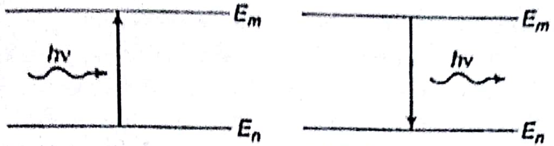
MOLECULAR SPECTROSCOPY

Spectroscopy deals with the transitions that a molecule undergoes between its energy levels upon absorption of suitable radiations determined by quantum mechanical selection rules.

Let us consider how a spectrum arises. Consider two molecular energy levels E_n and E_m, as shown in Fig.



(a) Absorption spectrum **(b) Emission spectrum**

Fig. : Spectroscopy Transitions between Molecular Energy Levels.

If a photon of frequency ν falls on a molecule in the ground state and its energy hν is exactly equal to the energy difference ΔE (= $E_m - E_n$) between the two molecular energy levels, then the molecule undergoes a transition from the lower energy level to the higher energy level with the absorption of a photon of energy hν. The spectrum thus, obtained is called the **absorption spectrum.** If the molecule falls from the excited state to the ground state with the emission of a photon of energy hν, the spectrum obtained is called the **emission spectrum.**

Basic Features of Different Spectrometers

The schematic diagram of the apparatus for absorption spectroscopy is given in Fig.

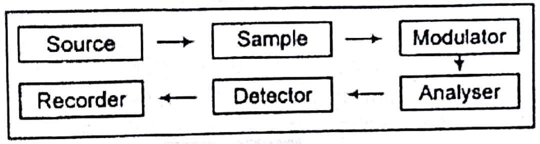


Fig. : Apparatus for Absorption Spectroscopy.

Source

The spectrometer is used when absorption occurs in infrared and ultraviolet regions of the electromagnetic spectrum. The source in a spectrometer produces radiation spanning a range of frequencies, but in a few cases (such as lasers), it is almost a monochromatic radiation. The radiation source in an absorption spectrometer is a heated ceramic filament coated with rare-earth oxides (a Nernst emitter or filament) for the infrared region. The source for the visible region of the spectrum is a tungsten filament which gives out intense white light : for the ultraviolet region the source is a hydrogen discharge lamp. A klystron (which is also used in radar installations and microwave ovens) or more commonly, a semiconductor device called Gunn diode, is used to generate microwaves. The radio-frequency radiation is generated by causing an electric current to oscillate in a coil of wire.

Dispersing Elements or Analyser

The variation of absorption with frequency is determined, traditionally, by analyzing the spectral radiation by means of a dispersing element which separates different frequencies into rays that travel in different directions. The simplest dispersing element is a glass or quartz prism but a diffraction grating is more widely used.

Detector

The third component of spectrometers is the detector, a device that converts the spectral radiation into an electrical signal that is passed on to a recording device operating synchronously with the analyzer, thus producing either a trace on a chart recorder or a computer record of the spectrum. Common detectors are the radiation-sensitive semiconductors. The radiation is chopped by a shutter that rotates in the beam so that an alternating signal is obtained from the detector (an oscillating signal is easier to amplify than a steady signal). A modulator is introduced to convert the signal to an alternating character. The procedure enables more AC electronics to be employed in the recording stages. In the microwave region the source frequency is varied and the analyser is not necessary.

Sample

The highest resolution is obtained when the sample is gaseous and at such low pressure that collisions between molecules are infrequent. Gaseous samples are essential for microwave (pure rotational) spectroscopy for molecules can freely rotate only in the gaseous state.

In order to achieve sufficient absorption, the path lengths of gaseous sample must be very long, of the order of metres. Long path lengths are achieved by multiple passage of the beam between two parallel mirrors at each end of the sample cavity. For infrared spectroscopy, the sample is typically a liquid held between windows of sodium chloride (which is transparent down to 700 cm^{-1}) or potassium bromide (down to 400 cm^{-1}). Other ways of preparing the sample include grinding it into a paste with 'Nujol', a hydrocarbon oil, or passing it into a solid disk, with powdered potassium bromide.

Fourier Transform Technique

Now-a-days, it is a common practice to use Fourier transform technique in spectroscopy, particularly with infrared (IR) and nuclear magnetic resonance (NMR) spectroscopies. In Fourier-transform infrared (FTIR) spectroscopy, a Michelson-type interferometer is used to analyse the spectrum. It functions by producing an interferogram which is the superposition of a series of waves, each of which represents a component in the spectrum in terms of intensity and wave number. A Fourier transformation of the interferogram then produces a well-resolved absorption spectrum of the species, with a good signal-to-noise (S/N) ratio, also abbreviated as SNR.

Selection Rules

The molecular spectra are governed by the so-called selection rules which specify the changes in the quantum numbers accompanying a particular transition. The chemist is lucky that selection rules exist which determine a spectrum. It there were no selection rules. The resulting spectrum would by very chaotic, indeed ! The selection rules are, in fact, the 'backbone' of spectroscopy and are obtained from the quantum theory of interaction of radiation with matter. Let us enumerate a few examples which would later be elucidated. For a diatomic molecule, such as H_2, NO, CO, etc., the selection rule for a pure rotational transition is $\Delta J = \pm 1$, where, J is the rotational quantum number. The selection rule for a pure vibrational transition is $\Delta V = \pm 1$, where, V is the vibrational quantum number.

The selection rules, however, are not always obeyed strictly. This is because certain approximations which have been used in the derivation of the selection rules are not valid strictly. The spectral transitions which obey a given selection rule are called **allowed transitions** whereas those which violate a selection rule are called **forbidden transitions.** In general, the allowed transitions are more intense (stronger) than the forbidden transitions which are weak.

The natural line width (or line-time broadening) of a spectral line is determined by the Heisenberg uncertainty principle, $\Delta E \Delta t \geq h / 4\pi$, where, ΔE is the uncertainty in the energy and Δt is the uncertainty in the life-time of the energy level. Since, for a photon $E = h\nu$ so that $\Delta E = h\Delta\nu$, hence the natural line width, $\Delta\nu$, is given by

$$\Delta\nu \geq (4\pi\Delta t)^{-1} \qquad ...(1)$$

Width and Intensity of Spectral Lines

When we analyse the spectrum of a molecule, the first thing we wish to know is how sharp and how intense (strong) is the spectral line. These two quantities are common to all branches of spectroscopy. fig. shows sharp spectral line having no width while fig. shows a spectral line having a width ΔE at half-height. The chemist would, indeed, be a happy person if the spectral lines were all very sharp and very intense. In practice, this is not so.

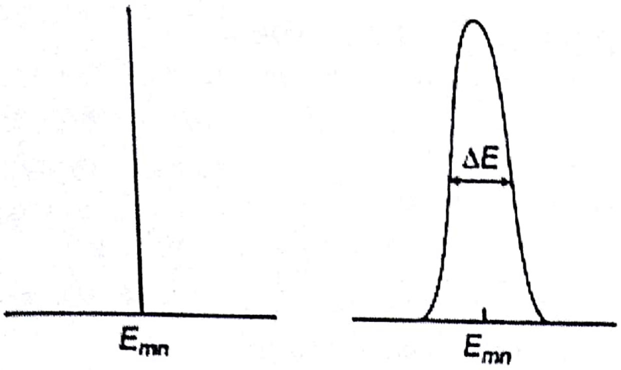


Fig. : (a) Sharp Spectral Line, (b) Spectral Line having a Width.

Two factors contribute to broadening of a spectral line : (i) The collision broadening and (ii) the Doppler broadening. The collision broadening is largely responsible for the width of spectral lines in the ultraviolet (UV) and visible regions. These transitions mostly take place between electrons in the outer shells in a molecule. When molecules in the gaseous or liquid phase collide with one another, they deform the charge clouds of the outer electrons thereby slightly perturbing the energy levels of these electrons. Hence, the spectral transitions between these perturbed energy levels are broadened.

The **Doppler broadening** arises when the molecule under investigation has a velocity relative to the observer or observing instrument. This is generally, the case with gaseous samples where the molecules are undergoing random motion according to the postulates of the kinetic theory of gases. If the molecule is moving towards the measuring instrument with velocity u, then the frequency v' of radiation 'seen' by the molecule is given by

$$v' = v(1 + u/c) \quad \text{...(2a)}$$

where, v is the radiation frequency and c is the velocity of light. If, on the other hand, the molecule is moving away from the measuring instrument, the frequency of radiation 'seen' by the molecule is given by

$$v' = v(1 - u/c) \quad \text{...(2b)}$$

Rearrange Eq. (2a), we obtain

$$(v - v')/v = \Delta v/v = - u/c \quad \text{...(3a)}$$

Similarly, rearranging Eq. (2b), we obtain

$$(v - v')/v = \Delta v/v = u/c \quad \text{...(3b)}$$

The quantity Δv is the Doppler broadening. From the kinetic theory of gases, it can be shown that the Doppler broadening of the spectral line of a molecule of mass m is given by

$$\Delta v/v = (2/c)\,(2kT \ln 2/m)^{1/2} \quad \text{...(4)}$$

Since, Δv/v is directly proportional to $T^{1/2}$, Doppler broadening can be reduced (and spectral lines of maximum sharpness can be obtained) by working with cold gaseous samples.

Intensity of Spectral Lines

The intensity of a spectral line is determined by (i) the Boltzmann population of the energy levels and (ii) the transition probability between the energy levels.

According to Boltzmann, if, at temperature T, N_0 is the number of molecules in the ground state, then the number of molecules, N, in the excited state is given by

$$N = N_0 e^{-\Delta E/kT} \quad \text{...(5)}$$

where, ΔE is the energy difference between the ground and excited states and k is the Boltzmann constant. The relative population at equilibrium is, thus, given by

$$N/N_0 = e^{-\Delta E/kT} \quad \text{...(6)}$$

Evidently, if ΔE is large, N/N_0 is small, i.e., the number of molecules in the excited state is less than that in the ground state. In fact, at room temperature, most of the molecules are in the ground state. Hence, the spectral lines originating from transitions from the ground state to a higher, say, third excited state would be more intense than those originating from transitions from the first excited state to the third excited state.

7. PURE ROTATION (MICROWAVE) SPECTRA

It is also called rotational spectroscopy.

Developed by Cleeton and Williams (1934)

Region of microwave spectroscopy = $3 \times 10^6 - 3 \times 10^8$ Hz

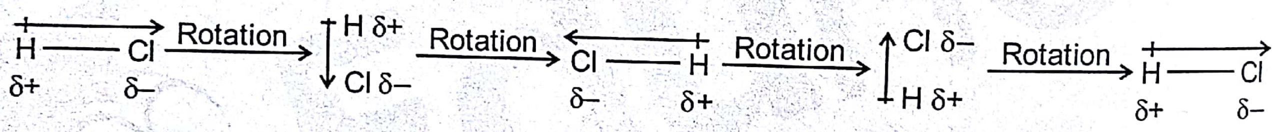
For light molecules the rotational spectra occur in the Far IR Region and for heavier diatomic and polyatomic molecules spectra arise in microwave region.

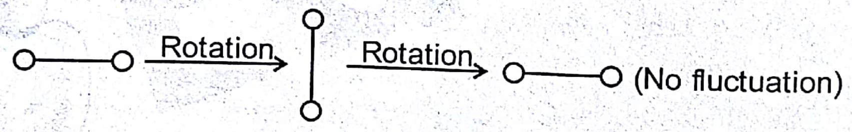
In microwave spectroscopy we deal's with the rotational energy of the molecules rotational energy of the molecules is always quantised.

