13/12/23

DOON UNIVERSITY, DEHRADUN

End-Semester Examination, First Semester, July 2023 – December 2023

Academic Year 2023–2024 (Odd Semester)

School of Physical Sciences, Department of Chemistry

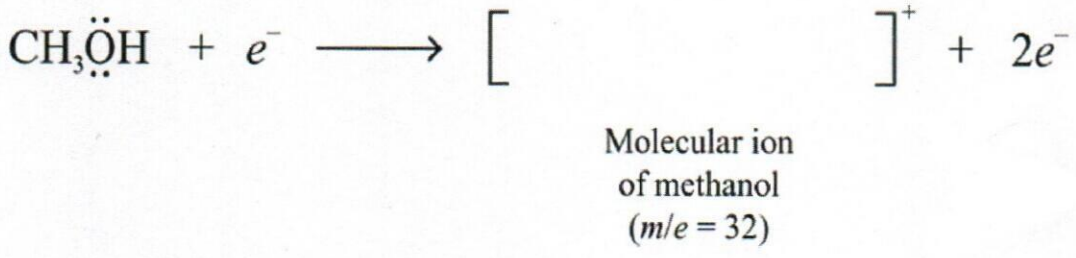
Programme Name: Undergraduate Certificate in Chemistry /Undergraduate Diploma in Chemistry /B.Sc. Hons. in Chemistry / B.Sc. Hons with Research in Chemistry

Course Code with Title: CYC-102; Organo-analytical Techniques.

***Time Allowed**: 1.5 Hours* ***Date**: 13th December 2023 (Wednesday)* ***Maximum Marks**: 30*

SECTION : A
(Very Short Answer Type Questions)

[1] When a molecule of methanol (CH_3OH) is bombarded with a beam of fast-moving electrons in the mass spectrometer, the following reaction will take place. Draw this reaction in your answer booklet, and write the correct structure of molecular ion inside the square bracket. [1]

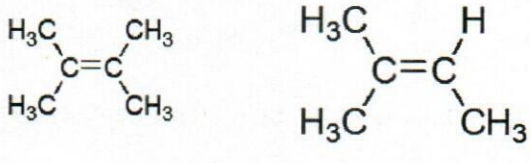


[2] Discuss the factors upon which the frequency of a given stretching vibration of a covalent bond is dependent. [1]

[3] (3.1) What kind of change occurs in the molecule after the absorption of a quantum of energy (hν) in IR radiation? [½]

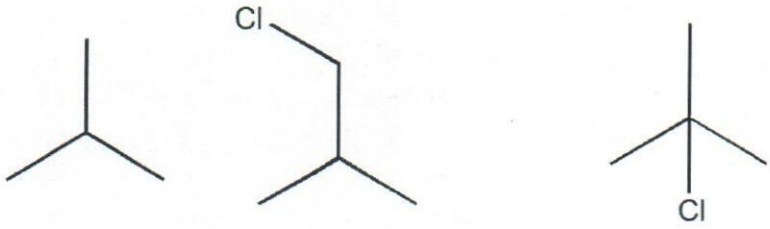
(3.2) Discuss the different types of regions in an IR spectrum. [½]

[4] How many sets of chemically equivalent protons are available in the following molecules.

