REV-01
MSC/41/14/17

2022/12

SET A

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

[USE OMR SHEET FOR OBJECTIVE PART]

Duration : 3 hrs. **Full Marks : 70**

(Objective)

Time: 30 min. **Marks: 20**

Choose the correct answer from the following: ***1X20=20***

1. In IR spectroscopy, for a specific bond, stretching frequency is
   a. greater than bending frequency
   b. equal to bending frequency
   c. lesser than bending frequency
   d. none of these

2. The number of fundamental vibrations in CO_2 molecule is
   a. 4
   b. 3
   c. 2
   d. 5

3. The constant in Hooke's law κ represent
   a. force constant
   b. dipole moment
   c. reduced mass
   d. none of these

4. The wavenumber corresponding to C≡C stretching is
   a. 1600 cm^{-1}
   b. 1700 cm^{-1}
   c. 3200 cm^{-1}
   d. 2100 cm^{-1}

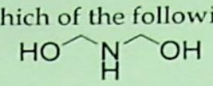
5. How many Hertz does 1 ppm correspond to a ^{1}H-NMR spectrometer operating at a radio frequency of 60 MHz?
   a. 6
   b. 60
   c. 600
   d. 0.6

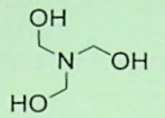
6. The distance between the centers of the peaks of doublet is called as?
   a. Chemical Shift
   b. Coupling Constant
   c. Spin constant
   d. Spin-spin coupling

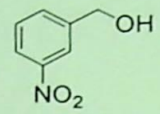
7. Which of the following organic compound with molecular formula $C_3H_6Cl_2$ exhibits only one signal in the ^{1}H-NMR spectrum?
   a. 2, 2-dichloropropane
   b. 1, 2-dichloropropane
   c. 1, 3-dichloropropane
   d. 1, 1-dichloropropane

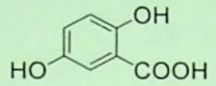
8. The J-value for an ortho-coupling of a proton in a benzene ring is
   a. 6-9 Hz
   b. 1-3 Hz
   c. 0-1 Hz
   d. 18-20 Hz

9. Which of the following compound is used as matrix in MALDI-MS?

a. 

b. 

c. 

d. 

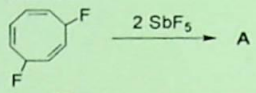
10. The base peak of benzaldehyde in EI-MS is

a. $[M-1]^+$ b. $[M-15]^+$
c. 77 d. $[M]^+$

11. The ionization of compound in FAB-MS is done by the high energy beam of

a. Electron b. Photon
c. Ar^+ d. Inert Gases

12. The molecular ion peak of the product 'A' for the following reaction will be in the EI^+ MS at



a. 52 b. 104
c. 123 d. 142

13. The compound which will show a prominent M+2 peak in EI-MS is

a. 4-nitrophenol b. 4-Chlorophenol
c. 4-aminophenol d. None of these

14. DEPT-135 of 4-bromobenzaldehyde will have total peak

a. 4 b. 3
c. 6 d. 5

15. Which of the following will show base peak within M, [M+2], and [M+4] peaks in the EI-MS?

a. 4-Bromo-3-chlorophenol b. 4-bromobenzylbromide
c. 2,4-dibromotoluene d. All of them

16. The retro Diels-Alder fragmentation in EI-MS is observed for molecule having core structure of

a. cyclopentene b. cyclopentadiene
c. cyclohexadiene d. cyclohexene .

17. The peak of D_4-1,2-dichloroethane in ^{13}C NMR will be

a. quintet b. quartet
c. triplet d. singlet

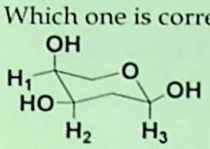
18. DBE (double bond equivalence) of the following molecule will be $C_{16}H_{16}N_2O_2$

a. 8 b. 9
c. 10 d. 11

19. If a molecule ($C_xH_yN_z$) shows molecular ion peak in EI-MS m/z = 80, a distinct peak at 2250 cm^{-1} in IR and a singlet (δ = 2.8 ppm, 2H) in ^{1}H-NMR, and DBE = 4, the correct formula will be

a. $C_3H_2N_3$
b. $C_4H_4N_2$
c. $C_4H_8N_2$
d. C_5H_6N

20. Which one is correct for the following molecule regarding its NMR study?



a. H_1-H_2: COSY & H_2-H_3 NOESY
b. H_1-H_3: NOESY & H_2-H_3 COESY
c. H_1-H_2: NOESY & H_2-H_3 COESY
d. H_1-H_3: COSY & H_2-H_3 NOESY