- Such type of Gaseous molecules which contain permanent dipole moment is microwave active molecule i.e., (rotational active molecule) e.g., CH_3Cl, H_2O(Vapour) OCS, SO_2, $CHCl_3$, HCl etc.
- Molecule which contain zero dipole moment not show rotational spectra (Rotational inactive molecule) e.g., CCl_4, SF_6, CO_2, H_2, N_2, Cl_2, SO_3 etc.
- When a molecule having permanent dipole moment and show rotation then Fluctuation of dipole moment takes place when it rotates.

Howevers if a molecules does not possess a permanent dipole moment, there is no fluctuating dipole on rotation. Thus the molecules which have permanent dipole moment can absorb or emit radiation by making transition between different rotation states the. Dipole moment fluctuate in a wave form just like electric field of electromegnetic radiation.

e.g.,





dipole = O

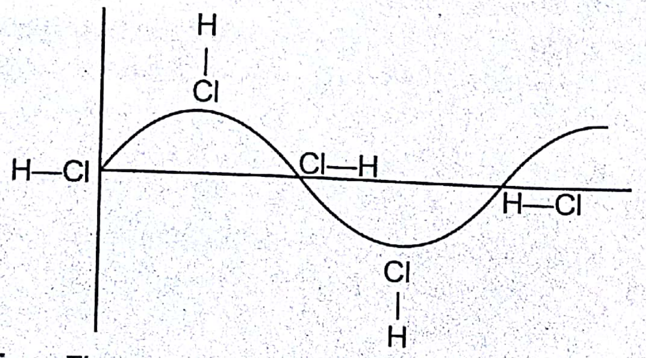


Fig. : Fluctuation of Dipole Moment with Rotation

Fluctuation of dipole moment and electric field of electromagnetic radiation interact with each other and result a rotational spectra.

Types of Molecules

In microwave spectroscopy rotation of molecules take on the basis of their moment of inertia (I) along with three perpendicular axis.

Thus a body has three principle moment of inertia, one about each axis usually called I_A, I_B and I_C.

Molecules can be divided into following categories.

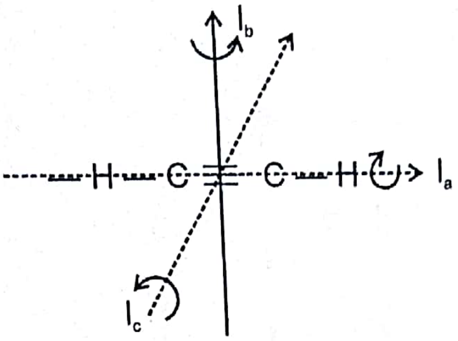
1. Linear Molecules : In linear molecules all the atoms are arranged in a straight line. Bond angle is always 180. Here three types of rotation take place :

(a) I_a : Along with principal axis or molecular axis or principle rotational axis.

(b) I_b : Perpendicular to the principal axis or end over end rotation in the plane of paper.

(c) I_c : $\perp$ to the principal axis or end over end rotation $\perp$ to the plane of paper.

e.g.,



For linear molecule $I_a = 0$

$I_b = I_c$

e.g., HCl, CO, OCS, HCN, N_2O, C_2H_2, HCCCl.

2. Symmetry Top Molecules : Symmetry top molecules have equal moment of inertia about two axes of rotation while the moment of inertia about the remaining axis is not equal to either of the other two moment of inertia.

So $I_a \neq I_b = I_c$

symmetry top molecules further divided in two categories.

(i) Prolate : (Rolling Pin Shaped)

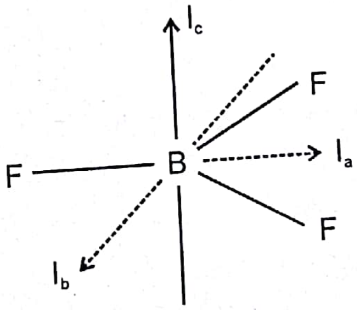
$I_a < I_b = I_c$

eg. CH_3Cl, CH_3F, $CHCl_3$, CH_3I

(ii) Oblate : (Disc or Knob Shaped)

$I_b = I_c < I_a$

eg. BF_3, C_6H_6 etc.



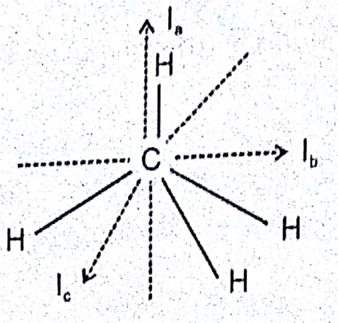
3. Spherical Top Molecule : Spherical top molecules have all the three moment of inertia equal i.e.

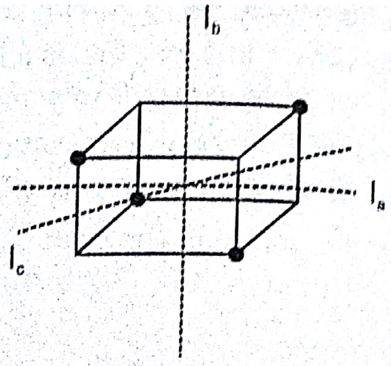
spherical top molecules has zero dipole moment.

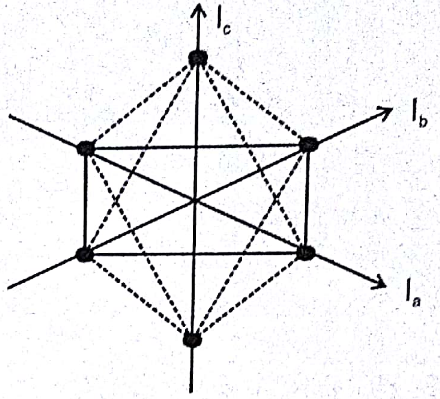
i.e. $I_a = I_b = I_c$

All regular tetrahedral and octahedral molecules are spherical top molecules

eg. CH_4, CCl_4, OSO_4, SF_6 etc.

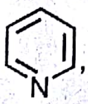


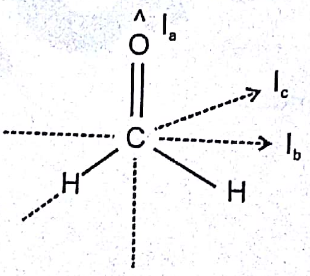




4. Asymmetric Top Molecules : The molecules for which all moment of inertia is different from each other is called asymmetric top molecules.

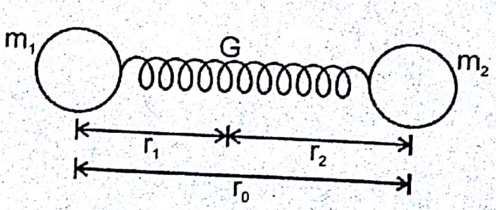
i.e. $I_a \neq I_b \neq I_c$

eg. H_2O, SO_2, HCHO, CH_3CHO, CH_2F_2,  , $CH_2 = CH - Cl$



Rigid Rotor

We consider a hetero diatomic molecule having two atom of mass m_1 and m_2 the inter nuclear distance blus m_1 and m_2 is r_0 and point G represent the centre of Gravity around which rotations take place.



the distance of m_1 particle from G is r_1
the distance of m_2 particle from G is r_2
From above diagram we can say that

$$r_0 = r_1 + r_2 \qquad \ldots(1)$$

The molecule is rotating around centre of gravity G

So we can say

$$m_1r_1 = m_2r_2 \qquad ...(2)$$

Now moment of inertia of rotating molecule is given by

$$I = m_1r_1^2 + m_2r_2^2 \qquad ...(3)$$

$$I = \sum m_i r_i^2$$

$$I = m_1r_1r_1 + m_2r_2r_2$$

$$I = m_2r_2r_1 + m_1r_1r_2$$

$$I = r_1r_2\,(m_1 + m_2) \qquad ...(4)$$

Now we determine the value of r_1 and r_2 from eq. (1) and (2)

From eq. (1)

$$r_0 = r_1 + r_2$$

$$r_2 = r_0 - r_1$$

$$m_1r_1 = m_2r_2 = m_2(r_0 - r_1) = m_2r_0 - m_2r_1$$

$$m_1r_1 = m_2r_0 - m_2r_1$$

$$m_1r_1 + m_2r_1 = m_2r_0$$

$$r_1(m_1 + m_2) = m_2r_0$$

$$r_1 = \frac{m_2r_0}{(m_1+m_2)} \qquad ...(A)$$

Such like that

$$r_2 = \frac{m_1r_0}{(m_1+m_2)} \qquad ...(B)$$

Now we put the value of (A) and (B) in eq. (4)

$$I = \frac{m_2r_0}{(m_1+m_2)} \times \frac{m_1r_0}{(m_1+m_2)}.(m_1+m_2)$$

$$I = \frac{m_1m_2r_0^2}{(m_1+m_2)}$$

$$\mu = \frac{m_1m_2}{m_1+m_2} = \text{reduced mass}$$

$$\boxed{I = \mu r_0^2} \qquad ...(5)$$

as we know For angular kinetic energy (Rotational energy) ...(6)

$$\because \quad E = \frac{1}{2}I\omega^2$$

$$E = \frac{1}{2}I.\omega.\omega$$

L = angular momentum

$$E = \frac{1}{2}L.\omega$$

ω = angular velocity

$$E = \frac{1}{2}I\omega^2 \times \frac{I}{I} = \frac{1}{2}\frac{I^2\omega^2}{I} = \frac{1}{2}\frac{L^2}{I}$$

$$\boxed{E = \frac{L^2}{2I}} \qquad ...(8)$$

But According to quantum mechanics it is provide that angular momentum is quantised and given by the equation

$$L = \sqrt{J(J+1)} \cdot \frac{h}{2\pi} \qquad ...(9)$$

Now put the value of eq. (9) in eq. (8)

$$E = \left[(J(J+1))^{1/2} \cdot \frac{h}{2\pi} \right]^2$$

$$E = \frac{J(J+1)}{2I} \frac{h^2}{4\pi^2} = \frac{h^2}{8\pi^2 I} \cdot J(J+1)$$

$$E = B.J(J + 1)$$

$$\because \qquad B = \frac{h^2}{8\pi^2 I} \text{ Joule}$$

We know that

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

$$\boxed{E = \frac{h^2}{8\pi^2 I} J(J+1)} \qquad ...(10)$$

From eq.(10) it is clear that rotational energy is quantised and it depends upon rotational quantum no.

