B.Sc.-III

Department of Physics,

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Chapter –II

Molecular Spectra

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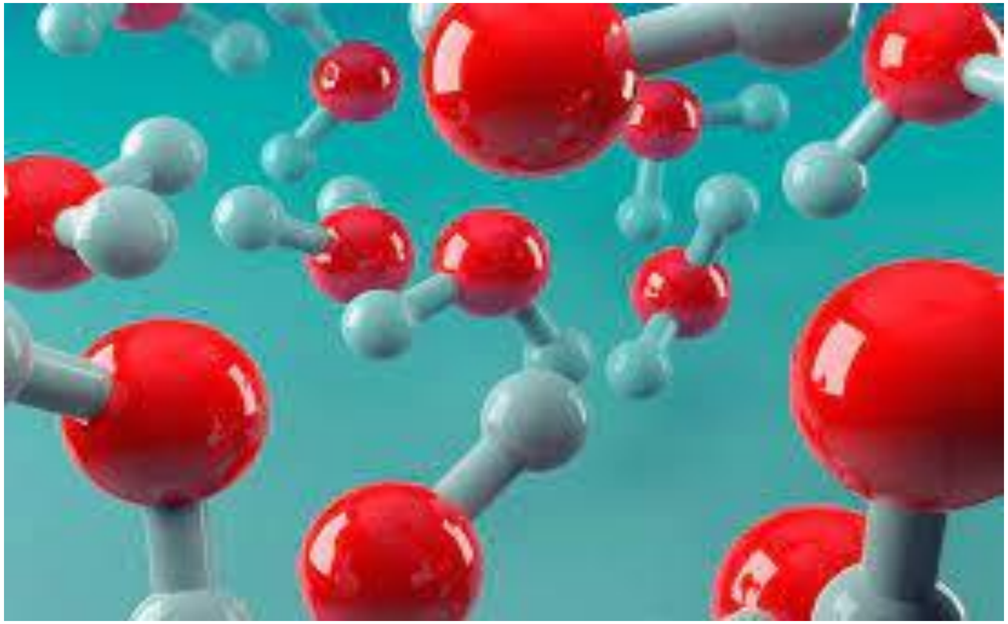
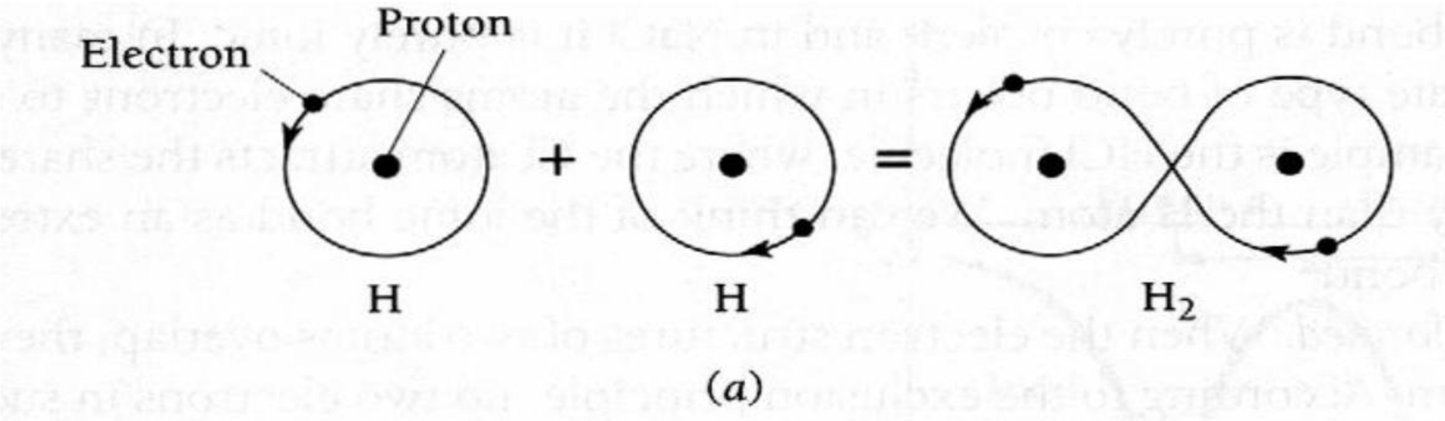
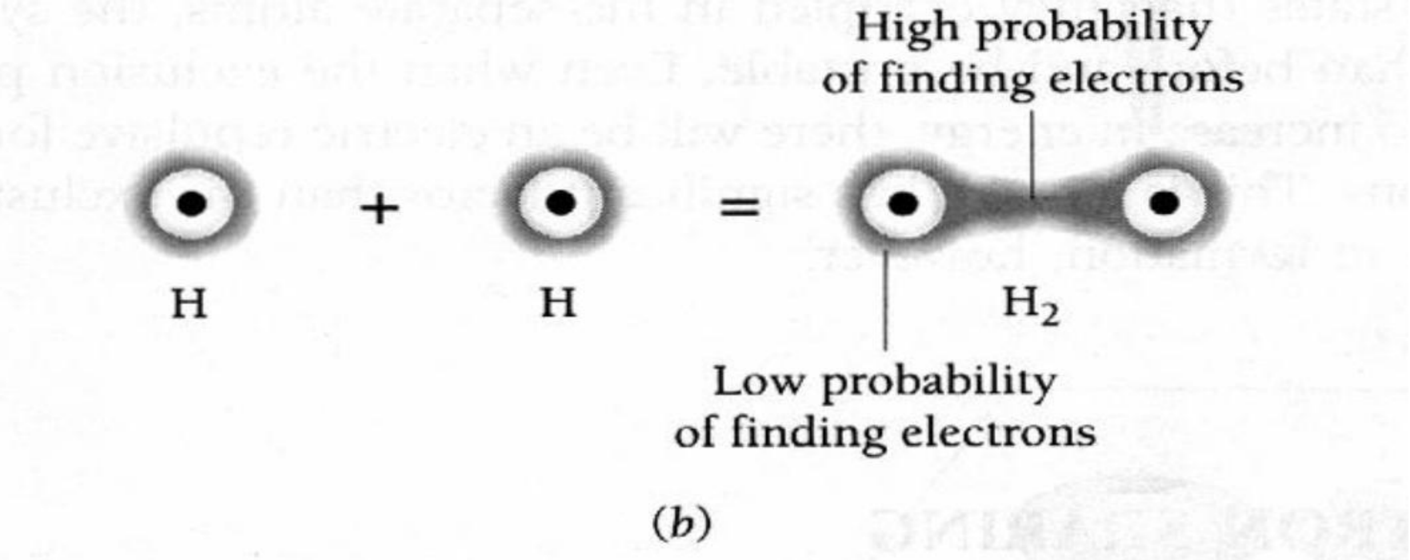
Molecular Bond

A **molecule**, is formed when atoms **bond** by sharing pairs of electrons. This sharing can occur from atom to atom, or from an atom to another **molecular bond**.





(a) Orbit model of the hydrogen molecule.



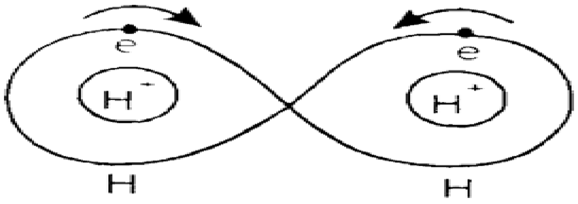
(b) Quantum-mechanical model of the hydrogen

❖ Types of molecular bond

- No bond form
- Covalent bond
- Ionic bond

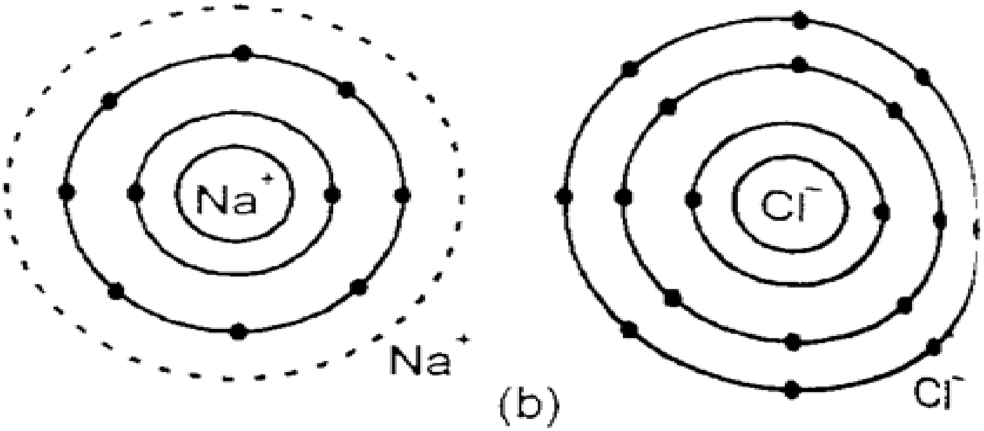
(i) No bond is formed : The two atoms when form a system, the electron structures overlap and according to Pauli's exclusion principle no two electrons can occupy the same quantum state. Hence, the electrons may be pushed into higher energy state. With higher energy the system becomes unstable. Consequently bond is not formed between the atoms and hence molecule is not formed.

(ii) Covalent bond : If two or more pairs of electrons are shared by the atom. example, in H_2-molecule two electrons, one from each atom, are shared by both atoms to form stable configuration and thus a stable molecule is formed as shown in Fig. (2.1(a)). Thus, a bonding is formed between H-atoms in H_2-molecule. Thus, a bond formed by sharing electrons is called **covalent bond**.

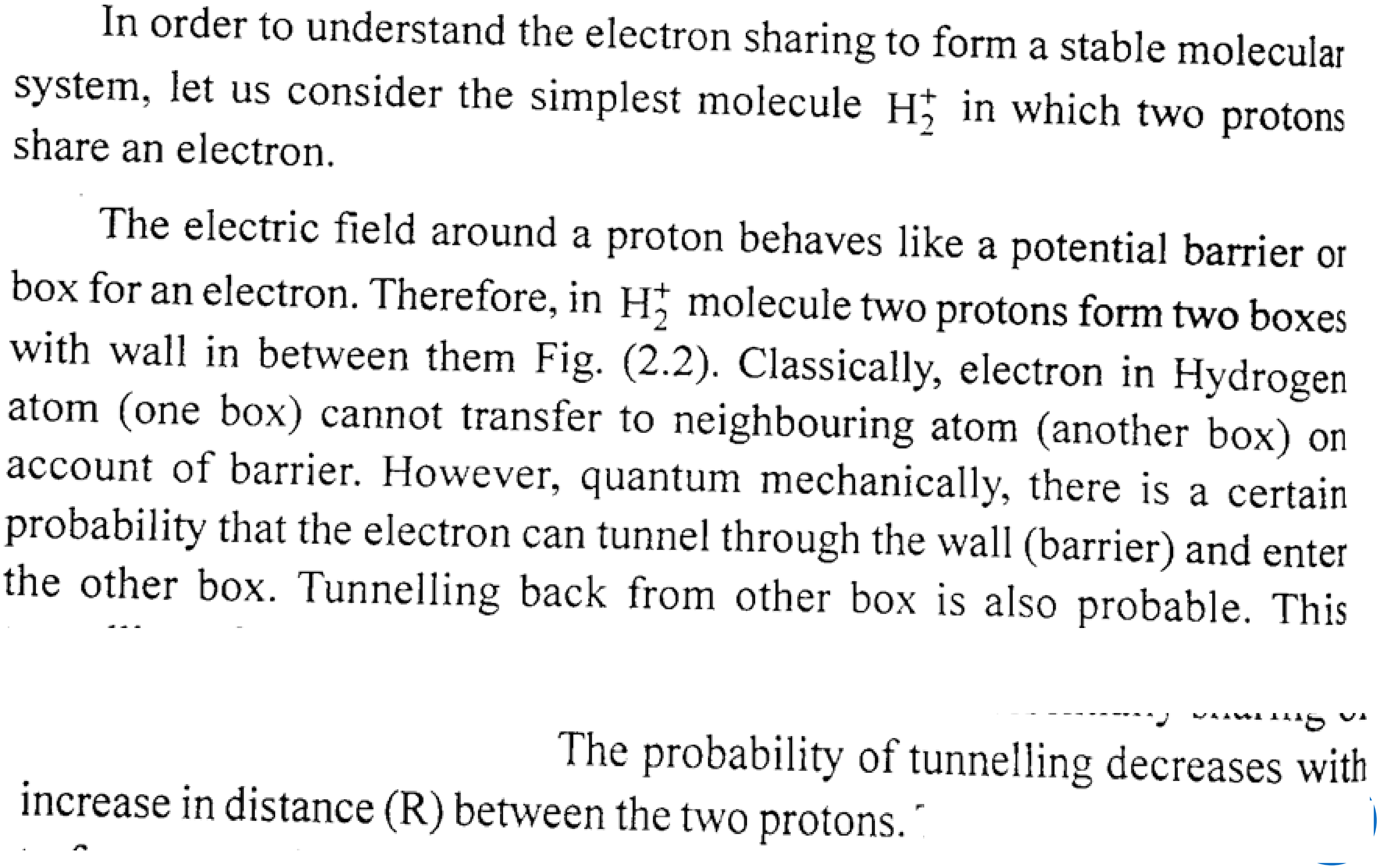


(a)

(iii) Ionic bond : If one or more electrons from one atom are transferred to other atom, then positive and negative ions are formed which strongly attract each other to form a stable system *i.e.* molecule. The bonding so formed is called **ionic bond**. For example, in NaCl molecule, Na^+ and Cl^- ions are formed by transfer of an electron from Na-atom to Cl-atom to complete their last orbits with their capacities *i.e.* octets are completed to achieve stability. The ions formed attract each other naturally.



❖ Electron Sharing



In order to understand the electron sharing to form a stable molecular system, let us consider the simplest molecule H_2^+ in which two protons share an electron.

The electric field around a proton behaves like a potential barrier or box for an electron. Therefore, in H_2^+ molecule two protons form two boxes with wall in between them Fig. (2.2). Classically, electron in Hydrogen atom (one box) cannot transfer to neighbouring atom (another box) on account of barrier. However, quantum mechanically, there is a certain probability that the electron can tunnel through the wall (barrier) and enter the other box. Tunnelling back from other box is also probable. This

The probability of tunnelling decreases with increase in distance (R) between the two protons.

The electron shared between two protons is less confined and hence according to Heisenberg's uncertainty principle (*viz.* $\Delta x \cdot \Delta p \sim \hbar$), the electron possesses less momentum and hence less kinetic energy. Thus, electron energy in H_2^+-system is less than that in ($H + H^+$) and hence H_2^+-system becomes a stable molecule.

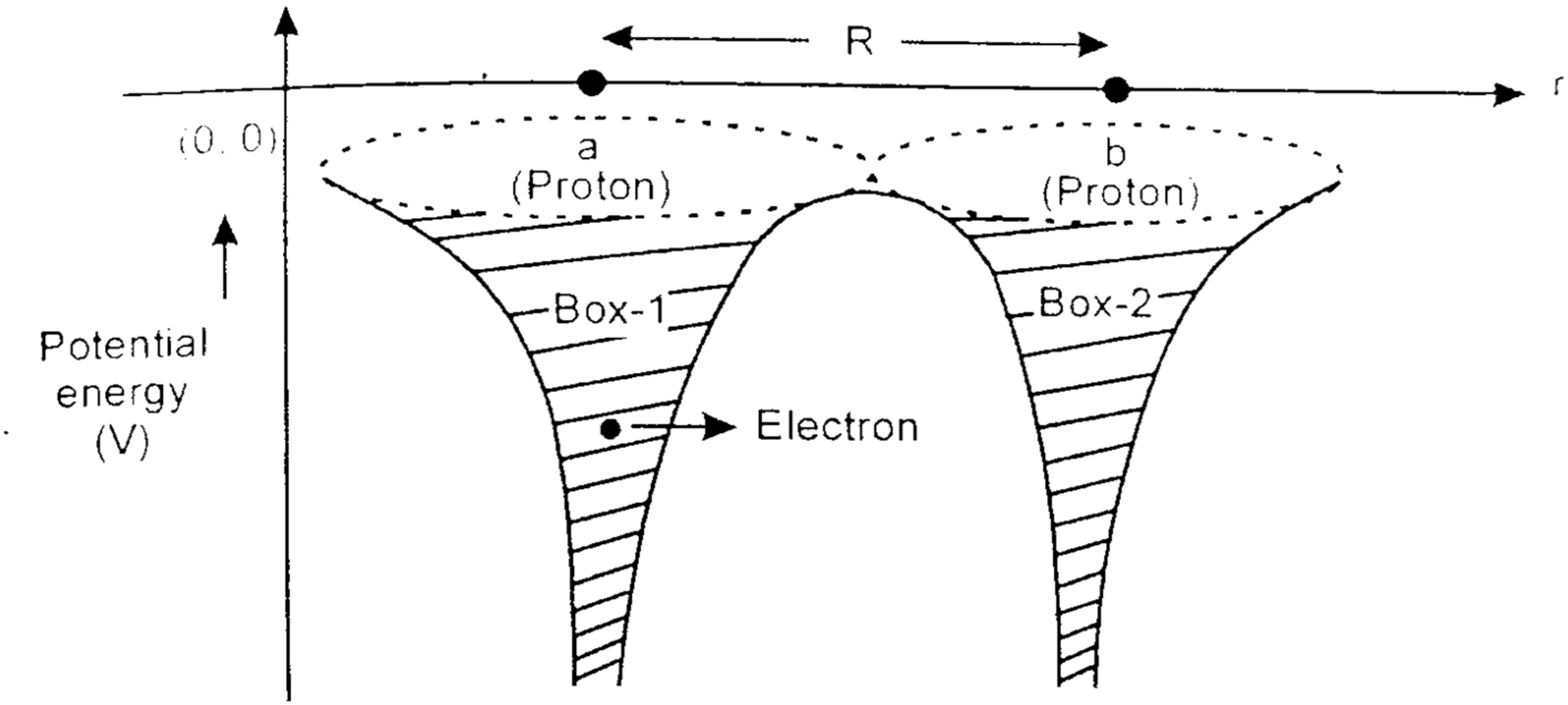
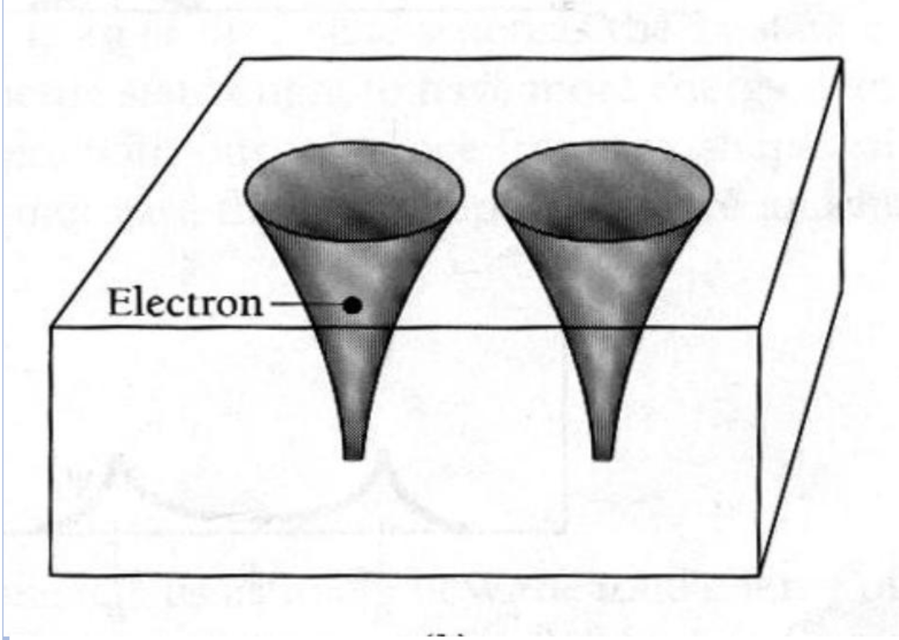
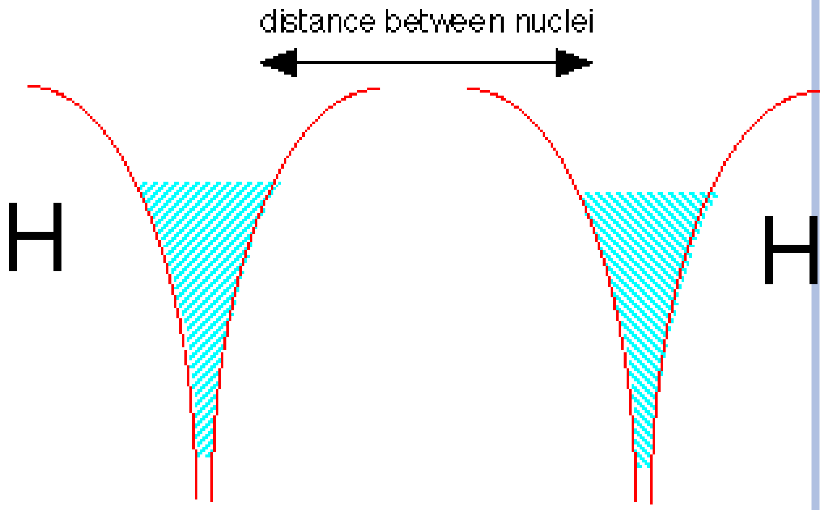
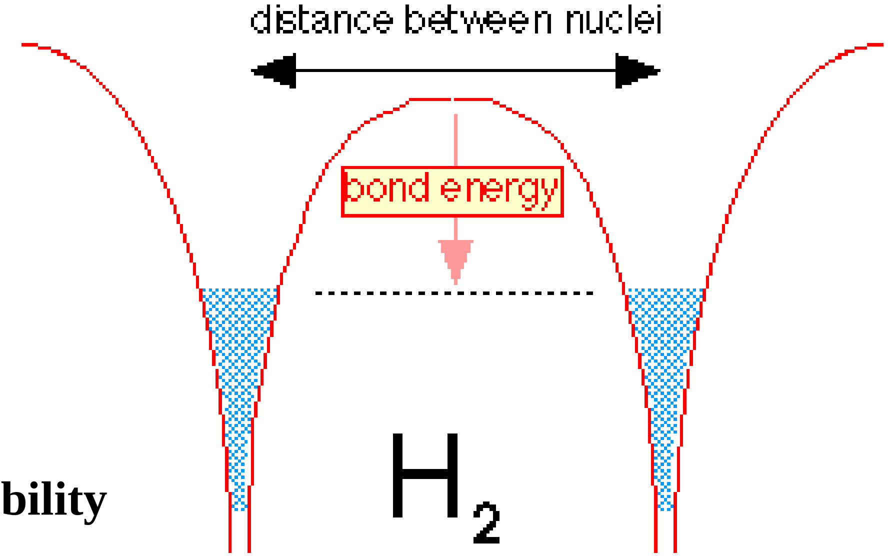


