SCHEDULE

	Date		Topic
1.	Wed	01.03.	Lec-1: Introduction
2.	Mon	06.03.	Lec-2: Crystal Chemistry & Tolerance parameter
3.	Mon	06.03.	EXERCISE 1
4.	Wed	08.03.	Lec-3: Crystal Chemistry & BVS
5.	Fri	10.03.	Lec-4: Symmetry & Point Groups
6.	Mon	13.03.	EXERCISE 2
7.	Wed	15.03.	Lec-5: Crystallography & Space Groups (Linda)
8.	Fri	17.03.	Lec-6: XRD & Reciprocal lattice (Linda)
9.	Mon	20.03.	EXERCISE 3 (Linda)
10.	Fri	31.03.	Lec-7: Rietveld (Linda)
11.	Mon	03.04	EXERCISE 4: Rietveld (Linda)
12.	Wed	12.04.	Lec-8: ND & GI-XRD
13.	Fri	14.04.	Lec-9: XRR (Topias)
14.	Mon	17.04.	EXERCISE 5: XRR (Topias)
15.	Wed	19.04.	Lec-10: Synchrotron radiation & XAS & EXAFS
16.	Fri	21.04.	Mössbauer
17.	Fri	21.04.	EXERCISE 6
18.	Thu	27.04.	Seminars: XPS, FTIR, Raman
19.	Fri	28.04.	Seminars: ED, HRTEM, SEM, AFM

EXAM

LINDA LECTURES / EXERCISES

- 15.03. WEDNESDAY: 14.15 – 16 (Ke3)
- 17.03. FRIDAY: 8.30 – 10 (Ke4)
- 20.03. MONDAY: 14.15 – 16 (Ke4)
- 31.03. FRIDAY: 8.30 – 10 (Ke4)
- 03.04. MONDAY: Two groups, 10-12 & 12-14 (details given later)

SEMINARS

IR	Fasiha Israr & Lisa Riedlsperger
Raman	Zonghang Song & Xueran Tao
XPS	Umaid Lone
SEM	Trang Pham & Erkka Koskenniemi
AFM	Joakim Kattelus & Matilda Antila
HRTEM	Luiza Souza & Henrik Stenbrink
ED	Christer Söderholm & Shadab Ishtiaq
EELS	Aleksi Rantanen

INSTRUCTIONS for SEMINAR PRESENTATIONS

- Topics: **IR, Raman, XPS, SEM, AFM, HRTEM, ED, EELS**
- Seminar presentation is mandatory
- Presentation slides will be put up in MyCourses afterwards
- **Seminars are part of the course content and it is likely that there will be questions in the exam related to these seminars**
- Given in a group of two students
- Evaluated in the scale: 10 ~ 20 points
- Presentation: 25+5 minutes
- Rough content of the presentation:

  - principle of the technique(s)

  - type of information gained

  - interpretation of the measured data

  - pros & cons

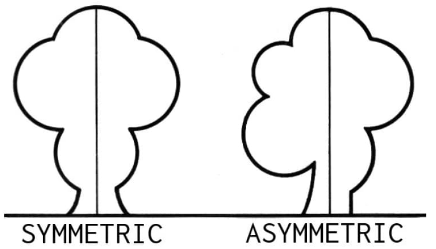
  - two to four research examples
  (you will be given some relevant research papers for an example)

LECTURE 4: SYMMETRY

- **Greek ”*symmetrein”* (= commensurate, yhteismitallinen)**
- **Symmetry elements/operations**
- **Molecular symmetry & Point groups**
- **Space groups & Crystallography in Lecture 5**

SYMMETRY

- Symmetry is common in nature
- Some people see beauty in symmetry, some in asymmetry



Kuva: Pearson Scott Foresman

IN CHEMISTRY …

MOLECULAR SYMMETRY

Important for understanding/explaining/classification

- **Molecule structures**
- **Crystal structures**
- **Quantum chemistry**
- **Spectroscopy (IR, Raman)**
- **Material properties, e.g. ferro/piezoelectricity**

SYMMETRY OPERATION

Operation that generates the same representation of an object (molecule)

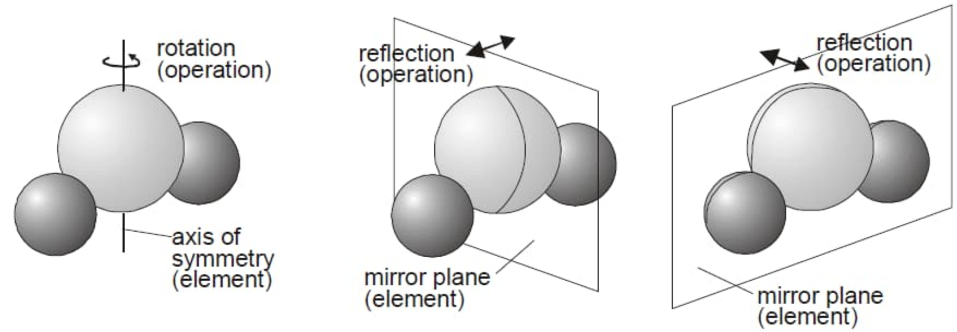
SYMMETRY ELEMENT

Each symmetry operation has a corresponding symmetry element (point, axis, plane) about which the operation takes place

MOLECULAR SYMMETRY

Operations & Elements

(historical Schönflies notation; used also in spectroscopy)



Molecular symmetry: at least one point remains unchanged

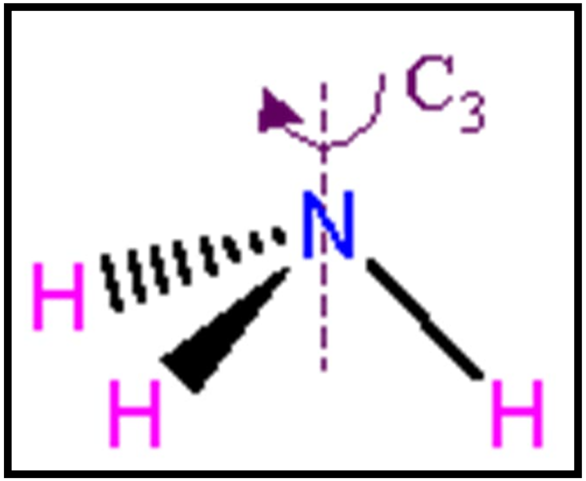
- **Identity (E; *German Einheit*):** No change; every molecule has E
- **Rotation axis (C_n):** Rotation by 360º/n (n = 1, 2, 3, …) about an axis, which leaves the molecule unchanged
- **Symmetry or mirror plane (σ):** Plane through which reflection leaves the molecule unchanged:

