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THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Final Examination — 2009/2010

CHU 3128/CHE 5128 — Special Topics in Spectroscopy

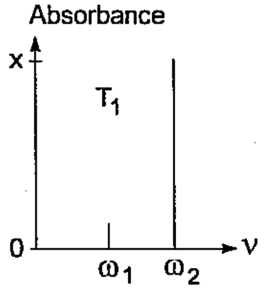
$\left(2\frac{1}{2}\text{ hours}\right)$

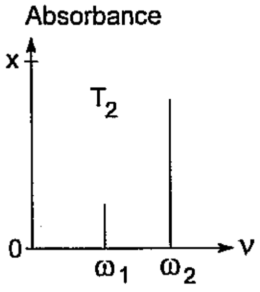
14th June 2010 (Monday) 1.30 p.m. — 4.00 p.m.

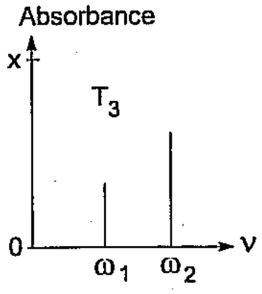
- There are six (06) questions and seven (07) pages (including the first page) in the paper.
- Answer any **04 (Four)** questions. If more than 04 questions are answered only the first 04 answers, *in the order they are written in the answer script*, will be marked.
- The use of a non-programmable calculator is permitted
- Cellular phones are not allowed.

Gas constant (R) = $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Avogadro constant (N_A) = $6.023 \times 10^{23} \text{ mol}^{-1}$
Faraday constant (F) = $96,500 \text{ C mol}^{-1}$
Planck constant (h) = $6.63 \times 10^{-34} \text{ J s}$
Velocity of light (c) = $3.0 \times 10^{8} \text{ m s}^{-1}$
Standard atmospheric pressure = $10^5 \text{ Pa} \left(\text{N m}^{-2}\right)$
π = 3.14159
$\text{Log}_e(X)$ = $2.303 \text{ Log}_{10}(X)$

1. (a) A student placed a gaseous sample of a stable diatomic molecule in a double beam absorption spectrometer and recorded its absorbance as a function of frequency, ν, in a portion of the IR region of the electromagnetic spectrum, at three different temperatures, T_1, T_2 and T_3 such that $T_1 < T_2 < T_3$. The results are schematically represented below.







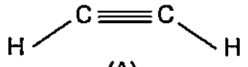
The line appearing at frequency ω_2 is known to be the fundamental line.

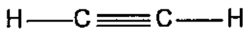
(i) Explain the intensity variation of the fundamental line observed in the above spectra.

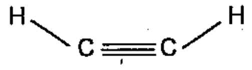
(ii) Giving reasons state the type of line/band appearing at frequency ω_1 and explain the variation of its intensity with temperature.

(40 marks)

(b) The displacements of hydrogen nuclei in a particular vibrational mode of acetylene molecule is shown in the following diagram.


(A)


(B)


(C)

Deduce whether it is a parallel mode or a perpendicular mode of vibration.

(20 marks)

(c) In standard notation, the vibrational energy levels (in wave number units), $\bar{E}_\alpha$, of a polyatomic molecule, which has only three normal modes, are given by the following expression.

$$\bar{E}_\alpha = \sum_{k=1}^{3}\left(\upsilon_k+\tfrac{1}{2}\right)\bar{\omega}_{e,k} + \sum_{j\le k}\bar{x}_{jk}\left(\upsilon_j+\tfrac{1}{2}\right)\left(\upsilon_k+\tfrac{1}{2}\right) \text{ where}$$

$\bar{\omega}_{e,1} = 3832.0\ \text{cm}^{-1}$	$\bar{\omega}_{e,2} = 1648.0\ \text{cm}^{-1}$	$\bar{\omega}_{e,3} = 3942.0\ \text{cm}^{-1}$
$\bar{x}_{11} = -43.0\ \text{cm}^{-1}$	$\bar{x}_{22} = -17.0\ \text{cm}^{-1}$	$\bar{x}_{33} = -48.0\ \text{cm}^{-1}$
$\bar{x}_{12} = -16.0\ \text{cm}^{-1}$	$\bar{x}_{13} = -166.0\ \text{cm}^{-1}$	$\bar{x}_{23} = -20.0\ \text{cm}^{-1}$

(i) Calculate the zero point energy of the molecule.