Fig. 2.2 : Potential barrier (or box) of electron in electric field of Protons





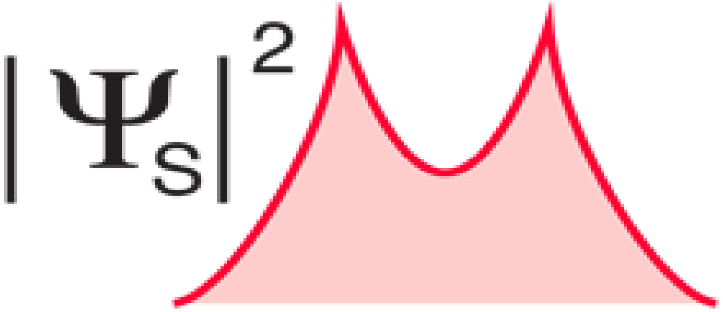
Minimum probability



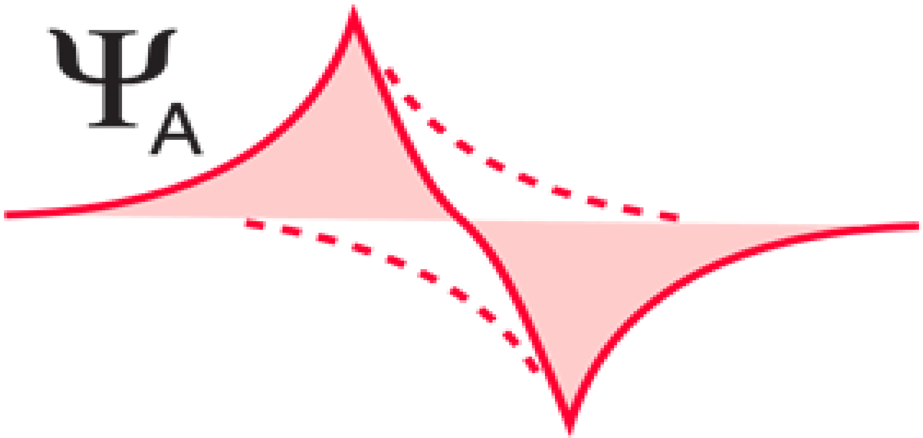
Maximum probability

Nature of wave function

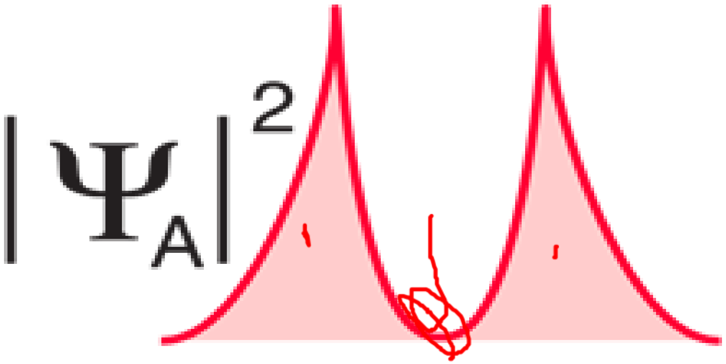
Symmetric wave function



Bonding



Anti-symmetric wave function



Anti-bonding

If there are two systems

$\psi_a(1)$

ψ – wave fun.

a – Quantum state

1 – particle

$\psi_b(2)$

ψ – wave fun.

b – Q. state

2 – particle..

2.4 : The H_2^+ Molecular Ion

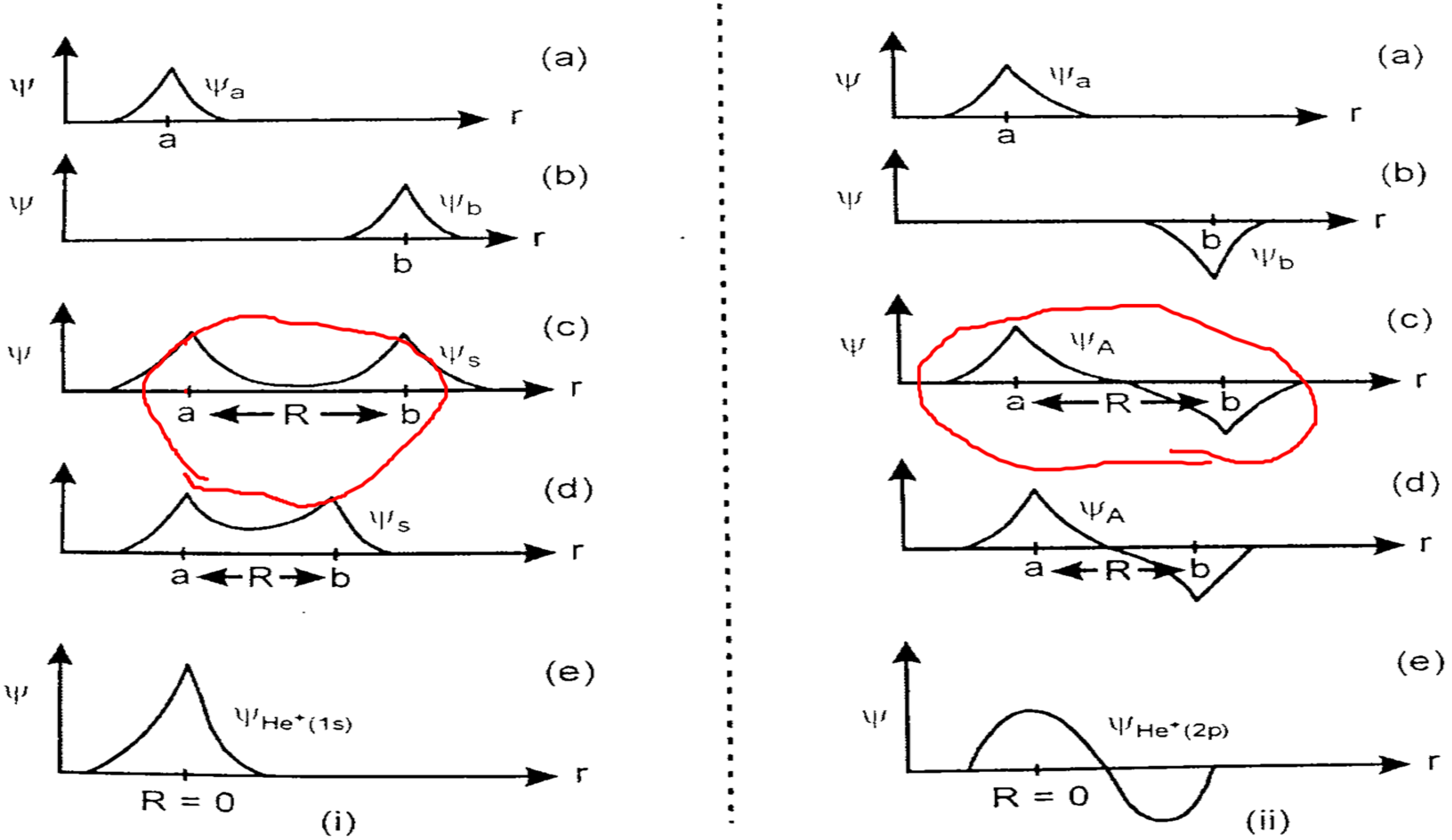


Fig. 2.3 : Combination of two 1s-wave functions of H-atom to form (i) symmetric (ψ_s) and (ii) antisymmetric (ψ_A) wave functions of H_2^+ - molecule

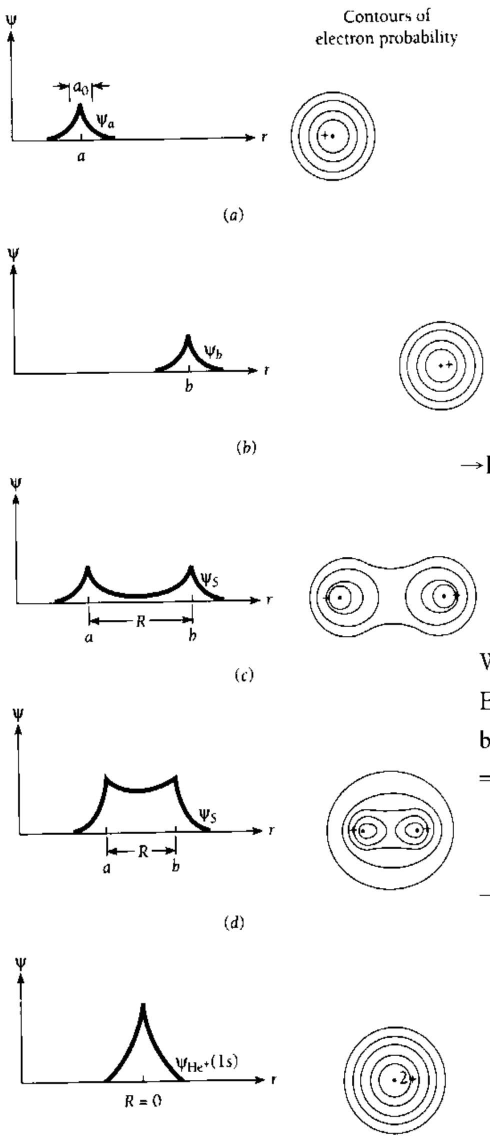


Figure 8.5 The combination of two hydrogen-atom 1s wave functions to form the symmetric H_2^- wave function ψ_S.

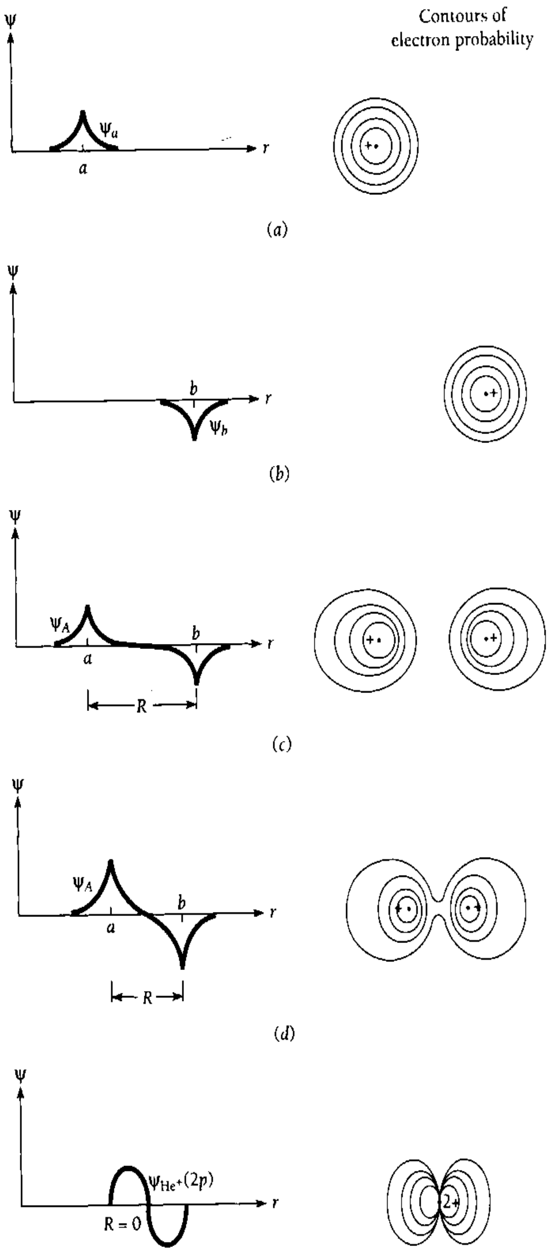
→look like 1s wave function of H

When R~a0,

Enhanced like hood of finding e' between protons.

=> sharing e' by protons

→He^- ion 1s wave function of He^-



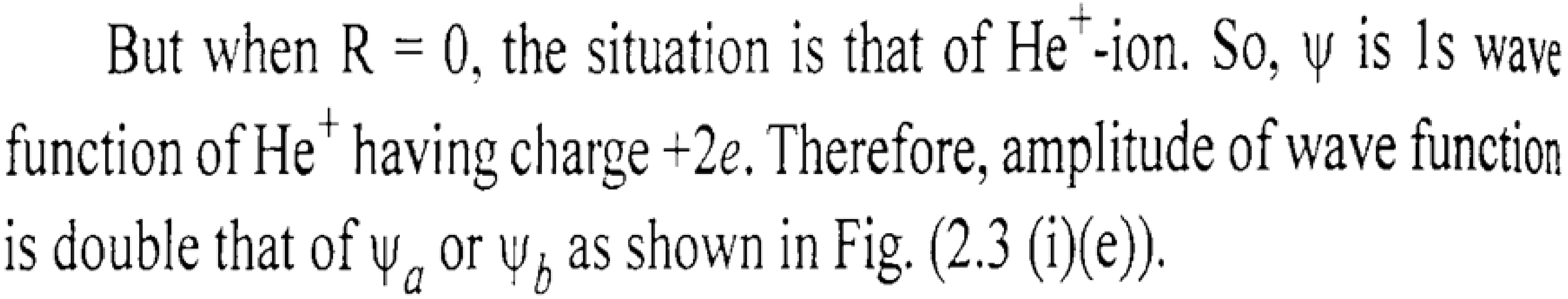
φ_A does not approach 2p wave function of He^+ which has a node at the origin.

There is a node between a & b where φ => reduce likehood of finding e' between protons

H_2 Molecular ion

The nature of wave function (ψ):

- Where, R be the radius which is very large as compared to bohr’s radius (a_0) of first orbit.
- Ψ be the wave function.
- Ψ_a be the wave function around proton a .
- Ψ_b be the wave function around proton b.



But when R = 0, the situation is that of He^+-ion. So, ψ is 1s wave function of He^+ having charge +2*e*. Therefore, amplitude of wave function is double that of ψ_a or ψ_b as shown in Fig. (2.3 (i)(e)).

- , Thus, with symmetric wave function ψ_s, there is a possibility of formation of stable molecular system.

(ii) On the other hand if we consider antisymmetric combination of ψ_a and ψ_b as shown in Fig. (2.3(ii)), it is clear that there is a node between *a* and *b*, where $\psi = 0$ *i.e.* probability of finding the electron in between protons becomes neglegibly small.

Thus, deficiency of negative charges results in repulsive forces between two protons *i.e.* with the antisymmetric wave function ψ_A, stable molecular system cannot be formed. As $R \rightarrow 0$,

Energy of H_2 molecule

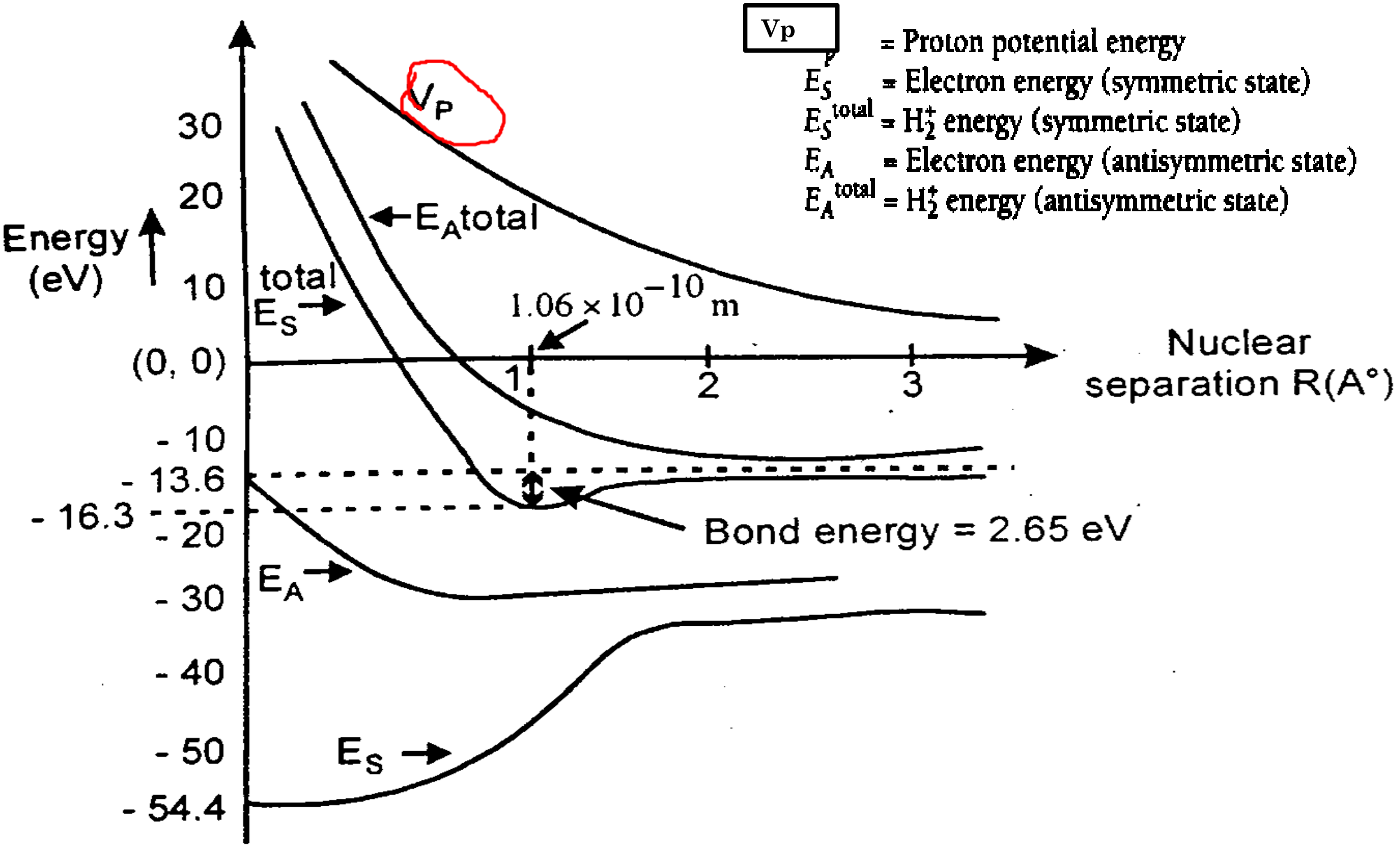


Fig. 2.4 : Energy of H_2^+ system with nuclear separation (R)

Energy of H_2^+ system with R : Let us estimate the total energy of H_2^+-system for various separations (R) of protons for both symmetric and antisymmetric states. In both the cases the electrostatic potential energy of protons is given by,

$$V_p = \frac{e^2}{4\pi \epsilon_0 R}$$

$\therefore V_p \to 0$ as $R \to \infty$ as shown in Fig. (2.4).

(i) For symmetric state ψ_s : At R = 0, the electron energy is that of ground state (1s) of He^+-ion, which is Z^2 times that of H-atom. But ground state (1s) energy of H-atom is – 13.6 eV. Hence, ground state energy of He^+ ion is $4 \times (-13.6) = -54.4$ eV. Also as, $R \to \infty$, $E_s \to -13.6$ eV since $\psi_s \to \psi_a$ or ψ_b.

$$\therefore \quad E_s^{total} = E_s + V_p \text{ , in general} \qquad \ldots 2.2$$

Thus, E_s^{total}, evidently shows a minimum at R = 1.06 A°, which corresponds to stable molecular state (H_2^+). The bond energy *i.e.* energy required to break the molecule H_2^+ into ($H + H^+$) is 2.65 eV. This value is verified experimentally.

