nu$ ). It is defined as the number of times a wave passes a given point in one second. It is denoted by  $\nu$  (nu) and is expressed in hertz (Hz), kilocycles or kilohertz (kHz), megacycles or megahertz (MHz)

$$1 \text{ MHz} = 10^3 \text{ kHz} = 10^6 \text{ Hz}$$

It is important to note that the wave of high frequency has a shorter wavelength, while a wave of low frequency has a longer wavelength.

(d) *Time period* ( $T$ ). It is the time-interval between two consecutive (successive) crests or troughs. It is denoted by ( $T$ ). Its unit is seconds.

(e) *Amplitude* ( $A$ ). It is the maximum displacement of oscillation or wave from propagation path in any one direction.

(f) *Wave front*. It is defined as the plane at right angle to the direction of propagation of wave.

(g) *Velocity*. It is defined as the distance through which the wave front of the given wave travels in one second along the direction of propagation. It is denoted by  $C$ .

The various types of electromagnetic radiations have different wavelengths and frequencies, but travel with the same speed (*i.e.*, speed of light) in the vacuum (space). This velocity is  $3.0 \times 10^{10}$  cm/sec; which is, in fact, the velocity of light.

*Inter-relationships of wave parameters.*

$$(a) \quad c = \nu \cdot \lambda$$

$$(b) \quad \bar{\nu} = \frac{1}{\lambda} = \frac{\nu}{c}$$

$$(c) \quad \nu = \frac{c}{\lambda} = c \cdot \bar{\nu}$$

$$(d) \quad \nu = \frac{1}{T}$$

$$(e) \quad c = \nu \cdot \lambda = \frac{\lambda}{T}$$



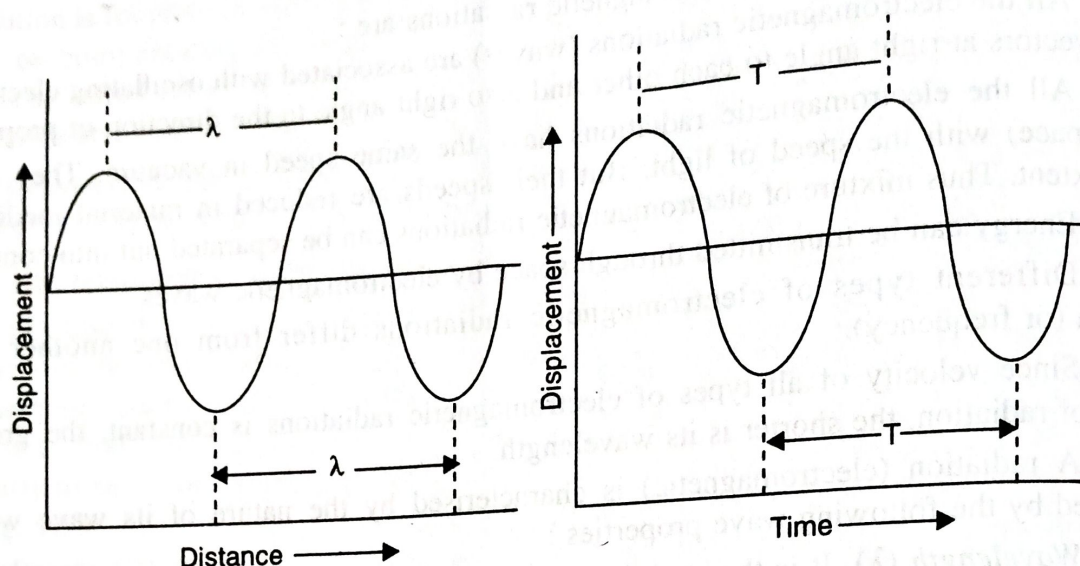


Fig. 9.16. Wave characteristics.

### III. Electromagnetic Theory of Light

In 1865 Maxwell postulated that light also was an electromagnetic phenomenon and thus electromagnetic theory of light was born, which established an essential identity between light and electricity. According to this theory, *light is considered as the result of rapidly alternating displacement currents in the medium, which give rise to magnetic effects. The two fields, the electric and magnetic, inseparably associated, the one varying proportionately with the other and the variation of one giving rise to the other, urge each other forward with a finite velocity, i.e., that of light.* The fact that the mutually perpendicular electric and magnetic fields are always confined to a plane perpendicular to the direction of propagation, accounts very well for the transverse nature of light.

### IV. Conclusions drawn from Electromagnetic Theory of Radiations

The following are conclusions drawn from electromagnetic theory of radiations :

1. *Unification of Various Types of Radiations – The Electromagnetic Spectrum.* The electromagnetic waves (or radiations) originate as a result of the periodic motion (oscillation) of the electric charges. Now if light waves be electromagnetic, they must have their origin also in periodic motion of electric charges. Spectroscopic study shows that each element has a characteristic spectrum which, it may be assumed, arises from the atoms and molecules of the element. From this we may conclude that the atoms and molecules contain electric charges, the vibrations of which send out electromagnetic radiations. The electromagnetic waves, emitted by gamut of radiations, cover a very wide range of frequencies or wavelengths, forming a long electromagnetic spectrum is the arrangement of various types of electromagnetic radiations in order of their increasing (or decreasing) wavelengths (or frequencies). This spectrum is shown in the chart below, where it is seen that essentially same electromagnetic radiation is called by different names, according to different frequencies and the corresponding wavelengths involved. All the electromagnetic radiations are propagated with the same velocity through space, devoid of matter and all consist of alternating electric and magnetic fields in mutually perpendicular directions. This wonderful synthesis of all types of radiations is one of the greatest achievements of the electromagnetic theory of Maxwell.



Electromagnetic Spectrum Chart

Class	Wavelength (cm)	Wave number (cm <sup>-1</sup> )	Frequency	Uses
Cosmic rays	$\sim 10^{-11}$	$\sim 10^{11}$	$\sim 10^{23}$	X-ray crystallography and medical diagnosis
$\gamma$ rays	$\sim 10^{-9}$	$\sim 10^9$	$6 \times 10^{23}$ to $3 \times 10^{18}$	
X-rays	$\sim 10^{-7}$	$\sim 10^7$	$6 \times 10^{19}$ to $6 \times 10^{15}$	
Far-ultraviolet	$\sim 10^{-5}$	$\sim 10^5$	} $2 \times 10^{16}$ to $8 \times 10^{14}$	} Electronic excitation of molecules
Ultraviolet	$< \sim 10^{-4}$	$> \sim 10^4$		
Visible	$\sim 10^{-4}$	$\sim 10^4$	$8 \times 10^{14}$ to $4 \times 10^{14}$	Electronic excitation of molecules
Near-infrared	$> 10^{-4}$	$< \sim 10^4$	$4 \times 10^{14}$	} Vibrational excitation of molecules
Far-infrared	$10^{-3}$	$\sim 10^3$	$1.5 \times 10^{13}$	
Microwaves	$\sim 10^{-2}$	$\sim 10^2$	$3 \times 10^{11}$	Electronic spin resonance; rotational excitation of molecules; radar
Television	$\sim 1$	$\sim 1$		
Nuclear Magnetic Resonance (NMR)	$10^4$	$10^{-4}$		
Radiowaves	$\sim 10^5$	$10^{-5}$	0.01 cm to 100 kilometers	Broadcasting

2. *An Accelerated Charge must Radiate Energy.* The electromagnetic theory provides also a clue to the inner mechanism of such radiation, by stating that any accelerated charge must radiate energy in the form of an electromagnetic pulse or wavetrain. Thus, even a single electron, subjected to a periodic motion, would send out a train of electromagnetic waves, i.e., radiate energy. It follows, therefore, that any accelerated charge must radiate energy. In other words the acceleration of a charge cannot take place without radiation of energy.

### V. Failure of Wave Nature of Radiant Energy—Quantum Theory of Radiation

The wave nature of electromagnetic radiation (radiant energy) completely fails to explain the phenomena that are associated with its absorption or emission. To explain these problems, Planck developed a theory called *Planck's Quantum Theory of Radiation*. According to this theory, *Radiation is considered corpuscular in nature, made up of discrete packets of energy, called quanta or photons, which are shot out with the velocity of light.* Thus energy changes take place only discontinuously and discretely, always as an integral multiples of small unit of energy (i.e., photon).



As a matter of fact, photon is a synthesis of the dual nature of radiation, wave and corpuscular, which two aspects are now regarded as complementary. The reason for this is that the wave nature of electromagnetic radiation cannot be completely given up, since that alone and not the quantum theory can account for the phenomena of diffraction and interference. On the other hand, only quantum concept of radiant energy can explain adequately the phenomenon of black body radiation, photoelectric effect (emission of electrons from metals when exposed to radiations of certain frequencies), etc. Hence, *if we wish to interpret satisfactorily all the radiation phenomena, we are forced to attribute a double aspect to radiation, i.e., wave and corpuscular natures.*

The energy of a photon is given by

$$E = h\nu$$

where

$h$  = Planck's constant

$\nu$  = Frequency of radiation

The energy of a photon is called quantum of energy. The value of quantum of energy is not constant, but depends on the frequency of radiation. The energy of a photon is independent of its intensity. The intensity gives the total number of photons in a beam and has no relation with the energy of individual photons in the beam. Thus the energy of the photon depends only on its intrinsic property.

The photon must possess mass of its own, given by the relation

$$m = \frac{h\nu}{C^2}$$

where

$h\nu$  = Energy of the photon

$C$  = Velocity of light

The photon is always in motion, it must also have a momentum which indicates its particle nature. However, all photons move with the same velocity (*i.e.*, velocity of light) while particles of material bodies move with variable and different velocities, which can never reach the velocity of light. The momentum of photon is given by the expression :

$$\text{Momentum of photon} = \text{Mass} \times \text{Velocity} = \frac{h\nu}{C^2} \times C = \frac{h\nu}{C}$$

where

$C$  = Velocity of light

The photons that constitute radiation are electrically neutral and are not therefore, affected by electric and magnetic fields; hence also they do not ionize directly by themselves.

### 3. MOLECULAR SPECTROSCOPY

#### I. Introduction

A *spectrum* is an array of waves, which is spread out according to the increasing or decreasing of some property, such as wavelength or frequency. The *molecular spectroscopy* is that area of study which describes the interactions of electromagnetic radiations with matter. The instruments used in such studies are called *spectrometers*. Compared to chemical analysis, spectroscopic methods are faster and more accurate, require less sample, and are usually nondestructive.

The *atomic spectrum* is the result of only transitions of electrons from one electronic state (electronic energy level) to another. Hence, atomic spectrum is due solely to changes of energy (absorption or emission) arising from the transition of electron from one energy level to another levels, in addition to electronic transitions. Hence, molecular spectrum is the result of changes of molecular rotational and molecular vibrational energy, as well as changes of energy due to



transitions of electrons from one molecular orbital to another. As a result, the spectra of molecules (molecular spectra) are much more complicated than spectra of atoms (atomic spectra). The atomic spectra consist of sharp lines, which are grouped into series. The frequency of the lines is determined from the difference in energy between two electronic states (energy levels) of the atom.

In early days of investigation, molecular absorption spectra were found as broad continuous bands. Hence molecular spectra were often mentioned as "*Band Spectra*" in distinction from *line-spectra* of atoms. But later on, with spectroscopes of high resolving power, the bands were found to consist of innumerable closely-packed lines. These lines could be classified into groups or closely related series called "*Bands*", the lines in each band becoming closer and closer until these merge into an edge called "*band head*". Again a large number of bands are found clustered together forming a "*band-group*". The molecular spectra provide most useful informations regarding the shape and size of molecules, the bond lengths, strength of bonds, bond dissociation energies and bond angles. Thus molecular spectroscopy is of great use in determining structure and constitution of compounds. This branch of science provides informations not only about the dimensions of molecules but also regarding the possible molecular energy levels, that is why spectroscopic method is the most useful of all the methods for the study of molecular structure and thermodynamic properties of the molecule.