From eq.(10) we can say that

$$E_0 = \frac{h^2}{8\pi^2 I} J(J+1) \text{ Joule.}$$

$$E = \frac{\varepsilon_{rot}}{hc} = \frac{h^2}{8\pi^2 I} \frac{J(J+1)}{hc} cm^{-1}$$

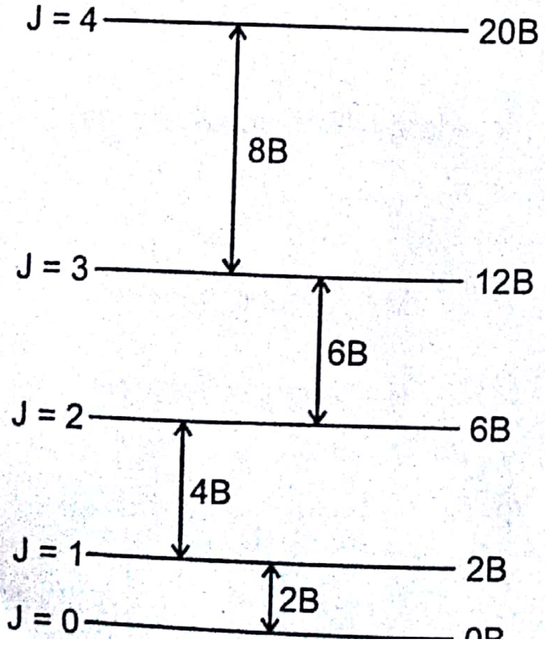
$$E = \frac{h}{8\pi^2 Ic} J(J+1)\ cm^{-1}$$

$E = B(J(J + 1)cm^{-1}$ $\qquad$ J = (0, 1, 2, ...) rotational ovantum no.

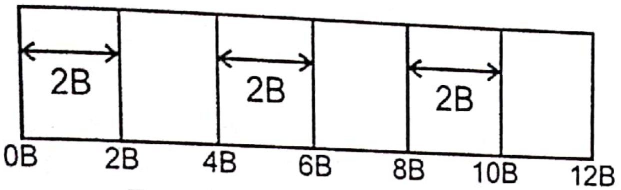
Energy Level Diagram of Rigid Rotator

We know that

$$E_j = B_j(J + 1)cm^{-1}$$



Spectrum of Rigid Rotator



Equally spaced line = 2B

but energy gap is not equal.

For Rigid rotor, the rotational spectra arise in such a way that all spectral lines are equally spaced the difference between two lines are 2B.

Now we can determine rotational constant by the help of rotational spectra.

When we solve schrodinger equation of rigid rotator, then it also provide information about selection rules.

Quantum mechanics say that selection rule for rigid rotor

$$\Delta J = \pm 1 \begin{cases} +1 \text{ Absorption} \\ -1 \text{ Emission} \end{cases}$$

Now we consider energy difference of rotational transition when molecules goes from rotational level J to J + 1

$$\Delta E = E_{J+1} - E_J = BJ^1(J^1 + 1) - BJ(J + 1)$$

$$\Delta E = B[J^1(J^1 + 1) - J(J + 1)]$$

$$\Delta E = B[J^2 + J^1 - J^2 - J]$$

$$\Delta E = B[(J + 1)^2 + (J + 1) - J^2 - J]$$

$$\Delta E = B[\cancel{J^2} + 1 + 2J + \cancel{J} + 1 - \cancel{J^2} - \cancel{J}]$$

$$\Delta E = B[2J + 2]$$

$$\boxed{\Delta E = 2B[J + 1]\text{cm}^{-1}} \qquad \text{...(11)}$$

Thus eq.(11) give the whole spectrum to be expected from a molecule.

Effect of Isotopic Substitution on Rotational Spectra

When a particular atom in a molecule is replaced by its isotope, the resulting substance is chemically identical with the original except for its atomic mass.

Here we assume that the bond length (inter nuclear distance) does not changed on isotopic substitution.

However a change in total mass moment of inertia and rotational constant of the molecule is occur.

Reduced mass

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

So we can say that if μ(↑) then moment of inertia I also (↑)

$$I = \mu r^2$$

But $B = \frac{h}{8\pi^2 IC}$

so the (↑)ing of I then the rotational constant B(↓) due to this energy is also (↓) because we know that

$$E = BJ(J + 1)$$

$$E \propto B$$

So energy is also (↓)

For original molecule

$$E_j \propto B \propto \frac{1}{I} \propto \frac{1}{\mu} \quad (1)$$

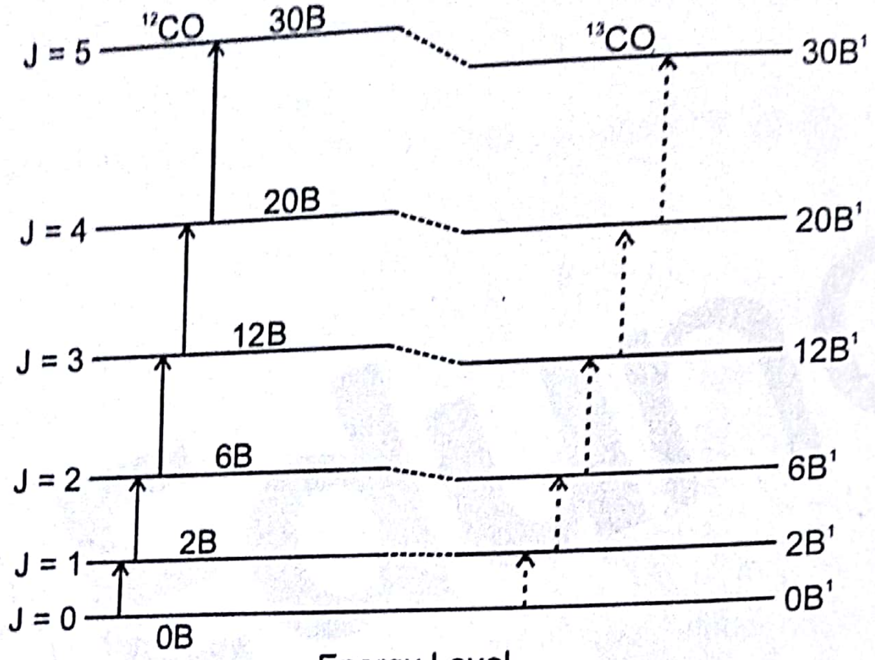
For isotopic substitution

$$E'_j \propto B' \propto \frac{1}{I'} \propto \frac{1}{\mu'} \quad (2)$$

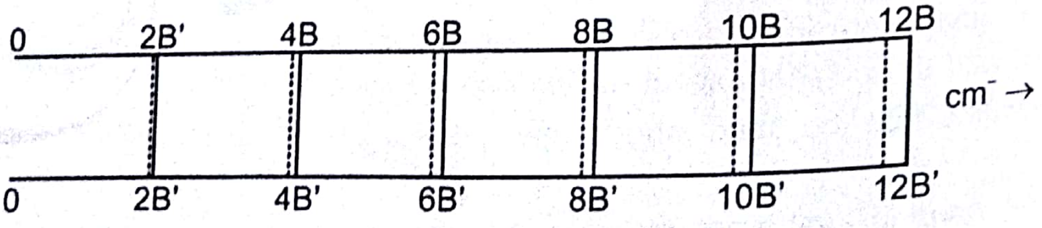
From eq.(1) and (2)

$$\frac{E'_j}{E_j} \propto \frac{B'}{B} \propto \frac{I}{I'} \propto \frac{\mu}{\mu'}$$

So we can draw a diagram



Energy Level



Rotational Spectrum

In the case of heavy isotope , the lines in rotational spectrum is not equispaced as well rotational energy level (↑) , the energy difference b/w two rotations level (↓) so rotational transition requ less amount of energy. So that line in spectrum get closure to each other.

Non Rigid Rotor : In rigid rotator the inter nuclear distance remains constant during the rotati if we rotate the molecule and (↑)es the rotational energy then centrifigal force will be dominant and t inter nuclear distance will (↑)es.

This type of rotator in which inter nuclear distance (↑) during the rotation is called non-rigid rotato

As the rotation (↑) centrifugal force (↑) the inter nuclear distance due to which the moment inertia is also (↑) So B and E also (↓)es. So the (↓) in energy is called centrifugal distortion effect.

We can say that

$$E_j \propto B \propto \frac{1}{I} \propto \frac{1}{r_0^2}$$

E_j' For non rigid rotator

$$\frac{E_j}{E_j'} = \frac{B}{B'} = \frac{I'}{I} = \frac{r'^2}{r^2}$$

the energy of non rigid system is given by

$$E_j = Bj(j + 1) - Dj^2 (j+ 1)^2$$

Here D is centrifugal distortion constant and the value of D is given by

$$D = \frac{h^3}{32\pi^4 r^2 I^2 KC}$$

K = Bond stretching force constant

Now we calculate energy difference when a molecule transition from J to J + 1 rotational level.

$$\Delta E_j = B_{J+1} - E_J$$

$$\Delta E_j = [Bj'(j' + 1) - Dj'^2(j' + 1)^2] - [Bj(j + 1) - Dj^2(j + 1)^2]$$

$$\Delta E_j = [Bj'(j' + 1) - Bj(j + 1) - [Dj'^2(j' + 1)^2 - Dj^2(j + 1)^2]$$

$$\Delta E_j = B[j'(j' + 1) - j(j + 1)] - D[j'^2(j' + 1)^2 - j^2(j + 1)^2]$$

$$\Delta E_j = B[j'^2 + j' - j^2 - j] - D[j'^2(j'^2 + 1 + 2j') - j^2(j^2 + 1 + 2j]$$

$$\Delta E_j = B[j'^2 + j' - j^2 - j] - D[j'^4 + j'^2 + 2j'^3 - j^4 - j^2 - 2j^3]$$

$$\Delta E_j = B[(j + 1)^2 + (j + 1) - j^2 - j] - D[(1 + j)^4 + (1 + j)^2 + 2\ (1 + j)^3 - j^4 - j^2 - 2j^3]$$

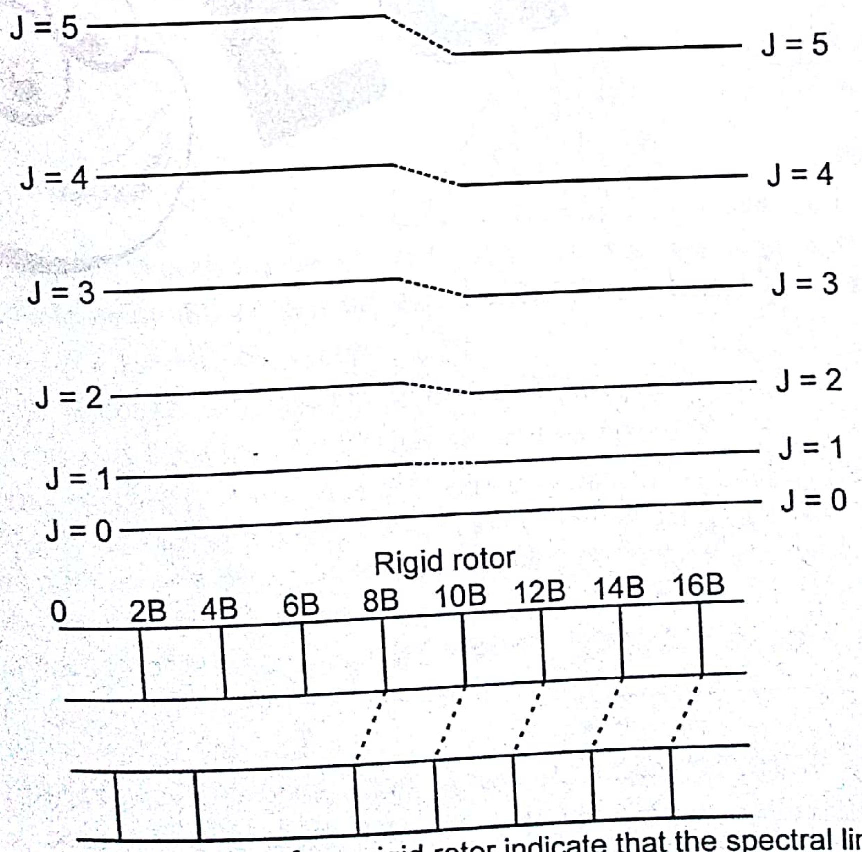
$$\Delta E_j = B[\ j^2 + 2j + 1 + j + 1 - j^2 - j]$$
$$- D[1 + 4j + 6j^2 + 4j^3 + j^4 + 1 + j^2 + 2j + 2\ (1+ j^3 +3j^2 + 3j) - j^4 - j^2 - 2j^3]$$

$$\Delta E_j = B[\ j^2 + 2j + 1 + j + 1 - j^2 - j]$$
$$- D[1 + 4j + 6j^2 + 4j^3 + j^4 + 1 + j^2 + 2j + 2 + 2j^3 + 6j^2 + 6j - j^4 - j^2 - 2j^3]$$

$$\Delta E_j = 2B[\ j + 1] - D[4 + 12j + 12j^2 + 4j^3]$$

$$\boxed{\Delta E_j = 2B(j+1) - 4D(j+1)^3}$$

Now the rotation spectrum of non rigid rotor is shown as



The rotational spectra of non rigid rotor indicate that the spectral line that's arises in the spectrum is not equispaced, as well as energy of rotation level (↑) the spectral line deviate and get closure to each other.

