

## THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Final Examination — 2010/2011

CHU 3128/CHE 5128 — Special Topics in Spectroscopy

(2½ hours)

14<sup>th</sup> December 2010 (Tuesday)

9.30 am — 12.00 noon

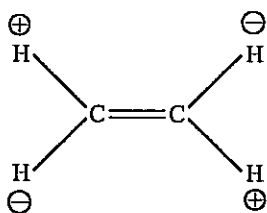
- There are six (06) questions and eight (08) pages (including the first page) in the paper.
- Answer any 04 (Four) questions. If more than 04 questions are answered only the first 04 answers, *in the order they are written in the answer script*, will be marked.
- Use of a non-programmable calculator is permitted
- Cellular phones are not allowed.

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Gas constant (R)	=	8.314 J K <sup>-1</sup> mol <sup>-1</sup>
Avogadro constant (N <sub>A</sub> )	=	6.023 × 10 <sup>23</sup> mol <sup>-1</sup>
Faraday constant (F)	=	96,500 C mol <sup>-1</sup>
Planck constant (h)	=	6.63 × 10 <sup>-34</sup> J s
Velocity of light (c)	=	3.0 × 10 <sup>8</sup> m s <sup>-1</sup>
Standard atmospheric pressure	=	10 <sup>5</sup> Pa (Nm <sup>-2</sup> )
π	=	3.14159
Log <sub>e</sub> (X)	=	2.303 Log <sub>10</sub> (X)

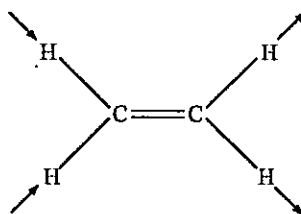
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1. (a) Indicate the number of normal modes in the following molecules/ion.  
 (i)  $C_{60}$  (buckyball)    (ii)  $C_{10}H_8$  (naphthalene)    (iii)  $C_5NH_5$  (pyridine)  
 (iv)  $C_2H_2$  (acetylene)    (v)  $NH_4^+$  (ammonium ion) (10 marks)
- (b) In standard notation, sketch the normal modes of a water molecule and identify them as symmetric stretching etc. (10 marks)
- (c) (i) State the gross selection rule in IR spectroscopy of molecules.  
 (ii) A *twisting* normal mode ethylene is indicated in the following figure (in standard notation).



CCH and HCH bond angles remain the same during vibration in this mode.

- (α) State why it is called a *twisting* mode?  
 (β) Giving reasons state whether it is IR active or not. (25 marks)
- (d) (i) Define the following as applied in IR spectroscopy.  
 (α) Parallel vibration  
 (β) Perpendicular vibration.  
 (ii) A stretching normal mode of ethylene is indicated in the following figure (in standard notation).



Giving reasons, state whether it is a parallel mode or a perpendicular mode.

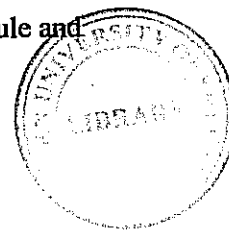
- (25 marks)
- (e)  $H^{35}Cl$  behaves as an anharmonic oscillator with  $\bar{\omega}_e = 2990 \text{ cm}^{-1}$  and  $x_e = 0.0174$  (with the symbols having their usual meaning).  
 (i) Write down an expression for the vibrational energy levels of  $H^{35}Cl$  in terms of  $\bar{\omega}_e$  and  $x_e$ , and identify all the parameters in it.

**[Question 1 is continued in the next page]**

(ii) Sketch the potential energy versus bond length of a  $\text{H}^{35}\text{Cl}$  molecule and indicate, on it, the dissociation energies,  $D_e$  and  $D_0$ .

(iii) Write down the mathematical relationship between  $D_e$  and  $D_0$ .

(iv) Calculate  $D_e$  of  $\text{H}^{35}\text{Cl}$  (in Jules) if  $D_0 = 8.2341 \times 10^{-19} \text{ J}$ .



(30 marks)

2. (a) Consider a polyatomic molecule with molecular formula,  $\text{XY}_3$ . Giving reasons suggest a structure for this molecule that

(i) shows a microwave spectrum.

(ii) does not show a microwave spectrum.

