RAJARATA UNIVERSITY OF SRI LANKA

FACULTY OF APPLIED SCIENCES

B.Sc. (Special) Degree in Chemistry

Fourth Year - Semester I Examination – June / July 2018

CHE 4210 – MOLECULAR AND SURFACE SPECTROSCOPY

Time: Two (02) hours

Answer **only four (04)** questions.

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

Boltzmaan constant, k = 1.381 × 10^{-23} J K^{-1}, N_A = 6.022×10^{23} mol^{-1}

Use of a non-programmable calculator is permitted.

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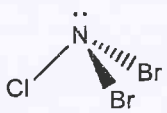
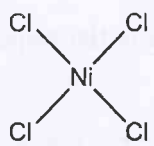
1. A) Show all the symmetry elements for the given molecules. (15 marks)

a)



b)



B) Find the point group of following molecules. Use the given flow chart to obtain your answers. (20 marks)

a) SF_5Br b) $CHCl_2F$ c) SOF_4 d) 1,3,5-tribromobenzene

C) The group D_2h has a C_2 axis perpendicular to the principal axis and a horizontal mirror plane. Show that the group must therefore have a centre of inversion. (20 marks)

D) How would you describe the symmetry element, "improper rotation" using CH_4 as an example? (15 marks)

E) Consider the C_3V symmetry group.

i. What is the order of the point group?

ii. Show whether the C_3V group is an Abelian group using a proper example.

(30 marks)

2. A) Briefly describe photoelectron spectroscopy (PES) as a surface analytical technique. (20 marks)

B) Splitting of PES peaks can be caused by the existence of multiple final states after photoelectron ejection. Discuss the factors affect on energetically different final states in PES in detail.

(50 marks)

C) Although energetically high X-rays are used to emit Auger electrons, those electrons possess energy comparable to that of UV radiation. Explain the reason for this observation. (30 marks)

3. A) Explain two types of radiations observed in Raman spectroscopy, Stoke radiation (ν_i-ν_k) and anti-Stokes radiation (ν_i-ν_k).

ν_i – the frequency of the incident radiation
ν_k – the frequency of the k^{th} normal mode of harmonic vibration (30 marks)

B) H_2O gas shows three (03) absorptions at 3651.1 cm^{-1}, 1595.0 cm^{-1} and 3755.8 cm^{-1} in the IR spectrum where as the IR spectrum of CO_2 gas consists of only two (02) absorptions which appear at 2349.0 cm^{-1} and 667.3 cm^{-1}. Explain the observations. Assign these absorptions to the respective vibrational modes for both. (30 marks)

C) Account for the diatomic vibrating rotor. Include the discussion of origination of the P, Q, R bands in your answer. (40 marks)

4. A) Predict the form of the rotational Raman spectrum of $^{14}NH_3$, for which B = 9.977 cm^{-1}, when it is exposed to monochromatic wavelength of 336.732 nm laser radiation. Spectral positions for the Stokes lines are given by the equation,

$$\bar{\nu}_{J \to J+2} = \bar{\nu}_i - 2B\,(2J+3).$$

Spectral positions for the anti-Strokes lines are given by the equation,

$$\bar{\nu}_{J \to J-2} = \bar{\nu}_i + 2B(2J-1).$$

(40 marks)

B) The microwave spectrum of $^{1}H^{127}I$ consists of a series of equally spaced lines each separated by 12.8 cm^{-1}.

The wave number for the spectral lines is given by the equation,

$$\bar{\nu}_{J \to J+1} = 2B(J+1) \quad \text{where the rotational constant } B = \frac{h}{8\pi^2 Ic}$$

and the moment of inertia $I = \mu r^2$

and the reduce mass $\mu = \frac{M_1 M_2}{(M_1+M_2)N_A}$

i. Calculate the spectral position of the first line in the spectrum.

ii. Calculate the spectral positions corresponding to J = 2 → J = 3 and J = 6 → J = 7 transitions.

iii. Calculate the moment of inertia and the internuclear distance of the HI molecule.

iv. Calculate the separation between the spectral lines in the microwave spectrum of $^{2}H^{127}I$.

v. Calculate the spectral positions corresponding to J = 2 → J = 3 and J = 6 → J = 7 transitions in the microwave spectrum of $^{2}H^{127}I$.

vi. Based on the values you calculated above, comment on the effect of the substitution of a heavier isotope on the value of the rotational constant and the spectral features. (40 marks)

5. A) Arrange the compounds, CH_4, CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 in an increasing order of

i. dipole moment ii) polarizability (20 marks)

B) Can matter change the velocity of propagation of light? Explain. (25 marks)

C) Mathematically show that the dipole moment of BF_3 is zero. (25 marks)

D) Classify following molecules according to their activity in microwave, Infra-Red and Raman spectroscopies: H_2, H_2O, O_2, CO, CO_2, CH_4, CH_3Cl, CH_2Cl_2, N_2, and NH_3.

