KIBABII UNIVERSITY

UNIVERSITY EXAMINATIONS
2021/2022 ACADEMIC YEAR

FORTH YEAR FIRST SEMESTER
MAIN EXAMINATIONS

FOR THE DEGREE OF BSC (CHEMISTRY)

COURSE CODE: SCH 411

COURSE TITLE: SPECTROSCOPY AND SEPARATION

DATE: 24/05/2022 **TIME: 2:00PM-4:00PM**

INSTRUCTIONS TO CANDIDATES
Time: 2 Hours

Answer question ONE and any other TWO of the remaining

QUESTION ONE [30 MARKS]

a) Name three functions of mass spectrometer **[3 marks]**

b) Explain the following observations in IR spectrum **[3 marks]**

i. Units in the x axis of IR spectrum is measured in wavenumbers rather than wavelength

ii. Lighter atoms have faster oscillation

iii. Weaker bonds have lower energy oscillations

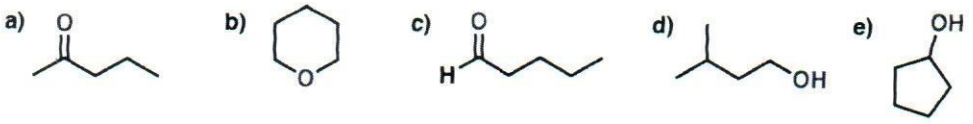
c) Using well labeled schematic diagram show the basic components of HPLC **[4 marks]**

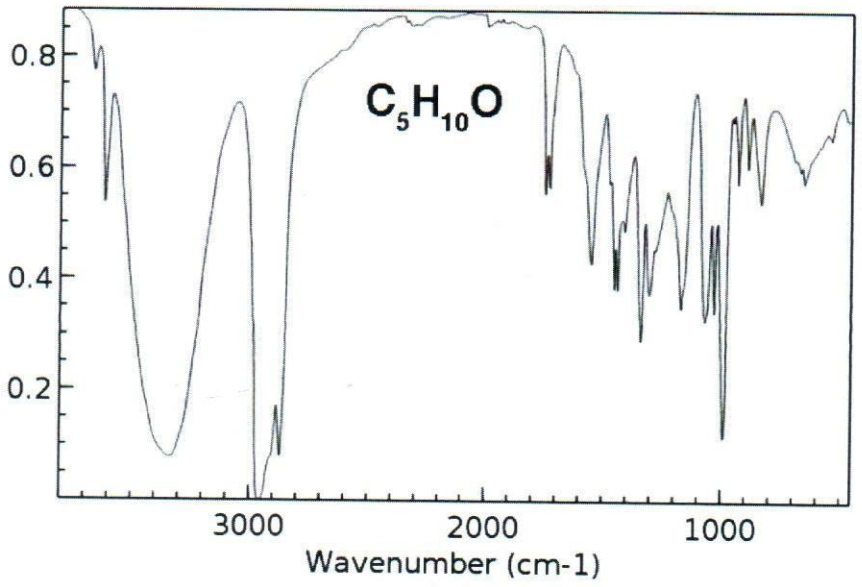
d) Gas chromatography (GC) is the technique of choice for separation of thermally stable and volatile compound

i. State any three properties of ideal carrier gas used in GC **[3 marks]**

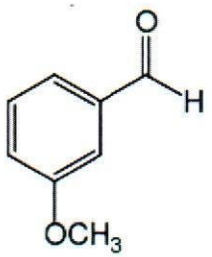
ii. With aid of diagram, explain working principle of thermal conductivity detectors used in GC **[4 marks]**

e) Unknown molecule has a molecular formula $C_5H_{10}O$. Based on IR spectrum below and citing reasons which of these five molecules is it most likely to be? **[3 marks]**

