



Univerzitet u Nišu  
Prirodno-matematički fakultet  
Departman za hemiju  
Katedra za neorgansku hemiju



# Hemija prelaznih metala sa koordinacionom hemijom

*Studijski program:* Hemija

*Vrsta i nivo studija:* Osnovne akademske studije

*Tip predmeta:* obavezni

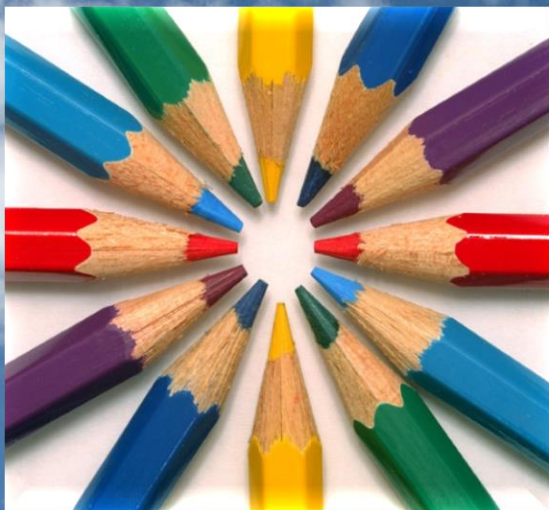
*Šifra predmeta:* H-111-B

*Fond časova:* 4+1+1

*Školska:* 2018/2019. godina

*SI\_P2*

**Prof. dr Nenad S. Krstić**



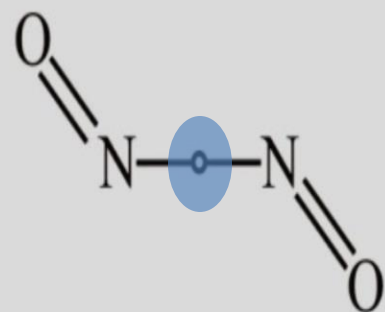
# Simetrija u hemiji



# ELEMENTI SIMETRIJE I SIMETRIJSKE OPERACIJE

Element simetrije	Oznaka	Simetrijska operacija
centar simetrije	$i$	inverzija
prava osa simetrije	$C_n$	rotacija (obrtnanje)
ravan simetrije	$\sigma$	refleksija
nesvojstvena osa	$S_n$	rotacija oko ose i refleksija u ravni normalnoj na osu

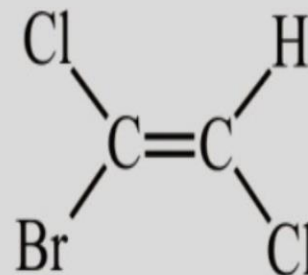
# Centar simetrije (i)



a)



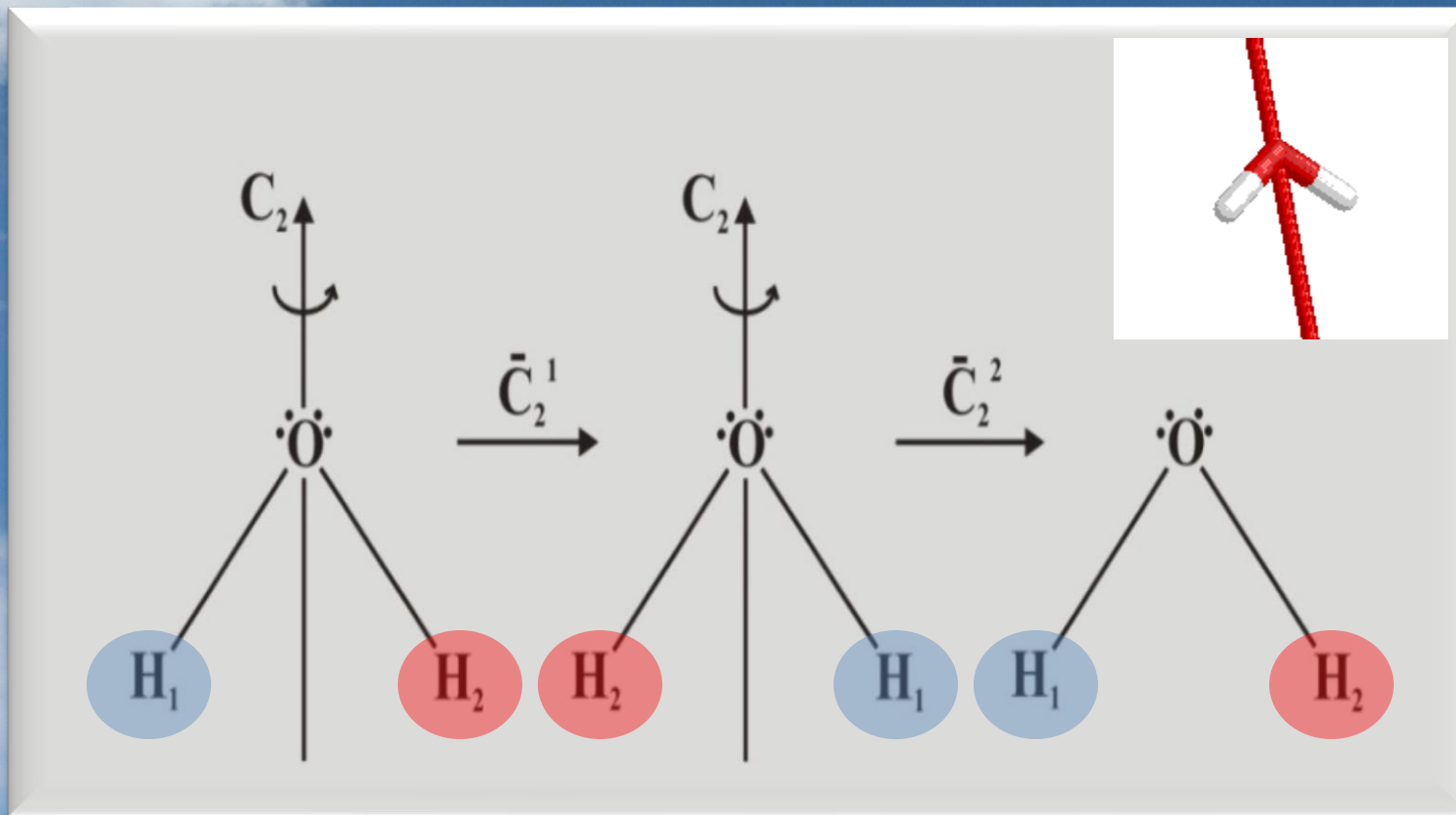
b)



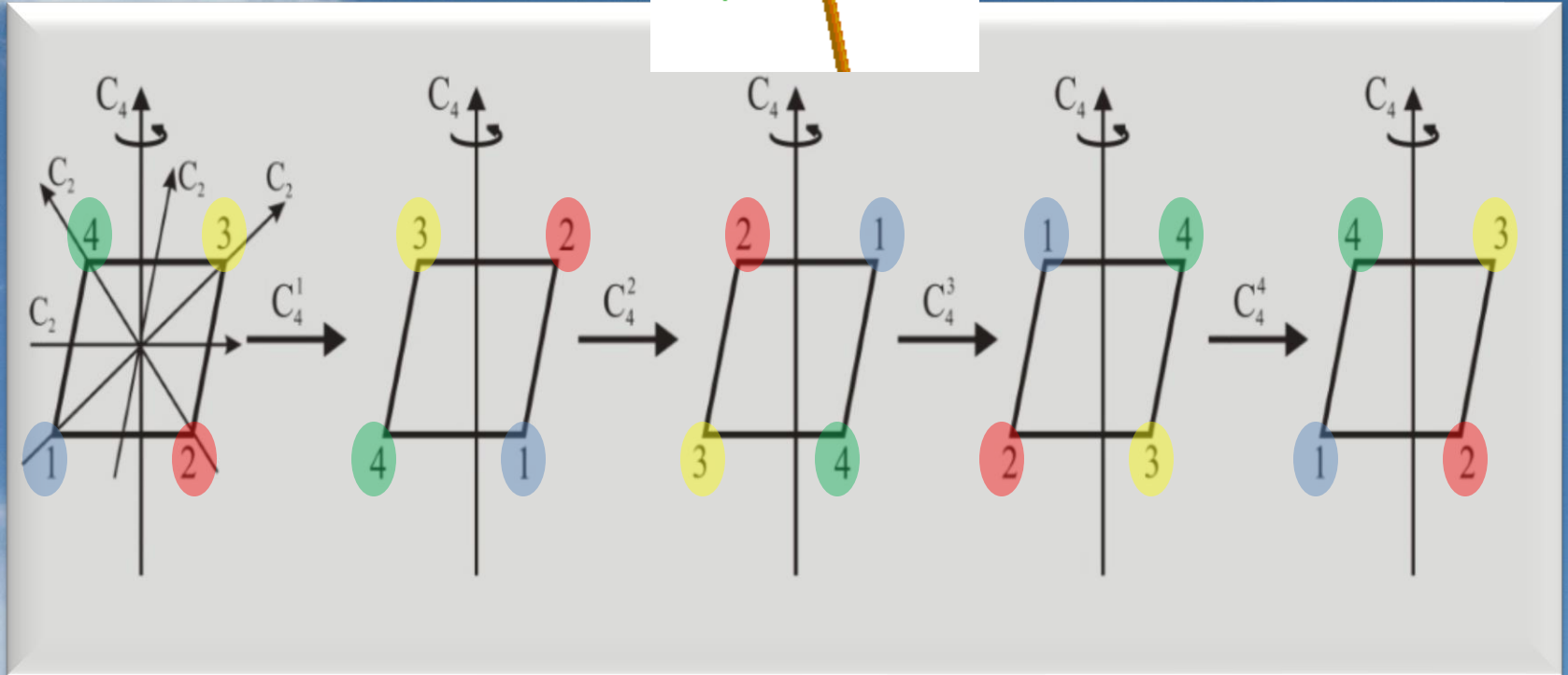
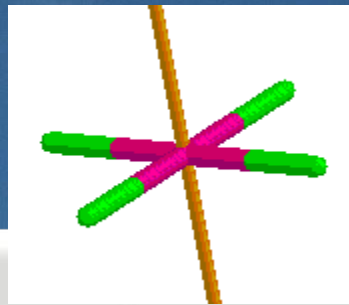
c)

