Part III Symmetry and Bonding

Chapter 1 Symmetry and Point Groups

第一章 对称性与点群

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http://pcoss.xmu.edu.cn/xlv/index.html

http://pcoss.xmu.edu.cn/xlv/courses/theochem/index.html

Recommended books

- Vincent A., *Molecular Symmetry and Group Theory*, 2nd edition, Wiley, 2001.
- Barrett J., *Structure and Bonding*, RSC, 2001
- Cotton F. A., *Chemical Applications of Group Theory*, 3rd edition, Wiley, 1990.
- Atkins P. W. & Friedman R. S., *Molecular Quantum Mechanics*, 4th edition, OUP, 2005
- *Physical Chemistry*, Donald A McQuarrie and John D. Simon

  University Science Books

  Good for other parts of the course too

1.1 Introduction

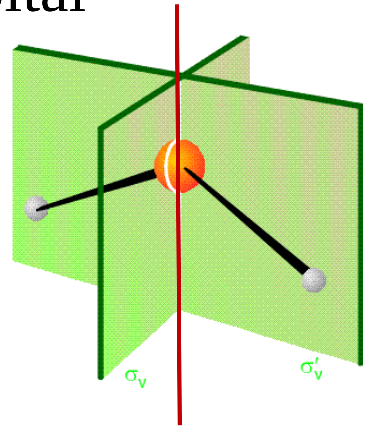
- In this course we will explore how ***the symmetry of molecules*** can be described precisely using ***Group Theory*** and how, armed with the concepts from this theory, we can go on to ***predict and understand important properties of molecules***.

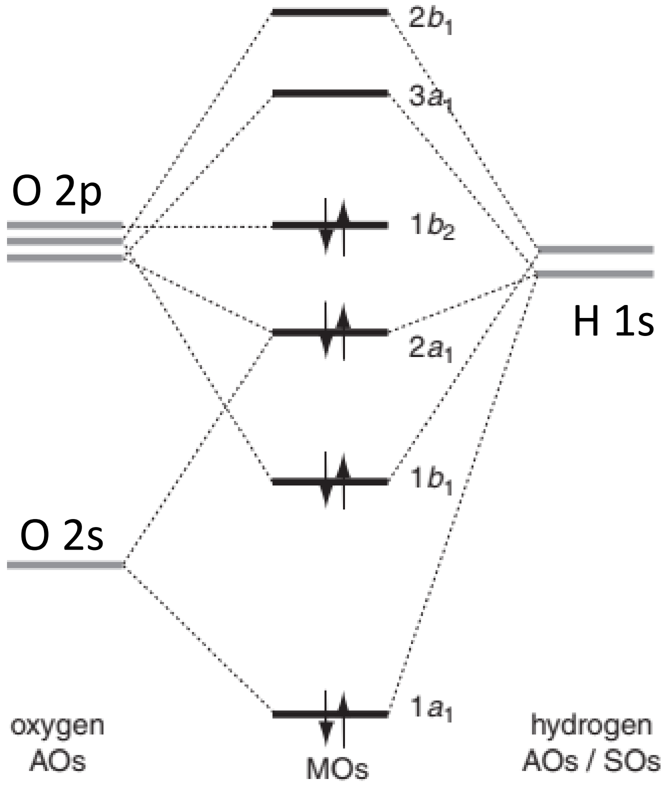
- In particular we shall focus on

  i) how symmetry helps us to construct molecular orbital diagrams;

  ii) how it helps in the calculation of the energies and precise form of the orbitals.

  iii) how to use symmetry to predict and describe the properties of the vibrational normal modes of molecules and their activity in ***IR and Raman spectra.***





Molecular orbital diagram for H_2O

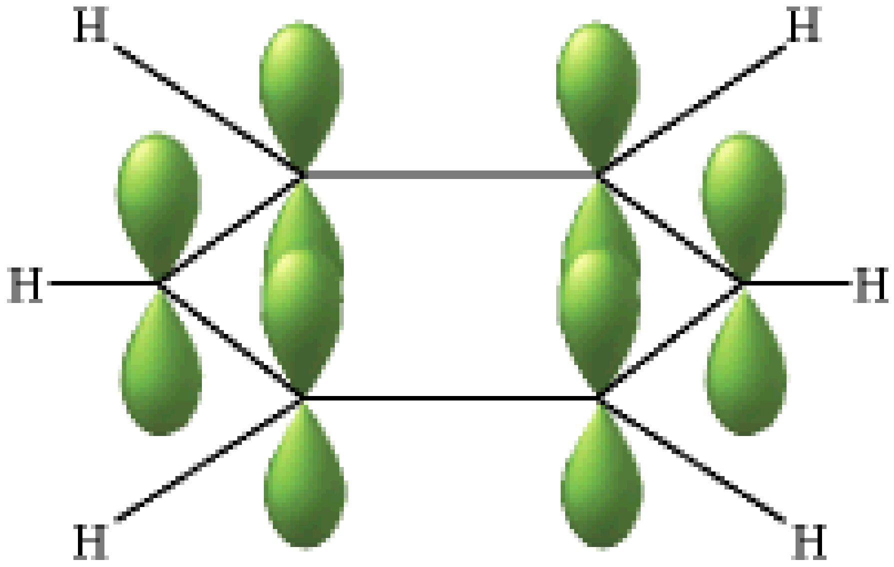
1.1.1 The Simple Powerfulness of Symmetry

- **The symmetry possessed by a molecule has a powerful influence on its properties.**
- **For example, *benzene* ~ high symmetry!**

➢ All of the carbon atoms are equivalent, thus having the same properties, such as chemical shift.

➢ Likewise, the electron density on each hydrogen is the same.

➢ If a calculation predicted that this was not so, we would immediately know that the calculation must be wrong.

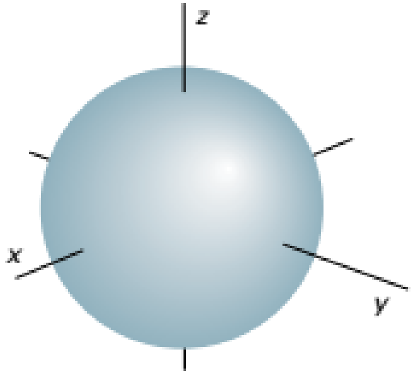


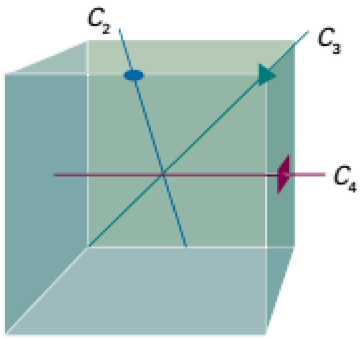
1.1.2 分子形状与对称性简介

- **对称与视觉美感**

对称物体 -- 由完全等同部件组成

对称之美 -- 日常生活中随处可见

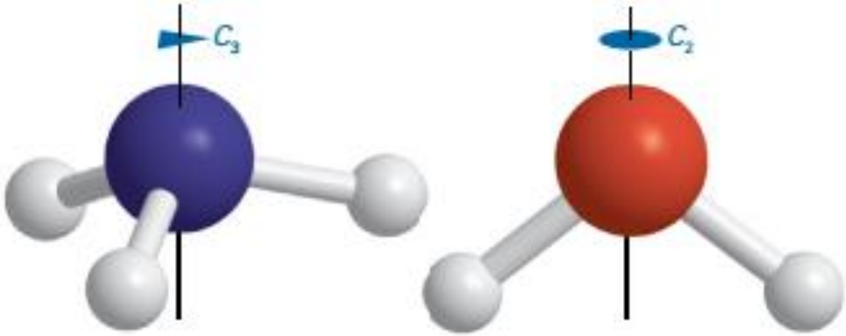




- **“更对称” -- ?**

球形 > 立方体

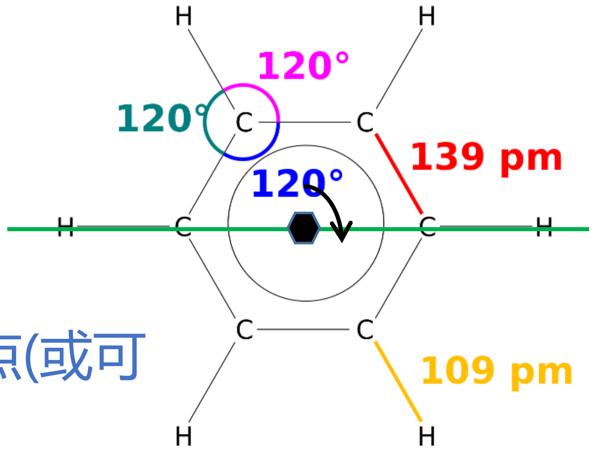
NH_3 > H_2O



- **分子对称性** – 因原子几何排列而具有一定的外形和对称性，可根据对称性特征对分子进行分类；

正四面体型：CH_4 vs SO_4^{2-} 三角锥型：NH_3 vs SO_3^{2-}

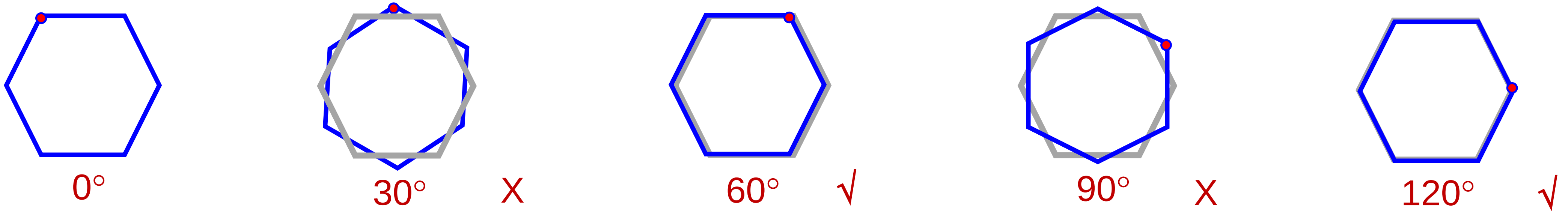
1.2 对称元素与对称操作



◆ 对称操作(symmetry operation)

对物体做一个动作(操作)后，物体的每一点都与原始物体的等价点(或可能是相同的点)相重合！简言之，就是完成动作后物体看似不动！

例1：以通过苯环心且垂直分子平面的直线为轴，顺时针旋转30°、60°、90°、120°，哪个为对称操作?



例2：苯分子，以1,4位碳原子连线为轴，旋转 90° 或 180°，哪个为对称操作?　后一动作

例3：苯分子, 以分子平面为镜面，做照镜子动作?　√

例4：苯分子，以环心为原点，所有原子坐标均做 $(x,y,z) \rightarrow (-x,-y,-z)$ 的反演变换　√

1.2 对称元素与对称操作

- **对称元素(symmetry element)**：

对称操作所据以进行的 点(对称中心或反演中心)、线(对称轴或旋转轴)、面(对称面或镜面)等几何元素。

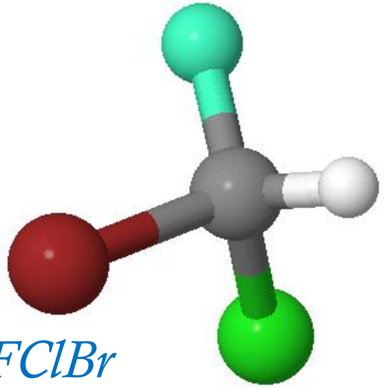
共有五类对称元素

对称元素产生对称操作!

