

# A.R COACHING CENTRE

PG-TRB, POLYTECHNIC-TRB, SET COACHING FOR PHYSICS  
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## PG TRB - 2019

### Unit VI - Spectroscopy

#### Electromagnetic spectrum:-

Electromagnetic theory, developed by Clark Maxwell. Electromagnetic radiation travel with velocity of light( $c$ ) and can be treated in terms of frequency ( $\nu$ ) of the oscillating electric and magnetic fields.

$$c = \nu \lambda ; \quad \lambda = \frac{c}{\nu} m ; \quad 1 \text{ \AA} = 10^{-10} m = 10^{-4} \mu m = 10^{-8} cm = 10^{-10} m.$$

In molecular spectroscopy very often instead of frequency ( $\nu$ ), wave number ( $\bar{\nu}$ ) is used.

$$\boxed{\bar{\nu} = \frac{\nu}{c} = \frac{1}{\lambda} \text{ cm}^{-1} \text{ (or) } m^{-1}} \quad 100 \text{ m}^{-1} = 1 \text{ cm}^{-1} \quad 1 \text{ micron} = 1 \mu m = 10^{-6} m.$$

#### Types of Molecular Energy:-

- (i) The transition energy ( $E_t$ ) due to the translational motion of the molecule.
- (ii) The electronic energy ( $E_e$ ) since the electrons associated with each atom (or) bond are in continuous motion.
- (iii) The vibrational energy ( $E_v$ ) due to the periodic displacement of its atom from their equilibrium position.
- (iv) The rotational energy ( $E_r$ ) by virtue of bodily rotation about its atom centre of gravity.

► Born and Oppenheimer, the various form of energies of a molecule are independent of each other.

$$\boxed{\therefore \text{Total energy } E_{total} = E_e + E_v + E_r \quad \text{(or)} \quad \psi = \psi_e \psi_{rv} \psi_r} \quad \text{(PG TRB-2013)}$$

Where,  $\psi_e, \psi_v$  and  $\psi_r$  are the electronic, vibrational and rotational wave functions.

- The quantized levels of these energies for diatomic molecule.
- The rotational, vibrational and electronic energy separation are of the order of  $1 - 300 \text{ cm}^{-1}$ ,  $300 - 4000 \text{ cm}^{-1}$  and  $10^6 \text{ cm}^{-1}$  respectively.

