PHYSICAL

SPECTRA

HAND MADE NOTES



ChemistryABC.com

quizes | posts | downloads | study materials more

www.ChemistryABC.com

25th-March-2015.

Physical spectra

Topics :-

1. Introduction.
2. Basics of spectroscopy.
3. Types of spectra.
4. Origin of spectra.
5. Molecular spectra.
   (a) Rotational spectra of diatomic molecules.
   (b) Vibrational spectra of Diatomic molecules.
   (c) Raman spectra.
   (d) Electronic spectra (UV. Visible spectra)
   (e) Basic principle of ESR & and NMR spectra.
6. Atomic spectra.
   (a) Term simpol.
   (b) Many electron system and Anti symmetoric principles.
7. Previous year questions.

Introduction:-

(2) Basics
   (a) Electromagnetic Radiation.
   (b) Quantum theory of EMR.
   (c) Intraction of EMR with matter.
   (d) Energy of EMR.
   (e) BORN-Oppenhimer approximation.

Spectroscopy.

Spectroscopy deals the transition induced in a chemical species by its interaction with the photon of electromagnetic radiation.

Spectroscopy technique are generally used to major th

free download all stuffs more notes and books www.ChemistryABC.com

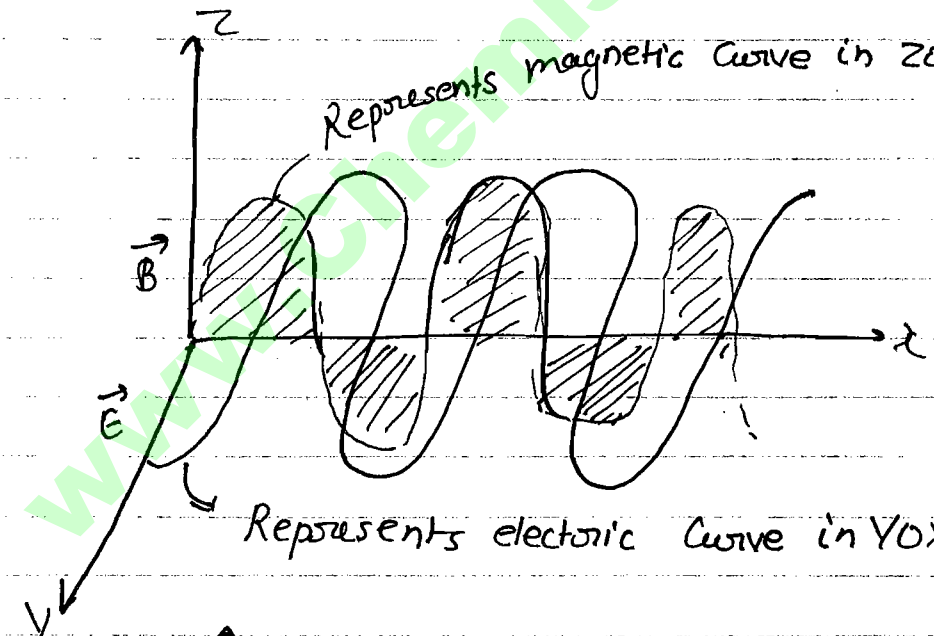
www.ChemistryABC.com

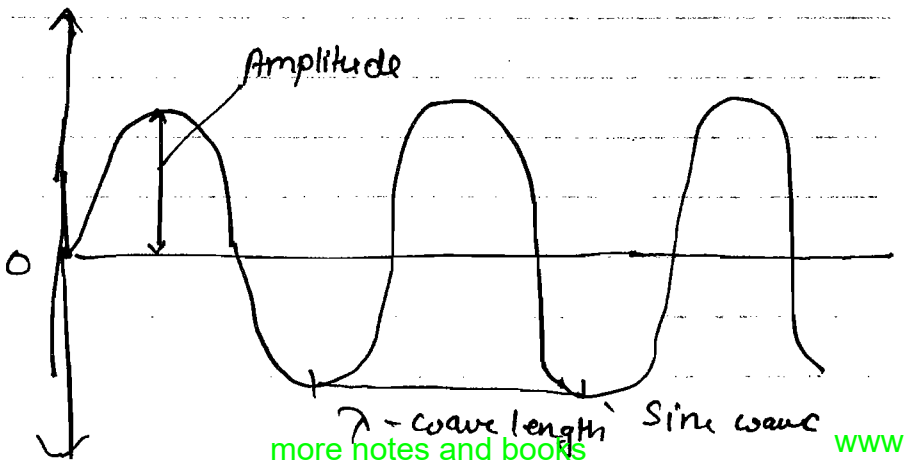
energy difference b/w various molecular energy level and to determine the atomic or molecular structure.

The instruments used in such studies called spectrophotometer and the spectrum of the molecules are presented as a continuous graph obtained by plotting either absorption or transmittance of EMR as a function of wave length or wave no. ~~spec~~ a over a particular range.

Electromagnetic radiation (EMR):-

Light is known as EMR it contains both electrical and magnetic components. According to Maxwell (1864) EMR is made up of two mutually perpendicular Sinusoidally (sine curve) oscillating electric and magnetic fields in planes.





free download all stuffs
more notes and books
www.ChemistryABC.com

www.ChemistryABC.com

* EMR shows dual nature i.e., wave and particles natur
* If EMR shows wave nature then. velocity of wave

$$\boxed{v = \nu\lambda}$$

for EMR

$$\boxed{c = \nu\lambda}$$

where c = Velocity of light

$c = 3 \times 10^8$ m/sec

$= 3 \times 10^{10}$ cm/sec

ν - Frequency of radiation.

λ = Wavelength.

Wave number = Reciprocal of λ

$$\boxed{\bar{\nu} = \frac{1}{\lambda}}$$

Units :-

Wave length = Cm or meter

frequency = Sec^{-1} or Hz

wave no. $\bar{\nu}$ = cm^{-1} or $meter^{-1}$

Kilo Hz = 10^3 Hz = KHz

Mega Hz = 10^6 Hz = MHz

Giga Hz = 10^9 Hz = GHz

Quantum theory of EMR :-

Wave nature of EMR does not explain the black body radiation, photoelectric effect, Compton effect. To explain these phenomena and oth theory is arises is called quantum theory.

According

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

to quantum theory EMR is consider a stream of energy packets called photons or quanta. which travels in the direction of propagating wave with the velocity of light.

The energy of photon is proportion to the frequency of radiation.

i.e., $E \propto \nu$

or $\boxed{E = h\nu}$

where, h = Planck's constant

$= 6.626 \times 10^{-23}$ J sec.

$= 6.626 \times 10^{-27}$ erg. sec.

Energy of EMR :-

Energy of EMR is calculated by

$$\boxed{E = h\nu}$$

Since $c = \nu\lambda$

$$\nu = \frac{c}{\lambda}$$

$$E = \frac{hc}{\lambda}$$

$$\boxed{E = hc\bar{\nu}} \quad \left\{\because \frac{1}{\lambda} = \bar{\nu}\right\}$$

It is basic eqn for energy of EMR.

Question :-

Calculate the energy of EMR having frequency 10^3 MHz

$E = 6.626 \times 10^{-34} \times 10^3$ MHz.

$E = 6.626 \times 10^{-34} \times 10^8 \times 10^3$,

$E = 6.626 \times 10^{-25}$ J sec.

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

To convert it J/mole, we multiply by it Avogadro's no.

$$E = 6.626 \times 10^{-25} \times 6.022 \times 10^{23} \text{ J/mole}$$
$$= 39.90 \times 10^{-2} \text{ J/mole.}$$
$$= 0.399 \text{ J/mole.}$$

Question:-

Calculate energy of EMR having wavelength 1986 A°

$$E = \frac{hc}{\lambda}$$
$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{1986 \times 10^{-10}}$$
$$= \frac{19.878 \times 10^{-26}}{19.86 \times 10}$$
$$= \frac{19.878 \times 10^{-16}}{19.8 \times 10}$$
$$= \frac{1.01 \times 10^{-16}}{0.01} \text{ Jule/sec.}$$
$$= 1.0 \times 10^{-18}$$
$$= 10^{-18}$$

Remember:-

$$hc = 19.87 \times 10^{-26}$$
$$1 \text{ cm}^{-1} = 11.96 \text{ J/mole}$$

Ques:-

Calculate the energy of EMR having wavenumber 1 cm^{-1}.

$\bar{\nu} = 1 cm^{-1}$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

$= 6.626 \times 10^{-34}\ J/sec \times 3 \times 10^{8}\ m/sec \times 1\ cm^{-1}$

$= 6.626 \times 10^{-34}\ J/sec \times 3 \times 10^{10}\ cm/sec \times 100\ 1\ cm^{-1}$

$= 19.87 \times 10^{-24}\ J$

$= 19.87 \times 10^{-24} \times 6.02 \times 10^{23}\ J/mole$

$= 119.6 \times 10^{-1}$

$= 11.96\ KJ/mole.$

Ques :-

Calculate the energy of EMR having wave no. 2000 cm^{-1}.

$= 6.626 \times 10^{-34}\ J/sec \times 3 \times 10^{10}\ cm/sec \times 2000\ cm^{-1}$

$= 6.626 \times 10^{-24} \times 3 \times 2000$

$= 19.87$

$= 39740 \times 10^{-24} = 3.97 \times 10^{-20}$

Ques :-

Calculate the λ of having 50 J mole

$$E = \frac{hc}{\lambda}$$

$$\lambda = \frac{hc}{E}$$

$$= \frac{6.626 \times 10^{-34} \times 3 \times 10^{8}}{50\ J\ mole}$$

$$= \frac{19.87 \times 10^{-26}}{50\ J\ mole.}$$

$$= 0.2 \times 10^{-26}$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

$$E = hc\bar{\nu}$$

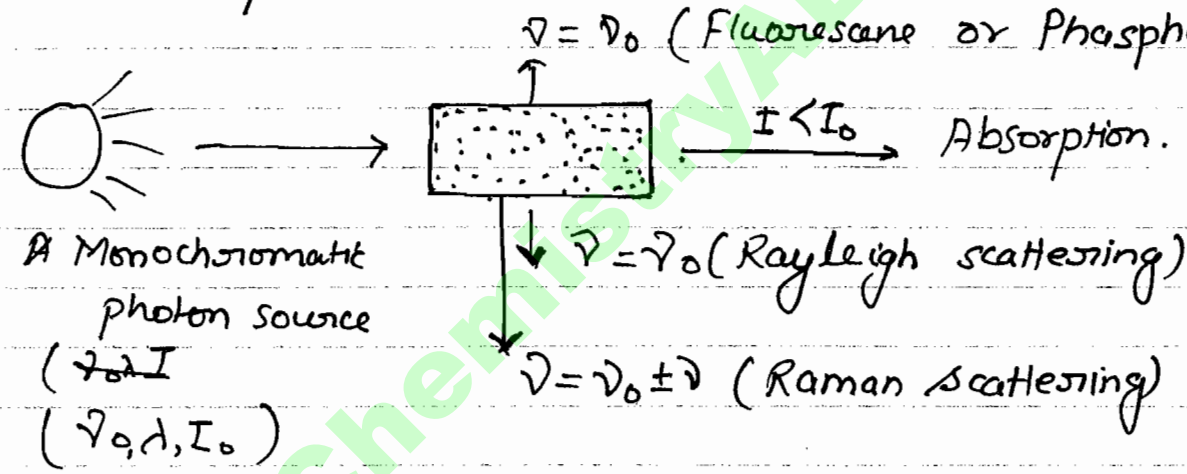
$$= \frac{50}{11.96}\ cm^{-1}$$

$$\bar{\nu} = 4.18\ cm^{-1}$$

$$\lambda = \frac{1}{\bar{\nu}} = \frac{1}{4.18}\ cm^{-1}$$

$$\lambda = 0.239\ cm^{-1}$$

Interaction of EMR with matter :-



(i) The direction of incident beam of light can change by reflection or refraction.

(ii) The scattered light may ~~ehil~~ exhibit the same frequ-ay an incident light which is reffered as rayleigh scattering.

(iii) If the scattered beam exhibit eq either higher or lowe-fo frequency it is called raman scattering higher fre-quency light gives antistockes and lower frequency gives stockes line.

(iv) If incident beam is plane polarised light the plane o/ polarization may be rotated by passing through compo-

free download all stuffs more notes and books www.ChemistryABC.com

└ Elec is very fast and
Evib — we cant calculate.

www.ChemistryABC.com

(v) The intensity of the incident beam gets reduced for even disappear when passed through the substance. It is called absorption of light.

(vi) The absorption of radiation by causes the atom or molecules to be in an excited state since excited state is short lived leaved (10^{-8}s). the e^- may return to its ground state with emission of certain amount of energy. When this emission of light is instentenious the phenamena is called fluorescene, if delayed it is called phosphorescene.

