



TECHNICAL UNIVERSITY OF MOMBASA

FACULTY OF APPLIED AND HEALTH SCIENCES

DEPARTMENT OF PURE & APPLIED SCIENCES

UNIVERSITY EXAMINATION FOR:

BACHELOR OF TECHNOLOGY IN APPLIED CHEMISTRY

ACH 4315: ORGANIC SPECTROSCOPY

END OF SEMESTER EXAMINATION

SERIES: DECEMBER Pick year

TIME: 2 HOURS

DATE: Pick Date Jul 2017

Instructions to Candidates

You should have the following for this examination

-Answer Booklet, examination pass and student ID

This paper consists of **FIVE** questions. Attempt question ONE (Compulsory) and any other TWO questions.

Do not write on the question paper.

Question ONE

(a) State the weaknesses of the following organic spectroscopy techniques in structural elucidation of organic molecules: [3 marks]

- i. UV
- ii. NMR
- iii. MS

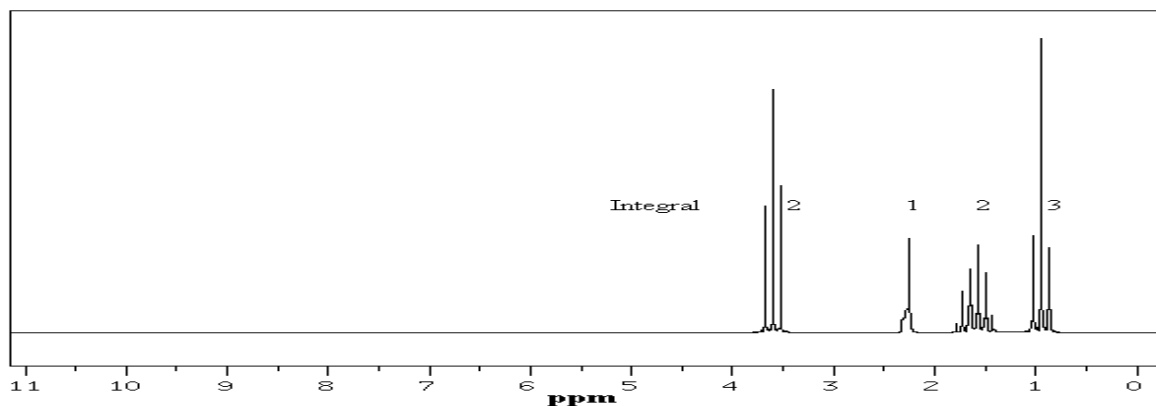
(b) Account for the following observations in NMR spectroscopy:

- i. The proton nuclei in different compounds behave differently in the NMR experiment resulting in to different chemical shift values. [2 marks]
- ii. The hydroxyl proton of carboxylic acids displays a resonance signal significantly down-field of other functions. [2 marks]
- iii. ^{13}C -NMR requires higher sample concentration than ^1H – NMR spectroscopy. [1 mark]

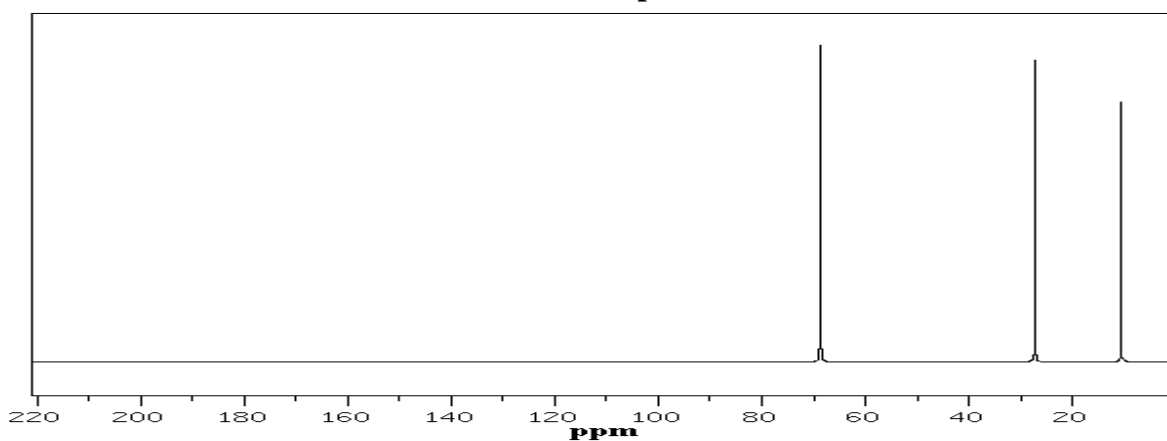
(c) Draw the patterns of the signals observed in each of the following spin multiplicities in ^1H -NMR spectroscopy. [4 marks]