Intensity of Spectral Line

As we know that the selection rule for rotational spectroscopy is ΔJ = ± 1

i.e. rotational transition may be possible from J to J + 1

Transition Probability b/w different rotational energy level affect the intensity of spectral lines.

In general consideration the probability of different type of transition i.e.

J = 0 to 1

J = 1 to 2

J = 2 to 3

So the intensity of spectral line must be equal but practically all spectral lines are not equally intense. So the intensity of spectral lines depends upon following two factors.

(I) Relative population of molecule in J level

(Boltzmann population)

⇒ in normal condition all the molecules occupied ground state i.e. at J = 0, g = 1.

Now we calculate the no. of molecule in a given energy level "J" that can be calculated on the basis of boltzmann distribution law.

According to this law the ratio of molecule in a particular J level can be given as :

$$\frac{N_j}{N_0} = e^{-(\Delta E_j / KT)}$$

Here $\Delta E = E_j - E_0$ but $E_0 = O$

$\Delta E = E_J$

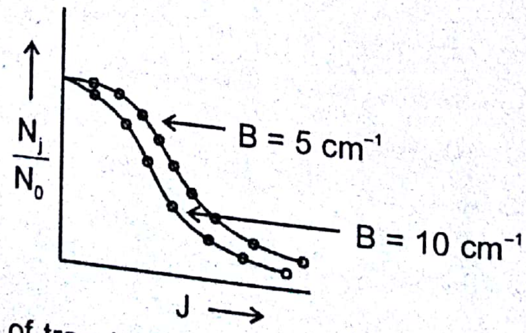
$$\frac{N_j}{N_0} = \exp\left(\frac{-E_j}{KT}\right) = \exp\left(\frac{-BhcJ(J+I)}{KT}\right) \quad ...(1)$$

$$\frac{N_j}{N_0} = \exp-\left(\frac{BhcJ(J+I)}{KT}\right) \quad ...(2)$$

$E_j = BJ(J + I)\text{cm}^{-1}$

$E_j = BJ(J + I) \times hc$ Joule

if we plot a graph between $\frac{N_j}{N_0}$ v/s J then it indicate that as well as the valve of J↑ the ratio of $\frac{N_j}{N_0}$↓ exponentially.



(II) The higher probability of transition between various energy levels will have higher intensity.

Degeneracy of Energy Level j : As we know that the rotational level is quantised From quantum mechanics, it is prove that the degeneracy of rotational energy level is

g = (2J + 1)

3. VIBRATIONAL OR I.R. SPECTROSCOPY

Vibrational spectroscopy is also called I.R. spectroscopy. IR Region of electromagnetic radiation.

$= 3 \times 10^{12}$ HZ – 3×10^{14} HZ

Complete IR Region 50 – 12500 cm^{-1}

Spectroscopic IR Region - 667 – 4000 cm^{-1}

Functional group
I.R. Region
[4000 – 1400 cm^{-1}]

Finger Print Region
[1400 – 667 cm^{-1}]

Far I.R. Region $\Rightarrow$ 50 cm^{-1} $\rightarrow$ 667 cm^{-1}

Near I.R. Region $\Rightarrow$ 4000 $\rightarrow$ 12500 cm^{-1}

0.8	2.5	15	(μ)	200μ wave length
Near I.R. Region	I.R. Region	Far I.R. Region		
12500	4000	667		50(cm^{-1}) wave number

if we fall I.R. Radiation on a molecule then vibration start. Due to this vibration I.R. spectra arises.

Condition of I.R. Activity : The molecule which contain permanent dipole moment or create dipole moment during the vibration will be I.R. Active molecule's

i.e. $\frac{du}{dr} \neq 0$

I.R. Active Molecule : H_2O, SO_2, HCl, HBr, H-I, $CHCl_3$, CO_2 (Asymmetric stretching), SF_6 (Asymmetric Stretching).

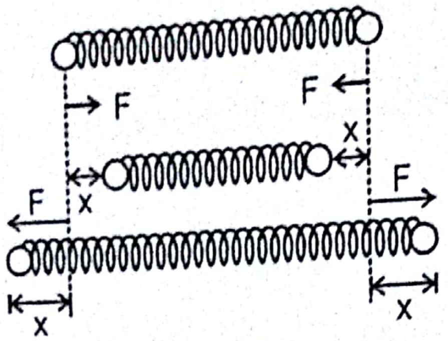
I.R. Inactive Molecule : Homodiatomic molecule (H_2, Br_2, Cl_2, F_2, O_2, N_2) and S_8, P_4, CO_2 and SF_6 (symmetrical stretching vibration)

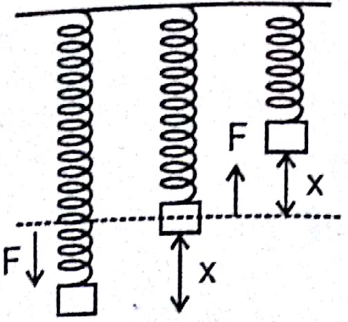
The vibrational spectra arises due to transition b/w different energy level.

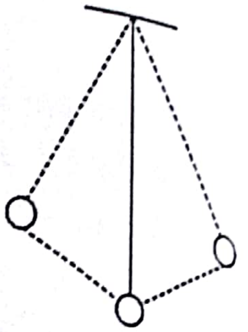
Principle of I.R. Spectroscopy : The absorption of I.R. radiation causes an excitation of molecule from a lower to higher vibrational level. We know that each vibrational level is associated to a no. of closely spaced rotational levels. So clearly the IR spectra is considered as vibrational-rotational spectra. All the bond in a molecule are not capable of absorbing I.R. energy but only those bonds which are accompanied by a change in dipole moment will absorb in the IR Region. Such vibrational transitions which are accompanied by a change in the dipole moment of the molecule are called IR active transitions thus these are responsible for absorbing the energy in the I.R. Region. On the other hand the vibrational transitions which are not accompanied by a change in dipole moment of the molecule are not directly observed and these are I.R. inactive.

Simple Harmonic Oscillator : The motion in which a particle or a system oscillate around its mean position is called simple Harmonic motion or simple Harmonic oscillation and the particle or system is called simple Harmonic oscillator.

The vibration of diatomic molecule take place around the mean position of the bond so diatomic molecule can be accepted as S.H.O.







SHO follow the book law

$F \propto x$ (x = displacement from mean position)

$F = -Kx$

k = force constant. ...(

Here –ve sign indicate that both force and displacement are opposite in direction. The potential energy of the SHO can be given as in the term of work done by system. According to classical mechanics

$$v = \int -F \cdot dx$$

$$v = -\int(-kx)dx = k\int x\, dx = k \cdot \frac{x^2}{2} \quad ...($$

$$v = \frac{1}{2}kx^2 \quad ...($$

The schrodinger equation of S.HO can be given as

$$\frac{d^2\Psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - V)\Psi = 0$$

From equation (3)

$$\frac{d^2\Psi}{dx^2} + \frac{8\pi^2 m}{h^2}(E - \frac{1}{2}kx^2)\Psi = 0$$

if we take diatomic molecule then m is replaced by μ then

$$\frac{d^2\Psi}{dx^2} + \frac{8\pi^2 \mu}{h^2}(E - \frac{1}{2}kx^2)\Psi = 0 \quad ...(4$$

When we solve schrodinger equation for S.H.O. and find out the energy then we found vibrational energy is quantisied i.e. it depends on the quantum no. called vibrational quantum no.(

So the vibrational energy can be given as :

$$E_V = \left(V + \frac{1}{2}\right) hv \quad ...(5)$$

$$E_V = \frac{Ev}{hc} = \left(V + \frac{1}{2}\right)\frac{hv}{hc} = \left(v + \frac{1}{2}\right) w_{osc}\, cm^{-1}$$

$$\boxed{\because w_{osc} = w_e = \frac{v}{c}}$$

$$\boxed{E_V = \left(v + \frac{1}{2}\right) w_e\, cm^{-1}} \quad ...(6)$$

$W_e = W_{osc}$ = Frequency of equilib

As we know that

$$E_v = \left(v + \frac{1}{2}\right)hv$$

at zero vibrational level v = 0 then

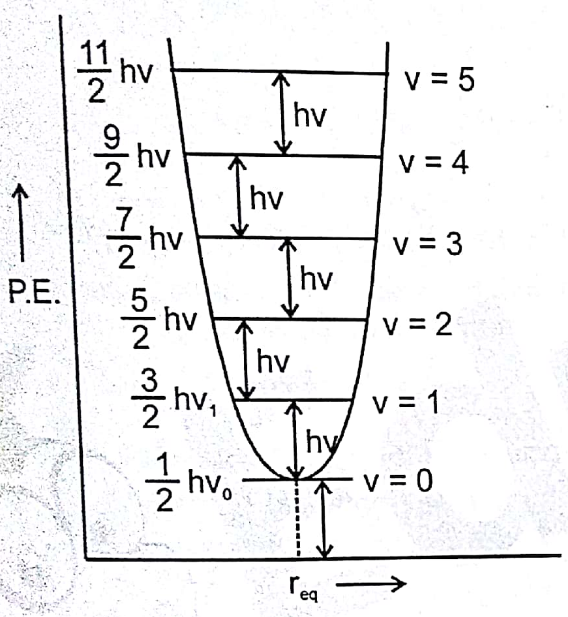
$$E_o = \frac{1}{2}\,hv \neq 0$$

So at v = 0 then E is not equal to zero but it possesses some value that is called zero point energy.

