Molecular Spectroscopy

Presented by

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MOLECULAR SPECTROSCOPY

Spectroscopy is that branch of science which deals with the study of interaction of electromagnetic radiations with matter.

ELECTROMAGNETIC RADIATION

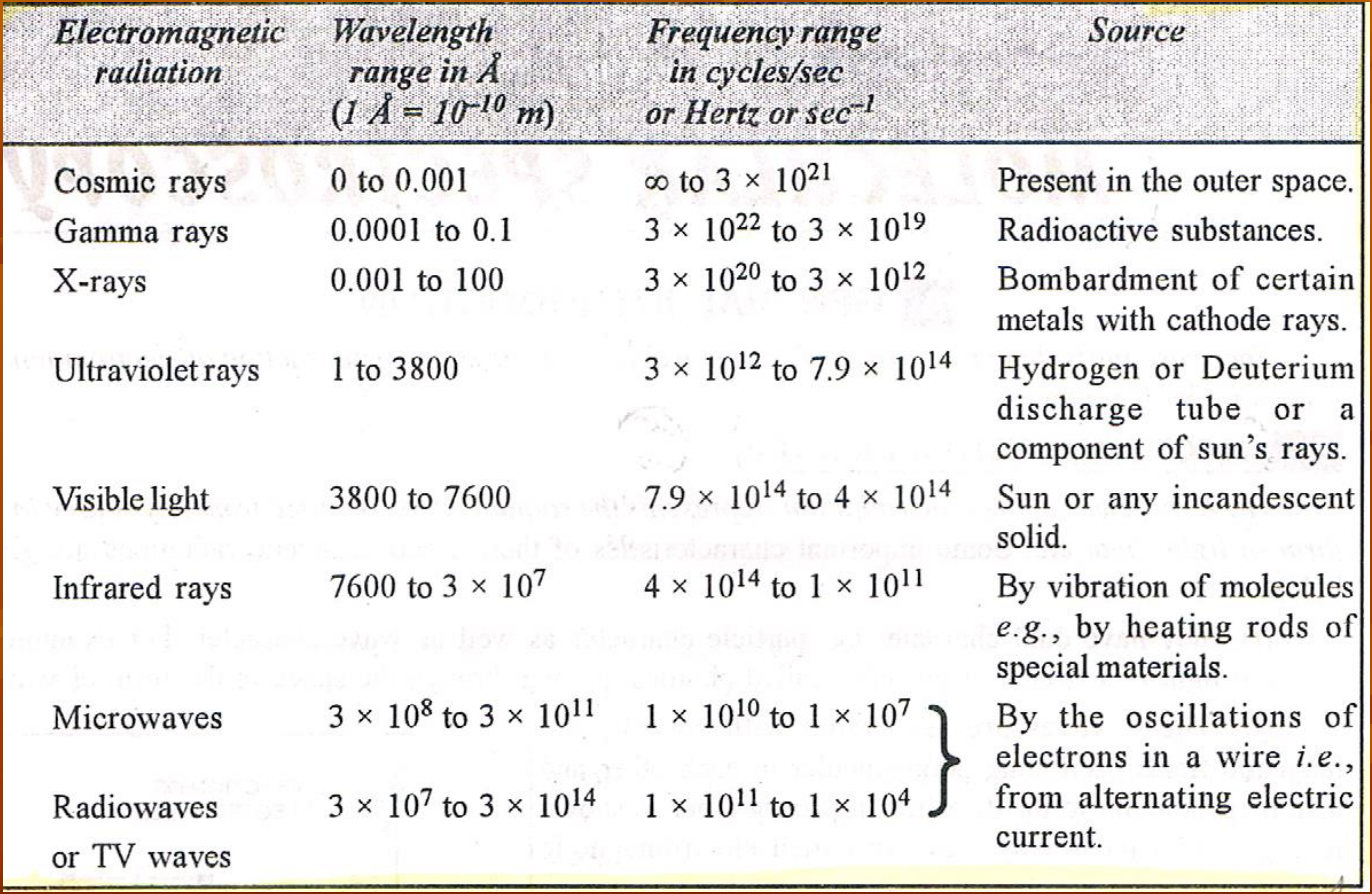
The term electromagnetic radiation represents the radiant energy emitted from any source in the form of light, heat etc. Some important characteristics of these electromagnetic radiations are given below :

(i) They have dual character i.e. particle character as well as wave character. For example, a beam of light is a stream of particles called photons moving through the space in the form of waves.