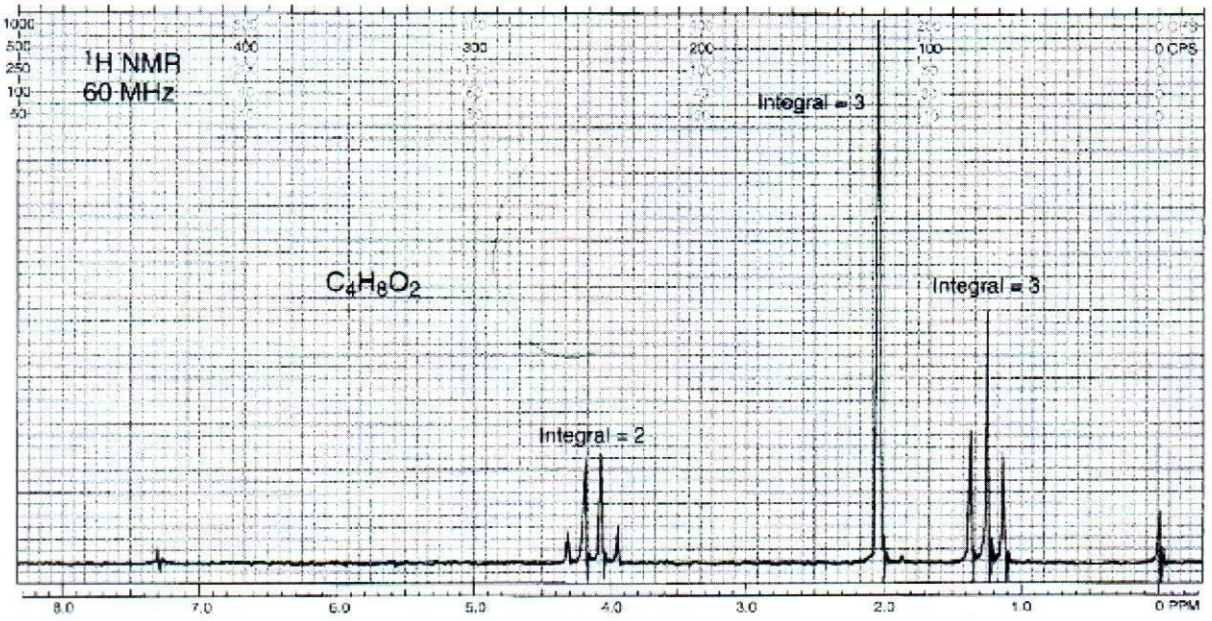




f) Draw what you would expect to see in the 1H NMR of this compound. Your drawing should clearly show the number of signals, their approximate chemical shift (within 1 ppm) and the expected splitting pattern **[5 marks]**



g) The following compound, with the formula $C_4H_8O_2$ is an ester. Deduce its structure and assign its chemical shift value **[5 marks]**



QUESTION TWO [20 MARKS]

a) Briefly explain working principle of mass spectrometer **[4 marks]**

b) Calculate the molecular formulas for the possible compounds with the molecular mass of 136, using Rule of Thirteen and calculate index of hydrogen deficiency for each molecular formula. You may assume that the only other atoms present in each molecule are carbon and hydrogen