对称元素	符号	对称操作(其符号为算符！)
对称心	i	***i***, 反演 (inversion) – 所有原子通过中心的反演
对称面	σ	σ, 反映(reflection) –从镜面的一侧反映到另一侧
对称轴	C_n	$\boldsymbol{C_n}$, 旋转(rotation) – 绕轴转动 (**360°/n**) 或其倍数角度
映转轴	S_n	$\boldsymbol{S_n}$, 旋转反映 (rotation-reflection) – 绕轴转动360°/n，再在垂直轴的平面中反映
恒等	E	***E***,恒等操作(identity) – 不动

1.2.1 恒等 （identity, E）

- 恒等元素E生成的对称操作为恒等操作$\boldsymbol{E}$ – 不动
- 所有物体均具恒等元素



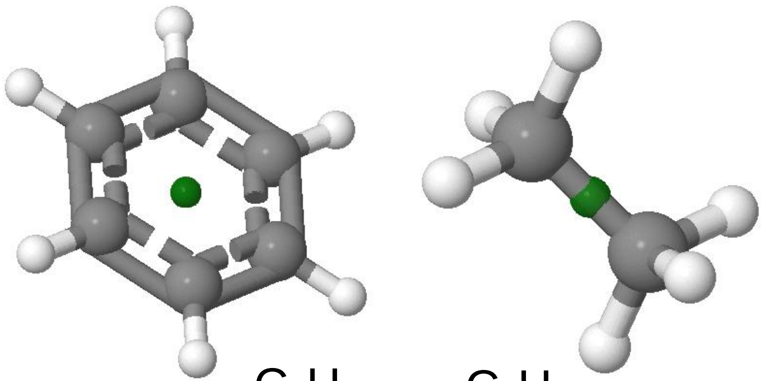
CHFClBr

(An asymmetric molecule)

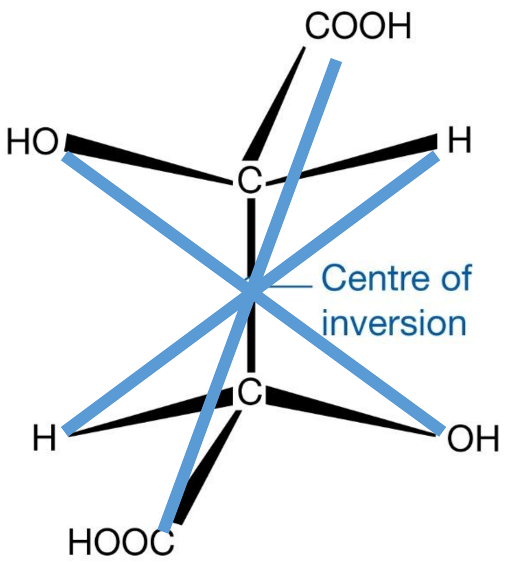
1.2.2 对称中心(center of symmetry)/反演中心(center of inversion)

- 将坐标原点位于分子中的某一点时，若把分子中每个原子的坐标(x,y,z)变为(-x,-y,-z)可使分子进入等价构型(看似不动!)，则原点所在点为对称中心或反演中心, 符号为*i*。

- 反演中心只生成一个操作—反演*i*: (x,y,z) → (-x,-y,-z)



C_6H_6 C_2H_6



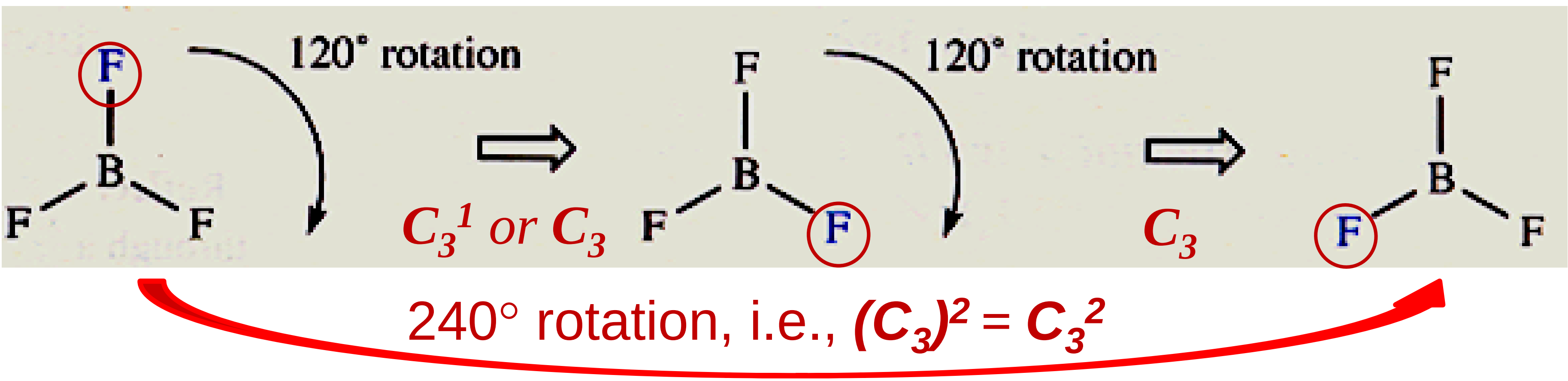
3 Meso-tartaric acid

1.2.3 对称轴(axis of symmetry, 或旋转轴) 与 转动(rotation)

- 将物体围绕一根直线旋转360°/n后，看似未动，物体具有C_n轴 (n次轴，n-fold axis of rotation)。

例：BF_3中的C_3

$(C_3)^3 = E$

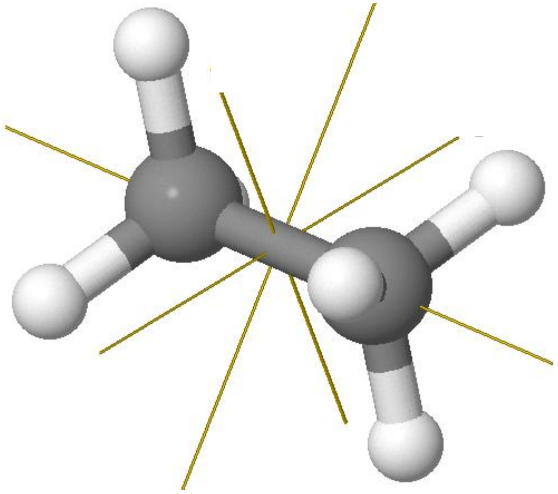


- C_n轴 生成n个相互独立的旋转操作C_n^m (转动m×360°/n , m= 1,2,…,n)， $C_n^n = E$。

Q：BF_3中是否还有其它对称轴?

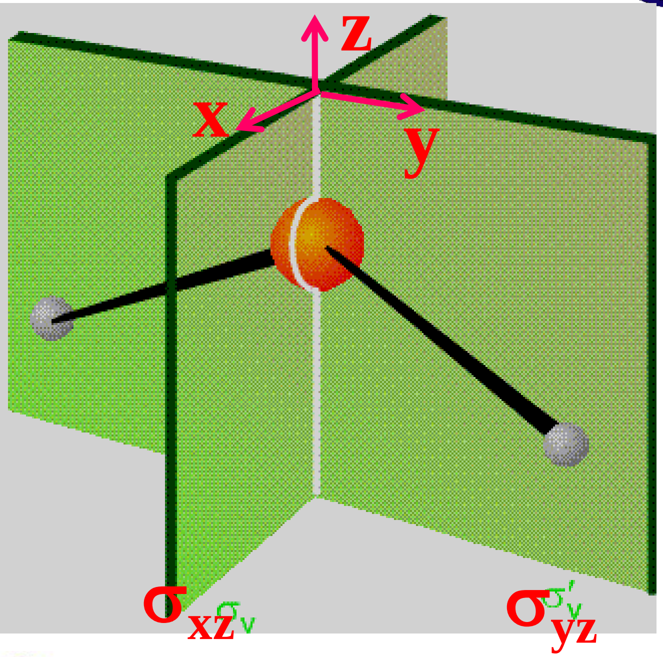
- 分子中有多根对称轴时，轴次n最大的为主轴 (principal axis)。

Q：乙烷(交叉式构象)中有哪些C_n轴？哪个为主轴?

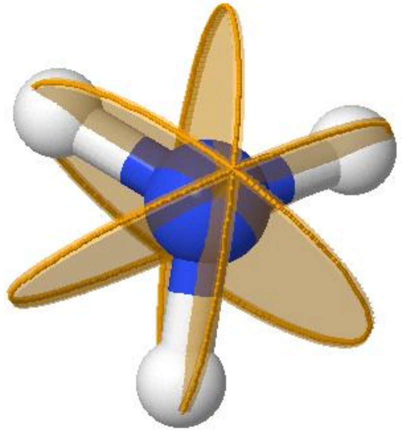


1.2.4 对称面(a plane of symmetry)/镜面(mirror plane), σ

- 将分子相对于一个平面做反映(reflection)操作, 分子看似不动，这个平面就是对称面（镜面）。例：H_2O



- 一个对称面 σ只生成一个反映操作。

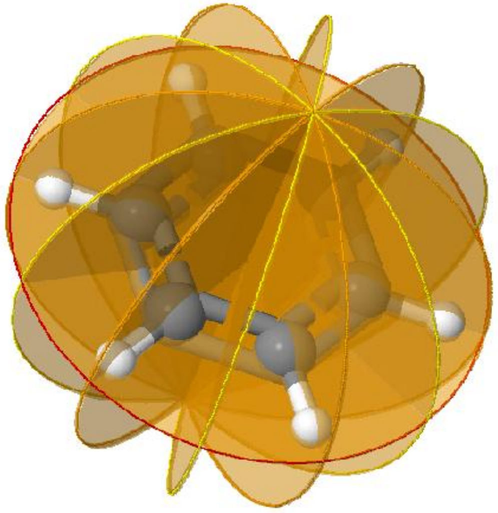


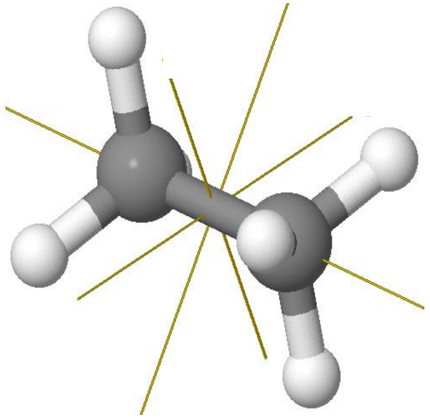
- 一个分子中可存在多个对称面，例: NH_3
- 一个分子中还可能存在多种对称面，例: 苯

i）垂直镜面σ_v：包含主轴的镜面.（v ~ vertical)

ii）水平镜面σ_h：垂直主轴的镜面. (h~ horizontal)

iii）二面镜面σ_d：特殊σ_v，将垂直主轴的两个C_2轴夹角平分！



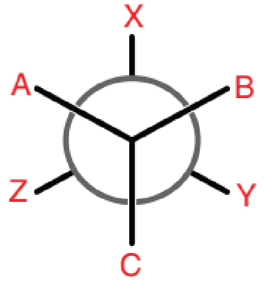


Q: 乙烷(交叉式构象)中有哪些镜面，属哪类镜面?

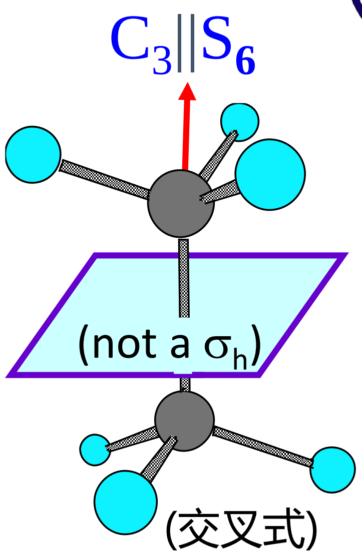
1.2.5 映转轴(rotation-reflection axis)/非真转动轴(improper rotation axis)

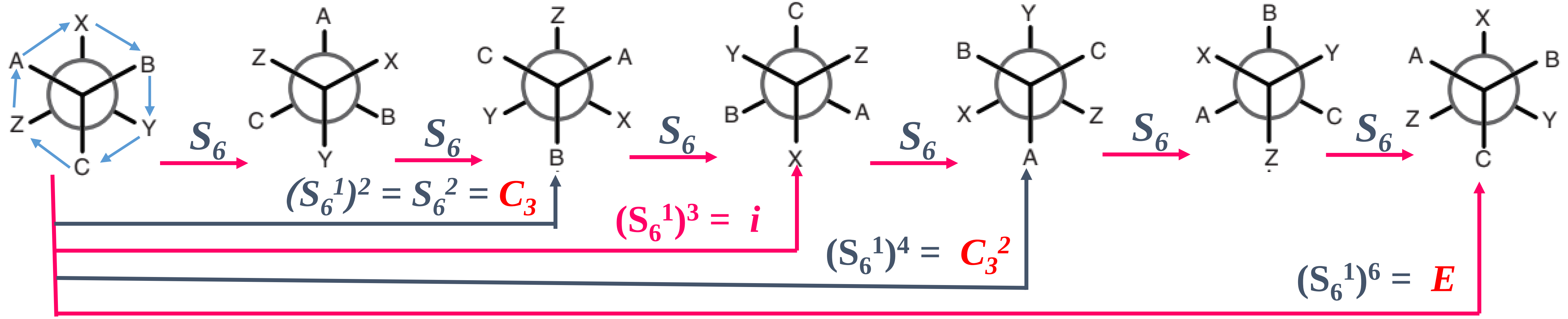
- S_n: 将分子绕一根直线旋转360°/n, 再做垂直该直线的镜面反映后，分子看似不动，则分子具有映转轴S_n。
- 分子中有S_n轴时，并不必要有C_n轴和σ_h。例：乙烷。
- S_n轴生成多个相互独立的映转操作S_n^m [$= (S_n)^m = (\sigma_h)^m C_n^m$]

