H-4/12/22

Roll No.

IV Semester Examination, 2022

M.Sc.

CHEMISTRY

Paper IV (Spectroscopy)

Time: 3 Hours] [Max. Marks: 80

Note: All questions are compulsory. Question Paper comprises of 3 sections. Section **A** is objective type/multiple choice questions with no internal choice. Section **B** is short answer type with internal choice. Section **C** is long answer type with internal choice.

SECTIONA

 $1\times8=8$

(Objective Type/Multiple Choice Questions)

Note: Attempt all the *eight* questions.

Choose the correct answer:

- **1.** Spin-spin coupling is not observed when the protons are separated by more than :
 - (a) One sigma bond
 - (b) Two sigma bond
 - (c) Three sigma bond
 - (d) Four sigma bond

P.T.O.

2. The ¹³C, NMR spectrom of a compound shows 6 peaks and ¹H NMR spectrum shows 5 peaks. Which of the following is this compound?

(a)
$$CH_3 - CH_2 - CH_2 - CH_2 - CH_3$$

(b)
$$CH_3 - C(CH_3)_2 - CH_2 - CH_2 - CH_3$$

(c)
$$CH_3 - CH(CH_3) - CH_2 - CH_2 - C(CH_3)_2 - CH_3$$

(d)
$$CH_3 - CH(CH_3) - CH_2 - CH_2 - CH_3$$

3. Which of the hydrogens a—d in the following molecule gives a triplet signal in normal ${}^{1}H$ NMR spectrum?

$$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3 - \text{C} - \text{CH}_2 - \text{CH} \left(\text{OCH}_3 \right)_2 \end{array}$$

- (a) hydrogen a
- (b) hydrogen c
- (c) hydrogen b
- (d) hyrogen d
- **4.** How many signals does the aldehyde $(CH_3)_3CCH_2CHO$ have in 1H NMR and ^{13}C NMR spectra?
 - (a) Five ¹H signals and six ¹³C signals
 - (b) Three ¹H signals and four ¹³C signals
 - (c) Five ¹H signals and four ¹³C signals
 - (d) Three ¹H signals and six ¹³C signals

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5. Hyperfine splitting that can be observed with two equivalent protons will be:

(a) 2

(b) 3

(c) 5

(d) 6

6. The number of ESR lines for the triphenyl methyl radicals are :

(a) 156

(b) 106

(c) 150

(d) 196

7. The peak at m/z 91 in the mass spectrum for alkyl benzene is due to which one of the followings:

- (a) Alpha fission
- (b) Retro Diels-Alder rearrangement
- (c) Mc-Laffartey rearrangement
- (d) Tropylium ion formation

8. Fe* very rapidly drops to the ground state Fe, the energy change ΔE involved being 2.30×10^{-28} J per nucleus. The frequency of emitted γ -rays is :

(a) $3.1 \times 10^{10} \text{ Hz}$

(b) $3.5 \times 10^{18} \text{ Hz}$

(c) $3.5 \times 10^{16} \text{ Hz}$

(d) $3.4 \times 10^{18} \text{ Hz}$

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P.T.O.

SECTION B

 $6 \times 4 = 24$

(Short Answer Type Questions)

Note: Attempt all the questions.

Unit-I

1. Discuss the contact and pseudo contact shifts with suitable examples.

Or

Discuss the karplus curve for the variation of coupling constant with the dihedral angle.

Unit-II

- **2.** Write an explainatory notes on the following :
 - (a) COSY technique,
 - (b) DEPT technique.

Or

What is carbon-13 NMR spectroscopy? Discuss the merits and demerits of C¹³ NMR and H¹ NMR spectroscopy.

Unit-III

3. Discuss the biological applications of ESR with examples.

Or

Explain symmetry and shapes of AB_2 , AB_4 and AB_5 types of molecules.

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Unit-IV

4. Describe the types of ions produced in a mass spectrometer.

Or

Discuss the formation of following Mossbaurer nucliders:

(a) ⁵⁷Fe

(b) 119 Sn

(c) ¹⁹¹Ir

SECTION C

 $12 \times 4 = 48$

(Long Answer Type Questions)

Note: Attempt all *Four* questions.

Unit-I

1. Write down all possible structural formulae of compound having molecular formula C₃H₆Cl₂. Is it possible to identify them on the basis of low or/and high resolution PMR spectra? Ignore the interaction of Cl atoms with H atom.

Or

- (a) Discuss the spectrum of CH_3CH_2OH in acidic medium and in presence of D_2O .
- (b) Write a note on contact shift reagents.

Unit-II

2. (a) Is spin-spin coupling between C¹³—C¹³ nuclei observed in C-13 NMR?

Discuss some techniques for simplification of C-13 NMR spectra.

(b) Discuss how C-13 NMR is applicable in the structure determination of carbonyl compound.

Or

Discuss the applications of photoacoustic spectroscopy in the chemical and surface analysis.

Unit-III

3. What do you understand by hyperfine splitting and hyperfine splitting constant in ESR? Explain the hyperfine splitting in CH₃ radical.

Or

Discuss the following:

- (a) Spin polarization for atoms & transition metal ions.
- (b) Application of resonance spectroscopy for the study of active sites of matalloproteins.

Unit-IV

4. Discuss the basic principle of Mössbauer spectroscopy and explain this technique to the study of bonding and structure of Sn²⁺ and Sn⁴⁺ compounds.

Or

Discuss general fragmentation mode in organic compounds in detail with suitable examples.

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