

where, $c =$ Velocity of light.

$h =$ Planck's Constant.

on combining eqs - (i) and - (ii) we get -

$$E \propto \nu \propto \bar{\nu} \propto \frac{1}{\lambda}$$

In other words, The energy increases, frequency increases, wave no. increases, but wave length decreases.

* Quantisation of Energy levels:-

In a molecule we have following energy viz. Translational, Rotational, Vibrational and Electronic energies.

A/c to Born-Oppenheimer approximation the total energy of a molecule is given by -

$$E = E_{\text{Trans}} + E_{\text{ROT}} + E_{\text{vib}} + E_{\text{ele.}}$$

where,

$$E_{\text{ele}} > E_{\text{vib}} > E_{\text{ROT}} > E_{\text{Trans}}$$

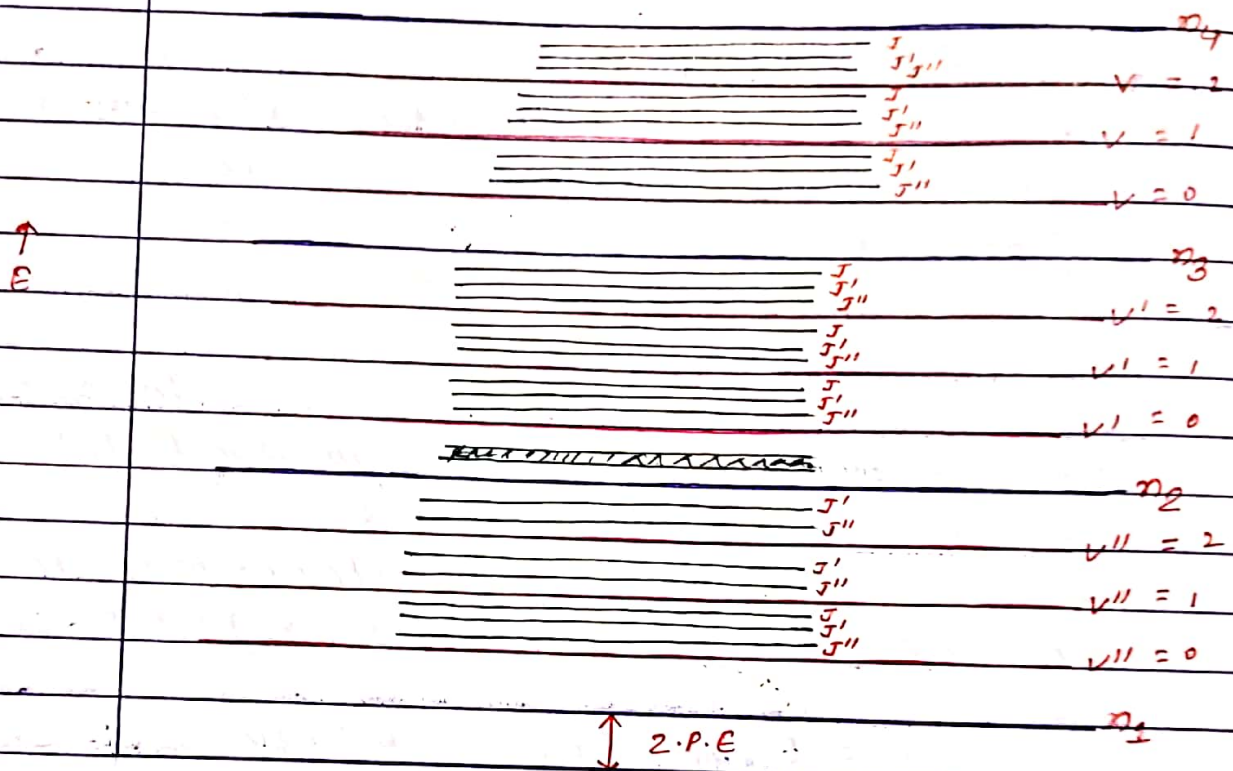
The translational energy is not quantised. Since, E_{Trans} is neglected.