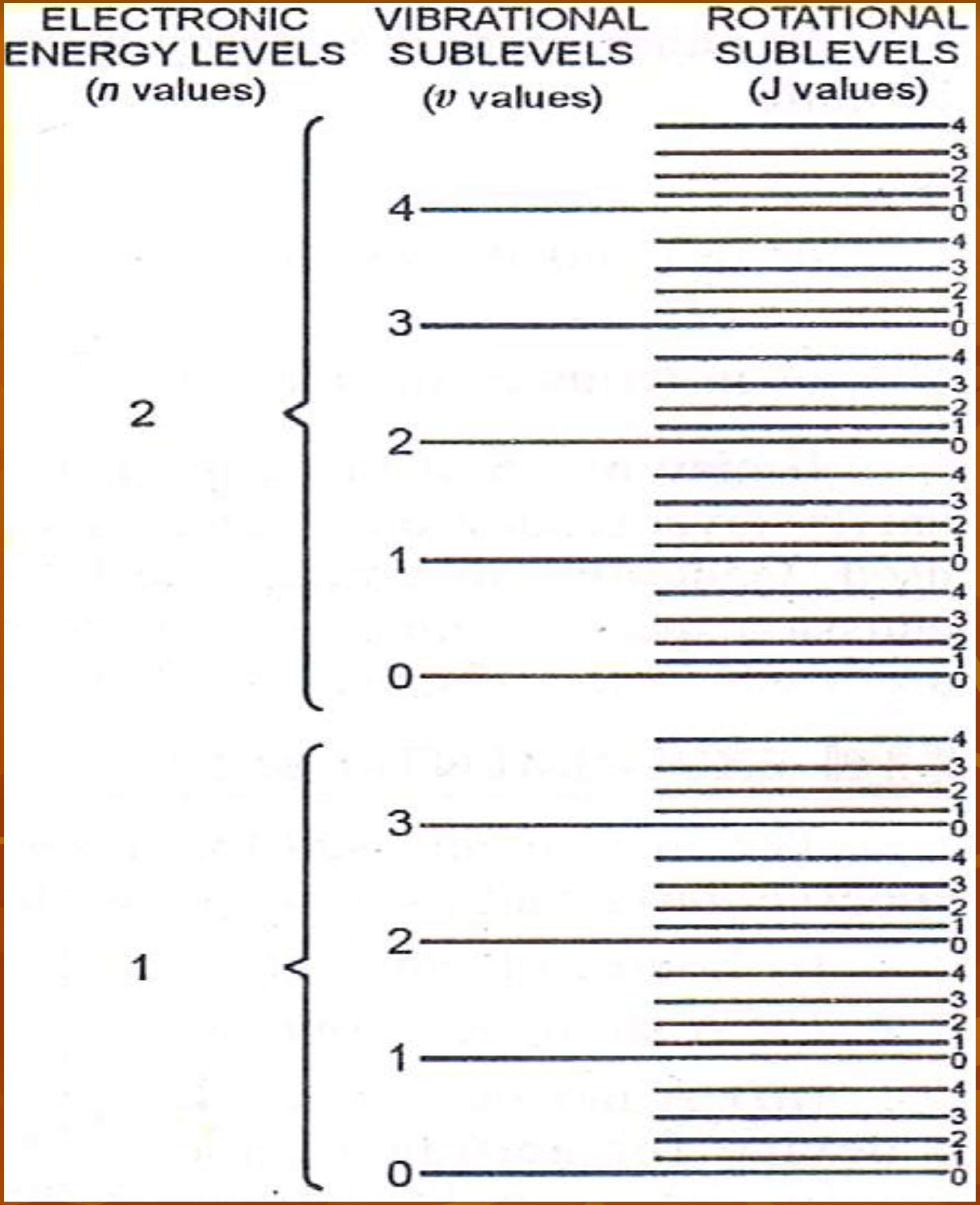
(ii) These waves are associated with electric and magnetic fields oscillating perpendicular to each other and also perpendicular to the direction of propagation.

(iii) All electromagnetic radiations travel with the velocity of light.

