

Subject: GENERAL CHEMISTRY CHEM F111

Mid-Semester Examination (Closed Book)

Max. Marks: 90

MODEL SOLUTION

Date: October 11, 2017

Q1. (a) Normalization constant = N

$$\Psi = \psi = N \sin \frac{n\pi x}{L} ; \quad \int_0^L \psi^2 dx = 1 \quad [1]$$

$$\int_0^L N^2 \sin^2 \frac{n\pi x}{L} dx = 1 ; \quad N = \sqrt{\left(\frac{2}{L}\right)} \quad [2]$$

The normalized wavefunction is $\sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$ [1]

(ii) $\psi = \sqrt{\frac{2}{L}} \sin \frac{\pi x}{L}$ for $n = 1$; Probability density $= \psi^2 = \frac{2}{L} \sin^2 \frac{\pi x}{L}$

Max Probability density is at $x = L/2$; Max. Prob density $\psi^2(max) = \frac{2}{L}$ [1]

$\frac{2}{L} \sin^2 \frac{\pi x}{L} = 1/2$ of $\psi^2(max)$; $\frac{2}{L} \sin^2 \frac{\pi x}{L} = \frac{1}{2} \left(\frac{2}{L}\right)$; $x = L/4$ and $3L/4$ [2]

(iii) $x = L/3$ and $2L/3$ [2]

(b) First energy level: Non degenerate

Second energy level: 2-fold degenerate [2]

Second energy level (1,2) or (2,1)

Fourth Energy level (1,3) or (3,1)

Energy difference $= 5h^2/8mL^2$ [2]

$= 3.01 \times 10^{-17} \text{ J}$ [1]

(c) Work function $= hc/\lambda = 3.52 \times 10^{-19} \text{ J}$ [1]

Kinetic energy of the ejected electron $= 4.84 \times 10^{-19} - 3.52 \times 10^{-19}$ [2]

$= 1.32 \times 10^{-19} \text{ J}$ [1]

Q2. (a) (i) $\psi(r, \theta, \phi) = R(r) \times Y(\theta, \phi) = \left(\frac{\sqrt{2}}{81\sqrt{\pi}}\right) \left(\frac{Z}{a_0}\right)^{\frac{3}{2}} \left(\frac{6Zr}{a_0} - \frac{Z^2 r^2}{a_0^2}\right) e^{-\frac{Zr}{3a_0}} \sin\theta \sin\phi$ [1]

Orbital is $3p_y$ [1]

(ii) Orbital angular momentum $= \sqrt{l(l+1)}\hbar = \sqrt{2}\hbar$ [2]

(iii) One radial node at $\frac{6Z}{a_0} - \frac{Z^2 r}{a_0^2} = 0$; i.e. $r = 6a_0$ as $Z = 1$ for hydrogen [2]

(iv) Energy $= -hcR_H/n^2 = -hcR_H/9 = 6.626 \times 10^{-34} \text{ Js} \times 3 \times 10^{10} \text{ cm/s} \times 109680 \text{ cm}^{-1}/9 = 2.42 \times 10^{-19} \text{ J}$ [2]

(b) $\psi_{\text{He}(1,2)} = (1/\sqrt{2})[(1s_1, \alpha)(1s_2, \beta) - (1s_1, \beta)(1s_2, \alpha)]$

Hence, $\psi_{\text{He}(2,1)} = (1/\sqrt{2})[(1s_2, \alpha)(1s_1, \beta) - (1s_2, \beta)(1s_1, \alpha)]$ [2]

$$= - (1/\sqrt{2})[(1s_1, \alpha)(1s_2, \beta) - (1s_1, \beta)(1s_2, \alpha)]$$

$$= -\psi_{\text{He}(1,2)} \quad [1]$$

Hence, wavefunction is antisymmetric. [1]

(c) Degeneracy of the term represented by the symbol $^3P = (2S+1)(2L+1) = 3(3) = 9$ [2]

Level associated with this term = $^3P_2, ^3P_1, ^3P_0$ [3]

Ground state term symbol = 3P_0 [1]

Q3. (a) Ans: $P_1/P_0 = (2J+1)\exp[-BhcJ(J+1)/kT];$ [1]

$$= 2.94$$
 [2]

When mass is less, I is less, B is large, relative population is less. [2]

(b) Gross selection rule: The molecular polarizability must change during vibration. [1]

Sym. mode of CO_2 is Raman active as polarizability changes during the molecular vibration. [1]

None of the others are Raman active as all these modes are IR active and for a molecule with center of inversion, mutual exclusion principle is valid. [1+1]

(c) $m_H = 1.67 \times 10^{-27}$ kg, so, $m_N = 23.4 \times 10^{-27}$ kg. [1]

$$\bar{\nu} = \nu/c = \frac{1}{2\pi c} \sqrt{\frac{k}{m_N m_H / (m_N + m_H)}} = 3347.7 \text{ cm}^{-1}$$
 [1+2]

$CH_3CH_2NH_2$ molecule will show two peaks as symmetric and anti-symmetric stretching in that region instead of one observed in case of CH_3NHCH_3 because symmetric and antisymmetric stretching frequencies are only possible for $CH_3CH_2NH_2$. [2]

(d) $A = \log(1/T) = -\log T = \log(100/20) = 0.698$ [1]

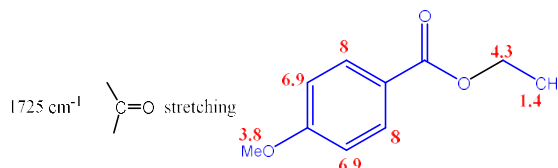
$A = \epsilon c$; $c = 2.3 \times 10^{-5}$ mole. dm^{-3} [2]

Q4. (a) Number of signals in 1H NMR and ^{13}C NMR will be 5 and 7 respectively. Carbonyl (C=O) carbon be most de-shielded carbon in ^{13}C NMR. [2+2+1]

(b) (i) $2.1 = \text{observed shift from TMS}/60 \times 10^6 \times 10^6 = 126 \text{ Hz}$ [3]

(ii) δ 2.1 ppm [2]

(c) [1+4+3]



5. (a) [2+2+1+1+1+1]

C_2	$1\pi_u < 2\sigma_g < 1\pi_g$	Diamagnetic	increases
O_2	$2\sigma_g < 1\pi_u < 1\pi_g$	Paramagnetic	decreases

(b) (i) [1+1+1+1] (ii) $A = H_2O, B = Cl, C = Cl, D = Cl$ [2]

5	2	3
3	0	0

(c) (i) $[TiCl_6]^{3-} < [Ti(H_2O)_6]^{3+} < [Ti(en)_3]^{3+}$ [2]

(ii) $[Co(NH_3)_6]^{3+} < [Rh(NH_3)_6]^{3+} < [Ir(NH_3)_6]^{3+}$ [2]