UNIVERSITY OF RUHUNA

BACHELOR OF SCIENCE SPECIAL DEGREE (LEVEL I) SEMESTER I
EXAMINATIONS – APRIL/MAY 2021

SUBJECT: Chemistry

COURSE UNIT: CHE 4132 (Quantum Chemistry & Molecular Spectroscopy)

TIME: Two (02) hours

Answer **All Three (03)** Questions

Avogadro constant (N_A)	$= 6.022 \times 10^{23}$ mol^{-1}
Atomic mass unit (amu)	$= 1.6606 \times 10^{-27}$ kg
Boltzmann constant (k_B)	$= 1.3806 \times 10^{-23}$ J K^{-1}
Electron charge (e)	$= -1.602 \times 10^{-19}$ C
Electron mass (m_e)	$= 9.109 \times 10^{-31}$ kg
Faraday constant (F)	$= 9.6485 \times 10^{4}$ C mol^{-1}
Gas constant (R)	$= 8.31446$ J K^{-1} mol^{-1}
	$= 0.08021$ dm^3 atm K^{-1} mol^{-1}
Planck constant (h)	$= 6.626 \times 10^{-34}$ J s
Proton mass (m_p)	$= 1.673 \times 10^{-27}$ kg
Speed of light (c)	$= 2.998 \times 10^{8}$ m s^{-1}
Vacuum permittivity (ε_0)	$= 8.854 \times 10^{-12}$ J^{-1} C^2 m^{-1}

1 atm = 760 mmHg = 1.01325 bar = 101325 Pa

2.303 (RT/F) = 59.15 mV at 298.15 K

1 eV = 1.6022 x 10^{-19} J

01. Answer **all** parts

(a) Consider the following Hamiltonian operator.

$$\hat{H} = \hat{H}_1(q_1) + \hat{H}_2(q_2) + \hat{H}_3(q_3)$$

where q_1, q_2 and q_3 are three independent sets of coordinates.

(i) If $\psi_i(q_i)$ and E_i are the eigenfunction and corresponding eigenvalue of the operator $\hat{H}_i(q_i)$, respectively, where $i = 1, 2, 3$, show that the eigenfunction of $\hat{H}$ are given by the product of the eigenfunctions ψ_i (i.e., $\psi(q_1, q_2, q_3) = \psi_1(q_1)\psi_2(q_2)\psi_3(q_3)$), and the eigenvalue of $\hat{H}$ is the sum of the eigenvalues E_i (i.e., $E = E_1 + E_2 + E_3$)

(20 marks)

(ii) The normalized wavefunction ψ and energy E of a particle in one-dimensional box are

$$\psi_{n_i} = \left(\frac{2}{L_i}\right)^{\frac{1}{2}} \sin\left(\frac{n\pi i}{L_i}\right) \qquad i = x, y, or\ z \quad and \quad n_i = 1, 2, 3, ...$$

$$E_{n_i} = \frac{n_i^2 h^2}{8mL_i^2}$$

where m and L_i are the mass of particle and box length, respectively.

(I) Using the relations that you derived in part (i) above, obtain expressions for the wavefunction and energy of a particle in a three-dimensional box of dimensions $L_x \times L_y \times L_z$.

(20 marks)

(II) Find the most probable location of a particle in a **cube** when it is in the ground state.

(10 marks)

(b) The diatomic rigid rotor can be viewed as a point with reduced mass μ moving freely on a surface of a sphere of radius r. The normalized wavefunction for a such system are called spherical harmonics Y_{l,m_l}, where $l = 0, 1, 2, ...$ and $m_l = 0, \pm1, \pm2, ..., \pm l$.

(i) Obtain the expressions for the energy and degeneracy g of a rigid rotor, if spherical harmonics satisfy the equations,

$$-\frac{\hbar^2}{2\mu r^2}\Lambda^2 Y = EY \quad and \quad \Lambda^2 Y = -l(l+1)Y$$

(20 marks)

(ii) If the frequency of the transition between the two lowest energy rotational states of $^1H^{35}Cl$ is $6.4 \times 10^{11} s^{-1}$, calculate its moment of inertia.

(15 marks)

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(iii) Calculate the magnitude of the angular moment for $l = 1$ state, components of the angular momentum along the z −axis, and the angles that the momentum vector makes to the z-axis.

(15 marks)

02. Answer **all** parts

Vibration-rotation spectrum of carbon monoxide ($^{12}C^{16}O$) was studied by Nairman et al. (Journal of Chemical Education, 1996). It has been reported that each absorption band is observed to be split into two sets of closely spaced peaks. The spectral data of the first few consecutive lines of first two spectra is given in the following table.

First Vibrational Band Line-spectra			
Left to the center /cm^{-1}		Right to the center/cm^{-1}	
1	2139.2	1	2146.9
2	2135.3	2	2150.7
3	2131.4	3	2154.1
Second Vibrational Band Line-spectra			
Left to the center /cm^{-1}		Right to the center/cm^{-1}	
1	4255.6	1	4263.2
2	4251.8	2	4267.2
3	4247.9	3	4270.6

(i) The vibration-rotation energy is given by

$$E_{total} = \tilde{B}J(J+1) - \tilde{D}J^2(J+1)^2 + (v+\frac{1}{2})\bar{v}_e - (v+\frac{1}{2})^2 x_e\bar{v}_e \quad cm^{-1}$$

Giving the assumptions you make, show that the general equations for the first vibrational transition that describe the appearance of two sets of line spectra is given by

$$\bar{v}_{spe} = \bar{v}_0 + 2\tilde{B}m \quad cm^{-1} \quad m = \pm1, \pm2, \pm3\ldots\ldots$$

All symbols have their general meanings.