i. A compound with two nitrogen atoms and one oxygen atom **[4 marks]**

ii. A compound with five carbon atoms and four oxygen atoms **[4 marks]**

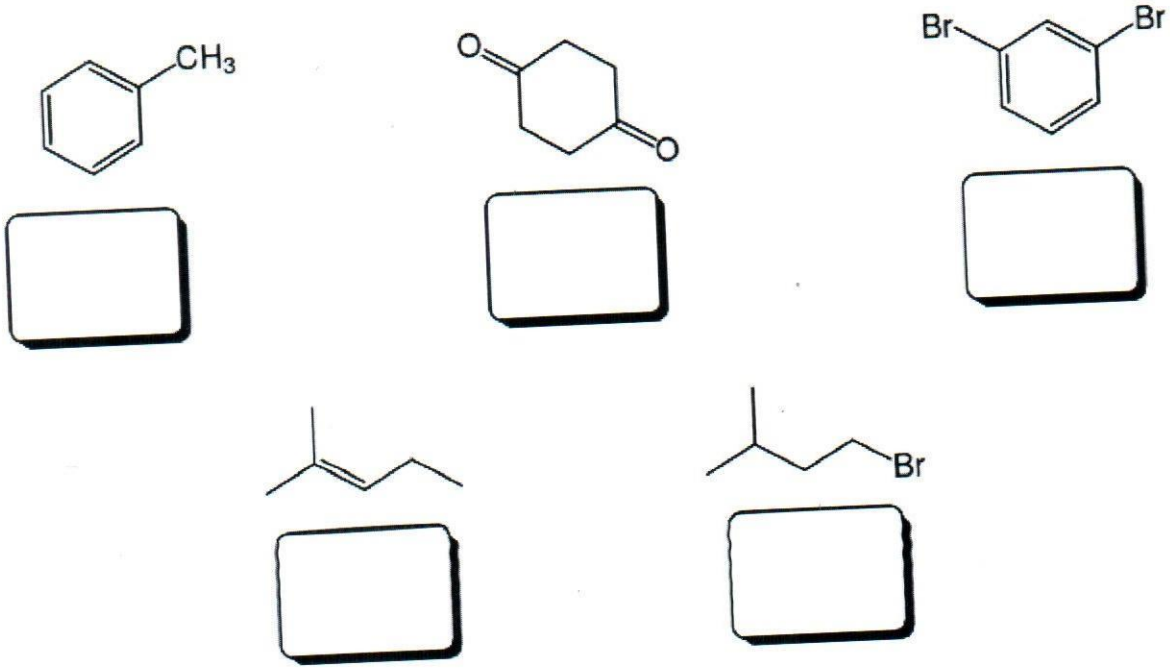
c) HPLC is a chromatographic technique used to separate compounds dissolved in solutions

i. Explain principle of separation in HPLC **[3 marks]**

ii. With aid of diagram, explain the working principle of UV detector used in HPLC **[5 marks]**

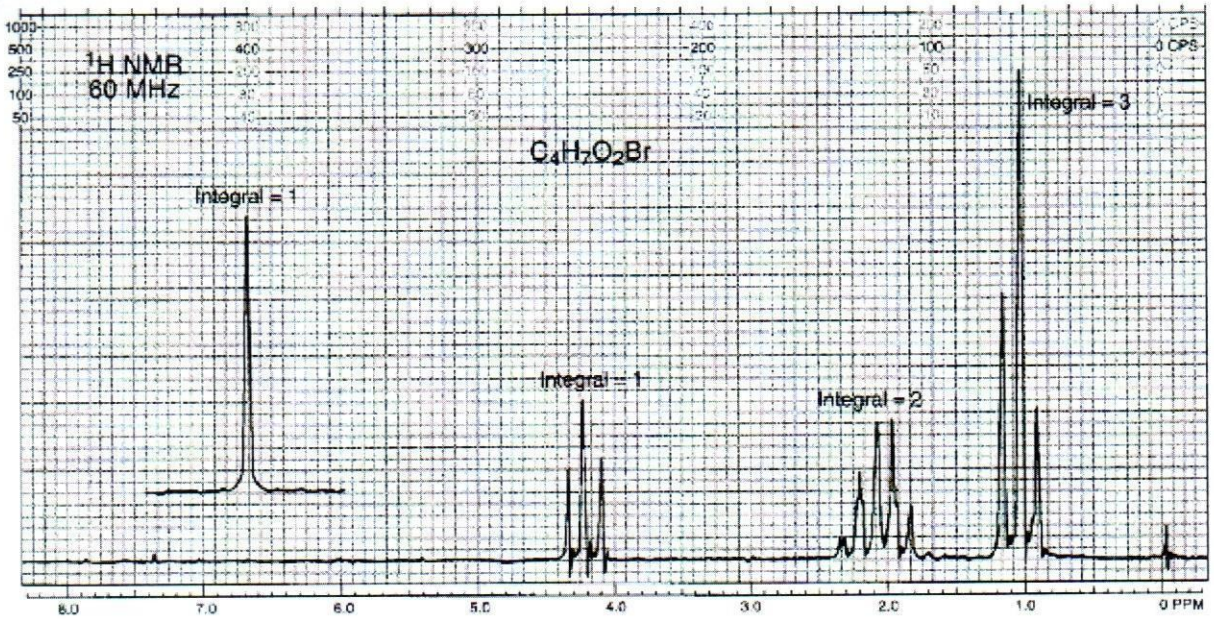
QUESTION THREE [20 MARKS]

