THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Final Examination — 2015/2016

CHU 3128/CHE 5128 — Special Topics in Spectroscopy

(*2 hours*)

4th January 2017 (Wednesday)	1.30 p.m. — 3.30 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 <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)	=	$8.314 \ \text{J} \ \text{K}^{-1} \ \text{mol}^{-1}$
Avogadro constant (N_A)	=	$6.023 \times 10^{23} \ \text{mol}^{-1}$
Faraday constant (F)	=	$96{,}500 \ \text{C} \ \text{mol}^{-1}$
Planck constant (h)	=	$6.63 \times 10^{-34} \ \text{J} \ \text{s}$
Velocity of light (c)	=	$3.0 \times 10^{8} \ \text{m} \ \text{s}^{-1}$
Standard atmospheric pressure	=	$10^{5} \ \text{Pa} \left(\text{N} \, \text{m}^{-2} \right)$
π	=	3.14159
$\text{Log}_e (X)$	=	$2.303 \ \text{Log}_{10} (X)$

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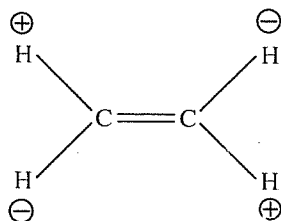

    CCH and HCH bond angles remain the same during vibration in this mode.

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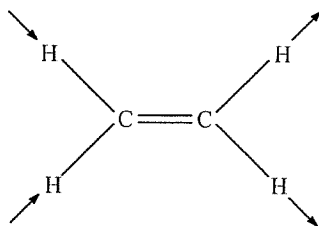
Giving reasons, state whether it is a parallel mode or a perpendicular mode.

(25 marks)

(e) $H^{35}Cl$ behaves as an anharmonic oscillator with $\bar{\omega}_e = 2990\ cm^{-1}$ 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]

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(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 $D_0 = 8.2341 \times 10^{-19}$ 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

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

(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 rigid rotor, are also indicated in the same graph (in the same frequency scale). Explain difference in frequency of the corresponding lines in the two spectra.
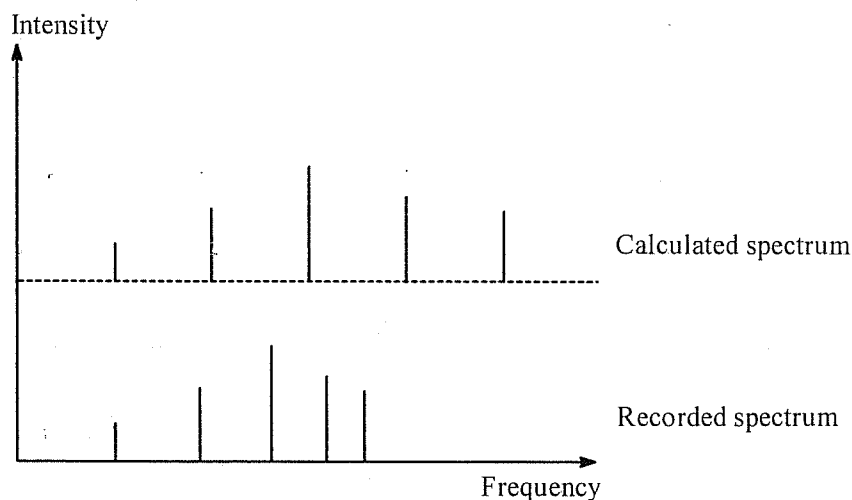
(20 marks)

(c) Giving an example in each, define the following terms as applied in molecular spectroscopy.

