Registration Number:

Date & session:

ST.JOSEPH'S UNIVERSITY, BENGALURU -27
M.Sc (CHEMISTRY) – II SEMESTER
SEMESTER EXAMINATION: APRIL 2023
(Examination conducted in May 2023)
CH 8421 – SPECTROSCOPY - II
(For current batch students only)

Time: 2 Hours **Max Marks: 50**

This paper contains FIVE printed pages and THREE parts
(Spectral data is given towards the end of this paper)

PART-A

Answer any **EIGHT** of the following questions. Each question carries **2** marks. [8x2 = 16 marks]

1. Mention the various factors influencing the magnitude of coupling constants (*J*) in ^{1}H NMR spectroscopy.
2. What is nuclear overhauser effect? What is the significance of NOE in structural elucidation?
3. What is HETCOR technique? How is COSY different from this technique?
4. What is the significance of DEPT-90 data in ^{13}C-NMR spectroscopy?
5. How does conjugation affect the position of λ_{max} of compounds in UV-visible spectrum?
6. How do you distinguish primary, secondary and tertiary amines from their IR spectra?
7. How does bond order effect the position of absorption bands in an IR spectrum?
8. What are base and isotope peaks in mass spectrometry?
9. To record Mössbauer spectrum of a sample containing Fe, a source 'X' was used. X after nuclear transformation with 'Y' gives gamma radiation. Identify 'X' and 'Y'.
10. Give a block diagram of mass spectrometer.

PART-B

Answer any **TWO** of the following questions. Each question carries **12** marks. [2x12 = 24marks]

11. (a) What is the frequency range of finger print region in an IR spectra? What is its main application in the structural analysis of organic compounds?

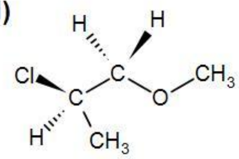
(b) Match the pattern of ^1H NMR signals of *N,N*-dimethylformamide given in column-I with the temperatures given in column-II.

Column-I	Column-II
(i) Two singlets for two types of protons at 2.87 and 2.97 ppm	25 °C
(ii) One sharp singlet for six protons at 2.92 ppm	120 °C
(iii) One broad signal for six protons	150 °C

(c) What is the total number of fine and hyperfine lines for octahedral Mn^{2+} ($I = 5/2$)?

(d) In Mössbauer studies why is the sample cooled in liquid nitrogen and the source moved with respect to the sample? (3+3+3+3)

12. (a) Identify each chemically distinct types of hydrogens in each of the compounds given below.

(i)


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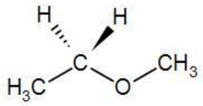

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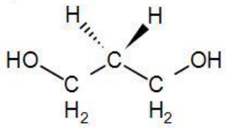

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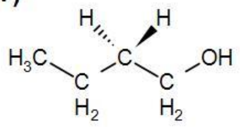
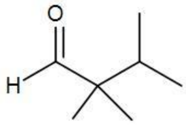


(b) How many ^{13}C signals (i.e. chemically distinct C atoms) would you expect for each of these compounds?

(i)


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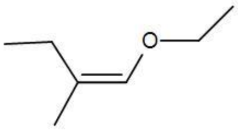

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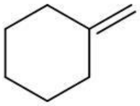

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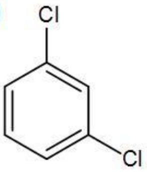
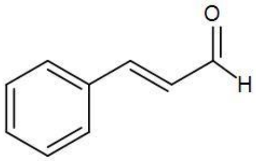


(c) Draw DEPT-45 and DEPT-135 spectra of following compounds.

(i)


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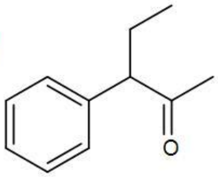


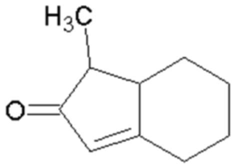
(4+4+4)

13.(a) Draw the mass spectra of ethanol indicating the major peaks.

(b) Explain recoil and Doppler effect in EPR spectra. How these factors affect resonance.

(c) Deduce λ_{max} values for the following compounds using the Woodward-Fieser rules.

(i)



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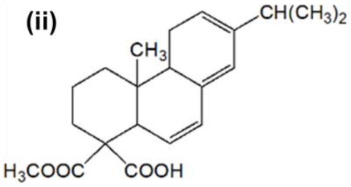


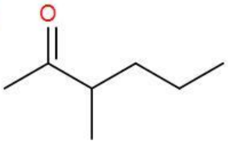
(4+4+4)

PART-C

Answer any **TWO** of the following questions. Each question carries **5** marks. [2x5 = 10marks]

14. (a) Among the following, identify the compound that gives base peak at m/z 72. Justify your answer.