(10 marks)

(b) (i) Briefly describe what is meant by a principal moment of inertia of a molecule.

(ii) What is the relationship among the three principal moments of inertia,  $I_a$ ,  $I_b$  and  $I_c$  of a molecule.

(iii) Giving an example each, define the following as applied in molecular spectroscopy.

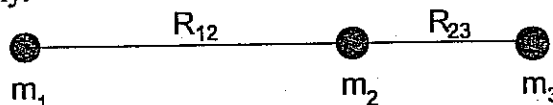
(α) Spherical top.

(β) Symmetric top.

(γ) Asymmetric top.

(30 marks)

(c) Consider the rigid linear triatomic molecule shown in the following figure where  $m_i$  and  $R_{ij}$  indicate the mass of the  $i^{\text{th}}$  nucleus and the distance between the  $i^{\text{th}}$  and  $j^{\text{th}}$  nuclei, respectively.



(i) Show that the moment of inertia,  $I$ , of the molecule about an axis that is perpendicular to the molecular axis and passing through the centre of mass of the molecule is given by

$$I = \frac{m_1 m_2 R_{12}^2 + m_1 m_3 R_{13}^2 + m_2 m_3 R_{23}^2}{m_1 + m_2 + m_3}$$

(ii) Write down the relationship between the rotational constant,  $B$ , of the molecule and  $I$ .

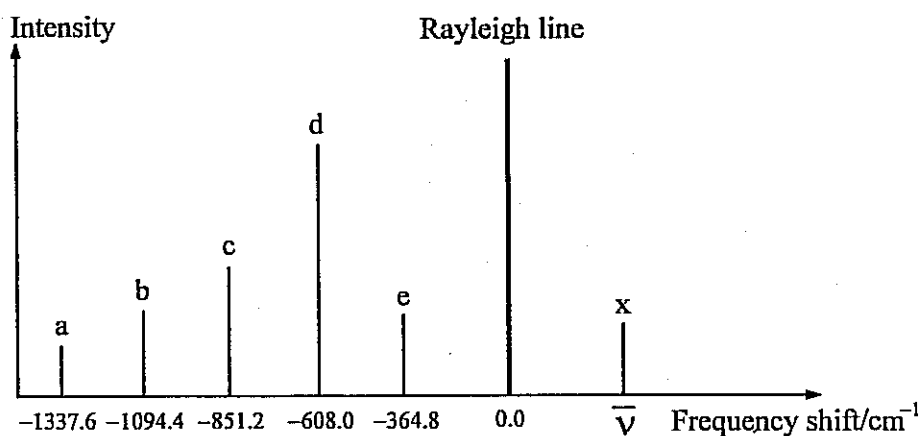
(iii) Write down the equation that relates the rotational energy of such a molecule to the rotational constant and rotational quantum number,  $J$ .

(iv) What is the specific selection rule in the microwave spectroscopy of such a molecule?

[Question 2 is continued in the next page]

- (v) Derive an equation for the positions (frequencies) of lines in the microwave spectrum of such a molecule starting with the equation mentioned in part (iii) above.
- (vi) CO and CS bond lengths in OCS are 0.1165 nm and 0.1158 nm respectively. Calculate the frequency of the line in the microwave spectrum of OCS due to the transition,  $J = 1 \rightarrow J = 2$ .  
State assumptions, if any, you make in the above calculation.  
[Relative atomic masses: O = 16, C = 12, S = 32]
- (60 marks)
3. Consider a diatomic molecule which behaves as a harmonic oscillator and a non-rigid rotor.
- (a) Write down a mathematical expression for the vibration-rotation energy levels of the molecule and identify all the terms in it.  
(10 marks)
- (b) Write down the specific selection rules for the vibration-rotational energy transitions.  
(06 marks)
- (c) Briefly describe how the P and R-branches in the IR spectrum of the molecule is created.  
(14 marks)
- (d) Derive expressions for the positions of lines in the P and R-branches in the IR spectrum of the molecule under Born-Oppenheimer approximation.  
(20 marks)
- (e) A series of adjacent lines in the fundamental band in the vibration-rotation spectrum of  $\text{H}^{35}\text{Cl}$  are located at wavenumbers (in  $\text{cm}^{-1}$ ) 3054.018, 3033.212, 3012.166, 2969.834, 2948.788, 2927.982.
- (i) Giving reasons deduce the position (in  $\text{cm}^{-1}$ ) of the band origin.
- (ii) Out of the above given set of lines identify the lines in the P branch and those in the R branch.
- (iii) Calculate the rotational constant and the centrifugal distortion constant of  $\text{H}^{35}\text{Cl}$ , in Born-Oppenheimer approximation, using the lines in the P branch.  
(50 marks)