So, we have -

$$E = E_{\text{ROT}} + E_{\text{vib}} + E_{\text{ele.}}$$

All the energies are quantised.

p.t.o.



where,

n = Electronic quantum no.
 = 0, 1, 2, 3,

v = vibrational quantum no.
 = 0, 1, 2, 3,

J = Rotational quantum no.
 = 0, 1, 2, 3,

* I.R active molecule :-

Molecules having
 Temporary dipole moment is called IR active molecule
OR Microwave inactive molecule.
 eg - O_2 .

* microwave Active molecule :-

molecules having permanent dipole moment is called microwave as well as I.R active molecule.

eg - HCl.

Homonuclear diatomic molecule (H_2, O_2, Cl_2 etc) are neither I.R. nor microwave active (Inactive).

Reason - Having no. Temporary as well as permanent dipole moment.

5/03/08.

* Intensity of spectral transitions :-

Intensity of spectral transitions depends upon :-

(i) Transition probability :-

It requires a knowledge of precise quantum mechanical wave functions of the two states between ^{which} the transition occurs. which is decided whether the transition probability is zero or non-zero. i.e. whether the transition is allowed or forbidden. so, the process will be the reduction of selection rule. which allow us to decide which level transition will give rise to spectral lines.

(ii) Population of states :-

If transition from two levels to a third one are probable then we get most intense spectral line from the level which initially has the greater population.

A/c to Boltzmann distribution law :-

$$\frac{N_{upper}}{N_{lower}} = \exp\left(\frac{-\Delta E}{kT}\right)$$

where.

N_{upper} = no. of molecules in upper energy level.

N_{lower} = no. of molecules in lower energy level.

k = Boltzmann constant.

$$= 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ molecule}^{-1}$$

when it is multiplied with 'N' (Avogadro's no.) then the unit becomes R per mole.

(iii) Path length of samples:—

A/c to Lambert-Beer law —

$$\frac{P}{I_0} = \exp(-\epsilon cl)$$

where,

c = Concentration of the sample.

l = length of the path sample.

ϵ = Molar absorption coefficient.

$$\text{OR} \quad \frac{P}{I_0} = 10^{-\epsilon cl} = T$$

(Transmittance)

$$\text{OR} \quad \frac{I_0}{P} = 10^{\epsilon cl}$$

Taking logarithms both side, we have —

$$\log \left(\frac{I_0}{P} \right) = \epsilon cl = A$$

Absorbance

OR optical density.

I_0 = Incident radiation.

P = Transmitted radiation.

$(I_0 - P)$ = Absorbed radiation.

(iv). width of spectral lines:—

~~spect~~

~~for width of~~

No molecular transition takes place at a single frequency but always over a range of frequency. As mechanical slits in spectrometers are not infinitely narrow, so, there must be a minimum width in any atomic or molecular transition. This width arises because, the energy levels of atomic and molecular systems are not precisely determined. Several factors may be assigned for this widening—

- (i) Collision Broadening —
- (ii) Doppler Broadening —
- (iii) ~~Higer~~ Heisenberg uncertainty principle —

(i) Collision Broadening:—

Since, atoms or molecules

in liquid and gaseous phase are colliding frequently. They cause some deformation of the particle and hence perturb to some extent. The energies of at least the outer electron in each. So, electronic, rotational or vibrational spectra are broadened. Since, collisions interfere with these motions. These collisions are more serious in liquid than in gaseous phase. and so, gas phase spectra exhibit sharper lines than those of the corresponding liquids.

(ii) Doppler Broadening:—

Since, the

motion is random (disordered) in a given sample. Hence, it causes absorption and emission frequencies to show a Doppler shift. In the spectral line shifts to both high

and low frequencies and hence it is broadest.

Doppler broadening predominates in the gaseous sample as compare to those of corresponding liquid samples.

(iii) Heisenberg Uncertainty principle :-

A/c to Heisenberg Uncertainty principle the energy levels are not sharp in an atom or a molecule.

If a system exists in an energy states for a limited Δt second (infinite time) then the energy of that state will be uncertain to an extent ΔE .

where —

$$\Delta E \cdot \Delta t \approx \frac{h}{2\pi}$$