**Prisustvo (a) i odsustvo (b, c) centra simetrije**

# Prava osa simetrije (C)

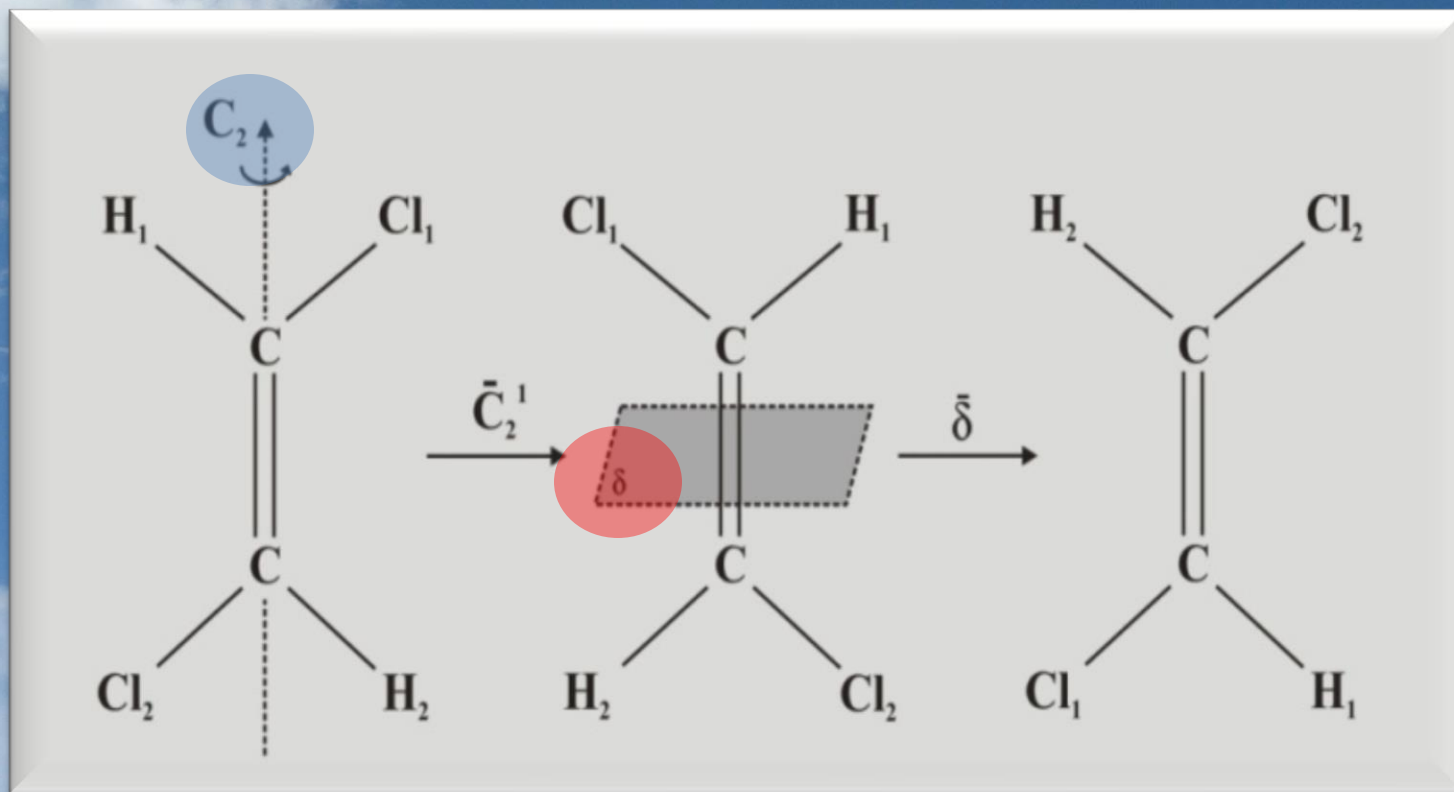


Rotacija molekula  $H_2O$  oko ose rotacije  $C_2$



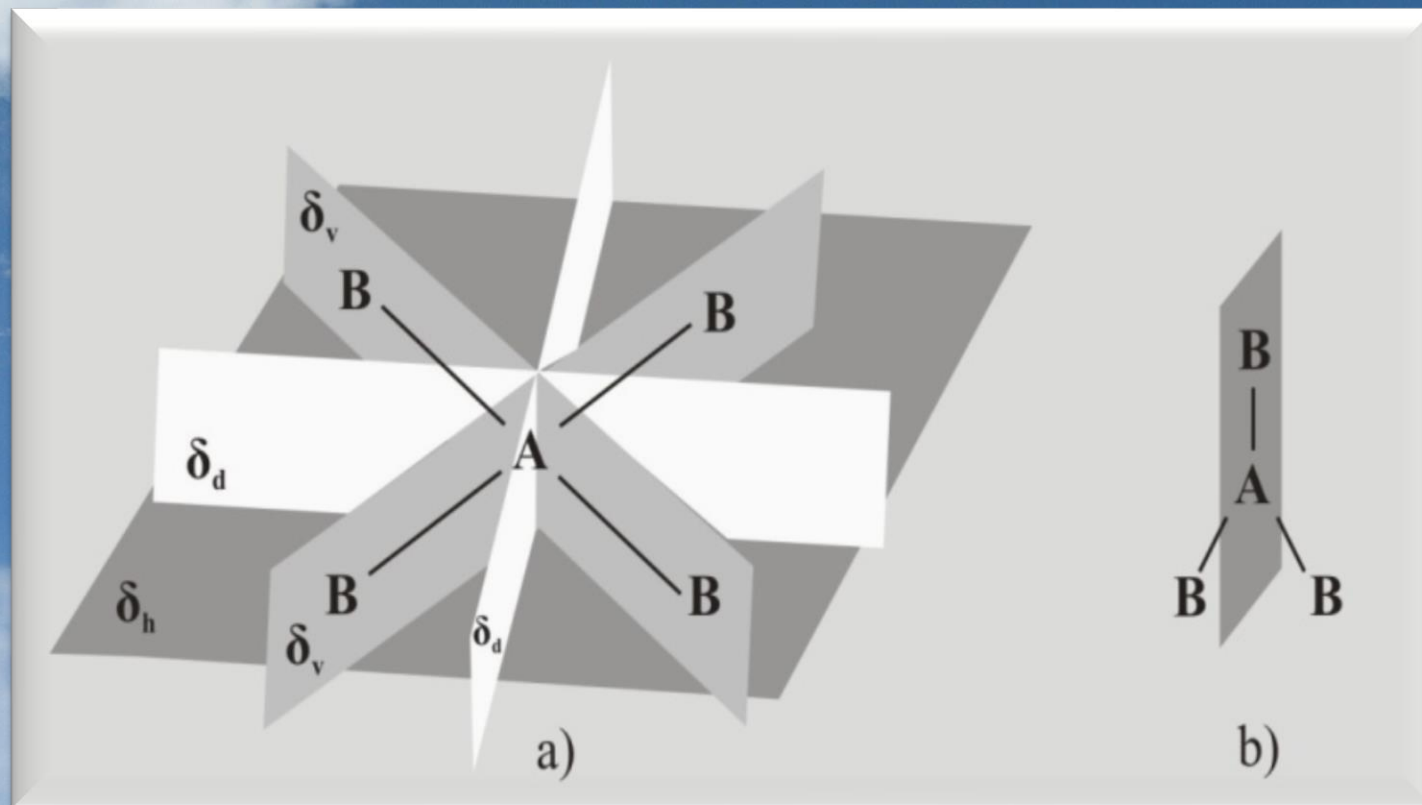
**Rotacija molekula tipa  $AB_4$  kvadratoplanarne strukture oko ose rotacije  $C_4$**

# Neprava osa simetrije ( $S_n$ )



Neprava osa simetrije duž C-C veze u molekulu 1,2-dihloretena

# Ravan simetrije ( $\sigma$ )



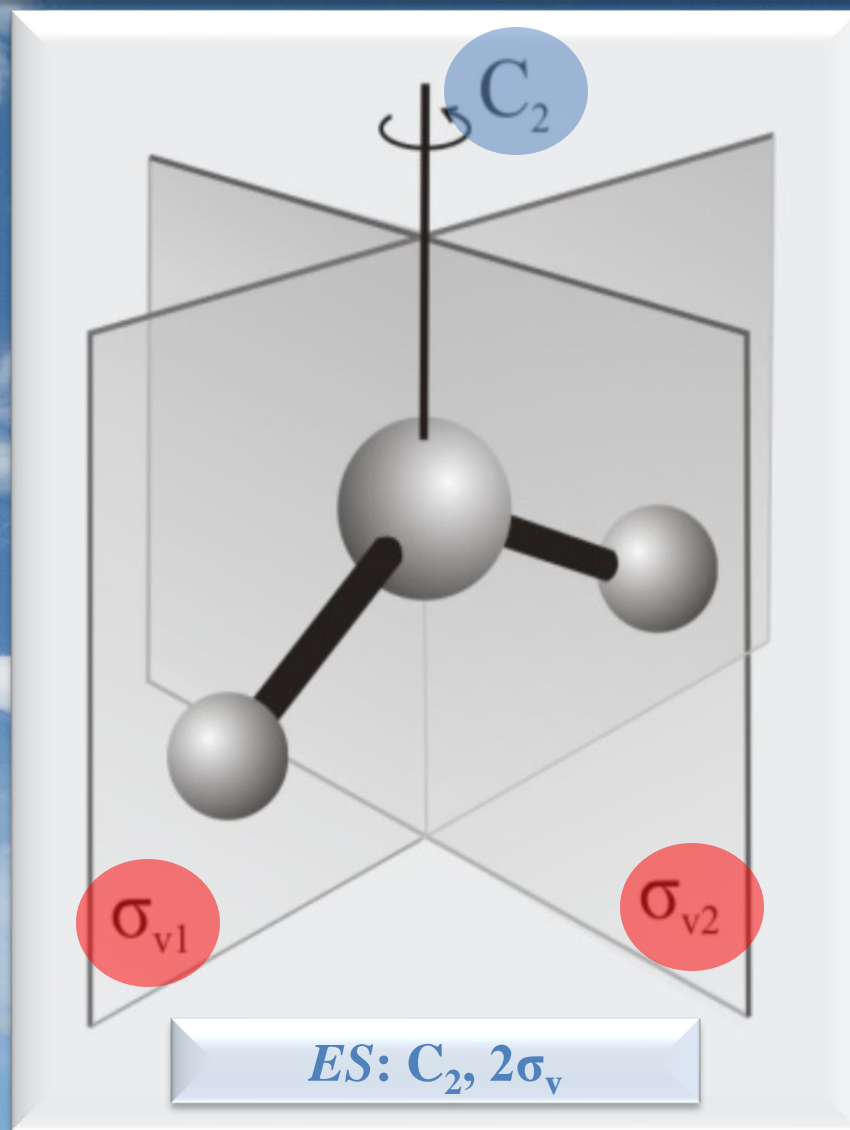
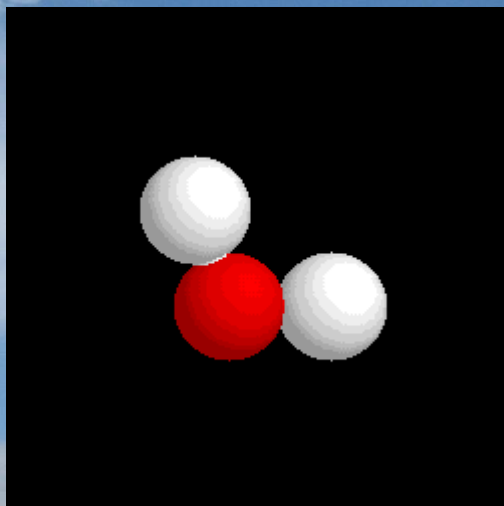
Horizontalne, vertikalne i dihedralne ravni u molekulu tipa  $AB_4$  kvadratnoplanarne strukture (a) i ilustracija vertikalne ravni u molekulu tipa  $AB_3$  (b)



