Molecular Symmetry and Group Theory
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(Wiley, 1988)
Chapter 2

Programme 2

Point Groups

Objectives

After completing this programme you should be able to:

1. State the point group to which a molecule belongs
2. Confirm that the complete set of symmetry operations of a molecule constitutes a group
3. Arrange a set of symmetry operations into classes

The first of these objectives is vital to the use of group theory and is the only one tested at the end of the programme.

Assumed Knowledge

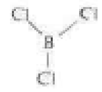
A knowledge of simple molecular shapes, and of the contents of programme 1 is assumed.

2.1 Write down the symbols of the FIVE elements needed to completely specify molecular symmetry.

2.2 E C S σ i

What are the names of these five elements of symmetry?

2.3 E — The identity element
C — Proper rotation axis
S — Improper rotation (or rotation-reflection) axis
σ — Plane of symmetry
i — Inversion centre

List all the symmetry elements of 

2.4 E C_3 $3C_2$ σ $3\sigma'$ S_3

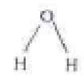
If you have got these three questions substantially correct you may proceed, otherwise return to programme 1 - symmetry elements and operations.

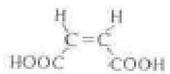
List all the symmetry elements of 

2.5 E C_3 $3C_2$ σ $3\sigma'$ S_3

i.e. exactly the same as BCl_3

There are many other examples of several molecules having the same set of symmetry elements, e.g. list all the symmetry elements of





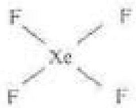
2.6 All four of these molecules (and many more!) have the element

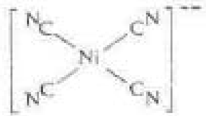
E C_2 σ σ '

In the same way all square planar molecules contain the elemen

E C_4 $C_2(=C_4^2)$ $4C_2$ σ $4σ'$ i S_4, regardle

of the chemical composition of the molecule e.g.

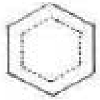




etc.

It is convenient to classify all such molecules by a single symb which summarises their symmetry. This symbol for a flat square molecule is D_{4h}.

Can you suggest the symbol for a flat hexagonal molecule like benzene:



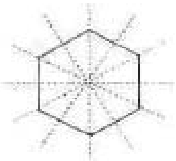
2.7 D_{6h} The symmetry is similar to that of the square planar case, but the principal axis is a 6-fold axis not a 4-fold axis.

The symmetry symbol consists of three parts:

The number indicates the order of the principal (i.e. high order) axis. This is conventionally taken to be vertical.

The small letter h indicates a horizontal plane.

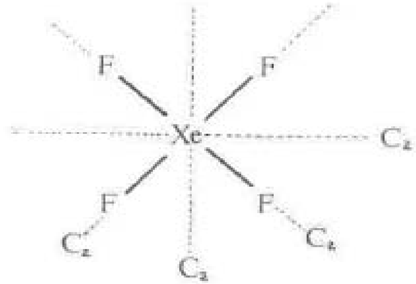
The capital letter D indicates that there are n(=6 for benz C_2 axes at right angles to the principal C_n axis (C_6 for benzene):



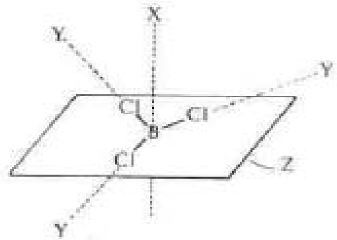
Two-fold axes

How many two-fold axes like this are there in a flat squa molecule like XeF_4?

2.8 4.



Let us look now at a flat triangular molecule, say BCl_3:



What are the symmetry elements labelled X, Y, and Z?

2.9 X = C_3 axis

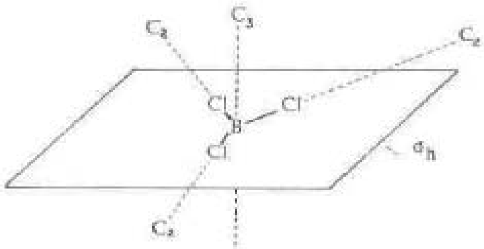
Y = C_2 axes

Z = plane of symmetry

The principal C_3 axis is taken, conventionally to be vertical, so the plane is a horizontal plane ($σ_h$), and there are three C_2 axes at right angles to the principal axis.

What, therefore, is the symmetry symbol of the BCl_3 molecule? (frame 2.7 may help).

