

Birla Institute of Technology & Science, Pilani, Rajasthan - 333 031
II Semester 2017-2018

GENERAL CHEMISTRY

CHEM F111

Mid-Sem Exam. Model Solution

Max. Marks: 90

Duration: 90 minutes

Date: March 10, 2018

Q1. a) Power of lamp = 100 W = 100 Js⁻¹. 1M

Energy of a photon of yellow light is given as

$$E_y = \frac{hc}{\lambda} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{560 \times 10^{-9}} = 3.55 \times 10^{-19} \text{ J} \quad 1\text{M}$$

Number of photons emitted per second = $\frac{100 \text{ J}}{3.55 \times 10^{-19} \text{ J}} = 2.8 \times 10^{20}$ 1M

Assumptions: Lamp has 100 % efficiency 1M

Q1. b) Energy of the electron after acceleration is E = 20000 x 1.602 x 10⁻¹⁹ J, 1M

Hence, $\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} = \frac{6.626 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 20000 \times 1.602 \times 10^{-19}}} = 8.65 \times 10^{-12} \text{ m}$ 1+1=2M

Q1. c

Entry	Entity of interest	Expression
1.	Wavefunction, $\psi(x, y)$	$\psi(x, y) = \frac{2}{\sqrt{L_1 L_2}} \sin \frac{n_x \pi x}{L_1} \sin \frac{n_y \pi y}{L_2}$
2.	Energy, if $L_1=2L_2$	$E = \frac{h^2}{32mL_2^2} (n_x^2 + 4n_y^2)$
3.	Quantum numbers for the first degenerate states when $L_1=2L_2$	$\psi_{4,1}(n_x = 4, n_y = 1) \text{ and } \psi_{2,2}(n_x = 2, n_y = 2)$

2M

2M 2+2=4M

Q1. d. $E_0 = (0 + \frac{1}{2})h\nu = \frac{1}{2} h\nu$

Either $E_0 = 1600/2 = 800 \text{ cm}^{-1}$,

or $E_0 = hc/2\lambda = 1600 \times 6.626 \times 10^{-34} \times 3 \times 10^8 / 2 = 1.59 \times 10^{-20} \text{ J}$ 2M

The lowest energy level has ZERO nodes 1M

Q2. a) i) $E = -\frac{e^4 \mu}{8\epsilon_0^2 h^2} \frac{Z_{eff}^2}{n^2}$

$E \propto -\frac{Z_{eff}^2}{n^2}$ (n = principal quantum number) 2M

$$\frac{E_{F8+}}{E_{Li2+}} = \frac{\frac{(9)^2}{(3)^2}}{\frac{(3)^2}{(2)^2}} = \frac{81 \times 4}{9 \times 9}$$

= 4 2M

ii) $L = \sqrt{l(l+1)}\hbar$

Here, 'l' for F⁸⁺ = 2, so, $L_{F8+} = \sqrt{6}\hbar$ 1M

'l' for Li²⁺ = 1, $L_{Li2+} = \sqrt{2}\hbar$ 1M

iii) $L_z = m_l \hbar$

m_l values for F⁸⁺ = +2 (from $\Psi_{3,2,2}$) 1M

$L_z = 2\hbar$ 1M

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Q2. b) $E_{IE} (Li^{2+}) = 13.6 \times Z^2 \text{ eV}$ 1M

$$= 13.6 \times (3)^2 \text{ eV}$$

$$= 122.4 \text{ eV} \quad \text{2M}$$

Q2. c) i) The most probable radius occurs when the radial distribution wavefunction is a maximum. At this point the derivative of the function with respect to either r or ρ equals zero.

