THE OPENUNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Final Examination — 2015/2016

CMU 3131/CME 5131 — Concepts in Spectroscopy

(2 *hours*)

12th July 2016 (Tuesday) 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.

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

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

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

$$\bar{\varepsilon}_{JK} = \bar{B}J(J+1) - \bar{D}_J J^2(J+1)^2 + \left(\bar{C}-\bar{B}\right)K^2 - \bar{D}_K K^4 - \bar{D}_{JK}J(J+1)K^2$$

$$\bar{\varepsilon}_{JK} = \bar{B}J(J+1) - \bar{D}_J J^2(J+1)^2 + \left(\bar{A}-\bar{B}\right)K^2 - \bar{D}_K K^4 - \bar{D}_{JK}J(J+1)K^2$$

$$N_i = \frac{g_i}{g_0}N_0 \times \exp\left[-\frac{(E_i - E_0)}{kT}\right] \qquad M = \left(\frac{h}{2\pi}\right)^2 \frac{N\gamma^2 B_0}{4kT} \qquad \nu = \frac{\gamma(1-\sigma)B_0}{2\pi}$$

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

Part A

Answer the following questions as applied to the linear triatomic molecule $A-B-A$. Assume that the molecule behaves as a harmonic oscillator in each of its normal modes. The vibrational quantum number in the i^{th} normal mode is indicated by υ_i.

(i) In standard notation, identify total vibrational energy levels of the molecule in terms of the vibrational quantum numbers in each of the normal modes. Briefly explain your answer.

(ii) Define the following terms and give an example each (relevant to $A-B-A$).

(α) Fundamental level

(β) Overtone level

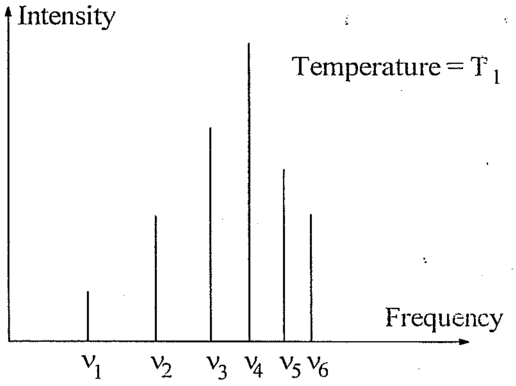
(iii) Using standard notation (as described in (i) above) identify all the fundamental levels.

(iv) State which fundamental level is degenerate and indicate its degeneracy. Briefly explain your answer.

(30 marks)

Part B

The first 6 lines in the microwave spectrum of a diatomic molecule AB, recorded at temperature T_1, is shown in the figure. Answer the following questions based on this spectrum.



(i) Giving reasons state whether AB behaves as a rigid rotor or a non-rigid rotor.

(ii) Assuming that the transition originating from the ground rotational level is observed in the spectrum, indicate the rotational transitions that produce the 6 lines in the spectrum.

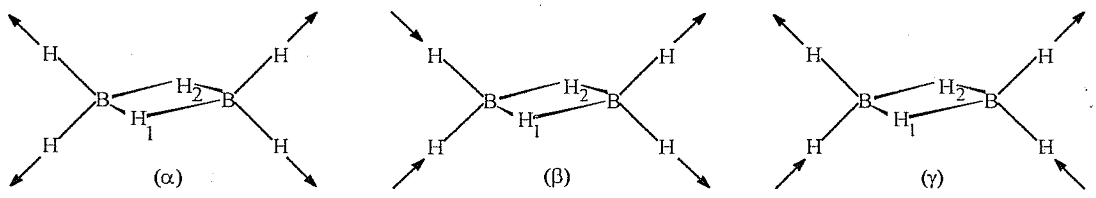
(iii) Giving reasons state what is expected with respect to the following if you were to record the microwave spectrum of AB at a temperature higher than T_1.

(α) Positions of the lines due to the transitions mentioned in part (ii) above.

