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THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Final Examination — 2013/2014

CHU 3128/CHE 5128 — Special Topics in Spectroscopy

(2 *hours*)

14th November 2014 (Friday) 2.00 p.m. — 4.00 p.m.

- There are **six (06) questions** and **eight (08) 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
- Mobile phones are **not** allowed.

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

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

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

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

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

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

π = 3.14159

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

1. (a) Indicate the number of normal modes in the following molecules and the ion.

(i) C_{60}^{-} (buckyball) (ii) $C_{10}H_8$ (naphthalene) (iii) C_5NH_5 (pyridine)

(iv) C_2H_2 (acetylene) (v) NH_4^+ (ammonium ion)

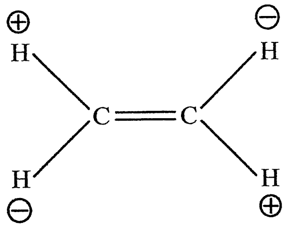
(10 marks)

(b) In standard notation, sketch the normal modes of a water molecule and identify them as symmetric stretching etc.

(10 marks)

(c) (i) State the gross selection rule in IR spectroscopy of molecules.

(ii) A *twisting* normal mode ethylene is indicated in the following figure (in standard notation).



CCH and HCH bond angles remain the same during vibration in this mode.

(α) State why it is called a *twisting* mode?

(β) Giving reasons state whether it is IR active or not.

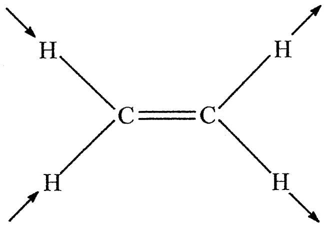
(25 marks)

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

(α) Parallel vibration

(β) Perpendicular vibration.

(ii) A stretching normal mode of ethylene is indicated in the following figure (in standard notation).



Giving reasons, state whether it is a parallel mode or a perpendicular mode.

(25 marks)

(e) $H^{35}Cl$ behaves as an anharmonic oscillator with $\bar{\omega}_e = 2990\ \text{cm}^{-1}$ and $x_e = 0.0174$ (with the symbols having their usual meaning).

(i) Write down an expression for the vibrational energy levels of $H^{35}Cl$ in terms of $\bar{\omega}_e$ and x_e, and identify all the parameters in it.

[Question 1 is continued in the next page]

(ii) Sketch the potential energy versus bond length of a $H^{35}Cl$ molecule and indicate, on it, the dissociation energies, D_e and D_0.

(iii) Write down the mathematical relationship between D_e and D_0.

(iv) Calculate D_e of $H^{35}Cl$ (in Jules) if $D_0 = 8.2341\times10^{-19}$ J.

(30 marks)

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

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

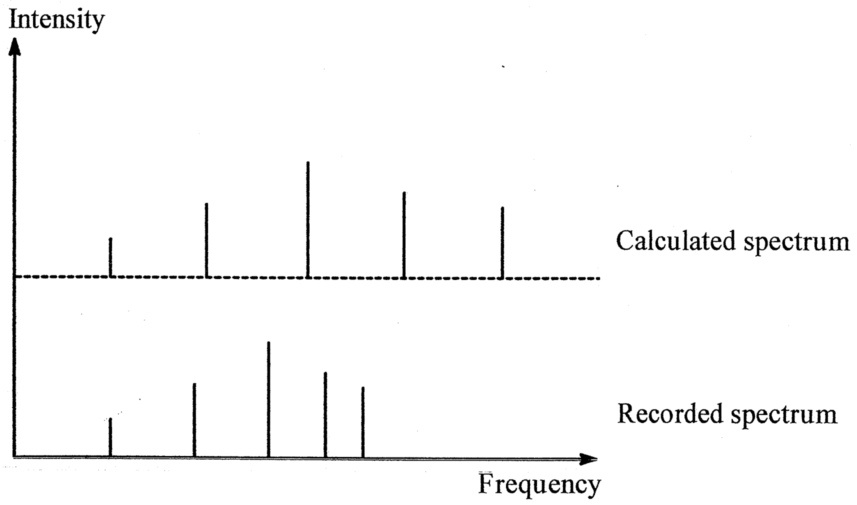
(i) Identify all the parameters in the above equation.

