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00140

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

Department	: Chemistry
Level	: 5
Name of the Examination	: Final Examination
Course Code and Title	: CYU5301, Concepts in Spectroscopy
Academic Year	: 2020/2021
Date	: 17/12/2021
Time	: 09.30 a.m.- 11.30 a.m.
Duration	: 2 hours
Index number	:

General Instructions

1. Read all instructions carefully before answering the questions.
2. This question paper consists of 4 essay questions in 11 pages.
3. Answer all questions.
4. Use the spectra given in pages 10 and 11 to answer the question number 03 and attach both pages with your answer script.
5. Answer for each essay question should commence from a new page
6. Non programmable calculators are permitted.
7. Having any unauthorized documents/ mobile phones in your possession is a punishable offense.
8. Use blue or black ink to answer the questions.
9. Circle the number of the questions you answered in the front cover of your answer script.
10. Clearly state your index number in your answer script.

Gas constant (R)	=	$8.314\ J\ K^{-1}\ mol^{-1}$
Avogadro constant (N_A)	=	$6.023 \times 10^{23}\ mol^{-1}$
Faraday constant (F)	=	$96{,}500\ C\ mol^{-1}$
Planck constant (h)	=	$6.63 \times 10^{-34}\ J\ s$
Velocity of light (c)	=	$3.0 \times 10^{8}\ m\ s^{-1}$
Standard atmospheric pressure	=	$10^5\ Pa\left(N m^{-2}\right)$
π	=	3.14159
$Log_e(X)$	=	$2.303\ Log_{10}(X)$

Some equations used in spectroscopy are given below in standard notation.

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

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

$$\bar{E}_{JK} = BJ(J+1) + (A-B)K^2 - D_J J^2 (J+1)^2 - D_{JK} J(J+1)K^2 - D_K K^4$$

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

$$E(\upsilon_1, \upsilon_2, \upsilon_3, \ldots) = \sum_{\substack{k = \text{All} \\ \text{normal} \\ \text{modes}}} h\left(\upsilon_k + \frac{1}{2}\right)\omega_{e,k} + \sum_{j \le k} h\, x_{jk}\left(\upsilon_j + \frac{1}{2}\right)\left(\upsilon_k + \frac{1}{2}\right) + h\, G_0$$

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

Part A

Copy the following table onto your answer script and fill out with appropriate values of the quantities (indicated in the first column) for the molecules (indicated in the first row) in their gaseous phase.

Quantity to be evaluated \ Molecule		He	Br_2	BF_3	C_{60}
(i)	Number of nuclei				
(ii)	Total number of degrees of freedom				
(iii)	Translational degrees of freedom				
(iv)	Rotational degrees of freedom				
(v)	Number of normal modes				

(24 marks)

Part B

A diatomic molecule, **AB**, behaves as an **anharmonic oscillator**.

(i) Sketch the potential energy curve for **AB** on a potential energy versus internuclear distance diagram and do the following on the same diagram.

(a) Using horizontal lines sketch the first four vibrational energy levels (the variation in relative separation of the energy levels should be visible)

(b) Using vertical arrows sketch the transitions corresponding to the fundamental and 2^{nd} overtone and label them

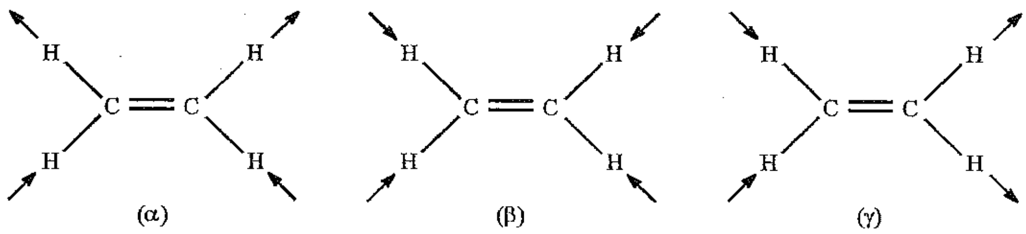
(c) Using double arrows, indicate the zero point energy, energy corresponding to the dissociation energies, D_0 and D_e, and label them

(ii) The equilibrium vibration frequency and the anharmonicity constant of AB are $2990\ cm^{-1}$ and 0.074 respectively.

Calculate the difference between D_0 and D_e for AB in units of cm^{-1}.