REGIONS OF ELECTROMAGNETIC SPECTRUM

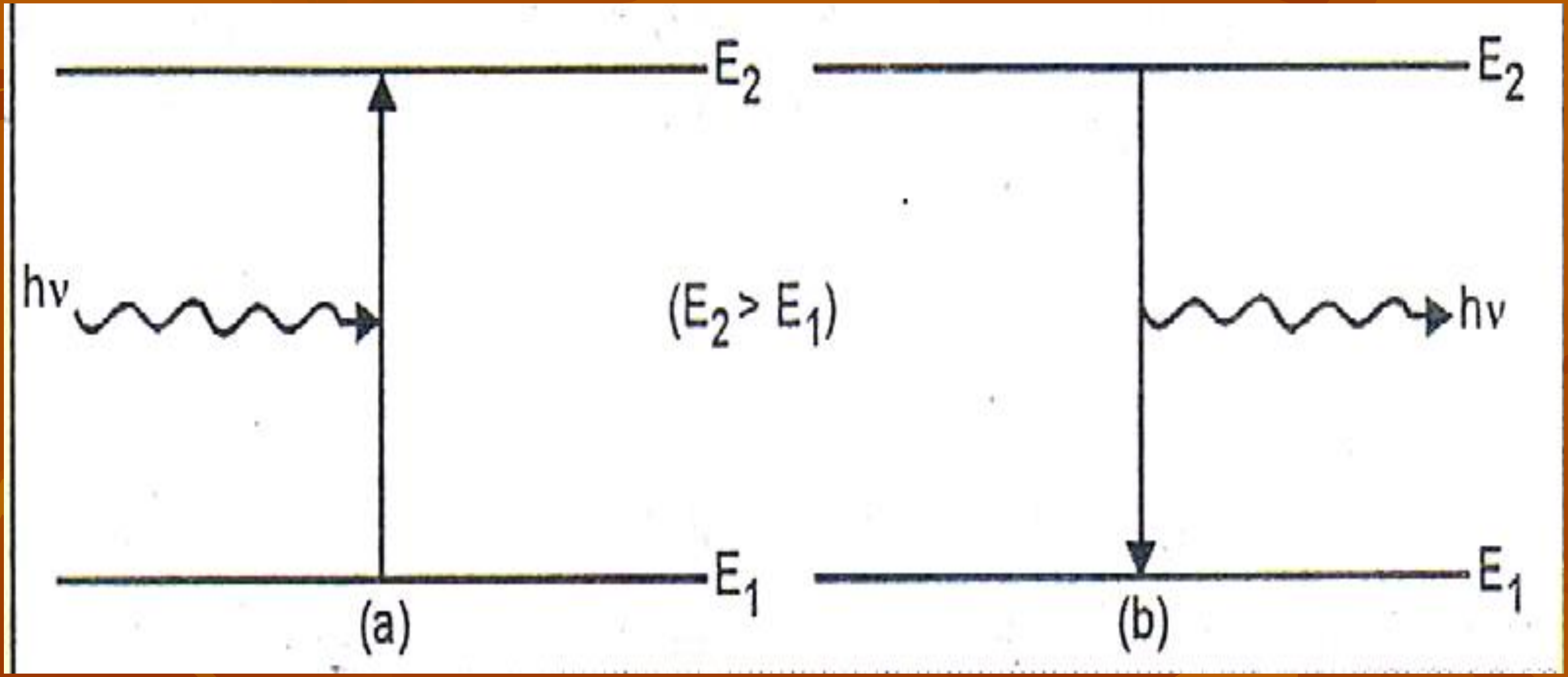


Electromagnetic radiation	*Wavelength range in Å ($1 Å = 10^{-10}$ m)*	*Frequency range in cycles/sec or Hertz or sec^{-1}*	*Source*
Cosmic rays	0 to 0.001	∞ to 3×10^{21}	Present in the outer space.
Gamma rays	0.0001 to 0.1	3×10^{22} to 3×10^{19}	Radioactive substances.
X-rays	0.001 to 100	3×10^{20} to 3×10^{12}	Bombardment of certain metals with cathode rays.
Ultraviolet rays	1 to 3800	3×10^{12} to 7.9×10^{14}	Hydrogen or Deuterium discharge tube or a component of sun's rays.
Visible light	3800 to 7600	7.9×10^{14} to 4×10^{14}	Sun or any incandescent solid.
Infrared rays	7600 to 3×10^{7}	4×10^{14} to 1×10^{11}	By vibration of molecules *e.g.*, by heating rods of special materials.
Microwaves	3×10^{8} to 3×10^{11}	1×10^{10} to 1×10^{7}	By the oscillations of electrons in a wire *i.e.*, from alternating electric current.
Radiowaves or TV waves	3×10^{7} to 3×10^{14}	1×10^{11} to 1×10^{4}	



MOLECULAR ENERGY LEVELS

ABSORPTION AND EMISSION SPECTROSCOPY



(a) Transition Involving absorption of photon
(b) Transition involving emission of photon.

According to Born-Oppenheimer approximation, the total energy of a molecule is the sum of translational, rotational, vibrational and electronic energies, i.e.

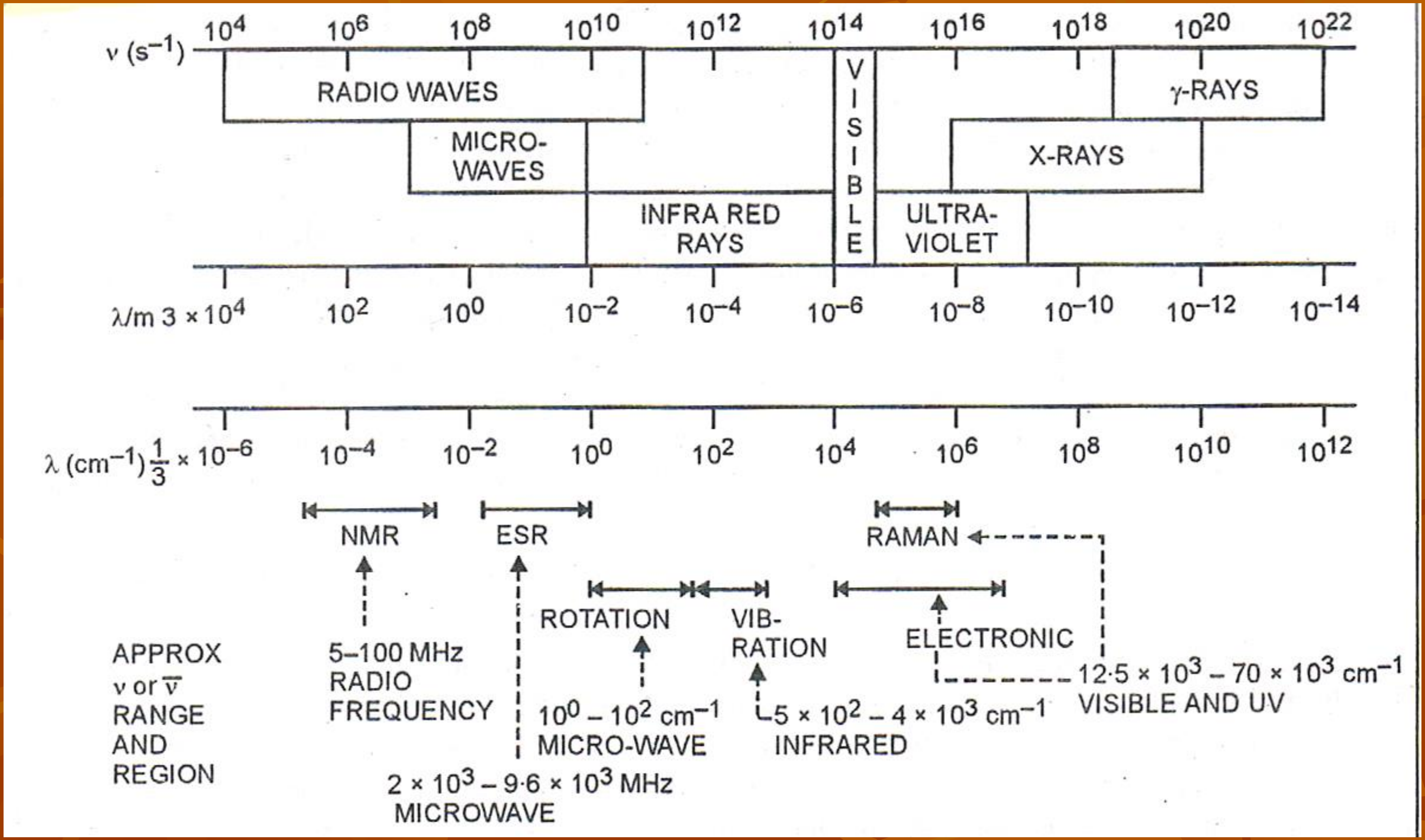
$$E = E_t + E_r + E_v + E_e$$

It is found that the translational energy is negligibly small. Hence Born-Oppenheimer approximation can be written as

