084

# THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

**Final Examination** — 2007/2008

**CHU 3128/CHE 5128** — Special Topics in Spectroscopy

$\left(2\frac{1}{2}\text{ hours}\right)$

31st December 2007 1.00 p.m. – 3.30 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
- Logarithm tables will be provided.

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Gas constant (R) = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$

Avogadro constant $(N_A)$ = $6.023\times10^{23} \text{ mol}^{-1}$

Faraday constant (F) = $96{,}500 \text{ C mol}^{-1}$

Planck constant (h) = $6.63\times10^{-34} \text{ J s}$

Velocity of light (c) = $3.0\times10^{8} \text{ m s}^{-1}$

Standard atmospheric pressure = $10^{5} \text{ Pa}\left(\text{N m}^{-2}\right)$

$\pi$ = 3.14159

$\text{Log}_e(X)$ = $2.303 \text{ Log}_{10}(X)$

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1. (a) Giving reasons state which of the following molecules can show a microwave spectrum and which cannot.
   (i) $SO_2$ (ii) HCN (iii) $CF_4$

(18 marks)

(b) (i) Define the following terms as applied in rotational spectroscopy of molecules.
   (α) Symmetric top
   (β) Prolate symmetric top
   (γ) Oblate symmetric top

(18 marks)

(ii) Consider a $BCl_3$ molecule.
   (α) Derive an expression for the moment of inertia of $BCl_3$ 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.
   (β) deduce whether $BCl_3$ is an oblate spherical top or a prolate spherical top.

(20 marks)

(c) (i) Write down the relationship between the rotational energy of a diatomic molecule and the rotational quantum number and identify all the terms in it.

(ii) State the specific selection rule in microwave spectroscopy of a diatomic molecule.

(iii) Deduce an expression for the positions of lines in the microwave spectrum of such a molecule.

(iv) For CuBr, the $J = 14 \leftarrow 13$ and $15 \leftarrow 14$ transitions occur at 84421.34 and 90449.25 MHz respectively. Calculate the rotational constant and the centrifugal distortion constant of CuBr.

(44 marks)

2. (a) Calculate the number of normal modes in each of the following molecules.
   (i) $BI_3$ (ii) Pyridine (iii) Cyclohexane (iv) HCN

(20 marks)

(b) The equilibrium vibration frequencies of the 9 normal modes of $CHD_3$ in units of $cm^{-1}$, with their degeneracies in parenthesis, are 993(1), 2142(1), 1003(3), 1291(2) and 1036(2).
   (i) Calculate the zero point energy of a $CHD_3$ molecule.
   (ii) State any assumption/s you make, if any, in the above calculation.

(20 marks)

(c) The $H^{35}Cl$ molecule is quite well described by the Morse potential with $D_e = 42934.9\ cm^{-1}$, $\bar{\omega}_e = 2989.7\ cm^{-1}$ and $x_e = 0.0174$.
   (i) Write down the expression for the vibrational energy levels of $H^{35}Cl$ and identify all the terms.
   (ii) Write down the relationship between $D_e$, the dissociation energy, $D_0$, and the zero point energy, $\varepsilon_0$.

***[Question 2 is continued in the next page]***

(iii) Calculate the dissociation energy of $H^{35}Cl$.

(iv) Calculate the dissociation energy of $D^{35}Cl$.

(v) State any assumptions you make in the calculation in part (iv) above.

[Relative atomic masses: H = 1, D = 2 and $^{35}Cl = 35$]

(60 marks)

3. (a) (i) Define the following terms.
   - (α) Perpendicular vibration
   - (β) Parallel vibration.

   (ii) Using the standard notation (arrows) draw the 3 normal modes of a water molecule and identify them as symmetric stretching, anti-symmetric stretching and bending. Classify each normal mode as parallel and perpendicular vibration.

(30 marks)

(b) Consider a diatomic molecule whose vibrational and rotational motions can be approximated by a harmonic oscillator and a rigid rotor respectively.

(i) Write down the expression for the vibrational-rotational energy levels of this molecule in terms of the vibrational and rotational quantum numbers and identify all the terms.

(ii) State the specific selection rules in vibrational-rotational spectroscopy of this molecule.

(iii) Deduce expressions for the positions of the lines in the P and R branches in the IR spectrum.

(35 marks)

(c) The first line in the P and R branches of the fundamental band of the IR spectrum of $H^{35}Cl$ appear at $2865.09\ cm^{-1}$.and $2906.25\ cm^{-1}$ respectively.

(i) Determine the equilibrium vibration frequency and the rotational constant of $H^{35}Cl$.

(ii) Write down the relationship between the separation of the P and R branch maxima in the IR spectrum of a diatomic molecule and the rotational constant and identify all the terms in it.

(iii) The separation between the P and R branch maxima of the fundamental band of the IR spectrum of a sample of $H^{35}Cl$ is $130.90\ cm^{-1}$. Calculate the temperature of the sample of $H^{35}Cl$.