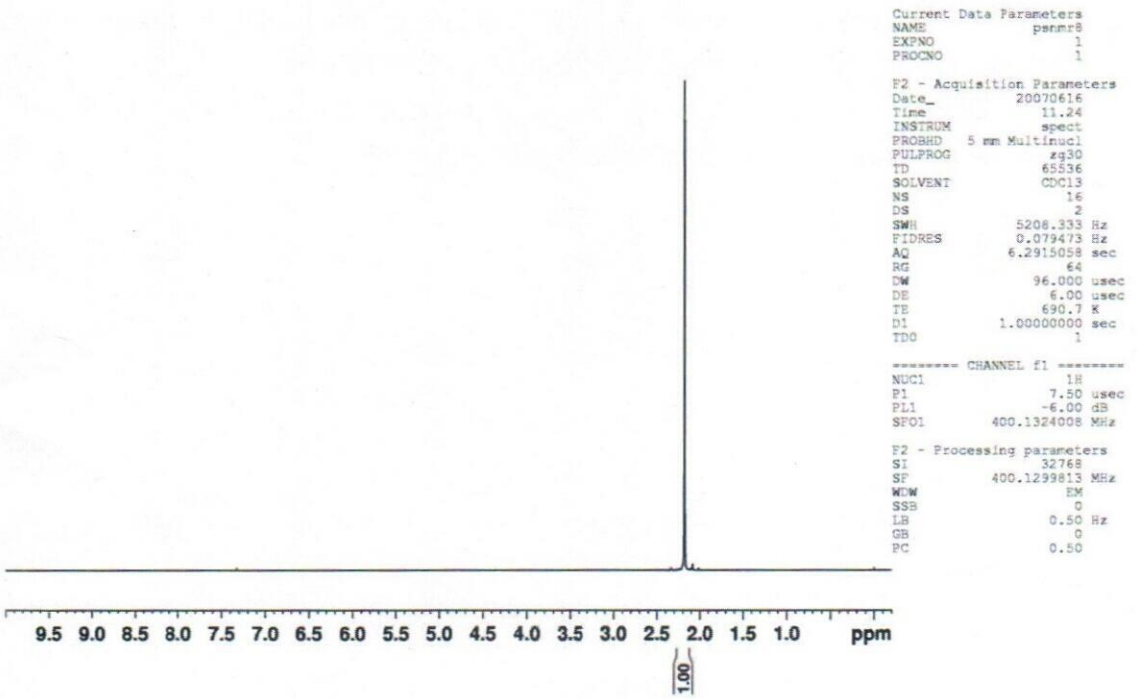


[5] (5.1) How many protons are available in following molecules. [½]

(5.2) How many sets of chemically equivalent protons are available, and how many signals will appear in ^{1}H-NMR Spectrum of the compounds? [½]



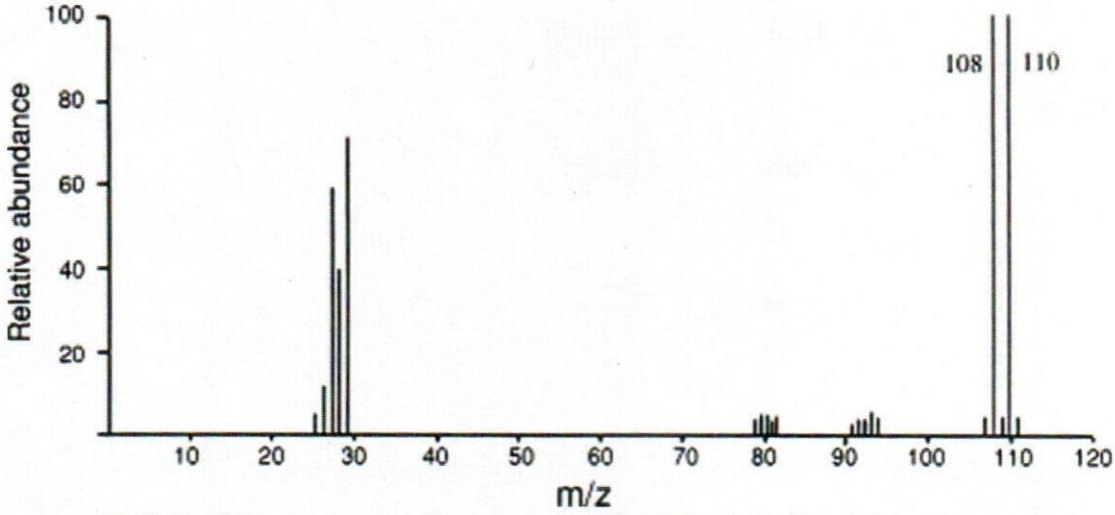
[6] Acetone gives following ^{1}H NMR spectrum. Why does it contain only one signal. [1]



