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MAIN EXAMINATION

JANUARY – APRIL 2019 TRIMESTER

FACULTY OF SCIENCE

DEPARTMENT OF NATURAL SCIENCE (CHEMISTRY)

REGULAR PROGRAMME

CHEM 305: ORGANIC SPECTROSCOPY

Date: APRIL 2019	**Duration: 2 Hours**
INSTRUCTIONS: Answer Question ONE and ANY OTHER TWO Questions	

Q1. a) Explain the following terms as used in the study of organic spectroscopy. Use appropriate examples. **(5 Marks)**

i) Chromophores
ii) IR stretches and bends
iii) Chemical shift
iv) Molecular ion

b) i) Explain the working principle of a UVvis spectrophotometer **(3 marks)**

ii) Given that, the correlations of conjugated diene according to Woodward-Feiser rules are as follows:

i) Base value for homoannular diene = 253 nm
ii) Base value for heteroannular diene = 214 nm
iii) Alkyl substituent or Ring residue attached to the parent diene = 5 nm
iv) Double bond extending conjugation = 30 nm
v) Exocyclic double bonds = 5 nm
vi) Polar groups: -OAc = 0 nm
-OAlkyl = 6 nm
-Cl, -Br = 5 nm

Calculate the absorption maximum for 1-methylcyclohexa-1,3-diene . **(2 marks)**

c) i) A sample of an organic compound with a mass of 1.224 g was completely burned in oxygen and found to produce 2.340 g of Carbon (IV) Oxide and 1.433 g of water only. The molecular mass of the compound was 46.0 a.m.u.

i) Calculate the empirical and molecular formula of the organic compound. **(3 marks)**

ii) Propose possible functional isomers of the compound. **(2 marks)**

ii) Consider the mass spectrum of benzoic acid **(Figure 1)** and identify the ions responsible for the major peaks. **(2 marks)**

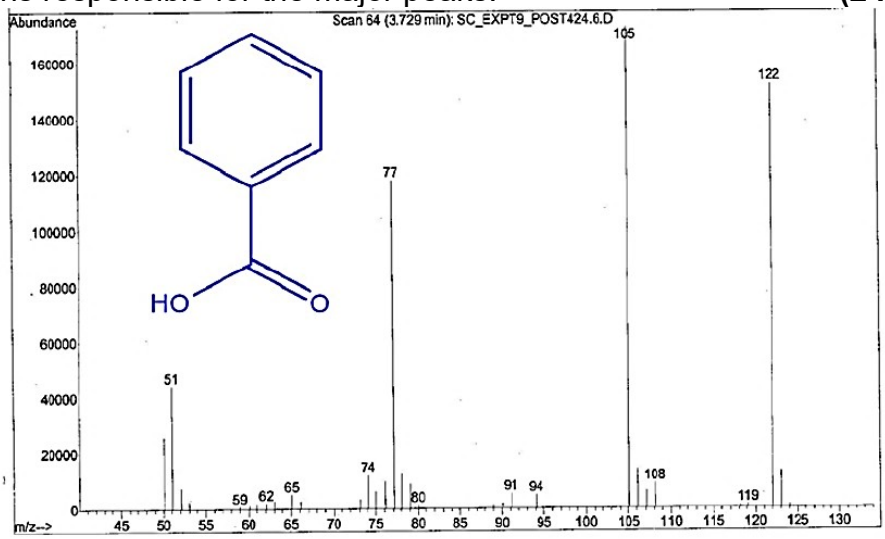


Figure 1

d) The IR spectra in **Figure 2 and 3** are of ethanol and ethanoic acid. Draw the full structural formula for both compounds, and then determine giving reasons, which spectrum is due to which compound. **(4 marks)**