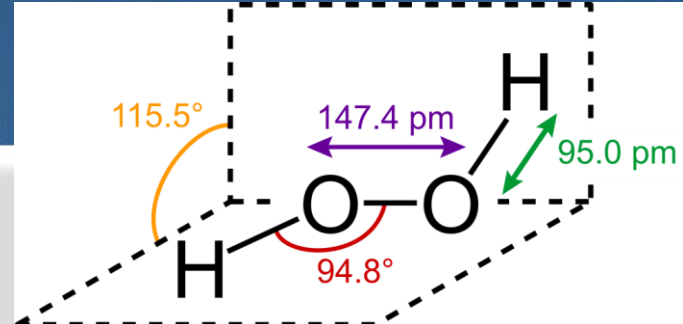
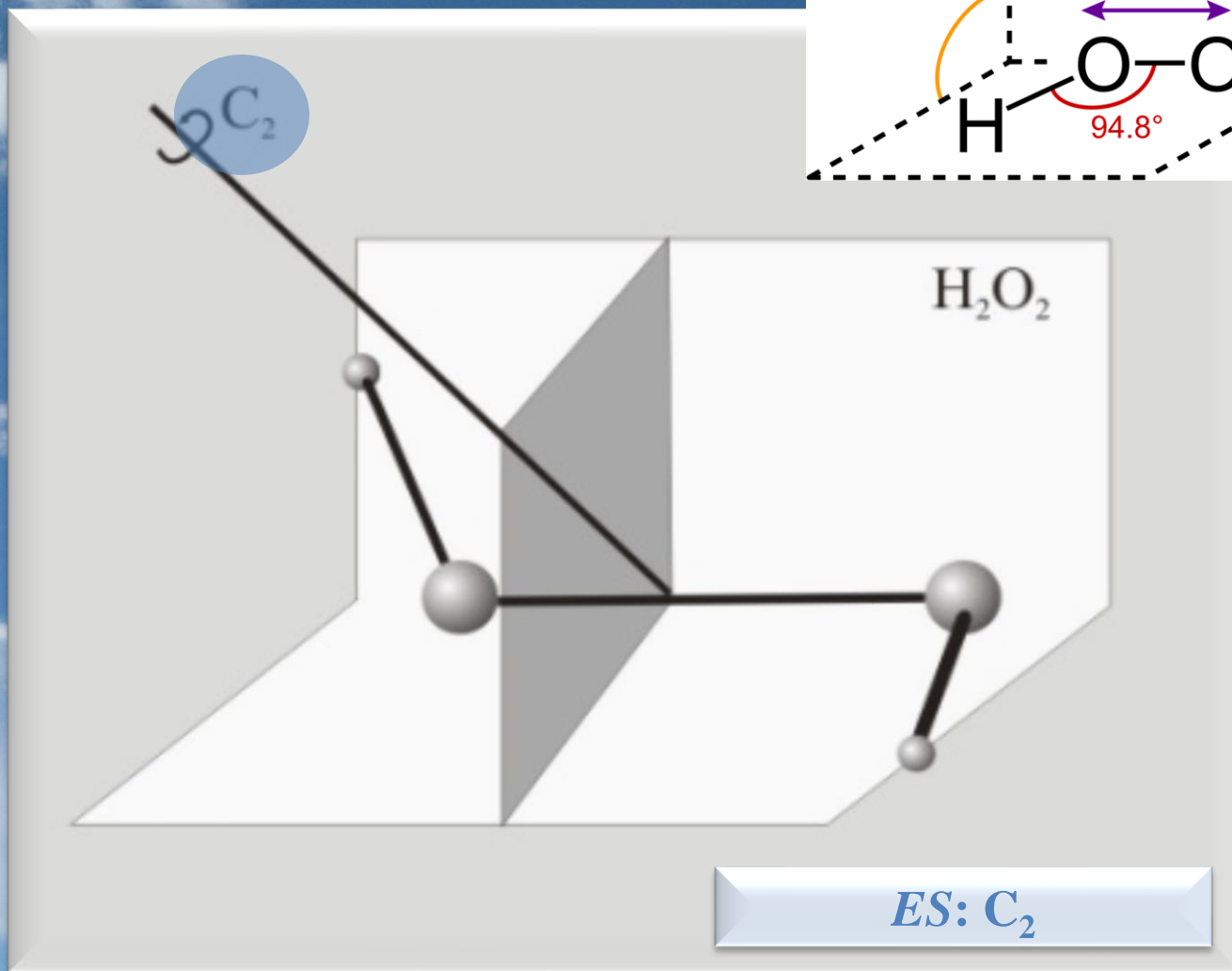
## Element identičnosti (**I**)

Poseduju gas svi molekuli, kada se svaki atom nekog molekula preslikava u samog sebe  $C = I$ , u literaturi se može sresti i **E** kao oznaka za identičnost.

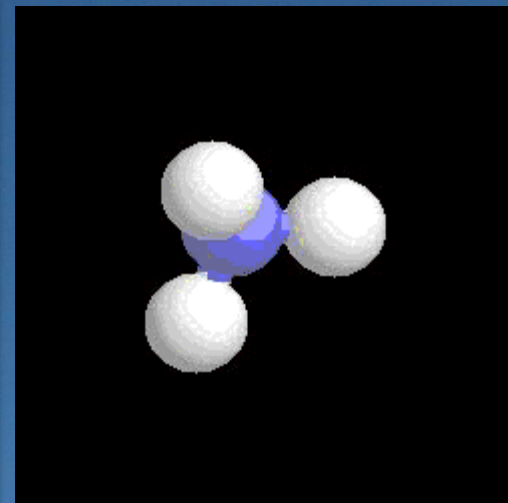
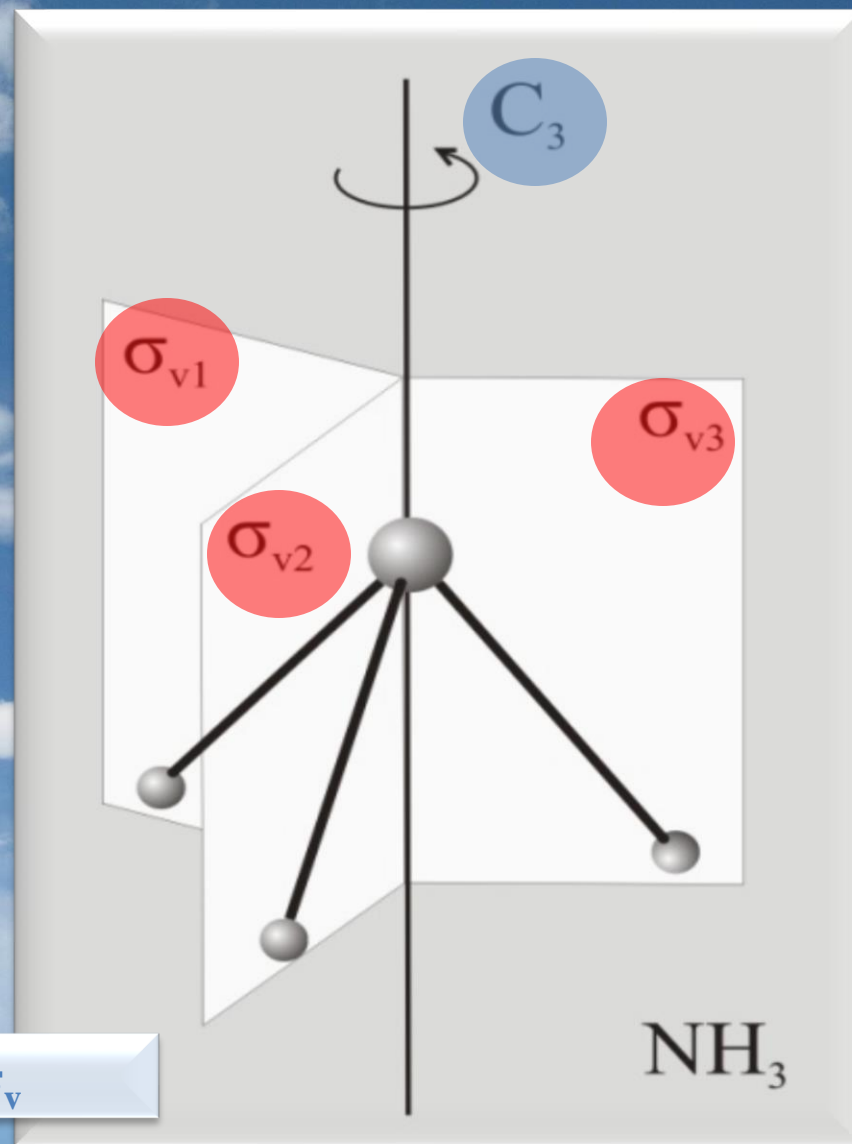
# Primeri



Molekul  $H_2O$

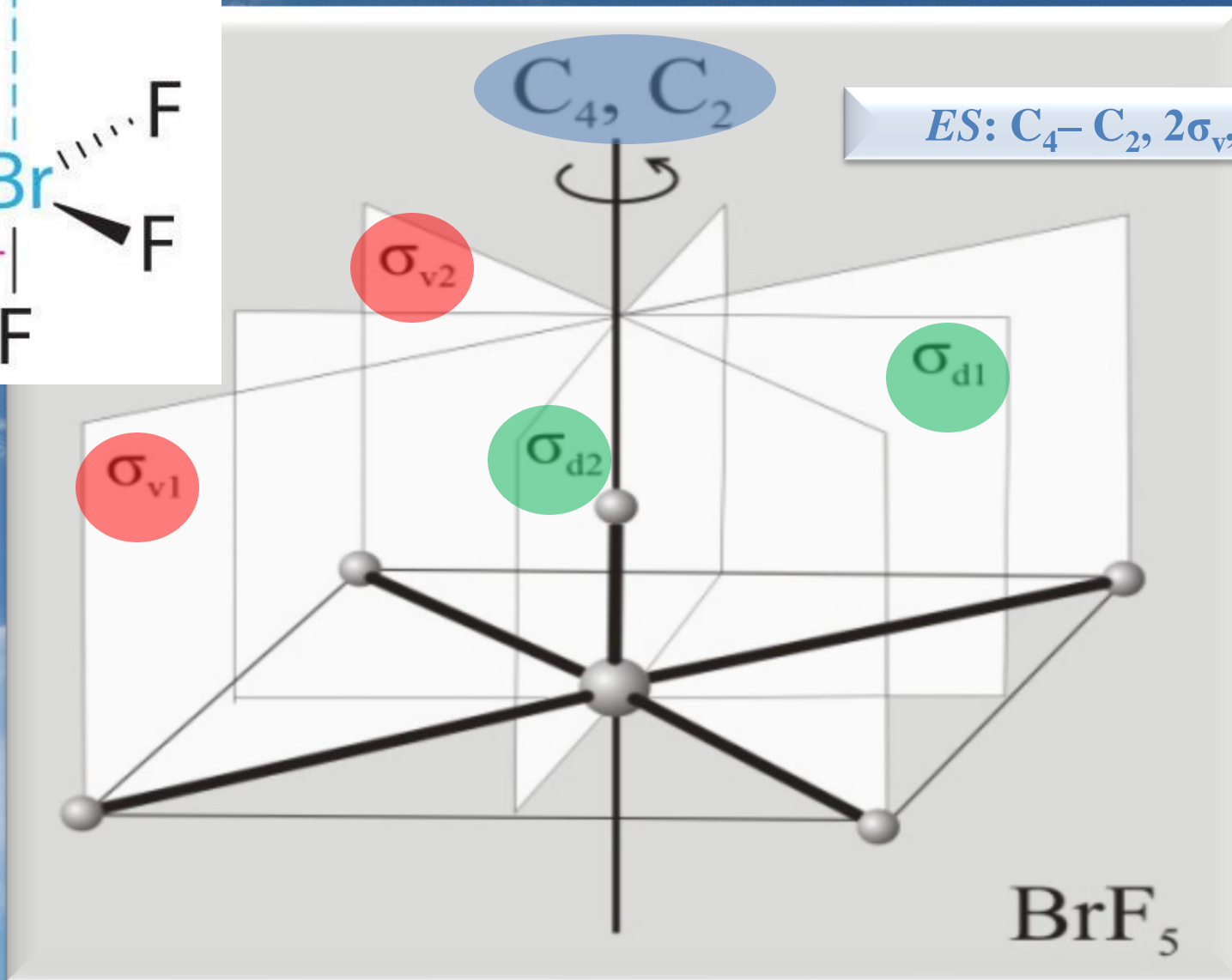
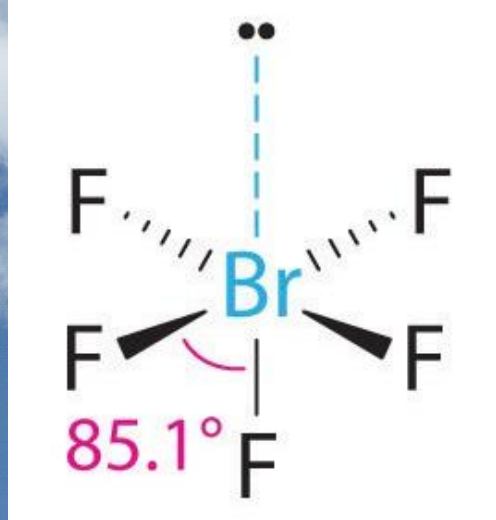


