Indian Institute of Technology, Jodhpur

Minor 1

Chemistry (CYL1010)

Total Marks [30]

Date: 8.09.23   Venue: LHB

NB: Calculations without units will fetch no marks. All questions are mandatory.

Q.1. You wish to carry out a photochemical reaction using a UV lamp filtered to generate 290 nm radiation with 25 W power. Your reactants are sufficiently concentrated to absorb all the radiation from this lamp, and the reaction's photochemical product (overall) quantum yield is 0.28. How many moles of product will you generate per hour of illumination?   [4]

Ans: 25-watt power = 25 Js^{-1}
Hence energy absorbed per hour = 25 × 3600 J
For 295 nm radiation energy corresponding to 1 mole of photons is
$$E = N_A h \frac{c}{\lambda}$$
$$E = \frac{6.022 \times 10^{23} mol^{-1} \times 6.626 \times 10^{-34} Js \times 3 \times 10^8 ms^{-1}}{295 \times 10^{-9} m} = 0.4057 \times 10^6 Jmole^{-1}$$
Hence, in one hour no. of moles of photons absorbed will be
$$no.\,of\,moles\,absorbed\,per\,hour = \frac{25 \times 3600\,J}{0.4057 \times 10^6 Jmole^{-1}} = 0.2218\,mole$$

$$\varphi = \frac{no.\,of\,moles\,of\,product}{no.\,of\,moles\,of\,photon\,absorbed}$$
Hence no. moles produced per hour will be
$$no.\,of\,moles\,produced\,per\,hour = 0.28 \times 0.2218\,moles = 6.211 \times 10^{-2} moles$$

Q.2. Why do spectral lines have natural linewidth? [2]

Ans: Spectral lines have natural linewidth because of Heisenberg uncertainty principle which states that the energy (E) and lifetime (τ) of an excited state cannot be determined simultaneously. In case the lifetime of an excited state is precisely known the energy (E) will have a range of values giving rise to a width of the line (Δv).

$$\Delta E \Delta \tau \geq h/4\pi$$

Q.3. Study the following Jablonski diagram very carefully and identify the misrepresentations (incorrect information) in the diagram. Reason out why do you think these are incorrect? In the diagram some arrows are curvy, and some are vertical. Why are they represented in that way? [2+2 = 4]
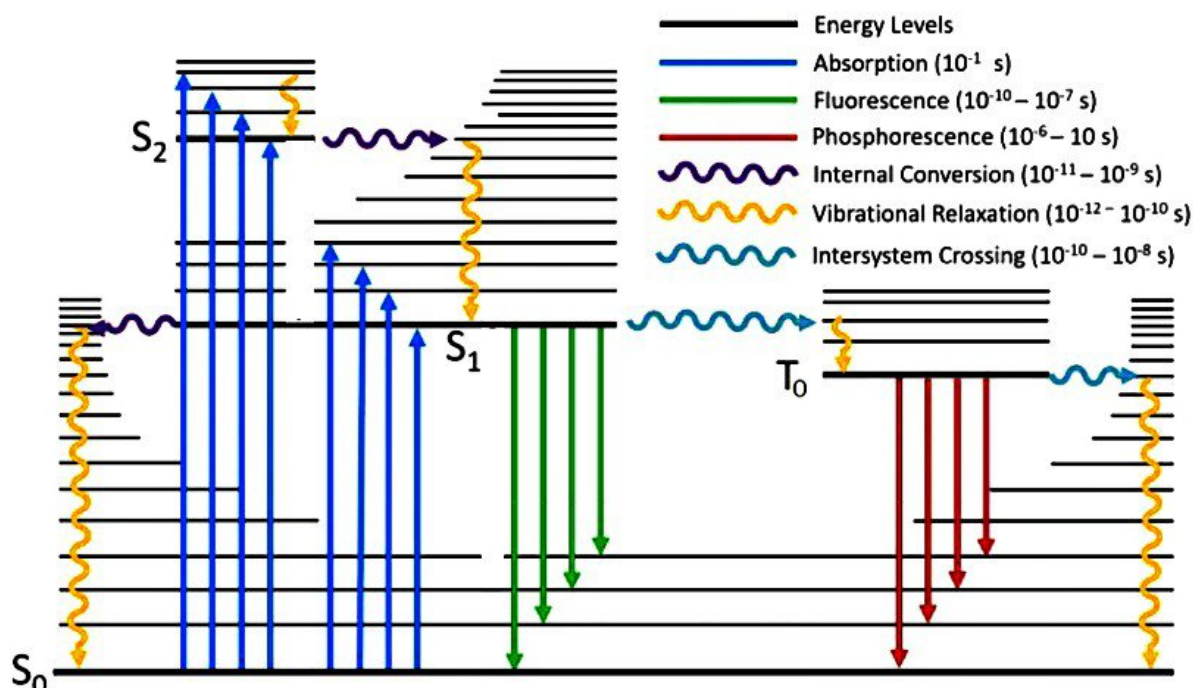
Ans: There are two mistakes in the above Jablonski diagram. I) Triplet ground state T0 is non-existent, however the diagram shows T0. A triplet state corresponds to two electrons with parallel spin orientation. Such arrangement is a higher energy state than the singlet state with two electrons having antiparallel spin orientation. Hence T0 does not occur.

