CHUKA UNIVERSITY

UNIVERSITY EXAMINATIONS

EXAMINATION FOR THE AWARD OF DEGREE OF BACHELOR OF SCIENCE IN CHEMISTRY

CHEM 345: MOLECULAR SPECTROSCOPY

STREAMS: MSC CHEM **TIME: 2 HOURS**

DAY/DATE: FRIDAY 17/04/2020 **11.30 A.M. – 1.30 P.M.**

INSTRUCTIONS:

- **Answer question ONE and any other TWO questions.**

USEFUL DATA

1ev= $1.60218 \times 10^{-19} J = 96.485\ KJ\ mol^{-1}$
$= 8065.5 cm^{-1}$
1 Cal = 4.184 J
$1A^0 = 10^{-10} m$
$C = 3 \times 10^8 m/s$
$e = 1.602176 \times 10^{-19} C$
Boltzmann constant (k) = $1.38065 \times 10^{-23} JK^{-1}$
h = 6.62608×10^{-34}JS
$N_A = 6.02214 \times 10^{23} mol^{-1}$
Atomic mass unit (u) =$1.66054 \times 10^{-27} KJ$ mass
Electron $m_e = 9.10938 \times 10^{-31} kg$
$m_p = 1.67262 \times 10^{-27} kg$
$m_n = 1.67493 \times 10^{-27} kg$

1. (a) Define the following terms:

(i) Chromophore ($\frac{1}{2}\ marks$)

(ii) Auxochrome ($\frac{1}{2}$ marks)

(iii) Bathochromic shift ($\frac{1}{2}$ marks)

(iv) Hypsochromic shift ($\frac{1}{2}$ marks)

(v) Hyperchromic effect ($\frac{1}{2}$ marks)

(vi) Hypochromic effect ($\frac{1}{2}$ marks)

(b) (i) Write short notes on various types of transitions in organic molecules. (8 marks)

(ii) In the determination of acetone in biological fluids the following calibration curve and unknown data were obtained.

Standard	Absorbance
mg acetone/100ml	
Reagent blank	0.053
2.0	0.097
4.0	0.143
6.0	0.190
8.0	0.221
10.0	0.238
Normal blood	0.119
Ketonic blood	0.222
Normal urine	0.150
Ketonic urine (diluted)	0.230

All the absorbance measurements were against a water blank. Determine the ketone concentrations in each of the four unknowns and assuming a 1:25 (initial: final) dilution was used, calculate the ketone concentration in the undiluted urine. (6 marks)

(iii) Explain how the ultraviolent spectrum can be used to decide between the following isometric systems

(c) (i) Outline six requirements for effective coupling interaction in infrared spectroscopy. (3 marks)

(ii) Outline four requirements which must be met before an attempt is made to interpret a spectrum. (2 marks)

(d) (i) Outline the four principles which can be used to decide about the structure of an unknown compound from its NMR spectrum. (2 marks)

(ii) List three terms which can be considered to be associated with the shifts of hydrogen bonding in metal chelates as well as in organic compounds in NMR spectrum. ($1\frac{1}{2}$ marks)

(iii) Explain how NMR can be used for identification of structure of CIF_3. (2 marks)

(iv) List five types of information which can be obtained from electron spin resonance spectroscopy spectrum.

QUESTION TWO (20 MARKS)

2. (a) (i) List factors attributing to decrease in resolution of mass spectrometer. ($3\frac{1}{2}$ marks)

(ii) Give seven types of ions produced in a mass spectrometer. ($3\frac{1}{2}$ marks)

(iii) What accelerating voltage is required to direct a singly charged water molecule through the exit shit of a magnetic sector mass spectrometer if the magnet has a field strength of 0.240 T (tesla) and the radius of curvature of the ion through the magnetic field is 12.7 cm?
$\{e = 1.602177 \times 10^{-19}C, N_A = 6.022141 \times 10^{23}$ particles per mole,
$1\ volt = 1kgm^2/s^2C, IT = V\ s/m^2$ (2 marks)

(b) Differentiate between Raman spectra and infrared spectra. (11 marks)

(c) Calculate the energy in Joules per quantum calories per mole and electron volts of photons of wavelength 3000 A^0
$\{h = 6.62 \times 10^{-34}J - S, C = 3 \times 10^8\ ms^{-1}, N_A = 6.02 \times 10^{23}mol^{-1}$
$1\ cal = 4.184\ Joules, 1\ ev = 1.60218 \times 10^{19}J\}$

QUESTION THREE (20 MARKS)

3. (a) Consider the molecules $CCI_4, CHCI_3 and\ CH_2CI_2$

(i) What kind of rotor are they (symmetric top, etc, do not bother with oblate or near-prolate, etc) ($1\frac{1}{2}$ marks)

(ii) Will they show pure rotational spectra? (1 mark)

(iii) Assume that ammonia shows a pure rotational spectrum. If the rotational constants are 9.44 and 6.20 cm^{-1}, use the energy expression
$E = (A - B)K^2 + BJ(J + 1)$
To calculate the energies (in cm^{-1}) of the first three lines (ie, those with lowest K, J quantum number for absorbing level) in the absorption spectrum (ignoring higher order terms in the energy expression)
($2\frac{1}{2}$ marks)

(iv) Determine whether the bond length in HBr the same as that in DBr {The wavenumbers of the $J = 1 \leftarrow 0$ rotational transitions for $H^{79}Br$ and $^{2}H^{79}Br$ are 16.68467 and 8.48572 cm^{-1}, respectively. Atomic masses are 1.007825u and 2.0140u for ^{1}H and ^{2}H respectively. The mass of ^{79}Br is 78.91833u.

$\hbar = \frac{h}{2\pi} = 1.05457 \times 10^{-34} JS$

$h = 6.62608 \times 10^{-34} JS$

$C = 2.99792558 \times 10^{8} ms^{-1}$

Atomic mass unit (u)=$1.66054 \times 10^{-27} Kg$
$1u = 1.66054 \times 10^{-27} Kg.$ (7 marks)

(b) (i) The use of Raman spectroscopy has historically not been as prevalent as IR spectroscopy. Describe two advantages that Raman spectroscopy holds over IR spectroscopy. What technological advance was the key to making Raman a feasible instrumental techniques? (7 marks)

(ii) Why does the ratio of anti-stokes to stokes intensities increase with sample temperature? (1 mark)

QUESTION FOUR (20 MARKS)

4. (a) (i) What are the advantages of a Fourier transform infrared spectrometer compared with a dispersive instrument? (5 marks)

(ii) How many vibrational modes are expected for HCN? Draw the normal vibrational modes. How many bands are expected in the IR spectrum? (6 marks)

(b) Explain how you can collect the spectrum given below and which of the two are closely resemble each other? A fluorescence emission spectrum, A fluorescence excitation spectrum, An absorption spectrum. (9 marks)
