UNIVERSITY OF RUHUNA

FACULTY OF FISHERIES AND MARINE SCIENCES & TECHNOLOGY

Academic Year 2023/2024

Bachelor of Science Honours in Marine and Freshwater Sciences Degree

Level III Semester I Examinations – Oct/Nov 2024

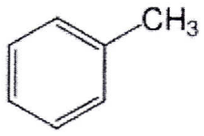
CHM 3122: Physical Chemistry II - Theory

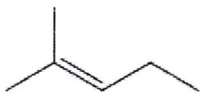
Part II - Answer all questions (70 Marks)

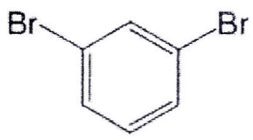
1) Answer all parts

a) NMR is a spectroscopic technique that gives information about the number of magnetically distinct atoms in a molecule.

I) Predict how many signals will be in the ^{13}C spectrum of the following molecules.

A. 

B. 

C. 

(06 marks)

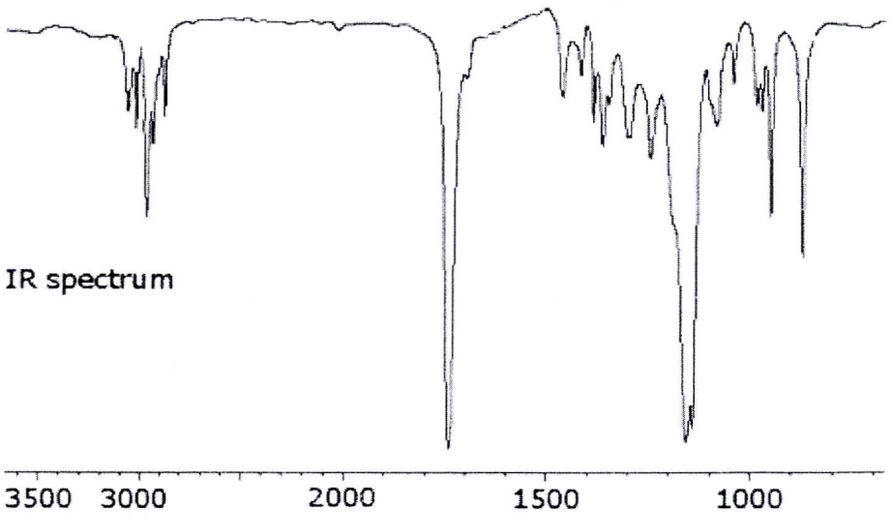
II) Briefly describe what 3-bond coupling is in NMR spectroscopy.

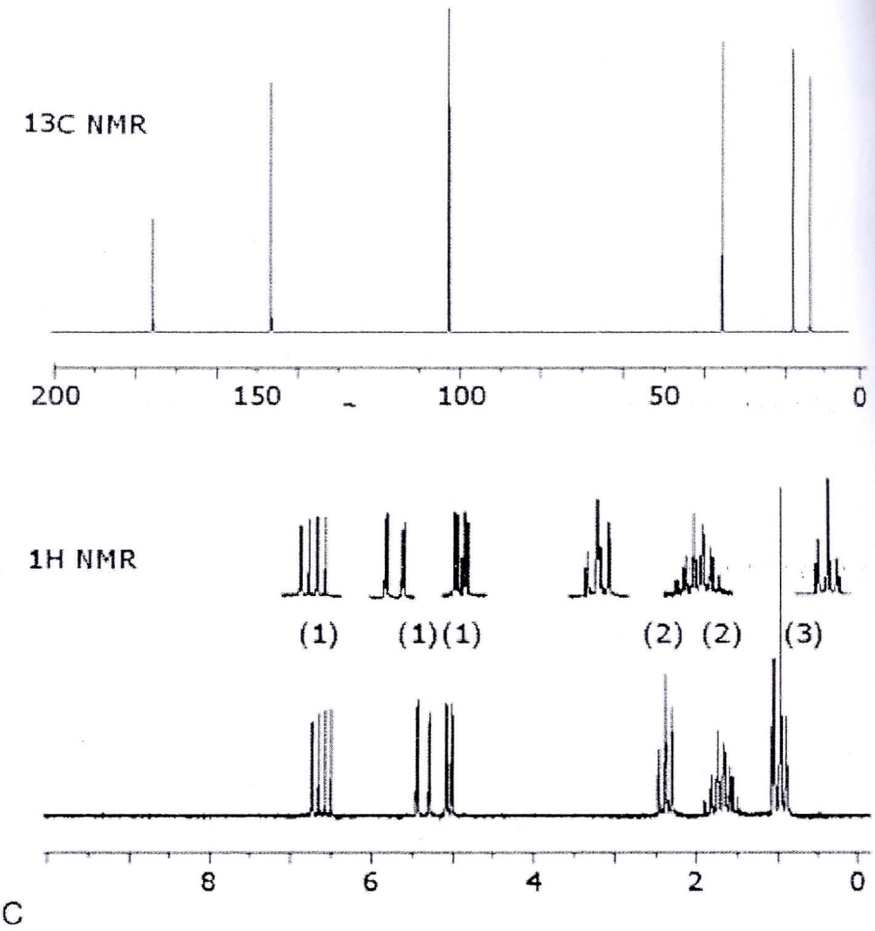
(04 marks)