(ii) For antisymmetric state (ψ_A) : At R = 0, the electron energy E_A is that of 2*p*-state of He^+ ion *i.e.* $\boxed{\frac{Z^2}{n^2}}$ times ground state (1s) energy of H-atom. Since $\underline{Z = 2}$ and $\underline{n = 2}$; $E_A = -13.6$ eV at R = 0. Again as $R \rightarrow \infty$, $E_A \rightarrow -13.6$ eV. Thus, electron energy for antisymmetric state shows a small dip between extreme values (*viz.* – 13.6 eV).

$$\therefore \quad E_A^{total} = E_A + V_P \qquad \ldots 2.3$$

It is evident that there is no minimum in total energy (E_A^{total})-curve for antisymmetric state as shown in Fig. (2.4). Thus, no stable system or molecular bond is formed with antisymmetric wave function Ψ_A.

2.5 : The Hydrogen Molecule (H_2)

The H_2 molecule contains two protons and two electrons. Now let us see, what could be the nature of complete wave function Ψ (1, 2) of a system of two electrons. The complete wave function is the product of spatial wave function ψ (1, 2) which describes the co-ordinate positions of electrons and spin function S (1, 2) which describes orientation of their spins.

$$\therefore \quad \Psi(1,2) = \psi(1,2) \cdot s(1,2) \qquad \text{... 2.4}$$

According to Pauli's exclusion principle, two electrons cannot be in the same state (*i.e.* cannot have same set of quantum numbers).

$\therefore \Psi(1,2)$ must be antisymmetric, which can result in two different ways *viz.*

(i) symmetric co-ordinate function $\psi(1,2)$ and antisymmetric spin function S_Λ

$$i.e.\quad \Psi = \underline{\psi_S S_A} \qquad \ldots 2.5$$

or (ii) antisymmetric co-ordinate function ψ_A (1, 2) and symmetric spin function S_S (1, 2).

$$i.e.\quad \Psi_A = \underline{\psi_A}\,\underline{S_S} \qquad \ldots 2.6$$

The antisymmetric spin function S_A corresponds to antiparallel spins as it reverses the sign when electrons are exchanged. Similarly S_S corresponds to parallel spins.

The Schroedinger equation for H_2 molecule can be solved by approximation methods whose results are plotted in the form of energy of (H + H) system against internuclear distance (R) as shown in Fig. (2.5).

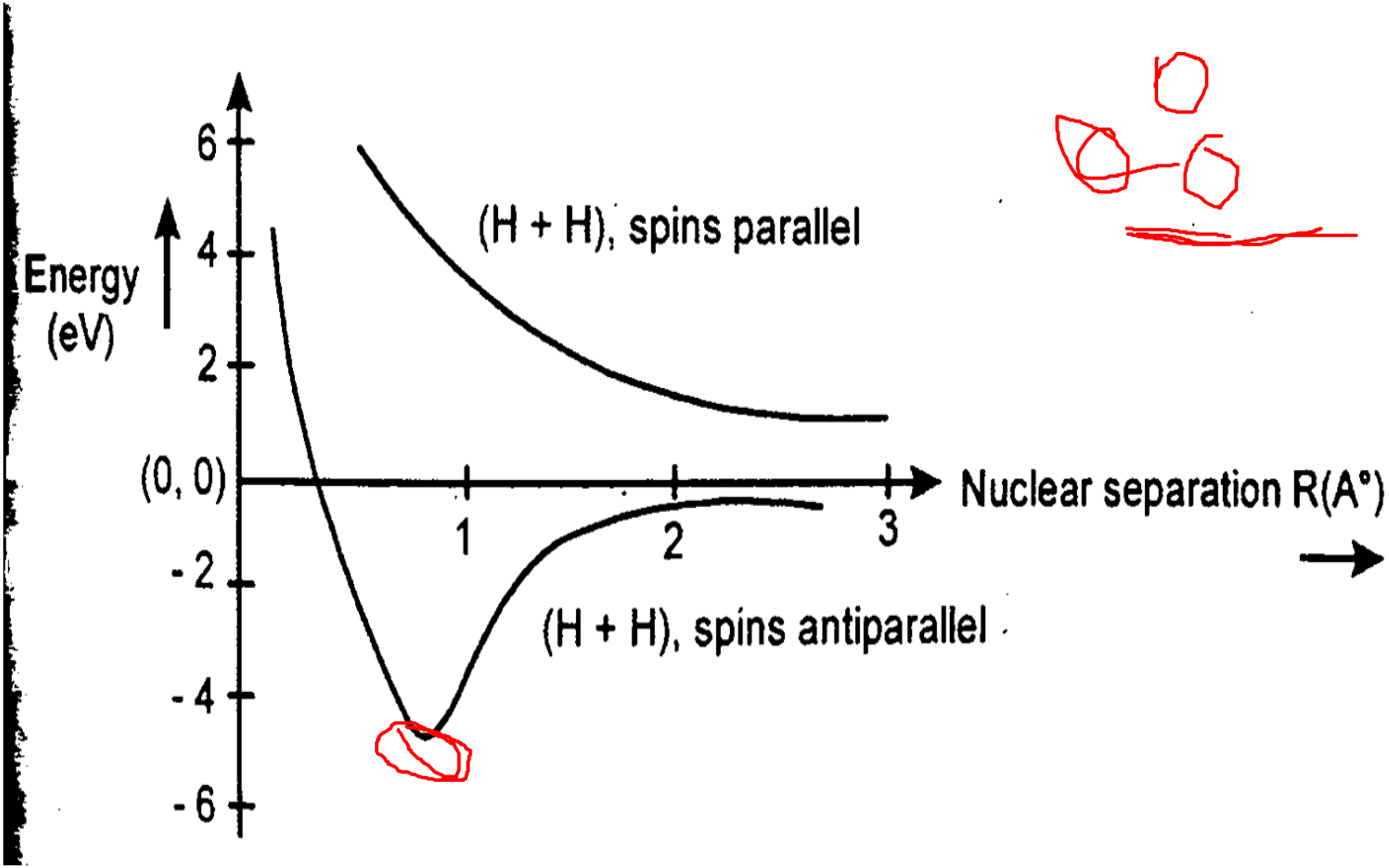


Fig. 2.5 : Variation of energy of (H + H) system with nuclear separation.

It is clear that when spins are parallel, the energy of the system (H + H) is always positive *i.e.* a bound system (or molecule) is not formed.

But with antiparallel spins, the energy of the system (H + H) becomes negative and reaches a minimum, indicating that a stable H_2 molecule is formed with a nuclear separation (R) about 0.74 A°. Therefore, according to equation (2.5), the spatial wave function for H_2 molecule must be symmetric wave function $\psi_S(1, 2)$.

As there are two electrons in H_2 molecule, the bond energy (or dissociation energy) must be expected to be double that in H_2^+ *i.e.* $2 \times 2.65 = 5.3$ eV. However, repulsion between two electrons, reduces this energy by a small amount and hence the observed bond energy is 4.5 eV.

Thus, the state function of H_2 molecule is $\Psi(1,2) = \psi_S(1,2) \cdot S_A$

i.e. two electrons with antiparallel spins are shared by two H-atoms.

2.6 : Rotational Energy Levels

The molcular energy states arising due to the rotation of molecule as a whole are rotational energy levels which are separated by very small intervals (~ 10^{-3} eV). For simplicity, let us discuss the rotational energy levels of diatomic molecules which can be considered as rigid rotators. Let m_1 and m_2 be the masses of two atoms with nuclear separation (R) called bond length. Let this molecular system rotate about an axis through its centre of mass (C.M.) and perpendicular to the line joining two atoms as shown in Fig. (2.6). *i.e.* end-over-end rotation.

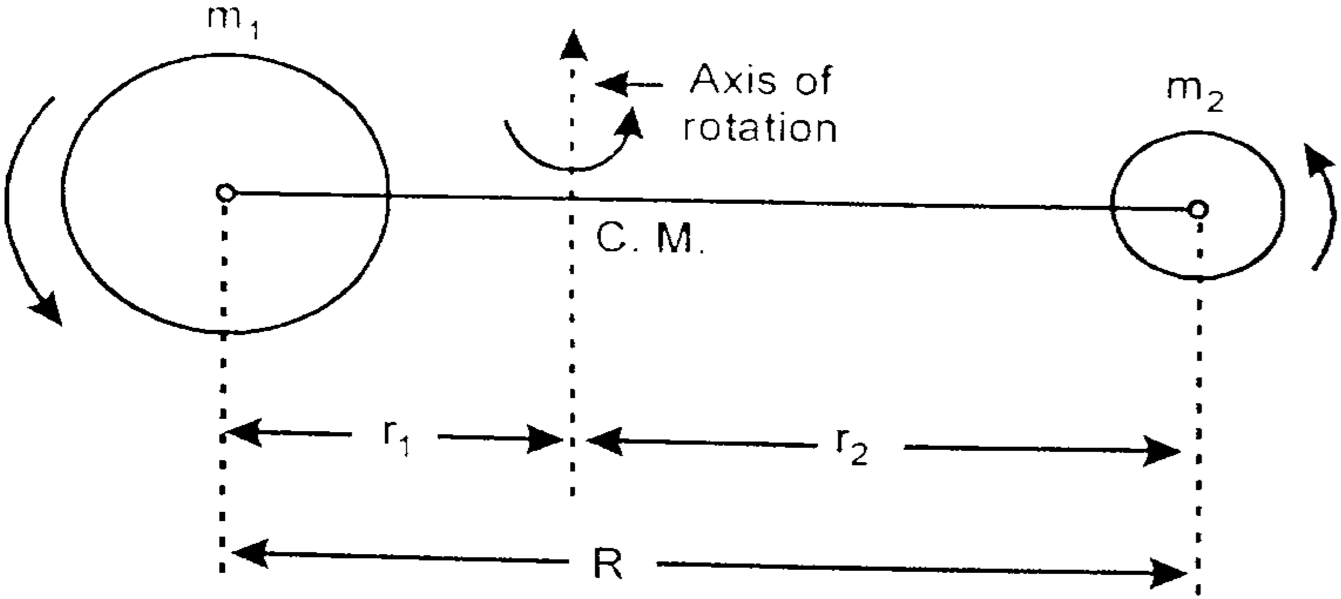


Fig. 2.6 : Rotation of diatomic molecule

$\therefore$ Moment of inertia of molecule, $I = m_1 r_1^{\,2} + m_2 r_2^{\,2}$

But $\quad m_1 r_1 = m_2 r_2$

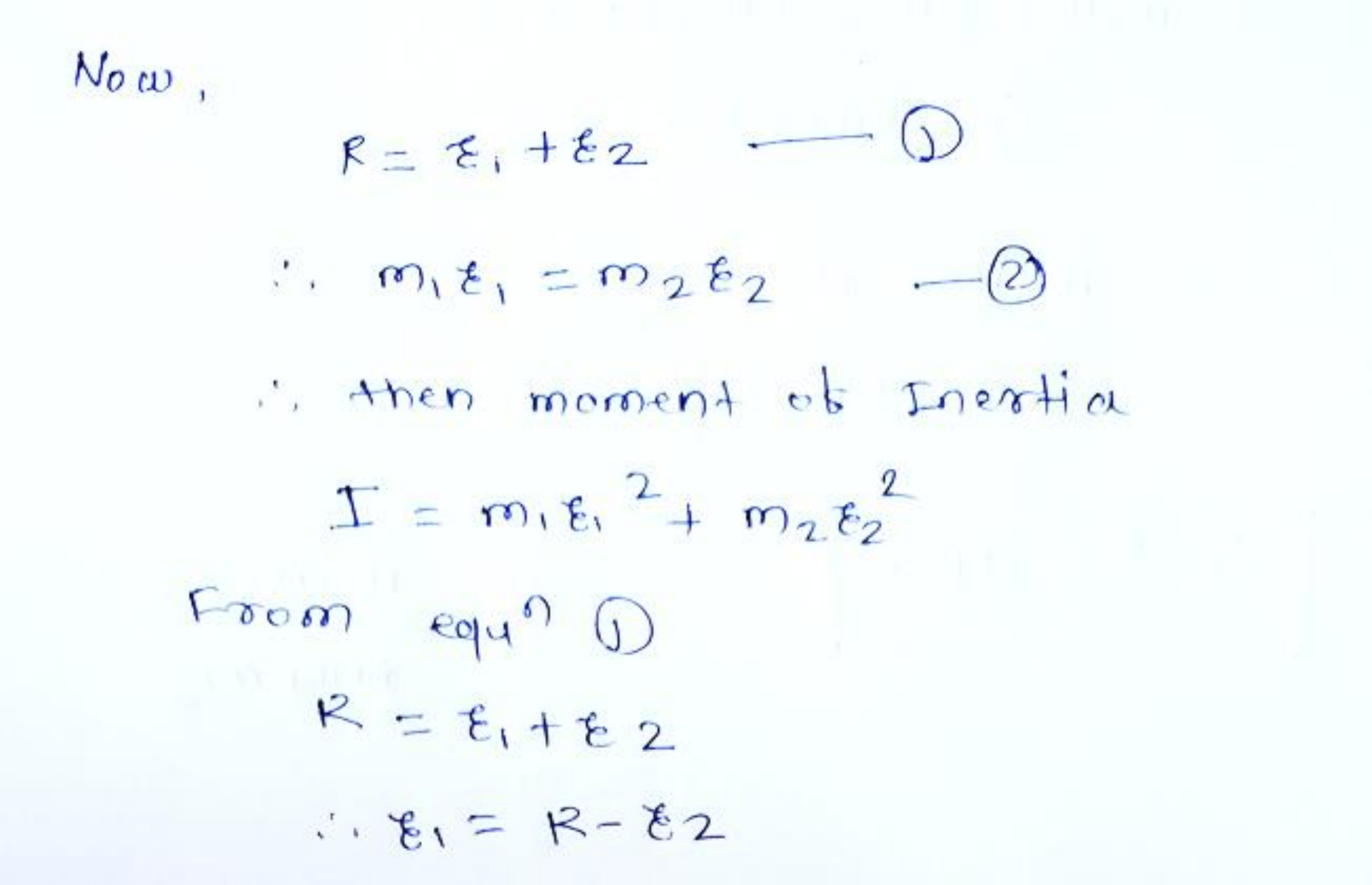
$$\therefore \quad R = r_1 + r_2 = \left(\frac{m_2}{m_1} + 1\right) r_2 = \frac{m_1 + m_2}{m_1} \cdot r_2$$

$$\therefore \quad r_2 = R \cdot \frac{m_1}{m_1 + m_2}$$

$$\therefore \quad I = \frac{m_2}{m_1}(m_1 + m_2) r_2^{\,2}$$

$$\boxed{= \frac{m_1 m_2}{m_1 + m_2}(r_1 + r_2)^2}$$

$$\boxed{\equiv \mu R^2}$$



Now,

$$R = r_1 + r_2 \longrightarrow ①$$

$$\therefore m_1 r_1 = m_2 r_2 \longrightarrow ②$$

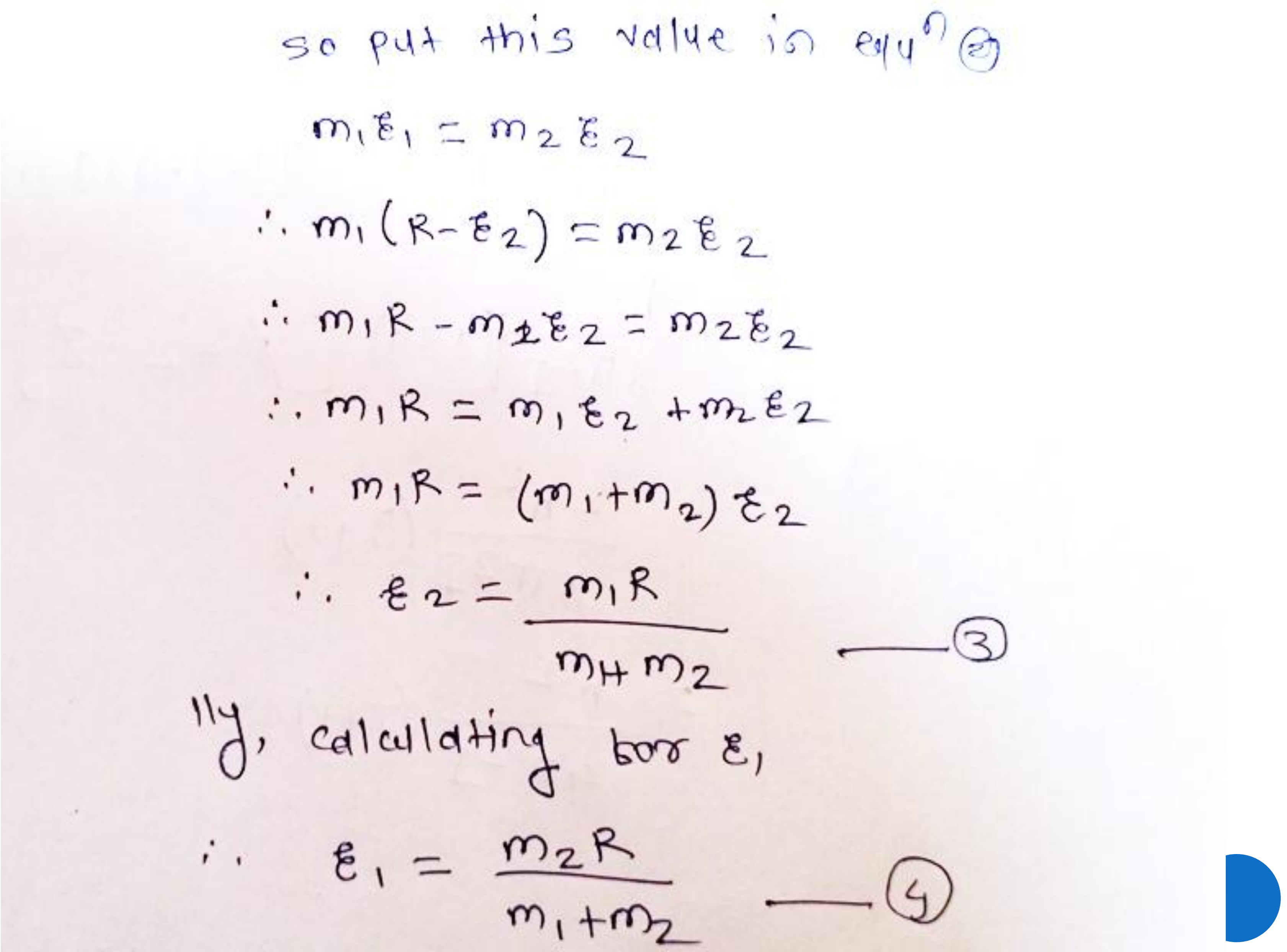
∴ then moment of Inertia

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

From equ^n ①

$$R = r_1 + r_2$$

$$\therefore r_1 = R - r_2$$



so put this value in equ^n ②

$$m_1 \varepsilon_1 = m_2 \varepsilon_2$$

$$\therefore m_1 (R - \varepsilon_2) = m_2 \varepsilon_2$$

$$\therefore m_1 R - m_1 \varepsilon_2 = m_2 \varepsilon_2$$

$$\therefore m_1 R = m_1 \varepsilon_2 + m_2 \varepsilon_2$$

$$\therefore m_1 R = (m_1 + m_2) \varepsilon_2$$

$$\therefore \varepsilon_2 = \frac{m_1 R}{m_1 + m_2} \quad \text{——— ③}$$

lly, calculating for ε_1

$$\therefore \varepsilon_1 = \frac{m_2 R}{m_1 + m_2} \quad \text{——— ④}$$

Now, we have to know equ^n of Inertia

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

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

$$= \frac{m_1 m_2 \cancel{(m_2+m_1)} R^2}{\cancel{(m_1+m_2)}^2}$$

$$= \boxed{\frac{m_1 m_2 R^2}{(m_1+m_2)}}$$

$$\boxed{\therefore\ I = \underline{\mu} R^2} \qquad \because\ \mu = \frac{m_1 m_2}{m_1+m_2}$$

where, $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ is called reduced mass.

The rotational motion of molecule is quantised *i.e.* the angular momentum, $L = I\omega$ is quantised, where ω is the angular velocity, such that,

$L = \sqrt{J(J+1)}\,\dfrac{h}{2\pi}$, where J = 0, 1, 2, ... is called rotational quantum number.

∴ Rotational kinetic energy is given by,

$$E_J = \frac{1}{2} I\omega^2$$

$$= \frac{L^2}{2I}$$

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

Thus, E_J is proportional to J (J + 1).

Since rotational energy is of the order of thermal energy ($kT \approx 10^{-3}$ eV) at room temperature, the molecules are excited in rotational states. However, the rotation about the axis of symmetry involves energy about a few eV, which is of the order of bond (or dissociation) energy. Hence, during excitation of these energy states, the molecule dissociates and therefore these states cannot be excited. So only significant rotation is end-over-end rotation *i.e.* about an axis passing through centre of mass and perpendicular to axis of symmetry *i.e.* line joining the two atoms.