2.10 D_{3h}



Point group symbol: D_3h

3C₂ axes (horizontal) — 3-fold principal axis (vertical) — horizontal plane

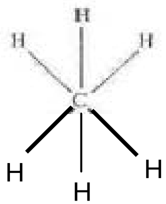
The molecule is said to belong to the D_{3h} POINT GROUP.

Let us now get a bit more general, and call the principal axis C_n, so that its order, n, can be any number.

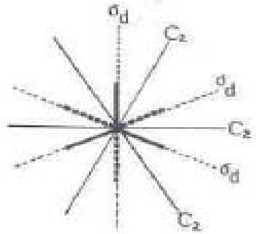
If there is no horizontal plane of symmetry, but there are n vertical planes as well as nC_2 axes, the point group is D_{nd}.

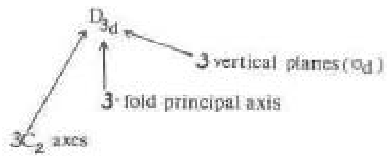
The D and the number mean the same as before but the small d stands for DIHEDRAL PLANES, because the n vertical planes lie between the nC_2 axes.

Ethane in the staggered conformation belongs to a D_{nd} point group. Decide on the value of n from the following diagram (looking down the principal axis), and hence state the point group to which ethane belongs.

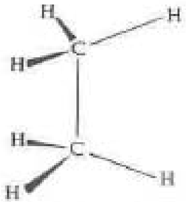


2.11 D_{3d} A model will help to convince you of the elements of symmetry in this case, but the following diagram is looking down the principal, vertical, 3-fold axis:





In the eclipsed conformation ethane has an additional element of symmetry. Can you see from the diagram (or a model) what the extra element is?



2.12 A horizontal plane of symmetry, σ_h

What does this make the point group of ethane in the eclipsed conformation?

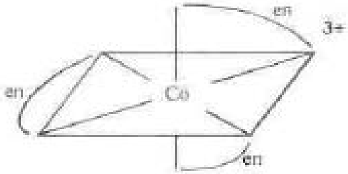
2.13 D_{3h} i.e. in the eclipsed conformation the horizontal plane takes precedence over the dihedral planes in describing the symmetry.

Some molecules have a principal C_n axis, and nC_2 axes at right angles, but no horizontal or vertical (dihedral) planes.

There is no need to include h or d in the symmetry symbol. If the principal axis is a three-fold axis what is the symmetry symbol in this case?

2.14 D_3 i.e., it has a threefold axis and three C_2 axes at right angles, hence D_3, but no σ_h or σ_d, so no additional symbol is necessary.

An example of an ion of this symmetry is:

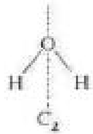


(en = $NH_2CH_2CH_2NH_2$)

You will probably need a model of the ion to see the axes.

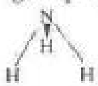
If the principal C_n axis is not accompanied by n C_2 axes, the first letter of the point group is C. A horizontal plane is looked for first, and is shown by a little h. If σ_h is not present, n vertical planes are looked for and are shown by a small v.

e.g.



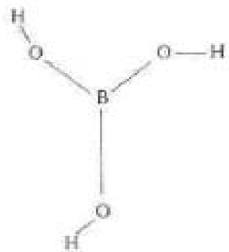
C_2, no C_2 at right angles no σ_h, but $2\sigma_v$ ∴ point group C_{2v}

What is the point group of



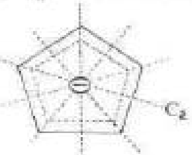
2.15 C_{3v} i.e. it has a principal C_3 axis and 3 vertical planes.

Remember that all flat molecules have a plane of symmetry in the molecular plane. Try to decide the point group of a free boric acid molecule which has no vertical planes or horizontal C_2 axes.



2.16 C_{3h} i.e. it has a principal C_3 axis, no horizontal C_2 axes, and a horizontal plane

What is the point group of the flat ion:



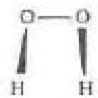
2.17 D_{5h} i.e. it has a C_5 (vertical), 5 C_2 axes at right angles, and a horizontal plane.

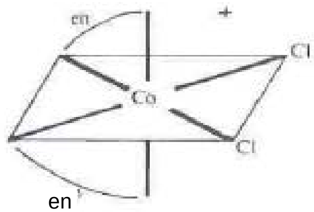
List the four symmetry elements of fumaric acid:

2.18 E, C_2, σ_h, i. What does this make the point group symbol?

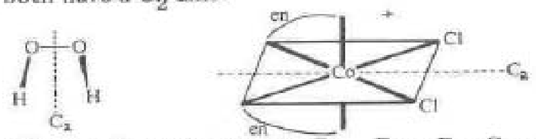
2.19 C_{2h} i.e. it has a C_2 axis and a horizontal plane.

