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THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Final Examination — 2013/2014

CMU 3131/CME 5131 — Concepts in Spectroscopy

(2 *hours*)

19th June 2014 (Thursday) 9.30 a.m. — 11.30 a.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
- Mobile phones are **not** allowed.

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

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

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

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

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

$$\bar{E}_{JK} = BJ(J+1)+(A-B)K^2 - D_J J^2(J+1)^2 - D_{JK}J(J+1)K^2 - D_K K^4$$

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

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

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

Part A

Copy the following table onto your answer script and fill out with appropriate values of the quantities (indicated in the first column) for the molecules (indicated in the first row) in their gaseous phase.

Molecule **Quantity to be evaluated**		He	Br_2	BF_3	C_{60}
(i)	Number of nuclei				
(ii)	Total number of degrees of freedom				
(iii)	Translational degrees of freedom				
(iv)	Rotational degrees of freedom				
(v)	Number of normal modes				

(24 marks)

Part B

A diatomic molecule, AB, behaves as an anharmonic oscillator.

(i) Sketch the potential energy curve for AB on a potential energy versus internuclear distance diagram and do the following on the same diagram.

(α) Using horizontal lines sketch the first four vibrational energy levels (the variation in relative separation of the energy levels should be visible)

(β) Using vertical arrows sketch the transitions corresponding to the fundamental and 2nd overtone and label them.

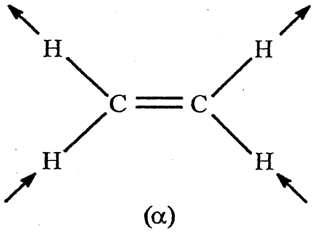
(γ) Using double arrows, indicate the zero point energy, energy corresponding to the dissociation energies, D_0 and D_e, and label them.

(ii) The equilibrium vibration frequency and the anharmonicity constant of AB are 2990 cm^{-1} and 0.074 respectively.

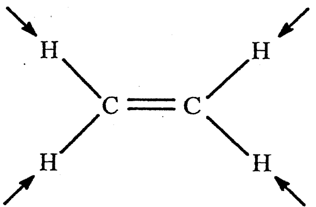
Calculate the difference between D_0 and D_e for AB in units of cm^{-1}.

(24 marks)

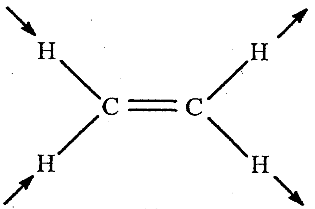
(b) Three normal modes, (α), (β) and (γ), of C_2H_4 molecule are shown in the following figure.



(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.

(26 marks)

(c) In standard notation the vibrational parameters for a water molecule are given, in units of cm^{-1}, as follows.

$\omega_{e,1} = 3832.2$ $\omega_{e,2} = 1648.5$ $\omega_{e,3} = 3942.5$

$x_{11} = -42.6$ $x_{22} = -16.8$ $x_{33} = -47.6$

$x_{12} = -15.9$ $x_{13} = -165.8$ $x_{23} = -20.3$

$G_0 = 1.6$

Consider the four vibrational energy levels $(0,0,0)$, $(0,0,2)$, $(1,1,0)$ and $(0,1,0)$.

(i) Identify the above levels as fundamental, overtone, ground, combination etc. levels.

(ii) Calculate the energy of each level, $(0,0,0)$, $(0,0,2)$ and $(1,1,0)$, in units of cm^{-1}.

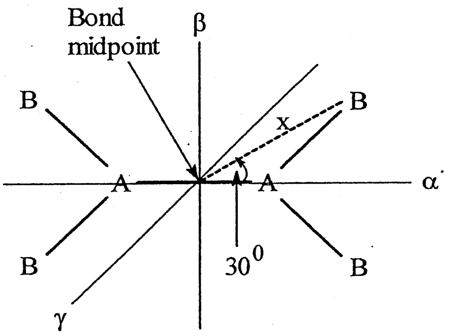
(iii) Calculate the wavenumbers of photons that bring about the following transitions.

$(\alpha)\ (0,0,0) \rightarrow (1,1,0)$ $(\beta)\ (1,1,0) \rightarrow (0,0,2)$

(iv) Identify the spectra due to each of the above transitions as fundamental, overtone, combination etc. bands.

