→ Vlad — 10

Question-1: Fill the below table for the specific selection rules (2 points x 5 = 10 points):

Spectroscopy	Rule (ex: ΔN=±3, for nuclear isotopes)	Symbols explination (ex: N is the number of atoms)
Microwave Spectroscopy for rigid linear molecule	$\Delta J = \pm 1$	J = Total angular moment of the molecule.
Infra-red spectroscopy for diatomic molecule	$\Delta V = \pm 1$	V = Vibrational Quantum number
Rotational-Vibrational Spectroscopy for diatomic molecule	$\Delta J = 0, \pm 1$	J = Rotational Quantum Number.
Rotational Raman Spectroscopy for rigid linear molecule	$\Delta J = 0, \pm 2$	J = Rotational Quantum Number
Microwave Spectroscopy for rigid symmetric top molecule	$\Delta J = 0, \pm 1, \Delta K = 0$	J = Total angular momentum of the molecule.

$$A = \epsilon C L$$

$$A = \log \frac{I_0}{I}$$ or $$A = -\log T$$

(1) → Vishal

Question-2(a): State Beer-Lambert Law, and explain all 'variables' in it. (2 point)

Ans:- It states for a given material sample path length and concentration of the sample are directly proportional to the absorbance of the light.

$$A = \epsilon C L$$

ϵ = Molar Extinction Coefficient

L = Distance Covered by the light through the Solution.

A = Amount of light absorbed for a particular wavelength by the sample.

C = Concentration of the absorbing species.

the sample.

Question-2(b) Demonstrate the use of Beer-Lambert Law, by way of an example (construct a numerical example) (2 point)

Ans - Beer-Lambert law is used to dertermine the Concentration of a solute in a solution.

Ex - Let a sol^n of red dye in ethanol, we want to determine the Conc^n of the dye using spectrophotometer that measures the absorbance of light at specific wavelength.

Let molar absorptivity (ε) of dye = $0.177 \, M^{-1} cm^{-1}$

Absorbance (A) = 0.372 , Conc^n = ?

Path length (L) = 1 cm

$A = \varepsilon C L$

$C = \dfrac{A}{\varepsilon L}$

$= \dfrac{0.372}{0.177 \times 1} = 2.10 \, mol/lit.$

Question-2(c) Provide a derivation of the Beer-Lambert Law. (3 points)

⇒ The decrease in intensity of light with thickness of the absorbing medium at any point is directly proportional to the intensity of light.

$$-\frac{dI}{dx} \propto I \longrightarrow ①$$

↳ Intensity of monochromatic light

$$\boxed{\left(\frac{-dI}{dx}\right) = a\,I \longrightarrow ②}$$
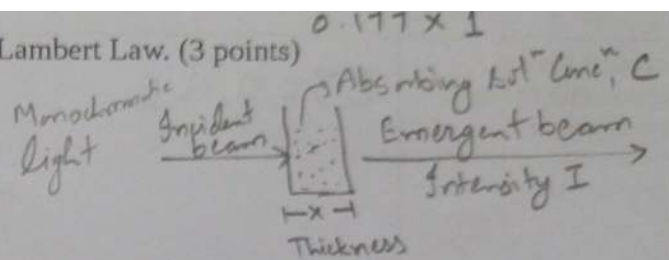
↳ Absorption co-efficient.

Rate of decrease of intensity with thickness dx

Integrating Eq② we get

$$-\ln I = ax + c \longrightarrow ③$$

At $x=0$, $I = I_0$, So, $c = -\ln I_0$

$$\ln \frac{I}{I_0} = -ax \longrightarrow ④$$

Monochromatic light

Incident beam → Absorbing substance; C → Emergent beam Intensity I

⊢x⊣

Thickness

Eq ④ can also be written as

$$I = I_0 e^{-ax} \longrightarrow ⑤$$

$$\log \frac{I}{I_0} = -\frac{a}{2.303} x \longrightarrow ⑥$$

$$\log \frac{I}{I_0} = -a'x \longrightarrow ⑦$$

Here, $a' = \frac{a}{2.303}$ is Extinction Co-efficient

$$-\ln \frac{I}{I_0}$$ is absorbance of the medium

$$A = \text{Absorbance}$$

Ques-② © Cont^d --

$$-\frac{dI}{dx} \propto C \longrightarrow ⑧$$

Two law Combined to write,

$$\frac{-dI}{dx} \propto I \times c$$

$$-\frac{dI}{dx} = b \times I \times C \longrightarrow ⑨$$

c = Conc^n (mol/L)

b = Molar absorption Coefficient.

