# MACHAKOS UNIVERSITY

**University Examinations 2020/2021 Academic Year**

**SCHOOL OF PURE AND APPLIED SCIENCES**

**DEPARTMENT OF PHYSICAL SCIENCES**

**FOURTH YEAR FIRST SEMESTER EXAMINATION FOR**

**BACHELOR OF EDUCATION (SPECIAL NEEDS)**

**BACHELOR EDUCATION (SCIENCE)**

**SCH 404: INSTRUMENTAL METHODS**

**DATE: 18/8/2021** **TIME: 8.30-10.30 AM**

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**INSTRUCTIONS:**

- The paper consists of **two** sections.
- Section **A** is **compulsory** (30 marks).
- Answer any **two** questions from section **B** (each 20 marks).

**Useful Data**

Planck constant = $6.626 \times 10^{-34}$ JS

$c = 3 \times 10^{8}$ $ms^{-1}$

**SECTION A**

**QUESTION ONE (30 MARKS)**

a) The UV-Visible region of the electromagnetic spectrum stretches from 10 nm to 1000 nm in terms of wavelength.

i. Express the boundary of the above region in terms of frequency in hertz. (3 marks)

ii. Determine the maximum and minimum energies for this region. (3 marks)

b) The UV-Visible spectra of molecules consist of a few humps rather than sharp lines.

i. Explain why the spectra consist of humps rather than sharp lines. (3 marks)

ii. Show with the help of an energy level diagram how various electronic transitions from the ground states to the excited states occur in a UV-Vis active molecule. (3 marks)

c) The position at which a molecule in the UV-Vis region absorbs is denoted as $\lambda_{max}$.

i. Explain what is $\lambda_{max}$. (3 marks)

ii. Explain briefly why a saturated molecule absorbs energy at a shorter wavelength than an unsaturated one. (3 marks)

iii. Explain why conjugation in unsaturated groups of molecules make molecules even to absorb in the visible region making the molecules to be coloured. (3 marks)

d) The amount of radiation absorbed by a UV-Vis active molecule is governed by the Beer-Lambert´s law.

i. Derive the equation describing the Beer Lambert law explaining each variable in the equation. (3 marks)

ii. The intensity of an incident monochromatic radiation is reduced to one-fourth of its initial value after passing through a solution of concentration of 0.06 M in a path length of 8 cm of the solution. Calculate the molar extinction coefficient (ε) of the solution. (6 marks)

**SECTION B**

**QUESTION TWO (20 MARKS)**

a) The Infrared spectra result from interactions of IR-active molecules with radiation of suitable frequency in the IR region defined by $v = ½ \Pi (k/\mu)^{½}$ where,

v = frequency

k = force constant

μ = reduced mass

i. From the equation above, what is the effect of varying k on the value of v? (1½ marks)

ii. What is the effect of varying μ on the value of v? (1½ marks)

iii. Describe briefly the trend of v as the bond of the molecule is changed from single to double and finally triple bond. (2 marks)

b) The absorption of energy by an IR-active molecule in the IR region is due to the transition from lower vibrational energy level (v) to higher vibrational energy level.

i. Explain what are requirements for a molecule to be IR-active. (2 marks)

ii. Based on the selection rules on the energy absorption by an IR active molecule, explain what are the fundamental absorption bands of a molecule. (2 marks)

iii. Explain what are overtone absorption bands. (2 marks)

iv. Explain why normally the observed fundamental bands are fewer than predicted theoretically. (3 marks)

c) Figure 1 below is an IR-spectrum of $CO_2$ gas. Four fundamental absorption peaks are predicted but only two peaks are observed.

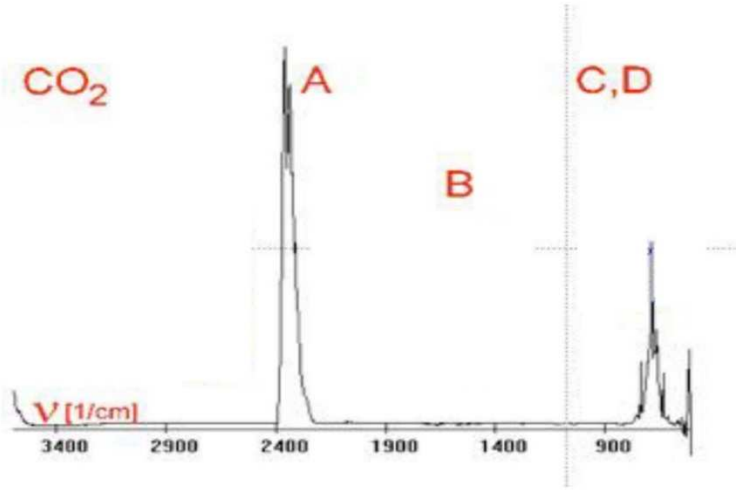



**Figure 1: IR spectrum of $CO_2$ gas**

i. Explain how the four peaks are arrived at theoretically. (2 marks)

ii. Assign the peaks expected at A, B, C, D. (2 marks)

iii. Explain why only two peaks are observed. (2 marks)

**QUESTION THREE (20 MARKS)**

Use the following information for this question

$v = (\mu/hI)H_o$

v = Resonance frequency of Radio waves of electromagnetic spectrum

h= Planck constant

$H_o$ =External magnetic field strength.