- i. Doublet
- ii. Triplet
- iii. Quartet
- iv. quintet

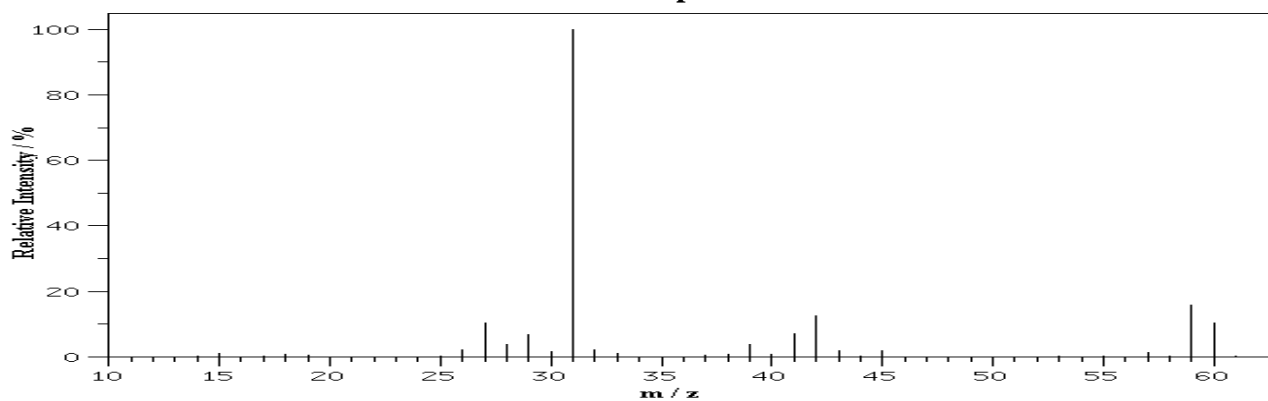
(d) An organic compound with molecular formula C_3H_8O registered a characteristic strong and broad IR absorption peak at 3350 cm^{-1} as well as a strong sharp peak at 1075 cm^{-1} . The molecule displays the following NMR and MS spectra:



$^1\text{H-NMR}$ Spectra



$^{13}\text{C-NMR}$ Spectra



MS Spectrum

- i. Determine the double bond equivalence of the molecule and state the possible functional group in the molecule. [2 marks]

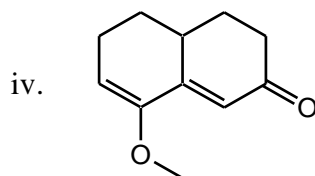
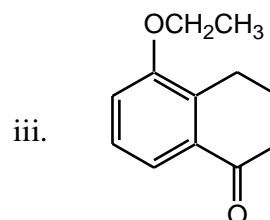
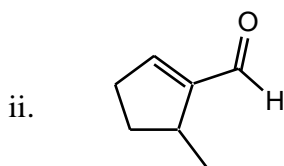
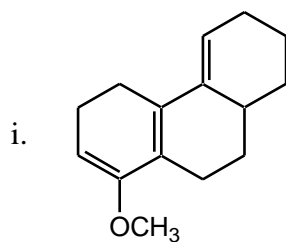
- ii. From the spectral data given in the figures above, work out the structure of compound. Clearly outline the pieces of information obtained from the ^1H NMR, ^{13}C NMR and MS spectra that leads to the suggested structure. [12 marks]
- iii. Make use of curly arrows to account for the fragment registered as the base peak ion. [4 marks]

Question TWO

(a) Define the following terms as applied in UV Spectroscopy. [4 marks]

