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PRESENTED BY  
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SUB:VIBRATIONAL SPECTROSCOPY

# INTRODUCTION

## SPECTROSCOPY

Spectroscopy deals with transition induced in chemical species by its interaction with photons of electromagnetic radiation .

The most important consequence of electromagnetic interaction is that the energy is absorbed or emitted by the matter in discrete amount called quanta .

Spectroscopy techniques are generally employed to measure the energy difference between various molecular energy levels and to determine atomic and molecular structures .

# VIBRATIONAL SPECTROSCOPY

Vibrational spectroscopy is one of the most powerful analytical techniques which provides information on molecular vibrations or more precisely on transitions between vibrational and rotational energy levels in molecules. In fact atoms in a molecule do not remain in a fixed relative position but vibrate about their mean position .

If excitation energy is sufficiently large to cause transition from one vibrational energy level to another in the in the same electronic level resulting in vibrational spectra of molecule.

Energy required for these spectra is available in infrared region of the electromagnetic spectrum and hence this spectra also known as Infrared spectra or Mid-infrared spectra or Near-infrared spectra .

# CONDITION

This type of spectra is shown only by those molecules which possess permanent dipole moment or by the molecules whose vibrational motion is accompanied by a change in dipole moment of the molecule. The polyatomic molecules, may or may not have permanent dipole moment of their own but when subjected to Infrared radiation it induces oscillating dipole moment such as polyatomic molecules, hence they show vibrational spectra.

As it has been mentioned earlier that the energy required for the rotational transition is much lower than vibrational transition. Hence the vibrational transition is generally accompanied by the rotational transition. Such spectra is called as VIBRATIONAL-ROTATIONAL spectra. In case of liquids, the rotational motion is quenched due to intermolecular interaction and hence pure vibrational spectra can be observed.

# VIBRATIONAL ENERGY LEVELS OF DIATOMIC MOLECULE

In order to understand the vibration in diatomic molecule, we assume that the vibrational motion is Simple Harmonic Oscillator . A Simple Harmonic Oscillator is one which oscillates under the action of restoring force.

This restoring force is proportional to the displacement from the mean position or equilibrium position.

It is given by Hooke' law.

This law states that force acting on a simple harmonic oscillator is directly proportional to its displacement from equilibrium position. This equation is as follows.

$$F \propto -x \text{ OR } F = -kx \text{ -----(1)}$$

Where, (k) is proportionality constant known as force constant.

For such an oscillator energy, the change in energy dE for small displacement dx is given by

$$dE = -F dx \text{ OR } dE = kx \cdot dx \text{ -----(2)}$$

On integrating equation ---(2) , we get

$$\int dE = k \int x dx$$

$$E = \frac{1}{2} kx^2 \text{ -----(3)}$$

We can make following observations from the equation-

- 1) This is the equation of parabola and so the value of energy changes with displacement in a parabolic manner.
- 2) At equilibrium position,  $x = 0$  and so potential energy is zero.
- 3) The increase in potential energy is continuous. But, according to quantum mechanics, vibrational energy levels are quantized and the energy is given by

$$E_v = (v + \frac{1}{2})h\nu \text{ ----- (4)}$$

Where,  $v$  = Vibrational quantum number which has only integral values like 0,1,2,----,etc,

$h$  = Plank's constant

$\nu$  = Vibrational frequency or oscillation frequency

Also,  $\nu = c\omega_e$  OR  $\bar{\nu} = \omega_e$

Where,  $\omega_e$  = equilibrium frequency in terms of wave number. So equation (4) becomes .....