(i)



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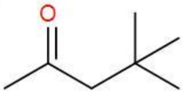

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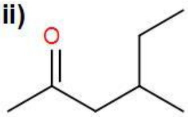

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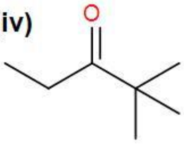
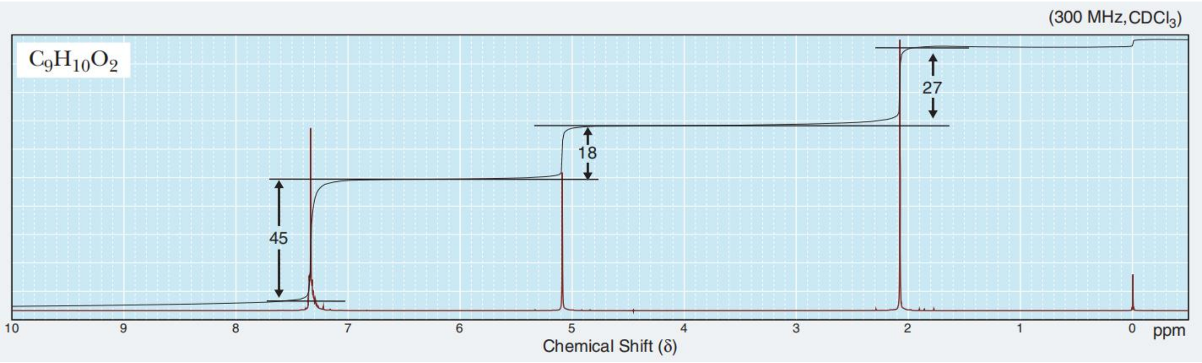


(b) $(R_3Ge)_2$ on photolysis gives a radical. Calculate the number of hyperfine lines shown by the radical, given I = 9/2 for ^{73}Ge. (3+2)

15. Following is the ^1H NMR spectrum for a compound with the molecular formula $C_9H_{10}O_2$. From the analysis of the integration height, calculate the number of hydrogens giving rise to each signal and identify the structure of the compound.



16. Deduce the structure of the compound (molecular formula $C_8H_8O_2$) from the IR, NMR and MS data given below:

IR: 1685 cm^{-1}
^{1}H NMR δ: 3.9 (singlet, 3H)
7.0 (doublet, J = 9Hz, 2H)
7.9 (doublet, J = 9Hz, 2H)
9.9 (singlet, 1H) ppm
^{13}C NMR δ: 55.6, 114.5, 130.2, 132.2, 164.9, 191.0 ppm
MS: 136 (M^+), 135, 107, 92, 78 m/z

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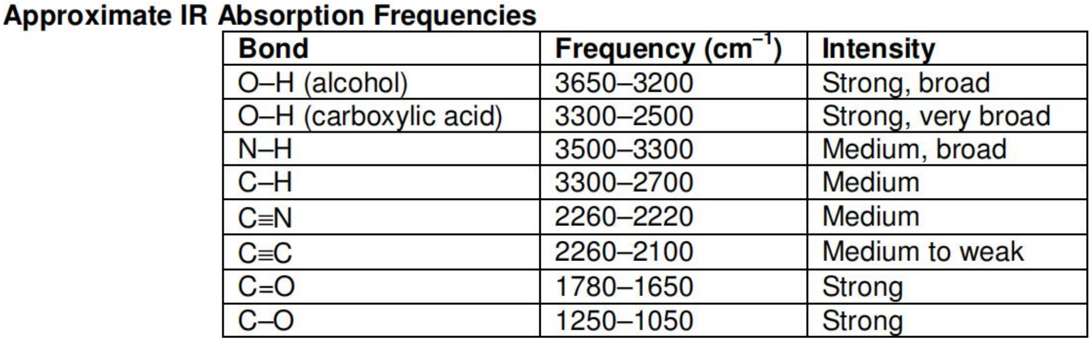
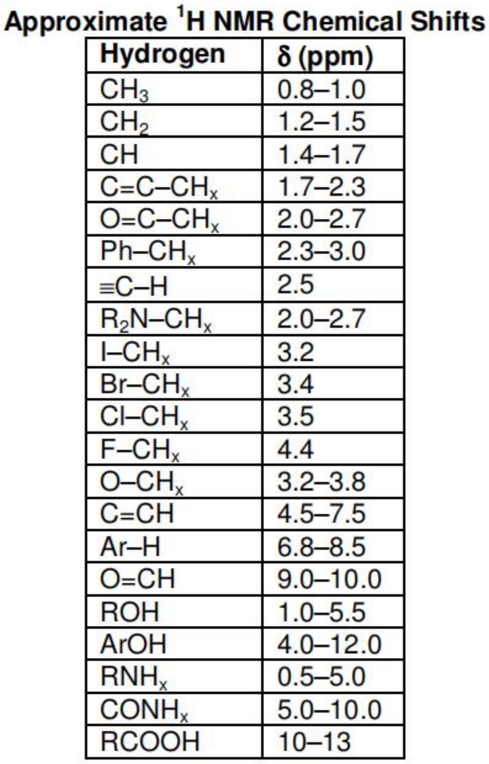


