**CHUKA UNIVERSITY**

**UNIVERSITY EXAMINATIONS**

**EXAMINATIN FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE**

**CHEM 345: MOLECULAR SPECTROSCOPY**

**STREAMS: BSC (CHEM)** **TIME: 2 HOURS**

**DAY/DATE: MONDAY 15/4/2019** **2.30 P.M. – 4.30 P.M.**

**INSTRUCTIONS: Answer question ONE and any other TWO questions**

**QUESTIONONE (20 MARKS)**

(a) (i) Why are pure rotational microwave spectra studied only in the gaseous states of atoms and molecules? [1½ marks]

(ii) Calculate the degeneracies of the following diatomic rotational energy levels:

(I) O [2 marks]

(II) $\frac{h^2}{4\pi^2 I}$ [1 mark]

(III) $6\frac{h}{4\pi^2 I}^2$ [1 mark]

Where I is the moment of inertia, h = Planck's constant.

(iii) Draw different figures representing linear molecule, spherical molecule, symmetric top molecule and asymmetric top molecule [2 marks]

(iv) From the microwave spectrum of Hcl, it is observed that the frequency difference between successive absorption lines is found to be 20.7 $cm^{-1}$ and is identified with 2B. Calculate the bond length of Hcl and separation between energy level J = 0 and J = 1

$$\left[B = rotational\ constant\ h = 6.62608\,x\,10^{10}\,cms^{-1}\ H = 1.008, Cl = 35.45\ N_A = 6.02214\,x\,10^{23}, 1\,A° = 10^{-10}\,m\right]$$

[4½ marks]

(b) (i) Accounts for all the peaks in the figure below showing electron spin resonance (ESR) spectrum of $Mn^{2+}$ ions in solution

$Spin\ quantum\ number\ of\ nucleus\ of\ Mn^{2+} = \frac{5}{2}$ [1½ marks]

(ii) Explain how the results obtained by derivative curves in electron spin resonance (ESR) can be interpreted [1½ marks]

(iii) Explain how the number of electrons in an unknown sample can be calculated from the results obtained by ESR spectrum [1 mark]

(iv) Predict the type of ESR spectrum to be obtained for 2, 3 – dichlorobenzoquinone [½ mark]

(c) (i) Describe how you can determine the location of groups on a benzene ring using Raman spectroscopy [1½ marks]

(ii) Briefly discuss how fluorescent spectroscopy differs from other spectroscopic techniques [1½ marks]

(iii) Distinguish between photoluminescence and chemiluminescence techniques as applied in molecular luminescence spectrometry [2 marks]

(d) (i) Discuss the strength and limitations of Mossbauer spectroscopy [3½ marks]

(ii) Give a brief discussion on properties of laser light which laser analytical spectroscopy utilizes for the purpose of analysis [5 marks]

**QUESTION TWO (20 MARKS)**

(a) Comment on the following statements

(i) The spectrum of aniline solution contains absorption peak which disappear when solution is made acidic [1½ marks]

(ii) Cyclonexane and heptane are solvents for near UV region which are not free from limitations [1 mark]

(iii) Distinguish the folloiwng:

Chromophores, chromogen and auxochrome [2 marks]

(iv) Which of the following pairs of compunds is likely to absorb radiation at the longer wavelength and with greater intensity? Give reasons

(I) $CH_3$ $CH_2$ CNS and SNC $CH_2$ $CH_2$ $CH_2$ CNS

para linked molecule and

meta linked molecule [2 marks]

(b) Phosphorus in urine can be determined by treating with molybdenum (VI) and then reducing the phosphomolybdatewith aminaphtholsulfonic acid to give the characteristic molybdenum blue colour. This absorbs at 690 nm. A patient excreted 1270 ml urine in 24h and the pH of the urine was 6.5. A 1.00 ml a aliquot of the urine was treated with molybdate reagent and aminophtholsulfonic acid and was diluted to a volume of 50.0ml. A series of phosphate standards was similarly treated.

