

Vigal - 10

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

Spectroscopy	Rule (ex: $\Delta N= \pm 1$ , for nuclear isotopes)	Symbols explanation (ex: N is the number of atoms)
Microwave Spectroscopy for rigid linear molecule	$\Delta J = \pm 1$	$J$ : Total angular momentum 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.

$$A = \epsilon CL$$

Q) Visited

$$A = \log \frac{I_0}{I} \quad \text{or}$$

$$A = -\log T$$

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.

$$A = \epsilon CL$$

$\epsilon$  = Molar Extinction Coefficient.

$L$  = Distance Covered by the light through the solution.

$C$  = Concentration of the absorbing species.

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

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 determine the Concentration of a solute in a solution.

Ex - Let a sol<sup>n</sup> of red dye in ethanol, we want to determine the Conc<sup>n</sup> of the dye using Spectrophotometer that measures the absorbance of light at specific wavelength.

Let molar absorptivity ( $\epsilon$ ) of dye =  $0.177 \text{ M}^{-1}\text{cm}^{-1}$        $A = \epsilon CL$

Absorbance ( $A$ ) = 0.372      , Conc<sup>n</sup> = ?

Path length ( $L$ ) = 1 cm

$$C = \frac{A}{\epsilon L}$$
$$= \frac{0.372}{0.177 \times 1} = 2.10 \text{ mol/lit.}$$

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.

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

↳ Intensity of monochromatic light

$$-\frac{dI}{dx} = a I \rightarrow ②$$

↳ Absorption Co-efficient

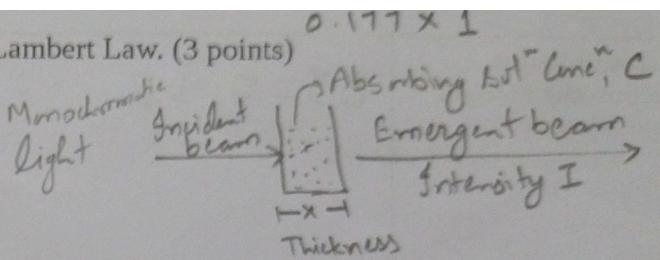
Rate of decrease of intensity with thickness  $dx$

Integrating Eq ② we get

$$-\ln I = ax + c \rightarrow ③$$

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

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



Eq ④ can also be written as

$$I = I_0 e^{-ax} \rightarrow ⑤$$

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

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

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

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

A = Absorbance

Ques - ② ③ Cond :-

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

Laws combined to write.

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

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

c = Concentration (mol/L)

b = molar absorption coefficient

$$\log \frac{I}{I_0} = \frac{-b}{2.303} \times c \times x \rightarrow 10$$

$$\log \frac{I}{I_0} = -E \times c \times x$$

→ 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,  $\nu$  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 correspond to specific wavelength ( $\lambda$ ) 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 ~~to~~ quantum mechanical principles. Selection rules determines allowed or forbidden transitions leading to characteristic line spectra observed for the atoms / molecules,

for example,

When,  $1s(e^-) \xrightarrow{\text{transits}} 2s \Rightarrow$  spherical charge migration  $\Rightarrow$  no dipole moment change  $\Rightarrow$  forbidden transition.

Again, when,  $1s(e^-) \xrightarrow{\text{transits}} 2p \Rightarrow$  dipole moment change  $\Rightarrow$  allowed transition

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

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

$h$  = Planck's constant  $\approx 6.626 \times 10^{-34} \text{ Js}$

$\nu$  = frequency of the transition.

Now, we know,  $\nu = c/\lambda$ , where,  $c$  = speed of light in vacuum  $\approx 3 \times 10^8 \text{ m s}^{-1}$ , and  $\lambda$  = wavelength of the transition  $= 2L$ , where

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

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

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

$\therefore$  frequency of lowest transition,

$$\nu = \Delta E / h = \frac{5.615 \times 10^{16} \text{ J}}{6.626 \times 10^{-34} \text{ Js}} \approx \underline{\underline{3.475 \times 10^{47} \text{ Hz}}}$$

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

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

$$\text{I} = \frac{8}{3} m(^{35}\text{Cl}) R_{\text{c-a}}^2 = \frac{8}{3} \times 5.812 \times 10^{-26} \text{ kg} \times (0.177 \times 10^{-9} \text{ m})^2 \\ = 4.855 \times 10^{-49} \text{ kg m}^2$$

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

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

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 ( $\text{NH}_3$ ) molecule has  $B = 9.977 \text{ cm}^{-1}$ , and  $A = 12.077 \text{ cm}^{-1}$ . Draw schematic diagram of the rotational spectrum, clearly indicate the frequencies, spacing etc.. [3 points]

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

*rotational spectra of diatomic molecule like  $\text{NH}_3$  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  
 $J$  = rotational quantum no. constant

~~constant~~

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

$$\text{so, } \Delta\nu = \frac{E_3 - E_0}{h}; \quad \text{when, } J=0, E=E_0=0$$

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

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

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

.....

