



## THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Final Examination — 2014/2015

CHU 3128/CHE 5128 — Special Topics in Spectroscopy

(2 hours)

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17<sup>th</sup> October 2015 (Saturday)

1.30 p.m. — 3.30 p.m.

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- There are **six (06) questions** and **six (06) 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.
  - The use of a non-programmable calculator is permitted
  - Mobile 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 (N m <sup>-2</sup> )
π	=	3.14159
Log <sub>e</sub> (X)	=	2.303 Log <sub>10</sub> (X)

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1. (a) Consider a heteronuclear diatomic molecule whose variation of potential energy as a function of internuclear distance is given by the Morse function. Sketch the curve of potential energy versus internuclear distance for the molecule. Indicate the *dissociation limit*, *ground energy level* and the *dissociation energies*  $D_e$  and  $D_0$  on the sketch you have drawn.

(10 marks)

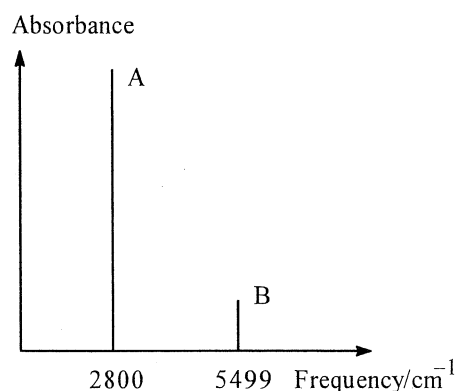
- (b) In standard notation the vibrational energy (in wavenumber units) of the diatomic molecule mentioned in part (a) above, is given by the following expression.

$$\bar{E}_v = \left( v + \frac{1}{2} \right) \bar{\omega}_e - \left( v + \frac{1}{2} \right)^2 x_e \bar{\omega}_e$$

- (i) Identify all the parameters in the above energy expression.  
 (ii) What is the selection rule in IR spectroscopy of the molecule?  
 (iii) Using the energy level expression and the selection rule, derive an expression for the wavenumber of the absorbed radiation due to a vibrational excitation originating from the ground state. [Hint:  $v = n$  for the excited state]  
 (iv) Deduce expressions for the wavenumbers of the fundamental and the first overtone from the expression you have derived in part (iii) above.

(30 marks)

- (c) At room temperature, the full pure vibrational spectrum of the molecule mentioned in part (a) above, recorded by a student shows only two lines as indicated in the figure.

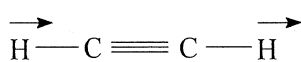


- (i) Giving reasons, identify the lines using standard nomenclature (fundamental and overtones etc.) and indicate the vibrational energy level transitions involved in producing each of these lines. (Assume that the student has not made any errors in recording the spectrum).

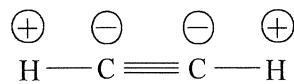
- (ii) Calculate  $x_e$  and  $\bar{\omega}_e$  for the molecule.

(40 marks)

- (d) Two vibrational normal modes of acetylene molecule are represented in standard notation in the following diagrams. Giving reasons identify each of them as a parallel or a perpendicular mode.



( $\delta$ )

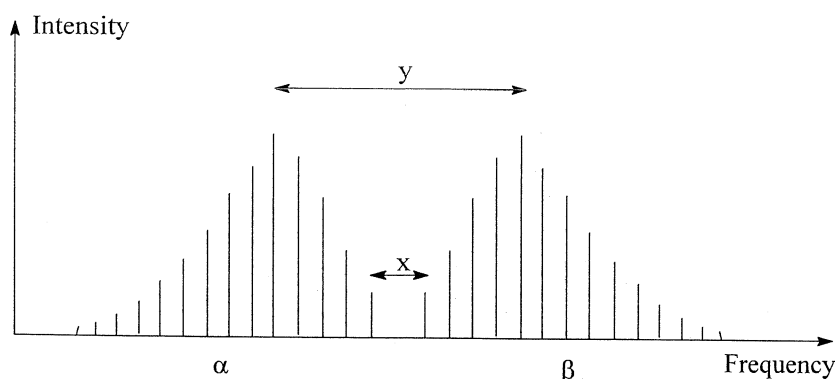


( $\lambda$ )

(20 marks)

