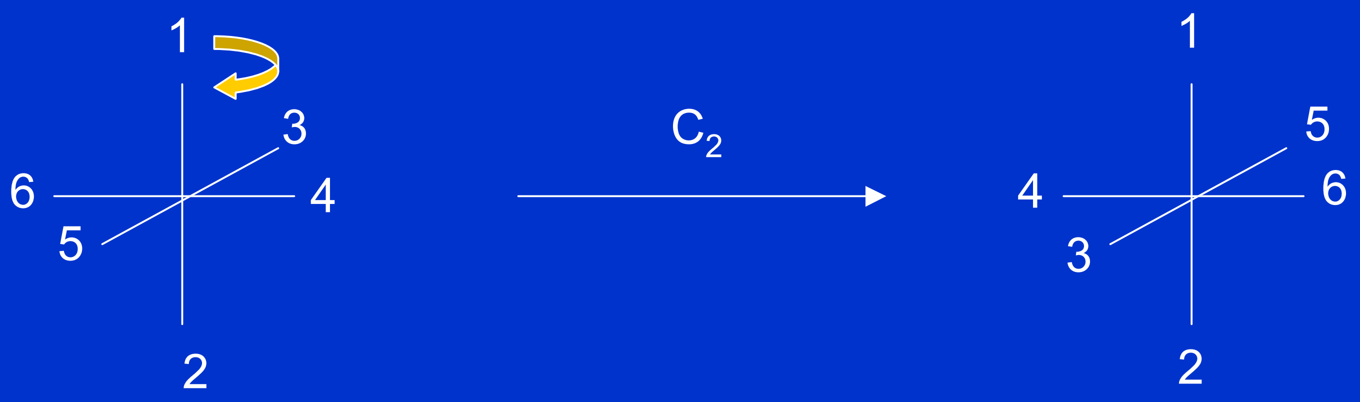
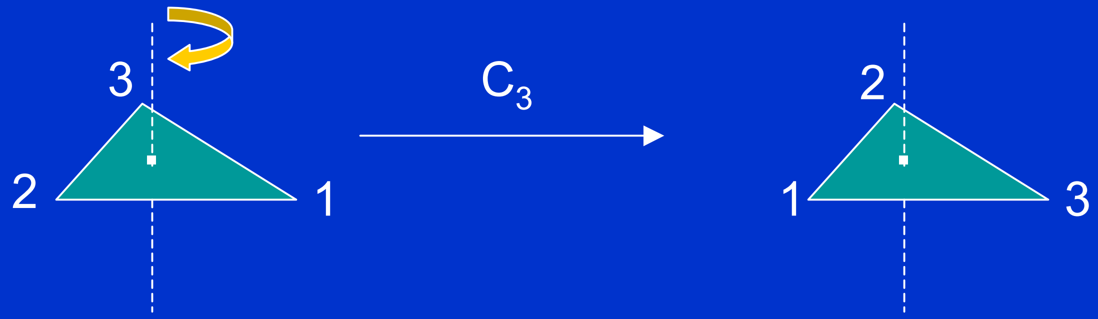
Cap 2. Simetria