$$\log \frac{I}{I_0} = \frac{-b}{2.303} \times C \times x \longrightarrow 10$$

$$\boxed{\log \frac{I}{I_0} = -\varepsilon \times C \times x} \longrightarrow Beer-Lambert's Law.$$

Question-2: What is the general rule for the transitions due to electro-magnetic radiation in atoms / molecules. Motivate this rule (4 points)

General rule for the transitions due to electro-magnetic radiation in atoms/molecules are —

i) Quantized Energy Levels: $e^-(s)$ in atoms/molecules exists in discrete energy levels or orbitals, represented by Quantum numbers (n, l, m, s) and correspond to specific electron configurations. The electrons occupy lowest available energy levels before moving (excited) to higher energy levels.

ii) Energy and Frequency Relationship: Energy of electro-magnetic radiation composed of photons, $E = h\nu$, where, ν is the freq. of the e.m. radiation). When an electronic transition occurs between energy levels, it can either absorb energy (move to a higher energy level) or emit energy (move to a lower energy level). And this energy difference between the energy levels, $\boxed{\Delta E = E_f - E_i} = h\nu =$ energy of absorbed/emitted photon.

$E_f =$ final state energy level, $E_i =$ initial state energy level

iii) Transitions and Spectral Lines: Transitions between energy levels result in the absorption or emission of photons with specific energies and therefore, specific frequencies (quantized). These ν correspond to specific wavelength (λ) in the e.m. spectrum, Because energy levels are quantized, only specific transitions are allowed; leading to the formation of discrete spectral lines in the spectrum.

iv) Selection Rules: The specific transitions that are allowed or forbidden are governed by selection rules, which depend on the Quantum numbers of the initial and final energy levels and are a consequence of conservation of angular momentum and other Quantum mechanical principles. Selection rules determines allowed or forbidden transitions leading to characteristic line spectra observed for the atoms/molecules,
for example,
when, $1s (e^-) \xrightarrow{transits} 2s \Rightarrow$ spherical change migration $\Rightarrow$ no dipole moment change $\Rightarrow$ forbidden transition.
Again, when, $1s (e^-) \xrightarrow{transits} 2p \Rightarrow$ dipole moment change $\Rightarrow$ allowed transition

Question-4: In carbon tetrachloride molecule (C Cl$_4$), the C-Cl bond is 0.177 nm. Find the frequency of lowest energy transtion. (nm is nano meters) [3 points]

we have, $\Delta E = h\nu$, where, $\Delta E =$ energy difference between two levels,

$h =$ Planck's constant $\approx 6.626 \times 10^{-34}$ Js
$\nu =$ frequency of the transition.

Now, we know, $\nu = c/\lambda$, where, $c =$ speed of light in vacuum $\approx 3 \times 10^8$ ms^{-1},

and $\lambda =$ wavelength of the transition $\simeq 2L$, where,

$L =$ bond length $= 0.177$ nm $= 0.177 \times 10^{-9}$ m (for C-Cl bond)

Thus, $\Delta E = h\nu = h\,c/\lambda = \dfrac{hc}{2L} = \dfrac{6.626 \times 10^{-34}\ \text{Js} \times 3 \times 10^8\ \text{ms}^{-1}}{2 \times 0.177 \times 10^{-9}\ \text{m}}$

$\Rightarrow \Delta E \approx 5.615 \times 10^{-16}$ J

$\therefore$ frequency of lowest transition,

$\nu = \Delta E / h = \dfrac{5.615 \times 10^{-16}\ \text{J}}{6.626 \times 10^{-34}\ \text{Js}} \approx 8.475 \times 10^{17}$ Hz