(n为偶数时，m =1,2, …, n; n为奇数时，m =1,2,…,2n)



Newman (viewed down C-C bond)





Q1：映转轴S_6必然与哪些对称元素共存？ i, C_3

Q2：上述哪些操作是仅由S_6映转轴生成的独特映转操作？ S_6, S_6^5

1.2.5 映转轴(rotation-reflection axis)/非真轴(improper axis)

$S_n^m = (S_n)^m = (\sigma_h)^m C_n^m$

注：$(\sigma_h)^m = E$ (m=偶数) / $= \sigma_h$ (m=奇数)

- 几种特殊情况：

i) $n = 1, m=1$ → $S_1 = \sigma_h E = \sigma_h$　　对称操作S_1就是反映操作σ

ii) $n = 2, m= 1$ → $S_2 = \sigma_h C_2 = i$　　对称操作S_2就是反演操作i

◆ 所有对称操作，要么是转动(C_n)，要么是映转(S_n)操作！

◆ 两个对称元素（E除外）共存时，会有其它对称元素共存！

例如，拥有C_{2n}轴和反演中心i的分子必然拥有σ_h！

拥有与C_n主轴垂直的1根C_2轴，必然还有(n-1)根垂直主轴的C_2轴！……

思考题：

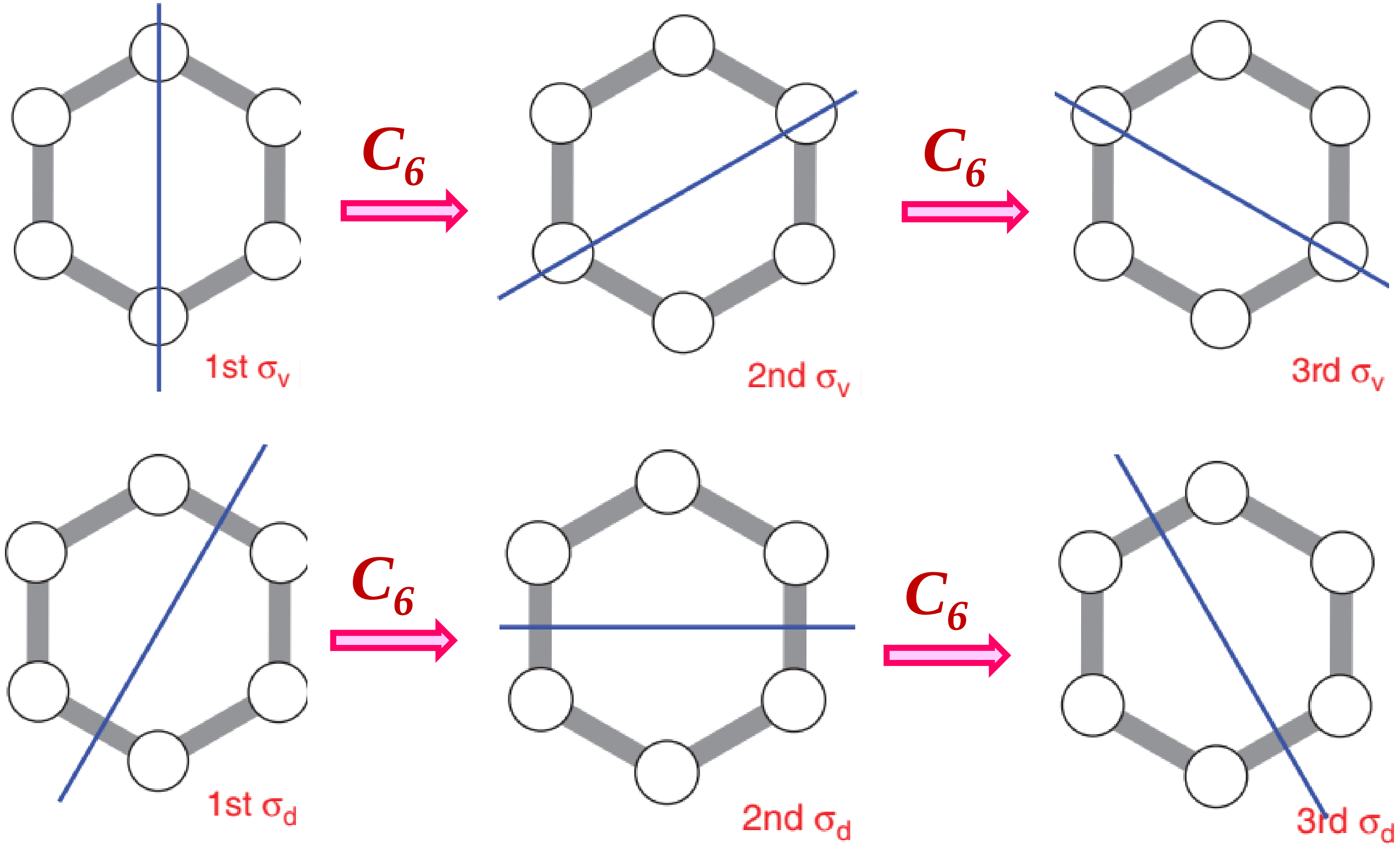
1）试判断S_{2n}轴是否同时也是C_n轴？试简要证明。

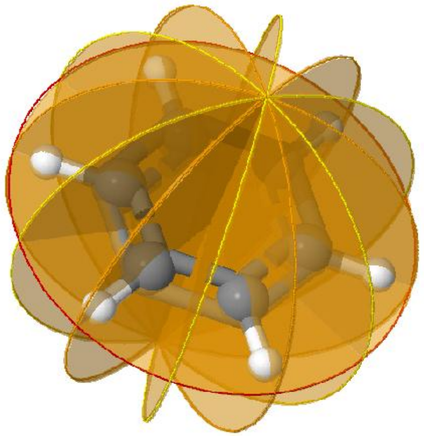
2）试判断具有S_{2n}轴(n为奇数)的分子是否具有反演中心？试简要证明。

1.2.6 Classes of operations（对称操作的分类）

In Group Theory two symmetry operations are said to be in the same ***class*** if they are related by another symmetry operation which the molecule possesses.

e.g., Benzene, σ_v planes





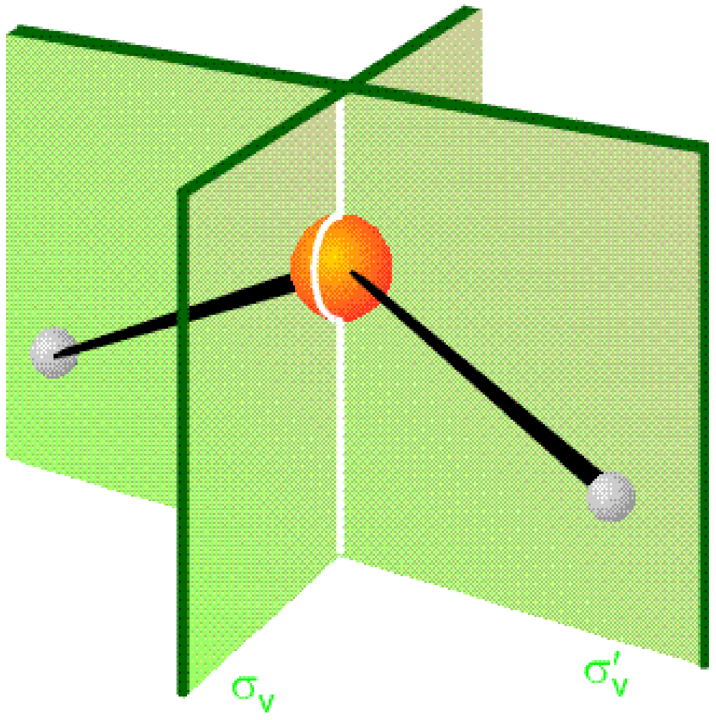
These three planes related by the C_6 rotation are in the same class.

These six mirror planes are not in the same class!

These three planes related by the C_6 rotation are in the same class.

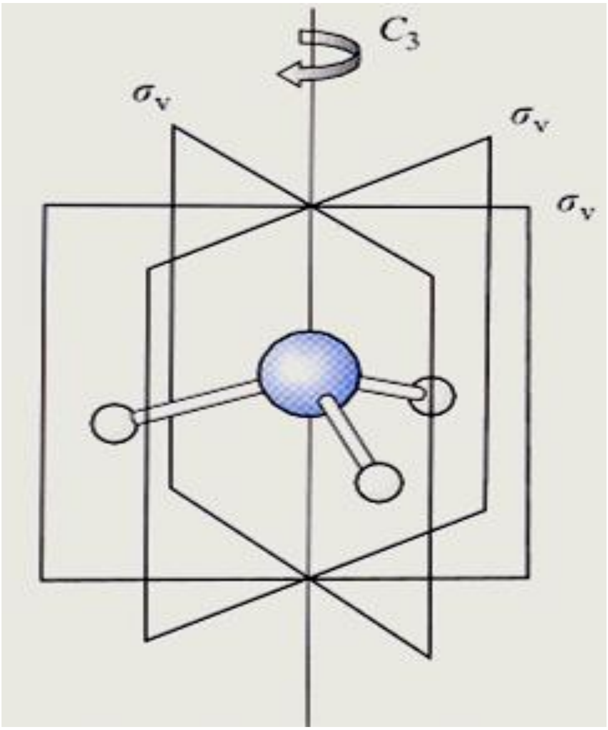
Q： Are the six C_2 operations (each generated by a C_2 axis) in the same class?

a) Are the two σ_v planes in the same class? Why?



H_2X (X= S,O)

b) Are the three σ_v planes in the same class? Why?



NH_3

Ex.3

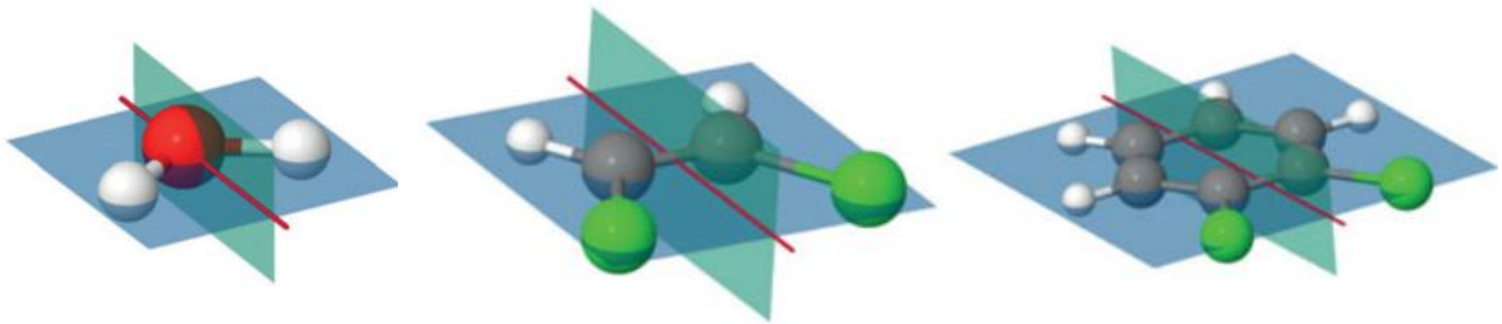
1.3 点群(point group) – 分子对称性的分类描述

◆ 准确描述某分子对称性 – 列出其所有对称元素（或所有可及对称操作）！ 繁琐！ 简便方法?

