



MANIPAL UNIVERSITY
DEPARTMENT OF SCIENCES
SECOND SEMESTER M. Sc. (CHEMISTRY)
END SEMESTER EXAMINATIONS
ORGANIC SPECTROSCOPY-II (CHM - 608)

Time: 3 Hours

Date:

Max. Marks: 50

Note: Answer any five full questions. Write diagrams, equations or examples wherever necessary.

1. A. Discuss about any two alternatives for magnetic/electrostatic focusing. Write two advantages of FTMS method.
 B. Explain the factors affecting chemical shift.
 C. Justify the following statements;
 (i) Isotopic substitution method could be used to study the reaction mechanism involved in hydrolysis of ester using mass spectrometry.
 (ii) TMS is used as a reference in NMR spectroscopy

(4 + 4 + 2)

2. A. Explain the energy levels and transition frequencies for excitation ($I_e = 3/2$) of a Mossbauer nucleus from ground level of spin, $I_g = 1/2$ due to magnetic hyperfine interactions.
 B. What are the basic components of ESR spectrometer? Explain the working of ESR spectrometer with a schematic diagram.
 C. Differentiate between ^1H NMR and ^{13}C NMR spectroscopic techniques

(4 + 4 + 2)

3. A. Discuss the basic fragmentation and rules by taking the example of alkanes, alkenes, cycloalkenes and alkyl benzenes.
 B. (i) Deduce the structure of the organic compounds having the following molecular formula and ^1H NMR spectral data
 (a) $\text{C}_4\text{H}_8\text{O}_2$

| Chemical Shift (ppm) | Peak area | Splitting |
|----------------------|-----------|-----------|
| 3.674 | 3 | Singlet |
| 2.324 | 2 | Quartet |
| 1.148 | 3 | triplet |

(b) CH_3NO

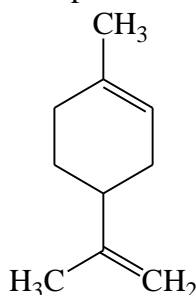
| Chemical Shift (ppm) | Peak area | Splitting |
|----------------------|-----------|-----------|
| 8.04 | 1 | Doublet |
| 7.39 | 2.13 | doublet |

- (ii) Explain the instrumentation involved in NMR spectrometer
- C. Differentiate between the following
 (i) Continuous wave NMR and FTNMR
 (ii) Hard and soft ionization techniques

(4 + 4 + 2)

4. A. Describe the energy levels, expected ESR spectrum, intensities of spectral lines and the frequencies of absorption of an unpaired electron coupling with two non-equivalent nuclei, each of spin, $I = \frac{1}{2}$.

- B. (i) Discuss the expected ^{13}C DEPT spectra of the following molecule



- (ii) Write a short note on ^{19}F and ^{31}P NMR spectroscopic techniques.

- C. The compound BCl_3 has C_3 axis. The NQR study of this compound yields $q_{zz} = 2 \times 10^{-25}$. Calculate the NQR frequency. Given: $e = 4.8 \times 10^{-10}$ esu, $q = -0.08 \times 10^{-24} \text{ cm}^2$.

(4 + 4 + 2)

5. A. Explain the principle involved in GC-MS technique. How its interface is different from the interface involved in HPLC- MS technique.

- B. (i) Illustrate the effect of deuterium exchange on NMR spectrum
(ii) How do you distinguish the following pairs using proton NMR spectra?
(a) propanal and propanone (b) 1-butyne and 2-butyne

- C. (i) An unknown substance has a molecular ion peak at $m/z = 107$, with a relative intensity of 100. The relative intensity of the $M + 1$ peak is 8.00, and the relative intensity of the $M + 2$ peak is 0.30. What is the molecular formula for this unknown?
(ii) An unknown substance shows a molecular ion peak at $m/z = 78$. The M and $M+2$ peak had a relative intensity of 3:1. What is the molecular formula of the unknown?

(4 + 4 + 2)

6. A. Predict the ^{13}C chemical shift values for the following molecules

- (i) n-octane
(ii) 2-Methylpentane (correction for branching $1^\circ(3^\circ) = -1.1$, $2^\circ(3^\circ) = -2.5$, $3^\circ(2^\circ) = -3.7$)
(iii) 3-hexanol (correction for internal OH substitution: α carbon = +41, β carbon = +8, γ carbon = -5)
(iv) 1-chlorobutane (correction for terminal Cl substitution: α carbon = +31, β carbon = +11, γ carbon = -4)

- B. The spin of ^{59}Co is $7/2$. Assume an axial field gradient, obtain expressions for frequencies of the NQR transitions.

- C. Explain, why FeSO_4 shows quadrupole splitting whereas $\text{K}_4\text{Fe}(\text{CN})_6$ does not show in Mossbauer spectroscopy?

(4 + 4 + 2)