## Region of Electromagnetic spectrum:

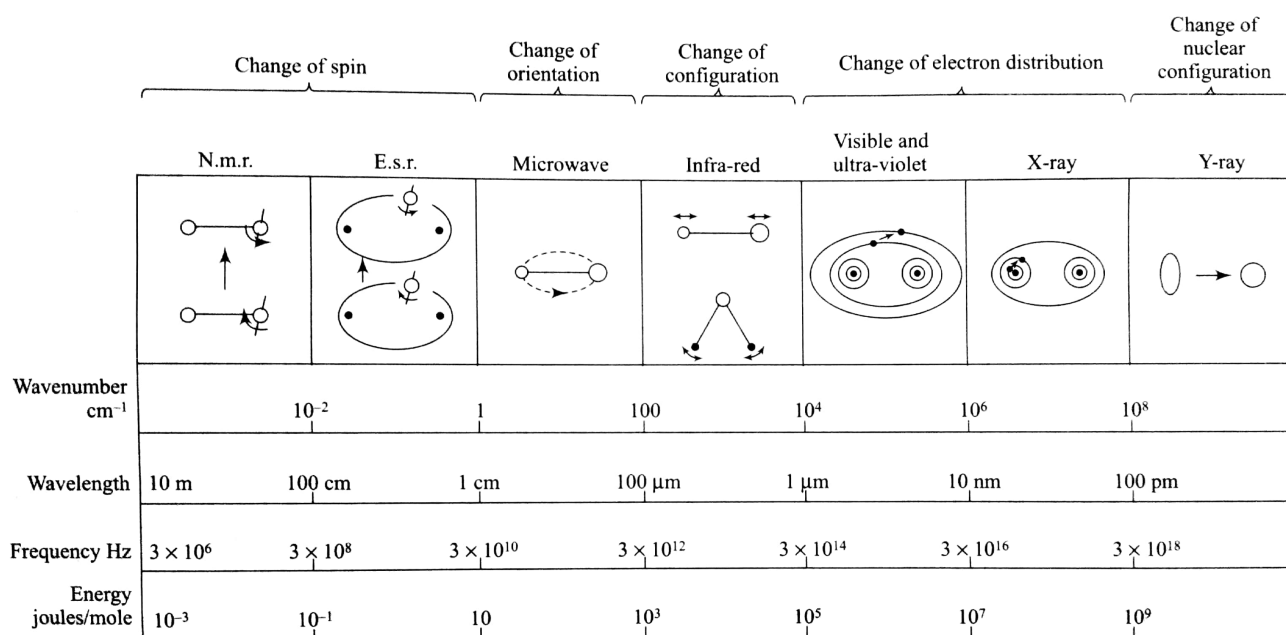


Figure 1: Electromagnetic Spectrum

### Rotation of spectra (or) Microwave spectra:-

#### Classification of molecule:

The molecules are usually classified into four groups base one of the relative values of principle moments of inertia.

#### [i] Linear Molecule:

All the atom of the molecules are arranged in a straight line.

Example:  $HCl$ ,  $CO_2$ ,  $OCS$ ,  $HCN$ ,  $C_2H_2$ , ..... etc

The three direction of rotation may be taken as,

- about the bond axis
- end-over-end rotation in the plane of the paper
- ene-over-end rotation at right angles to the plane.

► The moment of  $b$  and  $c$  are the same  $I_B = I_C$  while that of  $a$  is very small ( $I_A = 0$ ).

$$I_A = 0 ; \quad I_B = I_C$$

#### [ii] Symmetric Tops:

► Two of the principle moments of inertia are equal and all three are non-zero.

► Example: Methyl fluoride  $\rightarrow$  where the three hydrogen atoms are bonded tetrahedrally to the carbon. A molecule spinning about this axis can be imagined as a top.

- (1) Prolate Symmetric Top:- Example:  $CH_3Cl$ ,  $CH_3F$ ,  $CH_3CN$ ,  $NH_3$ . If as in methyl fluoride above  $I_B = I_C > I_A$ , then the molecule is called prolate symmetric top.
- (2) Oblate Symmetric Top:- Example:  $BF_3$ ,  $BCl_3$ , If  $I_B = I_C < I_A$  it is referred as oblate symmetric top.
- (3) Planer and Symmetrical:- Example: *Boron trichloride* ( $BCl_3$ ), If  $I_A = 2I_B = 2I_C$  - (PG TRB) palner and symmetrical.

### [iii] Spherical Tops:

When all the three principle moments of inertia of molecule are equal, it is called a spherical top molecule. Example:  $CH_4$ ,  $O_sO_4$ ,  $SF_6$ ,  $CCl_4$ , .....

- ▶ They have no dipole moment owing to their symmetry, rotation alone can produce no dipole change and hence no rotational spectrum is observable.
- ▶ Molecule structure for tetrahedral molecule methene ( $CH_4$ ) - (PG TRB)

### [iv] Asymmetric Top:

These molecule, to which the majority of substances belong, have all three moments of inertia are different.  $I_A \neq I_B \neq I_C$ .

Example: *Water* ( $H_2O$ ), *Vinyl chloride* ( $CH_2 = CHCl$ ),  $CH_3OH$ ,  $CH_2CHCl$ .

### Interaction of Radiation with rotating molecule:

(1) If the permanent dipole moment is zero there will not be any periodic variation. As homodiatomic molecules  $H_2$ ,  $N_2$ ,  $O_2$ , ..... etc, hetro nuclear molecule (linear molecule) such as  $CO_2$ ,  $CS_2$ , and spherical to molecules do not possess a permanent dipole moment, they show no rotational spectrum. (PG TRB). Even isotopic substitution does not produce activity, since it changes only the mass of the molecule.

(2) Rotation about bond axis for diatomic and linear molecules do not produce any change in dipole moment hence no spectrum.

### Selection rule for Rotating molecule:

1. Transitions are allowed only between adjacent rotational levels (i.e),
  - ▶  $\Delta J = \pm 1$  (+  $\rightarrow$  absorbtion), (-  $\rightarrow$  emission).