$\mu$ = magnetic moment of the spinning nucleus

a) The Nuclear Magnetic Resonance is a spectroscopic method which results from the transition of a nucleus from the ground state nuclear energy level to the excited state on absorbing radiofrequency radiation.

i. Describe how the nuclear spin quantum number I of 0, integers (1,2,…), half integers (1/2 , 3/2, 5/2….) are assigned to nuclei of various elements. 1 mark)

ii. Explain how the spinning nucleus in an applied external field Bo interacts with the radiofrequency radiation to generate the NMR signals. (1 mark)

iii. Determine the number of energy levels for the nucleus with a spin value of I = 2. (1 mark)

iv. With the help of an energy level diagram, show the various nuclear energy levels resulting from the interaction of the spinning nucleus with the applied magnetic field of strength Bo. (1 mark)

b) Table1 provides information of nuclei of isotopes which are NMR active. Use the table to answer the questions below.

**TABLE 1: MAGENETIC RESONANCE PROPERTIES OF SELECTED NUCLEI**

| | | | | NMR FREQUENCY, MHZ | | |
|---|---|---|---|---|---|---|
| **Isotopes** | **I value** | **μ ($JG^{-1}$)** | **Relative sensitivity** | | | |
| | | | **At constant $H_o$** | **at 14.09 kG** | **at 21.14 kG** | **at 23. 49 kG** |
| 1H | ½ | $1.41x10^{-30}$ | 100 | 60.000 | 90.000 | 100.000 |
| $^{2}H$ | 1 | $4.33x10^{-31}$ | 0.96 | 9.210 | 13.815 | 15.352 |
| $^{13}C$ | ½ | $3.55x10^{-31}$ | 1.59 | 15.086 | 22.629 | 25.147 |
| $^{19}F$ | ½ | $1.33x10^{-30}$ | 83.4 | 56.444 | 84.666 | 94.087 |
| $^{31}P$ | ½ | $5.71x10^{-31}$ | 6.64 | 24.288 | 36.432 | 40.485 |

i. From the table 1 provided, work out the NMR frequency in MHZ (megahertz) for $^{1}H$ and $^{13}C$ at the external field strengths, Ho of 14.09, 21.14 and 23.49 kg, respectively. (2 marks)

ii. From the table explain the effect of the value of magnetic moment of the respective nuclei on the NMR frequency which determines the sensitivity of the NMR spectrometer. (2 marks)

iii. Give two reasons why $^{1}H$ has the highest relative sensitivity at constant Ho (Applied external magnetic field) as shown in table 1 (2 marks)

iv. Give one advantage $^{13}C$ NMR has over $^{1}H$ NMR. (1 mark)

c) i Explain the term chemical shift as used in NMR spectroscopy. (1 mark)

ii Explain the term spin-spin coupling in NMR spectroscopy. (1 mark)

iii Explain why Tetra Methyl Silane (TMS) is used as a reference standard in NMR Spectroscopy measurement of chemical shifts of compounds. (1 mark)

d) The figure 2 below is an NMR spectrum of ethyl iodide ($CH_3CH_2I$) dissolved in deuterochloroform ($CDCl_3$).

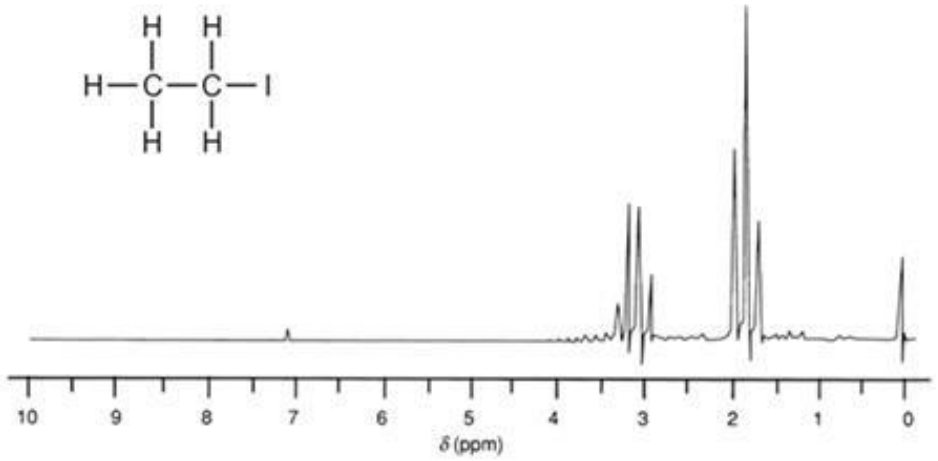



**Figure 2: $^1$H NMR spectrum of $CH_3CH_2I$**

i. Explain why deuterochloroform is used instead of chloroform itself to dissolve ethyl iodide. (2 marks)

ii. Identify the peaks at 0ppm, 1.8ppm, 3.2ppm and 7.25ppm. (2 marks)

iii. Explain why the peaks at 1.8 and 3.2 ppm are split into a triplet and quadruplet, respectively. (2 marks)

