

Write the following information in the first page of Answer Script before starting answer

ODD SEMESTER EXAMINATION: 2020-21

Exam ID Number _____

Course _____ Semester _____

Paper Code _____ Paper Title _____

Type of Exam: _____ (Regular/Back/Improvement)

Important Instruction for students:

1. Student should write objective and descriptive answer on plain white paper.
2. Give page number in each page starting from 1st page.
3. After completion of examination, Scan all pages, convert into a single PDF, rename the file with Class Roll No. **(2019MBA15)** and upload to the Google classroom as attachment.
4. Exam timing from 10am – 1pm (for morning shift).
5. Question Paper will be uploaded before 10 mins from the schedule time.
6. Additional 20 mins time will be given for scanning and uploading the single PDF file.
7. Student will be marked as ABSENT if failed to upload the PDF answer script due to any reason.

M.Sc. CHEMISTRY
THIRD SEMESTER
APPLICATIONS OF SPECTROSCOPY
MSC-304

Duration : 3 hrs.

Full Marks : 70

(PART-A : Objective)

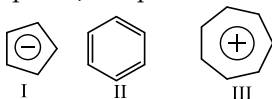
Time : 20 min.

Marks : 20

Choose the correct answer from the following:

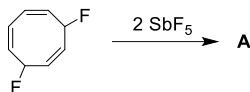
1X20=20

- What is the relation between restoring force, f to the displacement q in Hooke's law?
 - $f = -kq$
 - $f = kq$
 - $f = kq^2$
 - $f = -kq^2$
- The vibrations, without a center of symmetry are active in which of the following region?
 - Infrared but inactive in Raman
 - Raman but inactive in IR
 - Raman and IR
 - Inactive in both Raman and IR
- What is the order of decreasing vibrational frequency for C – Cl, C – Br, C – C, C – O and C – H?
 - C-H, C-C, C-O, C- Cl, C-Br
 - C- Cl, C-Br, C-C, C -H, C-O
 - C-O, C-H, C-Br, C- Cl, C-C
 - C-Br, C- Cl, C-C, C-O, C-H
- In IR spectroscopy, the vibration between atoms is caused by which of the following?
 - The overall molecular weight of the molecule
 - The number of protons in a nucleus
 - Dipole moments between atoms
 - The movement of electrons to higher energy levels
- Which of the following functional groups exhibits the highest frequency in an infrared (IR) spectrum?
 - Ester
 - Alcohol
 - Aldehyde or ketone
 - Nitrile
- In the 400 MHz ^1H NMR Spectrum, an organic compound exhibited a doublet. The two lines of the doublet are at δ 2.38 and 2.3. The coupling constant ' J ' value is:
 - 3 Hz
 - 6 Hz
 - 9 Hz
 - 12 Hz
- The correct match of the ^1H NMR chemical shift value δ of the following species/compounds are:



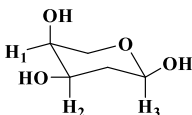
- I: 5.4; II: 7.2; III: 9.2
- I: 9.2; II: 5.4; III: 7.2
- I: 9.2; II: 7.2; III: 5.4
- I: 7.2; II: 9.2; III: 5.4

8. Which of the following $^1\text{H-NMR}$ spectrum of compound with molecular formula $\text{C}_4\text{H}_9\text{NO}_2$ shows δ 5.30 (broad, 1H), 4.10 (q, 2H), 2.80 (d, 3H), 1.20 (t, 3H) ppm?
- $\text{CH}_3\text{NHCOOCH}_2\text{CH}_3$
 - $\text{CH}_3\text{CH}_2\text{NHCOOCH}_3$
 - $\text{CH}_3\text{OCH}_2\text{CONHCH}_3$
 - $\text{CH}_3\text{CH}_2\text{OCH}_2\text{CONH}_2$
9. A proton H_b is coupled to four equivalent protons H_a . The multiplicity and the relative intensity of lines in the signal H_b is:
- Doublet, 1 : 4
 - Triplet, 1 : 4 : 6
 - Quintet, 1 : 4 : 6 : 4 : 1
 - Quartet, 1 : 4 : 6 : 4
10. Which among the following is not a NMR active?
- ^1H
 - ^{13}C
 - ^{16}O
 - ^{19}F
11. The compound which will show a prominent $\text{M}+2$ peak in EI-MS is:
- 4-Chlorophenol
 - 4-nitrophenol
 - 4-aminophenol
 - None of these
12. The molecular ion peak of the product 'A' for the following reaction will be in the EI⁺ MS at



