

2025

M.Sc. 3rd Semester Examination

CHEMISTRY

Paper : CEM - 301

(Advanced Spectroscopy-I)

Full Marks : 50

Time : Two Hours

*The figures in the margin indicate full marks.
Candidates are required to give their answers
in their own words as far as practicable.*

Group - A

Answer any *four* questions : $2 \times 4 = 8$

1. In addition to the use of microwave radiation, it is essential to apply external magnetic field for recording EPR spectrum of a sample. Comment on it.
2. What do you mean by "X-band frequency" and "Q-band frequency" in ESR spectroscopy? What are the advantages in using "Q-band frequency"?
3. Calculate the g value of an unknown radical shows ESR line at 1.301 T in a spectrometer operating at 39.41 GHz. (Given $\beta = 9.27 \times 10^{-24} \text{ JT}^{-1}$).
4. What do you mean by "adiabatic ionization energy" and "vertical ionization energy"?

P.T.O.

5. What is E-type delayed emission? Give example.
6. Show that the rate of the primary photophysical process (excitation) is equal to the intensity (I_0) of the radiation absorbed by the molecule.

Group - B

Answer any *four* questions : 4×4=16

7. What is meant by the static and dynamic quenching of fluorescence? How do you differentiate between the static and dynamic quenching of fluorescence? 2+2
8. What is meant by steady state and time resolved fluorescence spectroscopy? Give schematic diagram of the instrument for each of the steady state and time resolved fluorescence spectroscopy. 1+3
9. What is P-type delayed emission? Give example. Write down the mechanistic aspect to explain P-type delayed emission. 1+3
10. When the irradiation of malonic acid is done with X-ray, two products are obtained whose ESR spectrum consists of a dominant doublet and a weak triplet. Identify the products. 4
11. What do you mean by "zero field splitting"? Explain the appearance of three lines of different intensities in the ESR spectrum of naphthalene diradical. 4
12. Considering hyperfine coupling with copper(II) and nitrogen nucleus predict the ESR spectrum of bis-salicylaldehyde Cu(II) complex. 4

(3)

Group - C

Answer any *two* questions : $8 \times 2 = 16$

13. (a) Explain the photoelectron spectrum of hydrogen molecule.
- (b) Showing "crystal field splitting" and weak "zero-field splitting" predict the expected EPR spectrum of octahedral Cr(III) complex. $4+4$
14. (a) Explain the appearance of two lines in the atomic photoelectron spectrum of Ar.
- (b) Predict the intensity distribution in the hyperfine lines of the ESR spectrum of $[\text{NH}_2]$ radical.
- (c) Photoelectron spectrum of molecular nitrogen exhibits three vibrationally structured photoionizations at about 15.6, 17.0 and 18.8 eV and a detail of the spectrum is given below. Predict the nature of different molecular orbitals of N_2 molecule. (Vibrational frequency for the ground state of N_2 is 2345 cm^{-1}).

	Ionization at 15.6 eV	Ionization at 17.0 eV	Ionization at 18.8 eV
Most intense peak	adiabatic Ionization	vertical Ionization ($v = 0$ to $v = 1$)	adiabatic Ionization
Vibrational spacing	2150 cm^{-1}	1810 cm^{-1}	2390 cm^{-1}

$2+2+4$

P.T.O.

(4)

15. Write down the steps involved and the rate of each step for the biomolecular photophysical processes. Deduce Stern-Volmer equation. How do you obtain Stern-Volmer quenching constant (K_{SV}) using half quenching method? 2+4+2
16. What is meant by twisted intramolecular charge transfer (TICT) emission? Give example. Write down the characteristics of TICT emission. Explain the effect of polarity of the medium on TICT emission. 2+2+4

Internal Assessment : 10 marks
