KIBABII UNIVERSITY

UNIVERSITY EXAMINATIONS
2021/2022 ACADEMIC YEAR

FORTH YEAR FIRST SEMESTER
SUPPLIMENTARY/SPECIAL EXAMINATIONS

FOR THE DEGREE OF BSC (CHEMISTRY)

COURSE CODE: SCH 411

COURSE TITLE: SPECTROSCOPY AND SEPARATION

DATE: 17/11/2022 **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)

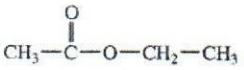
a) Differentiate between the following **(4 marks)**
   i. Wavelength and Wave number
   ii. Chromophore and Auxochrome

b) Determine index of hydrogen deficiency for the following compounds **(4 marks)**
   i. C_6H_{12}
   ii. $C_5H_8Br_2$
   iii. $C_5H_{11}N_3$
   iv. $C_6H_8Br_2O_3$

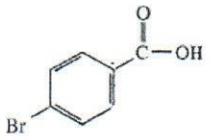
c) State any four application of UV-VIS spectroscopy **(4 marks)**

d) Predict the number of peaks that you would expect in proton-decoupled 13C spectrum of each of the following compounds **(4 marks)**

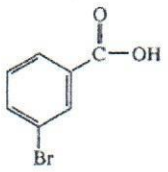
(a)



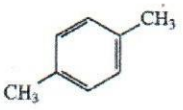
(b)



(c)



(d)



e) Define the following terms as used in Mass spectrometry **(4 marks)**

   i. Molecular ion peak
   ii. Base peak
   iii. Radical cation
   iv. Fragmentation ion

f) Briefly describe the processes and instrumentation involved in electron impact ionization techniques used in mass spectrometry **(3 marks)**

g) The spectrum seen here was taken as a KBr pellet and belongs to a compound with the formula C_2H_6O.

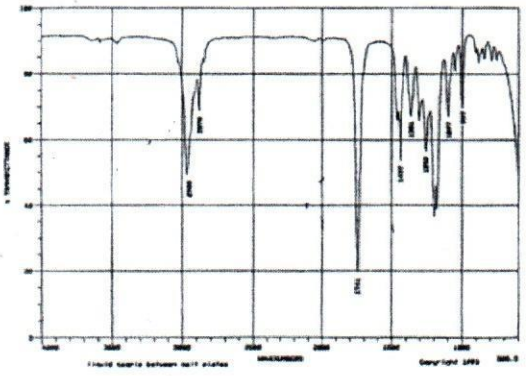
QUESTION TWO (20 MARKS)

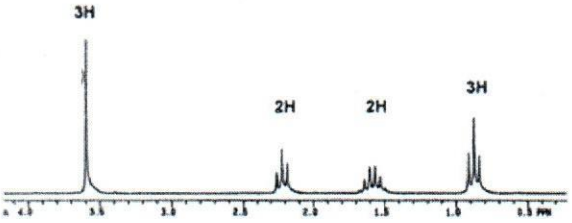
a) A proton has resonance 90 Hz downfield from TMS when the field strength is 1.41 Tesla and the oscillator frequency is 60 MHz

i. What will be its shift in Hertz if the field strenght is increased to 2.82 Tesla and the oscillator freqency is 120 MHz **(3 marks)**

ii. What will be its chemical shift in parts per million (δ) **(3 marks)**

b) Provide a structure of a compound having molecular formula $C_5H_{10}O_2$ that is consistent with the following spectra.
Show your work by assigning all the relevant peaks in IR and NMR spectra **(12 marks)**





QUESTION THREE (20 MARKS)

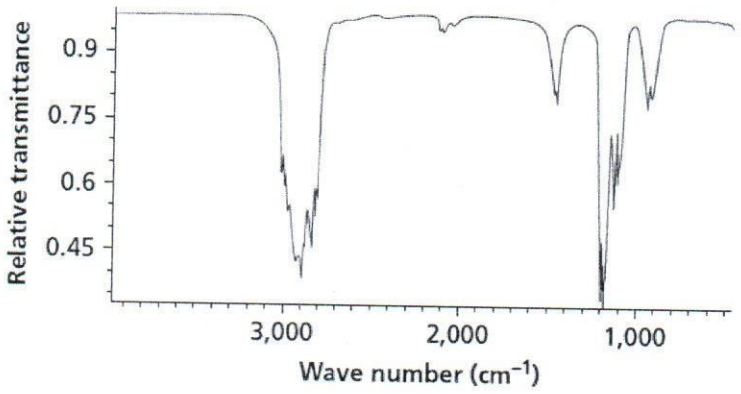
a) Show that

$$m/z = \frac{H^2 r^2}{2V}$$

(5 marks)

