086

The Open University of Sri Lanka
Faculty of Natural Sciences
B.Sc Degree Programme

Department : **Chemistry**
Level : **5**
Name of the Examination : **Final Examination**
Course Title and Code : **CYU5301 – Concepts of Spectroscopy**
Academic Year : **2021/2022**
Date : **22.10.2022**
Time : **9.30 a.m. – 11.30 a.m.**
Duration : **2 hours**

General Instructions

1. Read all instructions carefully before answering the questions.
2. This question paper consists of **four (04)** questions in **five (05)** pages.
3. Answer **all parts** of **all questions**. All questions carry equal marks.
4. Answer for each question should be started on a fresh page.
5. Answers to all parts of any question should be written together.
6. Draw fully labelled diagrams where necessary.
7. Involvement in any activity that is considered as an examination offense will lead to punishment.
8. Use blue or black ink to answer the questions.
9. Clearly state your index number on all pages of your answer script.
10. Use of non-programmable calculators will be allowed.
11. Mobile phones and other electronic equipment are not allowed. Switch off and leave them outside.
12. A list of constants and equations are provided overleaf for your reference.

List of important constants

Quantity	Symbol	Value	Unit
Speed of light	*c*	3 x 10^8	m s^{-1}
Faraday's constant	*F*	9.648 x 10^4	C mol^{-1}
Gas constant	*R*	8.314	J mol^{-1} K^{-1}
Plank's constant	*h*	6.63 x 10^{-34}	J s
Avagadro's constant	N_A	6.022 x 10^{23}	mol^{-1}
Standard atmospheric pressure	*atm*	1.01325 x 10^5	Pa
Pi	π	3.14159	
$Log_e(X)$		2.303 $Log_{10}(X)$	

Some equations used in spectroscopy in standard notation

$$\bar{E}_\upsilon = (\upsilon + 1/2)\bar{\omega} \qquad \bar{E}_\upsilon = (\upsilon + 1/2)\bar{\omega}_e - (\upsilon + 1/2)^2 x_e \bar{\omega}_e \qquad \bar{\nu}_J = 2\bar{B}(J+1) - 4\bar{D}(J+1)^3$$

$$\bar{B} = h/\left(8\pi^2 \mu c R^2\right) \qquad \bar{E}_J = \bar{B}J(J+1) - \bar{D}J^2(J+1)^2 \qquad \nu = \gamma(1-\sigma)B_0/2\pi$$

$$\bar{\nu}_0 = (1-2x_e)\bar{\omega}_e \qquad \bar{\nu}_1 = 2(1-3x_e)\bar{\omega}_e \qquad \bar{\nu}_2 = 3(1-4x_e)\bar{\omega}_e$$

$$D = 4B^3/\left(h^2\omega_e^2\right) \qquad \upsilon_m = 1/(2x_e) - 1 \qquad M = N\gamma^2 h^2 B_0/\left(16\pi^2 kT\right)$$

$$\nu = \gamma(1-\sigma)B_0/(2\pi) \qquad \bar{\nu} = 2\bar{B}(J+1) - 4\bar{D}_J(J+1)^3 - 2\bar{D}_{JK}(J+1)K^2$$

$$E_{J,K} = B\,J(J+1) + [A-B]\,K^2 \qquad E_{J,K} = B\,J(J+1) + [C-B]\,K^2$$

Question 1

a. The IR absorption spectrum of a non-linear triatomic molecule 'A' shows three strong lines at 3750 cm^{-1}, 3650 cm^{-1}, and 1600 cm^{-1}. Calculations reveal that they correspond to the excitations in asymmetric stretching, symmetric stretching, and bending modes, respectively. It is given that using the harmonic oscillator approximation, the ten (10) lowest energy vibrational levels of molecule 'A' can be labelled as (0,0,0), (0,1,0), (0,2,0), (1,0,0), (0,0,1), (1,1,0), (0,1,1), (2,0,0), (1,0,1), and (0,0,2) in order of increasing energy.

   i. Label the three equilibrium vibration frequencies (ω_e) of 'A' as $\omega_{e,1}$, $\omega_{e,2}$, or $\omega_{e,3}$.
   ii. Write an expression for the energy of a total vibrational level in terms of the quantum numbers of the set of normal modes (v_1, v_2, v_3) and the energies above.
   iii. Identify the **highest energy fundamental level** in molecule 'A'.
   iv. Identify the **lowest energy combination level** in molecule 'A'.
   v. Calculate the energy of the **ground energy level** of molecule 'A'.
   vi. Calculate the energy of the **lowest energy overtone level** of molecule 'A'.
   vii. Calculate the energy associated with the **lowest energy overtone band** in the vibrational spectrum of molecule 'A'.

   Hint: $\bar{E}(v_1, v_2, v_{3,\dots\dots}) = \sum_{k=all\ normal\ modes}\left\{\left(v_k + \frac{1}{2}\right)\bar{\omega}_{e,k}\right\}$

(50 marks)

b. Three (03) consecutive lines in the rotational spectrum of $H^{79}Br$ are observed at 84.544, 101.355 and 118.112 cm^{-1}. Assume that $H^{79}Br$ behaves as a non-rigid rotor.

   i. Assign the three (03) spectral lines to appropriate J" → J' transitions.
   ii. Determine the values of $\bar{B}$ and $\bar{D}$.