  σ_v: vertical mirror plane (in relation to rotation axis)

  σ_h: horisontal mirror plane (in relation to rotation axis)
- **Center of symmetry (i):** center through which inversion leaves the molecule unchanged
- **Improper rotation (or rotary-reflection) axis (S_n):** Rotation about an axis by 360°/n, followed by reflection in a plane perpendicular to the axis. Note: $S_1 = \sigma$; $S_2 = i$

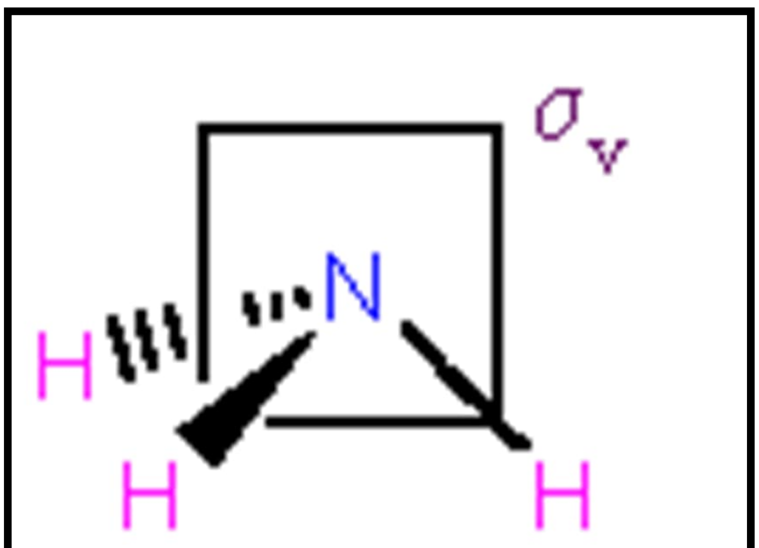
Proper: **Can be actually done on a molecule: E, C_n**

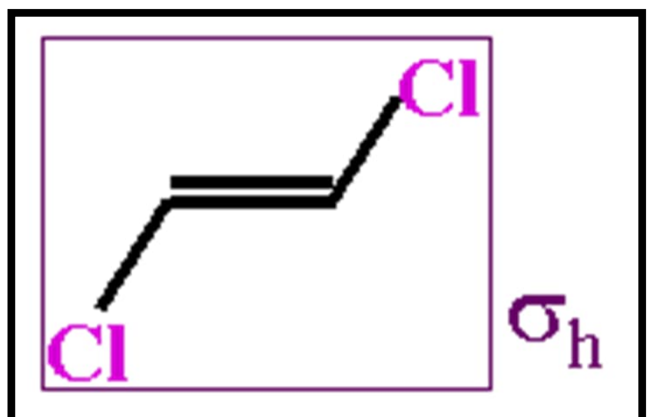
Improper: **Can be only imagined, not done: σ, I, S_n**
(drastic chemical bond rearrangements)