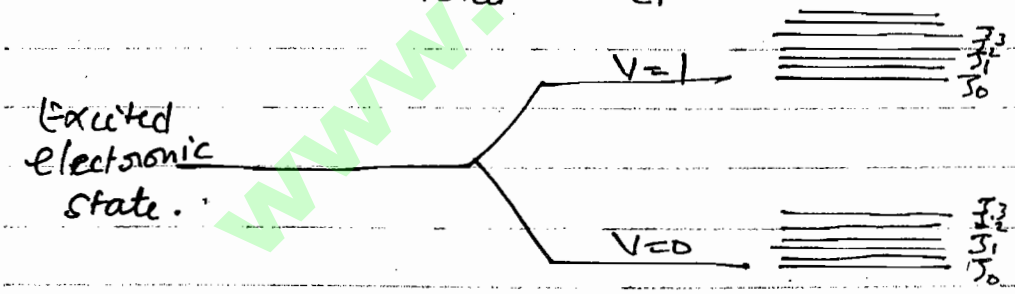
Born - Oppenhimer approximation :-

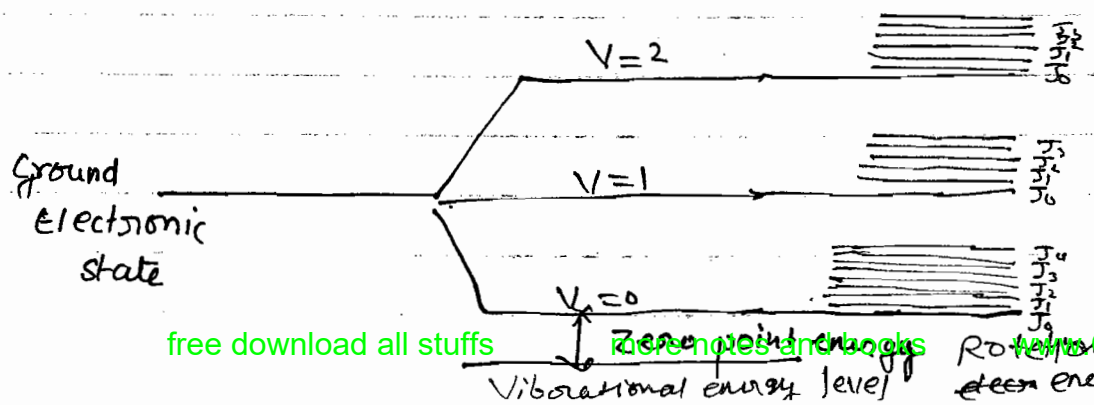
$$E = E_{trans} + E_{vibs} + E_{rot} + E_{el} + E_{spin} + E_{nuclear}.$$

$$E_{el} \gg E_{vib} \gg E_{rot} \gg E_{trans}$$

Opl Applying BOA

$$E_{Total} = E_{el} + E_{vib} + E_{rot}.$$





free download all stuffs notes and books www.ChemistryABC.com

www.ChemistryABC.com

Classification of spectra (Types of spectra):-

* Matter contains e and p, by the motion of these particles there is an induced E field and magnetic field ($\vec{B}$).
* EMR also contains electric and magnetic field.
* When EMR beam is interacts with any substance two types of interactions are possible

(a) = Electric interaction ($\vec{E} \times \vec{E}$)
(b) = Magnetic interaction ($\vec{B} \times \vec{B}$)

According to types of interaction following types of spectra are obtained.

(1) By Electric interaction:-
* Rotation spectra
* Vibrational spectra
* Electronic spectra.

(2) By magnetic ~~infra~~ interaction:-
* NMR - spectra
* ESR - spectra.

Types of Molecular spectra and Frequency Range:-

$\lambda = 10\ m$ 10^{-2} 10^{-4} 10^{-6} 10^{-8} 10^{-9} 10^{-10} 10^{-12} 10^{-14} 10^{-16}

Radiowave	Micro wave	IR ←	UV	X-rays	γ-rays	Cosmic rays-	IR.
* Extreemly low energy * No heating effect * No chemical shift * NMR and ESR spectra * Frequency Range $10^2 MH_2 - 0.1 MH_2$	* low energy * heating effect * No chemical shift * Rotational spectra * High energy ESR * $10^3 MH_2 - 10^5 MH_2$	* high energy * heating effect * Chemical shift Most are possible. * Electronic transition spectra * Frequency range $10^{10} H_2 - 4.0 \times 10^{14} MH_2$	380mm → Blue 780nm Red	* Very high energy * Penetrating inside the molecule * Bragg's spectra * Frequency range $10^{16} MH_2 - 10^{18} MH_2$	* Extremely high energy * Nuclear transition takes place * Mass-Bauer spectra $10^{18} MH_2$	No more inform. avail.	* Moderately high energy * Heating effect * Chemical effect * Vibration Spectra $10^8 MH_2 - 10^5 MH_2$

www.ChemistryABC.com
www.ChemistryABC.com
free download all stuffs more notes and books www.ChemistryABC.com

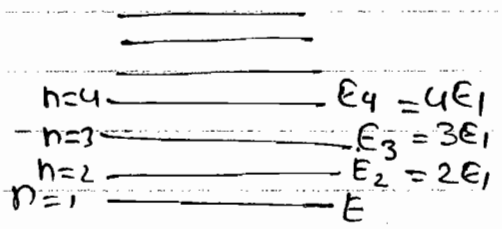
www.ChemistryABC.com

26th-March-2015

Origin of Spectra :-

(a) Quantum of energy.
(b) Absorption of EMR
(c) factors affecting the intensity.
(i) Selection rule
(ii) Population ratio b/w two energy states

(a) Quantum of energy :-



$$E_n = nE_1$$

① Generally all atoms and molecules have energy due to several type of motions such as translation energy, rotational energy, vibrational energy, electronic energy etc.

② All energies are quantised convinently the transition state involve the different type of energy levels usually occur in different part of electro magnetic spectrum.

③ Fixed energy have fixed state and energy of nth state is integral multiple of first energy state.

$$E_n = nE_1$$

④ A contineous system can not give spectra which is equal to translation energy.

⑤ Translational energy can not give spectra because the energy difference b/w two successive translational energy level is very low which is order of 10^{-60} J/mole.

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Q- So for a normal molecule translational energy is consi-dered to as very contineously.

C- Rest are all other motions are quantised the energy di-fference b/w two successive energy levels and correspon-ing wavelength is shown below:-

	ΔE/J/mol	λ (meter)
Rotational	10^{-23}	10^{-2}
Vibration	10^{-21}	10^{-4}
Electronic	10^{-19}	10^{-6}

(b) Absorption of Radiation :-



If,

$I > I_o$ → emmision

$I < I_o$ → Absorption

$I = I_o$ → No absorption.

Absorption of EMR is the way in which the energy of a photon is taken up by a matter, tipically by the e^- of an atom thus electromagnetic energy is transform into inter-nal energy of the matter, therefore the change in inten-sity of a light wave takes place.

Transmittance :-

$$T = \frac{I}{I_o}$$

free download all stuffs more notes and books www.ChemistryABC.com

Refractive index change at very high temperature

$$\eta = \frac{V_a}{V_{gas}}$$

www.ChemistryABC.com

---

and absorbance $(A) = \epsilon . l . c$

$$\boxed{A = \epsilon \cdot l \cdot c}$$

Lambert - Beer's law (Beer's law) :-

Lambert - Beer law is the linear relationship between ~~absorp~~ absorbance and concentration of an absorbing species. It is written as-

$$A = \epsilon \cdot l \cdot c$$

c = Concetration of ten sample

l = Optical path length (cm)

ϵ = Molar absorbance coefficient.
(Only depends upon nature of substance).

Example :-

1M $KMnO_4 \longrightarrow \epsilon_1$

1 M $KCl \longrightarrow \epsilon_2$

1M $(Ti(H_2O_6)^{+3} = \epsilon_3$

there

$$\epsilon_1 \neq \epsilon_2 \neq \epsilon_3$$

But for,

1M $KMnO_4$ and 1 M $KMnO_4$ (ϵ remains same)

Unit of ϵ :-

$$A = \epsilon \cdot l \cdot c$$

$$\epsilon = \frac{A}{l \cdot c} = \frac{1}{\text{cm} \times \text{mol/litre}}$$

$$\boxed{\text{Unit of } \epsilon = \text{lit cm}^{-1} \text{ mole}^{-1}}$$

$$\epsilon = \frac{1}{\text{cm} \times \text{mol/cm}^3}$$

$$\boxed{\epsilon = \text{cm}^2 \text{ mol}^{-1}}$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Physical significance of ϵ :-

From $\epsilon = cm^2\ mol^{-1}$

$$\boxed{\epsilon = \text{area/mol}}$$

(i.e.,) Molar absorbance coefficient is area transverse by EMR per unit mole of any substance (molecule).

Thus. Intensity $\propto \epsilon$

$$\boxed{I \propto \epsilon}$$

Where I = Intensity of spectral line.

Relation b/w A and T =

~~$A = -T$~~ $A = -\log T$

$$A = \log \frac{1}{T}$$

$$\boxed{A = \log\left(\frac{I_0}{I}\right) = \epsilon \cdot l \cdot c}$$

Ques:-

A solution of compound have absorbance 30%. Calculat its transmitance. ($\log 2 = 0.3$)

$A = 30\%$ 0.3

$A = \frac{100}{30}$ ~~T~~

$A = \log \frac{1}{T}$

$T = \frac{1}{2} = 0.5$

$T = 50\%$.

$\frac{1}{T} = 2$

$\frac{1}{T} = \text{Antilog } A$

$\frac{1}{T} = \text{Antilog}(0.3)$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Note:-

It is clear th from above calculation

$$\boxed{A + T \neq 100\%}$$

Therefore the loss of Radiation Causes the heating or scattering.

Ques:-

0.01M $KMnO_4$ solution has 50% absorbance in 1cm path length then calculate ϵ in unit liter $mol^{-1} cm^{-1}$.

$$\epsilon = \frac{A}{l \cdot c}$$

$$= \frac{0.5}{1 \times 0.01M}$$

$$\boxed{\epsilon = 0.50 \text{ litre } mol^{-1} cm^{-1}}$$

Ques:-

0.1M $K_2Cr_2O_7$ solution has absorbance of 0.2 calculate absorbance of 0.01 M $K_2Cr_2O_7$ soln.

$$\epsilon_1 = \epsilon_2 = \epsilon$$

$$l_1 = l_2 = l$$

$$A_1 = 0.2 \qquad A_2 = ?$$

$$C_1 = 0.1M \qquad C_2 = 0.01\ M.$$

$$\frac{A_2}{A_1} = \frac{\epsilon_2 C_2 l_2}{\epsilon_1 C_1 l_1}$$

$$\frac{A_2}{A_1} = \frac{C_2}{C_1} = \frac{A_2}{0.2} = \frac{0.01}{0.1}$$

$$A_2 = \frac{0.01 \times 0.2}{0.1} = \boxed{0.02}$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Ques:- absorbance / absorption of compound

Calculate Ratio of λ X and Y under a pathlength ratio 5:3, the molar absorbance coefficient is in ratio 2:3 an concentration is same.

A_1 F

A_1 =

(a) 10.9 (b) 9:10 (c) 5:10 (d) 10.5.

$$\frac{A_2}{A_1} = \frac{\epsilon_2 l_2}{\epsilon_1 l_1} = \frac{2}{3} \times \frac{5}{3} = \frac{10}{9} = 10:9$$

NET

Ques (2012)

Using Cuvettes of 0.5 cm of path length a 10^{-4}M sol^{n} of chromophore shows 50% transmittance at certain wavelength. The molar extinction coefficient of a chromophore of this wavelength is. ($\log 2 = 0.3010$)

(1) 1500 $M^{-1}cm^{-1}$ (2) 3010 $M^{-1}cm^{-1}$

(3) 5000 $M^{-1}cm^{-1}$ (4) 6020 $M^{-1}cm^{-1}$

$l = 0.5$ cm

$C = 10^{-4}$ M

T = 50%

$\epsilon = ?$

$A = \log \frac{1}{T}$

$A = \log \frac{1}{0.5}$

$= \log 2.$

$A = 0.3010$

$A = \epsilon C l$

$C = \frac{A}{l \times c}$

$= \frac{0.3010}{0.5 \times 10^{-4}}$

$= 0.602 \times 10^{4}$

$= 6020\ M^{-1}cm^{-1}$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

0.5ppm soln of organic compound having molecular weight 250 gm/mole has a absorbance of 80% under path-length of 1.cm calculate molar absorbone coefficient.

$\epsilon = ?$

$C = 0.5\,ppm$

$= 5 \times 10^{-6}$ gm/litre

Absorbance = 80%.

or $\frac{5.0 \times 10^{-6}\ gm}{250\ gm/mole}$ dissolve in 1 litre

i.e $= C = \frac{5 \times 10^{-6}}{250}$ mol litre

$C = 0.02 \times 10^{-6}$

$A = 0.8$

$l = 1$

$\epsilon = ?$

$\epsilon = \frac{A}{l.C} = \frac{0.8}{0.1 \times 0.02 \times 10^{-6}}$

$= .40 \times 10^{6}$

$= 4 \times 10^{7}$ mol^{-1} litre mol^{-1} cm^{-1}

* 2pp 25ppm of an organic compound having formula weight having 125 gm/mole molar absorbance coefficient 2.5×10^{3} litre mole^{-1} cm^{-1} calculate the absorbance under pathlength of 5cm.

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

$$C = \frac{25 \times 10^{-6}}{125 \text{ gm/mole}}$$

$$C = 0.2 \times 10^{-6}$$

$$A = \varepsilon l c.$$
$$= 2.5 \times 5 \times 0.2 \times 10^{-6} \times 10^{3}$$
$$= 12.5 \times 0.2 \times 10^{-6} \times 10^{3}$$
$$= 2.50 \times 10^{-3}$$
$$= 2.5 \times 10^{-3}$$

In an absorption cell the absorbance of ~~oll~~ transmitta of 0.1 M soln of a substance X in 80% and that 0.1 M soln of another substane Y is 60% at a given wavelength what is the transmittance of a the solution i.e., simoultaniously 0.1 M in X and 0.1 in Y.

