036

THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Final Examination — 2006/2007

CHU 3128/CHE 5128 — Special Topics in Spectroscopy

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

4th November 2006 1.00 p.m. — 3.30 p.m.

- 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.
- Cellular phones are not allowed.
- There are six (06) questions and 6 pages to this paper.

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

π = 3.14159

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

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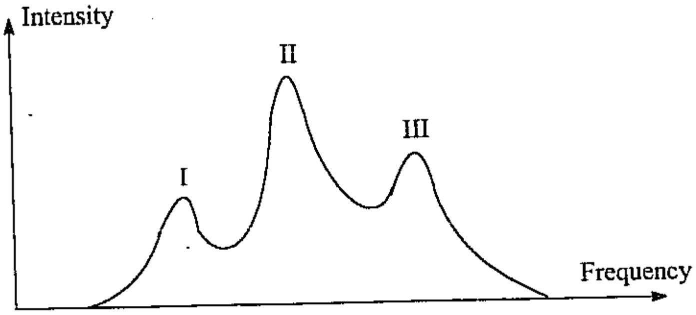
1. (a) Giving necessary equations, briefly describe how you would estimate the atmospheric temperature of a distant planet known to have high concentration of gaseous $H^{35}Cl$. You are provided with a powerful infrared absorption spectrometer (and a telescope). (You may assume that the temperature of the atmosphere of this planet is uniform).
(50 marks)

(b) (i) Briefly describe how P, Q and R branches in the IR spectrum due to a perpendicular vibrational mode of a linear molecule originate.

(ii) The first overtone band in the IR spectrum due to the bending mode of HCN under low resolution is indicated below.



(A) Identify the branches, I, II and III.

(B) Briefly describe why the intensity of II is higher that that of either I or III.
(40 marks)

(c) Identifying the branches, sketch the fundamental band in the IR spectrum due to the symmetric stretching mode of HCN under low resolution.
(10 marks)

2. (a) State two experimental observations that indicate that real diatomic molecules behave as anharmonic oscillators.
(10 marks)

(b) Define the following as applied in IR spectroscopy.

(i) Hot band

(ii) Parallel band

(iii) Perpendicular band
(15 marks)

(c) (i) Write down the relationship between the vibrational energy and the equilibrium vibrational frequency of a real diatomic molecule, AB, and identify all the terms in it.

(ii) What are the specific selection rules in vibrational spectroscopy of AB.

(iii) Using the answers to parts (i) and (ii) above, derive an expression for the positions of the fundamental and the first overtone lines in the vibrational spectrum of AB.

[Question 2 is continued in the next page]

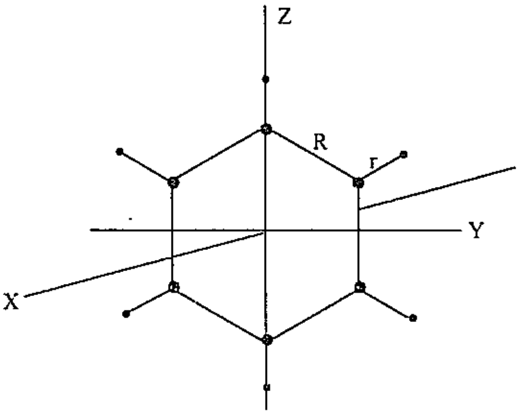
(iv) The first two lines in the vibrational spectrum of AB appear at $2886\,\text{cm}^{-1}$ and $5668\,\text{cm}^{-1}$.

(α) Calculate the equilibrium vibration frequency and the anharmonicity constant of AB.

(β) Calculate the position of the line due to the transition, $\nu = 1 \rightarrow \nu = 2$ in the vibrational spectrum of AB.

(75 marks)

3. (a) The following diagram indicates three axes, X, Y and Z, in a benzene molecule.



X is perpendicular to the plane of the molecule. Y and Z are in the plane of the molecule. All three axes passes through the centre of mass of the molecule and are mutually perpendicular. Denote the masses of C and H by M and m and C—C and C—H bond lengths by R and r.

(i) Derive an expression for the moment of inertia of benzene about X in terms of M, m, R and r.

(ii) Derive an expression for the moment of inertia of benzene about Z.

(iii) What is the shape of the ellipsoid of inertia of benzene?

(iv) Using the answer to (iii) above or by any other means, show that the moment of inertia about Y is the same as that about Z.

(v) Giving reasons identify the axes X, Y and Z as a, b and c.

(60 marks)

(b) In standard notation the rotational energy levels of a diatomic molecule, AB, are given by $\varepsilon_J = B\left(\text{cm}^{-1}\right)J(J+1) - D\left(\text{cm}^{-1}\right)J^2(J+1)^2$.

(i) Identify all the terms in the above expression.

(ii) What are the specific selection rules in the microwave spectroscopy of AB.

(iii) Using the answers to (i) and (ii) above, deduce an expression for the positions of lines in the microwave spectrum of AB.

[Question 3 is continued in the next page]

(iv) The experimental spectrum of AB fits well to the equation $\bar{\nu}/\mathrm{cm}^{-1} = 40.0(J+1) - 9.0\times10^{-3}\,(J+1)^3$. Calculate the rotational constant and the centrifugal distortion constant of AB

[You are given that $\sin(60^0) = \cos(30^0) = \sqrt{3}/2$ and $\cos(60^0) = \sin(30^0) = 1/2$.]