(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 <u>rigid rotor,</u> 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)

(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)

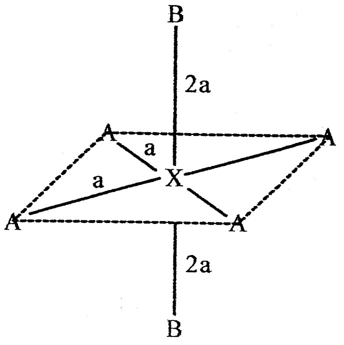
[Question 2 is continued in the next page]

(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)

3. Consider a diatomic molecule which behaves as a harmonic oscillator and a non-rigid rotor.

(a) Write down a mathematical expression for the vibration-rotation energy levels of the molecule and identify all the terms in it.

(10 marks)

(b) Write down the specific selection rules for the vibration-rotational energy transitions.

(06 marks)

(c) Briefly describe how the P and R-branches in the IR spectrum of the molecule is created.

(14 marks)

(d) Derive expressions for the positions of lines in the P and R-branches in the IR spectrum of the molecule under Born-Oppenheimer approximation.

(20 marks)

(e) A series of adjacent lines in the fundamental band in the vibration-rotation spectrum of $H^{35}Cl$ are located at wavenumbers $\left(\text{in cm}^{-1}\right)$ 3054.018, 3033.212, 3012.166, 2969.834, 2948.788, 2927.982.

(i) Giving reasons deduce the position $\left(\text{in cm}^{-1}\right)$ of the band origin.

(ii) Out of the above given set of lines identify the lines in the P branch and those in the R branch.

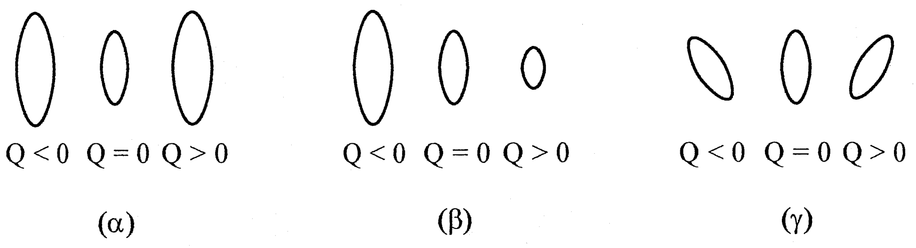
(iii) Calculate the rotational constant and the centrifugal distortion constant of $H^{35}Cl$, in Born-Oppenheimer approximation, using the lines in the P branch.

(50 marks)

4. (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.)



(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)

(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.

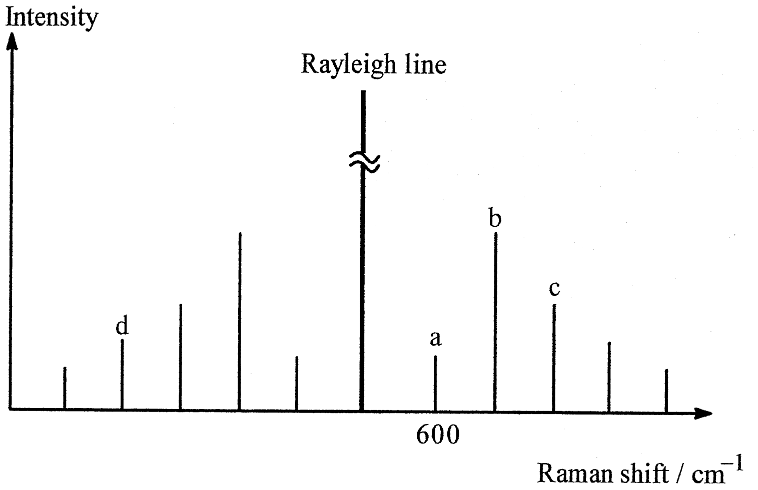
Frequency/ cm^{-1}	Raman spectrum	IR spectrum
1450.0	Strong peak	No peak
650.0	No peak	Strong peak
3400.0	No peak	Strong peak

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)

[Question 4 is continued in the next page]

(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.

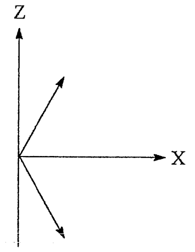
(ii) Calculate the rotational constant of the molecule.

(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) All allowed orientations of the spin vector of a proton are sketched in the following diagram. Similarly sketch all the allowed orientations of the spin vector of a magnetic nucleus with the spin quantum number $I = 3/2$.



