



061

THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Final Examination — 2008/2009

CHU 3128/CHE 5128 — Special Topics in Spectroscopy

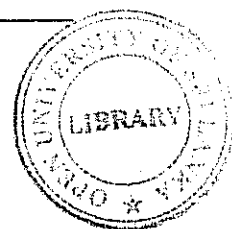
(2½ hours)

18th June 2009 (Thursday)

1.30 p.m. – 4.00 p.m.

- 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
- Cellular phones are not allowed.

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



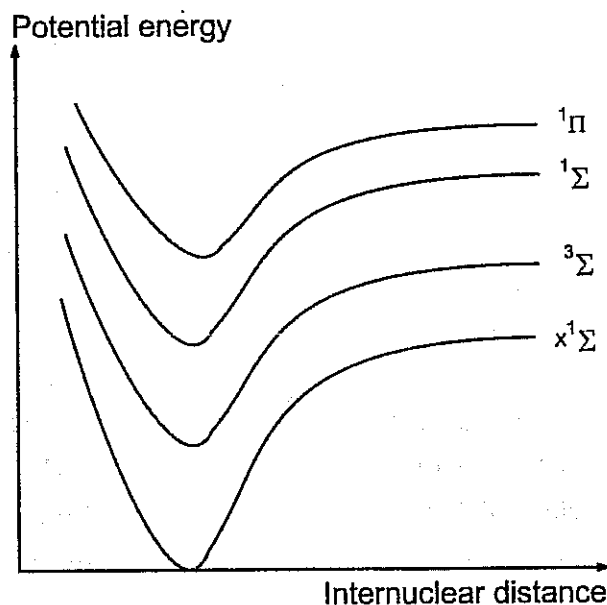
1. (a) Consider the ionic and molecular species, N_2^+ , N_2 and N_2^- in its ground state.
- (i) Write down the electronic configuration for each species.
 [Hint: The order of increasing energy of molecular orbitals (except in O_2 and F_2) is $\sigma_g 1s < \sigma_u^* 1s < \sigma_g 2s < \sigma_u^* 2s < \pi_u 2p < \sigma_g 2p < \pi_g^* 2p < \sigma_u^* 2p$]
- (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.
- (iv) Derive the electronic term symbol for the ground electronic state of each of the molecule/ion.

Electronic term symbols for different values of Λ (i.e. Z-component of angular momentum) are given below.

Λ	0	1	2	3
Electronic term symbol	Σ	Π	Δ	Φ

(60 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.

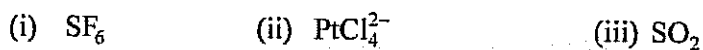


- (i) Copy this diagram on to your answer sheet and sketch all the allowed electronic transitions originating from the ground state.
- (ii) State the selection rule/s that is/are violated for the forbidden electronic transitions. (Consider all possible forbidden electronic transitions)

(40 marks)

2. (a) State an experimental observation that indicates the fact that a diatomic molecule does not behave as a rigid rotor as far as its rotational motion is considered. (10 marks)

- (b) Giving reasons identify each of the following molecules/ions as asymmetric top, symmetric top or spherical top.



(24 marks)

- (c) For an ammonia molecule, $I_b = 2.805 \times 10^{-47} \text{ kg m}^2$ and $I_c = 4.412 \times 10^{-47} \text{ kg m}^2$. In standard notation, the expression for the rotational energy levels of a symmetric top is given below.

$$\epsilon_{JK} = \begin{cases} BJ(J+1) - D_J J^2 (J+1)^2 + (C-B)K^2 - D_K K^4 - D_{JK} J(J+1)K^2 & \text{oblate} \\ BJ(J+1) - D_J J^2 (J+1)^2 + (A-B)K^2 - D_K K^4 - D_{JK} J(J+1)K^2 & \text{prolate} \end{cases}$$

- (i) Identify all the terms in the energy expression given above.
 (ii) What are the specific selection rules in microwave spectroscopy of a symmetric top molecule.
 (iii) Giving reasons state whether ammonia molecule is an oblate symmetric top or a prolate symmetric top.
 (iv) Starting with the appropriate energy expression, derive an expression for the position of lines in the microwave spectrum of an ammonia molecule.
 (v) Calculate the separation between two adjacent lines in the microwave spectrum of ammonia disregarding the centrifugal distortion.

(66 marks)

3. (a) Calculate the number of normal modes in each of the following molecules/ions.



(20 marks)

- (b) In standard notation, draw the representations of all the normal modes of a sulphur dioxide molecule and label them (as symmetric stretching etc.).

(10 marks)

- (c) Define the term accidental degeneracy.

(10 marks)

- (d) Consider a diatomic molecule which behaves as an anharmonic oscillator.