$$E_v = (v + \frac{1}{2})hc\omega_e \text{ ----- (5)}$$

We can make important conclusions from the equation –

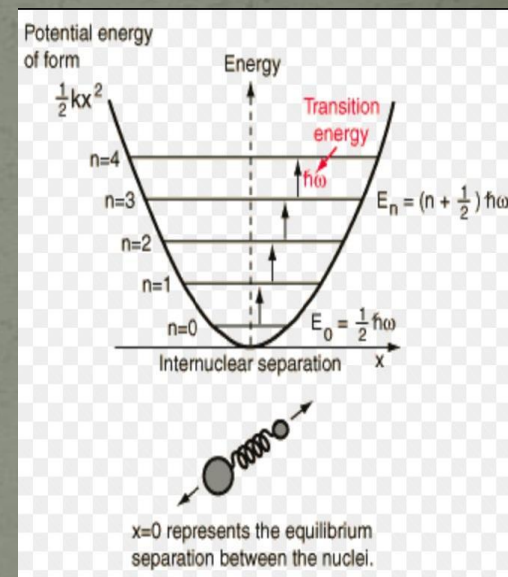
1) Putting different values of Vibrational Quantum Numbers ( $v$ ), we get different energy levels as

$$E_0 = \frac{1}{2} hc\omega \quad E_1 = \frac{3}{2} hc\omega$$

$$E_2 = \frac{5}{2} hc\omega$$

Hence each two vibrational energy levels are separated by equal energy  $hc\omega$

For  $v = 0$ ,  $E_0 = hc\omega$ . This energy is called as zero point energy. It is defined as the minimum amount of energy associated with a vibrating molecule.





# SELECTION RULES FOR PURE VIBRATIONAL SPECTRA

- 1) First and foremost condition for getting vibrational spectra is that the dipole moment of molecule must change due to vibration . The molecule need not have permanent dipole moment , but change in dipole moment should not be zero .
- 2) The change in vibrational quantum number should be unity. That is  $\Delta v = \pm 1$

$\Delta v = +1$  shows absorption of radiation while  $\Delta v = -1$  shows emission of radiation .

Other transitions are not allowed.

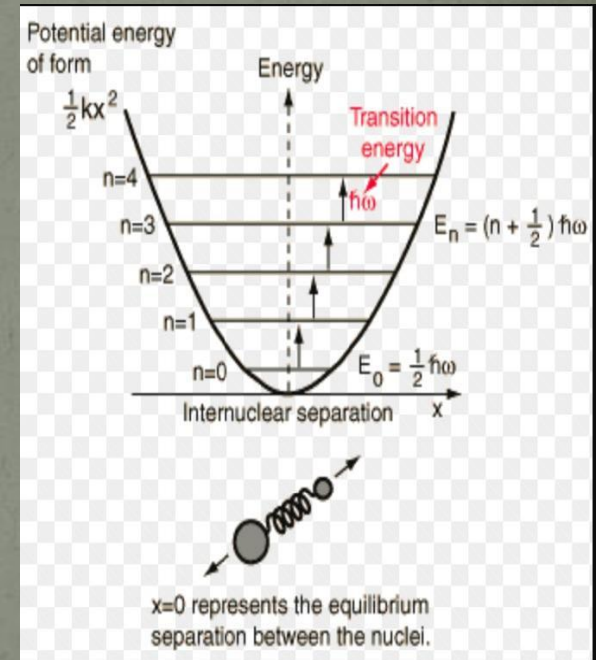
# PURE VIBRATIONAL SPECTRA OF SIMPLE HARMONIC OSCILLATOR

according to selection rules, vibrational transitions are allowed only between adjacent energy levels. Also two energy levels are separated by equal energy given by –

$$\Delta E = hc\nu_e$$

$$\therefore hc\nu = hc\nu_e$$

$$\therefore \nu = \nu_e$$



# VIBRATIONAL ENERGY LEVELS IN ANHARMONIC OSCILLATOR

In the case of anharmonic oscillator, the atoms come back to the equilibrium position from any distance. But it is not in case of real molecules. If the two bonded atoms are stretched to large separation, the restoring force decreases and the molecule dissociates. Such a molecule is called Anharmonic Oscillator