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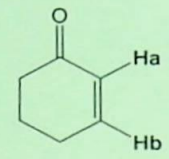
Descriptive

Time : 2 hrs. 30 mins. **Marks : 50**

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

1. **a.** Determine the number of fundamental modes of vibrations in the following molecules (i) CH_4, (ii) C_2HF, (iii) CH_3COCH_3 — 3

b. In the following compound, Ha or Hb which proton should show higher chemical shift? Explain your answer with schematic description. — 2



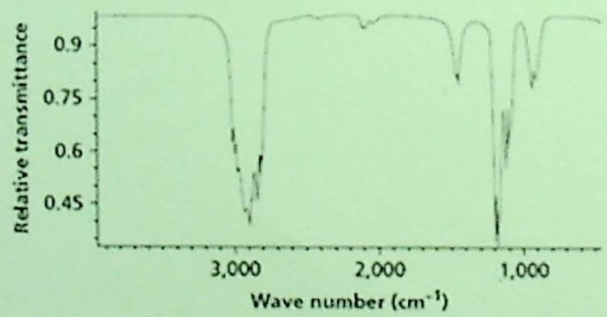
c. The $CDCl_3$ shows a singlet in ^1H-NMR, whereas that in ^{13}C-NMR gives triplet peaks. Explain it. — 2

d. Write a short note on retro Diels-Alder fragmentation in EI-MS. — 3

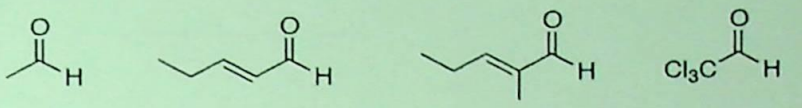
2. **a.** Assign the structure to a compound from following IR results with proper explanation — 3

M.F.$C_4H_8O_2$ to absorb the IR radiation at 2989-2880(m), 1740(s), 1240(s) & 1045 (s) cm^{-1}

b. A compound having molecular formula C_2H_6O showed the following spectrum in KBr pellet. Find the most possible structure with detailed explanation. — 2



c. Arrange the following four compounds with respect to their increasing order of frequency and put suitable explanation. **3**



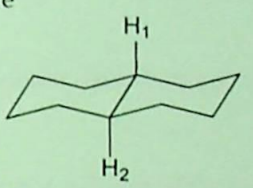
d. Arrange the following compounds in increasing order of their vibrational - C=O stretching frequency: **2**
cyclohexanone, cyclopentanone, cyclobutanone and cycloproanone

3. a. An organic compound X having molecular formula $C_6H_{12}O$ shows the following proton NMR. Suggest a structure of an organic compound X. The answer must be accompanied by proper explanation. **3+2+3+2=10**
IR (cm^{-1}): 1715
^{1}H-NMR: δ 2.1 (s) and 1.2 (s)

b. At 60 MHz the shift of the protons in CH_3Br is 162 Hz while at 100 MHz, the shift is 270 Hz from TMS. Calculate the δ value?

