

M.Sc. CHEMISTRY
Third Semester
SPECTROSCOPY-II
(MSC – 14)

Duration: 3Hrs.

Full Marks: 70

Part-A (Objective) =20
Part-B (Descriptive) =50

(PART-B: Descriptive)

Duration: 2 hrs. 40 mins.

Marks: 50

Answer any five of the following questions:

1. What are the different types of intensity distribution of the vibrational structures in electronic transitions? State Franck / Condon Principle and apply this Principle to explain the various intensity distributions of the vibrational structure in electronic transition. (4+2+4= 10)

Or

- (i) State the selection rule on the basis of symmetry properties of electronic states.
(ii) Calculate the frequency of R branch and the frequency of P branch of rotational fine structure in electronic vibrational transition.
(iii) What do you mean by dissociation and pre dissociation of a molecule? Give the expression of dissociation energy and suggest a method to determine it. (2+2+4= 10)

2. Explain the basic principle of ESR spectroscopy and deduce the condition of resonance. Write down the expression of "g" value and calculate it for a free electron. Why ESR spectra is obtained in derivative mode? [(4+2)+(2+1)+1=10]

Or

- (i) Explain what do you mean by fluorescence and phosphorescence.
(ii) What are the properties of Laser radiation?
(iii) Calculate the ESR frequency in a magnetic field of 20,000 gauss (Given that $\beta = 9.273 \times 10^{-24} \text{ JT}^{-1}$ and $g = 2.0$) (4+4+2=10)

3. Explain the principal of Mössbauer spectroscopy. Show that in order to have resonance absorption the line width must be equal or greater than the loss of γ ray energy due to recoil. Why the source and the sample are put in the crystal in Mössbauer spectroscopy? (5+3+2=10)

Or

- (i) What do you mean by Quadrupole moment? Discuss the quadrupole splitting of ^{57}Fe in an asymmetrical electric field. (2+3=5)
- (ii) What are different types of bands in ultra violet (UV) spectra of organic compounds? Discuss the factors that affect the position of UV absorption band. (3+2=5)
4. (i) Discuss the free electron model of conjugated polyene to calculate the wavelength of transition between HOMO and LUMO. Explain the effect of solvent polarity on $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition. (4+2=6)
- (ii) Write short notes on: (2+2=4)
- (a) Chromophores and (b) Auxochromes
5. (i) What do you mean by mass spectrum of a sample? State the essential components of mass spectrometer. Show that ions of $\frac{m}{e}$ value follow a circular path of radius "r" for a given value of accelerating voltage and magnetic field of the magnetic analyser. (2+2+3=7)
- (ii) Discuss the chemical ionization technique used in mass spectrometry. (3)

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Duration: 20 minutes

Marks - 20

(PART A - Objective Type)

I. Choose the correct answer:

1×20=20

- i. Electronic excitation occur in the range of wavelength from
(a) 200 nm to 780 nm (b) 300 nm to 600 nm only
(c) 70 nm to 300 nm only (d) 300 nm to 1200 nm only
- ii. Transition associated with highest wavelength is in
(a) $\pi \rightarrow \pi^*$ (b) $\sigma \rightarrow \sigma^*$
(c) $n \rightarrow \pi^*$ (d) $n \rightarrow \sigma^*$
- iii. The shift of absorption maximum toward longer wavelength is known as
(a) Batho chromic shift (b) Hypso chromic shift
(c) Hypo chromic shift (d) Hyper chromic shift
- iv. Mössbauer line split into a doublet in $\text{Na}_2 [\text{Fe} (\text{CN})_5 \text{NO}] 2\text{H}_2\text{O}$ due to extensive
(a) σ bonding in Fe - O linkage (b) π bonding in Fe - N - O linkage
(c) σ bonding in Na - Fe - Linkage (d) Isomeric shift
- v. The selection rule of P and R branch of rotational spectral line are respectively
(a) $\Delta J = +1$ and -1 (b) $\Delta J = -1$ and $+1$
(c) $\Delta J = 0$ and $+1$ (d) $\Delta J = -1$ and 0
- vi. ESR spectra is obtained in the region of
(a) Micro ware (b) Radio frequency
(c) Infra red (d) Ultra-violet
- vii. The transition in CH_4 molecule due to the absorption of ultra violet radiation is
(a) $\sigma \rightarrow \sigma^*$ (b) $\pi \rightarrow \pi^*$
(c) $n \rightarrow \pi^*$ (d) $n \rightarrow \sigma$
- viii. The m/z value for M^+ fragment in but anal is
(a) 70 (b) 72 (c) 75 (d) 68
- ix. A high resolution mass spectrometer is required for
(a) C_2H_4^+ , CH_2N^+ (b) CO^+
(c) N_2^+ (d) All

- x. The number of ESR spectral line of benzene anion is
 (a) One (b) Two (c) Five (d) Seven
- xi. The intensities of the ESR hyperfine spectral lines of the methyl radical is in the ratio
 (a) 1 : 3 : 3 : 1 (b) 1 : 2 : 1 : 2
 (c) 3 : 1 : 1 : 3 (d) 1 : 4 : 6 : 4 : 1
- xii. The electron spin resonance is an example of
 (a) Stark effect (b) Zeeman effect
 (c) Paschen-Back effect (d) L - S coupling
- xiii. Transmittance is
 (a) $10^{-\epsilon cl}$ (b) $10^{\epsilon cl}$ (c) ϵcl (d) $\frac{1}{\epsilon cl}$
- xiv. The region extending from 200 nm to 380 nm wavelength is called
 (a) Near UV (b) Vacuum UV
 (c) Quartz UV (d) Both (a) & (c)
- xv. Mössbauer effect is greater at lower temperature because it depends on
 (a) Recoil free fraction of γ rays emitting atoms (b) Dohhler shift
 (c) Isomer Shift (d) None of the above
- xvi. Which of the following transitions are allowed by selection rule
 (a) ${}^3\Sigma_g^- \leftrightarrow {}^3\Sigma_u^-$ (b) ${}^3\Sigma_g^- \leftrightarrow {}^3\Sigma_u^+$
 (c) ${}^3\Sigma_g^- \leftrightarrow 3\Delta_u$ (d) ${}^3\Sigma_g^- \leftrightarrow {}^1\Sigma_g^+$
- xvii. Mössbauer effect is related to
 (a) Resonance fluorescence of γ rays (b) Stark effect
 (c) Intra nuclear rather than electronic energy level (d) Both (a) & (c)
- xviii. Which of the following will not exhibit ESR spectrum?
 (a) NO (b) N₂ (c) CU⁺ (d) CO₂
- xix. The nucleus having nuclear spin $I = \frac{5}{2}$ is
 (a) ¹⁷O (b) ¹⁵N (c) ³⁵Cl (d) ¹¹B
- xx. The NMR spectra of H₂, CH₄, C₂H₆ and C₆H₆ exhibit
 (a) Singlet (b) Doublet (c) Triplet (d) Quintet
