THE CATHOLIC UNIVERSITY OF EASTERN AFRICA

A. M. E. C. E. A

P.O. Box 62157

00200 Nairobi - KENYA

Telephone: 891601-6

MAIN EXAMINATION

JANUARY – APRIL 2020 TRIMESTER

FACULTY OF SCIENCE

DEPARTMENT OF NATURAL SCIENCE (CHEMISTRY)

REGULAR PROGRAMME

CHEM 206: SPECTROCOPIC METHODS IN INORGANIC CHEMISTRY

Date: APRIL 2020	**Duration: 2 Hours**
INSTRUCTIONS: Answer Question ONE and ANY OTHER TWO Questions	

General Data and Fundamental Constants:

Speed of Light	$c = 2.998 \times 10^{8}\ m\,s^{-1}$
Planck constant	$h = 6.626 \times 10^{-34}\ J\,s$
Rydberg constant	$R_\infty = 1.0974 \times 10^{7}\ m^{-1}$
Avogadro constant	$N_A = 6.022 \times 10^{23}\ mol^{-1}$
atomic mass unit	$u = 1.661 \times 10^{-27}\ kg$
Boltzmann constant	$k = 1.3806 \times 10^{-23}\ J\,K^{-1}$
Electron volt	$1\ eV = 1.6022 \times 10^{-19}\ J$
Mass of an electron	$m_e = 9.109 \times 10^{-31}\ kg$
Atomic Mass of hydrogen:	1.0079

Equations:

$$p = \frac{h}{\lambda} \qquad E_{vib} = \hbar\omega_0(\mathrm{v} + \frac{1}{2}) \qquad E_{rot} = hc\tilde{B}J(J+1) \qquad \omega_0 = \sqrt{\frac{k}{m_R}}$$

$$\tilde{B} = \frac{h}{8\pi^2 cI} \qquad I = m_{\mathrm{R}}R_{\mathrm{e}}^2 \qquad \tilde{\nu} = R_\infty\left(\frac{1}{n''^2} - \frac{1}{n'^2}\right) \qquad n'' < n'$$

1. (a) i. Define spectroscopy. [2 marks]
   ii. What is the value of spectroscopy? [2 marks]
   iii. Distinguish clearly between emission and absorption spectroscopy. [2 marks]

   (b) Explain clearly what is meant by
   i. Balmer series [2 marks]
   ii. Line spectrum [2 marks]

   (c) One of the important types of spectroscopy is vibrational spectroscopy.
   i. Explain how the vibration of the covalent bond of a diatomic molecule is like that of a spring. [2 marks]
   ii. By means of equations explain how Hooke's law is applied to molecular vibrations. [2 marks]
   iii. Calculate the reduced mass of carbon monoxide. [2 marks]

   (d) Another important type of spectroscopy is rotation.
   i. Explain what is meant by "degrees of freedom". [2 marks]
   ii. A molecule can translate, vibrate and rotate. Determine the number of various degrees of freedom of HCl, CO_2 and H_2O and so complete the following table. [6 marks]

Molecule	Total	Translational	Rotational	Vibrational
HCl				
CO_2				
H_2O				

   (e) i. What is the difference between a harmonic oscillator and an anharmonic oscillator? [2 marks]
   ii. What is resonance and what is its importance in vibrational spectroscopy? [2 marks]
   iii. What is the "Born-Oppenheimer approximation"and how does it simplify the study of spectroscopy? [2 marks]

2. (a) Radiation in the ultraviolet region of the electromagnetic spectrum is usually described in terms of wavelength, λ, and is given in nanometers 10^{-9} m). Calculate the values of
   i. ν, [3 marks]
   ii. $\tilde{\nu}$, and [3 marks]
   iii. E [3 marks]
   for ultraviolet radiation with λ = 200 nm.