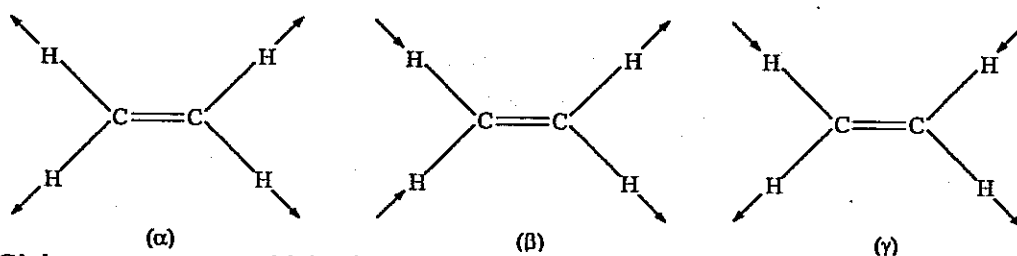
4. (a) (i) Describe what a Polaroid is. State how to keep it with respect to a beam of radiation when using for the intended purpose.
- (ii) In a spectroscopy lab a student found an old light source. A label on it stated that it gives out a parallel, plane polarized beam. The student also found a Polaroid. Briefly describe how the student could verify whether the source gives out a plane polarized beam or not using the Polaroid.
- (20 marks)
- (b) Consider a  $H_2$  molecule which behaves as a rigid rotor.
- (i) Write down an expression for its rotational energy levels of  $H_2$  and identify all the terms in it.
- (ii) Write down the specific selection rules in the pure rotational Raman spectroscopy of  $H_2$ .
- (iii) Derive an expression for the Raman shift of Stokes lines in the pure rotational Raman spectrum of  $H_2$ .
- (iv) Deduce an expression for the frequency separation between the first Stokes line and the first Anti-Stokes line in the pure rotational Raman spectrum of  $H_2$ .
- (v) Some adjacent lines in the observed pure rotational Raman spectrum of  $H_2$  is schematically represented in the following diagram.



- (α) Identify the Stokes and anti-Stokes lines in the above spectrum.
- (β) Determine the rotational constant of  $H_2$ .
- (γ) Determine the frequency shift,  $\bar{\nu}$ , of line x in the above spectrum.
- (60 marks)

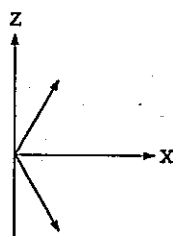
**[Question 4 is continued in the next page]**

(c) Three vibrational normal modes of ethylene are shown below.



Giving reasons state which of the above mode/s will give a polarised anti-Stokes band.

- (20)
5. (a) All allowed orientations of the spin vector of a proton are sketched in the following diagram. Similarly sketch all the allowed orientations of the spin vector of a magnetic nucleus with the spin quantum number  $I = 3/2$ .



(10 marks)

(b) (i) Define an AMX spin system.

(ii) A molecule has three chemically equivalent groups ( $G_1$ ,  $G_2$  and  $G_3$ ) of magnetic nuclei of the same atomic species with the nuclear spin quantum number  $I = 3/2$ . Groups  $G_1$ ,  $G_2$  and  $G_3$  have 2, 3 and 4 nuclei each, respectively. The nuclei satisfy the conditions of an AMX spin system in a particular NMR spectrometer. The highest shielded nuclei are in  $G_3$  and the lowest shielded nuclei are in  $G_1$ . There are no other magnetic nuclei in the molecule. The Larmor frequencies of nuclei in groups  $G_1$ ,  $G_2$  and  $G_3$ , in the spectrometer, are  $\nu_1$ ,  $\nu_2$  and  $\nu_3$  respectively. In standard notation, the scalar coupling constants are  $J_{12}$ ,  $J_{13}$  and  $J_{23}$ . Sketch the high resolution NMR spectrum of the molecule, on an intensity versus frequency diagram, recorded when the sample is simultaneously irradiated with radio waves of frequency  $\nu_3$ .

