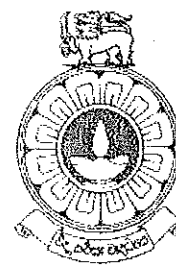


The Open University of Sri Lanka
Faculty of Natural Sciences
B.Sc/ B. Ed Degree Programme



Department	: Chemistry
Level	: 05
Name of the Examination	: Final Examination
Course Code and Title	: CYU5301/CMU3131/CME5131 Concepts in Spectroscopy
Academic Year	: 2019/2020
Date	: 5 th January 2019 (Sunday)
Time	: 9.30 a.m. – 11.30 a.m.
Duration	: 02 hours

1. Read all instructions carefully before answering the questions.
2. This question paper consists of **04** questions in **07** pages.
3. Answer **ALL 04** questions. All questions carry equal marks.
4. Answer for each question should commence from a new page.
5. Draw fully labelled diagrams where necessary.
6. Having any unauthorized documents/ mobile phones in your possession is a punishable offense.
7. Use blue or black ink to answer the questions.
8. Circle the number of the questions you answered in the front cover of your answer script.
9. Clearly state your index number in **ALL** pages of your answer script.

Some important universal constants are given below, in standard notation.

$$\begin{array}{lll}
 R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1} & N_A = 6.023 \times 10^{23} \text{ mol}^{-1} & F = 96,500 \text{ C mol}^{-1} \\
 h = 6.63 \times 10^{-34} \text{ Js} & c = 3.0 \times 10^8 \text{ ms}^{-1} & P_0 = 10^5 \text{ Pa (Nm}^{-2}\text{)} = 1 \text{ bar} \\
 e = 1.602177 \times 10^{-19} \text{ C} & \pi = 3.14159 & \text{Log}_e(X) = 2.303 \text{ Log}_{10}(X)
 \end{array}$$

Some equations used in chemistry are given below, in standard notation.

$$\begin{array}{lll}
 \nu_m = 1/(2x_e) - 1 & \nu = \gamma(1 - \sigma)B_0/2\pi & \bar{D}_e = (\nu_m + 1/2)\bar{\omega}_e - (\nu_m + 1/2)^2 x_e \bar{\omega}_e \\
 \bar{B} = h/(8\pi^2 \mu c R^2) & \bar{E}_J = \bar{B}J(J+1) - \bar{D}J^2(J+1)^2 & \bar{\nu}_J = 2\bar{B}(J+1) - 4\bar{D}(J+1)^3 \\
 \bar{\nu}_0 = (1 - 2x_e)\bar{\omega}_e & \bar{\nu}_1 = 2(1 - 3x_e)\bar{\omega}_e & \bar{E}_\nu = (\nu + 1/2)\bar{\omega}_e - (\nu + 1/2)^2 x_e \bar{\omega}_e \\
 \bar{\epsilon}_{JK} = \bar{B}J(J+1) - \bar{D}_J J^2(J+1)^2 + (\bar{C} - \bar{B})K^2 - \bar{D}_K K^4 - \bar{D}_{JK} J(J+1)K^2 \\
 \bar{\epsilon}_{JK} = \bar{B}J(J+1) - \bar{D}_J J^2(J+1)^2 + (\bar{A} - \bar{B})K^2 - \bar{D}_K K^4 - \bar{D}_{JK} J(J+1)K^2 \\
 E = -h \nu_1 m_{l_1} - h \nu_2 m_{l_2} + h J m_{l_1} m_{l_2} & \omega_e = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} & \nu = \frac{\gamma(1 - \sigma)B_0}{2\pi} \quad \nu_A = \frac{\gamma_A B_0}{2\pi}
 \end{array}$$

1. (a) Answer **either** Part (A) **or** Part (B) (but **NOT** both).

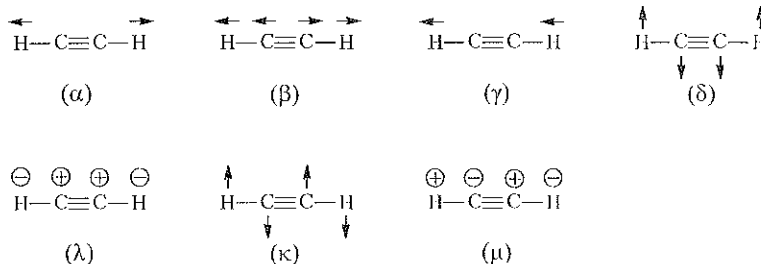
Part A

- (i) Define the following as applied in vibrational spectroscopy.