$$E = E_r + E_v + E_e$$

TYPES OF MOLECULAR SPECTRA

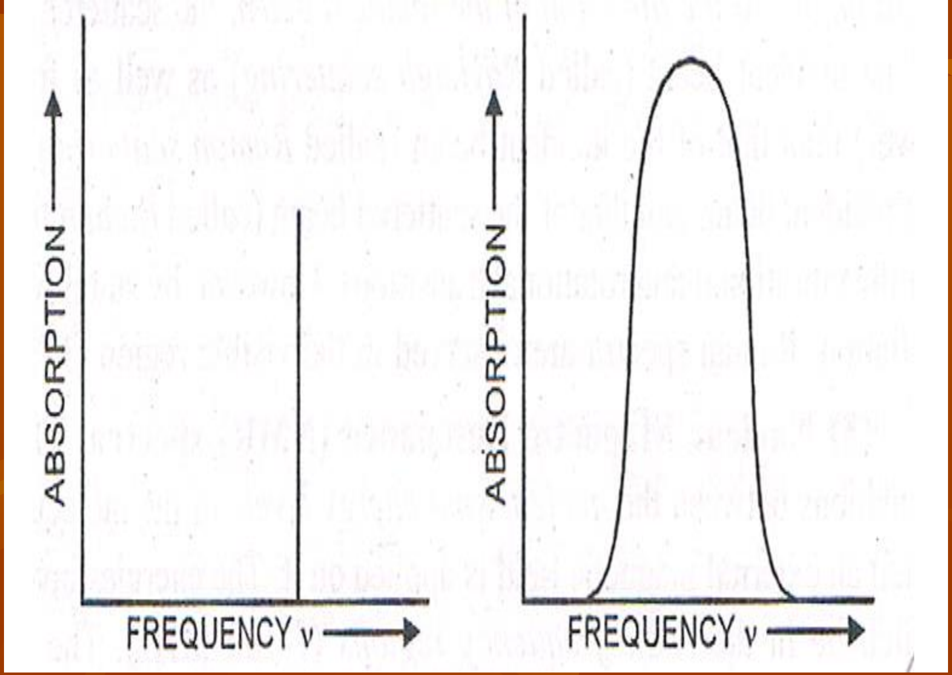
- Pure rotational (Microwave) spectra.
- Vibrational rotational spectra
- Electronic Band Spectra.
- Raman Spectra.
- Nuclear Magnetic Resonance (NMR)
- Electron Spin Resonance (ESR) Spectra.



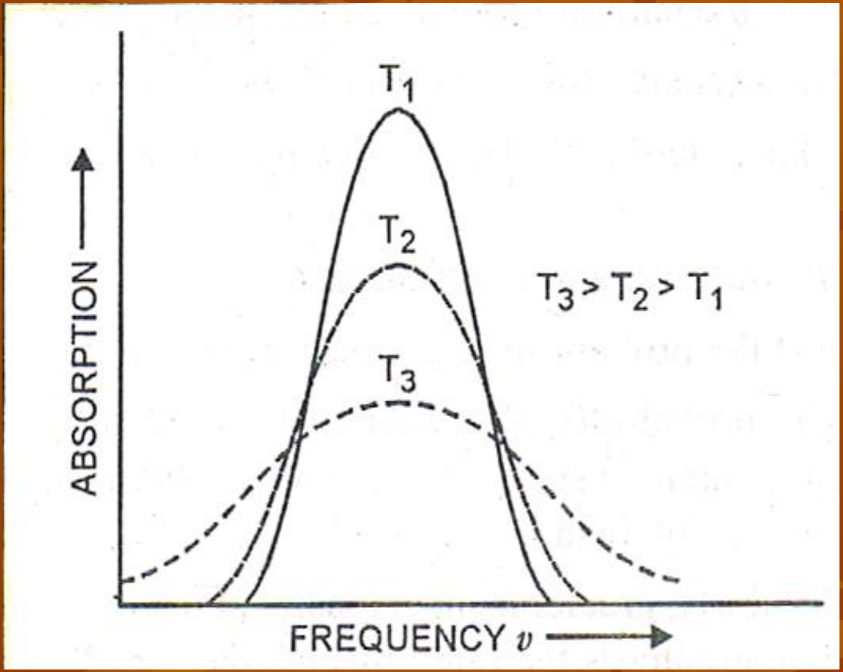
REGIONS OF THE ELECTROMAGNETIC SPECTRUM

WIDTHS AND INTENSITIES OF THE SPECTRAL LINES

Factors affecting the width of spectral lines. The two factors which contribute to the broadening of a spectral line are (i) Doppler Broadening and (ii) Lifetime broadening



(a) A sharp spectral line
(b) A spectral line having a width.

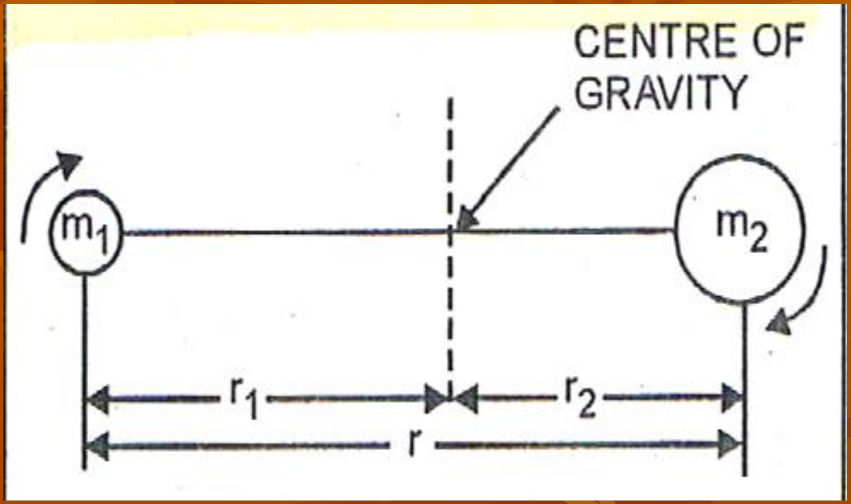


The line broadens as the temperature is increased.