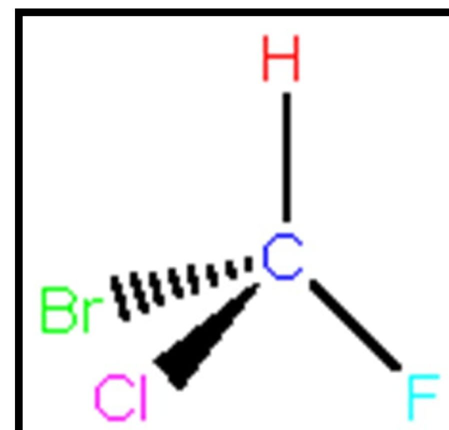

C_3
N
H
H
H


C_5

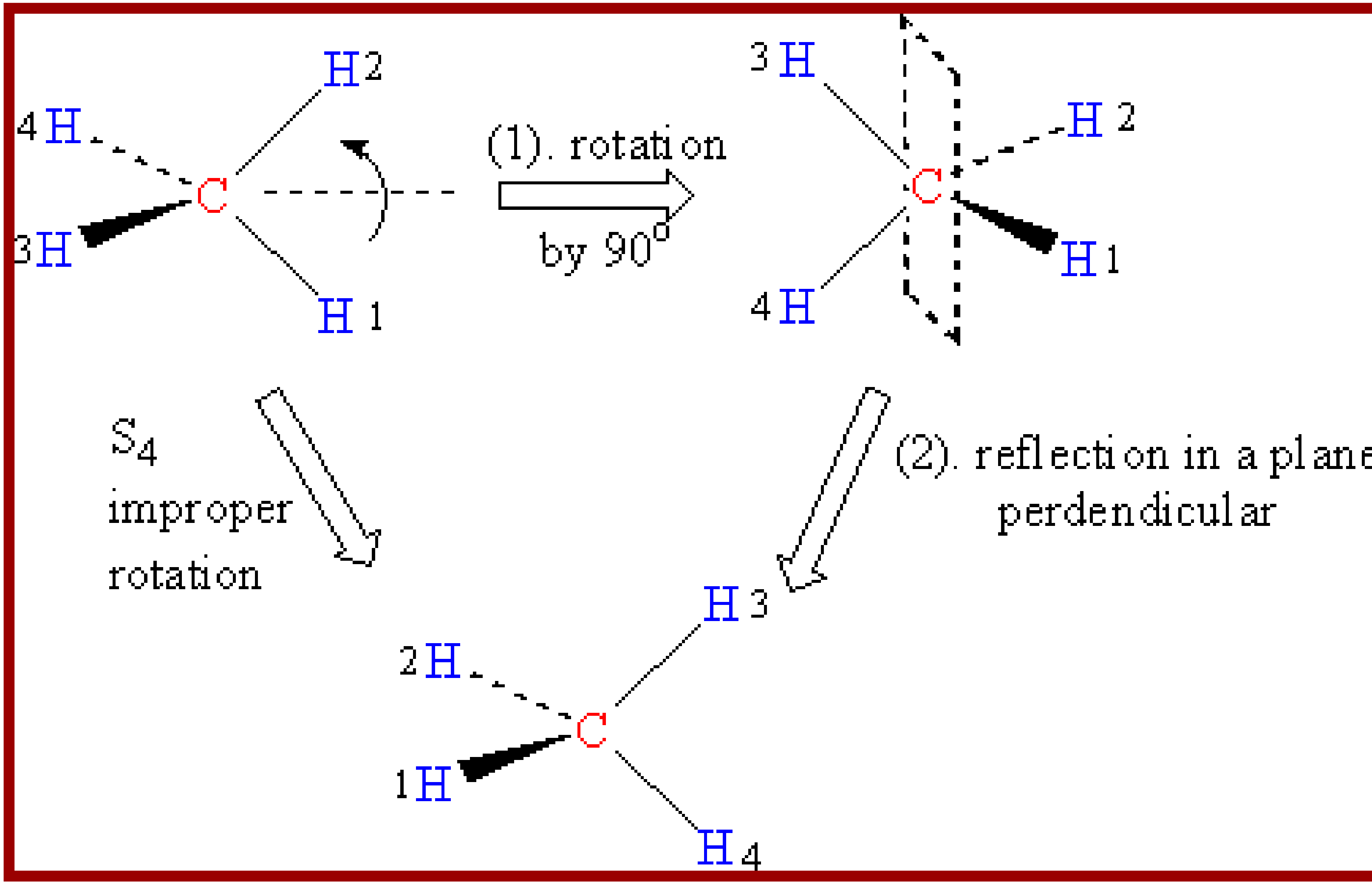

O—C—O
Invert through
centre
O—C—O


σ_v
N
H
H
H

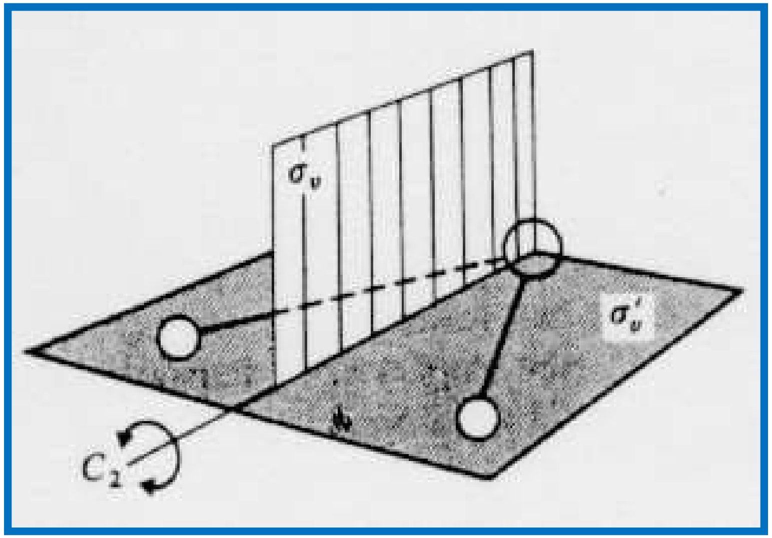

Cl
Cl
σ_h

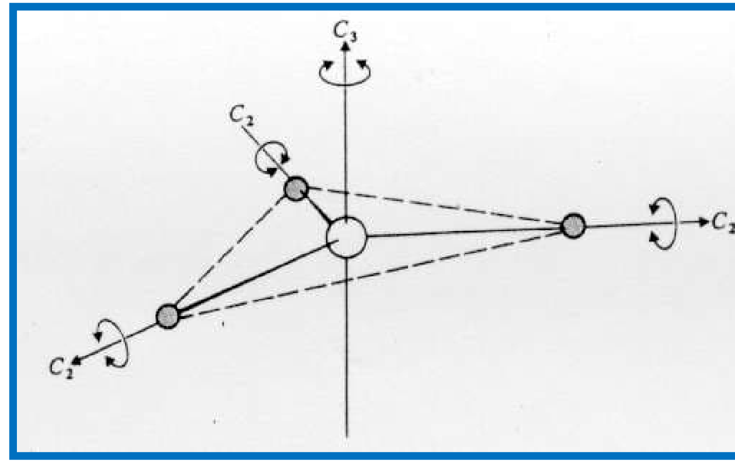

H
C
Br
Cl
F

Rotary-reflection: CH_4



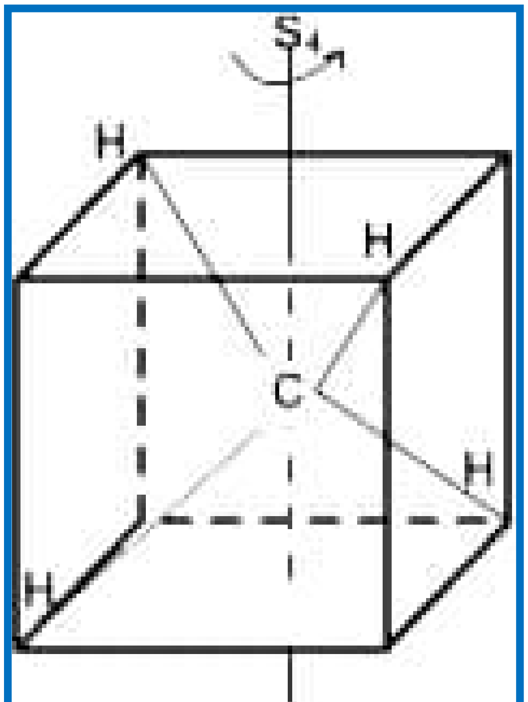
H_2O



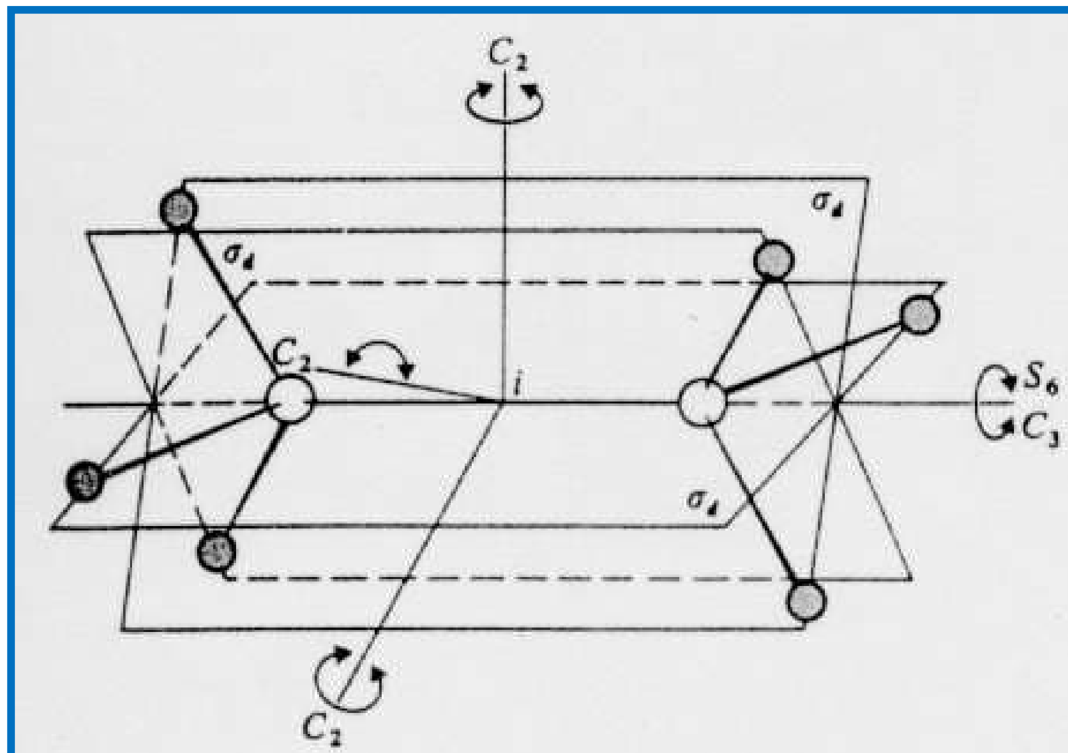


BF_3

CH_4