III) Using the Karplus curve describe how 3-bond coupling is affected by the dihedral angle.

(05 marks)

b) Given below are the IR, ^{13}C and ^{1}NMR spectra of a compound with molecular formula $C_6H_{10}O_2$.





C

I) Calculate the degree of unsaturation for the given compound

II) What does the signal at about 1740 suggest in the IR spectrum?

III) In the ^{13}C NMR, what does the chemical shift of the signal at about 105 suggest?

IV) In the ^{1}H NMR, what does the chemical shift of the signal at about 5.2 suggest?

V) In the ^{1}H NMR, what does the signal integration at about 2.3 suggest?

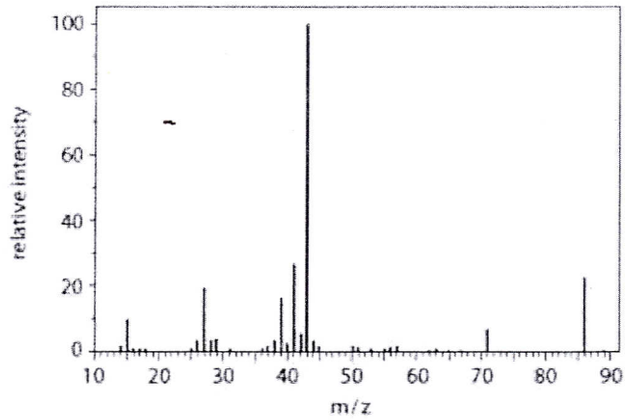
VI) In the ^{1}H NMR, what does the splitting pattern of the signal at about 1.0 suggest?

VII) Suggest a suitable structure for this molecule.

Answer all parts

Mass spectrometry (MS) is an analytical technique that separates ionized particles such as atoms, molecules, and clusters by using differences in the ratios of their charges to their respective masses (mass/charge; m/z), and can be used to determine the molecular weight of the particles.

I) The mass spectrum of pure 3-methylbutan-2-one is shown.



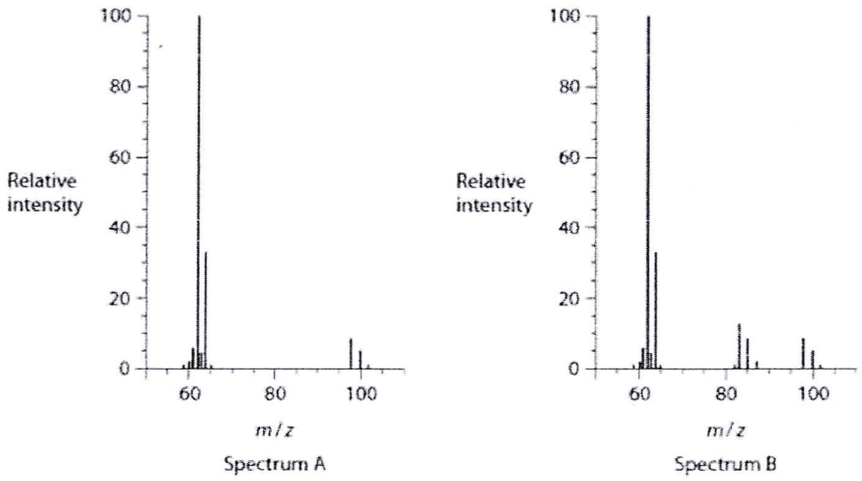
A. State how you would find the molar mass of 3-methylbutan-2-one from the mass spectrum.