## II. Origin of Molecular Spectra

The energy of the molecule, besides translational and nuclear energies (which do not interfere in spectroscopic analysis) can be considered to be made up of :

(i) *Electronic (transitional) energy*. Which is the energy associated with motion of electrons in the molecule.

(ii) *Vibrational Energy*. Which is the energy associated with the vibrations of the constituent atoms in the molecule.

(iii) *Rotational Energy*. Which is the energy associated with the rotation of the molecule as a whole.

Hence the total energy of the molecule (for spectroscopic purpose) can be written as

$$E_{total} = E_{electronic} + E_{vibrational} + E_{rotational}$$

Each one of these energies is quantized and can exist with some discrete values. This means that these energies have to follow quantum restrictions. The discrete values (quantized) of these energies depend on the properties of the molecules *i.e.*, size, shape, flexibility, as well as on the type of motion. Hence we can say that quantum restrictions become more prominent as the region in which particle is free to move gets smaller.

If a molecule is placed in an electromagnetic field (*e.g.*, light), a transfer of energy from the electromagnetic field to the molecule occurs when,

$$\Delta E = h \nu$$

$h$  = Planck's constant

$\nu$  = Frequency of light

$\Delta E$  = Difference in energy between two quantized states.

The molecule absorbs energy when it is excited from the lower energy state ( $E_1$ ) to higher energy state ( $E_2$ ) and emits radiations of the same frequency when the molecules reverts from higher energy state to lower energy state. Hence

For Emission :

$$\Delta E = E_2 - E_1$$

For Absorption :

$$\Delta E = E_1 - E_2$$



Thus, when a molecule absorbs energy, there may be three types of changes in the molecule:

- (i) There may be a change in rotational levels.
- (ii) There may also be a change in vibrational levels on which rotational change may be superimposed.
- (iii) An electronic state may change simultaneously with changes in both vibrational and rotational energies.

As a result, even with a simple diatomic molecule, there is a possibility of a large number of changes in energy states, producing many spectral lines.

The various energy levels in the molecule are shown in the Fig. 9.17. Suppose  $A$  and  $B$  are the two electronic states (Energy states) of a molecule. In each of electronic states, there are the two vibrational energy levels, indicated by quantum number  $V$  ( $= 0, 1, 2, 3, 4, \dots$ ). Again for each vibrational state (energy level), there exist several rotational energy levels, indicated by quantum number  $J$  ( $= 0, 1, 2, 3, 4, \dots$ ). A possible transition in any one of these energy levels will lead to a change in energy content and hence give rise to spectral lines.

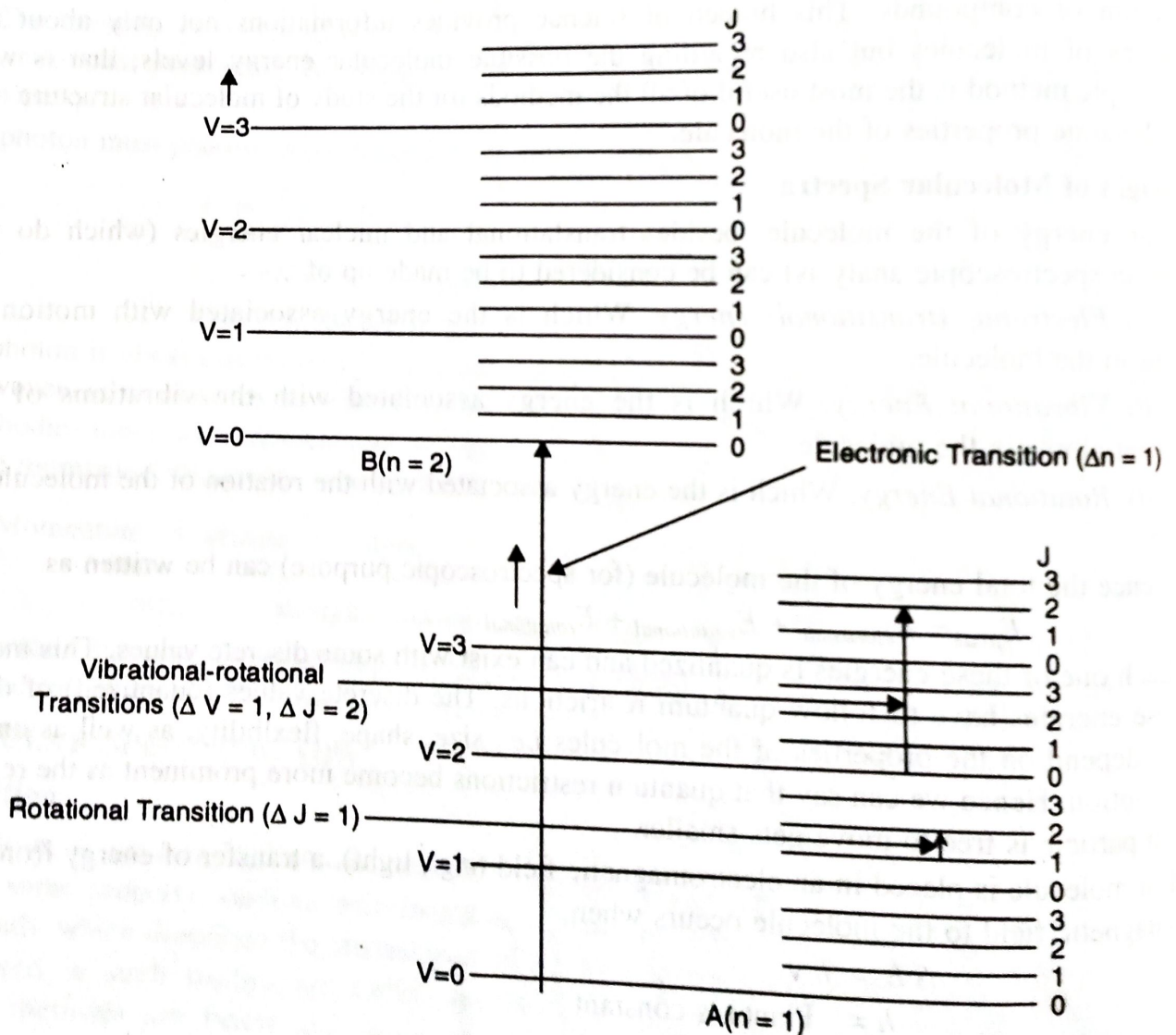


Fig. 9.17. Molecular energy level diagram.

### III. Classification of Molecular Spectra

There are three types of molecular spectra, corresponding to three types of energy changes in a molecule:

1. Rotational spectra
2. Vibrational-rotational spectra
3. Electronic spectra



1. **Rotational Spectra.** These spectra are produced due to change of energy in rotational quantum levels within a vibrational level. Thus pure rotational spectra are the simplest molecular spectra. Rotational spectra involve very small energy change of the order of 0.005 e.v. The frequency of rotational spectral line is given by

$$\nu = \frac{\Delta E}{h} = \frac{0.005 \times 1.6 \times 10^{-12} \text{ ergs}}{6.6 \times 10^{-27}}$$

$$\begin{aligned} \text{or } \lambda &= \frac{c}{\nu} = \frac{3 \times 10^{10} \times 6.6 \times 10^{-27}}{0.005 \times 1.6 \times 10^{-12}} \\ &= 25 \times 10^5 \text{ \AA} = 250 (10^4 \times 10^{-8}) \text{ cm} \\ &= 250 \times 10^{-4} \text{ cm} \end{aligned}$$

Since 1 micron ( $\mu$ ) =  $10^{-4}$  cm

Hence

$$\lambda = 250 \mu$$

The rotational energy levels are relatively close to each other and hence energy changes taking place in rotational transitions are of small amounts. That is why pure rotational spectra appear in *far infrared* and *microwave* regions (i.e.,  $10^4 \mu$  to  $10^2 \mu$  range). Hence rotational spectroscopy is also known as *microwave or far infra-red spectroscopy*.

2. **Vibrational-Rotational Spectra.** The separation of vibrational energy levels is greater as compared to rotational levels; hence the transitions between vibrational levels involve energies of the order of 0.1 e.v. That is

$$\begin{aligned} \lambda &= \frac{c}{\nu} = \frac{c \times h}{\Delta E} = \frac{3 \times 10^{10} \times 6.6 \times 10^{-27}}{0.1 \times 1.6 \times 10^{-12}} = 1,25,000 \text{ \AA} \\ &= 12.5 \times 10^4 \times 10^{-8} \text{ cm} = 12.5 \times 10^{-4} \text{ cm} \end{aligned}$$

$$\lambda = 12.5 \mu$$

The vibrational spectra would, therefore, appear in the *mid-infrared regions* ( $10^2 \mu$  to  $1 \mu$  range). During a vibrational change, the rotational energy also changes and the energy emitted or absorbed is the sum of two energy changes. That is why the *mid-infrared* spectrum is called the *vibrational-rotational spectrum*.

3. **Electronic Spectra.** The electronic energy levels (denoted by the quantum number  $n$ ) are far apart. Hence a change in electronic state is associated with a larger difference in energy, of the order of 5 e.v. per molecule. The wavelength ( $\lambda$ ) of the spectral lines produced from electronic transition (on which vibrational and rotational transitions are superimposed) is given by

$$\lambda = \frac{c}{\nu} = \frac{c \times h}{\Delta E} = \frac{3 \times 10^{10} \times 6.6 \times 10^{-27}}{5 \times 1.6 \times 10^{-12}}$$

$$\lambda = 2500 \text{ \AA} = 0.25 \times 10^{-4} \text{ cm} = 0.25 \mu$$

Hence the electronic spectra appear in the visible and ultraviolet region ( $1 \mu$  to  $0.1 \mu$  range). That is why *electronic spectroscopy is also called visible and ultraviolet spectroscopy*.

The range in electromagnetic spectrum extending from  $\lambda = 0.8$  to  $200 \mu$  is commonly referred to as the *infrared region*. This region is divided into three :

1. *Near infrared region.* It extends from  $0.8$  to  $2.5 \mu$ .
2. *Mid-infrared region.* This region extends from  $2.5$  to  $15 \mu$ . This region is also referred to as *ordinary (conventional) infrared region*.
3. *Far infrared region.* It extends from  $15$  to  $200 \mu$ .



The far infrared region deals with pure rotational motion of molecule and because of experimental difficulties in the generation and detection at low frequencies, far infrared has not been so extensively explored as mid-infrared.

#### IV. Rotational or Microwave (or Far Infrared) Spectroscopy

Pure rotational molecular spectra are produced in the far infrared region, caused by the rotations of the molecules. The molecules possessing permanent dipoles give rotation spectra. During rotational motion, the direction of the dipole undergoes a periodic change, resulting in periodic fluctuations in the magnitude of a component of the dipole, as shown in Fig. 9.18.

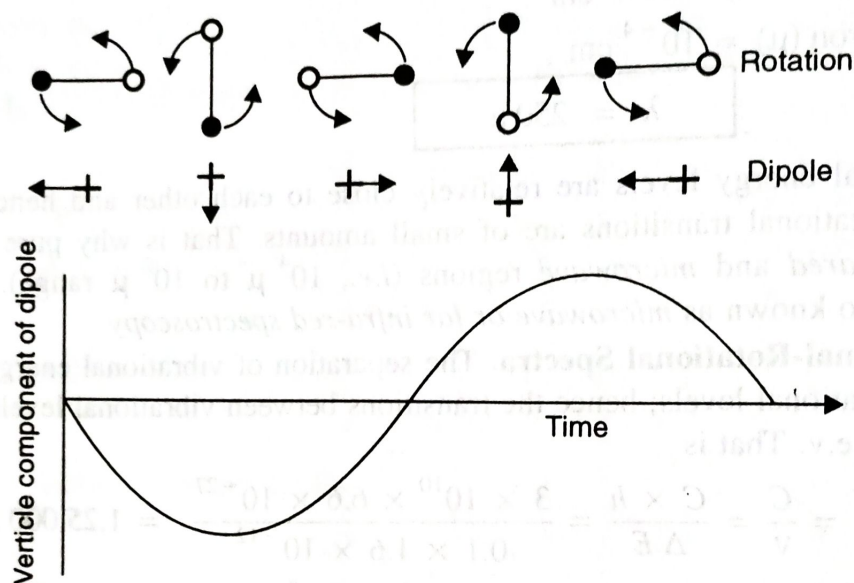


Fig. 9.18. Rotation of a diatomic molecule (●—●) possessing a permanent dipole.

