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THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. Degree Programme — Level 5

Final Examination — 2017/2018

CYU5301/CMU 3131/CME 5131 — Concepts in Spectroscopy

(2 *hours*)

27th September 2018 (Thursday) 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) = $8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}$
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.

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

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

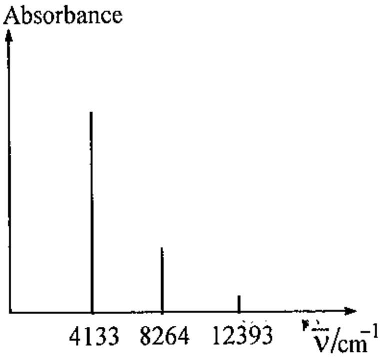
$$\bar{E}_{JK} = \bar{B}J(J+1) + (\bar{A}-\bar{B})K^2 - \bar{D}_J J^2(J+1)^2 - \bar{D}_{JK}J(J+1)K^2 - \bar{D}_K K^4$$

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

$\bar{\nu}_0 = (1-2x_e)\bar{\omega}_e$ $\bar{\nu}_1 = 2(1-3x_e)\bar{\omega}_e$ $\bar{\nu}_2 = 3(1-4x_e)\bar{\omega}_e$ $\omega_e = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

$J_{max} = \frac{1}{2}\sqrt{\frac{2kT}{\bar{B}hc}} - \frac{1}{2}$ $\bar{\nu}_P = \bar{\omega}_0 - 2\bar{B}J''$ $\bar{\nu}_R = \bar{\omega}_0 + 2\bar{B}(J''+1)$

1. (a) The IR spectrum of a diatomic molecule, AB, is schematically represented in the figure. It is known that only the ground vibrational energy level of AB is populated at the temperature this spectrum was recorded. The reduced mass of AB is 0.944 g mol^{-1}.



(i) Explain why more than one absorption line appears in the IR spectrum of AB.

(ii) Calculate the following quantities for AB.

(α) Equilibrium vibration frequency and the anharmonicity constant.

(β) Zero point energy (in units of cm^{-1}).

(γ) Force constant of the AB bond.

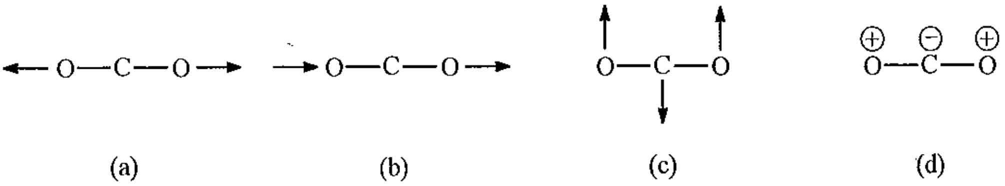
(50 marks)

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

Part A

(i) Define *normal mode* of vibration of a polyatomic molecule.

(ii) The four normal modes of CO_2 are represented in the following figure.



(α) Identify each of the above normal modes (as symmetric stretching etc.).

(β) How many fundamental bands will appear in the IR spectrum of CO_2? Briefly explain your answer.

(30 marks)

Part B

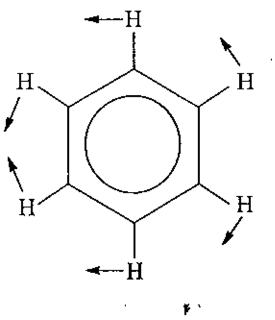
A particular polyatomic molecule has only four normal modes with equilibrium vibration frequencies, $\bar{\omega}_{e,1} = 650 \text{ cm}^{-1}$, $\bar{\omega}_{e,2} = 1150 \text{ cm}^{-1}$, $\bar{\omega}_{e,3} = 2200 \text{ cm}^{-1}$ and $\bar{\omega}_{e,4} = 2700 \text{ cm}^{-1}$.

(i) Identify the energy levels designated (in standard notation) by $(0,0,0,0)$, $(0,0,3,0)$, $(2,0,0,1)$ 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 $(1,0,0,0) \rightarrow (1,0,2,0)$ assuming the vibrational energy in each normal mode to be given by that of a harmonic oscillator.

(30 marks)

(c) An IR active normal mode of benzene is shown the figure. The carbon nuclei do not move in this normal mode and the hydrogen nuclei move in the plane of the molecule.



   (i) Copy the figure of this normal mode of benzene onto your answer script and draw the axis on which the dipole moment changes during the vibration in this normal mode.

   (ii) Giving reasons, identify this normal mode as parallel or perpendicular.

(20 marks)

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

Part A

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

   (α) Symmetric top

   (β) Prolate symmetric top

   (γ) Oblate symmetric top

(ii) Without using moments of inertia, show that $[PtCl_4]^{2-}$ is a symmetric top ion.

(ii) By evaluating moments of inertia about appropriate axes, determine whether $[PtCl_4]^{2-}$ is an oblate symmetric top or a prolate symmetric top.

(35 marks)

Part B

Answer the following questions as applicable to bromine pentafluoride (BrF_5) which behaves as a non-rigid rotor. Use the following data.

For bromine pentafluoride, three rotational constants, in units of cm^{-1}, are $\bar{A} = 0.10331$, $\bar{B} = 0.10331$ and $\bar{C} = 0.071537$. Three centrifugal distortion constants, in standard notation, in units of cm^{-1}, are $\bar{D}_J = 1.811 \times 10^{-9}$, $\bar{D}_K = 1.093 \times 10^{-9}$ and $\bar{D}_{JK} = -1.517 \times 10^{-8}$.

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

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

(iii) Calculate the lowest rotational energy (in units of cm^{-1}) a bromine pentafluoride molecule can have when its rotational quantum number, $J = 2$.