(30 marks)

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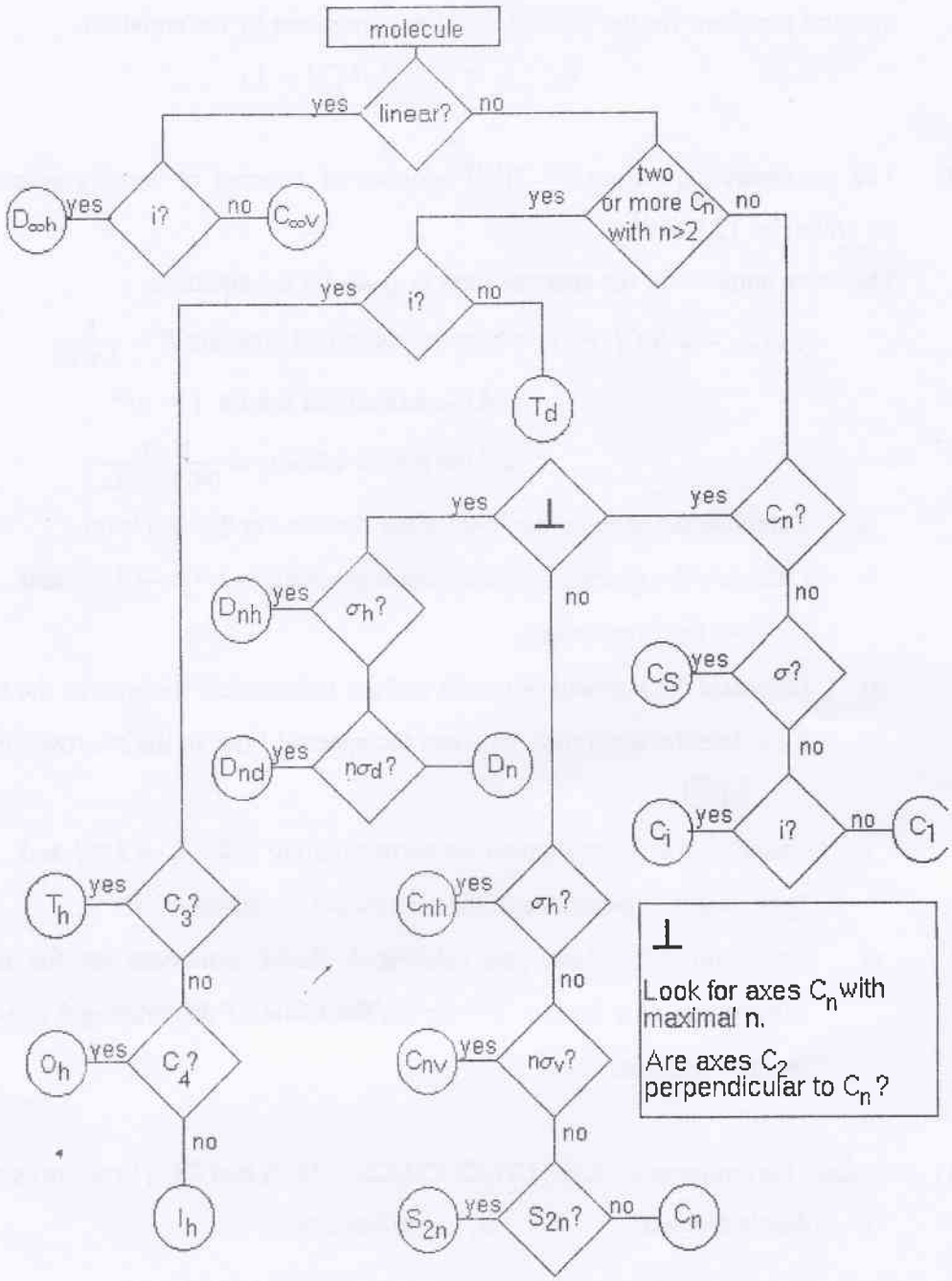
molecule
linear?
yes
no
$D_{\infty h}$
i?
$C_{\infty v}$
two or more C_n with n>2
T_d
⊥
C_n?
D_{nh}
σ_h?
D_{nd}
$n\sigma_d$?
D_n
C_S
σ?
C_i
C_1
T_h
C_3?
O_h
C_4?
I_h
C_{nh}
C_{nv}
$n\sigma_v$?
S_{2n}
S_{2n}?
C_n
⊥
Look for axes C_n with maximal n.
Are axes C_2 perpendicular to C_n?