2. (b) (i) Define the following terms as applied in rotational spectroscopy of molecules.  
 ( $\alpha$ ) Prolate symmetric top  
 ( $\beta$ ) Oblate symmetric top  
 (20 marks)
- (ii) Consider a  $\text{BCl}_3$  molecule.  
 ( $\alpha$ ) Derive an expression for the moment of inertia of  $\text{BCl}_3$  about its  $C_3$  axis and a  $C_2$  axis in terms of the masses of Cl, B-Cl bond length and the Cl-B-Cl bond angle.  
 ( $\beta$ ) deduce whether  $\text{BCl}_3$  is an oblate spherical top or a prolate spherical top.  
 (30 marks)
- (c) (i) Write down the relationship between the rotational energy and the rotational quantum number of a real diatomic molecule and identify all the terms in it.  
 (ii) State the specific selection rule in microwave spectroscopy of such a diatomic molecule.  
 (iii) Deduce an expression for the positions of lines in the microwave spectrum of such a molecule.  
 (iv) For  $\text{CuBr}$ , the  $J = 14 \leftarrow 13$  and  $15 \leftarrow 14$  transitions occur at 84421.34 MHz and 90449.25 MHz respectively. Calculate the rotational constant and the centrifugal distortion constant of  $\text{CuBr}$ .  
 (50 marks)

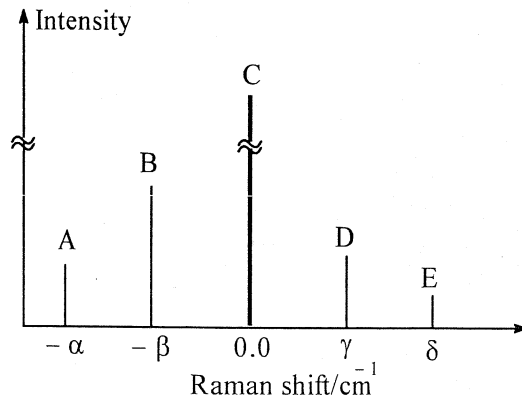
3. (a) Giving an example in each, define the following terms as applied in molecular spectroscopy.  
 (i) parallel vibration                      (ii) perpendicular vibration  
 (24 marks)
- (b) The first overtone band in the high resolution IR spectrum of a gaseous diatomic molecule, which behaves as a rigid rotor, is shown below where  $x = 12.0 \text{ cm}^{-1}$  is the separation between the first line in branch  $\alpha$  and the first line in branch  $\beta$ .



- (i) Identify the branches  $\alpha$  and  $\beta$  in standard nomenclature.  
 (ii) Calculate the value of  $y$ , separation between the lines with highest intensity in the two branches.  
 (iii) Estimate the temperature of the sample of molecules used in obtaining the above spectrum.

(76 marks)

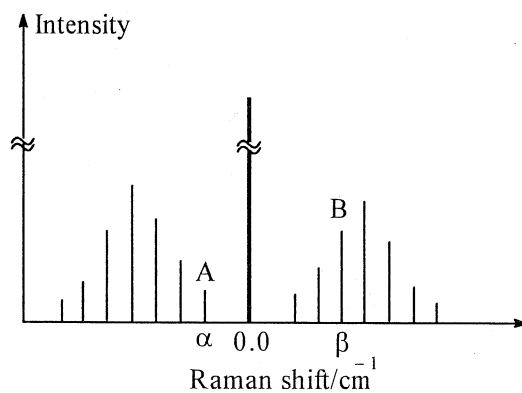
4. (a) Pure vibrational Raman spectrum corresponding to the fundamental and first overtone transitions of a diatomic molecule are schematically represented in the figure. The lines are designated as A, B, C, D and E. The Raman shifts are denoted by  $-\alpha$ ,  $-\beta$ ,  $\gamma$  and  $\delta$ .



- Identify the line with zero Raman shift (i.e. line C).
- Identify the lines A, B, D and E as Stokes and anti-Stokes lines.
- State the relationship between  $\beta$  and  $\gamma$ .
- State the relationship between  $\alpha$  and  $\delta$ .
- Giving reasons identify the lines corresponding to the fundamental and first overtone transitions, respectively.
- State the approximate relationship between ( $\alpha$  and  $\beta$ ).