Question-6: In carbon tetrachloride molecule (C Cl$_4$), the C-Cl bond is 0.177 nm. Find the frequency of lowest energy transtion. (nm is nano meters) [3 points]

$$m\left(^{35}Cl\right) \approx 35 \text{ amu}$$

$$I = \frac{8}{3} m\left(^{35}Cl\right) R^2_{C-Cl} = \frac{8}{3} \times 5.812 \times 10^{-26} \text{ kg} \times \left(0.177 \times 10^{-9} \text{ m}\right)^2$$

$$= 4.855 \times 10^{-45} \text{ kg m}^2$$

Rotational Constant   (assuming $c = 3 \times 10^8 \text{ ms}^{-1}$)

$$\tilde{B} = \frac{\hbar}{4\pi c I} \approx 5.7656 \text{ m}^{-1} \approx 0.057656 \text{ cm}^{-1}$$

freq. of lowest transition, for $J = 0$, $J' = J+1 = 1$

$$\tilde{F}(J+1) - \tilde{F}(J) = \tilde{B}(J+1)(J+2) - \tilde{B} J (J+1)$$

$$= 2\tilde{B}(J+1) = 2 \times 0.057656 \text{ cm}^{-1}$$

$$\approx 0.1153 \text{ cm}^{-1}$$

$$\approx 3.46 \times 10^9 \text{ Hz}$$

Question-5: Ammonia (N H_3) molecule has B = 9.977 cm^{-1}, and A = 12.077 cm^{-1}. Draw schematic diagram of the rotational spectrum, clearly indicate the frequencies, spacing etc.. [3 points]

we have, $A = 12.077$ cm^{-1} $= 3.6206 \times 10^{11}$ Hz, $B = 9.977$ cm^{-1} $= 2.9910 \times 10^{11}$ Hz

rotational spectra of diatomic molecule like NH_3 can be described by

$$E_J = B \cdot J \cdot (J+1) - D \cdot J^2 (J+1)^2 \quad , \text{where,}$$

B = rotational constant, D = centrifugal distortion constant
J = rotational quantum no.

And, we have, $D = A - 2B = -2.3614 \times 10^{11}$ Hz

So, $\nu = \dfrac{E_J - E_0}{h}$;

when, $J=0$, $E = E_0 = 0$

$J=1$, $E_1 = 2B - 4D$, $\nu_1 = \dfrac{2B-4D}{h}$

$J=2$, $E_2 = 6B - 36D$, $\nu_2 = \dfrac{6B-36D}{h}$

$J=3$, $E_3 = 12B - 144D$, $\nu_3 = \dfrac{12B-144D}{h}$

$\therefore$ transition from, $J_{1 \to 0} = 0 \leftarrow 1$, $\nu_{1 \to 0} = \dfrac{2B-4D}{h}$

$J_{2 \to 0} = 0 \leftarrow 2, \nu_{2 \to 0} = \dfrac{6B-36D}{h}$; $J_{2 \to 1} = 1 \leftarrow 2$, $\nu_{2 \to 1} = \dfrac{4B-32D}{h}$

$J_{3 \to 0} = 0 \leftarrow 3, \nu_{3 \to 0} = \dfrac{12B-144D}{h}$; $J_{3 \to 1} = 1 \leftarrow 3$, $\nu_{3 \to 1} = \dfrac{10B-140D}{h}$; $J_{3 \to 2} = 2 \leftarrow 3$, $\nu_{3 \to 2} = \dfrac{6B-108D}{h}$

symmetric top, $\Delta K = 0$

6

NH$_3 \rightarrow$ Symmetric rotor, $\}\rightarrow I_1 = I_2 \neq (I_3 \neq 0)$

rigid molecule $\} \Rightarrow \tilde{F}(J,K) = \tilde{B}J(J+1) + (\tilde{A}-\tilde{B})K^2$