$T = ?$

$$A = A_1 + A_2$$

$$X = A = \log \frac{1}{T} = \log \frac{1}{80.8}$$

$$= \log 1.25.$$

$T =$

$$A_X = 0.096$$

$$A_Y = 0.202 + 0.096 =$$
$$A = 0.3188$$
~~$A = 1.25 + 0.20$~~
~~$= 1.45$~~

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

$$\frac{I_o}{I} = \text{anti log } 0.3188$$

$$T = \frac{I_o}{I} = 2.084$$

$$= \frac{1}{2.084}$$

$$T = 0.48$$

$$\boxed{T = 48\%}$$

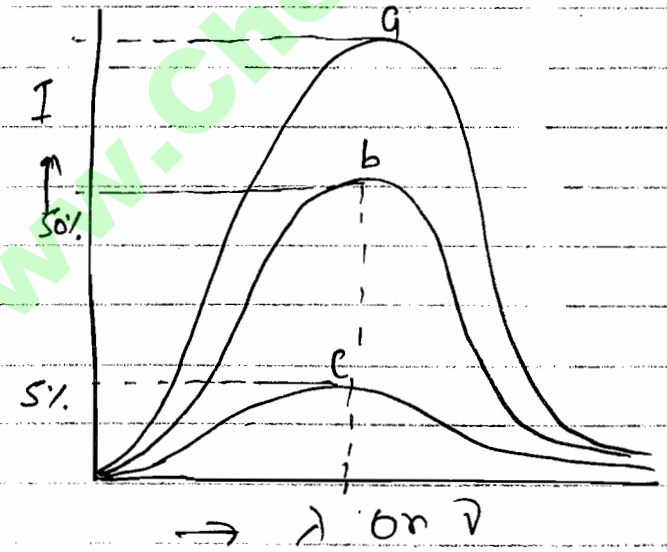
(C) Factors affecting the intensity:-

(i) ~~Sectre~~ Selection rule:-

The set of quantum mechanical rules which decides transition b/w two energy states called selection rule.

(i) Every spectra is associated with selection rule.

(ii) Selection rule allowed spectra is always intense. but partial allow and forbidden spectra have low intensity as shown in the plot.



Curve a = allowed spectra ($\epsilon > 10^4$)

Curve b = Partial allowed spectra ($\epsilon = 10^2 - 10^4$)

Curve c = forbidden ($\epsilon < 10^2$)

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

$I \propto \epsilon$

Selection rule for different spectra :-

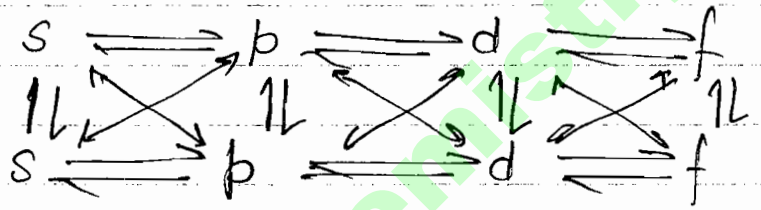
(1) For electronic spectra :-

Δn = Anything (Allowed)
= 1, 2, 3, 4 ...

$\Delta l = \pm 1$ (Laporte selection rule)

$\Delta S = 0$ (Spin selection rule)

$s \rightarrow s$
$p \rightarrow p$
$d \rightarrow d$
$f \rightarrow f$
} Not allowed transition
$\Delta l = 0$



Horizontal → allowed ($\Delta l \pm 1$)
Digonal → allowed ($\Delta l \pm 1$)
Vertical → Not allowed ($\Delta l = 0$)
Jumping → Not allowed ($\Delta l = \pm 2, \pm 3$)

(2) Rotational spectra :-

Selection rule for rot - spectra is change in rotational quantum no. is ± 1

i.e, $\boxed{\Delta J = \pm 1}$

(3) Vibrational spectra :-

Selection rule for Vib spectra is change in Vibrational quantum Number is ± 1

i.e., $\boxed{\Delta V = \pm 1}$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

4- Rotational-Vibration spectra :-

Selection rule :- $\Delta J = \pm 1$

$\Delta V = \pm 1, \pm 2, \pm 3 \cdots$

Intense spectra obtained due to population effect at G-S,

For P- Branch = $\Delta J = -1$, $\Delta V = \pm 1, \pm 2, \cdots$

R - Branch = $\Delta J = +1$, $\Delta V = \pm 1, \pm 2, \cdots$

Q - Branch = $\Delta J = 0$, $\Delta V = \pm 1, \pm 2 \cdots$

O - Branch = $\Delta J = -2$, $\Delta V = \pm 1, \cdots$

S - Branch = $\Delta J = +2$, $\Delta V = \pm 1, \cdots$

(5) For Raman spectra :-

Selection rule for raman spectra.

(1) Rot. $\Delta J = \pm 2$

↓

Because it is 2-photon process. one for stokes and other for antistokes line.

(2) Vibrational Raman

$\Delta V = \pm 1$

(3) Rotational - Vibrational raman spectra (O and S branch

$\Delta V = \pm 1, \pm 2, \cdots$

$\Delta J = \pm 2$

(6) For NMR - Spectra :-

Selection rule for NMR spectral

$\Delta m_I = \pm 1$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Δm_I = Difference b/w two nuclear spin stat

For EPR and ESR :-

$\Delta M_S = \pm 1$ (when no hyper fine splitting)

$\Delta M_I = 0$ (when hyper fine splittings is take place).

Se 30th-March-2015.

Ques :-

Which is intense transition :-

(a) $7f \longrightarrow 4f$ $\Delta l = 0$

(b) $5f \rightarrow 3p$ $\Delta l = \pm 2$

(c) $2d \longrightarrow 3p \longrightarrow$ Not allowed

(d) $3d \longrightarrow 4p$ $\Delta l = \pm 1$

Electronic spectra :-

Δn = Anything

$\Delta l = +1$

$\Delta S = 0$

Ques :-

Which is intense transition.

(a) $1s^{\uparrow\downarrow} \longrightarrow 1s^{\uparrow} 2s^{\uparrow}$ $\Delta S = 1$ $\Delta l = 0$, $\Delta S = +1$

(b) $2p_x^{\uparrow\downarrow} \longrightarrow 2p_x^{\uparrow} 3d^{\uparrow}$ $\Delta S = 1$ $\Delta l = +1$ $\Delta S = +1$

(c) $2s^{\uparrow\downarrow} \longrightarrow 2s^{\uparrow} 2p^{\uparrow}$ $\Delta s = 0$ $\Delta l = 1$ $\Delta S = 0$ — (Intense.)

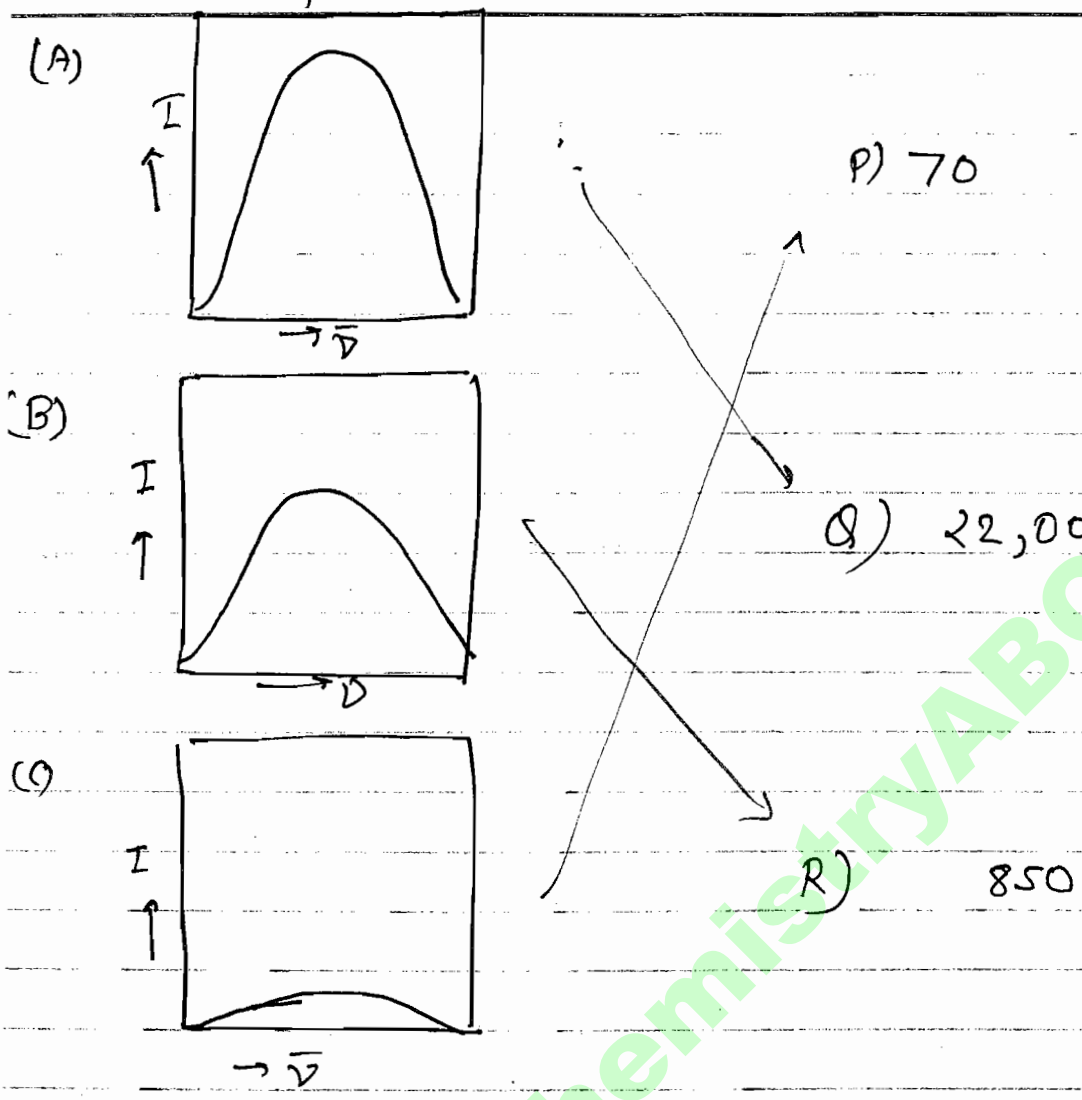
(d) $3d^{\uparrow\downarrow}_{x^2y^2} \longrightarrow 3d^{\uparrow}_{x^2y^2}\ 3d^{\downarrow}_{xy}$

Ques :- Match the following graph with their molar absorban coefficient.

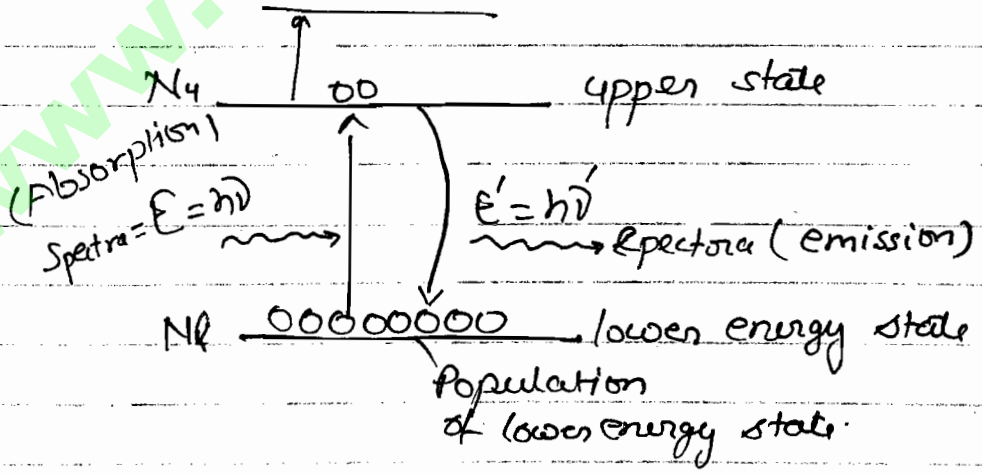
free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Spectra. G (cm⁻¹ mL²)



(ii) Population ratio between two state :-



Intensity of any spectra depends upon population difference b/w two states if population of low state is N_l and upper state is N_u then $\frac{}{}$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Intensity $\propto (N_l - N_u)$

From Boltzmann partition function the population ratio of two states are -

$$\frac{N_u}{N_l} = g \cdot \exp\left(\frac{\Delta E}{KT}\right)$$

Where g = Degeneracy factor for
$g = 1$ for all spectra (except rotational spectra
$g = (2J+1)$ (For rotational spectra)

ΔE = Energy difference b/w two states.
K = Boltzman constant.

Intensity

Suppose $N_l = 10$ $N_u = 1$

$(N_l - N_u) = 9$

$$\frac{N_u}{N_l} = 0.1$$

If $N_u = 9$ $N_l = 10$

$(N_l - N_u) = 1$

$$\frac{N_u}{N_l} = 0.9$$

therefore

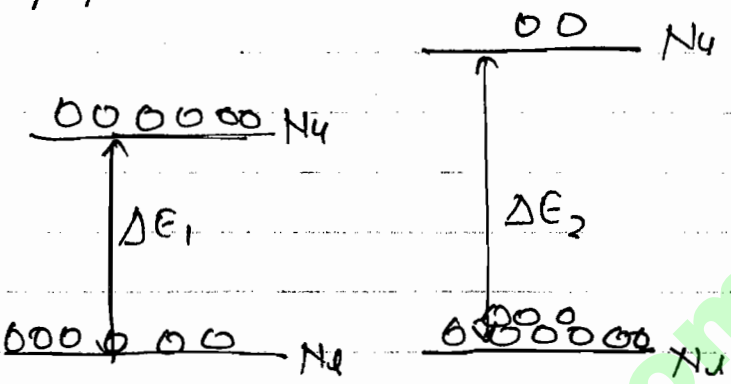
$$I \propto (N_l - N_u)$$

$$I \propto \frac{1}{(N_u/N_l)}$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Mathamatical analysis of formula:-



If, $\Delta E_1 < \Delta E_2$

* Higher the energy gap the population of lower state is high and lower higher state is low.

$$\frac{N_4}{N_1} = \text{low}$$

and Intensity of spectra will be high.

* Lower the energy gap, higher will be population of N_4 i.e.,

$$\frac{N_4}{N_1} = \text{high}$$

and intensity of spectral will be low.

* As temperature increases N_4 becomes more and more populated and N_4/N_1 increase then intensity decreases.