◆ 一些分子（或离子）拥有同一套特征对称元素。e.g., CH_4 & SO_4^{2-}， BF_3& SO_3& CO_3^{2-}

◆ 点群(point group): 一个分子所拥有的全部特征对称元素即定义了其所归属的点群。

- 点群名称与所包含的特征对称元素有关。 e.g., H_2O, $E, C_2, 2\sigma_v$ → C_{2v}

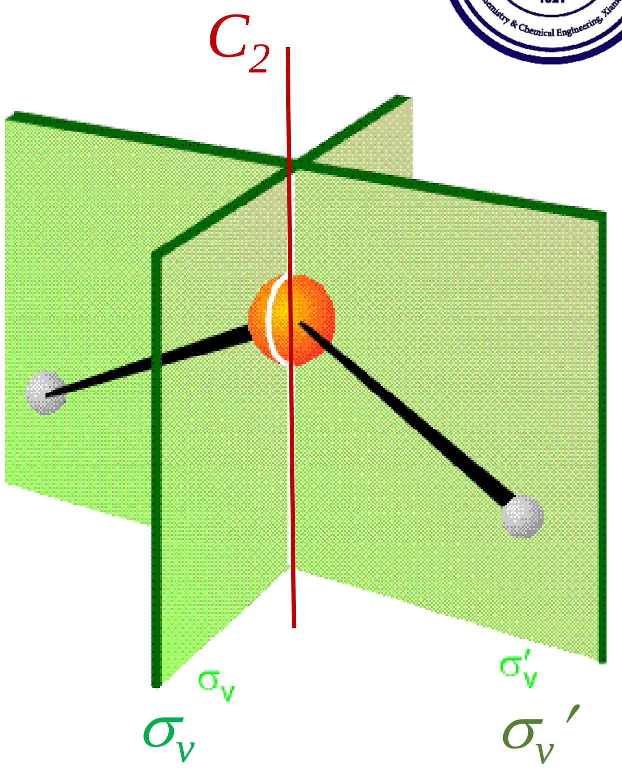


- 拥有相同特征对称元素的分子都属于同一点群。 e.g., 以上三个分子均属于C_{2v}
- 使用点群的名称符号快捷表示分子的对称性。

1.3 点群(point group) – 分子对称性的分类描述

◆ 何为点群 or 为何称为点群?

In Geometry, a ***point group*** is a mathematic group of symmetry operations that have a common fixed point.



1）分子(或物体)中所有对称元素所生成的全部独特对称操作之集合；

e.g.,H_2O中共有四个独特对称操作 $\{E, C_2, \sigma_v, \sigma_v'\}$，为$C_{2v}$ 点群。

2）该对称操作集合$\{\hat{R}_1, \hat{R}_2, \ldots \hat{R}_i, \ldots, \hat{R}_n\}$满足代数中群的定义。即必有恒等操作$E$，每个群元素有其逆元素(操作)且亦为群元素，任意两个群元(操作)相乘仍是该群的一个元素(操作)…

e.g., C_{2v}，C_2 操作即为其自身的逆，$C_2 \cdot C_2 = E$;

$C_2 \cdot \sigma_v(x,y,z) = \sigma_v'(x,y,z)$; $\sigma_v \cdot \sigma_v'(x,y,z) = C_2(x,y,z)$, …

3) 分子中所有对称元素至少有一个公共点, 这个公共点在所有可及对称操作下不动。

◆ 群元数(即对称操作总数)即为群阶h (order) 。e.g., C_{2v}点群的群阶为4。

1.3 点群(point group) – 分子对称性的分类描述

◆ 使用点群 -- 对分子对称性进行分类：

- 无轴点群: C_1 C_s C_i
- 单轴群(仅拥有单根C_n旋转轴的点群)：C_n C_{nh} C_{nv} S_{2n}
- 二面体群（拥有一个C_n轴及n根与之垂直的C_2轴的点群）：

  D_n D_{nd} D_{nh}

- 多面体群或立方体群 （拥有多根 C_n (n >2) 轴的点群）：

  T_d T T_h (四面体群);

  O_h O (八面体群);

  I_h I (二十面体群);

  (K_h –球对称)

◆ 子群： A群的所有元素是B群的部分元素，则A为B的子群。

◆ 判断点群要点：

找出特征对称轴、面、心等

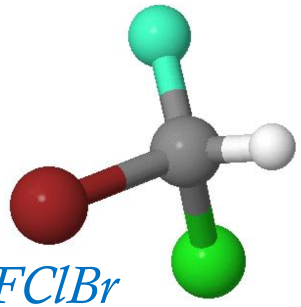
1.3.1无轴点群: C_1, C_s, C_i

- C_1: 只有恒等元素E, $h=1$

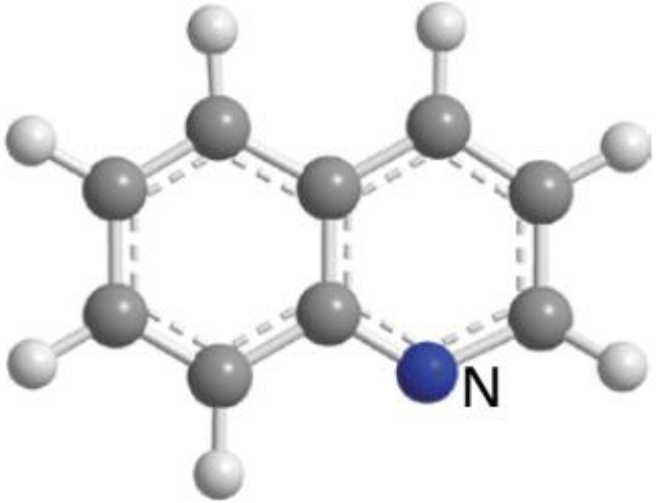
- C_i: 只有一个对称心i , $h=2$

  (plz always count E!)

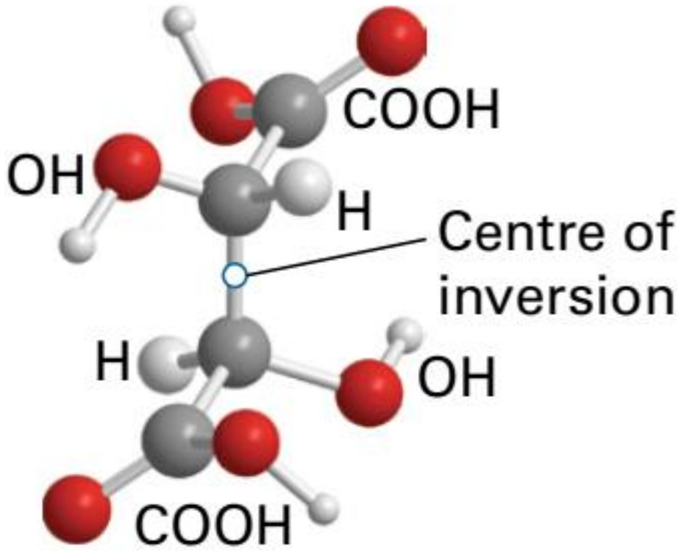
- C_s : 只有一个对称面σ , $h=2$



CHFClBr



Quinoline, C_9H_7N
喹啉



Meso-tartaric acid, HOOCCH(OH)CH(OH)COOH
内消旋酒石酸

厦大**长汀时期**化学系系主任刘椽先生

1946年刘椽与妹妹刘惠的全家福

前排左起：

刘芳苯、刘芳蒽、刘芳桂、俞小梅、俞晓松、刘芳萘；

后排左起：

刘椽、刘椽夫人高佩兰、刘光夏、刘惠、俞浩鸣(刘椽妹夫)

刘惠和俞浩鸣都是厦门大学老师，刘惠教英文，俞浩鸣教土木建筑；

刘芳萘供图

"南方之强"由来：1940–41两次全国大学生学业竞赛蝉联冠军！！！！！！

忆恩师刘椽先生，张永巽，大学化学，2021, 36(4): 2102049-0
http://www.dxhx.pku.edu.cn/article/2021/1000-8438/20210403.shtml
https://chem.xmu.edu.cn/info/1141/2644.htm (卢嘉锡先生回忆笔录)

1.3.2 单轴点群： C_n, C_{nv}, C_{nh} ($n \geq 2$，主轴轴次)

名称	特征对称元素	h
C_n	E, C_n	n
C_{nv}	E, C_n, $n\sigma_v$	$2n$
C_{nh}	E, C_n, σ_h	$2n$*

*未列出全部对称元素！

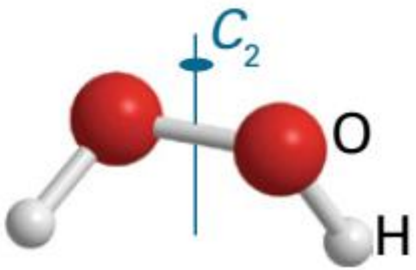
- 某些特征元素共存时会派生出其他对称元素：

  e.g., C_n & σ_h → S_n

  (对称操作： $C_n \cdot \sigma_h = S_n$)

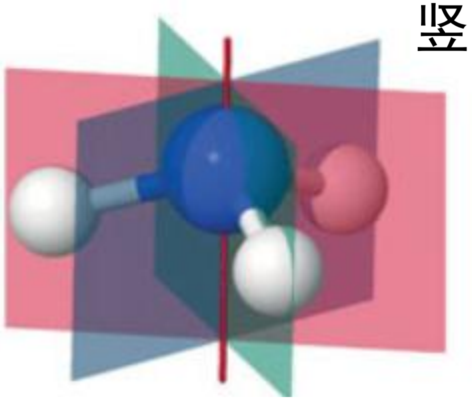
  e.g., C_2 & σ_h → i

  (对称操作： $C_2 \cdot \sigma_h = i$)

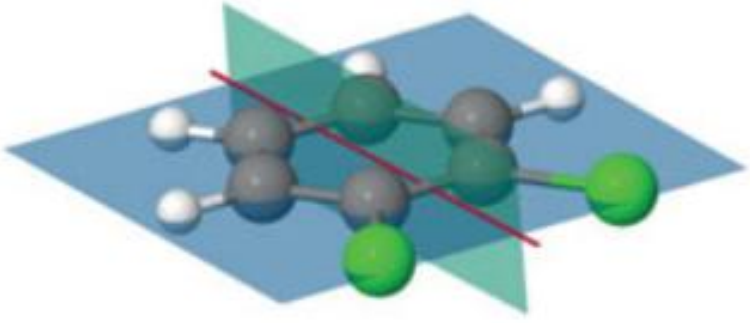


H_2O_2

竖直镜面σ_v

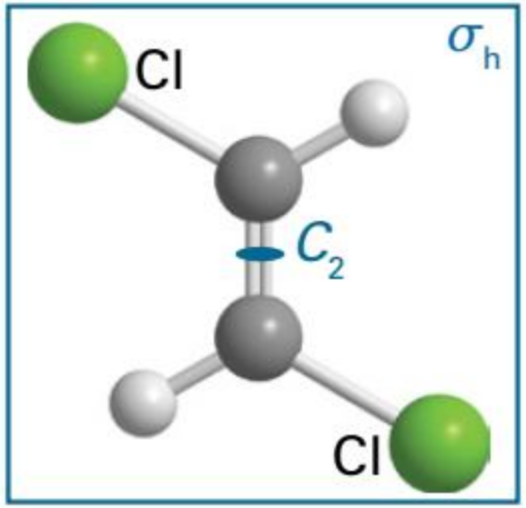


NH_3

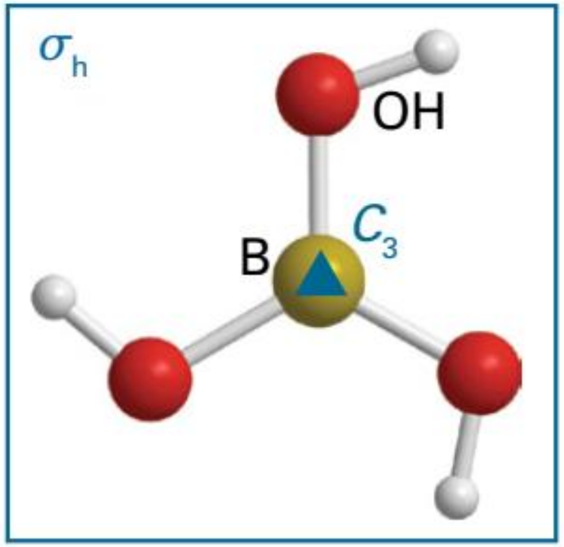


邻二氯苯

水平镜面σ_h



9 *trans*-CHCl=CHCl



10 $B(OH)_3$

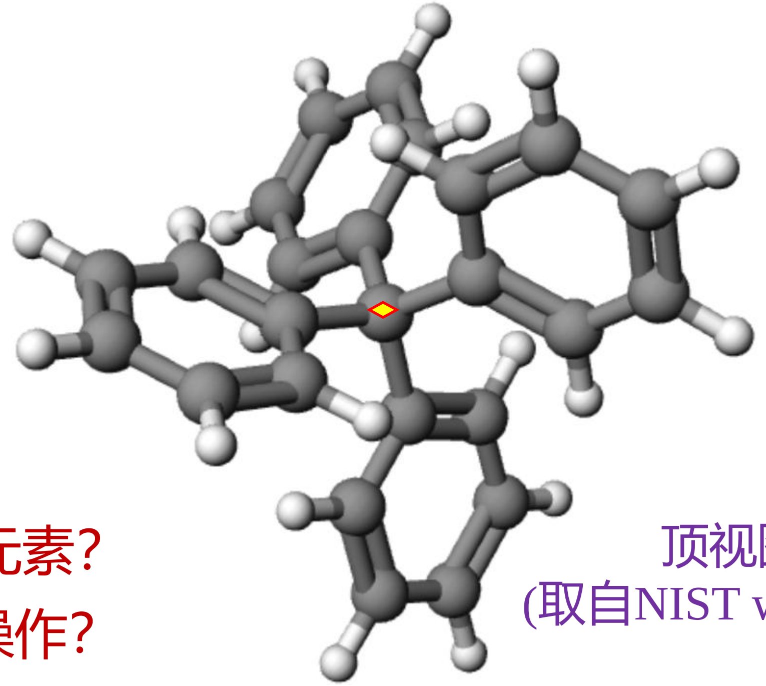
1.3.3 $\boldsymbol{S_n}$ ($\boldsymbol{n}$ =2m， m ≥2) 点群