(β) The position of the line with highest intensity.

(30 marks)

(b) Three normal modes, α, β and γ, of B_2H_6 (diborane) molecule are shown in the following figure in standard notation.



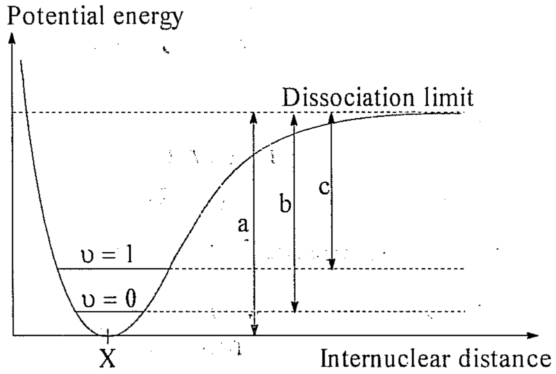
(α) (β) (γ)

[In B_2H_6 molecule, two B nuclei and hydrogen nuclei 1 and 2 are in a plane. The other four hydrogen nuclei are in a plane perpendicular to it. The movements of hydrogen nuclei in the normal modes shown above are along the relevant B-H bonds.]

(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) The potential energy versus internuclear distance of a diatomic molecule XY is shown in the figure. Also shown are the first two vibrational energy levels. It is also known that $a = 42880.8\ \text{cm}^{-1}$, $b = 41397.7\ \text{cm}^{-1}$ and $c = 38512.9\ \text{cm}^{-1}$.

(i) Write down the relationship among the vibrational energy, equilibrium vibrational frequency and the anharmonicity constant of XY and identify all the parameters in it.

(ii) Calculate the equilibrium vibrational frequency and the anharmonicity constant of XY.

(40 marks)

2. (a) A diatomic molecule, XY, behaves as anharmonic 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 vibration-rotation energy expression derive an expression for the positions of lines in the R branch in the fundamental band in the IR spectrum of XY in post Born-Oppenheimer approximation.

(iv) A student found out that the experimentally determined spectral lines, $\bar{\nu}_{R}$'s, in the R branch of the fundamental band in the vibrational-rotational spectrum of XY are given by the expression;

$$\bar{\nu}_R/\text{cm}^{-1} = -0.01786(J''+1)^2 + 3.8301(J''+1) + 2143.2680\,.$$

Where J'' has its usual meaning. Deduce the following quantities for XY.

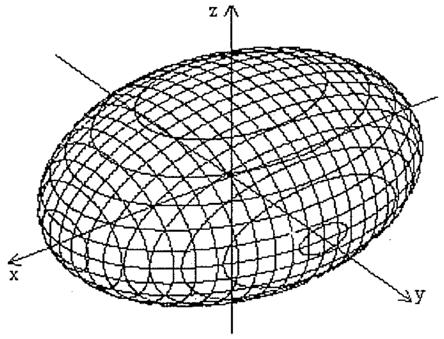
(α) Position of the fundamental line in the pure vibrational spectrum of XY.

(β) Rotational constants in the ground and first excited vibrational levels of XY.

(40 marks)

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

Part A



A sketch of the ellipsoid of inertia of the molecule *tarns*-XA_3B_2, which has a trigonal bipyramidal geometry is shown in the figure. It is an ellipsoid of rotation about the x-axis. Its major radius lies on the x-axis.

(i) State whether the ellipsoid of inertia of *tarns*-XA_3B_2 is a prolate ellipsoid or an oblate ellipsoid.
Briefly explain your answer.

(ii) Out of the three principal axes of the ellipsoid of inertia, i.e. x, y and z shown in the figure, which one coincides with the B-X-B axis of the molecule?
Briefly explain your answer.