Selection Rule : $\Delta J = \pm 1$,

$\Delta K = 0$

$\Delta M_J = 0, \pm 1$ $\therefore \tilde{\lambda}_{obs}$ (wave no.) $= [\tilde{F}(J',K') - \tilde{F}(J,K)]$

$= 9.977 \text{ cm}^{-1}. (J)(J+1) + 2.1 \text{ cm}^{-1}.(K^2)$

for $J \rightarrow (J+1)$, $\tilde{\lambda}_{obs} = \tilde{B}(J+1)(J+2) - \tilde{B}(J)(J+1) = 2\tilde{B}(J+1)$

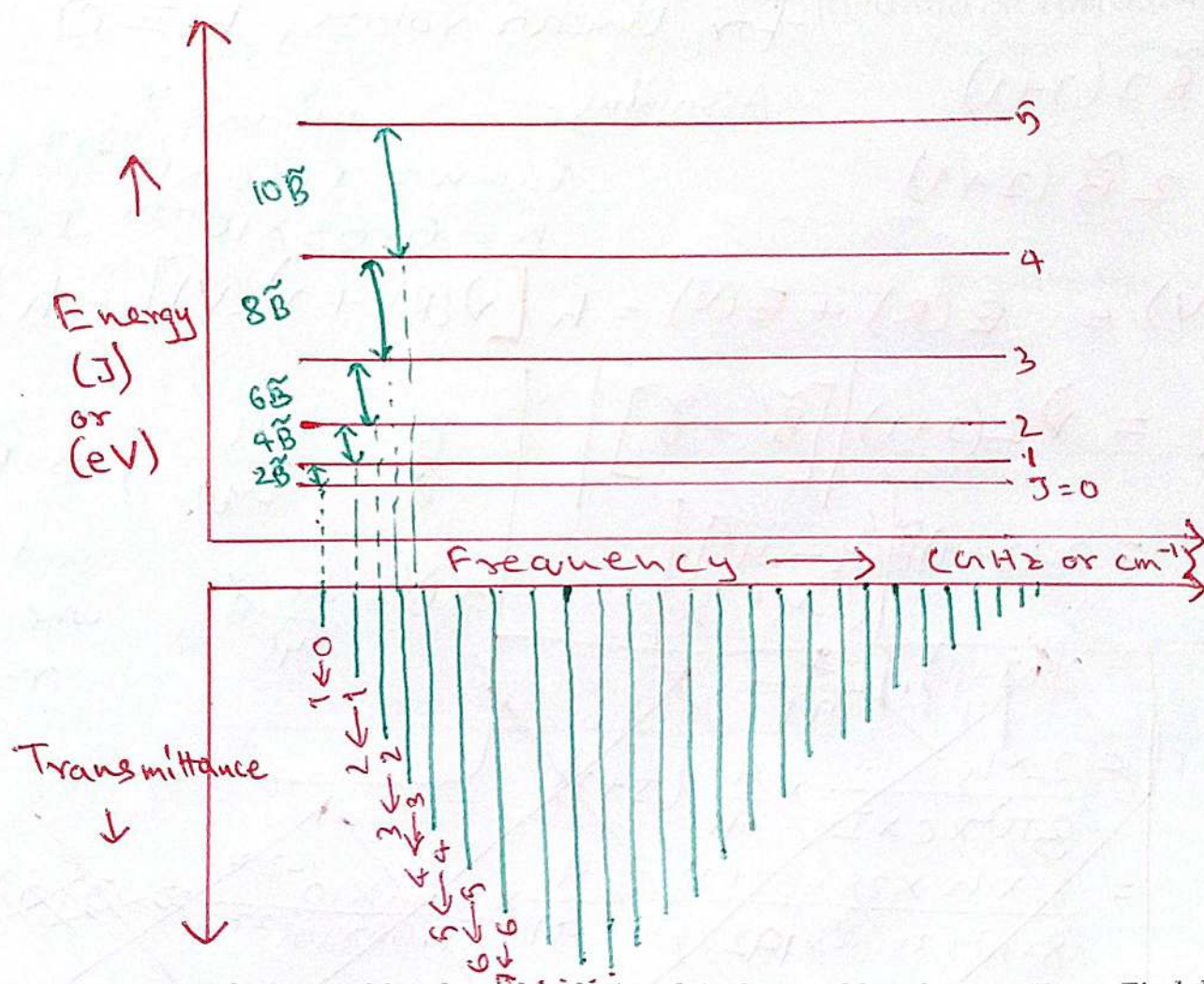| J	0	1	2	3 ...
$\tilde{\nu}/(\text{cm}^{-1})$	19.95	39.91	59.86	79.82
$\nu/(\text{GHz})$	598.2	1196	1795	2393

