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THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Final Examination — 2012/2013

CMU 3131 — Concepts in Spectroscopy

(2 *hours*)

27th November 2013 1.30 p.m. — 3.30 p.m.

- There are four (04) questions and six (07) 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.

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.

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

$$\Delta\bar{v}=\sqrt{(8kT\bar{B}/hc)} \qquad \upsilon_m=(1/2x_e)-1 \qquad \nu=\gamma B_0/2\pi$$

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

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

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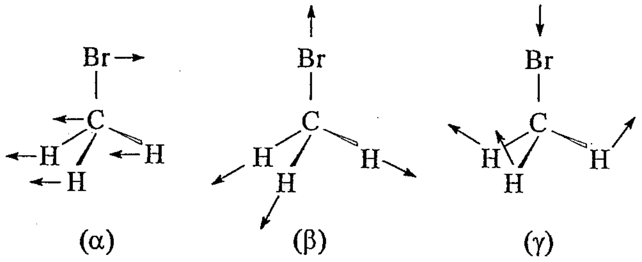
1. (a) Methyl bromide, CH_3Br, has been widely used in pest control. However, its use has been banned because it is an ozone depleting agent. It is also a Greenhouse gas because of the $C-Br$ stretching vibration, fundamental band of which appears at $611\ cm^{-1}$. A weak overtone of this stretching mode appears at $1215\ cm^{-1}$. In this stretching mode, $C-H$ bonds in the CH_3 group do <u>not</u> stretch and the CH_3 group behaves as a big atom.

(i) How many normal modes of vibration does methyl bromide has?

(ii) Write down the equation that relates the vibrational energy levels associated with the $C-Br$ stretching normal mode to its equilibrium vibration frequency and the anharmonicity constant and identify all the parameters in it.

(iii) Calculate the equilibrium vibration frequency and the anharmonicity constant for the $C-Br$ stretching mode.

(iv) A student suggested the modes, $(\alpha), (\beta)$ and (γ), shown in the figure as possible normal modes of methyl bromide. Giving reasons identify the mode which **<u>cannot</u>** be a normal mode of methyl bromide.

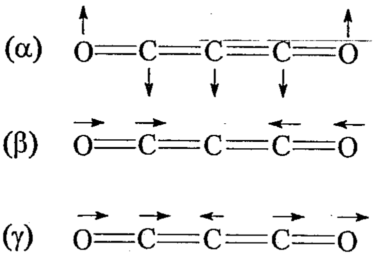


(50 marks)

(b) Three normal modes, $(\alpha), (\beta)$ and (γ), of carbon suboxide are shown in the figure.

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

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



(25 marks)

(c) Answer **either** <u>Part (A)</u> **or** <u>Part (B)</u> (but **NOT** both).

<u>Part A</u>

The equilibrium vibration frequency and the anharmonicity constant of a diatomic molecule XY are $3000\ cm^{-1}$ and 0.018 respectively. Estimate the minimum energy required to dissociate <u>1 molecule</u> of XY which is in the ground vibrational energy level.

(25 marks)

Part B

A particular polyatomic molecule has only four non-degenerate normal modes with equilibrium vibration frequencies, $\bar{\omega}_{e,1} = 600\ \text{cm}^{-1}$, $\bar{\omega}_{e,2} = 1100\ \text{cm}^{-1}$, $\bar{\omega}_{e,3} = 2300\ \text{cm}^{-1}$ and $\bar{\omega}_{e,4} = 2900\ \text{cm}^{-1}$.

(i) Identify the energy levels designated (in standard notation) by $(0,0,0,0)$, $(0,1,0,0)$, $(2,0,0,1)$ and $(2,0,0,0)$ as ground, overtone, combination, fundamental etc. levels.

(ii) Calculate the position of the line in the IR spectrum that originates from the transition $(2,0,0,0) \rightarrow (2,0,0,1)$ assuming each normal mode to behave as a harmonic oscillator.

(25 marks)

2. (a) A student observed lines in the microwave spectrum of $H^{35}Cl$ at the following wavenumbers (in cm^{-1}); $\bar{\nu} = 83.32$, 104.13, 124.73, 145.37, 165.89, 186.23, 206.60 and 226.86. Using the above mentioned wavenumbers, he made a straight line plot of $\bar{\nu}_J/(J+1)$ versus $(J+1)^2$ where J is the rotational quantum number of the lower energy level involved in the rotational transition producing the line at $\bar{\nu}_J$. His straight line plot was given by the equation, $y = -0.0021\,x + 20.867$.

(i) Write down a relationship between the rotational energy of $H^{35}Cl$ and rotational quantum number and identify all the parameters in it.

(ii) What is the selection rule in microwave spectroscopy of a diatomic molecule?

(iii) Deduce a relationship for the wavenumber of a line in the microwave spectrum of a diatomic molecule and the rotational quantum number, J, of the lower energy level involved in the transition producing that line.