(24 marks)

(b) Three normal modes, (α), (β) and (γ), of C_2H_4 molecule are shown in the following figure.



(i) Giving reasons identify these normal modes as parallel or perpendicular.

(ii) Giving reasons identify the normal modes which can show an infrared spectrum.

(26 marks)

(c) In standard notation the vibrational parameters for a water molecule are given, in units of cm^{-1}, as follows.

$$\omega_{e,1} = 3832.2 \quad \omega_{e,2} = 1648.5 \quad \omega_{e,3} = 3942.5$$

$$x_{11} = -42.6 \quad x_{22} = -16.8 \quad x_{33} = -47.6$$

$$x_{12} = -15.9 \quad x_{13} = -165.8 \quad x_{23} = -20.3$$

$$G_0 = 1.6$$

Consider the four vibrational energy levels (0,0,0), (0,0,2), (1,1,0), and (0,1,0).

(i) Identify the above levels as fundamental, overtone, ground, combination etc. levels.

(ii) Calculate the energy of each level, (0,0,0), (0,0,2), and (1,1,0) in units of cm^{-1}

(iii) Calculate the wavenumbers of photons that bring about the following transitions.

$$(\alpha) \quad (0,0,0) \rightarrow (1,1,0) \qquad (\beta) \quad (1,1,0) \rightarrow (0,0,2)$$

(iv) Identify the spectra due to each of the above transitions as fundamental, overtone, combination etc. bands.

(50 marks)

02. (a) In standard notation, the rotational energy levels (in wavenumber units) of a heteronuclear diatomic molecule are given by the equation $\bar{E}_J = \bar{B}J(J+1) - \bar{D}J^2(J+1)^2$

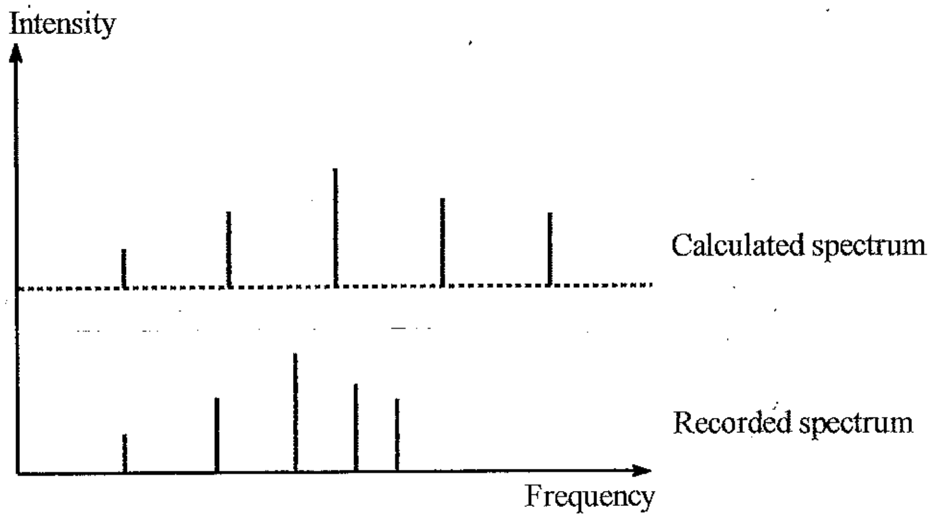
(i) Identify all the parameters in the above equation.

(ii) What is the selection rule in the microwave spectroscopy of this molecule ?

(iii) Derive an expression for the position of lines in the microwave spectrum of the molecule.

(25 marks)

(b) Following diagram indicates the first 5 lines in the microwave spectrum of a real diatomic molecule recorded by a student in intensity versus frequency graph. The positions of the same lines calculated by the student, assuming the molecule to behave as a rigid rotor, are also indicated in the same graph (in the same frequency scale). Explain difference in frequency of the corresponding lines in the two spectra.



(20 marks)

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

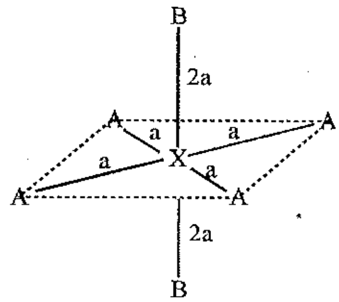
Part A

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

(A) Prolate symmetric top molecule

(B) Oblate symmetric top molecule

(ii) A molecule of *trans*-XA_4B_2 has a square bipyramidal structure (see the figure). X-A and X-B bond lengths are a and 2a respectively. The atomic mass of B is larger than the atomic mass of A. By calculating appropriate moments of inertia, deduce whether *trans*-XA_4B_2 is a prolate symmetric top or an oblate symmetric top.



