RAJARATA UNIVERSITY OF SRI LANKA
FACULTY OF APPLIED SCIENCES

B.Sc. (Honours) Degree in Chemistry
Fourth Year - Semester I Examination – September / October 2019

CHE 4210 – MOLECULAR AND SURFACE SPECTROSCOPY

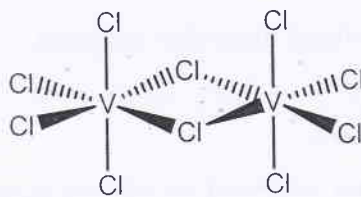**Time: Two (02) hours**

Answer <u>question 2 and any 3</u>

$R = 8.314$ J K^{-1} mol^{-1}, $e = 1.602 \times 10^{-19}$ C, $1D = 3.336 \times 10^{-30}$ C m, $h = 6.63 \times 10^{-34}$ J s,

Boltzmaan constant, $k = 1.381 \times 10^{-23}$ J K^{-1}, $N_A = 6.022 \times 10^{23}$ mol^{-1}, $c = 3.0 \times 10^{8}$ m s^{-1}

Use of a non-programmable calculator is permitted.

1. a) Show all the symmetry elements for the given molecules.

    i)

    (16 marks)

    ii)

    b) Find the point group of following molecules. Use the given flow chart to obtain your
       answers. (see page 04)

        i. SF_3Br_3 ii. PBr_3 iii. $P(Ph)_3$ iv. $B(OH)_3$ (24 marks)

    c) Give an example for each point group given below.

        i. C_{2v} ii. D_{3h} iii. $D_{\infty h}$ (15 marks)

    d) Describe the symmetry element "improper rotation" by means of staggered C_2H_6 as an
       example.   (15 marks)

e) Consider the molecule CHF_3.

    i. Write down the point group of CHF_3.

    ii. Find the order of the point group of CHF_3?

    iii. For the above point group, multiplication of two symmetry elements are said to be not commuted. Illustrate what that means. (30 marks)

2. a) Discuss briefly the instrumentation and the theory behind of X-ray photoelectron spectroscopy (XPS). (40 marks)

  b) What chemical information could be obtained by XPS analysis? (30 marks)

  c) Auger electron spectroscopy (AES) is one of the techniques for surface analysis.

    (i) What is an Auger electron and how it is generated?

    (ii) Sketch the Auger electron for a metal at KL_2L_3

    (iii) State the advantages and limitations of AES.

(30 marks)

3. a) 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),

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

Obtain relationships for the frequency (v) and the wave number ($\tilde{v}$).

(40 marks)

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

    i. Assign the above lines to $J\,(J+1) \rightarrow$ 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. (3x20 marks)

Assume that you are given access to a 532 nm excitation source and a 785 nm excitation source for a Raman spectrometer. The power of the 532 nm source is 50 mW where the power of the other source is 350 mW. Assuming that sample will not absorb neither of above energies, predict which source will give the highest Raman intensities. Justify your answer.

(30 marks)

The rotational spectrum of $^1H^{127}I$ consists of a series of equally spaced lines each separated by 12.8 cm^{-1}. Elaborate the effect of the substitution of a heavier isotope on the value of the rotational constant and the spectral features. Use $^2H^{127}I$ as the example. Give all the necessary calculations required.

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

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

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

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

(70 marks)

Defend the statement "Energy and matter interact with each other".

(30 marks)

Determine which of the following molecules may show only pure rotational microwave absorption spectra. PH_3, CS_2, N_2O, H_2O, CBr_4, H_2O_2.   (15 marks)

Determine which of the following molecules may show only pure rotational Raman absorption spectra. CCl_4, CO_2, $CHCl_3$, H_2, HBr, SF_6.