名称	特征对称元素	h
S_n	E, S_n	n

- 罕见 $\boldsymbol{S_n}$ ($\boldsymbol{n}$ >4) 点群分子。

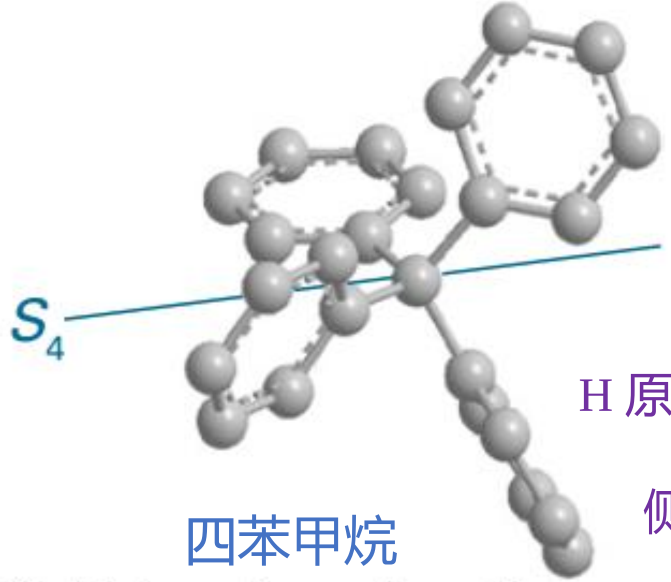
Q: $\boldsymbol{S_4}$点群有哪些对称元素？

共有哪些对称操作？



顶视图

(取自NIST webbook)

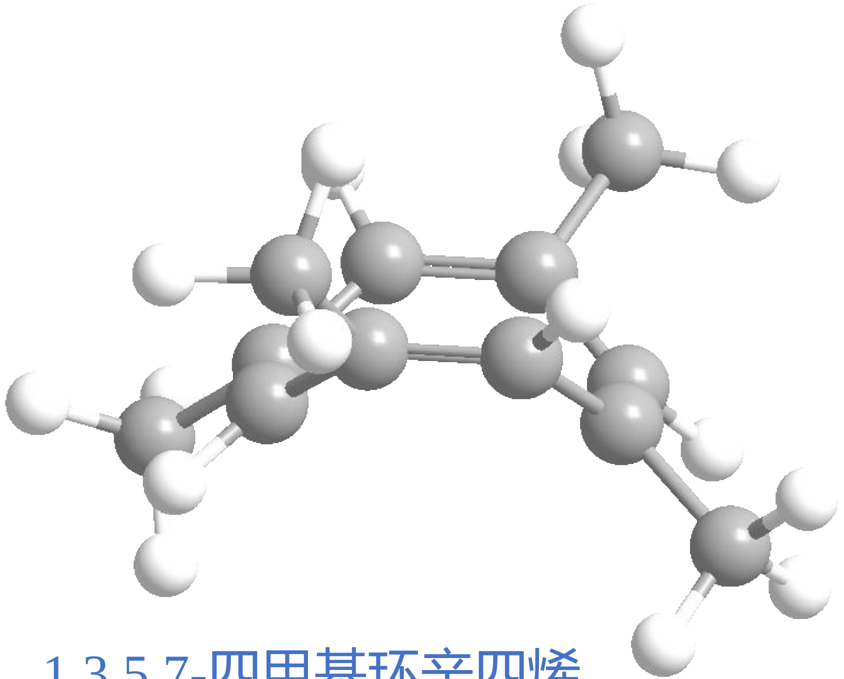


H 原子未显示

侧视图

四苯甲烷

14 Tetraphenylmethane, $C(C_6H_5)_4$ (S_4)



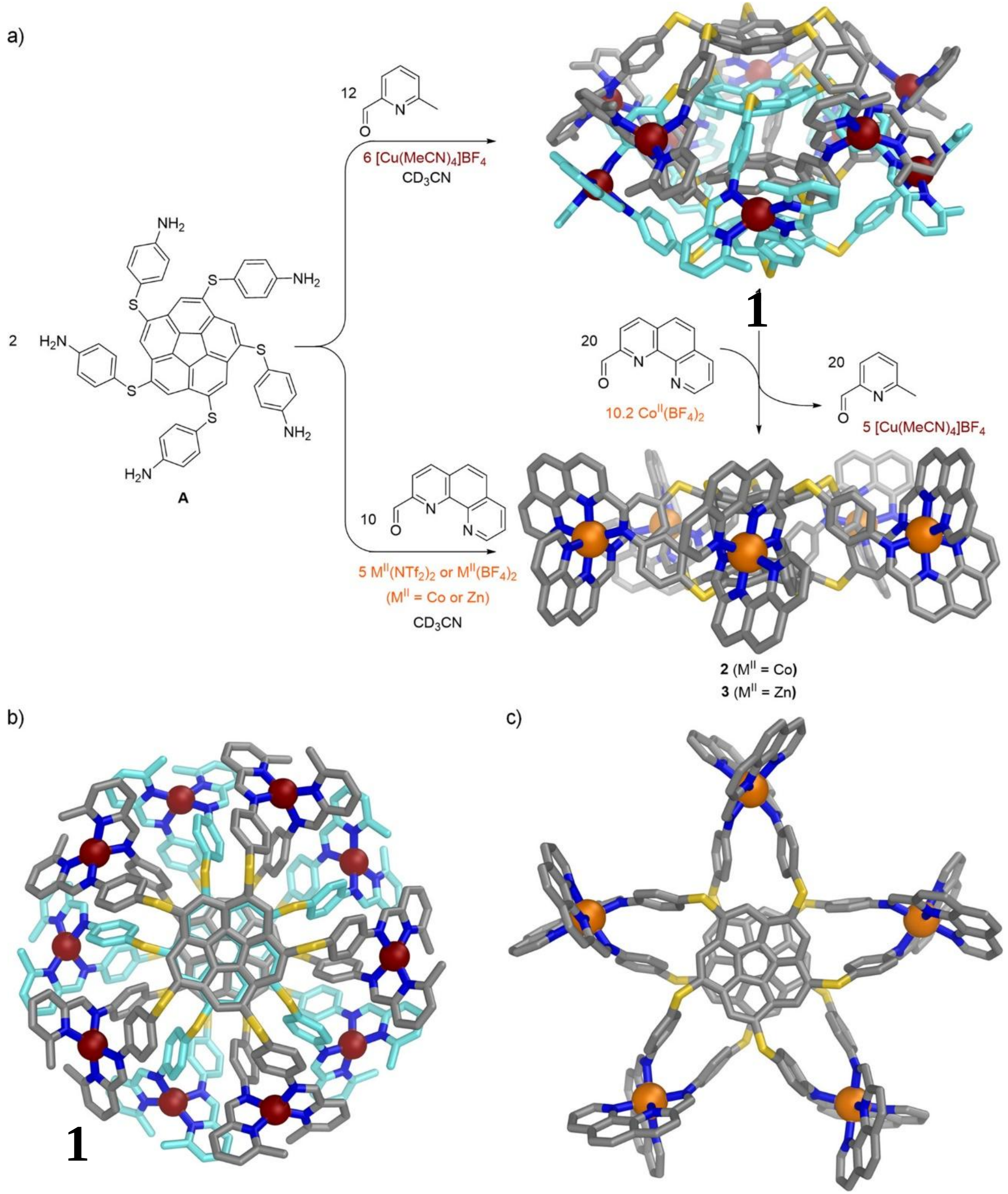
1,3,5,7-四甲基环辛四烯

Funny Structures

An S_{10}-Symmetric 5-Fold Interlocked [2]Catenane

By T.K. Ronson et al.,
J. Am. Chem. Soc., 2020, 142, 10267.

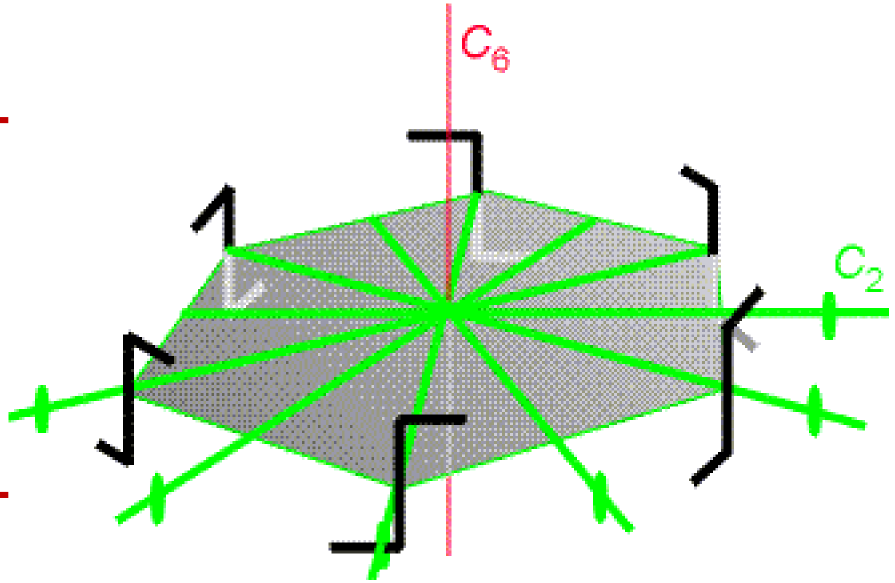
Compound **1** is S_{10}-symmetric.

