[This question paper contains 4 printed pages.]

Your Roll No.....

Sr. No. of Question Paper : 9902 **K**

Unique Paper Code : 2173010041

Name of the Paper : DSE: Advanced Molecular Spectroscopy and Applications

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

Semester : VII

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. Q. No. **1** is compulsory.
3. Attempt **FOUR** questions in all.
4. **All** questions carry equal marks.
5. Use of scientific calculators is allowed.

1. Attempt **any five** (3 marks each). (3 x 5 = 15)

   a. Name any two factors that affect the width of spectral lines. Discuss how the linewidth depends on temperature and molecular mass, and explain why lighter molecules exhibit broader lines?

   b. A 2.5 x 10^{-3} M solution in a cell of path length 1 cm has an absorbance of 0.75 at 560 nm. What is the molar absorptivity coefficient of the substance? Calculate the absorbance and transmittance if the concentration of the solution is 7.5 x 10^{-4} M.

   c. Show that if the ground and excited vibrational states of a molecule have identical potential energy curves, then the (0,0) transition is the most intense. Which principle dictates this observation?

   d. List **two** main points of difference between charge transfer transitions and *d-d* tranitions. Explain the origin of the intense purple colour of potassium permanganate in terms of electronic transitions.

P.T.O.

e. How does conjugation effect $\pi \rightarrow \pi^*$transitions in a molecule? Anthracene is colourless, but tetracene is bright orange. Justify this observation.

f. With suitable reasons, explain the increasing order of chemical shift in complexes of Fe, Fe^{2+} and Fe^{3+} ions, in Mössbauer spectroscopy.

g. i. Why does fluorescein fluoresce but a similar molecule phenophthalein does not?
ii. $n \rightarrow \pi^*$transitions are *blue-shifted* in the presence of H-bonding solvents. Why?

2. a. Derive the following expression for the probability of transition from state *l* to state *m* when a molecule interacts with a time-dependent electromagnetic field. (5)

$$P_{l \rightarrow m} = |c_m|^2 = \frac{4\varepsilon_{0x}{}^2 |\mu_{xlm}{}^2|}{\hbar^2 \omega^2} sin^2 \frac{\omega t}{2}$$

b. Derive the selection rules for the n-π^*, π-π^*, n-σ^* and σ-π^* transitions of formaldehyde using the symmetry principle. (5)

Character table of C_{2v} is given as

	E	C_2	σ_{xz}	σ_{yz}		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	-1	-1	R_z	xy
B_1	1	-1	1	-1	x, R_y	xz
B_2	1	-1	-1	1	y, Rx	yz

c. How many signals are observed in the following complexes and explain it briefly with their spectral transition diagram. (5)
i. $[Fe(CN)_6]^{3-}$
ii. $[Fe(H_2O)_6]Cl_3$
iii. $[Fe(CN)_4(CO)_2]$

3. a. Write the time-dependent Schrödinger wave equation. Show that the total wavefunction for a system that varies with time is given by the expression (5)

$$\Psi(q,t) = \phi(q) e^{\frac{-iEt}{\hbar}}$$

b. What do you understand by the term "fluorescence quenching". Derive Stern- (5)

Volmer equation and explain the significance of this plot.

c. For each of the following electronic transitions, determine whether the transition is *allowed* or *forbidden* based on the selection rules: (5)

(i) $^1\Sigma^+ \rightarrow {}^1\Sigma^-$
(ii) $^1\Sigma^+ \rightarrow {}^1\Pi$
(iii) $^3\Pi \rightarrow {}^1\Sigma^+$
(iv) $^1\Delta \rightarrow {}^1\Sigma^-$

Also, the transition between the O_2 states $^3\Sigma_g$ and $^1\Delta_g$ violates three selection rules. Name them.

4. a. Derive the relationship between Einstein coefficients A_{ml} and B_{ml}, and show that (5)

$$A_{ml} = \frac{8\pi h\nu^3}{c^3} B_{ml}$$

b. The rotational lines crowd closely together with increasing m on the R-branch side, while the P-branch lines become widely spaced as m increases, where m is ($m = B_1 - B_0$). Using relevant equations, explain this. (5)

OR

Write the expression for the wavenumbers of the P and R branch lines in terms of rotational constants B_1 and B_0, for vibrational state v=1 and v=0, respectively. The observed spectroscopic lines in the spectrum of CO is given by

$$\bar{\nu}_{spect} = 2143.28 + 3.813\, m - 0.0175\, m^2 \text{cm}^{-1}$$

Determine the value of B_1 and B_0. Comment on why the value of $B_0 > B_1$.

c. Using appropriate electronic state potential energy diagrams, explain how the dissociation energy of a diatomic molecule such as I_2 can be determined? (5)

5. a. The lifetime τ of a certain transition in sodium atom at 589 nm has been measured as 16 ns. Determine the Einstein coefficients, A and B, alongwith their suitable units. (5)

b. The Mössbauer spectrum of a high-spin Fe^{2+} complex shows a quadrupole doublet, while that of a low-spin Fe^{3+} complex shows a sextet at low temperature. Explain. (5)

c. Explain the concept of fluorescence polarization and how do molecular rotation and fluorescence lifetime influence the observed polarization of emitted light? (5)

OR

Derive the expressions for fluorescence and phosphorescence lifetimes based on their radiative and non-radiative rate constants. Why is the phosphorescence lifetime generally greater than fluorescence lifetime?

6. Write short notes on the following **(any three)** 5 x 3

a. Jablonski diagram and mirror-image relationship

b. Circular Dichroism

c. Effect of polarity of solvent on n to π^* and π to π^* transitions

d. Isomer Shift in Mössbauer spectroscopy

e. Vibronic coupling and its relevance in electronic spectrocpy

f. Recoil energy, and Doppler effect in Mössbauer spectroscopy

g. Fluorescence Correlation Spectroscopy

(1000)