- 52
- 104
- 123
- 142

13. The base peak of benzaldehyde in EI-MS is:
- $[\text{M}-15]^+$
 - $[\text{M}-1]^+$
 - $[\text{M}]^+$
 - 77
14. The ionization of compound in FAB-MS is done by the high energy beam of:
- Photon
 - Electron
 - Inert Gases
 - Ar^+
15. Which of the following will show base peak within M , $[\text{M}+2]$, and $[\text{M}+4]$ peaks in the EI-MS?
- 4-Bromo-3-chlorophenol
 - 4-bromobenzylbromide
 - 2,4-dibromotoluene
 - All of them
16. DEPT-135 of 4-Chlorobenzaldehyde will have total peak:
- 3
 - 4
 - 5
 - 6
17. The peak of D_4 -1,2-dichloroethane in ^{13}C NMR will be:
- Quintet
 - Quartet
 - Triplet
 - Singlet
18. Which one is correct for the following molecule regarding its NMR study?



- $\text{H}_1\text{-H}_2$: COSY & $\text{H}_2\text{-H}_3$ NOESY
- $\text{H}_1\text{-H}_2$: NOESY & $\text{H}_2\text{-H}_3$ COESY
- $\text{H}_1\text{-H}_3$: COSY & $\text{H}_2\text{-H}_3$ NOESY
- $\text{H}_1\text{-H}_3$: NOESY & $\text{H}_2\text{-H}_3$ COESY





(PART-B : Descriptive)

Time : 2 hrs. 40 min.

Marks : 50

[Answer question no.1 & any four (4) from the rest]

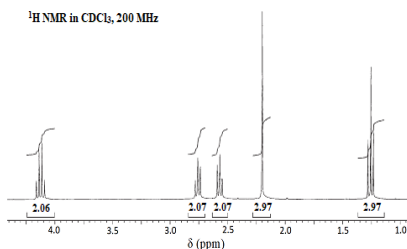
1. a) Write the correct increasing order of IR stretching frequencies with suitable justification for the organic compounds having the $C \equiv C$, $C = C$ and $C - C$? 3
- b) Depict the EI-MS of benzaldehyde and comment on the base peak. 2
- c) In the 60 MHz 1H NMR of acetone the signal for methyl proton appears at 122.4 Hz downfield from TMS. Determine the chemical shift of the signal in δ scale. What should be the resonance frequency for the same signal from TMS in a 300 MHz spectrum? 3
- d. The $CDCl_3$ shows a singlet in 1H -NMR, whereas that in ^{13}C -NMR gives triplet peaks. Explain it. 2
2. a) What are the factors on which the normal IR stretching frequency of carbonyl bonds depends on? 3
- b) Match the following ketone with their IR stretching frequencies- 2

1		1780 cm^{-1}
2		1740 cm^{-1}
3		1700 cm^{-1}
		1680 cm^{-1}

- c) Write the approximate IR stretching frequency of (i) alcohol (ii) Nitrile (iii) carbonyl compound and (iv) ester. 2
- d) The IR stretching frequency of $[Cr(CO)_6]$ is lower than that of $[Mn(CO)_5]$. Explain with suitable justification. 3
3. a) Explain why certain nuclei can be detected and others cannot in NMR? 3
- b) Why "F" is unable to give a signal in 1H NMR? 2
- c) Explain the term with suitable example- (i) Chemical shift and (ii) Coupling constant used in NMR spectroscopy. Which one among the two depends on operating frequency? 3
- d) Why TMS is chosen as a standard of reference in NMR spectroscopy? 2
4. a) Explain why 1H -NMR spectrum of benzene is observed at a lower field whereas that of acetylene is observed at a higher field strength. 3