(10 marks)

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

(ii) A molecule has three chemically equivalent groups (G_1, G_2 and G_3) of magnetic nuclei of the same atomic species with the nuclear spin quantum number $I = 3/2$. Groups G_1, G_2 and G_3 have 2, 3 and 4 nuclei each, respectively. The nuclei satisfy the conditions of an AMX spin system in a particular NMR spectrometer. The highest shielded nuclei are in G_3 and the lowest shielded nuclei are in G_1. There are no other magnetic nuclei in the molecule. The Larmor frequencies of nuclei in groups G_1, G_2 and G_3, in the spectrometer, are ν_1, ν_2 and ν_3 respectively. In standard notation, the scalar coupling constants are J_{12}, J_{13} and J_{23}. Sketch the high resolution NMR spectrum of the molecule, on an intensity versus frequency diagram, recorded when the sample is simultaneously irradiated with radio waves of frequency ν_3.

Label the multiplets using the relevant group label G_1, G_2 or G_3.

Clearly indicate the relevant chemical shifts and the separation in adjacent lines in each multiplet on the diagram.

Disregard the variation of intensity of lines and use lines of the same height in sketching the spectrum.

Briefly explain your answer

(25 marks)

(c) (i) Define the δ scale for chemical shifts using a mathematical expression and identify all the parameters in it.

(ii) In general the resonance frequency of magnetic nucleus placed in an NMR spectrometer depends on the strength of the static magnetic field, B_0. However, show that the chemical shift expressed in δ scale is independent of B_0.

(25 marks)

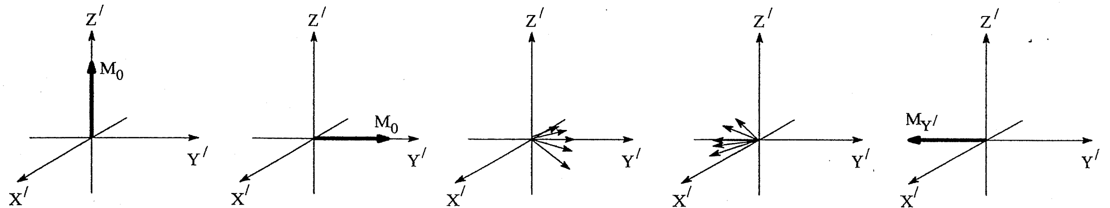
(d) Define the following terms as applied in NMR spectroscopy.

(i) Longitudinal relaxation

(ii) Transverse relaxation.

(10 marks)

(e) The behavior of the macroscopic magnetization and individual spins in the rotating frame during a pulse–delay sequence in a spin echo experiment of a magnetic nucleus in a particular environment is sketched (in standard notation) in the following figure.



(α) (β) (γ) (δ) (λ)

(i) Indicate the pulse–delay sequence (e.g. $180^0_{Y'}$ pulse – delay $\tau - 90^0_{X'}$ pulse –....) involved in going from $(\alpha) \to (\beta) \to (\gamma) \to (\delta) \to (\lambda)$.

(ii) Explain why the components of spins fan out when going from $(\beta) \to (\gamma)$.

(iii) Explain why the components of spins come together when going from $(\delta) \to (\lambda)$.

(30 marks)

6. (a) State the Frank-Condon principle. How would you apply this principle in electronic spectroscopy?

(20 marks)

(b) (i) What is the selection rule governing vibrational transitions?

(ii) Consider the vibrational coarse structure in an electronic transition of a diatomic molecule. Explain why the above selection rule is not strictly applied during electronic-vibrational transitions.

(iii) Sketch all the vibrational transitions that <u>honour (obey) the above selection rule</u> and occur from $n'' = 0,1,2,3$ to $n' = 0,1,2$ during an electronic transition in a diatomic molecule, where n'' represents vibrational states in the ground electronic state and n' represents the vibrational states in the excited electronic state. Copy the following table and fill in the blanks with respect to the above transitions.

n'	n''	Δn for the transition

(40 marks)

(c) Vibrational energy (including corrections for anharmonisity) can be given in wave number terms as, $G(n) = (n + 1/2)\varpi_e - (n + 1/2)^2 \varpi_e x_e$ where all the symbols have their usual meanings. Following table gives the absorption wave numbers in the vibrational coarse structure of the electronic spectrum of carbon monoxide.

n' (excited electronic state)	n'' (ground electronic state)	Absorption wave number (cm^{-1})
0	0	64758
1	0	66234
2	0	67682
3	0	69089
4	0	70467

Use above data (deriving necessary equations) to calculate the bond anharmonisity constant (x_e) and ϖ_e for carbon monoxide.

(40 marks)