$$R(r) = A \rho e^{-\frac{\rho}{2}}; \quad A = \text{constant}$$

$$P(r) = r^2 \rho^2 e^{-\rho} dr; \quad \text{1M}$$

$$\frac{d[P(r)]}{dr} = 0 \quad \text{1M}$$

$$\text{By putting, } \rho = \frac{2Zr}{na_0}; \frac{d}{dr} \left[r^4 e^{-\frac{Zr}{a_0}} \right] = 0 = e^{-\frac{Zr}{a_0}} \left(4r^3 - \frac{Z}{a_0} r^4 \right) \quad \text{2M}$$

$$r = \frac{4a_0}{Z} \quad \text{1M}$$

ii) Here, probability = $\int \Psi^2 \delta v \approx \Psi^2 \delta v$ with $\delta v = 1.0 \text{ pm}^3$

$$\text{Probability} = \Psi^2 \quad \text{1M}$$

$$\Psi = \left(\sqrt{\frac{1}{32\pi a_0^3}} \right) \left(2 - \frac{r}{a_0} \right) e^{-r/2a_0};$$

$$\text{At } r = 2a_0,$$

$$\text{Probability, } \Psi^2 = 0 \quad \text{1M}$$

Q3. a) Since hybrid orbitals are orthogonal

$$\text{So, } \int_{\text{All space}} \left[S - \sqrt{\frac{3}{2}} p_z - \sqrt{\frac{1}{2}} p_x \right] \left[S + A p_z + B p_x \right] d\tau = 0 \quad \text{1M}$$

Applying the given condition of orthogonality and orthonormality the integration will provide

$$1 - \sqrt{\frac{3}{2}} A - \sqrt{\frac{1}{2}} B = 0 \text{-----eq (1)} \quad \text{2M}$$

Since hybrid orbitals are orthonormal

$$\int_{\text{All space}} \left[\sqrt{\frac{1}{3}} \{ S + A p_z + B p_x \} \right]^2 d\tau = 1 \quad \text{1M}$$

$$\text{Gives } A^2 + B^2 = 2 \text{-----eq (2)} \quad \text{2M}$$

$$\text{Solving eq (1) and eq (2) } A = \sqrt{\frac{3}{2}} \quad \text{and } B = -\sqrt{\frac{1}{2}} \quad \text{2 + 2=4M}$$

Orbital is in XZ plane. 1M

Q3. b) The spatial arrangement possible for $3p^1$ is 3 and spin arrangement possible is 2.

So, totally 6 arrangements are possible for one electron in $3p$.

Similarly one electron can be placed by 10 different ways in $3d$ orbital.

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So as a whole there will be $6 \times 10 = 60$ states possible. 2M

Triplet states are $^3F, ^3D, ^3P$ 3M

Min. energy for 3F 2M

Q 4. a) $\log\left(\frac{I}{I_0}\right) = -\epsilon cl$ 1M

$\frac{I}{I_0} = \frac{16}{100} = 0.16$ and $c = \frac{3.9 \text{ g/L}}{78 \text{ g/mol}} = 0.05 \text{ mol/L}$ 1M

molar absorption coefficient (ϵ) = $\frac{-\log(0.16)}{0.05 \text{ mol/L} \times 0.1 \text{ cm}}$ 1M

= $159.2 \text{ L mol}^{-1} \text{ cm}^{-1}$ 1M

b) $J_{max} = \left(\frac{kT}{2Bhc}\right)^{\frac{1}{2}} - \frac{1}{2}$ 1M

$4 = \left(\frac{298 \text{ K} \times 1.38 \times 10^{-23} \text{ J/K}}{2B \times 6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^{10} \text{ cm s}^{-1}}\right)^{\frac{1}{2}} - \frac{1}{2}$ 1M

$B = \frac{298 \text{ K} \times 1.38 \times 10^{-23} \text{ J/K}}{2 \times 4.5 \times 4.5 \times 6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^{10} \text{ cm s}^{-1}} = 5.108 \text{ cm}^{-1}$ 1 + 1 = 2M

Separation between Stokes or anti-Stokes lines in the rotational Raman spectrum = $4B = 20.4 \text{ cm}^{-1}$ 1M

