Date:

Registration number:

ST. JOSEPH'S COLLEGE (AUTONOMOUS), BENGALURU-27
M.Sc. CHEMISTRY - II SEMESTER
SEMESTER EXAMINATION: APRIL 2022
(Examination conducted in July 2022)

CH8421 - SPECTROSCOPY– II

Time- 2 ½ hours Max Marks-70

This question paper contains 5 printed pages and three parts

Part A

Answer any SIX of the following. (6 x2 = 12)

1. Calculate the number of allowed spin states for ^{11}B (I = 3/2) and ^{17}O (I = 5/2) nuclei. List the value of *m* (nuclear spin quantum number) for each state from highest to lowest energy.
2. At what magnetic field strength do protons (^{1}H nuclei) precess at a frequency of 300 MHz? Magnetogyric ratio of ^{1}H nucleus $\gamma = 267.512 \times 10^{6}$ rad $T^{-1}\,s^{-1}$.
3. Why FT-NMR spectroscopy is preferred over continuous wave as a technique for ^{13}C NMR?
4. Write any two criteria for choosing an appropriate solvent for UV spectroscopy.
5. What are the IR spectral peaks that distinguish alkenes from alkanes?
6. How does the O-H stretching frequency differ for methanol vapour and liquid methanol? Give reason for the difference.
7. Draw a block diagram of the mass spectrometer instrument.
8. Briefly explain the principle of ESR spectroscopy.

Part B

Answer any FOUR of the following. (4 x12 = 48)

9. a) What is allylic and propargylic coupling in ^{1}H NMR?
   b) With proper reasoning, predict the structure of an organic compound with molecular formula $C_{10}H_{16}O_{6}$. The ^{1}H NMR data and IR data of the compound is given below.
   IR: 1740 cm^{-1}
   NMR: 1.3 ppm (triplet, 9H)
   4.2 ppm (quartet, 6H)
   4.4 ppm (singlet, 1H)

   c) With the help of molecular orbital diagram explain why 1, 3-butadiene absorbs at 217nm (λ_{max}) and ethylene absorbs at 175nm (λ_{max} values). Also, explain why the molar absorption of 1, 3-butadiene is higher than ethylene.

   (4+4+4)

10. a) What is cross polarization? Discuss how cross polarization explains the origin of nuclear overhauser effect.
    b) Explain HETCOR technique with a suitable example.

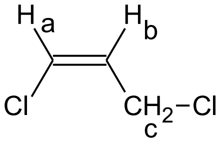
    (7+5)

11. a) Give reason for the following:

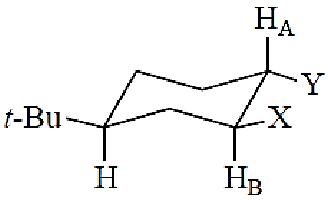
    i) The ^{1}H NMR spectrum of N,N-dimethylformamide at room temperature is different from that obtained at 140º C.

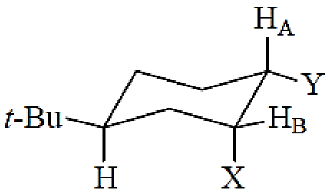
    ii) Chemical shift values of acetylenic protons (-C≡C-H) are anomalously lower than that of vinylic protons (-C=C-H)

    b) With the help of a tree diagram, describe the splitting pattern expected for the protons labelled as “b” and “c” in the following molecule.



    c) Using Karplus equation, predict the coupling constant, J_{AB} for the protons H_A and H_B in the following molecules.

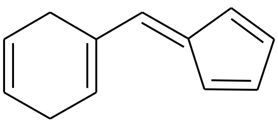




(6+3+3)

12. a) Distinguish between the following pair of compounds using UV spectroscopy.

    i)



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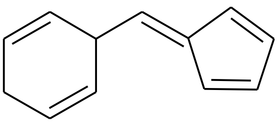
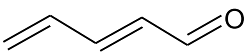


    ii)



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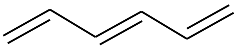


    b) Draw a diagram and explain the ion production in MALDI (matrix assisted laser desorption ionization) technique of mass spectrometric analysis.

    c) Using an example discuss the McLafferty rearrangement in (i) alkylbenzene (ii) ketone.

(4+4+4)

13. a) The C=C stretching vibration occurs at 1680 cm^{-1}. Calculate the force constant of the double bond. (^{12}C = 12.011amu, Avogadro’s number = 6.022×10^{23} /mole and c = 3×10^{10} cm/s)

    b) Chlorine has two isotopes ^{35}Cl and ^{37}Cl with relative abundance 3:1. Sketch a typical mass spectrum of chlorine gas molecule representing all the isotopic peaks with appropriate intensities.

    c) Explain isomer shift in Mossbauer studies. Discuss any two factors affecting isomer shift.

