



THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Final Examination — 2011/2012

CMU 3131 — Concepts in Spectroscopy

(2 hours)

15th June 2012 (Friday)

1.30 p.m. — 3.30 p.m.

- There are four (04) questions and six (06) pages (including the first page) in the paper.
 - Answer **ALL FOUR** (04) questions.
 - The use of a non-programmable calculator is permitted
 - Cellular phones are not allowed.
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Gas constant (R)	=	8.314 J K ⁻¹ mol ⁻¹
Avogadro constant (N _A)	=	6.023 × 10 ²³ mol ⁻¹
Faraday constant (F)	=	96,500 C mol ⁻¹
Planck constant (h)	=	6.63 × 10 ⁻³⁴ J s
Velocity of light (c)	=	3.0 × 10 ⁸ m s ⁻¹
Standard atmospheric pressure	=	10 ⁵ Pa (Nm ⁻²)
π	=	3.14159
Log _e (X)	=	2.303 Log ₁₀ (X)

1. (a) Consider a heteronuclear diatomic molecule whose variation of potential energy as a function of internuclear distance is given by the Morse function. Sketch the curve of potential energy versus internuclear distance for the molecule. Indicate the *dissociation limit*, *ground energy level* and the *dissociation energies* D_e and D_0 on the sketch you have drawn.

(10 marks)

- (b) In standard notation the vibrational energy (in wavenumber units) of the diatomic molecule mentioned in part (a) above, is given by the following expression.

$$\bar{E}_v = \left(v + \frac{1}{2} \right) \bar{\omega}_e - \left(v + \frac{1}{2} \right)^2 x_e \bar{\omega}_e$$

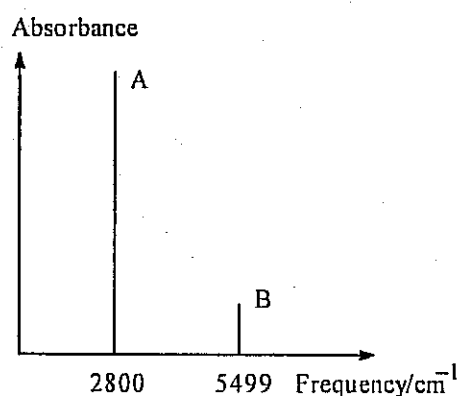
- (i) Identify all the parameters in the above energy expression.
 (ii) What is the selection rule in IR spectroscopy of the molecule?
 (iii) Using the energy level expression and the selection rule, derive an expression for the wavenumber of the absorbed radiation due to a vibrational excitation originating from the ground state. [Hint: $v = n$ for the excited state]
 (iv) Deduce expressions for the wavenumbers of the fundamental and the first overtone from the expression you have derived in part (iii) above.

(30 marks)

- (c) Answer either Part (α) or Part (β) (but NOT both).

- (α) At room temperature, the full pure vibrational spectrum of the molecule mentioned in part (a) above, recorded by a student shows only two lines as indicated in the figure.

- (i) Giving reasons, identify the lines using standard nomenclature (fundamental and overtones etc.) and indicate the vibrational energy level transitions involved in producing each of these lines. (Assume that the student has not made any errors in recording the spectrum).



- (ii) Calculate x_e and $\bar{\omega}_e$ for the molecule.

(40 marks)

- (β) In standard notation, $\bar{\omega}_e = 1903.98 \text{ cm}^{-1}$ and $x_e = 0.007332$ for a heteronuclear diatomic molecule, XY.

- (i) For XY, derive a relationship among $\bar{\omega}_e$, x_e and v_m where v_m is the vibrational quantum number of the vibrational energy level with maximum energy.
 (ii) Calculate v_m for XY.
 (iii) Estimate the energy required to dissociate a molecule of XY which is in its first vibrational excited state.

(40 marks)

- (d) Two vibrational normal modes of acetylene molecule are represented in standard notation in the following diagrams. Giving reasons, identify each of them as a parallel or a perpendicular mode.



(20 marks)

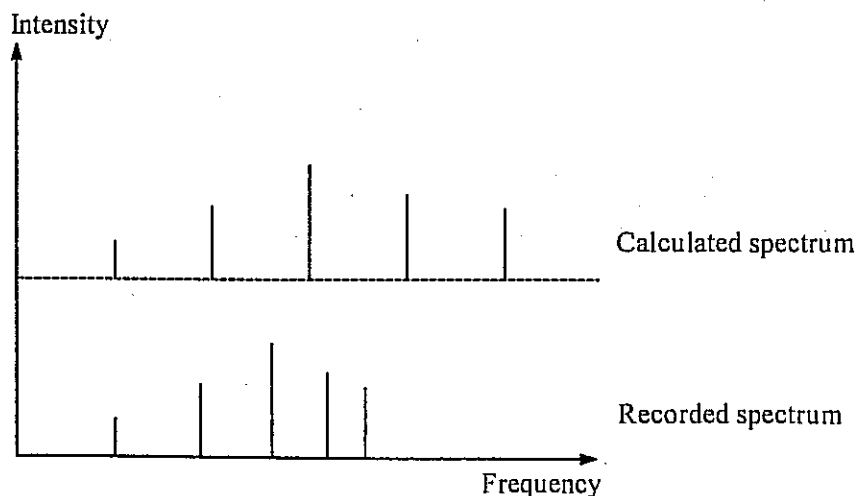
2. (a) In standard notation, the rotational energy levels (in wavenumber units) of a heteronuclear diatomic molecule are given by the equation

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

- (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 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.