2.7 : Rotational Spectra

The transitions among rotational levels give rise to rotational spectra. Only those molecules which possess electric dipole moment can interact with the electric field of electromagnetic radiations and hence they can emit or absorb electromagnetic radiations during these transitions. So non-polar diatomic molecules like H_2, N_2 etc. as well as symmetric polyatomic molecules like CO_2, CH_4 etc. do not exhibit rotational spectra. But polar molecules like CO, HCl etc. can give rise to rotational spectra.

The rotational transitions are governed by the selection rule,

$$\Delta J = \pm 1 \qquad \text{... 2.10}$$

i.e. the quantum number J, changes by only one unit.

Generally, rotational spectra are obtained in absorption. Therefore, if we represent initial and final states by J and (J + 1) respectively, then change in energy (ΔE) during the transiton is,

$$\underset{(J\rightarrow J+1)}{\Delta E} = \frac{h^2}{8\pi^2 I}\left[(J+1)(J+2) - J(J+1)\right] \equiv E_{J+1} - E_J$$

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

$$\therefore \Delta E = \frac{h^2}{8\pi^2 I}\left[(J+1)(J+2) - J(J+1)\right]$$

$$= \frac{h^2}{8\pi^2 I}(J+1)\left[\cancel{J} + 2 - \cancel{J}\right]$$

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

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

This difference in energy corresponds to radiation of frequency (ν), which is absorbed,

ΔJ

$$\therefore \quad \nu = \frac{\Delta E}{h} = \frac{h}{4\pi^2 I}(J+1) \qquad (\because E = h\nu) \qquad \ldots 2.11$$

$$\therefore \quad \Delta\nu = \frac{h\cdot\Delta J}{4\pi^2 I} = \text{Constant} \qquad (\because \Delta J = \pm 1) \qquad \ldots 2.11(a)$$

Thus, rotational spectrum consists of equispaced lines as shown in Fig. (2.7). Since energy differences are very small, the pure rotational spectrum occurs in far-infra-red [*i.e.* wavelength, $\lambda \approx (10^2\mu - 10^3\mu)$; where $\mu = 10^{-6}\,\text{m} = 10^4\,\text{A}^\circ$] or microwave $(10^3\mu - 10^4\mu)$ region. The measurement of frequencies or difference in frequency of the rotational spectral lines provides a method of estimating the moment of inertia (I) using equations (2.11) or (2.11(a)) and thereby bond length (R) can be computed using equation (2.8).

$\Delta J = \pm 1$

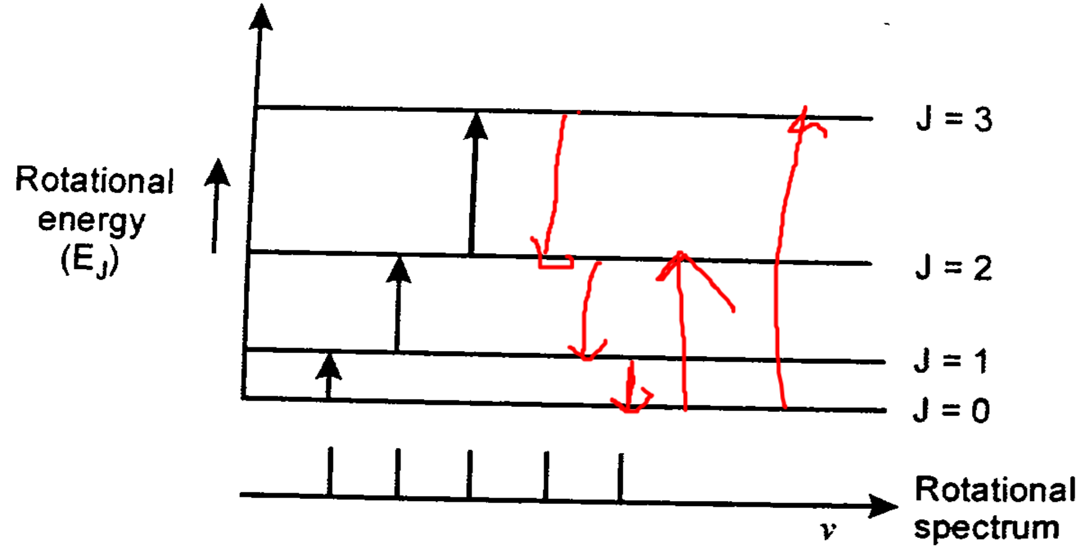


Fig. 2.7 : Rotational energy levels and spectrum

Vibrational energy levels

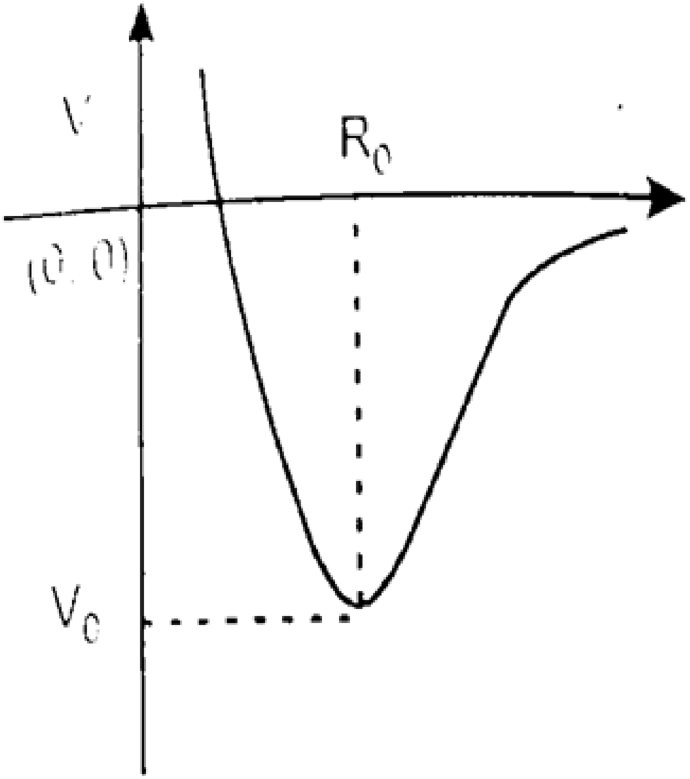
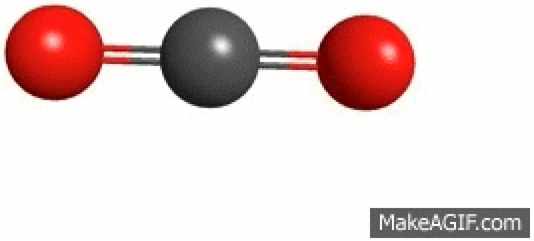


Fig. 2.8 : Potential energy curve of a diatomic molecule



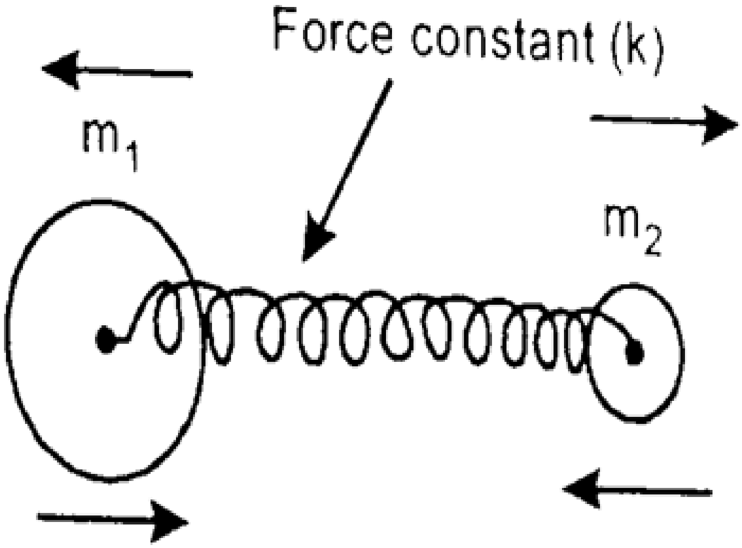


Fig. 2.9 : A two body oscillator

To understand the nature of vibrational level, let us consider the variation of potential energy (V) of diatomic molecule with internuclear distance (R) as shown in Fig. (2.8). In the neighbourhood of equilibrium separation (R_0), the curve is almost parabolic in nature. Therefore, the potential energy in this region, may be written as,

$$V = V_0 + \frac{1}{2}k(R - R_0)^2$$

∴ Restoring force responsible for this potential is,

$$F = -k(R - R_0)$$

where k is force constant (or spring constant).

Eq^n. (2.13) shows that F is a restoring force in simple harmonic oscillator with force constant (k). Therefore, the frequency (ν_0) of oscillation of mass (m) connected to a spring of force constant k is,

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \qquad \text{... 2.14}$$

But diatomic molecule is a two-body oscillator *i.e.* two masses m_1 and m_2 attached to the ends of a spring with force constant k, and oscillating back and forth relative to the centre of mass as shown in Fig. (2.9).

The frequency (ν_0) of oscillation of such a two-body oscillator is expressed in terms of their reduced mass, $\mu = \dfrac{m_1 m_2}{m_1 + m_2}$ as,

$$\nu_0 = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \text{... 2.15}$$

According to quantum mechanics, the vibrational energy (E_v) is also quantised, such that

$$E_v = \left(v + \frac{1}{2}\right) h\nu_0 \qquad \text{... 2.16}$$

where, v = 0, 1, 2, ... is vibrational quantum number.

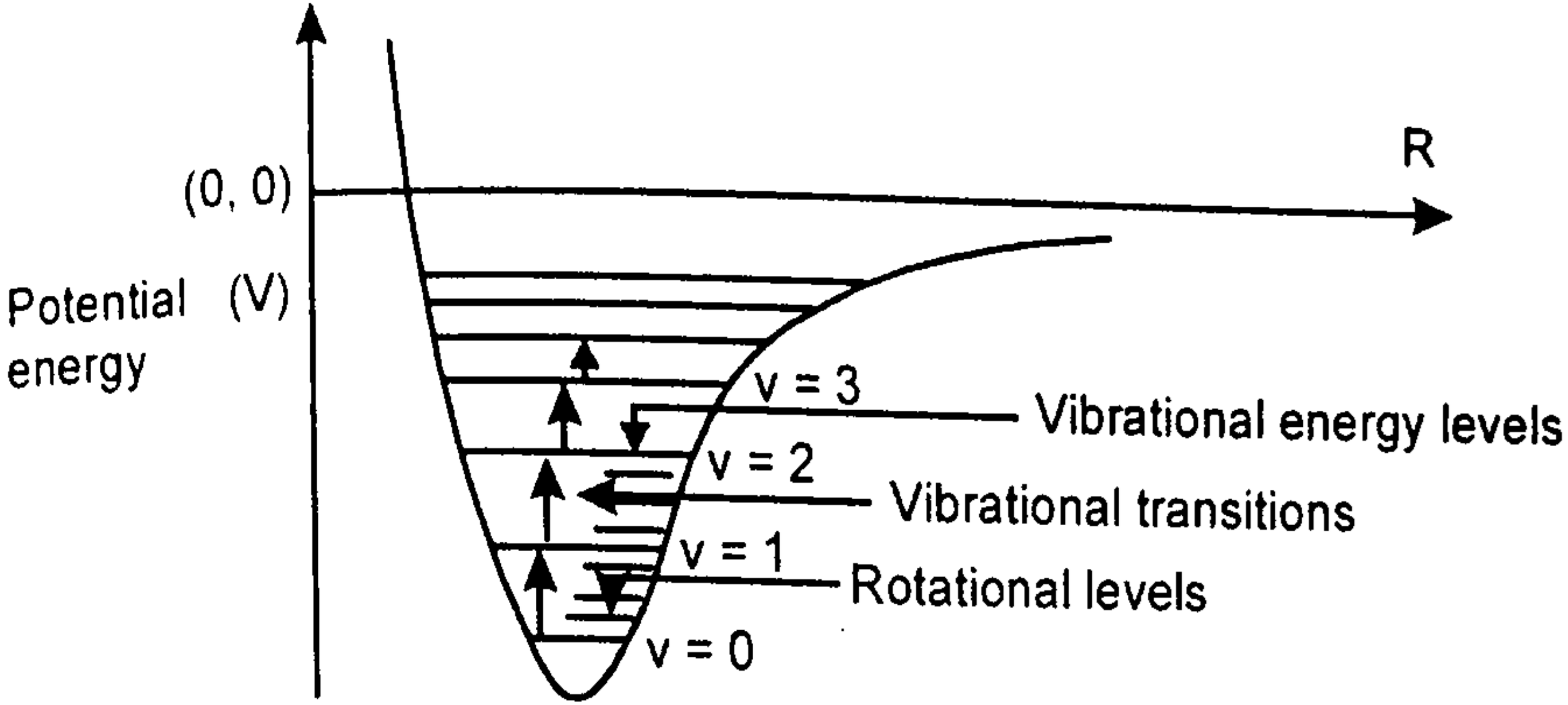
The lowest energy state with v = 0, also possesses a finite energy $\frac{1}{2}h\nu_0$, called *zero point energy*.

$$\therefore \quad E_v = \left(v + \frac{1}{2}\right) - \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} \qquad \text{... 2.17}$$

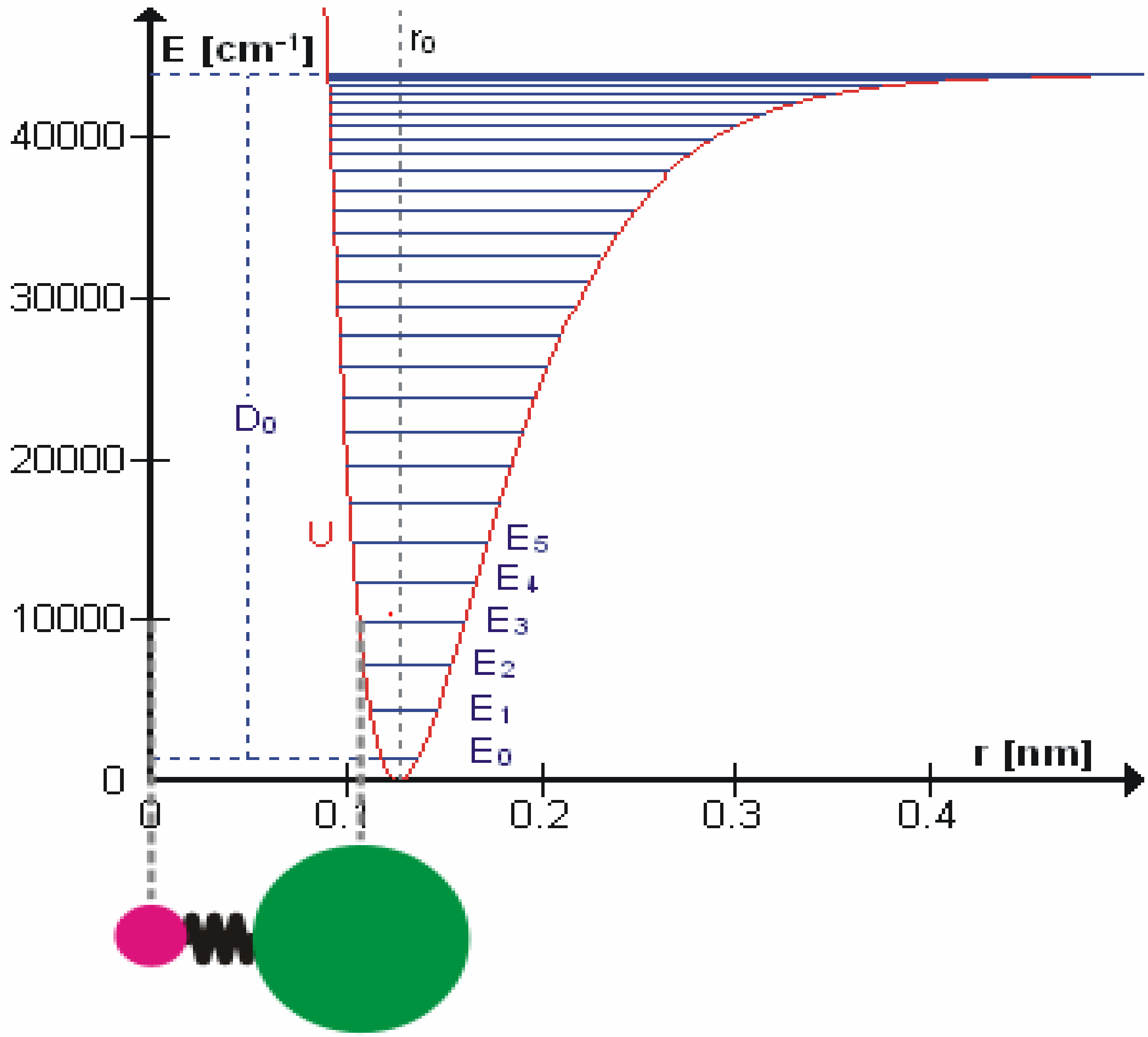
This eq^n. (2.17) gives vibrational energy levels. The vibrational energy is of the order of 0.1 eV which is, generally, larger than the thermal energy $(kT = 2.6 \times 10^{-2}\,\text{eV})$. Hence, molecules are mostly found in the lowest energy state with $v = 0$.

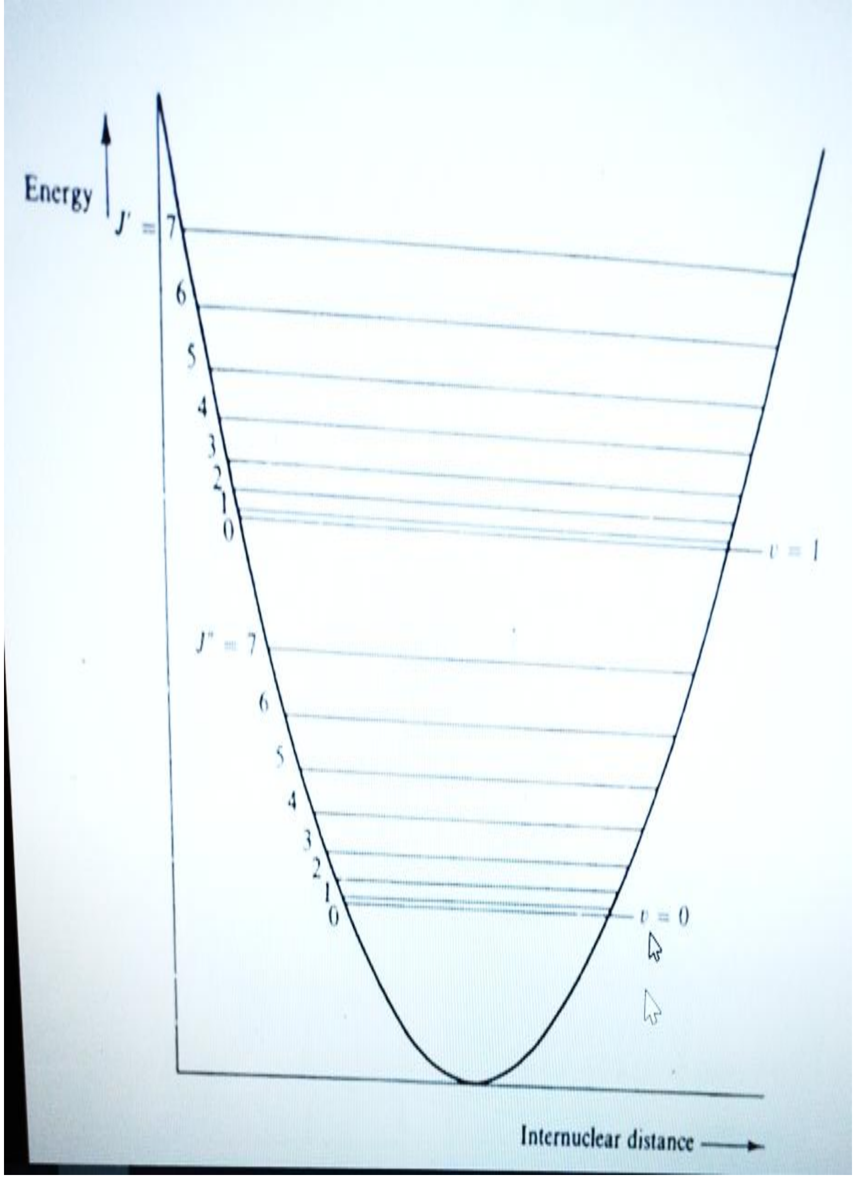
2.9 : Vibrational Spectra

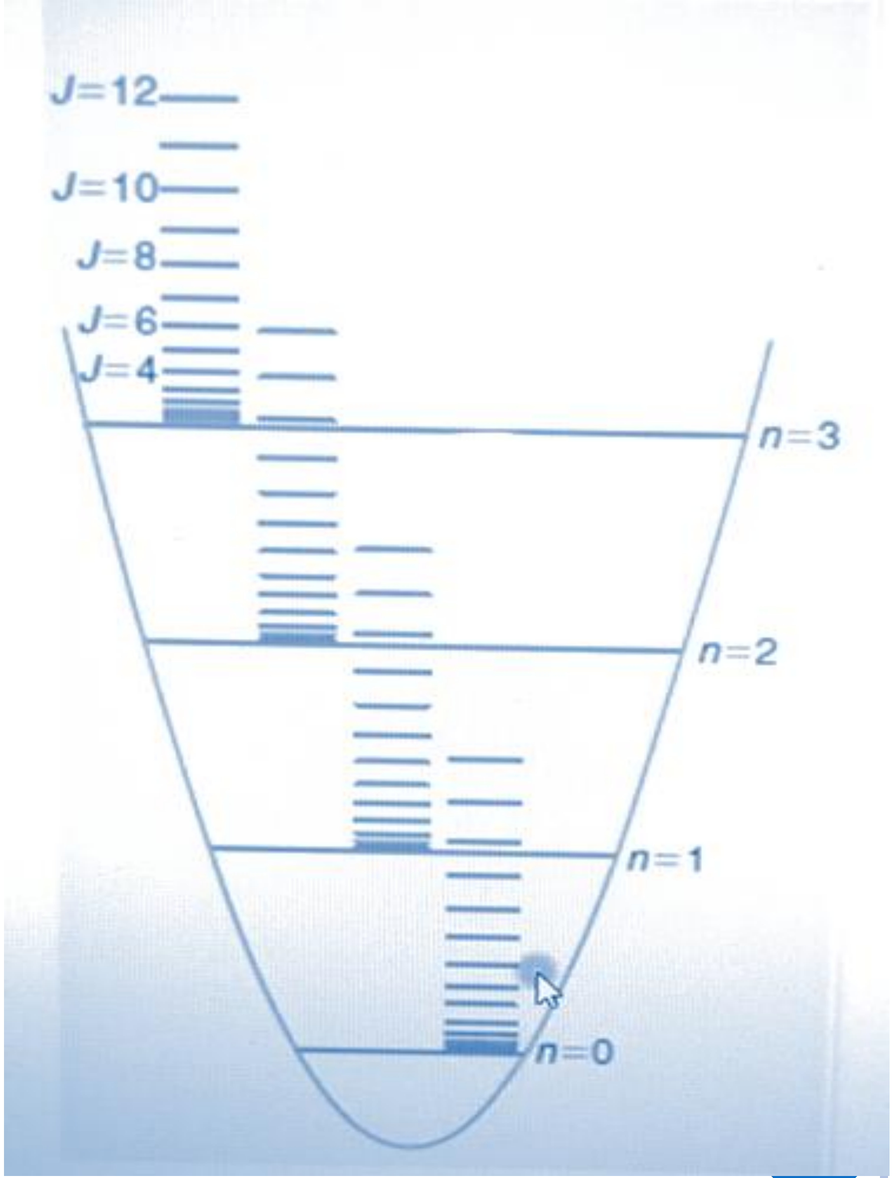
From eq^n. (2.17), it is seen that the vibrational energy levels are equispaced, since $E_v \propto \left(v + \frac{1}{2}\right)$. However, at higher v-values, the harmonic oscillator approximation is not valid as the shape of potential energy curve deviates from parabolic nature. Therefore, the spacing between energy levels goes on decreasing with increase in vibrational quantum number v, as shown in Fig. (2.10) for an harmonic oscillator.

