Inorganic Chemistry

Week 04

Symmetry and group theory

Department of Applied Chemistry
Prof. Chan Woo Lee

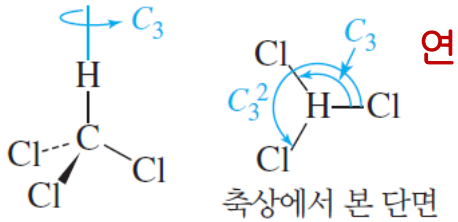
4.1 대칭 요소와 대칭 조작

- **대칭 요소(symmetry element):** 거울면(mirror plane), 회전축(rotation axes), 반전 중심(inversion center)
- **대칭 조작(symmetry operation):** 거울면, 회전축, 반전 중심을 이용하여 이동시키는 것
- 대칭조작을 하기 전과 후에 분자 모양이 같을 경우, 분자는 그 대칭조작에 대해 대칭성을 가진다고 볼 수 있다.

G. L. Miessler, 무기화학 제 5판, 자유아카데미, 2015, p. 88

4.1 대칭 요소와 대칭 조작

- 회전 조작(rotation operation, C_n): 대칭축을 중심으로 360°/n 돌리는 것
- 주회전축(principal axis): n값이 가장 큰 C_n 축
- 동등 조작(indentity operation): $C_n{}^n \equiv E$

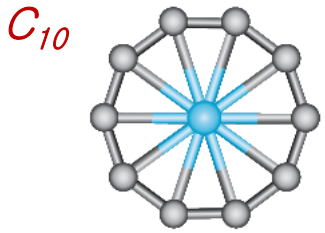


축상에서 본 단면

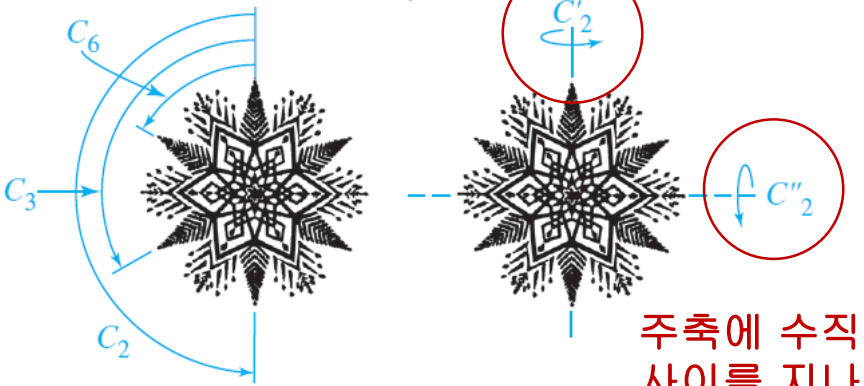
$CHCl_3$의 C_3회전

연속 조작: $C_3{}^2$

주축에 수직이며 원자를 지나는 축: C_2'



기체 상태 TaB_{10}^- 에너지 상태가 가장 낮은 이성질체 구조



눈서리의 C_2, C_3와 C_6 회전축

주축에 수직이며 원자 사이를 지나는 축: C_2''

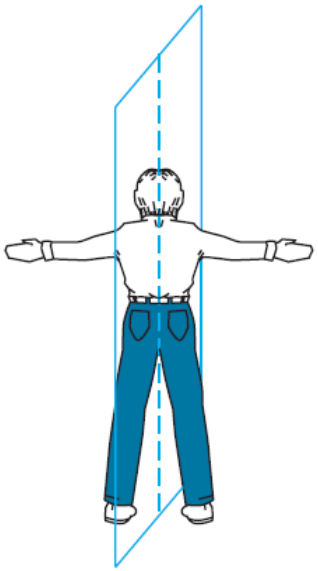
회전각	대칭 조작	회전각	대칭 조작
60°	C_6	240°	$C_3{}^2 (\equiv C_6{}^4)$
120°	$C_3 (\equiv C_6{}^2)$	300°	$C_6{}^5$
180°	$C_2 (\equiv C_6{}^3)$	360°	$C_6{}^6 (\equiv E)$

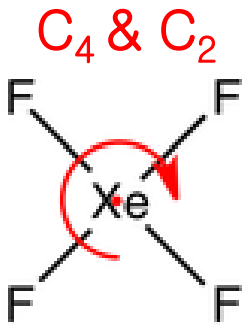
G. L. Miessler, 무기화학 제 5판, 자유아카데미, 2015, p. 89

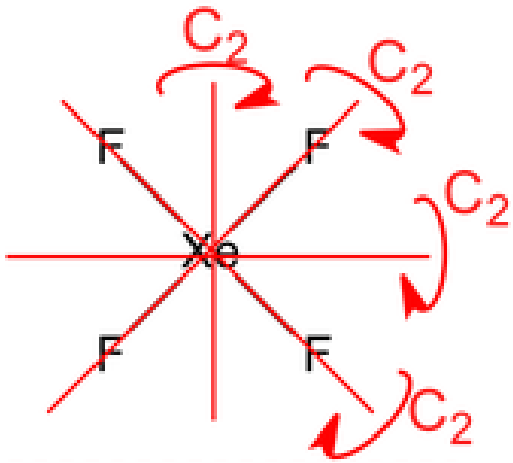
4.1 대칭 요소와 대칭 조작

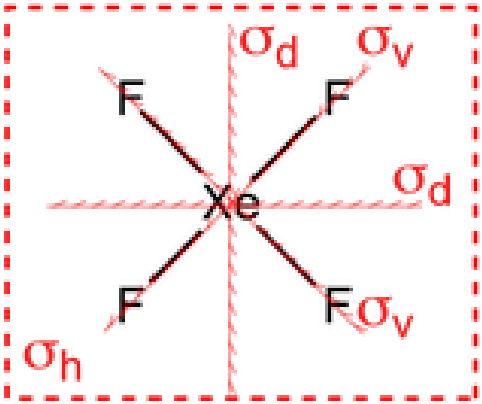
- **반사조작(reflection operation, σ)**: 거울면에 대해 수직으로 같은 거리에 이동. 반사조작은 좌-우를 바꾼다

- σ_h(horizontal mirror): 거울면이 주축에 대하여 수직인 경우
- σ_v(vertical mirror): 거울면이 주축과 평행한 경우
- σ_d(dihedral mirror): 2개의 회전축 사이를 양분하는 vertical mirror