II) the time taken to absorb a photon is 10^{-15}s while the diagram shows 10^{-1}s. Absorption of photon is the fastest process in the Jablonski diagram and therefore cannot be of the order of 10^{-1}s.

In the diagram curvy arrows represent energy dissipation due to vibrational transition or internal conversion or intersystem crossing. These processes are non-radiative in nature and therefore do not involve photon absorption or emission. During these processes the nuclear coordinates can change. On the other hand, the vertical straight lines represent radiative processes such as photon absorption and emission. During these processes the nuclear coordinates do not change since the electron's motion is much faster that the nuclear motion. This is because of Frank-Condon principle.

Q.4. Select the correct statements regarding a C–H bond vibration assuming a force constant of 4.89×10^2 N/m. [Please justify your selection with proper calculation, there is no mark for only writing the correct option]   [6]

a) The absorption frequency of the bond appears at 3004.89 cm^{-1}.
The statement is correct. In the following the required calculation is shown. If we use exact atomic mass the result will be in 3004.89 cm^{-1}. Since approximations are taken the value deviates a bit.

Absorption frequency of the C-H bond can be given as

$$\bar{v}(cm^{-1}) = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

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

Now m1 = 12.01 g/mole; m2 = 1.00 g/mole

$\mu = \frac{m_1 m_2}{m_1 + m_2}$ g/mole = 0.9231 g/mole

Reduced mass can be written in kg/molecule as follows:

$$\mu = \frac{0.9231\,g}{mole} \times \frac{1\,kg}{1000\,g} \times \frac{1\,mole}{6.02 \times 10^{23}\,molecules} = 1.5329 \times 10^{-27}\,kg/molecule$$

$$\bar{v} = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}} = \frac{1}{2 \times 3.141 \times 2.99 \times 10^{8} ms^{-1}} \sqrt{\frac{4.89 \times 10^{2}\,N/m}{1.5329 \times 10^{-27}\,kg/molecule}}$$

$$= \frac{1}{18.783 \times 10^{8} ms^{-1}} \sqrt{\frac{4.89 \times 10^{2}\,kg\,m\frac{s^{-2}}{m}}{1.5329 \times 10^{-27}\frac{kg}{molecule}}}$$

$$\bar{v} = \frac{1}{18.783 \times 10^{8}} \times 0.564 \times 10^{15}\,m^{-1} = 3002.715\,cm^{-1}$$

b) In case deuterium replaces the H in the CH bond the vibrational frequency shift towards shorter wavelength.

One can use the similar calculation to calculate the vibrational frequency. The mass of D will be 2g/mole. This statement is incorrect. Since as we increase the molecular mass, the vibrational frequency reduces hence the wavelength moves to the longer wavelength.

c) The reduced mass for the CH bond is 1.536×10^{-27} kg.
The above statement is correct and can be checked using the reduced mass calculation.

d) The CH bond does not scatter photon.
The above statement is incorrect. All bond vibrations scatter photons as Rayleigh scattering.

e) 3.32 μm of IR light is absorbed by the CH bond.
This is the wavelength of the C-H bond vibration. When vibration frequency is converted into wavelength this is the value of the λ. This can also be check from the first set of equation. The statement is therefore correct.