Ethane (staggered): CH_3-CH_3

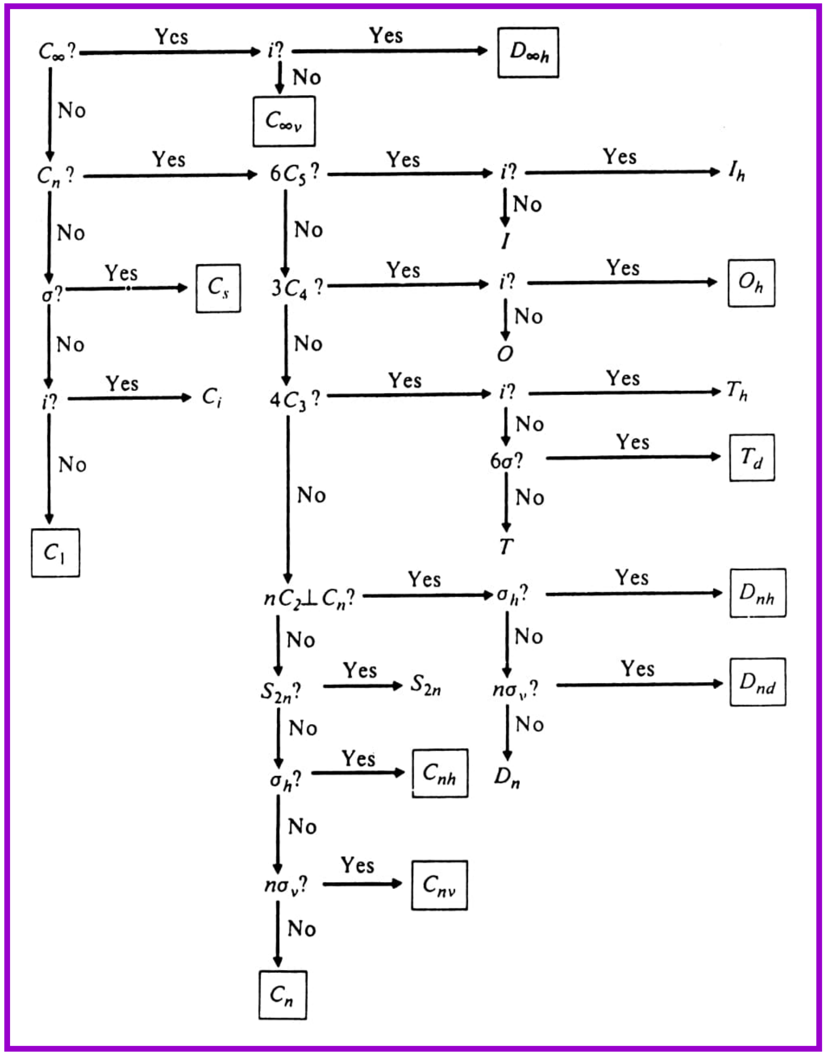


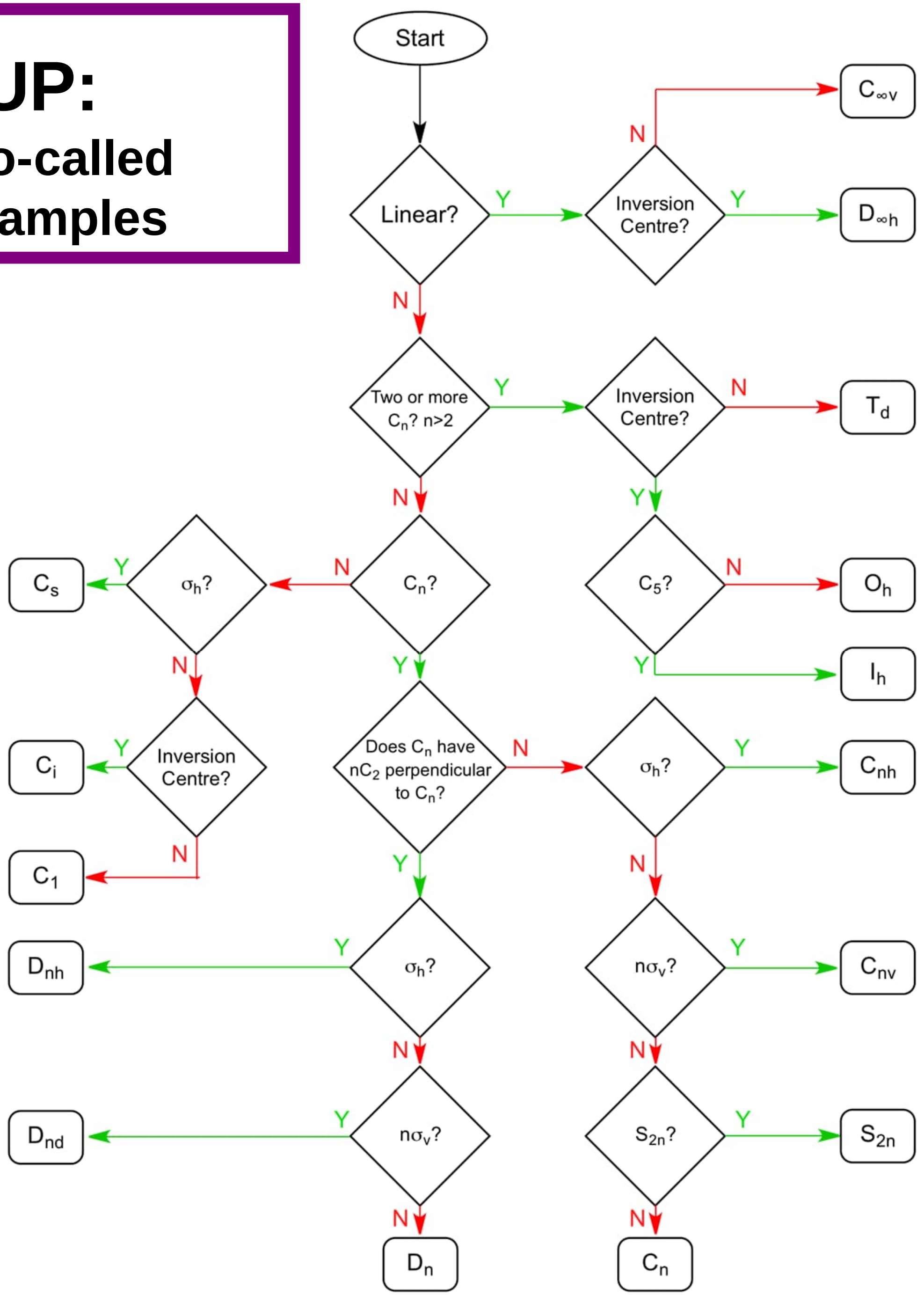
POINT GROUP

- **Summarizes all the symmetry operations that can be performed on a certain molecule**
- **Describes unambiguously the symmetry of the molecule**
- **In principle there are infinite number of point groups (combinations of symmetry elements); in practice ca. 40 different point groups are enough to classify all the known molecules**