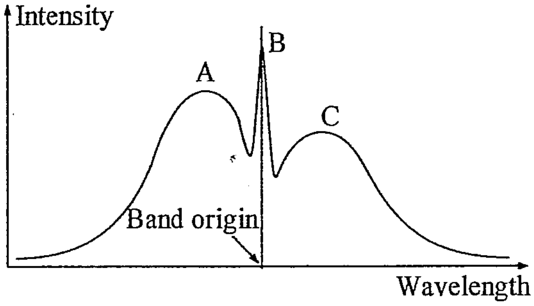
(iv) Determine the rotational constant and the centrifugal distortion constant of $H^{35}Cl$.

(30 marks)

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

Part (A)

The fundamental band of the low resolution IR spectrum of a linear molecule observed by a student is shown in the figure as the intensity versus wavelength plot.



(i) Identify the branches A, B and C in the above figure as P, Q and R.

(ii) Giving reasons state whether the normal mode that created the spectrum given in the figure is a *perpendicular mode* or a *parallel mode* of vibration.

(25 marks)

Part (B)

In order to estimate the atmospheric temperature of a plant, which is known to have a particular diatomic molecule AB, a student generated the IR spectrum of AB in the planet. He found out that the separation between the P and R maxima to be $75\ \mathrm{cm}^{-1}$. The rotational constant of AB is known to be $10\,\mathrm{cm}^{-1}$.

(i) Write down an equation relating the separation between P and R branch maxima and the rotational constant and identify all the parameters in it.

(ii) Estimate the atmospheric temperature of the planet.

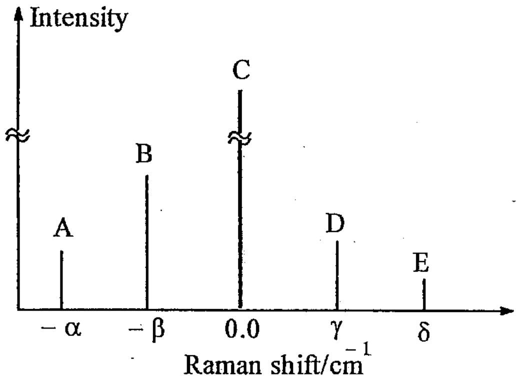
(25 marks)

(c) Giving reasons identify the following molecules as spherical, symmetric and/or asymmetric tops.

(i) NH_3 (ii) SF_6 (iii) H_2O

(15 marks)

(d) Pure vibrational Raman spectrum corresponding to the fundamental and first overtone transitions of a diatomic molecule are schematically represented in the figure. The lines are designated as A, B, C, D and E. The Raman shifts are denoted by $-\alpha$, $-\beta$, γ and δ.



(i) Identify the line with zero Raman shift (i.e. line C).

(ii) Identify the lines A, B, D and E as Stokes and anti-Stokes lines.

(iii) State the relationship between β and γ.

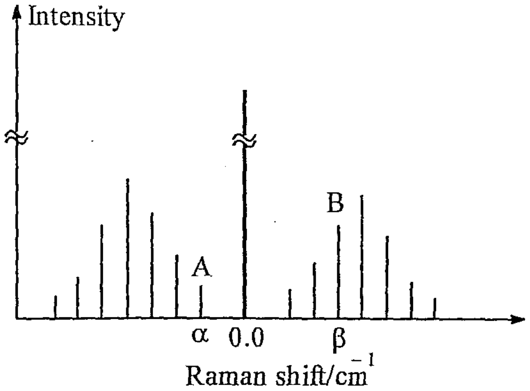
(iv) State the relationship between α and δ.

(v) Giving reasons identify the lines corresponding to the fundamental and first overtone transitions, respectively.

(vi) State the approximate relationship between (α and β).

(30 marks)

3. (a) Pure rotational Raman spectrum of a diatomic molecule (which behaves as a rigid rotor) is schematically represented in the figure. There, α and β are the Raman shifts of the lines A and B respectively and $\alpha = -120$.



(i) State the specific selection rule in pure rotational Raman spectroscopy.

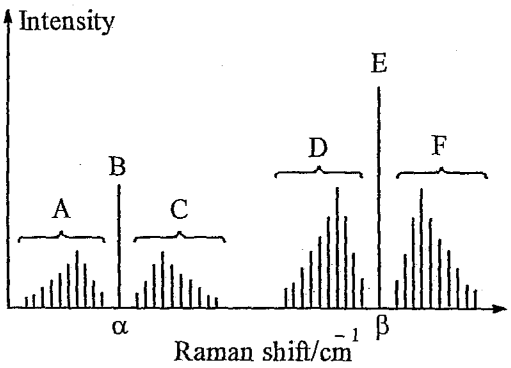
(ii) Starting with the expression for rotational energy levels of the diatomic molecule derive an expression for α in terms of the rotational constant.