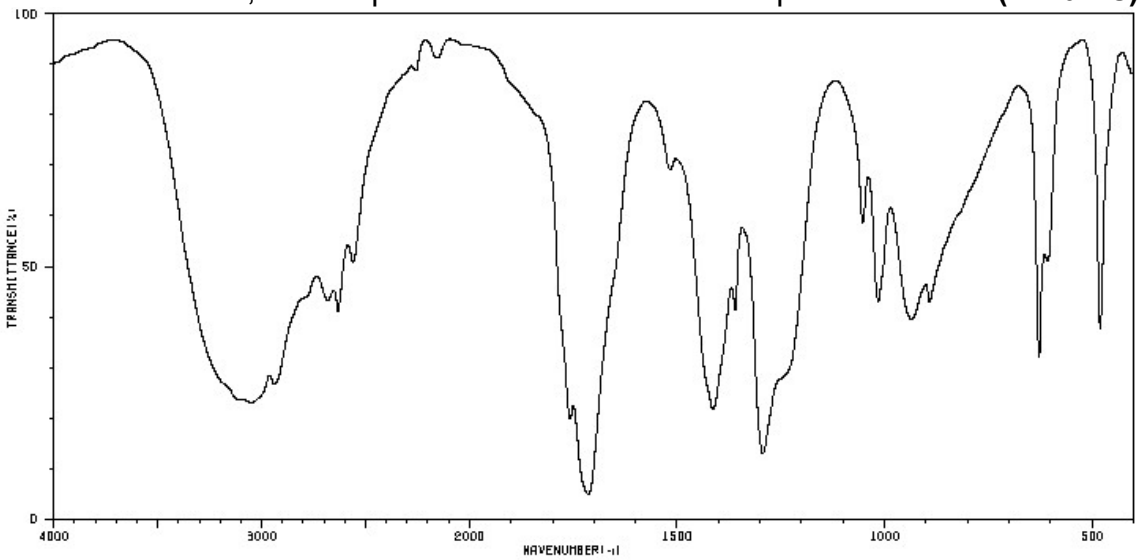


Figure 2

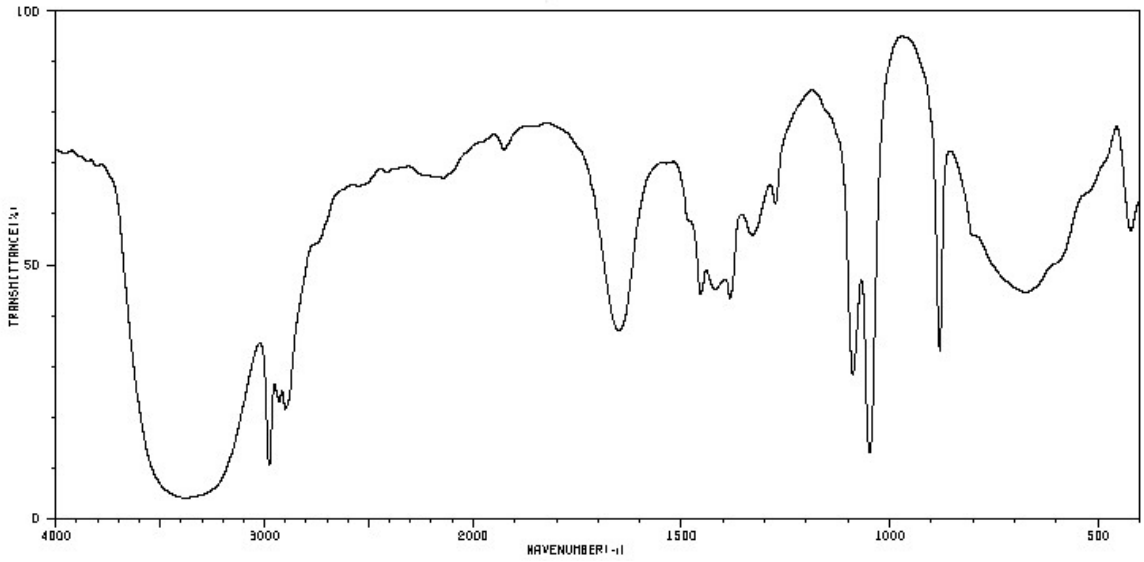


Figure 3

e) Predict the multiplicities of the signals in the proton NMR spectra of the following compounds. **(5 Marks)**

i) $CH_3CH(Cl)CH_2CH_2Cl$

ii) $CH_3CO_2CH(CH_3)CH_2CH_3$

f) The following is data from IR **(Figure 4a)** and ^1H NMR spectra (300 MHz) **(Figure 4b)** of a compound A. The molecular formula of compound A is $C_4H_8O_2$ and it contains one unsaturation. **(4 marks)**

