Reg. No.

MANIPAL
ACADEMY of HIGHER EDUCATION
(Deemed to be University under Section 3 of the UGC Act, 1956)

DEPARTMENT OF SCIENCES
III SEMESTER M.Sc. (Chemistry)
END SEMESTER EXAMINATIONS, DECEMBER 2021

Spectroscopy – II [CHM 6101]
(CBCS Scheme)

Time: 3 Hours Date: 09 Dec 2021 MAX. MARKS: 50

Note: (i) Answer **ALL** questions.
(ii) Draw diagrams, and write equations wherever necessary
(iii) Given: Planck's constant (h) = 6.626×10^{-34} Js;
Avogadro number (N) = 6.023×10^{23} mol^{-1}.
Velocity of light (c) = 3×10^{8} m/s

1 A. Explain the instrumentation involved in continuous wave proton NMR. Why is TMS preferred as the internal standard in Proton NMR?

1 B. Why do protons appear at different chemical shift values? Describe how the anisotropic effect and hydrogen bonding affect chemical shift values.

1 C. Give reason
i) Presence of carboxylic acid group in a sample is indicated by highly deshielded signal in ^{1}H NMR spectra
ii) In ^{1}H NMR spectra of molecules with terminal alkene groups, a doublet of doublet peak appears instead of a triplet signal. **(4+4+2)**

2 A. i) Deduce the structure of compound using the data given below;
Molecular formula $C_5H_{10}O_2$

Chemical Shift (ppm)	Peak area	Splitting
11.8	1.01	Singlet
2.2	1.92	Triplet
1.47	1.91	Multiplet
1.21	1.9	Multiplet
0.78	3.0	Triplet

ii) The mass spectrum of a liquid compound gave a molecular ion which appears as a pair of peaks with equal intensity at m/z of 122 and 124. Small fragment ion peaks are observed at m/z of 107 and 109 (equal intensity), and at m/z of 79, 80, 81 and 82 (all are of roughly equal size). Large fragment ions are found at m/z of 43 (base peak), 41 and 39. Write the molecular formula of this compound.

2 B. i) Explain the principle involved in HPLC -mass spectrometry.
ii) Illustrate with appropriate examples the application of isotope labelling in mass spectrometry to determine the mechanism of reactions.

2 C. Explain how do you differentiate heptane and 2,2,3-trimethyl butane using proton NMR and mass spectra? **(4+4+2)**

3 A. **i)** Describe how chemical exchange affects the ^{1}H NMR spectra?
ii) Fragmentation of the molecular ion of methylbutanone, $(CH_3)_2CHCOCH_3$, gives rise to dominant peaks at $m/z = 71$ and m/z 43. Construct a balanced equation to show how fragmentation of the molecular ion gives rise to the peak at $m/z = 71$.

3 B. Discuss the principles of Electron Spin Resonance Spectroscopy and obtain the mathematical equation for frequency of absorption in it.

3 C. Explain the principles of ^{19}F NMR spectroscopy with an example. **(4+4+2)**

4 A. Explain the instrumentation and working of Nuclear Quadrupole Resonance spectrometer.

4 B. Compute the ^{13}C chemical shift (δ) values of all carbons in the following
(i) (*Z*)-3-methyl-2-pentene (correction for Z-cis is -1.1)
(ii) 1-fluoro-2-nitrobenzene (Incremental shift of ^{13}C are as follows)

Substituent	*Ipso*	*ortho*	*meta*	*para*
F	+35.1	-14.3	+0.9	-4.5
NO_2	+19.6	-5.3	+0.9	+6.0

4 C. Calculate the recoil velocity and energy of free Mössbauer nucleus, ^{119}Sn when emitting a γ–ray of frequency 6.98×10^{18} Hz. **(4+4+2)**

5 A. Discuss the broad band decoupled and off resonance decoupled ^{13}C NMR spectra of 4-ethoxybenzaldehyde.

5 B. Explain the main hyperfine interactions that can be observed in the Mössbauer spectroscopy.

5 C. A free electron is placed in a magnetic field of strength 1.3 T. Find out the resonance frequency of absorption, when $g = 2.0023$ and Bohr magnetron (μ_B) is 9.2732×10^{-24} J/T. **(4+4+2)**

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