ST. JOSEPH'S COLLEGE (AUTONOMOUS), BENGALURU-27.

M.SC., CHEMISTRY – II SEMESTER

SEMESTER EXAMINATION – APRIL 2022
(Examination conducted in July 2022)

CH 8418: SPECTROSCOPY – II

Time: 2 hr 30 min. **Max marks: 70**

This question paper contains three printed pages and three parts.

Part A

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

1. What is COSY technique in NMR?
2. In an organic compound, three kinds of protons appear at 60, 100 and 180 Hz when the spectrum is recorded at 60 MHz NMR spectrometer. What will be their relative positions (in Hz) when 90 MHz spectrometer is used?
3. Mention two advantages of using ^{13}C NMR under broad band decoupled conditions?
4. A compound of molecular formula C_6H_{10} gives three signals in its ^1H NMR spectrum with the following integration units: 13, 33, 73 units. How many protons are responsible for each signal?
5. What are molecular ion and isotope peaks in mass spectrometry?
6. How would the following compound differ in the IR spectra?
   CH_3CHO and CH_3COOH
7. List the electronic transitions of formaldehyde and arrange them in the increasing order of energy.
8. What is zero field splitting in EPR? Give an example.

Part B

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

9. a) Propose a structure for a hydrocarbon with molecular formula, $C_{11}H_{16}$, that has the following ^{13}C NMR spectral data:
   Broadband decoupled: 29.5, 31.8, 50.2, 125.5, 127.5, 130.3, 139.8 ppm
   DEPT-90: 125.5, 127.5, 130.3 ppm
   DEPT-135: positive peaks at 29.5, 125.5, 127.5, 130.3 ppm; negative peak at 50.2 ppm.
   b) In an attached proton test (APT) experiment, explain why a methine carbon gives an inverted peak while a methylene carbon gives a normal peak? (5+7)

10. a) The ^1H NMR spectrum of N,N-dimethyl formamide recorded at room temperature is different from that recorded at 140 °C. Explain.
    b) The ^1H NMR spectrum of phenol (C_6H_5OH) shows three absorptions in the aromatic region: 6.70 (2 ortho H's), 7.14 (2 meta H's), and 6.80 (1 para H) ppm. Explain why the ortho and para absorptions occur at lower chemical shift than the meta absorption.

c) Propose a suitable structure for **C**: molecular formula $C_6H_{12}O_3$; strong IR absorption at 1718 cm^{-1}
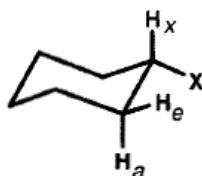

^{1}H NMR of C
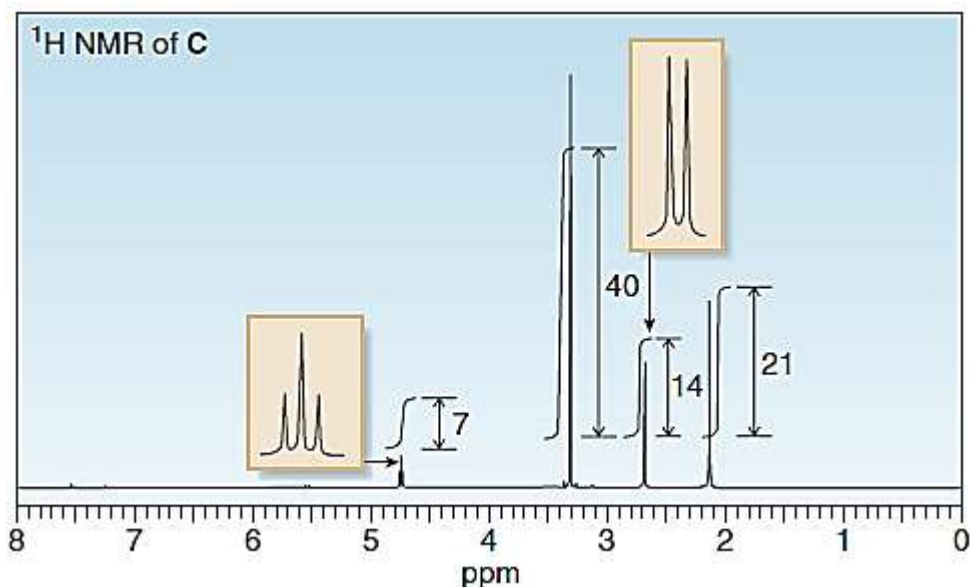
(4+4+4)

11. a) What is diamagnetic anisotropy? Why does the following molecule show two signals in the ^{1}H NMR spectrum, one at 8.8 ppm and the other at −1.9 ppm?

b) What is Karplus equation? Using this equation, predict ^3J coupling values for H_x–H_e and H_x–H_a in the cyclohexane molecule represented below.

c) What is nuclear overhauser effect? How is it useful in ^{13}C-NMR spectroscopy?.