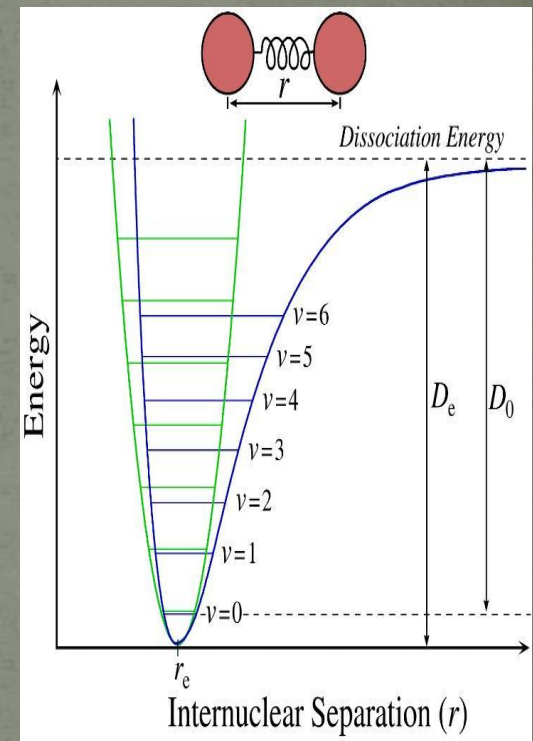
P.M. Morse studied the effect of stretching on vibrational energy of molecules. He put forward an equation called as Morse Equation. It is given by –

$$E = D_e \{1 - e^{n(r-r_e)}\}^2$$

$D_e$  = Dissociation energy of molecule ,

$r$  = Internuclear distance at any position ,

$r_e$  = Equilibrium distance



When Schrodinger wave equation was solved using this value of potential energy, the vibrational energy levels are given by -----

$$E_v = (v + \frac{1}{2})hc\omega - (v + \frac{1}{2})^2 hc x_e \omega$$

Where,  $x_e$  is called as anharmonicity constant.

It can be seen that the separation of each two energy levels is less by a factor of -----  $(v + \frac{1}{2})^2 hc x_e \omega$

In the case of anharmonic oscillator, the selection rule changes to  $v = 0$  to  $1$ ,  $0$  to  $2$ ,  $0$  to  $3$ , etc.

Hence we get different bands in spectrum. Most intense band for transition  $v = 0$  to  $1$ . This intense band is called fundamental vibrational band and the absorption corresponds to this is called fundamental absorption.

The weak intensity band corresponds to the transition from  $v = 0$  to  $2$  is called first overtone and that corresponds to transition from  $v = 0$  to  $3$  is called second overtone.

# VIBRATIONAL - ROTATIONAL SPECTRA

In the case of gaseous state, the molecules are rotating continuously irrespective of their vibrational state. The energy required for rotational transition is extremely small as compared to vibrational transition. Because of this reason such gaseous molecules show vibrational rotational spectra.

The energy of vibrating rotor is given by the sum of vibrational and rotational energy .

$$E_{v,J} = E_v + E_J, \text{ But we know that } E = hc\bar{\nu}$$

$$hc\bar{\nu}_{v,J} = hc\bar{\nu}_v + hc\bar{\nu}_J$$

$$\bar{\nu}_{v,J} = \bar{\nu}_v + \bar{\nu}_J$$

Putting the values of  $\bar{\nu}_v$  and  $\bar{\nu}_J$  we get,

$$\bar{\nu}_{v,J} = B_J (J+1) + (v+1/2)\omega_e - (v+1/2)^2 x_e \omega_e$$

Where  $\nu, J$  represents the number of energy level given by vibrational quantum number  $\nu$  and rotational quantum number  $J$ .