(α) Degenerate normal modes

(β) Accidental degeneracy

- (ii) The seven normal modes of an acetylene molecule are shown in the figure. Giving reasons, identify all the degenerate sets of normal modes.



- (iii) Two equilibrium vibration frequencies of a nonlinear triatomic molecule has the relationship $\omega_{e,3} = 4\omega_{e,2}$. The molecule behaves as a harmonic oscillator in each of its normal modes. Identify two accidentally degenerate vibrational energy levels of this molecule.

(40 marks)

Part B

The equilibrium vibration frequencies, corresponding to the three normal modes of a non-linear triatomic molecule, A_2B , are $\bar{\omega}_{e,1} = 3652 \text{ cm}^{-1}$, $\bar{\omega}_{e,2} = 1595 \text{ cm}^{-1}$ and $\bar{\omega}_{e,3} = 3756 \text{ cm}^{-1}$. In each normal mode A_2B behaves as a harmonic oscillator.

(i) Define the following vibrational energy *levels* of A_2B molecule.

(α) Fundamental level

(β) Overtone level

(γ) Combination level

(ii) Calculate the wave numbers corresponding to the following transitions and classify them as producing fundamental, overtone or combination *bands* in the infrared spectrum of A_2B .

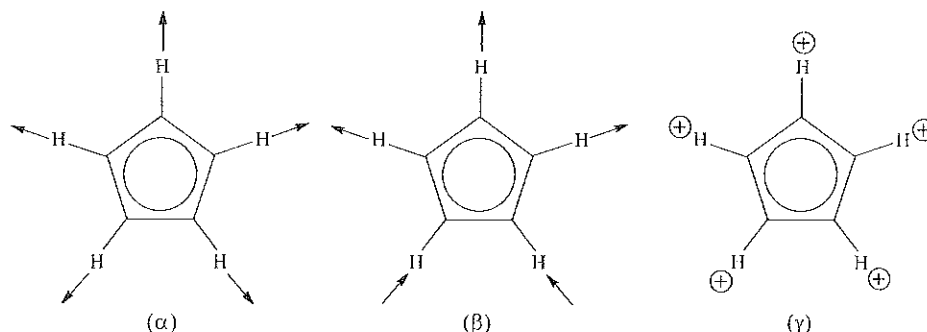
(α) $(0,0,0) \rightarrow (1,2,0)$

(β) $(0,0,0) \rightarrow (1,0,0)$

(γ) $(0,0,0) \rightarrow (0,0,3)$

(40 marks)

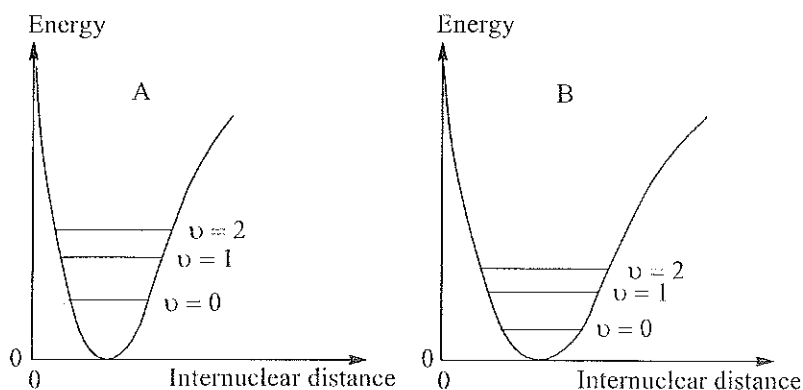
(b) Three normal modes, α , β and γ , of the planar anion, $C_5H_5^-$ (cyclopentadienyl) are shown in the following figure in standard notation.



Giving reasons identify the parallel and perpendicular normal modes.

(10 marks)

(c) Consider two diatomic molecules, A and B, having the *same* reduced mass, μ , and the *same* anharmonicity constant, x_e . The figure shows their potential energy curves on the *same* energy scale. Also shown are the first three vibrational energy levels in A and B.

