Reg. No. ☐☐☐☐☐☐☐☐☐☐

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

(Make–up)
exam.

DEPARTMENT OF SCIENCES
III SEMESTER M.Sc. (Chemistry)
END SEMESTER EXAMINATIONS, JANUARY 2022

Spectroscopy – II [CHM 6101]
(CBCS Scheme)

Time: 3 Hours   Date: 10 Jan 2022   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

1A. Define coupling constant. Discuss the factors affecting coupling constant.

1B. Describe the instrumentation involved in Field Ionization Mass Spectrometer.

1C. Explain the process of deuteration. What kind of data could be obtained from it?

(4+4+2)

2A. Explain the basic fragmentation types with appropriate examples.

2B. Discuss the working principle of the following;
i) Quadrupole MS   ii) Ion Cyclotron MS

2C. Compare the ^{1}H NMR and mass spectra of chlorobenzene and benzyl chloride.

(4+4+2)

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.

3B. Discuss the reasons for Isomer shift (δ) of a Mössbauer nucleus and deduce the mathematical expression for it.

3C. Give reason
i) The variation in the concentration of solution affects the OH peak intensity in ^{1}H NMR spectra of p-nitro phenol but not in o-nitro phenol
ii) Strong molecular ion peak is observed in the mass spectra of aryl chlorides but not in aryl iodides

(4+4+2)

4A. **(i)** Give reasons for the following
    (a) ^{13}C NMR spectra are more difficult to record than ^{1}H NMR spectra.
    (b) Number of peaks in ^{13}C spectrum of *n*-butyl chloride and *t*-butyl chloride are different.
  (ii) Discuss the principles of ^{31}P NMR spectroscopy with an example.

4B. Discuss the expected ESR spectrum and the relative intensities of the spectral lines for the following
    (i) Methyl radical   (ii) p-Nitrobenzoate dianion

4C. What is meant by a Nuclear Quadrupole? Explain the forms of Nuclear quadrupoles and the criteria for a nucleus to behave as a Nuclear Quadrupole.   **(4+4+2)**

5A. Explain the principle of NQR spectroscopy. Why NQR cannot be used for liquid or gaseous samples? How is NQR used for studying the nature of chemical bond?

5B. Compute the ^{13}C chemical shift (δ) values of all carbons in the following
    (i) n-Hexane
    (ii) 3-Methylpentane (correction for branching $1°(3°) = -1.1$, $2°(3°) = -2.5$, $3°(2°) = -3.7$)
    (iii) 3-Pentanol (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 $= -4$)

5C. The electron in atomic hydrogen has 'g' value of 2.0032. An ESR spectrometer working at 9.250 GHz shows two lines from Hydrogen atom at 357.3 and 306.3 mT. Calculate the hyper fine coupling constant. Given: $\beta = 9.2732 \times 10^{-24}$ J/T.   **(4+4+2)**

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