When frequency of electromagnetic radiation coincides with that of molecular rotation, the electromagnetic radiation interacts with the molecular dipole and keeps pushing the molecule to a higher rotational energy level. This absorption of radiation thus gives the pure rotational spectrum of the molecule.

The emission or absorption of electromagnetic radiation in rotational energy levels would occur only if a change in dipole moment is associated with it. That is, molecule must be polar (*i.e.*, must possess permanent dipole) in order to produce a rotational spectrum *e.g.*, HCl, CO. etc. Such molecules are called *microwave active*. The homonuclear molecules like  $H_2$ ,  $Cl_2$ ,  $N_2$  do not produce rotational bands, as their dipole moment is zero. Such molecules are called *microwave inactive*.

(a) **Theory of the Pure Rotation Spectra.** Consider a diatomic molecule to rotate as a whole about the axis through its centre of gravity. The diatomic molecule can be pictured as :

1. Rigid Rotator Model
2. Non-rigid Rotator Model

1. **Rigid Rotator Model.** In this simple picture, the diatomic molecule is supposed to be a system consisting of two atoms of masses  $m_1$  and  $m_2$  connected by a rigid rod of length  $r$  (representing bond length) and  $r_1$  and  $r_2$  be the distances of two atoms from the centre of gravity of the system.

(i) **Moment of Inertia.** The molecule has a natural rotation about the axis through its centre of gravity. The moment of inertia of this system is given by



$$I = m_1 r_1^2 + m_2 r_2^2 \quad \dots (1)$$

As the system is balanced about its centre of gravity, one can write

$$m_1 r_1 = m_2 r_2 \quad \dots (2)$$

Also  $r = r_1 + r_2 \quad \dots (3)$

On solving equations (2) and (3), we get

$$r_1 = \frac{m_2 r}{m_1 + m_2}; \quad r_2 = \frac{m_1 r}{m_1 + m_2} \quad \dots (4)$$

From equations (1) and (4), we can write

$$I = \frac{m_1 m_2^2 r^2}{(m_1 + m_2)^2} + \frac{m_2 m_1^2 r^2}{(m_1 + m_2)^2}$$

or

$$I = \frac{m_1 m_2 (m_2 + m_1) r^2}{(m_1 + m_2)^2}$$

or

$$I = \frac{m_1 m_2 r^2}{(m_1 + m_2)} = \mu r^2 \quad \dots (5)$$

where

$\mu$  = Reluctant or reduced mass of the system

$$= \frac{m_1 m_2}{(m_1 + m_2)}$$

Equation (5) defines the moment of inertia, in terms of masses and bond length.

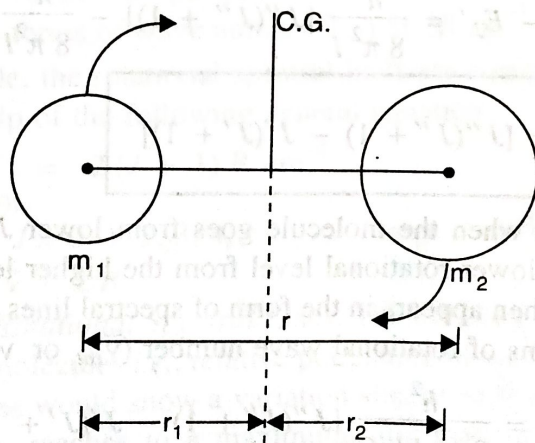


Fig. 9.19. Rigid rotator model for a diatomic molecule.

(ii) *Kinetic Energy of Rotation.* The kinetic energy of rotation of a rigid rotator is given by

$$E_{rot} = \frac{1}{2} m_1 \cdot v_1^2 + \frac{1}{2} m_2 \cdot v_2^2$$

where  $v_1$  and  $v_2$  are the linear velocities of masses  $m_1$  and  $m_2$  respectively. Since  $r_1$  and  $r_2$  are assumed to remain unchanged during rotation, the above equation can be written as (by using the relation  $\omega = \frac{v}{r}$ , where  $\omega$  = angular velocity).

$$\begin{aligned} E_{rot} &= \frac{1}{2} m_1 (\omega \cdot r_1)^2 + \frac{1}{2} m_2 (\omega \cdot r_2)^2 \\ &= \frac{1}{2} \omega^2 (m_1 r_1^2 + m_2 r_2^2) \end{aligned}$$



But,  $I = m_1 r_1^2 + m_2 r_2^2$

Hence  $E_{rot} = \frac{1}{2} I \omega^2$  ... (6)

The rotational energy is quantized, the molecule can have only certain permitted values of rotational energy, depending on the shape and size of the molecule under consideration. Since the molecule is a rigid rotator, the potential energy is zero. The quantized (permitted) rotational energy values are obtained by solving the Schrodinger equation

$$\nabla^2 \psi + \frac{8 \pi^2 I E_{rot}}{h^2} \psi = 0$$

This equation, when solved for  $E_{rot}$  (also written as  $E_J$ ), gives the following expression for  $E_J$

$$E_J = \frac{h^2}{8 \pi^2 I} [J(J + 1)] \text{ ergs} \quad \dots (7)$$

where  $J$  = Rotational quantum number, having integral values 0, 1, 2, 3, . . . .

The equations (7) gives the rotational energy of the molecule in a given rotational energy level.

(iii) *Frequency of Spectral Line.* Consider the transition of molecule from lower rotation level ( $J'$ ) to higher rotational level ( $J''$ ). The difference of rotational energy between these two rotational energy levels will be given by

$$\Delta E_J = E_{J''} - E_{J'} = \frac{h^2}{8 \pi^2 I} [J''(J'' + 1)] - \frac{h^2}{8 \pi^2 I} [J'(J' + 1)]$$

or 
$$\Delta E_J = \frac{h^2}{8 \pi^2 I} [J''(J'' + 1) - J'(J' + 1)] \quad \dots (8)$$

This energy is absorbed when the molecule goes from lower  $J$  to higher  $J$  and is emitted when the molecule returns to lower rotational level from the higher level. According to quantum theory, the energy evolved is then appears in the form of spectral lines. The frequency of rotational spectral lines expressed in terms of rotational wave number ( $\bar{\nu}_{rot}$  or  $\bar{\nu}_J$ ) is given by

$$\bar{\nu}_{rot} = \frac{\Delta E_J}{h C} = \frac{h^2}{8 \pi^2 I h C} [J''(J'' + 1) - J'(J' + 1)]$$

or 
$$= \frac{h}{8 \pi^2 I \cdot C} [J''(J'' + 1) - J'(J' + 1)]$$

The quantity  $(h/8 \pi^2 I C)$  is a characteristics of the molecule and is called the *rotational constant*, denoted by  $B$ . Thus,

if 
$$B = \frac{h}{8 \pi^2 I C} \text{ cm}^{-1}$$

then 
$$\bar{\nu}_{rot} = B [J''(J'' + 1) - J'(J' + 1)] \quad \dots (9)$$

(iv) *Quantum Mechanical Restrictions i.e., Selection Rule for Rotational Spectra.* For a molecule to show rotational spectra, it must have a dipole moment, but all transitions involving arbitrarily any two rotational levels are not permissible. The quantum mechanics permits only those rotational transitions in which there is an increase or decrease of unity in the rotational



quantum number ( $J$ ). That is, the transition in rotational energy levels is limited to only adjacent rotational levels. Mathematically

$$J'' - J' = \Delta J = \pm 1 \quad \dots (10)$$

This is called *selection rule* for a rotational transition for a diatomic rigid molecule. Thus, according to this rule, the rotational transitions  $J = 0 \rightarrow 2$ ,  $J = 1 \rightarrow 3$ ,  $J = 2 \rightarrow 0$  etc., are not possible, because in such cases  $\Delta J \neq (\pm 1)$ .

(v) *Rotational Spectrum Consists of Equidistant Spectral Lines.* The rotational spectra are known only in absorption. We know that

$$\bar{\nu}_{rot} = B [J''(J'' + 1) - J'(J' + 1)] \quad \dots (11)$$

Hence variety of rotational transitions with  $\Delta J = (\pm 1)$  would be possible, if appropriate energies are made available to the system. Thus

when  $J' = 0$  and  $J'' = 1$ , then

$$\bar{\nu}_{rot} = B [1(1 + 1) - 0(0 + 1)] = 2B \text{ cm}^{-1}$$

when  $J' = 1$  and  $J'' = 2$ , then

$$\bar{\nu}_{rot} = B [2(2 + 1) - 1(1 + 1)] = 4B \text{ cm}^{-1}$$

when  $J' = 2$  and  $J'' = 3$ , then

$$\bar{\nu}_{rot} = B [3(3 + 1) - 2(2 + 1)] = 6B \text{ cm}^{-1}$$

when  $J' = 3$  and  $J'' = 4$ , then

$$\bar{\nu}_{rot} = B [4(4 + 1) - 3(3 + 1)] = 8B \text{ cm}^{-1}$$

Thus we see that rotational spectrum consists of a series of spectral lines with frequency separation (expressed in terms of wave number  $\bar{\nu}_{rot}$ ) of  $2B \text{ cm}^{-1}$  between the two consecutive lines. Thus, on frequency scale, the rotational spectral lines are equidistant. The frequency scale can be constructed with the help of the following general equation.

$$\bar{\nu}_{rot} = 2(J + 1)B \text{ cm}^{-1} \quad \dots (12)$$

where  $J = 0, 1, 2, 3, 4, 5, \dots$  respectively.

$$\text{or} \quad \Delta \bar{\nu} = 2B \quad \dots (13)$$

(vi) *Intensity of Rotational Spectral Lines.* The intensity of the spectral lines is governed by the relative number of molecules *i.e.*, relative population of various rotational levels. Therefore, the intensity of spectral lines would show a variation similar to that shown by the population. That is, intensity first increases, reaches to a maximum, and then decreases. The position of the most intense spectral line is given by the following equation :

$$J_{Max} = \sqrt{kT/2BhC} - \frac{1}{2} \quad \dots (14)$$

where  $k =$  Boltzmann constant

$T =$  Temperature in  $\text{\AA}$

$$B = \frac{h}{8\pi^2 IC} \text{ cm}^{-1}$$

$C =$  Velocity of light

$h =$  Planck's constant

$I =$  Moment of inertia of diatomic molecule.

(vii) *Isotopic Effect on the Rotational Spectra.* The diatomic molecule having different isotopes of the same element, such as HCl, DCl, show different rotational spectra. This is because of the fact that masses of the isotopic atoms are different and hence the reduced mass, moment of inertia, as well as frequencies of rotation, would be different. It has been established that



$$B \propto \frac{1}{\mu}$$

Thus spectrum of heavier species will show smaller value of  $B$  and hence smaller separation between the spectral lines. This fact has been used in the evaluation of precise atomic weights.

