1. Symmetry of Molecules

1.1 Symmetry Elements

- Symmetry operation: Operation that transforms a molecule to an equivalent position and orientation, i.e. after the operation every point of the molecule is coincident with an equivalent point.
- Symmetry element: Geometrical entity (line, plane or point) which respect to which one or more symmetry operations can be carried out.

In molecules there are only four types of symmetry elements or *operations*:

- Mirror planes: *reflection* with respect to plane; notation: σ
- Center of inversion: *inversion* of all atom positions with respect to inversion center, notation i
- Proper axis: *Rotation* by $2\pi/n$ with respect to the axis, notation C_n
- Improper axis: *Rotation* by $2\pi/n$ with respect to the axis, followed by *reflection* with respect to plane, perpendicular to axis, notation S_n

Formally, this classification can be further simplified by expressing the inversion i as an improper rotation S_2 and the reflection σ as an improper rotation S_1. Thus, the only symmetry elements in molecules are C_n and S_n.

Important: Successive execution of two symmetry operation corresponds to another symmetry operation of the molecule. In order to make this statement a general rule, we require one more symmetry operation, the identity E.

(1.1: Symmetry elements in CH4, successive execution of symmetry operations)

1.2. Systematic classification by symmetry groups

According to their inherent symmetry elements, molecules can be classified systematically in so called symmetry groups. We use the so-called Schönfliess notation to name the groups, which is the usual notation for molecules. An alternative scheme is the so called crystallographic notation which will be introduced in chapter 2.

Classification algorithm:

(1) Special groups:

(a) Does the molecule possess more than one axes with n>2? Yes: It belongs to one of the special groups $\mathbf{T}$, $\mathbf{T_h}$, $\mathbf{T_d}$, $\mathbf{O}$, $\mathbf{O_h}$, $\mathbf{I}$, $\mathbf{I_h}$ (discussed in section 1.3)

(b) Does the molecule possess rotational symmetry? Yes: It belongs to $\mathbf{C_{¥v}}$ (no perpendicular mirror plane) or $\mathbf{D_{¥h}}$ (perpendicular mirror plane).

(2) Does the molecule possess an proper / improper axis? No: $\mathbf{C_1}$ (no symmetry element apart from E), $\mathbf{C_s}$ (only one σ and E), $\mathbf{C_i}$ (only i and E).

(3) Is the only symmetry element an even improper axis? Yes: $\mathbf{S_4}$, $\mathbf{S_6}$, $\mathbf{S_8}$, $\mathbf{S_{10}}$,...

(4) Identify the "principal symmetry axis" C_n with highest n

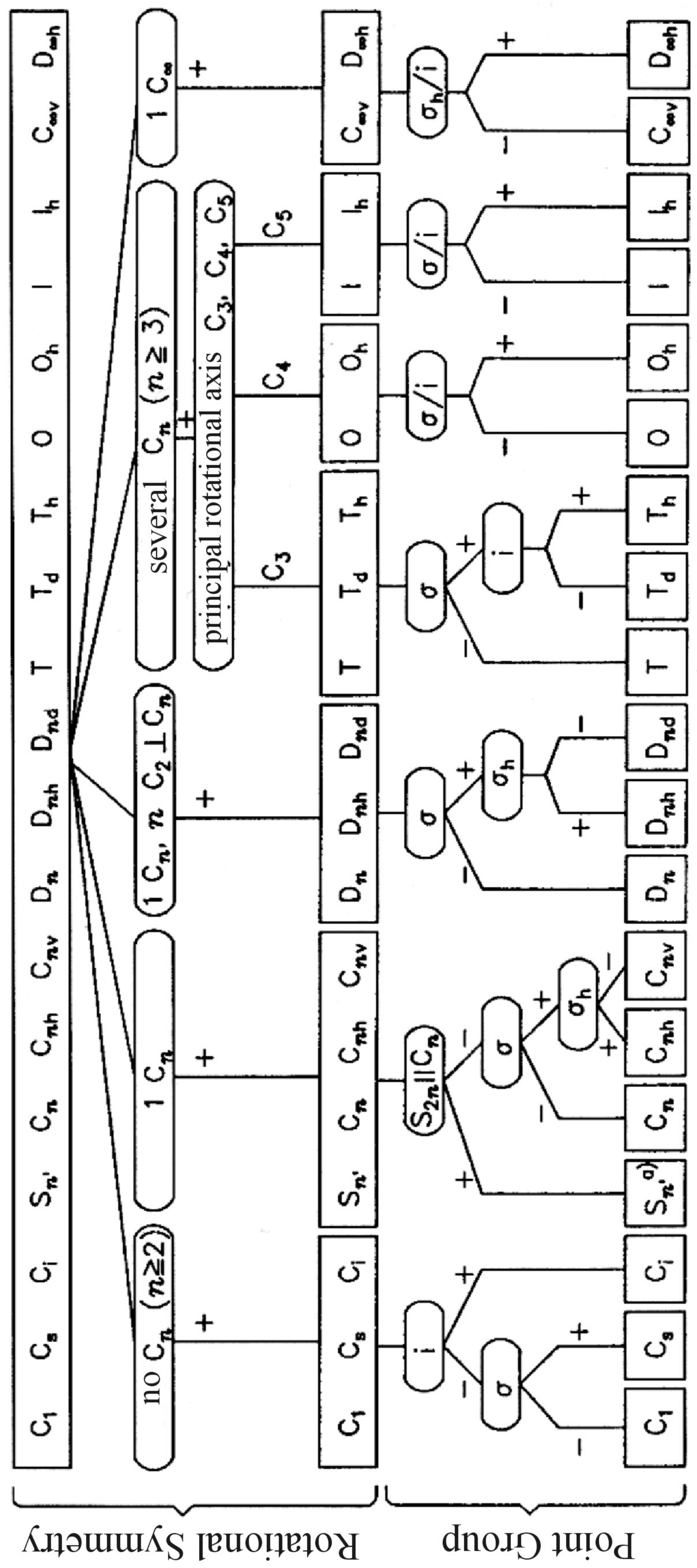
(5) Are there C_2 axes perpendicular to C_n?