(50 marks)

Question 2

a. A hypothetical molecule 'B' has only five (05) energy levels.

   i. What is the **maximum possible number of Stokes lines** that may appear in the Raman spectrum of molecule 'B'?
   ii. Using a suitable energy level diagram, indicate **all above Stokes lines** using arrows to represent each transition.
   iii. Do you expect all energy transitions that you have indicated above to give rise to lines in the Raman spectrum of molecule 'B'? Briefly explain.

(30 marks)

b. Derive an expression for the **separation** between the **first Stokes line** and the **first anti-Stokes line**, in the pure rotational Raman spectrum of a linear molecule in terms of $\bar{B}$. If the above separation for a molecule 'C' is reported to be 3190 cm^{-1}, determine the value of $\bar{B}$ for molecule 'C'.

(40 marks)

c. Equilibrium vibration frequencies of the symmetric stretching, bending and the anti–symmetric stretching modes of H_2O, in units of cm^{-1}, are 3651, 1595 and 3756 respectively. Calculate the wavenumbers at which you expect to observe the **fundamental Stokes and anti-Stokes lines** in the vibrational Raman spectrum of H_2O obtained using radiation of 5000 cm^{-1}? (Assume H_2O to behave as a harmonic oscillator)

(30 marks)

Question 3

a. Magnetic quantum number of an electron in an antibonding molecular orbital, φ, of a homonuclear diatomic molecule is found to be equal to −3. The orbital φ has the property, $\hat{\imath}\,\varphi = -\,\varphi$, with respect to inversion, $\hat{\imath}$, through the bond midpoint. Deduce the symbol for the molecular orbital φ. Clearly show all your workings.

(20 marks)

b. In the electronic absorption spectrum of a diatomic molecule, a rotational band head is formed in the P branch. It was observed that the rotational lines corresponding to two rotational quantum numbers (J") and (J"+7) are overlapped. If the ratio B'/ B" is 1.125, determine the value of J".

(30 marks)

c. Consider a molecule 'D' of Hund's case (a) where total orbital angular momentum and total spin angular momentum are not coupled.

   i. State the selection rules applicable in the electronic spectroscopy of molecule 'D'.
   ii. Based on your answer above, state whether the electronic transition b $^1\Sigma_g^+ \leftarrow$ X $^3\Sigma_g^-$ in D is allowed. If not, state the selection rule/s that forbid the transition.

(30 marks)

d. Using a sketch of a Jablonski diagram, clearly indicate and label the electronic transitions associated with **fluorescence, phosphorescence, vibrational relaxation, internal conversion, and intersystem crossing** using arrows to indicate each type of transition.

(20 marks)

Question 4

a. Consider the molecule 1,1,2-trichloroethane ($CHCl_2$-CH_2Cl) having three (03) protons.

   i. What is the 'gross selection rule' for NMR spectroscopy?

   ii. What is/are the 'specific selection rule/s' for NMR spectroscopy?

   iii. Using α or β to denote the two possible spin state of each proton, write all the possible combinations of states that the molecule may be in.

   iv. Indicate the above spin states in a suitable energy level diagram and indicate all possible transitions using arrows to represent each transition.

   v. Based on the diagram drawn in part (ii) determine the number of peaks and their relative intensities in the NMR spectrum of 1,1,2-trichloroethane.

(50 marks)

b. A student observed a complex multiplet pattern in the NMR spectrum of a compound 'E', which he believes is due to spin–spin coupling. One of the peaks observed in the spectrum is due to the $-^{13}CH_3$ group in compound 'E'. Since the ^{13}C spin is coupled with three equivalent protons, he observed a 1:3:3:1 quartet for the ^{13}C NMR spectrum. Since, the spectrum was challenging to analyze and interpret, he decided to simplify the spectrum via the two (02) methods: (1) recording the NMR spectrum of that compound at a higher magnetic field, or (2) removing multiplet splitting by decoupling the spin–spin interaction which causes the splitting.

   i. What is the Larmor frequency of ^{13}C, if the above spectrometer is operating at a field of 15.2 T and the magnetogyric ratio of ^{13}C is 6.7283×10^7 rad s^{-1} T^{-1}?

   ii. State two (02) reasons s to how recording an NMR spectrum of a compound at a higher magnetic field would help to simplify an NMR spectrum.

   iii. State the two (02) modes in which decoupling in NMR spectra could be conducted.

   iv. Briefly describe what would happen to the quartet peak due to the $-^{13}CH_3$ group when a decoupling experiment is performed on 'E', where coupling between ^{13}C and ^1H is removed.

   v. Sketch two (02) clearly labelled NMR spectra (in the proper scale), before and after decoupling, to indicate the spectral changes that you explained in part (iv) above.

(50 marks)

-- End of examination paper --