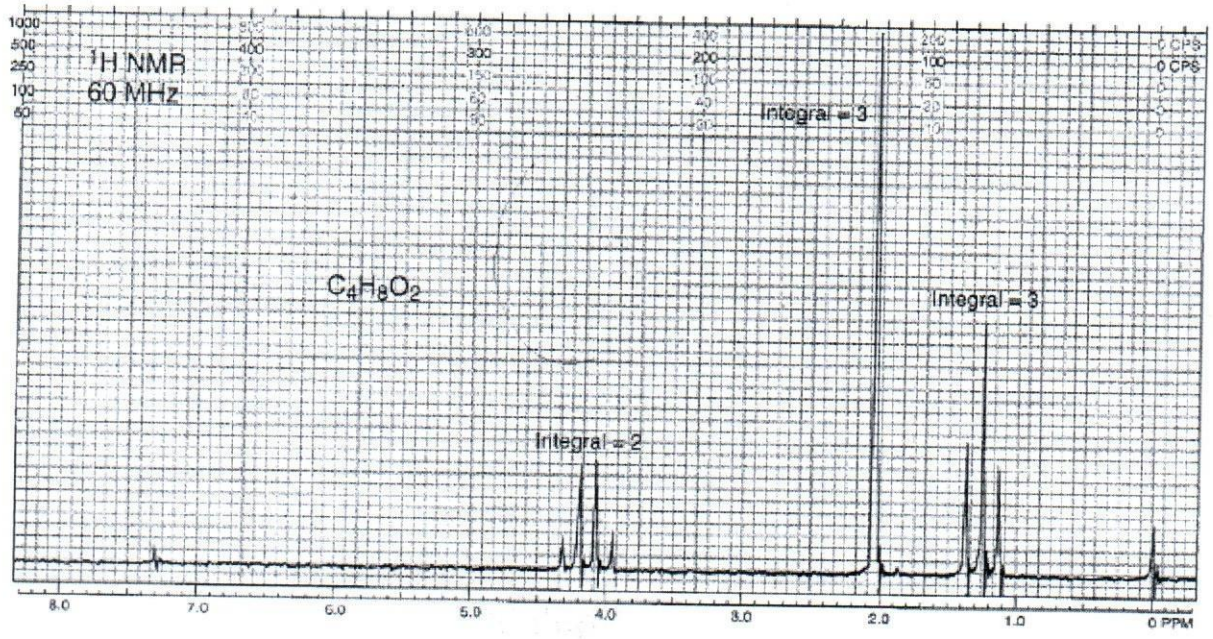
b) An unknown compound has the mass spectrum shown below. The infrared spectrum of the unknown shows significant peaks at

3102 cm^{-1}	3087	3062	3030	1688
1598	1583	1460	1449	1353
1221	952	746	691	

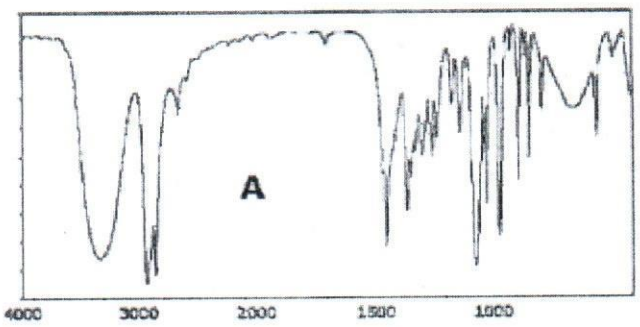


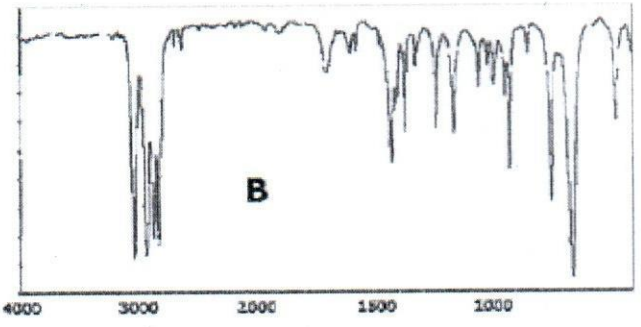
Determine the identity of the compound. **(3 marks)**

