RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (Special) Degree in Chemistry
Fourth Year - Semester I Examination – Oct/Nov 2017

CHE 4210 – MOLECULAR AND SURFACE SPECTROSCOPY

Answer **only four** questions. **Time: Two (2) hours**

$R = 8.314\ J\ K^{-1}mol^{-1}$ $e = 1.602 \times 10^{-19}\ C$ $h = 6.63 \times 10^{-34}\ J\ s$ $c = 3.0 \times 10^{8}\ m\ s^{-1}$

Boltzmaan constant, $k = 1.381 \times 10^{-23}\ J\ K^{-1}$

Answer **all** the questions in **Part A** and select any **two** questions from **Part B**. Only first four answers will be graded.

Part A

1.

a) Find the point group of each molecule using the given flow chart (showing steps is **not** required). (4×5 marks)

i. SbF_5 ii. 1,3,5-chlorobenzene iii. Cyclohexane iv. SOF_4

b) Draw three types of molecules that fall into each point group given below (For examples, H_2O and CH_2Cl_2 are two types of molecules that fall into the C_2V point group. Non-real molecules are accepted as answers).

(2×15 marks)

i. D_{4h} ii. C_{3v}

c) Consider the molecule, PH_3

i. What is the point group of PH_3? (2.5 marks)

ii. What is the order of the point group of PH_3? (7.5 marks)

iii. For the above point group, multiplication of two symmetry elements are said to be not commuted. Illustrate what that means. (10 marks)

iv. What is an Abelian group? (10 marks)

d) Some of the molecular properties can be established by identifying the point group of a molecule. Give two examples and write a **brief** note for each.

(20 marks)

2.

a) Compare and contrast the ultraviolet photoelectron spectroscopy over Auger electron spectroscopy. What are the advantages and limitations of each technique?

(70 marks)

b) The 3d photoemission of Pd is in fact split between two peaks, one at binding energy of 334.9 eV and the other at binding energy of 340.2 eV, with an intensity ratio of 3:2. Explain. The inner core electronic configuration of the initial state of the Pd is : $(1s)^2\ (2s)^2\ (2p)^6\ (3s)^2\ (3p)^6\ (3d)^{10}$ ....

(30 marks)

Part B

3. The rotational energy of a non-rigid diatomic molecule is given by the equation $E_J = Bhc\ J(J+1) - Dhc\ J^2(J+1)^2$

Where the rotational constant,

$$B = \frac{h}{8\pi^2 Ic}$$

and the centrifugal distortion constant,

$$D = \frac{h^3}{32\pi^4 I^2 r^2 kc}$$

Also given that square of oscillation wave number (vibrational frequency),

$$\tilde{\nu}^2_{osc} = \frac{4B^3}{D}$$

a) Obtain relationshipsfor the frequency (ν) and the wave number ($\tilde{\nu}$) for the $J \rightarrow (J+1)$ transitions and use the latter in the part (b).

(40 marks)

b) Three consecutive lines in the rotational spectrum of $H^{35}Cl$ are observed at 104.13, 124.73, and 145.37 (wave numbers in cm^{-1}).

i. Assign the above lines to $J \rightarrow (J+1)$ transitions.

ii. Calculate the value of rotational constant, B and the centrifugal distortion constant, D.

iii. Calculate the force constant for the $H^{37}Cl$ bond.

(3×20 marks)

4.

a) Account for the interaction of electromagnetic radiation (EMR) with matter.

(25 marks)

b) Define the dipole moment. Calculate the theoretical dipole moment, μ_{cal} of KBr and hence the percentage ionic character of KBr. Given that bond distance of KBr = 282 pm and observed dipole moment, $\mu_{obs} = 3.473 \times 10^{-29}$ Cm (K= 39.0983, Br =79.904).

(15 marks)

c) Account for two of followings (2×15 marks)

i. line broadening. ii. light scattering. iii. refractive index

d) What are the four types of molecular rotors? Include relationships between I_x, I_y, I_z for each type in your answer. (10 marks)

e) Specify the molecules which may show only pure rotational microwave absorption spectra. N_2O, H_2O, CCl_4, H_2O_2, NH_3, CO_2 (10 marks)

f) Specify the molecules which may show only pure rotational Raman absorption spectra.CO_2, H_2, CH_4, HCl, SF_6,CH_3Cl (10 marks)

5.

a) What is the criteria of a molecule to be IR active? (10 marks)

b) Given that the fundamental vibrational frequency of $H^{35}Cl$ is 2890 cm^{-1}.

(2×20 marks)

i. Calculate the force constant of HCl.