a) Predict how many signals you would see in the ^{13}C NMR spectrum of each of these molecules. **[5 marks]**



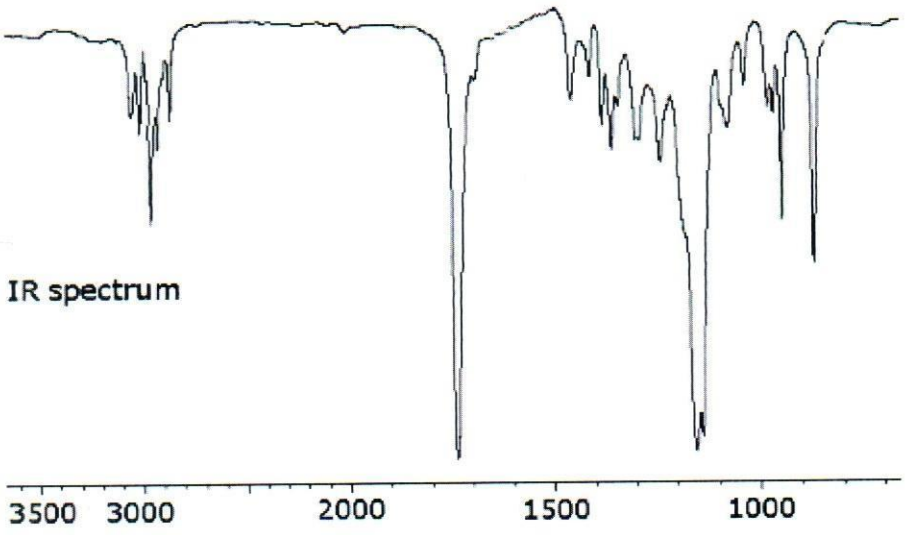
b) Calculate the chemical shift in parts per million (δ) for a proton that has resonsance 128 Hz downfield from TMS on the spectrometer that operates at 60 MHz **[4 marks]**