* If $N_4 \geq N_1$ $g = 1$

$N_4 = N_1$,

$$\frac{N_4}{N_1} = g \cdot \exp\left(\frac{-\Delta E}{KT}\right)$$

$$I = \exp^{\left(\frac{-\Delta E}{KT}\right)}$$

$$e^0 = e^{-\Delta E/KT}$$

$$\boxed{\frac{\Delta E}{K} = 0}$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Since $\Delta E \neq 0$

$T = \infty$

But T never be ∞ infinite, so, the condition $N_4 = N_0$ and $N_4 > N_1$ Not possible. Thus the population of upper state is always Less then lower state.

* Intensity is directly proportional to $\left(\frac{\Delta E}{T}\right)$

ΔE		$\frac{N_4}{N_1}$	
increase			decrease
T	intensity		
	↑		

Ques:-

Which one of the following spectra is more inte -nse which ΔE = values are given below.

(a) 30 KJ (b) 400KJ (c) 5000J (d) 3 KJ

$I \propto \Delta E$ = 5KJ

Ques:- Which of the following spectra is more intence which temp. are given.

(a) 500K (b) 50°K (c) 23°c (d) 1°c

-273

$227°c$

$I \propto \frac{1}{T}$

$\frac{273}{30}$

303

Ques:- Which of the sp following spectra is more intence

	ΔE	Tem.	
(a)	300	30°c	$\Delta E/T = \frac{300}{303} = 0.01$
(b)	50	5°c	$\Delta E/T = \frac{50}{278} =$
(c)	400	400°c	$\Delta E/T = \frac{400}{673}$
(d)	5	3K	$\Delta E/T = \frac{5}{276} =$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Calculate the palpulation ratio b/w two states having energy gap of 300K ~~via~~ K where K is Boltzman constant at 27°c take degeneracy $g = 1$

$$\frac{N_4}{N_l} = ?$$

$\Delta E = 300K$

$T = 27°c = 300K$ $\quad T = 300K$

$$\frac{N_4}{N_l} = e^{-\frac{300}{300K}}$$

$$\frac{N_4}{N_l} = \frac{1}{e}$$

**Ali In a diatomic molecule population of lower state is 1000 then calculate the population of upper state which is seperated by the energy gap of $13.8 \times 10^{-23} J$

$T = 10K$

$g = 1$

$K = 3.8 \times 10^{-23} JK^{-1}$

$$\frac{N_4}{N_l} = e^{-\frac{13.8 \times 10^{-23}}{1.3.8 \times 10^{-23} \times 10}}$$

$$1000 = \frac{1}{e}$$

$$N_4 = N_l e \left(\frac{N_l}{e}\right) = \frac{1000}{2.71} = 369$$

Rotational spectra :-

1- Definition.
2- Moment of Inertia.
3- Rigid rotor.

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

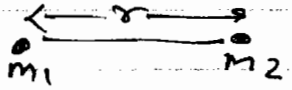
4- Energy of rotating molecule.
(5) - Essential condition for rotional spectra.
(6) - Selection and rule for rotation spectra.
(7) - Intensity of rotational spectra.
8 - Effect of isotopic substitution on Rotational constant
(9) Non - rigid rotor

(1) Difination :-

Transitions b/w rotational levels belon -ging to particular vibration level are observed in micro wave region of Electromagnetic spectrum. ($\lambda = 10^{-2}$ to 10^{-4} meter) called vibration spectra. It is arises due to rotation of molecule about bond axis are perpendicular to bond axis.

The rotational property of a rigid bo are characterised by its moment of inertia so the rotati -onal spectra of a molecule depends upon moment of inertia.

Moment of inertia :-



For a diatomic molecule.

Moment of inertia (I) = mr^2

or $I = \mu r^2$

$\mu = \frac{m_1 m_2}{m_1 + m_2}$ reduced mass

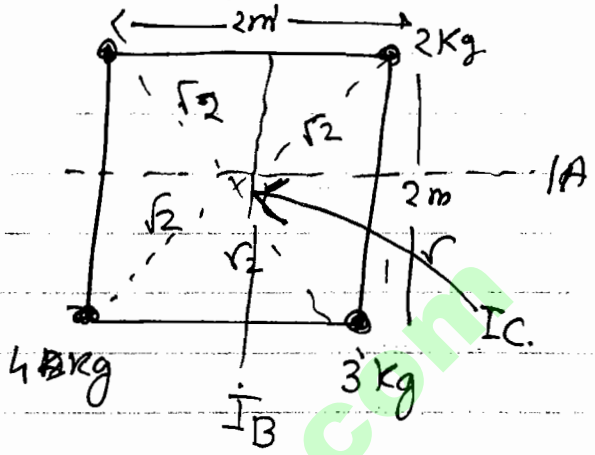
For polyatomic molecule moment of inertia

$$I = \sum_{n=1}^{n=i} m_i r_i^2$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

In poly ~~atom~~ atomic molecule the moment of inertia.



Along A axis.

$$I_A = 1Kg \times (1)^2 + 2Kg \times (1)^2 + 3Kg\,(1)^2 + 4Kg\,(1m)^2$$

$$I_A = 10\,kg\,m^2.$$

Along B-axis

$$I_B = 10\,kg\,m^2$$

Along c-axis:-

$$I_C = 1\times(\sqrt{2})^2 + 2(\sqrt{2})^2 + 3(\sqrt{2})^2 + 4(\sqrt{2})^3$$

$$I_C = 2 + 4 + 6 + 8$$

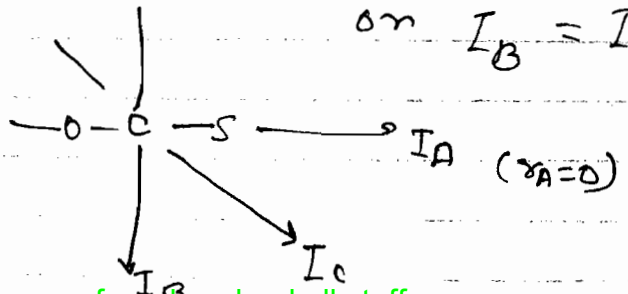
$$\boxed{I_C = 20\,kg\,m^2}$$

For the purpose of studing spectra rotational spectra in a molecule we have to classify the molecule according to moment of inertia.

(1) Linear top molecule for linear molecules such as, HCl, CO_2, O-C-S etc moment of intertia core

$$I_B = I_C \text{ and } I_A = 0$$

or $I_B = I_C > I_A$



$I_B = I_C > I_A$

O-C-S etc bo, Dooh.

free download all stuffs more notes and books www.ChemistryABC.com

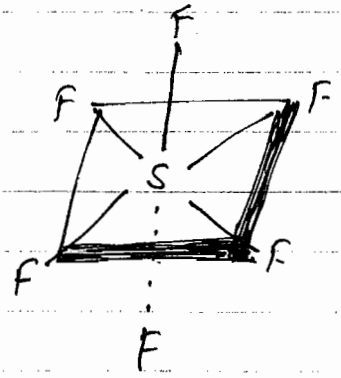
www.ChemistryABC.com

* Spherical top molecule:-

When a molecule have all three moment of inertia identical called spherical top molecule.

i.e., $I_A = I_B = I_C$

Example:- Octahedral molecules (Oh), tetrahedra molecule (Td) and Icosahedral (Ih)., SF_6, CH_4, CCl_4, UF_6, SO_4^{--} etc.



* Symmetrical top molecule :-

In symmetrical top molecules.

$I_B = I_C \neq I_A$ and $I_A \neq 0$

Generally symmetrical rotator have C_n axis with $n \geq 3$ or S_4-a
It is two types (a) Oblet : $I_B = I_C < I_A$ { BF_3, C_6H_6 and squar planner)

(c) Prolate: $I_C = I_B > I_A$ { CH_3I, CH_3F, CH_3F, CH_3 $CHCl_3$, NH_3 etc).

* Asymmetric to or Non-Symmetric Top molecule:-

The molecules having all the moment of inertia different passes Asymmetric top,

$I_A \neq I_B \neq I_C$

Example:- H_2O, Vinyl chloride.

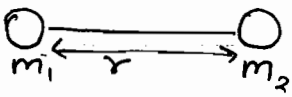
free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Formaldehyde, Chlorobenzene etc. (C_2-axis)

6th - April - 2015

Rigid ~~roto~~ rotor :-



When masses m_1 and m_2 are joined by a ~~rid~~ rigid bar (bond) whose length is r, called rigid rotor.

There is no change in bond length during rotation ($\Delta r = 0$).

Any rotating molecule having angular momentum.

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

$$\vec{L} = \sqrt{J(J+1)}\;\hbar$$

where - $J = 0, 1, 2, 3 \ldots$

J = Rotational quantum no.

$J = 0 \rightarrow \vec{L} = \sqrt{0(0+1)}\;\hbar$

G.S. $\rightarrow$ $\vec{L} = 0$

$J = 1 \rightarrow \vec{L} = \sqrt{1(1+1)}\;\hbar$

$= \sqrt{2}\;\hbar$

$J = 2 \rightarrow \vec{L} = \sqrt{2(2+1)}\;\hbar$

$= \sqrt{6}\;\hbar$

$J = 3 \rightarrow \vec{L} = \sqrt{3(3+1)}\;\hbar$

$= \sqrt{12}\;\hbar = 2\sqrt{3}\;\hbar$

$J = 4 \; \vec{L} = \sqrt{20}\;\hbar$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

" Angular momentum of rotating molecule are ~~quatised~~ quantised.

4- Energy of rotating molecule :-

For linear motion kinetic energy of the body

$K.E = \frac{p^2}{2m}$ — Linear momentum
m — mass.

For rotational motion of rigid rotor.

$$\text{Energy} = E = \frac{\vec{L}^2}{2I}$$

Where, L = Angular momentum.
I = moment of inertia.

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

Then $= E = \frac{\left(\sqrt{J(J+1)}\ \frac{h}{2\pi}\right)^2}{2I}$

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

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

In term of wave no. $\bar{\nu}$, is.

$$E = hc\bar{\nu} \quad — (2)$$

From e⁻ ① and (2) =

$$hc\bar{\nu} = \frac{J(J+1)\ h^2}{8\pi^2 I} \qquad \bar{\nu} = \frac{J(J+1)\ h}{8\pi^2 I c} \quad — (3)$$

$$\text{或 } c\bar{\nu} = \frac{J(J+1)\ h}{8\pi^2 I}$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

$$\bar{\nu} = J(J+1)B \quad -(4)$$

B = Rotational constant.

$$B = \frac{h}{8\pi^2 Ic} \quad -(5)$$

Thus :-

$$B \propto \frac{1}{I}$$

$I = \mu r^2$ $\qquad$ $B \propto \frac{1}{\mu}$ $\qquad$ $\mu = \frac{m_1 m_2}{m_1 + m_2}$

(r = Constant in case of rigid rotor)

Thus rotational constant inversionally proportional to moment of Inertia and reduced mass.

* Energy in terms of wave no.

We know that,

$$E = hc\bar{\nu}$$

and $\bar{\nu} = J(J+1)B.$

$$E = J(J+1)Bhc \text{ Joule.}$$

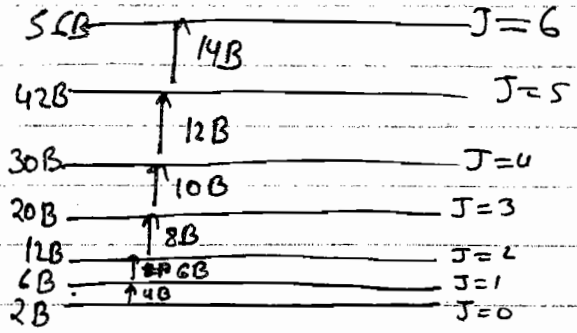
$$\bar{E} = J(J+1)B$$

Both energy as well as momentum of rotating molecule is quantised.

~~$L = \sqrt{J}$~~	$L = \sqrt{J(J+1)}\,\hbar$	$E = J(J+1)Bhc$	$\bar{E} = J(J+1)B$
J	L	E	E
0	0	0	0
1	$\sqrt{2}\,\hbar$	$2Bhc$	$2B$
2	$\sqrt{6}\,\hbar$	$6Bhc$	$6B$
3	$\sqrt{12}\,\hbar$	$12Bhc$	$12B$
4	$\sqrt{20}\,\hbar$	$20Bhc$	$20B$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com



(5) Essential condition for rotational spectra:-

* A molecule must be polar ($\mu \neq 0$), then it shows rotational spectra and molecule is called microwave active molecule.

* If a molecule have dipole moment zero than it does not show spectra. Thus it i.e., the molecule is microwave inactive.

Example:-

	Microwave active	Microwave inactive.
diatomic molecule	HCl, HBr, HI, CO, NO, etc.	H_2, N_2, O_2 I_2 etc.

Triatomic molecule.

$S=C=O$

$H-C\equiv N$

$SnCl_2$ (Cl, Sn, Cl)

SO_2, H_2O etc.

$O=C=O$, $S=C=S$

Cl – Be – Cl etc.

* If a molecule have does not permanent dipole moment can not generate oscillating electric field and can not interact with electric field of radiation and hence such a molecule does not show rotational spectra. So the essential condition for a molecule to be m

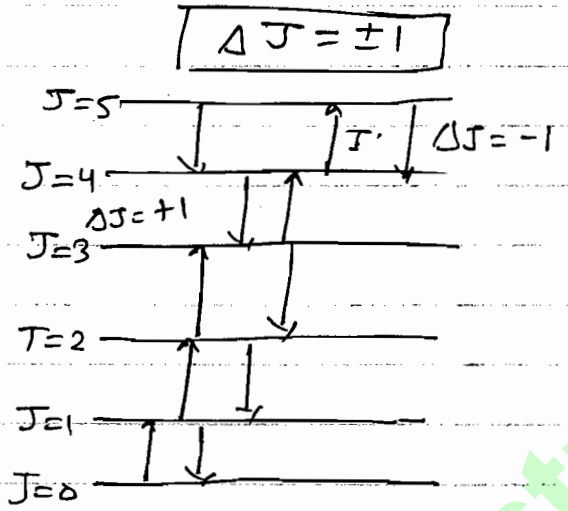
free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

- wave active is that it should have permanent dipole moment.