(30 marks)

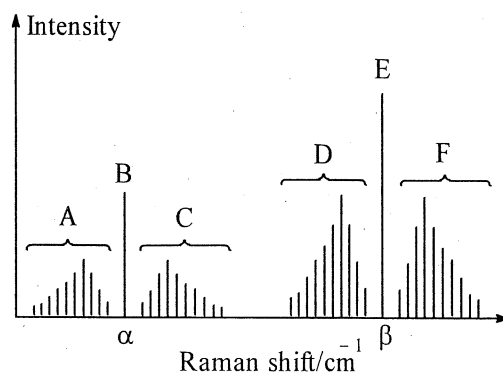
- (b) Pure rotational Raman spectrum of a diatomic molecule (which behaves as a rigid rotor) is schematically represented in the figure. There,  $\alpha$  and  $\beta$  are the Raman shifts of the lines A and B respectively and  $\alpha = -120$ .



- State the specific selection rule in pure rotational Raman spectroscopy.
- Starting with the expression for rotational energy levels of the diatomic molecule derive an expression for  $\alpha$  in terms of the rotational constant.
- Determine the rotational constant of the diatomic molecule.
- Derive an expression for the separation between adjacent anti-Stokes lines.
- Determine  $\beta$ .

(35 marks)

- (c) Two consecutive bands (with rotational fine structure) corresponding to the fundamental and the first overtone in the vibration-rotation Raman spectrum of a diatomic molecule are schematically represented in the figure. Raman shifts  $\alpha$  and  $\beta$  has the relationship,  $\alpha < \beta$ .



- (i) Giving reasons identify the sets of lines corresponding to the fundamental and the first overtone transitions respectively.
- (ii) Giving reasons state whether the lines in the spectrum in the figure are Stokes lines or anti-Stokes lines.
- (iii) Giving reasons identify the branches A, C, D and F as O, P, Q, R, S etc.

(35 marks)

5. (a) The energy of an unshielded nucleus (or a subatomic particle) placed in a magnetic field is given by  $E = -\gamma \left( \frac{h}{2\pi} \right) m_I B_0$ . Identify all the terms in this expression.

(15 marks)

- (b) A scientist investigates the possibility of neutron spin resonance and has available a commercial NMR spectrometer with a variable applied magnetic field.
- (i) Deduce the number of nuclear magnetic energy levels of a neutron placed in this spectrometer?
- (ii) What are the specific selection rules?
- (iii) Calculate the strength of the magnetic field for resonance at 300 MHz.
- (iv) Calculate the lowest energy of a neutron under resonance conditions.

[ For a neutron  $I = 1$  and  $\gamma = -1.831 \times 10^8 \text{ rad s}^{-1} \text{ T}^{-1}$  ]

(60 marks)

- (c) Clearly indicating the frequencies, sketch the Fourier transform of  $f(t) = 2.5 \times \sin(9\pi t) + 5.2 \times \exp(-9.3t)$  in intensity versus frequency plot.

(25 marks)

6. (a) Write down the occupation of molecular orbitals in the ground state of  $\text{He}_2^+$  molecular ion.

(10 marks)

- (b) The equation given below can be used to calculate the energy absorbed during an electronic transition.

$$\Delta E = \Delta E_E + \left( n' + \frac{1}{2} \right) h \nu' - \left( n'' + \frac{1}{2} \right) h \nu'' + \frac{h^2}{8\pi^2 I'} J' (J' + 1) - \frac{h^2}{8\pi^2 I''} J'' (J'' + 1)$$

- (i) What are the quantum numbers of the lower vibrational and rotational states? What is the moment of inertia of the lower electronic state?
- (ii) Sketch four transition/s allowed by the selection rules,  $\Delta n = 1$  and  $\Delta J = 1$  originating from the ground vibrational and rotational state of the lower electronic state and ending at the upper electronic state. Label all the relevant vibrational and rotational states with the quantum numbers.

(40 marks)

- (c) (i) Copy the following table (twice) on to your answer script and fill it for  $\text{He}_2^+$  and  $\text{He}_2$ . Modify the table if it is necessary.

Combination	Molecular orbital $\sigma_g 1s$				Molecular orbital $\sigma_u^* 1s$				$M_L$	$M_S$
	Electron 1		Electron 2		Electron 3		Electron 4			
	$m_l$	S	$m_l$	S	$m_l$	s	$m_l$	s		
I										
II										

- (ii) Derive the electronic state symbols for  $\text{He}_2^+$  and  $\text{He}_2$ .

(50 marks)