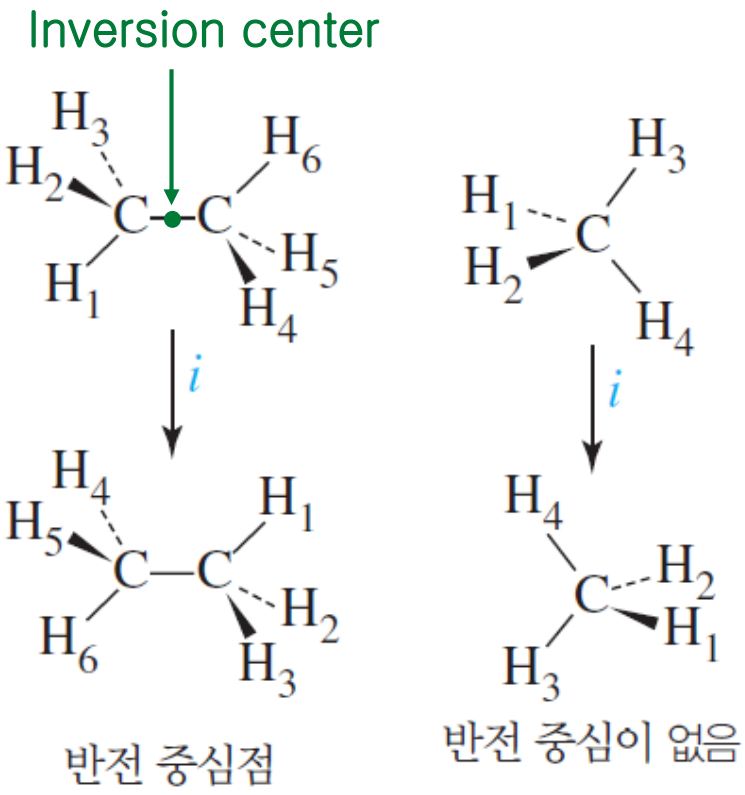


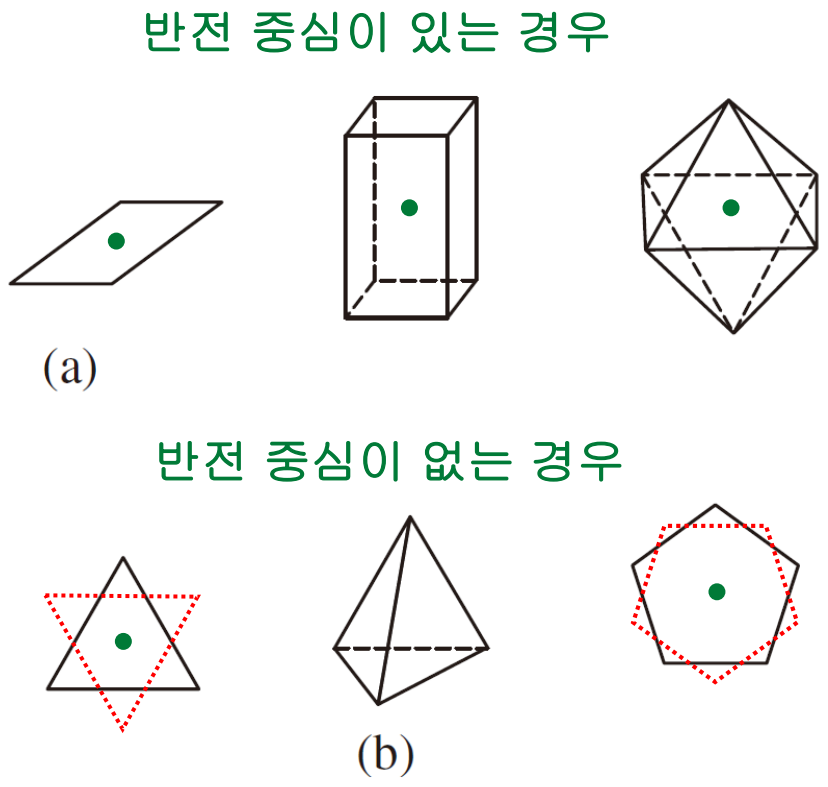


G. L. Miessler, 무기화학 제 5판, 자유아카데미, 2015, p. 89

4.1 대칭 요소와 대칭 조작

- **반전(inversion, i):** 각 점이 분자의 중심점에 대해 반대방향의 같은 거리로 이동
- Ethane 은 반전중심을 가지지만, 메탄은 가지지 않는다.



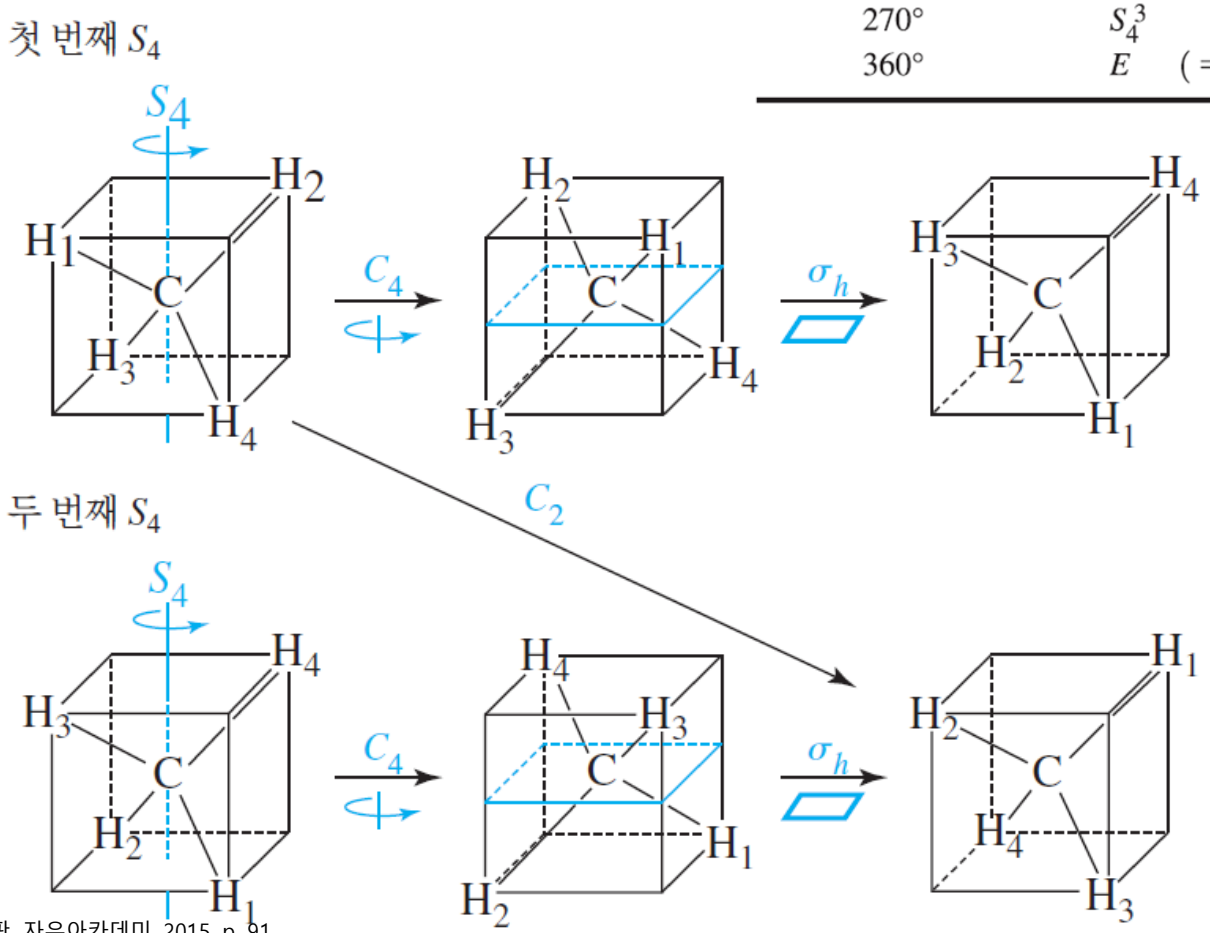


G. L. Miessler, 무기화학 제 5판, 자유아카데미, 2015, p. 90

4.1 대칭 요소와 대칭 조작

- **회전 반사 조작(rotation-reflection operation, S_n)**: 대칭축을 중심으로 360°/n 만큼 회전시킨 후 회전축 수직면에 반사시키는 대칭 조작
- S_2 = 반전조작 i, S_1 = 반사 조작 σ_h

회전각	대칭 조각
90°	S_4
180°	C_2 $(= S_4^2)$
270°	S_4^3
360°	E $(= S_4^4)$



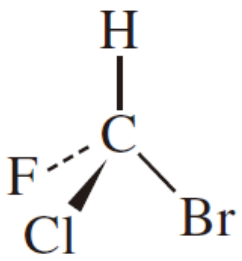
G. L. Miessler, 무기화학 제 5판, 자유아카데미, 2015, p. 91

4.1 대칭 요소와 대칭 조작

대칭 요소와 조작의 예

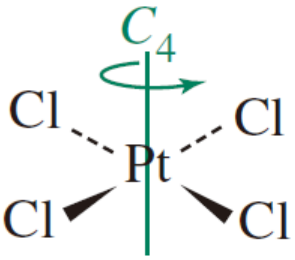
E

CHFClBr



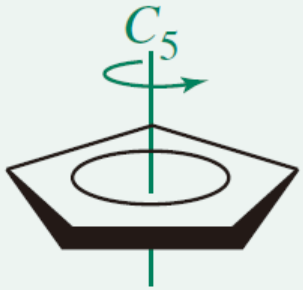
C_4

$[PtCl_4]^{2-}$



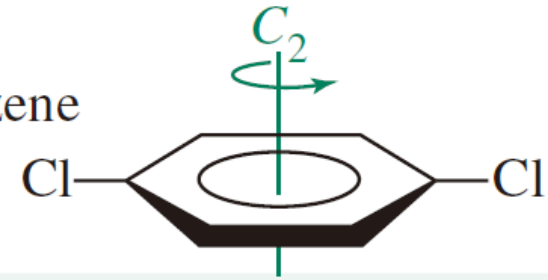
C_5

Cyclopentadienyl group



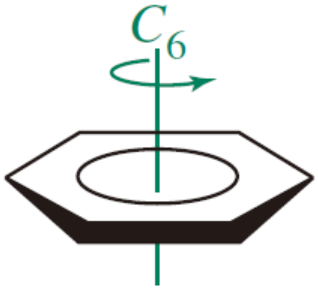
C_2

p-dichlorobenzene



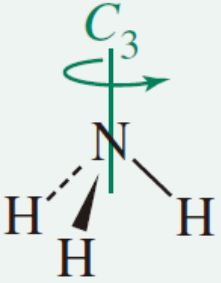
C_6

Benzene



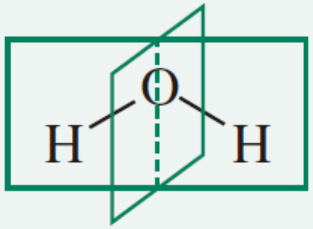
C_3

NH_3



σ_v

H_2O



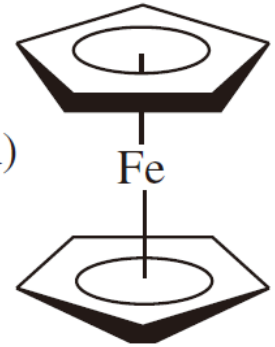
G. L. Miessler, Inorganic Chemistry 5th Ed., Pearson Educaion. Inc,, 2014, p. 79