The molecule H_2O_2 and the ion *cis*$[Co(en)_2Cl_2]^+$ both have only the identity and one proper axis of symmetry. They both belong to the same point group. Can you say which one it is? (A model, or the diagrams below, might help.)

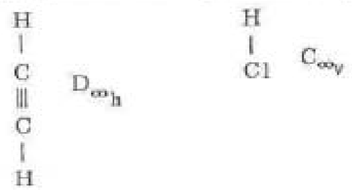




2.20 C_2. They both have a C_2 axis:

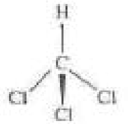


We have so far seen the point groups, D_{nh}, D_{nd}, D_n, C_{nh}, C_{nv} and C_n. These groups cover many real molecules, even simple linear ones which have an infinity-fold axis e.g.



There are three additional groups for highly symmetrical molecules, octahedral molecules belong to the group O_h, tetrahedral molecules to T_d, and icosahedral structures to I_h. You must realise that T_d refers to the symmetry of the whole molecule e.g. CH_4 and CCl_4 both belong to the T_d group, but $CHCl_3$ does not.

What is the point group of $CHCl_3$?



(cf. NH_3)

2.21 C_{3v}

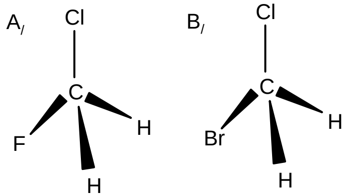
Some rather rare molecules possess only two elements of symmetry, and these are given a special symbol:

E and i only	C_i
E and σ only	C_s
E and S_n only	S_n

Many molecules have no symmetry at all (i.e. their only symmetry element is the identity, E. Such molecules belong to the C_1 point group.

The following are examples of molecules with only one or two symmetry elements .

What are their point groups?

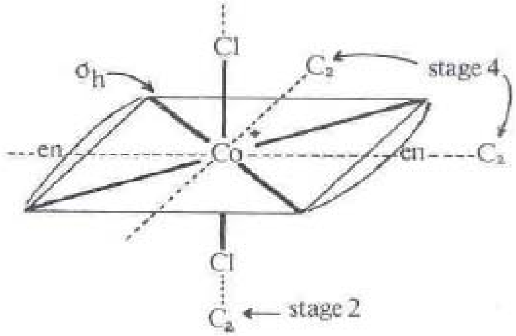


2.22 A. C_s

B. C_1

There is a simple way of classifying a molecule into its point group, and a sheet at the end of this programme gives this. You will see that the tests at the bottom of the scheme are similar to those used to introduce the nomenclature in this programme. The scheme does not test for all the symmetry elements of a molecule, only certain key ones which enable the point group to be found unambiguously.

Have a look at the sheet, and try to follow it through for the ion:



Stage 1 - it is not one of these special groups

Stage 2 - there is a C_2 axis - ∴ n = 2

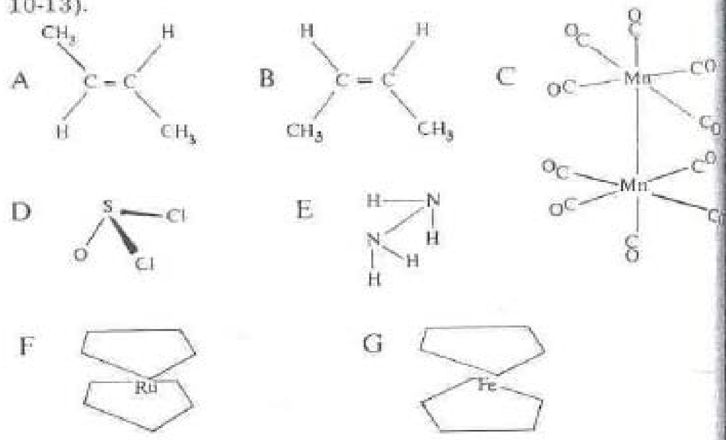
Stage 3 - there is no S_4 colinear with C_2

Stage 4 - there are two C_2 axes at right angles there is a horizontal plane.

What point group have you arrived at? (Remember the value of n found in Stage 2.)