(50 marks)

2. (a) A planar molecule, A_2B_4, has the geometry shown in the figure. A-A bond axis is labelled as α. The axes β and γ pass through the bond midpoint and are perpendicular to α. All three axes, α, β and γ are C_2 axes. The distance from the bond midpoint to any B nucleus is x. The angle between α and the line joining the bond midpoint and a B nucleus is 30^0. A-A bond length is 2y. The mass of an A nucleus and a B nucleus are represented by M and m respectively. $\left[\sin(30^0) = 1/2,\ \cos(30^0) = \sqrt{3}/2\right]$



(i) Derive expressions for the moment of inertia of the molecule about the three axes α, β and γ.

(ii) Giving reasons, state whether A_2B_4 is a spherical, symmetric or an asymmetric top.

(35 marks)

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

Part A

The first four lines in the high resolution microwave spectrum of $^{2}H^{19}F$ appear at $22.0180\ cm^{-1}$, $44.0218\ cm^{-1}$, $65.9970\ cm^{-1}$ and $87.9295\ cm^{-1}$. [Relative atomic masses: $^{2}H = 2;\ ^{19}F = 19$]

(i) Deduce whether $^{2}H^{19}F$ behaves as a rigid rotor or a non-rigid rotor.

(ii) Write down an expression for the wavenumber of the line in the microwave spectrum of $^{2}H^{19}F$ due to the rotational transition $J \rightarrow J+1$ and identify all the parameters in it.

(iii) Using the wavenumbers of minimum number of lines as is required, calculate the rotational constant of $^{2}H^{19}F$. [Plotting of a graph is NOT necessary]

(iv) Calculate the H-F bond length.

(35 marks)

Part B

Consider a non-rigid oblate symmetric top molecule, X whose rotational energy levels, ε_{JK}, are given by the following equation.

$$\varepsilon_{JK} = BJ(J+1) - D_J J^2 (J+1)^2 + (C-B)K^2 - D_K K^4 - D_{JK} J(J+1)K^2$$

where B, C, D_J, D_K and D_{JK} are positive constants.

(i) Write down the gross and specific selection rules in microwave spectroscopy of X?

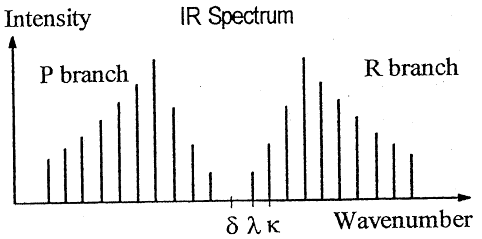
(ii) Starting with the above given energy expression, derive an expression for the position of lines in the microwave spectrum of X.

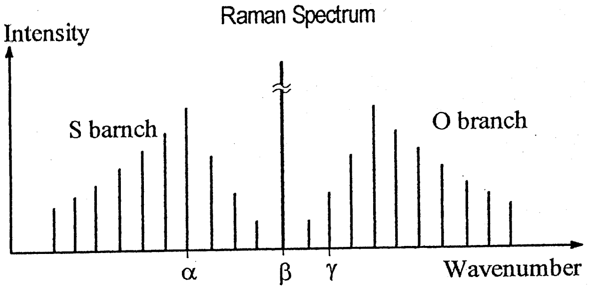
(iii) Represent an allowed transition in microwave (absorption) spectroscopy of X by $(J'', K'') \rightarrow (J', K')$. Write down all possible allowed transitions originating from rotational energy levels with $J'' = 3$ using the above representation.

(iv) Sketch the high resolution microwave spectrum of due to transitions originating from the levels with $J'' = 3$ on intensity versus frequency diagram and identify each line with the associated value/s of K.
Use a vertical line to represent each spectral line.
Disregard the variation in intensity among the spectral lines.
The variation of relative spacing between adjacent lines must be clearly visible.

(35 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.





P and O branches are due to rotational de-excitations. R and S branches are due to rotational excitations. It is observed that, in the IR spectrum the P branch appears at lower wavenumber than the R branch. However, in the Stokes Raman spectrum the O branch appears at higher wavenumber than the S branch. Explain this observation.

(30 marks)

3. (a) Consider a diatomic molecule, Y, which behaves as an anharmonic oscillator and a rigid rotor.

   (i) Write down an expression of the vibration-rotation energy of Y in terms of the vibrational and rotational quantum numbers and identify all the parameters in it.