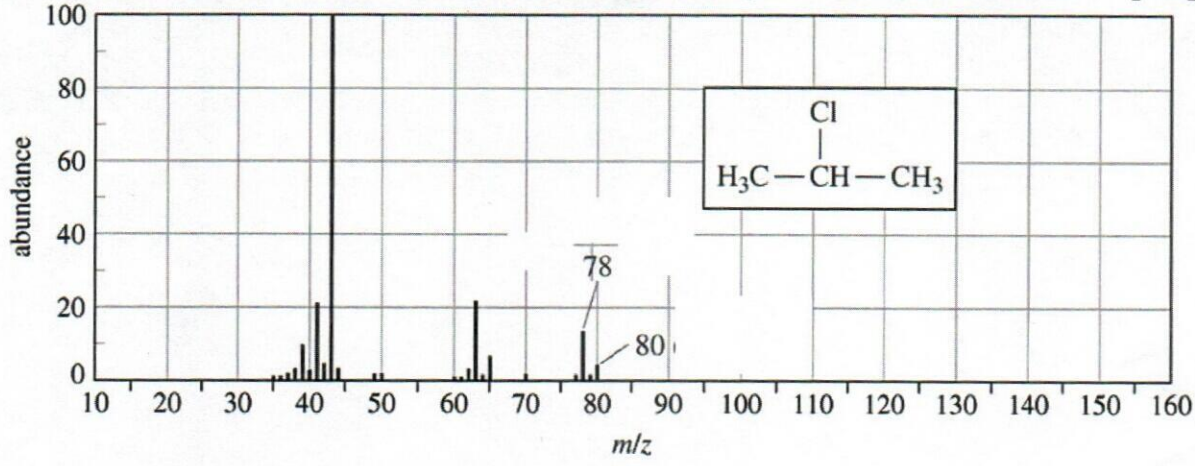
SECTION : B
(Short Answer Type Questions)

[7] Discuss all types of vibrations which can take place in bond upon irradiation by IR. [3]

[8] (8.1) The following is the mass spectrum of bromoethane (C_2H_5Br). Interpret the peaks at 108 and 110. [1.5]



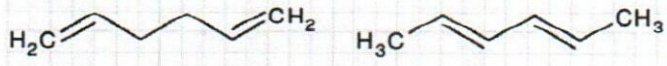
(8.2) 2-Chloropropane (Isopropyl chloride) gives the following mass spectrum. Identify the molecular ion peak. Interpret the peaks at m/z 78 and 80. [1.5]



[9] (9.1) Discuss the reason for the difference in the following: [1]

1,5 - hexadiene has λ_{max} = 178 nm

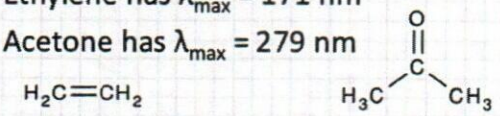
2,4 - hexadiene has λ_{max} = 227 nm



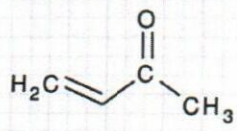
(9.2) Discuss the reason for the difference in the following: [1]

Ethylene has λ_{max} = 171 nm

Acetone has λ_{max} = 279 nm



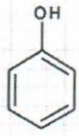
Crotonaldehyde has λ_{max} = 290 nm



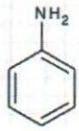
(9.3) Discuss the reason for the difference in the following: [1]