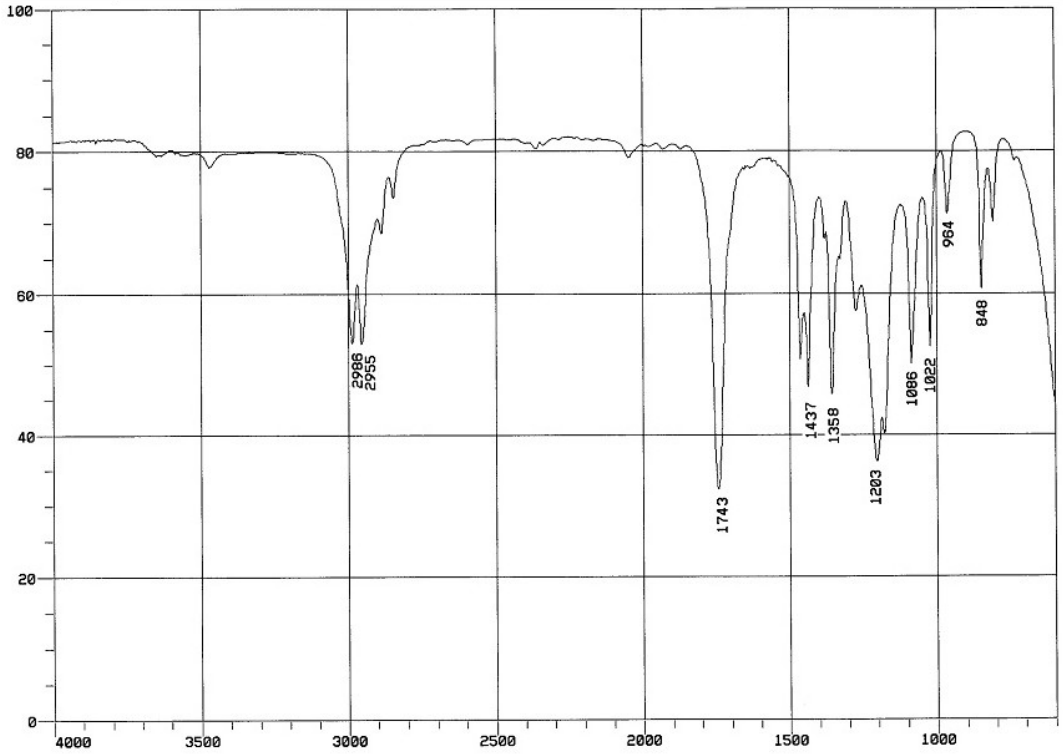


Figure 4a

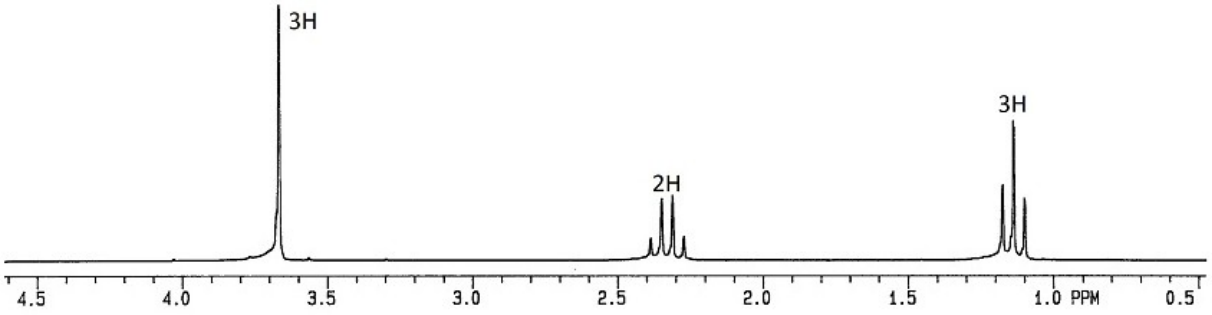


Figure 4b

Q2. a) The spectra provided below **(Figure 5 a – d)** were obtained when a molecule was analyzed. Use the spectra to provide a structure that is consistent with the data. (Give your reasoning). **(10 marks)**