- **Point groups are named: C_2, C_{2v}, D_{3h}, O_h, T_d … (Schönflies)**

Finding the POINT GROUP:

There are a number of routes or so-called symmetry trees; here are some examples





Point Groups

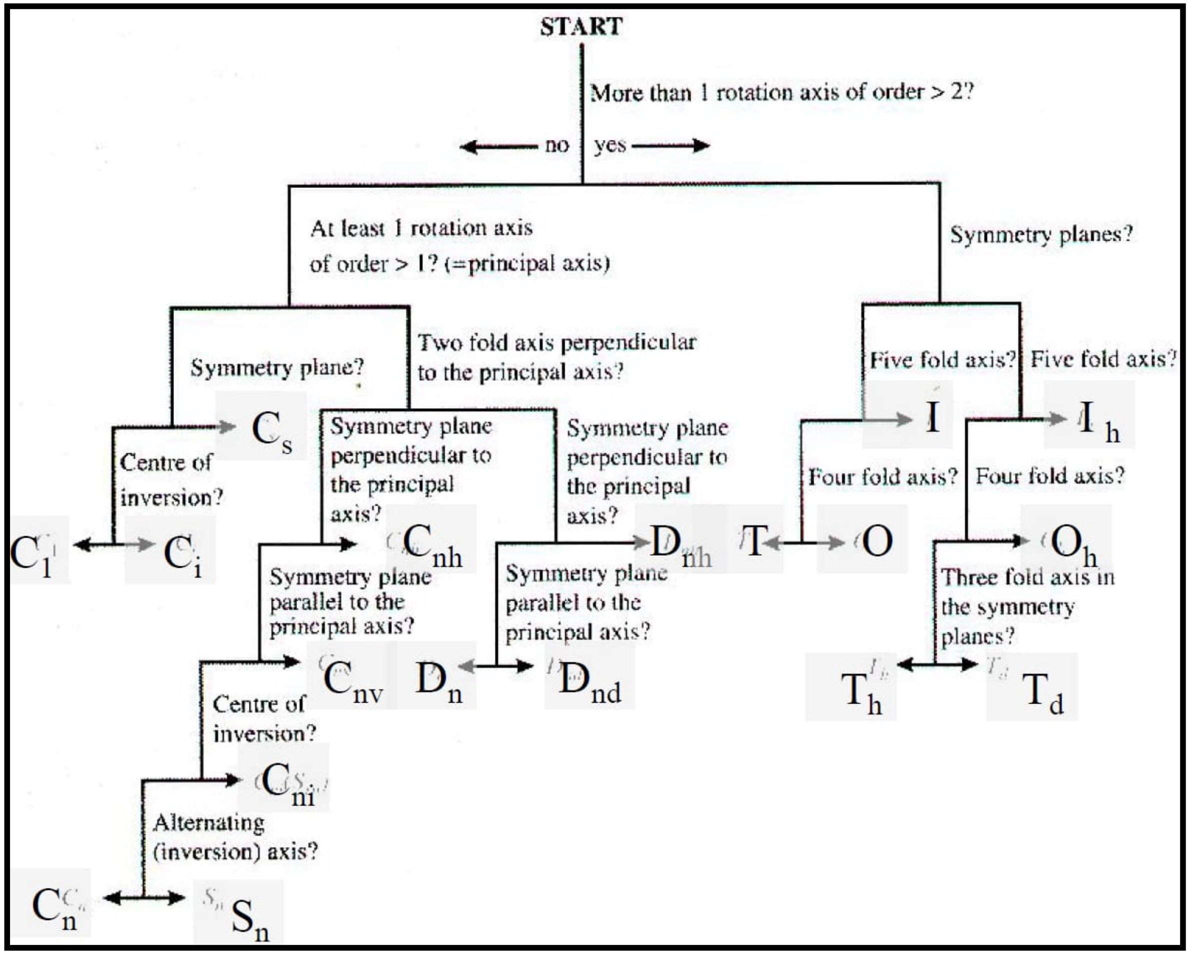
Every molecule has a set of symmetry elements.
This set is called the Point Group of the molecule.