Label the multiplets using the relevant group label  $G_1$ ,  $G_2$  or  $G_3$ .

Clearly indicate the relevant chemical shifts and the separation in adjacent lines in each multiplet on the diagram.

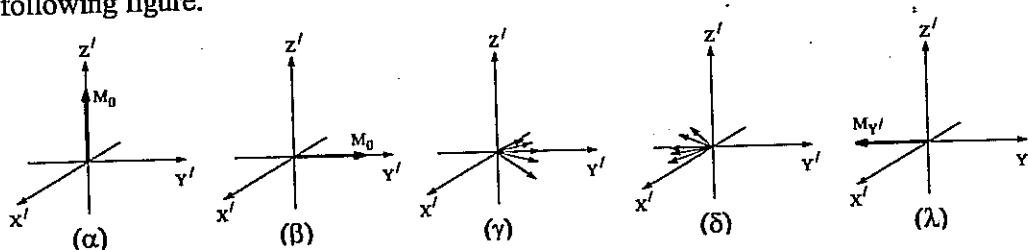
Disregard the variation of intensity of lines and use lines of the same height in sketching the spectrum.

Briefly explain your answer

(25 marks)

**[Question 5 is continued in the next page]**

- (c) (i) Define the  $\delta$  scale for chemical shifts using a mathematical expression and identify all the parameters in it.
- (ii) In general the resonance frequency of magnetic nucleus placed in an NMR spectrometer depends on the strength of the static magnetic field,  $B_0$ . However, show that the chemical shift expressed in  $\delta$  scale is independent of  $B_0$ .  
(25 marks)
- (d) Define the following terms as applied in NMR spectroscopy.
- (i) Longitudinal relaxation
- (ii) Transverse relaxation.  
(10 marks)
- (e) The behavior of the macroscopic magnetization and individual spins in the rotating frame during a pulse–delay sequence in a spin echo experiment of a magnetic nucleus in a particular environment is sketched (in standard notation) in the following figure.



- (i) Indicate the pulse–delay sequence (e.g.  $180^\circ_{y'}$  pulse – delay  $\tau$  –  $90^\circ_{x'}$  pulse – ....) involved in going from  $(\alpha) \rightarrow (\beta) \rightarrow (\gamma) \rightarrow (\delta) \rightarrow (\lambda)$ .
- (ii) Explain why the components of spins fan out when going from  $(\beta) \rightarrow (\gamma)$ .
- (iii) Explain why the components of spins come together when going from  $(\delta) \rightarrow (\lambda)$ .  
(30 marks)
6. (a) State the Frank-Condon principle. How would you apply this principle in electronic spectroscopy?  
(20 marks)
- (b) (i) What is the selection rule governing vibrational transitions?
- (ii) Consider the vibrational coarse structure in an electronic transition of a diatomic molecule. Explain why the above selection rule is not strictly applied during electronic-vibrational transitions.
- (iii) Sketch all the vibrational transitions that honour (obey) the above selection rule and occur from  $n'' = 0, 1, 2, 3$  to  $n' = 0, 1, 2$  during an electronic transition in a diatomic molecule, where  $n''$  represents vibrational states in the ground electronic state and  $n'$  represents the vibrational states in the excited electronic state. Copy the following table and fill in the blanks with respect to the above transitions.

[Question 6 is continued in the next page]

$n'$	$n''$	$\Delta n$ for the transition

(40 marks)

- (c) Vibrational energy (including corrections for anharmonicity) can be given in wave number terms as,  $G(n) = (n + 1/2)\omega_e - (n + 1/2)^2\omega_e x_e$  where all the symbols have their usual meanings. Following table gives the absorption wave numbers in the vibrational coarse structure of the electronic spectrum of carbon monoxide.

$n'$ (excited electronic state)	$n''$ (ground electronic state)	Absorption wave number ( $\text{cm}^{-1}$ )
0	0	64758
1	0	66234
2	0	67682
3	0	69089
4	0	70467

Use above data (deriving necessary equations) to calculate the bond anharmonicity constant ( $x_e$ ) and  $\omega_e$  for carbon monoxide.

(40 marks)