(i) parallel vibration   (ii) perpendicular vibration

(25 marks)

[Question 2 is continued in the next page]

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(d) (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.
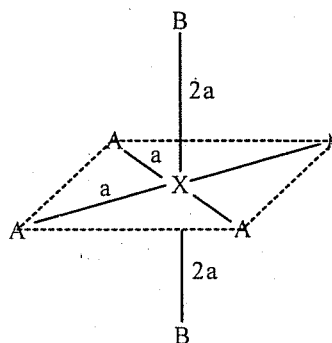
(30 marks)

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.
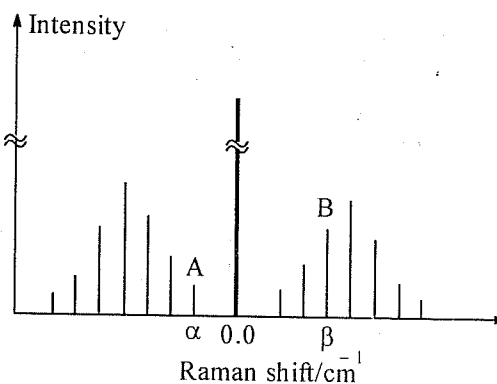
(50 marks)

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4. (a) Pure vibrational Raman spectrum corresponding to the fundamental and first overtone transitions of a diatomic molecule are schematically represented in the figure. The lines are designated as A, B, C, D and E. The Raman shifts are denoted by $-\alpha$, $-\beta$, γ and δ.

(i) Identify the line with zero Raman shift (i.e. line C).

(ii) Identify the lines A, B, D and E as Stokes and anti-Stokes lines.

(iii) State the relationship between β and γ.

(iv) State the relationship between α and δ.

(v) Giving reasons identify the lines corresponding to the fundamental and first overtone transitions, respectively.

(vi) State the approximate relationship between (α and β).

(30 marks)

(b) Pure rotational Raman spectrum of a diatomic molecule (which behaves as a rigid rotor) is schematically represented in the figure. There, α and β are the Raman shifts of the lines A and B respectively and $\alpha = -120$.


(i) State the specific selection rule in pure rotational Raman spectroscopy.

(ii) Starting with the expression for rotational energy levels of the diatomic molecule derive an expression for α in terms of the rotational constant.

(iii) Determine the rotational constant of the diatomic molecule.

(iv) Derive an expression for the separation between adjacent anti-Stokes lines.

(v) Determine β.

(35 marks)

(c) Two consecutive bands (with rotational fine structure) corresponding to the fundamental and the first overtone in the vibration-rotation Raman spectrum of a diatomic molecule are schematically represented in the figure. Raman shifts α and β has the relationship, $\alpha < \beta$.

(i) Giving reasons identify the sets of lines corresponding to the fundamental and the first overtone transitions respectively.

(ii) Giving reasons state whether the lines in the spectrum in the figure are Stokes lines or anti-Stokes lines.

(iii) Giving reasons identify the branches A, C, D and F as O, P, Q, R, S etc.

(35 marks)

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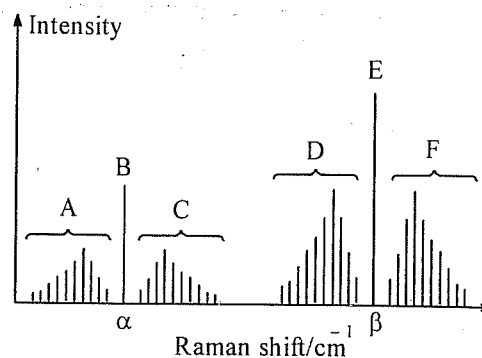
5. (a) The energy of an unshielded nucleus (or a subatomic particle) placed in a magnetic field is given by $E = -\gamma \left(\dfrac{h}{2\pi} \right) m_I B_0$. Identify all the terms in this expression.

(15 marks)

(b) A scientist investigates the possibility of neutron spin resonance and has available a commercial NMR spectrometer with a variable applied magnetic field.

(i) Deduce the number of nuclear magnetic energy levels of a neutron placed in this spectrometer?

(ii) What are the specific selection rules?

(iii) Calculate the strength of the magnetic field for resonance at $300\,\text{MHz}$.

(iv) Calculate the lowest energy of a neutron under resonance conditions.

[For a neutron $I = 1$ and $\gamma = -1.831 \times 10^8 \ \text{rad s}^{-1} \ \text{T}^{-1}$]

(60 marks)

(c) Clearly indicating the frequencies, sketch the Fourier transform of $f(t) = 2.5 \times \sin(9\pi t) + 5.2 \times \exp(-9.3\,t)$ in intensity versus frequency plot.

(25 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 obey the above selection rule 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)

[Question 6 is continued in the next page]

(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)