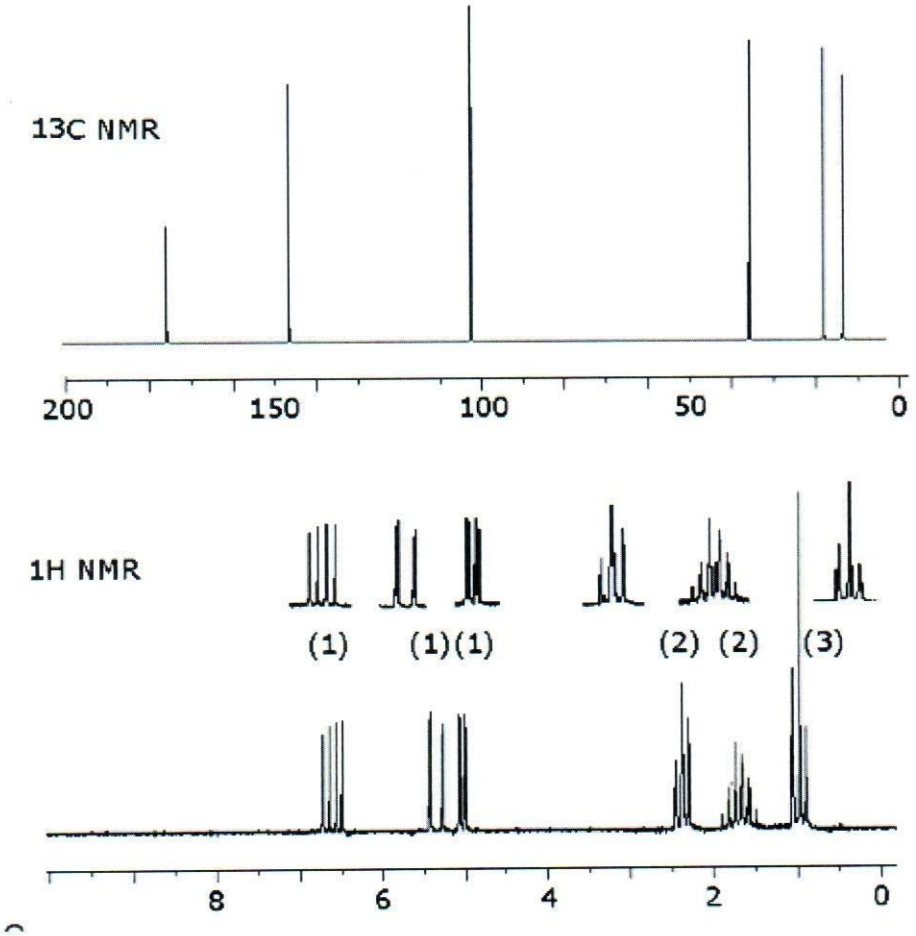
c) The following compound is a carboxylic acid that contain a bromine atom: $C_4H_7O_2Br$. The peak at 10.97 ppm was moved onto the chart (which runs only from 0 to 8 ppm) for clarity. Deduce the structure of the compound **[11 marks]**



QUESTION FOUR [20 MARKS]

Study the IR, ^{13}C NMR and ^{1}H NMR spectra for an unknown compound with the formula $C_6H_{10}O_2$, then answer the question on the next page.





i. Determine degrees of unsaturation in this compound and explain its significance **[4 marks]**

ii. In the IR, what does the signal at about 1740 suggest? **[2 marks]**

iii. In the ^{13}C NMR, what does the chemical shift of the signal at about 105 suggest? **[2 marks]**

iv. In the ^{1}H NMR, what does the chemical shift of the signal at about 5.2 suggest? **[2 marks]**

v. In the ^{1}H NMR, what does the integration of the signal at about 2.3 suggest? **[2 marks]**

vi. In the ^{1}H NMR, what does the splitting pattern of the signal at about 1.0 suggest? **[2 marks]**

vii. Deduce the structure of this unknown compound **[6 marks]**

APPENDICES

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

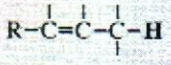
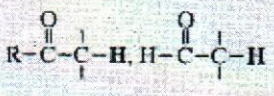
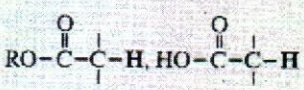
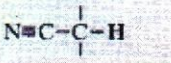
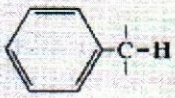
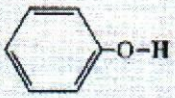
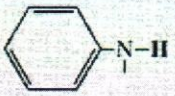
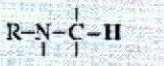
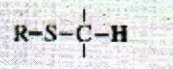
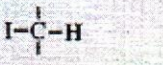
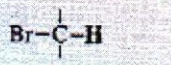
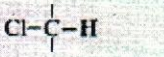
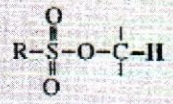
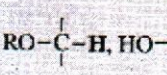
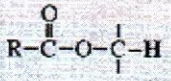
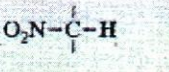
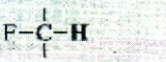
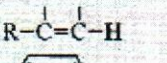
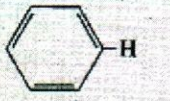
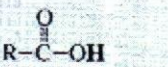
Approximate ^{13}C NMR Chemical Shifts