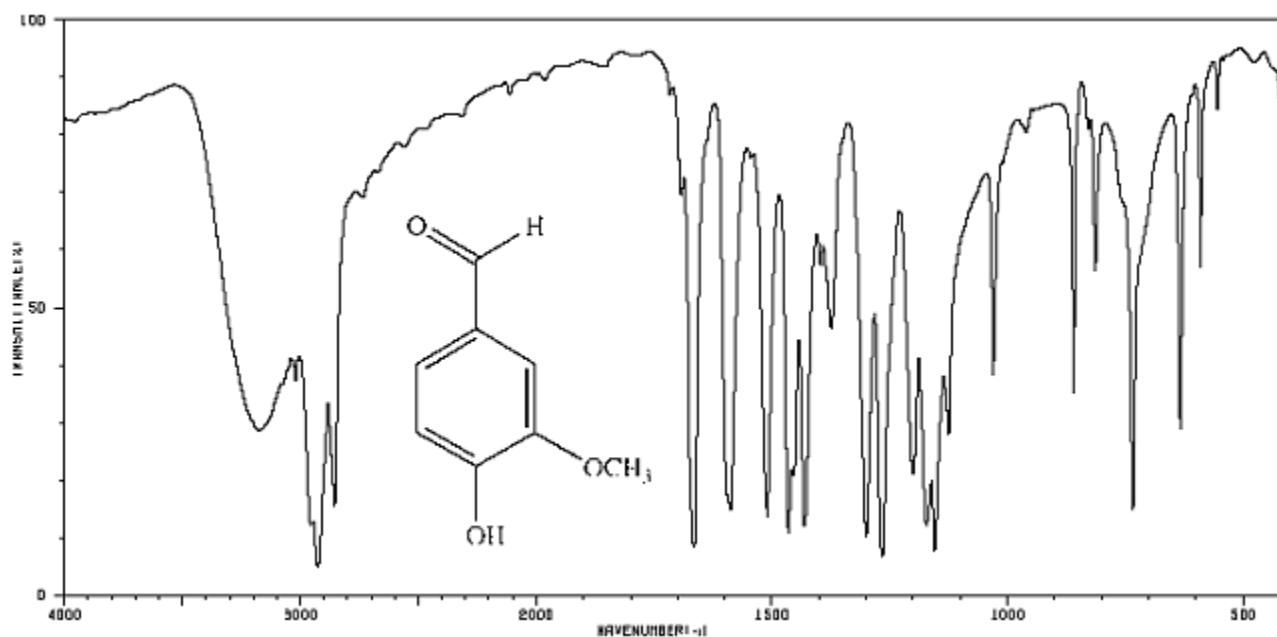
- i. Auxochrome
- ii. Red shift
- iii. Hypochromic effect
- iv. Blue shift

(b) Calculate the expected UV absorption λ_{max} for the following compounds in ethanol by applying Woodward-Fieser and Scott's rules: [16 Marks]



Question THREE

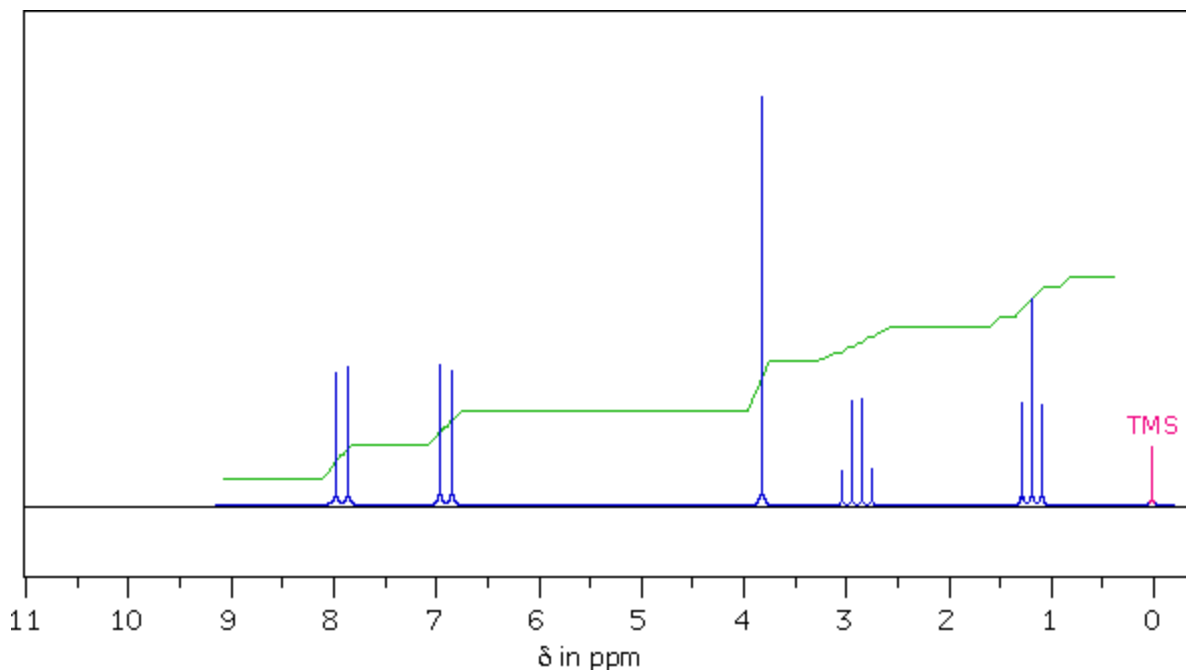
- (a) State three limitations of IR spectroscopy in structural elucidation of organic molecules. [3 marks]
- (b) Explain how the following factors influence the vibrational frequencies in IR spectroscopy. [4 marks]
- Hydrogen bonding
 - Hybridization of carbon atom
- (c) The following is IR spectrum for Vanillin obtained from a solution of the compound in nujol which is a liquid mixture of high molecular-weight alkanes.