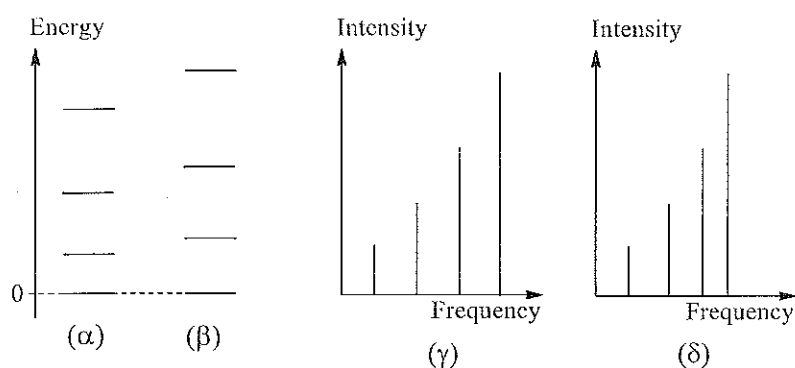


shown are the first three vibrational energy levels in A and B.

- (i) Giving reasons state the molecule (out of A and B) which has the *lower* zero point energy.
- (ii) Using relevant equations find out the molecule which has the *larger* force constant.
- (iii) Define the dissociation energies, D_e and D_0 , of a diatomic molecule.
- (iv) Write down the relationship between D_e and D_0 .
- (v) Find out, by way of deduction, whether the molecule A or molecule B has a lower D_e value.

(50 marks)

2. (a) A student calculated the first few rotational energy levels and the first four lines in the microwave spectrum of a diatomic molecule, AB, assuming it to be a rigid rotor. Another student performed



the same calculation assuming AB to be a non-rigid rotor. Their results are schematically represented in the figures (which are NOT in any particular order). [Figures, (α) and (β) represent the first four energy levels calculated by the students on the *same* energy scale.]

- (i) Out of (α) and (β) , identify the energy levels that were calculated assuming AB to be a rigid rotor. Using relevant equations, briefly explain your answer.
- (ii) Out of (γ) and (δ) , identify the spectrum generated using the energy levels in (β) . Using relevant equations, briefly explain your answer.

(40 marks)

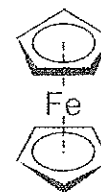
- (b) Answer **either Part (A) or Part (B)** (but NOT both).

Part A

- (i) Define the following terms as applied in rotational spectroscopy.

- (α) Spherical top
- (β) Symmetric top
- (γ) Asymmetric top

- (ii) Consider a ferrocene molecule, $\text{Fe}(\text{C}_5\text{H}_5)_2$ whose structure is shown in the figure. [It has two C_5H_5^- ions whose planes are parallel to each other. Fe^{2+} is held in the *middle* (i.e. equidistant from C_5H_5^-) on the axis passing through the centres of C_5H_5^- .] Assume it to behave as a rigid rotor.



- (α) Using symmetry of the molecule, deduce whether ferrocene is a spherical top, symmetric top or an asymmetric top.
- (β) Giving reasons state whether ferrocene can show a microwave spectrum.

(30 marks)