4.1 대칭 요소와 대칭 조작

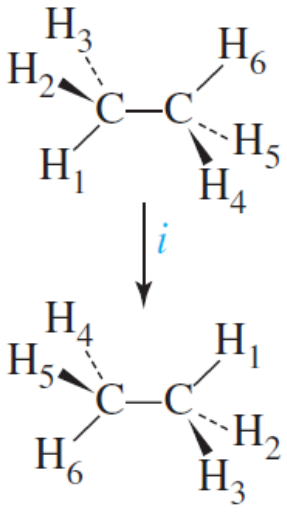
대칭 요소와 조작의 예

i

Ferrocene (staggered)



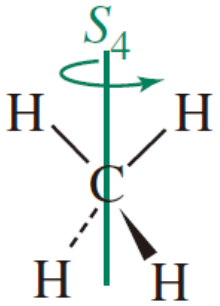
i



반전 중심점

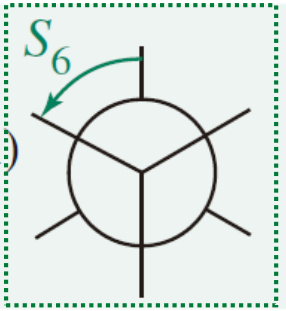
S_4

CH_4



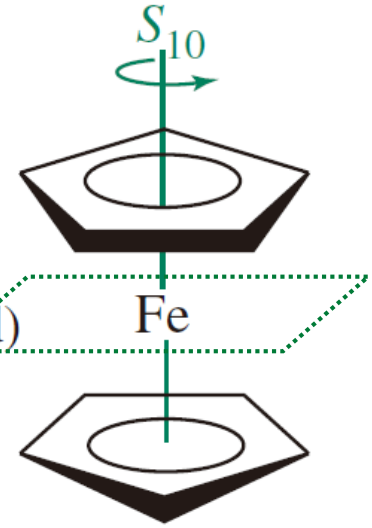
S_6

Ethane (staggered)



S_{10}

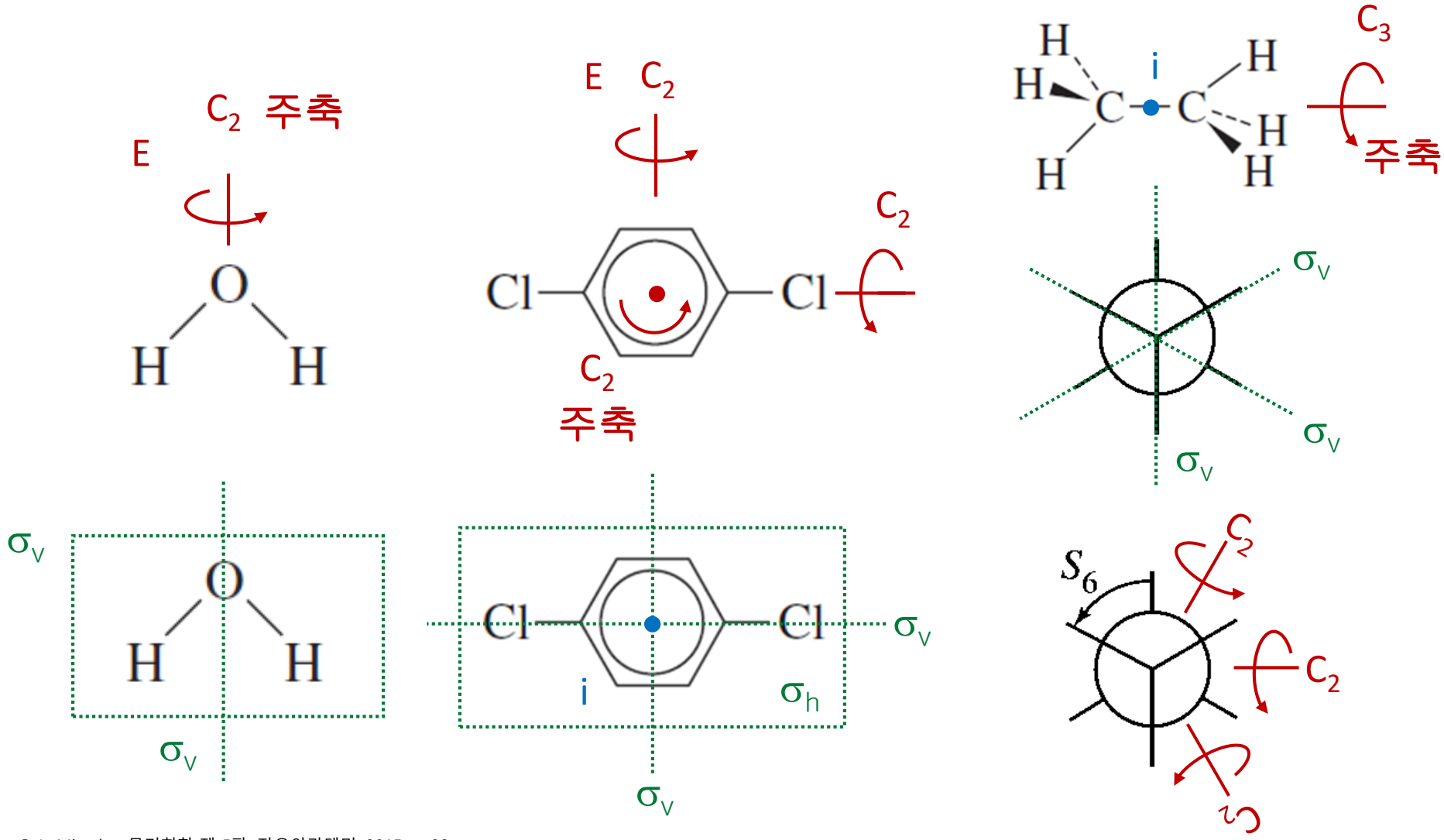
Ferrocene (staggered)



G. L. Miessler, Inorganic Chemistry 5th Ed., Pearson Educaion. Inc,, 2014, p. 79

4.1 대칭 요소와 대칭 조작

(예제문제 4.1) 다음 분자의 대칭 요소를 모두 찾아라. 대칭성을 결정할 때는 원자만 고려하라. 분자 대칭성은 원자의 기하학적 형태로 결정된다.

