Regd. No.										

MANIPAL UNIVERSITY

DEPARTMENT OF SCIENCES

SECOND SEMESTER M. Sc. (CHEMISTRY)
END SEMESTER EXAMINATIONS

ORGANIC SPECTROSCOPY-II (CHM - 608)

Time: 3 Hours | Date: 11th May 2016 | Max. Marks: 50

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

1. A. A Mossbauer nucleus having an axially symmetric electric field tensor gets excited from a ground state with spin $I_g = 3/2$ to the excited state with spin $I_e = 5/2$. Obtain the energy level schemes and expressions for quadrupole splittings.

B. (i) A free electron gives a resonance at a frequency of 9.5 GHz in a magnetic field of 0.34 T. At what frequency, the resonance occurs if the magnetic field is 1.3 T?
(ii) Explain the principle of ESR spectroscopy.

C. The NQR frequencies ν_+ and ν_- for a nitrogen containing compound in the solid state are 20 and 18 kHz respectively. Find η and the quadrupole coupling constant ($e^2 qQ$) in frequency unit.

(4 + 4 + 2)

2. A. (i) Draw the possible molecular structures for compounds which meet the following ^{1}H NMR

(a) Molecular formula, $C_8H_8O_2$

Chemical Shift (ppm)	Peak area	Splitting
7.78	0.19	Doublet of doublets
7.22	0.10	triplet
7.11	0.19	Triplet
3.58	0.30	Singlet

(b) Molecular formula, $C_5H_{12}O$

Chemical Shift (ppm)	Peak area	Splitting
2.4	1	Singlet
1.4	2.03	quartet
1.1	5.98	Singlet
0.8	3.01	triplet

(ii) How do you distinguish the following pairs by ^{1}H NMR spectra?
(a) 1-bromopropane and 2-bromopropane
(b) ethyl acetate ($MeCO_2Et$) and methyl propanoate ($EtCO_2Me$)

B. Discuss the following;
(i) Quadrupole MS (ii) Factors affecting the coupling constant

C. Justify the statements:
(i) Abundant molecular ions were found in the mass spectrum of aniline but not in 2-methyl 2-propylamine.
(ii) Inductive effect shifts the normal position of a proton signal in NMR.

(4 + 4 + 2)

3. **A.** Discuss the various types of interactions that contribute to the total Hamiltonian of an electron in a system.

B. (i) Explain the influence of electronegative moieties on ^{13}C chemical shift values with an example.

(ii) Explain the ^{13}C chemical shift values of carbons with different hybridizations.

C. How is the Mossbauer spectroscopy useful in surface studies?

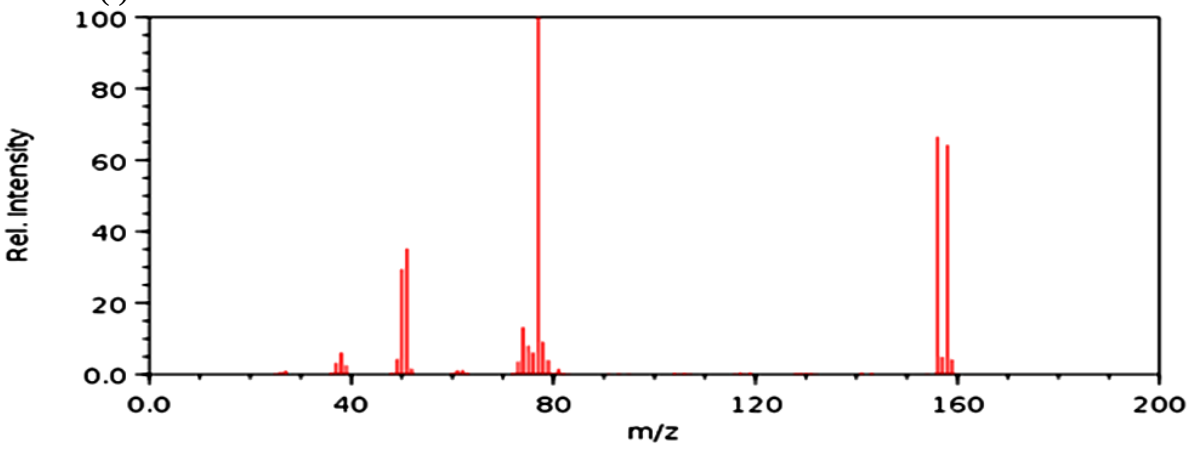
(4 + 4 + 2)