Selection rule :- (Rotational spectra) :-

Change in rotational quantum no. $= \pm 1$



Ques :-

Which of the following transition are possible.

a) = $J=0 \longrightarrow J=3$

(b) $J=3 \longrightarrow J=2$ ✓

(c) $J=3 \longrightarrow J=1$

(d) $J=\pm 1 \longrightarrow J=+3$

* Energy of difference between two states and Spectrum between two successive spectral line.

Suppose for tansition.

$J \longrightarrow J'$

lower higher.

$\Delta E = E_{J'} - E_J$ ---(i)

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Suppose $J' = J+1$

$$\Delta E = J'(J'+1)Bhc - J(J+1)Bhc.$$

$$\Delta E = (J+1)(J+1+1)Bhc - J(J+1)Bhc$$

$$\Delta E = 2J(J+1)BHC(1+1) - J$$

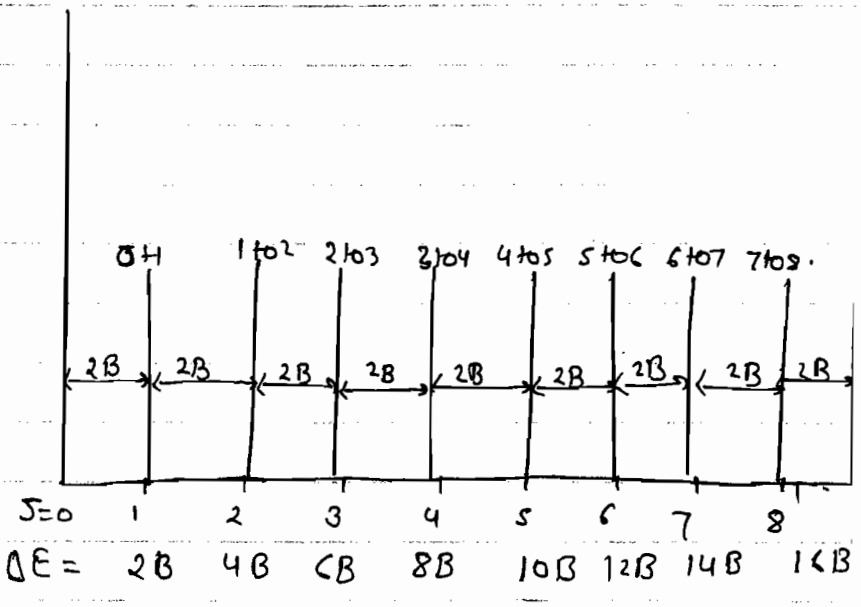
$$\boxed{\Delta E = 2(J+1)Bhc} \text{ Joule}$$

$$\boxed{\Delta \tilde{E} = 2(J+1)B} \text{ cm}^{-1}.$$

Transition	ΔE
$J=0 \rightarrow 1$	$2B$] $2B$
$J=1 \rightarrow 2$	$4B$] $2B$
$J=2 \rightarrow 3$	$6B$] $2B$
$J=3 \rightarrow 4$	$8B$] $2B$
$J=4 \rightarrow 5$	$10B$] $2B$
----------	So on.

Note:-

Separation b/w two successive



free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Ques:-

In the rotional spectra of CO the first and fift line is 24 cm^{-1} calculate the rotational constant.

$$\Delta E = 2(2+1)B = 8B$$

$$24 = 2(2+1)B = 8B = 24$$

$$B = 4\ cm^{-1}$$

* In rotational spectra of HCl molecule separation b/w two adjacent line is 2cm^{-1} calculate the energy of 4th rotational state.

$$2B = 2cm^{-1}$$

$$B = = 1$$

$$J = 4 = J(J+1)B$$

$$= 4(4+1)1$$

$$E = 20$$

* In the rotation spectra of CO separation b/w any two adjacent line is six 6 cm^{-1} calculate the moment of inertia.

$$2B = 6cm^{-1}$$

$$B = \frac{6}{2} = 3cm^{-1} \qquad \text{tm} \quad 1cm^{-1} = 100\ m^{-1}$$

$$= 100m^{-1}$$

We know that:- $B = \frac{h^2}{8\pi^2 IC}$

$$I = \frac{h^2}{8\times\pi^2 BC.} = 6.6\times10^{-3}$$

$$\frac{6.626\times10^{-34}}{78.87\times300\times8}$$

$$\frac{6.626\times10^{-34}}{8\times(3.14)^2\times300m\cdot\times8\times10^{9}}$$

$$I = \frac{6.626\times10^{-34}\ J/sec}{8\times(3.14)^2\times300m\cdot\times8\times10^{9}}$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

$I = 9.34 \times 10^{-47}\ kg\ m^{-2}$.

Ques:-

Calculate the rotational energy of $^{14}NO^{16}$ corresponding to $J=1$ level in Joule and cm^{-1} assuming it to be rigid rotator. The atomic masses of ^{14}N and ^{16}O are

^{14}N → 14.004 amu ^{16}O → 15.9994 amu respectively.

Bond length = ~~10~~ 115 pm.

$= 115 \times 10^{-12}$ m.

$$\mu = \frac{14.004 \times 15.9994}{14.004 + 15.9994} \frac{10^{-27} \times 10^{-27}}{10^{-27} + 10^{-27}}$$

$1\ amu = 1.66 \times 10^{-27}$ kg. $= 23.2466 \times 10^{-27}$ kg (N)

$= 15.9994 \times 10^{-27} = 26.559 \times 10^{-27}$ kg

$$= \frac{617.4064}{49.8056} = 12.3963 \times 10^{-27}\ kg$$

$I = \mu r^2$

$I = 12.39 \times 13225 \times 10^{-24} \times 10^{27}$

$I = 163857.7 \times 10^{-51}$

$I = 1.638 \times 10^{-46}$

$$E = \frac{h^2}{4\pi^2 \mu r^2} = \frac{(6.626 \times 10^{-34})^2\ J\,sec}{4 \times 9.8 \times 12.39 \times 10^{-27} (115 \times 10^{-12})^2}$$

$$E_1 = 6.79 \times 10^{-21}\ Joule.$$

$$\bar{E} = \frac{6.797 \times 10^{-21}}{hc} = \frac{6.797 \times 10^{-21}}{6.626 \times 10^{-34} \times 3 \times 10^{8}}\ cm^{-1}$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

$$= \frac{6.797 \times 10^{-21}}{19.87 \times 10^{-26}} \qquad \bar{E} = 0.3420 \times 10^{5}$$

$$= 34.2 \times 10^{3}$$

Intensity of rotation spectra :—

$$\Delta E = 2B(J+1) \qquad D = J(J+1)B$$

Give only position of line in rotational spectra but it does not tells anything about intensity of lines. However it is observed that the intensity of line of spectra are not seen some lines are more intense than others. (The relative intensity of spectral lines would be therefore be expected to depends on factors namely -

(a) The propability of transition b/w various energy level. The higher probability of transition will have higher intensity.

Relative population of various rotational levels.

Therefore the quantum mechanical calculation show that the probability of all transitions corresponding to selection rule ($\Delta J = \pm 1$) is same.

www.ChemistryABC.com

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

www.ChemistryABC.com

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

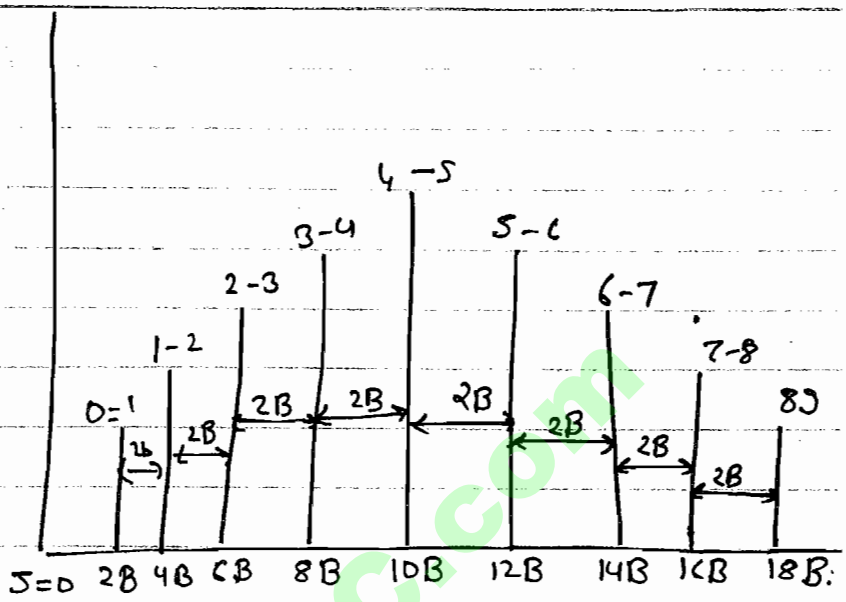
www.ChemistryABC.com

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

7th-April-2015.

$J_{max} = \sqrt{\frac{kT}{2Bhc}} - \frac{1}{2}$



$J_{max} = 0.6\sqrt{\frac{T(K)}{B(cm^{-1})}} - \frac{1}{2} = 0.6\sqrt{\frac{T(K)}{B(cm^{-1})}} - \frac{1}{2}$

* Separation b/w any two line in the spectra of CO is 6cm^{-1} calculate J_{max} at 27°C.

$2B = 6\ cm^{-1}$

$B = \frac{6}{2} = 3\ cm^{-1}$

$J = 0.6\sqrt{\frac{300K}{3/}} - \frac{1}{2}$

$J = 0.6\sqrt{100} - \frac{1}{2}$

$J = 0.6 \times 10 - \frac{1}{2}$

$J = 5.5 \approx 6$

www.ChemistryABC.com

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

* The most populated rotational state for HCl ($B = 8.5\ cm^{-1}$) at 300k is.

$$J_{max} = 0.6\sqrt{\frac{300}{8.5}} - \frac{1}{2}$$

$$= 0.6\sqrt{35.29} - \frac{1}{2}$$

$$= 0.6 \times 5.94 - 0.5$$

$$= 3.56 - 0.5$$

$$\boxed{J_{max} = 3.06 \simeq 3}$$

* If the two diatomic molecules AX and AY have rotational constants $6\ cm^{-1}$ and $10\ cm^{-1}$ respectively calculate the ratio of temp. at which Jmax for both is equal.

$$J_{max}(AX) = J_{max}(AY)$$

$$0.6\sqrt{\frac{T_1}{6\ cm^{-1}}} - \frac{1}{2} = 0.6\sqrt{\frac{T_2}{10\ cm^{-1}}} - \frac{1}{2}$$

$$\frac{T_1}{B_1} = \frac{T_2}{B_2}$$

$$\frac{T_1}{T_2} = \frac{B_1}{B_2} = \frac{6}{10} = \frac{3}{5}$$

$$\boxed{T_1/T_2 = 3:5}$$

www.ChemistryABC.com

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

* Degeneracy of rotational spectra is 11 calculate angular momentum L_J and energy E_J.

$$J_J = \sqrt{J(J+1)}\,\hbar$$

$$E_J = J(J+1)Bhc.$$

$$g_J = 2J+1 = 11$$

$$2J = 11-1$$

$$J = \frac{10}{2} = 5$$

$$L_J = \sqrt{5(5+1)}\,\hbar$$

$$\boxed{L_J = \sqrt{30}\,\hbar}$$

$$\boxed{E_J = 5(5+1)Bhc = 30Bhc}$$

* Calculate the relative population of the first two rotational levels for HCl at 300k. Given that the value of Rotation constant of the molecule. 10.59 cm^{-1}

$$\text{O.C.} \sqrt{\frac{T(K)}{B\ cm^{-1}}} - \frac{1}{2} \times$$

$$\frac{N_J}{N_0} = (2J+1)\, e^{\left(\frac{J(J+1)Bhc}{KT}\right)}$$

Given :-

$$B = 10.59\ cm^{-1} = 10.59 \times 100\ m^{-1}$$

$$T = 300k$$

$$h = 6.626 \times 10^{-34}\ Joule/sec$$

$$c = 3 \times 10^{8}\ m/sec$$

$J = 0$ $\quad g_J = 1$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

$$\frac{N_J}{N_0} = (2\times 0+1)\,e^{0} = 1$$

We know that the rotational energy in the lowest state is zero since $J=0$ so if we have N_0 molecules in this states than the No. of molecules in any higher state is geiven by.

$$\frac{N_J}{N_0} = e^{-\frac{J(J+1)Bhc}{KT}}$$

$$\frac{N_1}{N_0} = e^{-\frac{1(1+1)Bhc}{KT}}$$

$$= e^{-\frac{2Bhc}{KT}}$$

~~$\log \frac{N_1}{N_0} = \ldots$~~

$$\ln \frac{N_1}{N_0} = -\frac{2Bhc}{KT}$$

or $$\log \frac{N_1}{N_0} = \frac{-2Bhc}{2.303KT}$$

$$= \frac{-2\times 10.59\times 10^{2}\times 6.626\times 10^{-34}\times 3.0\times 10^{8}}{2.303\times 1.38\times 10^{-23}\times 300} = \frac{421.01}{}$$

$$\log \frac{N_1}{N_0} = 0.44$$

Taking Antilog $\boxed{\frac{N_1}{N_0} = 0.363}$

www.ChemistryABC.com

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

* In the rotational spectrum of CO absorption lines are observed at a constant separation of 3.84 cm^{-1} calculate the angular velocity in radian/sec in J=1 level. ($I_{CO} = 14.5094 \times 10^{-47}$ kg/m

$$2B = 3.84\ cm^{-1}$$

$$B = \frac{3.8\ cm^{-1}}{2}$$

$$B = 1.92\ cm^{-1}$$

$$\frac{1}{2} I \omega^2 = J(J+1) BhC$$

$$\frac{1}{2} I \omega^2 = 2 \times 1.92 \times 6.626 \times 10^{-34} \times 3 \times 10^{8}$$

$$\frac{1}{2} \times 14.5094 \times 10^{-47}\ kg/m^3 = 3.84 \times 6.626 \times 10^{-34} \times 3 \times 10^{8}$$

$$7.2847 \times 10^{-47} \omega^2 = 25.4438 \times 10^{-34} \times 3 \times 10^{8}$$

$$7.2847 \times 10^{-47} \omega^2 = 76.3315 \times 10^{-26}$$

$$\omega^2 = \frac{76.3315 \times 10^{26}}{7.2847 \times 10^{-47}}$$

$$\omega^2 = 10.4783 \times 10^{23}$$

$$\omega^2 = \sqrt{10.478 \times 10^{23}}$$

$$\omega =$$

~~$\omega = 3.2354 \times 10^{23}$~~

$$\omega = \sqrt{104.78 \times 10^{22}}$$

$$\omega = 10.23 \times 10^{11}\ \text{Radian/sec}$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

8)- Effect of isotopic Substitution or Rotational constant :-

we know that.

$$B = \frac{h}{8\pi^2 c I}$$

Therefore, or $B \propto \frac{1}{I}$

or $\boxed{B \propto \frac{1}{\mu}}$

$\{ I = \mu r^2 \}$
$\{ \Rightarrow I \propto \mu \}$

i) As the value of μ increases the value of rotational constant decrease i.e; all lines becomes more closer to each other in isotopic molecule.

