KIBABII UNIVERSITY

UNIVERSITY EXAMINATIONS
2020/2021 ACADEMIC YEAR

THIRD YEAR SECOND SEMESTER
SPECIAL/SUPPLEMENTARY EXAMINATIONS

FOR THE DEGREE OF BACHELOR OF CHEMISTRY

COURSE CODE: SCH 327

COURSE TITLE: SYMMETRY, MOLECULAR STRUCTURE AND PROPERTIES

DURATION: 2 HOURS

DATE: 20/1/2022 **TIME:** 8-10AM

INSTRUCTIONS TO CANDIDATES

- Answer **QUESTION ONE** (Compulsory) and any other two (2) Questions.
- Indicate **answered questions** on the front cover.
- Start every question on a new page and make sure question's number is written on each page.

This paper consists of **5** printed pages. Please Turn Over

QUESTION ONE.COMPULSORY

(a) Define the following terms; (4 marks)
   (i) Symmetry element
   (ii) Symmetry operation

(b) Calculate the number of vibrational modes in CO_2 and CH_4 (4 marks)

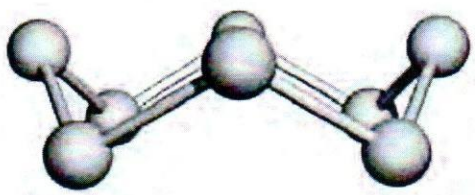
(c) The symmetry operators for NH_3 are E, C_3 and $3\sigma_v$.
   (i) Draw the structure of NH_3. (2 marks)
   (ii) What is the meaning of the E operator? (2 marks)
   (iii) Draw a diagram to show the rotation and reflection symmetry operations. (2 marks)

(d) What symmetry elements do BCl_3 and PCl_3
   (i) have in common and (2 marks)
   (ii) Not have in common? (2 marks)

(e) Determine the point group of PF_5. (3 marks)

(f) To what point group does $POCl_3$ belong? (3 marks)

(g) Three projections of the cyclic structure of S_8 are shown below all S-S bond distances are equivalent, as are all S-S-S bond angles. To what point group does S_8 belong? (5 marks)



(h) The IR spectrum of $SnCl_2$ exhibits absorptions at 352, 334 and 120 cm^{-1}. What shape do these data suggest for the molecule, and is this result consistent with VSEPR theory? (5 marks)

(i) Determine the point group of trans-N_2F_2. (2 marks)

QUESTION TWO

(a) The oxalate ligand, $[C_2O_4]^{2-}$, is a bidentate ligand and the structure of the complex ion $[Fe(ox)_3]^{3-}$ is shown below. Confirm that the point group to which the ion belongs is D_3 and that members of this point group are chiral. (5 marks)

(b) How do the rotation axes and planes of symmetry in cis- and trans-N_2F_2 differ? (5 marks).

(c) Draw the structures of each of the following species and confirm that each possesses a center of symmetry: CS_2, $[PF_6]^-$, XeF_4, I_2, $[ICl_2]^-$ (10 marks)

QUESTION THREE

(a) Assign a point group to each member in the series (i) CCl_4, (ii) CCl_3F, (iii) CCl_2F_2, (iv) $CClF_3$ and (v) CF_4. (5 marks)

(b) Determine the number of degrees of vibrational freedom for each of the following: (i) SO_2; (ii) SiH_4; (iii) HCN; (iv) H_2O; (v) BF_3 (5 marks)

(c) Explain what is meant by (i) Chiral (ii) Enantiomer (iii) Helical Chain (3 marks)

(d) How many normal modes of vibration are IR active for (i) H_2O, (ii) SiF_4, (iii) PCl_3, (iv) $AlCl_3$, (v) CS_2 and (vi) HCN? (6 marks)

(a) The point group of $[AuCl_2]^-$ is D∞h. What shape is this ion? (1 mark)

QUESTION FOUR

(a) Using VSEPR theory, draw the structures of CF_4, XeF_4 and SF_4. Assign a point group to each molecule. Show that the number of degrees of vibrational freedom is independent of the molecular symmetry. (10 marks)

(b) How many degrees of freedom do each of the following possess: $SiCl_4$, BrF_3, $POCl_3$ (3 marks)

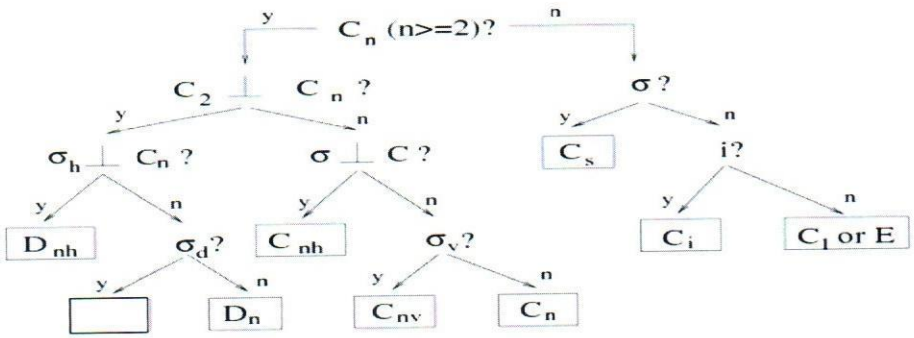
(c) The IR spectrum of SF_2 has absorption at 838, 813 and 357cm^{-1}. Explain why these data are consistent with SF_2 belonging to the C_{2v} rather than D∞h point group. (3 marks)