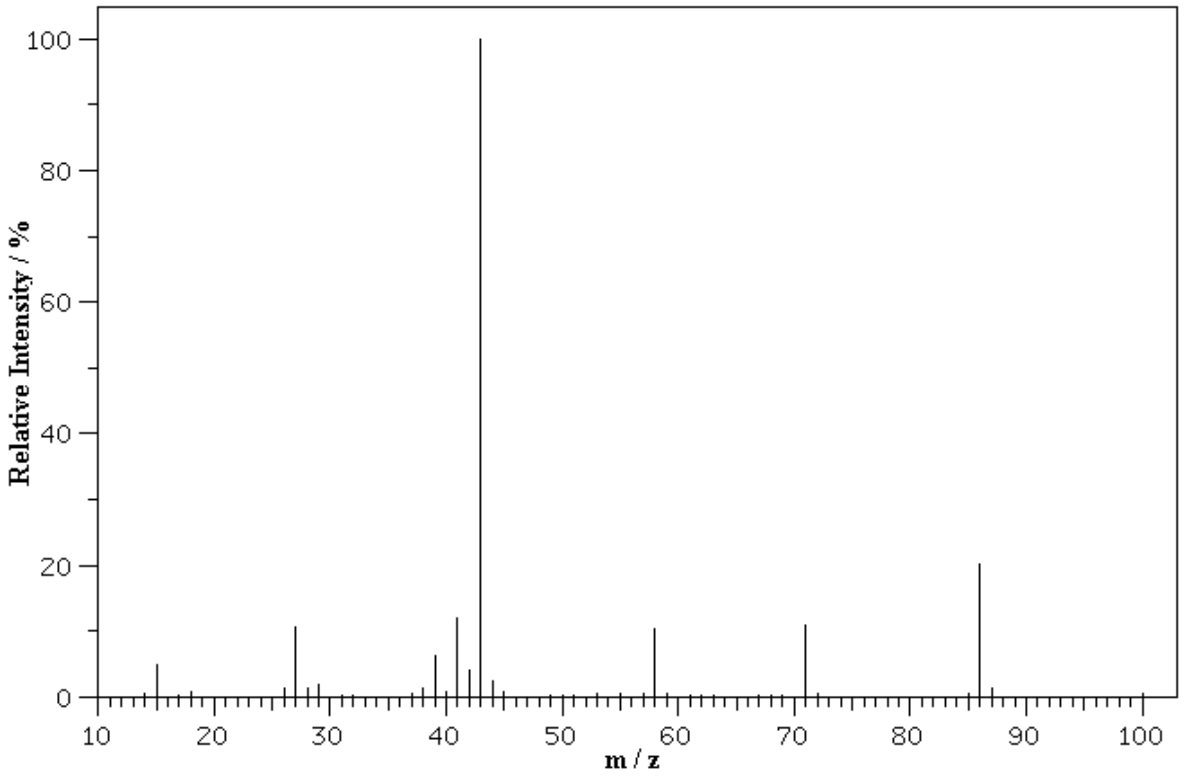


Figure 5a

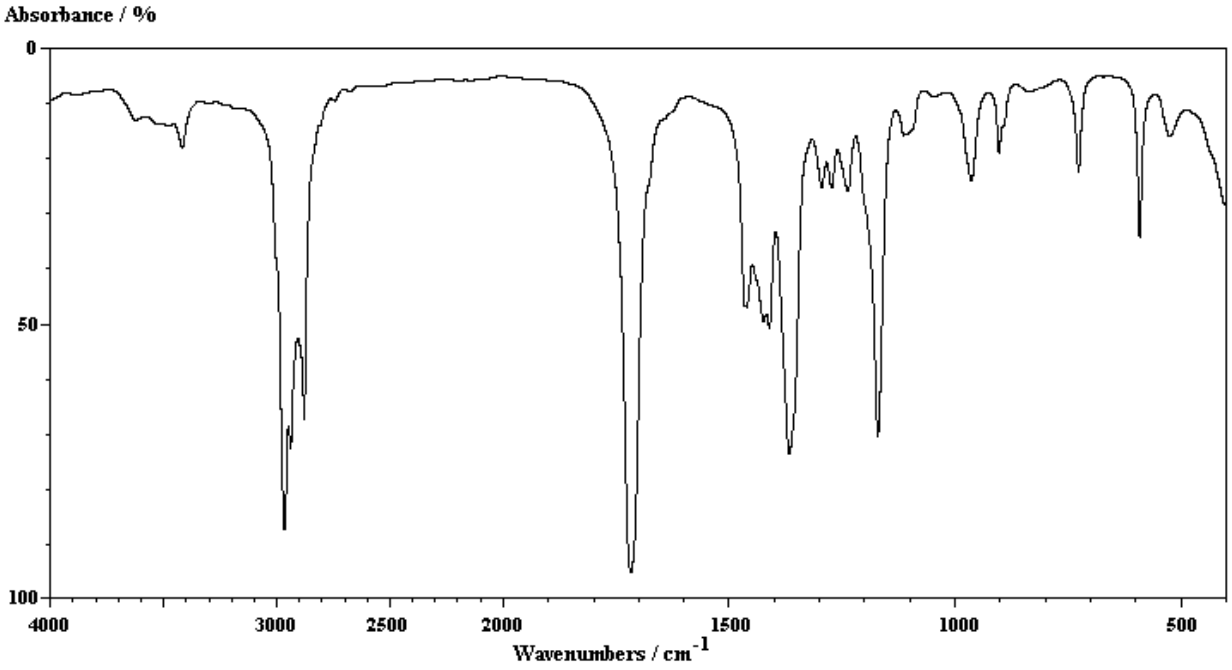


Figure 5b

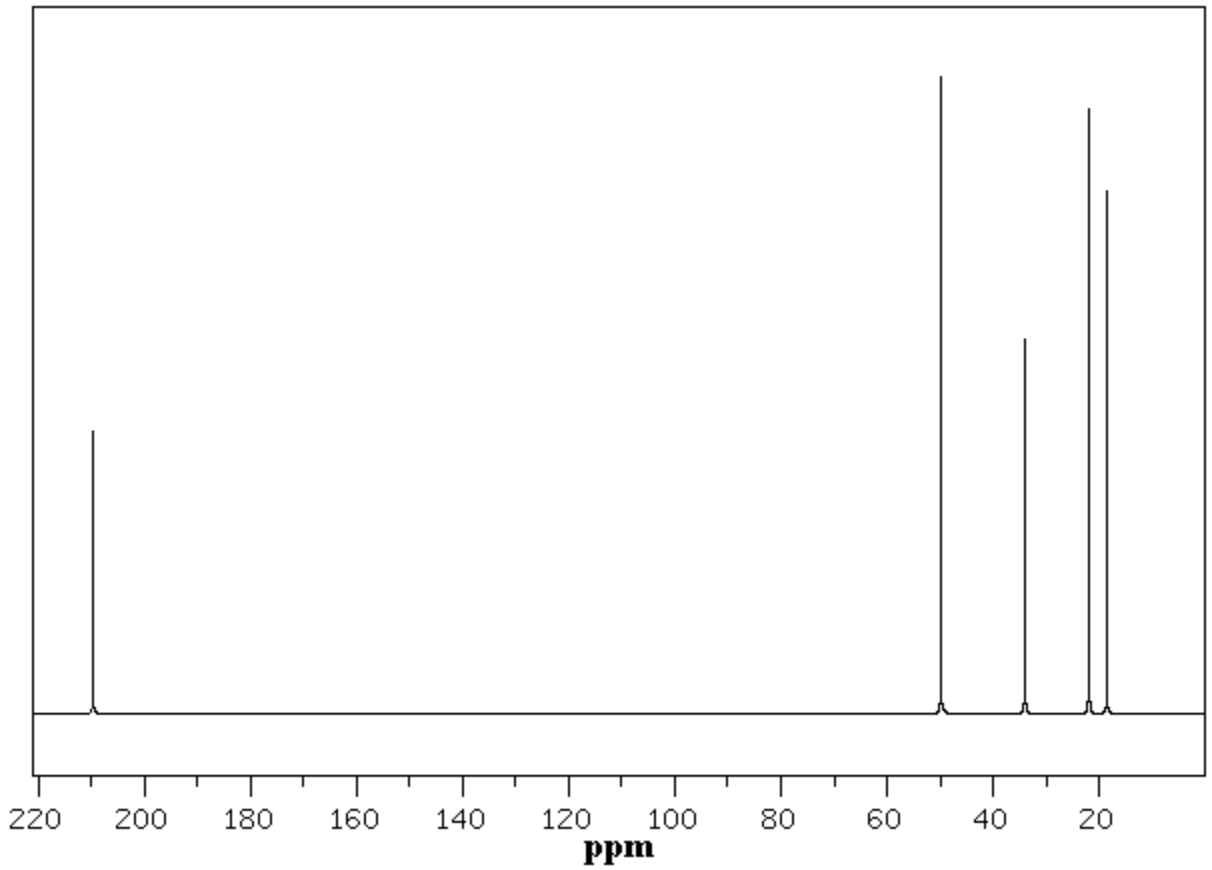