(25 marks)

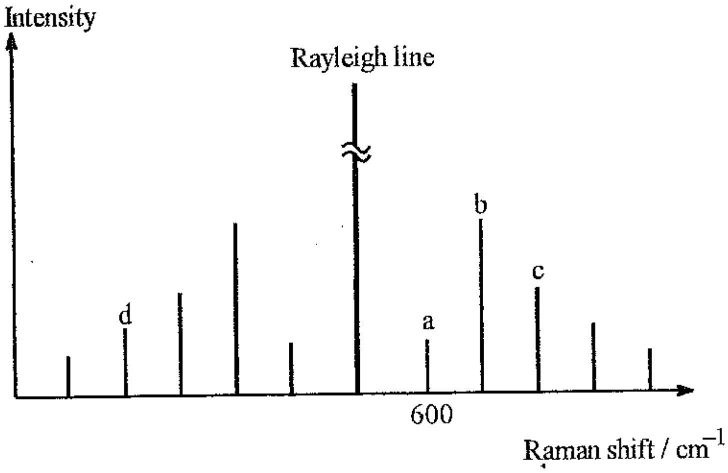
Part B

(i) Briefly describe how the P, Q and R branches in the IR spectrum of a linear polyatomic molecule arise.

(ii) Explain why the IR spectrum of the bending mode of HCN shows P, Q and R branches and the IR spectrum of the symmetric stretching mode of HCN shows only P and R branches.

(25 marks)

(d) The pure rotational Raman spectrum of a diatomic molecule is schematically represented in the following figure. The Raman shift of the spectral line a is $600\ \text{cm}^{-1}$.



(i) Write down (no proof required) the relationship between the Raman shift of the spectral line a and the rotational constant, B, of the molecule.

(ii) Calculate the rotational constant of the molecule.

(iii) Giving reasons (no derivation of equations is required) calculate the Raman shift of the spectral line b.

(iv) Giving reasons (no derivation of equations is required) calculate the Raman shift of the spectral line d.

(30 marks)

03. (a) Consider the ionic and molecular species, N_2^+, N_2 and N_2^- in their ground states.

(i) Write down the electronic configuration for each species.
Hint: The order of increasing energy of molecular orbitals (except in O_2 and F_2) is :

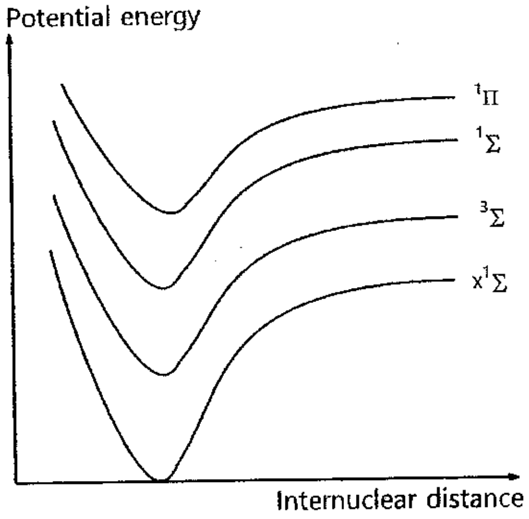
$$\sigma\ 1s < \sigma^*1s < \sigma\ 2s < \sigma^*\ 2s < \pi\ 2p < \sigma\ 2p < \pi^*\ 2p < \sigma^*\ 2p$$

(ii) Calculate the bond order of each of the above molecule/ion.

(iii) Write down the spin multiplicity of each of the above molecule/ion.

(40 marks)

(b) Potential energy curves for electronic states of a heteronuclear diatomic molecule are given below. **The ground electronic state is labelled with the letter X.**



(i) Sketch all the allowed electronic transitions **originating from the ground state** on the spectrum given in ***page 10*** (make sure to attach it to your answer script)

(ii) Sketch all the **forbidden** electronic transitions on the spectrum given in ***page 11***. state the selection rule/s that is/are violated for the forbidden electronic transitions. (Consider all possible forbidden electronic transitions, make sure to attach your answer sheet to the answer script)

(60 marks)

04. (a) Consider N_1 mol of ethyl alcohol molecules (CH_3CH_2OH) at temperature T_1 placed in a uniform magnetic field of strength B_1. Under these conditions the difference in the number of methyl protons in α and β nuclear spin states in this sample is M_1.