(d) The vibrational modes of XeF_2 are at 555, 515 and 213cm^{-1} but only two are IR active. Explain why this is consistent with XeF_2 having a linear structure. (4 marks)

QUESTION FIVE

(a) Use the flow chart below to assign the point groups to the following molecules (10 marks)

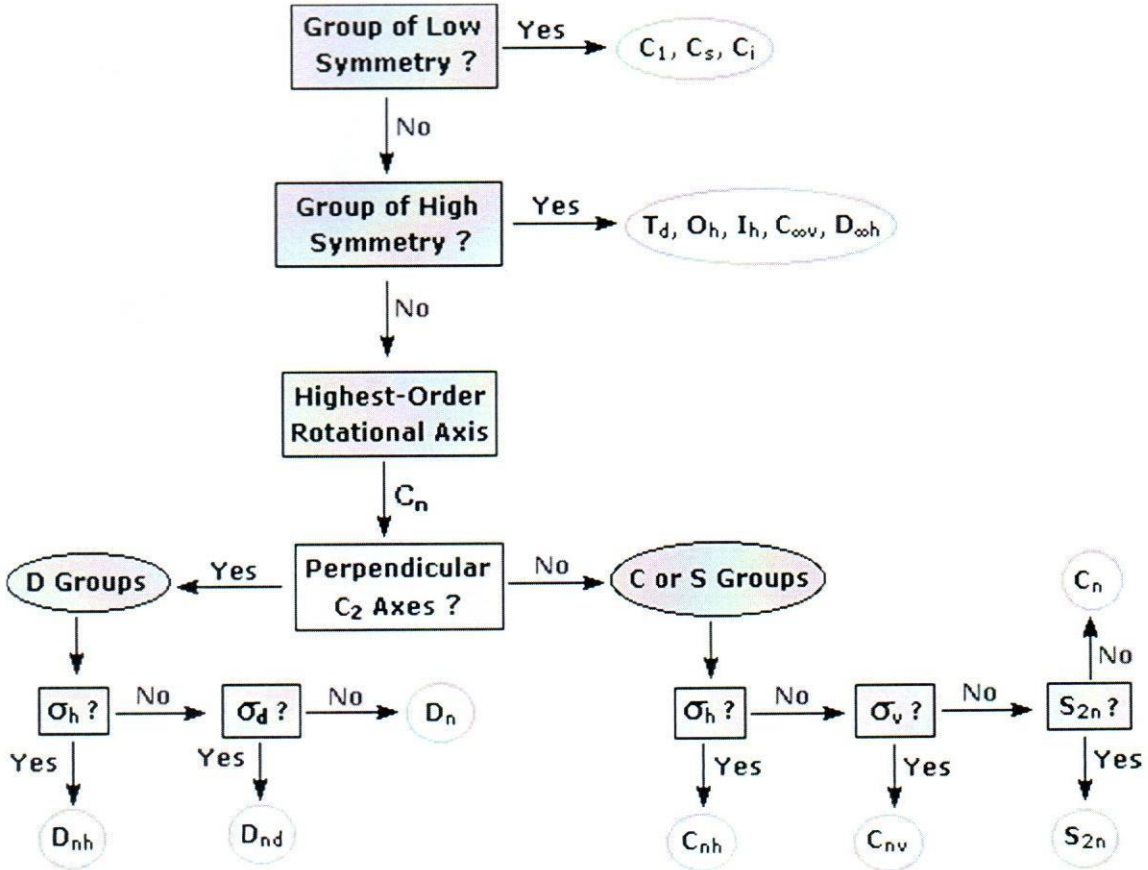
(i)Ammonia, (ii) acetone, (iii) dimethylcyclopentane, (iv) ethanediol, (v) propanediene



(b) The $[PdCl_4]^{2-}$ ion gives rise to three absorptions in its IR spectrum (150, 321 and 161 cm^{-1}). Rationalize why this provides evidence for a D_{4h} rather than a T_4 structure. (5 marks)

(c) The IR spectrum of gaseous ZrI_4 shows absorption at 55 and 254 cm^{-1}. Explain why this observation is consistent with molecules of ZrI_4 having T_4 symmetry. (5 marks)

Additional data for use


Group of Low Symmetry ?
Yes
C_1, C_s, C_i
No
Group of High Symmetry ?
Yes
T_d, O_h, I_h, $C_{\infty v}$, $D_{\infty h}$
No
Highest-Order Rotational Axis
C_n
Perpendicular C_2 Axes ?
Yes
D Groups
No
C or S Groups
σ_h ?
No
σ_d ?
No
D_n
Yes
Yes
D_{nh}
D_{nd}
σ_h ?
No
σ_v ?
No
S_{2n} ?
No
C_n
Yes
Yes
Yes
C_{nh}
C_{nv}
S_{2n}