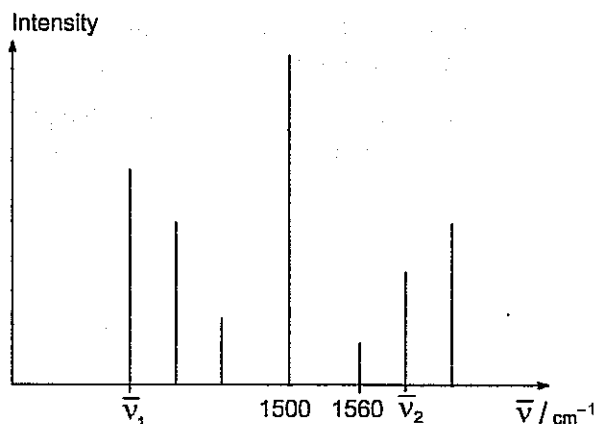
- (i) Write down an expression for the vibrational energy and identify all the parameters in it.
 (ii) What are the specific selection rules in the vibrational spectroscopy of the molecule.
 (iii) Using the answers in parts (i) and (ii) above derive an expression for the positions of the fundamental and the first overtones in the IR spectrum of the molecule.
 (iv) The fundamental and the 1st overtone in the IR spectrum of $^{14}\text{N}^{16}\text{O}$ appear at 1876.06 cm^{-1} and 3724.20 cm^{-1} respectively. Calculate the equilibrium vibration frequency and the anharmonicity constant of $^{14}\text{N}^{16}\text{O}$.

(60 marks)

4. Consider a diatomic molecule which behaves as a harmonic oscillator and a non-rigid rotor.
- Write down a mathematical expression for the vibration-rotation energy levels of the molecule and identify all the terms in it. (10 marks)
 - Write down the specific selection rules for the vibration-rotational energy level transitions. (10 marks)
 - Briefly describe how the P and R-branches in the IR spectrum of the molecule is created. (20 marks)
 - Derive expressions for the positions of lines in the P and R-branches in the IR spectrum of the molecule. (20 marks)
 - Derive expressions for the separation between two adjacent lines in the P-branch as well as separation between two adjacent lines in the R-branch in the IR spectrum of the molecule. (20 marks)
 - Show that the spacing of lines in the P-branch decreases with decreasing frequency and the spacing of lines in the R-branch decreases with increasing frequency. (20 marks)
5. (a) Define the following terms as applied in Raman spectroscopy. (15 marks)
- Rayleigh line
 - Stoke's line
 - Anti-Stokes line
- (b) Consider an HCN molecule placed on the plane of this paper so that the molecular axis is horizontal and parallel to the paper. Sketch the cross section of the polarisability ellipsoid of this molecule on the plane of the paper. Indicate the positions of the H, C and N nuclei on the same sketch. (10 marks)
- (c) Consider an HCN molecule which behaves as a rigid rotor.
- Write down an expression for its rotational energy levels and identify all the terms in it.
 - Write down the specific selection rules in the pure rotational Raman spectroscopy of HCN.
 - Derive an expression for the Raman shift of a Stokes line in the pure rotational Raman spectrum of HCN.
 - Derive an expression for the Raman shift of an Anti-Stokes line in the pure rotational Raman spectrum of HCN.
 - 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 HCN.
 - Deduce an expression for the frequency separation between two adjacent Stokes lines in the pure rotational Raman spectrum of HCN. (55 marks)

[Question 5 is continued in next page]

- (d) The first three Stokes and anti-Stokes lines in the pure rotational Raman spectrum of a rigid linear molecule is shown below. The Rayleigh line appears at 1500 cm^{-1} and the first anti-Stokes line appears at 1560 cm^{-1} .



Determine $\bar{\nu}_1$ and $\bar{\nu}_2$ (i.e the positions of the 3rd Stokes line and the 2nd anti-Stokes line)

(20 marks)

6. (a) (i) Write down a mathematical expression which defines the chemical shift (δ - scale) in part per million, ppm, and identify all the parameters in it.
 (ii) A student performing a proton NMR experiment learned that he has run out of TMS which is the usual proton NMR reference compound. However, he found another substance, X, which could be used as a reference in place of TMS. It gives a single strong resonance at 499.800000 MHz in a 500 MHz NMR spectrometer. In the same spectrometer, the protons in CH and NH groups in a compound, A, gave resonances at 500.000683 MHz and 500.001973 MHz respectively. Calculate the chemical shifts, in ppm, of the CH and NH protons in A in a scale where X is the reference.

(30 marks)

- (b) Briefly describe what is meant by a 90°_Y pulse in a spin echo experiment.

(10 marks)

- (c) (i) Briefly describe what is meant by an AMX spin system.
 (ii) Briefly describe what is meant by homonuclear decoupling and how it is done.
 (iii) Three protons in a molecule, Y, form an AMX spin system. The molecule has no other nuclei with spin. The resonance frequencies of the three nuclei, in a particular NMR spectrometer, are denoted by ν_A , ν_M and ν_X . They obey the relationships $\nu_A > \nu_M > \nu_X$, $\nu_A - \nu_X = 350 \text{ MHz}$ and $\nu_A - \nu_M = 250 \text{ MHz}$. The coupling constants are given by $J_{AX} = 15 \text{ MHz}$, $J_{AM} = 5 \text{ MHz}$ and $J_{MX} = 2 \text{ MHz}$.

[Question 6 is continued in next page]