NATIONAL OPEN UNIVERSITY OF NIGERIA
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FACULTY OF SCIENCES
DEPARTMENT OF CHEMISTRY
OCTOBER EXAMINATION 2022

COURSE CODE: **CHM 402**
COURSE TITLE: **Theory of Molecular Spectroscopy**
TIME: **2 Hours**
INSTRUCTION: **Answer question one and any two questions.**

QUESTION ONE

1. (a) State Beer-Lambert's law of spectrophotometry and explain how a calibration curve can be prepared. Hence sketch a typical pattern expected for the calibration curve (7 marks)

(b) Given that a solution of a compound has a molar absorptivity of 12000 $M^{-1}dm^3cm^{-1}$ and the absorbance (measured at the solution maximum wavelength of absorption) reading is 0.60 at λ_{max} of 480 nm while the path length is 1 cm. Calculate the concentration of the solution. (6 marks)

(c) The absorbance of a solution whose concentration is 0.25 M was measured as 0.76. What would be the concentration of another solution of the same compound whose absorbance reading is 0.62. (6 marks)

d. Use the quantization principle to explain the process of absorption and emission of photon.

e. State the application of nuclear quadrupole resonance spectroscopy in the mining industries and highlight the basic instrumentation for such application (5 marks)

QUESTION TWO

2. (a)(i) Write an equation that can be used to calculate the moment of inertia of a rigid rotor (3 marks)

(ii) Write an expression for the quantized rotational energy of a molecule in its original form and in terms of the rotational constant, B. (5 marks)

(b)(i) What is the model behind the rotational symmetry of a diatomic molecule having reduced mass and moment of inertia given as μ and I respectively (radius created by the rotation = r). Write appropriate equation to support your answer (4 marks)

(ii) State why samples meant for microwave spectroscopic analysis should preferably be in the gaseous state instead of solid or liquid states. (2 marks)

(iii) How can the sensitivity of a radio spectroscope be increased? Hence define the Stark and Zeeman effect. (6 marks)

QUESTION THREE

3.a(i) Write expressions for the vibrational energy of a molecule under the consideration of a harmonic oscillator. Also write the quantum mechanics equation for the calculation of the vibrational energy of a molecule (5 marks)

(ii) Write an equation that is relevant for the calculation of the vibrational energy of an anharmonic system. Hence what is the selection rule for harmonic and anharmonic systems (4.5 marks)

b. What is the selection rule for vibration-rotation, hence define P, R and Q branch transitions (6 marks)

c. What is the analytical usefulness of the near, mid and far-infrared regions (4.5 marks)

QUESTION FOUR

4. a(i) Highlight the main characteristics of the two major spectra that gas-phase molecules exhibit? (5 marks)

(ii) What is the major challenges of Raman spectroscopy with reference to the Raleigh scattering and how can this challenge be overcome (4 marks)

b. What are the major features of the fingerprint region of the infrared spectrum and how are they useful in chemical analysis? (5 marks)

(c) State the major differences between Raman spectroscopy and infrared spectroscopy (6 marks)

QUESTION FIVE

5.(a) Answer the following questions on chemical shift

(i) What is chemical shift? (2 mark)

(ii) Why is it necessary to consider chemical shift in NMR spectroscopy (2 mark)

(iii) What is the reference compound used in NMR to standardized chemical shift? (2 mark)

(iv) How many chemically and magnetic equivalent protons are found in the reference compound stated in (iii) above. Hence what is its resonance position (2 mark)

(v) What is the formulation that is suitable for use as internal standard in NMR instrument (2 mark)

b. Write equations for the two factors that can be used to calculate chemical shift. Define all the terms in the equations (5 marks)

(ii) State six intra and intermolecular factors that affect chemical shift (5 marks)