(i) State whether the difference in the number of methyl protons in α and β nuclear spin states in the above mentioned sample become larger, smaller or remain at M_1 when the magnetic field strength is increased keeping the temperature constant at T_1.

(ii) Briefly explain your answer in part a (i) above using relevant equations.

(40 marks)

(b) The δ scale of chemical shift is defined by the equation,

$$\delta = \frac{\nu_{Sample} - \nu_{Reference}}{\nu_0} \times 10^6$$

(i) Identify all the parameters in the above equation.

(ii) Write down the relationship between Larmor frequency of a nucleus and the shielding constant and identify all the parameters in it.

(iii) Show that the chemical shift of a particular nucleus on δ scale is independent of the strength of the static magnetic field, B_0, of the NMR spectrometer.

(iv) Explain why the chemical shift on δ scale has to be negative for nuclei which are more shielded than the nuclei in the reference.

(30 marks)

(c) A student recorded the NMR spectrum of methyl protons in ethyl alcohol (CH_3CH_2OH), in duplicate. In both recordings, A and B, he took the same amount of alcohol from the same bottle, added a little TMS in sample and inserted into the same NMR spectrometer. **Sketch** the spectra (A and B) separately, that he recorded (at the same temperature) schematically. Please note the following in constructing your spectra: (a) Both spectra recorded on the same scale (b) student accidentally added little excess of TMS in sample B compared to sample A.

(30 marks)

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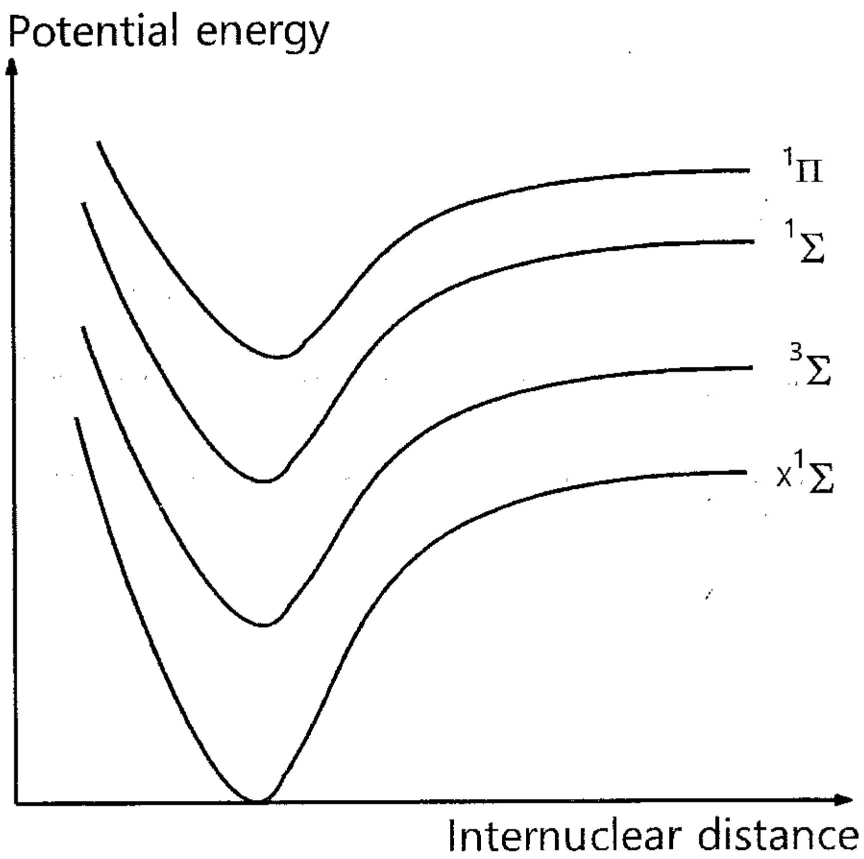
(03)

b

(i)



Name: …………………………..

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(03)

b

(ii)