Zero point energy of SHO

$$\boxed{E_0 = \frac{1}{2}hv_0}$$

the vibrational level of SHO can be shown as



we know that $E_v = \left(V + \frac{1}{2}\right)hv$

if $v = 1$ then $E = \frac{3}{2}hv$

if $v = 2$ then $E = \frac{5}{2}hv$

if $v = 3$ then $E = \frac{7}{2}hv$

if $v = 4$ then $E = \frac{9}{2}hv$

A/c to quantum mechanics the selection rule for S.H.O. is given by

$$\Delta v = \pm 1 \begin{cases} \nearrow +1 \text{ Absorption} \\ \searrow -1 \text{ Emission} \end{cases}$$

the energy gap v → (v + 1)

$$\underset{V\to V+1}{\Delta E} = \underset{V+1}{E} - E_V$$

$$= \left(v' + \frac{1}{2}\right)hv - \left(v + \frac{1}{2}\right)hv = \left[\left(V + \frac{1}{2}\right) - \left(V + \frac{1}{2}\right)\right]hv$$

$$\underset{V\to V+1}{\Delta E} = \left[\left((V+1) + \frac{1}{2}\right) - \left(V + \frac{1}{2}\right)\right]hv$$

$$\underset{V\to V+1}{\Delta E} = \left[(V+1) + \cancel{\frac{1}{2}} - V - \cancel{\frac{1}{2}}\right]hv = \left[\cancel{V} + 1 - \cancel{V}\right]hv$$

$$\boxed{\underset{V\to V+1}{\Delta E} = hv}$$

Anharmonic oscillator : In real molecules when we stretch a bond then a point comes the bond is break, so the molecule dissociates into atoms. So real molecules behave as an oscillator.

P.M. morse study the anharmonicity and give a formula show the energy of an harmonic that can be given as :

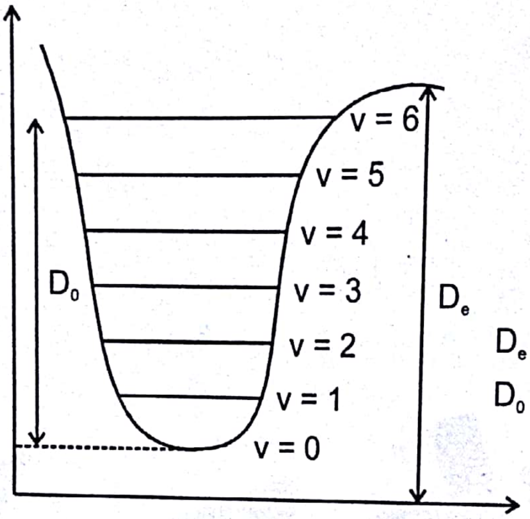
$$E = D_e\left[1-\exp\left[a(r_{eq}-r)\right]\right]^2$$

D_e = Dissociation energy

a = constant

r_{eq} = internuclear distance at equilibrium.

The p.m. morse potential diagram curve for an harmonic oscillator can be shown as :



D_e = theoritical dissociation energy

D_0 = experimental dissociation energy from ground state

According to morse potential curve the dissociation energy is represented as De and Do Theoritical dissociation energy is calculated by the well potential curve from E = 0 to max. b experimentally dissociation energy D_0 will be calculated from the ground vibrational level i.e. From. V = 0 to V = max.

or $E = \frac{1}{2}h\nu_0$ to max.

So we can say that

$$\boxed{D_e = D_0 + \frac{1}{2}h\nu_0}$$

- due to the anharmonicity of molecule the upper vibrational energy level get closure to each other
- When we solve schrodinger eq. for anharmonic oscillator then energy is arise as :

$$\varepsilon_v = \left(V+\frac{1}{2}\right)\bar{\omega}_e - \left(V+\frac{1}{2}\right)^2 \bar{\omega}_e x_e \ \text{cm}^{-1}$$

x_e = Anharmonicity constant

if v = 0 then $\varepsilon_0 = \frac{1}{2}\bar{\omega}_e - \frac{1}{4}\bar{\omega}_e x_e$

if v = 1 then $\varepsilon_1 = \frac{3}{2}\bar{\omega}_e - \frac{9}{4}\bar{\omega}_e x_e$

if v = 2 then $\varepsilon_2 = \frac{5}{2}\bar{\omega}_e - \frac{25}{4}\bar{\omega}_e x_e$

if v = 3 then $\varepsilon_3 = \frac{7}{2}\bar{\omega}_e - \frac{49}{4}\bar{\omega}_e x_e$

if v = 4 then $\varepsilon_4 = \frac{9}{2}\bar{\omega}_e - \frac{81}{4}\bar{\omega}_e x_e$

- The selection rule for anharmonce oscillator is given by Δv = ±1, ±2, ±3, ±4 .... Now we take different type of transition

(1) Fundamental Band : From v = 0 to v = 1 $\boxed{\Delta v = \pm 1}$

$$\underset{v=0\text{ to }v=1}{\Delta\omega}\ \varepsilon_1 - \varepsilon_0 = \left(\frac{3}{2}\bar{\omega}_e - \frac{9}{4}\bar{\omega}_e x_e\right) - \left(\frac{1}{2}\bar{\omega}_e - \frac{1}{4}\bar{\omega}_e x_e\right)$$

$$\Delta\varepsilon = \frac{3}{2}\bar{\omega}_e - \frac{9}{4}\bar{\omega}_e x_e - \frac{1}{2}\bar{\omega}_e + \frac{1}{4}\bar{\omega}_e x_e$$

$$\Delta\varepsilon = \left(\frac{3}{2}\bar{\omega}_e - \frac{1}{2}\bar{\omega}_e\right) + \left(\frac{1}{4}\bar{\omega}_e x_e - \frac{9}{4}\bar{\omega}_e x_e\right)$$

$$\Delta\varepsilon = \bar{\omega}_e\left(\frac{3}{2} - \frac{1}{2}\right) + \bar{\omega}_e x_e\left(\frac{1}{4} - \frac{9}{4}\right)$$

$$\Delta\varepsilon = \bar{\omega}_e + \bar{\omega}_e x_e \times -2$$

$$\Delta\varepsilon = \bar{\omega}_e - 2\bar{\omega}_e x_e = \bar{\omega}_e(1 - 2x_e)$$

$$\boxed{\underset{v=0\text{ to }v=1}{\Delta\varepsilon} = \bar{\omega}_e(1 - 2x_e)}$$

(2) Ist Overtone : (v = 0 to v = 2) Δv = ±2

$$\Delta E = E_2 - E_0$$

$$\underset{v=0\text{ to }v=2}{\Delta E} = \left(\frac{5}{2}\bar{\omega}_e - \frac{25}{4}\bar{\omega}_e x_e\right) - \left(\frac{1}{2}\bar{\omega}_e - \frac{1}{4}\bar{\omega}_e xe\right)$$

$$\Delta E = \frac{5}{2}\bar{\omega}_e - \frac{25}{4}\bar{\omega}_e x_e - \frac{1}{2}\bar{\omega}_e + \frac{1}{4}\bar{\omega}_e xe$$

$$\Delta E = \frac{5}{2}\bar{\omega}_e - \frac{1}{2}\bar{\omega}_e + \frac{1}{4}\bar{\omega}_e x_e - \frac{25}{4}\bar{\omega}_e xe$$

$$\Delta E = \bar{\omega}_e\left(\frac{5}{2} - \frac{1}{2}\right) + \bar{\omega}_e x_e\left(\frac{1}{4} - \frac{25}{4}\right)$$

$$\Delta E = 2\bar{\omega}_e + \bar{\omega}_e x_e \times -6$$

$$\underset{v=0\text{ to }v=2}{\Delta E} = 2\bar{\omega}_e - 6\bar{\omega}_e x_e = 2\bar{\omega}_e(1 - 3x_e)$$

Such like that

For IInd overtone Δv = ±3

$$\underset{v=0\text{ to }v=3}{\Delta E} = 3\bar{\omega}_e(1 - 4x_e)$$

For IIIrd overtone Δv = ±4

$$\Delta E = 4\bar{\omega}_e(1 - 5x_e)$$

(3) Hot Band : v = 1 to v = 2 (Δv = ±1)

First hot band (v = ±1)

$$\Delta E = E_2 - E_1$$

$$\Delta E_{v=2\text{ to }v=1} = \left(\frac{5}{2}\bar{\omega}_e - \frac{25}{4}\bar{\omega}_e x_e\right) - \left(\frac{3}{2}\bar{\omega}_e - \frac{9}{4}\bar{\omega}_e x_e\right)$$

$$\Delta E = \frac{5}{2}\bar{\omega}_e - \frac{25}{4}\bar{\omega}_e x_e - \frac{3}{2}\bar{\omega}_e + \frac{9}{4}\bar{\omega}_e x_e$$

$$\Delta E = \frac{5}{2}\bar{\omega}_e - \frac{3}{2}\bar{\omega}_e + \frac{9}{4}\bar{\omega}_e x_e - \frac{25}{4}\bar{\omega}_e x_e$$

$$\Delta E = \bar{\omega}_e\left(\frac{5}{2} - \frac{3}{2}\right) + \bar{\omega}_e x_e\left(\frac{9}{4} - \frac{25}{4}\right)$$

$$\Delta E = \bar{\omega}_e + \bar{\omega}_e x_e \times -4$$

$$\boxed{\Delta E_{v=2\to 1} = \bar{\omega}_e - 4\bar{\omega}_e x_e \Rightarrow \bar{\omega}_e(1 - 4x_e)}$$ Ist hot band

Such like for IInd Hot band

v = 1 to v = 3 (Δv = ±2).

$$\Delta E_{v=1\text{ to }v=3} = E_3 - E_1 = \left[\frac{7}{2}\bar{\omega}_e - \frac{49}{4}\bar{\omega}_e x_e\right] - \left[\frac{3}{2}\bar{\omega}_e - \frac{9}{4}\bar{\omega}_e x_e\right]$$

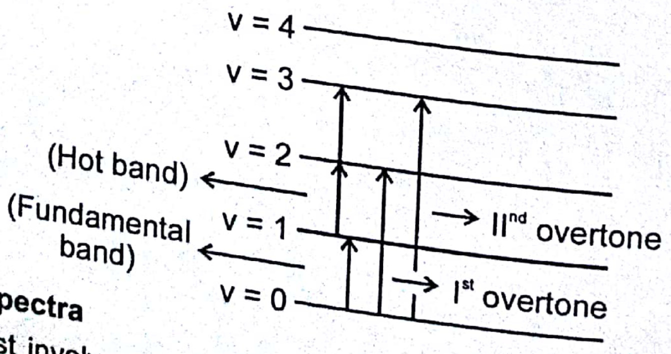
$$\Delta E_{v=1\text{ to }v=3} = E_3 - E_1 = \frac{7}{2}\bar{\omega}_e - \frac{49}{4}\bar{\omega}_e x_e - \frac{3}{2}\bar{\omega}_e + \frac{9}{4}\bar{\omega}_e x_e$$

$$\Delta E = \left[\frac{7}{2}\bar{\omega}_e - \frac{3}{2}\bar{\omega}_e\right] + \left[\frac{9}{4}\bar{\omega}_e x_e - \frac{49}{4}\bar{\omega}_e x_e\right]$$

$$\Delta E = \bar{\omega}_e\left[\frac{7}{2} - \frac{3}{2}\right] + \bar{\omega}_e x_e\left[\frac{9}{4} - \frac{49}{40}\right]$$

$$\Delta E = 2\bar{\omega}_e - 10\bar{\omega}_e x_e = 2\bar{\omega}_e\left[1 - 5x_e\right]$$

Different type of transitions can be shown as :



Condition for Vibration Spectra

(1) Vibration must involve a change in dipole moment.