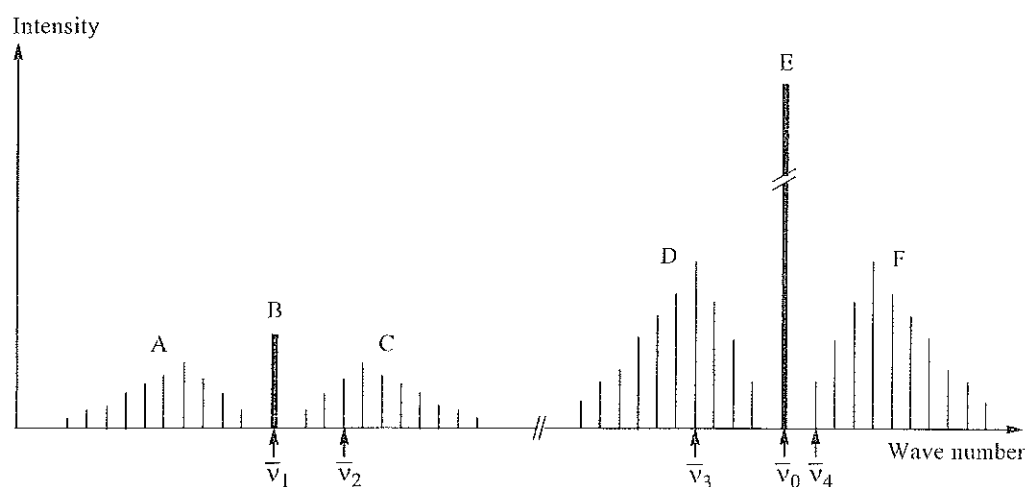
Part B

A trigonal bipyramidal molecule, MX_4Y , behaves as a non-rigid oblate symmetric top.

- (i) Write down the expression for the rotational energy of MX_4Y and identify all the parameters in it.
- (ii) Write down the specific selection rules in microwave spectroscopy of MX_4Y .
- (iii) Using the energy expression and the selection rules, deduce the maximum number of lines that may be observed in the microwave spectrum of MX_4Y due to the transition $J = 5 \rightarrow J = 6$ (where J has its usual meaning).

(30 marks)

- (c) A diatomic molecule XY behaves as an anharmonic oscillator and a rigid rotor. A student recorded its Raman spectrum using (incident) radiation with wavenumber $\bar{\nu}_0 = 19500 \text{ cm}^{-1}$. The Raman spectrum she obtained is schematically represented in the following figure. It shows the pure rotational Raman spectrum and a fundamental vibrational-rotational Raman band.

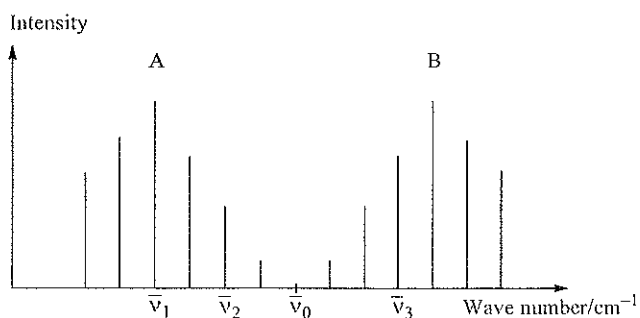


In standard notation, for XY , $\bar{\omega}_e = 384.3 \text{ cm}^{-1}$, $x_e \bar{\omega}_e = 1.5 \text{ cm}^{-1}$ and $\bar{B} = 0.2 \text{ cm}^{-1}$.

- (i) Identify the branches/lines designated by A, B, C, D, E and F in the figure.
- (ii) Calculate $\bar{\nu}_1$, $\bar{\nu}_2$, $\bar{\nu}_3$ and $\bar{\nu}_4$.

(30 marks)

3. (a) A diatomic molecule, XY, behaves as an anharmonic oscillator and a rigid rotor. Part of the fundamental band (close to the band origin) in the IR spectrum of XY is schematically represented in the figure. There



$\bar{\nu}_0 = 2886 \text{ cm}^{-1}$ is the band origin and $\bar{\nu}_2 = 2843.6 \text{ cm}^{-1}$. The anharmonicity constant, x_e , and reduced mass, μ , of XY are 0.0174 and $9.722 \times 10^{-4} \text{ kg mol}^{-1}$, respectively.

- Identify the two branches, A and B, in the spectrum.
- Calculate the equilibrium vibration frequency of XY.
- Calculate the rotational constant of XY.
- Calculate $\bar{\nu}_1$ and $\bar{\nu}_3$.
- State the rotational transitions that produce the lines at $\bar{\nu}_1$ and $\bar{\nu}_3$.
- Calculate the bond length of XY.