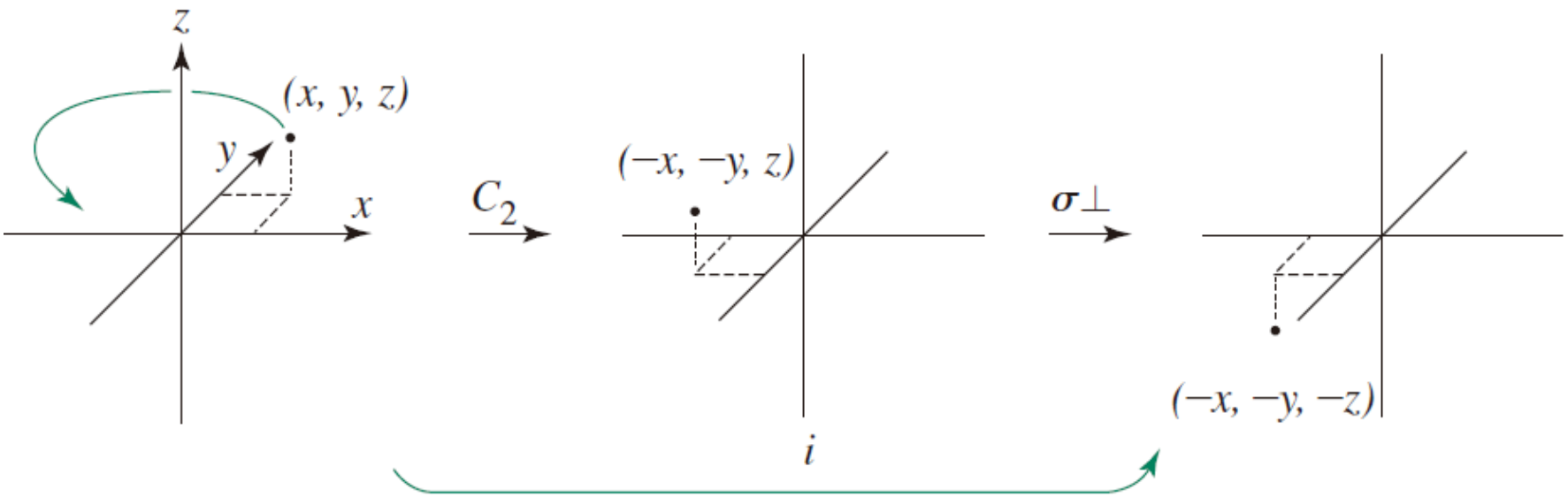


G. L. Miessler, 무기화학 제 5판, 자유아카데미, 2015, p. 92

4.1 대칭 요소와 대칭 조작

(기본문제 4.1) 카디션 좌표(cartesian coordinate)의 한 점을 사용하여 $S_2 = i$, $S_1 = \sigma$임을 보여라.

S_2 is made up of C_2 followed by $\sigma_\perp$, which is shown in the figure below to be the same as i.

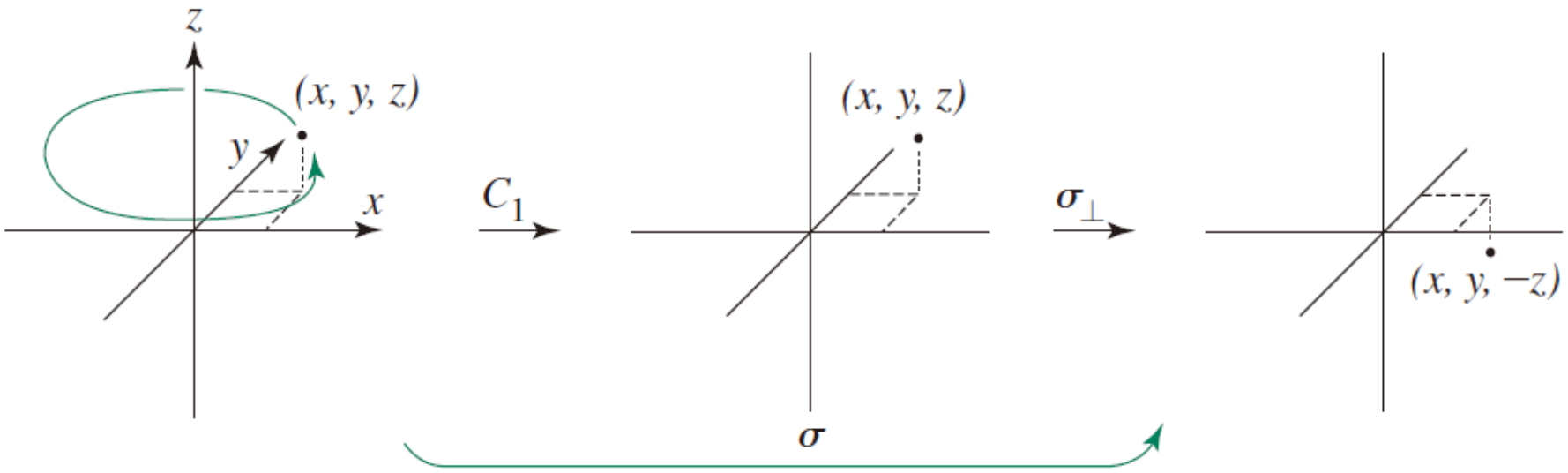


G. L. Miessler, 무기화학 제 5판, 자유아카데미, 2015, p. 93

4.1 대칭 요소와 대칭 조작

(기본문제 4.1) 카디션 좌표(cartesian coordinate)의 한 점을 사용하여 $S_2 = i$, $S_1 = \sigma$임을 보여라.

S_1 is made up of C_1 followed by $\sigma_\perp$, which is shown in the figure below to be the same as σ.



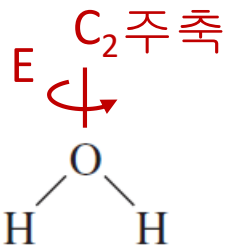
G. L. Miessler, 무기화학 제 5판, 자유아카데미, 2015, p. 93

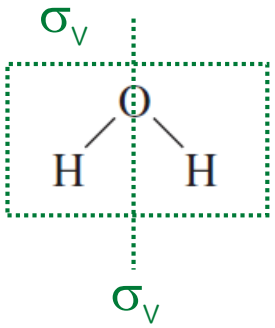
4.2 점군

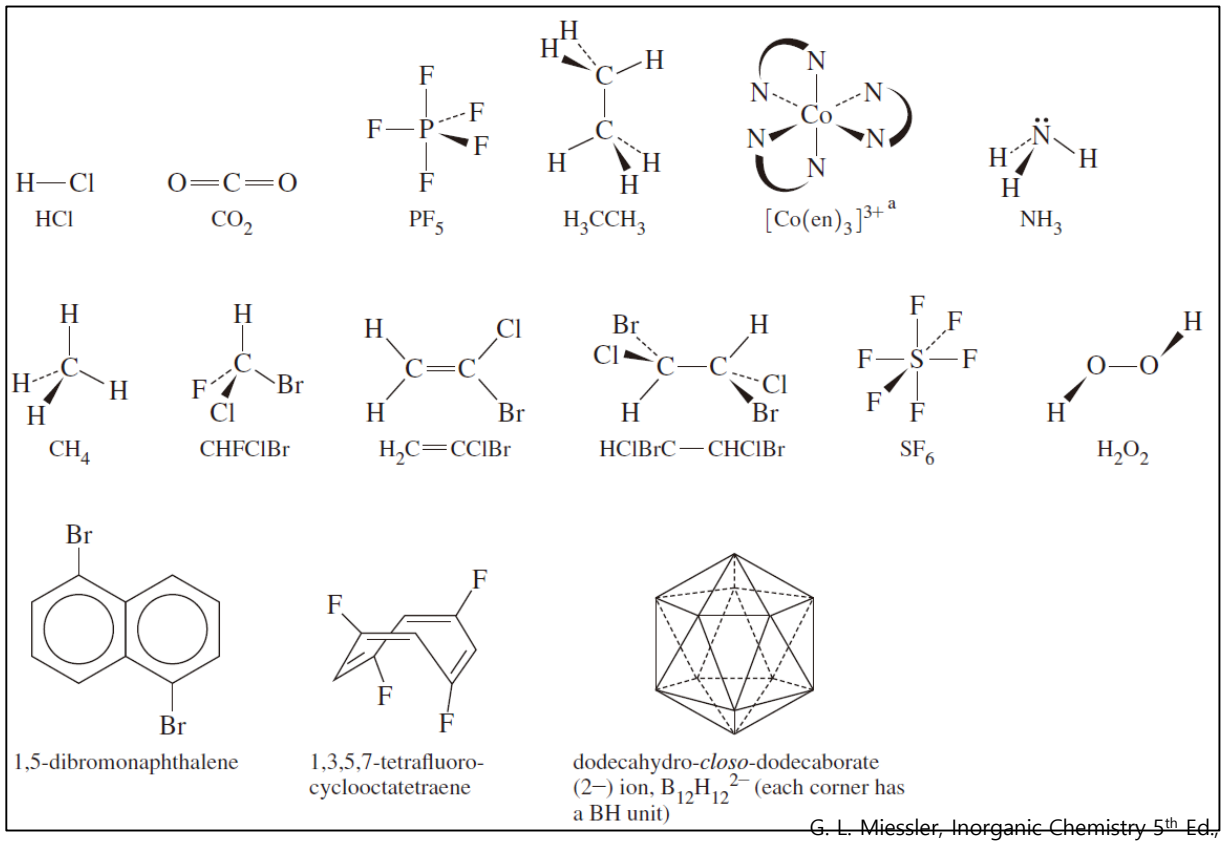
- **점군(point group)**: 분자가 가지는 대칭조작들을 그룹화한 것
- **군론(group theory)**: 대칭성을 연구할 때 사용하는 수학적 이론