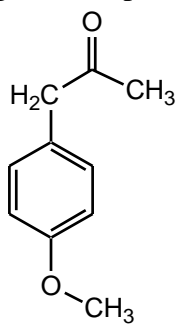
- Trace the structure of Vanillin and label all the functional groups in the molecule. [3 marks]
- Which absorbances in the range 4000-1400 cm⁻¹ of IR spectrum correspond to nujol, and which to vanillin? Indicate which bond vibration is responsible for each identified absorbance. [10 marks]

Question FOUR

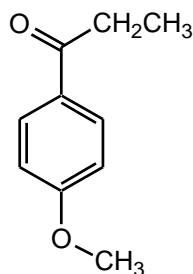
- (a) The following is a ¹H-NMR spectrum obtained on a 90 MHz spectrometer of a compound with a molecular formula C₁₀H₁₂O₂.



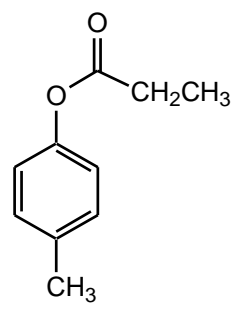
- i. Ignoring the TMS signal at $\delta = 0$, how many discrete groups of proton signals are present in this spectrum? [1 mark]
- ii. State the chemical shift values and spin multiplicity of all the discrete groups identified in i. above. [5 marks]
- iii. Using the integrator trace and the formula of the sample, assign the number of protons responsible for each signal in the spectrum. [3 marks]
- iv. In units of Hertz (Hz) how far is each signal from the TMS signal? [5 marks]
- v. From multiplet line separations (Js), which of the signals are coupled to each other? [2 marks]
- vi. Three structural formulas of some possible candidates for this compound are presented below. After reviewing the chemical shifts, coupling patterns and integration values shown in this spectrum, select the structure most likely to give this spectrum. [2 marks]



A



B



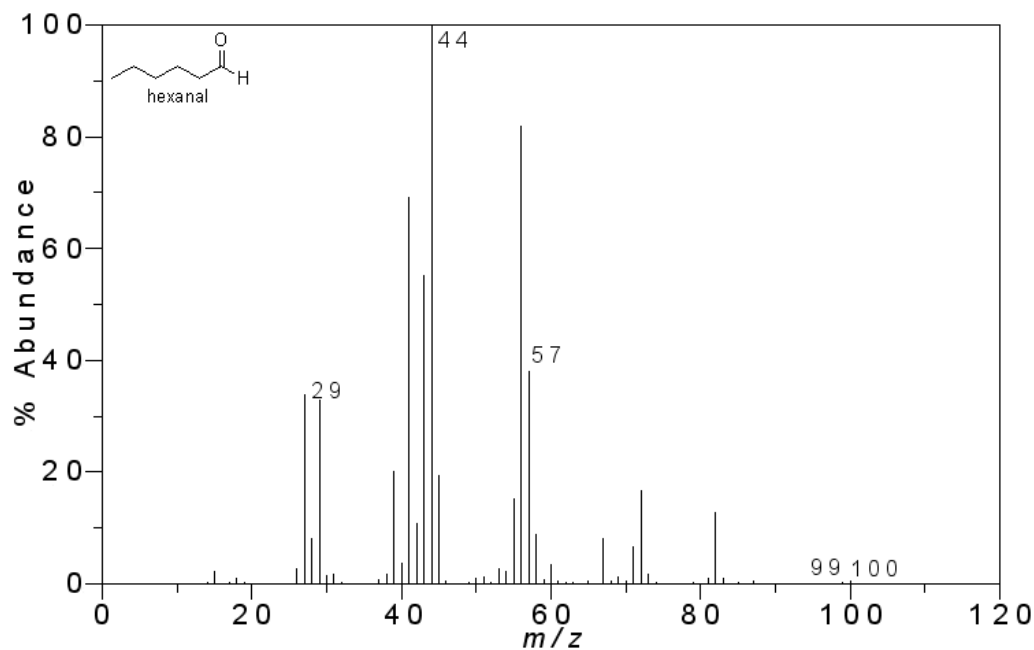
C

Question FIVE

(a) State four major components of a mass spectrometer and outline their functions.

[6 marks]

(b) The complete mass spectrum of hexanal is given in the figure below.



- Provide molecular formula of hexanal and determine its molecular mass. [2 marks]
- Make use of curly arrows to provide a scheme detailing the important α - and β -cleavage patterns as well as the McLafferty rearrangement to account for the registered m/z peaks in the mass spectrum of hexanal. [12 marks]