**Molekul  $\text{H}_2\text{O}_2$**



*ES:  $C_3, 3\sigma_v$*

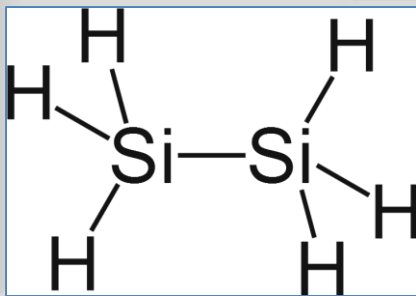
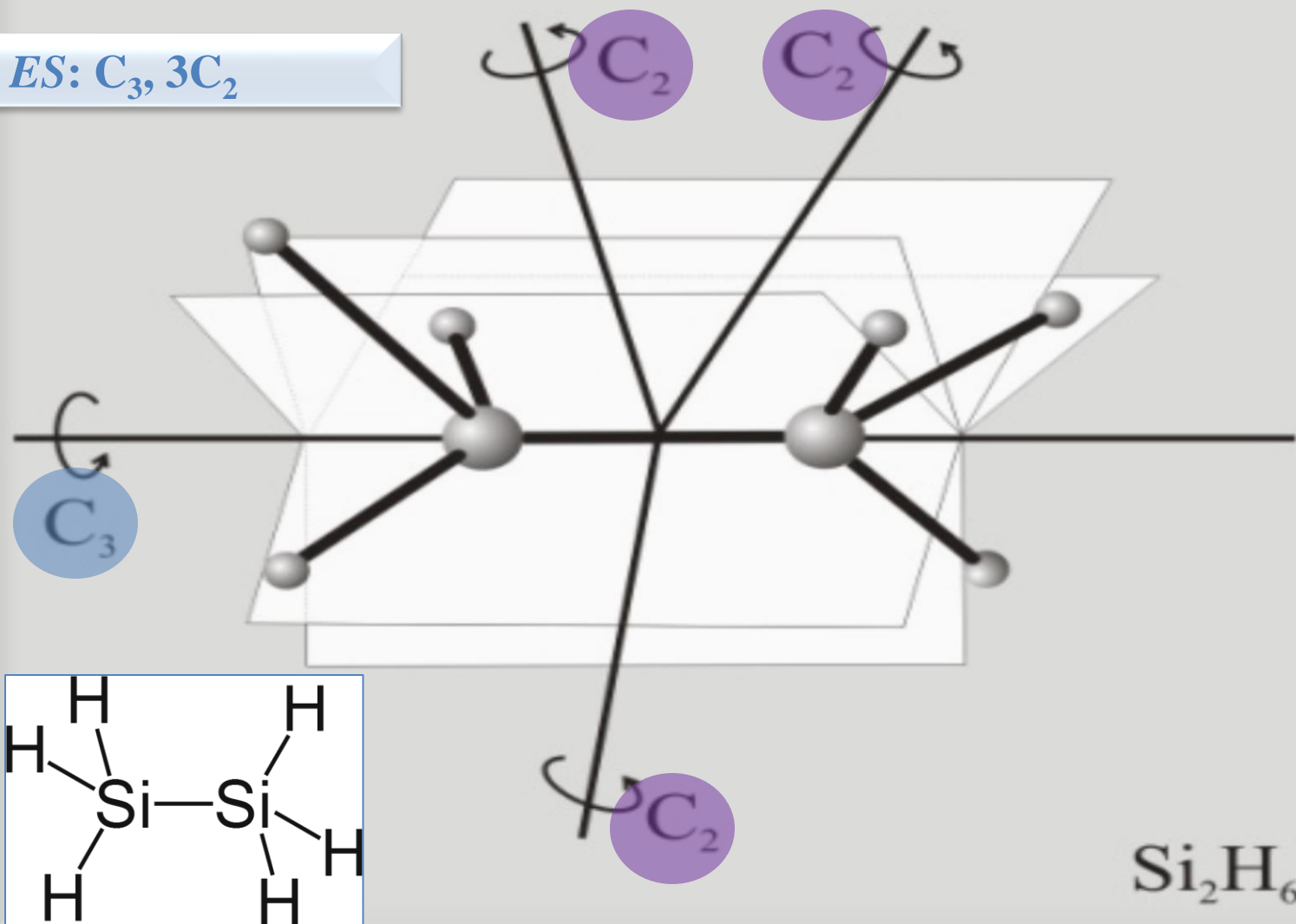
**Molekul  $NH_3$**



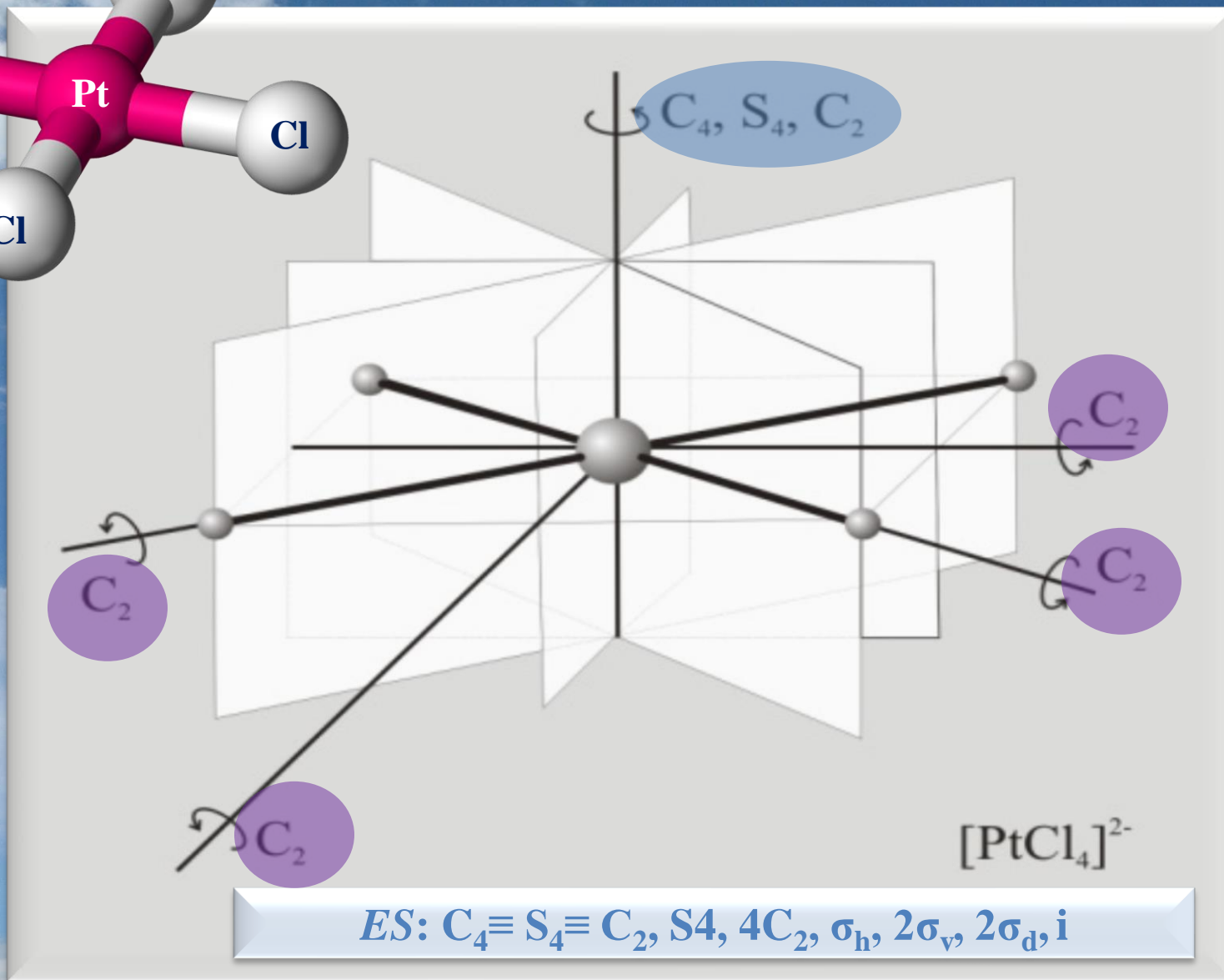
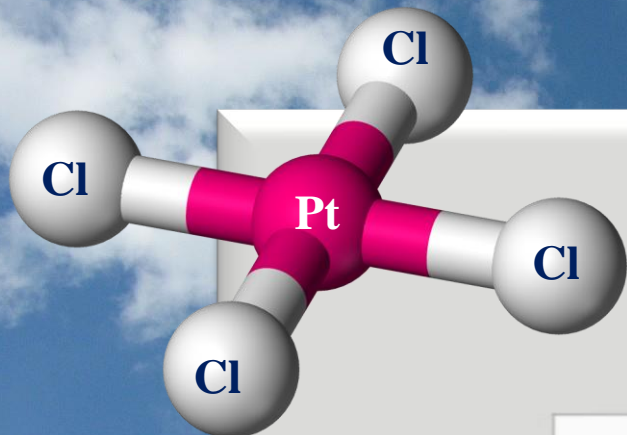
*ES:  $C_4 - C_2, 2\sigma_v, 2\sigma_d$*

**Molekul  $\text{BrF}_5$**

ES:  $C_3, 3C_2$

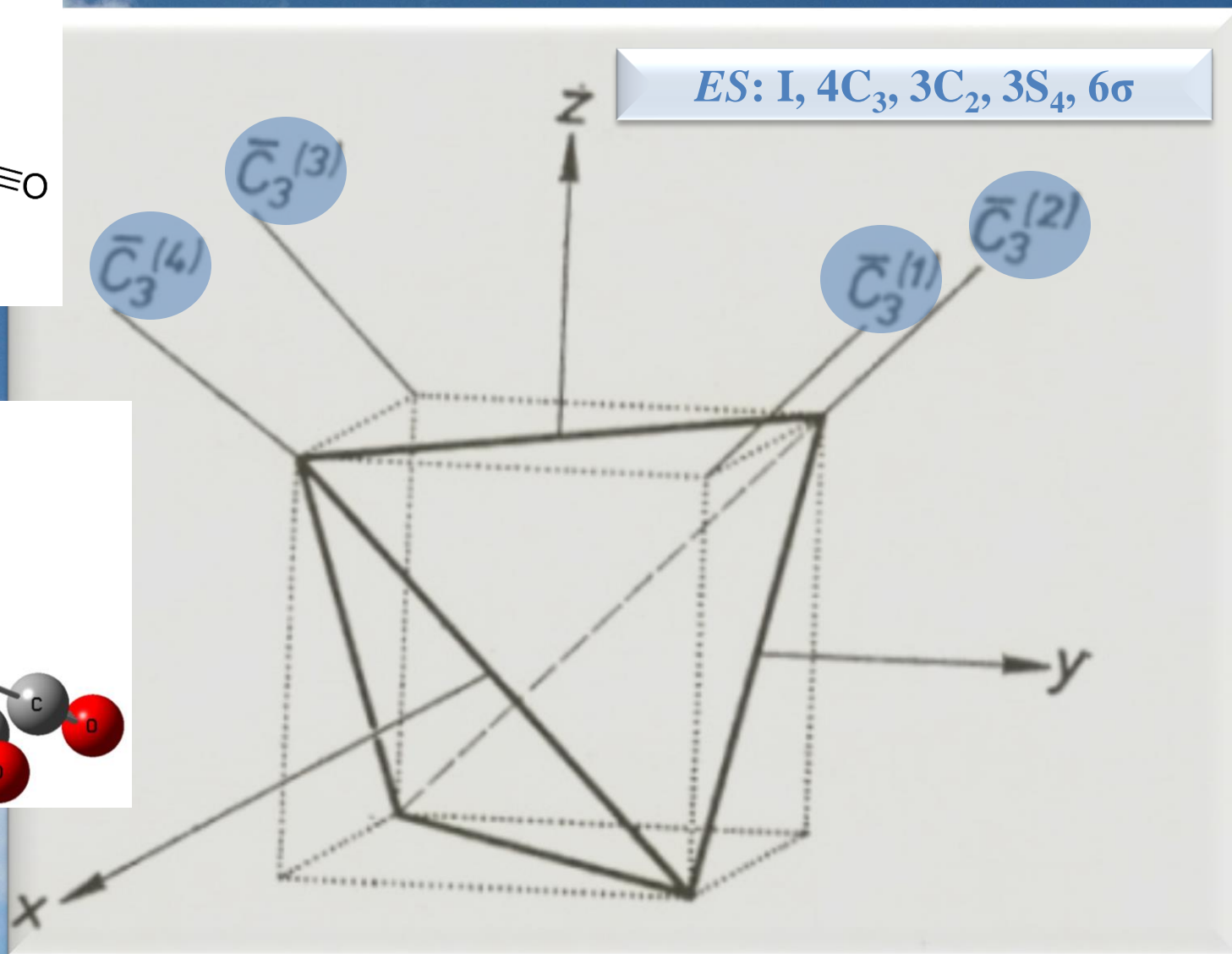
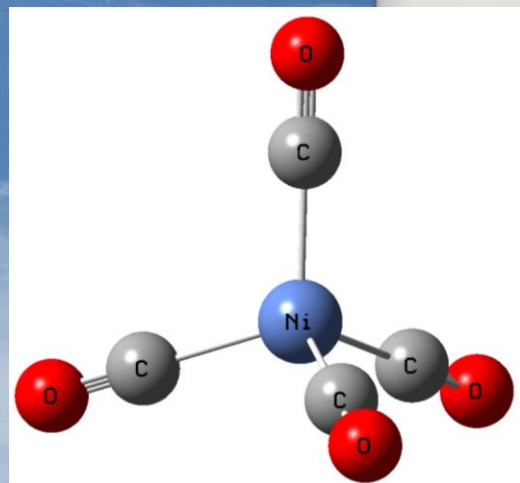
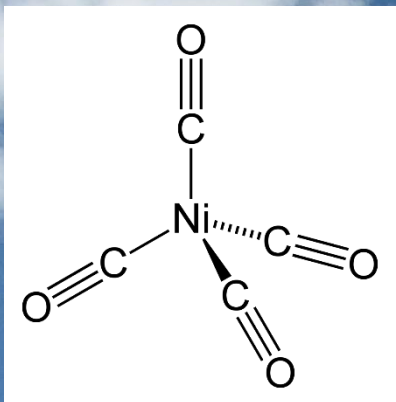