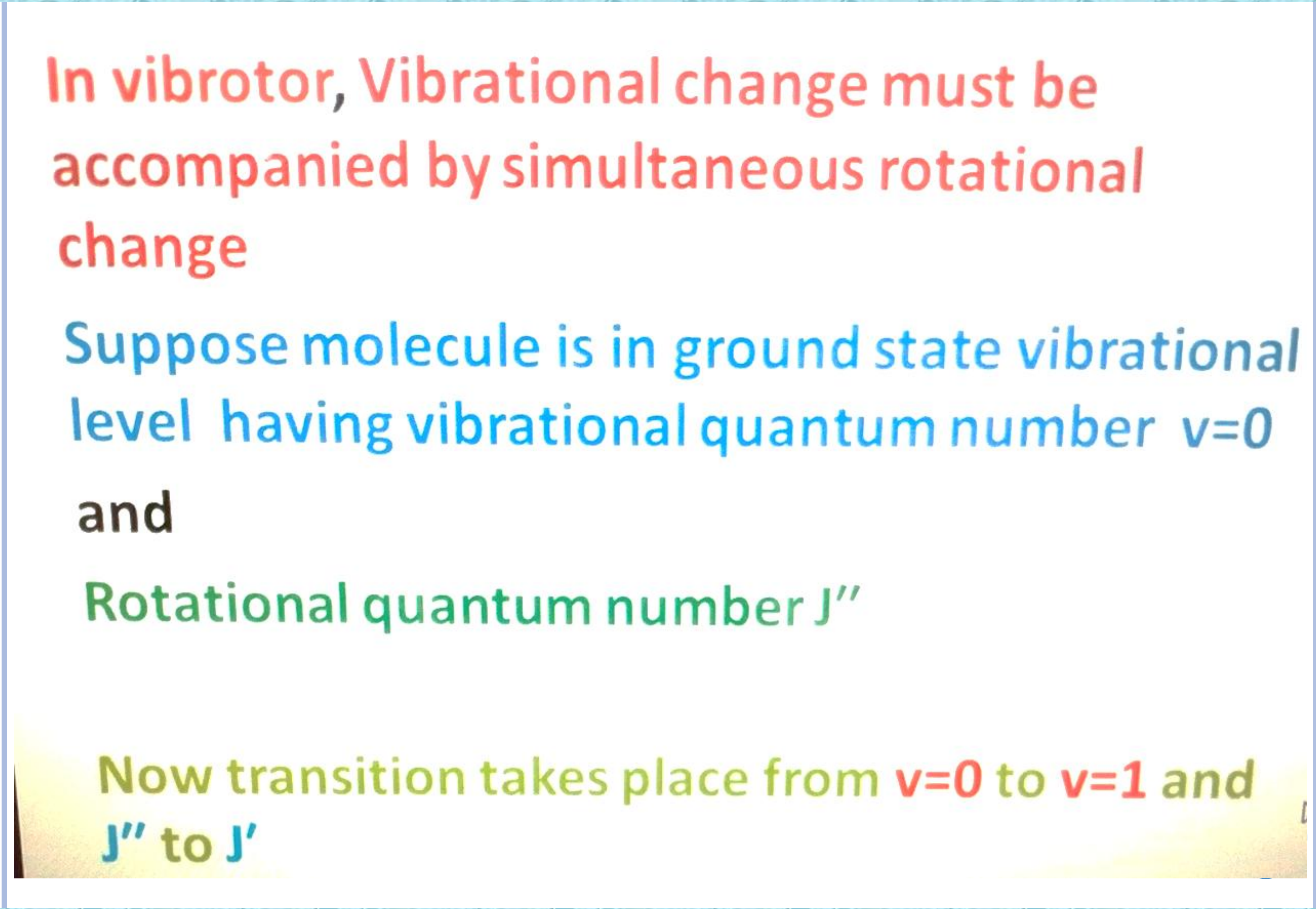


Vibrational transitions for an harmonic oscillator


E [cm⁻¹]
r₀
40000
30000
20000
10000
0
D₀
U
E₅
E₄
E₃
E₂
E₁
E₀
r [nm]
0
0.1
0.2
0.3
0.4


Energy
J' = 7
6
5
4
3
2
1
0
v = 1
J'' = 7
6
5
4
3
2
1
0
v = 0
Internuclear distance


J=12
J=10
J=8
J=6
J=4
n=3
n=2
n=1
n=0



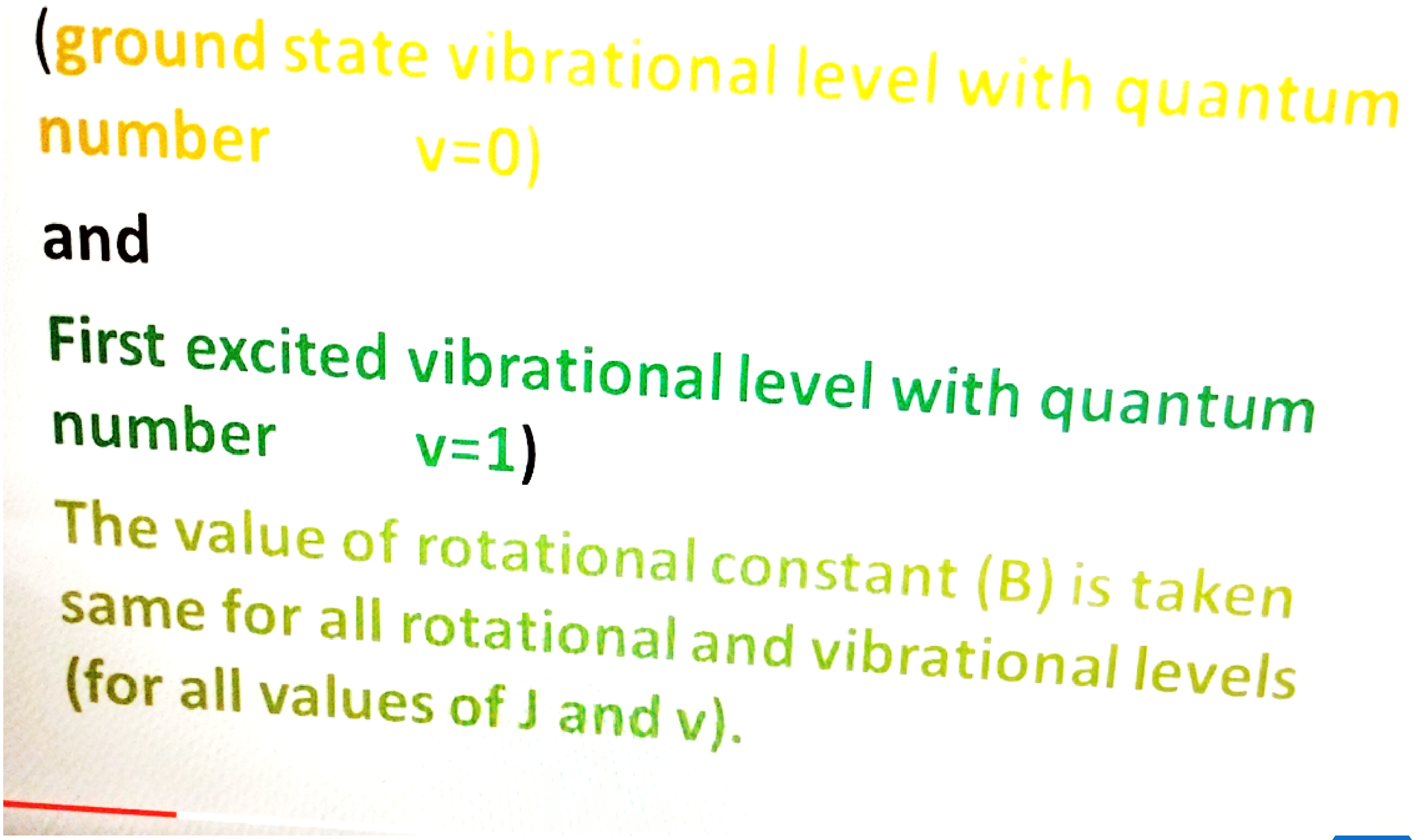
In vibrotor, Vibrational change must be accompanied by simultaneous rotational change

Suppose molecule is in ground state vibrational level having vibrational quantum number v=0

and

Rotational quantum number J″

Now transition takes place from v=0 to v=1 and J″ to J′



(ground state vibrational level with quantum number v=0)

and

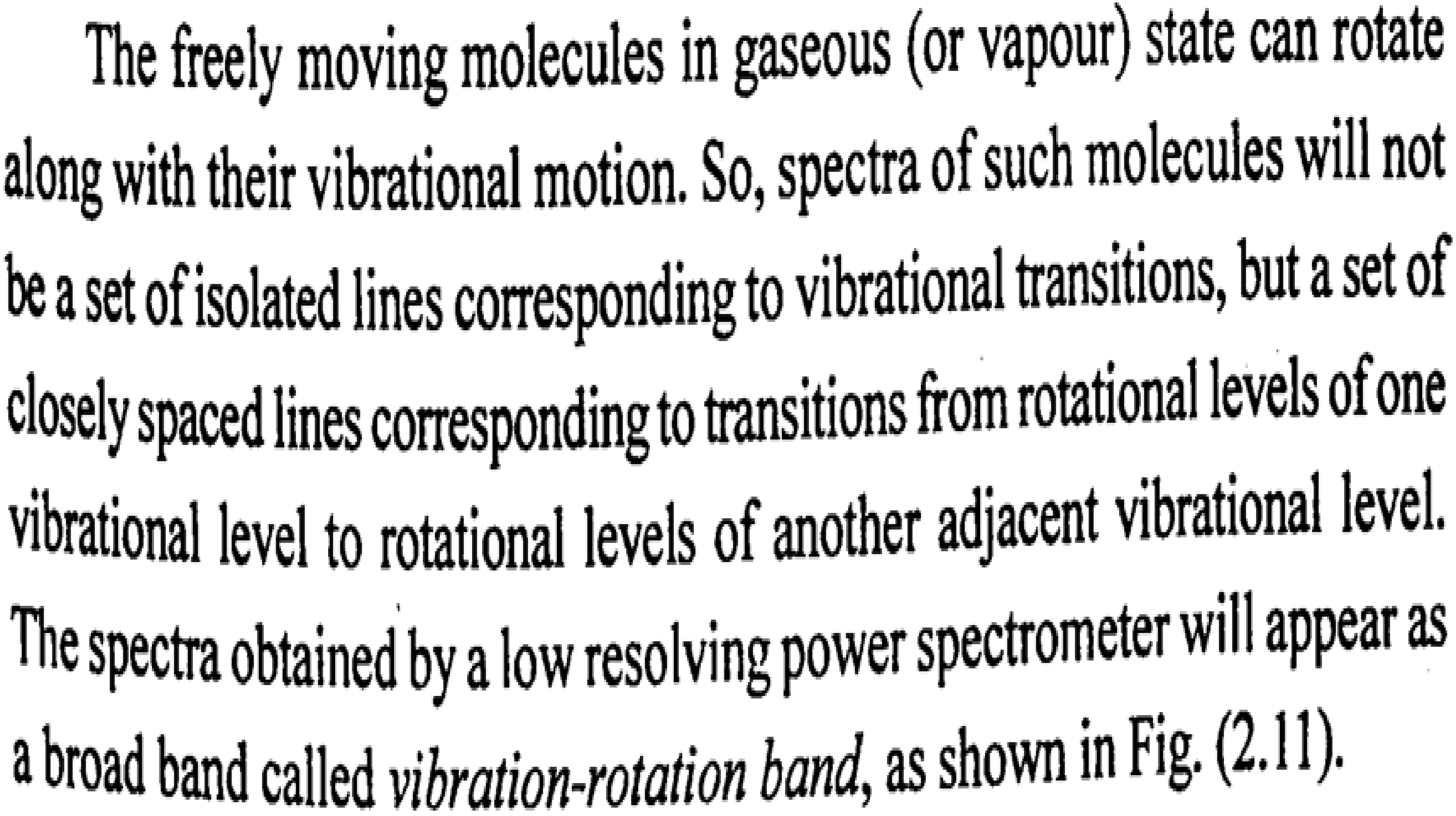
First excited vibrational level with quantum number v=1)

The value of rotational constant (B) is taken same for all rotational and vibrational levels (for all values of J and v).

An oscillating electric dipole of frequency v_0 can emit or absorb electromagnetic radiation of same frequency. Hence, energy change of hv_0 can occur at a time. Therefore, the selection rules for the vibrational transitions are,

$$\Delta v = \pm 1 \qquad \text{... 2.18}$$

Rotational-Vibrational spectra:



The freely moving molecules in gaseous (or vapour) state can rotate along with their vibrational motion. So, spectra of such molecules will not be a set of isolated lines corresponding to vibrational transitions, but a set of closely spaced lines corresponding to transitions from rotational levels of one vibrational level to rotational levels of another adjacent vibrational level. The spectra obtained by a low resolving power spectrometer will appear as a broad band called *vibration-rotation band*, as shown in Fig. (2.11).