### Rotational spectra of rigid diatomic molecule:

A diatomic molecule may be considered as a rigid rotator consisting of atomic masses  $m_1$  and  $m_2$  connected by a rigid bond of length  $r$ . Considered the rotation of this rigid rotor about an axis perpendicular to its molecular axis and passing through the centre of gravity.

The solution of the schrodinger equation for the rigid rotor gives the energy eigen values.

$$E_J = \frac{\hbar^2}{2I} J(J+1) \text{ joules} \quad J = 0, 1, 2, \dots \quad (\text{PG TRB-2013})$$

$J \rightarrow$  rotational quantum number and each level is  $(2J + 1)$  fold degenerate

$I \rightarrow$  moment of inertia

$$I = m_1 r_1^2 + m_2 r_2^2 ; \quad m_1 r_1 = m_2 r_2 ; \quad r = r_1 + r_2$$

$$\text{Reduced mass } \mu = \frac{m_1 m_2}{m_1 + m_2} ; \quad \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2} \quad (\text{PG TRB-2012})$$

$$\therefore I = \frac{m_1 m_2}{m_1 + m_2} r^2 = \mu r^2$$

► Often it is convenient to analyse the rotational energy spectrum in wavenumber (*unit*  $\rightarrow \text{cm}^{-1}$ ) unit.

$$E_J = \frac{h^2}{8\pi^2 I} J(J+1) \text{ joule}$$

$E_J = B J(J+1)$  joule ;  $\rightarrow$  Eigen energy value of Rotational spectra for diatomic molecule.

$$\therefore \epsilon_J = \frac{E_J}{hC} = \frac{h}{8\pi^2 IC} J(J+1) \text{ cm}^{-1}$$

$$\epsilon_J = B J(J+1) \text{ cm}^{-1} \quad \rightarrow \text{where } B \text{ is the rotational constant.}$$

$$B = \frac{h}{8\pi^2 IC} \text{ cm}^{-1} = \frac{h^2}{8\pi^2 I} \text{ joules} \quad (\text{TRB-2012})$$

$$\text{Selection rule } \Delta J = \pm 1 \quad (\text{TRB})$$

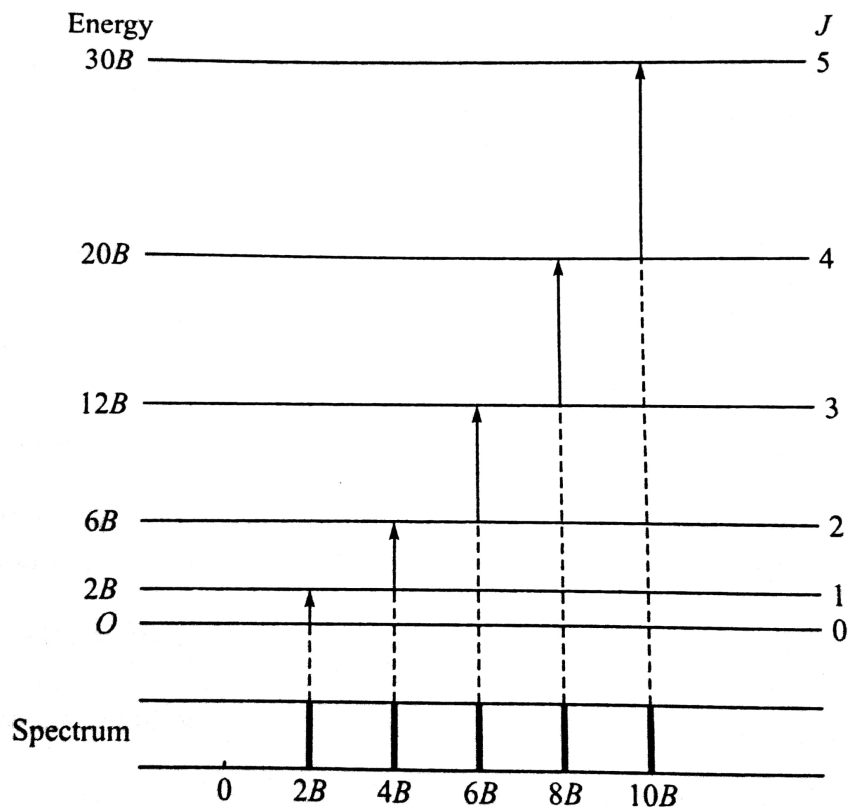


Figure 2: Rotational energy levels and transition for a rigid diatomic molecule.