Molekul  $Si_2H_6$



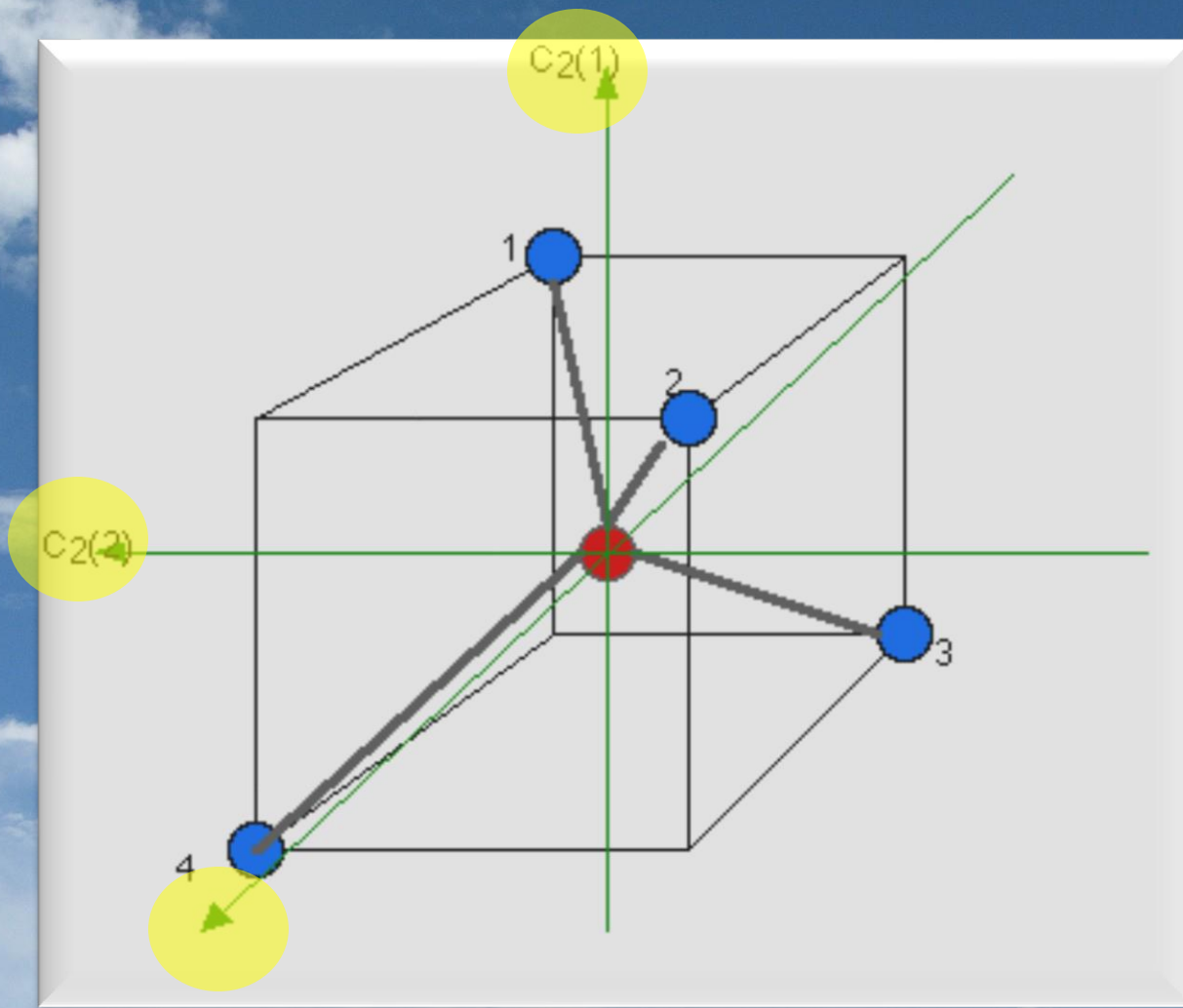
*ES:  $C_4 \equiv S_4 \equiv C_2, S_4, 4C_2, \sigma_h, 2\sigma_v, 2\sigma_d, i$*

**Kompleksni jon  $[\text{PtCl}_4]^{2-}$**

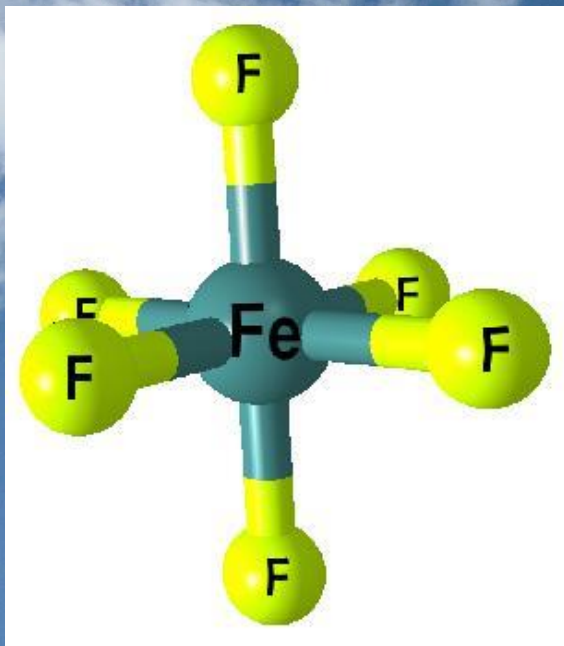


**Kompleks [Ni(CO)<sub>4</sub>]**

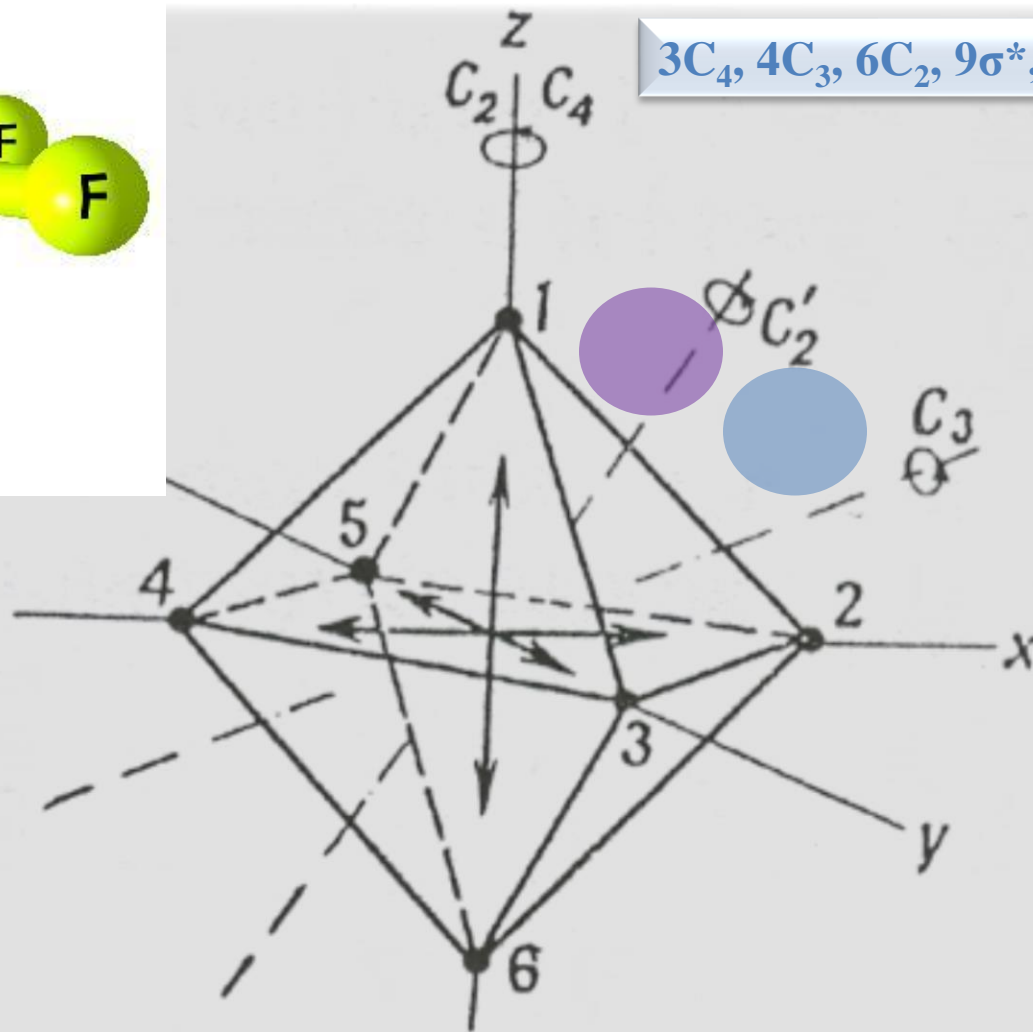




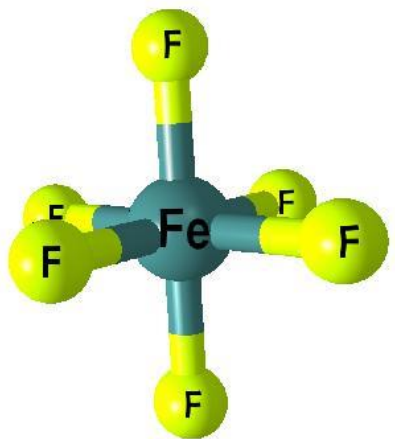
**Kompleks  $[\text{Ni}(\text{CO})_4]$**