Figure 5c

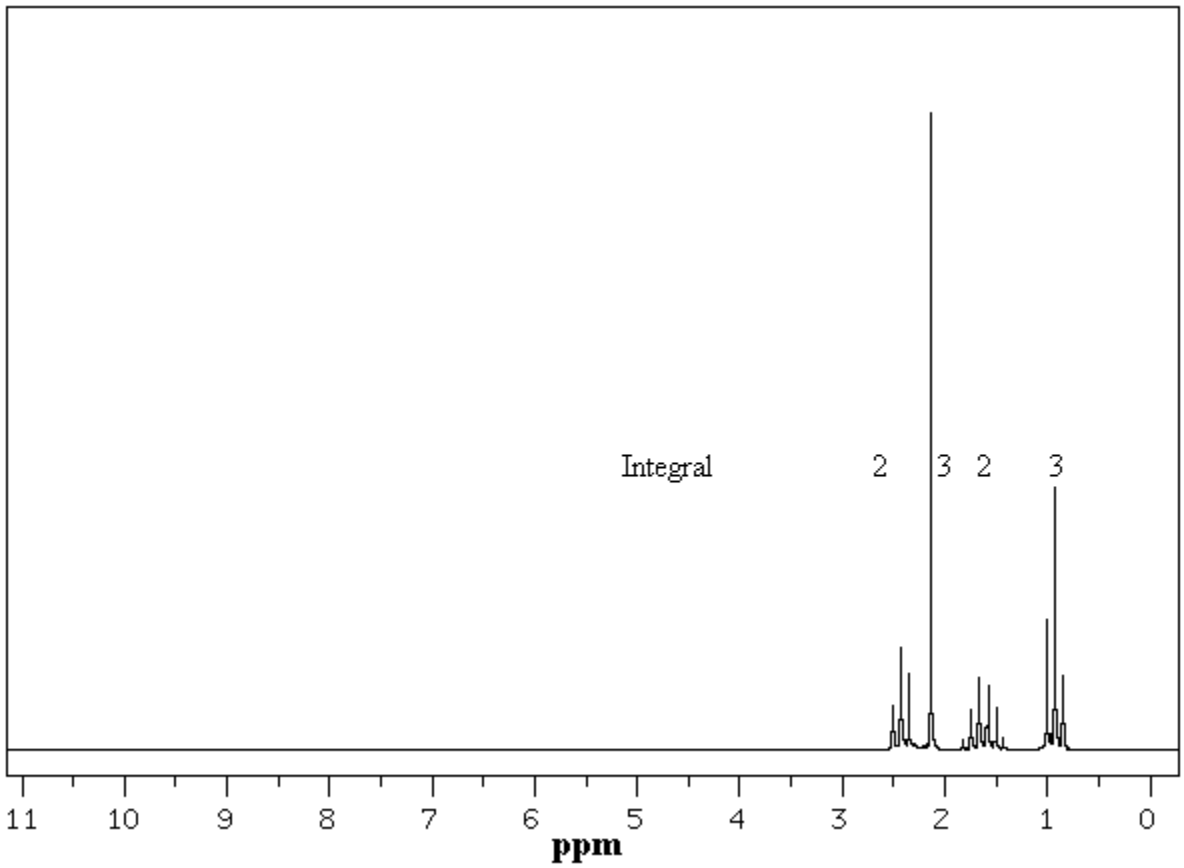


Figure 5d

b) Give structure(s) consistent with each of the following sets of NMR data:

i) M.F. $C_9H_{11}Br$
^1H NMR: δ 2.15 (2H quintet), δ 2.75 (2H, singlet), 3.38 (2H, triplet) and δ 7.22 (5H, singlet) (Hint 5H singlet represent protons on benzene ring)
^{13}C NMR: 128.0, 138.8. 34.2, 36.2, 32.5 **(5 marks)**

ii) M.F. C_6H_{10}
^1H NMR: δ 7.2 (4H, singlet), δ 2.91 (4H, triplet), and δ 2.04 1H quintet
^{13}C NMR: 128.0, 125.9, 138.8. 34.2, 36.2, 25.2 **(5 marks)**

Q3. a). The most intense peak in the mass spectrum of 2,2-dimethylbutene occur at m/z 29 and 86. Account for the peaks and show the carbocations associated with the peaks **(4 Marks)**

b). i) Two isomeric compounds J and K with the same molecular formula $C_6H_{12}O_2$ have the following NMR peaks.
J: ^1H NMR : δ 1.44 (9H, singlet) and 1.95 (3H, singlet)

^{13}C NMR: δ 19.5, 212.8, 49.8 and 22.7

K: ^{1}H NMR : δ 1.01 (6H, singlet), 2.15(1H multiplet), 2.52 (1H, multiplet) and 11.0 1H singlet)
^{13}C NMR: δ 12.2, 19.5, 27.8, 49.8 and 179.5

Compounds J and K have IR peaks at 1715 – 1750 cm^{-1}.Compound K has a very strong and broad band covering a wide range between 2800 and 3500 cm^{-1}

I. Draw all the possible functional isomers for the compound with molecular formula $C_6H_{12}O_2$ **(4 marks)**

II. Suggest the structures of J and K. Show your reasoning. **(6 marks)**

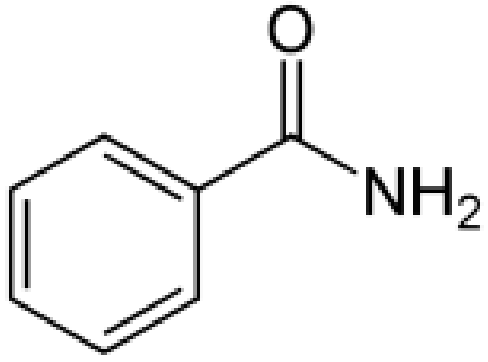
c) Explain the working principle of (i) IR (ii). UV-Vis spectroscopy. **(6 marks)**

Q4. a) Listed below are some spectra and molecular formulae of some organic molecules. Propose with reasons, a structure that is consistent with each set of data.

i) MF: C_4H_8O; IR: 1720 cm^{-1}, ^{1}H NMR δ 1.05 (3H, t), 2.13 (3H,s) and 2.49 (3H, t)^{13}C NMR: δ24.5, 207.1, 36.1 and 7.3 **(5 marks)**

ii) MF: C_7H_8O; IR: 3550 - 3200 cm^{-1}, ^{1}H NMR δ 2.43 (1H, s), 4.58 (2H,s) and 7.28 (5H,m) ^{13}C NMR: δ 128.7, 140.8, and 68.5 **(5 marks)**

b) Predict the main IR absorption peaks one would expect in the spectrum of benzamide. **(5 marks)**



Benzamide

c) Predict the ^{13}C and ^{1}H NMR peaks that one would expect in the spectrum of benzamide. Show your reasoning. **(5 marks)**

Q4. a) The spectra provided below (Figure 6 a- d) were obtained when a molecules C_7H_8O was analyzed. Use the spectra to identify the molecule (Give your reasoning).Hint: the compound is aromatic. **(10 marks)**