(viii) *Validity of the Theory of Rotational Spectroscopy.* The validity of the theory of rotational spectra can now be tested by considering the following examples :

(a) *Carbon Monoxide Molecule.* The first rotational spectral lines corresponds to the transition from  $J = 0$  to  $J = 1$  and appears at  $\bar{\nu}_{rot} = 3.84235 \text{ cm}^{-1}$ . We know that

$$\bar{\nu}_{rot} \quad [J \rightarrow (J+1)] = 2B(J+1) \text{ cm}^{-1}$$

$$\therefore \bar{\nu}_{rot} \quad [J=0 \rightarrow 1] = 2B(0+1) = 2B \text{ cm}^{-1} = 3.84235$$

$$\text{Hence } B = 3.84235/2 = 1.92118 \text{ cm}^{-1}$$

The moment of inertia of CO is given by

$$I_{CO} = \frac{h}{8\pi^2 CB} = \frac{6.624 \times 10^{-27}}{8 \times (3.14)^2 \times 2.9978 \times 10^{10} \times 1.92118}$$

$$= 1.45673 \times 10^{-39} \text{ gm cm}^{-2}$$

Reduced mass of CO is given by

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \cdot \frac{1}{N}$$

Now  $m_1 = 12 \text{ gm}$  (carbon);  $m_2 = 15.9949 \text{ gm}$  (oxygen);

$$N = 6.023 \times 10^{23}$$

$$\mu = \frac{12 \times 15.9949}{12 + 15.9949} \times \frac{1}{6.023 \times 10^{23}}$$

$$\text{or } \mu = 1.138365 \times 10^{-23} \text{ gram per molecule}$$

The bond length of CO molecule can be calculated by the equation

$$I = \mu \cdot r^2$$

where  $I$  = Moment of inertia

$\mu$  = Reduced mass of the molecule

$r$  = Bond length, i.e., internuclear distance between two atoms

$$\therefore r_{CO} = \left( \frac{I}{\mu} \right)^{\frac{1}{2}} = \left( \frac{1.456773 \times 10^{-39}}{1.138365 \times 10^{-23}} \right)^{\frac{1}{2}} \text{ cm}$$

$$\text{or } r_{CO} = 1.131 \times 10^{-8} \text{ cm} = 1.131 \text{ \AA}$$

This value of bond length of CO molecule is in good agreement with experimental value. This indeed is the most accurate determination of bond length. From rotational spectra we can also calculate the rotational energy at any level and moment of inertia of the molecule.

(b) *HCl Molecule.* For HCl, the frequency difference (separation) between two successive rotational spectral lines, in terms of wave number, has been found to be  $20.3 \text{ cm}^{-1}$ . Hence

$$\text{Wave number difference} = \Delta \bar{\nu} = 2B = 20.3$$

Putting value of  $B$ , we get

$$\frac{2h}{8\pi^2 I C} = 20.3$$



Substituting  $h = 6.624 \times 10^{-27}$

$$C = 2.9978 \times 10^{10} \text{ cm/sec}$$

$$\pi = 3.14$$

we have

$$I = 2.7 \times 10^{-40} \text{ gm cm}^2$$

Again for HCl, H = 1.008; Cl = 35.46;  $N = 6.023 \times 10^{23}$

$$\begin{aligned} \therefore \mu &= \frac{m_1 \cdot m_2}{(m_1 + m_2) N} \\ &= \frac{1.008 \times 35.46}{(1.008 + 35.46) (6.023 \times 10^{23})} \\ &= 1.63 \times 10^{-24} \text{ gm} \end{aligned}$$

$$\begin{aligned} \therefore \text{Bond length of HCl} &= \sqrt{\frac{I}{\mu}} = \left( \frac{2.7 \times 10^{-40}}{1.63 \times 10^{-24}} \right)^{\frac{1}{2}} \\ &= 1.29 \text{ \AA} \end{aligned}$$

The above results are in good agreement with experimental values.

**2. Non-rigid Rotator Model.** (i) *Limitations of Rigid Rotator Model.* The constant equal separation between consecutive rotational spectral lines is true only at lower values of  $J$ . At higher values of  $J$ , the rigid character of the rotator is affected, because the velocity of rotation increases and there is a tendency for the bond to stretch and also the moment of inertia increases. Whereas in the theory proposed above, moment of inertia is assumed to be constant and independent of the angular velocity  $\omega$ .

As a result of the variation of  $I$ , the rotational energy levels corresponding to higher  $J$  values must lie somewhat lower than that given in the theory of rigid rotator model. The lines corresponding to transitions involving higher  $J$  values must, therefore, have somewhat lower wave number  $\bar{\nu}$  than they would if  $I$  were constant. It thus appears that the rigid rotator model for a diatomic model may serve as a reasonably good approximation but cannot be regarded as a true picture of the real molecules.

(ii) *Non-rigid Rotator Model.* It is quite obvious that the molecule cannot be a strictly rigid rotator, when it is also able to perform vibrations. Therefore, a better model for representing the rotations of the molecule is to consider the diatomic molecule as a rotating system consisting of two atoms connected by a massless spring. This simple picture of a diatomic molecule is commonly known as *non-rigid rotator model*. The energy of rotation is then expressed as

$$E_J = \frac{h^2}{8\pi^2 I} [J(J+1)] - Dh [J^2(J+1)^2] \text{ ergs} \quad \dots (15)$$

in which  $D$  is the centrifugal distortion constant and is of order of  $10^{-4} B$ . It is a small positive quantity and is given by

$$D = \frac{4B^3}{(\bar{\nu}_0)^2} \quad \dots (16)$$

where  $\bar{\nu}_0$  = Fundamental vibrational frequency

As  $\bar{\nu}_0$  is always very much greater than  $B$  and, therefore, according to equation (16),  $D$  will be much smaller than  $B$ .

In rotational region, spectra are usually expressed in terms of wave numbers, so it is useful to consider energies expressed in these units.

Rotational energy in terms of wave number



$$\begin{aligned}
 &= \frac{E_J}{hC} = \frac{h^2}{8\pi^2 h C I} [J(J+1)] - D [J^2(J+1)^2] \\
 &= BJ(J+1) - D J^2(J+1)^2 \text{ cm}^{-1} \quad \dots (17)
 \end{aligned}$$

The selection rule  $[\Delta J = (\pm 1)]$  is valid, whether the rotator is rigid or non-rigid. The frequency (in terms of wave number  $\bar{\nu}_{rot}$ ) of rotational spectral line, representing the transition for  $J$  to  $(J+1)$  is given by

$$\begin{aligned}
 \bar{\nu}_{rot} &= (\text{Rotational energy in terms of wave number for } (J+1) \text{ level}) \\
 &\quad - (\text{Rotational energy in terms of wave number for } J \text{ level})
 \end{aligned}$$

Hence from equation (17) we have

$$\begin{aligned}
 \bar{\nu}_{rot} &= [B(J+1)(J+1+1) - D(J+1)^2(J+1+1)^2] \\
 &\quad - [BJ(J+1) - DJ^2(J+1)^2] \text{ cm}^{-1} \\
 &= [B(J+1)(J+2) - D(J+1)^2(J+2)^2] - [BJ(J+1) - DJ^2(J+1)^2] \text{ cm}^{-1} \\
 &= [B(J+1)(J+2) - BJ(J+1)] - [D(J+1)^2(J+2)^2 - DJ^2(J+1)^2] \text{ cm}^{-1} \\
 &= B(J+1)[J+2-J] - D(J+1)^2[(J+2)^2 - J^2] \text{ cm}^{-1} \\
 \therefore \bar{\nu}_{rot} &= 2B(J+1) - 4D(J+1)^3 \text{ cm}^{-1} \quad \dots (18)
 \end{aligned}$$

Equation (18) gives the frequency of rotational spectral line for the transition from  $J$  to  $(J+1)$  or  $(J+1)$  to  $J$  rotational energy levels. Hence from equation (18) we get

$$\begin{aligned}
 \bar{\nu}_{rot} &= 2B(0+1) - 4D(0+1)^3 = (2B - 4D) \text{ cm}^{-1} \\
 &\quad J=0 \rightarrow 1 \\
 \bar{\nu}_{rot} &= 2B(1+1) - 4D(1+1)^3 = (4B - 32D) \text{ cm}^{-1} \\
 &\quad J=1 \rightarrow 2 \\
 \bar{\nu}_{rot} &= 2B(2+1) - 4D(2+1)^3 = (6B - 108D) \text{ cm}^{-1} \\
 &\quad J=2 \rightarrow 3
 \end{aligned}$$

Thus we see that the spectral lines are no longer exactly equidistant but their separation distance decreases with increasing value of  $J$ , as shown below

$$\Delta \bar{\nu} \text{ between 1st and 2nd lines} = (4B - 32D) - (2B - 4D) = (2B - 28D) \text{ cm}^{-1}$$

$$\Delta \bar{\nu} \text{ between 2nd and 3rd lines} = (6B - 108D) - (4B - 32D) = (2B - 76D) \text{ cm}^{-1}$$

Since the values of  $D$  are much smaller as compared to  $B$ , the effect of frequency separation is not so much pronounced.

(b) **Applications of Microwave-Spectroscopy.** At lower quantum levels of rotation, the spectral lines are equidistant. This fact has been utilized in the most accurate determination of bond-distances in diatomic molecules. The knowledge of rotational spectra is also helpful in determining the moment of inertia and reduced mass of the diatomic molecules.

By microwave spectroscopy, only those molecules can be studied which possess dipole moment e.g., HCl, CO etc. The molecules such as H<sub>2</sub>, N<sub>2</sub>, Cl<sub>2</sub> etc., do not show rotational spectra as their dipole moments are zero.

The far infrared (microwave) region deals with the rotational motion of molecule and because of the experimental difficulties in the generation and detection at low frequencies (longer wavelengths), far infrared has not been so extensively explored as mid-infrared.

Polyatomic linear molecules have several internuclear distances, hence these quantities cannot be determined from their single values of moment of inertia.

The far infrared spectra are not observed in liquids and solids, because in condensed state,



no well defined rotational energy levels exist. All the microwave spectroscopic studies should be done in *gaseous state*, because in gaseous state the rotation of the molecule is free.

### V. Vibrational-Rotational (Mid-infrared) Spectroscopy

The vibrational spectra appear in mid-infrared region, as the energy changes in the vibrational transitions are larger than those in pure rotational transitions. In general, vibrational changes are always accompanied by so many rotational changes in the gas phase. Hence it is difficult to get pure vibrational spectra; we actually get vibrational-rotational spectra in the *near and mid-infrared regions*. Such spectra are shown by only those molecules which possess permanent dipole moment. The homonuclear diatomic molecules, like  $O_2$ ,  $N_2$ ,  $Cl_2$  etc., have zero dipole moment and, therefore, do not show vibrational-rotational spectra. The polyatomic molecules, have no permanent dipole moment of their own, but when subjected to electromagnetic radiation, it induces an oscillating dipole moment in such polyatomic molecules and excite them to undergo vibrational-rotational transitions. The studies of vibrational-rotational spectra of molecules lead to the conclusion that the molecules are flexible *i.e.*, both angles and bond lengths can be distorted from their original value in the equilibrium configuration of the molecule. The *mid-infrared spectroscopy is highly useful in the determination of molecular structure*.

(a) **Theory of Vibrational-Rotational Spectroscopy.** In general, a diatomic molecule may rotate and vibrate simultaneously, so that the total internal energy is partly rotational and partly vibrational.

$$E_{vib-rot} = E_{vib} + E_{rot}$$

Any given change of state may involve simultaneous change of both types of energy. That is, energy  $h\nu$  of a given radiation emitted or absorbed by the molecule may come partly from vibrational energy and partly from rotational energy of the molecule. We will first consider the spectra arising due to only vibrational changes (pure vibrational spectra) and then vibrational changes on which rotational changes are superimposed (vibrational-rotational spectra).

Let us consider a diatomic molecule, namely (1) *Harmonic Oscillator Model*, and (2) *Anharmonic Oscillator Model*.

1. **Harmonic Oscillator Model.** In this model, the diatomic molecule is supposed to be a system of two atoms connected by a spring capable of executing vibrations similar to the vibrations of a linear harmonic oscillator, about their mean positions.