Elementos de Simetria

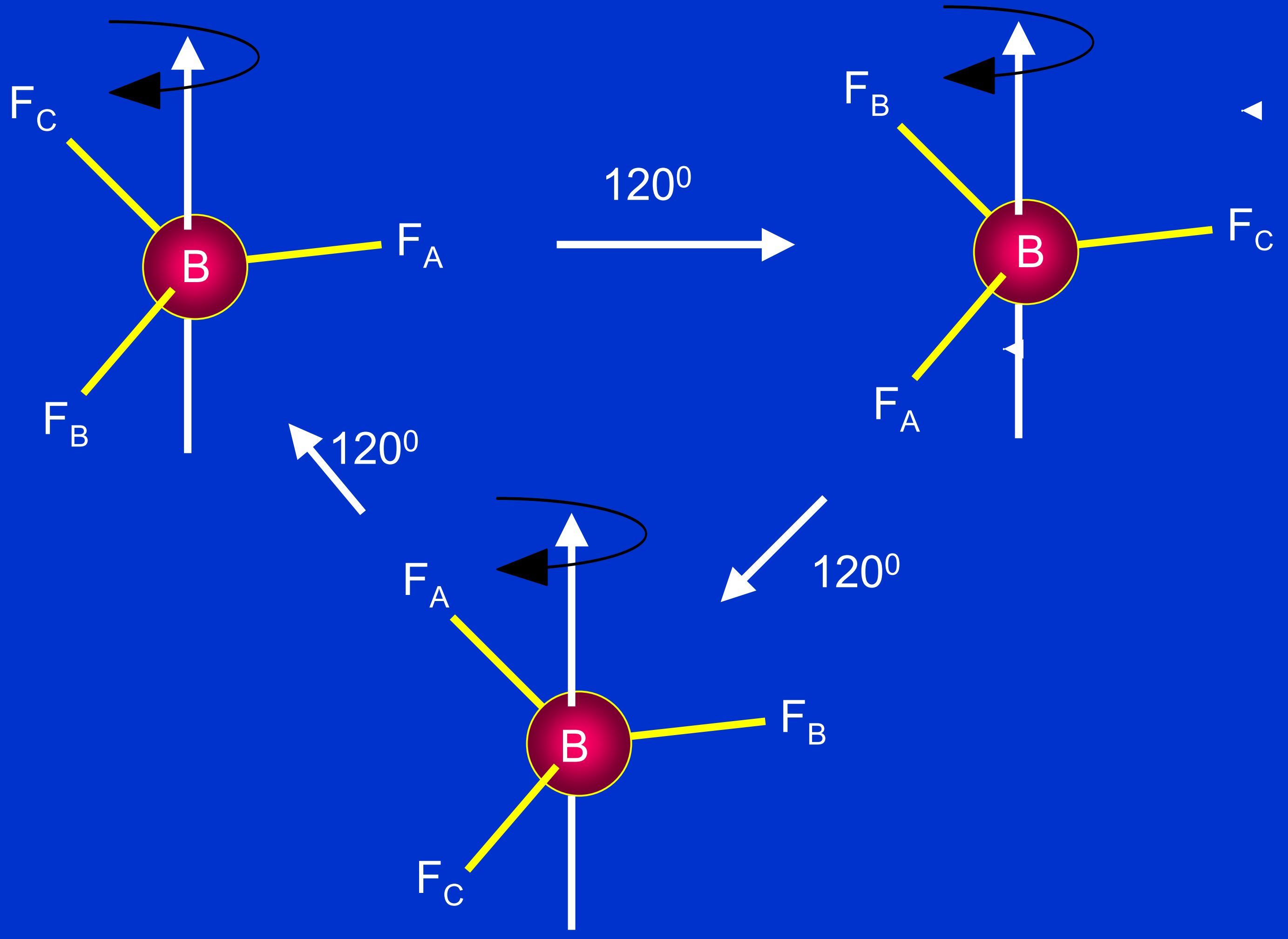
Grupo Pontual

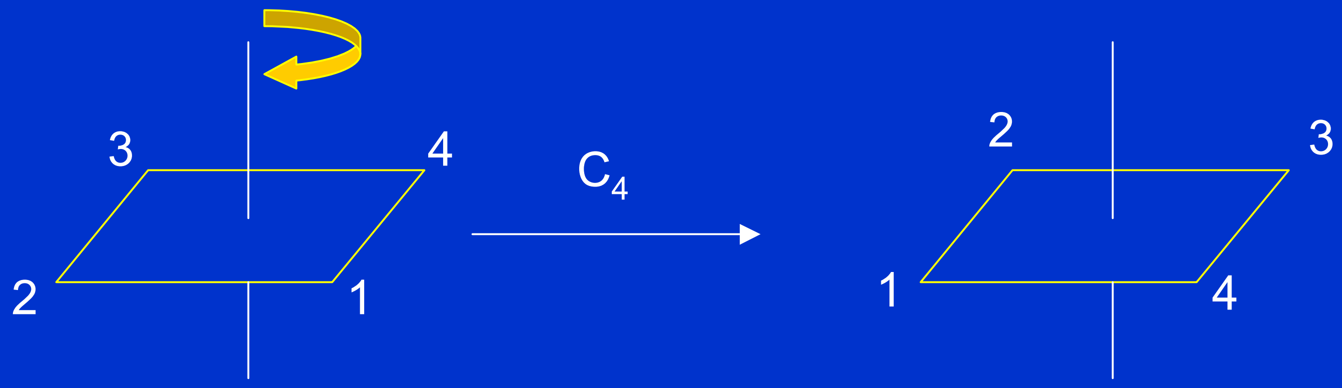