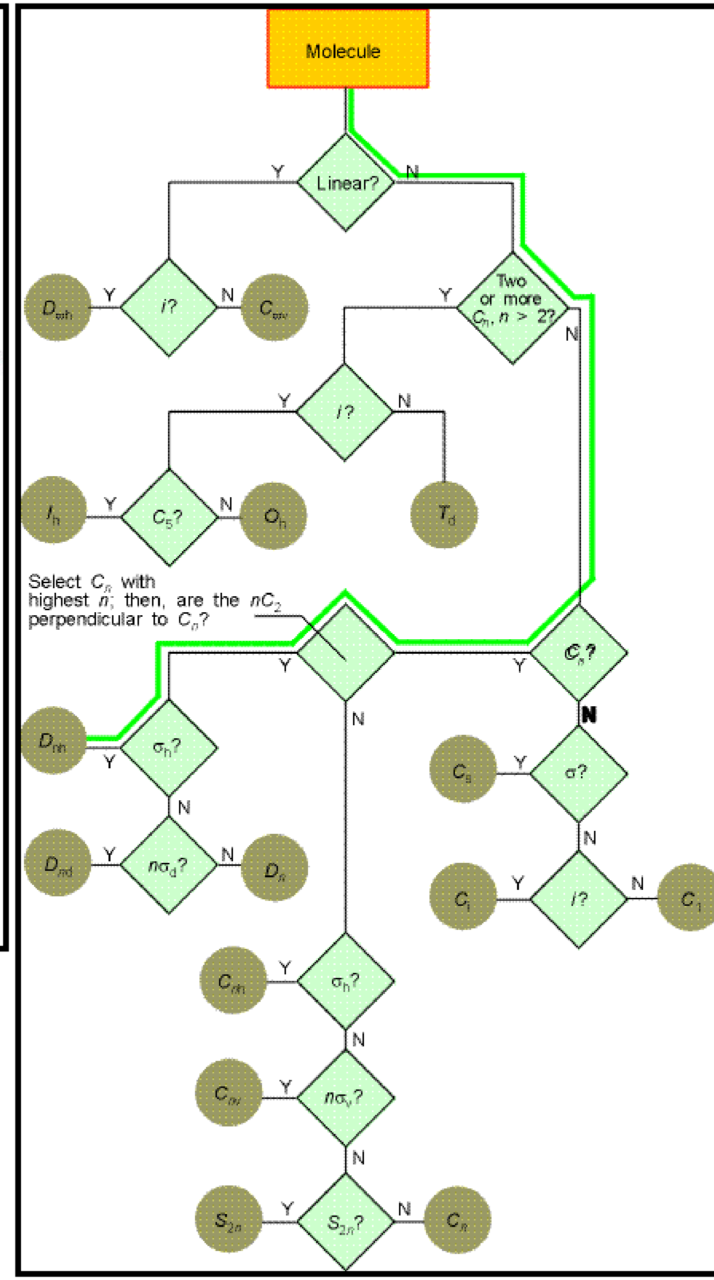
Nonaxial	**C_n**	**C_{nv}**	**C_{nh}**	**D_n**	**D_{nh}**	**D_{nd}**	**S_n**	**Higher**	**Linear**
C_1	C_2	C_{2v}	C_{2h}	D_2	D_{2h}	D_{2d}	S_4	T_d	$C_{\infty v}$
C_s	C_3	C_{3v}	C_{3h}	D_3	D_{3h}	D_{3d}	S_6	O_h	$D_{\infty h}$
C_i	C_4	C_{4v}	C_{4h}	D_4	D_{4h}	D_{4d}	S_8	I_h	
	C_5	C_{5v}	C_{5h}	D_5	D_{5h}	D_{5d}	S_{10}		
	C_6	C_{6v}	C_{6h}	D_6	D_{6h}	D_{6d}			

Character table for D_{3h} point group

	E	$2C_3$	$3C'_2$	σ_h	$2S_3$	$3\sigma_v$	linear, rotations	quadratic

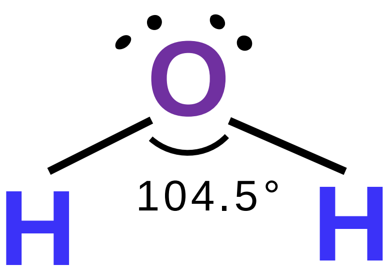
http://www.webqc.org/symmetry.php


START
More than 1 rotation axis of order > 2?
no
yes
At least 1 rotation axis of order > 1? (=principal axis)
Symmetry planes?
Symmetry plane?
Two fold axis perpendicular to the principal axis?
Five fold axis?
Five fold axis?
I
I h
C s
Centre of inversion?
Symmetry plane perpendicular to the principal axis?
Symmetry plane perpendicular to the principal axis?
Four fold axis?
Four fold axis?
C 1
C i
C nh
D nh
T
O
O h
Symmetry plane parallel to the principal axis?
Symmetry plane parallel to the principal axis?
Three fold axis in the symmetry planes?
C nv
D n
D nd
T h
T d
Centre of inversion?
C ni
Alternating (inversion) axis?
C n
S n

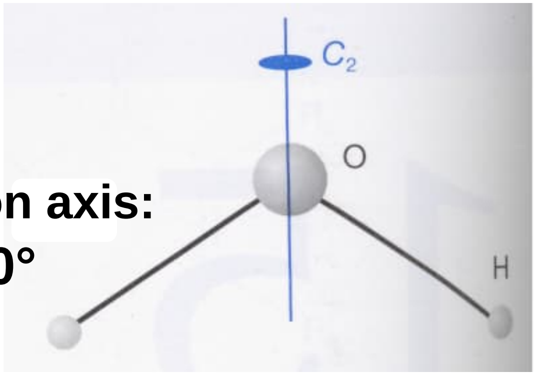

Molecule
Linear?
Y
N
i?
D∞h
C∞v
Two or more Cn, n > 2?
i?
C5?
Ih
Oh
Td
Select Cn with highest n; then, are the nC2 perpendicular to Cn?
Cn?
σh?
Dnh
nσd?
Dnd
Dn
σ?
Cs
i?
Ci
C1
σh?
Cnh
nσv?
Cnv
S2n?
S2n
Cn

