Unique Paper code : 32171502

Name of the course : B.Sc. (Hons) Chemistry

Name of the paper : Chemistry C-XII Physical Chemistry V:
Quantum Chemistry and Spectroscopy

Semester : V

Duration : 3 hours

Maximum Marks : 75

Instructions for Candidate:

1. **Attempt any FOUR questions in all.**
2. **Each question carries 18.75 marks.**
3. **Preferably attempt all parts of a question together.**
4. **Please show all calculations as each step carries marks.**
5. **Use of scientific calculators is allowed.**

Physical constants

Atomic mass unit : 1.66×10^{-27} kg

Planck's constant : 6.626×10^{-34} J s

Velocity of Light : 3×10^{8} m s^{-1}

Boltzmann constant : 1.381×10^{-23} J K^{-1}

Mass of Electron : 9.1×10^{-31} kg

Avogadro's number : 6.023×10^{23} mol^{-1}

Nuclear magneton : 5.047×10^{-27} J T^{-1}

Bohr magneton : 9.274×10^{-24} J T^{-1}

1. (a) Giving reason, state which of the following are acceptable wave functions in the indicated interval: (i) sin x (0, 2π), (ii) $e^{x}(-\infty, \infty)$, (iii) $\frac{1}{x}$ (0, ∞)

(b) Showing relevant calculations arrange the following in order of increasing magnitude:

$10\ \text{cm}^{-1}$, 1×10^{-23} J, 0.01 m, 1 MHz

(c) Explain why only one absorption line could be observed in the vibrational spectra of a diatomic molecule. Illustrate your answer with a suitable diagram.

(d) The electronic spectrum of a ketone shows the following two peaks:

λ_{max} /nm	280	190
ε at λ_{max} / L mol^{-1} cm^{-1}	15	100

Identify the electronic transition for each peak with justification and compare the intensities of the two peaks.

(4.5, 4.75, 4.75, 4.75)

2. (a) Determine whether the following functions are eigen functions of the given operator. If so, evaluate their eigen values.

(i) $\left(\frac{d^2}{dx^2} + 2\,\frac{d}{dx} + 3\right)\{\exp(ax)\}$

(ii) $\nabla^2\{(\cos ax)(\cos by)(\cos cz)\}$

(b) A particle of mass m exists in a one-dimensional box of length L. Find the probability of finding the particle in the range $0 \le x \le \frac{L}{4}$ for the states $n = 1$ and $n = 2$.

(c) The microwave spectrum for the $^{1}H^{80}Br$ molecule is observed as a series of equally spaced lines separated by $16.92\ \text{cm}^{-1}$. Evaluate the bond length of this molecule.

(d) What is the ‘formal’ selection rule for pure rotational Raman spectroscopy? Show that the Raman lines appear at wavenumbers given by $\bar{\upsilon} = \bar{\upsilon}_0 \pm 4B\,(J + \frac{3}{2})$, where $\bar{\upsilon}_0$ corresponds to the wavenumber of the Rayleigh line. Draw the possible theoretical pure rotational Raman spectrum.

(4.5, 4.75, 4.75, 4.75)

3. (a) Show that operators corresponding to $\hat{\boldsymbol{x}}$ and $\hat{\boldsymbol{p}}_{\boldsymbol{x}}$ do not commute. Give the physical significance of your result.

(b) Write the expression for the Hamiltonian operator for Li atom explaining all the terms involved. Write the modified Hamiltonian operator and the expression for the corresponding Schrodinger’s equation after applying Born Oppenheimer approximation.

(c) Arrange the following groups in the order of their increasing IR frequencies. Give justification.

(i) C−F, C−Cl, C−Br, C−H (ii) C−C, C=C, C≡C

(d) A molecule AB_2 has the following infrared and Raman spectra:

Wave number (cm^{-1})	Infrared	Raman
3756	Very strong	−
3652	Strong	Strong (polarized)
1595	Very strong	−

Suggest the possible geometry of the molecule and assign the observed lines to the corresponding vibrations. Give suitable explanation for the assignment.

(4.5, 4.75, 4.75, 4.75)

4. (a) Draw the energy level diagram and explain bonding in the heteronuclear diatomic molecule HF.

   (b) The ESR spectrum of atomic hydrogen was recorded on a spectrometer working at 9.302 GHz. The value of hyperfine coupling constant was found to be 50.7 mT. Find the value of the external applied magnetic field, *B* at which the two lines of atomic hydrogen will be observed. ($g_e = 2.0023$)

   (c) Show that the separation between the maxima of the P and R branches of the vibrational-rotational spectra of heteronuclear diatomic molecules is given by: $\sqrt{\frac{8kTB}{hc}}$

   (d) A monosubstituted aromatic compound with molecular formula C_9H_{12} gives four ^1H NMR signals (p_1-p_4). Their relative intensity ratios $p_1 : p_2 : p_3 : p_4$ are as follows:

   5 (singlet) : 2 (quartet) : 2 (quartet) : 3 (triplet)

   Suggest a possible structure of the molecule if δ values are in the order $p_1 > p_2 > p_3 > p_4$.

(4.5, 4.75, 4.75, 4.75)

5. (a) The normalized **1*s*** atomic orbital for the hydrogen atom is:

   $\psi(r) = \frac{1}{\sqrt{\pi a_0^3}} \exp(^{-r}/_{a_0})$ where a_0 represents the Bohr radius.

   Evaluate <***r***> for the electron in this orbital given that $\int r^n \exp(-ar)\, dr = \frac{n!}{a^{(n+1)}}$

   (b) Consider the *FEMO* description of the linear butadiene molecule. What is the minimum excitation energy given that the average C−C bond distance is 140 pm. The β-carotene molecule which has a long-conjugated C−C structure is coloured. Explain this on the basis of the *FEMO* model.

   (c) With the help of a diagram explain the difference between predissociation and dissociation.

   (d) Evaluate the rotational energy corresponding to the rotational level with the maximum population $\boldsymbol{J_{max}}$. How can this expression be simplified if the rotational constant, *B*, is small? Suggest a reason for your answer.

(4.5, 4.75, 4.75, 4.75)

6. Write short notes on the following:
   (a) Configuration Interaction
   (b) Fluorescence and phosphorescence
   (c) Larmor precession and Larmor precessional frequency
   (d) Variation theorem

(4.5, 4.75, 4.75, 4.75)