1. Eixos de Rotação





Molécula com eixo de rotação C_3

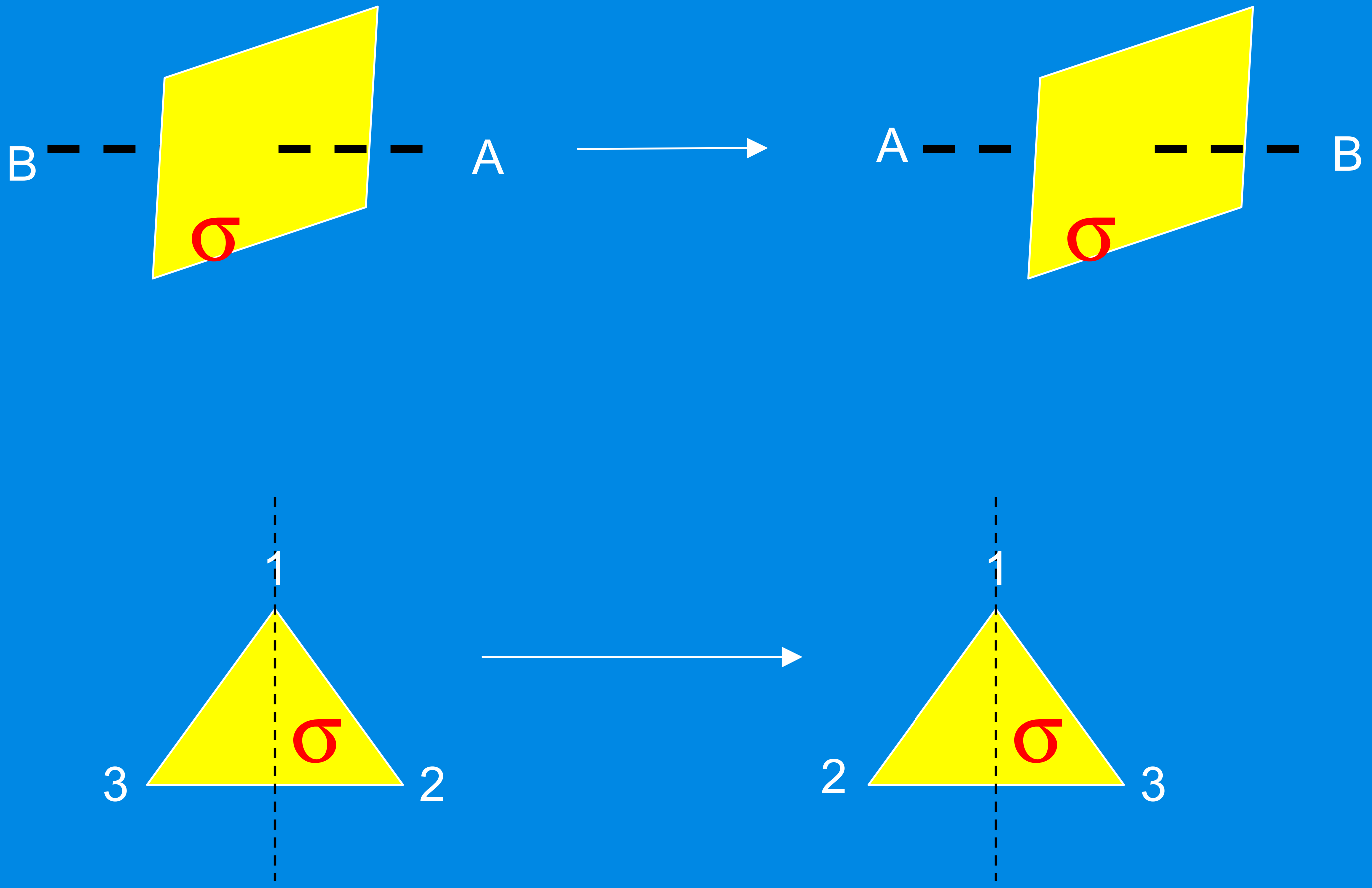


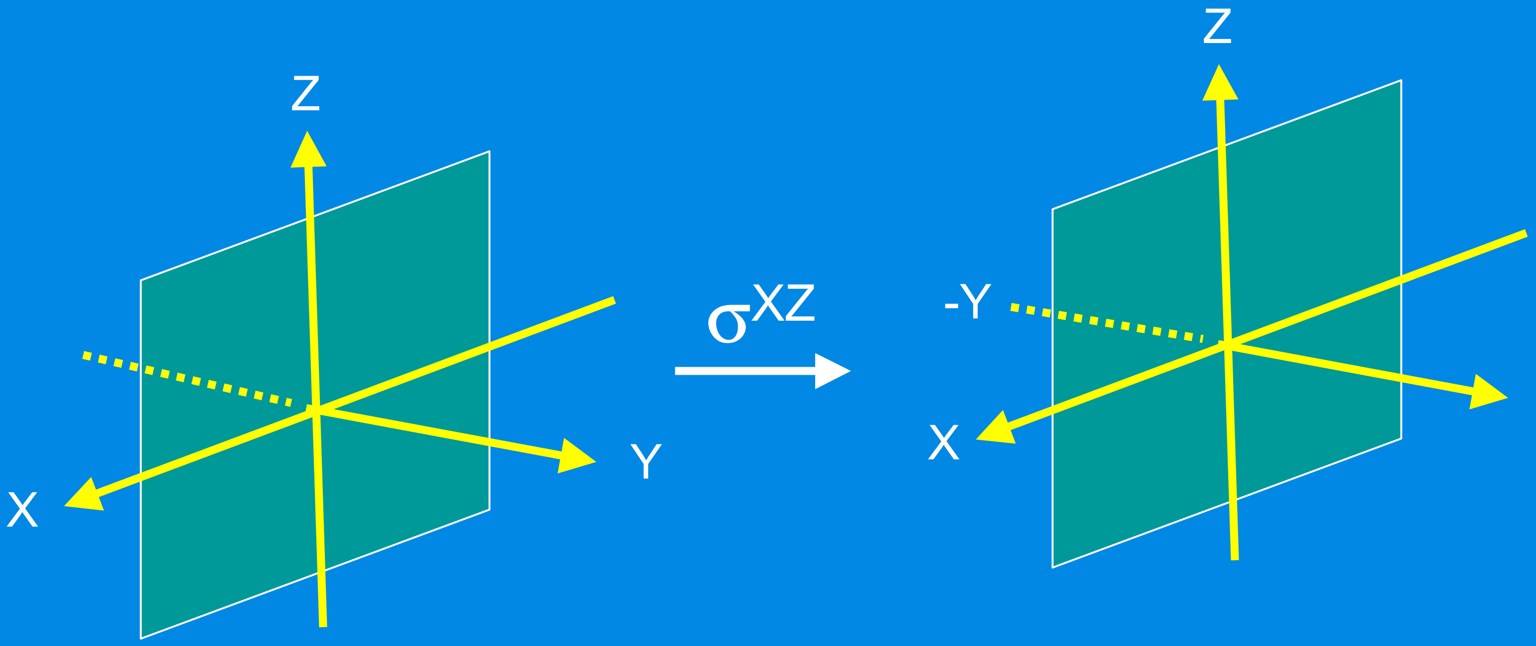


