MANIPAL ACADEMY of HIGHER EDUCATION

Reg.No.

DEPARTMENT OF SCIENCES, MIT MANIPAL
III SEMESTER M.Sc. (Chemistry)
END SEMESTER EXAMINATIONS, Nov-December 2023
Spectroscopy II [CHM 6101]
(CHOICE BASED CREDIT SYSTEM - 2020)

Time: 3 Hours | Date: 28/11/2023 | MAX. MARKS: 50

Note : (i) Answer **ALL** questions

(ii) Draw diagrams, and write equations wherever necessary

Q No	Question	Marks	CO	BL
1A	Compare the ^{1}H NMR and mass spectra of benzene, chlorobenzene and benzyl chloride	4	4	2
1B	How do non-first order NMR spectra work? Explain about the three techniques for resolving non-first-order spectra.	4	1	2
1C	A compound P with the molecular formula C_4H_7BrO is a volatile liquid. Suggest a method to obtain P for analysis from the mixture of volatile liquids. IR spectrum of this compound gave a peak at 1725 cm^{-1}. Identify the bond responsible for this absorption. The mass spectrum of this compound showed a molecular ion peak at $m/z = 150$ and a M+2 peak at 152. Suggest why these two peaks appeared and comment on their relative intensity. A base peak appeared at $m/z = 57$. Write the structural formula of this fragment.	2	3	3
2A	Explain the instrumentation of Secondary ion mass spectrometry. Differentiate between hard and soft ionization techniques.	4	3	2
2B	Describe how chemical exchange affects the ^{1}H NMR spectra.	4	1	2
2C	Give reason i) The presence of isotopes affect the mass spectra ii) Strong molecular ion peak is observed in the mass spectra of aryl chlorides but not in aryl iodides	2	3	3
3A	Compound A has the molecular formula $C_{10}H_{12}O_2$. The mass spectrum of A contains molecular ion peak at m/z 164. It also has a base peak at m/z 119. The other prominent peaks found are 136, 91 and 65. In its ^{1}H NMR spectrum the peaks appeared at δ 7.8 (doublet, peak area 2), 7.3 (doublet, peak area 2), 4.3 (quartet, peak area 2), 2.4 (singlet, peak area 3) and 1.4 (triplet, peak area 3). Deduce the structure of A.	4	1	3
3B	(i) Differentiate between ESR and NMR spectroscopic techniques. (ii) Calculate the 'g' value, if the methyl radical shows ESR signal at 33300 G in a spectrometer operating at 9590 MHz (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)	4	2	4 3
3C	Discuss about the various designs of interface between HPLC and MS.	2	3	2

4A	(i) Predict and describe the proton decoupled ^{13}C spectrum of 4-propyloxy-ethylbenzoate (ii) Discuss the various chemical shift ranges for ^{19}F in common organic environments	4	1	4 2
4B	Discuss the Mössbauer spectra of a nucleus with $I = \frac{1}{2}$ in ground state and $I = 3/2$ in excited state when it has quadrupole interactions and magnetic hyperfine interactions, independently.	4	2	3
4C	Compute the frequency of absorption of the NQR spectrum of ^{14}N ($I = 1$, axially symmetric nucleus). The eigen values of the system are $E_m = \frac{e^2qQ\left[3m_I^2 - I(I+1)\right]}{4I(2I-1)}$	2	3	3
5A	Compute the chemical shift values of various carbons in ^{13}C NMR spectra of the following (i) *n*-heptane 1,3-dihydroxybenzene (incremental shifts for –OH group are +26.6 for ipso, -12.7 for ortho, +1.6 for meta, -7.3 for para substituents)	4	1	3
5B	Discuss the instrumentation and working of ESR spectrometer.	4	2	2
5C	Illustrate the applications of NQR spectroscopy in determining the Hydrogen bonding interactions	2	3	3

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