Benzene λ_{max} = 255 nm

Phenol λ_{max} = 270 nm



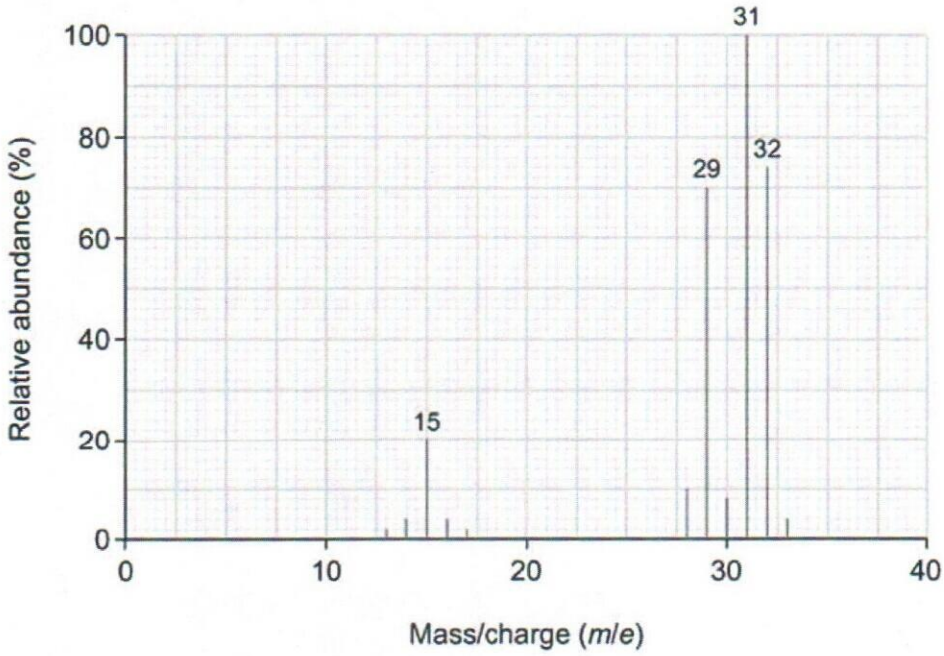
Aniline λ_{max} = 280 nm



[10] Discuss Mc Lafferty Rearrangement with suitable example. [3]

SECTION : C
(Long Answer Type Questions)

[11] The mass spectrum of methanol molecule is shown below. Draw it in your answer booklet.

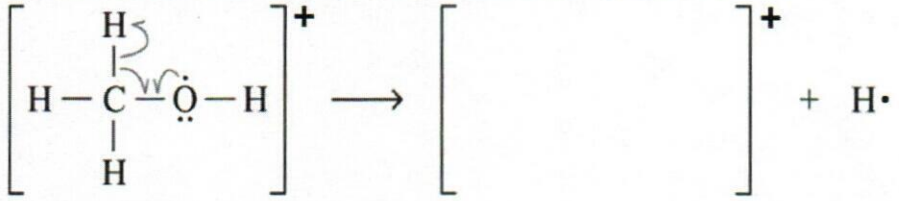


(11.1) Identify the *molecular ion peak*, *base peak* and *fragment ion peaks* in the spectrum. What is the percentage of the intensity of the *base beak*? How is this intensity given this value? [1]

(11.2) Identify the ions which give peaks at 32, 31, 29 and 15. Mention such ions the below given table: [1]

m/e ratio	Corresponding ion
32	
31	
29	
15	

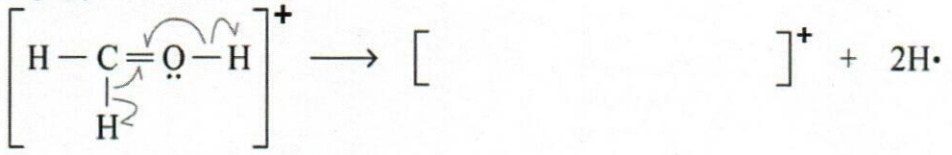
(11.3) The peak at *m/e* 31 corresponds to a particular ion which is formed due to the loss of one hydrogen atom from the molecular ion in the following manner. Write the structure of the ion inside the square bracket. [1]



m/e = 32 *m/e* = 31

(11.4) Why is the ion which gives peak at *m/e* 31 very much stable? Describe the reasons behind high stability of this ion? [1]

(11.5) Mention the structure of the ion (which gives peak at *m/e* 29) in the following square bracket. [½]