**QUESTION FOUR (20 MARKS)**

a) In atomic spectroscopy, normally atoms of compounds interact with radiation in order to for the compound to absorb radiation and therefore, determine the compound at atomic state both qualitatively and quantitatively.

i. Briefly outline with the help of diagrams the principles of the three types of atomic spectroscopy: atomic absorption, atomic emission and atomic fluorescence spectroscopy. (10 marks)

ii. Explain stepwise process of conversion of the compound from solution to its atomic state by the flame method before determination by the methods described in (i). (4 marks)

b) Describe how the hollow cathode lamp generates the resonance radiation in the analysis of the relevant element in atomic spectroscopic method. (6 marks)

**QUESTION FIVE (20 MARKS)**

a) Mass spectrommetry (MS) is considered as the most outstanding among analytical methods and is applied widely in many fields.

i. Outline what happens whenever a compound collides with an electron in the gas phase in the initial stage of the MS technique. (2 marks)

ii. Define what is m/z ratio in MS. (1 mark)

iii. In the mass spectrum what is molecular ion? (2 marks)

iv. What is the base peak in the mass spectrum? (2 marks)

b) There are two methods of generating ions from compounds in the MS technique, the electron ionization and the chemical ionization

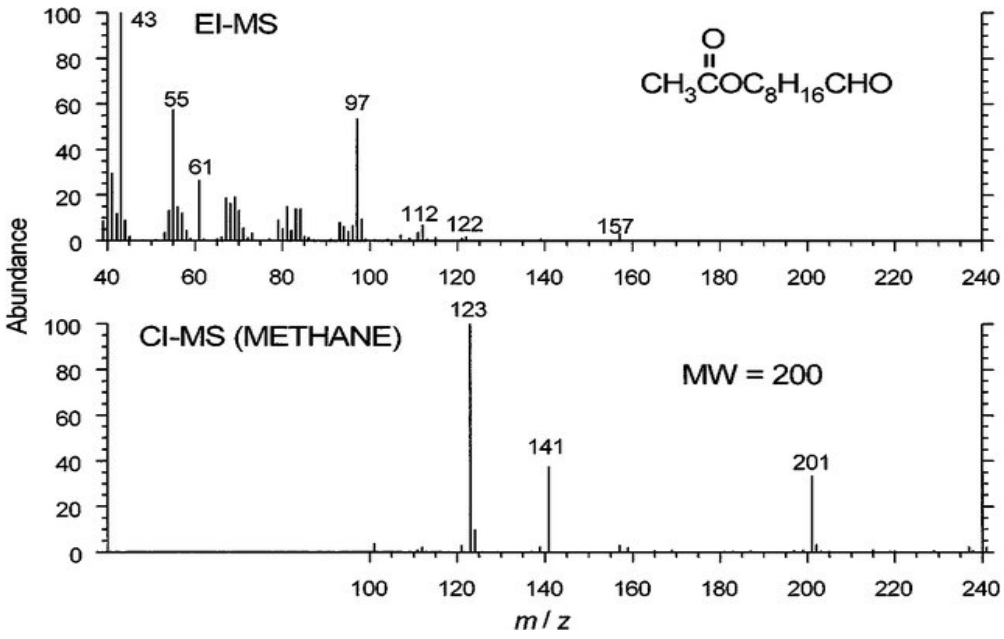
i. Explain the major difference between the two methods of ionization. (3 marks)

ii. Name and explain the behaviour of the three reagent gases used in chemical. (3 marks)

iii. Ionization

iv. Using $CH_4$ as a reagent gas in chemical ionization, describe in details with the help of chemical equations how chemicasl ionization generates the ions analyzed in the MS technique. (2 marks)

c) The figures below are mass spectra of diketopiperazine produced by electron ionization (EI) in the upper figure and by chemical ionization (CI) with methane as a reagent in the lower figure.




Figures 3a and b: Mass spectra of diketopiperazine

From the figures;

i. What is the molecular mass of the compound? (½ mark)

ii. What major difference do you see between the upper and lower spectra? (½ mark)

iii. Identify the molecular peak in the two spectra (2 marks)

iv. Identify both peaks m/z 157 and m/z 201, respectively (2 marks)