(40 marks)

- (b) Determine all possible electronic state/s arising out of the following electronic configuration of a particular exotic heteronuclear diatomic molecule/ion.

$$(\sigma 1s)^2 (\sigma^* 1s)^2 (\sigma 2s)^2 (\sigma^* 2s)^2 (\sigma 2p)^2 (\pi 2p)^4 (\pi^* 2p)^2.$$

(20 marks)

- (c) In standard notation, the positions of lines in the rotational fine structure in the vibronic absorption spectrum of a heteronuclear diatomic molecule is given by
- $$\bar{\nu} = (\bar{T}' - \bar{T}'') + [\bar{\omega}'_e (v' + 1/2) - \bar{\omega}''_e (v'' + 1/2)] + [\bar{B}' J' (J' + 1) - \bar{B}'' J'' (J'' + 1)].$$

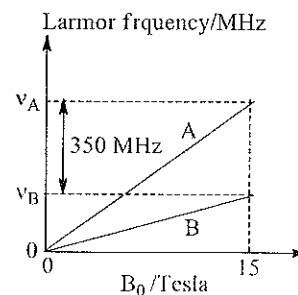
- What are the specific selection rules associated with the vibrational and rotational quantum numbers leading to rotational structure in vibronic spectroscopy?
- Briefly describe how P, Q and R branches arise in rotational fine structure in a vibronic spectrum of a heteronuclear diatomic molecule.
- Starting with the above equation deduce an equation for the position of lines in the P branch associated with a vibronic transition involving the fundamental vibrational transition (i.e. $v'' = 0 \rightarrow v' = 1$).
- A student found out that the wave numbers of the lines in the P branch of the vibronic spectrum involving the fundamental vibrational transition of a diatomic molecule could be given by the following equation.

$$\bar{\nu}_{J''}(\text{P})/\text{cm}^{-1} = 1.059(J'')^2 - 20.121 \times J'' + 5000$$

Calculate \bar{B}' and \bar{B}'' for this molecule.

(40 marks)

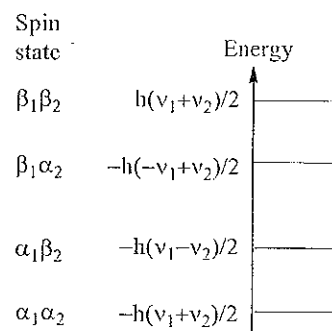
4. (a) Variation of the Larmor frequency with the applied magnetic field for two (bare) nuclei A and B are shown in the figure. The difference in Larmor frequencies at a magnetic field of 15 Tesla is, $\nu_A - \nu_B = 350$ MHz. For A, the magnetogyric ratio, $\gamma_A = 2.6752 \times 10^8 \text{ rad s}^{-1} \text{ T}^{-1}$.



- (i) Calculate ν_A .
- (ii) Calculate the magnetogyric ratio of B, γ_B .

(20 marks)

- (b) A molecule has two protons, labelled 1 and 2, in two different chemical environments. In an NMR spectrometer of magnetic field strength B_0 , their Larmor frequencies are ν_1 and ν_2 , respectively, with $\nu_1 > \nu_2$. The figure shows the energy levels of this two spin system when the spins are **NOT** scalar coupled.



- (i) What is the specific selection rule in NMR spectroscopy of this two spin system?
- (ii) Copy the energy level diagram on to your answer script and (using vertical arrows as usual) indicate possible transitions that gives rise to lines in the NMR spectrum. State the possible *number* of transitions.
- (iii) Using your answer in (ii) above, show that the possible transitions gives rise to two lines in the NMR spectrum at frequencies ν_1 and ν_2 .
- (iv) Now assume that the two spins form an AX system and are coupled with a scalar coupling constant, J . Then, in standard notation, the energy of the two spin system is given by $E = -h\nu_1 m_{I_1} - h\nu_2 m_{I_2} + hJ m_{I_1} m_{I_2}$.
- (α) On the energy level diagram you have drawn in (ii), draw the energy levels when coupling is present.
- (β) On the energy level diagram draw the transitions that can give lines in the NMR spectrum.
- (γ) Using your answer to part (β) show that each line appearing at ν_1 and ν_2 , when there is no coupling, is now split into two (forming a doublet).
- (δ) Show that the frequency separation between the two lines formed in each doublet is J .

(60 marks)

- (c) Indicating the frequencies at lines/peaks sketch the NMR spectra resulting from the following Free Induction Decay (FID) signals on an intensity versus frequency diagram. (The time, t , in the following expressions is in seconds.)

- (i) $f(t) = 10.3 \times \exp(-8.3t) \times \sin(15\pi t)$
- (ii) $f(t) = 14.0 \times \exp(-16.0t) \times \sin(16\pi t) - 9.2 \times \sin(10\pi t)$

(20 marks)