(ii) Calculate the wave number of the photon that brings about the vibrational energy transition, $(0,0,0)\rightarrow(0,1,0)$.

(40 marks)

2. (a) (i) State the gross selection rule in microwave spectroscopy.
   (ii) State which of the following molecules/ion can show a microwave spectrum and which cannot.

   (α) $C_5H_5^-$ (β) cis$-C_2H_2Cl_2$ (γ) C_2H_2 (δ) CH_3Cl

(20 marks)

(b) List <u>three</u> molecular parameters that have been determined using microwave spectroscopy.

(12 marks)

(c) (i) Giving reasons state whether an SF_6 molecule, in its most stable configuration, is an asymmetric top, a symmetric top or a spherical top.

(09 marks)

(ii) Denote the S–F bond length in an SF_6 molecule, in its most stable configuration by r. Now imagine creating a distorted SF_6 molecule by pulling out one F nucleus, without changing any of the bond angles, so that the S–F bond length for that F nucleus becomes 2r. Denote the mass of an F nucleus by m.

(α) Giving reasons deduce the axis of revolution of the ellipsoid of inertia of the distorted SF_6 molecule?

(β) By calculating the moment of inertia, in terms of r and m, of the distorted SF_6 about the axis of revolution of the ellipsoid of inertia and an axis perpendicular to it and passing through two F nuclei and the S nucleus, deduce whether this distorted SF_6 molecule is an oblate symmetrical top or a prolate symmetrical top.

(24 marks)

(d) The rotational energy levels of a linear polyatomic molecule, X, are given by the expression $\bar{E}_J = \bar{B}J(J+1) - \bar{D}J^2(J+1)^2 - \bar{H}J^3(J+1)^3$ where J is the rotational quantum number (which can take values 0, 1, 2, 3, ... as usual) and, $\bar{B}, \bar{D}$ and $\bar{H}$ are non-zero constants. X shows a microwave spectrum and the specific selection rule in microwave spectroscopy is $\Delta J = +1$. A student recorded the microwave spectrum of a gaseous sample of X using a spectrometer which can record the absorption peak positions to a precision of $0.001\ \text{cm}^{-1}$.

(i) Giving reasons state whether X behaves as a rigid rotor or a non–rigid rotor.

(ii) Derive an expression for the positions of lines in the microwave spectrum of X.

(iii) Calculate the positions of the first <u>two</u> lines in the recorded microwave spectrum of X if $\bar{B} = 20.000\ \text{cm}^{-1}$, $\bar{D} = 0.010\ \text{cm}^{-1}$ and $\bar{H} = 0.002\ \text{cm}^{-1}$.

(35 marks)

3. (a) (i) Define the following as applied in a study of vibration of a polyatomic molecule
   (α) Skeletal vibrations.
   (β) Group vibrations.

   (ii) State which vibrations, out of (α) and (β) indicated above, lead to the finger print bands in the IR spectrum of a polyatomic molecule.

[Question 3 is continued in the next page]

(iii) State <u>one</u> use of characteristic group frequencies in chemistry.

(20 marks)

(b) In post Born-Oppenheimer approximation, the vibration rotation energy levels in wave number units, $\overline{E}_{v_k,J}$, in a particular normal mode, k, of oblate and prolate symmetric top molecules are given by the following expressions, respectively.

$$\overline{E}_{v_k,J} = \left(v_k + \tfrac{1}{2}\right)\overline{\omega}_{e,k} - \left(v_k + \tfrac{1}{2}\right)^2 x_{e,k}\,\overline{\omega}_{e,k} + \overline{B}_{v_k}\,J(J+1) + \left(\overline{C}_{v_k} - \overline{B}_{v_k}\right)K^2$$