PURE ROTATIONAL (MICROWAVE) SPECTRA OF DIATOMIC MOLECULES

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

$$I = \frac{m_1 m_2}{m_{1+} m_2} r_0^2 = \mu r_o^2$$



Where m1 and m2 are the atomic masses of the two atoms of the diatomic molecule and

$$\frac{m_1 m_2}{m_{1+} m_2} = \mu$$

Derivation of the expression for rotational energy.

$$I = \mu r_0^{2}$$

$$L = I\,\omega$$

$$L = \sqrt{J(J+1)}\,\frac{h}{2\pi}$$

Where J = o,1,2,3……., called the rotational quantum numbers

$$E = I\omega^{2}$$

$$E_r = \frac{1}{2} I\omega^{2} = \frac{I\omega 2}{2I} = \frac{L2}{2I}$$

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

$$E_r = \frac{h2}{8\pi^2 I}\,J\,(J + I)$$

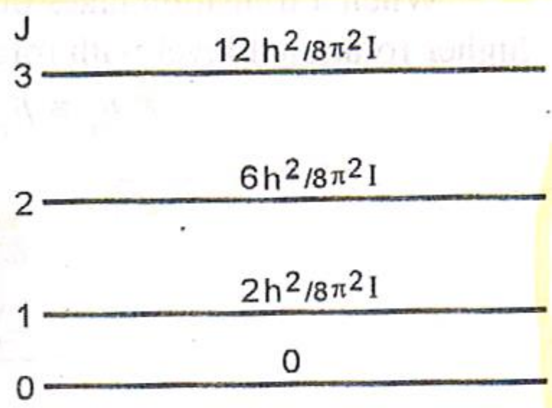


FIGURE 3.18

Rotational energy levels of a diatomic molecule treating it as a rigid rotator.

ROTATIONAL SELECTION RULES

$$\Delta J = \pm 1$$

The transition J = +1 corresponds to absorption and J = -1 corresponds to emission.

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

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

As E = hv, therefore in terms of frequency,

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

$$= BJ\,(J+1)$$

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

$$= BJ\,(J+1)$$

$$\Delta E_r = E^{i}_{r} - E_r \text{ (or } E_y - E_j\text{)}$$

$$= \frac{h^2}{8\pi^2 I} \; J'\,(J'+1) - \frac{h^2}{8\pi^2 I} \; j\,(J+1)$$

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

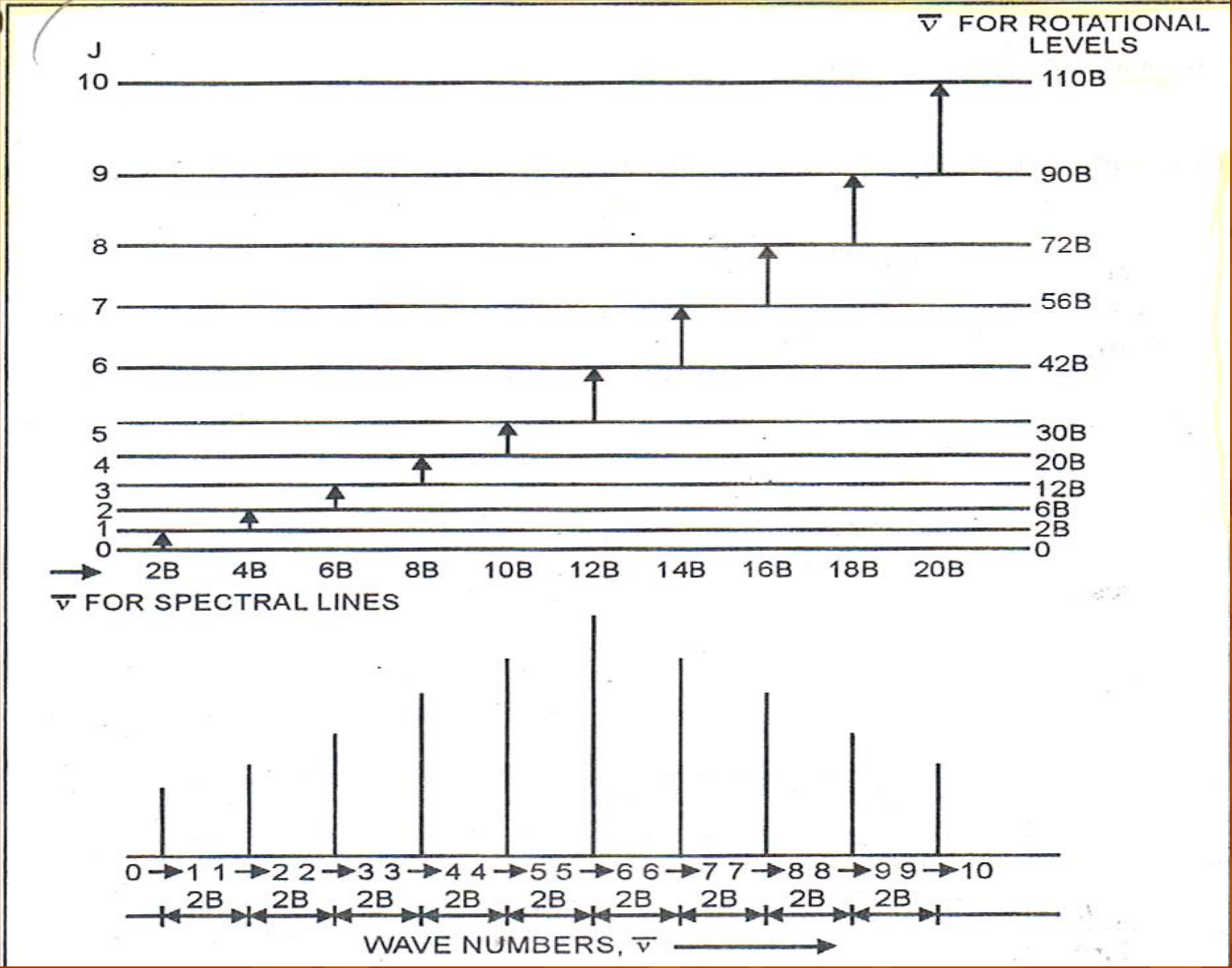
$$\Delta Er = \frac{h^2}{8\pi^2 I} \ [J' (J' +1) \ (J '+ 2) - J(J + 1)]$$