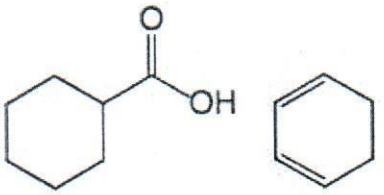
h) The HNMR spectrum below is for an ester compound the formula $C_4H_8O_2$. Provide its structure **(3 marks)**

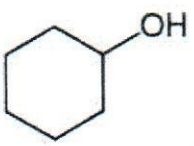


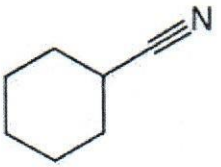
b) Below are the IR spectra A and B for two of four compounds





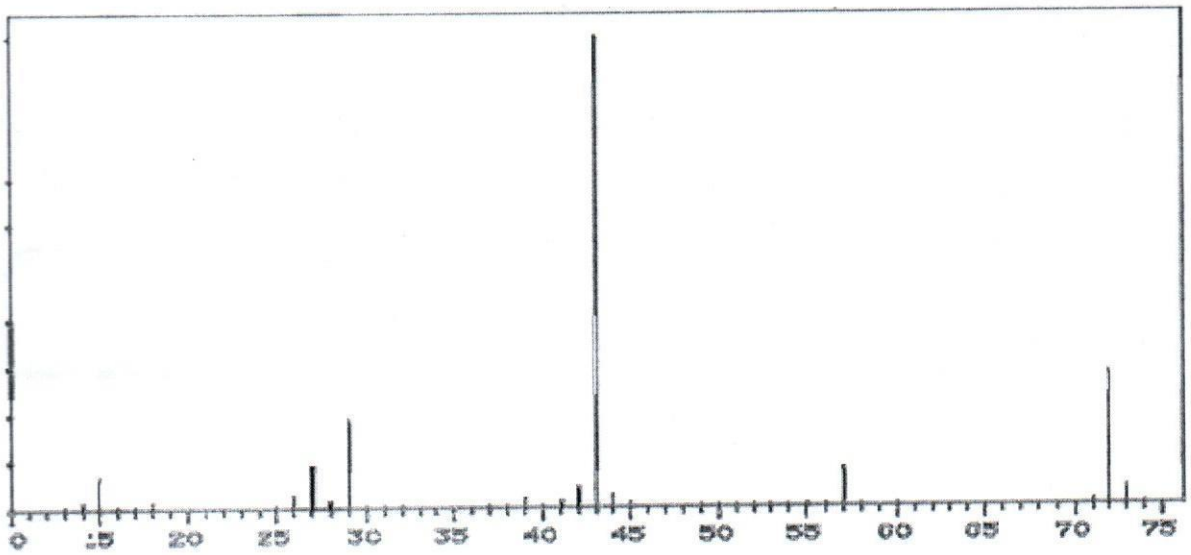




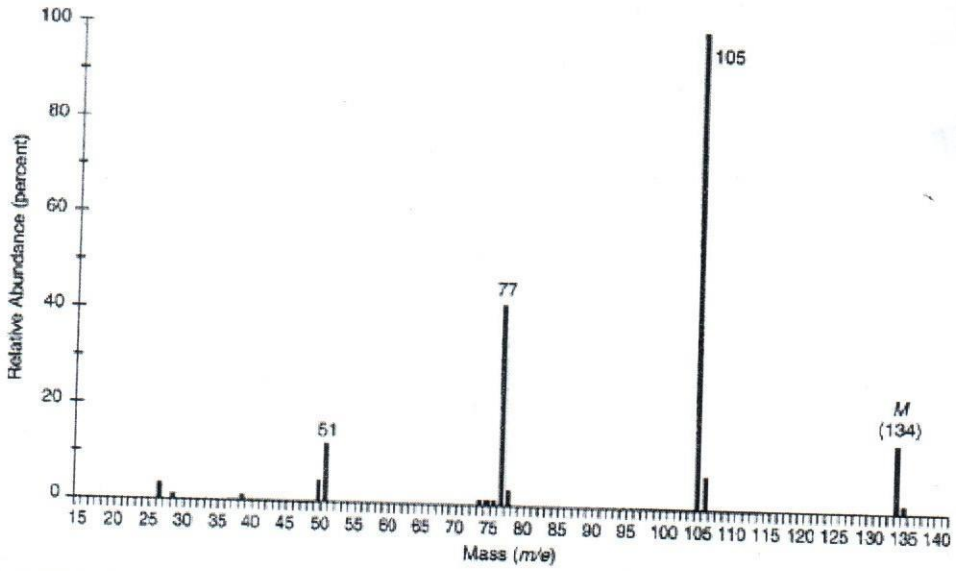


With reason, determine which spectrum belong to which compound **(8 marks)**

c) Below is the mass spectrum of 2-butanone. Explain the large peak at 43 and the small peak at 73 **(6 marks)**