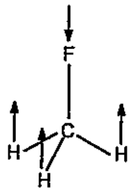
$$\overline{E}_{v_k,J} = \left(v_k + \tfrac{1}{2}\right)\overline{\omega}_{e,k} - \left(v_k + \tfrac{1}{2}\right)^2 x_{e,k}\,\overline{\omega}_{e,k} + \overline{B}_{v_k}\,J(J+1) + \left(\overline{A}_{v_k} - \overline{B}_{v_k}\right)K^2$$

The selection rules in vibration rotation spectroscopy of symmetric top molecules are given by the following equations.

$$\left.\begin{array}{l}\Delta v_k = \pm 1, \pm 2, \pm 3, \ldots \\ \Delta J = 0, \pm 1; \quad \Delta J = 0 \quad \text{forbidden if } K = 0 \\ \Delta K = 0\end{array}\right\} \quad \text{for parallel vibrations.}$$

$$\left.\begin{array}{l}\Delta v_k = \pm 1, \pm 2, \pm 3, \ldots \\ \Delta J = 0, \pm 1; \\ \Delta K = \pm 1\end{array}\right\} \quad \text{for perpendicular vibrations.}$$

A student recorded the vibration rotation spectrum corresponding to the following normal mode of CH_3F.



The 2nd, 3rd and 4th lines in the R branch in the first overtone band was found to be at $2084.72\ \text{cm}^{-1}$, $2086.25\ \text{cm}^{-1}$ and $2087.75\ \text{cm}^{-1}$ respectively. The student assumed that the vibration- rotation energy levels of CH_3F are give by the above expressions.

(i) Identify all the parameters in the above mentioned energy expressions.

(ii) Giving reasons state whether CH_3F vibrates as a harmonic oscillator or an anharmonic oscillator and rotates as a rigid rotor or a non-rigid rotor according to the assumption made by the student.

(iii) Giving reasons state whether the above mentioned vibrational mode of CH_3F is a parallel mode or a perpendicular mode.

(iv) Using the above energy expressions and selection rules given above, derive an expression for the positions of lines in the R branch of the first overtone band of CH_3F.

(v) Calculate the band origin, $\overline{B}_0$ and $\overline{B}_2$ for CH_3F.

(80 marks)

4. (a) Consider the electronic states $^3\Sigma^-$, $^3\Sigma^+$, $^1\Delta$ and $^4\Pi_{3/2}$.

Give the following information for these electronic states by filling the following table (copy the table to your answer script).

Electronic state	Total spin angular momentum quantum number	Orbital angular momentum quantum number	Whether the molecule has a centre of symmetry	Reflection symmetry of the wave function corresponding to the electronic state (only for sigma electronic states)
$^3\Sigma^-$				
$^3\Sigma^+$				
$^1\Delta$				
$^4\Pi_{3/2}$				

(30 marks)

(b) State the Hunds rules for the identification of the ground state of a diatomic molecule. Which of the following electronic states may be the ground electronic state of a diatomic molecule?

$^1\Sigma^+$ $^3\Sigma^+$ $^1\Sigma^-$ $^1\Delta$

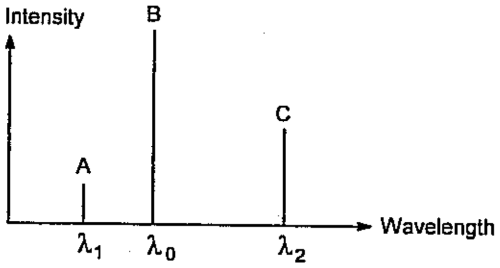
(30 marks)

(c) Sketch and label the following processes in a Jablonski diagram for a diatomic molecule.

(i) Absorption of radiation
(ii) Vibrational relaxation
(iii) Internal conversion
(iv) Fluorescence
(v) Intersystem crossing

(40 marks)

5. (a) A sketch of the intensity versus the wavelength of scattered radiation in the Raman spectrum of a hypothetical molecule having only two energy levels obtained with incident radiation of wavelength λ_0 is shown below.



(i) Giving reasons identify A, B and C as Rayleigh, Stokes and ant-Stokes lines.

(ii) Briefly explain why the magnitudes of the wave length shifts (from λ_0) of lines A and C are different.