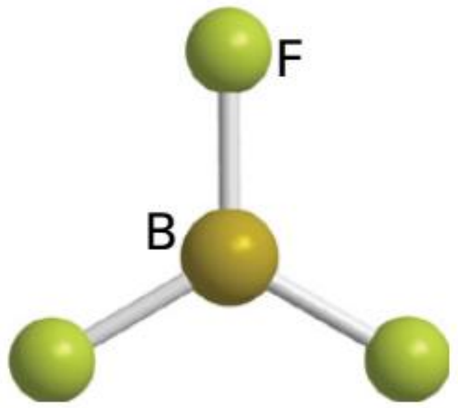


1.3.4 二面群： D_n, D_{nd}, D_{nh}

名称	特征对称元素	h
D_n	$E, C_n, nC_2'(\perp Cn)$	$2n$
D_{nh}	$E, C_n, nC_2'(\perp Cn), \sigma_h$	$4n$*
D_{nd}	$E, C_n, nC_2'(\perp Cn), n\sigma_d$	$4n$*

*未列出全部对称元素

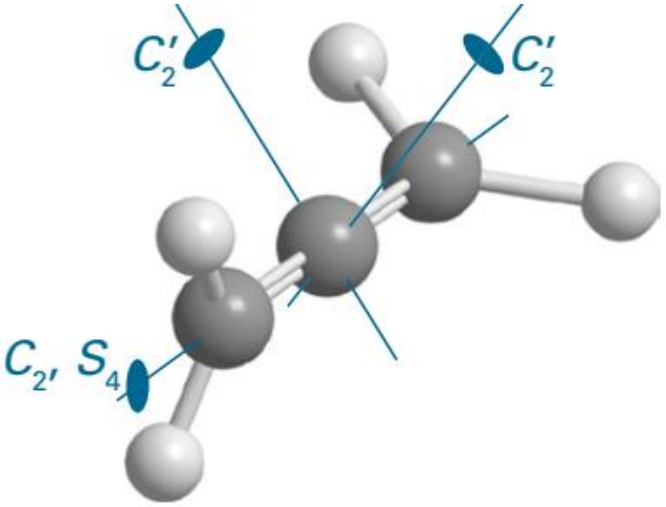




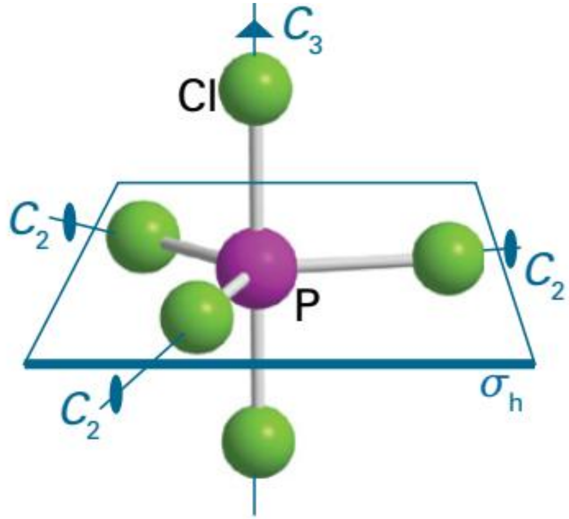
Boron trifluoride, BF_3

Q1: 试列出D_{3h}点群的全部对称元素以及全部群元(同类可合并)；

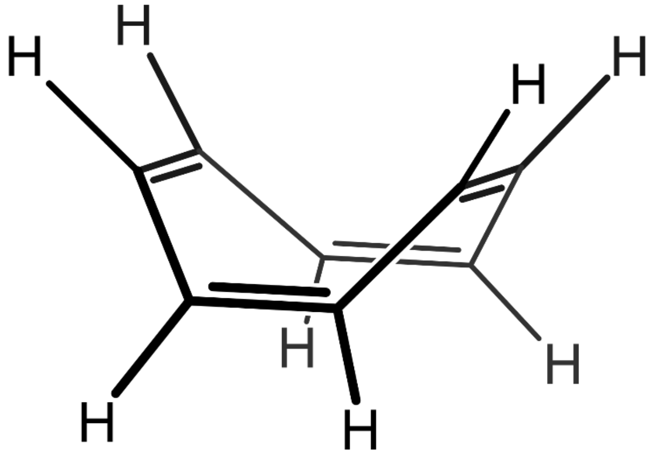
Q2: 试列出D_{3d}点群的全部对称元素以及全部群元(同类可合并)；



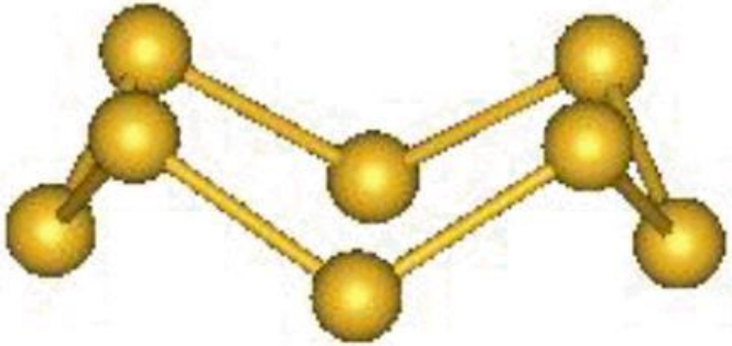
13 Propadiene, C_3H_4 (D_{2d})



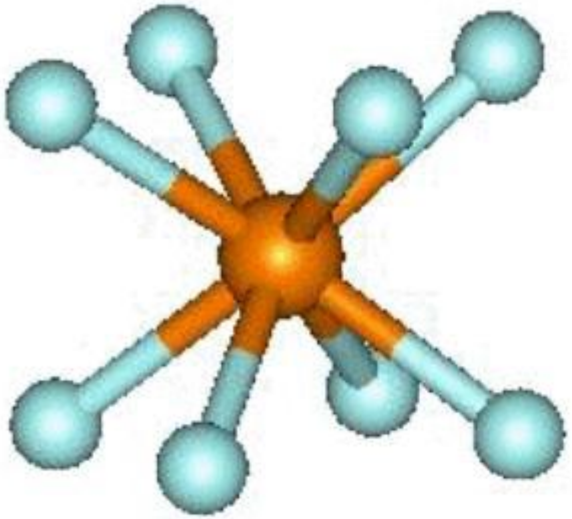
Phosphorus pentachloride, PCl_5 (D_{3h})



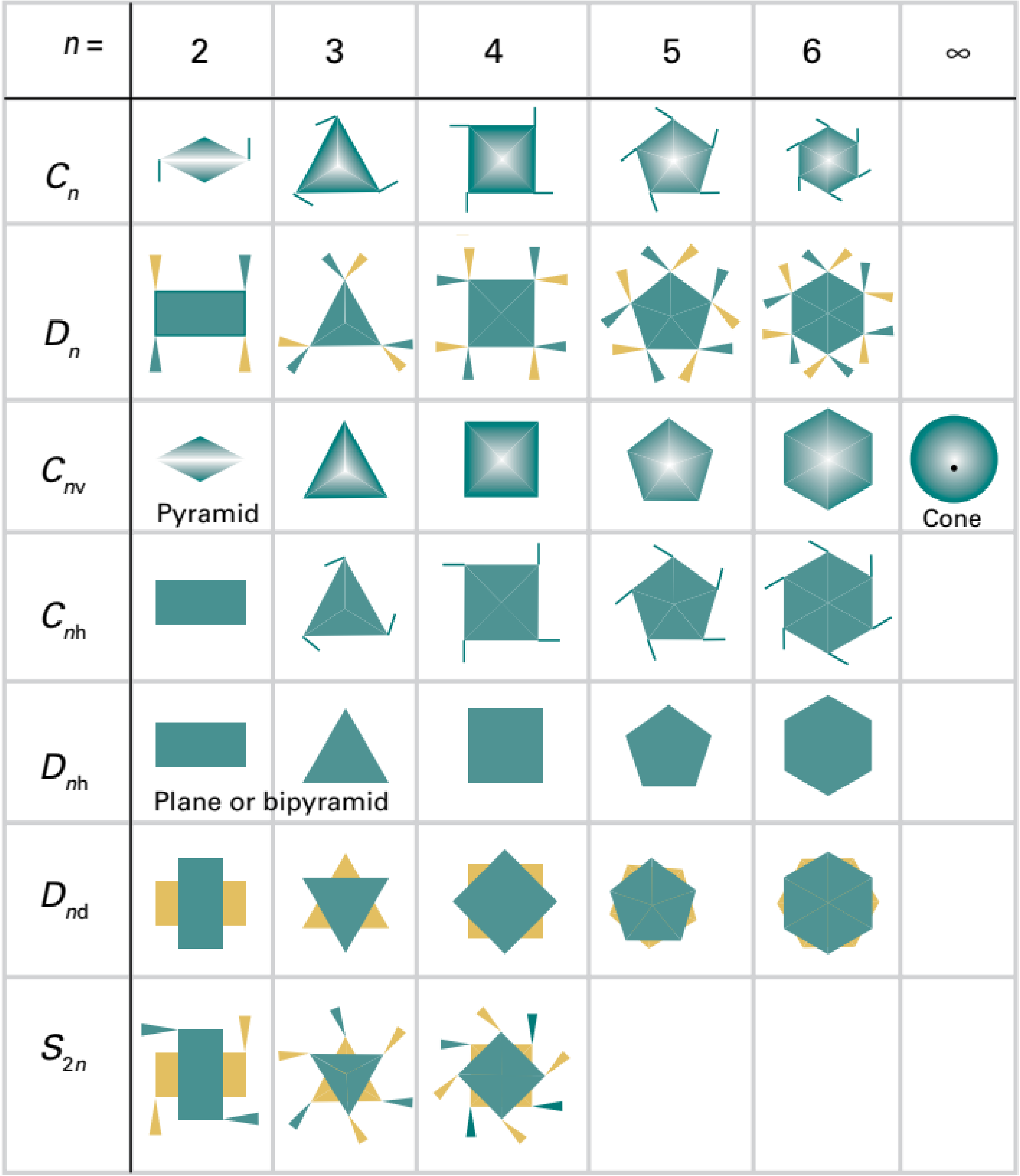
C_8H_8



S_8



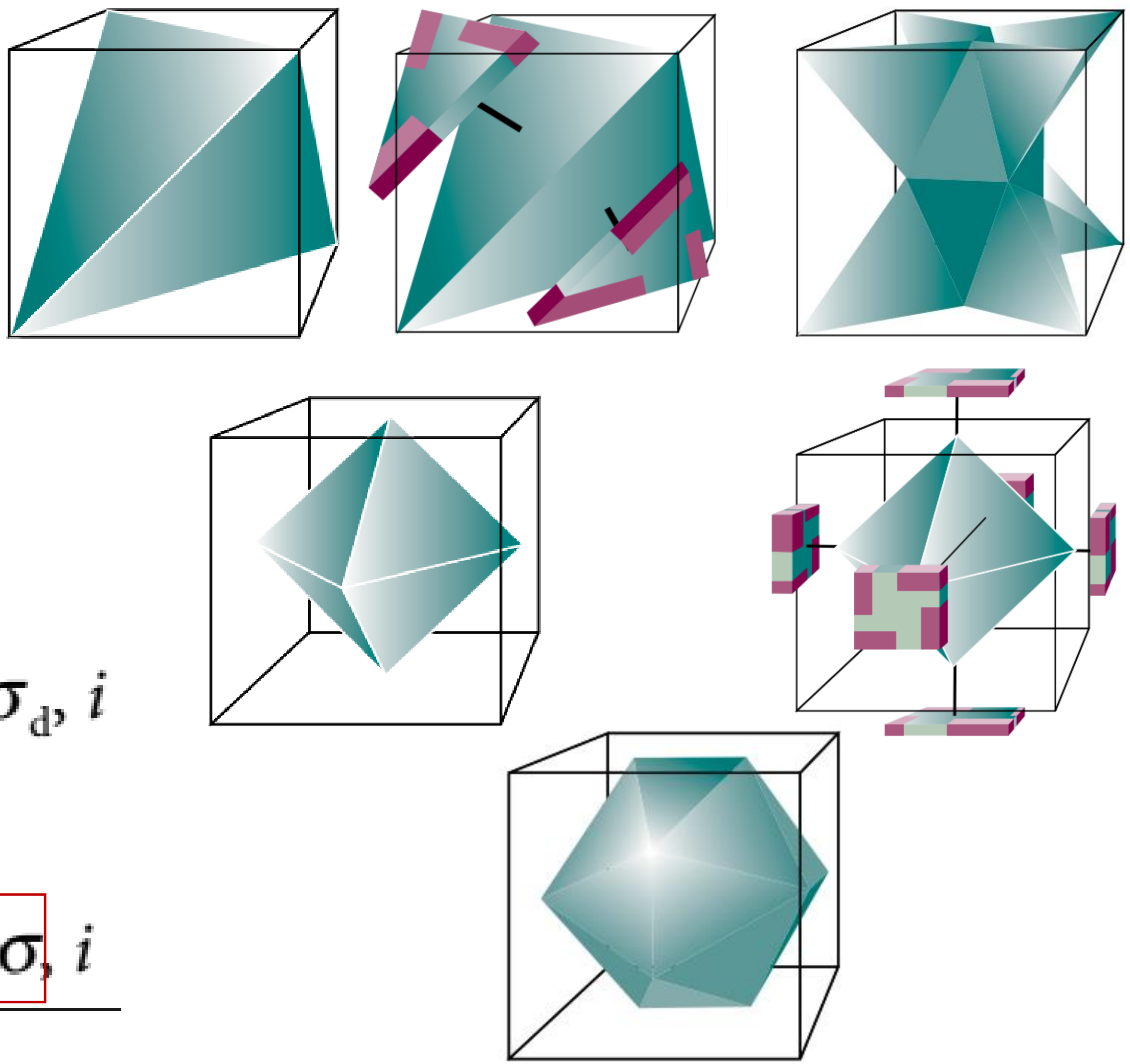
$[TaF_8]^{3-}$

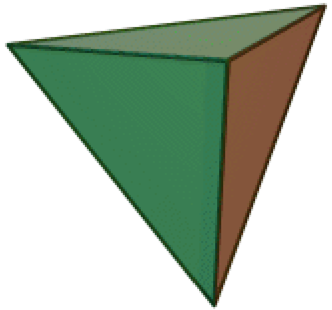

n =
2
3
4
5
6
∞
C_n
D_n
C_{nv}
Pyramid
Cone
C_{nh}
D_{nh}
Plane or bipyramid
D_{nd}
S_{2n}