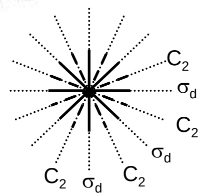
2.23 D_{2h}

Use the scheme to find the point group of each of the following: (C, E, F and G are a bit tricky without a model, but you may ge[t] C, F and G right by analogy with ethane as discussed in Frames 10-13).



2.24 A. C_{2h} B. C_{2v} C. D_{4d} D. C_s E. C_2 F. D_{5h} G. D_{5d}

The hardest of these examples are probably C and G which are both D_{nd} molecules. It is often very difficult to see the n two-fo[ld] axes on such a molecule and you may need to ask advice on this. Frame 2.11 shows the axes in the case of a D_{3d} molecule. The corresponding diagram, looking down the principal four-fol[d] axis of $Mn_2(CO)_{10}$ is:



A simple rule to remember is that any n-fold staggered structure (like C_2H_6, $Mn_2(CO)_{10}$ etc) belongs to the point group D_{nd}, and you may find it easier to remember this rule.

We have said that the symbol represents the POINT GROUP of the molecule. This is because all the symmetry elements of a molecule always pass through one common point (sometimes through a line or a plane, but always through a point).

Where is the point for examples A and G above?

2.25 A — the centre of the C = C double bond
G — the Fe atom

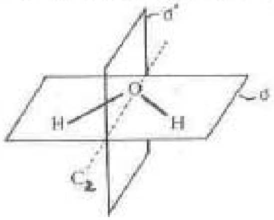
At this stage, the programme begins to look at what mathematicians call a GROUP. If you have had enough for one sitting, this is a convenient place to stop, but in any case it is not absolutely vital for a chemist to know about the rules defining a group, although I strongly recommend you to work through the rest of the programme. You should now be able to classify a molecule into its point group, which is absolutely vital to the use of Group Theory, and the test at the end of the programme tests only this classification.

The term GROUP has a precise mathematical meaning, and the set of symmetry OPERATIONS of a molecule constitutes a mathematical group. A group consists of a set of members which obey four rules:

a. The product of two members, and the square of any member is also a member of the group.
b. There must be an identity element.
c. Combination must be associative i.e. (AB)C = A(BC).
d. Every member must have an inverse which is also a member i.e. $AA^{-1} = E$, the identity, if A is a member, A^{-1} must also be.

N.B. Some texts use the word *element* for the members of a group. This convention has not been followed here in order to avoid confusion with the term *symmetry element*. It is the set of *symmetry operations* which form the group.

Let us take the C_{2v} group (e.g. H_2O) and confirm these rules. The group has four operations, E, C_2, σ, σ':



We have already seen the effect of combining two operations in the programme on elements and operations.

Set up the complete multiplication table for the group operations (in Programme 1 you used a little arrow on H to help do this).

	E	C_2	σ	σ'
E				
C_2				
σ				
σ'				

2.26

	E	C_2	σ	σ'
E	E	C_2	σ	σ'
C_2	C_2	E	σ'	σ
σ	σ	σ'	E	C_2
σ'	σ'	σ	C_2	E

If you did not get this result, look back at the first programme, frames 1.29-1.32.

We can see immediately from this table that rules a. and b. are true for this set of operations.

What about rule d. what is the inverse of σ', i.e. what multiplies with σ' to give E?

2.27 σ', it is its own inverse, σ' σ' = E. This is true for all the operations of this group.

Consider the C_3 element in a D_{3h} molecule. What is the inverse of the C_3 operation, or what *operation* will bring the shape back to the starting poing (I'd rather you didn't say C_3 in the opposite direction!)

2.28 C_3^2, i.e. apply the C_3 operation clockwise a further two times. Thus $C_3^2\ C_3 = C_3^3 = E$. (Remember that this means C_3 followed by C_3^2)

Note particularly that it is the symmetry **OPERATIONS**, not the elements which form a group.

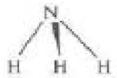
Confirm rule c. for the elements C_2, σ, and σ' of the C_{2v} group, i.e. work out the effect of (C_2 σ) σ' and of C_2 (σ σ').

2.29 $(C_2\sigma)\sigma' = \sigma' \ \sigma' = E$

$C_2(\sigma\sigma') = C_2 C_2 = E$

i.e. the operations are associative.

The C_{2v} point group only has four operations, so it is a simple matter to set up the group multiplication table. There is, however, a further feature of groups which can only be demonstrated by using a rather larger group such as C_{3v}. Ammonia belongs to the C_{3v} group. Can you write down the five symmetry *elements* of ammonia?