(ii) Isotopic substitution increases the value of μ and hence the rotational constant decreases.

$$\frac{B_{isotope}}{B_{Normal}} = \frac{\mu_{normal}}{\mu_{isotope}}$$

Since, $\mu_{isotope} > \mu_{Normal}$

$$\Rightarrow \frac{\mu_{isotope}}{\mu_{Normal}} > 1 \quad \text{or} \quad \frac{\mu_{Normal}}{\mu_{isotope}} < 1$$

$$\Rightarrow \frac{B_{isotope}}{B_{Normal}} < 1$$

$$\boxed{B_{isotope} < B_{normal}}$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

* If rotational constant of H^1Cl^{35} is 2cm^{-1} then what will be rotational constant of D^2Cl^{35}.

$$\frac{B_{D^2Cl^{35}}}{B_{H^1Cl^{35}}} = \frac{\mu_{H^1Cl^{35}}}{\mu_{D^2Cl^{35}}} = \frac{\mu_{HCl}}{\mu_{D^2Cl^{35}}} = \frac{35}{36}$$

$$= \frac{\mu_{D^2Cl^{35}}}{\mu_{D^2Cl^{35}}} = \frac{70}{37}$$

$$= \frac{35}{36} \times \frac{37}{70}$$

$$= \frac{37 \times 35}{36 \times 2} = 18 = \frac{37 \times 18}{}$$

$$= 0.513$$

$$\frac{B_{D^2Cl^{35}}}{B_{H^1Cl^{35}}} = \frac{1}{2}$$

$$B_{D^2Cl^{35}} = \frac{1}{2} \times 2 = 1\,cm^{-1}$$

* Calculate B of H^1Cl^{37}, if B of H^1Cl^{35} is 3 cm^{-1}

$$\frac{B_{H^1Cl^{37}}}{B_{H^1Cl^{35}}} = \frac{37}{38} \times \frac{36}{35}$$

$$\frac{B_{H^1Cl^{37}}}{B_{H^1Cl^{35}}} = 0.998$$

$$B_{H^1Cl^{37}} = 0.998 \times B_{H^1Cl^{35}}$$

$$B_{H^1Cl^{37}} = 0.998 \times 3$$

$$= 2.994\,cm^{-1}$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Note :-

Therefore isotopic substitution decreases the value of B but effect will be more when ever smaller atom is replaced by its haviour isotopes.

Question :-

For J=0 to J=1 transition in case of $^{12}C^{16}O$ takes plac at 115.4 GHz while in case of $^{*}C^{16}O$ takes place at 110.2 GHz. Calculate the mass No. of unknown isotope of carbon.

$$B_{^{12}C^{16}O} = 115.4\ GHz$$

$$B_{^{*}C^{16}O} = 110.2\ GHz.$$

$$\frac{\mu_{^{*}C^{16}O}}{\mu_{^{12}C^{16}O}} = \frac{B_{^{12}C^{16}O}}{B_{^{*}C^{16}O}}$$

$$\frac{16x}{16+x} \times \frac{16+12}{16\times 12} = \frac{115.4}{110.2}$$

$$\frac{28x}{12\times 16+x} = 1.04$$

$$\frac{(7x)}{3(16+x)} = 1.04$$

$$7x = 1.04\,(48+3x)$$

$$7x = 1.04\times 48 + 1.04\times 3x$$

$$7x - 3.12x = 1.04\times 48$$

$$3.88x = 49.92$$

$$= 12.8$$

$$\simeq 13$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

* Match the following molecule with their rotational constants.

Molecule		B(cm-1)
A = $^{1}H^{35}Cl$ (35)	..... (P)	2.00
B = $^{1}H^{37}Cl$ (37)	---(Q)	1.97
C = $^{2}H^{37}Cl$ (74)	(R)	1.00
D = $^{2}H^{35}Cl$ (76)	(S)	0.98

The correct matching is:-

(a) A → P , B → Q , C → R , D → S

(b) A → P , B → Q , C → S , D → R

(c) A → Q , B → P , C → S , D → R

(d) A → Q , B → R , C → P , D → S

More the product of mass & less will be the rotational constant.

(9) Non- Rigid rotor :-

Whenever rotation becomes very fast, bond length changes i.e., moment of inertia changes and therefore B, value also changes, such a rotation called non - rigid rotation.

Fo Example:- Rot-spectra of HF molecule is -

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

	$(2B)cm^{-1}$
$J = 0 \rightarrow 1$	$20\ cm^{-1}$
$J = 1 \rightarrow 2$	$20\ cm^{-1}$
$J = 2 \rightarrow 3$	$20\ cm^{-1}$
= = — —	
— — —	
— —	
$J = 10-11$	$19.93\ cm^{-1}$
$J = 11-12$	$19.85\ cm^{-1}$
$J = 12-B$	$19.38\ cm^{-1}$

*from above spectra it is clear that for the higher rotational state the value of B decreases and 'r' increases, rotation takes place with change in bond length and behaviour of ~~motion~~ rotation non-rigid. Non rigid behaviour is observed with increase in angular momentum.

* When molecule rotate the bond length increases because of centrifugal distortion.

* The effect of centrifugal distortion on a diatomic molecule is ~~too~~ to stretch the bond and hence to increase the moment of Inertia. As a result of ~~centr~~ centrifugal distortion rotational constant decreases.

* The effect of centrifugal distortion is usually taken into account by substracting a term from the energy and written as —

$$E_J = B \cdot J(J+1) - DJ^2(J+1)^2 \ cm^{-1} \quad —(1)$$

where D = Centrifugal distortion constant and it is very small quantity.

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

* The centrifugal distortion constant of a diatomic molec-le is related to vibrational wave no. of the bond.

$$D = \frac{4B^3}{\bar{\nu}^2} \quad -(2)$$

Since; $B = \frac{h}{8\pi^2 I.c} = \frac{h}{8\pi^2 \mu r^2 c.}$

$$\bar{\nu} = \frac{1}{4\pi c}\sqrt{\frac{k}{\mu}}$$

$$D = \frac{4 \times \frac{h^3}{8 \times 8\pi^4 \times I^3 c^3}}{\frac{1}{16\pi^2 c^2} \cdot \frac{k}{\mu}}$$

$$D = \frac{h^3 \mu}{32\pi^4 I^3 . c . k} \quad -(3)$$

$$D = \frac{h^3}{32\pi^4 I^2 . c . k} \quad -(4)$$

Ques:-

For HF molecule the rotational constant is $10\ cm^{-1}$ and vibration wave no. $1000\ cm^{-1}$ then calculate centr-fegal distortion constant

$B = 10\ cm^{-1}$

$\bar{\nu} = 1000\ cm^{-1}$

$$D = \frac{4 \times (10)^3}{(1000)^2} = \frac{4 \times 1000}{1000 \times 1000} = \frac{4}{10^3} = 4 \times 10^{-3}$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Ques:-

For a molecule of HBr the complete ~~J-to~~ rotational relationship is -

$$E_J = 8J(J+1) - 4 \times 10^{-3} \times [J(J+1)]^2$$

Calculate the value of B, D, $\bar{\nu}$ vibrational.

$$E_J = BJ(J+1) - D \cdot [J(J+1)]^2$$

$B = 8\ cm^{-1}$

$D = 4 \times 10^{-3}\ (m^{-1})$

$$D = \frac{4B^3}{\bar{\nu}^2}$$

$$4 \times 10^{-3} = \frac{4 \times (8)^3}{\bar{\nu}^2}$$

$$\bar{\nu}^2 = \frac{4 \times (8)^3}{4 \times 10^{-3}}$$

$$\bar{\nu}^2 = \frac{4 \times 8 \times 8 \times 8}{4 \times 10^{-3}}$$

$$\bar{\nu}^2 = \frac{4 \times 512}{4 \times 10^{-3}}$$

$$\bar{\nu}^2 = 512 \times 10^3$$

$$\bar{\nu} = \sqrt{8 \times 8 \times 8 \times 10^3}$$

$$\bar{\nu} = \sqrt{5120 \times 10^2}$$

$$= 8\sqrt{8 \times 10 \times 10^2}$$

$$\bar{\nu} = 712\ cm^{-1}$$

$$= 8 \times 10\sqrt{80}$$

$$= 80 \times 8.9$$

$$= 712\ cm^{-1}$$

64
×8
512
2048

www.ChemistryABC.com

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Non-Rigid Rotor :-

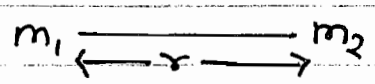
$$E_J = B \cdot J(J+1) - D \cdot J^2(J+1)^2 \ cm^{-1}$$

$$D = \frac{4B^3}{\bar{\nu}^2}$$

Where $\bar{\nu} = \frac{1}{4\pi c}\sqrt{\frac{K}{\mu}}$

Ques:- The B value of HF molecule is $10.00\ cm^{-1}$ for J=0 to J=1 For J=10 to J=11 B' value is $9.8\ cm^{-1}$ calculat the % of change of Bond length.

$\frac{\Delta r}{r} = ?$



$\frac{\Delta r}{r} \times 100 = ?$

$B = 10.00\ cm^{-1}$

$B' =$ value is $9.8\ cm^{-1}$

$B \propto \frac{1}{r^2}$

$\frac{B}{B'} = \left(\frac{r'}{r}\right)^2$

or $\frac{r'}{r} = \sqrt{\frac{B}{B'}} = \sqrt{10.00\ cm^{-1}}$

% Change

$\frac{r'}{r} - 1 = \sqrt{\frac{B}{B'}} - 1$

$\frac{r'-r}{r} = \sqrt{\frac{B}{B'}} - 1$

$\frac{\Delta r}{r} = \sqrt{\frac{B}{B'}} - r$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

% Change in Bond length for J

$$\frac{\Delta r}{r} \times 100 = \left(\sqrt{\frac{B}{B'}} - 1\right) \times 100$$

$$= \sqrt{\frac{10}{9.8}} - 1 \times 100$$

$$= 1.01 - 1 \times 100$$

$$= 0.01 \times 100$$

$$= 1\ \%$$

Question:-

For a molecule AB rotational transition at lower J value is observed that 10 cm^{-1} if bond length of molecule is 150 pm which becomes 160 pm due to non rigid rotation calculate rotational constant for the higher transition.

Solution:- given,

$B = 10.00\ cm^{-1}$

$r = 150\ pm$

$r' = 160\ pm$

$B' = ?$

$$\frac{r'}{r} = \sqrt{\frac{B'}{B}}$$

$$\frac{B'}{B} = \left(\frac{r}{r'}\right)^2 \quad \therefore \quad \frac{B'}{10} = \frac{(150 \times 10^{-12})^2}{(160 \times 10^{-12})^2} = \frac{22500}{25600}$$

$$\frac{B'}{B} = 0.87 \times 10 = 8.789\ cm^{-1}$$

$$= 8.8\ cm^{-1}$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Question :-

For the fast rotational spectra B value of Ax molecule is 20 cm^{-1} what will be the actual value of B if increase in bond length is 75% from slow to fast transtion.

Solution :- % Change in bond length $\left(\frac{\Delta r}{r} \times 100\right) = 75$

$$\frac{\Delta r}{r} \times 100 = \left(\sqrt{\frac{B}{B'}} - 1\right) 100$$

$$75 = \sqrt{\frac{B}{B'}} - 1 \times 100$$

$$\sqrt{\frac{B}{B'}} = \frac{75}{100} + 1$$

$$\sqrt{\frac{B}{B'}} = \frac{175}{100} = 1.75$$

$$\frac{B}{B'} = (1.75)^2$$

$$B = B'(1.75)^2 \times 20$$

$$\boxed{B = 61.25\ cm^{-1}}$$

Applications of rotational spectra :-

* To find the bond leng of a ~~mol~~ diatomic molecule by calculating the moment of inertia

$$r = \sqrt{\frac{I}{\mu}}$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

* To calculate the molecular weight of isotope.
* To determine the dipole moment of molecule.
* By using non-rigid rotar model we can calculate approximately the force constant.