There is also a band from aliphatic C-H stretching from 2879 to 2979 cm^{-1}

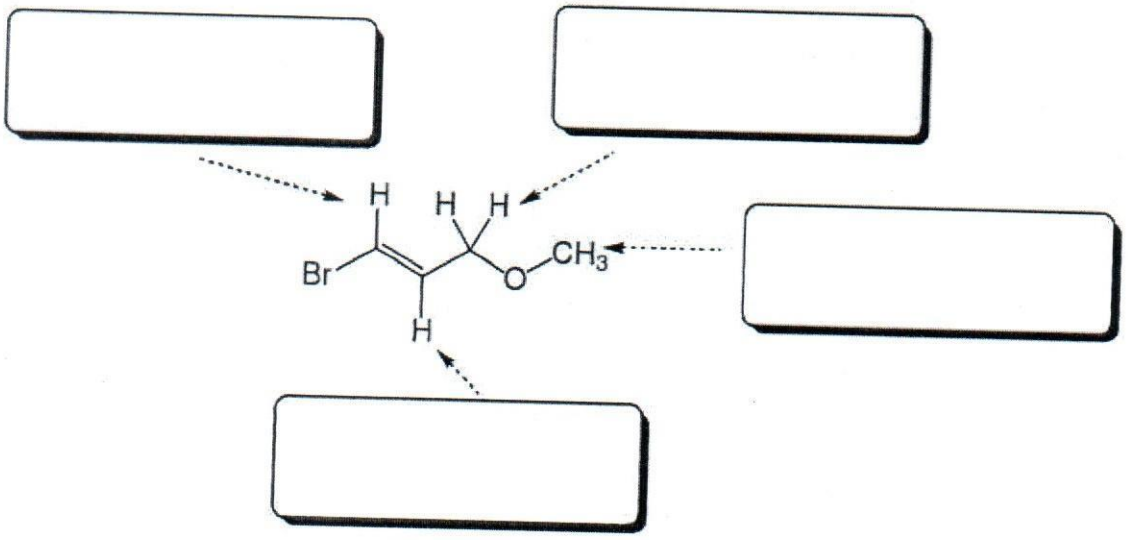


Deduce the structure

(15 marks)

QUESTION FOUR (20 MARKS)

a) The ^1H NMR of this compound should have four signals. Predict the splitting patterns (singlet, doublet, doublet of doublet etc) you would see for each signal **(4 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

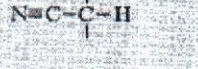
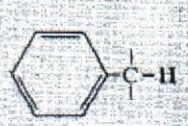
Approximate ^{13}C NMR Chemical Shifts

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
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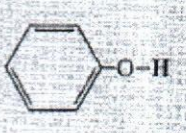
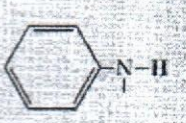
	var	4.0 – 7.0[b]
	var	3.0 – 5.0[b]
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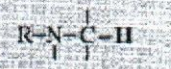
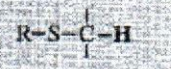
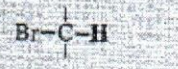
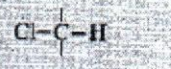
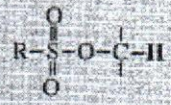
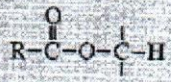
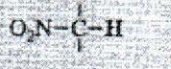
		2.2 – 2.9
		2.0 – 3.0
		2.0 – 4.0
		2.7 – 4.1
		3.1 – 4.1
		ca. 3.0
		3.2 – 3.8
		3.5 – 4.8
		4.1 – 4.3
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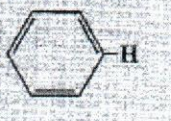
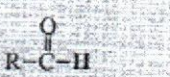
		6.5 – 8.0
		9.0 – 10.0
		11.0 – 12.0