ex. H_2O의 point group = C_{2v}

→ 주축으로 C_2축과
주축을 포함하는 mirror plane



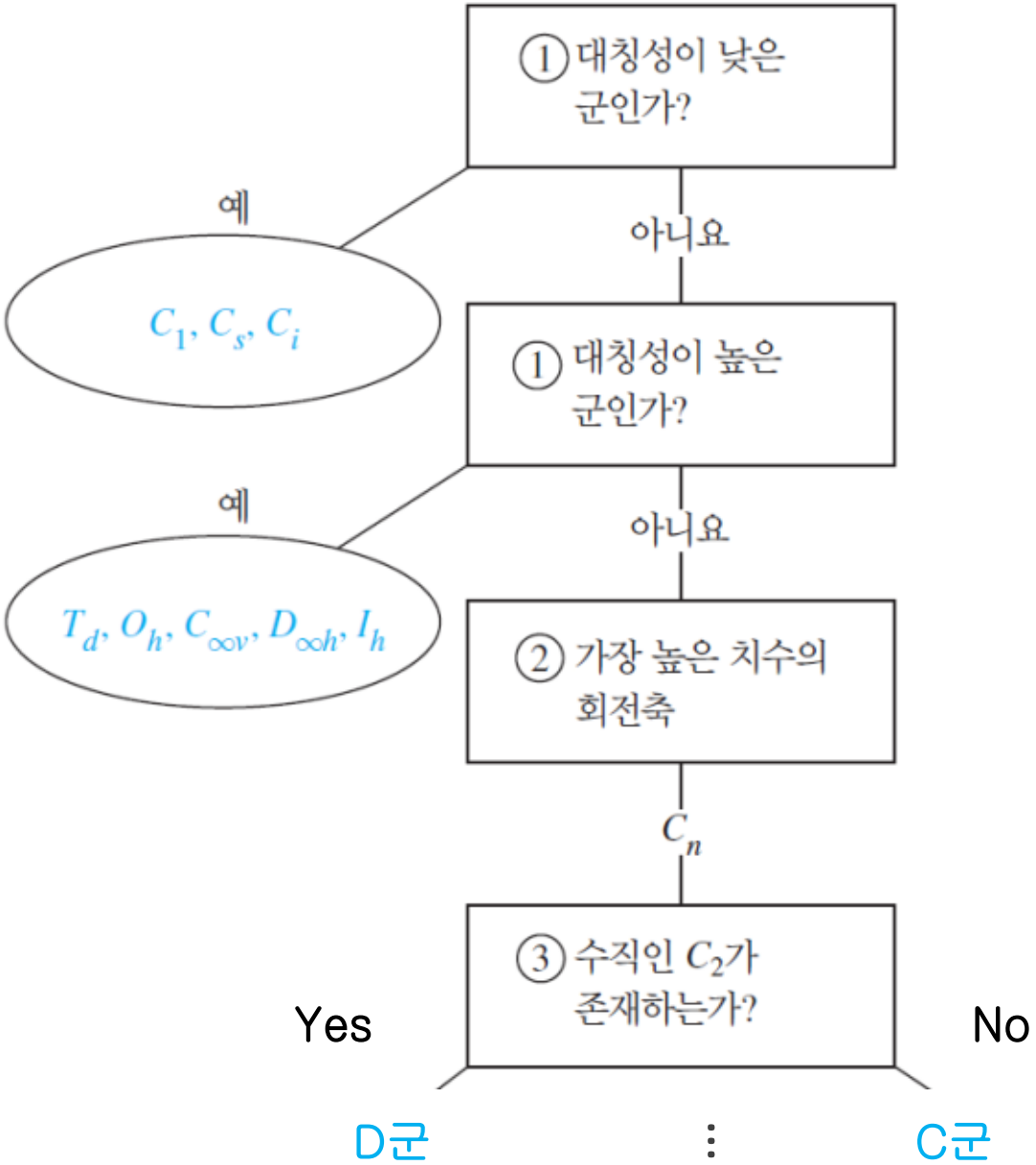




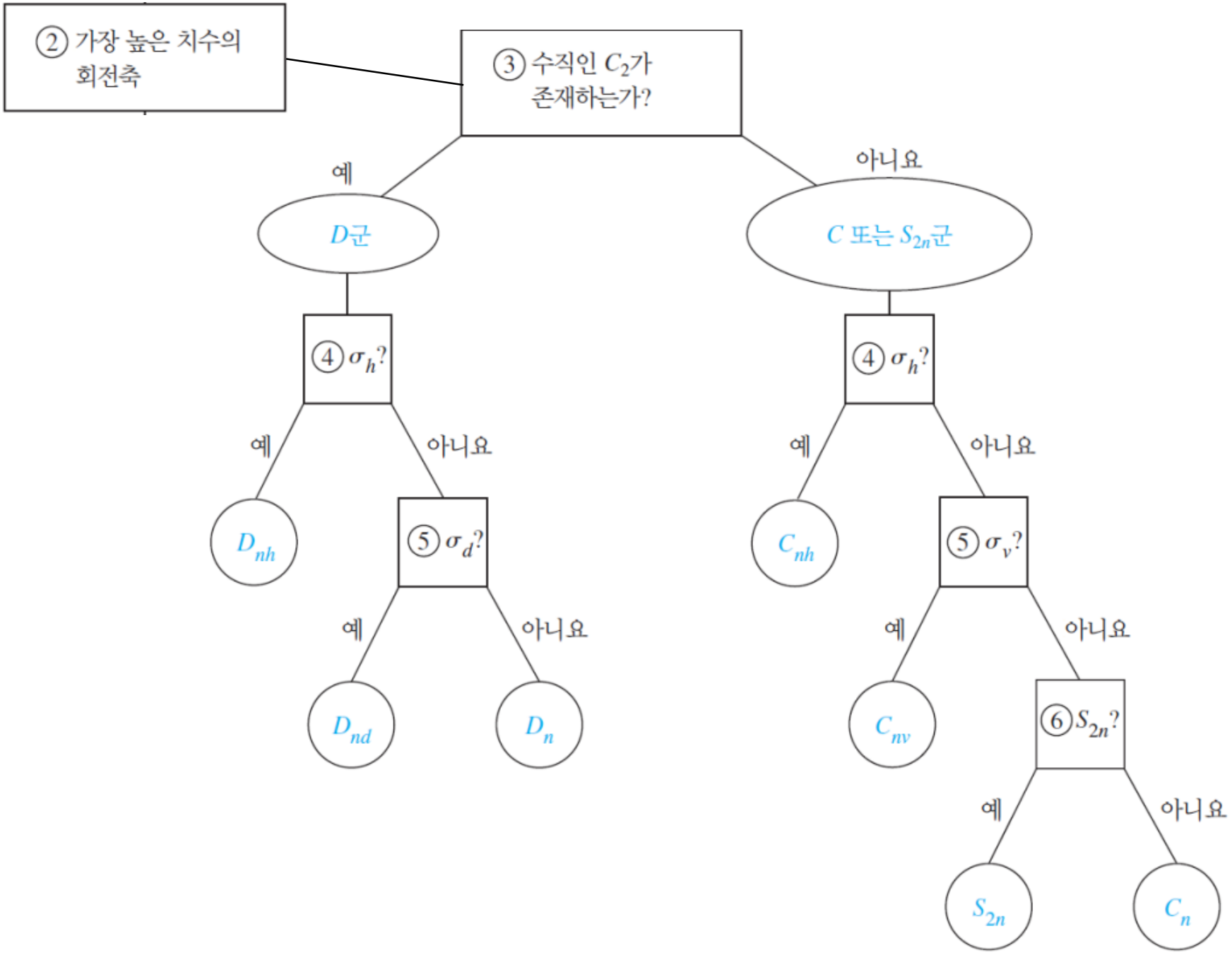
각 분자들의
점군을 나타내보자

G. L. Miessler, Inorganic Chemistry 5th Ed., Pearson Educaion. Inc,, 2014, p. 82

4.2 점군을 결정하는 단계



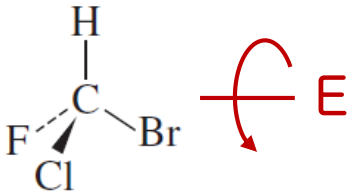
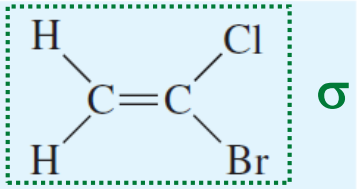
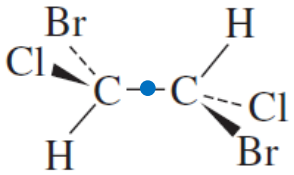
G. L. Miessler, 무기화학 제 5판, 자유아카데미, 2015, p. 94