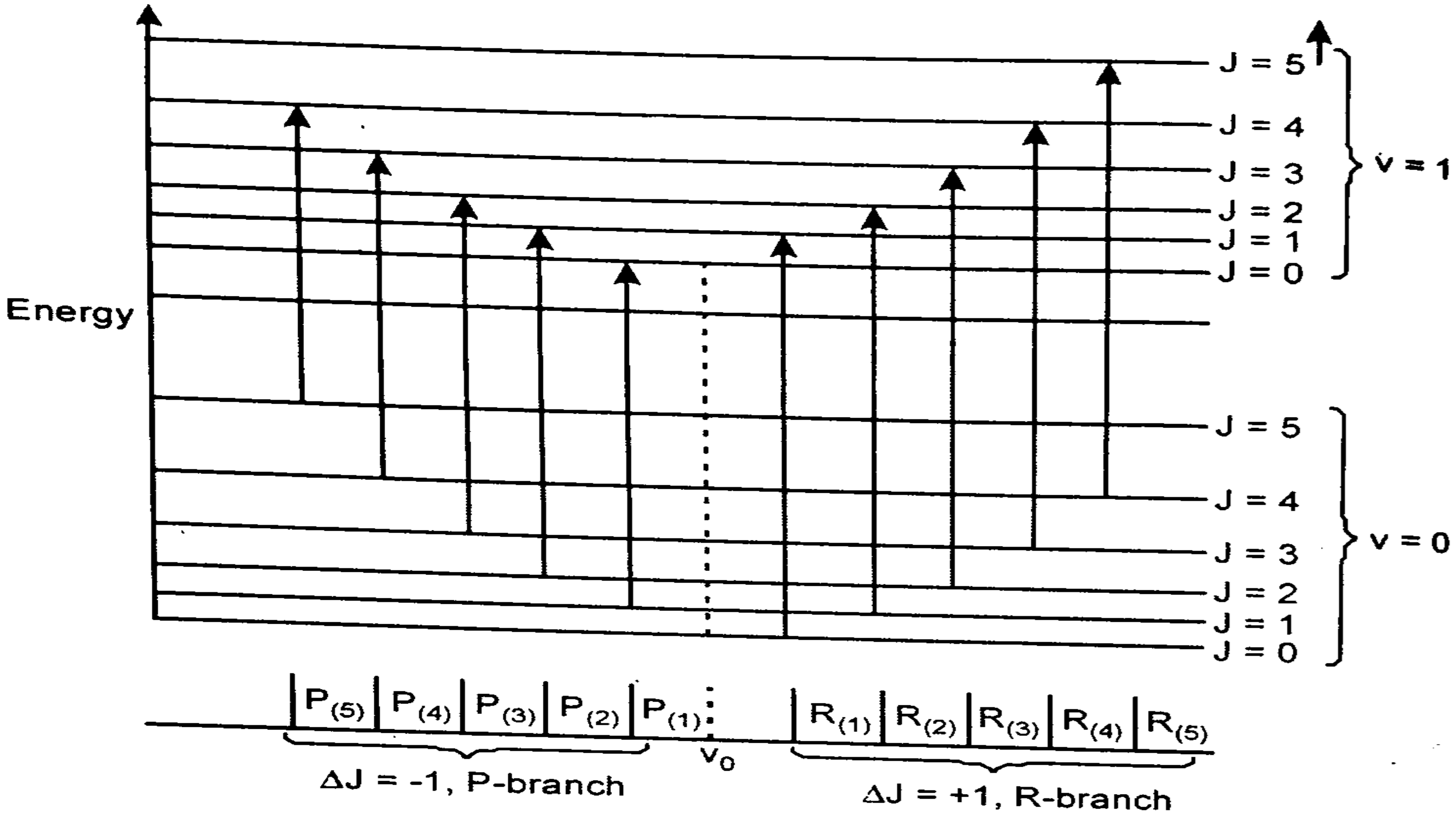
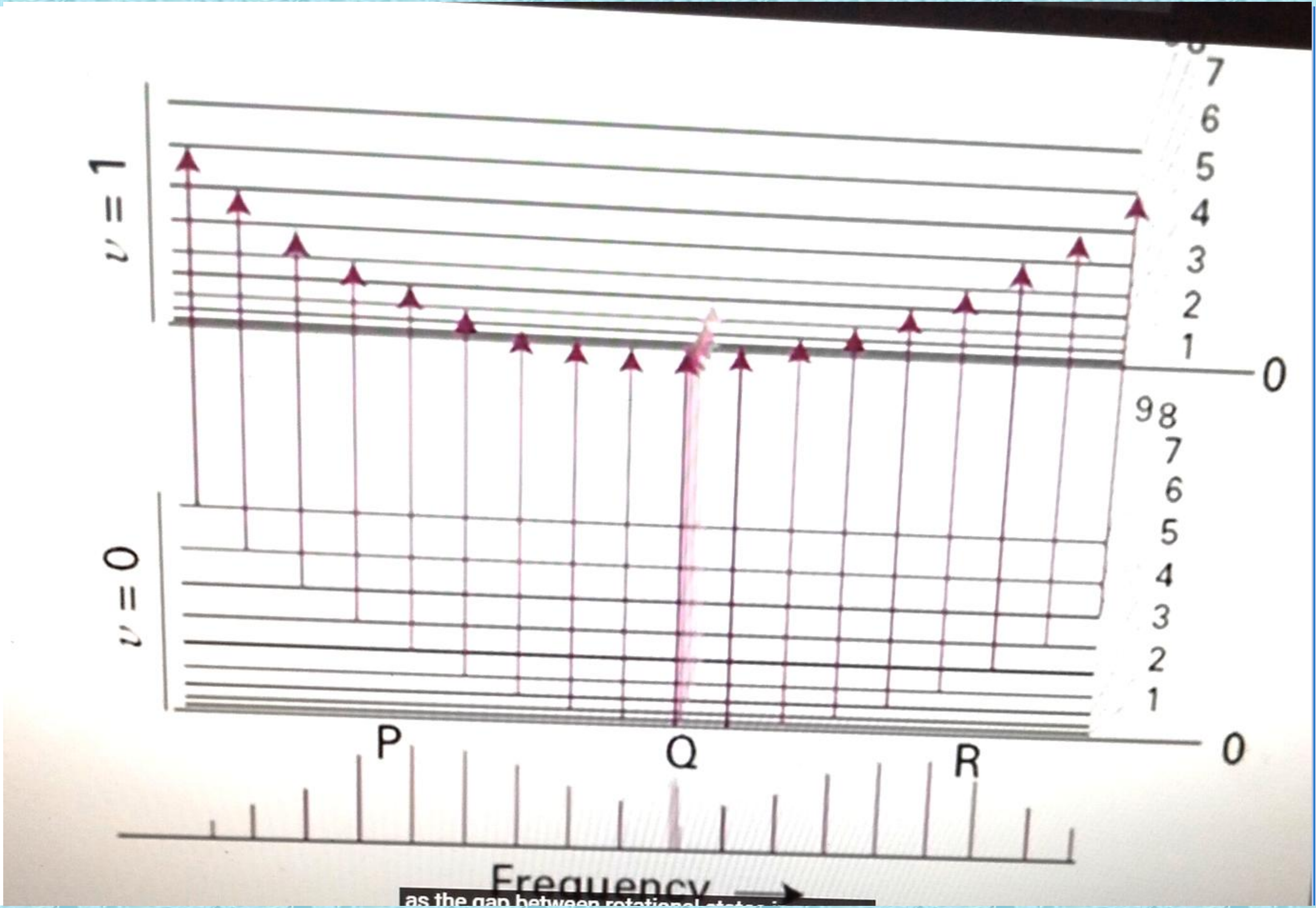
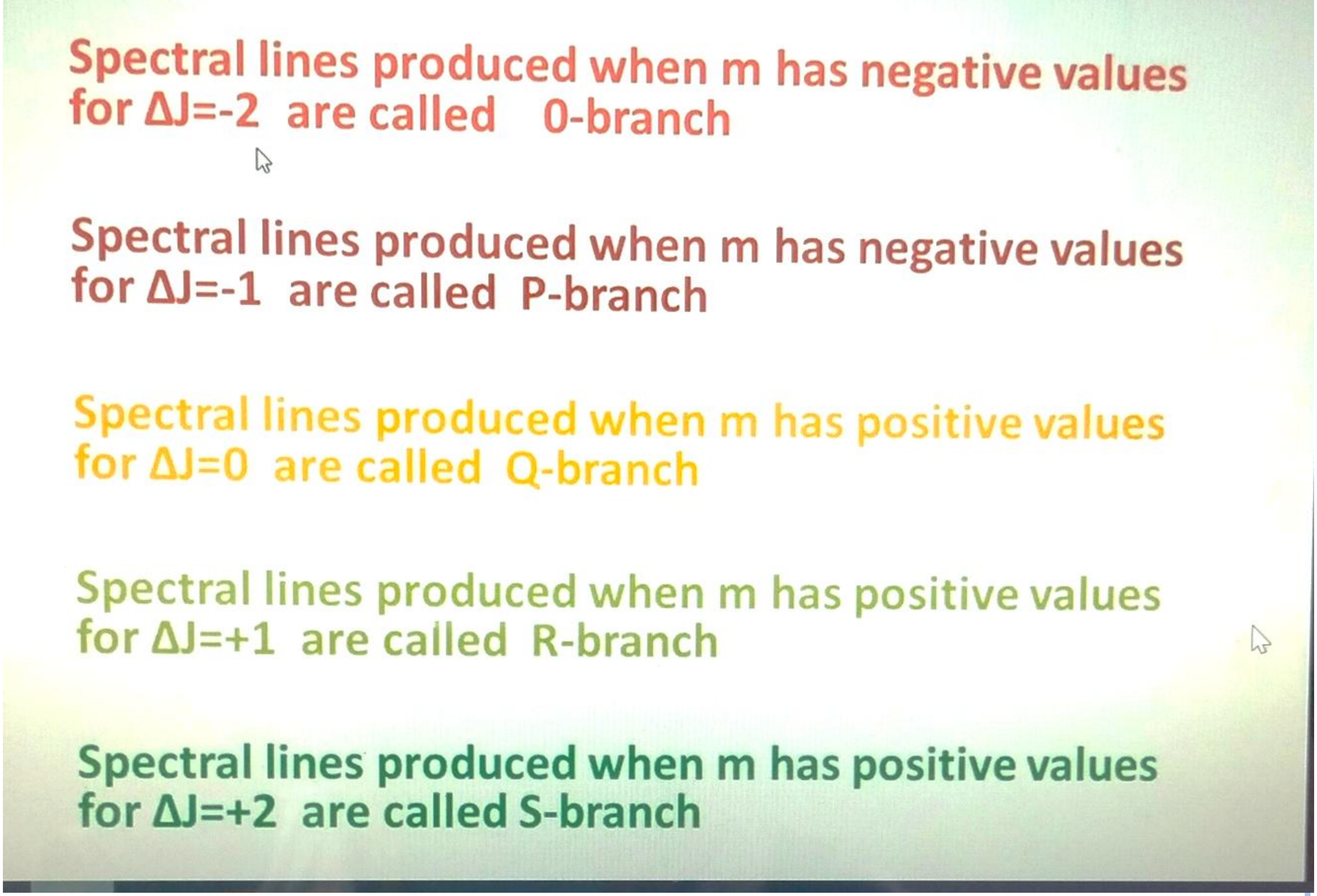


Fig. 2.11 : Vibration-rotational transitions (fine structure of vibration spectra)



as the gap between rotational states i



Spectral lines produced when m has negative values for ΔJ=-2 are called 0-branch

Spectral lines produced when m has negative values for ΔJ=-1 are called P-branch

Spectral lines produced when m has positive values for ΔJ=0 are called Q-branch

Spectral lines produced when m has positive values for ΔJ=+1 are called R-branch

Spectral lines produced when m has positive values for ΔJ=+2 are called S-branch

To a first approximation, we may consider that a diatomic molecule can rotate and vibrate independently. Thus, neglecting the interaction between rotational and vibrational motions, the total energy of molecule may be written as,

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

$v + \frac{1}{2}$

$$\therefore \quad E_{v,J} = E_v + E_J$$

$$\therefore \quad E_{v,J} = \underline{\left(v + \frac{1}{2}\right)} \cdot \frac{h}{2\pi}\sqrt{\frac{k}{\mu}} + \frac{h^2}{8\pi^2 I} \cdot J(J+1) \qquad \ldots 2.19$$

(from eqn^s. 2.9 and 2.17)

Fig. (2.11) shows fine structure of vibrational transitions from v = 0 to v = 1, vibrational states of a diatomic molecule. The selection rules for the transitions are,

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

Thus, the vibration-rotational transitions can be grouped into two parts *viz.*

(i) $\Delta v = +1$ and $\Delta J = -1$, called **P-branch.**

and (ii) $\Delta v = +1$ and $\Delta J = +1$, called **R-branch.**

$\therefore$ Frequency of spectral lines in P and R branches are given by,

(i) For P-branch lines,

$$h\nu_p = \left[E_{1,J-1} - E_{0,J}\right] = \Delta E_{v,J} \qquad (v = 0 \rightarrow 1 \text{ and } J \rightarrow J-1)$$

$$\therefore h\nu_p = \underset{(v=0\rightarrow 1)}{\Delta E_v} + \underset{(J\rightarrow J-1)}{\Delta E_J}$$

Energy change for this transition

$$\Delta\varepsilon_{J,v} = \varepsilon_{J'v=1} - \varepsilon_{J''v=0} \text{-----}(7)$$

$$\therefore \nu_p = \left(\frac{3}{2} - \frac{1}{2}\right)\frac{1}{2\pi}\sqrt{\frac{k}{\mu}} + \left[(J-1)J - J(J+1)\right]\frac{h}{8\pi^2 I}$$

$$= \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} - \frac{h}{4\pi^2 I}\cdot J$$

$$= \nu_0 - \frac{h}{4\pi^2 I}\cdot J \qquad \text{where, } J = 1, 2, 3, \ldots \qquad \ldots 2.20$$

Eq^n. (2.20) gives frequencies of P-branch lines.

Similarly, the frequency of R-branch lines is given by,

$$\nu_R = \nu_0 + [(J+1)(J+2) - J(J+1)]\frac{h}{8\pi^2 I}$$

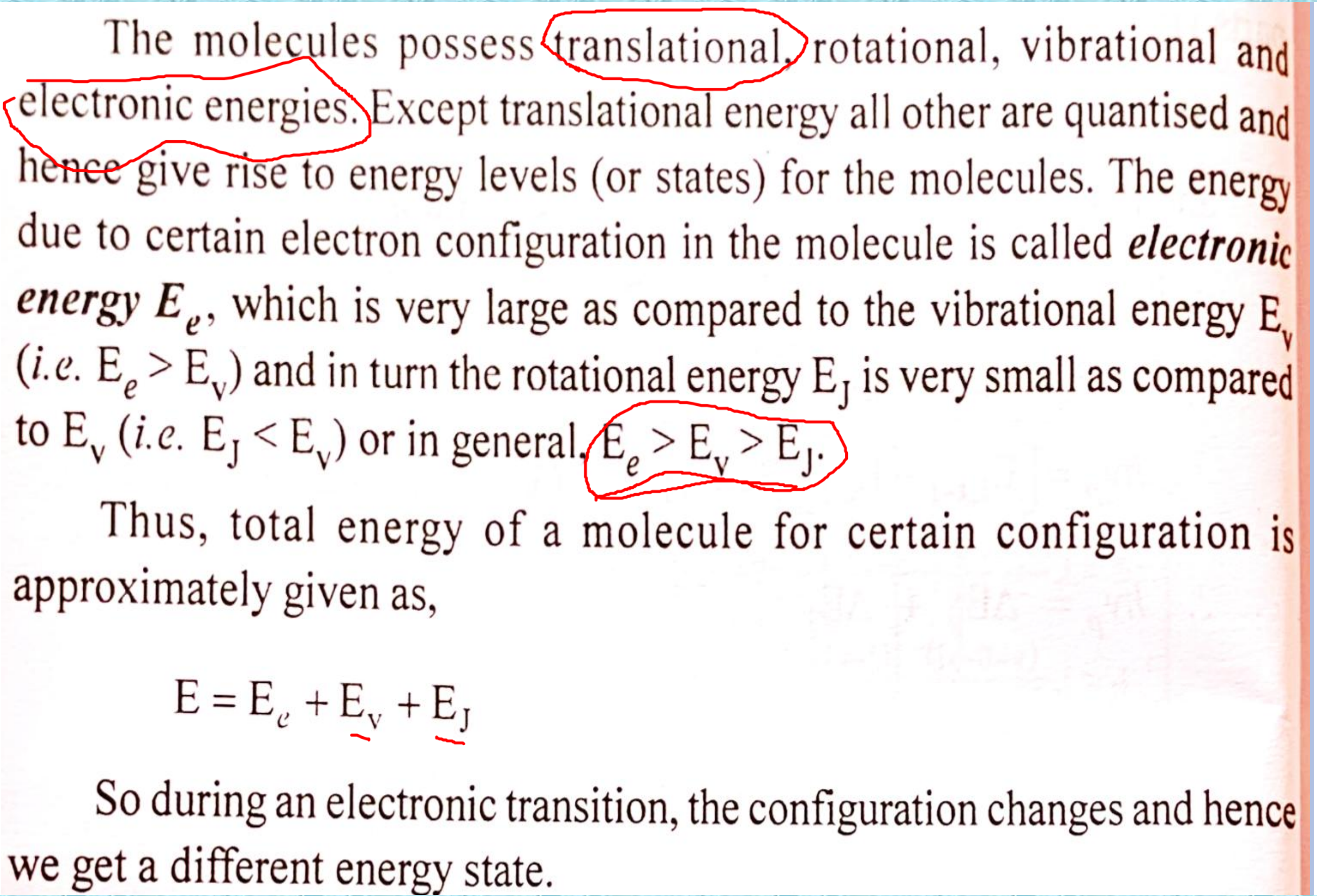
$$= \nu_0 + \frac{h}{4\pi^2 I}(J+1) \qquad \text{where, } J = 0, 1, 2, \ldots \qquad \ldots 2.21$$

Since, $\Delta J = 0$ is forbidden transition, there is no line corresponding to frequency $\nu = \nu_0$, called **band origin**.

The spacing between P-branch as well as R-branch lines is $\frac{h}{4\pi^2 I}$ [from eq^{ns}. (2.20) and (2.21)] *i.e.* rotational lines are equispaced in a vibrational band. [(v = 0, v = 1), say].

Thus, the study of vibration-rotation spectra in infra-red region provides a method to estimate *moment of inertia* (I) of the molecule and thereby the *bond length* (R), if reduced mass of molecule is known.

Electronic Spectra of Diatomic Molecules



The molecules possess translational, rotational, vibrational and electronic energies. Except translational energy all other are quantised and hence give rise to energy levels (or states) for the molecules. The energy due to certain electron configuration in the molecule is called ***electronic energy*** E_e, which is very large as compared to the vibrational energy E_v (*i.e.* $E_e > E_v$) and in turn the rotational energy E_J is very small as compared to E_v (*i.e.* $E_J < E_v$) or in general, $E_e > E_v > E_J$.

Thus, total energy of a molecule for certain configuration is approximately given as,

$$E = E_e + E_v + E_J$$

So during an electronic transition, the configuration changes and hence we get a different energy state.

$\therefore$ Change in total energy may be obtained as,

$$\Delta E = \Delta E_e + \Delta E_v + \Delta E_J$$

$\therefore$ $\Delta E = h\nu$, where ν is the frequency of radiation emitted or absorbed

during the transition from one electronic state to another electronic state of a molecule. Since the change in electronic configuration is always associated with a change in electric dipole moment, all the molecules (polar as well as non-polar) exhibit electronic spectra. But we know that to observe pure rotational spectrum, the molecule should possess a dipole moment and to observe vibrational spectra, there should be a change in dipole moment.

Thus, the study of electronic spectra of molecules provides a technique to obtain informations like moment of inertia (I), bond length (R) etc. even for non-polar molecules like H_2, N_2 etc.

The frequency of radiation involved in the electronic transitions is,

$$\nu = \nu_e + \nu_v + \nu_J$$

Since electronic transitions involve large change in energy, the electronic spectra occur in visible and ultraviolet region.

(i) The electronic energy (E_e) is the energy of electron plus the potential energy of nuclei. Hence, for diatomic molecules the electronic energy state may be represented by an almost parabolic curve.

(ii) The vibrational energy states are associated with each electronic state. They are almost equispaced at lower v-values, but the spacing decreases with increasing v-values at higher v-values.

(iii) Every vibrational level is associated with a set of closely spaced rotational levels. The spacing between the rotational levels goes on increasing with J-value. The electronic, vibrational and rotational levels are as shown in Fig. (2.10).

The transitions from one electronic state to another means from one rotational level in a vibrational level of an electronic level to another rotational level in a vibrational level of another electronic level. Hence, there are several such transitions giving a large number of spectral lines. When observed through a low resolving power spectroscope, we observe a *system of bands*. Each band has an intense *band-head* which fades away on the other side as shown in Fig. (2.12).

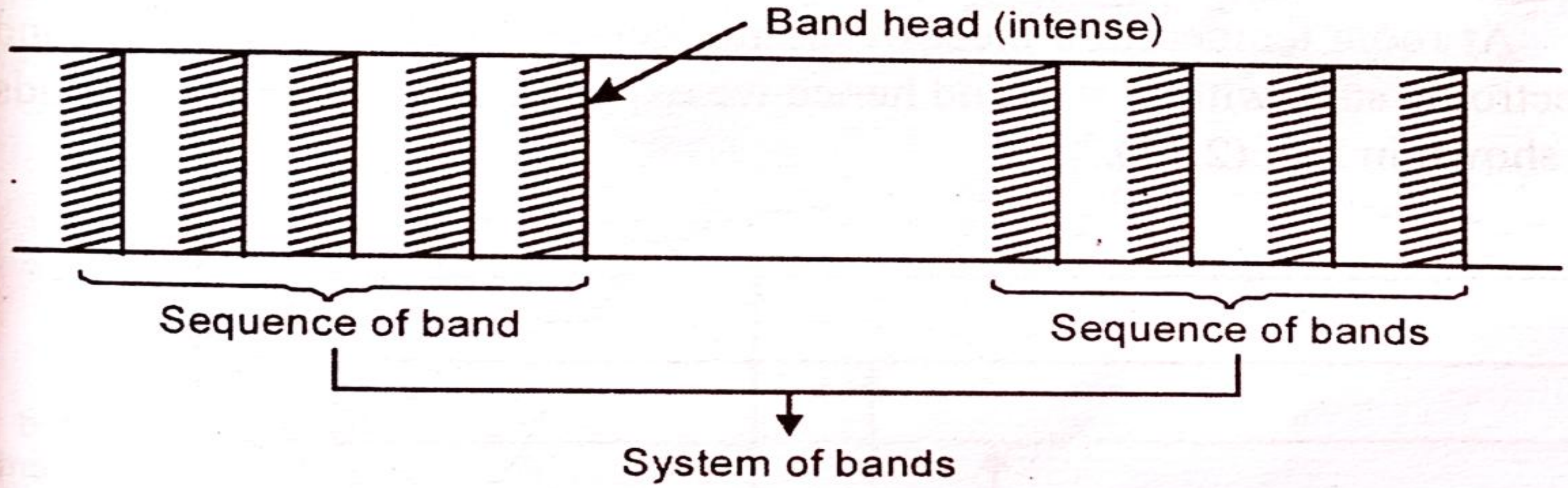
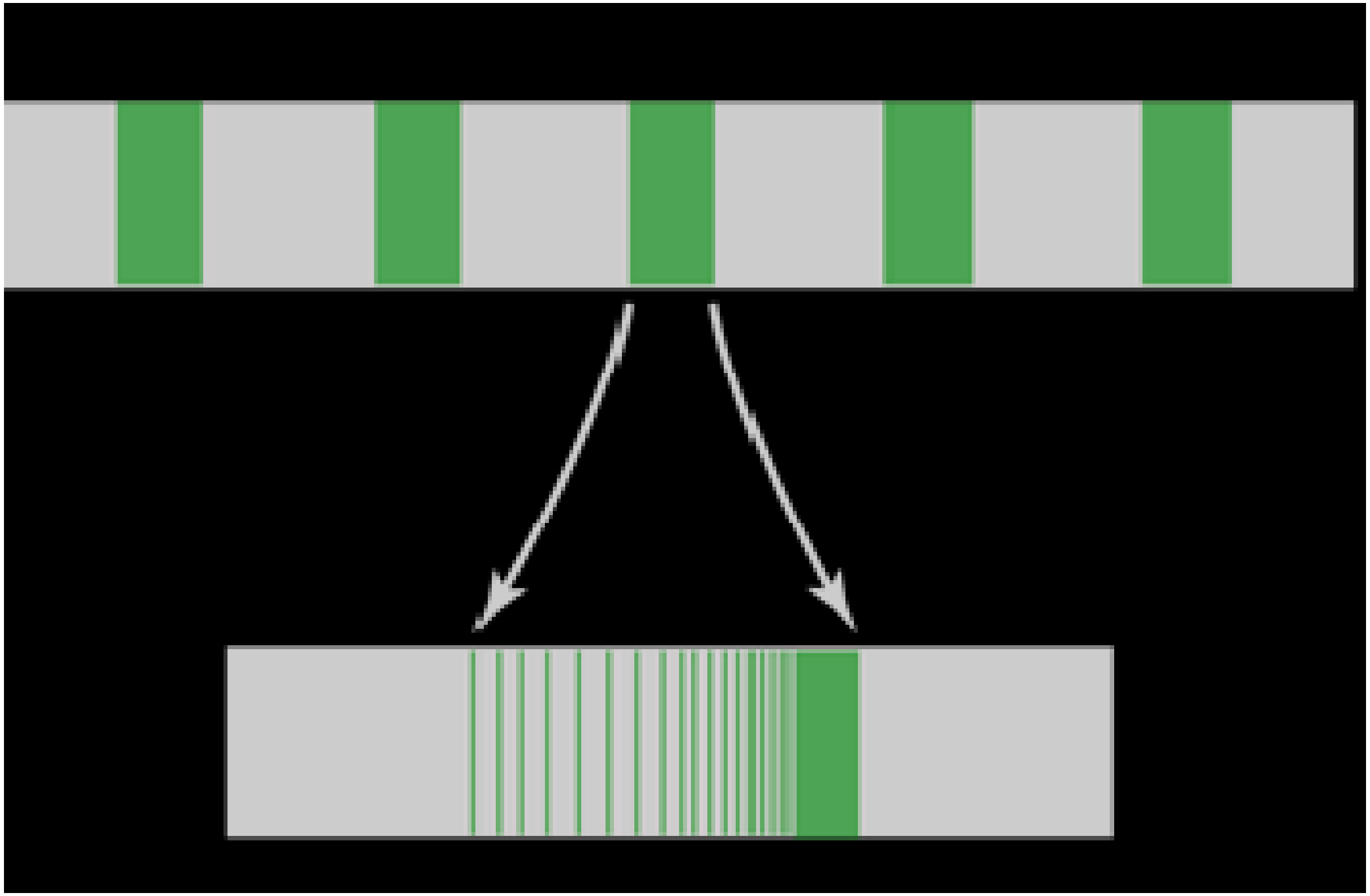
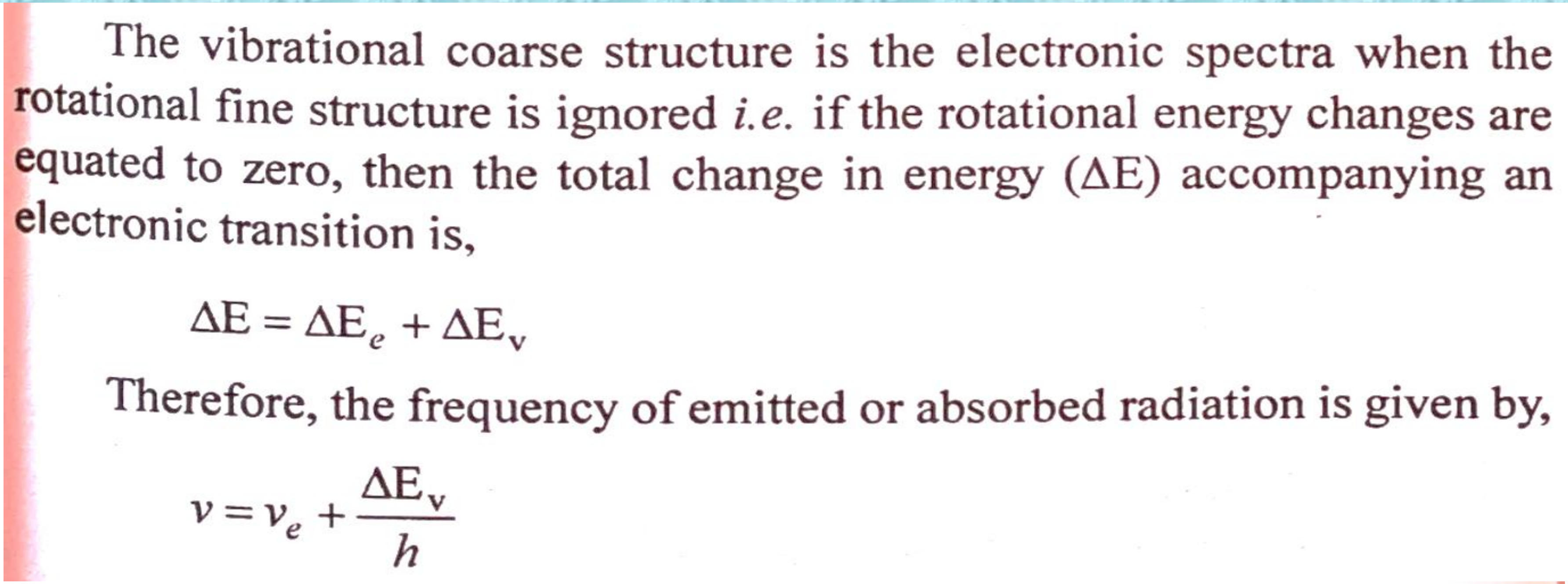