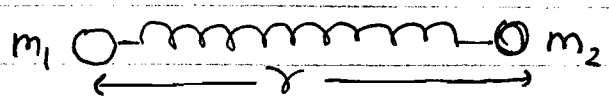
Vibrational spectra (IR-spectra):-

(1) Introduction and Simple Harmonic oscillater.
(2) Effect of bond Strength and isotopes on vibration frequency.
(3) Condition for Vibrational spectra.
(4) Nature of vibrations and Degree of freedom.
(5) Selection rule and intensity of transition.
(6) Anharmonic Oscillator.
(7) Selection rule of Anharmonic Oscillator.
(8) Calculate dissociation energy.

(1) Introduction and Simple Harmonic oscillator:-

Vibrational spectra as arises due to vibration of atoms about its mean position in the IR region of EMR. Suppose a diatomic molecule with atomic masses m_1 and m_2 joined by a chemical bond vibrates as one dimensional simple harmonic oscillator.

Frequency of SHO is given as

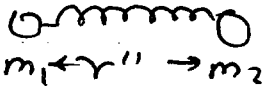


$$\nu = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}} \quad -(1)$$



and energy of SHO is

$$E = \left(v + \frac{1}{2}\right)h\nu \quad -(2)$$



free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Where, K = force Constant which measure the Bond strength

μ = Reduced mass $= \frac{m_1 m_2}{m_1 + m_2}$

V = Vibrational quantum No.

$V = 0, 1, 2, 3, 4 \cdots$

Energy of V^{th} state is given by,

$$E_V = (V + \tfrac{1}{2}) h\nu$$

or $$\boxed{E_V = (V + \tfrac{1}{2}) \frac{h}{2\pi} \sqrt{\frac{K}{\mu}}} \quad -(3)$$

Energy in terms of wave number.

$$\boxed{\bar{E}_V = (V + \tfrac{1}{2}) \frac{h}{2\pi c} \cdot \sqrt{\frac{K}{\mu}}} \quad -(4)$$

or $$\boxed{\bar{E}_V = (V + \tfrac{1}{2}) \bar{\nu}} \quad -(5)$$

If $V = 0$

$$E_0 = (0 + \tfrac{1}{2}) h\nu$$

$$\boxed{E_0 = \tfrac{1}{2} h\nu}$$

It is called zero point energy.

* In vibration motion zero point energy is not zero.

It is only mathamatical explanation to Hisenberg uncertainity principle even if all the motions of molecule stop. the molecule

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Remains vibrating with zero point energy so both position and momentum is not fixed.

(2) Effect of bond strength and isotopes of on vibrational spectra :-

Vibration energy of a system is.

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

Where $\bar{\nu} = \frac{1}{2\pi}\sqrt{\frac{K}{\mu}}$

or $\boxed{\bar{\nu} = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}}$

$\Rightarrow \boxed{\bar{\nu} \propto \sqrt{K}}$

$\boxed{\bar{\nu} \propto \frac{1}{\sqrt{\mu}}}$

* Bond strength and vibrational frequency :-

Since K is bond constant and depends upon. (force constant)

Nature of atom and bond

i.e., $A - B \Rightarrow K = x$

$A = B \Rightarrow K = 2x$

$A \equiv B \Rightarrow K = 3x$

$\bar{\nu}_{A-B} \propto \sqrt{x}$ — (1)

$\bar{\nu}_{A=B} \propto \sqrt{2x}$ — (2)

$\bar{\nu}_{A\equiv B} \propto \sqrt{3x}$ — (3)

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

From (1) and (2)

$$\frac{\bar{\nu}_{A-B}}{\bar{\nu}_{A=B}} = \frac{\sqrt{x}}{\sqrt{2x}} = \sqrt{\frac{1}{2}}$$

$$\boxed{\bar{\nu}_{A-B} = \frac{\bar{\nu}_{A=B}}{\sqrt{2}}}$$

Similarly

$$\frac{\bar{\nu}_{A=B}}{\bar{\nu}_{A\equiv B}} = \frac{\sqrt{2x}}{\sqrt{3x}} = \frac{\sqrt{2}}{\sqrt{3}}$$

$$\boxed{\frac{\bar{\nu}_{A=B}}{\sqrt{2}} = \frac{\bar{\nu}_{A\equiv B}}{\sqrt{3}}}$$

$$\boxed{\bar{\nu}_{A-B} = \frac{\bar{\nu}_{A=B}}{\sqrt{2}} = \frac{\bar{\nu}_{A\equiv B}}{\sqrt{3}}}$$

Question:-

If vibrational frequency of C≡O is 2100 cm^{-1}

C=O ?

$$\Rightarrow \frac{\bar{\nu}_{A=B}}{\sqrt{2}} = \frac{\bar{\nu}_{A\equiv B}}{\sqrt{3}}$$

$$\Rightarrow \frac{\bar{\nu}_{A=B}}{\sqrt{2}} = \frac{2100\,cm^{-1}}{\sqrt{3}}$$

$$\Rightarrow \frac{\bar{\nu}_{A=B}}{\sqrt{2}} = \frac{2100}{1.73}$$

$$\Rightarrow \bar{\nu}_{A=B} = \sqrt{2} \times 1214.4 = 1.414$$

$$\Rightarrow \boxed{1714\,(cm^{-1})}$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Ques:-

If $\nu_{C\equiv N}$ is 2200 cm^{-1} Calculate $\bar{\nu}_{C-N}$.

$$\nu_{C-N} = \frac{\nu_{C\equiv N}}{\sqrt{3}}$$

$$= \frac{2200}{1.73} = \boxed{1270.2\ cm^{-1}}$$

Effect of isotopes :-

$$\bar{\nu} \propto \frac{1}{\sqrt{\mu}}$$

$$\boxed{\frac{\bar{\nu}_1}{\bar{\nu}_2} = \sqrt{\frac{\mu_2}{\mu_1}}}$$

Ques:-

In $[Co(NH_3)_5H]$ the Co–H bond frequency is 1700 cm^{-1} calculate the Co – D bond frequency in $[Co(NH_3)_5D]$

$$\frac{\mu_{Co-H}}{\mu_{C_o-D}} = \frac{1}{2}$$

$$\frac{\nu_{Co-D}}{\nu_{C_o-H}} = \sqrt{\frac{\mu_{Co-H}}{\mu_{C_o-D}}} = \sqrt{\frac{1}{2}}$$

$$\frac{\nu_{C_o-D}}{1700} = \sqrt{\frac{1}{2}} = \frac{1700}{\sqrt{2}} = \frac{1700}{1.414} = \underline{1202\ cm^{-1}}$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Ques:-

If frequency of $H^{35}Cl$ is 1900 cm^{-1} - Calculate the frequency of $H^{37}Cl$ = ?

$$\mu_{H^{35}Cl} = \frac{35}{35+1} = \frac{35}{36}$$

$$\mu_{H^{37}Cl} = \frac{37}{38}$$

$$\frac{\mu H^{35}Cl}{\mu H^{37}Cl} = \sqrt{\frac{\mu H^{35}Cl}{\mu H^{37}Cl}} = \sqrt{\frac{35/36}{37/38}}$$

$$= \sqrt{\frac{0.972}{0.973}} = \sqrt{\frac{35 \times 38}{36 \times 37}}$$

$$= \sqrt{\frac{1330}{1332}} \times 1900$$

$$\chi = 0.274 \times$$
$$= 520.09\ cm^{-1}$$

35
× 38
280
105×
0

Note:-

Isotopic substitution decreases absorption frequency but effect will be more if lower atom is replaced by haviour isotope.

List I	$m_1 \times m_2$	List II	
(A) $^1H^{79}Br$	(79)	P	775 cm^{-1}
(B) $^2D-^{80}Br$	(160)	Q	772 cm^{-1}
(C) $^1H-^{80}Br$	(80)	R	480 cm^{-1}
(D) $^2D-^{79}Br$	(158)	S	487 cm^{-1}

www.ChemistryABC.com
free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

More the value of product of Mass less the ~~value~~ will be frequency.

Question:- Which of the following shows highest frequency

(a) $^{12}C\,^{16}O$
(b) $^{13}C\,^{17}O$
(c) $^{13}C\,^{18}O$
(d) $^{12}C\,^{17}O$

Ques:-

For a ~~A-B~~ or AB molecule and for CD molecule masses ~~is~~ for ratio 9:4 and their bond constant is in ratio of ~~three~~ & 3:2 If the ~~for~~ absorption frequency of AB is 1400 cm^{-1} calculate the ~~f~~ absorption frequency of CD

$$\frac{\mu_{AB}=9/4}{\mu_{CD}=3/2} \quad \frac{\nu_{C-D}}{\nu_{A-B}} = \sqrt{\frac{K_{CD}}{K_{AB}} \times \frac{\mu_{AB}}{\mu_{CD}}} = \sqrt{\frac{2}{3} \times \frac{9}{4}} \times 1400$$

$$= \sqrt{\frac{9}{4} \times \frac{3}{2}} \times 1400$$

$$= \frac{27}{8} \times 1400 \qquad = 1715\ cm^{-1}$$

$$= \frac{5.196}{2.82} \times 1400 \qquad = 2579.57\ cm^{-1}$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Ques:-

In C≡O absorption frequency is 2100cm^{-1} and absorption frequency is of C≡N is 2400cm^{-1} if their reduced mass are equal then calculate the ratio of Bond Constant.

$$\frac{K_{C\equiv O}}{K_{C\equiv N}} = ?$$

Ques:- Condition of vibrational spectra :-

(1) The interaction b/ radiation and vibrating molecule is through the fluxtuating (oscillating) electric field of radiation and similar field generated by vibration of the molecule is suitable condition for vibrational spectra.

(2) The essential condition of vibrational spectra is during vibration dipole moment changes if during vibration dipole moment changes then molecule is IR-active if

if. $\Delta \mu \neq 0 \Rightarrow$ IR-active

$\Delta \mu = 0 \Rightarrow$ IR-inactive.

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Example:- For Diatomic molecules :-

IR-active molecules are :-

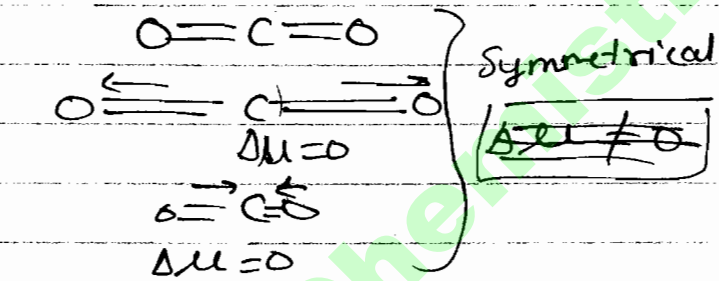
HCl , HBr , H, I , NO , CO etc.

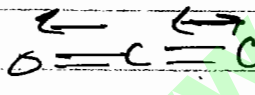
IR-inactive:-

H_2 , O_2 , N_2 , C_2 , Br_2 Etc.

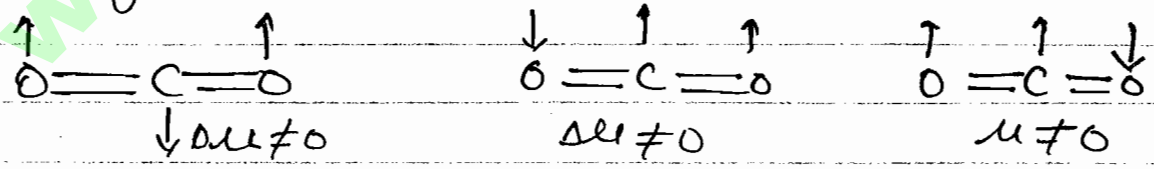
(3) For poly atomic molecule those modes of vibration in which dipole moments changes for IR active but all those mode of vibration the dipole does not changes are IR-inactive.

Example:- CO_2 molecule.




Assymetrical streching IR-active.

(all Bending. modes are IR active.



For N_2O molecule :-

$N \equiv \overset{\oplus}{N} - O^{\ominus}$

2- Streching mode
2- Bending mode. } IR-active.

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Nature of vibrations and Degree of freedom:-

Vibrational mod

are mainly two types:-

(1) Streching mode

↓

Change in bond length at constat Bin Bond angle

i.e., $\Delta r \neq 0$, $\Delta\theta = 0$

* It two types:-
  - → Symmetrical Streching
  - → Asymmetrical streching

(2) Bending mode

Change in bond angle at constant bond length.

$\Delta r = 0$

$\Delta\theta \neq 0$

→ It is also two types.

→ In plane bending or out of plane bending

→ Out of plane bending

Twisting Wegging.

Degree of freedom:-

If a molecule contain ~~N~~ a N atoms and the position of each atom is specifing by three co-ordinates (x, y and z axis) Thus total no. of co-ordinate value is 3N coordinates and we can say that the molecu have 3-degree of freedom. Since molecule is free move in 3D-space as a whole ~~without~~ ~~s~~ ~~coh~~ without change of shape such type of momement of position of its centre of gravity of any instant requirred a value of three co-or-inates. This translational movement cogo useses three degr-ee of freedom leaving (3N-3) degree of freedom.

For linear molecule there are two degree of rotation while for non linear there are three degree of rotation there-ore total vibrational degree of freedom for linear molecule.

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

is (3N-5) ; And non linear molecule is (3N-6)

For linear molecule — (3N-5) fundamental vib'
For nonlinear " — (3N-6) fundamental vib.

No. of streching vibration = (N-1) For all type of molecule
No. of Bending Vibration = ((2N-4) for linear.
= (2N-5) For Non-linear

Molecules (No. of atoms (N))	Total Degree of freedom (3N)	Translational degree of freedom (3)	Rotnal DOF	Vib DOF (3N-5) linear (3N-6) Non lin	Streching (N-1)	Bending (2N-4) lin (2N-5) Non lin
CO_2 linear	9	3	2	4	2	2
SO_2 Non linear	9	3	3	3	2	1
CH_4 Non linear	15	3	3	9	4	5
NO_3^- Non linear	12	3	3	6	3	3
C_6H_6 Non lin	36	3	3	30	11	19

www.ChemistryABC.com
free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Ques:-

The vibrational degree of freedom for O_2, N_2O, CH_2O, C_6H_6, and $CHCl_3$ are respectively.