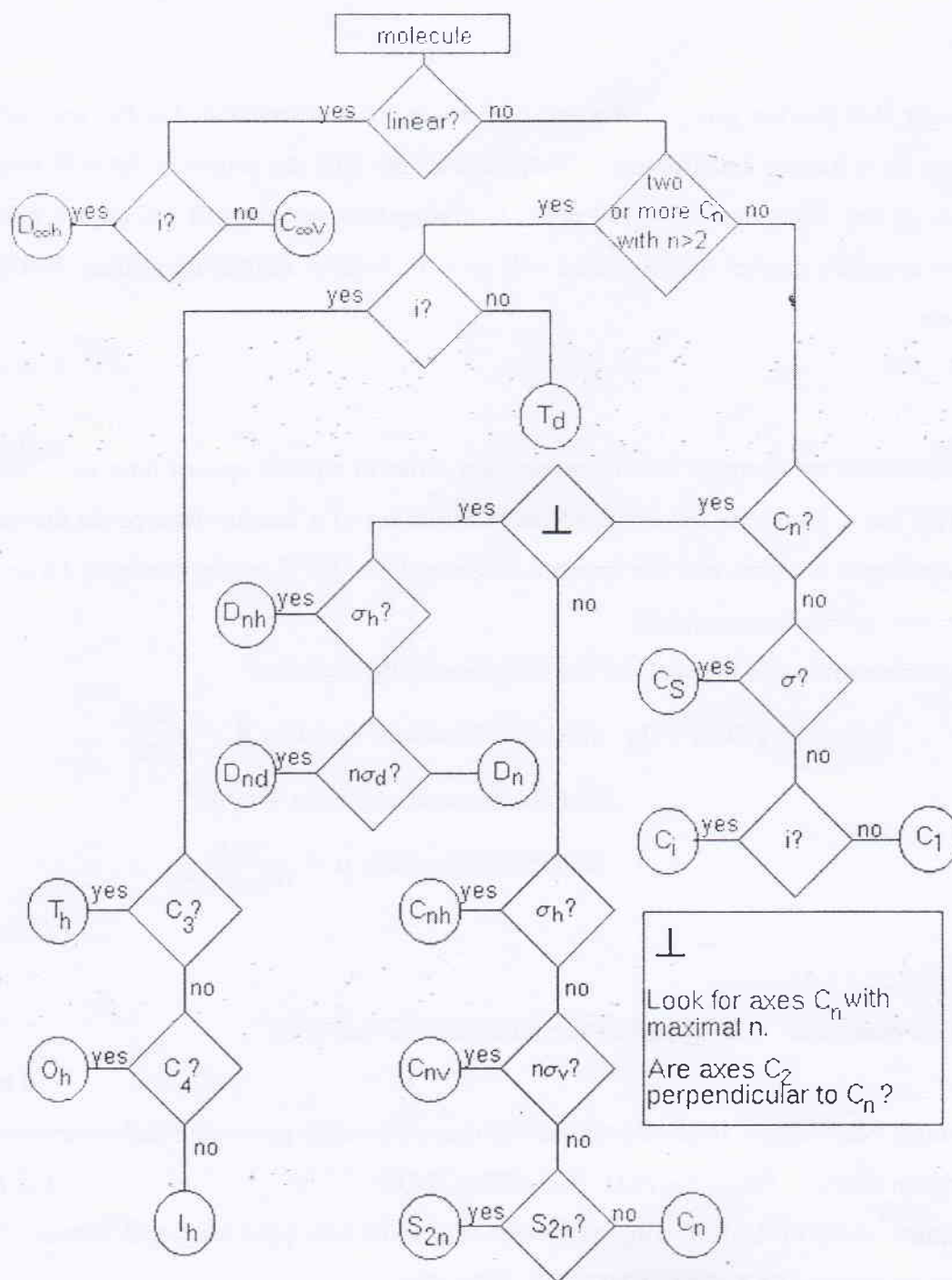(15 marks)

Calculate the dipole moment of H_2S. H-S-H Bond angle is 92.11 and H-S bond distance is 1.335 Å.   (20 marks)

In an electronic spectrum two bands were appeared with λ_{max} 195 nm and 277 nm with 10000 and 20 ε values respectively. Clarify this observation.   (20 marks)

molecule

linear?
— yes → i? — yes → $D_{\infty h}$
— yes → i? — no → $C_{\infty v}$
— no → two or more C_n with $n>2$
  — yes → i?
    — yes → ⊥
    — no → T_d
  — no → C_n?

⊥
— yes → σ_h? — yes → D_{nh}
  — σ_h? — no → $n\sigma_d$? — yes → D_{nd}
    — $n\sigma_d$? — no → D_n
— no → σ_h? — yes → C_{nh}
  — σ_h? — no → $n\sigma_v$? — yes → C_{nv}
    — $n\sigma_v$? — no → S_{2n}? — yes → S_{2n}
      — S_{2n}? — no → C_n

C_n?
— yes → ⊥
— no → σ? — yes → C_s
  — σ? — no → i? — yes → C_i
    — i? — no → C_1

C_3? — yes → T_h
C_3? — no → C_4? — yes → O_h
  C_4? — no → I_h

⊥
Look for axes C_n with maximal n.
Are axes C_2 perpendicular to C_n?

— END —