(4+4+4)

12. a) Explain ion production in mass spectral analysis by the following methods: i) field desorption and ii) fast atom bombardment.

b) What is hyperfine splitting? How many hyperfine lines are seen in the case of quinone and biphenyl radicals? (6+6)

13. a) In Mossbauer spectra a source emitting at 3.48×10^{18} Hz had to be moved towards absorber at 2.2 mm/sec for resonance. Find the shift of frequency between source and the absorber?

b) Using Woodward rules, predict the UV maximum for each of the following.
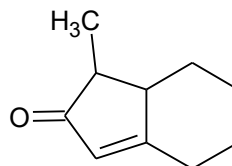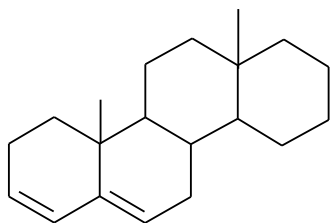
c) Explain Recoil and Doppler effect in EPR spectroscopy and how these factors affect the resonance.

(4+4+4)

14. a) Explain with suitable example the effect of i) conjugation ii) inductive and iii) hydrogen bonding effects on the position of vibrational frequency of carbonyl bond.

b) A given alkyl halide shows M+, M + 2 and M + 4 peaks in the intensity of 9:6:1. Answer the following with proper justification.

i) Identify the halogen; ii) how many halogens are present in the molecule

(6+6)

Part C

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

15. Deduce the structures of compounds **A** and **B,** two of the major components of jasmine oil, from the given data.

Compound **A**: $C_9H_{10}O_2$; IR absorptions at 3091–2895 and 1743 cm^{-1}; ^{1}H NMR signals at 2.06 (singlet, 3H), 5.08 (singlet, 2H), and 7.33 (broad singlet, 5H) ppm.

Compound **B**: $C_{14}H_{12}O_2$; IR absorptions at 3091–2953 and 1718 cm^{-1}; ^{1}H NMR signals at 5.35 (singlet, 2 H) and 7.26–8.15 (multiplets, 10 H) ppm.

16. The absorption peak of Co – H bond in Co(CO)$_4$H is seen at 1934 cm^{-1}. Then what is the absorption frequency of Co – D bond in Co(CO)$_4$D ?

17. a) Which of the following technique can distinguish between *cis* and *trans* 1,2 dichloro ethene. Explain your choice.

UV-Visible spectroscopy ii) Infrared spectroscopy iii) Mass spectrometry iv) EPR
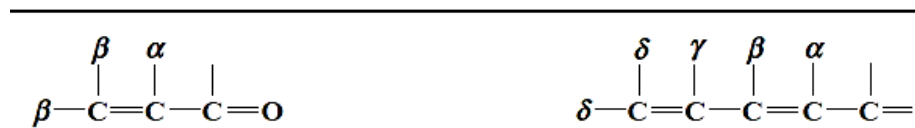
b) A sample of 2,5- dimethyl, 2,4 hexadiene in methanol in a 1.00 cm cell shows an absorbance of 0.65 at 242.5 nm. What is the concentration of the diene? The molar absorptivity at this wavelength is 13,100.

(2+3)

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EMPIRICAL RULES FOR DIENES

	Homoannular (cisoid)	Heteroannular (transoid)
Parent	$\lambda = 253$ nm	$\lambda = 214$ nm
Increments for:		
Double-bond-extending conjugation	30	30
Alkyl substituent or ring residue	5	5
Exocyclic double bond	5	5
Polar groupings:		
—OCOCH$_3$	0	0
—OR	6	6
—Cl, —Br	5	5
—NR$_2$	60	60

EMPIRICAL RULES FOR ENONES

$$\overset{\beta}{\underset{}{}}\;\overset{\alpha}{\underset{}{}}$$
$$\beta\!-\!C\!=\!C\!-\!C\!=\!O \qquad\qquad \delta\!-\!C\!=\!C\!-\!C\!=\!C\!-\!C\!=$$

with labels $\beta\ \alpha$ over the first structure and $\delta\ \gamma\ \beta\ \alpha$ over the second.

Base values:		
Six-membered ring or acyclic parent enone		= 215 nm
Five-membered ring parent enone		= 202 nm
Acyclic dienone		= 245 nm
Increments for:		
Double-bond-extending conjugation		30
Alkyl group or ring residue	α	10
	β	12
	γ and higher	18
Polar groupings:		
—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	12
—Br	α	25
	β	30
—NR$_2$	β	95
Exocyclic double bond		5
Homocyclic diene component		39
Solvent correction		Variable
λ_{max}^{EtOH}(calc) = Total		

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
(benzene ring)	~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 9.1 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, $R_2C=C-CH_3$ (R)	1.6–1.9	Vinylic, $R_2C=CH$ (R)	5.2–5.7
Ketone, $RCCH_3$ (O)	2.1–2.6	Aromatic, ArH	6.0–8.5
Benzylic, $ArCH_3$	2.2–2.5	Aldehyde, RCH (O)	9.5–10.5
Acetylenic, $RC≡CH$	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, $RCOH$ (O)	10–13[a]