(2) A molecule undergoing vibrational change must satisfy the selection rule for vibrational transition.

$$\Delta v = \pm 1$$

(3) The frequency of emitted or absorbed radiati

$$\Delta E = h\nu$$

Rotational-Vibrational Spectra : When a molecule absorbs radiation, which is enough to causes change in vibrational energy of the molecule, its rotational energy may also change because each vibrational energy level contains very closely spaced rotational level. Hence each absorption band which is due to a particular vibrational energy change, will exhibit a no. of closely spaced absorption lines due to change in rotational energy. Such type of spectrum is called Rotational-vibrational spectra.

The rotational and vibrational energy of molecules are quantisied. So the total energy of the molecule can be given as

$$E_t = E_r + E_v \qquad \text{...(1)}$$

$$E_t = \left[BJ(J+1) - DJ^2(J+1)^2\right] + \left[\left(V+\frac{1}{2}\right)w_e - \left(V+\frac{1}{2}\right)^2 w_e x_e\right] \qquad \text{...(2)}$$

In rotational-vibrational spectrum we consider a molecule as Non-rigid rotor and Anharmonic oscillator.

in eq. (2) we can neglect the centrifugal distortion constant D because it has very minor valve (effect) on the spectrum.

So equation (2) can be shown as

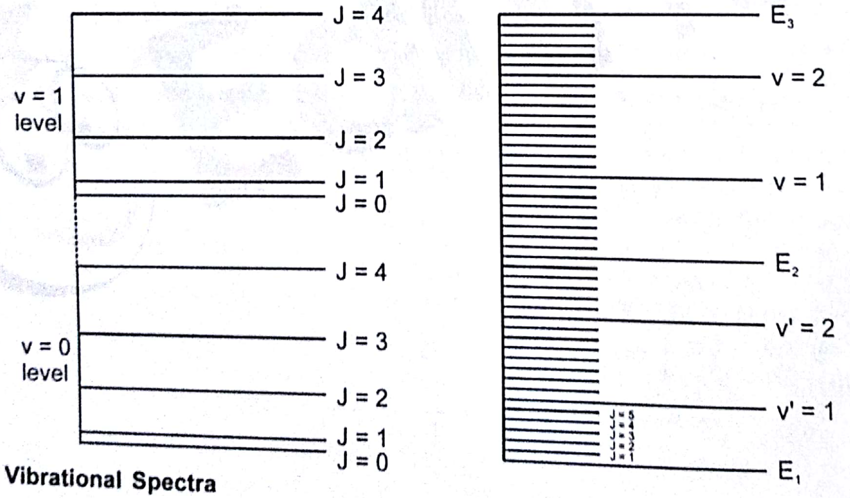
$$E_{J,V} = BJ(J+1) + \left(V+\frac{1}{2}\right)w_e - \left(V+\frac{1}{2}\right)^2 w_e x_e$$

According to quantum mechanics the selection rule for rotational vibrational spectra can be given as

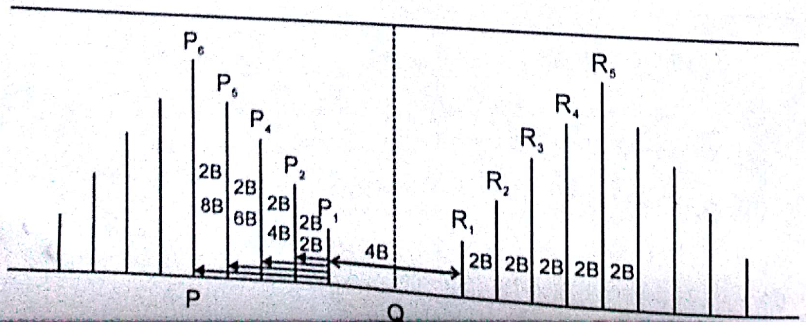
$\Delta J = 0, \pm 1, J = 0 = Q$ line

$\Delta V = \pm 1, \pm 2, \pm 3,$ --------------

Now different rotational and vibrational energy level of a molecule can be shown as :



Rotational Vibrational Spectra



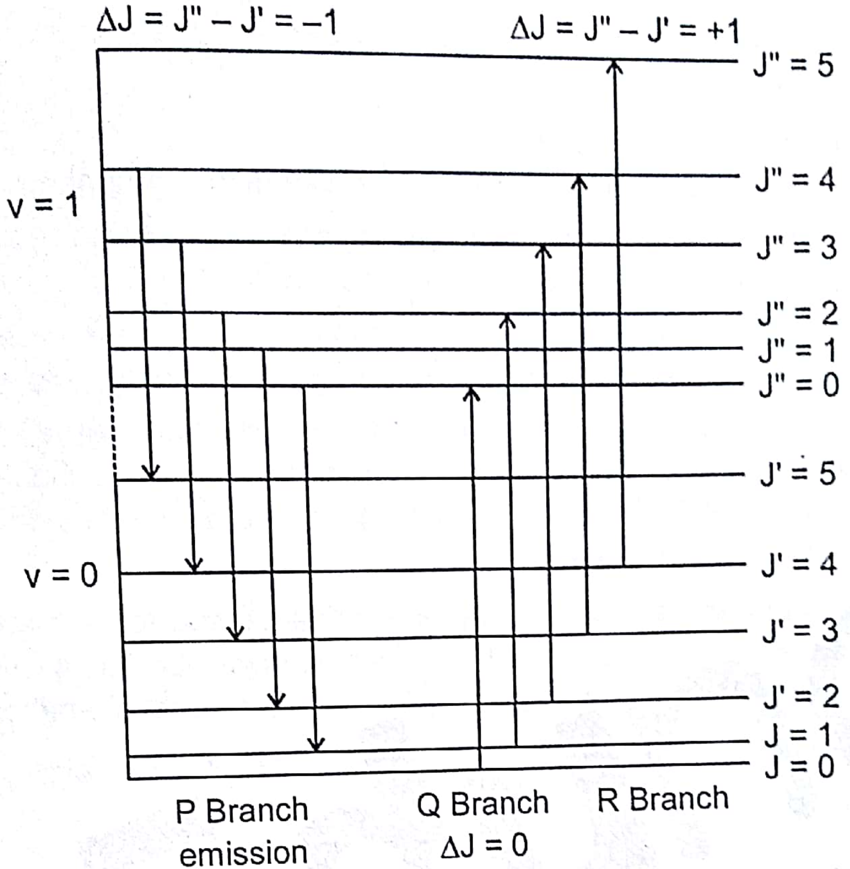
Explanation : The rotational-vibrational spectra arises due to the selection rule.

$\Delta J = \pm 1, 0$

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

In rotational-vibrational spectra different lines are arises, the explanation of line's can be given as

Name of lines →	O	P	Q	R	S
Selection rule (ΔJ)	–2	–1	0	+1	+2



(i) For P Branch : Spectral lines on low frequency side of band centre ($\bar{v}_0$) corresponding to ΔJ = –1 and Δv = 1 are called P Branch (or the negative branch since mass m is –ve) of the vibration-rotation.

$\boxed{\Delta v = \pm 1}$

i.e. $\Delta J = -1$ or $J'' - J' = -1$

$v_P = v_Q - 2B'(J + 1)$

different P lines observed at Branch

$v_P = v_Q - 2B$	P_1
$v_P = v_Q - 4B$	P_2
$v_P = v_Q - 6B$	P_3
$v_P = v_Q - 8B$	P_4

(ii) For R Branch : Spectral lines on high frequency side of v_o (band centre) corresponding to Δv = 1, ΔJ = 1 are known as R Branch (or the positive branch, since m is +ve) of the vibration-Rotation band their frequency is given as

$\boxed{\Delta v = \pm 1}$

$\Delta J = +1$ i.e. $J'' - J' = +1$

$v_R = v_Q + 2B'(J + 1)$

different R lines observed at

$v_R = v_Q + 2B$	R_1	
$v_R = v_Q + 4B$	R_2	
$v_R = v_Q + 6B$	R_3	
$v_R = v_Q + 8B$	R_4	Branch

10. ELECTRONIC SPECTRA

The electronic band spectra of molecules are observed in the ultraviolet and visible regions of the electromagnetic spectrum. Their complexity arises from the fact that a transition between two electronic states is almost invariably accompanied by simultaneous transitions between the vibrational and rotational energy levels as well. This is expressed by saying that electronic spectra have **vibrational fine structure** and **rotational fine structure.** According to the Born-Oppenheimer approximation, the total energy of molecule in the lower (ground) state is given by

$$E'' = E''_{el} + E''_{vib} + E''_{rot} \qquad ...(1)$$

neglecting the translational energy, E''_{tr}, which is not quantized. Here, E''_{el}, E''_{vib} and E''_{rot} are respectively, the electronic, vibrational and rotational energies. Assuming that the Born-Oppenheimer approximation is valid in the upper (excited) state as well, the excited state energy E' is given by

$$E' = E'_{el} + E'_{vib} + E'_{rot} \qquad ...(2)$$

The energy change for an electronic transition is given by

$$\Delta E = E' - E'' = (E'_{el} - E''_{el}) + (E'_{vib} + E''_{vib}) + (E'_{rot} - E''_{rot}) \qquad ...(3)$$

$$= \Delta E_{el} + \Delta E_{vib} + \Delta E_{rot} \qquad ...(4)$$

Considerable simplification of spectra results by recognizing that

$$\Delta E_{el} >> \Delta E_{vib} >> \Delta E_{rot} \qquad ...(5)$$

The frequency for the electronic transition is given by the Bohr frequency condition, viz.,

$$\bar{v} = \frac{\Delta E}{hc} = \frac{\Delta E_{el} + \Delta E_{vib} + \Delta E_{rot}}{hc}\ \text{cm}^{-1} \qquad ...(6)$$

Eq. 6 shows how an electronic transition possesses the vibrational and rotational fine structure.

Franck-Condon Principle

A very useful guiding principle for investigating the vibrational structure of electronic spectra is provided by the well known Franck-Condon principle which states that an electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition. This principle is, to a first approximation, true since the electrons move so much faster than the nuclei that during the electronic transition the nuclei do not change their position. Hence, an electronic transition may be represented by a vertical line on a plot of potential energy versus the internuclear distance.

Let us demonstrate the Franck-Condon principle for the electronic transition of a diatomic molecule. Consider fig. where we have shown two potential energy curves for the molecule in the ground electronic state (E_0) and in the first excited electronic state (E_1). Since, the bonding in the excited state is weaker than in the ground state, the minimum in the potential energy curve for the excited state occurs at a slightly greater inter-nuclear distance than the corresponding minimum in the ground electronic state. Also, quantum mechanically it is known that the molecule is in the centre of the ground vibrational level of the ground electronic state. Thus, when a photon falls on the molecule, the most probable electronic transition, according to the Franck-Condon principle, takes place from v'' = 0 to v' = 2 (written schematically as 0 → 2). Transitions to other vibrational levels of the excited electronic state occur with lower probabilities so that their relative intensities are smaller than the intensity of the 0 → 2 transition, as shown in fig.