(40 marks)

(ii) Calculate the oscillation frequency ($\bar{v}_e$) and the anharmonicity constant (x_e)

(15 marks)

(iii) Taking the assumption that $2\tilde{B}$ in the equation in above part (i) can be approximated to $(\tilde{B}_v + \tilde{B}_0)$, where$v\neq0$, Calculate the rotation-vibration constant (α), and the rotational constant at the equilibrium bond distance (B_e).

(30 marks)

(iv) Deduce the following relationship for the second vibration transition that describes the appearance of two sets of line spectra,

$$\bar{v}_{spe} = 4259.4 + 3.86m \quad cm^{-1} \quad m = \pm1, \pm2, \pm3\ldots\ldots$$

(15 marks)

3

03. Answer **all** parts

(a)

   (i) State spin selection rule and orbital symmetry selection rule pertaining to electronic transitions.

                                               (20 marks)

   (ii) Explain why the $n \rightarrow \pi^*$ electronic transitions show weak absorption compared to that of the $\pi \rightarrow \pi^*$ electronic transitions.
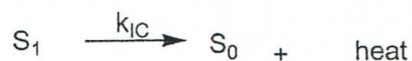
                                               (15 marks)

(b) Following diagram shows how the electronic and vibrational energy levels in the ground state (S_0) and first excited state (S_1) of molecule A are related to the absorption and fluorescence emission spectra.
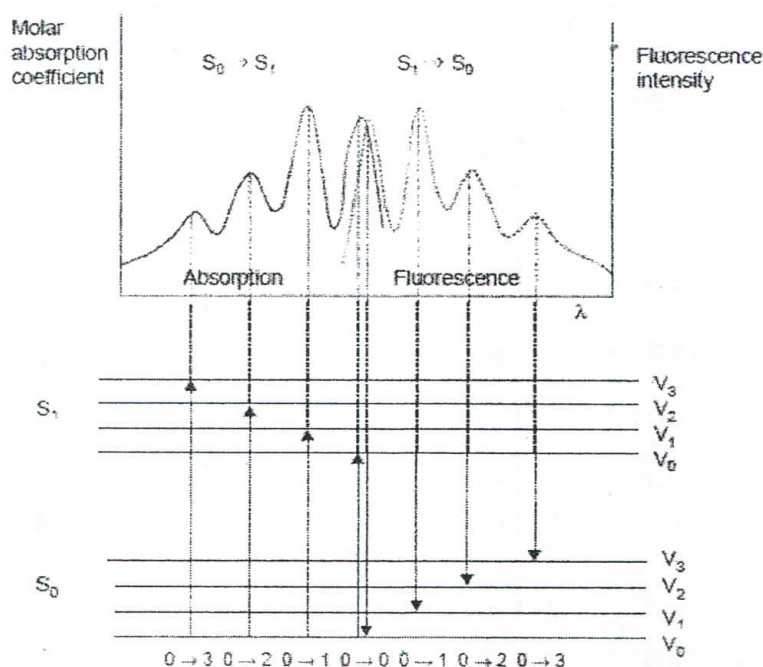
Explain why 0-0 band at slightly different wavelength even though we would expect the 0-0 band for absorption and emission to occur at the same wavelength according to the energy level diagram.

                                               (10 marks)

(c) Consider the following reaction sequence for the deactivation process of the excited S_1 state in the presence of quencher Q.

$$S_1 \xrightarrow{k_f} S_0 + h\nu$$

$$S_1 \xrightarrow{k_{ISC}} T_1 + \text{heat}$$

$$S_1 \xrightarrow{k_{IC}} S_0 + \text{heat}$$

$$S_1 + Q \xrightarrow{k_Q} S_0 + Q^*$$

(i) Write expressions for the rate of deactivation of S_1 energy state in the presence and absence of the quencher.

(10 marks)

(ii) Derive the expression for the ratio of quantum yield of fluorescence in the presence (Φ_f) and absence (Φ_f°) of Q

(15 marks)

(iii) Show that

$$\frac{\Phi_f^\circ}{\Phi_f} = 1 + K_Q\,[Q]\ ,\ \text{where } K_Q \text{ is the Stern- Volmer Quenching constant.}$$

(05 marks)

(iv) When tetra(ketocarboxamide) is added to a dilute solution of anthracene in DMF fluorescence observed in anthracene is quenched. If you have facilities to measure excited singlet state lifetime in the laboratory how would you determine the bimolecular rate constant for quenching of anthracene singlet excited state by tetra(ketocarboxamide)?

(10 marks)

(d)

(i) Write an equation using standard notation to show triplet-triplet energy transfer between donor (D) and acceptor (A) molecules.

(05 marks)

(ii) Draw an appropriate diagram to show electron movement occurring in triplet-triplet energy transfer by the exchange mechanism.

(10 marks)

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