THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Final Examination — 2011/2012

CHU 3128/CHE 5128 — Special Topics in Spectroscopy

(2 *hours*)

15th June 2012 (Friday)   1.30 p.m. — 3.30 p.m.

- There are six (06) questions and seven (07) pages (including the first page) in the paper.

- Answer any **04 (Four)** questions. If more than 04 questions are answered <u>only</u> 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

- Cellular phones are **not** allowed.

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
$Log_e(X)$	=	$2.303 \ Log_{10}(X)$

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.
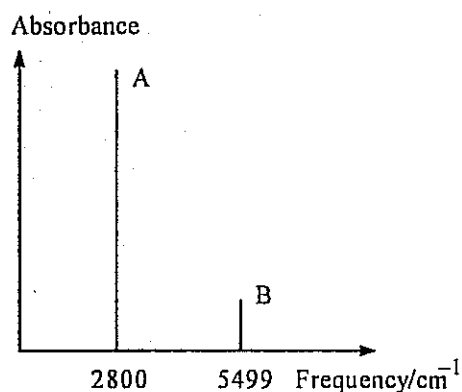
$$\overline{E}_\upsilon = \left(\upsilon + \frac{1}{2}\right)\overline{\omega}_e - \left(\upsilon + \frac{1}{2}\right)^2 x_e \overline{\omega}_e$$

(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: $\upsilon = n$ 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 <u>full</u> pure vibrational spectrum of the molecule mentioned in part (a) above, recorded by a student shows <u>only</u> two lines as indicated in the figure.

(i) <u>Giving reasons,</u> 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 <u>not</u> made any errors in recording the spectrum).
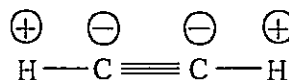
(ii) Calculate x_e and $\overline{\omega}_e$ for the molecule.

(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 <u>parallel</u> or a <u>perpendicular</u> mode.

$$\overrightarrow{H} \!-\! C \equiv C \!-\! \overrightarrow{H}$$

(δ)

$$\overset{\oplus}{H} \;\; \overset{\ominus}{-\!C} \equiv \overset{\ominus}{C\!-} \overset{\oplus}{H}$$

(λ)

(20 marks)

2. (a) In standard notation, the rotational energy levels (in wavenumber units) of a heteronuclear diatomic molecule are given by the equation

$$\overline{E}_J = \overline{B}J(J+1) - \overline{D}J^2(J+1)^2.$$

(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.
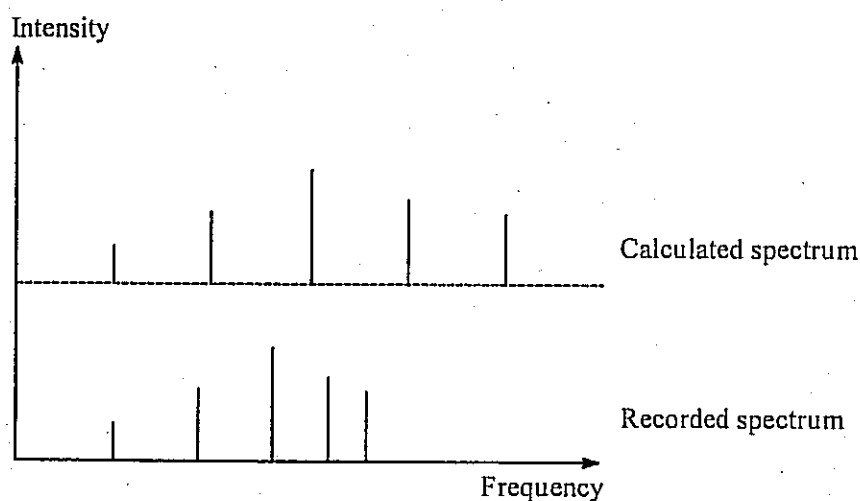
(20 marks)

(c) (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.
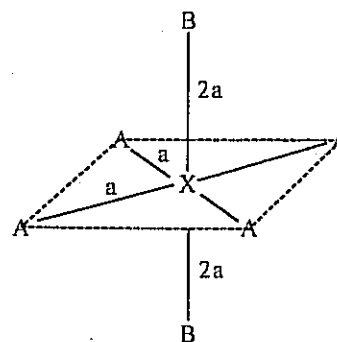
(30 marks)

[Question 2 is continued in the next page]

(d) (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)

3. (a) A linear molecule has the chemical formula X_2Y. Its microwave spectrum shows only one strong series of lines at 20, 40, 60, ...MHz. Is the structure of the molecule XXY or XYX?

   Briefly explain your answer.

(20 marks)

   (b) In standard notation, for an ammonia molecule $I_a = I_b = 2.805 \times 10^{-47} \text{kg m}^2$,

   $I_c = 4.412 \times 10^{-47} \text{kg m}^2$ and

   $\varepsilon_{JK} = BJ(J+1) - D_J J^2(J+1)^2 + (C-B)K^2 - D_K K^4 - D_{JK} J(J+1)K^2$.

   (i) Is an ammonia molecule a prolate symmetric top or an oblate symmetric top? Briefly explain your answer.

   (ii) Identify the terms D_J, D_K and D_{JK}. In general, why are they non–zero for a real molecule.

   (iii) State the selection rule in microwave spectroscopy of ammonia if it behaves as a rigid rotor.

   (iv) Starting with the above given energy expression and the selection rule derive an expression for the separation between two adjacent lines in the microwave spectrum of ammonia if it behaves as a rigid rotor.