Operação de rotação própria

$$C_n = \frac{2\pi}{n}$$

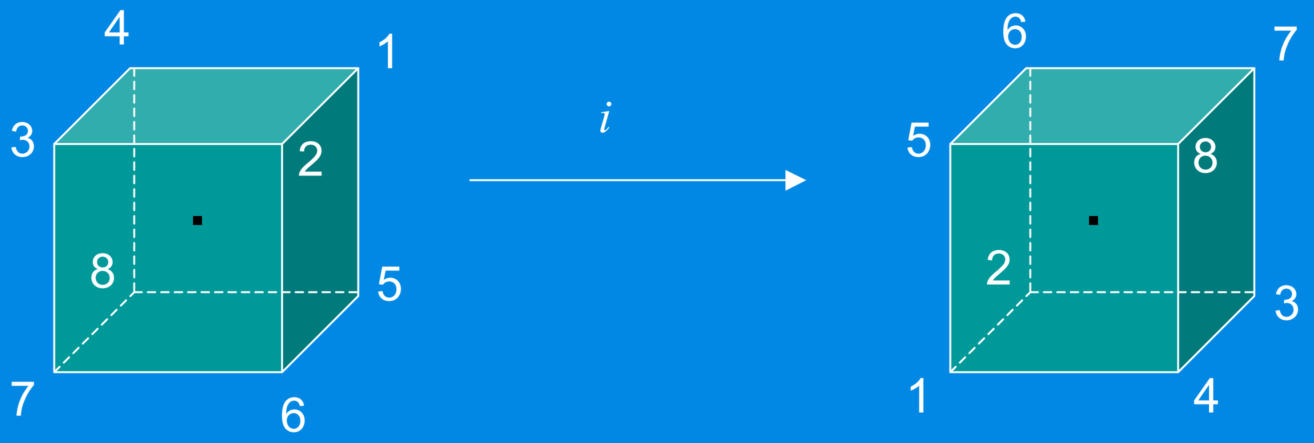
2. plano