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

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

$$\tilde{v} = \frac{h}{8\pi^2 Ic} \ x \ 2 (J +1) = 2B (J +1)$$

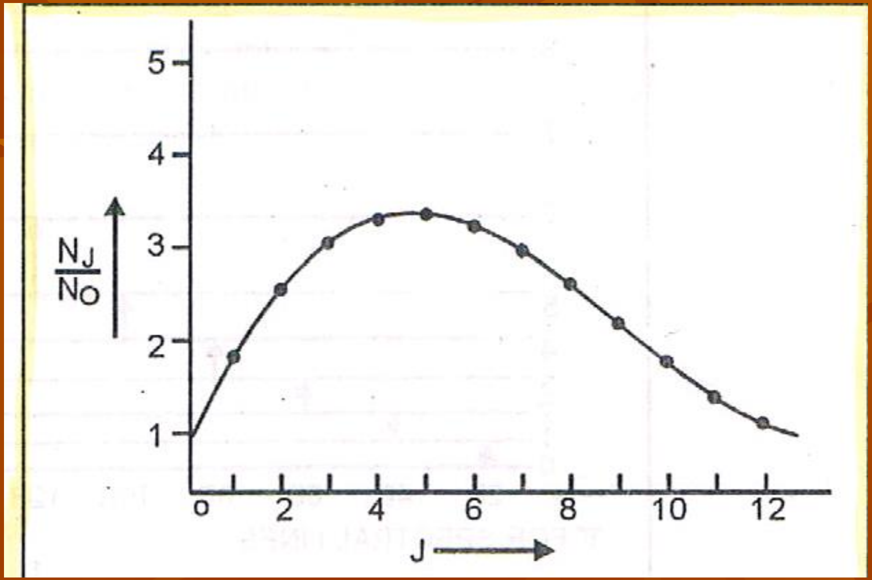
$$B = \frac{h}{8\pi^2 Ic}$$ is rotational constant


$\bar{\nu}$ FOR ROTATIONAL LEVELS
J
10
9
8
7
6
5
4
3
2
1
0
110B
90B
72B
56B
42B
30B
20B
12B
6B
2B
0
2B
4B
6B
8B
10B
12B
14B
16B
18B
20B
$\bar{\nu}$ FOR SPECTRAL LINES
0→1
1→2
2→3
3→4
4→5
5→6
6→7
7→8
8→9
9→10
2B
2B
2B
2B
2B
2B
2B
2B
2B
WAVE NUMBERS, $\bar{\nu}$

RELATIVE INTENSITIES OF ROTATIONAL SPECTRAL LINES

Population of a rotational energy level with quantum number J (relative to that of the ground level for which j = 0 is given according to Boltzmann distribution law by the equation.

$$\frac{N_J}{N_0} = e^{-\frac{Ei}{2kt}}$$



$$\text{Intensity}\alpha \frac{N_J}{N_0} = (2J + 1)e^{-\frac{Ei}{2kt}}$$

$$\frac{N_J}{N_0} = (2J + 1)e^{-hc\,BJ\,(J + I)\,/kT}$$

VIBRATIONAL ENERGY LEVELS OF A SIMPLE HARMONIC OSCILLATOR

A simple harmonic oscillator is the one in which the restoring force is proportional to the displacement in accordance with Hook 's law i.e.

$$F = -kx$$

Where k is called the force constant.

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

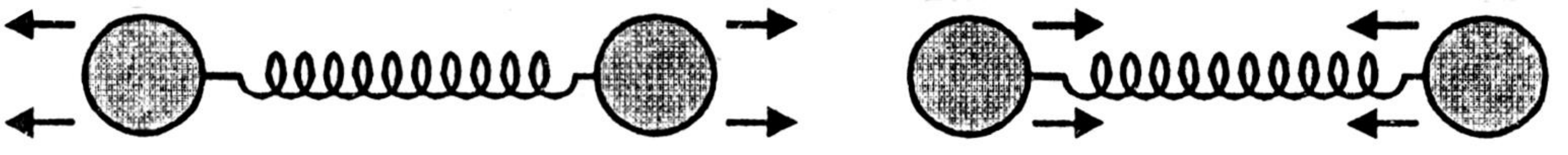
Where v is the frequency of vibration and v is the vibrational quantum number

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

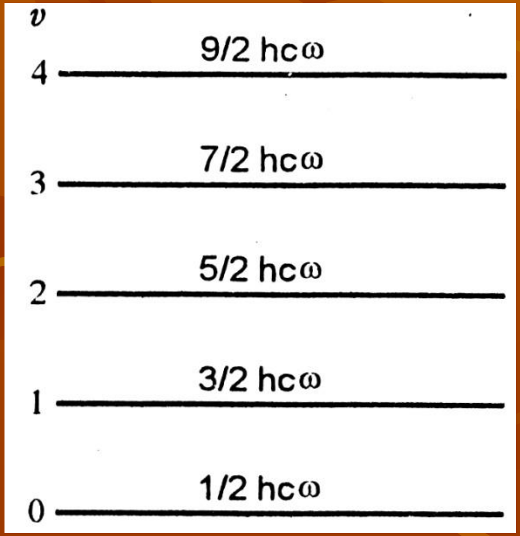
For the lowest vibrational level, v = 0. The energy for this level will, therefore, be

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

This is called zero point energy. It implies that even at absolute zero when all translational and rotational motion ceases in a crystal, the residual energy of vibration E_0 still remains, i.e., the vibrational motion still exists.