(30 marks)

Part B

The vibrational normal modes of a non-linear triatomic molecule AB_2 may be approximated by harmonic oscillators. For this molecule the three equilibrium vibrational frequencies which are different from each other are denoted by $\omega_{e,1}$, $\omega_{e,2}$ and $\omega_{e,3}$. However, they satisfy the relationship, $\omega_{e,1} = 4\,\omega_{e,3}$.

(i) Briefly describe what is meant by accidental degeneracy (in vibrational energy).

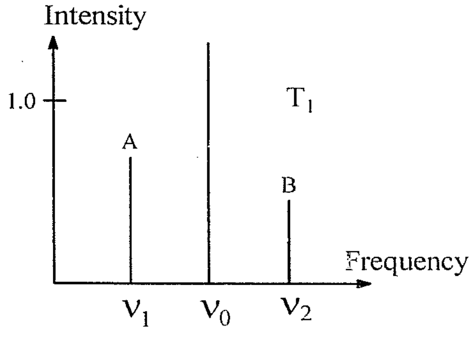
(ii) Write down the relationship between the total vibrational energy of the molecule and the three equilibrium vibrational frequencies and identify all the terms in it.

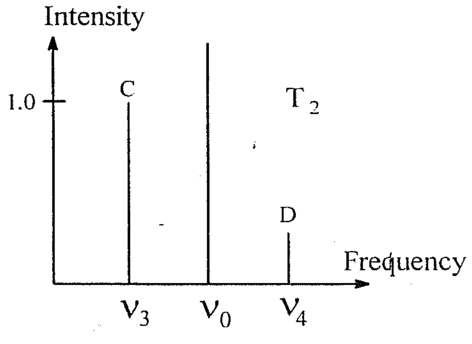
(iii) Deduce two vibrational energy levels which are accidentally degenerate and identify them in standard notation (using vibrational quantum numbers in normal modes).

(30 marks)

(c) (i) Briefly describe how Stokes and anti-Stokes lines in a Raman spectrum originate.

(ii) Answer the following questions based on the expected Raman spectra of a (hypothetical) molecule having only two energy levels at two different temperatures, T_1 and T_2, which are shown in the figure. The separation between the two energy levels is ΔE and ν_0 is the frequency of the radiation used in recording the spectrum.





(α) Giving reasons identify the Stokes and anti-Stokes lines in the above mentioned spectra.

(β) Giving reasons identify the higher temperature out of T_1 and T_2.

(γ) Deduce the relationship between ν_1 and ν_2 in terms of ΔE.

(δ) Deduce the relationship between ν_1 and ν_3 in terms of ΔE.

(λ) Deduce the relationship between ν_2 and ν_4.

(30 marks)

3. (a) Answer the following questions as applicable to methyl bromide which behaves as a non-rigid rotor. Use the following data.

For methyl bromide, three rotational constants, in units of cm^{-1}, are $A = 5.24631$, $B = 0.32192$ and $C = 0.32192$. Two centrifugal distortion constants, in standard notation, are $D_J = 3.29\times10^{-7}\ \text{cm}^{-1}$ and $D_{JK} = 4.29\times10^{-6}\ \text{cm}^{-1}$.

(i) Giving reasons classify methyl bromide as spherical top, prolate symmetric top, oblate symmetric top or asymmetric top.

(ii) Write down the relationship between the rotational energy of methyl bromide and the rotational constants and centrifugal distortion constants.

(iii) Write down the specific selection rules in pure rotational spectroscopy of methyl bromide.

(iv) Using your answers to (ii) and (iii) above, show that the position of a line in the microwave spectrum is given by $\bar{\nu} = 2\bar{B}(J+1) - 4\bar{D}_J(J+1)^3 - 2D_{JK}(J+1)K^2$.

(v) Giving reasons state how many lines can one observe in the microwave spectrum arising from the transition, $J = 3 \rightarrow J = 4$.

(vi) Calculate the position of all the lines that can be observed in the microwave spectrum arising from the transition, $J = 3 \rightarrow J = 4$.