$\therefore$  transition from,  $J=0 \leftarrow 1$ ,  $\Delta\nu_{1\leftarrow 0} = \frac{2B - 4D}{h}$

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

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

Question-5: Ammonia ( $\text{NH}_3$ ) molecule has  $\tilde{B} = 9.977 \text{ cm}^{-1}$ , and  $\tilde{A} = 12.077 \text{ cm}^{-1}$ . Draw schematic diagram of the rotational spectrum, clearly indicate the frequencies, spacing etc.. [3 points]

$\text{NH}_3 \rightarrow$  symmetric rotor,  $\tilde{I} = \tilde{I}_1 + (\tilde{I}_3 \neq 0)$

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

$$\begin{aligned} \text{Selection Rule: } & \Delta J = \pm 1, \\ & \Delta K = 0 \\ & \Delta M_J = 0, \pm 1 \quad \therefore \tilde{\lambda}_{\text{obs}}^{(\text{wave})} = [\tilde{F}(J', K') - \tilde{F}(J, K)] \\ & \text{for } J \rightarrow (J+1), \quad \tilde{\lambda}_{\text{obs}} = \tilde{B}(J+1)(J+2) - \tilde{B}(J)(J+1) = 2\tilde{B}(J+1) \end{aligned}$$

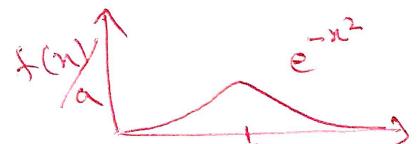
$J$	0	1	2	3	...
$\tilde{\lambda}/(\text{cm}^{-1})$	19.95	39.91	59.86	79.82	
$\tilde{\lambda}/(\text{GHz})$	598.2	1196	1795	2393	

Line spacing:  $19.95 \text{ cm}^{-1}$  or  $(598.1) \text{ GHz}$

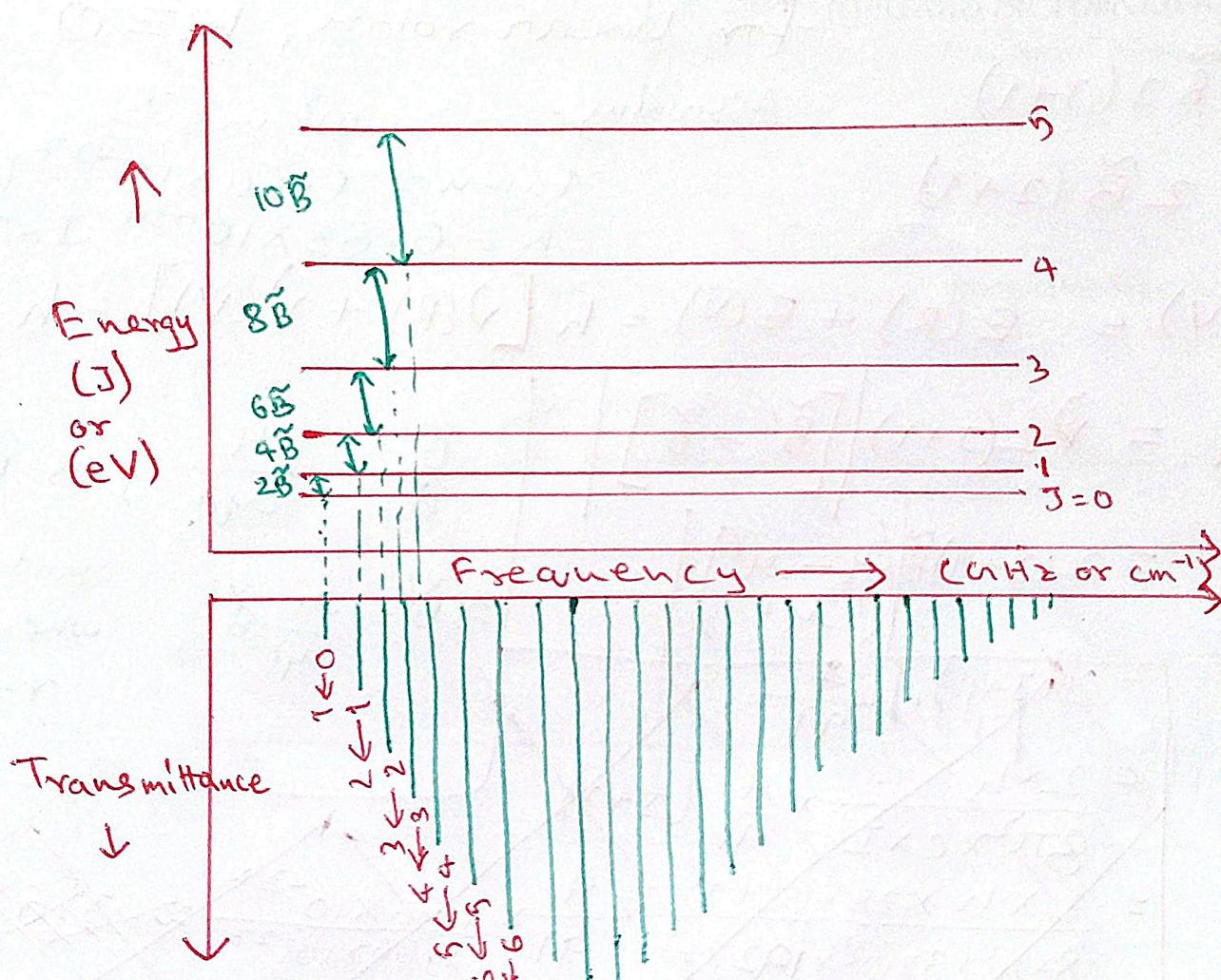
Intensity  $I$  of a transition at  $\tilde{\lambda}_{\text{obs}}$