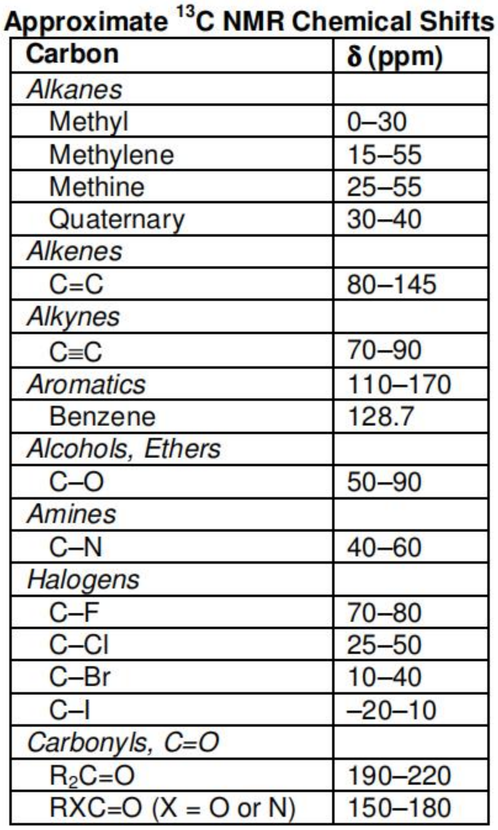
Approximate IR Absorption Frequencies

Bond	Frequency (cm^{-1})	Intensity
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
C≡N	2260–2220	Medium
C≡C	2260–2100	Medium to weak
C=O	1780–1650	Strong
C–O	1250–1050	Strong



Approximate ^{1}H NMR Chemical Shifts

Hydrogen	δ (ppm)
CH_3	0.8–1.0
CH_2	1.2–1.5
CH	1.4–1.7
$C=C-CH_x$	1.7–2.3
$O=C-CH_x$	2.0–2.7
$Ph-CH_x$	2.3–3.0
≡C–H	2.5
R_2N-CH_x	2.0–2.7
$I-CH_x$	3.2
$Br-CH_x$	3.4
$Cl-CH_x$	3.5
$F-CH_x$	4.4
$O-CH_x$	3.2–3.8
C=CH	4.5–7.5
Ar–H	6.8–8.5
O=CH	9.0–10.0
ROH	1.0–5.5
ArOH	4.0–12.0
RNH_x	0.5–5.0
$CONH_x$	5.0–10.0
RCOOH	10–13



Approximate ^{13}C NMR Chemical Shifts

Carbon	δ (ppm)
Alkanes	
Methyl	0–30
Methylene	15–55
Methine	25–55
Quaternary	30–40
Alkenes	
C=C	80–145
Alkynes	
C≡C	70–90
Aromatics	110–170
Benzene	128.7
Alcohols, Ethers	
C–O	50–90
Amines	
C–N	40–60
Halogens	
C–F	70–80
C–Cl	25–50
C–Br	10–40
C–I	–20–10
Carbonyls, C=O	
$R_2C=O$	190–220
RXC=O (X = O or N)	150–180

Empirical Rules for Dienes

	Homoannular (cisoid)	**Heteroannular (transoid)**
Parent	253 nm	214 nm
Increments for		
Double bond for extending conjugation	30	30
Alkyl substituent or ring residue	5	5
Exocyclic double bond	5	5
Polar grouping		
-$OCOCH_3$	0	0
-OR	6	6
-Cl, -Br	5	5
-NR_2	60	60

Base values:	
Six-membered ring or acyclic parent enone	215 nm
Five-membered ring	202 nm
Acyclic dienone	245 nm
Increments for:	
Double-bond-extending conjugation	30
Alkyl group or ring residue	α 10
	γ and higher 18
Polar grouping:	
-OH	α 35
	β 30
	δ 50
-$OCOCH_3$	α, β, δ = 6
-OCH_3	α 35
	β 30
	γ 17
	δ 31
-Cl	α 15
	β 30
-Br	α 25
	β 30
-NH_2	β 95
Exocyclic double bond	5
Homocyclic diene component	39