THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Final Examination — 2014/2015

CMU 3131/CME 5131 — Concepts in Spectroscopy

(2 *hours*)

13th May 2015 (Wednesday) 9.30 a.m. — 11.30 a.m.

- There are four (04) questions and seven (07) pages (including the first page) in the paper.
- Answer **ALL FOUR** (04) questions.
- 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
$\mathrm{Log}_e(X)$	=	$2.303\ \mathrm{Log}_{10}(X)$

Some equations used in spectroscopy are given below in standard notation.

$$E_\upsilon = (\upsilon + 1/2)\bar{\omega} \qquad \bar{E}_\upsilon = (\upsilon+1/2)\bar{\omega}_e - (\upsilon+1/2)^2 x_e\bar{\omega}_e \qquad \bar{\nu}_J = 2\bar{B}(J+1) - 4\bar{D}(J+1)^3$$

$$\bar{B} = h/\left(8\pi^2\mu c R^2\right) \qquad \bar{E}_J = \bar{B}J(J+1) - \bar{D}J^2(J+1)^2 \qquad \nu = \gamma(1-\sigma)B_0/2\pi$$

$$\bar{\nu}_0 = (1-2x_e)\bar{\omega}_e \qquad \bar{\nu}_1 = 2(1-3x_e)\bar{\omega}_e \qquad \bar{\nu}_2 = 3(1-4x_e)\bar{\omega}_e$$

$$E(\upsilon_1, \upsilon_2, \upsilon_3, \ldots) = \sum_{\substack{k = \text{All} \\ \text{normal} \\ \text{modes}}} h\left(\upsilon_k + \frac{1}{2}\right)\omega_{e,k} + \sum_{j \le k} h x_{jk}\left(\upsilon_j + \frac{1}{2}\right)\left(\upsilon_k + \frac{1}{2}\right) + hG_0$$

$$N_i = \frac{g_i}{g_0} N_0 \times \exp\left[-\frac{(E_i - E_0)}{kT}\right] \qquad M = \left(\frac{h}{2\pi}\right)^2 \frac{N\gamma^2 B_0}{4kT}$$

1. (a) Answer **either** Part (A) **or** Part (B) (but **NOT** both).

Part A

For the $^{127}I^{19}F$ molecule, the spectroscopic parameters (in standard notation) are $\bar{\omega}_e = 610.258\ \text{cm}^{-1}$ and $\bar{\omega}_e x_e = 3.141\ \text{cm}^{-1}$.

(i) Write down relationship among the vibrational energy and the abovementioned parameters of $^{127}I^{19}F$ and identify all parameters in it.

(ii) Starting with the energy expression in part (i) above, derive an expression for the position of a line in the IR spectrum due to a vibtational energy level transition $\upsilon'' \to \upsilon'$.

(iii) Determine the positions $\left(\text{in cm}^{-1}\right)$ of the following in the IR spectrum of $^{127}I^{19}F$.

(α) The first overtone.

(β) Lowest frequency hot band that should appear first when the sample used in recording the IR spectrum is heated from low temperatures where only the ground vibrational level is appreciably populated.

(30 marks)

Part B

Consider a diatomic molecule, AB, which behaves as a non-rigid rotor.

(i) Write down the relationship between the rotational energy levels of AB and the rotational quantum number, and identify all the parameters in it.

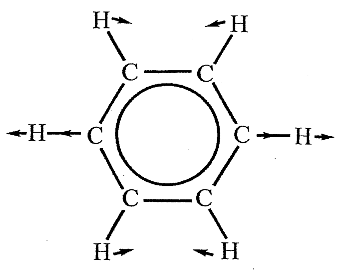
(ii) Write down the specific selection rule in the microwave spectroscopy of AB.

(iii) Using the answers to parts (i) and (ii) above, show that the positions of lines in the microwave spectrum of AB are given by $\bar{\nu}_J = 2\bar{B}(J+1) - 4\bar{D}(J+1)^3$.

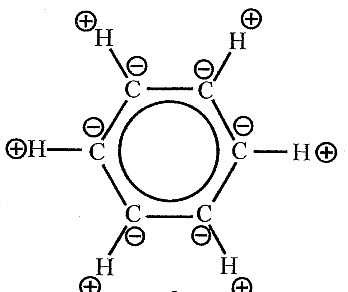
(iv) Using the equation in part (iii) above, explain which property of AB makes the separations between adjacent lines in the microwave spectrum NOT equal.