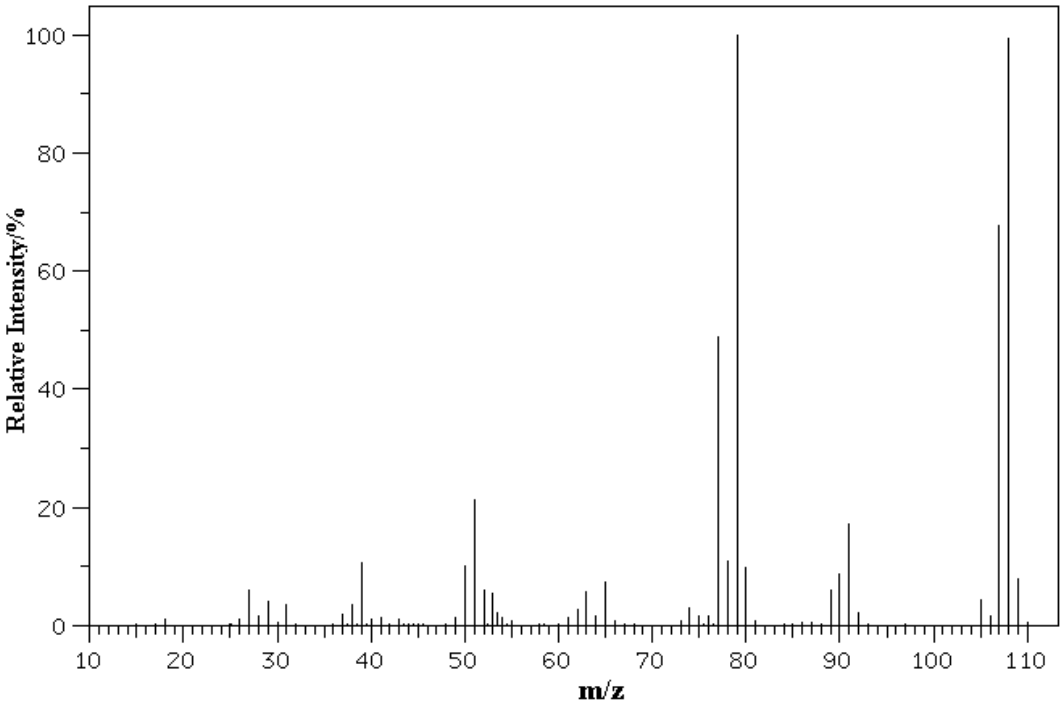


Figure 6a

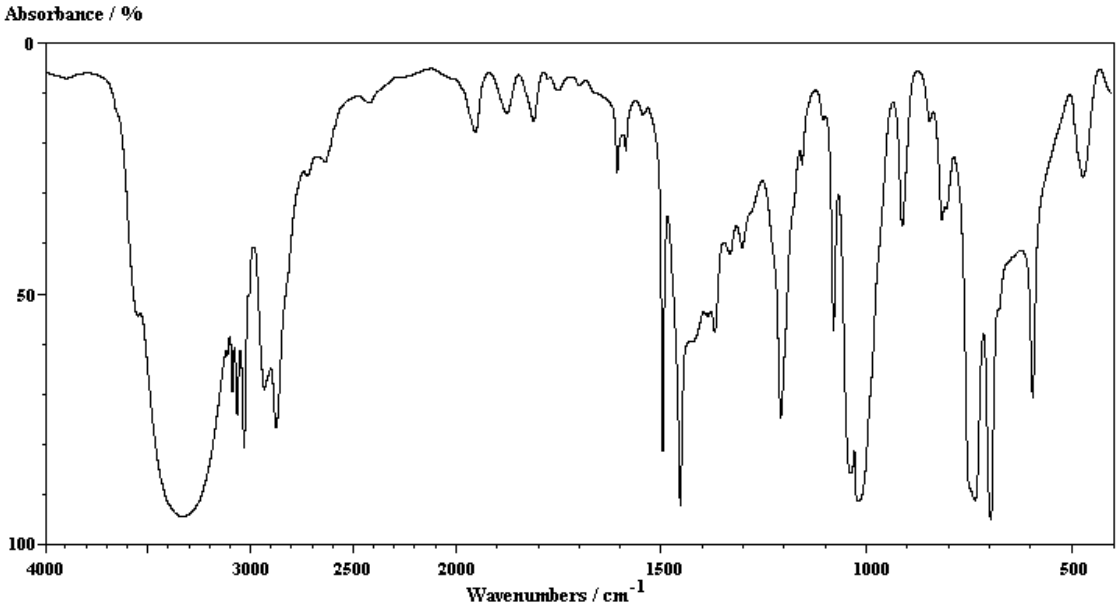


Figure 6b

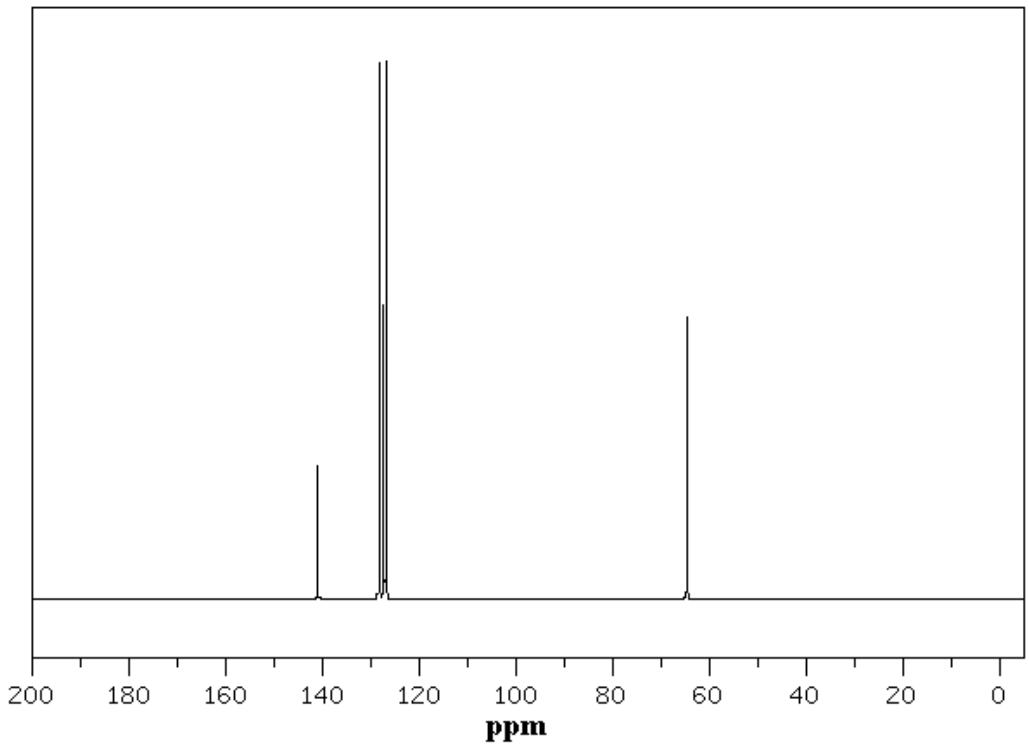


Figure 6c

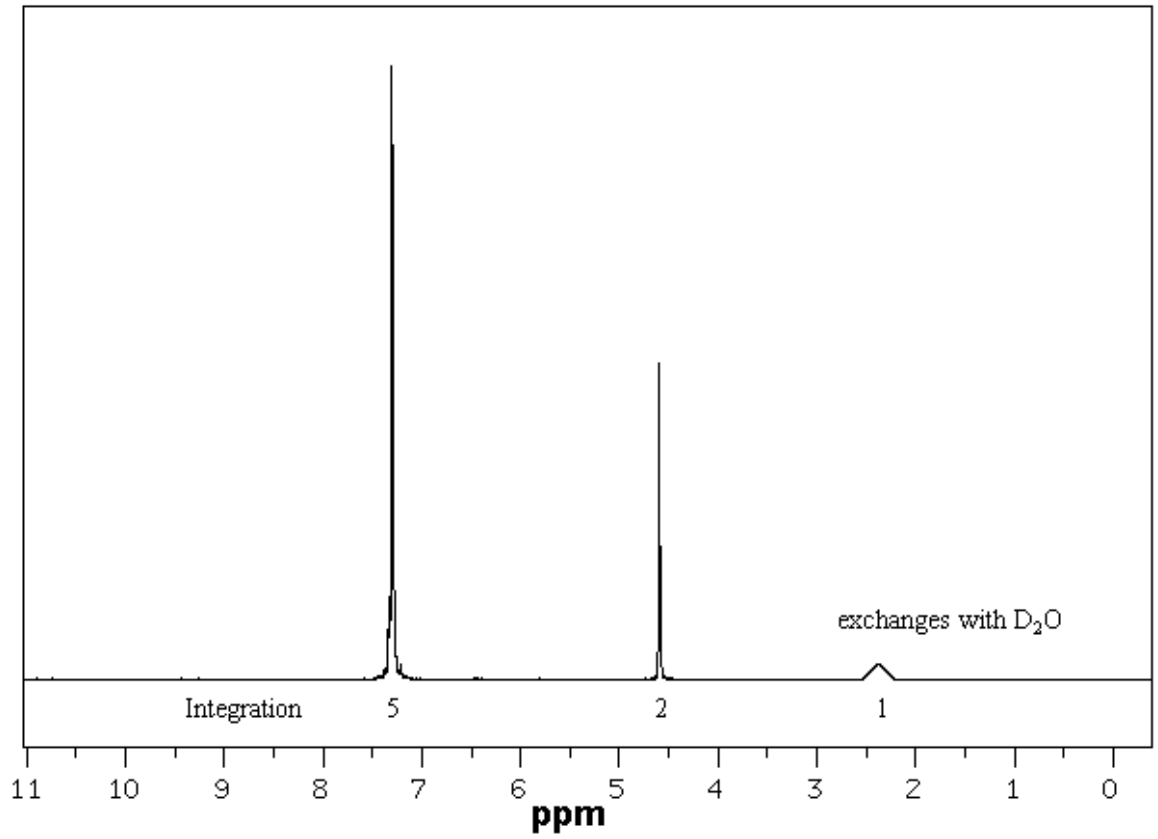


Figure 6d

b) i) Draw block diagrams of a Mass Spectrophotometer (MS). **(3 marks)**

ii) Explain the function of each part of the MS and explain how it is used to obtain spectra **(6 marks)**

END