[This question paper contains 4 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 1763 **L**

Unique Paper Code : 2172013603

Name of the Paper : DSC: PHOTOCHEMISTRY AND SPECTROSCOPY

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

Semester / Scheme : VI / NEP-UGCF-2022

Duration : 2 Hours Maximum Marks : 60

Instructions for Candidates

1. Write your Roll No. on the top immediately on receipt of this question paper.
2. Attempt any **four** questions out of **six**.
3. Question no. **1** is compulsory'
4. Attempt all parts of a question together.
5. Use of scientific calculators and log tables is allowed.

Physical constants

Atomic mass unit	:	1.66×30^{-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	:	6.022×10^{23} mol^{-1}
Nuclear magneton	:	5.047×10^{-27} J T^{-1}
Bohr magneton	:	9.274×10^{-24} J T^{-1}

1. Attempt **any five** of the following :

   (a) Explain why aromatic protons generally resonate at higher chemical shift values (δ 7-8 ppm) than aliphatic protons in NMR spectroscopy.

(b) Why is DPPH used as the practical reference standard in ESR spectroscopy instead of a free electron? Mention the properties that make it suitable for this purpose.

(c) Explain Fermi resonance with appropriate example.

(d) Which of the following molecules will be microwave active and why?

$$H_2,\ NO,\ CO_2,\ CCl_4$$

(e) Photosynthesis is a photosensitized reaction. Explain.

(f) Why phosphorescence is delayed and has a longer lifetime than fluorescence.

(3×5=15)

2. (a) Determine the value of the rotational quantum number J for which $\frac{N_J}{N_0}$ is maximum for the molecule $^{12}C^{16}O$ at 25°C, given that the rotational constant is 1.9302 cm^{-1}. Which transition will be most intense?

(b) What is the essential condition for a molecule to be infrared active? Give the selection rule and the energy expressions for a molecule undergoing (i) harmonic oscillation (ii) anharmonic oscillation.

(c) Assuming that the force constants of HCl and DCl are same calculate the fundamental vibrational frequency of DCl if the fundamental vibrational frequency of HCl is 2890 cm^{-1}. Calculate the zero-point energies of both the molecules if the vibration is assumed to be harmonic in nature.

(5,5,5)

3. (a) Differentiate between dissociation and predissociation. Explain their spectral significance with the help of a diagram.

(b) Two molecules A and B absorb one photon each of same energy. Molecule A dissociates directly while molecule B undergoes predissociation. Explain the difference in their excited state behaviour with the help of potential energy diagram.

(c) Describe how the Beer-Lambert law is used in determining concentration of a coloured solution. Under what conditions does it fail. (5,5,5)

4. (a) State the selection rules for pure rotational and pure vibrational Raman spectroscopy and the condition for the molecule to be Raman active. Explain why symmetric vibrational modes are often intense in Raman spectra but weak or absent in infrared spectra.

(b) For A_2B, the following spectroscopic data are available. Giving proper explanation predict the geometry of the molecule. Assign the wave number to specific vibrations.

Wavenumber (cm^{-1})	Infrared	Raman
589	Active (PQR)	Inactive
1285	Active (PR)	Active (polarized)
2224	Active (PR)	Active (depolarized)

(c) Define quantum yield and discuss the role of chemical actinometer in its measurement. Explain the factors responsible for high and low quantum yield. (5,5,5)

5. (a) Draw and explain the low-resolution and high-resolution PMR spectra of (i) methanol and (ii) acetone, indicating the chemical shift positions of different proton environments, relative signal intensities, and splitting patterns observed in each case.

(b) What is meant by chemical shift in NMR spectroscopy? Calculate the resonance frequency(v) for ^1H in a magnetic field of 1.50 T. Given: $g_n = 5.585$, $\beta_n = 5.050 \times 10^{-27}$ JT^{-1}.

(c) Draw the ESR spectrum of methyl radical and explain the observed hyperfine splitting pattern on the basis of electron-nuclear spin interaction.

(5,5,5)

6. Write short notes on **any three** of the following :

(a) Frank-Condon Principle

(b) Factors affecting the intensity of spectral lines

(c) Photostationary state and Quenching

(d) Larmor precession (5×3=15)