

CHUKA



UNIVERSITY

## UNIVERSITY EXAMINATIONS

EXAMINATION FOR AWARD OF DEGREE OF BACHELOR OF SCIENCE  
(CHEMISTRY)

## CHEM 345: MOLECULAR SPECTROSCOPY

STREAMS:

TIME: 2 HOURS

DAY/DATE: WEDNESDAY 14/07/2021

11.30 A.M. – 1.30 P.M.

## INSTRUCTIONS

- Answer question one and any two questions
- Do not write on the question paper

 $\text{\AA} = \text{angstrom} = 10^{-10}\text{m} = 10^{-8}\text{cm} = 10^{-4} \text{ micrometer}$ 
 $\text{nm} = \text{nanometer} = 10^{-9}\text{m} = 10\text{\AA} = 10^{-3} \text{ micrometer}$ 
 $\mu\text{m} = \text{micrometer} = 10^{-6}\text{m} = 10^4 \text{ angstroms}$ 

## QUESTION ONE (30 MARKS)

1. a) (i) From the definitions of the centre of mass and moment of inertia I show that for a diatomic molecule

$$I = \mu r^2$$

Where  $r$  = the length between two atoms

$\mu = \frac{m_1 m_2}{m_1 + m_2}$  Reduced mass (3 marks)

- ii) Write short notes on the following:

- I. spherical TOP molecules (1½ marks)
- II. symmetric TOP molecules (2 marks)
- III. Asymmetric TOP molecules (1½ marks)

- iii) Consider the molecules  $\text{CCl}_4$ ,  $\text{CHCl}_3$  and  $\text{CH}_2\text{Cl}_2$

- I. What kind of rotor are they? (1½ marks)

- II. Will they show pure rotational spectrum? (1½ marks)
- III. Assume that ammonia shows a pure rotational spectrum. If the rotational constants are 9.44 and 6.20 cm<sup>-1</sup>, use the energy expression.  
 $E = (A-B)K^2 + BJ(J+1)$  to calculate the energies (in cm<sup>-1</sup>) of the first three lines (i.e. those with lowest K, J quantum number for the absorbing level) in the absorption spectrum (ignoring higher order terms in the energy expression.) (2 marks)
- IV. The first rotational line in the rotational spectrum of CO is observed at 3.84235 cm<sup>-1</sup>. Calculate the rotational constant (B) and the bond length of CO. The relative atomic weight C=12.0 and O = 15.9994, the absolute mass of H = 1.67343 x 10<sup>-27</sup> kg  
 $h = 6.626 \times 10^{-34}$ ,  $N_A = 6.024 \times 10^{23}$ ,  $1 \text{ \AA} = 10^{-8} \text{ cm}$  (3 marks)

b (i) Show that, the vibrational frequency in a diatomic molecule is given by

$$V_m = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}$$

Where  $V_m$  = Vibrational Frequency

$\mu$  = Reduced mass

K = Force constant (3 marks)

ii) A diatomic molecule  $Hx$  (x is an unknown) has a harmonic vibrational force constant  $K = 9.6800 \times 10^5 \text{ g/S}^2$ . The harmonic vibrational frequency in wave number is 4143.3 cm<sup>-1</sup>.

- I. Calculate the reduced mass of the molecule. (1 mark)
- II. Determine element X {C = 2.99792558 x 10<sup>8</sup> m/s,  $N_A = 6.02214 \times 10^{23} \text{ Mol}^{-1}$ , H = 1.0079 amu, 1 amu = 1.66053892173 x 10<sup>-27</sup> kg} (1½ marks)

iii) Consider the diatomic molecule LiH to be an anharmonic oscillator. Use the spectroscopic constants given below: LiH,  $\omega_e = 1405.7 \text{ cm}^{-1}$  and  $x_e = 0.0165$ .

- I. Determine the fundamental vibrational transition. (1½ marks)
- II. The first and second overtone transition. (1 mark)

c. Write short notes on the following:

- (i) R – branch (1 mark)
- (ii) P – branch (1 mark)
- (iii) Q – branch (1 mark)

d. Outline the five advantages and the disadvantage of using pellet technique when recording the IR spectra. (3 marks)

