THE OPENUNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Final Examination — 2016/2017

CMU 3131/CME 5131 — Concepts in Spectroscopy

(2 *hours*)

31st July 2017 (Monday) 9.30 a.m.. — 11.30 a.m.

- There are four (04) questions and five (05) 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)	=	$8.314\ J\ K^{-1}\ mol^{-1}$
Avogadro constant (N_A)	=	$6.023\times10^{23}\ mol^{-1}$
Faraday constant (F)	=	$96,500\ C\ mol^{-1}$
Planck constant (h)	=	$6.63\times10^{-34}\ J\ s$
Velocity of light (c)	=	$3.0\times10^{8}\ m\ s^{-1}$
Standard atmospheric pressure	=	$10^5\ Pa\left(N m^{-2}\right)$
π	=	3.14159
$Log_e(X)$	=	$2.303\ Log_{10}(X)$

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

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

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

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

$$D = 4B^3/\left(h^2\omega_e^2\right) \qquad \upsilon_m = 1/(2x_e) - 1 \qquad M = N\gamma^2 h^2 B_0/\left(16\pi^2 kT\right)$$

$$\nu = \gamma(1-\sigma)B_0/(2\pi) \qquad \bar{\nu} = 2\bar{B}(J+1) - 4\bar{D}_J(J+1)^3 - 2\bar{D}_{JK}(J+1)K^2$$

$$E_{J,K} = BJ(J+1) + [A-B]K^2 \qquad E_{J,K} = BJ(J+1) + [C-B]K^2$$

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

Part A

(i) State two experimental observations that shows a real diatomic molecule does not behave as a harmonic oscillator.

(ii) Write down the expression for the vibrational energy levels (in wave number units) of a diatomic molecule which behaves as an anharmonic oscillator and identify all the parameters in it.

(iii) Starting with the energy expression you have written above, show that the vibrational quantum number, υ_m, of the highest vibrational energy level is given by $\upsilon_m = \frac{1}{2x_e} - 1$.

(30 marks)

Part B

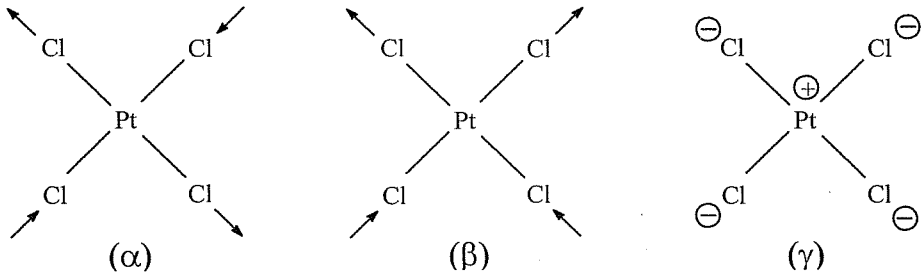
(i) Write down the expression for the vibrational energy levels (in wave number units) of a diatomic molecule which behaves as an anharmonic oscillator and identify all the parameters in it.

(ii) Starting with the energy expression you have written above, derive expressions for the wave numbers for the fundamental and the hot band due to the transition $1 \rightarrow 2$ in a diatomic molecule.

(iii) For a CO molecule the fundamental and the hot band due to the transition $1 \rightarrow 2$ appear at 2143.1 cm^{-1} and 2116.1 cm^{-1} respectively. Calculate the anharmonicity constant and the equilibrium vibration frequency of a CO molecule.

(30 marks)

(b) Three normal modes, α, β and γ, of planar $[PtCl_4]^{2-}$ ion are shown in the following figure in standard notation.



(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) A polyatomic molecule has four non-degenerate normal modes. It produces four lines, corresponding to the 1st, 2nd, 3rd and 4th normal modes, in the IR spectrum at frequencies ν_1, ν_2, ν_3 and ν_4 respectively. Assume that the molecule behaves as a harmonic oscillator in each of these normal modes.

(i) Giving reasons identify the vibrational energy levels $(1,1,0,0)$, $(0,0,2,0)$, $(0,1,2,0)$ and $(0,1,0,0)$ as fundamental or overtone or combination levels.

(ii) Write down the relationship among the total vibrational energy, E_V, of the molecule and ν_1, ν_2, ν_3 and ν_4.

(iii) Deduce the frequencies in of the lines in the IR spectrum due to the transitions $(0,1,0,0) \leftarrow (0,0,0,0)$, $(0,0,3,0) \leftarrow (0,0,2,0)$ and $(0,0,1,2) \leftarrow (0,0,0,1)$.

(iv) Deduce the relationship between ν_2 and ν_3 if the energy levels $(1,3,4,0)$ and $(1,4,2,0)$ are accidentally degenerate.

(40 marks)

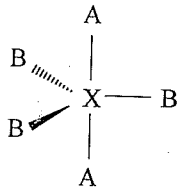
2. (a) Consider a diatomic molecule AB, which behaves as a non-rigid rotor. Using relevant equations, explain why the separation of adjacent lines in the microwave spectrum of AB becomes smaller with increasing frequency.

(30 marks)

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

Part A

The molecule, XB_3A_2 has a trigonal bipyramidal geometry as shown in the figure. Bond lengths X-A and X-B are equal. All three B-X-B angles are equal. Mass of an A nucleus is twice as much as that of B. (i.e. $m_A = 2m_B$).



(i) Using symmetry, show that XB_3A_2 is a symmetric top molecule.