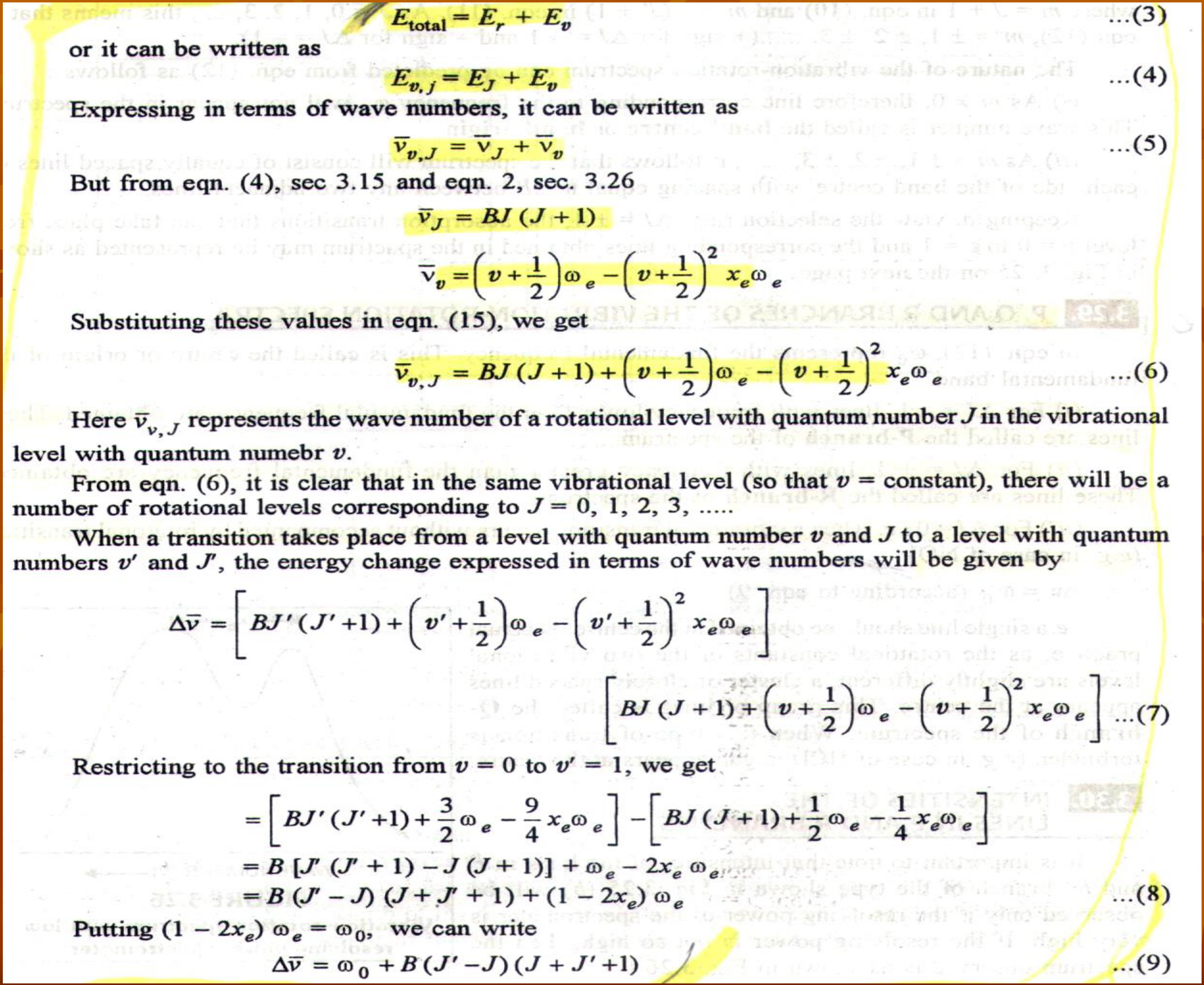


VIBRATORY MOTION OF A DIATOMIC MOLECUTE



EQUALLY SPACED VIBRATIONAL ENERGY LEVEL OF A SIMPLE HARMONIC OSCILLATOR

VIBRATIONAL – ROTATIONAL SPECTRA



$$E_{\text{total}} = E_r + E_v \qquad \ldots(3)$$

or it can be written as

$$E_{v,j} = E_J + E_v \qquad \ldots(4)$$

Expressing in terms of wave numbers, it can be written as

$$\bar{\nu}_{v,J} = \bar{\nu}_J + \bar{\nu}_v \qquad \ldots(5)$$

But from eqn. (4), sec 3.15 and eqn. 2, sec. 3.26

$$\bar{\nu}_J = BJ\,(J+1)$$

$$\bar{\nu}_v = \left(v+\frac{1}{2}\right)\omega_e - \left(v+\frac{1}{2}\right)^2 x_e\omega_e$$

Substituting these values in eqn. (15), we get

$$\bar{\nu}_{v,J} = BJ\,(J+1) + \left(v+\frac{1}{2}\right)\omega_e - \left(v+\frac{1}{2}\right)^2 x_e\omega_e \qquad \ldots(6)$$

Here $\bar{\nu}_{v,J}$ represents the wave number of a rotational level with quantum number J in the vibrational level with quantum numebr v.