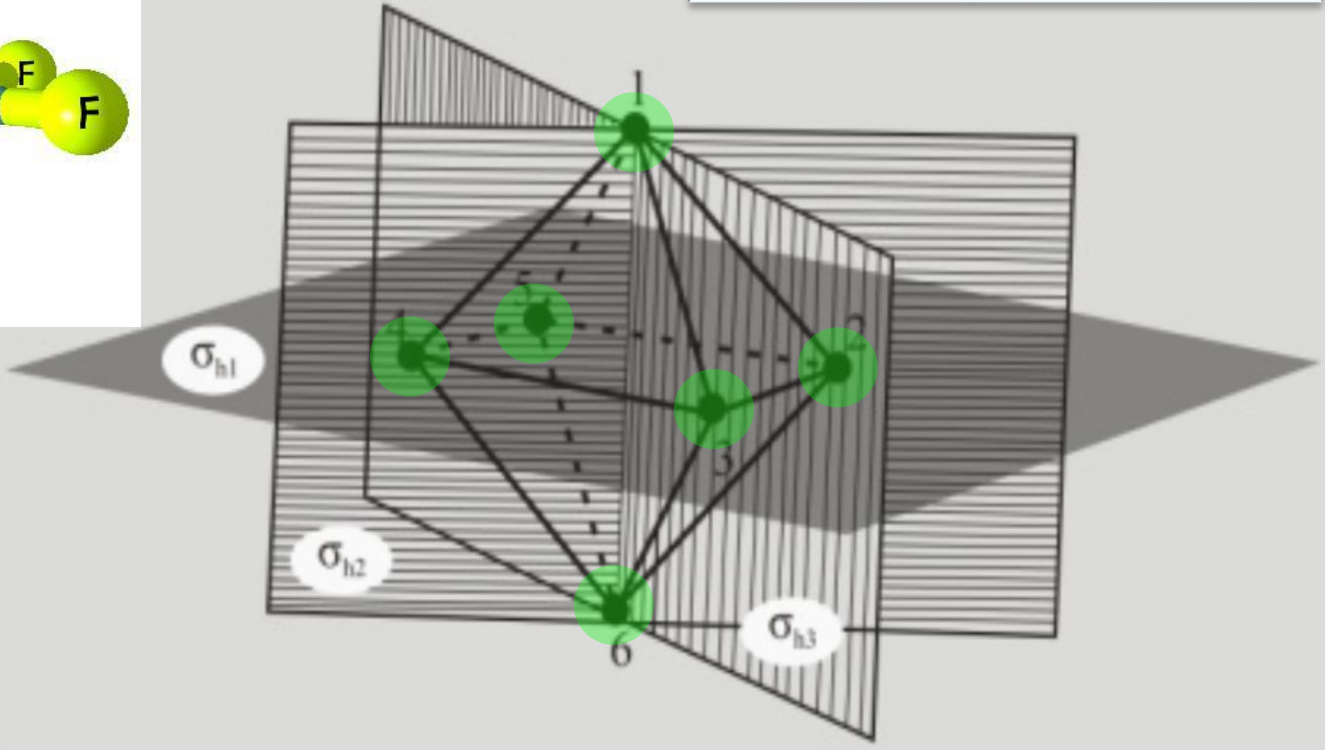
$3C_4, 4C_3, 6C_2, 9\sigma^*, 3S_6, 3S_4, i$



**Kompleksni jon  $[\text{FeF}_6]^{3-}$**



$3C_4, 4C_3, 6C_2, 9\sigma^*, 3S_6, 3S_4, i$



\*Od  $9\sigma$ :

- **3 su horizontalne** ( $\sigma_{h1}$ - sadrži  $F^-$  jone označene brojevima 2, 3, 4 i 5;  $\sigma_{h2}$ - sadrži  $F^-$  jone označene brojevima 1, 2, 6 i 4; i  $\sigma_{h3}$ - sadrži  $F^-$  jone označene brojevima 1, 3, 6 i 5),
- **6 su verikalne** i polove naspramne ivice oktaedra.

**Kompleksni jon  $[FeF_6]^{3-}$**

# MNOŽENJE SIMETRIJSKIH OPERACIJA

“Proizvod” simetrijskih operacija je njihovo postupno izvodenje po pravilu „s desna na levo“, prvo desna pa leva operacija u proizvodu.

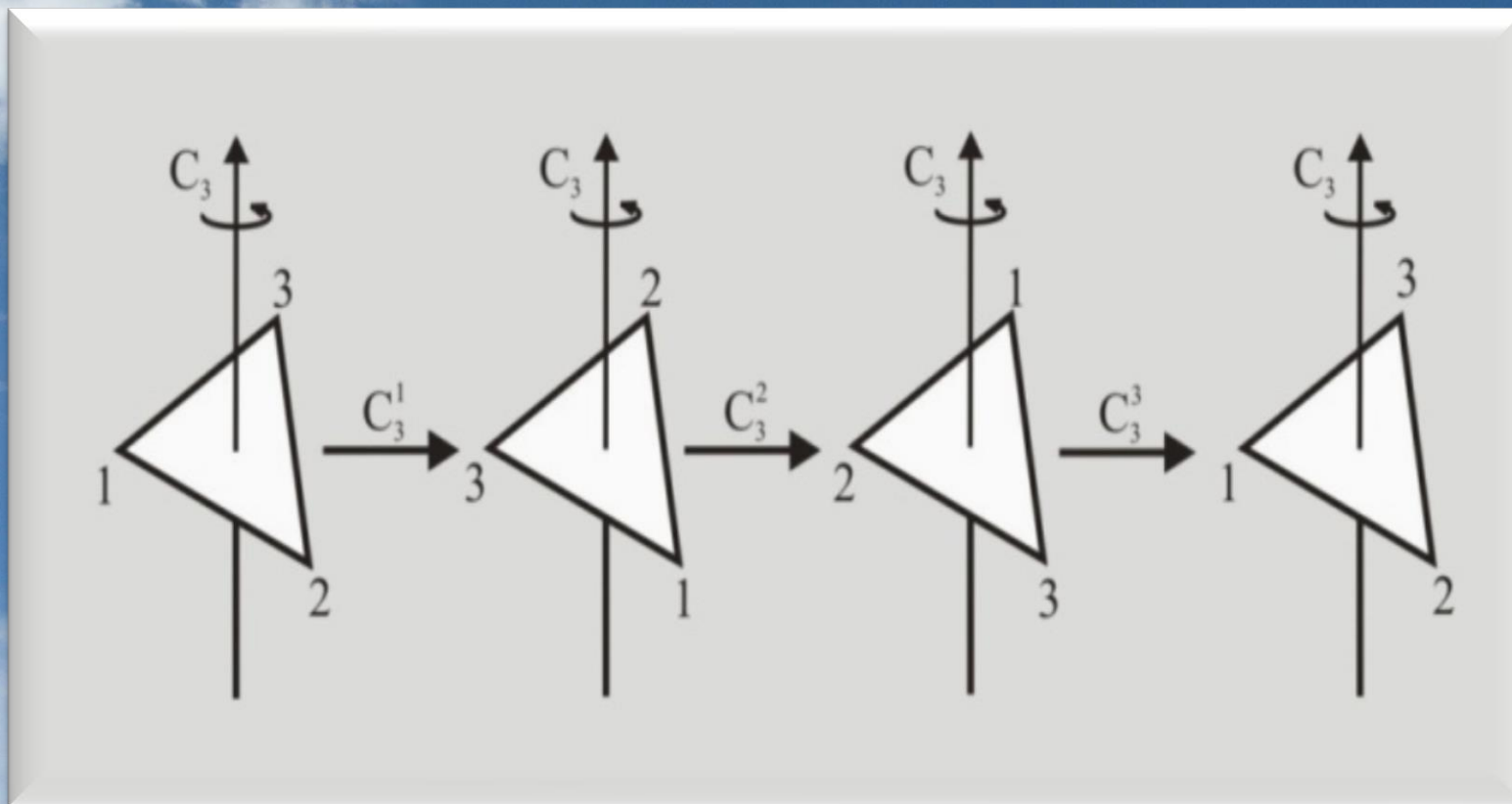
*Molekul: (NH<sub>3</sub>)*

Simetrijska grupa tačke:  $C_{3v}$

Elementi simetrije:  $C_3, 3\sigma_v$

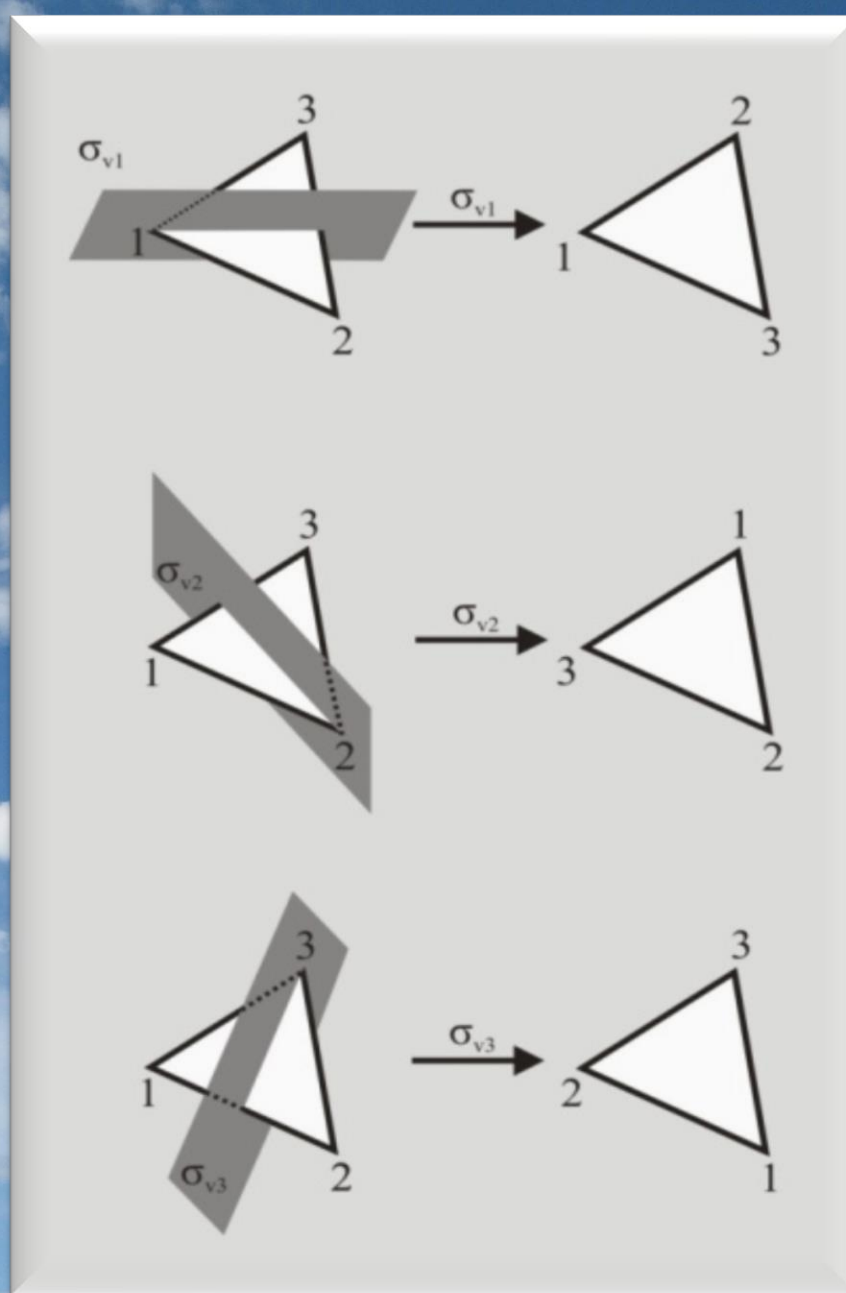
Operacije simetrije:  $I, C, C, C \equiv I, \sigma_{v1}, \sigma_{v2}, \sigma_{v3}$