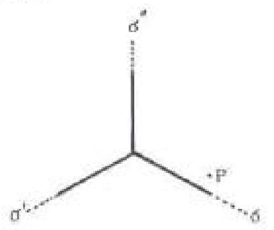


2.30 E C_3 3σ

What operations do these elements generate?

2.31 E C_3 C_3^2 σ σ' σ'' (or 3σ)

We can set up the 6 x 6 multiplication table for these operations by considering the effect of each operation on a point such as P in the diagram below, which has the C_3 axis perpendicular to the paper:

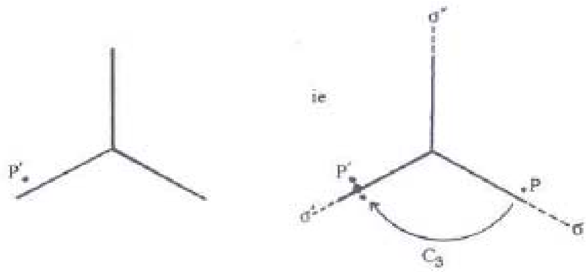


The C_3 and C_3^2 operations are clockwis

Draw the position of point P after applying C_3 and then σ'

(call the new position P')

2.32

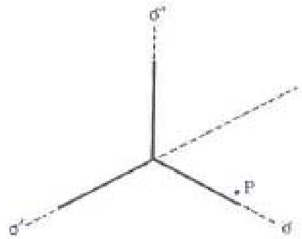


What single operation would take P to P '?

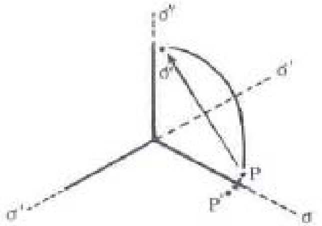
2.33 σ''

i.e. $\sigma' C_3 = \sigma''$ (remember that this means C_3 followed by σ' has the same effect as σ'' — we write the operations in reverse order)

What happens if we do it the other way round, i.e. what is σ' followed by C_3 ($= C_3\sigma'$)?



2.34 σ



In this case σ ′ C_3 does not equal C_3 σ ′ - we say that these two operations do not **COMMUTE.**

Use the effect of the group operations on the point P to see which of the following pairs of operations commute:

C_3 and C_3^2 σ and C_3 σ and σ′ E and C_3^2

2.35 $C_3 C_3^2 = E$; $C_3^2 C_3 = E$ i.e. C_3 and C_3^2 commute

σ C_3 = σ ′ ; C_3 σ = σ ″ i.e. σ and C_3 do not commute

σ σ ′ = C_3 ; σ ′ σ = C_3^2 i.e. σ and σ ′ do not commute

$EC_3^2 = C_3^2$; $C_3^2 E = C_3^2$ i.e. E and C_3^2 commute, it shou be obvious that E commutes with everything — it does not matt if you do nothing before or after the operation!

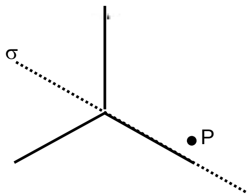
We will now consider briefly the subject of **CLASSES** of symme operations. Two operations A and B are in the same class if there is some operation X such that :

$$XAX^{-1} = B \quad (X^{-1} \text{ is the inverse of X, i.e. } XX^{-1} = E$$

We say that B is the *similarity transform* of A, and that A and B are *conjugate*

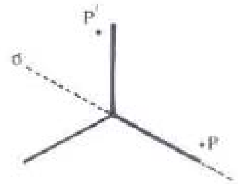
Since any σ is its own inverse we can perform a similarity transformation on the operation C_3 by finding the single operation equivalent to σ C_3 σ .

Work out the position of point P after carrying out these three operations.

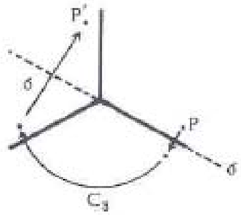


C_3 is clockwise

2.36



i.e.

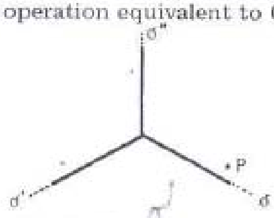


What single operation is the same as σ C_3 σ ?

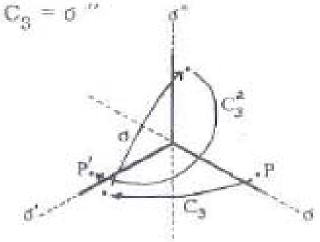
2.37 C_3^2. Thus C_3 and C_3^2 are in the same class.