(30 marks)

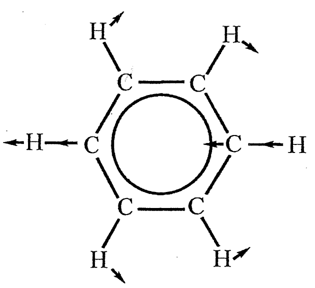
(b) Three normal modes, α, β and γ, of C_6H_6 (benzene) molecule are shown in the following figure in standard notation.



α



β



γ

(i) Giving reasons identify these normal modes as parallel or perpendicular.

(ii) Giving reasons identify the normal modes which can show an infrared spectrum.

(30 marks)

(c) Consider a CO_2 molecule which behaves as a harmonic oscillator in each of its normal modes.

(i) Draw (in standard notation) the four normal modes of it.

(ii) Indicate the degenerate modes out of the normal modes you have drawn above.

(iii) Write down the total vibrational energy of a CO_2 molecule in terms of the equilibrium vibration frequency of the normal modes and identify all the parameters in it.

(iv) Energy (in units of cm^{-1}) of the total vibrational levels $(0,1,0)$, $(0,2,0)$ and $(1,0,0)$ of CO_2 are 2840, 3507 and 3503, respectively. In the above notation of energy levels, the first and the third quantum numbers refer to the stretching vibrational normal modes of CO_2. Calculate the position (in units of cm^{-1}) of the line due to the transition $(0,0,0) \rightarrow (0,1,0)$ in the IR spectrum of CO_2.

(40 marks)

2. (a) A diatomic molecule, XY, behaves as a harmonic oscillator and a rigid rotor.

(i) Write down an expression for the vibration-rotation energy levels of XY, *in wave number units*, and identify all the parameters in it.

(ii) Write down the specific selection rules in the vibration-rotation spectroscopy of XY.

(iii) Starting with the energy level expression derive expression for the positions of lines in the P and R branches in the fundamental band in the IR spectrum of XY.

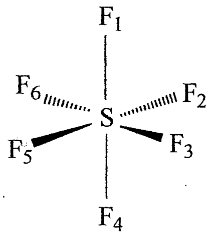
(iv) Derive an expression for the separation, $\Delta\bar{v}$, between the P and R branch maxima in the fundamental band in the IR spectrum of XY, if the rotational quantum number of the rotational energy level with highest population is given by $J_{max} = \frac{1}{2}\sqrt{\frac{2kT}{\bar{B}hc}} - \frac{1}{2}$, in standard notation.

(40 marks)

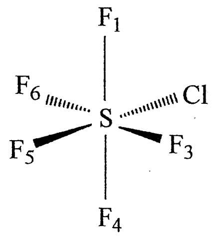
(b) Answer **either** Part (A) **or** Part (B) (but **NOT** both).

Part A

Consider the molecules of SF_6 and SF_5Cl which are shown in the following figure as (α) and (β), respectively. (β) is obtained by replacing the fluorine atom at position 2 in (α) with a chlorine atom. Assume that the bond angles and bond lengths do not change in this replacement process.



(α)



(β)

(i) Stating whether each is an ellipse or a circle, draw the cross sections of the ellipsoid of inertia of (α) on the two perpendicular planes $SF_1F_3F_4F_6$ and $SF_1F_2F_4F_5$. On your diagrams, clearly indicate the relevant axes out of F_1SF_4, F_3SF_6 and F_2SF_5. In case of an ellipse, indicate the major and minor radii on your diagram.

(ii) Stating whether each is an ellipse or a circle, draw the cross sections of the ellipsoid of inertia of (β) on the two perpendicular planes $SF_1F_3F_4F_6$ and $SF_1ClF_4F_5$. On your diagrams, clearly indicate the relevant axes out of F_1SF_4, F_3SF_6 and $ClSF_5$. In case of an ellipse, indicate the major and minor radii on your diagram.

(iii) Briefly explain your answer in part (ii) above.

(30 marks)

Part B

The following 7 bands have been measured in the infrared spectrum of a bent triatomic molecule A-B-A.