(35 marks)

4. (a) State the specific selection rule in vibrational transitions in a diatomic molecule which behaves as a harmonic oscillator.

(10 marks)

(b) Consider the following vibrational transitions of a diatomic molecule;

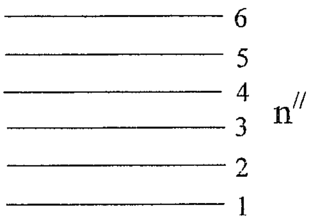
($\alpha$) within an electronic state

($\beta$) between two electronic states

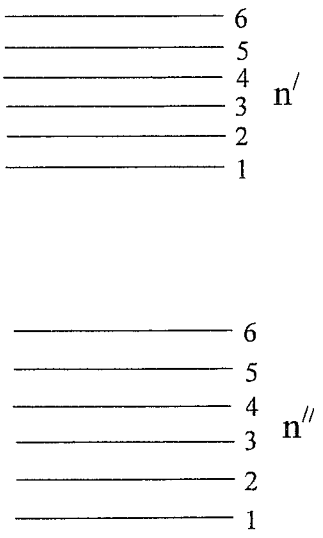
(i) Describe how the selection rule mentioned in part (a) above is obeyed in these two situations.

(20 marks)

(ii) Copy the following sketch of the vibrational energy levels on to your answer sheet and using vertical arrows, sketch/indicate <u>four</u> allowed transitions in the two cases mentioned above.



vibrational energy levels
within an electronic state



vibrational energy levels
of two electronic states

(40 marks)

Indicate whether the vibrational selection rule is obeyed for the transitions you have drawn and explain why they are possible if selection rules are not obeyed.

(10 marks)

(c) Write down the ground electronic configuration of $N_2^+$ and deduce its bond order.

(20 marks)

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

(18 marks)

(b) Giving reasons identify the molecules that may show a pure rotational Raman spectrum.

(i) $N_2$ (ii) $CCl_4$ (iii) $CH_2Cl_2$ (iv) $SF_6$

(16 marks)

(c) Vibrational-rotational Raman spectroscopy can be used to calculate the rotational constant of a diatomic molecule. Consider such a molecule whose vibrational and rotational motions can be approximated by a Morse oscillator and a rigid rotor respectively.

(i) Write down the expression for the vibrational-rotational energy levels of this molecule in terms of the vibrational and rotational quantum numbers and identify all the terms.

(ii) State the specific selection rules in vibrational-rotational Raman spectroscopy of this molecule.

(iii) Deduce expressions for the positions of the lines in the O and S branches in the fundamental anti-Stokes band of the vibrational-rotational Raman spectrum.

(iv) Write down the expression for the quantum number of rotational energy level with maximum population at temperature T and identify all the terms in it.

(v) Show that the separation, $\Delta v$, between the O and S-branch maxima in the fundamental anti-Stokes band of the vibrational-rotational Raman spectrum is given by $\Delta v = \sqrt{\frac{32BkT}{h^2}}$ where B is the rotational constant and the other terms have their usual meaning.

(66 marks)

6. (a) (i) Write down the relationship between the Larmor frequency of a bare nucleus and the magnetic field strength and identify all the terms in it.

(ii) Calculate the magnetic field strength if the Larmor frequency of a $^{31}P$ nucleus placed in it is 500 MHz. $[\gamma = 1.083 \times 10^8 \text{ rad s}^{-1}\,T^{-1} \text{ for } ^{31}P]$

(20 marks)

(b) (i) Briefly describe what is meant by shielding in NMR spectroscopy.

(ii) Write down the relationship between the Larmor frequency of a nucleus in a molecule and the magnetic field strength and identify all the terms in it.

(iii) The values of proton shielding constants for HF and HI are $2.871 \times 10^{-5}$ and $4.447 \times 10^{-5}$ respectively. Calculate the frequency separation of the proton resonances of HF and HI in a 500 MHz NMR spectrometer.

(30 marks)

***[Question 6 is continued in the next page]***

(c) Sketch the multiplet structure of the proton and nitrogen resonances in the NMR spectrum of $^{14}N^{1}H_3$. Identify the multiplets due to proton and nitrogen on the sketch. Disregard the variation of intensity of lines and you may use lines of equal height. Assume that the resonance frequency of protons is higher than that of nitrogen. Nuclear spin quantum number, $I = 1$ for $^{14}N$.

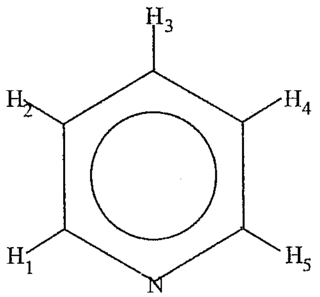
(20 marks)

(d) (i) Define the following terms as applied in NMR spectroscopy.

(α) Chemically equivalent nuclei.

(β) Magnetically equivalent nuclei.

(ii) Identify the chemically equivalent and magnetically equivalent nuclei in the following (pyridine) molecule.



(30 marks)