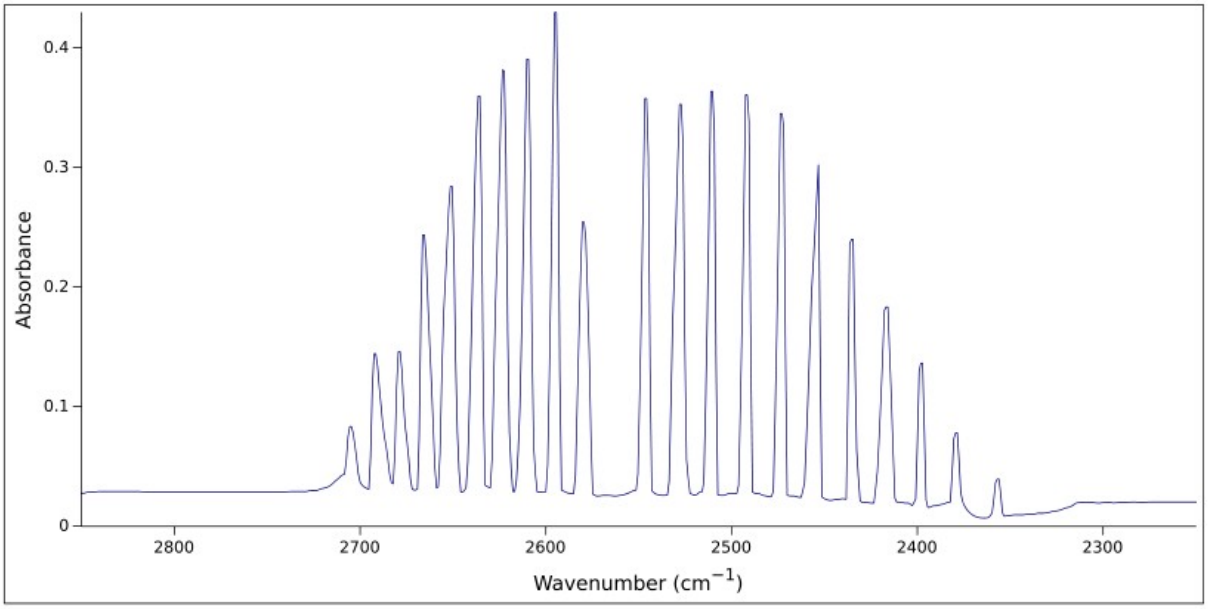
   (b) i. Referring to the equation given above for the wave number of an electronic transition of hydrogen, what would be the value of n' corresponding to the ionization of hydrogen? [2 marks]
   ii. Calculate the ionization energy of the hydrogen atom using this value in the equation. [9 marks]

3. (a) The infrared spectrum of $^{75}Br^{19}F$ consists of an intense line at $380\,cm^{-1}$. Calculate the force constant of $^{75}Br^{19}F$. [10 marks]

(b) The equilibrium internuclear distance of $H^{127}I$ is 160.4 pm. Calculate the value of $\tilde{B}$ in wave numbers and megahertz.

i. Calculate the moment of inertia, I, of the molecule and, hence, [5 marks]

ii. the value of $\tilde{B}$ in wave numbers and megahertz. [5 marks]



4. The image above shows the infrared absorption spectrum of HBr.

(a) On the separate copy of the image (to be handed in with your answer booklet if you attempt this question) indicate

i. the position of $\tilde{\nu}_0$ [3 marks]

ii. The P and R branches [4 marks]

iii. How the gaps between the peaks are related to the rotational constant $\tilde{B}$. [3 marks]

(b) Clearly explain the two factors that affect the heights of the absorption peaks and how they are related. [6 marks]

(c) Clearly explain the absence of a central peak between the P and R branches in terms of the rotational selection rule for ΔJ. [4 marks]