G. L. Miessler, 무기화학 제 5판, 자유아카데미, 2015, p. 94

4.2 점군

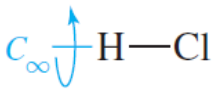
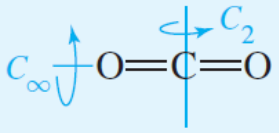
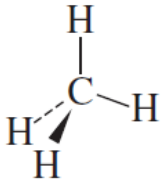
표 4.2 대칭성이 낮은 군

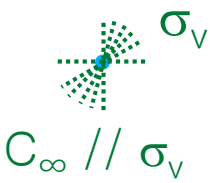
군	대칭성	예	
C_1	동등 대칭 조작 외에 다른 대칭성이 없음	CHFClBr	
C_s	하나의 거울면	$H_2C=CClBr$	
C_i	반전 중심 (분자의 예가 많지 않음)	HClBrC—CHClBr (엇갈린 형태)	

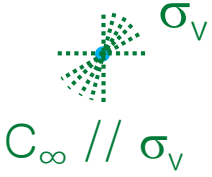
C_1, C_s, C_i, T_d, O_h, I_h, $C_{\infty v}$, $D_{\infty h}$

G. L. Miessler, 무기화학 제 5판, 자유아카데미, 2015, p. 95

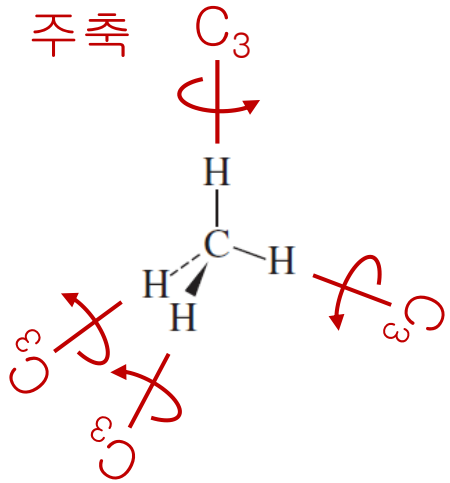
표 4.3 대칭성이 높은 군

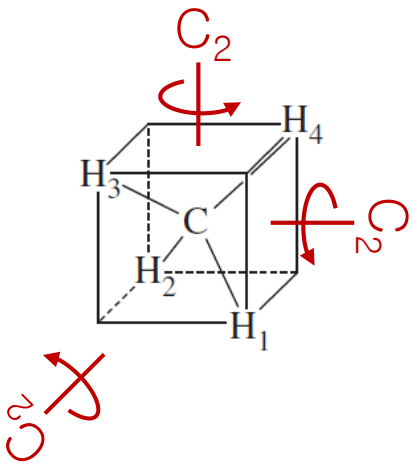
군	대칭성	예
$C_{\infty v}$	선형 구조이며, 무한 개의 회전축과 회전축을 포함하는 무한 개의 반사면을 가진다. 이 군은 반점 중심을 가지고 있지 않다.	
$D_{\infty h}$	선형 구조이며, 무한 개의 회전축과 회전축을 포함하는 무한 개의 반사면을 가진다. 이 군은 주축에 수직인 C_2축과 반사면, 반전 중심을 가진다.	
T_d	대부분의 분자는 사면체의 기하학적 구조를 가진다. 이 군에서는 C_4 축이 없으며, 4개의 C_3, 3개의 C_2, 3개의 S_4와 6개의 σ_d 평면이 있다.	

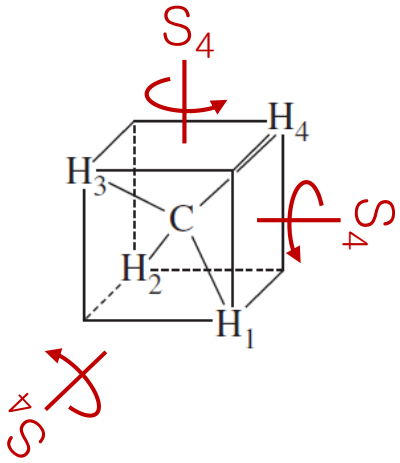


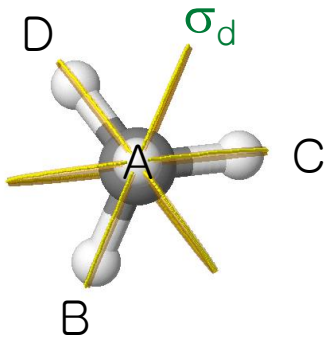


tetrahedron









A–B, A–C, A–D
B–C, B–D
C–D

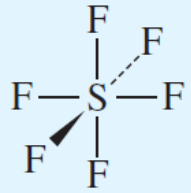
C_1, C_s, C_i, T_d, O_h, I_h, $C_{\infty v}$, $D_{\infty h}$

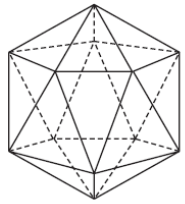
G. L. Miessler, 무기화학 제 5판, 자유아카데미, 2015, p. 96

4.2 점군

표 4.3 대칭성이 높은 군

O_h	정팔면체 구조를 가지며, 정육면체의 구조도 같은 대칭 조작 세트를 가진다. 총 48개의 대칭 조작 중 4개의 C_3, 3개의 C_4와 반전 중심이 있다. octahedron
I_h	정십이면체 구조는 6개의 C_5축이 있다(다른 대칭 조작을 포함하여 총 120개의 대칭 조작이 가능하다). icosahedron





$B_{12}H_{12}^{2-}$, BH는 정십이면체의 꼭짓점에 위치한다.

TABLE 4.5 Symmetry Operations for High-Symmetry Point Groups and Their Rotational Subgroups

Point Group	Symmetry Operations									
I_h	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$	i	$12S_{10}$	$12S_{10}^3$	$20S_6$	15σ
I	E	$12C_5$	$12C_5^2$	$20C_3$	$15C_2$					
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(\equiv C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
O	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(\equiv C_4^2)$					
T_d	E	$8C_3$		$3C_2$			$6S_4$			$6\sigma_d$
T	E	$4C_3$	$4C_3^2$	$3C_2$						
T_h	E	$4C_3$	$4C_3^2$	$3C_2$		i	$4S_6$	$4S_6^5$	$3\sigma_h$	

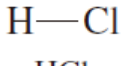
C_1, C_s, C_i, T_d, O_h, I_h, $C_{\infty v}$, $D_{\infty h}$

G. L. Miessler, 무기화학 제 5판, 자유아카데미, 2015, p. 94

G. L. Miessler, Inorganic Chemistry 5th Ed., Pearson Educaion. Inc,, 2014, p. 89

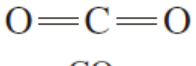
en: ethylenediamine = $NH_2CH_2CH_2NH_2$

$C_{\infty v}$

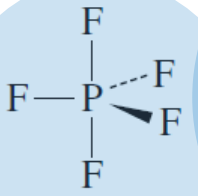


HCl

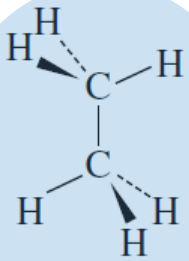
$D_{\infty h}$



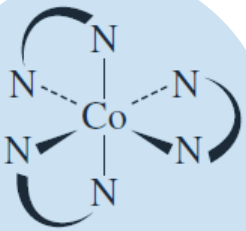
CO_2



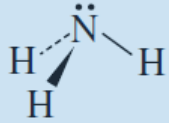
PF_5



H_3CCH_3

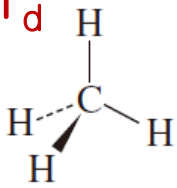


$[Co(en)_3]^{3+}$ [a]