(i) For absorption spectra  $\Delta J = +1$  (i.e)  $J \rightarrow J + 1$

$$\boxed{\bar{\nu}_J = 2B (J + 1) \text{ cm}^{-1}} \quad \bar{\nu}_J = \Delta \epsilon_J \quad J = 0, 1, 2, \dots$$

(ii) For emission spectra  $\Delta J = -1$  (i.e)  $J + 1 \rightarrow J$

$$\boxed{\bar{\nu}_J = 2B J \text{ cm}^{-1}} \quad J = 0, 1, 2, \dots$$

The rotational constant  $B$  is assumed to be the same in both lower and upper rotational state.

- ▶ Thus a series of spectrum with wave number  $\bar{\nu}$  values are equally spaced ( $2B, 4B, 6B, \dots \text{ cm}^{-1}$ ) is expected for the rotational spectrum a rigid diatomic molecule.
- ▶ The separation between any two adjacent (spacing) lines is  $2B$ . (PG TRB)
- ▶ Allowed energy or eigen value of a diatomic molecule.

$J$	0	1	2	3	4	5	6
$E_J$	0	2B	6B	12B	20B	30B	42B

### Isotope Effect in Rotational Spectra:

An atom when replaced by one of its isotopes, the inter bond distance remains the same as the electron charge distribution does not change. However, the mass of the nucleus changes leading to a change in the moment of inertia.

$$\Delta \bar{\nu} = 2B (J + 1) (1 - \rho^2)$$

$$\therefore \frac{I}{I'} = \frac{\mu}{\mu'} = \rho^2$$

- ▶ As  $\rho \simeq 1$  in most of the cases, the shift will be extremely small.
- ▶ When there is a mass increases,  $\rho^2 < 1$  giving a positive value for  $\Delta \bar{\nu}$ .
- ▶ Isotope shift increases with value of  $J$ .
- ▶ Measurement of isotope shift allows precise determination of atomic weight of atoms.

- (i)  $J = \sqrt{\frac{KT}{2BhC}} - \frac{1}{2} \rightarrow$  This is  $J$  value will have the maximum population (or) Maximum intensity.
- (ii) Linear polyatomic molecules can also be treated similar to the diatomics.
- (iii) The quantity  $e^2 q Q \rightarrow$  Rotational quatrapole coupling constant.

### Microwave spectrometer:-

Various types of microwave component,

(i) Source-Klystron, (ii) Measurement of frequency, (iii) Guidance of the radiation to the absorbing substance, (iv) Sample cell, (v) Crystal detector, (vi) Crystal detector, (vii) Vacuum pump, (viii) Stark electrode, (ix) Pre-amplifier, (x) Square wave moderator (xi) Lock in amplifier, (xii) Oscillator or Recorder.

- (1) Frequency measuring device:- Frequency counter using beats technique.
- (2) Sample cell:- Sample cell background characteristics are determined in stark modulation spectrograph.
- (3) Detector:- A silicon crystal mounted in a coaxial cartridge is the most commonly used detector.

**Information derived from Rotational Spectra and Uses:**

- (i) Molecular structure:
- Moment of inertia
  - Molecular constant
  - Force constant( $K$ )  $K = \frac{16\pi^2 C^2 \mu B^2}{D}$ .
- (ii) Dipole moment.
- (iii) Atomic mass:  $\frac{B}{B'} = \frac{I'}{I} = \frac{\mu'}{\mu}$
- (iv) Nuclear quadrupole moment.

**Rotational spectra result:**

- Only it is asymmetric (heteronuclear) will this spectrum be observed.
- Homonuclear there will be no dipole moment change during the rotation.
- $HCl$  and  $CO$  will show a rotational spectrum while  $N_2, O_2$  will no.

**Infrared Spectroscopy (or) Vibrational Spectroscopy:-****Vibrational energy of the diatomic molecule:**

The vertical oscillations of a mass ' $m$ ' connected to a stretched spring of a force constant ' $K$ ' whose other end is fixed.