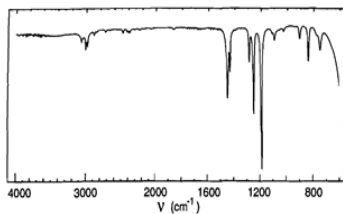
- b) What spin-spin coupling patterns do you expect for each distinct set of H nuclei in the following molecules: CH_3CHCl_2 , $\text{CH}_3\text{CHClCH}_3$ and $\text{CH}_3\text{OCH}_2\text{CH}_3$. 3
- c) (i) How many NMR signals do you expect for pure ethanol? Also discuss the splitting pattern. 4
(ii) Explain clearly what will happen if the ethanol contains moisture?
5. a) An organic compound $\text{C}_7\text{H}_{12}\text{O}_2$ shows the following data in the ^1H NMR spectra- δ 7.10 (1H, dt, $J = 16$ and 7.2 Hz), 5.9 (1H, dt, $J = 16$ and 2 Hz), 4.1 (2H, q, $J = 7.2$ Hz), 2.1 (2H, m), 1.25 (3H, t, $J = 7.2$ Hz), 0.9 (3H, t, $J = 7.2$ Hz) ppm. Predict the correct structure of the organic compound from the given data. 3
- b) ^1H NMR of olefinic compound often shows the presence of two isomers (E and Z) having different J-value ranging from approximately 10-17 Hz. How could you differentiate them with the help of NMR spectroscopy? 2
- c) What is retro Diels-Alder cleavage? Explain with example. 2
- d) Discuss the McLafferty rearrangement in EI-MS with suitable example. 3
6. a) Draw the all possible isomers of formula C_5H_{12} and show their fragmentation pattern in EI-MS. Depict their most probable mass spectrum (EI-MS). Find out the base peak of each of the isomer. 6
- b) Identify the active species which are responsible for base peaks in EI-MS of ortho-xylene and ethylbenzene. 4
7. a) The proton NMR spectrum of an organic compound-A with exact mass of 144.0786 is shown below. The coupling constant for the triplet at 1.25 ppm is of the same magnitude as the one for the quartet at 4.15 ppm. The pair of distorted triplets at 2.56 and 2.75 ppm are coupled to each other. The infrared spectrum displays strong bands at 1720 and 1738 cm^{-1} . The proton-decoupled ^{13}C -NMR and the DEPT experimental results are shown below. Draw the structure of this compound with justification. 6

Normal Carbon	DEPT-135	DEPT-90
14 ppm	Positive	No peak
28	Negative	No peak
30	Positive	No peak
38	Negative	No peak
61	Negative	No peak
173	No peak	No peak
207	No peak	No peak

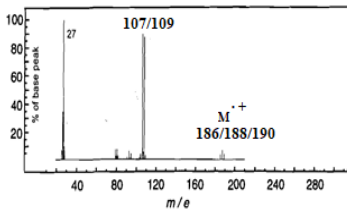
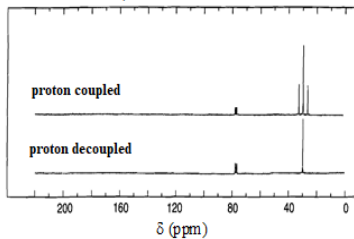
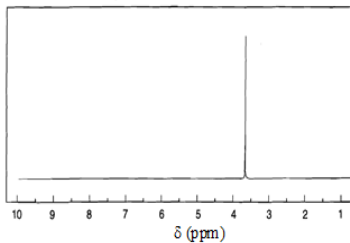


- b) Depict the COSY (^1H - ^1H) spectrum of the organic compound-A. 4
8. a) A halogenated hydrocarbon compound-X has one isomer 'Y'. Compound-X has the following spectroscopic information. Identify the compound-X. 6

IR Spectrum



EI-MS

 ^{13}C NMR in CDCl_3 , 50 MHz ^1H NMR in CDCl_3 , 200 MHz

- b) Write the structure of the isomeric compound-Y and depict its ^1H -NMR as well as proton decoupled ^{13}C NMR spectra.

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