(02 marks)

B. The mass spectrum shows a peak at m/z = 43. Draw the displayed formulae of two fragment ions that might be responsible for this peak.

(06 marks)

II) The mass spectra of the two isomers of dichloroethane are shown.



A. Deduce the molecular formulae of the species responsible for the molecular ion peaks at m/z 98, 100 and 102. The molecular formulae for the species producing these peaks are the same in both spectra.

(06 marks)

B. State why in both spectra the peaks at 98, 100 and 102 have different relative intensities.

(02 marks)

C. Explain how the presence of the peaks at 83, 85 and 87 in spectrum B allo identification of the isomer responsible for this spectrum.

(04

b) ESR (Electron Spin Resonance) spectroscopy is a useful form of spectroscopy used to molecules or atoms with an unpaired electron.

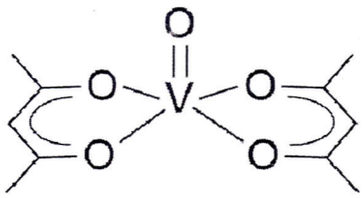
I) State what is meant by saturation in the ESR process.

(05 m

II) State the reason for the saturation in ESR process.

(02 m

III) Predict the ESR spectrum of vanadyl acetylacetonate, $VO(acac)_2$ using nec calculations. The structure of $VO(acac)_2$ is given below. (I = 7/2 for V)



(05

IV) State 03 applications of ESR spectroscopy.

(03 m

@@@@@@@@@@@@@@@

Degree of Unsatura

Degree of unsat
0
1
2
3
4

NMR correlatio

Approximate ^{1}H NM

Hydrogen
CH_3
CH_2
CH
C=C–CH_x
O=C–CH_x
Ph–CH_x
≡C–H
R_2N–CH_x
I–CH_x
Br–CH_x
Cl–CH_x
F–CH_x
O–CH_x
C=CH
Ar–H
O=CH
ROH
ArOH
RNH_x
$CONH_x$
RCOOH

in spectrum B allows th

(04 marks

troscopy used to study

(05 marks

(02 marks

ac)$_2$ using necessary

)

(05 arks

(03 marks

Degree of **Unsaturation**

Degree of unsaturation	Description
0	No unsaturated Carbon atoms
1	1-π bond or ring without unsaturated Carbon atoms
2	2-π bonds or ring with 1-π bond
3	3-π bonds or ring with 2-π bonds
4	A ring with 3-π bonds

NMR **correlation data**

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

IR Correlation data

Functional group	Frequency (cm^{-1})	Intensity
Water O-H stretch	3700-3100	Strong
Alcohol O-H stretch	3600-3200	Strong
Phenol	3350	Broad
O-H (hydrogen bonded)	3400-3000	Broad
O-H (non-hydrogen bonded)	3650-3600	Strong
Carboxylic acid O-H stretch	3600-2500	Strong, Very broad
N-H Amine	3500-3350	Weak spikes
N-H Amide	3400-3000	Medium
≡C-H stretch	~3300	Strong
=C-H stretch	3100-3000	Weak
-C-H stretch	2950-2840	Weak
-C-H Aldehyde stretch	2900-2800	Variable
C≡N stretch	~2250	Strong
C≡C stretch	2260-2100	Variable
C=O Aldehyde	1740-1720	Strong
C=O Anhydride	1840-1800, 1780-1740	Weak, Strong
C=O Ester	1750-1720	Strong
C=O Ketone	1745-1715	Strong
C=O Carboxylic acid	1730-1700	Strong
C=O Acid chloride	1810-1775	Strong
C=O Amide	1700-1500	Strong
C=C Alkene	1680-1600	Weak
C=C Aromatic	1600, 1475	2 Bands, Medium to Strong
CH_2 Bend	1480-1440	Medium
CH_3 Bend	1465-1440, 1390-1365	Medium
C-O Ether	1250-1050	Strong
C-O Alcohol	1260-1000	Strong
C-O Anhydride	1300-900	Multiple bands
C-O Carboxylic acid	1320-1210	Medium
C-O Ester	1300-1000	2 or more bands
N=O stretch	1600-1500 and 1400-1300	Strong, Medium
C-F stretch	1400-1000	Strong
C-Cl stretch	800-600	Strong
C-Br stretch	750-500	Strong
C-I stretch	~500	Strong