(iii) Determine the rotational constant of the diatomic molecule.

(iv) Determine β.

(25 marks)

(b) Two consecutive bands (with rotational fine structure) corresponding to the fundamental and the first overtone in the vibration-rotation Raman spectrum of a diatomic molecule are schematically represented in the figure. Raman shifts α and β has the relationship, $\alpha < \beta$.



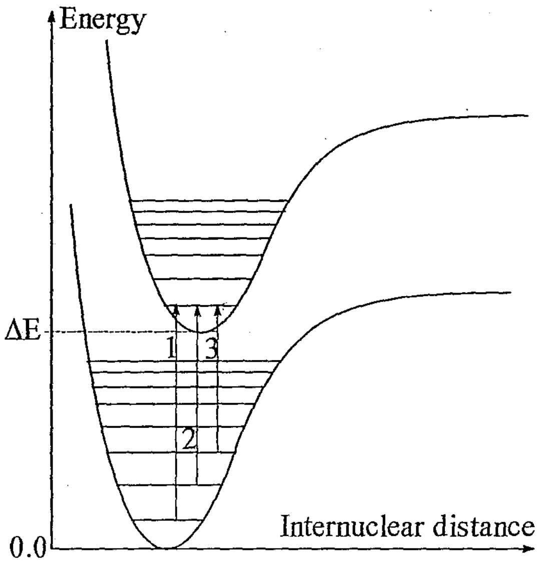
(i) Giving reasons identify the sets of lines corresponding to the fundamental and the first overtone transitions respectively.

(ii) Giving reasons state whether the lines in the spectrum in the figure are Stokes lines or anti-Stokes lines.

(iii) Identify the branches A, C, D and F as O, P, Q, R, S etc.

(25 marks)

(c) The figure shows three electronic-vibrational (vibronic) transitions in a diatomic molecule. The three transitions are designated as 1, 2 and 3 and are indicated using vertical arrows (as usual) in the figure. Horizontal lines indicate consecutive vibrational energy levels associated with each electronic state starting with the ground vibrational level. ΔE is the difference in electronic energy of the two states as indicated in the figure. The absorption waven umbers for the above mentioned transitions are $65176\ \mathrm{cm}^{-1}$, $66176\ \mathrm{cm}^{-1}$ and $67624\ \mathrm{cm}^{-1}$.



(i) Assign the above three wave numbers to the three transitions 1, 2 and 3 by copying and filling the following table

Transition	Wave number/ cm^{-1}
1	
2	
3	

(ii) Starting with the expression for the vibronic energy levels of a molecule which behaves as an anharmonic oscillator, derive an expression for the spacing between two consecutive lines among the above three lines in terms of the vibrational quantum numbers, anharmoinicity constants and the equilibrium vibration frequencies of the two electronic states.

(iii) Calculate the equilibrium vibration frequency and the anharmonicity constant of the lower energy electronic state; i.e. $\omega_e^{//}$ and $x_e^{//}$.

(50 marks)

4. Magnetogyric ratios of some nuclei are given below.

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

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

(a) (i) Consider a bare nucleus placed in a magnetic field. Write down the equation relating the Larmor frequency the nucleus to the magnetic field strength and identify all the parameters in it.

(ii) Define the spectrometer frequency of a NMR spectrometer.

(iii) The field strength of the magnet in an NMR spectrometer is 18.8 Tesla. Calculate the spectrometer frequency of this NMR spectrometer.

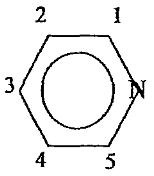
(25 marks)

(b) (i) Define the following terms as applied in NMR spectroscopy.

(α) Chemically equivalent nuclei in a molecule.

(β) Magnetically equivalent nuclei in a molecule.

(ii) Giving reasons, identify the chemically equivalent and magnetically equivalent groups of nuclei, if any, in the pyridine molecule shown in the figure. The five carbon nuclei are numbered from 1 to 5 as shown. The carbon and nitrogen nuclei in the molecule are not magnetic.



(25 Marks)

(c) A molecule has a $^{13}CH_2$ group. It has no other magnetic nuclei. In this molecule the Larmor frequencies of ^{13}C and H are ν_C and ν_H, respectively and $\nu_C > \nu_H$, The scalar coupling constant between ^{13}C and H is δ. Briefly explaining the origin of the number of lines, sketch the following spectra, recorded under high resolution, on intensity versus frequency plots. Clearly indicate ν_C, ν_H and δ on these sketches. Assume that all the spectral lines have the same intensity and the said nuclei form an AX_2 spin system.

(i) NMR spectrum of a sample of the molecules.

(ii) NMR spectrum of a sample of the molecules recorded while the sample is irradiated with electromagnetic radiation of frequency equal to ν_C.

(40 marks)

(d) 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)

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