REV-01
MSC/32/37

2025/06

SET A

M.Sc. CHEMISTRY
SECOND SEMESTER
MOLECULAR SPECTROSCOPY II
MSC – 205

[USE OMR FOR OBJECTIVE PART]

Duration: 1:30 hrs. **Full Marks: 35**

Objective

Time: 15mins. **Marks: 10**

Choose the correct answer from the following: ***1×10=10***

1. Spin-spin coupling in NMR gives rise to:
   a. Integration
   b. Chemical shift
   c. Multiplets
   d. Relaxation

2. Which of the following nuclei is NMR active?
   a. ^{16}O
   b. ^{14}N
   c. ^{12}C
   d. ^{4}He

3. In a high-resolution ^{1}H NMR spectrum, a quartet with a 1:3:3:1 intensity ratio is typically due to:
   a. 1 neighboring proton
   b. 2 neighboring protons
   c. 3 neighboring protons
   d. 4 neighboring protons

4. What is the typical range of chemical shifts for ^{13}C NMR?
   a. 0–20 ppm
   b. 0–240 ppm
   c. 0–1000 ppm
   d. 0–10 ppm

5. The Franck–Condon principle is based on the assumption that:
   a. Electronic transitions are much slower than nuclear motions
   b. Vibrational transitions require high energy
   c. Rotational transitions occur simultaneously with electronic ones
   d. Electronic transitions are much faster than nuclear motions

6. Which isotope is most commonly used in Mössbauer spectroscopy?
   a. Fe-56
   b. Fe-57
   c. Co-60
   d. I-131

7. The isomer shift in Mössbauer spectra depends on
   a. Gamma ray energy
   b. Nuclear spin
   c. s-electron density at the nucleus
   d. p-orbital population

8. The Mössbauer spectrum of a paramagnetic substance at room temperature typically shows
   a. No splitting
   b. Doublet
   c. Triplet
   d. Sextet

9. In ESR, the energy splitting of spin states is caused by
   a. External magnetic field
   b. Electric field
   c. Spin-orbit coupling
   d. Thermal vibrations

10. The intensity of an ESR signal is directly proportional to
   a. The number of nuclear spins
   b. The energy gap between spin state
   c. The microwave power
   d. The number of unpaired electrons

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(Descriptive)

Time:1 hr. 15 mins. **Marks: 25**

[Answer question no.1 & any two (2) from the rest]

1. **a.** At a magnetic flux density of 1.65 T, the frequency separation between protons in benzene and tetramethylsilane is 510.5 Hz. What is the chemical shift in δ and τscales. (Given $g_N = 5.585$ and $\beta_N = 5.051 \times 10^{-27}$ JT^{-1}) 3+2=5

   b. Draw the splitting of ESR signals due to the interaction of one electron with two equivalent nuclei having 'I' value ½.

2. **a.** Sketch a potential energy diagram for a molecule with two electronic states. Indicate possible Franck–Condon transitions and explain which is the most probable. 4+3+3 =10

   b. Calculate the precessional frequency of a proton in a field of 1.8T. (Given $g_N = 5.585$ and $\beta_N = 5.051 \times 10^{-27}$ JT^{-1}).

   c. What is shielding and deshielding in NMR? How do they affect chemical shifts?

3. **a.** Why is TMS (tetramethylsilane) used as a reference in NMR? 2+3+1+3 +1=10

   b. Which of the following molecules will show spin-spin coupling in their NMR spectra? Give the multiplicity of each kind of proton where the coupling is observed?
   CH_3Cl, CH_3COCH_3, CH_2ClCH_2Br, $CH_2ClCHCl_2$

c. In a ^1H NMR spectrum, a doublet has peaks separated by 8.4 Hz. What is the coupling constant?

d. What is spin-spin coupling, and how does it arise in NMR spectroscopy?

e. A ^1H NMR spectrum of a diene shows J = 15 Hz between two vinyl (-CH=CH-) protons. Are they cis or trans?

4. a. How many number lines can be observed in the ESR spectra of $(Ph)_3C\bullet$ and $\bullet NH_2$? Draw the spike diagram showing all the intensity ratios for $\bullet NH_2$ and calculate the overall intensity ratio. **3+2+2+3 =10**

b. Find number of lines and draw the spike diagram for CD_3-$CD_2\bullet$.

c. What will be the number of ESR lines and their intensity ratio of $\bullet NH_2$ if A_N = 20 mT and A_H= 10 mT, where A is the hyperfine splitting constant.

d. Explain Doppler Effect and how the recoiling energy losses can be minimized.

5. a. For a radical species, an ESR spectrum was observed at 3810 Gauss magnetic field and 9600 MHz microwave frequency. What will be the g-value? **(1 T = 10^4 Gauss)** **3+2+2+1 +2=10**

b. Find if quadruple splitting is present or not in $[Fe(CO)_5]$ and $[Fe(H_2O)_6]^{2+}$ complex?

c. Arrange in increasing order of isomer shift and give explanation for the following: SnF_4, $SnCl_4$, $SnBr_4$, SnI_4

d. Among CH_3 and NH_3, which one will have higher hyperfine splitting constant.

e. Write about different factors that affect the Isomer Shift.

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