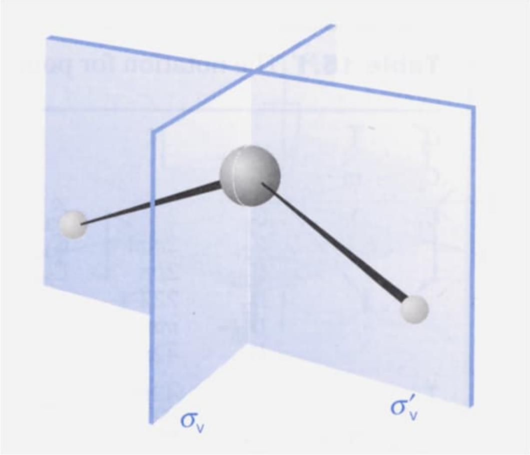
EXAMPLE: H_2O

C_{2v}

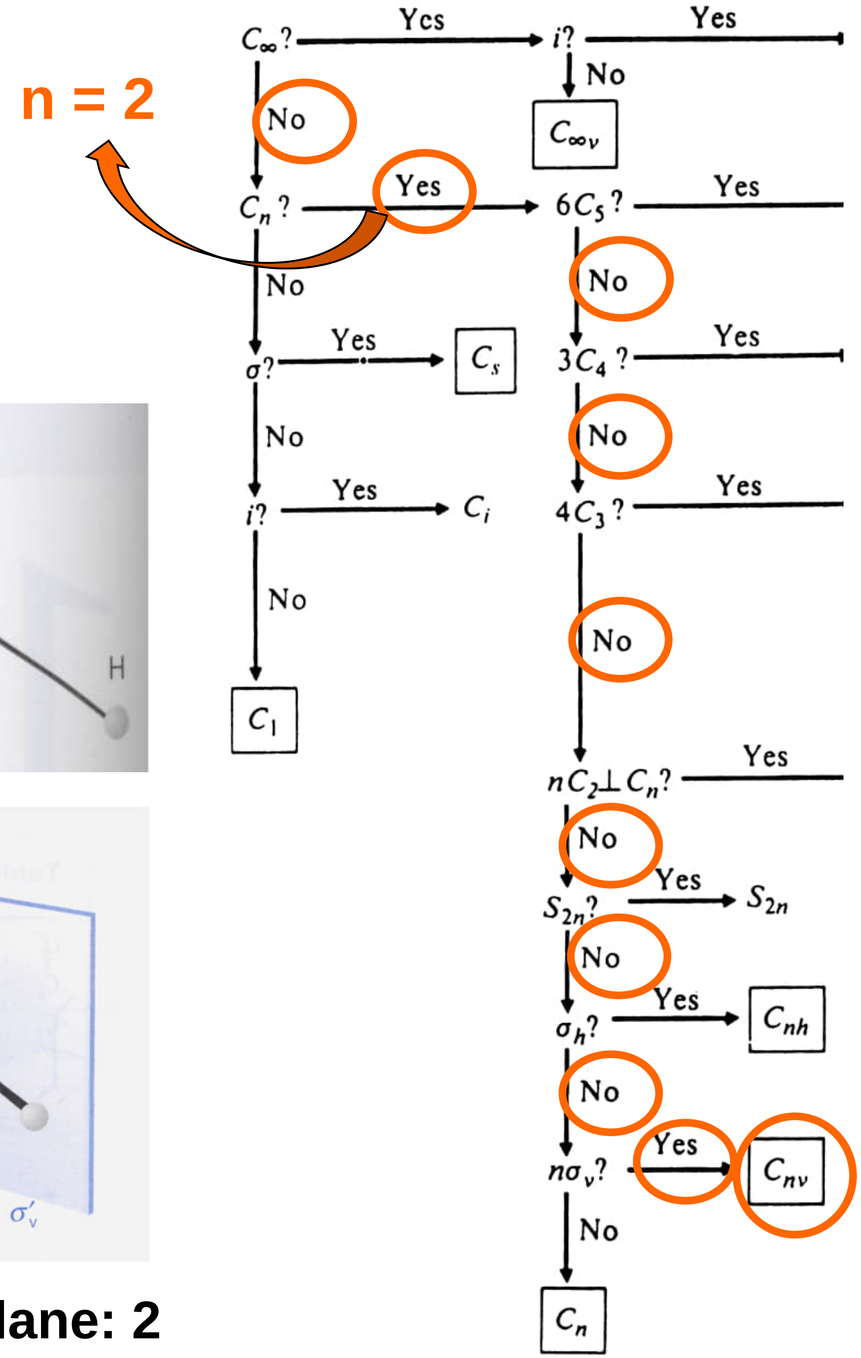


Rotation axis: 180°

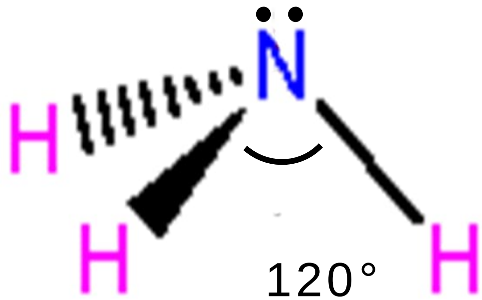


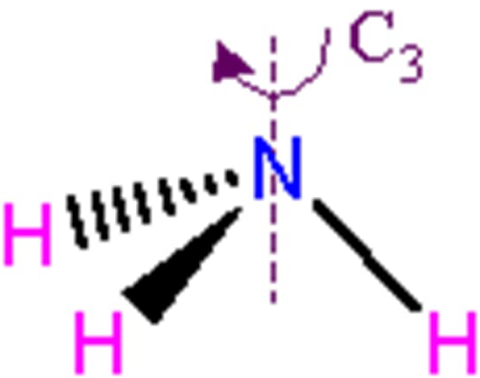


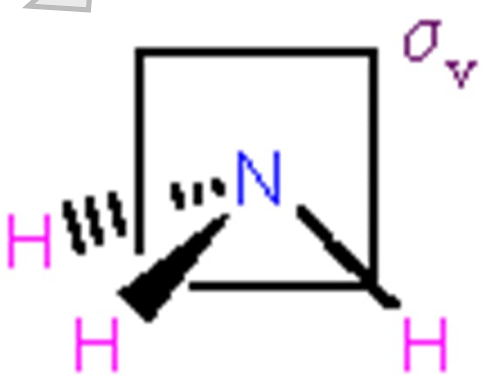
Vertical mirror plane: 2



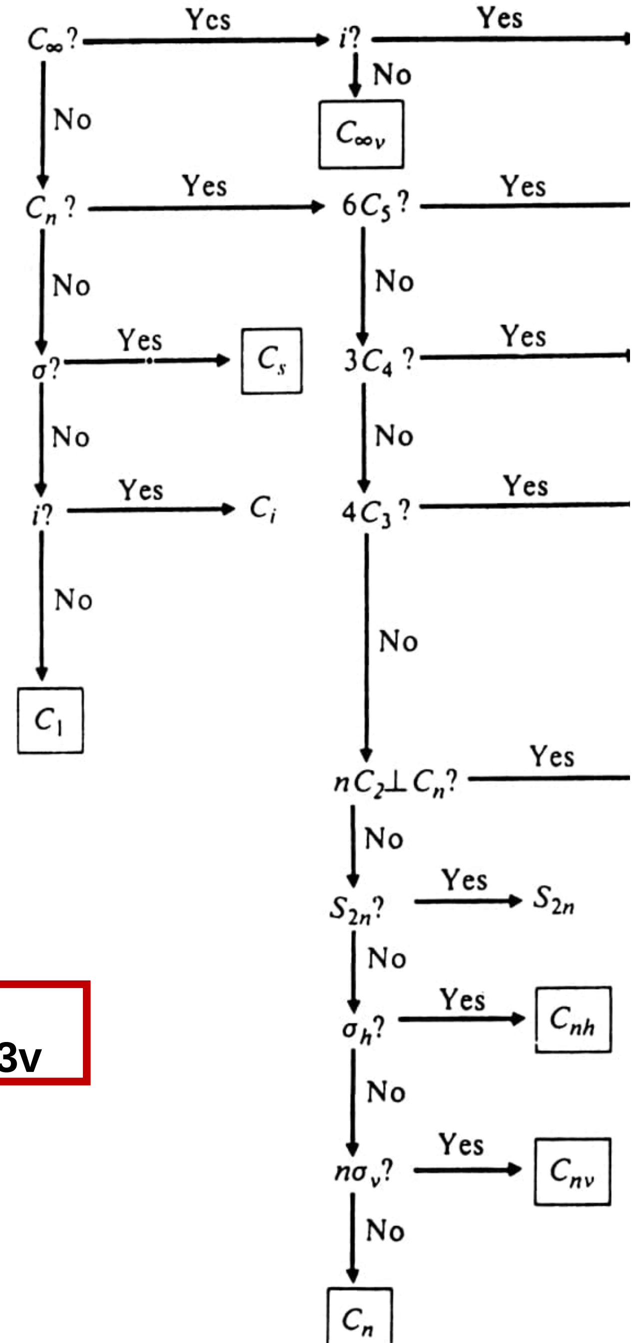
EXAMPLE: NH_3







C_{3v}



EXAMPLES

HCl

∞-fold rotation axis along the H-Cl bond, but no inversion center → $C_{\infty v}$