(24 marks)

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

(i) $C_5H_5^-$ (ii) C_2H_2 (iii) CH_3Cl (iv) SF_6

(16 marks)

(c) In standard notation the rotational energy levels of a rigid linear polyatomic molecule <u>without</u> a centre of symmetry is given by $E_J = B\left(cm^{-1}\right)J\left(J+1\right)$ where $J = 0, 1, 2, 3, 4, \ldots\ldots.$

(i) What is the selection rule in pure rotational Raman spectroscopy of a linear poly atomic molecule?

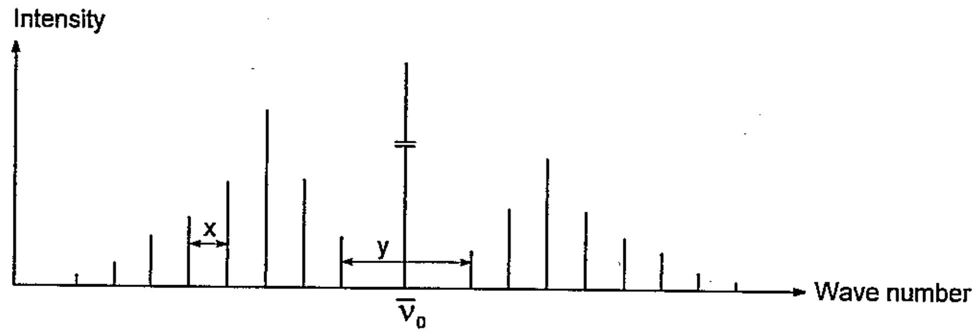
(ii) Derive an expression for the Raman shift of Stokes line in the pure rotational Raman spectrum of a linear polyatomic molecule without a centre of symmetry in terms of the rotational quantum number, J, of the initial rotational energy level.

(iii) Deduce an expression for the Raman shift of an anti-Stokes line in a linear polyatomic molecule without a centre of symmetry.

(iv) State how this expression for Raman shift is applied to a linear polyatomic molecule having a centre of symmetry.

(v) The rotational constant of a rigid linear molecule, AB_2 is $2.5\ cm^{-1}$. In AB_2, the nucleus A is located at the centre of symmetry and the nuclear spin quantum number of any B nucleus is zero. The pure rotational Raman spectrum, recorded by a student using a gaseous sample of AB_2 with an incident beam of electromagnetic radiation of wave number, $\overline{\nu}_0$, is schematically represented in the diagram below.

[Question 5 is continued in the next page]



Calculate the frequency separations x and y indicated in the diagram above.

(60 marks)

6. (a) State the following as applied in NMR spectroscopy.
   (i) Gross selection rule.
   (ii) Specific selection rule.

(14 marks)

(b) (i) Briefly describe what AX and AB spin systems are.

(ii) The Larmor frequency of a magnetic nucleus, X, is given by $\nu_X = \dfrac{\gamma_X(1-\sigma_X)B_0}{2\pi}$. Identify all the parameters in it.

(iii) Starting with the above equation for the Larmor frequency of a magnetic nucleus deduce a relationship between the Larmor frequency difference of two chemically non-equivalent nuclei in a molecule and the applied magnetic field strength.

(iv) Using the expression deduced in part (ii) above, show that an AB spin system can be converted into an AX spin system by increasing the magnetic field strength.

(40 marks)

(c) Briefly explain the statement "pulsed Fourier Transform NMR spectroscopy is an emission spectroscopy".

(16 marks)

(d) Three ^{13}C nuclei in a molecule placed in a particular NMR spectrometer form an AMX spin system. The scalar coupling constants are given by, $J_{AM} = 14\ \text{Hz}$, $J_{AX} = 6\ \text{Hz}$ and $J_{MX} = 2\ \text{Hz}$. The Larmor frequencies of the three nuclei satisfy the relationship, $\nu_X < \nu_M < \nu_A$. Sketch the high resolution NMR spectrum of these three ^{13}C nuclei. Clearly indicate the relative heights of the NMR spectral lines, spacing between lines in each multiplet (due to a nucleus) and placing of multiplets with respect to ν_X, ν_M and ν_A.

(30 marks)