## Prvi korak



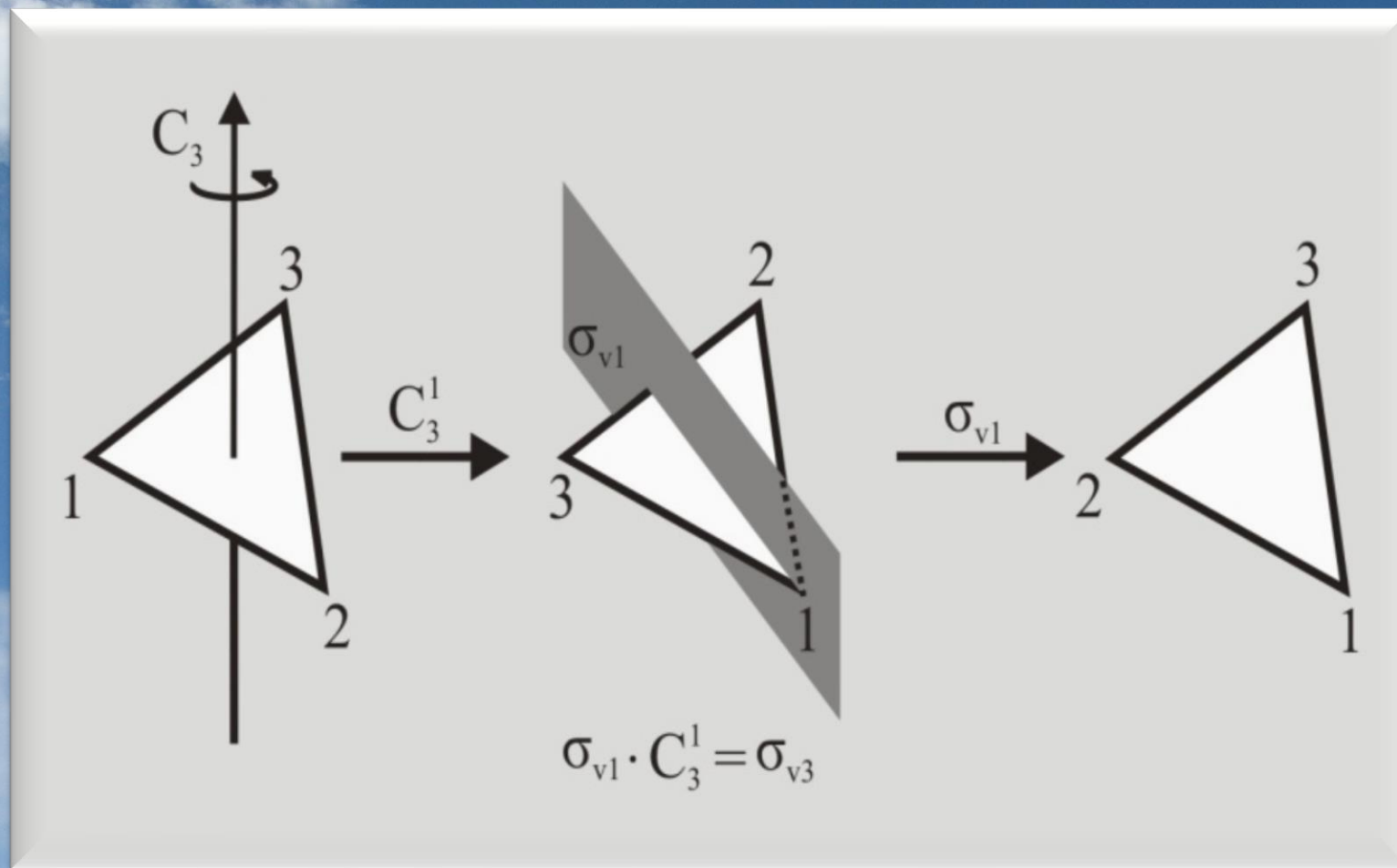
Rotacija molekula  $\text{NH}_3$  oko ose rotacije  $C_3$

## Drugi korak



Refleksija molekula  $\text{NH}_3$  u ravnima  $\sigma_{v1}$ ,  $\sigma_{v2}$ ,  $\sigma_{v3}$

## Treći korak



Ilustracija množenja simetrijskih operacija  $\sigma_{v1} \cdot C$  kod molekula  $\text{NH}_3$

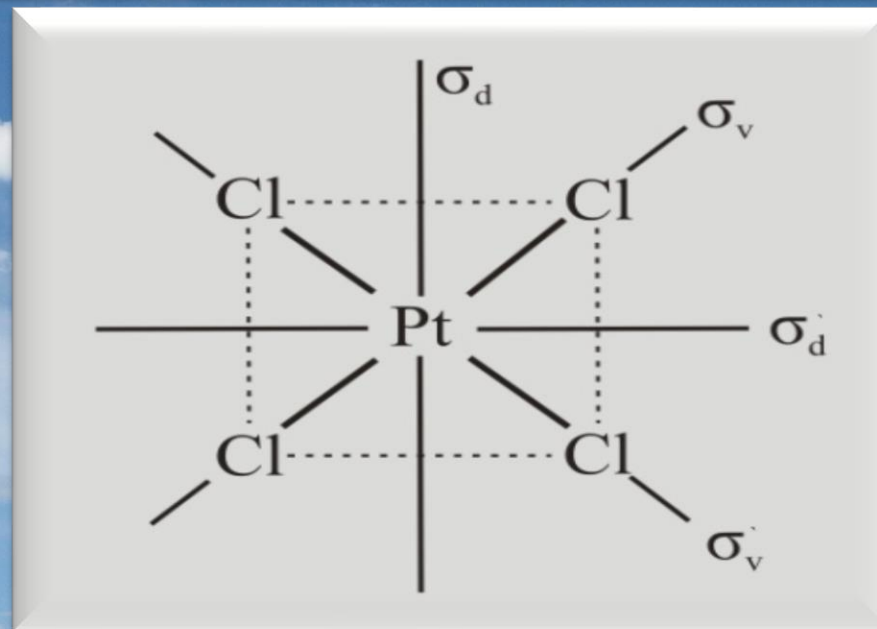
Tablica množenja simetrijskih operacija za  $C_{3v}$  grupu tačke

$C_{3v}$	I	$C_3^1$	$C_3^2$	$\sigma_{v1}$	$\sigma_{v2}$	$\sigma_{v3}$
I	I	$C_3^1$	$C_3^2$	$\sigma_{v1}$	$\sigma_{v2}$	$\sigma_{v3}$
$C_3^1$	$C_3^1$	$C_3^2$	I	$\sigma_{v3}$	$\sigma_{v1}$	$\sigma_{v2}$
$C_3^2$	$C_3^2$	I	$C_3^1$	$\sigma_{v2}$	$\sigma_{v3}$	$\sigma_{v1}$
$\sigma_{v1}$	$\sigma_{v1}$	$\sigma_{v2}$	$\sigma_{v3}$	I	$C_3^1$	$C_3^2$
$\sigma_{v2}$	$\sigma_{v2}$	$\sigma_{v3}$	$\sigma_{v1}$	$C_3^2$	I	$C_3^1$
$\sigma_{v3}$	$\sigma_{v3}$	$\sigma_{v1}$	$\sigma_{v2}$	$C_3^1$	$C_3^2$	I



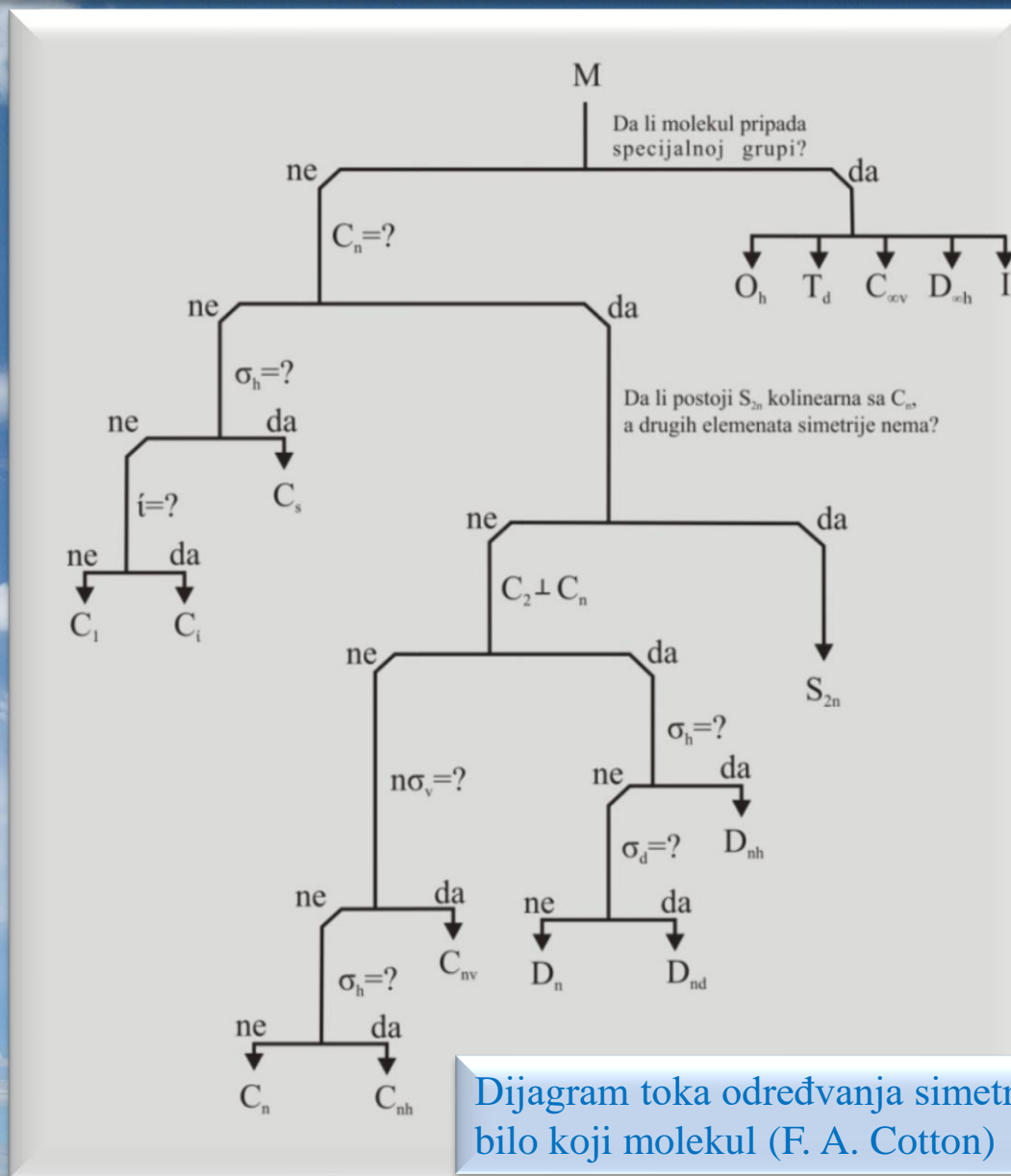
## Klase elemenata

- Elementi grupe se mogu razdvajati u manje skupove i ako su svi elementi u takvom skupu konjugovani (povezani transformacijama sličnosti) oni čine **klase**.
- Dve klase elemenata nemaju zajedničkih elemenata.
- Ekvivalentni elementi su oni koji se mogu prevesti jedni u druge pomoću operacija simetrije.