line spacing : 19.95 cm^{-1} or (598.1) GHz

Intensity I of a transition at ν_{obs}

$I(\nu_{obs}) = e^{-\frac{mc^2(\nu_{obs}-\nu_0)^2}{2\nu_0^2 k_B T}}$ [Gaussian function]

$f(x) = ae^{-(x-b)^2/2\sigma^2}$
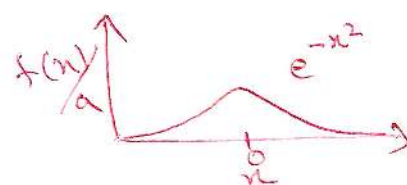
e^{-x^2}

$f(x)$

a

b

x

Question-5: Ammonia (NH_3) molecule has $B = 9.977$ cm^{-1}, and $A = 12.077$ cm^{-1}. Draw schematic diagram of the rotational spectrum, clearly indicate the frequencies, spacing etc.. [3 points]

Question-6: In carbon tetrachloride molecule (CCl_4), the C-Cl bond is 0.177 nm. Find the frequency

Rotation-Vibrational spectroscopy of a gas mixture of $^{12}C^{16}O$ and $^{13}C^{16}O$ has each peak as a doublet (twin peak) with small frequency difference. Find this frequency difference.

$\Rightarrow$ due to Isotope Effect,

$$m_{^{12}C} < m_{^{13}C}$$

$$\therefore \mu_{^{12}C^{16}O} = \frac{12 \times 16}{12+16} = \frac{192}{28} \text{ amu}$$

and, $\mu_{^{13}C^{16}O} = \frac{13 \times 16}{13+16} = \frac{208}{29} \text{ amu}$

Now, we have, $E_{Total} = E_{(R)} + E_{(V)}$

and, the ro-vibrational spectra can be defined by

$$\tilde{S}(v, J) = \underbrace{\tilde{G}(v)}_{\text{vibrational}} + \underbrace{\tilde{F}(J)}_{\text{rotational}}$$

where,

$$\tilde{G}(v) = (v + \tfrac{1}{2})\tilde{v} \; ; \; \tilde{v} = \frac{v}{c} = \frac{1}{2\pi c}\sqrt{\frac{k_f}{\mu}}$$

and,

$$\tilde{F}(J) = \tilde{B}J(J+1) + (\tilde{A} - \tilde{B})K^2$$

$\therefore$ CO is a linear molecule, $K \equiv 0$

$$\therefore \tilde{F}(J) = \tilde{B}J(J+1) \; ; \; \tilde{B} = \frac{\hbar}{4\pi c I}$$

$$\therefore I = \mu R^2 \Rightarrow \tilde{B} = \frac{h}{8\pi^2 c \mu R^2}$$

and R is $C \equiv O$ bond length

Assuming $C \equiv O$ is a harmonic oscillator, selection rule, $\Delta v = \pm 1$,

$$\Delta\tilde{G}_{v+1/2} = \tilde{G}(v+1) - \tilde{G}(v) = \tilde{v}$$

and we have,

P branch transitions ; $\Delta J = -1$;
$$\tilde{\nu}_P(J) = \tilde{\nu} - 2\tilde{B}J$$

Q branch transitions ; $\Delta J = 0$;
$$\tilde{\nu}_Q(J) = \tilde{\nu}$$

R branch transitions ; $\Delta J = +1$;
$$\tilde{\nu}_R(J) = \tilde{\nu} + 2\tilde{B}(J+1)$$