Q.5. Answer the following questions: [1+1+1+1 = 4]
a) Why is IR spectroscopy called spectroscopy of heat?
The wavelength of infrared waves is sufficient to set atoms and molecules into vibrational motion. Hence whenever an object is encountered with infrared radiations, produces heat due to the vibrations of atoms. This is the reason why infrared waves are called spectroscopy of heat.

b) What are the factors affecting intensities and position of IR bands?
The most important factor that influences the intensity of an IR absorption band is the change in dipole moment that occurs during a vibration.

-Strongly polar bonds such as carbonyl groups (C=O) produce strong bands.
-Medium polarity bonds and asymmetric bonds produce medium bands.
-Weakly polar bond and symmetric bonds produce weak or non-observable bands.

| STRONG | MEDIUM | WEAK | NOT OBSERVABLE |
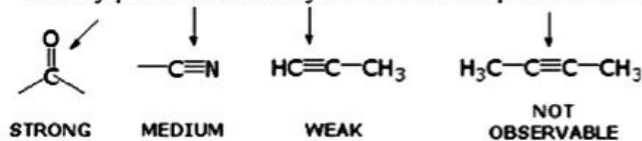
Or

The intensity of an absorption band depends on the polarity of the bond, and a bond with higher polarity will show a more intense absorption band. The intensity also depends on the number of bonds responsible for the absorption, and an absorption band with more bonds involved has a higher intensity.

c) Raman scattering is intrinsically low in intensity – what do we need to do to increase the same?

Ans: We need to use Laser beams as incident photons. Laser beams corresponds to high intensity radiation with a narrow wavelength range. Since incident photons are increased in numbers, the Raman scatter photons also increases in numbers resulting higher intensity.
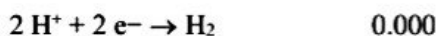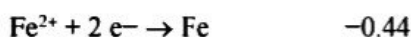
d) What is the basic difference between a Raman scattered photon and a fluorescence photon?

Ans: A Raman scattered photon is generated due to inelastic collisions of an incident photon with molecular bond vibrations. Such a collision causes transition of the molecule to a virtual vibrational energy level. On the other hand, fluorescence photon is emitted from an excited singlet state because of absorption of an incident photon. This process involves transition of electrons from ground singlet state to an excited singlet state.

Q.6. For how many minutes could a Cu/Zn cell keep a 100-watt lamp lit if 1 mole of reactants are transformed into product and that the cell voltage is 90 % of the $E°$. [3]
[Consider the Cu/Zn galvanic cell and note that $1 \text{ J s}^{-1} = 1$ watt]

Given:

$Zn^{2+} + 2 \text{ e}- \rightarrow Zn$	−0.763
$Fe^{2+} + 2 \text{ e}- \rightarrow Fe$	−0.44
$2 H^+ + 2 \text{ e}- \rightarrow H_2$	0.000
$Cu^{2+} + 2 \text{ e}- \rightarrow Cu$	+0.337

From the above table one may calculate $E_0 = 1.10$ V. 90% of the E_0 is 1.0 V.

The free energy change ΔG^0 per mole of reaction $= -n FE_0 = (-2) (96500 \text{ amp-sec mol}^{-1}) 1.0 \text{ V} = -193000$ watt-sec mol^{-1}

Hence 100-watt lamp will lit for $(193000/100) \text{ s} = 32.16$ minutes for a mole of reactants transformed in to product.
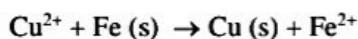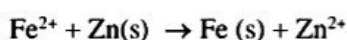
Q.7. Iron in presence of Zinc does not corrode while in presence of copper undergoes galvanic corrosion. Reason out the statement by inspecting the above table of standard reduction potentials. For both the cases write the half-cell reactions and the net cell reactions. [3]

The standard reduction potential of Fe2+/Fe is more positive than Zn2+/Zn, hence, iron can not be oxidized by Zinc when coupled to form a galvanic cell. Since corrosion refers to oxidation hence in presence of zinc, iron does not corrode. On the other hand, standard reduction potential of Cu2+/Cu is more positive than Fe2+/Fe and therefore in a galvanic cell Copper will play the role of cathode and iron will be the anode where iron will be oxidized or undergo galvanic corrosion.