(a) 3, 1, 6, 6, 30 (b) 4, 3, 9, 30, 9 (c) 1, 4, 6, 30, 9

(d) 1, 4, 6, 9, 30

(5) Selection Rule and itensity of transition:-

A moleule undergoing vibrational change within an electronic state must satisfy the selection rule for vibration transition.

$$\boxed{\Delta V = \pm 1}$$

$\Delta V = 0 \longrightarrow 1$

$V = 1 \longrightarrow 2$

$V = 2 \longrightarrow 3$

$V = 3 \longrightarrow 4$

$V = 4 \longrightarrow 5$

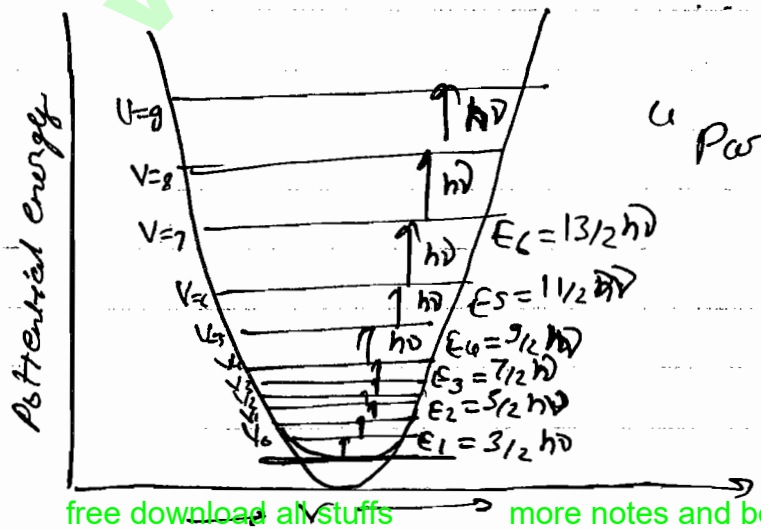
$E_V = (v + \frac{1}{2})h\nu$

$E_1 = 3/2\ h\nu$

$E_2 = 5/2\ h\nu$

$E_3 = 7/2\ h\nu$

$E_4 = 9/2\ h\nu$



(Parabolic graph)

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Note :-

(1) Only one transition $V=0 \rightarrow V=1$ is intense because population of N_{V+1} level is only 0.08 of N_4 level

$$\frac{N_{v+1}}{N_v} = 0.08$$

or $$\boxed{\frac{N_{v+1}}{N_v} = 8\%}$$

* According to selection rule suppose any transition is takes place $v \longrightarrow v'$.

$v \longrightarrow v'$

lower higher level

$\Delta E = E_{v'} - E_v$

$= (v' + 1/2)\, h\nu - (v + 1/2)\, h\nu$

But $v' = v+1$.

$\Delta E = (v + \frac{3}{2})h\nu - (v + \frac{1}{2})h\nu$

$$\boxed{\Delta E = h\nu}$$

or $$\boxed{\Delta \bar{E} = \bar{\nu}\ cm^{-1}}$$

Therefore in vibrational spectra the frequency of emmited or absorbed radiation must satisfied Bohrs condition i.e.,

$$\boxed{\Delta E = h\nu}$$

$$E_0 = \frac{1}{2} h\nu$$

$$\boxed{E_0 = \frac{\bar{\nu}}{2}}$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

Question :-

In a molecule of HI an intense band is observed at 670 cm^{-1} calculate the zero point energy

$$E_{0-1} = h\nu = 670\ cm^{-1}$$

$$\text{Zero point energy} = \frac{1}{2} h\nu = \frac{\bar{\nu}}{2}$$

$$= \frac{670}{2} = 335\ cm^{-1}$$

$$\text{Zero point energy} = 335 \times 11.96\ J\,mol^{-1}$$

$$= 4006.6\ J\,mol^{-1}$$

$$\Rightarrow 4.006\ KJ\,mol^{-1}$$

Question :-

Zero point energy of a molecule is 100 cm^{-1} and reduced mass 10^{-27} kg calculate the bond constant.

Solution :- $\bar{E}_0 = \frac{1}{2}\bar{\nu} = 100\ cm^{-1} = 10^4\ m^{-1}$

$K = ?$ $\quad \mu = 10^{-27}\ kg$

$K = ?$

We know that

$$\bar{E}_0 = \frac{1}{2}\bar{\nu} = \frac{1}{2} \cdot \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}}$$

$$\bar{E}_0 = \frac{1}{4\pi c} \cdot \sqrt{\frac{K}{\mu}}$$

$$\bar{E}_0^2 = \frac{1}{16\pi^2 c^2} \frac{K}{\mu}$$

$$K = 16\pi^2 c^2 \bar{E}_0^2 \mu$$

$$K = 10^{-27} \times (100)^2 \mu$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

$$K = (4 \times 3.14 \times 3.0 \times 10^8 \times 10^4)^2 \cdot 10^{-27}$$

$$K = (37.68 \times 37.68 \times 10^8 \times 10^8 \times 10^4 \times 10^4) \; 10^{-27}$$

$$K = 1408 \times 10^{24} \times 10^{-27}$$

$$K = 1419.7 \times 10^{-3}$$

$$\boxed{K = 1.4197 \text{ Nm}^{-1}}$$

Calculate the zero point energy of Cl_2 molecule. assuming harmonic oscillation if the value of bond constant of Cl_2 is 480 Nm^{-1}

$$K = 480 \text{ Nm}^{-1}$$

μ = in kg.

Zero point energy $= (E_0) = \frac{1}{2} h\nu$

$$(E_0) = \frac{1}{2} \frac{h}{2\pi} \sqrt{\frac{K}{\mu}} \quad \text{---(1)}$$

But for $\mu_{Cl_2} = \frac{M_A \cdot M_B}{(M_A + M_B) N_0} =$

$$= \frac{M_u}{2N_0} = \frac{35.5 \times 10^{-3}}{2 \times 6.022 \times 10^{23}}$$

1 amu = 1.66

$$= 2.94 \times 10^{-26} \text{ Kg}$$

$$E_0 = \frac{1}{2} \frac{6.626 \times 10^{-34}}{4 \times 3.146} \sqrt{\frac{480}{2.94 \times 10^{-26}}}$$

$$= \frac{6.626 \times 10^{-34}}{4 \times 3.14} 10^{13} \sqrt{463.2653}$$

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

$$= \frac{6.626 \times 10^{-34}}{4 \times 3.14} \times 10^{13} \times 12.777$$

$$= \frac{84.6639 \times 10^{-21}}{12.56}$$

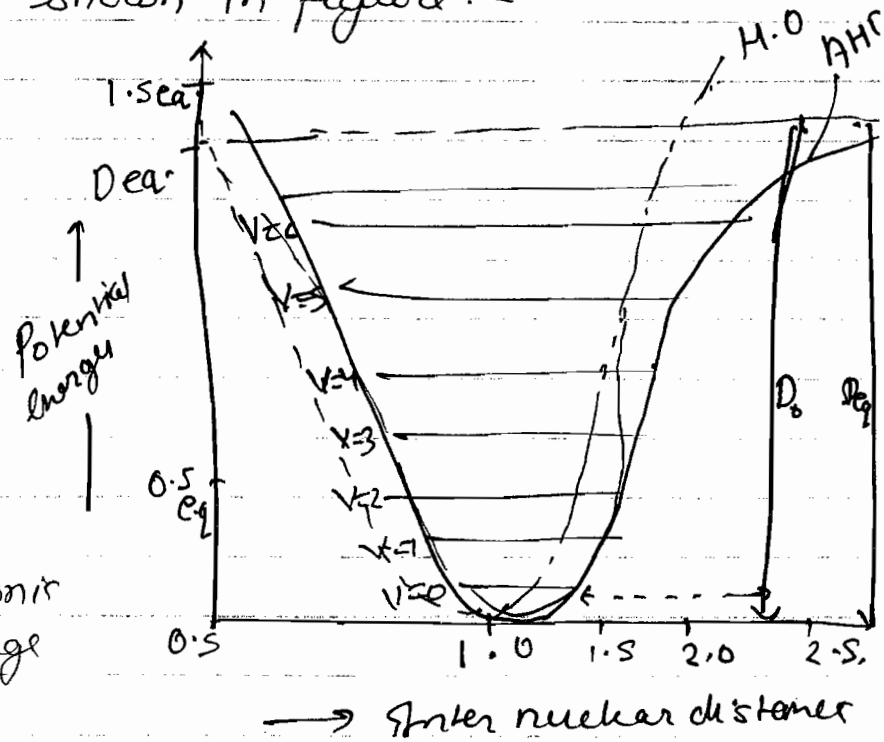
$$= 6.74 \times 10^{-21} \text{ Joule}$$

Anharmonic Oscillator :-

Anharmonic oscillator in which without vibrate any limit and can vibrates by any speed but behaviour of actual molecule does not always at ~~hea~~ harmonic oscillator they undergo dissociation after a certain elastic limit thus behaviour of actual molecule is regarded as anharmonic oscillator. It does not follow the hooks law. The potential energy of any anharmonic oscillator is derived empirically by P.M Morse and called the Morse potential which shown in figure :-

(1) There is no difference in behaviour of actual molecule and harmonic oscillator if displacement is small (about 10% of bond length).

(2) There is deviation b/w actual molecule and harmonic oscillator in higher range of bond length.



free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com

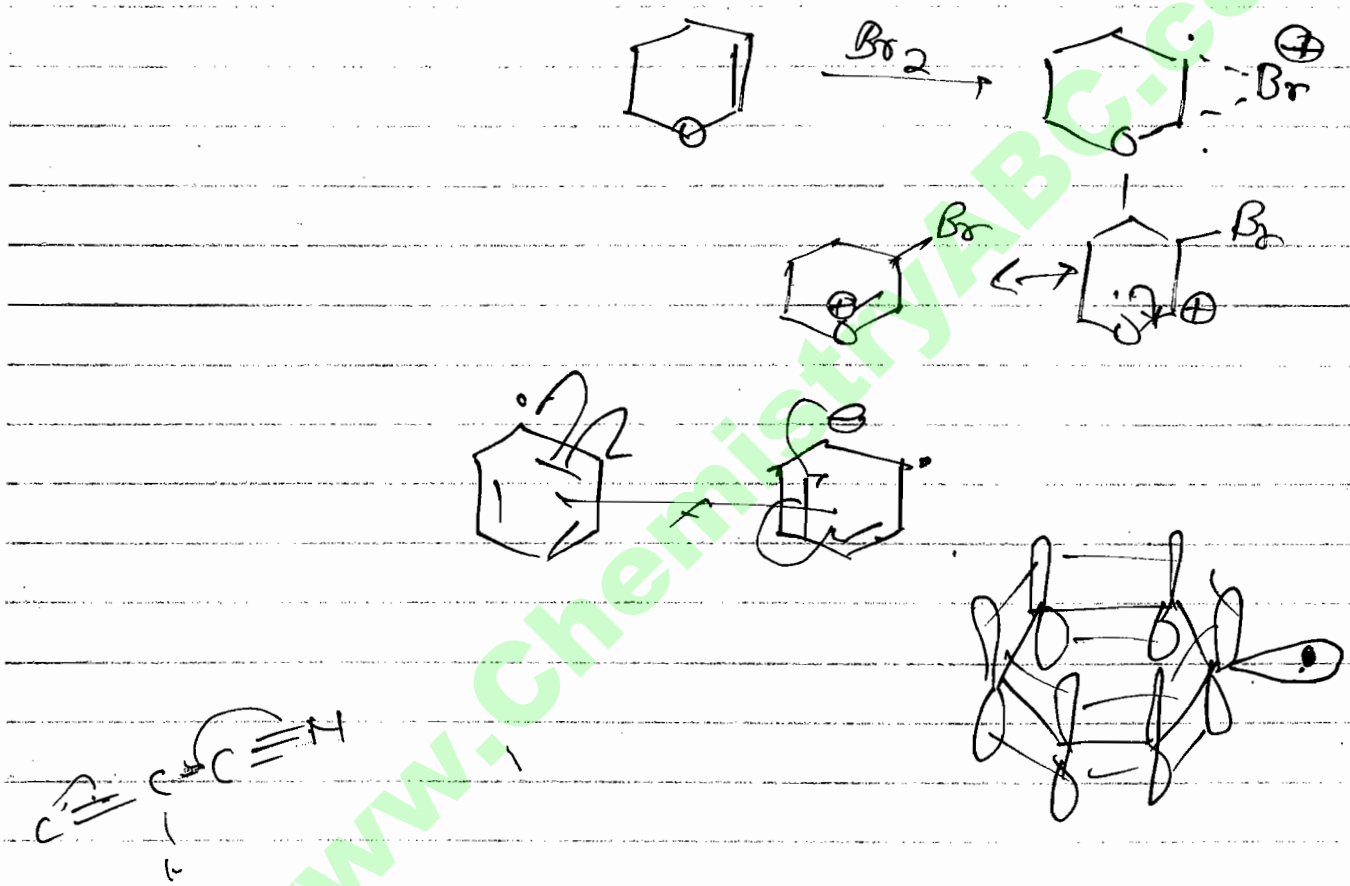
* In the highest range of bond length molecule dissociated into atoms after a certain limit of energy which is called dissociation limit. and corresponding energy is called disociation energy.

Harmonic range :-

www.ChemistryABC.com

free download all stuffs more notes and books www.ChemistryABC.com

www.ChemistryABC.com



www.ChemistryABC.com

free download all stuffs more notes and books www.ChemistryABC.com