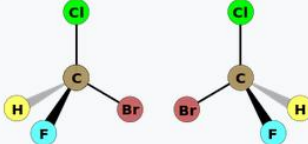
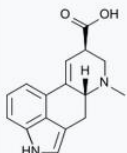
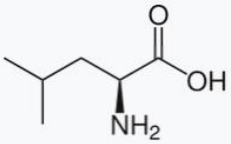



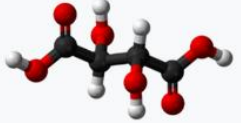
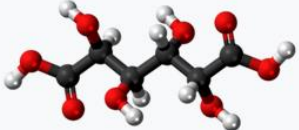

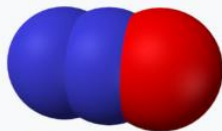
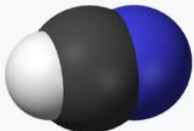


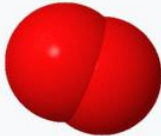

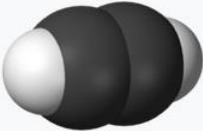
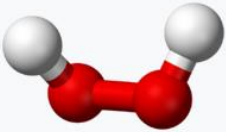

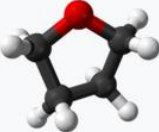

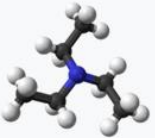
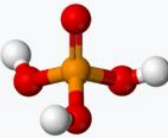
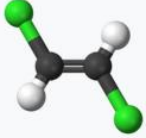

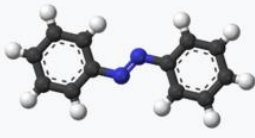
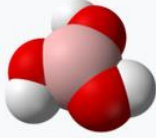
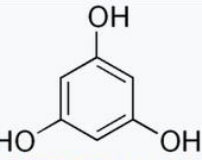
Vertikalne i dihedralne ravni u kompleksnom jonu  $[\text{PtCl}_4]^{2-}$


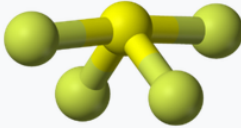

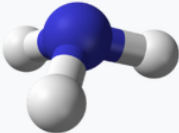

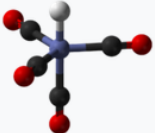

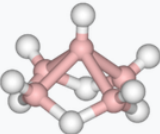
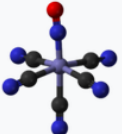
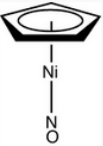
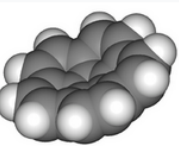
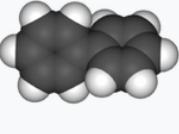
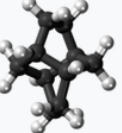
# Sistematsko razvrstavanje molekula prema simetrijskim elementima

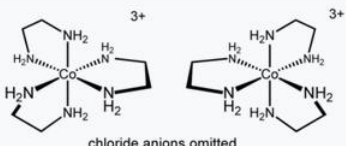
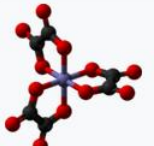

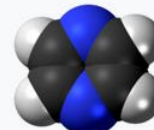




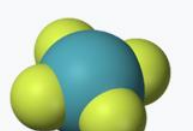

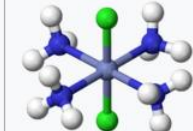







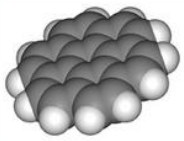

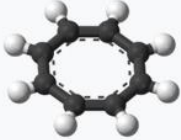

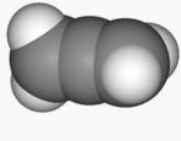
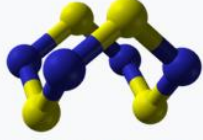
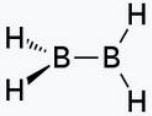



Dijagram toka određivanja simetrijske grupe tačke za bilo koji molekul (F. A. Cotton)

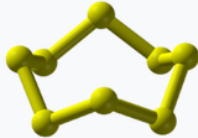
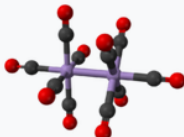

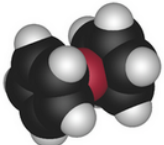
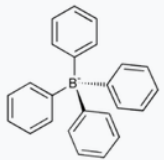

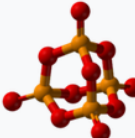
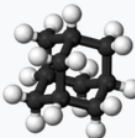
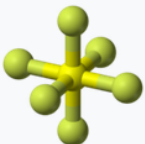

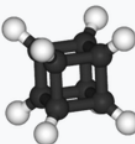
Point group	Symmetry operations	Simple description of typical geometry	Example 1	Example 2	Example 3
$C_1$	E	no symmetry, chiral	 <p>bromochlorofluoromethane (both enantiomers shown)</p>	 <p>lysergic acid</p>	 <p>L-leucine and most other <math>\alpha</math>-amino acids except glycine</p>
$C_s$	$E \sigma_h$	mirror plane, no other symmetry	 <p>thionyl chloride</p>	 <p>hypochlorous acid</p>	 <p>chloriodomethane</p>
$C_i$	$E i$	inversion center	 <p>meso-tartaric acid</p>	 <p>mucic acid (meso-galactaric acid)</p>	(S,R) 1,2-dibromo-1,2-dichloroethane ( <i>anti</i> conformer)
$C_{\infty v}$	$E 2C_{\infty} \infty\sigma_v$	linear	 <p>hydrogen fluoride (and all other heteronuclear diatomic molecules)</p>	 <p>nitrous oxide (dinitrogen monoxide)</p>	 <p>hydrocyanic acid (hydrogen cyanide)</p>

$D_{\infty h}$	$E 2C_{\infty} \infty\sigma_i / 2S_{\infty} \infty C_2$	linear with inversion center	 <p>oxygen (and all other homonuclear diatomic molecules)</p>	 <p>carbon dioxide</p>	 <p>acetylene (ethyne)</p>
$C_2$	$E C_2$	"open book geometry," chiral	 <p>hydrogen peroxide</p>	 <p>hydrazine</p>	 <p>tetrahydrofuran (twist conformation)</p>
$C_3$	$E C_3$	propeller, chiral	 <p>triphenylphosphine</p>	 <p>triethylamine</p>	 <p>phosphoric acid</p>
$C_{2h}$	$E C_2 / \sigma_h$	planar with inversion center	 <p><i>trans</i>-1,2-dichloroethylene</p>	 <p><i>trans</i>-dinitrogen difluoride</p>	 <p><i>trans</i>-azobenzene</p>
$C_{3h}$	$E C_3 C_3^2 \sigma_h S_3 S_3^5$	propeller	 <p>boric acid</p>	 <p>phloroglucinol (1,3,5-trihydroxybenzene)</p>	

$C_{2v}$	$E C_2 \sigma_v(xz) \sigma_v'(yz)$	angular ( $H_2O$ ) or see-saw ( $SF_4$ )	 water	 sulfur tetrafluoride	 pyrrole
$C_{3v}$	$E 2C_3 3\sigma_v$	trigonal pyramidal or tetrahedral	 ammonia	 phosphorus oxychloride	 cobalt tetracarbonyl hydride, $HCo(CO)_4$
$C_{4v}$	$E 2C_4 C_2 2\sigma_v 2\sigma_d$	square pyramidal	 xenon oxytetrafluoride	 pentaborane(9), $B_5H_9$	 nitroprusside anion $[Fe(CN)_5(NO)]^{2-}$
$C_{5v}$	$E 2C_5 2C_5^2 5\sigma_v$	'milking stool' complex	 $Ni(C_5H_5)(NO)$	 corannulene	
$D_2$	$E C_2(x) C_2(y) C_2(z)$	twist, chiral	 biphenyl (skew conformation)	 twistane ( $C_{10}H_{16}$ )	cyclohexane twist conformation

$D_3$	$E C_3(z) 3C_2$	triple helix, chiral	 <p>chloride anions omitted Tris(ethylenediamine)cobalt(III) cation</p>	 <p>tris(oxalato)iron(III) anion</p>	
$D_{2h}$	$E C_2(z) C_2(y) C_2(x) i \sigma(xy) \sigma(xz) \sigma(yz)$	planar with inversion center	 <p>ethylene</p>	 <p>pyrazine</p>	 <p>diborane</p>
$D_{3h}$	$E 2C_3 3C_2 \sigma_h 2S_3 3\sigma_v$	trigonal planar or trigonal bipyramidal	 <p>boron trifluoride</p>	 <p>phosphorus pentachloride</p>	 <p>cyclopropane</p>
$D_{4h}$	$E 2C_4 C_2 2C_2' 2C_2 i 2S_4 \sigma_h 2\sigma_v 2\sigma_d$	square planar	 <p>xenon tetrafluoride</p>	 <p>octachlorodimolybdate(II) anion</p>	 <p>Trans-[Co<sup>III</sup>(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]<sup>+</sup> (excluding H atoms)</p>
$D_{5h}$	$E 2C_5 2C_5^2 5C_2 \sigma_h 2S_5 2S_5^3 5\sigma_v$	pentagonal	 <p>cyclopentadienyl anion</p>	 <p>ruthenocene</p>	 <p>C<sub>70</sub></p>

$D_{6h}$	$E 2C_6 2C_3 C_2 3C_2' 3C_2'' i 2S_3 2S_6 \sigma_h 3\sigma_d 3\sigma_v$	hexagonal	 benzene	 bis(benzene)chromium	 coronene ( $C_{24}H_{12}$ )
$D_{7h}$	$E C_7 S_7 7C_2 \sigma_h 7\sigma_v$	heptagonal	 tropylium ( $C_7H_7^+$ ) cation		
$D_{8h}$	$E C_8 C_4 C_2 S_8 i 8C_2 \sigma_h 4\sigma_v 4\sigma_d$	octagonal	 cyclooctatetraenide ( $C_8H_8^{2-}$ ) anion	 uranocene	
$D_{2d}$	$E 2S_4 C_2 2C_2' 2\sigma_d$	90° twist	 allene	 tetrasulfur tetranitride	 diborane(4) (excited state)
$D_{3d}$	$E 2C_3 3C_2 i 2S_6 3\sigma_d$	60° twist	 ethane (staggered rotamer)	 dicobalt octacarbonyl (non-bridged isomer)	 cyclohexane chair conformation

$D_{4d}$	$E 2S_8 2C_4 2S_8^3 C_2 4C_2' 4\sigma_d$	45° twist	 <p>sulfur (crown conformation of <math>S_8</math>)</p>	 <p>dimanganese decacarbonyl (staggered rotamer)</p>	 <p>octafluoroxenate ion (idealised geometry)</p>
$D_{5d}$	$E 2C_5 2C_5^2 5C_2 / 3S_{10}^3 2S_{10} 5\sigma_d$	36° twist	 <p>ferrocene (staggered rotamer)</p>		
$S_4$	$E 2S_4 C_2$		 <p>tetraphenylborate anion</p>		
$T_d$	$E 8C_3 3C_2 6S_4 6\sigma_d$	tetrahedral	 <p>methane</p>	 <p>phosphorus pentoxide</p>	 <p>adamantane</p>
$O_h$	$E 8C_3 6C_2 6C_4 3C_2 / 6S_4 8S_6 3\sigma_h 6\sigma_d$	octahedral or cubic	 <p>sulfur hexafluoride</p>	 <p>molybdenum hexacarbonyl</p>	 <p>cubane</p>



# Tabele karaktera

Simbol grupe tačke

- Elementi grupe
- Klase simetrijskih operacija pomnožene sa brojem operacija u klasi

$D_3$	E	$2C_3$	$2C_2$	
$A_1$	1	1	1	z, $R_z$ (x, y) ( $R_x, R_y$ )
$A_2$	1	1	-1	
E	2	-1	0	

Oznake nesvodljivih predstavljanja grupe tačke

Oznake koordinata ili nekih njihovih funkcija

Karakteristi nesvodljivih predstavljanja

# Označavanje nesvodljivih predstavljanja matrica

**A**



**jednodimenzionalne** matrice (reprezentacije) koje rotacijom za ugao  $\varphi$  oko glavne ose  $C_n$  imaju karakter **+1**.

**B**



**jednodimenzionalne** matrice (reprezentacije) koje rotacijom za ugao  $\varphi$  oko glavne ose  $C_n$  imaju karakter **-1**.

**E**



**dvodimenzionalne** matrice (reprezentacije)

**T**



**trodimenzionalne** matrice (reprezentacije)

**indeks 1**



... karakter **+1** za pravu ili nepravu rotaciju oko ose najvišeg reda, i refleksije u ravni  $\sigma_v$  ukoliko nema rotacije

**indeks 2**



... karakter **-1** za pravu ili nepravu rotaciju oko ose najvišeg reda, i refleksije u ravni  $\sigma_v$  ukoliko nema rotacije

slovo **g**



Karakter **+1** u odnosu na centar inverzije

slovo **u**



Karakter **-1** u odnosu na centar inverzije

superskript **'**



Karakter **+1** u odnosu na  $\sigma_h$

superskript **''**



Karakter **-1** u odnosu na  $\sigma_h$