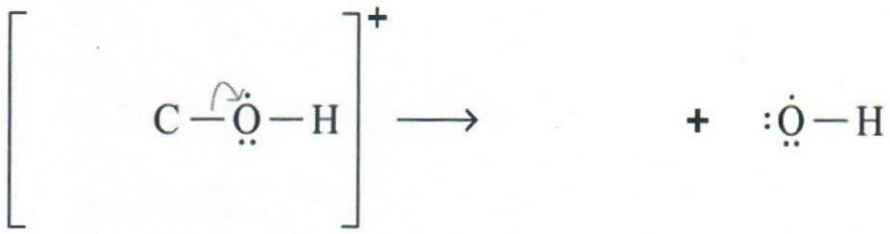


m/e = 31 *m/e* = 29

(11.6) The ion (which gives peak at *m/e* 29) in the mass spectrum of methanol has a good stability. Write justification and also correct structures of both structures in the following image to justify your answer. [½]

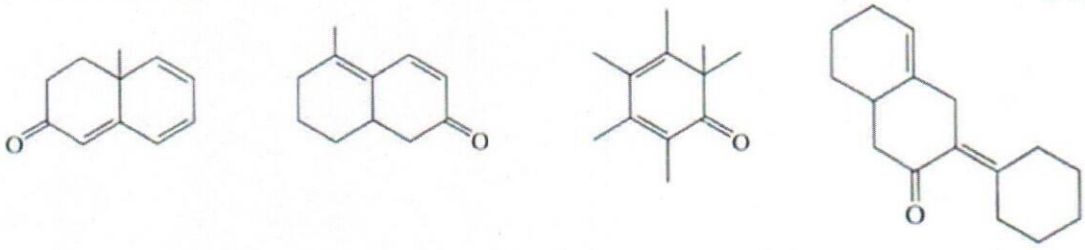
m/e = 29

(11.7) Complete the following to suggest the formation of the ion or carbocation (which gives peak at *m/e* 15) in the mass spectrum of methanol. Write the correct structures in the following image to justify your answer. [1]



$m/e = 32$ Carbocation $m/e = 15$

[12] Experimentally observed values of λ_{max} of the compounds, shown below, are 305, 349 and 360 nm. Correlate these three values with the compounds. Use the Woodward-Fieser rules and estimate value of λ_{max} for following molecules systematically. Identify the presence of the following components in the molecules and add the values for those components which are present in each molecule: [6]



(1) For Parent α,β-Unsaturated Carbonyl compound

For acyclic, six membered, or larger ring ketone		= .....
OR		
For five membered ring ketone		= .....
OR		
For aldehyde molecules		= .....
OR		
For acid molecules or ester molecules		= .....
(2) α-substituents	@.....**each**	= .....
(3) β-substituents	@.....**each**	= .....
(4) γ, δ, etc. substituents	@.....**each**	= .....
(5) Extra Conjugation	@ .....**each**	= .....
(6) Homoannular Diene (i.e. Frozen s-cis)	@ ..... **each**	= .....
(7) Polar - OH group at α-position	@ ..... **each**	= .....
(8) Polar - OH group at β -position	@ ..... **each**	= .....
(9) Polar - OH group at δ-position	@ ..... **each**	= .....
(10) Polar - O- Ac group at α, β or δ carbon	@ ..... each	= .....
(11) Polar - OR group at α-position	@ ..... **each**	= .....
(12) Polar - OR group at β-position	@ ..... **each**	= .....
(13) Polar - OR group at γ-position	@ ..... **each**	= .....
(14) Polar - OR group at δ-position	@ ..... **each**	= .....
(15) Polar - SR group	@ .....each	= .....
(16) Polar - Cl group at α-position	@ ..... **each**	= .....
(17) Polar - Cl group at β position	@ ..... **each**	= .....
(18) Polar - Br group at α-position	@ ..... each	= .....
(19) Polar - Br group at β position	@ ..... each	= .....
(20) Polar —NR2 at β-position	@ ..... **each**	= .....
Lamda (max)		=