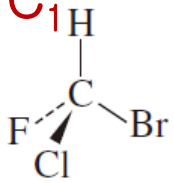
NH_3

T_d



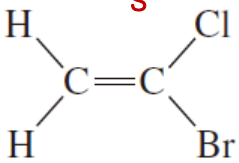
CH_4

C_1



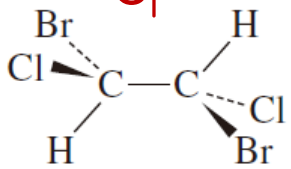
CHFClBr

C_s



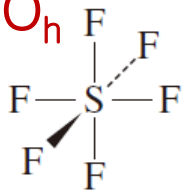
$H_2C{=}CClBr$

C_i

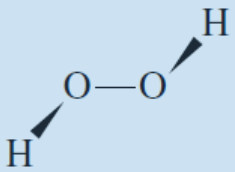


HClBrC—CHClBr

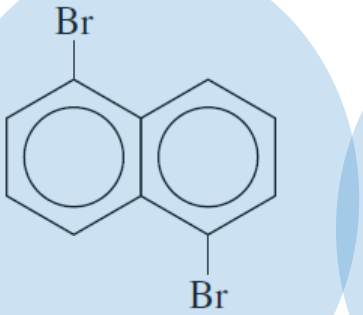
O_h



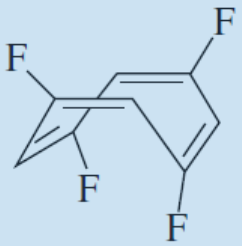
SF_6



H_2O_2

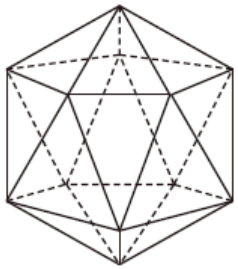


1,5-dibromonaphthalene



1,3,5,7-tetrafluoro-cyclooctatetraene

I_h

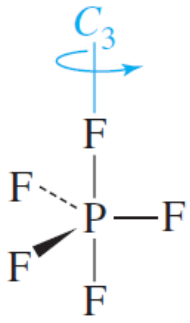


dodecahydro-*closo*-dodecaborate (2−) ion, $B_{12}H_{12}^{2-}$ (each corner has a BH unit)

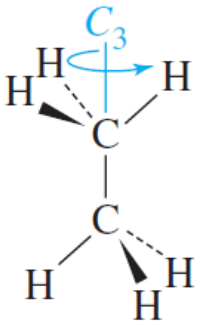
G. L. Miessler, Inorganic Chemistry 5th Ed., Pearson Educaion. Inc,, 2014, p. 82

4.2 점군

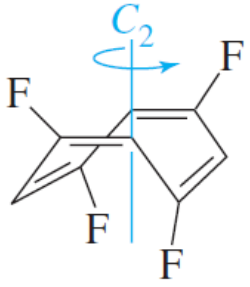
2) 가장 큰 n 값을 가진 주축 C_n은?



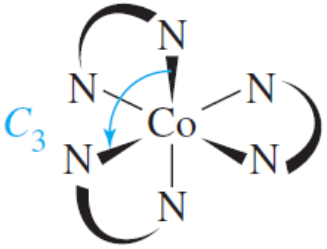
PF_5



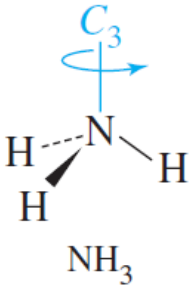
H_3CCH_3



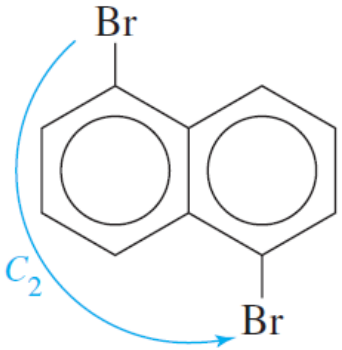
1,3,5,7-테트라플루오로
사이클로옥타테트라엔



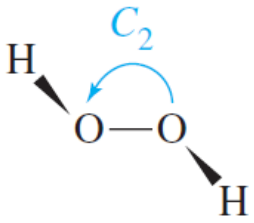
C_3는 종이면에 수직
$[Co(en)_3]^{3+}$



NH_3



C_2는 분자면에 수직
1,5-다이브로모나프탈렌



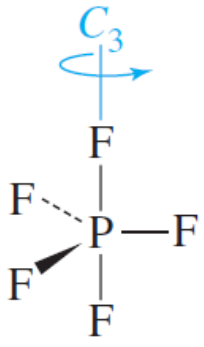
H_2O_2

G. L. Miessler, 무기화학 제 5판, 자유아카데미, 2015, pp. 97-99

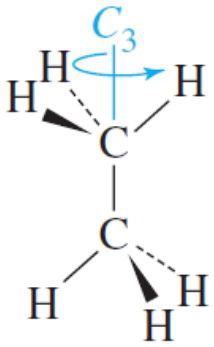
4.2 점군

3) 주축 C_n에 수직인 C_2축이 존재하는가?

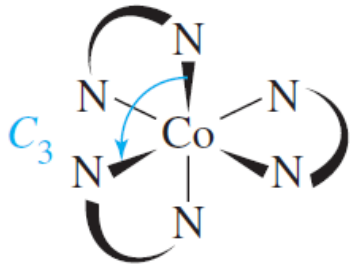
→ 존재하면 D



PF_5

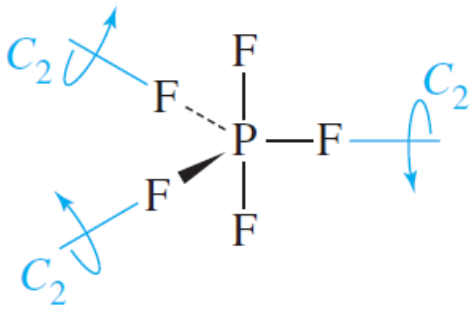


H_3CCH_3



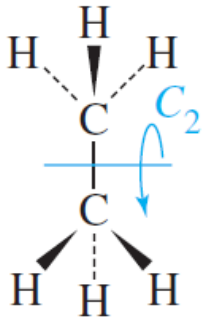
C_3는 종이면에 수직

$[Co(en)_3]^{3+}$



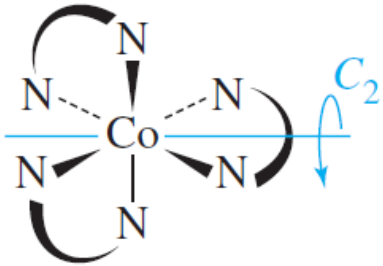
PF_5

예



H_3CCH_3

예



$[Co(en)_3]^{3+}$

예

G. L. Miessler, 무기화학 제 5판, 자유아카데미, 2015, pp. 97-99

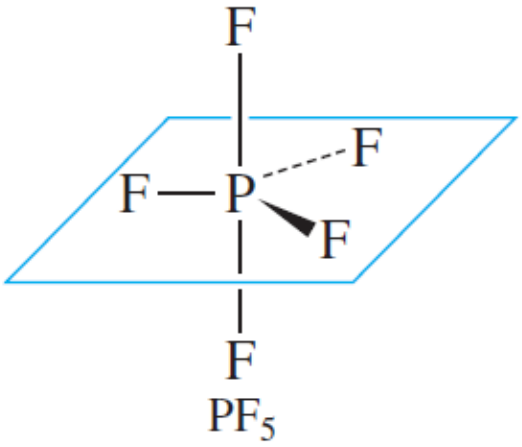
4.2 점군

4) 주축 C_n에 수직인 거울면 σ_h 이 존재하는가? D_{nh}

5) 주축 C_n을 포함하는 거울면 σ 이 존재하는가? D_{nd}

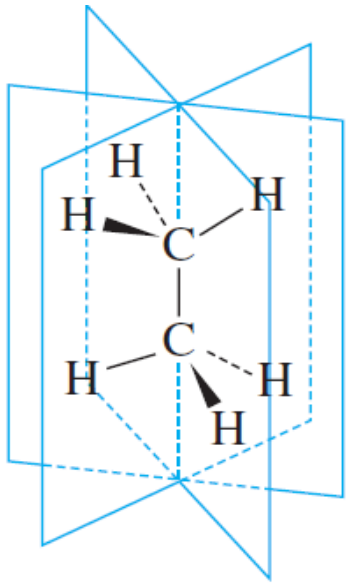
6) 모두 다 아니면 D_n

D_{3h}



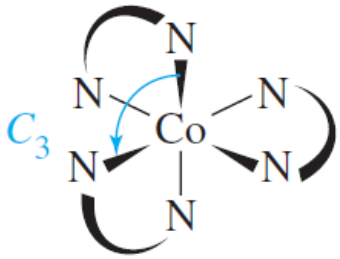
PF_5

D_{3d}



H_3CCH_3

D_3



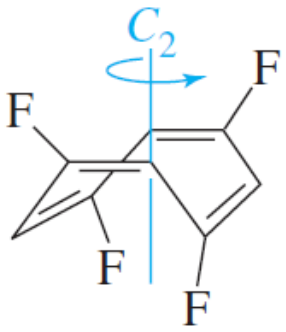
C_3는 종이면에 수직

$[Co(en)_3]^{3+}$

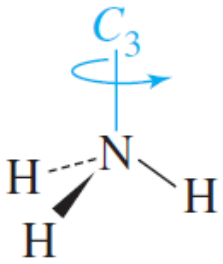
G. L. Miessler, 무기화학 제 5판, 자유아카데미, 2015, pp. 97-99