$$I(\tilde{\lambda}_{\text{obs}}) = e^{-\frac{mc^2(\tilde{\lambda}_{\text{obs}} - \tilde{\lambda}_0)^2}{2\tilde{\lambda}_0^2 k_B T}} \quad [\text{Gaussian function}]$$

$$f(x) = ae^{-\frac{(x-\mu)^2}{2\sigma^2}}$$



Question-5: Ammonia ( $\text{NH}_3$ ) molecule has  $B = 9.977 \text{ cm}^{-1}$ , and  $A = 12.077 \text{ cm}^{-1}$ . Draw schematic diagram of the rotational spectrum, clearly indicate the frequencies, spacing etc.. [3 points]



Question-6: In carbon tetrachloride molecule ( $\text{CCl}_4$ ), the C-Cl bond is  $0.177 \text{ nm}$ . Find the frequency

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Rotation-Vibrational Spectroscopy of  
a gas mixture of  $^{12}\text{C}^{16}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$   
has each peak as a doublet

(twin peak) with small frequency  
difference. Find this frequency difference

⇒ due to Isotope Effect,

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

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

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

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

and, the ro-vibrational spectra can be defined by

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

where,

$$\tilde{C}_v(v) = (v + \frac{1}{2})\tilde{\nu}; \tilde{\nu} = \frac{J}{c} = \frac{1}{2\pi c} \sqrt{\frac{kT}{\mu}}$$

and,

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

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

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

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

and R is C=O bond length

Assuming C=O is a harmonic oscillator, Selection rule,  $\Delta J = \pm 1$ ,

$$\Delta \tilde{C}_{v+\frac{1}{2}} = \tilde{C}_{v+\frac{1}{2}} - \tilde{C}_v = \tilde{\nu}$$

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

$$J = 0, -1$$

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

$$\therefore \tilde{s}(\nu, J) = \tilde{G}(\nu) = (\nu + \gamma_2) \tilde{\nu}$$

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

(assumption  $\Rightarrow C = 0$  is a harmonic oscillator)

$$\Delta \tilde{s}(\nu, J) = \tilde{\nu} \cancel{\nu} = \gamma / c$$

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

$$\Delta \nu = |\nu_{^{12}\text{C}^{16}\text{O}} - \nu_{^{13}\text{C}^{16}\text{O}}|$$

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

Question-6: Rotation-vibrational spectroscopy of a gas mixture of  $^{12}\text{C}^{16}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$  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 ~~isotopes~~ contributes to the freq. difference between the doublet peaks in the rotation-vibrational spectrum of a gas mixture of  $^{12}\text{C}^{16}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$ .

$$\text{So, } \Delta\nu = |\nu_1 - \nu_2| = \frac{1}{2\pi} \cdot \sqrt{k_f} \cdot \left( \frac{1}{\sqrt{M_1}} - \frac{1}{\sqrt{M_2}} \right), \text{ where,}$$

$\Delta\nu$  = freq. difference.

$\nu_1$  and  $\nu_2$  = freq. of doublet peak of  $^{12}\text{C}^{16}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$  respectively.

$k_f$  = force constant for the bond ( $\text{C=O}$ )

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

$M_1$  and  $M_2$  = reduced mass of  $^{12}\text{C}^{16}\text{O}$  and  $^{13}\text{C}^{16}\text{O}$  respectively

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

$^{13}\text{C} = 13 \text{ amu}$

$^{16}\text{O} = 16 \text{ amu}$

$$\text{So, } M_1 = \frac{12 \times 16}{12 + 16} \text{ amu} = 6.857 \text{ amu} = 6.857 \times 1.66054 \times 10^{-27} \text{ kg}$$

$$\text{and, } M_2 = \frac{13 \times 16}{13 + 16} \text{ amu} = 7.172 \text{ amu} = 7.172 \times 1.66054 \times 10^{-27} \text{ kg}$$

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

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

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

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

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

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

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