(40 marks)

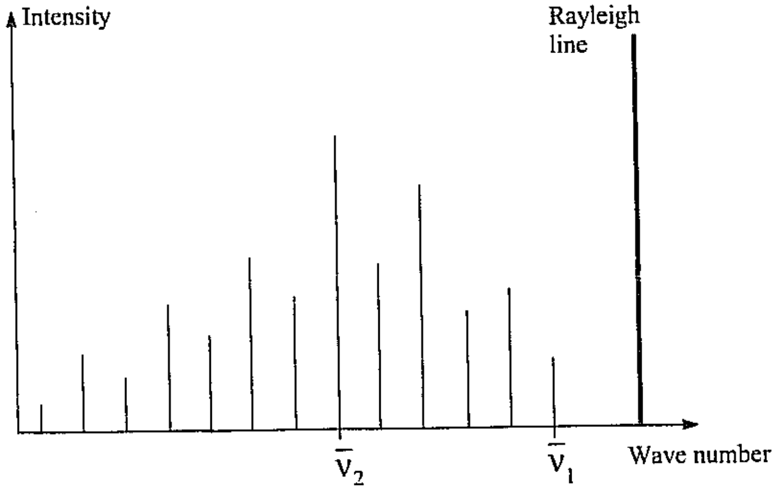
4. (a) (i) Giving reasons describe the shape of the polarizability ellipsoid of the following molecules.

(α) Methane (β) Ammonia (γ) Dichloromethane

(ii) Giving reasons indicate the molecule/s, out of the above three, which can show a pure rotational Raman spectrum.

(20 marks)

(b) Part of the pure rotational Raman spectrum of a molecule, with the chemical formula AB_3C and having a rotational axis of symmetry of order 3, is shown below.



In standard notation the rotational energy levels are given by $E_{J,K} = B(\mathrm{cm}^{-1})J(J+1) + [A(\mathrm{cm}^{-1}) - B(\mathrm{cm}^{-1})]K^2$ where $A(\mathrm{cm}^{-1}) = 8.0\,\mathrm{cm}^{-1}$ and $B(\mathrm{cm}^{-1}) = 7.0\,\mathrm{cm}^{-1}$

The selection rules in pure rotational Raman spectroscopy of this molecule are

for $K = 0$ $\Delta K = 0$ and $\Delta J = 0, \pm 2$

for $K \neq 0$ $\Delta K = 0$ and $\Delta J = 0, \pm 1, \pm 2$

(i) Identify all the terms in the above given energy expression.

(ii) Giving reasons indicate whether the given spectrum belongs to a Stokes band or an Anti-Stokes band.

(iii) Starting with energy expression and the selection rules derive expression/s that gives/give the positions of the spectral lines in the spectrum given above.

[Question 4 is continued in the next page]

(iv) Explain why there is a series of lines with enhanced intensity in the above spectrum.

(v) Calculate $\bar{v}_1$ and $\bar{v}_2$.

(vi) Indicate the rotational transitions that produce the line at $\bar{v}_1$ and the line at $\bar{v}_2$.

(80 marks)

5. (a) Write down the ground electronic configurations and ground electronic term symbols for the following homonuclear diatomic species.

(i) H_2^+ (ii) H_2 (iii) Be_2^+ (iv) B_2 (v) F_2

(50 marks)

(b) The energy change associated with an electronic transition in a diatomic molecule can be given by

$$\Delta E = \Delta E_e + \Delta E_v + hc\left[B'J'\left(J'+1\right) - B''J''\left(J''+1\right)\right] \text{ where}$$

ΔE_e = electronic energy change

ΔE_v = vibrational energy change

J' = rotational quantum number in the upper state

B' = rotational constant in the upper state

J'' = rotational quantum number in the lower state

B'' = rotational constant in the lower state

(i) Derive an expression to get the wave number of the spectral lines in P and R branches of the rotational fine structure in terms of J'', B', B'', ΔE_v and ΔE_e.

(ii) If $B' = 11\,\text{cm}^{-1}$ and $B'' = 9\,\text{cm}^{-1}$ find where the band head shall form.

(50 marks)

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

(ii) (α) Write down a relationship between the resonance frequency and the shielding constant of a nucleus in a molecule placed in a magnetic field and identify all the terms in it.

(β) A particular proton in a molecule resonates at a frequency $29.87\,\text{MHz}$ in a magnetic field of $1.0\,\text{T}$. Calculate the shielding constant of this proton in the molecule.

$\left[\text{for } ^1\text{H},\ \gamma = 2.6752\times10^8\ \text{rad}\,\text{s}^{-1}\,\text{T}^{-1}\right]$

(34 marks)

[Question 6 is continued in the next page]

(b) List three properties an NMR reference compound should have.

(15 marks)

(c) (i) Write down the relationship between the chemical shift, δ, of a nucleus in a molecule and its resonance frequency and identify all the terms in it.

(ii) A proton A resonates at 500.001973 MHz in a 500 MHz NMR spectrometer. The protons in TMS resonate at 499.997473 MHz in the same spectrometer. Calculate the chemical shift of A.

(30 marks)

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

(i) Spin-lattice relaxation.

(ii) Spin-spin relaxation

(iii) Spin-spin relaxation time.

(21 marks)