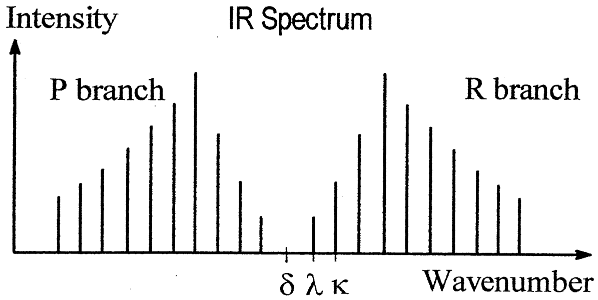
Wave number (cm^{-1})	**Intensity**	**Wave number (cm^{-1})**	**Intensity**
1200	Very strong	3600	Weak
2400	Medium strong	3870	Medium strong
2670	Very strong	4700	Medium strong
3500	Very strong		

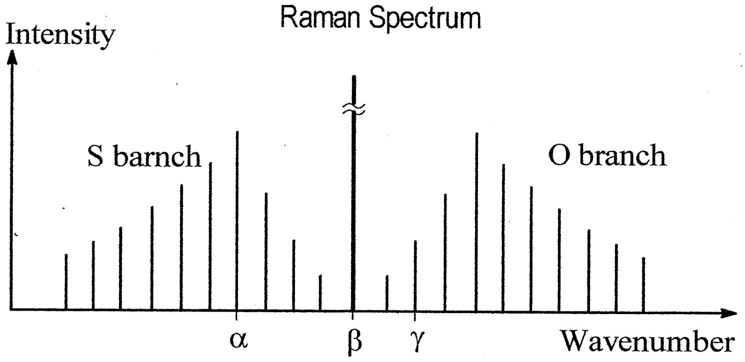
(i) Giving reasons identify each band as fundamental, overtone and combination band. In the case of an overtone band indicate whether it is 1st, 2nd, 3rd etc. overtone.

(ii) Denote the energy level transition associated with each band in standard notation.

(30 marks)

(c) The rotational fine structure of the fundamental band in the vibration-rotation IR and Stokes Raman spectra of a diatomic molecule are shown in the next page. The molecule behaves as a harmonic oscillator and a rigid rotor. Also it is known that $\delta = 2990\ cm^{-1}$ and $\lambda = 3010\ cm^{-1}$. The Raman spectrum has been recorded with incident radiation of wave number $8000\ cm^{-1}$.





Giving reasons deduce the values of α, β and γ.

(30 marks)

3. (a) The rotational energy levels of a prolate symmetric top molecule are given by $\bar{E}_{J,K} = \bar{B}\, J(J+1) + \left[\bar{A} - \bar{B}\right] K^2$. The selection rules in pure rotational Raman spectroscopy of such a molecule are given as follows.

For $K = 0$ energy levels: $\Delta K = 0$ and $\Delta J = 0, \pm 2$

For $K \neq 0$ energy levels: $\Delta K = 0$ and $\Delta J = 0, \pm 1, \pm 2$

(i) Identify all the parameters in the above energy level expression.

(ii) Derive expressions for the line positions of the R and S branches of the pure rotational anti-Stokes Raman spectrum of a prolate symmetric top molecule. Assume the wave number of the incident radiation beam to be $\bar{\nu}_0$.

(iii) Show that every line in the above mentioned S branch coincides with a line in the above mentioned R branch.

(iv) Show that some lines in the above mentioned R branch do NOT coincide with a line in the above mentioned S branch.

(50 marks)

(b) The ground state electronic configuration of Cr is $1s^2 2s^2 2p^6 3s^2 3p^6 3d^4 4s^2$. Write down, in standard notation, all possible occupations of electrons in the 3p- and 3d-levels in the above mentioned configuration. [Denote the three p-orbitals and the five d-orbitals by p_{-1}, p_0, p_{+1}, d_{-2}, d_{-1}, d_0, d_{+1} and d_{+2}.]