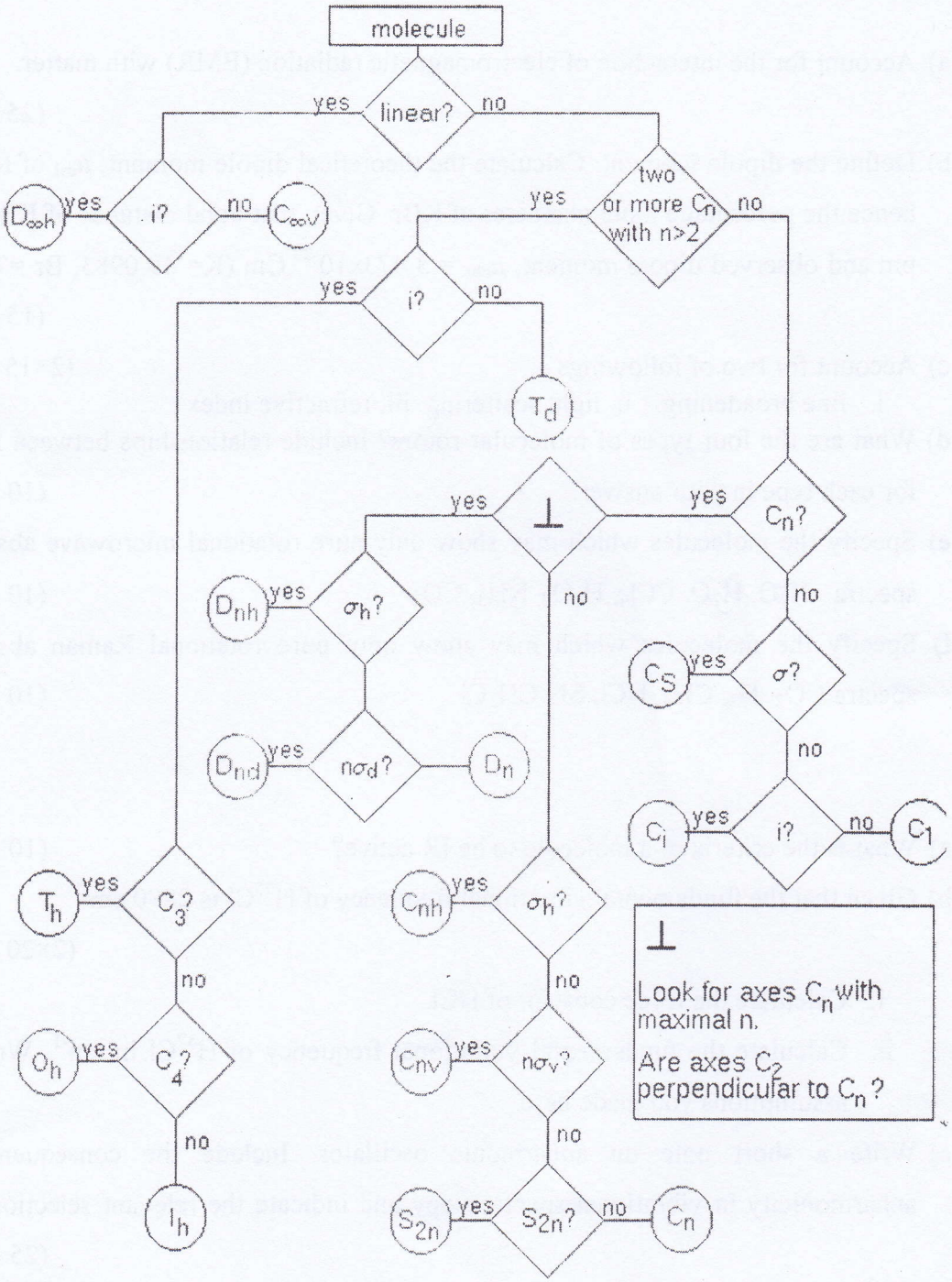
ii. Calculate the fundamental vibrational frequency of $H^{37}Cl$ in cm^{-1}. Write any assumptions you made here.

c) Write a short note on anharmonic oscillator. Include the consequences of anharmonicity in vibrational spectroscopy and indicate the relevant selection rules.

(25 marks)

d) Write a short note on rotational Raman spectroscopy. Use the terms isotropically polarizable, anisotropically polarizable, strokes and antistrokes in your explanation.

(25 marks)


molecule
linear?
yes
no
$D_{\infty h}$
i?
$C_{\infty v}$
two or more C_n with n>2
T_d
⊥
C_n?
D_{nh}
σ_h?
C_S
σ?
D_{nd}
$n\sigma_d$?
D_n
C_i
C_1
T_h
C_3?
C_{nh}
O_h
C_4?
C_{nv}
$n\sigma_v$?
I_h
S_{2n}
S_{2n}?
C_n
⊥
Look for axes C_n with maximal n.
Are axes C_2 perpendicular to C_n?