The respective half cell reactions are:

$Fe^{2+} + 2e^- \rightarrow Fe\ (s)$

$Zn^{2+} + 2e^- \rightarrow Zn(s)$

$Cu^{2+} + 2e^- \rightarrow Cu(s)$
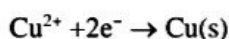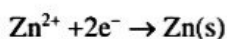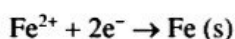
The net cell reaction in each case is:

$Fe^{2+} + Zn(s) \rightarrow Fe\ (s) + Zn^{2+}$

$Cu^{2+} + Fe\ (s) \rightarrow Cu\ (s) + Fe^{2+}$

Q.8. Consider a cell Ni/Ni2+ (0.01M) ‖ Cu2+ (0.5M)/Cu. The standard reduction potential of Ni and Cu are -0.25 and 0.34 V, respectively. Calculate the EMF of the cell. [3]

E_{ocell} = $E_{ocathode}$ − E_{oanode} = EoCu+2/Cu - EoNi+2/Ni = 0.34 (-0.25) = 0.59 V

EMF of the cell can be written as

$$E_{cell} = E^0_{cell} - \frac{0.0591}{n} log \frac{[Ni^{2+}]}{[Cu^{2+}]}$$
$$= 0.59 - \frac{0.0591}{2} log \frac{[0.01]}{[0.5]} = 0.64\ V$$

Q.9. What is an electrode concentration cell? [1]
Ans: An electrode concentration cell is a type of galvanic cell where two electrodes of the same substance but of different concentrations are dipped in the same solution.

$G.626 \times 10^{-34}$

1. Find whether the following statements are correct or not with proper justification- Writing true and False/Correct and Incorrect carry no marks [2+1+1+1+1]

a) If the wave function for a particle in one-dimensional box can be represented as $\psi(x) = i\sqrt{\frac{2}{3}}\psi_1 + \sqrt{\frac{1}{3}}\psi_2$, where ψ_1 and ψ_2 are the ground and first exited state wave functions, respectively then the average energy of the particle will be $\frac{5h^2}{8ml^2}$.

b) If the wave function of the particle in part (a) is $\psi(x) = \sqrt{\frac{1}{4}}\psi_1 + \sqrt{\frac{1}{4}}\psi_2 + \sqrt{\frac{1}{2}}\psi_3$, then the average momentum of the particle in will be 0.

c) For the position and momentum operator $[x, p_x^n] = inh p_x^{n-1}$.

d) One can measure eigen values corresponding to the quantum mechanical operator d/dx in an experiment.

e) $\psi = \sqrt{\frac{1}{2}}\psi_1 + \psi_2$ is a normalized wave function.

2. Consider a particle moving in a two-dimensional box of length a and breadth b such that its wave function and energy can be represented as $\psi = \sqrt{\frac{4}{ab}} Sin\left(\frac{n_x \pi x}{a}\right) Sin\left(\frac{n_y \pi y}{b}\right)$ $\left.\begin{array}{l} n_x = 1,2,3,..... \\ n_y = 1,2,3,..... \end{array}\right\}$ and

$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right)$, respectively. [3]

(a) Find the average position of the particle inside the box.
(b) Draw the first four energy levels of the particle considering $a = b$, i.e., the box to be a square.

3. Considering hexatriene to be a linear molecule whose length can be estimated as sum of lengths of all double bonds plus all single bonds plus the distance of a carbon atom radius at each end, evaluate the frequency of transition from highest occupied molecular orbital to lowest occupied molecular orbital. [3]
Note: $C=C$ bond length: 135 pm; $C-C$ bond length: 154 pm; radius of C atom 77 pm

4. Consider $|\Psi_1\rangle$ and $|\Psi_2\rangle$ to be the normalized eigen states of an operator $\hat{A}$ representing an observable A with eigen values a_1 and a_2, respectively. Similarly, consider $|\Phi_1\rangle$ and $|\Phi_2\rangle$ to be the normalized eigen states of an operator $\hat{B}$ representing an observable B with eigen values b_1 and b_2, respectively. Further, the eigen states of two operators are related by

$$|\Psi_1\rangle = \frac{1}{\sqrt{2}}[|\Phi_1\rangle + |\Phi_2\rangle]; \quad |\Psi_2\rangle = \frac{1}{\sqrt{2}}[|\Phi_1\rangle - |\Phi_2\rangle]$$