In this case, the selection rule is given by  $\nu = \pm 1$  and  $J = \pm 1$ . Since, most of the molecules are in ground vibrational state, consider a vibrational rotational transition from  $\nu = 0$  to  $1$  accompanied by rotational transition  $J$  to  $J'$ . The wave number corresponds to this is given by –

$$\Delta \bar{\nu}_{\nu, J} = [B J' (J' + 1) + (1 + \frac{1}{2}) \omega_e - (1 + \frac{1}{2})^2 X_e \omega_e] - [B J (J + 1) + (0 + \frac{1}{2}) \omega_e - (0 + \frac{1}{2})^2 X_e \omega_e]$$

$$\begin{aligned} \Delta \bar{\nu}_{\nu, J} &= B [J' (J' + 1) - J (J + 1)] + \omega_e - 2 X_e \omega_e \\ &= B (J' - J) (J + J' + 1) + (1 - 2 X_e) \omega_e \end{aligned}$$

Putting  $(1 - 2 X_e) \omega_e = \omega_0$ , we get

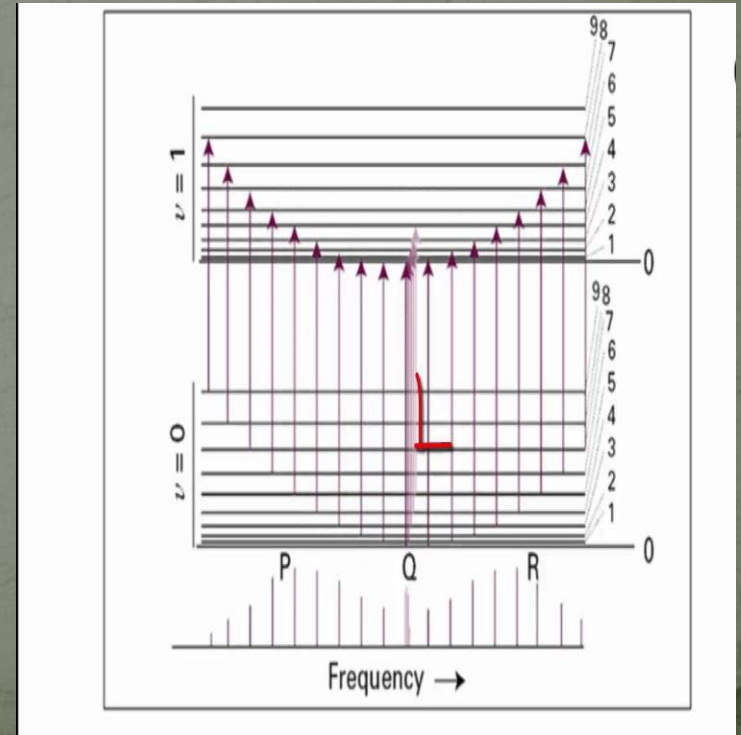
$$\Delta \nu_{\nu, J} = \omega_0 + B (J' - J) (J + J' + 1)$$

for transition with ( $\Delta J = +1$ ) , we get  
 $\Delta\nu_{\nu,J} = \omega + 2B(J+1)$       Where,  $J = 0,1,2$   
 for transition with ( $\Delta J = -1,$ ), we get  
 $\Delta\nu_{\nu,J} = \omega - 2B(J'+1)$       Where,  $J' = 0,1,2,$

## APPLICATIONS OF VIBRATIONAL-ROTATIONAL SPECTRA

$$B = h/8\pi^2 I c$$

Hence  $I$  can be calculated from this equation . Also,  $I$  is related to bond length as  $I = \mu r_0^2$



Another application is in the calculation of force constant 'K'. It is related to vibrational frequency by equation,

$$\omega = \frac{1}{2\pi} \sqrt{k/\mu} \text{ / sec}$$

$$\text{or, } K = 4\pi^2 \omega_e^2 \mu \text{ ----- (1)}$$

Dividing by velocity of light c in cm/sec

$$\omega_e/c = \tilde{\nu} = 1/2\pi c \sqrt{K/\mu} \text{ /cm or /m}$$

$$\text{or } K = 4\pi^2 c^2 \tilde{\nu}^2 \mu \text{ -----(2)}$$

where, 'μ' is the reduced mass of syste and is given--

$$\mu = m_1 m_2 / m_1 + m_2 \text{ -----(3)}$$