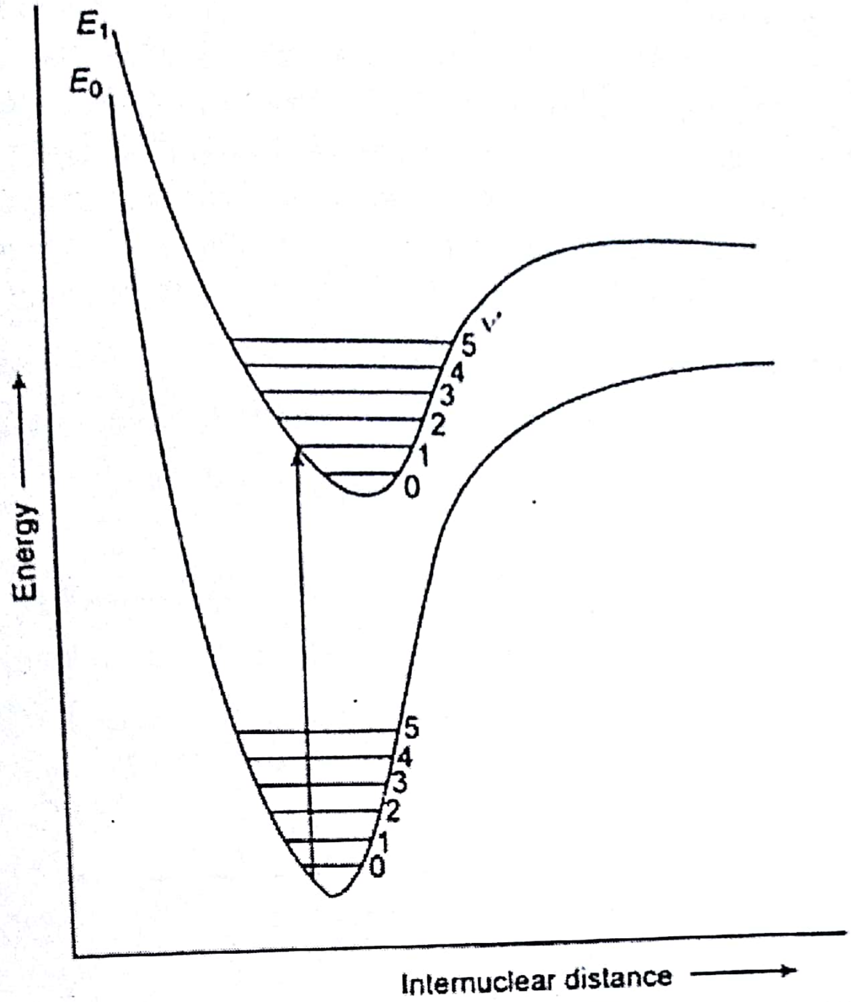


Fig. : Electronic Transition in A Diatomic Molecule.

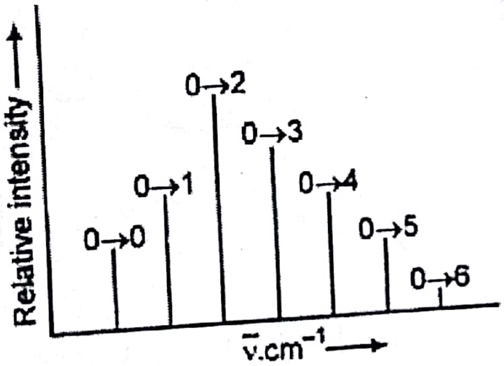


Fig. : Electronic Spectrum of A Diatomic Molecule.

Consider now a slightly different case of a diatomic molecule which has a potential energy curve E_0 in ground state and two potential energy curves E_1 and E_2 in excited states.

The potential energy curve E_2 does not have a minimum, as shown in fig.

The equilibrium internuclear distance is longer in E_1 than in E_0 since the bond is weaker in the excited state. The transition indicated by arrow a has, according to the Franck-Condon principle, maximum intensity. Other possible transitions are from the first excited vibrational level of the ground electronic state; they are indicated by the duplication of the vertical arrows b_1 and b_2. The transition b_1 ends in the lowest vibrational level of the first excited electronic state where the molecule is still held firmly. However, the transition b_2 promotes the molecule to a point where its energy is far above the potential energy plateau of state E_1 at large distance with the result that the molecule dissociates.

The molecule will also dissociate if it is excited to a level below the plateau in E_1 but above point c where the potential energy curves for E_1 and E_2 cross. At an inter-nuclear distance corresponding to the point c, the molecule may undergo a crossover from one state to the other without energy change and continue to dissociate

Considerable simplification of spectra results by recognizing that

$$\Delta E_{el} >> \Delta E_{vib} >> \Delta E_{rot} \quad ...(92)$$

The frequency for the electronic transition is given by the **Bohr frequency condition,** *viz.*,

$$\bar{\nu} = \frac{\Delta E}{hc} = \frac{\Delta E_{el} + \Delta E_{vib} + \Delta E_{rot}}{hc} \text{ cm}^{-1} \quad ...(93)$$

Eq. 93 shows how an electronic transition possesses the vibrational and rotational fine structure.

A very useful guiding principle for investigating the vibrational structure of electronic spectra is provided by the well known **Franck–Condon principle** which states that *an electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition.* This principle is, to a first approximation, true since the electrons move so much faster than the nuclei that during the electronic transition the nuclei do not change their position. Hence, *an electronic transition may be represented by a vertical line on a plot of potential energy versus the internuclear distance.*

Let us demonstrate the Franck–Condon principle for the electronic transition of a diatomic molecule. Consider Fig. 23. where we have shown two potential energy curves for the molecule in the ground electronic state (E_0) and in the first excited electronic state (E_1). Since the bonding in the excited state is weaker than in the ground state, the minimum in the potential energy curve for the excited state occurs at a slightly greater internuclear distance than the corresponding minimum in the ground electronic state. Also, quantum mechanically it is known that the molecule is in the *centre* of the ground vibrational level of the ground electronic state. Thus, when a photon falls on the molecule, the most probable electronic transition, according to the Franck–Condon principle, takes place from v″=0 to v′=2 (written schematically as 0 → 2). Transitions to other vibrational levels of the excited electronic state occur with lower probabilities so that their relative intensities are smaller than the intensity of the 0 → 2 transition, as shown in Fig. 24.

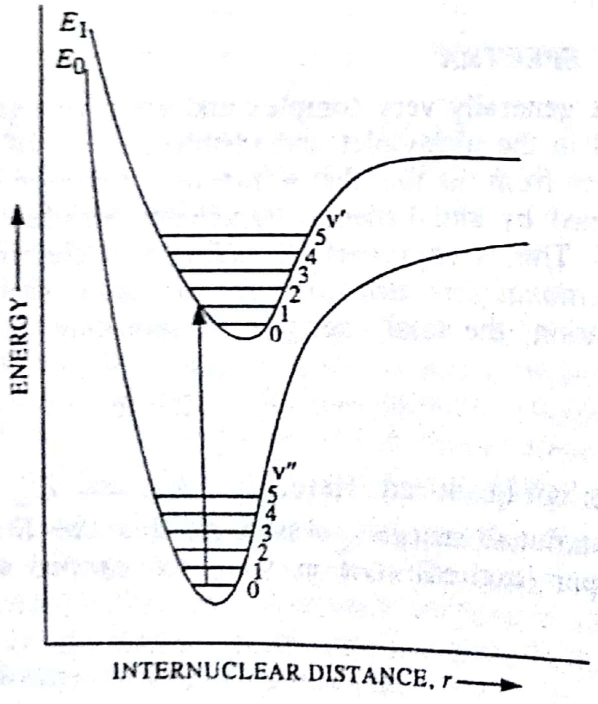


Fig. 23. Electronic transition in a diatomic molecule.

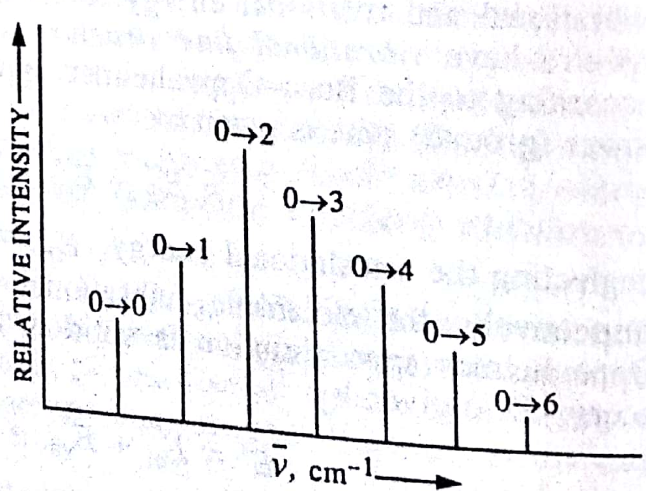


Fig. 24. Electronic spectrum of a diatomic molecule.

Consider now a slightly different case of a diatomic molecule which has a potential energy curve E_0 in ground state and two potential energy curves E_1 and E_2 in excited states.

The potential energy curve E_2 does not have a minimum, as shown in Fig. 24.

The equilibrium internuclear distance is longer in E_1 than in E_0 since the bond is weaker in the excited state. The transition indicated by arrow *a* has, according to the Franck-Condon principle, maximum intensity. Other possible transitions are from the first excited vibrational level of the ground electronic state ; they are indicated by the duplication of the vertical arrows b_1 and b_2. The transition b_1 ends in the lowest vibrational level of the first excited electronic state where the molecule is still held firmly. However, the transition b_2 promotes the molecule to a point where its energy is far above the potential energy plateau of state E_1 at large distance with the result that the molecule dissociates.

The molecule will also dissociate if it is excited to a level below the plateau in E_1 but above point *c* where the potential energy curves for E_1 and E_2 cross. At an internuclear distance corresponding to the point *c*, the molecule may undergo a crossover from one state to the other without energy change and continue to dissociate.

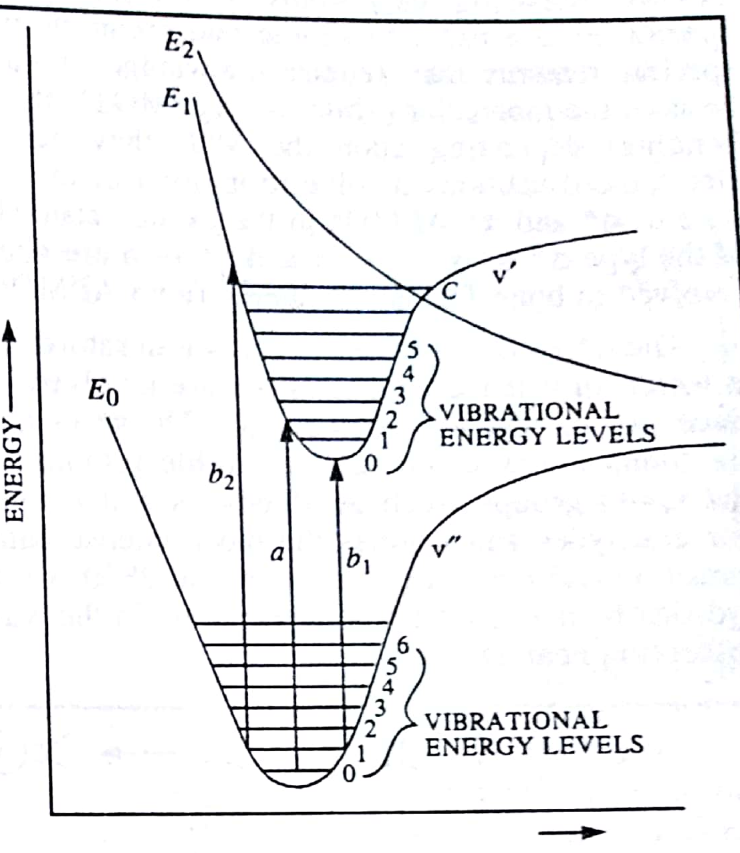


Fig. 25 Potential energy curves for the ground state and two excited states of a diatomic molecule. The curve E_2 crosses the curve E_1.