(3+4+5)

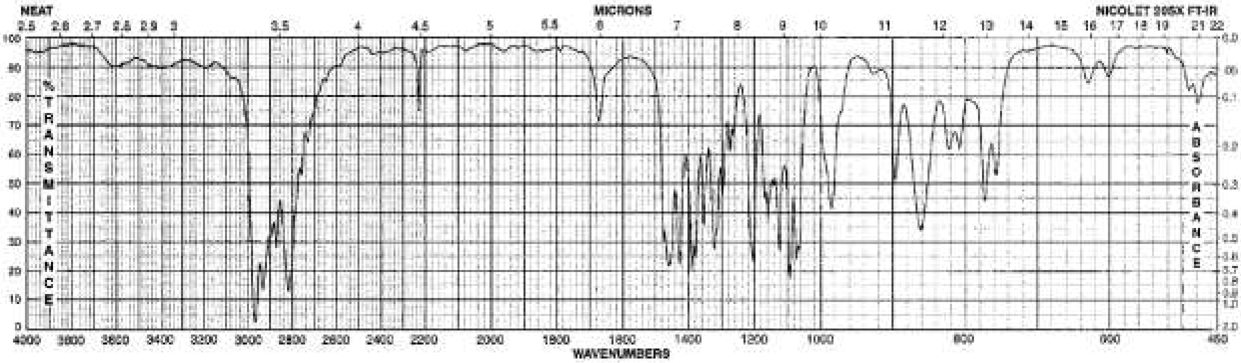
14. a) Arrange the following functional groups according to their increasing order of carbonyl stretching frequency. Explain the various electronic factors responsible for this order.
    Aldehyde, ketone, carboxylic acid, ester, amide, acid halide, acid anhydride.
    b) Using the energy level diagram explain the hyperfine splitting pattern in the ESR spectrum of p-benzoquinone radical anion.
    c) Explain the ESR spectra of $Cu(H_2O)_6{}^{2+}$ complex. ($I_{Cu}=3/2$)

(4+4+4)

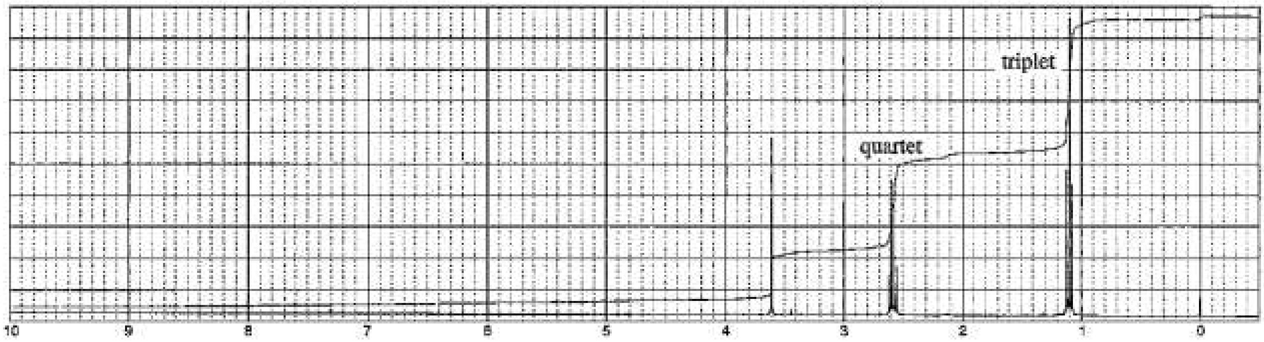
Part C

Answer any TWO of the following. **(2 x 5 = 10)**

15. The following is the spectral data of an organic compound with molecular formula $C_6H_{12}N_2$. What is the structure of the compound?
    IR spectrum:



^1H NMR spectrum

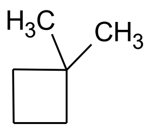


^{13}C NMR data

Normal Carbon	DEPT-135	DEPT-90
13 ppm	Positive	No peak
41 ppm	Negative	No peak
48 ppm	Negative	No peak
213 ppm	No peak	No peak

16. How many ^1H NMR signals does each compound give?

i



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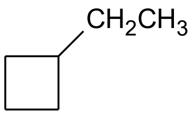

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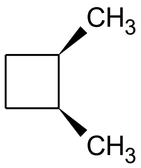

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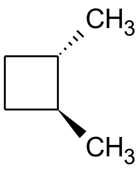

17. Deduce the structure of an organic compound with molecular formula C_9H_8O which shows following spectral data.

IR: 1690 cm^{-1} (strong)