4. **A.** What is a non-first order spectrum? Give examples. Explain any two methods to simplify complex proton NMR spectra.

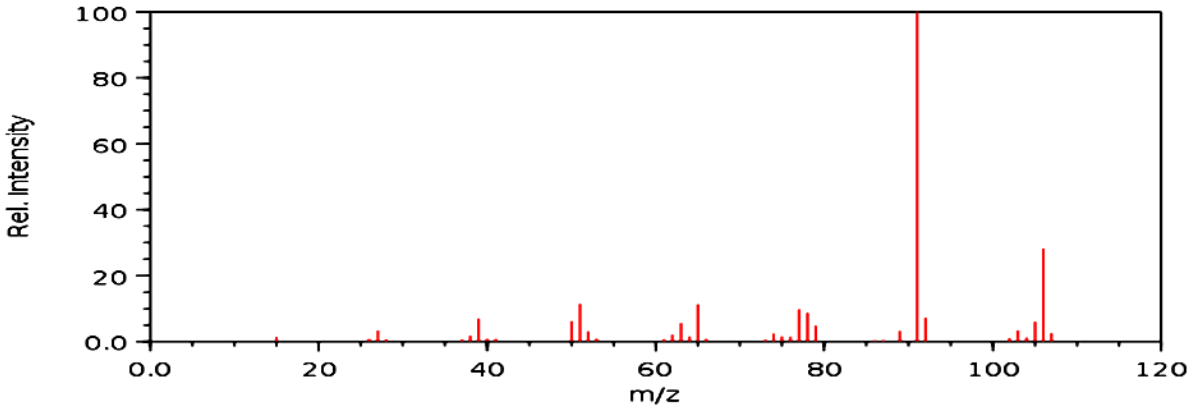
B. Describe the processes and instrumentation involved in the following techniques used in mass spectrometry: a) chemical ionization; b) field desorption c) fast atom bombardment d) thermospray.

C. Assign the structure using the following mass spectra

(i)



(ii)



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5. **A.** Predict the ^{13}C chemical shift values for the following molecules:

(i) n-nonane

(ii) 2-hexamine (correction for internal NH_2 substitution: α carbon = +24, β carbon = +10, γ carbon = − 5)

(iii) Nitrobenzene (correction for substituent NO_2: C_1 = + 19.6, C_2 = − 5.3, C_3 = +0.9, C_4 = + 6.0)

(iv) 1-fluoro-2-nitrobenzene (correction for substituent NO_2: C_1 = + 19.6, C_2 = −5.3, C_3 = + 0.9, C_4 = + 6.0) (correction for substituent F: C_1 = + 35.1, C_2 = −14.3, C_3 = + 0.9, C_4 = − 4.5)

B. 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?

C. A Mossbauer nucleus, ^{57}Fe make a transition from the excited state of energy 14.4 kev to the ground state. Calculate its recoil momentum and recoil velocities. Given: 1ev = 1.6×10^{-19}J.

(4 + 4 + 2)

6. A. What is Zeeman effect? Write the requirements for a nucleus to show NMR signal. Show that the ffrequency of absorbed/emitted by a nucleus in moving from one energy level to another is directly proportional to the applied magnetic field.

B. Explain the principle and instrumentation involved in continuous wave NMR spectrometer

C. Differentiate between the following
(i) Chemical and magnetic equivalence
(ii) Electron impact ionization and electrospray ionization

(4 + 4 + 2)

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