The absorbance of the solution at 690nm, measured against a blank, were as follows:

| Solution | Absorption |
|---|---|
| 1.00 PPm P | 0.205 |
| 2.00 PPm P | 0.410 |
| 3.00 PPm P | 0.615 |
| 4.00 ppm P | 0.820 |
| Urine sample | 0625 |

(i) Calculate the concentration of phosphorus in urine in g/L [5 marks]

(ii) Calculate the number of grams of phosphorus excreted per day [1 mark]

(iii) Calculate the ratio of $HPO_4^{2-}$ to $H_2PO_4^{-}$ in the sample

$$K_1 = 1.1 x 10^{-2}, K_2 = 7.5 x 10^{-8}, K_3 = 4.8 x 10^{-13}$$

[½ mark]

(c) Titanium (IV) and Vanadium (V) form coloured complexes when treated with hydrogen peroxide in 1M sulphuric acid. The titanium complex has an absorption maximum at 415 nm and the vanadium complex has an absorption maximum of 455 nm. A $1.00 x 10^{-3} M$ solution of the titanium complex exhibits an absorbance of 0.805 at 415nm and of 0.465 at 455nm, while a $1.00 x 10^{-2} M$ solution of the vanadium complex exhibits absorbances of 0.400 and 0.600 at 415 and 455 nm respectively. A 1.000g sample of an alloy containing titanium and vanadium was dissolved treated with excess hydrogen peroxide, and diluted to a final volume of 100ml. the absorbance of the solution was 0.685 at 415 nm and 0.513 at 455 nm. Calculate the percentages of titanium and vanadium in the alloy. [5 marks]

**QUESTION THREE (20 MARKS)**

(a) (i) If chloroform (trichloromethane) exhibits an infrared peak at 3018 cm$^{-1}$ due to the C – H stretching vibration, calculate the wave number of the absorption band corresponding to the C-D stretching vibration in deuterochloroform (experimental value 2253 cm$^{-1}$) [3 marks]

(ii) A ketone possesses an absorption band with a peak centred around 1710cm$^{-1}$. From this information deduce a value of the force constant of the C = 0 double bond [2 marks]

(b) The following experiment is used to determine the vinyl acetate (VA) level in an ethylene vinyl acetate (EVA) commercial packaging film infrared spectra packaging films with known vinyl acetate contents are recorded. The absorbance peak at 1030 cm$^{-1}$ used to determine the content of the vinyl acetate was measured by the baseline method

$(A=\log I_0/I)$ . The following results were obtained

| (EVA) | °G VA | $A_{1030}$ | $A_{720}$ | $D(\mu m)$ |
|---|---|---|---|---|
| 1 | 0 | 0.01 | 1.18 | 56 |
| 2 | 2 | 0.16 | 1.55 | 80 |
| 3 | 7.5 | 0.61 | 1.49 | 82 |
| 4 | 15 | 0.36 | 0.45 | 27 |

(i) Taking into account the film thickness, determine, from the data in the table, the best line $A_{1030}=f(VA)$ , using linear regression for a film thickness of 1 $\mu m$

[3½ marks]

(ii) Explain why the polyethylene peak at 720cm$^{-1}$ may be chosen as an internal standard, then calculate the ratio $A_{1030}/A_{720}$ for the four films [3½ marks]

(iii) Using both above methods calculate the vinyl acetate content $()$ of an unknown EVA film (given $d=90\mu m,$ $A_{1030}$ =0.7 and $A_{720}=1.54¿$

[1 mark]

(c) (i) Give the functions of IR spectroscopy, nuclear magnetic resonance, mass spectroscopy and UV spectroscopy in qualitative analysis of an unknown organic compound

[2½ marks]

(ii) Assign the peaks in the organic compound spectrum given in figure 1 [2½ marks]

(iii) Explain how you can distinguish the two organic compounds one shown in figure I from that in figure 2 [2 marks]

**QUESTION FOUR (20 MARKS)**

(a) (i) Discuss the use of NMR for studying the hydrogen bonding in metal chelates and in organic compounds [5 marks]

(ii) Distinguish between spin-spin coupling and coupling constant [1½ marks]

(iii) Account for the peaks in low resolution and high resolution spectrum of $CH_3CHO$ shown below

[3½ marks]

(iv) The low resolution proton $^1H$ NMR spectrum of the formula C4H4O2 shows two peaks of equal intensity. Assign the structure consistent with this information [½ marks]

(v) Briefly explain how aromatic compounds can be identify using $^1H$ NMR spectroscopy [3 marks]

(b) (i) Discuss Faraday cup detectors in mass spectrometer [3 marks]

(ii) State seven factors which contributes to decrease of the resolution of mass spectrometer [2 marks]

(iii) A singly protonated ion having m/Z = 375.9 is initially accelerated by an electric potential of 5000V. After it is accelerated, it enters a homogeneous magnetic field with a strength of 4T applied perpendicular to the path of the ions travel. Calculate the resultant radius of curvature in this ion in the magnetic field [1½ marks]

---