(35 marks)

(b) In standard notation, the rotational energy of a linear polyatomic molecule, X, is given by $\bar{E}_J = \bar{B}J(J+1) - \bar{D}J^2(J+1)^2 + \bar{H}J^3(J+1)^3$. The values of $\bar{B}, \bar{D}$ and $\bar{H}$, in units of cm^{-1}, are 6.0000, 0.0100 and -0.0001 respectively. The selection rule in pure rotational spectroscopy of this molecule is $\Delta J = \pm 1$.

(i) Giving reasons state whether X is a rigid rotor or a non-rigid rotor.

(ii) Calculate positions, in units of cm^{-1}, of the first two lines in the microwave spectrum of X.

(35 marks)

(c) (i) Write down the specific selection rules in vibrational-rotational Raman spectroscopy of a real diatomic molecule.

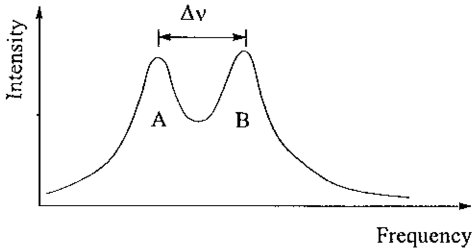
(ii) Assume that a $^{14}N_2$ behaves as a harmonic oscillator and a rigid rotor. The rotational constant of $^{14}N_2$ in different vibrational energy levels are different.

(α) Starting with the vibrational rotational energy expression for $^{14}N_2$, derive an expression for the Raman shift of a line in the Q-branch of the fundamental anti-Stokes band in the vibrational rotation Raman spectrum of $^{14}N_2$.

(β) Explain why the Q-branch mentioned above has more than one line.

(30 marks)

3. (a) The fundamental band of the low resolution IR (vibration-rotation) spectrum of a diatomic molecule, X, is shown in the figure. It has been recorded at temperature T_1. $\Delta\nu$ is the frequency separation between the intensity maxima. Assume X to behave as a harmonic oscillator and a rigid rotor.



(i) Giving reasons state whether X is a homonuclear diatomic molecule or a heteronuclear diatomic molecule.

(ii) Giving reasons identify the branches A and B in the spectrum.

(iii) Identify all the teams in the equation, $J_{max} = \frac{1}{2}\sqrt{\frac{2kT}{Bhc}} - \frac{1}{2}$, applicable to the rotational energy levels of a diatomic molecule.

(iv) Briefly explain how the rotational lines are generated in branches A and B and why there are maxima in intensity.

(v) State whether $\Delta\nu$ will increase or decrease when T_1 is increased. Briefly explain your answer.

(50 marks)

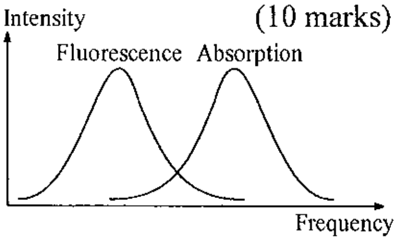
(b) (i) <u>Derive</u> the electronic state symbol for the ground state of He_2^+.

(20 marks)

(ii) All molecular orbital energy levels, except two π levels, of a diatomic molecule are filled. The configuration in the partially filled levels is of the from $\pi\pi'$. Hence, the possible electronic states of the molecule are $^1\Sigma^+$, $^1\Sigma^-$, $^3\Sigma^+$, $^3\Sigma^-$, $^1\Delta$ and $^3\Delta$. Identify the ground electronic state of this molecule? Briefly explain your answer.

(10 marks)

(iii) A typical electronic absorption band and the corresponding fluorescence band of a diatomic molecule are shown in the figure. Explain why the fluorescence band is shifted to lower frequency compared to the absorption band.



(20 marks)

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4. Magnetogyric ratios of some nuclei are given below.

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

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

(a) (i) Calculate the ratio, $\nu_0(\mathrm{H})/\nu_0(\mathrm{D})$ where $\nu_0(\mathrm{H})$ and $\nu_0(\mathrm{D})$ are the Larmor frequencies of bare proton and bare deuteron, respectively, in any NMR spectrometer.

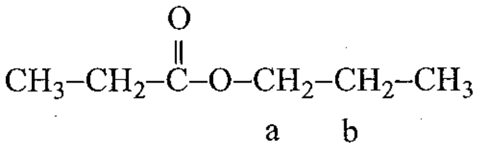
(ii) Briefly explain why deuterated trichloromethane $(\mathrm{CDCl_3})$ is often used, instead of trichloromethane, as a solvent in proton NMR spectroscopy.

(20 marks)

(b) (i) Define the δ -scale of chemical shift (using an equation) and identify all the terms in it.

(ii) State how the chemical shift of a nucleus (on δ -scale) changes when shielding is increased.

(iii) A student observed two lines of equal intensity at $\delta = 22.7$ ppm and $\delta = 68.9$ ppm in the low resolution ^{13}C NMR spectrum of the molecule whose structural formula is shown here. Only the carbons labelled as a and b are ^{13}C. Giving reasons state (deduce) the chemical shifts of carbons a and b.



$$\mathrm{CH_3{-}CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}\underset{a}{CH_2}{-}\underset{b}{CH_2}{-}CH_3}$$

(40 marks)

(c) Sketch the high resolution proton NMR spectrum of $\mathrm{CH_3COCH_2CH_3}$ (methyl ethyl ketone) on an intensity versus frequency diagram. Take the height of the shortest spectral line to be unity (one) and indicate the heights of all the spectral lines. Indicate equal separations between lines in multiplets using appropriate symbols. [All C in the molecule are ^{12}C]
Briefly explain your answer.

(40 marks)