Fig. 2.12 : System of bands



Vibrational Coarse Structure

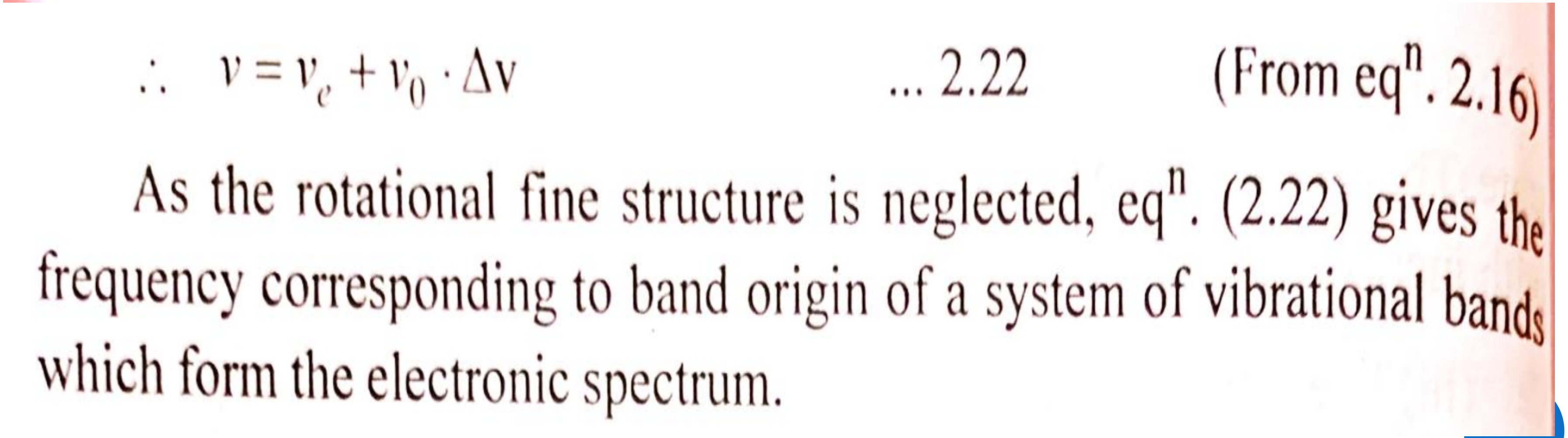


The vibrational coarse structure is the electronic spectra when the rotational fine structure is ignored *i.e.* if the rotational energy changes are equated to zero, then the total change in energy (ΔE) accompanying an electronic transition is,

$$\Delta E = \Delta E_e + \Delta E_v$$

Therefore, the frequency of emitted or absorbed radiation is given by,

$$\nu = \nu_e + \frac{\Delta E_v}{h}$$



$$\therefore \quad \nu = \nu_e + \nu_0 \cdot \Delta v \qquad \ldots 2.22 \qquad (\text{From eq}^n.\ 2.16)$$

As the rotational fine structure is neglected, eq^n. (2.22) gives the frequency corresponding to band origin of a system of vibrational bands which form the electronic spectrum.

During electronic transitions, there are no selection rules for vibrational quantum number v. Thus, Δv can be positive, negative or zero. If a group of bands correspond to same electronic transition, then they are called a **system of bands**. The bands are named by the vibrational quantum numbers of upper and lower electronic states (v', v'') as shown in Fig. (2.13).

There is a convenient way of classification of bands *viz.*

(i) if $\Delta v = (v' - v'')$ is a constant, then a series of such bands is called a **sequence.**

(ii) A set of bands corresponding to same v' and different values of v'' or same value of v'' and different values of v' is called a **progression.**

e.g. $v'' = 0$ and $v' = 0, 1, 2, 3, ...$ gives a progression.

At room temperature most of the molecules will be found in ground electronic state with v" = 0, and hence we expect a set of absorption bands as shown in Fig. (2.13).

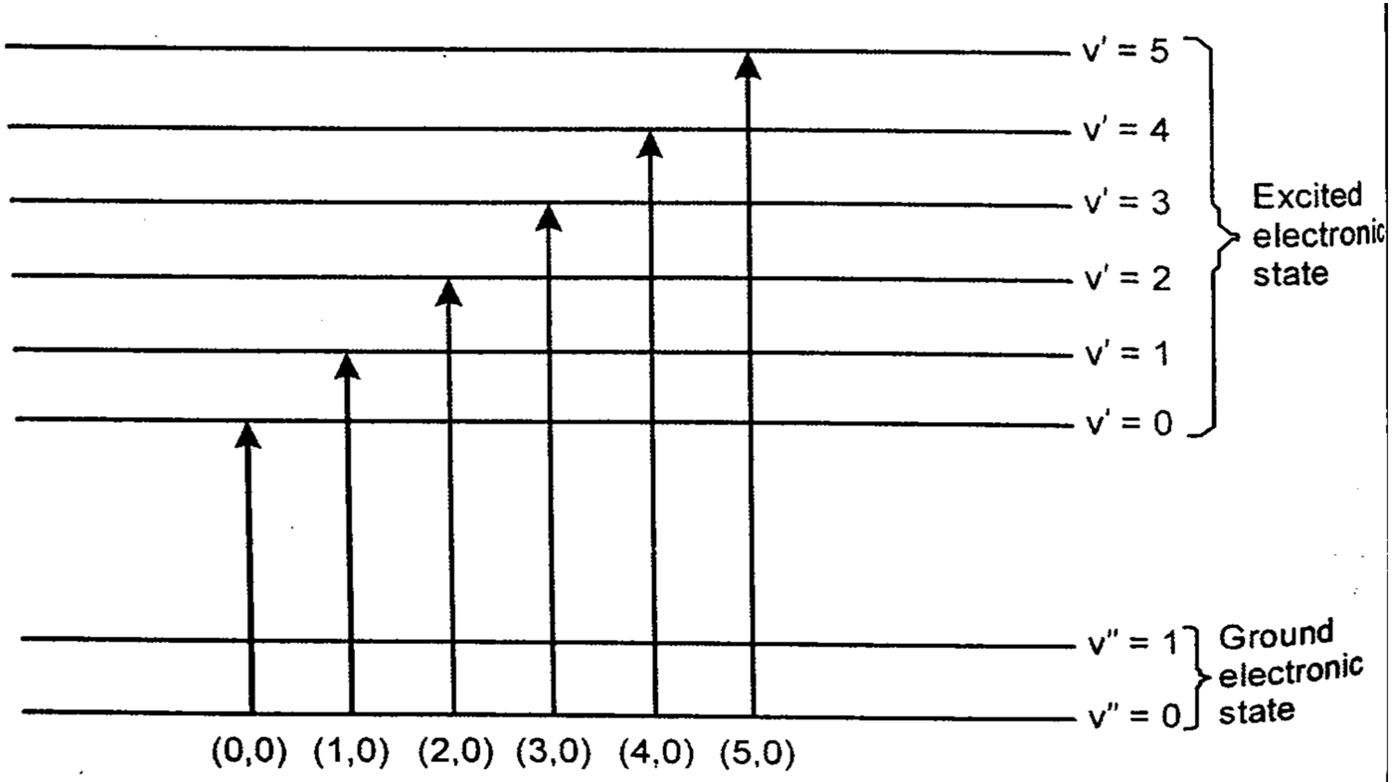
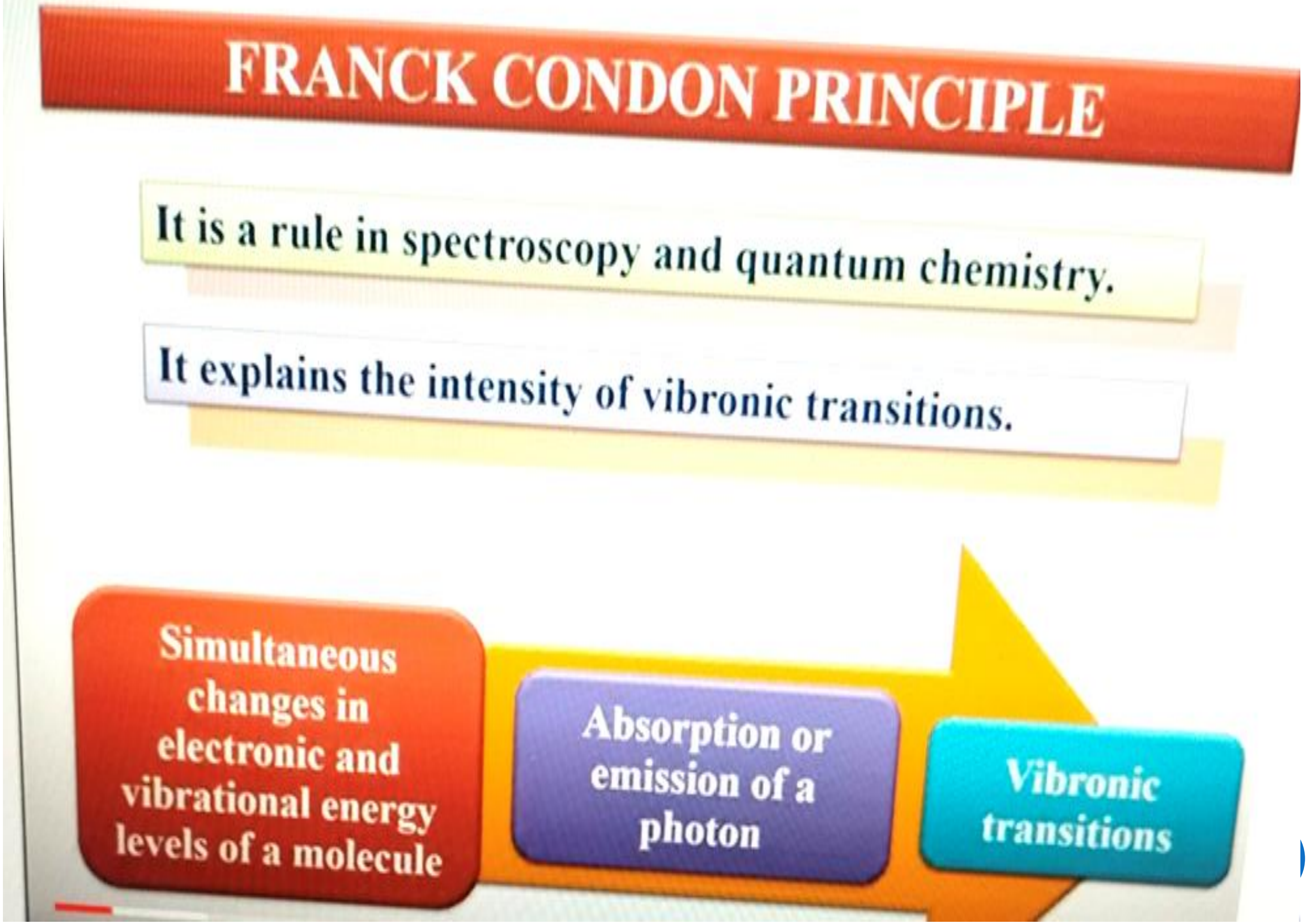


Fig. 2.13 : Vibrational coarse structure of absorption bands formed during electronic transitions from ground state to excited states.



FRANCK CONDON PRINCIPLE

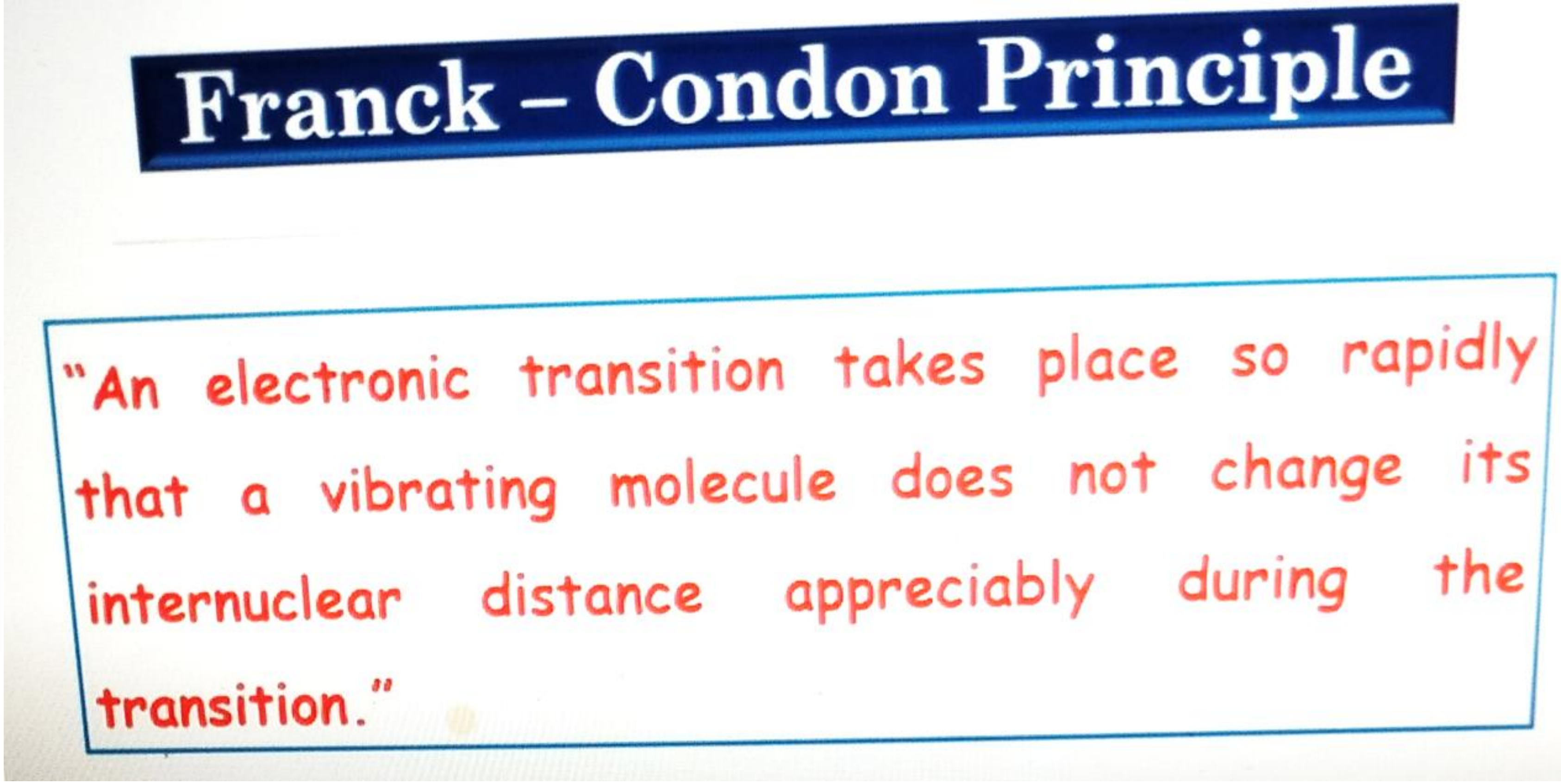
It is a rule in spectroscopy and quantum chemistry.

It explains the intensity of vibronic transitions.