BFClBr (planar, B in a middle of triangle)

Only symmetry plane (where the atoms are) → C_s

trans-$N_2O_2^{2-}$ (planar)

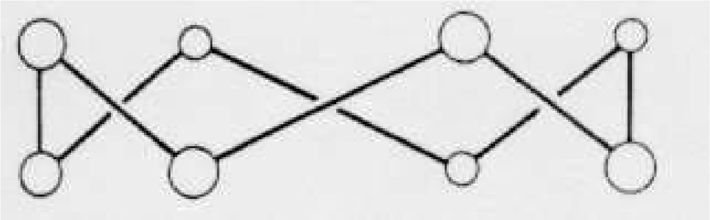
One C_2 rotation axis perpendicular to the plane where the atoms are, no S_4 rotary-reflecion axis, but horizontal symmetry plane → C_{2h}

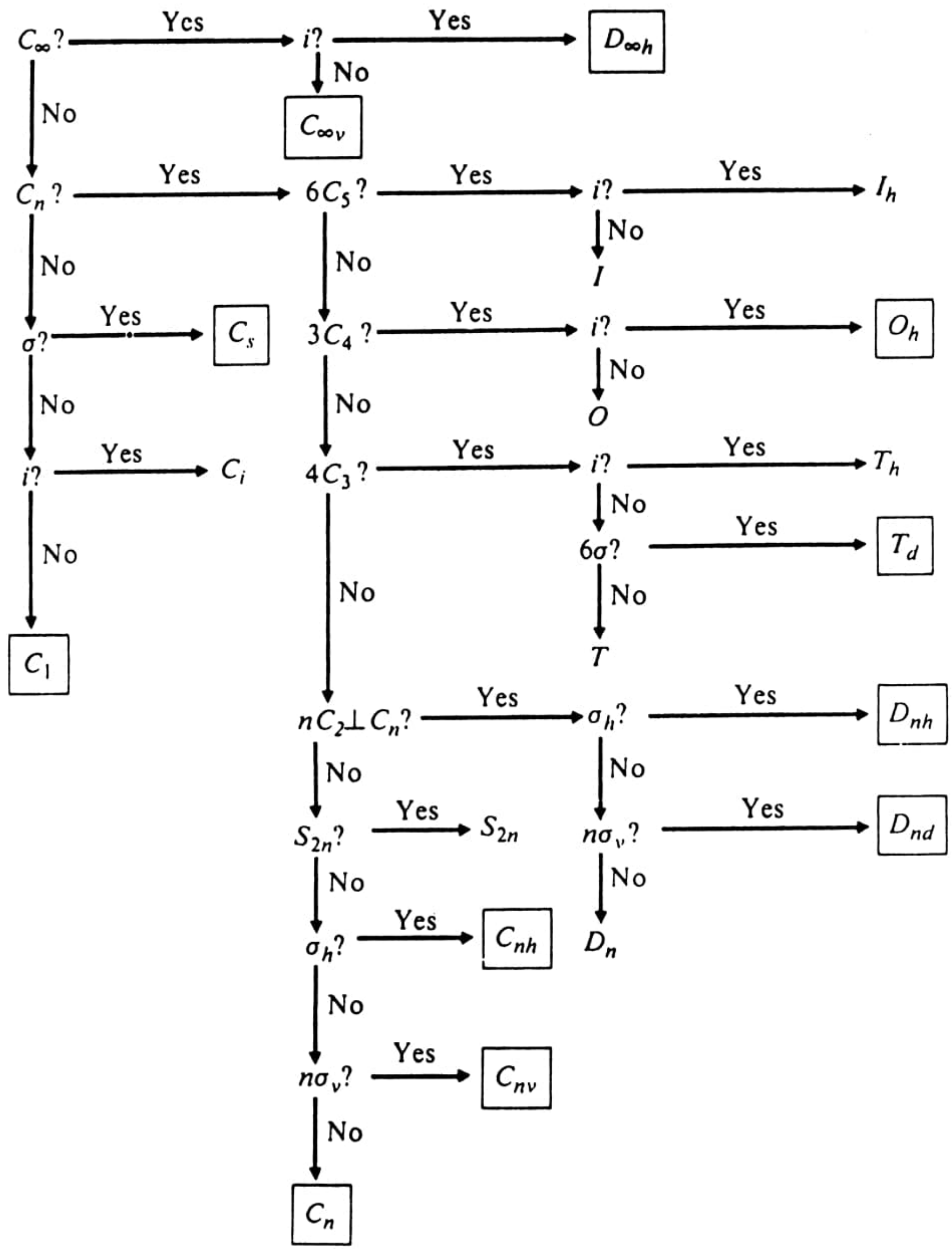
CH_4 (tetraedric)

Four C_3 rotation axes, no inversion center, six symmetry planes → T_d

S_8

One C_4 and four C_2 rotation axes perpendicular to C_4, no horizontal symmetry plane, but four vertical symmetry planes → D_{4d}




C_∞?
Yes
i?
Yes
$D_{\infty h}$
No
No
$C_{\infty v}$
C_n?
Yes
$6C_5$?
Yes
i?
Yes
I_h
No
I
No
No
σ?
Yes
C_s
$3C_4$?
Yes
i?
Yes
O_h
No
O
No
No
i?
Yes
C_i
$4C_3$?
Yes
i?
Yes
T_h
No
6σ?
Yes
T_d
No
T
No
No
C_1
$nC_2 \perp C_n$?
Yes
σ_h?
Yes
D_{nh}
No
No
S_{2n}?
Yes
S_{2n}
$n\sigma_v$?
Yes
D_{nd}
No
No
D_n
σ_h?
Yes
C_{nh}
No
$n\sigma_v$?
Yes
C_{nv}
No
C_n