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

A SIMPLIFIED CORRELATION CHART

Type of Vibration			Frequency (cm^{-1})	Intensity	Page Reference
C–H	Alkanes	(stretch)	3000–2850	s	29
	$-CH_3$	(bend)	1450 and 1375	m	
	$-CH_2-$	(bend)	1465	m	
	Alkenes	(stretch)	3100–3000	m	31
		(out-of-plane bend)	1000–650	s	
	Aromatics	(stretch)	3150–3050	s	41
		(out-of-plane bend)	900–690	s	
	Alkyne	(stretch)	ca. 3300	s	33
	Aldehyde		2900–2800	w	54
			2800–2700	w	
C–C	Alkane		Not interpretatively useful		
C=C	Alkene		1680–1600	m–w	31
	Aromatic		1600 and 1475	m–w	41
C≡C	Alkyne		2250–2100	m–w	33
C=O	Aldehyde		1740–1720	s	54
	Ketone		1725–1705	s	56
	Carboxylic acid		1725–1700	s	60
	Ester		1750–1730	s	62
	Amide		1680–1630	s	68
	Anhydride		1810 and 1760	s	71
	Acid chloride		1800	s	70
C–O	Alcohols, ethers, esters, carboxylic acids, anhydrides		1300–1000	s	45, 48, 60, 62, and 71
O–H	Alcohols, phenols				
	Free		3650–3600	m	47
	H-bonded		3400–3200	m	47
	Carboxylic acids		3400–2400	m	61
N–H	Primary and secondary amines and amides				
	(stretch)		3500–3100	m	72
	(bend)		1640–1550	m–s	72
C–N	Amines		1350–1000	m–s	72
C=N	Imines and oximes		1690–1640	w–s	75
C≡N	Nitriles		2260–2240	m	75
X=C=Y	Allenes, ketenes, isocyanates, isothiocyanates		2270–1940	m–s	75
N–O	Nitro ($R-NO_2$)		1550 and 1350	s	77
S–H	Mercaptans		2550	w	79
S–O	Sulfoxides		1050	s	79
	Sulfones, sulfonyl chlorides, sulfates, sulfonamides		1375–1300 and 1350–1140	s	80
C–X	Fluoride		1400–1000	s	83
	Chloride		785–540	s	83
	Bromide, iodide		<667	s	83

APPROXIMATE CHEMICAL SHIFT RANGES (PPM) FOR SELECTED TYPES OF PROTONS[a]

$R-CH_3$		0.7 – 1.3
$R-CH_2-R$		1.2 – 1.4
R_3CH		1.4 – 1.7
		1.6 – 2.6
		2.1 – 2.4
		2.1 – 2.5
		2.1 – 3.0
		2.3 – 2.7
$R-C\equiv C-H$		1.7 – 2.7
$R-S-H$	var	1.0 – 4.0[b]
	var	0.5 – 4.0[b]
$R-O-H$	var	0.5 – 5.0[b]
	var	4.0 – 7.0[b]
	var	3.0 – 5.0[b]
	var	5.0 – 9.0[b]
		2.2 – 2.9
		2.0 – 3.0
		2.0 – 4.0
		2.7 – 4.1
		3.1 – 4.1
		ca. 3.0
		3.2 – 3.8
		3.5 – 4.8
		4.1 – 4.3
		4.2 – 4.8
		4.5 – 6.5
		6.5 – 8.0
		9.0 – 10.0
		11.0 – 12.0