Simultaneous changes in electronic and vibrational energy levels of a molecule

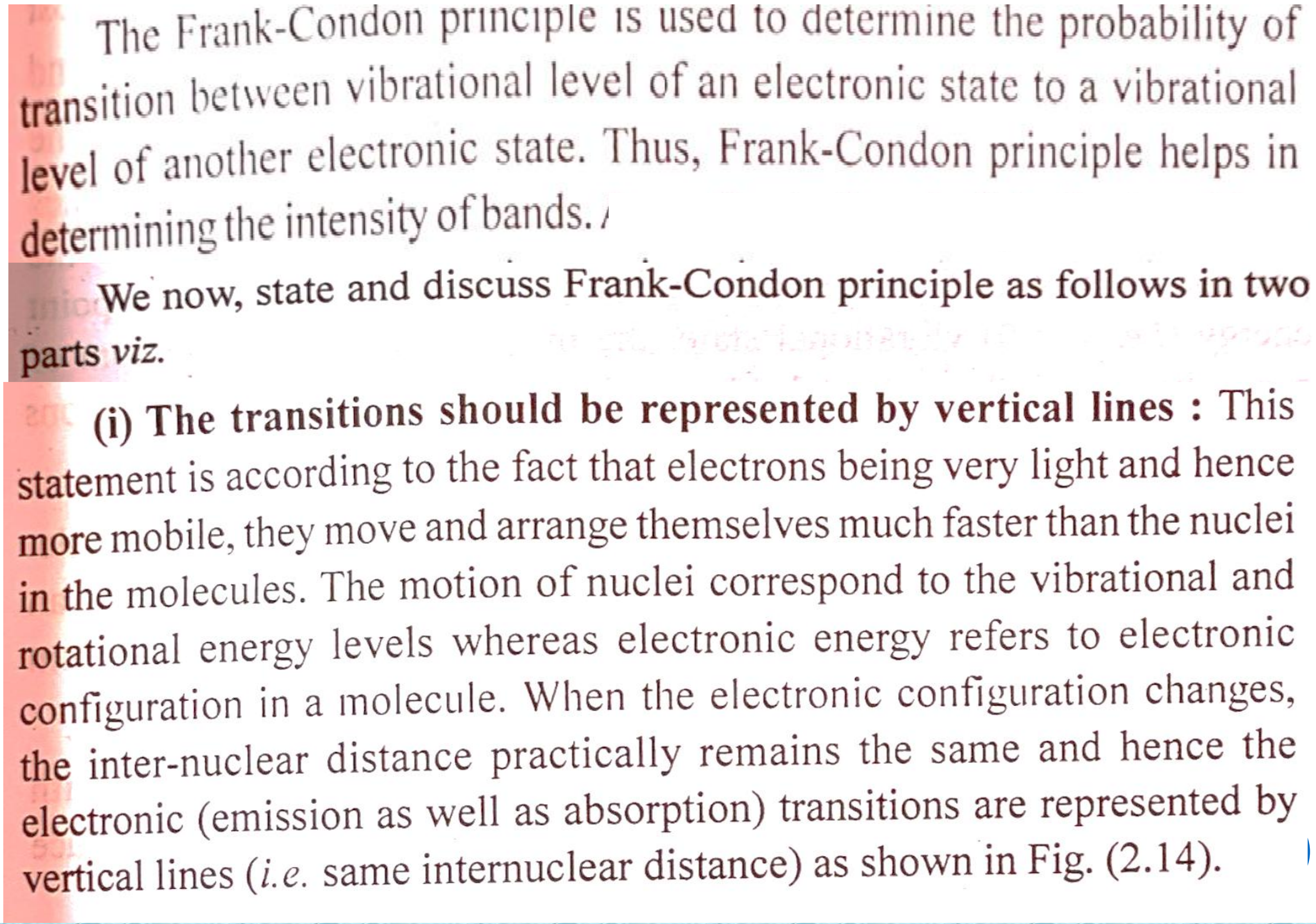
Absorption or emission of a photon

Vibronic transitions



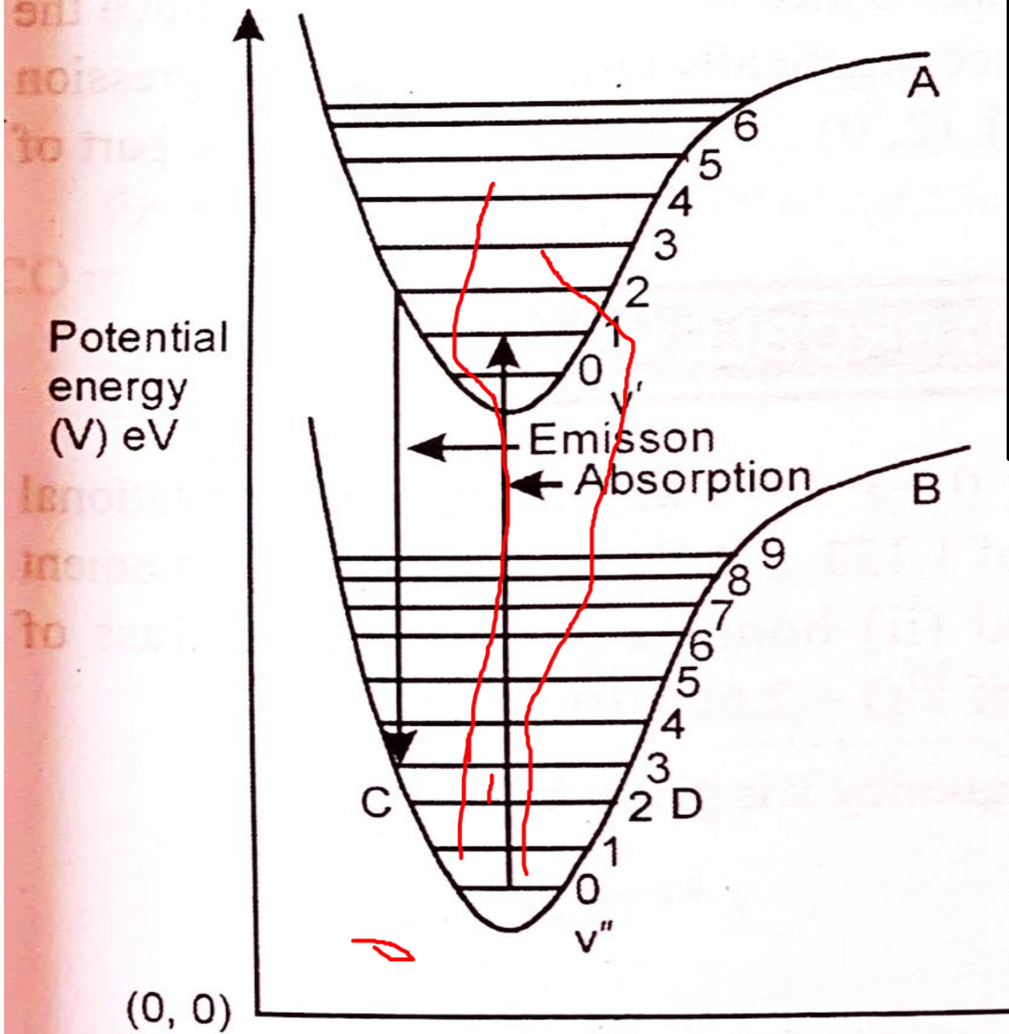
Franck – Condon Principle

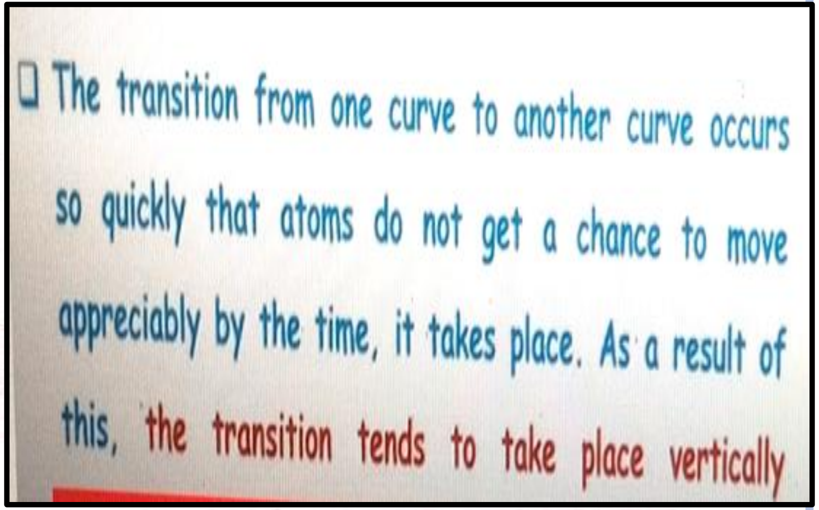
"An electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition."


The Frank-Condon principle is used to determine the probability of transition between vibrational level of an electronic state to a vibrational level of another electronic state. Thus, Frank-Condon principle helps in determining the intensity of bands.

We now, state and discuss Frank-Condon principle as follows in two parts *viz.*

(i) The transitions should be represented by vertical lines : This statement is according to the fact that electrons being very light and hence more mobile, they move and arrange themselves much faster than the nuclei in the molecules. The motion of nuclei correspond to the vibrational and rotational energy levels whereas electronic energy refers to electronic configuration in a molecule. When the electronic configuration changes, the inter-nuclear distance practically remains the same and hence the electronic (emission as well as absorption) transitions are represented by vertical lines (*i.e.* same internuclear distance) as shown in Fig. (2.14).





- The transition from one curve to another curve occurs so quickly that atoms do not get a chance to move appreciably by the time, it takes place. As a result of this, the transition tends to take place vertically

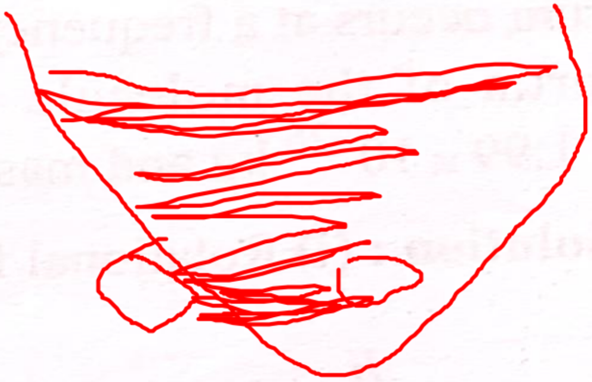
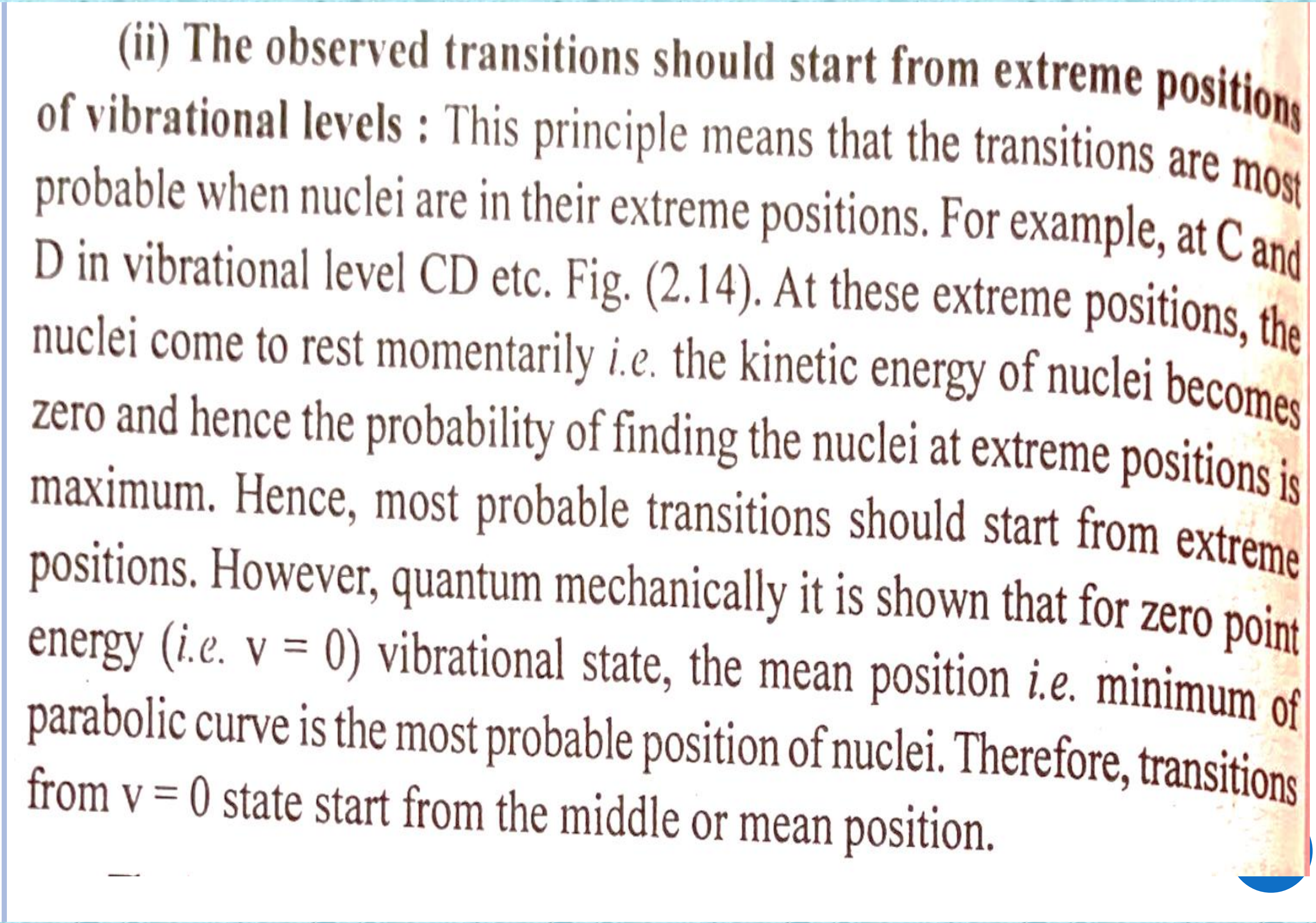
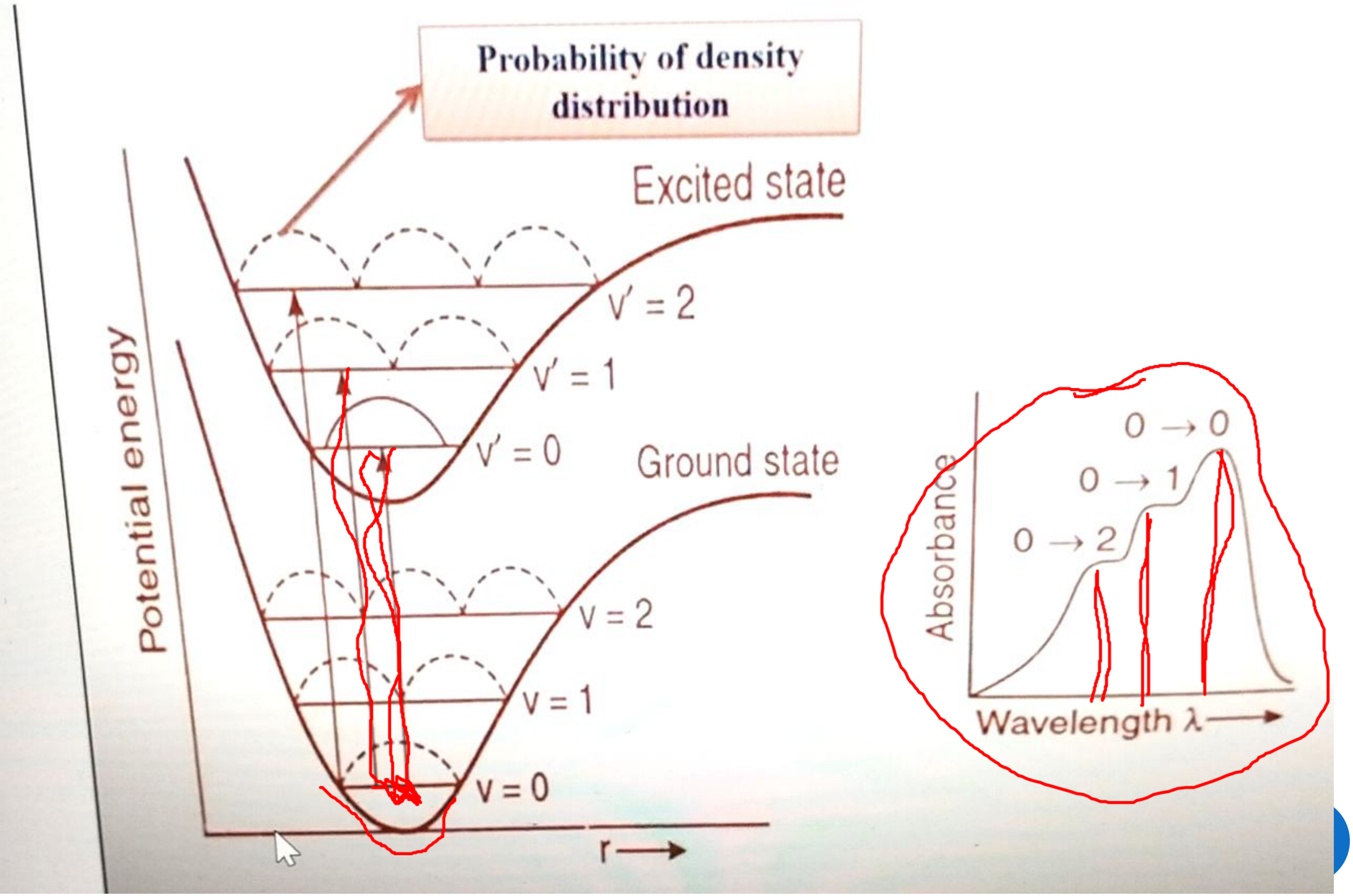
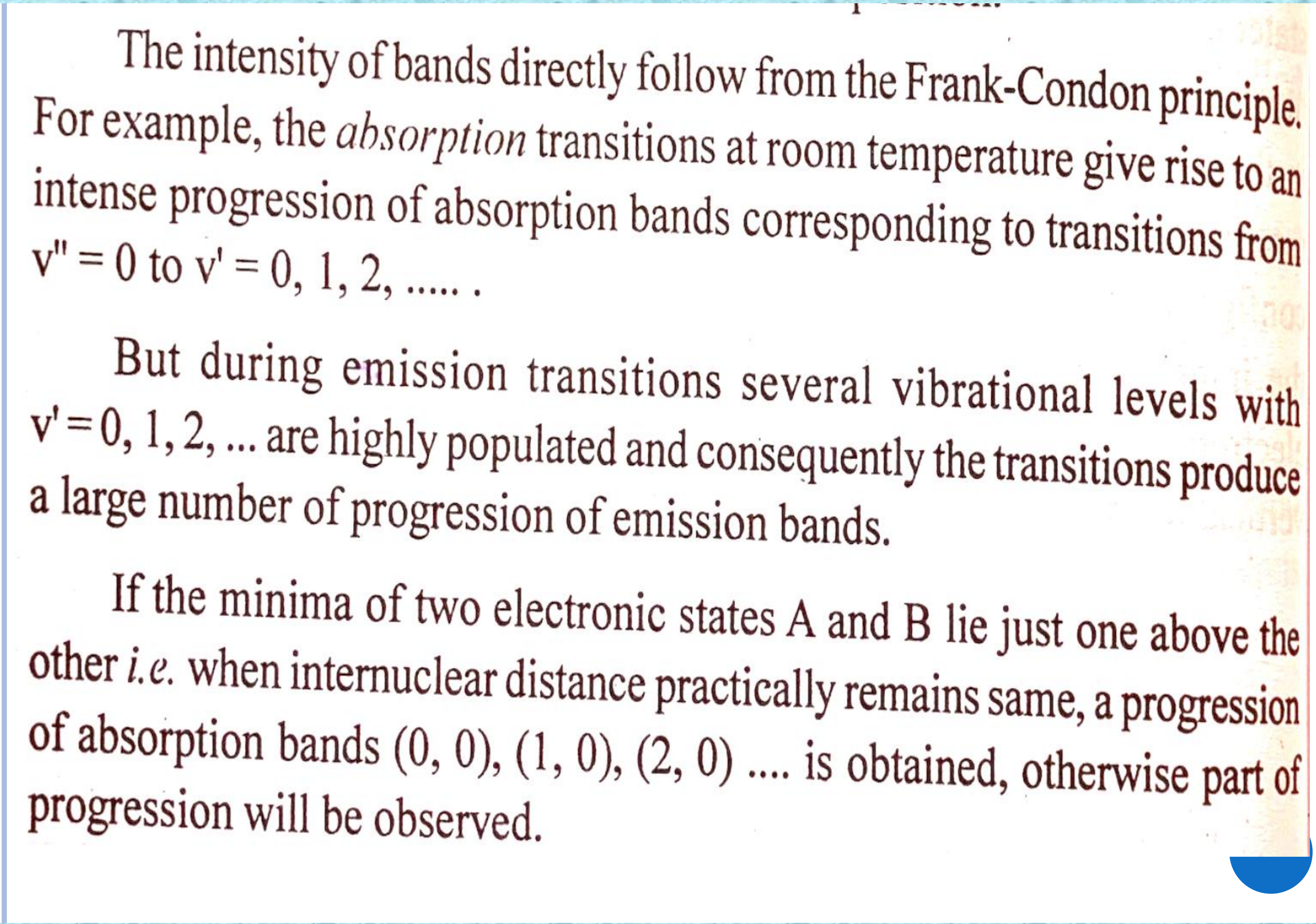


Fig. 2.14 : Vibrational energy levels and transitions corresponding to two electronic states A and B.



(ii) The observed transitions should start from extreme positions of vibrational levels : This principle means that the transitions are most probable when nuclei are in their extreme positions. For example, at C and D in vibrational level CD etc. Fig. (2.14). At these extreme positions, the nuclei come to rest momentarily *i.e.* the kinetic energy of nuclei becomes zero and hence the probability of finding the nuclei at extreme positions is maximum. Hence, most probable transitions should start from extreme positions. However, quantum mechanically it is shown that for zero point energy (*i.e.* v = 0) vibrational state, the mean position *i.e.* minimum of parabolic curve is the most probable position of nuclei. Therefore, transitions from v = 0 state start from the middle or mean position.


Probability of density distribution
Excited state
V′ = 2
V′ = 1
V′ = 0
Ground state
V = 2
V = 1
V = 0
Potential energy
r →
Absorbance
0 → 0
0 → 1
0 → 2
Wavelength λ →



The intensity of bands directly follow from the Frank-Condon principle. For example, the *absorption* transitions at room temperature give rise to an intense progression of absorption bands corresponding to transitions from v" = 0 to v' = 0, 1, 2, ...

But during emission transitions several vibrational levels with v' = 0, 1, 2, ... are highly populated and consequently the transitions produce a large number of progression of emission bands.

If the minima of two electronic states A and B lie just one above the other *i.e.* when internuclear distance practically remains same, a progression of absorption bands (0, 0), (1, 0), (2, 0) .... is obtained, otherwise part of progression will be observed.

Thank You!!!!!