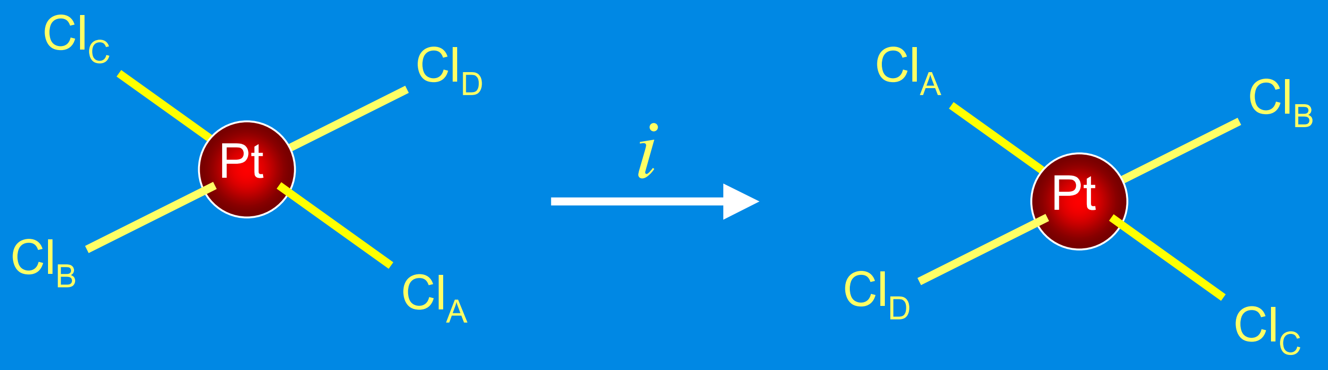


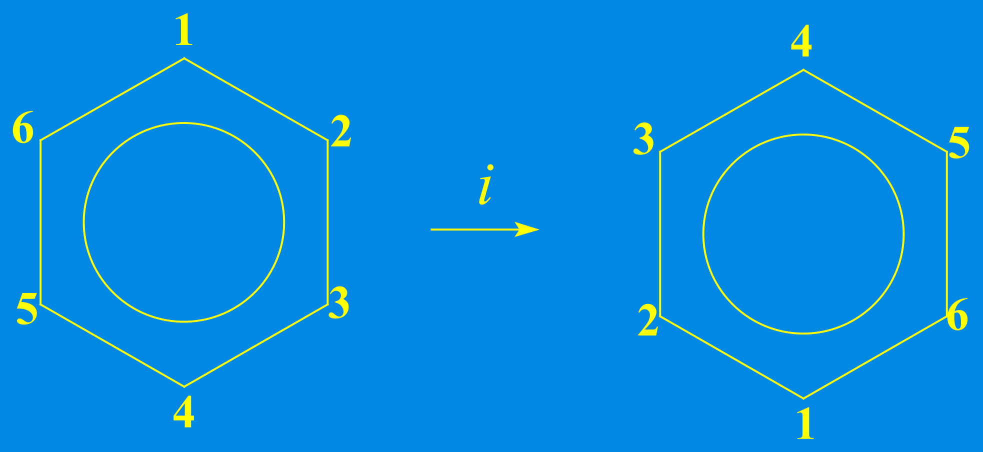
$$(X,Y,Z) \xrightarrow{\sigma^{XZ}} X,-Y,Z)$$