(i) *Harmonic Oscillator but not Rotator (only Vibration Spectra).* Let  $m_1$  and  $m_2$  be the masses of two atoms A and B of the diatomic molecule. Both atoms oscillate against one another harmonically. That is, Hook's law is obeyed during oscillations. In other words, the force tending to restore an atom to its original state, is proportional to the displacement of the vibratory atom from the original position.

Let  $r_e$  = Equilibrium atomic distance (equilibrium bond length)

$r$  = New bond length, when the molecule is stretched

$$\therefore x = r - r_e \quad \dots (1)$$

The two atoms shift (displace) by  $-x_1$  and  $+x_2$  in two directions (see Fig. 9.20)

$$\therefore x = -x_1 + (+x_2) = -x_1 + x_2 \quad \dots (2)$$

By Hook's law,

Restoring force on each atom  $\propto$  displacement

$$f = -kx$$

or

where  $x$  = Displacement or shift of each atom.

Hence, restoring forces on each atom of the diatomic molecule would be

$$f_1 = -kx_1 \quad \text{and} \quad f_2 = -kx_2$$



where  $k =$  Force constant of the spring (bond) and is regarded as a measure of its stiffness or bond strength.

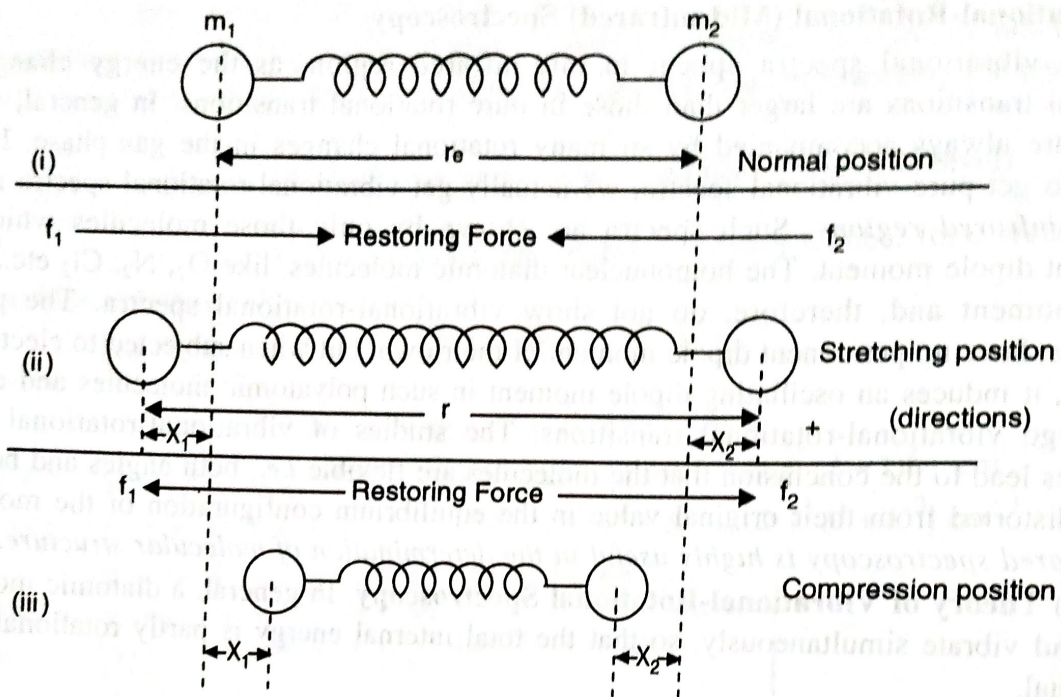


Fig. 9.20. Showing different modes of vibrations of a diatomic molecule and restoring force.

The net restoring force on the whole molecule would be the algebraic sum of  $f_1$  and  $f_2$ . Hence

$$\therefore f = f_2 + (-f_1) = f_2 - f_1$$

$$\text{or } f = (-kx_2) - (-kx_1)$$

$$\text{or } f = -k(x_2 - x_1) \quad \dots (3)$$

From equations (2) and (3) we get

$$f = -kx \quad \dots (4)$$

The accelerations of the two particles are respectively

$$-\frac{d^2x_1}{dt^2} \quad \text{and} \quad +\frac{d^2x_2}{dt^2}$$

Now force = (Mass  $\times$  Acceleration)

$$\therefore -k(x_2 - x_1) = m_1 \left( \frac{-d^2x_1}{dt^2} \right) = -m_1 \left( \frac{d^2x_1}{dt^2} \right) \quad \dots (5)$$

$$\text{and } -k(x_2 - x_1) = m_2 \left( \frac{+d^2x_2}{dt^2} \right) = +m_2 \left( \frac{d^2x_2}{dt^2} \right) \quad \dots (6)$$

The displacement of both atoms are harmonic; hence the equations for the displacements of both the atoms are

$$x_1 = A_1 \sin 2\pi \nu_0 t$$

$$\text{and } x_2 = A_2 \sin 2\pi \nu_0 t \quad \dots (7)$$

$$\text{where } A_1 \text{ and } A_2 = \text{Amplitudes of vibrations of both atoms respectively} \quad \dots (8)$$

$$\nu_0 = \text{Fundamental frequency of vibration (oscillation)}$$



Equations (7) and (8), on double differentiation with respect to  $t$ , give

$$\frac{d^2 x_1}{dt^2} = -4\pi^2 \nu_0^2 A_1 \sin 2\pi \nu_0 t \quad \dots (9)$$

$$\frac{d^2 x_2}{dt^2} = -4\pi^2 \nu_0^2 A_2 \sin 2\pi \nu_0 t \quad \dots (10)$$

From equations (5), (7) and (9), we get

$$-k \cdot \sin 2\pi \nu_0 t (A_2 - A_1) = -m_1 (-4\pi^2 \nu_0^2 A_1 \sin 2\pi \nu_0 t)$$

$$\text{or } -k(A_1 - A_2) = 4\pi^2 \nu_0^2 A_1 m_1 \quad \dots (11)$$

Combining equations (6), (8) and (10)

$$-k(A_2 - A_1) = 4\pi^2 \nu_0^2 A_2 m_2 \quad \dots (12)$$

Equations (11) and (12), on simplification, give

$$k A_2 = -A_1 (4\pi^2 \nu_0^2 m_1 - k) \quad \dots (13)$$

$$k A_1 = -A_2 (4\pi^2 \nu_0^2 m_2 - k) \quad \dots (14)$$

Equations (13) and (14), on multiplication and cancelling  $A_1 A_2$  yield

$$k^2 = (4\pi^2 \nu_0^2 m_1 - k)(4\pi^2 \nu_0^2 m_2 - k) \quad \dots (15)$$

$$\text{or } 4\pi^2 \nu_0^2 [4\pi^2 \nu_0^2 m_1 m_2 - k(m_1 + m_2)] = 0$$

$$\text{or } 4\pi^2 \nu_0^2 m_1 m_2 - k(m_1 + m_2) = 0$$

$$\text{or } 4\pi^2 \nu_0^2 m_1 m_2 = k(m_1 + m_2)$$

$$\text{or } 4\pi^2 \nu_0^2 = k \left( \frac{m_1 + m_2}{m_1 m_2} \right)$$

$$\text{But the reduced mass } (\mu) = \frac{m_1 m_2}{m_1 + m_2}$$

$$\therefore 4\pi^2 \nu_0^2 = \frac{k}{\mu}$$

$$\text{or } \boxed{\nu_0 = \frac{1}{2\pi} \sqrt{k/\mu}} \quad \dots (16)$$

The restoring force is related to the potential energy ( $V$ ) as

$$f = -\frac{\partial V}{\partial x} \quad \text{or } V = \frac{1}{2} k x^2$$

The vibrational energy may now be determined from Schrodinger wave equation (only  $x$ -direction of oscillation being considered).

$$\nabla^2 \Psi + \frac{8\pi^2 \mu}{h^2} [E_{vib} - \frac{1}{2} k x^2] \Psi = 0$$

The allowed solutions of this equation are given by

$$\boxed{E_{vib} = \frac{h}{2\pi} \sqrt{k/\mu} \left( v + \frac{1}{2} \right) \text{ ergs}} \quad \dots (17)$$



Combining equations (16) and (17), we get

$$E_{vib} = \left( v + \frac{1}{2} \right) h \nu_0 \text{ ergs} \quad \dots (18)$$

where  $v$  = Vibrational quantum number and has values 0, 1, 2, 3, ..., integers

Equation (17) or (18) gives the value of energy in different vibrational energy levels.

From equation (18) when  $v = 0$ , we have

$$E_0 = \left( 0 + \frac{1}{2} \right) h \nu_0 = \frac{1}{2} h \nu_0 \text{ ergs} \quad \dots (19)$$

This equation means that even at the lowest vibrational level ( $v = 0$ ) the molecule has vibrational energy equal to  $1/2 h \nu_0$ . This energy is called *zero point energy*. In other words *the molecules can never have zero vibrational energy, i.e., atoms can never be at absolute rest. Thus even at absolute zero ( $-273^\circ\text{K}$ ) when rotational and translational motions stop, vibrational motions still persist.*

The infrared spectra are usually studied in absorption. In vibrational transition from  $v'$  to  $v''$  levels, energy change is

$$\Delta E = E''_{vib} - E'_{vib} = \left( v'' + \frac{1}{2} \right) h \nu_0 - \left( v' + \frac{1}{2} \right) h \nu_0$$

or

$$\Delta E = (v'' - v') h \nu_0 \quad \dots (20)$$

The selection rule is also valid for vibrational transitions *i.e.*,  $\Delta v = \pm 1$ . That is  $v'' - v' = 1$ . Hence under this condition, equation (20) becomes

$$\Delta E = h \nu_0 \quad \dots (21)$$

Let the frequency of vibrational transition be  $\nu$ , then

$$\Delta E = h \nu \quad \dots (22)$$

Hence from equation (21) and (22), we get

$$\nu = \nu_0 = \frac{1}{2\pi} \sqrt{k/\mu} \text{ hertz} \quad \dots (23)$$

Equation (23) says that frequency of absorbed or emitted radiation, during vibrational transition, is the same as the fundamental frequency of vibration ( $\nu_0$ ) of the molecule, no matter what the  $v$  value of initial level may be. It means that *all the vibrational lines obtained from an harmonic oscillator are of same frequency.*

The energy in spectroscopic units ( $\text{cm}^{-1}$ ) is given by

$$\text{Energy in } \text{cm}^{-1} \text{ unit} = \frac{E_{vib}}{h C} = \frac{h}{2\pi h C} \sqrt{\frac{k}{\mu}} \left( v + \frac{1}{2} \right)$$

$$= \frac{1}{2\pi C} \sqrt{\frac{k}{\mu}} \left( v + \frac{1}{2} \right) \text{cm}^{-1}$$

$$= \frac{\nu_0}{C} \left( v + \frac{1}{2} \right) \text{cm}^{-1}$$

But

$$\frac{\nu_0}{C} = \bar{\nu}_0 \text{ cm}^{-1}$$



$$\therefore \text{Energy in cm}^{-1} \text{ unit} = \bar{\nu}_0 \left( v + \frac{1}{2} \right) \text{cm}^{-1}$$