1.3.4 立方体群

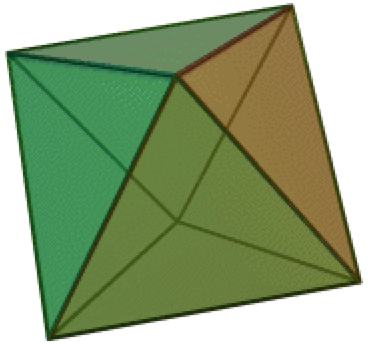
Name	Elements
T	$E, 4C_3, 3C_2$
T_d	$E, 3C_2, 4C_3, 3S_4, 6\sigma_d$
T_h	$E, 3C_2, 4C_3, i, 4S_6, 3\sigma_h$
O	$E, 3C_4, 4C_3, 6C_2$
O_h	$E, 3S_4, 3C_4, 6C_2, 4S_6, 4C_3, 3\sigma_h, 6\sigma_d, i$
I	$E, 6C_5, 10C_3, 15C_2$
I_h	$E, 6S_{10}, 10S_6, 6C_5, 10C_3, 15C_2, 15\sigma, i$

* 特征对称元素

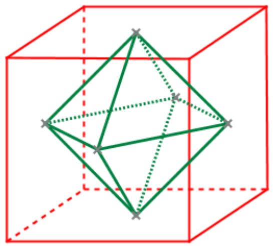




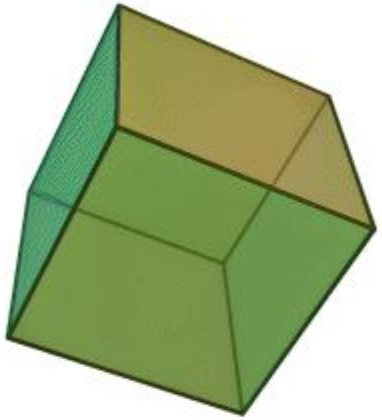
正四面体 (T_d)
Tetrahedron



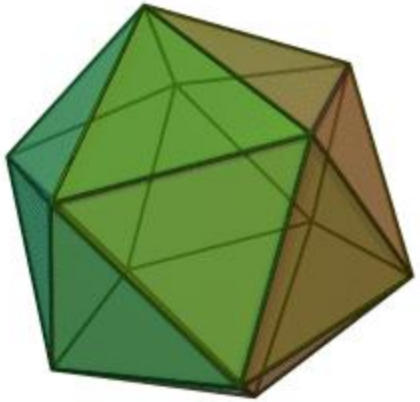
正八面体 (O_h)
Octahedron



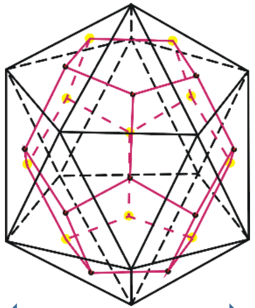
对偶多面体



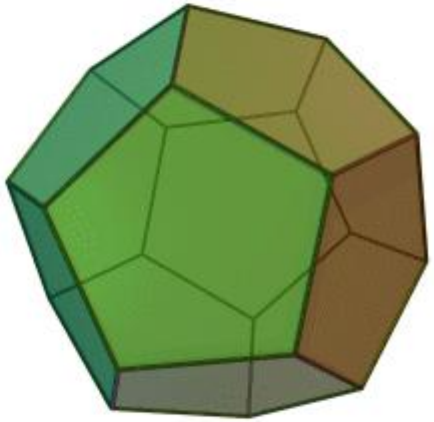
立方体 (O_h)
Cube



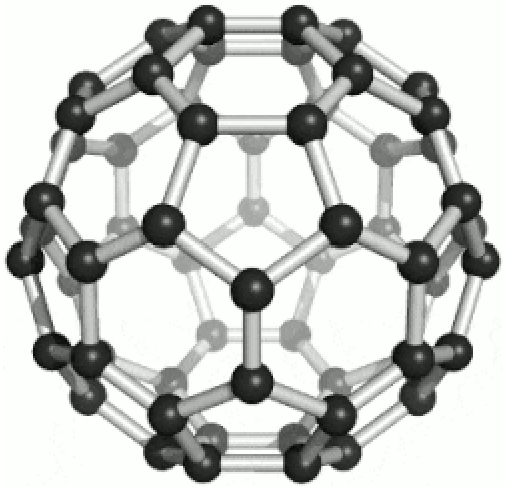
正二十面体 (I_h)
Icosahedron



对偶多面体



正十二体 (I_h)
Dodecahedron

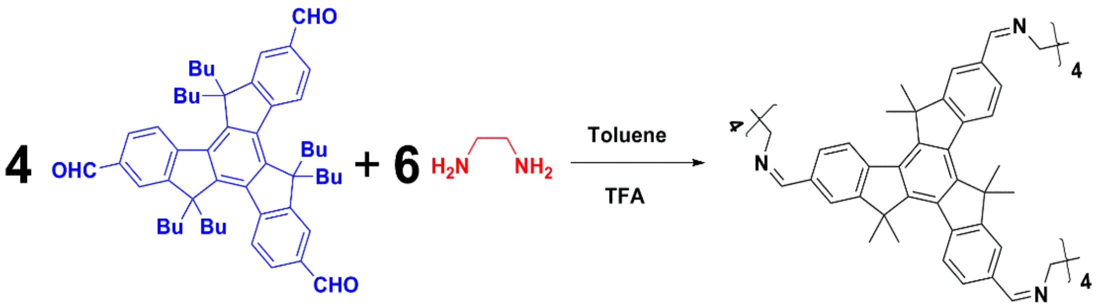


$\boldsymbol{I_h}$ - C_{60}

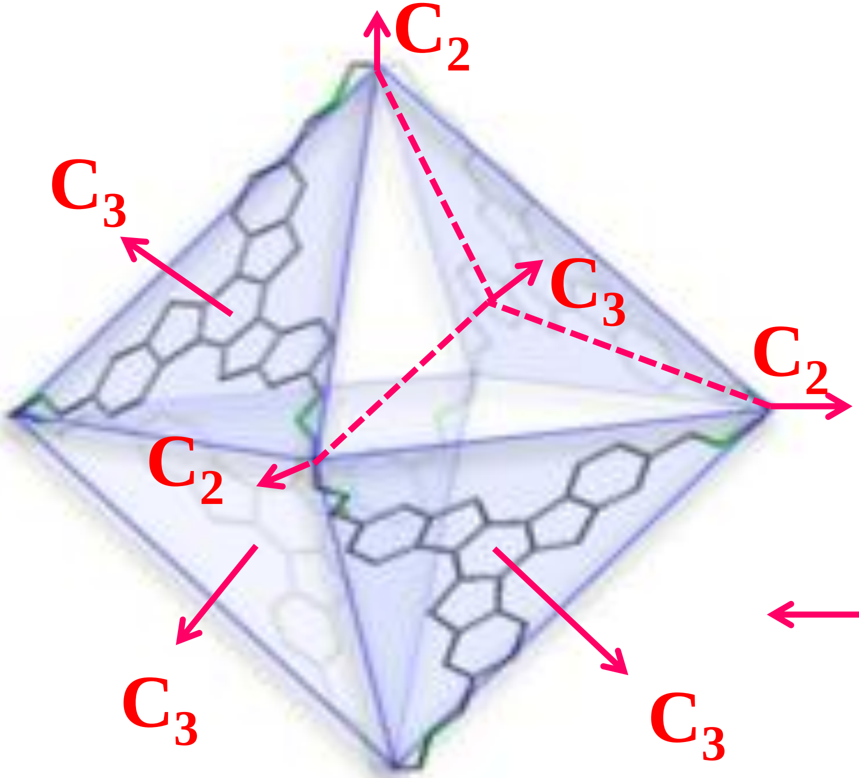
* 以上动图取自https://zh.wikipedia.org/

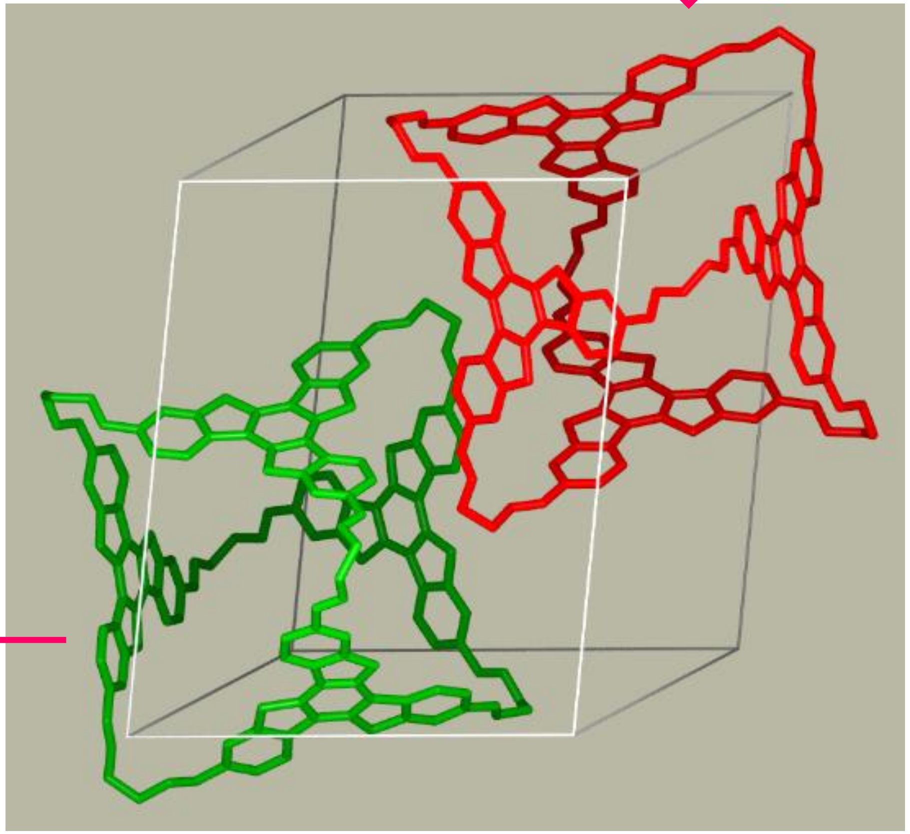
Example: **T**

Molecules of T-group symmetry are chiral!