^1H NMR:
6.7 (1H, dd, J=16Hz and J=8Hz)
7.4 (5H, m)
7.45 (1H, d, J= 16 Hz)
9.75 (1H, d, J = 8Hz) ppm

Note: dd= doublet of doublet

MASS:
Molecular ion at m/z=132
Base peak at m/z=131
Significant peak at m/z= 103, 77, 51

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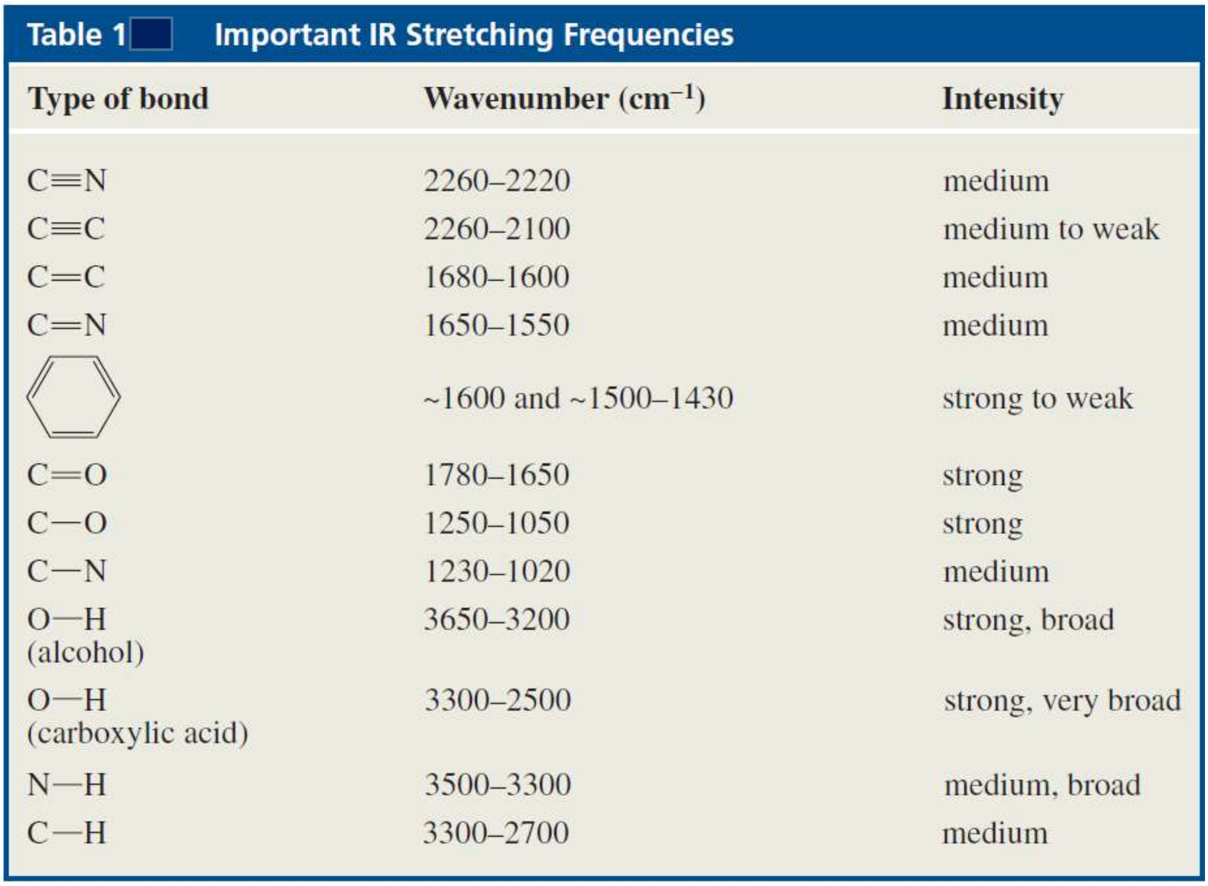

Table 1 **Important IR Stretching Frequencies**

Type of bond	Wavenumber (cm^{-1})	Intensity
C≡N	2260–2220	medium
C≡C	2260–2100	medium to weak
C=C	1680–1600	medium
C=N	1650–1550	medium
⌬	~1600 and ~1500–1430	strong to weak
C=O	1780–1650	strong
C—O	1250–1050	strong
C—N	1230–1020	medium
O—H (alcohol)	3650–3200	strong, broad
O—H (carboxylic acid)	3300–2500	strong, very broad
N—H	3500–3300	medium, broad
C—H	3300–2700	medium