The allowed vibrational energy levels for a simple harmonic oscillator can be computed using equation

$$E_{vib} = \left( v + \frac{1}{2} \right) h \nu_0$$

when  $v = 0, E_{vib} = \frac{h}{2} \nu_0$

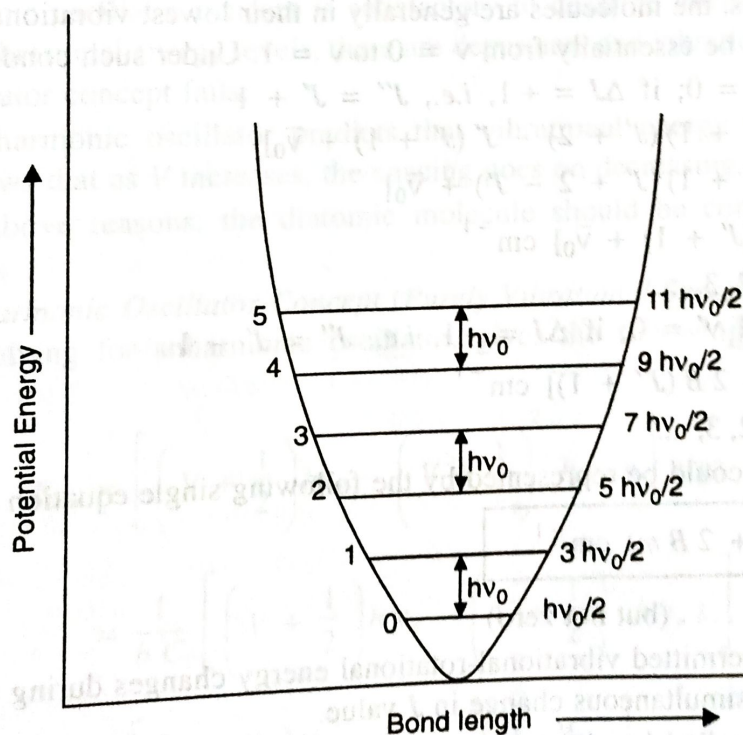
$$v = 1, E_{vib} = \frac{3}{2} h \nu_0$$

$$v = 2, E_{vib} = \frac{5}{2} h \nu_0$$

$$v = 3, E_{vib} = \frac{7}{2} h \nu_0 \quad \text{and so on.}$$

The spacing between the adjacent vibrational levels is always equal to  $h\nu_0$ . That is, *the vibrational levels of simple harmonic oscillator are equidistant.*

This is shown in the following Fig. 9.21.



**Fig. 9.21.** Equidistant vibrational energy levels of diatomic harmonic oscillator.

(ii) *Harmonic Oscillator Undergoing Simultaneously Rotational Motions (Vibrational-Rotational Spectra).* Upon the vibrational motions of the simple harmonic oscillator, is superimposed the rotation of the molecule. Hence the total energy of the molecule is given by

$$\begin{aligned} E_{Total} &= E_{vib} + E_{rot} \\ &= (E_v + E_r) \text{ ergs} \end{aligned}$$

In terms of spectroscopic unit ( $\text{cm}^{-1}$ )



$$\text{Total energy} = \frac{(E_v + E_J)}{h \cdot C} \text{ cm}^{-1}$$

Considering the molecule executing rotational and vibrational motions simultaneously and neglecting the centrifugal distortion effects, the permissible rotation-vibrational energies are given by

$$E_{v,J} = \left[ B J(J+1) + \bar{\nu}_0 \left( v + \frac{1}{2} \right) \right] \text{ cm}^{-1}$$

where  $J = 0, 1, 2, 3, \dots$

and  $v = 0, 1, 2, 3, \dots$

The selection rule is also obeyed here, *i.e.*,

$$\Delta J = \pm 1 \text{ and } \Delta v = \pm 1$$

The energy change for the transition from  $v', J'$  to  $v'', J''$  levels is given by

$$\begin{aligned} \Delta E_{v,J} &= E''_{v,J} - E'_{v,J} \\ &= \left[ \left\{ B J''(J''+1) + \bar{\nu}_0 \left( v'' + \frac{1}{2} \right) \right\} - \left\{ B J'(J'+1) + \bar{\nu}_0 \left( v' + \frac{1}{2} \right) \right\} \right] \text{ cm}^{-1} \end{aligned}$$

$$\text{or } \Delta E_{v,J} = [B \{ J''(J''+1) - J'(J'+1) \} + \bar{\nu}_0(v'' - v')] \text{ cm}^{-1}$$

At lower temperatures, the molecules are generally in their lowest vibrational level ( $v = 0$ ). Hence the transition would be essentially from  $v = 0$  to  $v = 1$ . Under such condition

(a)  $v'' = 1$  and  $v' = 0$ ; if  $\Delta J = +1$ , *i.e.*,  $J'' = J' + 1$

$$\begin{aligned} \text{Then, } \Delta E_{v,J} &= [B(J'+1)(J'+2) - J'(J'+1) + \bar{\nu}_0] \\ &= [B(J'+1)(J'+2 - J') + \bar{\nu}_0] \end{aligned}$$

$$\text{or } \Delta E_{v,J} = [2B(J'+1) + \bar{\nu}_0] \text{ cm}^{-1}$$

where  $J' = 0, 1, 2, 3, \dots$

(b)  $v'' = 1$  and  $v' = 0$ ; if  $\Delta J = -1$ , *i.e.*,  $J'' = J' - 1$

$$\text{Then, } \Delta E_{v,J} = [\bar{\nu}_0 - 2B(J''+1)] \text{ cm}^{-1}$$

where  $J'' = 0, 1, 2, 3, \dots$

Both the expressions could be represented by the following single equation

$$\Delta E_{v,J} = (\bar{\nu}_0 + 2Bm) \text{ cm}^{-1}$$

where  $m = \pm 1, \pm 2, \pm 3, \dots$  (but not zero)

This equation gives permitted vibrational-rotational energy changes during transition, from  $v = 0$  to  $v = 1$ , involving simultaneous change in  $J$  value.

*Discussion.* 1.  $\bar{\nu}_0$  is called *band origin* or *band centre*.

2. The vibrational-rotational spectrum would consist of the series of lines with equal spacing of  $2B \text{ cm}^{-1}$ , on either side of the band origin at  $\bar{\nu}_0$ .

3. The band centre itself will not appear because of the condition that  $m$  is not equal to zero.

4. The spectral lines corresponding  $\Delta J = -1$  (where  $m = \text{negative}$ ) *i.e.*, at lower frequency side of  $\bar{\nu}_0$  are called *P-branch lines*.

5. The spectral lines corresponding to  $\Delta J = +1$  (when  $m = +ve$ ) *i.e.*, at higher frequency side of  $\bar{\nu}_0$  are called *R-branch lines*.



6. The vibrational-rotational spectral lines corresponding to  $\Delta J = -2, -1, 0, +1, +2$  are called *O, P, Q, R* and *S branch lines* respectively.

*Intensity of Spectral Lines in each Branch.* The expressions for maximum intensity of spectral lines in *P* and *R* branches are as follows :

$$P\text{-branch : } \bar{\nu}_{max} = \bar{\nu}_0 - 2B \left( \sqrt{\frac{kT}{2BhC}} + \frac{1}{2} \right) \text{ cm}^{-1}$$

$$R\text{-branch : } \bar{\nu}_{max} = \bar{\nu}_0 + 2B \left( \sqrt{\frac{kT}{2BhC}} + \frac{1}{2} \right) \text{ cm}^{-1}$$

*Frequency Separation between two most Intense Lines.* This is given by the following equation

$$\Delta \bar{\nu}_{max} = 4B \left( \sqrt{\frac{kT}{2BhC}} + \frac{1}{2} \right)$$

$$\Delta \bar{\nu}_{max} = \left( \sqrt{\frac{8kTB}{hC}} + 2B \right)$$

## 2. Anharmonic Oscillator Model. (i) Weaknesses of Harmonic Oscillator Model.

1. The harmonic oscillator concept is satisfactory to describe lowest vibrational energy levels. But at higher vibrational energy levels, there are departures and vibrations become anharmonic *i.e.*, harmonic oscillator concept fails.

2. The harmonic oscillator predicts that vibrational energy levels are equispaced. But experiment shows that as  $V$  increases, the spacing goes on decreasing.

Due to above reasons, the diatomic molecule should be considered as an anharmonic oscillator.

(ii) *Anharmonic Oscillator Concept (Purely Vibrational Spectra).* The Schrodinger wave equation, on solving for anharmonic oscillator, gives the following expression for vibrational energy

$$E_{vib} = \left[ \left( V + \frac{1}{2} \right) h\nu_e - \left( V + \frac{1}{2} \right)^2 h\nu_e x \right] \text{ ergs}$$

or

$$= \frac{1}{hC} \left[ \left( V + \frac{1}{2} \right) h\nu_e - \left( V + \frac{1}{2} \right)^2 h\nu_e x \right] \text{ cm}^{-1}$$

$$= \left[ \left( V + \frac{1}{2} \right) \frac{\nu_e}{C} - \left( V + \frac{1}{2} \right)^2 \frac{\nu_e}{C} x \right] \text{ cm}^{-1}$$

$$E_{vib} = \left[ \left( V + \frac{1}{2} \right) \bar{\nu}_e - \left( V + \frac{1}{2} \right)^2 \bar{\nu}_e x \right] \text{ cm}^{-1}$$

where

$\bar{\nu}_e$  = Equilibrium oscillation frequency (wave number)

$x$  = Anharmonicity constant. It has small magnitude



**Selection Rule.** Because of anharmonicity, the vibrational transitions are not confined to adjacent levels only, but may also occur between different levels. So that  $\Delta V = \pm 1, \pm 2, \pm 3, \dots$

The above expression is the selection rule for anharmonic oscillator regarding the vibrational transitions.

The transitions involving  $\Delta V > 1$ , however, would be less probable because at room temperature, only lowest vibrational level ( $V = 0$ ) is occupied, and therefore, most of transitions would originate from  $V = 0$  level.

The energy changes, frequencies of lines from different transitions can be expressed as follows :

Transitions	$\Delta E_v$	Frequencies
$\Delta V = +1, \text{ i.e., } v=0 \text{ to } V=1$ $0 \rightarrow 1$	$\Delta E_v = h\nu = h\nu_e(1 - 2x)$ $0 \rightarrow 1$	$\nu = (1 - 2x) \cdot \nu_e$ $0 \rightarrow 1$
$\Delta V = +2, \text{ i.e., } v=0 \text{ to } V=2$ $0 \rightarrow 2$	$\Delta E_v = h\nu = 2h\nu_e(1 - 3x)$ $0 \rightarrow 2$	$\nu = (1 - 3x) \cdot 2\nu_e$ $0 \rightarrow 2$
$\Delta V = +3, \text{ i.e., } v=0 \text{ to } V=3$ $0 \rightarrow 3$	$\Delta E_v = h\nu = 3h\nu_e(1 - 4x)$ $0 \rightarrow 3$	$\nu = (1 - 4x) \cdot 3\nu_e$ $0 \rightarrow 3$
$\Delta V = +1, \text{ i.e., } v=1 \text{ to } V=2$ $1 \rightarrow 2$	$\Delta E_v = h\nu = h\nu_e(1 - 4x)$ $1 \rightarrow 2$	$\nu = (1 - 4x) \cdot \nu_e$ $1 \rightarrow 2$

Each different vibrational transition will lead to a separate line in the spectrum, with frequencies as indicated above.

(a) The line appearing due to transition from  $V = 0 \rightarrow V = 1$  is called fundamental band.

(b)  $V = 0 \rightarrow V = 2$  transition gives the line called *first overtone band* (second anharmonic).

(c)  $V = 0 \rightarrow V = 3$  transition produces the spectral lines called *second overtone band* (third anharmonic).

(d)  $V = 0 \rightarrow V = 4$  will correspond to *third overtone band* (fourth anharmonic) etc.

The intensity of these overtones keeps on falling with the increase in their degree.

**Hot Bands.** At room temperature only, the lowest vibrational energy level ( $V = 0$ ) is occupied. Thus most of vibrational transitions originate from level ( $V = 0$ ). As the temperature rises, molecules migrate from lowest level to  $V = 1$ . Thus a sufficient number of molecules occupy level  $V = 1$  at higher temperatures, thereby permitting vibrational transitions to originate from  $V = 1$ . Such transitions from  $V = 1$  to higher levels produce the spectral lines called *hot bands*. As the temperature rises, the intensity of hot bands increases.