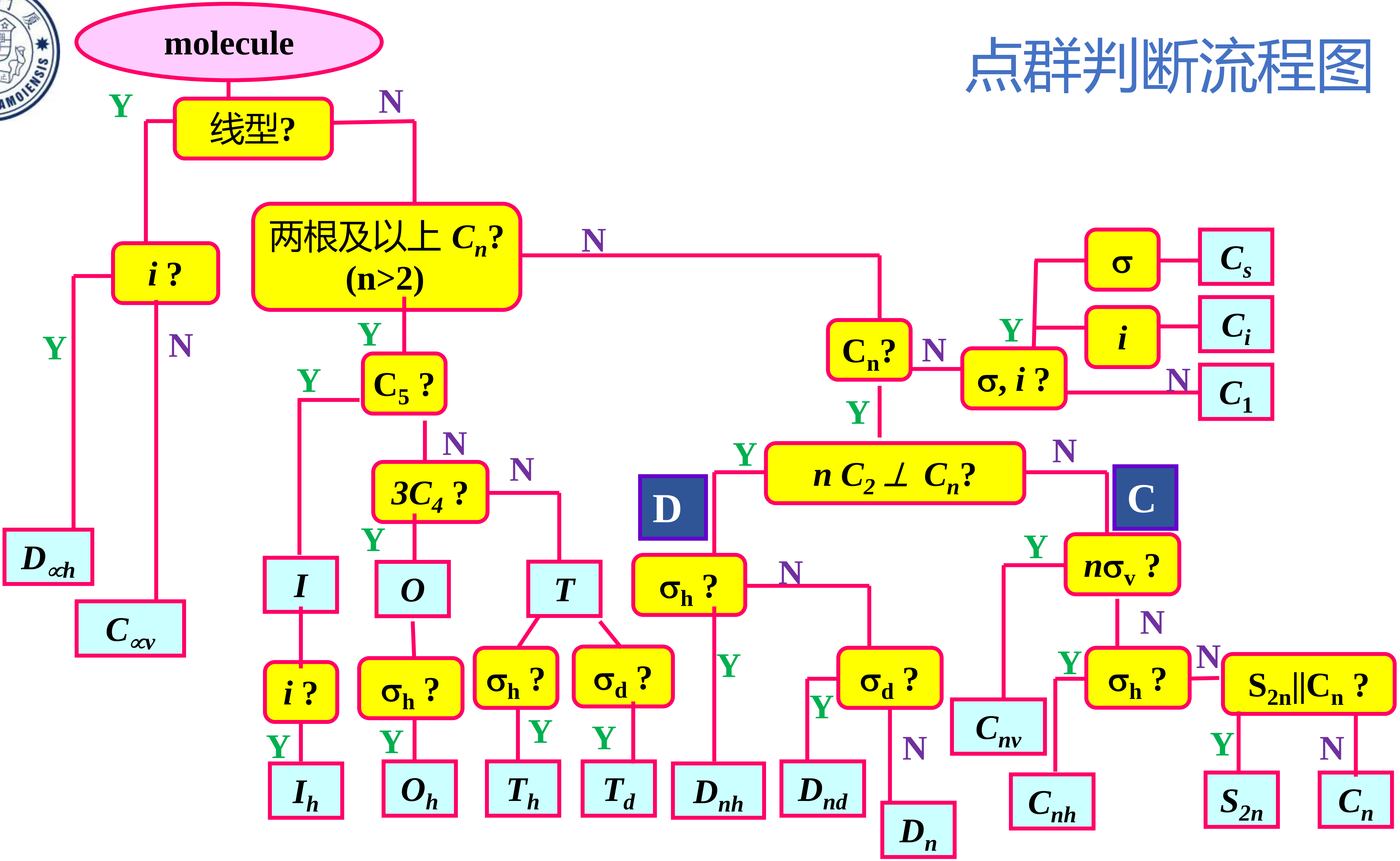
crystallization





Wang XC et al. Nature Comm., 2016, 7, 12469

点群判断流程图



molecule
线型?
Y
N
i ?
Y
N
$D_{\infty h}$
$C_{\infty v}$
两根及以上 C_n? (n>2)
Y
N
C_5 ?
Y
N
I
i ?
Y
I_h
$3C_4$?
Y
N
O
σ_h ?
Y
O_h
T
σ_h ?
Y
T_h
σ_d ?
Y
T_d
C_n?
Y
N
σ, i ?
Y
σ
C_s
i
C_i
N
C_1
$n C_2 \perp C_n$?
Y
N
D
C
σ_h ?
Y
N
D_{nh}
σ_d ?
Y
N
D_{nd}
D_n
$n\sigma_v$?
Y
N
C_{nv}
σ_h ?
Y
N
C_{nh}
$S_{2n}||C_n$?
Y
N
S_{2n}
C_n

1.4 Character tables (特征标表)

Much of the useful information we need to apply Group Theory is summarised in the ***character table*** for a group, e.g., the character table for the C_{2v} group.

- ***Symmetry operations*** listed class-by-class, also known as ***elements of a point group***.

- The rows labelled A_1, A_2 etc. are the ***irreducible representations(IRs)***, each row containing the symmetry species, characters, and simple basis functions of the corresponding ***IR***.

The character table for C_{2v}

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz

Symmetry species (对称种类—不可约表示的Mulliken符号)

Characters (特征标)

typical basis (典型的基)

1.4 Character tables

D_{3h} (e.g., BF_3): The symmetry elements possessed by BF_3 include

a C_3 axis, three C_2 axes, a σ_h plane, an S_3 axis, and three σ_v planes.

- Two C_3 operations, C_3 and C_3^2, belonging to the same class are indicated as $2C_3$, so do the $3C_2$, $3\sigma_v$ and $2S_3$ (S_3^1 and S_3^5) operations.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$			
A_1'	1	1	1	1	1	1			$x^2+y^2; z^2$
A_2'	1	1	−1	1	1	−1		R_z	
E'	2	−1	0	2	−1	0	(x, y)		$(x^2-y^2, 2xy)$
A_1''	1	1	1	−1	−1	−1			
A_2''	1	1	−1	−1	−1	1	z		
E''	2	−1	0	−2	1	0		(R_x, R_y)	(xz, yz)

1.4 Character tables

D_{6h} : Benzene has a six-fold axis of symmetry and this generates several symmetry operations. It turns out that C_6^+ and C_6^- are in the same class, and so are listed as '$2C_6$'.Similarly $(C_6^+)^2$ and $(C_6^-)^2$ are in the same class, and are listed as '$2C_6^2$'. $(C_6)^3$ is in a class of its own.

(C_6^1, C_6^5) → $2C_6$

(C_6^2, C_6^4) → $2C_6^2$

(S_3^1, S_3^5) → $2S_3$

(S_6^1, S_6^5) → $2S_6$

D_{6h}	E	$2C_6$	$2C_6^2$	C_6^3	$3C_2$	$3C_2'$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1
...	...	...	...	...	...	...	...	...	...	...	...	...

To save space, only one of the irreducible representations is given

Q: please figure out the symmetry operation(s) that relates the operations of the same class.

1.5 Summary

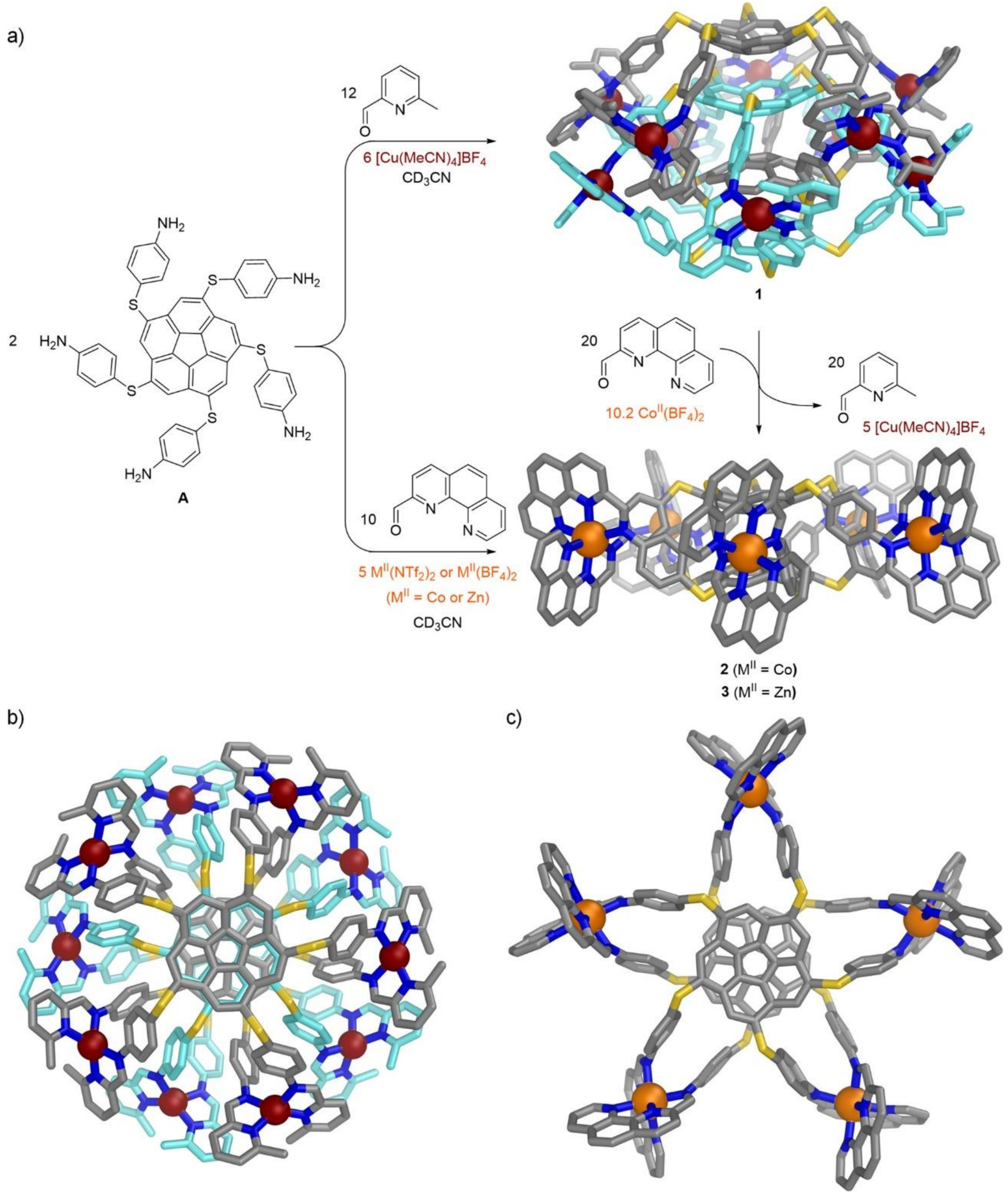
- A molecule may possess ***several*** ***symmetry elements.***
- The possible symmetry elements are: ***the identity***; ***n-fold axis of symmetry***; ***mirror plane***; ***centre of symmetry***; ***n-fold axis of improper rotation.***
- Each *symmetry element* generates one or more symmetry operations.
- The action of any ***symmetry operation*** is to leave the molecule in an indistinguishable orientation from that in which it starts.
- The *symmetry elements* which a molecule possesses defines the point group to which it belongs.
- *Symmetry operations* are in the same class if they are related by another symmetry operation of the group.
- **Each point group** has a ***character table*** which, amongst other things, gives the symmetry operations of the group, arranged into classes.

Funny Structures

An S_{10}-Symmetric
5-Fold Interlocked [2]Catenane

By T.K. Ronson et al.,
J. Am. Chem. Soc., 2020, 142, 10267.

Compound 2 belongs to _____-symmetry.



Definition of group (群的定义)

A ***group*** in mathematics is a collection of transformations, $\mathbf{G = \{R_1, R_2, \ldots, R_i, \ldots\}}$, that satisfy four criteria,

a) **Closure.** The product of any two elements R_i and R_j is another element in the group, i.e. $R_i \cdot R_j = R_k$, $R_m^2 = R_n$, …

b) **Identity.** One of the transformations is the identity E.

c) **Inversion.** For every transformation R in G, the inverse transformation R^{-1} is in the collection so that $R \cdot R^{-1} = R^{-1} \cdot R = E$.

d) **Associative rule.** $(R_i \cdot R_j) \cdot R_m = R_i \cdot (R_j \cdot R_m)$.

The order of a group (群阶):

The number of elements in a group!

Atkins' *Phyical Chemistry*, 11th ed., pp.390-397

Point Groups

- The collection of all allowed symmetry operations of a molecule (or an object) forms a mathematical group.

- These symmetry operations have at least one common **point** unchanged (e.g., the O atom in H_2O).

- *Such a group of symmetry operations is thus called **point group**.*

- Accordingly, it is quite convenient to represent the symmetry of a molecule by the very ***point group***!

- ***Subgroup***: if group **A** contains all elements of group **B**, group **B** is said to be a ***subgroup*** of group **A**.

The symmetry of an object (molecule) can be conveniently represented by a point group that contains all allowed unique symmetry operations arising from its available symmetry elements.

Objects/

Molecules

If they have a common

set of symmetry elements

They must have a common set of symmetry operations!

They belong to the same type of ***point group*.**

Symmetry classification of molecules in terms of point group!