

**M.Sc. CHEMISTRY  
THIRD SEMESTER  
SPECTROSCOPY-II  
MSC-304**

Duration: 3 Hrs.

Marks: 70

PART : A (OBJECTIVE) = 20  
PART : B (DESCRIPTIVE) = 50

**[ PART-B : Descriptive ]**

Duration: 2 Hrs. 40 Mins.

Marks: 50

**[ Answer question no. One (1) & any four (4) from the rest ]**

1. What are the different types of intensity distributions of the vibrational bands in electronic transitions? State the principle behind it and apply it to explain the different types of intensity distributions. (4+2+4=10)
2. Explain fluorescence and phosphorescence. Mention the selection rule on the basis of symmetry properties of electronic state. Calculate the frequencies of 'R' & 'P' branches of rotational and fine structure in electronic vibrational transition. What is band head? [(2+2)+1+(2+2)+1=10]
3. Deduce the condition of resonance in ESR spectroscopy. Why ESR spectrum is obtained in derivative mode? Calculate 'g' value for free electron used in ESR spectroscopy. State the cause of hyperfine structure in ESR spectral line. Find the value of the Bohr magneton if in a magnetic field of 9506.690 Tesla resonance is found at 0.34 MHz. (Given that  $g=2.0023$ ) (2+2+2+2+2=10)
4. Discuss the basic principle of Mössbauer spectroscopy and show that in order to have resonance absorption the line width must be equal or greater than the loss of gamma ( $\gamma$ ) ray energy due to recoil. Explain why the source and the sample are put in the crystal in Mössbauer spectroscopy? (4+3+3=10)
5. Explain what do you mean by dissociation and predissociation. Deduce the expression for dissociation energy of a molecule. Suggest a method to determine the dissociation energy of a molecule when no continuum appears in the vibrational bands in electronic transition. (2+2+3+3=10)
6. Explain the basic principle in mass spectroscopy. How a mass spectrum is represented? Mention the essential components of a mass spectrometer. Show that ions of  $m/e$  value follow a circular path of radius  $r$  for a given value of the accelerating voltage and magnetic field of the magnetic analyser. Discuss the chemical ionization technique used in mass spectroscopy. (2+1+1+3+3=10)



7. (i) What are different types of electronic transitions? State the selection rules in electronic transition. (3+2=5)
- (ii) State Beer-Lambert law and explain why the colour of  $\text{KMnO}_4$  solution is violet. (2+3=5)
8. Write short notes on *any two* of the following: (2×5=10)
- (i) Laser action and properties of laser radiation.
- (ii) Ultra-violet absorption spectrum of  $\alpha$ ,  $\beta$  unsaturated carbonyl Compounds.
- (iii) McLiafferty rearrangement.

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[ PART-A : Objective ]

Choose the correct answer from the following :

1×20=20

- The range of frequencies  $3 \times 10^{12}$  Hz –  $3 \times 10^{14}$  Hz is in the region of:
  - Infrared
  - Visible
  - Microwave
  - Radio frequency
- Boron trichloride molecule has:
  - $I_B = I_C < I_A$
  - $I_B = I_C > I_A$
  - $I_B = I_C = I_A$
  - $I_B \neq I_C \neq I_A$
- The lowest frequency is associated with the transition:
  - $n \rightarrow \pi^*$
  - $\pi \rightarrow \pi^*$
  - $n \rightarrow \sigma^*$
  - $\sigma \rightarrow \sigma^*$
- Which of the following will not show ESR spectrum?
  - $Zn^{2+}$
  - $Cu^{2+}$
  - $CO_2^-$
  - NO
- $CH_3NH_2$  molecule undergoes transition:
  - $n \rightarrow \sigma^*$  and  $\sigma \rightarrow \sigma^*$
  - $n \rightarrow \pi^*$  and  $\sigma \rightarrow \sigma^*$
  - $\pi \rightarrow \pi^*$  only
  - $\sigma \rightarrow \sigma^*$  only
- R band is found in:
  - benzene
  - acetaldehyde
  - phenol
  - nitro-benzene
- The e.s.r hyperfine spectrum line of benzene radical is a:
  - Quartet
  - Septet
  - Octate
  - Pentate
- Band head occurs in the P branch of the rotational spectral line when:
  - $r_e' = r_e''$
  - $r_e' < r_e''$
  - $r_e' > r_e''$
  - $r_e' \gg r_e''$
- The intensities of hyperfine lines of  $CH_3$  radical in e.s.r spectroscopy are in the ratio:
  - 3:1:1:3
  - 1:3:3:1
  - 1:3:1:3
  - 3:1:3:1
- Hypsochromic effect is related with:
  - Increase of  $\epsilon_{max}$
  - Increase in frequency
  - Decrease in frequency
  - Decrease of  $\epsilon_{max}$
- The intensity distribution of the vibrational bands in the absorption spectra during electronic transition of Iodine molecule shows that:
  - $r_e' \approx r_e''$
  - $r_e' \leq r_e''$
  - $r_e' > r_e''$
  - $r_e' < r_e''$
- Transmittance is expressed as:
  - $\epsilon cl$
  - $10^{\epsilon cl}$
  - $10^{-\epsilon cl}$
  - $\frac{1}{\epsilon cl}$
- Increase in polarity of solvent shift the absorption maximum of carbonyl compound to shorter wavelength in:
  - $\sigma \rightarrow \sigma^*$
  - $\pi \rightarrow \pi^*$
  - $n \rightarrow \pi^*$
  - $n \rightarrow \sigma$



14. Mössbauer effect is greater at lower temperature because it depends on:
- Isomer shift
  - Doppler shift
  - Recoil free fraction of total  $\gamma$  ray emitting atoms
  - Half life of the excited atoms
15. The selection rule for the transition among energy levels due to quadrupole splitting is:
- $\Delta m_l = 0$
  - $\Delta m_l = 1$
  - $\Delta m_l = 0, \pm 1$
  - $\Delta m_l = -1$
16. In Mössbauer spectroscopy, the main hyperfine interaction(s) is/are:
- Isomer shift
  - Quadrupole splitting
  - Nuclear Zeeman splitting
  - All
17. Number of translational, rotational and vibrational degrees of freedom in  $\text{CO}_2$  molecule are respectively:
- 2, 3, 4
  - 4, 3, 2
  - 4, 2, 3
  - 3, 2, 4
18. The electron which contribute to isomer shift in Mössbauer spectroscopy are:
- d electron
  - p electron
  - f electron
  - s electron
19. Mössbauer spectra of  $[\text{Fe}(\text{CN})_6]^{4-}$  and  $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$  consist of respectively:
- 1 line each
  - 2 lines each
  - 2 and 4 lines
  - 1 and 2 lines
20. The  $m/e$  value for  $\text{M}^+$  fragment in butanol is:
- 70
  - 68
  - 75
  - 72

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Course : .....

Semester : ..... Roll No : .....

Enrollment No : ..... Course code : .....

Course Title : .....

Session : ..... 2017-18 ..... Date : .....

## Instructions / Guidelines

- The paper contains twenty (20) / ten (10) questions.
- Students shall tick ( $\checkmark$ ) the correct answer.
- No marks shall be given for overwrite / erasing.
- Students have to submit the Objective Part (Part-A) to the invigilator just after completion of the allotted time from the starting of examination.

Full Marks	Marks Obtained
20	

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Scrutinizer's Signature.....  
Examiner's Signature.....  
Invigilator's Signature