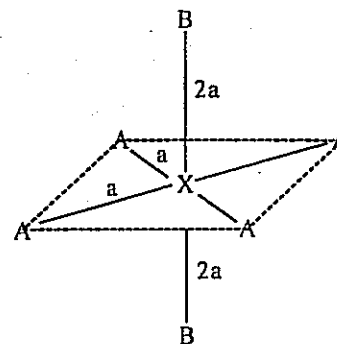


(20 marks)

- (c) Answer either Part (α) or Part (β) (but **NOT** both).

- (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). $\text{X}-\text{A}$ and $\text{X}-\text{B}$ 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.

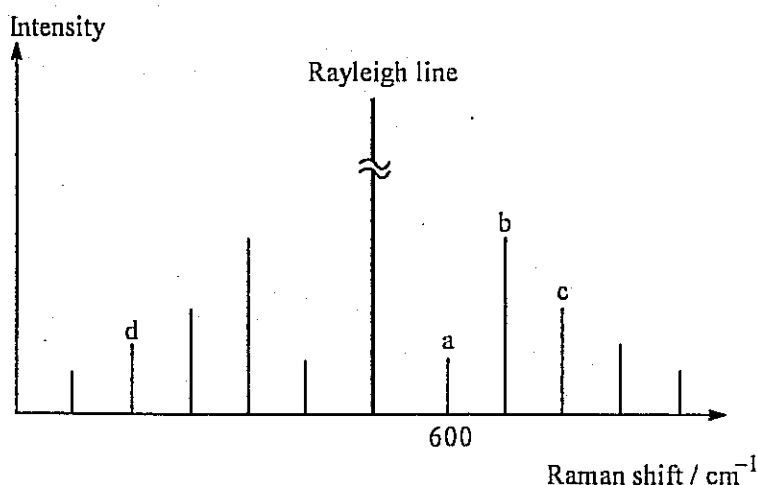


(25 marks)

- (β) (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)

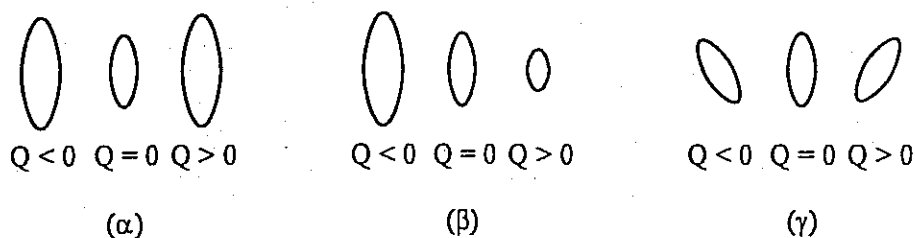
- (d) The pure rotational Raman spectrum of a diatomic molecule is schematically represented in the following figure. The Raman shift of the spectral line a is 600 cm^{-1} .



- (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)

3. (a) 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)
- (b) (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)

- (c) Write down the occupation of molecular orbitals in the ground state of He_2^+ molecular ion. (10 marks)
- (d) The equation given below can be used to calculate the energy absorbed during an electronic transition.

$$\Delta E = \Delta E_E + \left(n' + \frac{1}{2}\right) h \nu' - \left(n'' + \frac{1}{2}\right) h \nu'' + \frac{h^2}{8\pi^2 I'} J' (J' + 1) - \frac{h^2}{8\pi^2 I''} J'' (J'' + 1)$$

- (i) What are the quantum numbers of the lower vibrational and rotational states? What is the moment of inertia of the lower electronic state?
- (ii) Sketch four transition/s allowed by the selection rules, $\Delta n = 1$ and $\Delta J = 1$ originating from the ground vibrational and rotational state of the lower electronic state and ending at the upper electronic state. Label all the relevant vibrational and rotational states with the quantum numbers.

(40 marks)

4. (a) The δ scale of chemical shift is defined by the equation,

$$\delta = \frac{\nu_{\text{Sample}} - \nu_{\text{Reference}}}{\nu_0} \times 10^6.$$

- (i) Identify all the parameters in the above equation.
- (ii) Write down the relationship between Larmor frequency of a nucleus and the shielding constant and identify all the parameters in it.
- (iii) Show that the chemical shift of a particular nucleus on δ scale is independent of the strength of the static magnetic field, B_0 , of the NMR spectrometer.
- (iv) Explain why the chemical shift on δ scale has to be negative for nuclei which are more shielded than the nuclei in the reference.

(35 marks)

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

- (ii) Three sets of protons in a molecule (which has no other magnetic nuclei) forms an AMX spin system in a particular NMR spectrometer. The sets corresponding to A, M and X has 1, 2 and 1 protons, respectively (so that one can also say that they form an AM_2X spin system). The scalar coupling constants are, $J_{AM} = 5$ Hz, $J_{MX} = 8$ Hz and $J_{AX} = 20$ Hz. The relationship among the resonance frequencies of A, M and X protons in the spectrometer is $\nu_A > \nu_M > \nu_X$. Sketch the high resolution NMR spectrum of these protons in intensity versus resonance frequency plot. Clearly indicate the spacing (in Hz) of the lines and centre of the multiplet due to each set of protons. Also indicate the intensity of each line on a scale where the shortest line has intensity one (1).

(35 marks)

- (c) Sketch the NMR spectrum generated by the free induction decay (FID) signal $f(t) = 3.6 \exp(-2.67t) \sin(9\pi t) + 4.89 \sin(20\pi t)$ on intensity versus frequency plot. Clearly indicate the frequency corresponding to the peaks/lines. (The intensity of all peaks/lines may be taken to be the same.)

(10 marks)

- (d) (i) Briefly describe what is meant by the double resonance method in NMR spectroscopy.
- (ii) Briefly describe how the double resonance method could be used to simplify an NMR spectrum of a molecule.

(20 marks)