MANIPAL UNIVERSITY

Reg. No.										

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DEPARTMENT OF SCIENCES, M. Sc. (C)
II SEMESTER END SEMESTER EXAMINATIONS, JUNE 2017

SUBJECT: ORGANIC SPECTROSCOPY – II [CHM 608]

(REVISED CREDIT SYSTEM)

Time: 3 Hours | Date: 17th June, 2017 | MAX. MARKS: 50

Note: Answer **any five full** questions.

1.A. Predict and explain the hyperfine ESR spectrum of $H_3C - {}^{*}CH_2$ and ${}^{*}CF_2D$ free radicals.

1.B. Discuss the principles of Mossbauer spectroscopy along with the conditions for resonant and non-resonant absorptions.

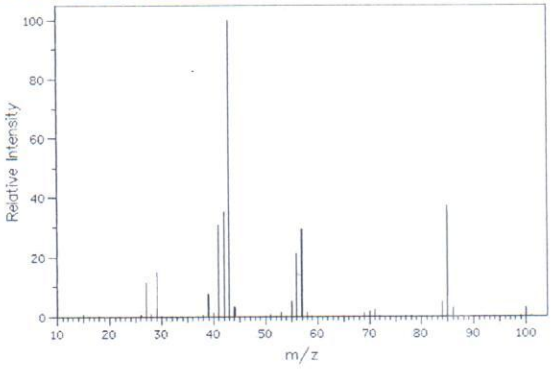
1.C. Explain, how to distinguish the n-butyl alcohol and sec-butyl alcohol by ^{13}C NMR spectroscopy?

[4+4+2]

2.A. Discuss the following;
(i) Internal standard used in NMR spectroscopy
(ii) Deuteriation

2.B. Discuss two of the alternative means to magnetic/electrostatic focusing for mass separation in mass spectrometry. Write their advantages.

2.C. The mass spectrum of 2-methylhexane is given below. What is the *m/z* value of the M+ peak and of the base peak? Give possible structures of the fragments giving rise to the large peaks at *m/z* = 85, 57, and 43.



[4+4+2]

3.A. Write a note on ^{19}F and ^{31}P NMR spectroscopic techniques. Why $CFCl_3$ is considered as a standard for ^{19}F spectroscopy?

3.B. Discuss the principles of ESR spectroscopy. What are the different terms involved in the total Hamiltonian of the system?

3.C. What is meant by isomer shift? Explain the reasons for isomer shift.

[4+4+2]

4.A. Differentiate between the following;
(i) Electron impact ionization and chemical ionization
(ii) Continuous wave NMR and FTNMR

4.B. (i) Deduce the structure of the organic compound using the NMR data given below;

(I) Molecular formula, $C_4H_6O_2$			**(II) Molecular formula, $C_8H_8O_2$**		
Chemical Shift (ppm)	Peak area	Splitting pattern	Chemical Shift (ppm)	Peak area	Splitting pattern
12.5	1	singlet	7.78	0.19	doublet of doublets
6.22	1	singlet	7.22	0.10	triplet
5.62	1	singlet	7.11	0.19	triplet
1.9	3.06	singlet	3.58	0.30	singlet

(ii) Explain any two methods used for the simplification of complex proton NMR spectra.

4.C. What are metastable ions? Write their significance. Calculate the m/z value for the parent ion (m1) that produce the normal daughter ion (m2) having m/z value of 61 and metastable daughter ion (m*) having m/z value of 31.8.

[4+4+2]

5.A. What is meant by the γ-effect of a carbon substituent on the chemical shift values in ^{13}C spectroscopy? Describe the various regions of ^{13}C chemical shift (δ) values of functionalized hydrocarbons with examples.

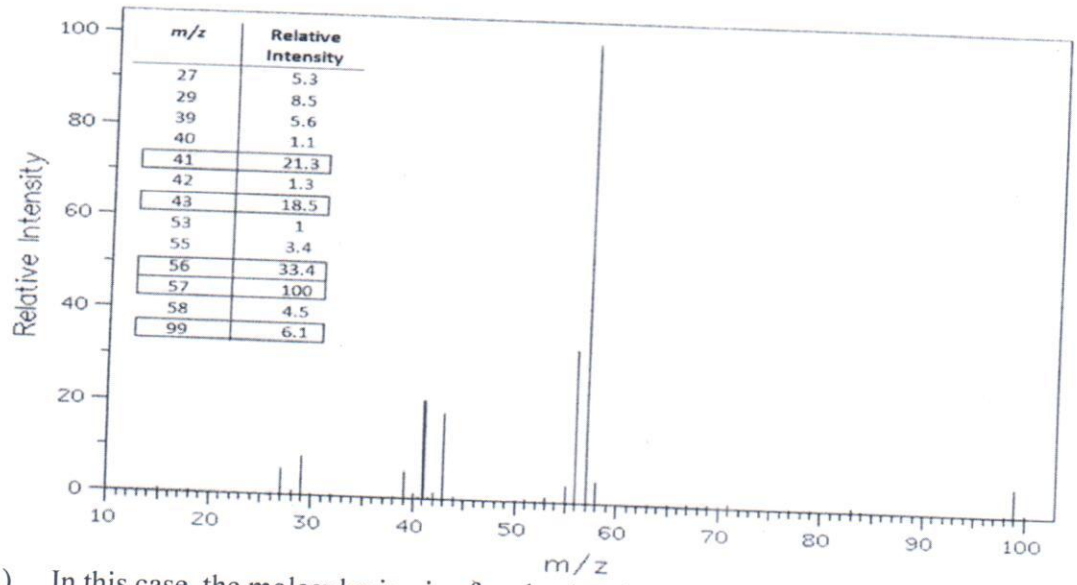
5.B. Describe the theory of NQR transitions for axially symmetric systems.

5.C. Explain the following:
(i) $FeSO_4$ has quadrupole splitting but $K_4Fe(CN)_6$ does not show quadrupole slitting.
(ii) The Mossbauer spectrum of ^{127}I is a single line for $IF_6^+AsF_6^-$, but in $CsIF_6$ it shows a large quadrupole splitting.

[4+4+2]

6.A. Explain the factors affecting coupling constant.

6.B. Using the mass spectrum of 2,2,4-trimethylpentane shown below, answer the questions that follow about its fragmentation.



m/z	Relative Intensity
27	5.3
29	8.5
39	5.6
40	1.1
41	21.3
42	1.3
43	18.5
53	1
55	3.4
56	33.4
57	100
58	4.5
99	6.1

(i) In this case, the molecular ion is of such a low intensity it is not detected. Draw the structure of molecular ion and determine its m/z value.

(ii) Draw a likely structure of molecular ion that produces a base peak signal at m/z of 57.

(iii) Draw a fragmentation mechanism that could produce the ion responsible for the signal at m/z =56 from the base peak ion?

(iv) Draw likely structures for the ions that produce the signals at m/z=43 and 41.

6.C. Discuss the factors influencing the fragmentation of organic compounds.

[4+4+2]

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