

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

1. Answer the following questions: (any five)

5 × 5=25

- a) Write the selection rule for P, Q and R branches of rotational fine structure and calculate the frequencies of each branch in terms of rotational constant. Explain, how a band head is formed?
- b) State Frank-Condon principle and apply this principle to explain the intensity distribution of vibrational bands in electronic transitions of diatomic molecules.
- c) Give the basic principles of ESR spectroscopy and deduce the expression for the frequency of ESR spectral line.
- d) What do you mean by hyperfine structure in ESR spectral line? State the causes of it. Draw the ESR spectra of ethyl radical anion.
- e) What is Mossbauer effect? Discuss the principle of it and calculate the condition to observe the Mossbauer shift.
- f) Discuss the properties of Mossbauer nuclides. Calculate the expression for isomeric shift in terms of electron density.
- g) What are different types of electronic transitions in organic molecules? State the selection rules of these transitions. What changes can you expect if the solvent is polar?

2. Answer the following questions: (any five)

5 × 5 = 25

- a) Write down the principles of mass spectrometry and show that this technique is different from conventional spectroscopic technique. What do you mean by molecular ion peak?
- b) Discuss the chemical ionization (CI) technique used in mass spectrometry.
- c) Show how you can separate ions of various (m/e) values with the help of magnetic sector analyser. Distinguish magnetic scanning and electric voltage scanning. Define resolving power of a mass spectrometer.
- d) Discuss how the presence of isotopes of an element can be detected in the mass spectra. Explain it with the help of mass spectra of 1-bromohexane.
- e) Write short notes on:
(i) Metastable ion peak, (ii) phosphorescence
- f) Write down the properties of LASER radiation. State the conditions to obtain LASER radiation and explain how can you achieve it.
- g) Consider benzene in a circular ring. Assume C-C bond length in benzene is 1.40 Å. Find the wavelength of the first electronic band in benzene. Assume C-C bond length is equal to radius of the ring.

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(The figures in the margin indicate full marks for the questions)

Duration: 20 minutes

Marks – 20

PART A- Objective Type

I. Select and put '✓' mark on the appropriate answer: 1×20=20

1. The shift of an absorption maximum towards longer wavelength is known as:
(a) Hypsochromic effect
(b) Hyperchromic effect
(c) Bathochromic effect
(d) Hypochromic effect
2. Movement of nuclei is negligible during the time taken by an electronic transition. It is called:
(a) Frank Condon principle
(b) Born-Oppenheimer approximation
(c) Lambert Beer law
(d) Hund's rule
3. Electronic excitations occur in the range of:
(a) 200 nm to 780 nm
(b) 220 nm to 500 nm
(c) 250 nm to 700 nm
(d) 290 nm to 1000 nm
4. Increase of polarity of solvents shift $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ band respectively to:
(a) Shorter and longer wavelength
(b) Shorter and shorter wavelength
(c) longer and shorter wavelength
(d) longer and longer wavelength

5. The correct order of energies in the transition is:
- $\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \pi^*$
 - $n \rightarrow \sigma^* > \pi \rightarrow \pi^* > \sigma \rightarrow \sigma^* > n \pi^*$
 - $\pi \rightarrow \pi^* > n \rightarrow \sigma^* > \sigma \rightarrow \sigma^* > n \pi^*$
 - $n \rightarrow \sigma^* > n \rightarrow \pi^* > \pi \rightarrow \pi^* > \sigma \rightarrow \sigma^*$
6. The correct order of shift of wavelength in disubstituted benzene is:
- para > meta > ortho
 - ortho > meta > para
 - meta > ortho > para
 - ortho > para > meta
7. Transitions involving d-orbitals are:
- Laporte forbidden
 - Laporte allowed
 - Spin allowed
 - Spin forbidden
8. Laporte allowed transitions involved:
- $g \rightarrow g$
 - $g \rightarrow u$
 - $u \rightarrow u$
 - all
9. Optical rotation and circular dichroism together are known as:
- Optical rotator dispersion (ORD)
 - Cotton effect
 - Frank-Condon principle
 - Stark effect
10. When, $I_x < I_y = I_z$, then the molecule is:
- oblate
 - prolate
 - asymmetric top
 - linear
11. The rotational spectrum of a rigid diatomic rotor consists of equally spaced lines with spacing equal to (B is rotational constant)
- 2B
 - B
 - B/2
 - 3B
12. The increasing order of stretching frequencies for $C \equiv C$, $C = C$, $C - C$ is:
- $C - C < C = C < C \equiv C$
 - $C \equiv C < C = C < C - C$
 - $C \equiv C < C - C < C = C$
 - $C = C < C \equiv C < C - C$
13. For two equivalent protons, the numbers ESR lines are:
- 1
 - 2
 - 3
 - 4

14. The system which will not show ESR spectrum is:
- (a) CO_2
 - (b) CH_3
 - (c) Cu^{2+}
 - (d) Na^+
15. Spectroscopically detectable energy are called:
- (a) Term
 - (b) Orbitals
 - (c) Microstates
 - (d) None
16. In alkali metal spectra every component level is:
- (a) Doublet excluding S level
 - (b) Quartet excluding S level
 - (c) Triplet
 - (d) Singlet
17. Charge transfer transition may be regarded as:
- (a) Internal redox process
 - (b) Oxidation process
 - (c) Adsorption
 - (d) Absorption
18. The vibrations, without a centre of symmetry are active in:
- (a) Infrared but inactive in Raman
 - (b) Raman but inactive in IR
 - (c) Both (a) and (b)
 - (d) None
19. The expression for calculating the frequency of vibration of a diatomic molecule is:
- (a) $v = \frac{1}{2\pi c} \sqrt{\frac{k}{\mu}}$
 - (b) $v = \frac{1}{2\pi^2} \cdot \frac{k}{\mu}$
 - (c) $v = \sqrt{\frac{k}{\mu^2}}$
 - (d) $v = \frac{1}{2\pi} \cdot \frac{k^2}{\mu}$
20. Mossbauer effect is greater at lower temperatures because it depends on:
- (a) Recoil free fraction of the total γ ray emitting atoms
 - (b) Doppler shift
 - (c) Isomers shift
 - (d) None