(ii) **Anharmonic Oscillator Undergoing Rotational Motions Simultaneously (Vibrational-Rotational Spectra).** The total energy of anharmonic vibrating rotator is given by the following expression :

$$E_{v,J} = \left[ BJ(J+1) + \bar{\nu}_e \left( V + \frac{1}{2} \right) \left[ 1 - x \left( V + \frac{1}{2} \right) \right] \right] \text{ cm}^{-1}$$

In such case, the selection rules would be given by

$$\Delta J = \pm 1$$

and

$$\Delta V = \pm 1, \pm 2, \pm 3, \dots \quad \text{etc.}$$

Consider the transition from  $V = 0$  to  $V = 1$  involving a rotational change from level  $J'$  to  $J''$ . Under this condition the change in energy will be expressed as

$$\Delta E_{v,J} = [\bar{\nu}_e(1 - 2x) + B(J'' - J')(J'' + J' + 1)] \text{ cm}^{-1}$$

the rotational level  $J''$  is higher and  $J'$  is lower.

In the above equation if  $\Delta J = +1$ , i.e.,  $J'' - J' = 1$ , then

$$\Delta E_{v,J} = \bar{\nu}_e(1 - 2x) + B(1 + J' + J' + 1)$$



where 
$$= \nu_e (1 - 2x) + 2B (J' + 1) \text{ cm}^{-1} \quad \dots (1)$$

when  $J' = 0, 1, 2, \dots$

$\Delta J = -1$ , i.e.,  $J'' - J' = -1$ , then

where 
$$\Delta E_{v,J} = \bar{\nu}_e (1 - 2x) - 2B (J'' + 1) \text{ cm}^{-1} \quad \dots (2)$$

$J'' = 0, 1, 2, \dots$

The equations (1) and (2) can be expressed by the following single equation :

where 
$$\Delta E_{v,J} = \bar{\nu}_e (1 - 2x) + 2B \cdot m \text{ cm}^{-1} \quad \dots (3)$$

$m = \pm 1, \pm 2, \pm 3, \dots$  (but not zero)

In the equation (3) the frequency  $\bar{\nu}_e (1 - 2x)$  is called *band centre*. Hence the rotational-vibration spectrum of the diatomic molecule would have the series of lines on either side of the band centre.

In the above equation the frequency  $\bar{\nu}_e (1 - 2x)$  is equal to fundamental frequency  $\bar{\nu}_0$ . Hence

$$\Delta E_{v,J} = [\bar{\nu}_0 + 2B m] \text{ cm}^{-1} \quad \dots (4)$$

The value of  $m$  cannot be zero, because this will mean that value of  $J''$  or  $J'$  be negative, which is not possible. The spectrum contains equispaced lines, with a spacing of  $2B$  on either side of band centre (band origin). The two cases may arise :

(a) *For Negative Value of  $m$* . The spectral lines will appear on the lower frequency side of the centre of band frequency ( $\bar{\nu}_0$ ). Such spectral lines constitute *P-branch*.

(b) *For Positive Value of  $m$* . The spectral lines will appear on the higher frequency side of  $\bar{\nu}_0$ . Such spectral lines constitute *R-branch*.

The theoretical predictions made from equation (4) about vibrational-rotational spectra have been found in good agreement with experimental results.

(b) **Modes of Molecular Vibrations.** A molecule, consisting of  $n$ -atoms, has total degrees of freedom equal to  $3n$ .

(1) *For Linear Molecule :*

Rotational degrees of freedom = 2

Translational degrees of freedom = 3

$\therefore$  Vibrational degrees of freedom = (Total degrees of freedom) - (Rotational + Translational degrees of freedom)

=  $3n - (3 + 2)$

$\therefore$  Vibrational degrees of freedom =  $(3n - 5)$

Hence linear molecule has  $(3n - 5)$  fundamental vibrational modes. Hence for a diatomic molecule ( $n = 2$ ), modes of vibrations will be  $(3 \times 2 - 5)$  i.e., 1.

(2) *For Non-linear Molecule :*

Rotational modes = 3

Translational modes = 3

Vibrational modes =  $3n - (3 + 3)$

=  $(3n - 6)$

Thus non-linear molecule has  $(3n - 6)$  vibrational degrees of freedom.

**Types of Molecular Vibrations.** There are two types of molecular vibrations :

1. **Stretching Vibrations.** In these vibrations the distance between two atoms increases or decreases, but the atoms remain in the same bond axis. Such a mode of vibration does not cause any dipole change in the symmetrical molecule e.g.,  $\text{O}=\text{C}=\text{O}$  and, therefore, is not *infrared active vibration*.

When the stretching and compression occurs in a symmetrical fashion, we call it *symmetric*



stretching. But when one bond is compressing while the other bond is stretching, then it is known as *asymmetric stretching*.

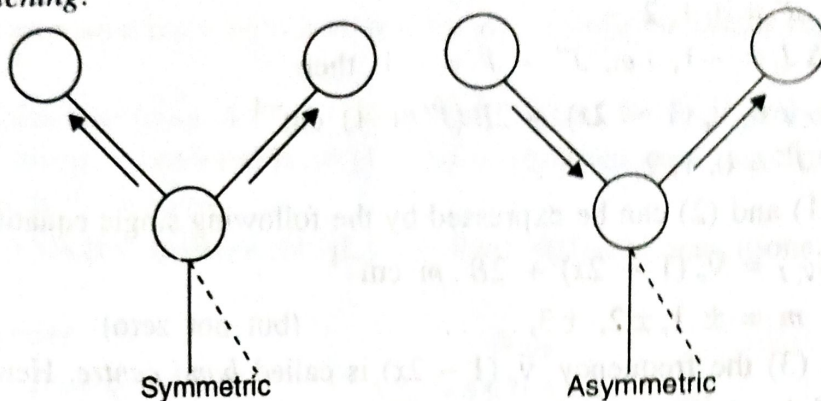


Fig. 9.22. Kinds of stretching vibrations.

**2. Bending (Deformation) Vibrations.** In such vibrations, atoms move in and out of the bond axis plane. Hence these vibrations involve change in bond angle or a movement of a group of atoms with respect to the remainder of the molecule, without movement of atom in the group with respect to one another. Thus bending mode of vibrations involves oscillations of atom perpendicular to its chemical bond. The bending modes are of four types :

(i) *Rocking*. In this mode of vibration, the two atoms joining a central atom, move back and forth in the plane of the molecule.

(ii) *Scissoring*. In this deformation, the two atoms, joined to a central atom, move towards and away from each other. In this mode, the bond angle changes.

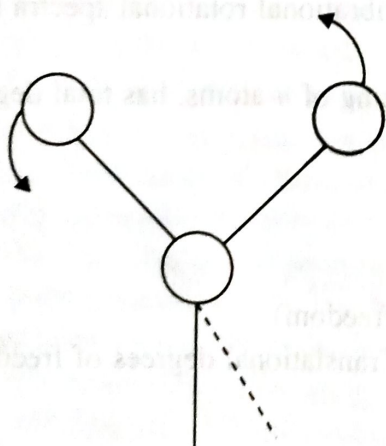


Fig. 9.23. Rocking mode of vibration.

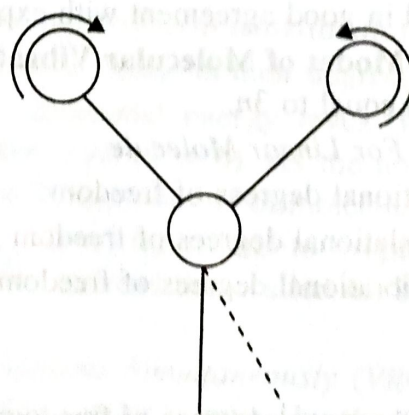


Fig. 9.24. Scissoring mode of vibration.

(iii) *Twisting*. In this deformation, the structural unit rotates about the bond, which joins it to the rest of the molecule.

(iv) *Wagging*. In this kind of vibration, the structural unit moves back and forth, out of the plane of molecule.

Let us consider vibrational modes of some particular cases.

**Diatomic Molecules.** The diatomic molecule is invariably linear. Hence

$$\begin{aligned} \text{No. of modes of vibrations} &= 3n - 5 \\ &= 3 \times 2 - 5 = 1 \end{aligned}$$

Thus there can be only one mode of vibration. In case of homonuclear diatomic molecules, because of their zero dipole moment for all bond lengths, no vibrational energy exchange would be possible, and as a result, such molecules would be *infrared inactive*.



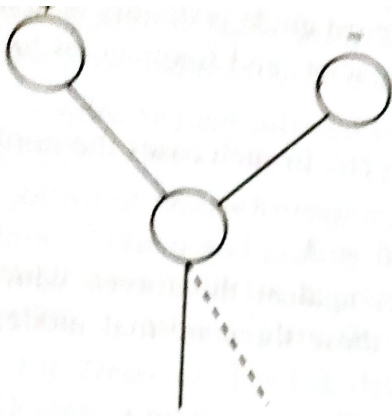


Fig. 9.25. Twisting mode of vibration. + or - sign signifies vibrations perpendicular to the plane of paper.

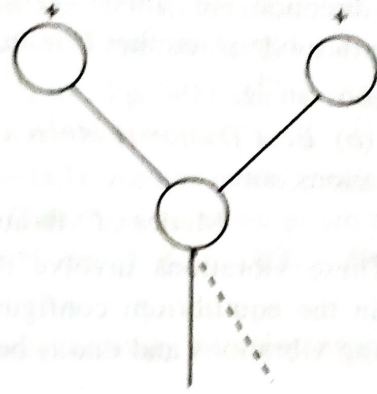


Fig. 9.26. Wagging mode of vibration. The + sign means vibrations perpendicular to the plane of paper.

In any heteronuclear diatomic molecule, e.g., HCl, CO, NO etc., the changes in the dipole moment, due to fluctuations in the bond-length, would make these molecules *infrared active*.



Fig. 9.27. Stretching in diatomic molecule.

**Polyatomic Molecules.** There are certain polyatomic molecules, which, although do not possess a permanent dipole, but because of certain modes of vibrations, develop a fluctuating dipole and respond to the infrared region of electromagnetic radiation.

Let us now consider some *linear* and *bent triatomic molecules*.

(a) *Linear Triatomic Molecule* e.g.,  $\text{CO}_2$ . It has the following vibrational modes

$$\begin{aligned} \text{Vibrational modes} &= (3n - 5) \\ &= 3 \times 3 - 5 = 4 \end{aligned}$$

Thus, allowed modes of vibrations are 4. These are shown in the following Fig. 9.28.

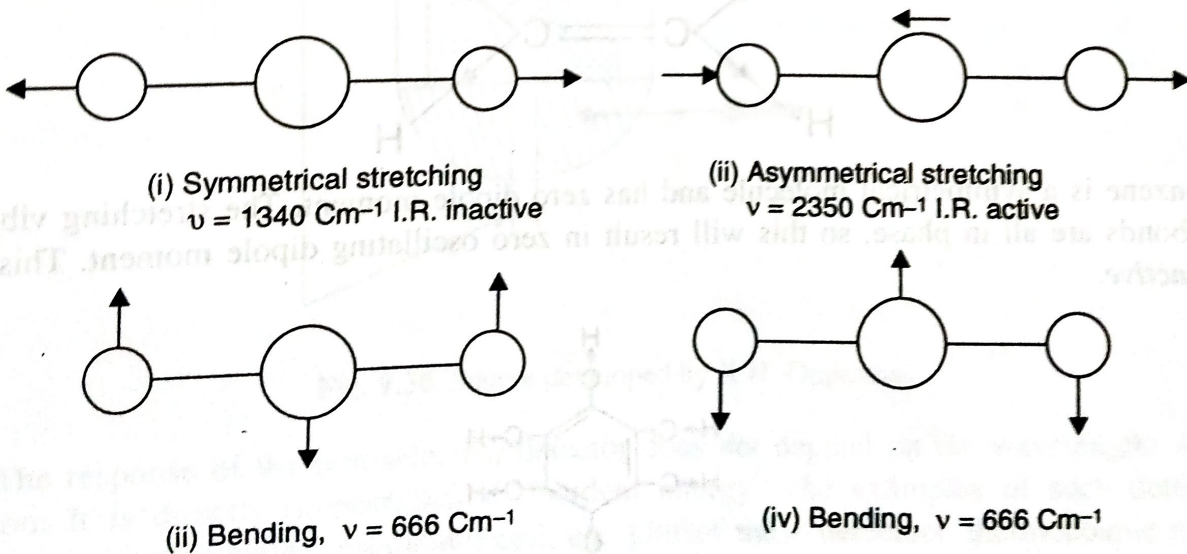


Fig. 9.28. Stretching in a linear triatomic molecule e.g.,  $\text{CO}_2$ .