The mass executes simple harmonic motion with a fundamental frequency,

$$\nu_o = \frac{1}{2\pi} \sqrt{\frac{K}{m}}$$

If two mass  $m_1, m_2$  are connected,

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

$$\therefore \text{fundamental frequency } \nu_o = \frac{1}{2\pi} \sqrt{\frac{K}{\mu}}$$

The vibrational energy of such harmonic system

$$E_\nu = \left(\nu + \frac{1}{2}\right) h\nu_o \quad \text{Joule} \quad \nu = 0, 1, 2, \dots$$

$\nu \rightarrow$  Vibrational quantum number .

The vibrational energy in  $cm^{-1}$ ,

$$\therefore \varepsilon_\nu = \frac{E_\nu}{hC} = \left(\nu + \frac{1}{2}\right) \frac{\nu_o}{C}$$

$$\varepsilon_\nu = \left(\nu + \frac{1}{2}\right) \bar{\nu}_o \quad cm^{-1} \quad \therefore \bar{\nu} = \frac{\nu_o}{C}$$

where,  $\bar{\nu}_o \rightarrow$  wave number in  $cm^{-1}$

These energy levels are equally spaced and the energy of the lowest state ( $\nu = 0$ ),

$$\boxed{\varepsilon_0 = \frac{1}{2} \bar{\nu}_0 \text{ cm}^{-1} \quad (\text{or}) \quad E_\nu = \frac{1}{2} h\nu_0 \text{ joule}} \rightarrow \text{It is called zero point energy.}$$

That is the vibrational energy is not zero even the lowest vibrational level indicating that a molecule must vibrate always.

In diatomic molecules, the actual potential energy curve is not of the simple harmonic type but is given by,

$$\boxed{U(r) = D_e (1 - \exp[-a(r - r_e)])^2} \quad \text{..... (A)}$$

$D_e$   $\rightarrow$  Dissociation energy,  $a$   $\rightarrow$  Constant ,  
 $r_e$   $\rightarrow$  Inter nuclear distance at equilibrium condition .

