



**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  $12000 \text{ M}^{-1}\text{dm}^3\text{cm}^{-1}$  and the absorbance (measured at the solution maximum wavelength of absorption) reading is 0.60 at  $\lambda_{\text{max}}$  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  $\mu$  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 spectroscopy 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 Rayleigh 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)