Thus we see that the fourth mode of vibration is identical with third one. The frequencies



associated with the fourth and third are identical. Such motions, which are identical in all respects, except direction, are called *degenerates*. Thus in case of  $\text{CO}_2$ , third mode is doubly degenerate, i.e., the fourth mode is another bending type, identical in the character and frequencies to the third ( $\nu = 666 \text{ cm}^{-1}$ ).

(b) *Bent Triatomic Molecules*. Examples are  $\text{H}_2\text{O}$ ,  $\text{NO}_2$  etc. In such cases the normal modes of vibrations are –

$$\text{Modes of vibration} = 3n - 6 = 3 \times 3 - 6 = 3$$

These vibrations involve the movement of the nuclei against the forces which tend to maintain the equilibrium configuration of the molecule. Of these three normal modes, two are stretching vibrations and one is bending vibration.

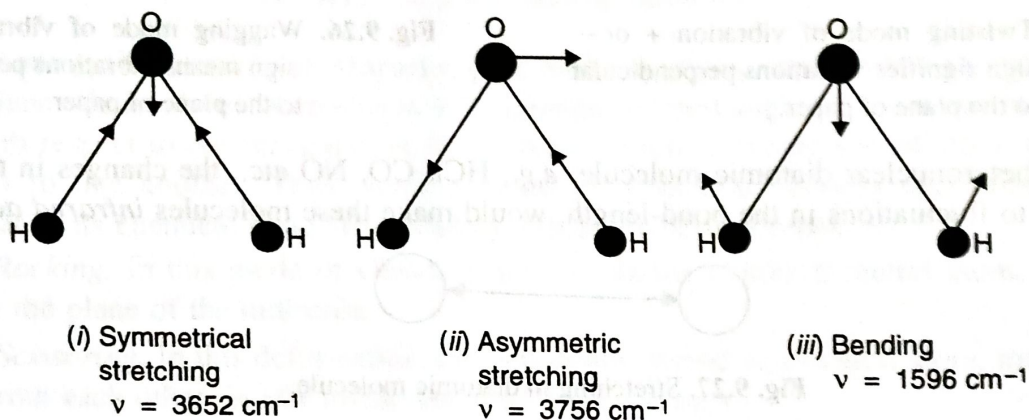
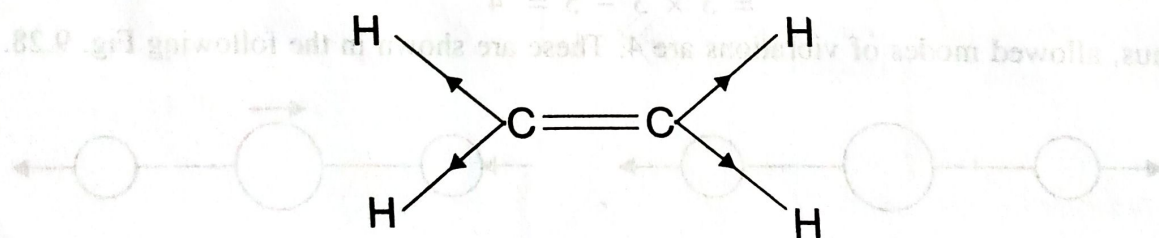


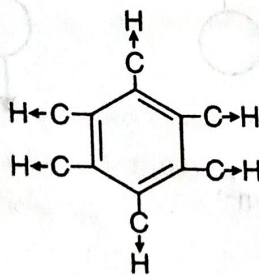
Fig. 9.29. Stretching in nonlinear triatomic molecule e.g.,  $\text{H}_2\text{O}$ .

The above figures reveal that bending frequencies are considerably much lower than stretching frequencies. All these three vibrations are *infrared active*.

(c) *Other Examples of Polyatomic Molecules*. For example  $\text{C}_2\text{H}_4$  shows the oscillating dipole moment, hence it is *infrared active*.



Benzene is a symmetrical molecule and has zero dipole moment. The stretching vibrations of C–H bonds are all in phase, so this will result in zero oscillating dipole moment. This is not *infrared active*.



**Instrumentation.** The instrument used to study I.R. spectra is called infrared spectrometer (spectrophotometer). There are four major components of an infrared spectrometer. These are :

1. *Source of I.R. Radiation.* The source of I.R. radiation is primarily an incandescent solid



- where
- $K$  = Force constant of the bond
  - $C$  = Velocity of light
  - $\bar{\nu}_0$  = Fundamental vibrational rotational frequency in terms of wave number
  - $\mu$  = Reduced mass of the molecule

Therefore, force constant for diatomic molecules can be calculated by determining  $\bar{\nu}_0$  and using the above equations. Calculation of force constant is not possible in polyatomic molecules. The force constants of some bonds are given below :

Bond	Force constant ( $K$ ) (dynes/cm)
C - C	$4.6 \times 10^5$
C = C	$9.5 \times 10^5$
C $\equiv$ C	$15.8 \times 10^5$
C = O	$12.3 \times 10^5$

From this table, it is inferred that  $K$  increases from a single to double and from a double to triple bond. Hence  $K$  gives useful information regarding the type of bond present in a compound.

(ii) **Identification of Compounds.** Every pure substance has its own characteristic I.R. spectrum, different from that of any other substance. The spectral picture thus helps in confirming and identifying an unknown sample of the pure variety or the components of a mixture. What we actually do is that the I.R. spectrum of the unknown compound is compared with the reference I.R. spectra and from the resemblance of the two spectra, the nature of the unknown compound is established.

(a) **Identification of Organic Compounds.** The regular recurrence of some absorption bands, when certain groups are present in the molecule, points to the fact that these bands are the characteristic of those groups. Thus the presence or absence of these groups may be established by the appearance or non-appearance of the absorption bands associated with these groups. These frequencies have been called *group frequencies*, which have provided a powerful tool in the identification of a covalent compound. In addition to the group frequencies, there are several bands in the I.R. spectrum of the compound, which cannot be associated with any group. These have been sometimes called *fingerprint bands*. The characteristic frequencies of some of the groups are given below :

Groups	Band Frequencies ( $\text{cm}^{-1}$ )
$\begin{array}{c}   \\ -\text{C}-\text{H} \\   \end{array}$	2880-3030
$\begin{array}{c} =\text{C}-\text{H} \\   \end{array}$	3000-3120
$\equiv\text{C}-\text{H}$	3340
$>\text{C}=\text{O}$	1660-1870
$>\text{C}=\text{C}<$	1600-1680
$-\text{C}\equiv\text{C}-$	2200-2260
$-\text{O}-\text{H}$	3500-3700
$\rightarrow\text{N}-\text{H}$	3300-3500

In a mixture, the positions and intensities of the I.R. bands for a particular substance are not affected by the presence of other components. So, in a mixture of closely related compounds, the identification, as well as quantitative estimation of a particular component, can be spectroscopically ascertained, even if the chemical methods fail.

(b) **Identification of Inorganic Ions and Compounds by I.R. Spectroscopy.** So far we have



non-aqueous samples and AgCl for aqueous samples). Gases can be studied in suitable gas cells, made of glass with "windows".

**Principle of I.R. Spectrometer.** The flow sheet diagram of the I.R. spectrometer is given in the Fig. 9.31.

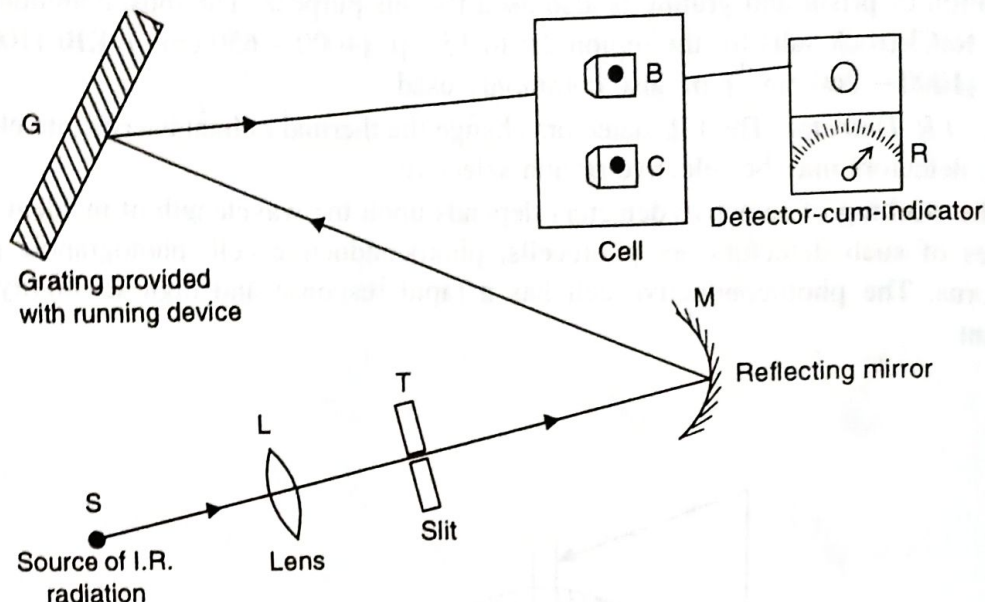


Fig. 9.31. Flow sheet diagram of I.R. spectrometer.

The beam of I.R. radiation from the source  $S$  is allowed to pass by means of lens  $L$ , through a narrow slit  $T$ . Then this beam is focussed by means of mirror  $M$  on the grating  $G$ , which is provided with a rotating device. The radiations of a desired wavelength emerge from  $G$ . Such radiations are allowed to pass through a cell  $B$ , containing the solution under test and from there to the detector-cum-indicator  $R$ . The intensity of the thermo-electric current, which is a measure of the intensity the radiation, is recorded. The cell  $B$  is then replaced by a cell containing pure solvent and again the intensity of radiation is recorded as before. If

$I$  = Intensity of radiation when the radiation passes through the solution.

$I_0$  = Intensity of the same radiation when it passes through the solvent.

Then  $I / I_0$  = Transmittance or transmittancy.

The transmittance is determined at different wavelengths and thus I.R. spectra is obtained.

## VI. Applications of Mid-Infrared Spectroscopy

The mid-infrared spectra of the molecule is said to be its finger prints since it is the characteristic of the molecule. The growing importance of this branch is based on the fact that no two organic compounds possess completely identical I.R. spectra. The I.R. spectroscopy finds a large variety of applications in the field of identification, chemical constitution determination, conformational studies, etc. Some of the important applications are :

(i) **Calculation of the Force Constant.** The force constant is the restoring force per unit displacement. The fundamental frequency at which absorption of I.R. radiation by the molecule occurs is related to the force constant of the corresponding bond by the following equation :

$$\bar{\nu}_0 = \frac{1}{2\pi C} \sqrt{K/\mu}$$

$$K = 4\pi^2 C^2 (\bar{\nu}_0)^2 \mu$$