(a) Suppose observable A is measured and if the measurement outcome is a_1, then what is the state of the system after the measurement?
(b) After the measurement in part (a), observable B is measured. What are the possible results and associated probabilities?
(c) After the measurement of part (a), suppose that B is measured but we do not learn the measurement outcome. Assuming that A is measured again, then what is the probability of getting the result a_1. [1+1+1]

---------------Best of Luck ☺ ---------------

$\cos(x) = \textcircled{2}1 - 2\sin^2 x$

$\sin^2 x = \frac{1 - \cos(2x)}{2}.$

$12 \times 6 + 8 \implies 80 \times 1.6 \times 10^{-19}$

$\sin^2 x = \dfrac{1-\cos(2x)}{2}.$ अतः पहले के है .

Solution- Minor I   ①

I (a) $\psi(x) = i\sqrt{\dfrac{2}{3}}\,\psi_1 + \sqrt{\dfrac{1}{3}}\,\psi_2$

Average energy $= \langle H \rangle = \dfrac{\langle \psi | H | \psi \rangle}{}$

$$= \int_0^l \psi^* H \psi \, dx$$

$$= \int_0^l \left(-i\sqrt{\tfrac{2}{3}}\,\psi_1 + \sqrt{\tfrac{1}{3}}\,\psi_2\right) H \left(i\sqrt{\tfrac{2}{3}}\,\psi_1 + \sqrt{\tfrac{1}{3}}\,\psi_2\right) dx$$

Note : $\psi_1, \psi_2, \psi_3 \ldots$ are orthonormal and are all real

$$E = \int_0^l \left(-i\sqrt{\tfrac{2}{3}}\,\psi_1 + \sqrt{\tfrac{1}{3}}\,\psi_2\right)\left(i\sqrt{\tfrac{2}{3}}\,H\psi_1 + \sqrt{\tfrac{1}{3}}\,H\psi_2\right) dx$$

$$= \int_0^l \left(-i\sqrt{\tfrac{2}{3}}\,\psi_1 + \sqrt{\tfrac{1}{3}}\,\psi_2\right)\left[i\sqrt{\tfrac{2}{3}}\left(\tfrac{h^2 \psi_1}{8ml^2}\right) + \sqrt{\tfrac{1}{3}}\left(\tfrac{4h^2\psi_2}{8ml^2}\right)\right]$$

$$\because H\psi_n = E_n \psi_n$$
$$E_n = n^2 h^2 / 8ml^2$$

$$= \frac{2}{3}\cdot\frac{h^2}{8ml^2}\int_0^l |\psi_1|^2 dx + \frac{1}{3}\cdot\frac{4h^2}{8ml^2}\int_0^l |\psi_2|^2 dx$$

$$= \frac{2h^2}{24ml^2} + \frac{4h^2}{24ml^2} = \frac{6h^2}{24ml^2} = \frac{h^2}{4ml^2}$$

(b) $\langle p_x \rangle$ for particle in a box 'n zero irrespective of n

$$\langle p_x \rangle = \int \psi^* \hat{p}_x \psi \, dx = \frac{1}{4}\int_0^l \psi_1^* p_x \psi_1 \, dx + \frac{1}{4}\int_0^l \psi_2^* p_x \psi_2 \, dx$$

$$+ \frac{1}{2}\int_0^l \psi_3^* p_x \psi_3 \, dx = 0$$

All cross integrals are not considered as ψ_1, ψ_2 & ψ_3 are orthogonal to each other and hence will vanish

(c) $[x, p_x^n] = [x, p_x\cdot p_x^{n-1}] = [x,p_x]p_x^{n-1} + p_x[x,p_x^{n-1}]$

$[A, BC] = [A,B]C + B[A,C]$

$$= i\hbar p_x^{n-1} + p_x[x, p_x\cdot p_x^{n-2}]$$

$$= i\hbar p_x^{n-1} + p_x\left\{[x,p_x]p_x^{n-2} + p_x[x, p_x^{n-2}]\right\}$$

$$\cdots i\hbar\, p_x''' + p_x \left\{ i\hbar\, p_x'' + p_x \left[x, p_x \cdot p_x''' \right] \right\}$$

$$= 2 i\hbar\, p_x^{n-1} + p_x^2 \left[x, p_x \cdot p_x^{n-3} \right]$$

$$\vdots$$

$$= n\, i\hbar\, p_x^{n-1}$$

(d) $\frac{d}{dx}$ is not a Hermitian operator; its eigenva[lue]
can be real or complex