   (v) Calculate the expected separation of two adjacent lines in the microwave spectrum of a gaseous sample if an ammonia molecule behaves a rigid rotor.

(80 marks)

4. (a) 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 <u>more</u> shielded than the nuclei in the reference.

(35 marks)

[Question 4 is continued in the next page]

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

(ii) Three sets of protons in a molecule (which has no other magnetic nuclei) forms an AMX spin system in a particular NMR spectrometer. The sets corresponding to A, M and X has 1, 2 and 1 protons, respectively (so that one can also say that they form an AM_2X spin system). The scalar coupling constants are, $J_{AM} = 5\,Hz$, $J_{MX} = 8\,Hz$ and $J_{AX} = 20\,Hz$. The relationship among the resonance frequencies of A, M and X protons in the spectrometer is $\nu_A > \nu_M > \nu_X$. Sketch the high resolution NMR spectrum of these protons in intensity versus resonance frequency plot. Clearly indicate the spacing (in Hz) of the lines and centre of the multiplet due to each set of protons. Also indicate the intensity of each line on a scale where the shortest line has intensity one (1).

(35 marks)

(c) Sketch the NMR spectrum generated by the free induction decay (FID) signal $f(t) = 3.6\exp(-2.67\,t)\sin(9\pi t) + 4.89\sin(20\pi t)$ on intensity versus frequency plot. Clearly indicate the frequency corresponding to the peaks/lines. (The intensity of all peaks/lines may be taken to be the same.)

(10 marks)

(d) (i) Briefly describe what is meant by the double resonance method in NMR spectroscopy.

(ii) Briefly describe how the double resonance method could be used to simplify an NMR spectrum of a molecule.

(20 marks)

5. (a) Define the following as applied in Raman spectroscopy.
   (i) Stokes scattering
   (ii) Anti Stokes scattering

(20 marks)

(b) Consider a planer polyatomic molecule. The variation of the cross section of the polarisability ellipsoid of the molecule, on the plane of the molecule, during vibration in three normal modes, α, β and γ, is shown in the following diagram. (Q is the normal coordinate.)

Q < 0 Q = 0 Q > 0   Q < 0 Q = 0 Q > 0   Q < 0 Q = 0 Q > 0

(α)   (β)   (γ)
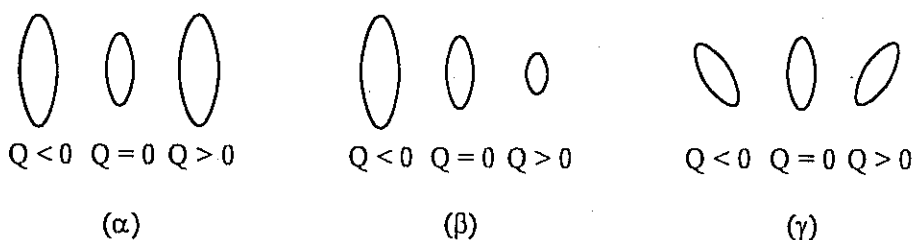
(i) Giving reasons identify the normal mode/s which can give a vibrational Raman spectrum.

(ii) Giving reasons identify the normal mode/s which can give a polarised vibrational Raman spectrum.

(25 marks)

[Question 5 is continued in the next page]

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(c) (i) State the rule of mutual exclusion in vibrational spectroscopy.

(ii) A linear molecule, A_2B, show the following characteristics in vibrational Raman spectrum and the IR spectrum.

Frequency/ cm^{-1}	Raman spectrum	IR spectrum
1450.0	Strong peak	No peak
650.0	No peak	Strong peak
3400.0	No peak	Strong peak

Giving reasons, state whether you can determine the structure of the molecule is $A-B-A$ or $A-A-B$ from the above observations?
If possible, what is the structure?

(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 $600 \, cm^{-1}$.
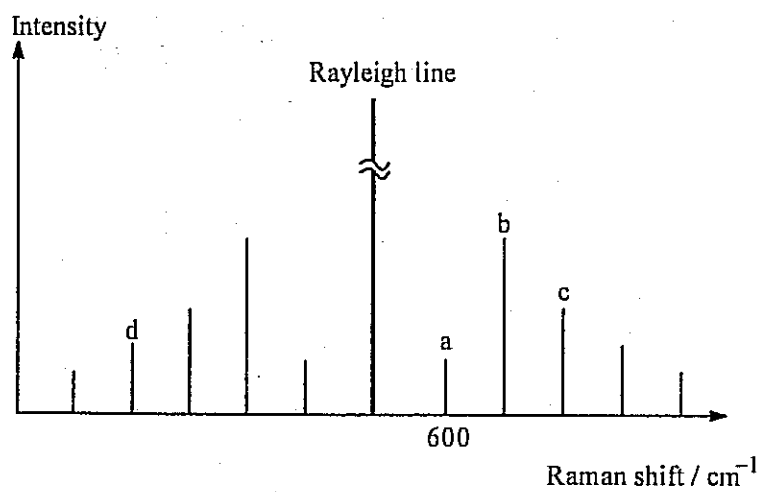
(i) Write down (no proof required) the relationship between the Raman shift of the spectral line a and the rotational constant, B, of the molecule.

(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)

5. (a) Write down the occupation of molecular orbitals in the ground state of He_2^+ molecular ion.

(10 marks)

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

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

(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 He_2^+ and 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 He_2^+ and He_2.

(50 marks)