**QUESTION TWO (20 MARKS)**

2. a. (i) Compare the sample handling procedures in Raman spectrometry with that in IR spectrometry. (3 marks)

ii) Explain why a laser is the ideal source to use for measuring Raman Spectra. (2 marks)

iii) The molecule carbon tetrachloride ( $\text{CCl}_4$ ) has three Raman active absorptions that occur at 218, 314 and 459  $\text{cm}^{-1}$  away from the laser line. Draw a representation of the Raman spectrum of  $\text{CCl}_4$  that includes both the stokes and anti-stokes line. (3 marks)

iv) Explain how to interpret Raman spectrum data. (2 marks)

b (i) How many Raman and Rayleigh scatter be identified within a fluorescence emission spectrum? (1½ marks)

ii) What is the limiting effect of Raman scatter when added to the sample measurement? (½ marks)

iii) When Raman scatter does interfere, what four alternatives does the analyst possess for eliminating it. (1½ marks)

c) i) A sample gives a stokes line at  $4458\text{\AA}$  when the exciting radiation of wavelength  $4358\text{\AA}$  is used. Deduced the wavelength of the anti-stokeness line. (2 marks)

ii) Justify the following statement “Aniline fluorescence but nitrobenzene does not” (2½ marks)

iii) Explain why correction for the spectral response of the detector is required for measuring an excitation spectrum in a fluorometer but not needed when measuring uv-visible absorption. (1 mark)

iv) Consider benzene and naphththalene.

I. Which molecule would you expect to have a larger quantum yield? (½ marks)

- II. Which molecule would you expect to have a shorter peak wavelength for fluorescence? (½ marks)

**QUESTION THREE (20 MARKS)**

3. a) i) Predict the part of the quinine molecule that is most likely to behave as the chromophore and fluorescent center. (1 mark)

ii) Calculate the electron spin resonance (ESR) frequency of an unpaired electron in a magnetic field of 0.030T

$$g = 2.0, \beta = 9.273 \times 10^{-24} \text{ JT}^{-1}, h = 6.626 \times 10^{-34} \text{ JS} \quad (1 \text{ mark})$$

iii) Predict the number of lines in the ESR spectrum of each of the following

- I. (CF<sub>2</sub>H) (1 mark)  
II. (<sup>13</sup>CH<sub>3</sub>) (½ mark)  
III. CF<sub>2</sub>D (½ mark)

iii) ESR spectra of free radicals formed from three substrates during enzyme oxidation by peroxide H<sub>2</sub>O<sub>2</sub> are given below. Match each of the spectra with the corresponding free radicals.

A) From reductic

B) From dihydroxy fumaric acid

C) From Ascorbic

Spectrum 1

Spectrum 2

Spectrum 3

iv) Compare NMR and ESR spectroscopy.

(3½ marks)  
(4 marks)

IV. Compare NMR spectroscopy and ESR spectroscopy.

(3 marks)

b. i) Explain why Hydrogen bonding lowers the absorption frequency using hydroxyl compounds as an example.

(2 marks)

ii) Distinguish between inter-and intra molecular hydrogen bondings.

(3½ marks)

#### QUESTION FOUR (20 MARKS)

4. i) Explain the formation of prominent ion peaks at  $m/e$  72, 71, 57 and 43 in the mass spectrum of 2-methylbutane. Indicate the ion responsible for the base peak. (20 marks)

ii) An organic compound gave a peak at  $m/z$  122(w) and another peak of nearly equal intensity at  $m/z$  124 in its mass spectrum. What is the likely molecular formula of the compound? (1½ marks)

iii) ion clusters formed by sodium trifluoroacetate during electrospray ionization can be used to calibrate mass analyzers. What is the error in mass accuracy (ppm) if the  $[\text{Na}_3 (\text{CF}_3\text{COO})_2]^+$  ion was recorded to have an  $m/z$  ratio of 294.9357?

$^{23}\text{Na} = 22.989221$ ,  $^{12}\text{C} = 12.00000$ ,  $^{19}\text{F} = 18.998403$ ,  $^{16}\text{O} = 15.994915$  (2 marks)

b) Comment on the number of signals and their splitting, if any, in the  $^1\text{H}$ NMR

(i) (2 marks)

(ii) (1½ marks)

(iii) (1 mark)

c) In an organic compound, three kinds of protons appear at 60, 100 and 180 HZ when the spectrum is recorded at 60MHz NMR spectrometer. What will be their relative positions (in Hz) when 90 MHz spectrometer is used. (2 marks)

d) Explain what you understand by the method validation. (1 mark)

e. (i) In electrochemical atomic absorption spectrophotometry with graphite – probe atomization, the concentration of lead was measured by its absorbance of light. Ten reagent blanks were also measured and gave values of 0.0009, 0.0013, 0.0025, 0.0004, 0.0019, 0.0007, 0.0029, 0.0011, 0.0025, 0.0008. Calculate LOD at 95% CI and 99% CI and LOQ. (2 marks)

ii) A calibration curve was conducted using a series of load standard solutions. The concentrations and the absorbance of the standards are listed in the following table.

Conc (ppb)	0.01	0.1	0.5	1.0	2.50
Absorbance	0.0078	0.0880	0.4467	0.8980	1.8770

Determine

- I. Regression equation. (2 marks)
  - II. LOD and LOQ in ppb. (2 marks)
  - III. Lambert – Beer's Law range using ringborn plot method. (3 marks)
-