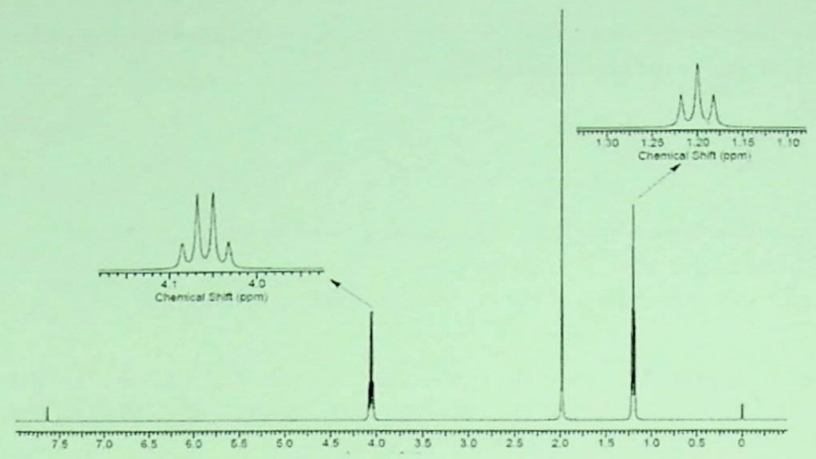
c. Write down structure and full form of TMS and why it is used in NMR spectroscopy?

d. Write down the Karplus Equation and calculate the J-value for the H_1 and H_2 proton of the given structure



4. a. Explain the four factors that affect the value of chemical shift. **2+2+4+2=10**

b. The ^{1}H-NMR spectrum of ethyl acetate is given below. Identify the different protons, their splitting and match with the spectrum. Explain your answer in detail.



c. In ^1H NMR spectroscopy of Benzene the protons gives peak in between 6 to 8 ppm, in ethylene the protons shows peak in between 5 to 6 ppm whereas in acetylene proton shows comparatively up-field shift in between 1.5 to 2.5 ppm. Why? Explain in details with diagram.

d. Draw the structure of [18] annulene and show which protons will give negative chemical shift value.

5. a. Write short note on CI MS — 5

b. Discuss about different fragmentation pathways related to mass spectrometric analysis. — 5

6. a. Both acetophenone & 4-methylbenzaldehyde have exact mass 120.0575. How to characterize them by EI-MS spectra? — 4

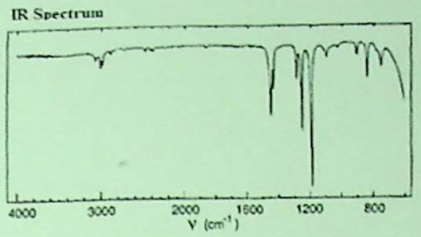
b. Depict the EI-MS of tert-butanol and n-butanol — 4

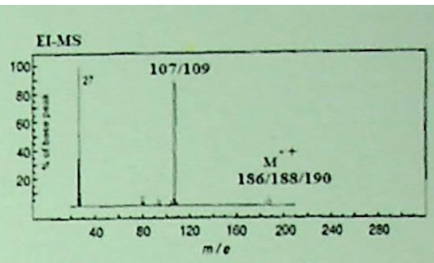
c. Discuss the McLafferty rearrangement in EI-MS with suitable example. — 2

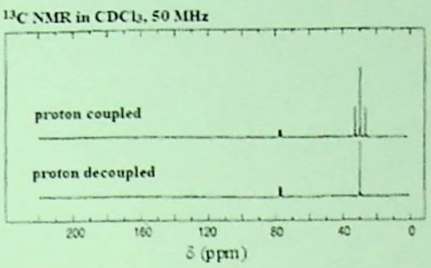
7. a. Depict the molecular ion peaks of Br_2 and Cl_2 in EI-MS and mention the notable differences about the nature of their peaks. (Given: relative abundance ^{79}Br =100, ^{81}Br = 98 and ^{35}Cl =100, ^{37}Cl = 32.5) — 5

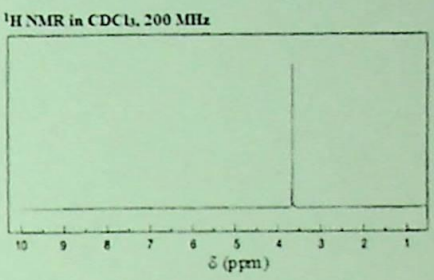
b. Depict the ^{1}HNMR and COSY spectrum of ethyl acetate. — 5

8. a. A halogenated hydrocarbon ($C_2H_4Br_2$) compound-X has one isomer 'Y'. Compound-X has the following spectroscopic information. Identify the compound-X. — 6









b. Write the structure of the isomeric compound-Y and depict its ^{1}H-NMR as well as proton decoupled ^{13}C NMR spectra. 4

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