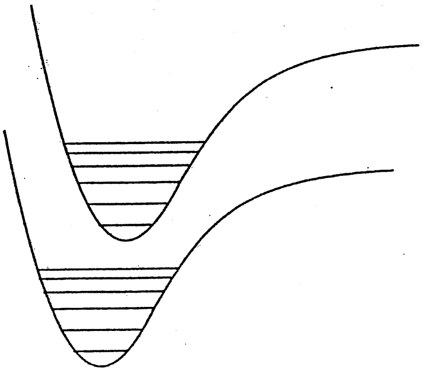
   (ii) What are the specific selection rules in vibration-rotation Raman spectroscopy of Y.

   (iii) Starting with the energy expression written in part (i) above, derive an expression for the frequency shift of the lines in the S branch of the fundamental band in the Stokes Raman spectrum of Y.

   (iv) Assume that the rotational fine structure of the fundamental band in the vibration-rotation Stokes Raman spectrum of Y is shown in the figure in question 2(c) above, with $\beta = 10,000\ \text{cm}^{-1}$. Calculate α if the rotational constant, $\bar{B} = 20\ \text{cm}^{-1}$, for Y.

(50 marks)

(b) (i) A sketches of potential energy curves and few consecutive vibration energy levels of two electronic states of a diatomic molecule are shown in the diagram to the right. Copy it on to your answer script and mark five vibronic transitions that could be used in calculating the dissociation energy of the molecule in its ground electronic state.



(15 marks)

(ii) State the selection rule in pure vibrational spectroscopy of the molecule. State why is this rule is not obeyed by the vibrational transitions between different electronic states.

(10 marks)

(iii) Briefly describe how the dissociation energy in the ground state could be calculated if the wave numbers of the transitions described in part (b)(i) above are $\bar{v}_1, \bar{v}_2, \bar{v}_3, \bar{v}_4$ and $\bar{v}_5$.

(25 marks)

4. Magnetogyric ratios of some nuclei are given below.

$\gamma\left({}^{1}\mathrm{H}\right)=2.6752\times10^{8}\ \mathrm{rad\ s^{-1}\ T^{-1}}$, $\gamma\left({}^{2}\mathrm{H}\right)=4.1066\times10^{7}\ \mathrm{rad\ s^{-1}\ T^{-1}}$,

$\gamma\left({}^{13}\mathrm{C}\right)=6.7283\times10^{7}\ \mathrm{rad\ s^{-1}\ T^{-1}}$

(a) A molecule, X, has only three protons and has no other magnetic nuclei. X produces a single line in its high resolution NMR spectrum at 500.00789 MHz when placed in a 500 MHz NMR spectrometer. Molecule Y is obtained by substituting all three protons in X with deuterium.

(i) Giving reasons state how many lines you expect to observe in the high resolution NMR spectrum of Y recorded using a 500 MHz NMR spectrometer.

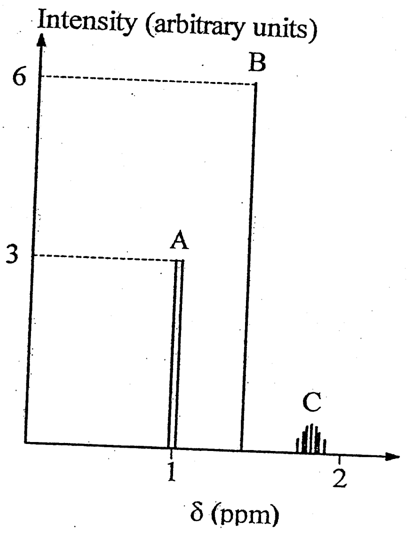
(ii) Calculate the position of the NMR line/s of Y when recorded with the same NMR spectrometer.

(30 marks)

(b) A molecule has protons in three different chemical environments denoted by A, B and C. The Fourier Transform proton NMR spectrum of these protons produces three lines of equal intensity at 600.000015 MHz, 600.000025 MHz and 600.000055 MHz respectively when recorded using a 600 MHz FT-NMR spectrometer. Giving reasons and indicating the frequencies, sketch the NMR spectrum corresponding to the FID signal if the detector is placed in a frame rotating at 600.000015 MHz.

(20 marks)

(c) A schematic representation of the high resolution proton NMR spectrum of $\mathrm{CCl(CH_3)_2-CH(CH_3)_2}$ is shown in the figure to the right. It has three sets of lines, A, B and C. (Assume that the protons form a AMX spin system.)



(i) Identify the protons which form each set of lines A, B and C.

(ii) Briefly explain the relative positioning of sets of lines A and B on the δ scale.

(iii) Briefly explain the multiplet structure in A, B and C.

(iv) Briefly explain the relative intensity of lines in A and B.

(50 marks)