So, when $J = 0$; $\tilde{\nu}_P(J) = \tilde{\nu}_Q(J) = \tilde{\nu}$ and $J = -1$; $\tilde{\nu}_R = \tilde{\nu}_Q = \tilde{\nu}$

again at $J = 0, -1$

$$\tilde{F}(J) = \quad 0$$

$$\therefore \quad \tilde{S}(\nu, J) = \tilde{G}(\nu) = (\nu + \tfrac{1}{2})\tilde{\nu}$$

Applying selection rule, $\Delta \nu = \pm 1$

(assumption $\Rightarrow$ $C \equiv O$ is a harmonic oscillator)
$$\Delta \tilde{S}(\nu, J) = \tilde{\nu} \quad = \quad \tilde{\nu}/c$$

Thus; frequency difference between doublet peak of gas mixture of $^{12}C^{16}O$ and $^{13}C^{16}O$ is

$$\Delta \tilde{\nu} = \left| \tilde{\nu}_{^{12}C^{16}O} - \tilde{\nu}_{^{13}C^{16}O} \right|$$

$$= \frac{1}{2\pi} \left| \left(\sqrt{\frac{k_f}{M_{^{12}C^{16}O}}} - \sqrt{\frac{k_f}{M_{^{13}C^{16}O}}} \right) \right|$$

Question-6: Rotation-vibrational spectroscopy of a gas mixture of ^{12}C ^{16}O and ^{13}C ^{16}O has each peak as a doublet (twin peak) with a small frequency difference. Find this freq difference; for the all variables not given take reasonable values and state them clearly. (4 pts)

Isotope effect arising due to masses of atoms in the molecules contributes to the freq. difference between the doublet peaks in the rotation-vibrational spectrum of a gas mixture of ^{12}C ^{16}O and ^{13}C ^{16}O.

So, $\Delta \nu = |\nu_1 - \nu_2| = \frac{1}{2\pi} \cdot \sqrt{k_f} \left(\frac{1}{\sqrt{\mu_1}} - \frac{1}{\sqrt{\mu_2}} \right)$, where,

$\Delta \nu$ = freq. difference.

ν_1 and ν_2 = freq. of doublet peak of ^{12}C ^{16}O and ^{13}C ^{16}O respectively.

k_f = force constant for the bond $(C=O)$

(assuming k_f to be similar in both the cases for diatomic molecule like CO) {a reasonable value for CO bond is $\sim 1900 \, Nm^{-1}$}

μ_1 and μ_2 = reduced mass of ^{12}C ^{16}O and ^{13}C ^{16}O respectively

The reasonable value for mass of $^{12}C = 12$ amu

$^{13}C = 13$ amu

$^{16}O = 16$ amu

So, $\mu_1 = \frac{12 \times 16}{12 + 16}$ amu $= 6.857$ amu $= 6.857 \times 1.66054 \times 10^{-27}$ kg

and, $\mu_2 = \frac{13 \times 16}{13 + 16}$ amu $= 7.172$ amu $= 7.172 \times 1.66054 \times 10^{-27}$ kg

Thus, $\nu_1 = \frac{1}{2\pi} \cdot \sqrt{\frac{1900 \, kg \, s^{-2}}{6.857 \times 1.66054 \times 10^{-27} \, kg}} \approx 6.501 \times 10^{13}$ Hz

and, $\nu_2 = \frac{1}{2\pi} \cdot \sqrt{\frac{1900 \, kg \, s^{-2}}{7.172 \times 1.66054 \times 10^{-27} \, kg}} \approx 6.357 \times 10^{13}$ Hz

$\therefore \Delta \nu = |\nu_1 - \nu_2| = (6.501 - 6.357) \times 10^{13}$ Hz

$= 0.144 \times 10^{13}$ Hz

$= 1.44 \times 10^{12}$ Hz

$\approx 4800 \, m^{-1}$

$\Rightarrow \boxed{\Delta \nu \approx 48 \, cm^{-1}}$