(50 marks)

(b) Determine all possible electronic state/s arising out of the following electronic configuration of a particular exotic heteronuclear diatomic molecule/ion.

$(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p)^2(\pi 2p)^4(\pi^* 2p)^3$.

(10 marks)

(c) In standard notation the positions of lines in the rotational fine structure in the vibronic absorption spectrum of a heteronuclear diatomic molecule is given by

$\bar{\nu} = (\bar{T}' - \bar{T}'') + \left[\bar{\omega}'_e(\upsilon' + 1/2) - \bar{\omega}''_e(\upsilon'' + 1/2)\right] + \left[\bar{B}' J'(J'+1) - \bar{B}'' J''(J''+1)\right]$.

(i) What are the specific selection rules associated with the vibrational and rotational quantum numbers leading to rotational structure in vibronic spectroscopy?

(ii) Briefly describe how P, Q and R branches arise in rotational fine structure in a vibronic spectrum of a heteronuclear diatomic molecule.

(iii) Starting with the above equation deduce an equation for the position of lines in the R branch associated with a vibronic transition involving the fundamental vibrational transition (i.e. $\upsilon'' = 0 \rightarrow \upsilon' = 1$) when $\bar{\omega}'_e = \bar{\omega}''_e$.

(iv) Calculate the position of the first two lines in the R branch in the vibronic spectrum of a heteronuclear diatomic molecule involving the fundamental vibrational transition for which $\left(\bar{T}' - \bar{T}''\right) = 10000\ \text{cm}^{-1}$, $\bar{\omega}'_e = \bar{\omega}''_e = 2990\ \text{cm}^{-1}$, $\bar{B}' = 10\ \text{cm}^{-1}$ and $\bar{B}'' = 12\ \text{cm}^{-1}$.

(40 marks)

4. (a) (i) A molecule is placed in a magnetic field. Write down the relationship between the Larmor frequency of a magnetic nucleus in the molecule and the strength of the applied magnetic field and identify all the parameters in it.

(ii) Define the δ scale used in measuring the chemical shift in NMR spectroscopy.

(iii) An NMR spectrometer with a 18.8 Tesla superconducting magnet was used to obtain a ^{13}C NMR spectrum of a molecule with two chemically different ^{13}C nuclei. The separation between the two ^{13}C resonances was found to be 800 Hz. Calculate the chemical shift difference between the two ^{13}C nuclei.

$$\left[\gamma\left(^{13}C\right) = 6.7283 \times 10^{7}\ \text{rad s}^{-1}\ \text{T}^{-1}\right]$$

(40 marks)

(b) (i) Briefly describe what is meant by an AMX spin system in NMR spectroscopy.

(ii) Two protons, labelled as M, in a molecule are chemically equivalent. Together with two other protons, labelled as A and X, they form an AMX spin system. The Larmor frequencies of these three types rpotons, A, M and X, in the molecule are ν_A, ν_M and ν_X, respectively. They satisfy the relationship $\nu_A < \nu_M < \nu_X$. In standard notation the spin-spin couplings are $J_{AM} = 12\ \text{Hz}$, $J_{AX} = 5\ \text{Hz}$ and $J_{MX} = 10\ \text{Hz}$. Sketch the high resolution NMR spectrum of these four protons on an intensity versus frequency diagram. You must clearly indicate the following on the diagram.

(α) Positions of ν_A, ν_M and ν_X on the frequency axis.

(β) Height of each NMR spectral line on a scale where the highest line/s in the spectrum has/have a height of one.

(γ) The spectral line separations.

(40 marks)

(c) Indicating the frequencies at lines/peaks sketch the NMR spectra resulting from the following Free Induction Decay (FID) signals on an intensity versus frequency diagram.

(i) $f(t) = 3.3 \times \exp(-5.3t) \times \sin(9\pi t)$

(ii) $f(t) = 4.0 \times \exp(-6.0t) \times \sin(8\pi t) - 5.2 \times \sin(10\pi t)$

(20 marks)