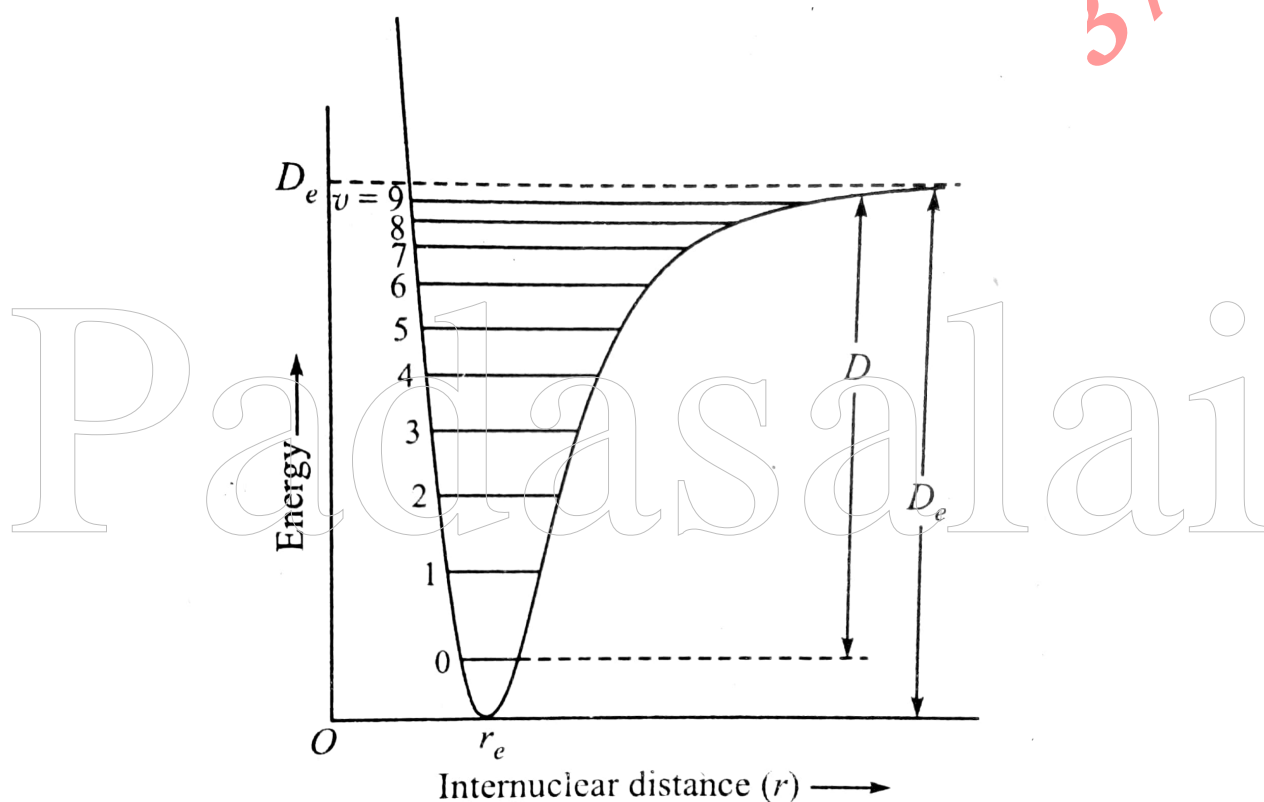


Figure 3: **The Morse curve and the energy levels of a diatomic molecules.**

- ▶ This potential function is due to P.M.Morse and is called the Morse function.
- ▶ The shape of this function where is one atom is fixed ( $r = 0$ ) while the other oscillates between the two branches of the Morse curve.
- ▶ With the potential in equation (A) , the Schrödinger equation of such an anharmonic oscillation gives the allowed energy eigen values.

$$\varepsilon_\nu = \left(\nu + \frac{1}{2}\right) \bar{\nu}_e - \left(\nu + \frac{1}{2}\right)^2 x_e \bar{\nu}_e + \left(\nu + \frac{1}{2}\right)^3 y_e \bar{\nu}_e \dots \quad \nu = 0, 1, 2, 3, \dots$$

Where,

$\nu = \bar{\nu}_e C$   $\rightarrow$  equilibrium oscillation frequency.

$x_e, y_e$   $\rightarrow$  anharmonic constant which very small, positive.

- The first anharmonic term, we get

$$\varepsilon_\nu = \left(\nu + \frac{1}{2}\right) \bar{\nu}_e - \left(\nu + \frac{1}{2}\right)^2 x_e \bar{\nu}_e \quad \text{cm}^{-1} \quad \nu = 0, 1, 2, 3, \dots$$

**The exact zero-point energy for anharmonic:**

$$\varepsilon_0 = \frac{1}{2} \left(1 - \frac{1}{2} x_e\right) \bar{\nu}_e$$

∴ The oscillation frequency of the harmonic oscillator having same vibrational energy as the anharmonic one,

$$\bar{\nu}_o = \bar{\nu}_e \left[1 - \left(\nu + \frac{1}{2}\right) x_e\right]$$

- The anharmonic oscillator behave like the harmonic oscillator but with oscillation frequency that decrease with increasing  $\nu$ .
- If we see  $\nu = -\frac{1}{2} \implies \varepsilon_\nu = 0$  and  $\bar{\nu}_o = \bar{\nu}_e$ . It is observed in the region  $50 - 4000 \text{ cm}^{-1}$  as IR or Raman band.

### IR Spectra Spectrum Result

- The energy of the diatomic molecule can never have zero.
- The selection rule for the harmonic oscillator undergoing vibrational changes.  $\Delta\nu = \pm 1$
- Vibrational energy only observable spectrum ( $\Delta\nu = +1$ ).
- Vibrational change produce when changes of electric dipole moment of the molecule. (TRB)

(i.e)  $\text{Condition for infrared activity} \quad \left(\frac{\partial \mu_i}{\partial Q}\right)_o \neq 0$

$\mu_i \rightarrow$  dipole moment. ( $\mu_i = \mu_x, \mu_y, \mu_z$ ) and  
 $Q \rightarrow$  The normal coordinate.

- Vibrational spectra observable only in heteronuclear diatomic molecule since homonuclear molecule have no dipole moment.
- Vibrational levels changes are equally spaced. (TRB)
- Pure vibrational spectra are observed only in liquid. (to be continue... )

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