(i) CF, CCl, CBr, CH

(ii) C-C, C=C, C=C (4.5,4,4)

8. (a) A ^1H NMR spectra of an organic compound with the molecular formula $C_3H_6Br_2$ gives three signals (p1, p2 and p3) with their respective intensity ratios as follows: 1(sixtet): 2 (doublet): 3(doublet) (δ values are in the order p1>p2> p3). Write the probable structure and justify your answer.

(b) Write short notes on any **two** of the following :

(i) Difference between internal conversion and intersystem crossing.

(ii) Factors affecting the intensity of transition.

(iii) Larmor precession. (4.5,4,4)

[This question paper contains 8 printed pages.]

Your Roll No.............

Sr. No. of Question Paper : 1041 **C**

Unique Paper Code : 32171502

Name of the Paper : Physical Chemistry V: Quantum Chemistry & Spectroscopy

Name of the Course : **B.Sc. (Hons) Chemistry**

Semester : V

Duration : 3 Hours Maximum Marks : 75

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt **six** questions in all, **three** questions each from Sections **A** and **B**.
3. Attempt all part of a question together.
4. **All** questions carry equal marks.
5. Use of a non-programmable scientific calculator is allowed.

Physical constants

Atomic mass unit	$=1.66 \times 10^{-27}$ kg
Planck's constant	$= 6.626 \times 10^{-34}$ J s
Velocity of Light	$= 3 \times 10^{8}$ m s^{-1}
Boltzmann constant	$= 1.381 \times 10^{-23}$ J K^{-1}
Mass of Electron	$= 9.1 \times 10^{-31}$ kg
Avogadro's number	$= 6.023 \times 10^{23}$ mol^{-1}
Nuclear magneton	$= 5.05 \times 10^{-27}$ J T^{-1}
Bohr magneton	$= 9.274 \times 10^{-24}$ J T^{-1}

SECTION A

(Quantum Chemistry)

1. (a) Discuss the postulates of quantum mechanics.

(b) Write the complete Hamiltonian operator for Li atom explaining all the terms. Write the modified Hamiltonian operator after applying Born Oppenheimer approximation.

(c) Show that the eigenvalues of a Hermitian operator are always real. (4.5,4,4)

(c) The fundamental and first overtone transitions of $^{14}N^{16}O$ are centered at 1876.06 cm^{-1} and 3724.20 cm^{-1}, respectively. Calculate the equilibrium vibration frequency and anharmonicity constant. (4.5,4,4)

7. (a) A molecule AB_2 has the following Infrared and Raman spectra :

ν (cm^{-1})	Infrared	Raman
519	Active (PQR)	Active (Polarized)
1151	Active(PQR)	Active (Polarized)
1367	Active(PQR)	Active (Depolarized)

Predict the geometry of the molecule with justification and assign the observed wavenumbers to the specific vibration mode.

(b) What is Raman effect? Explain the origin of Stokes and Anti-Stokes line.

(c) Arrange the following groups in increasing order of their absorption frequencies: Give Justification

SECTION B

(Spectroscopy)

5. (a) Chlorine gas is microwave and infra-red inactive but Raman active. Explain.

(b) How will the microwave spectrum of HCl^{35} change if Cl^{35} is replaced by Cl^{37}?

(c) The rotational spectrum of $^{79}Br^{19}F$ shows a series of equidistant lines 0.71433 cm^{-1} apart. Calculate the rotational constant, B, the moment of inertia and bond length of the molecule. (4.5,4,4)

6. (a) How do the P, Q and R branches arise in the Vibrational-Rotational spectrum. Why is Q branch not observed for most of the heteronuclear diatomic molecules?

(b) What is the ratio of the number of protons in each spin state at temperature 300 K, given that the ^1H NMR spectrometer is operating at 60MHz and $g_n = 5.585$ for the ^1H nucleus.

2. (a) A particle of mass m, in a one-dimensional box of length a can be represented by the function,

$\psi_n = \sin\frac{n\pi x}{a}$ (n = 1,2,3...) Normalize the given function ψ_n and find whether it is an eigen function of (i) $\widehat{p_x}$ (ii) $\widehat{p_x^2}$.

(b) A particle of mass, m, in a one-dimensional box of length a can be represented by the following normalized trial wave function where N is the normalization constant.

$$\psi_{trial} = N\{x(a-x)\}$$

(i) Calculate the expectation value of energy, (E), of this particle in the ground state using the trial wave function.

(ii) Compare this energy with the actual energy. Calculate the percentage error.

(iii) Is the trial wave function acceptable? Explain on the basis of variation theorem. (4.5,(4,2,2))

3. (a) Plot the radial functions and radial probability distribution functions for an electron in hydrogen atom for all wave functions having n = 2. Write the number of nodes in each case.

(b) Evaluate the expectation value of the radius, $\langle r \rangle$, at which the electron in the ground state of Hydrogen atom (Z=1) is found. Given the wave function for this state is

$$\psi_{1,0,0} = \frac{1}{\sqrt{\pi}}\left(\frac{z}{a_o}\right)^{\frac{3}{2}} e^{\frac{-Zr}{a_o}}$$ where a_o is the Bohr radius

and $\int_0^{\infty} r^n e^{-ar}\, dr = \frac{n!}{a^{(n+1)}}$.

(c) Giving reason, state which of the following are acceptable wave functions in the indicated interval.

(i) $\sin x$ $(0,\ 2\pi)$

(ii) e^{-x} $(-\infty,\ \infty)$

(iii) $\frac{1}{x}$ $(0,\ \infty)$

(iv) $\sin^{-1} x$ $(-1,\ 1)$

(4.5,4,4)

4. (a) By applying the procedure of separation of variables on the following Schrodinger equation for an electron in a hydrogen atom, derive three equations, one dependent on variable, r, second dependent on variable, θ and third dependent on variable, ϕ. In this equation $\psi(r, \theta, \phi)$ is the function of three independent variables r, θ and ϕ. Considering $\psi(r, \theta, \phi) = R(r) * \Theta(\theta) * \Phi(\phi)$,

$$\left[-\frac{h^2}{8\pi^2 \mu r^2}\left\{\frac{d}{dr}\left(r^2 \frac{d}{dr}\right) + \frac{1}{\sin\theta}\frac{d}{d\theta}\left(\sin\theta \frac{d}{d\theta}\right) + \frac{1}{\sin^2\theta}\frac{d^2}{d\varphi^2}\right\} - \frac{z e^2}{r}\right] \psi = E\psi$$

(b) Set up the Hamiltonian operator for a particle oscillating about a mean position (a simple harmonic oscillator). Explain the significance of zero-point energy of a simple harmonic oscillator.

(c) Starting from the expression for total energy of a rigid rotator, setup the Schrodinger equation for the system in Cartesian coordinates.

(4.5,4,4)