Yes: (6) Are there mirror planes?	Perpendicular to C_n: $\mathbf{C_{nh}}$
	Containing C_n: $\mathbf{C_{nv}}$
	None: $\mathbf{C_n}$
No: (6) Are there mirror planes?	Perpendicular to C_n: $\mathbf{D_{nh}}$
	Between C_2's: $\mathbf{C_{nd}}$
	None: $\mathbf{D_n}$

(1.2: Determine the molecular symmetry groups: ferrocene ecliptic configuration, ferrocene in staggered configuration)

(1.3: Examples of for specific point groups)

Classification scheme for molecular symmetry groups (from D. Steinborn):



1.3 Higher symmetries an the platonic solids

(1.4: "Stars" by M. C. Escher, 1948)

(1.5: "Platonic solids and the elements of ancient Greek mythology")

The so called platonic solids are regular polyhedra, i.e. solids,

(a) which faces are all one regular polygon (regular triangles, squares,...)

(b) the faces, edges and corners are all equivalent (are interchangeable by symmetry operations).

(1.6: How many platonic solids do exist?)

There are only 5 platonic solids:

(1) Tetrahedron

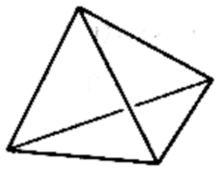
(2) Octahedron

(3) Icosahedron

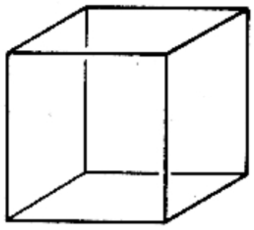
(4) Cube

(5) Dodecahedron

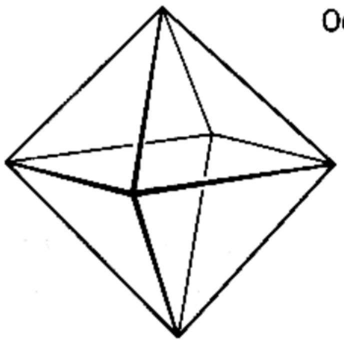
Platonic solids (from A. Cotton):



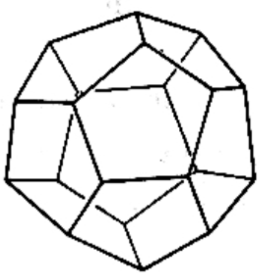
Tetrahedron
Faces: 4 equilateral triangles
Vertices: 4
Edges: 6



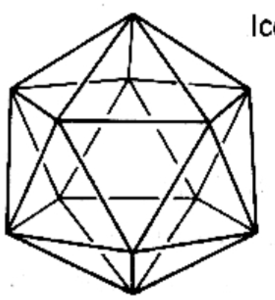
Cube
Faces: 6 squares
Vertices: 8
Edges: 12



Octahedron
Faces: 8 equilateral triangles
Vertices: 6
Edges: 12



Dodecahedron
Faces: 12 regular pentagons
Vertices: 20
Edges: 30



Icosahedron
Faces: 20 equilateral triangles
Vertices: 12
Edges: 30

We derive the symmetry elements and the symmetry operations of the platonic solids:

(1.7: What are the symmetry elements of a tetrahedron?)

(1.8: What are the symmetry operations of a tetrahedron?)

a. Tetrahedron:

- symmetry elements: 4 C_3 axes, 3 C_2 axes, 3 S_4 axes, 6 mirror planes
- 24 symmetry operations: E, 8C3, 3C2, 6S4, 6σd; group $\mathbf{T_d}$

Remark: It is possible to remove all mirror planes. The remaining group of symmetry operations is denoted as **T** (12 symmetry operations).

b. Octahedron:

- 48 symmetry operations: E, $8C_3$, $6C_4$, $6C_2$, $3C_2$, i, $6S_4$, $8S_6$, $3\sigma_h$, $6\sigma_d$: group $\mathbf{O_h}$

without mirror planes: **O** (24 symmetry operations)

Important: octahedron and cube have the same symmetry!

(1.9: Cube and octahedron have the same symmetry, identify the equivalent symmetry elements)

(1.10: Transition from cube to octahedron: cuboctahedron)

(1.11: Physical example for cubocahedral objects: metal nanoparticles with fcc structure, minimization of surface free energy, Wulff construction) have the same symmetry, identify the equivalent symmetry elements)

c. Icosahedron

- 120 symmetry operations: E, $12C_5$, $12C_5^2$, $20C_3$, $15C_2$, i, $12S_{10}$, $12S_{10}^3$, $20S_6$, 15σ

without mirror planes: **I** (60 symmetry operations)

Important: icosahedron and dodecahedron have the same symmetry!

(1.12: Example for the transition from dodecahedron to icosahedron: soccer ball)

(1.13: Chemical example for icosahedral symmetry: fullerene molecule C_{60})