$B = \frac{h}{8\pi^2 Ic} \Rightarrow I = \frac{h}{8\pi^2 Bc}$ or $r = \sqrt{\frac{h}{8\pi^2 B\mu c}}$ 1M

$\mu = \frac{m_1 \times m_2}{m_1 + m_2} = \frac{1 \times 35 \times 10^{-3}}{(1+35)6.023 \times 10^{23}} = 1.61 \times 10^{-27} \text{ kg}$ 1M

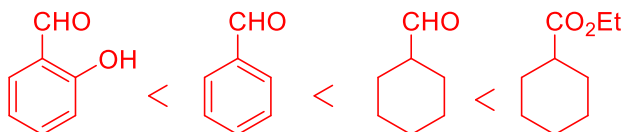
$r = \sqrt{\frac{h}{8\pi^2 B\mu c}} = \sqrt{\frac{6.626 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{8\pi^2 \times 5.108 \text{ cm} \times 1.61 \times 10^{-27} \text{ kg} \times 3 \times 10^{10} \text{ cm s}^{-1}}}$ 1M

= $0.0184 \times 10^{-8} \text{ m}$ 1M

c) For N_2O , number of normal vibrational mode = $3N - 6 = 3 \times 3 - 6 = 3$ 1 + 1 = 2M

For $\text{CH}=\text{CH}$, number of normal vibrational mode = $3N - 5 = 3 \times 4 - 5 = 7$ 1M

d) Increasing order of the C=O stretching frequency in IR spectra is 2M



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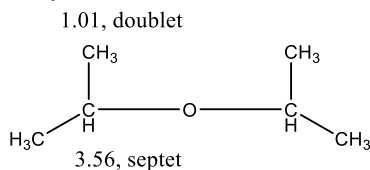
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Q 5. a)



[3 Marks for correct structure {no partial marks for incorrect structure}, 1.5 marks each for correct assignment]

b) Same, 7.2 Hz

2M

(c) Fill in the information for the following compound (*in the given format*)

2+2=4M

Compound	Most Shielded proton in ^1H NMR spectrum	No. of signals (peaks) in proton decoupled ^{13}C NMR spectrum
	<p>Methoxy OCH₃</p>	<p>6</p>

(d)

(i) $E_{1/2} (\alpha \text{ state}) = -\gamma_N \hbar B_0 m_l$ [or $= -g_N \mu_N B_0 m_l$] 1M
 $[1.084 \times 10^8 \text{ T}^{-1} \text{ s}^{-1} \times 1.055 \times 10^{-34} \text{ Js} \times 0.5 \times 7.04 \text{ T}] = -4.025 \times 10^{-26} \text{ J}$ 1M
 $E_{-1/2} (\beta \text{ state}) = 4.025 \times 10^{-26} \text{ J}$ 1M

(ii) $E_\beta - E_\alpha = h\nu$ 1M
 Resonance frequency $= \nu = E_\beta - E_\alpha / h$ 2M
 $= [4.025 \times 10^{-26} - (-4.025 \times 10^{-26})] / 6.626 \times 10^{-34} = 1.2149 \times 10^8 \text{ Hz} = 121.5 \text{ MHz}$

Alternatively,

Resonance frequency $= \gamma_N B_0 / 2\pi$ 1M
 $= [(1.084 \times 10^8 \text{ T}^{-1} \text{ s}^{-1} \times 7.04 \text{ T}) / (2 \times 3.14)] = 1.215 \times 10^8 \text{ Hz} = 121.5 \text{ MHz}$ 2M

Alternatively,

Resonance frequency $= g_N \mu_N B_0 / h$ 1M
 $= 2.263 \times 5.051 \times 10^{-27} \text{ J T}^{-1} \times 7.04 \text{ T} / 6.626 \times 10^{-34} \text{ Js} = 121.44 \text{ MHz}$ 2M