From eqn. (6), it is clear that in the same vibrational level (so that v = constant), there will be a number of rotational levels corresponding to $J = 0, 1, 2, 3, \ldots..$

When a transition takes place from a level with quantum number v and J to a level with quantum numbers v' and J', the energy change expressed in terms of wave numbers will be given by

$$\Delta\bar{\nu} = \left[BJ'(J'+1) + \left(v'+\frac{1}{2}\right)\omega_e - \left(v'+\frac{1}{2}\right)^2 x_e\omega_e\right]$$

$$\left[BJ\,(J+1) + \left(v+\frac{1}{2}\right)\omega_e - \left(v+\frac{1}{2}\right)^2 x_e\omega_e\right] \qquad \ldots(7)$$

Restricting to the transition from $v = 0$ to $v' = 1$, we get

$$= \left[BJ'(J'+1) + \frac{3}{2}\omega_e - \frac{9}{4}x_e\omega_e\right] - \left[BJ\,(J+1) + \frac{1}{2}\omega_e - \frac{1}{4}x_e\omega_e\right]$$

$$= B\,[J'\,(J'+1) - J\,(J+1)] + \omega_e - 2x_e\,\omega_e$$

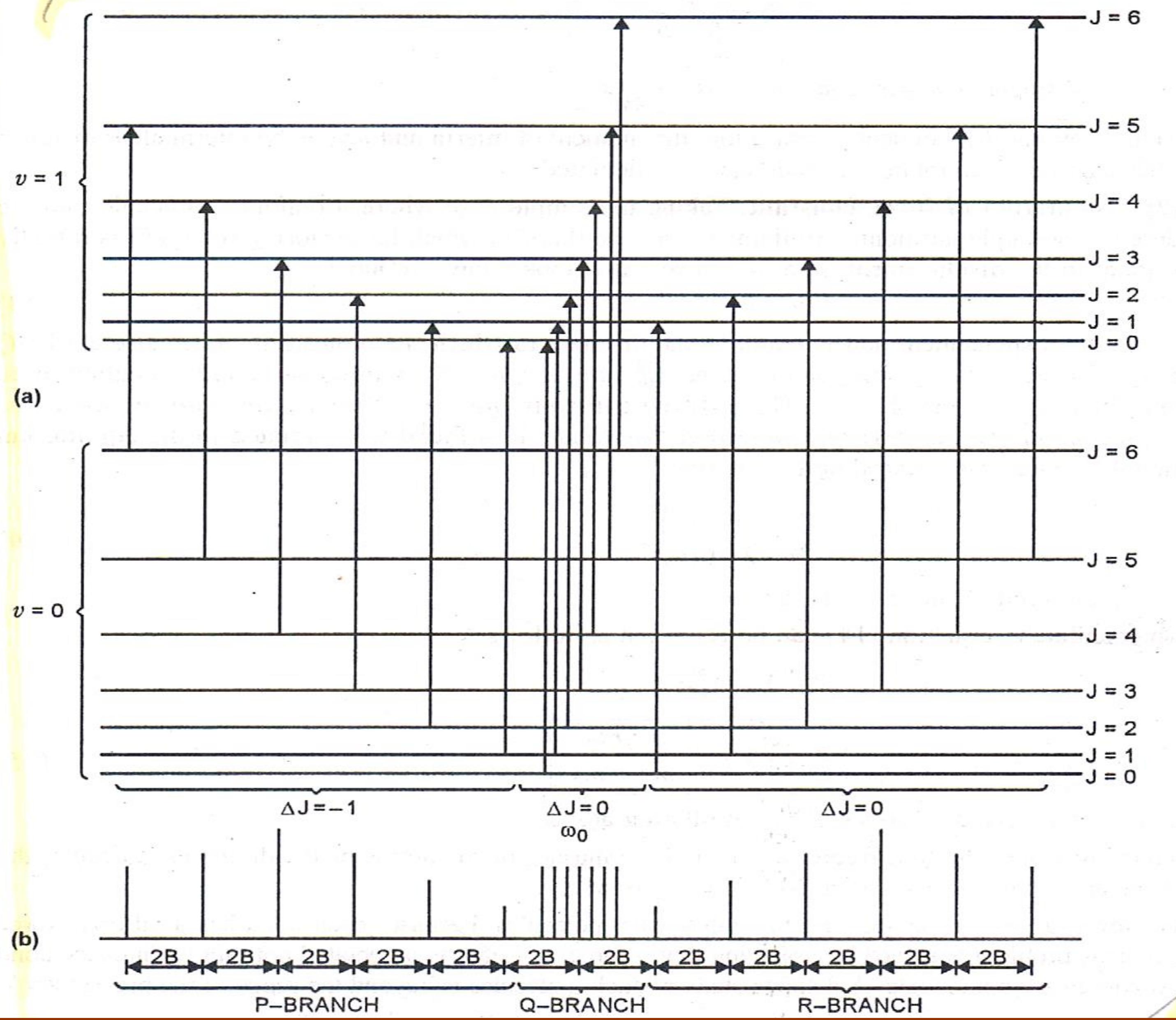
$$= B\,(J'-J)\,(J+J'+1) + (1-2x_e)\,\omega_e \qquad \ldots(8)$$

Putting $(1-2x_e)\,\omega_e = \omega_0$, we can write

$$\Delta\bar{\nu} = \omega_0 + B\,(J'-J)\,(J+J'+1) \qquad \ldots(9)$$

P , Q AND R BRANCHES OF THE VIBRATION – ROTATION SPECTRA

- For ∆J = -1 lines with frequency lower than the fundamental frequency are obtained. These lines are called the P-branch of the spectrum.
- For ∆J = +1 , lines with frequency greater than the fundamental frequency are obtained. These lines are called the R-branch of the spectrum.
- For ∆J = 0 i.e. when a vibrational transition occurs without accompanied by rotational transition (e.g. in case of NO)


J = 6
J = 5
J = 4
J = 3
J = 2
J = 1
J = 0
v = 1
v = 0
(a)
J = 6
J = 5
J = 4
J = 3
J = 2
J = 1
J = 0
ΔJ=−1
ΔJ=0
ω_0
ΔJ=0
(b)
2B
P–BRANCH
Q–BRANCH
R–BRANCH