(e) $\psi = \frac{1}{\sqrt{2}}\psi_1 + \psi_2$ $\qquad \left| \begin{array}{l} |c_1|^2 + |c_2|^2 = \left(\frac{1}{\sqrt{2}}\right)^2 + (1)^2 \\ = \frac{1}{2} + 1 = 3/2 \quad \therefore \text{ Not normali}[zed] \end{array} \right.$

2. $\psi = \sqrt{\frac{4}{ab}}\, \sin\left(\frac{n_x\pi x}{a}\right) \sin\left(\frac{n_y \pi y}{b}\right)$ $\qquad \begin{array}{l} n_x = 1, 2, 3, \cdots \\ n_y = 1, 2, 3, \cdots \end{array}$

$$E = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2}\right)$$

(a) for a 2-d box position vector r
$$\vec{r} = x\,\hat{i} + y\,\hat{j}$$

$$\langle \vec{r} \rangle = \langle x \rangle\,\hat{i} + \langle y \rangle\,\hat{j}$$

$$\Rightarrow \langle \vec{r} \rangle = \int_0^a \int_0^b \psi^*(x,y)\, \vec{r}\, \psi(x,y)\, dx\, dy$$

clearly $\langle x \rangle = \int_0^a \int_0^b \sqrt{\frac{4}{ab}} \sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_x \pi y}{b}\right) x \sqrt{\frac{4}{ab}}$

$\qquad\qquad\qquad\qquad\qquad\qquad \sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n}{?}\right) dx\, dy$

$$= \int_0^a \frac{2}{a} \sin\left(\frac{n_x\pi x}{a}\right) x \sin\left(\frac{n_x\pi x}{a}\right) dx \underbrace{\int_0^{b} \frac{2}{b} \sin^2\left(\frac{n_y\pi y}{b}\right) d}_{\substack{\overset{\shortparallel}{1} \text{ as i} \\ \text{is normalize}}}$$

$$\underbrace{}_{\overset{\shortparallel}{a/2}\ (\text{we know it})}$$

$$= a/2$$

similarly $\langle y \rangle = b/2$

$$\Rightarrow \langle \vec{r} \rangle = \frac{a}{2}\,\hat{i} + \frac{b}{2}\,\hat{j}$$

(b) energy level diagram

$10.h^2/8ml^2$ ——— $(1,3)$ ——— $(3,1)$ $\{$ $n_1=1, n_2=3$ or $n_1=3, n_2$

$8.h^2/8ml^2$ ——— $(2,2)$ $\{$ $n_1=2, n_2=2$ $\}$ $\{$ $n_1=2, n_2=2$ $\}$

$5.h^2/8ml^2$ ——— $(1,2)$ ——— $(2,1)$ $\{$ $n_1=1, n_2=2$ or $n_1=2, n_2=$

$2.h^2/8ml^2$ ——— $(1,1)$ $(n_1=1, n_2=1)$

$$E = \left(n_x^2 + n_y^2\right)\frac{h^2}{8ma^2} \quad \{a=b\}$$

3. Hexatriene $\Rightarrow$ 6 π electrons : every energy level can accomodate a max. of 2 e⁻

$n=4$

$\Rightarrow$ transition 'n' from $n=3$ to $n=4$

—⇅— $n=3$

—⇅— $n=2$

—⇅— $n=1$

$\Rightarrow$ $\Delta E = h\nu = n_4^2 - n_3^2$ $\left(4^2-3^2\right)\frac{h^2}{8ml^2}$

$\Rightarrow$ $\nu = \frac{7h}{8ml^2}$

$l = 3 \times (135\ pm) + 2 \times (154\ p)$
$+ 2 \times (77\ pm)$

$m = 9.1 \times 10^{-31}$ kg
$h = 6.636 \times 10^{-34}$ Js

4. Solved in Assignment / Practice Set I