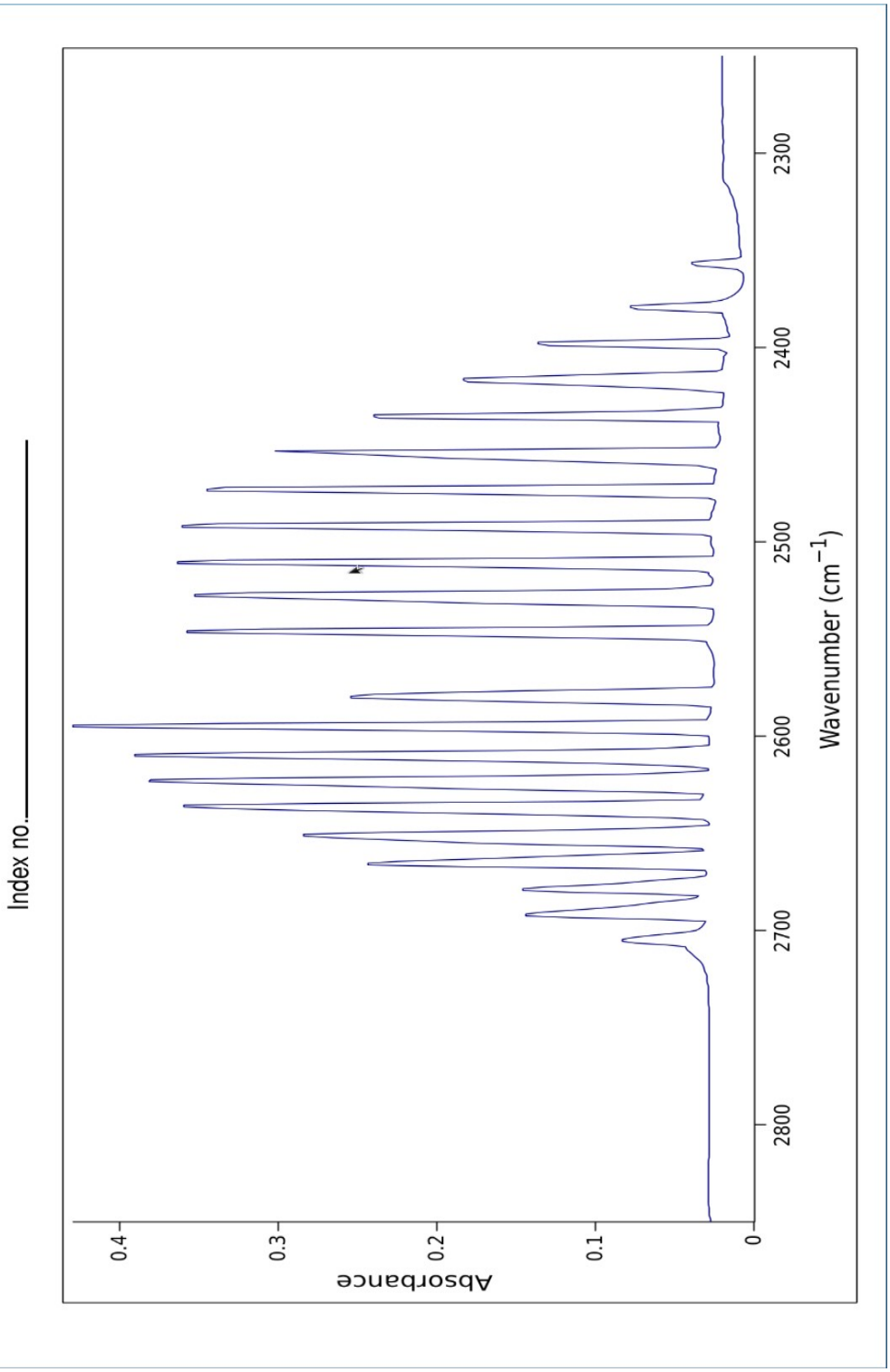
5. Use appropriate diagrams to answer the following questions:

   (a) What is the Franck-Condon principle? Explain assuming the anharmonic (Morse potential) potential energy curves. [5 marks]

   (b) Although there are no quantum mechanical restrictions on the change in the vibrational quantum number during an electronic transition, the probabilities and intensities of such vibrational changes during electronic transitions are not the same. Explain. [5 marks]

   (c) Show that if the ground and excited vibrational states have identical potential energy curves, the (0,0) transition is the most intense. [5 marks]

   (d) Explain the process of fluorescence. [5 marks]



END