4.2 점군

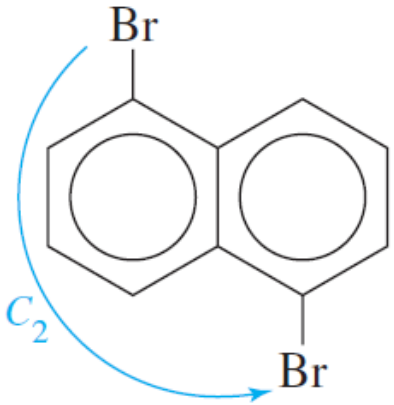
3) 주축 C_n에 수직인 C_2축이 존재하는가?
→ 존재하지 않으면 C



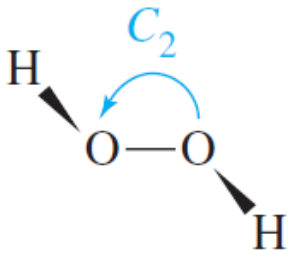
1,3,5,7-테트라플루오로
사이클로옥타테트라엔



NH_3



C_2는 분자면에 수직
1,5-다이브로모나프탈렌

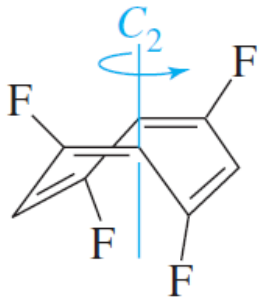


H_2O_2

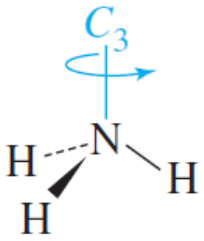
G. L. Miessler, 무기화학 제 5판, 자유아카데미, 2015, pp. 97-99

4.2 점군

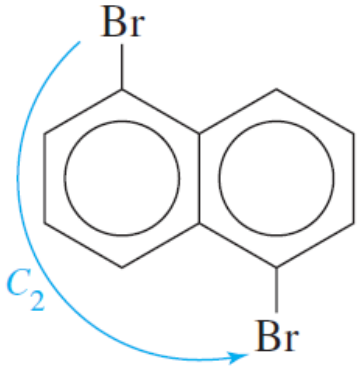
4) 주축 C_n에 수직인 거울면 σ_h 이 존재하는가? C_{nh}
5) 주축 C_n을 포함하는 거울면 σ_v 이 존재하는가? C_{nv}
6) 주축인 C_n과 일치하는 S_{2n}축이 존재하는가? S_{2n}
7) 모두 다 아니면 C_n



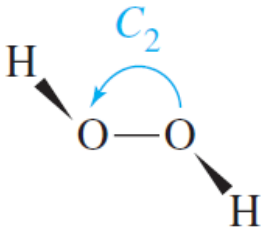
1,3,5,7-테트라플루오로
사이클로옥타테트라엔



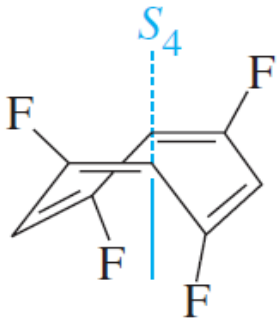
NH_3



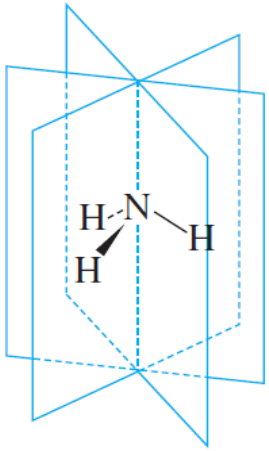
C_2는 분자면에 수직
1,5-다이브로모나프탈렌



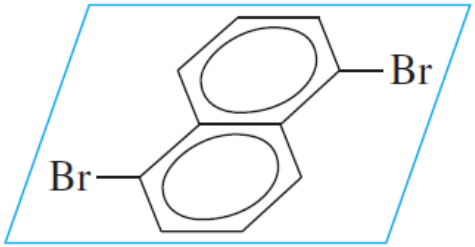
H_2O_2



S_4



C_{3v}



C_{2h}

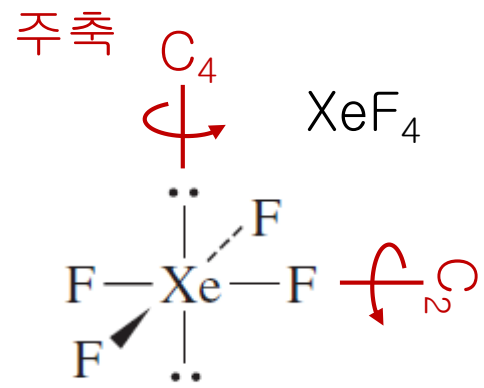
C_2

G. L. Miessler, 무기화학 제 5판, 자유아카데미, 2015, pp. 97-99

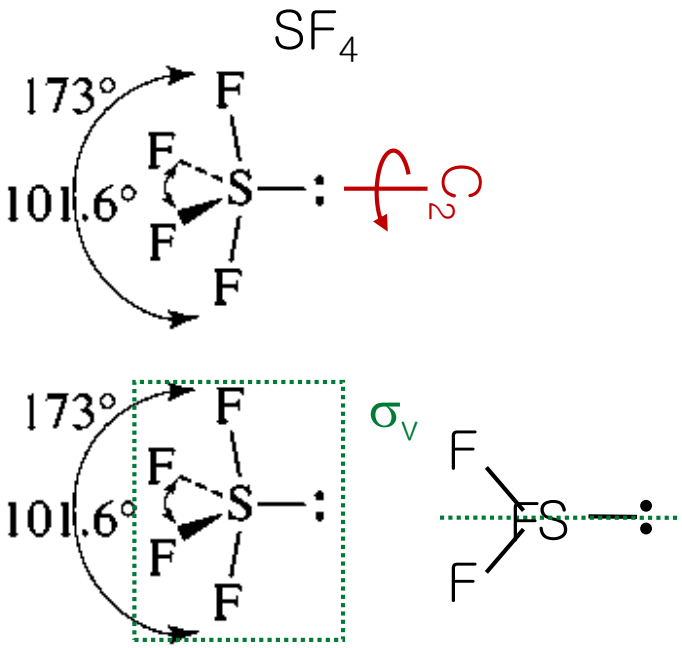
4.2 점군

(예제문제 4.2) 다음 분자와 이온의 점군을 결정하라.

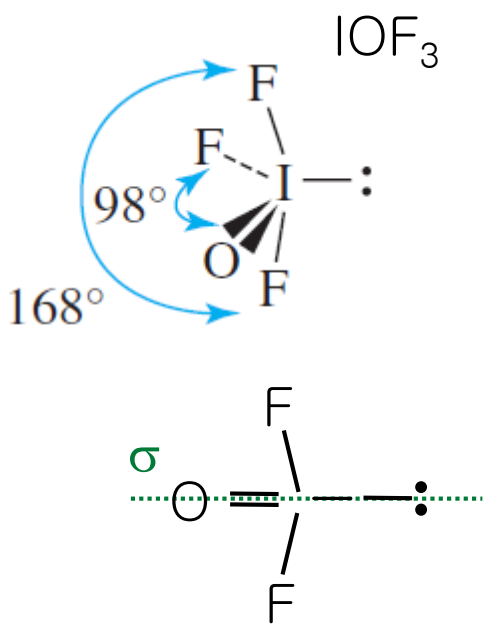
C_1, C_s, C_i, T_d, O_h, I_h, $C_{\infty v}$, $D_{\infty h}$ → C_n → 주축에 수직인 C_2 → D: σ_h → σ_d
→ C: σ_h → σ_v → S_{2n}



D_{4h}



C_{2v}



C_s

G. L. Miessler, 무기화학 제 5판, 자유아카데미, 2015, p. 102