In the case of homonuclear diatomic molecules such as H_2 and N_2, the highest occupied molecular orbital (HOMO) in the ground state is a bonding molecular orbital (BMO) whereas the lowest unoccupied molecular orbital (LUMO) is an antibonding molecular orbital (ABMO). The HOMO and LUMO orbitals are collectively referred to as *Frontier Molecular Orbitals* (FMOs). The electronic transition HOMO → LUMO takes place, *i.e.*, the electron, upon absorption of a photon, undergoes a transition from HOMO to LUMO. This lies in the short wave length side of the ultraviolet (UV) region. An exception is provided by the oxygen molecule O_2 that has two unpaired electrons in the ground state which is thus a *triplet state*. The electronic transition occurs from the triplet ground state to the triplet excited state (rather than to the singlet excited state). The electronic spectrum of O_2 molecule is, of course, complex.

Though the heteronuclear diatomic molecules such as CO, HCl, NO, BH, etc., have more complex structures in terms of the molecular orbitals occupied by the various electrons in them, their electronic spectra are essentially similar to those of the homonuclear diatomics, consisting of absorption bands in the near ultraviolet region.

The electronic spectra of polyatomic molecules show greater degree of complexity. The vibrational structure and the rotational fine structure of electronic spectra can only be observed in the gaseous states of small molecules. In solution, the rotational energy levels are not well defined ; moreover, large molecules have very high moments of inertia. Hence, the rotational fine structure is totally wiped out in solution. Even vibrational transitions are broad, as shown by the Franck-Condon principle. Thus, the electronic spectra of molecules in solution appear as large unresolved bands rather than as sharp peaks. This is a characteristic feature of electronic spectra in condensed media and must be borne in mind. It also follows that if the rotational and vibrational structure of an electronic band can be fully resolved in the gaseous state, considerable information can be obtained from the electronic spectrum.

Organic compounds, particularly those containing groups like C=C, C=O, –N=N– and extensively conjugated systems, form a special class of polyatomic molecules whose electronic spectra are amenable to simple interpretation even though the investigation of their detailed spectral features may require knowledge of quantum mechanics and group theory. On the basis of the molecular orbital theory (MOT), the electrons can be classified as σ, π or n (non-bonding) depending upon the MOs they occupy. For organic carbonyl compounds, the electronic transitions involve promotion of the electrons in n, σ and π orbitals in the ground state to σ^* and π^* ABMOs in the excited state (Fig. 26). In other words, only the transitions of the type $\sigma^* \leftarrow \sigma$, $\pi^* \leftarrow \pi$ and $\pi^* \leftarrow n$ are allowed. Since electrons in the n orbitals are not involved in bond formation, there are no ABMOs associated with them.

The $\sigma^* \leftarrow \sigma$ transitions occurring in saturated hydrocarbons and other types of compounds in which all valence shell electrons are involved in single bonds, are found in ultraviolet region since they involve very high energy. The $\pi^* \leftarrow \pi$ and the $\pi^* \leftarrow n$ transitions, on the other hand, are found either in the UV or visible regions. The unsaturated molecules containing C=C and C=O groups (such as aldehydes and ketones) show $\pi^* \leftarrow n$ and $\pi^* \leftarrow \pi$ transitions. For aldehydes and ketones the more intense band near 1800 Å (180 nm) is due to $\pi^* \leftarrow \pi$ transition and the weaker band around 2850 Å (285 nm) is due to $\pi^* \leftarrow n$ transition. Olefinic hydrocarbons show a $\pi^* \leftarrow \pi$ transition in the wave length 160 – 170 nm. Acetylene shows an absorption near 180 nm.

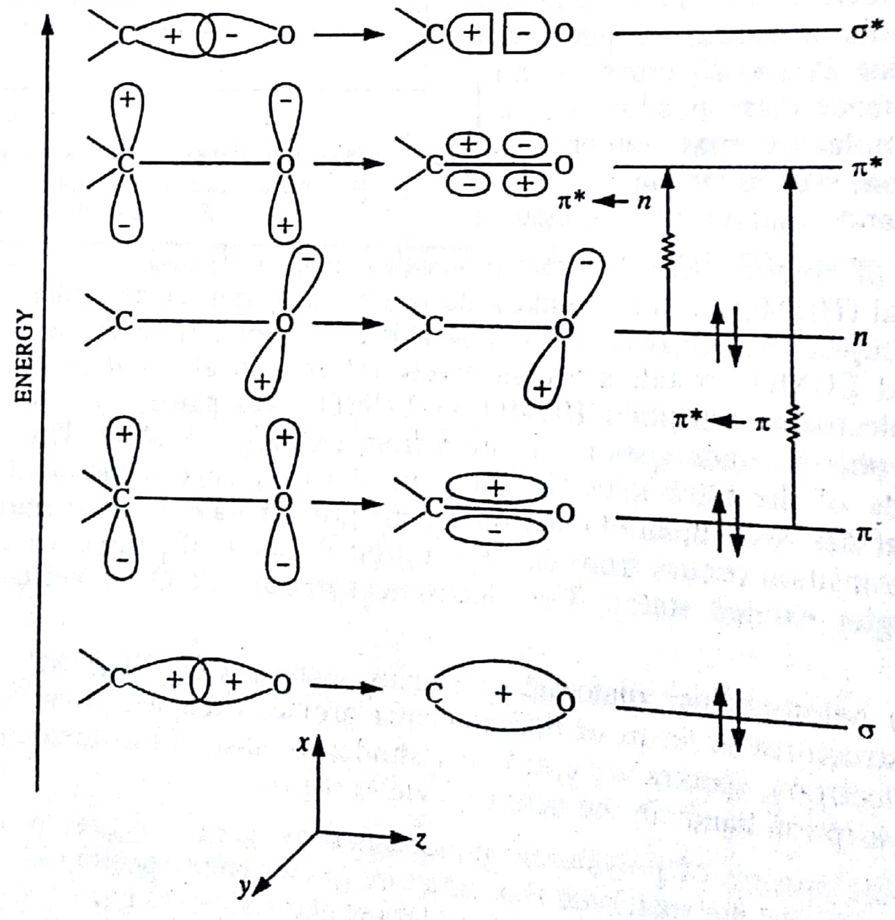


Fig. 26. Localized molecular orbitals and electronic transitions for the carbonyl group.

Functional groups such as C=C, –N=N– which absorb at wave lengths longer than 180 nm, are called **chromophores.** Other chromophores are nitro, nitroso, carbonyl, thiocarbonyl, sulphoxide groups as well as aromatic rings.

Molecules such as methylamine and methyl iodide which do not contain a π orbital, show $\sigma^* \leftarrow n$ transitions.

In extensively conjugated systems, the π-electrons are delocalized over the entire skeletal frame-work. Such systems are treated in terms of the 'free-electron model' and it is found that *the absorption bands shift to longer wave lengths as the extent of conjugation increases.* Thus, in the compound $C_6H_5-(CH=CH)_n-C_6H_5$, the $\pi^* \leftarrow \pi$ transition lies in the UV region when $n=1$ or 2. As n increases, the electronic transition shifts to the visible region. This aspect is dealt with later in this chapter. This phenomenon is shown schematically in Fig. 27.

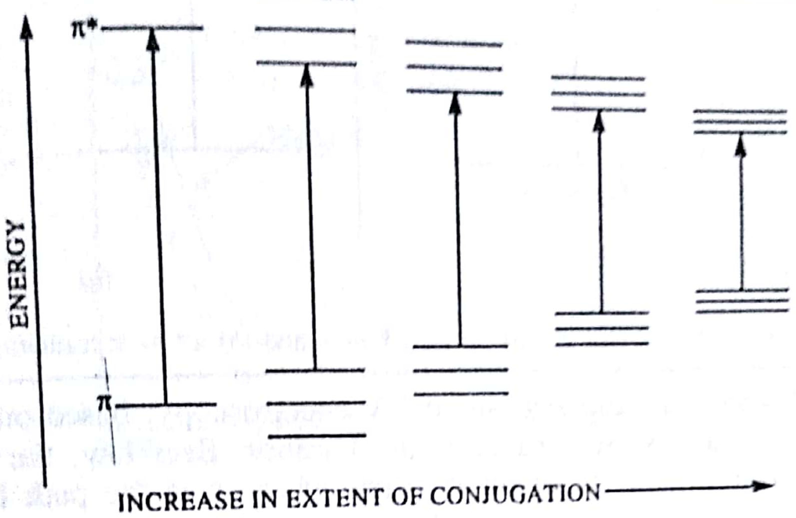


Fig. 27. Energy level diagram showing that in a conjugated π electron system, the wave length of absorption maximum is directly proportional to the extent of conjugation.

The intensity of an electronic band is determined by the extent of overlap of the wave functions in the ground and excited states. Since there is very poor overlap of wave functions of the ground and excited states in the $\pi^* \leftarrow n$ transition and there is considerable overlap of the corresponding wave functions in the $\pi^* \leftarrow \pi$ transitions, the $\pi^* \leftarrow n$ transitions are less intense (*i.e.*, weaker) than the $\pi^* \leftarrow \pi$ transitions. Also, in strongly acidic media, the $\pi^* \leftarrow n$ band disappears due to the protonation of lone pair of electrons. In fact, the protonation may increase the excitation energy to such an extent that the $\pi^* \leftarrow n$ transition may shift far out into the UV region and may not be observed.

The protonation of a functional group introduces profound changes in the spectra. Thus, the spectrum in such cases is strongly dependent upon *p*H. Solvent effects, too, are useful in identifying the nature of these transitions. The $\pi^* \leftarrow n$ transitions are altered by the solvent effects in cases where the lone pair electrons in oxygen or nitrogen-containing systems interact with polar solvents. It is customary in spectroscopic literature to refer to the shifts in absorption bands and their intensity changes as follows :

1. *Bathochromic shift* (or, the *red shift*) : a shift of λ_{max} to longer wave lengths.
2. *Hypsochromic shift* (or, the *blue shift*) : a shift of λ_{max} to shorter wave lengths.
3. *Hyperchromic shift* : an increase in the intensity of an absorption band, usually with reference to its molar extinction coefficient ε_{max}.
4. *Hypochromic shift* : a decrease in the intensity of an absorption band with reference to ε_{max}.

The term *auxochrome* refers to an atom or a group of atoms which does not give rise to an absorption band on its own but, when in conjugation with a chromophore, causes a bathochromic shift and a hyperchromic effect. For instance, $>C=C<$ group is a chromophore in ethylene; when one of the hydrogens is replaced by a halogen atom, a bathochromic shift and a hyperchromic effect are produced. This is because the lone pair on the halogen atom conjugates with the alkene double bond. We conclude that the halogen atom acts as an auxochrome.