What is the inverse of C_3?

2.38 C_3^2. Work out the similarity transform of σ by C_3, i.e. decide the operation equivalent to C_3^2 σ C_3.



2.39 $C_3^2 \sigma C_3 = \sigma''$



Thus σ and σ'' are in the same class

The complete set of symmetry operations of the C_{3v} point group, grouped by classes, is as follows:

E (always in a class by itself)

C_3 C_3^2

σ σ' σ''

The operations are commonly written in classes as:

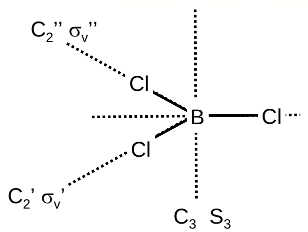
E $2C_3$ 3σ

It is not necessary to go through the whole procedure of working out similarity transformations in order to group operations into classes. A set of operations are in the same class if they are *equivalent operations* in the normally accepted sense. This is probably fairly evident for the example above.

The D_{3h} group (e.g. BCl_3) consists of the operations

$E \; C_3 \; C_3^2 \; C_2 \; C_2' \; C_2'' \; \sigma_h \; S_3 \; S_3^5 \; \sigma_v \; \sigma'_v \; \sigma''_v$

Group these operations into their six classes



2.40 E

$2C_3$

$3C_2$

σ_h

$2S_3$

$3\sigma_v$ (all equivalent but different from σ_h)

You should now be able to:

State the point group to which a molecule belongs.
Confirm that a set of operations constitutes a group.
Arrange a set of operations into classes.

The assignment of a molecule to its correct point group is a vital preliminary to the use of group theory, and this is the subject of the test which follows. The other two objectives of this programme are not tested because it is known in all cases that the symmetry operations of a molecule do constitute a group, and the tables (character tables) which are used in working out problems show the operations grouped by classes.

Point Groups

Revision notes

The set of symmetry operations of any geometrical shape forms a mathematical group, which obeys four rules:

i. The product of two members of the group, and the square of any member is also a member of the group.

ii. There must be an identity element.

iii. Combination must be associative, i.e. (AB)C = A(BC)

iv. Every member must have an inverse. i.e. if A is a member, then A^{-1} must also be a member, where $AA^{-1} = E$.

Symmetry operations do not necessarily commute, i.e. AB does not always equal BA.

A molecule can be assigned to its point group by a method which does not require the listing of all symmetry operations of the molecule; the method merely involves looking for certain key symmetry elements. The symbol for most molecular symmetry groups is in three parts e.g.

C_{4v} C_{2h} D_{3h} D_{6d}

These have the following meanings:

i. The number indicates the order of the principal (highest order) axis. This axis conventionally defines the vertical direction.

ii. The capital letter is D if an n-fold principal axis is accompanied by n two-fold axes at right angles to it; otherwise the letter is C.

iii. The small letter is h if a horizontal plane is present. If n vertical planes are present, the letter is v for a C group but d (=dihedral) for a D group. (N.B. h takes precedence over v or d). If no vertical or horizontal planes are present, the small letter is omitted

Systematic classification of molecules into point groups

C = rotation axis i = inversion centre

S = improper axis (alternating axis) σ = plane of symmetry

1. Examine for special groups
   a. Linear, no σ perpendicular to molecular axis — $C_{\infty v}$
   b. Linear, σ perpendicular to molecular axis — $D_{\infty h}$
   c. Tetrahedral — T_d
   d. Octahedral — O_h
   e. Dodecahedral or icosahedral — I_h

2. Examine for a C_n axis

- C_n absent
  - σ present — C_s
  - i present — C_i
  - no symmetry elements other than E — C_1
- C_n present
  - Find C_n of highest n or a unique C_n — this axis is then taken to be vertical by convention → 3.

3. Examine for S_{2n} colinear with C_n

- S_{2n} present
  - No other symmetry elements present, except i — S_{2n}
  - Other symmetry elements present → 4.
- S_{2n} absent → 4.

4. Examine for n horizontal C_2 axes

- n C_2 axes present
  - Horizontal plane (σ_h) present – D_{nh}
  - n Vertical planes (dihedral planes, σ_d, bisecting angles between C_2 axes) present – D_{nd}
  - Absent - D_n
- n C_2 axes absent
  - Horizontal plane (σ_h) present – C_{nh}
  - n Vertical planes present (σ_d) – C_{nv}
  - Absent - C_n