(ii) Determine whether it is a prolate symmetric top or an oblate symmetric top. $\left[\sin(60^0) = \sqrt{3}/2, \quad \cos(60^0) = 1/2\right]$.

(40 marks)

Part B

The rotational and centrifugal distortion constants for CH_3I are listed below

$\overline{B} = 0.25022\ cm^{-1}$ $\quad \overline{A} = 5.1739\ cm^{-1}$ $\quad \overline{D}_J = 2.09\times10^{-7}\ cm^{-1}$

$\overline{D}_{JK} = 3.29\times10^{-6}\ cm^{-1}$ $\quad \overline{D}_K = 87.6\times10^{-6}\ cm^{-1}$

(i) Write down an expression of the positions of lines in the microwave spectrum of CH_3I and identify all the parameters in it.

(ii) Giving reasons determine the positions of all the lines originating due to the transition $J = 3 \rightarrow J = 4$.

(40 marks)

(c) (i) State the selection rules in rotational Raman spectroscopy of a rigid symmetric top molecule.

(ii) Using the expression for the rotational energy levels of a symmetric top (prolate or oblate) derive an expression for the frequencies of the Stokes lines in the R and S branches in the pure rotational Raman spectrum of a rigid symmetric top molecule in terms of the rotational constant, B, the rotational quantum number, J and the frequency of the incident radiation, ν_0.

(30 marks)

3. (a) A student prepared an exotic molecule, AB_4 (where A and B represent atoms) which is a spherical top. It behaves as a harmonic oscillator in its vibrational normal modes. It behaves as a rigid rotor in rotational motion. The student observed the vibrational-rotational spectrum in one of its (asymmetric) normal modes.

(i) Write down the relationship among the vibrational-rotational energy levels in a normal mode of AB_4, equilibrium vibrational frequency, rotational constant and the relevant quantum numbers.
Identify all the parameters in the energy level expression you have written.

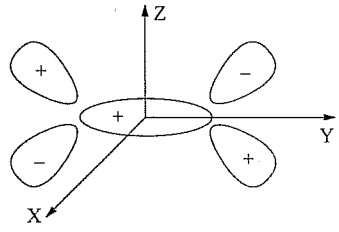
(ii) What are the specific selection rules in the vibrational-rotational spectroscopy of AB_4?

(iii) From the selection rules, deduce what branches (out of P, Q and R) may be observed in the vibrational-rotational spectrum of AB_4?

(iv) Derive expressions for the positions of lines in each branch in the vibrational-rotational spectrum of AB_4.

(50 marks)

(b) A molecular orbital is schematically represented in the figure, in standard notation. When you disregard the positive and negative signs, the orbital has C_2 rotational symmetry with respect the X-, Y- and Z-axes.



(i) Giving reasons state whether it is a gerade orbital or an ungerade orbital.

(ii) State the nature of the reflection symmetry of the orbital with respect to the XY-, XZ- and YZ-planes.

(20 marks)

(c) Birge-Sponer extrapolation is used in estimating the dissociation energy, D_0, of a diatomic molecule using its vibronic spectrum. A linear fit, $y = mx + c$, is used for this purpose.

(i) Identify y and x in the Birge-Sponer extrapolation.

(ii) The first 3 vibrational energy levels $\left(\text{in units of } cm^{-1}\right)$ in the ground electronic state of NaI are 142.81, 427.31 and 710.31. Using Birge-Sponer extrapolation, calculate D_0 of NaI in its ground electronic state.

(30 marks)

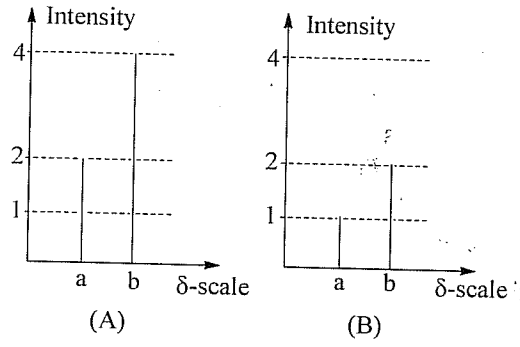
4. (a) (i) Using an appropriate mathematical equation, define the $\delta-$ scale of chemical shift.

(ii) State three essential characteristics of a compound used as a reference in NMR spectroscopy.

(iii) Two molecules A and B produce only one line each in their high resolution proton NMR spectra. These lines appear at chemical shifts 7.5 ppm and 3.2 ppm, respectively, when TMS is used as the reference. Calculate the chemical shift (in $\delta-$ scale) of the proton NMR line of B if A is used as the reference.

(40 marks)

(b) A student recorded the proton NMR spectrum of a compound X using a 200 MHz spectrometer and a 400 MHz NMR spectrometer. He used the same solution of X in both spectrometers. The high resolution NMR spectra he obtained, on the same intensity and chemical shift scales, are schematically represented in the figure. [The spectrometers have the same components except the static magnetic field and there is no scalar coupling among protons in the molecule.]



(i) Which spectrum may have been recorded with the 400 MHz NMR spectrometer?
Briefly explain your answer using an argument based on populations of NMR energy levels of protons.

(ii) Brief explain why the intensity ratio of the two lines (= 1:2) in each spectrum is the same.

(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) $f(t) = 17.32 + 10.0 \times \sin(20\pi t)$

(ii) $f(t) = 14.0 \times \exp(-12.0t) \times \sin(10\pi t) - 7.8 \times \sin(16\pi t)$

(20 marks)