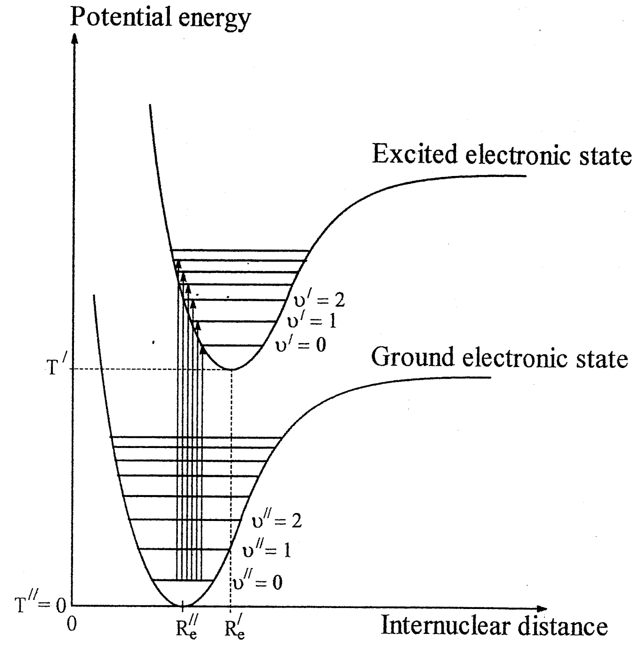
(20 marks)

(c) Consider a diatomic molecule whose potential energy curves of two electronic states are shown in the figure to the right with the following set of parameters.

$T^{//} = 0$ $\quad$ $T^{/} = 80,000\ \text{cm}^{-1}$

$\bar{\omega}_e^{//} = 3000\ \text{cm}^{-1}$ $\quad$ $x_e^{//} = 0.090$

$\bar{\omega}_e^{/} = 2000\ \text{cm}^{-1}$ $\quad$ $x_e^{/} = 0.040$



(i) Explain why ω_e and x_e in one electronic state is different to the corresponding quantities in the other electronic state even though they belong to the same molecule.

(ii) Calculate the position (in wave number units) of the line in the electronic spectrum of the molecule due to the vibronic transition $\upsilon^{//} = 1 \rightarrow \upsilon^{/} = 2$.

(30 marks)

4. (a) Consider N_1 mol of ethyl alcohol molecules (CH_3CH_2OH) at temperature T_1 placed in a uniform magnetic field of strength B_1. Under these conditions the difference in the number of methyl protons in α and β nuclear spin states in this sample is M_1.

(i) State whether the difference in the number of methyl protons in α and β nuclear spin states in the above mentioned sample become larger, smaller or remain at M_1 when the magnetic field strength is increased keeping the temperature constant at T_1.

(ii) Briefly explain your answer in part a (i) above using relevant equations.

(35 marks)

(b) (i) Briefly describe what is meant by the macroscopic magnetisation of an NMR sample.

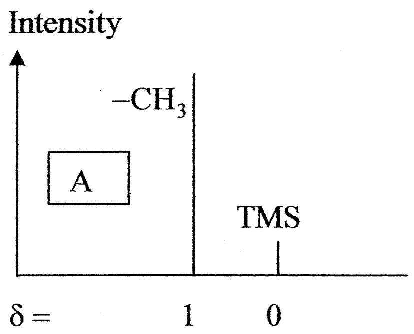
(ii) Write down a relationship between the static magnetic field strength of an NMR spectrometer and the macroscopic magnetisation of a sample placed in it under high temperature conditions and identify all the parameters in it.

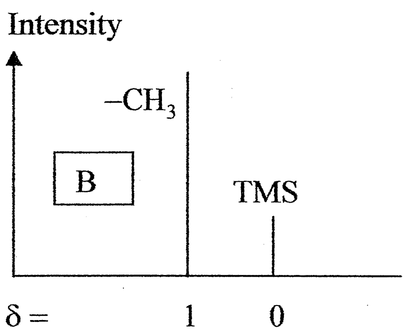
(iii) Consider one mole of ^1H nuclei placed in a magnetic field of strength 11.4 T. Calculate the macroscopic magnetisation of this sample of nuclei at 25^0C ?

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

(35 marks)

(c) A student recorded the NMR spectrum of methyl protons in ethyl alcohol, in duplicate. In both recordings, A and B, he took the same amount of alcohol from the same bottle, added a little TMS and injected into the same NMR spectrometer. The spectra he recorded (at the same temperature) are schematically represented in the following figure. In both spectra (recorded on the same scale) the intensity of the line due to methyl protons is the same. However, in A the intensity of the line due to TMS is smaller than that in B. Briefly explain why the intensity of the lines due to methyl protons is the same while that of lines due to TMS is different in A and B.





(30 marks)