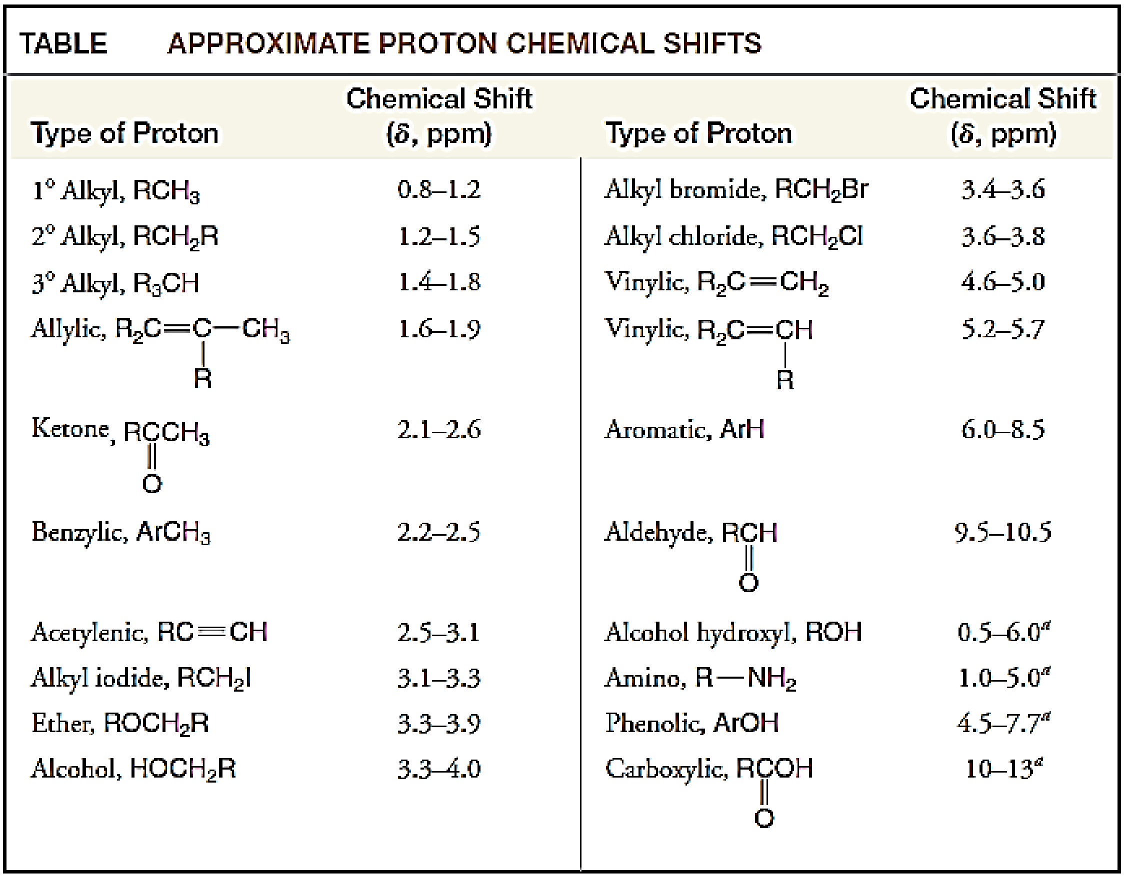

TABLE APPROXIMATE PROTON CHEMICAL SHIFTS

Type of Proton	Chemical Shift (δ, ppm)	Type of Proton	Chemical Shift (δ, ppm)
1° Alkyl, RCH_3	0.8–1.2	Alkyl bromide, RCH_2Br	3.4–3.6
2° Alkyl, RCH_2R	1.2–1.5	Alkyl chloride, RCH_2Cl	3.6–3.8
3° Alkyl, R_3CH	1.4–1.8	Vinylic, $R_2C{=}CH_2$	4.6–5.0
Allylic, $R_2C{=}\underset{\underset{R}{\vert}}{C}{-}CH_3$	1.6–1.9	Vinylic, $R_2C{=}\underset{\underset{R}{\vert}}{C}H$	5.2–5.7
Ketone, $R\underset{\underset{O}{\Vert}}{C}CH_3$	2.1–2.6	Aromatic, ArH	6.0–8.5
Benzylic, $ArCH_3$	2.2–2.5	Aldehyde, $R\underset{\underset{O}{\Vert}}{C}H$	9.5–10.5
Acetylenic, $RC{\equiv}CH$	2.5–3.1	Alcohol hydroxyl, ROH	$0.5–6.0^a$
Alkyl iodide, RCH_2I	3.1–3.3	Amino, $R{-}NH_2$	$1.0–5.0^a$
Ether, $ROCH_2R$	3.3–3.9	Phenolic, $ArOH$	$4.5–7.7^a$
Alcohol, $HOCH_2R$	3.3–4.0	Carboxylic, $R\underset{\underset{O}{\Vert}}{C}OH$	$10–13^a$