3. Centro de inversão

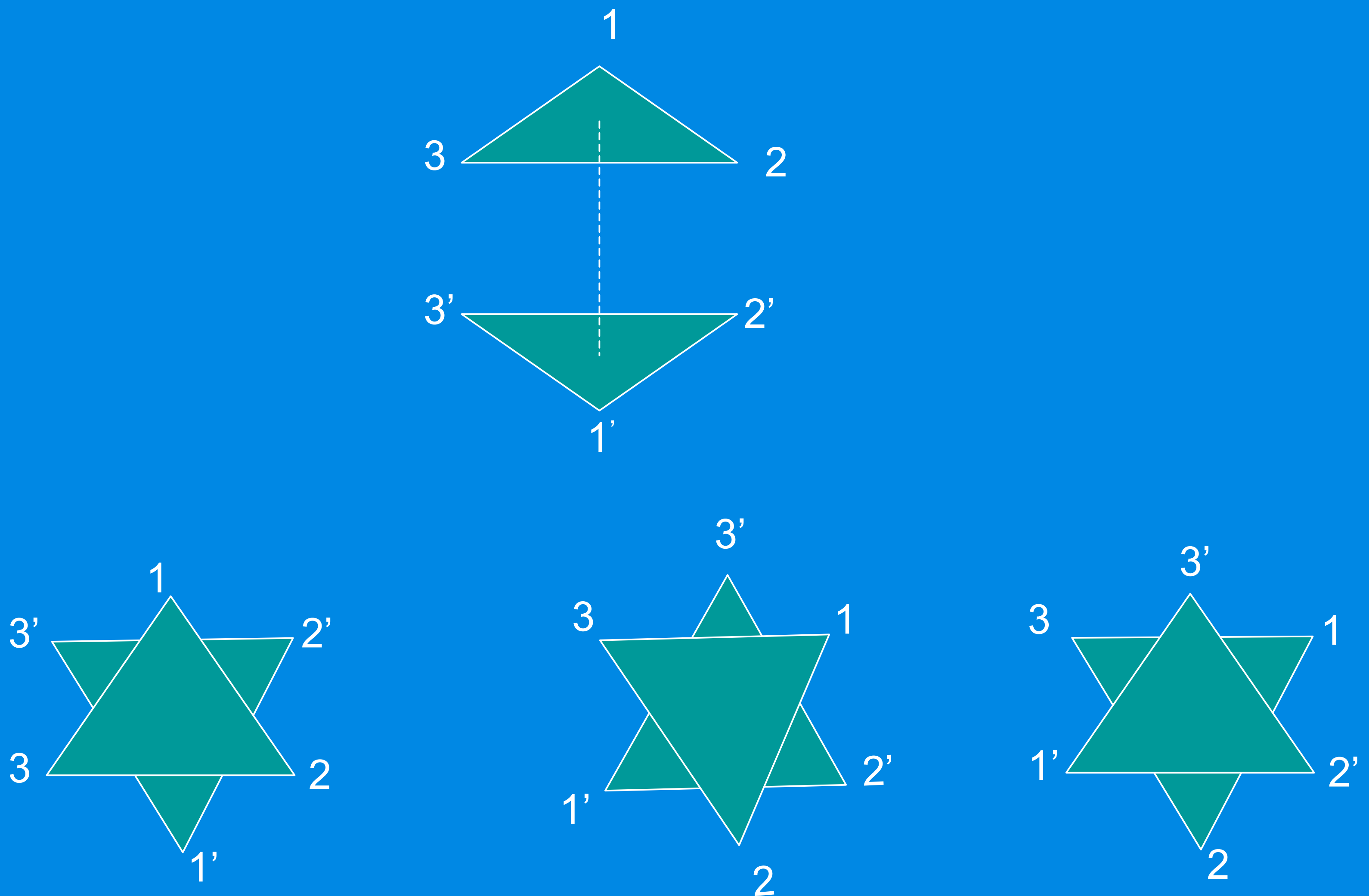


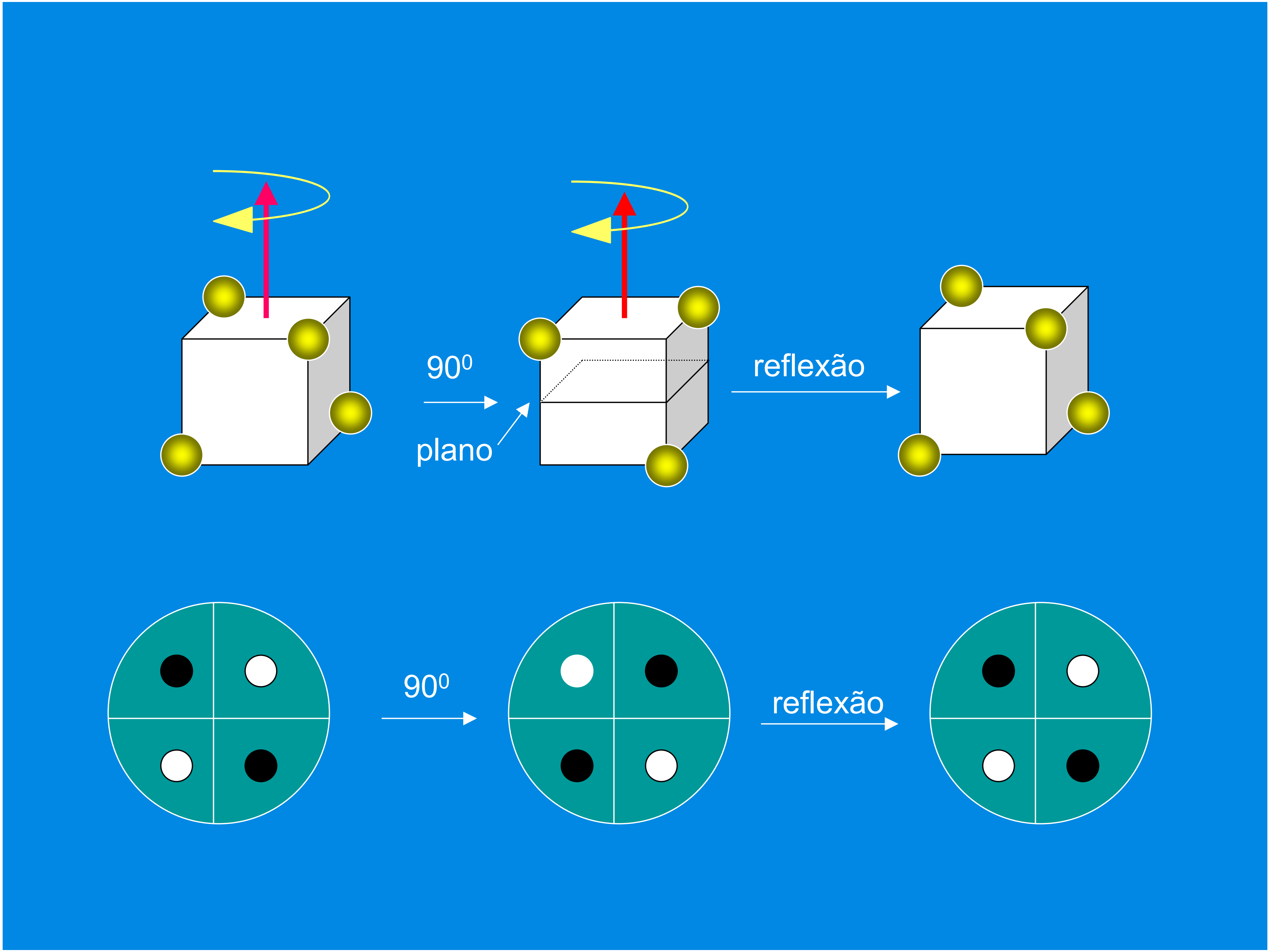
$$[x,y,z] \xrightarrow{i} [-x,-y,-z]$$


Cl$_C$
Cl$_D$
Pt
Cl$_B$
Cl$_A$
i
Cl$_A$
Cl$_B$
Pt
Cl$_D$
Cl$_C$


1
6
2
5
3
4
i
4
3
5
2
6
1

4. Rotação reflexão (rotaçãoimprópria)





90⁰
plano
reflexão
90⁰
reflexão

Classificação das Simetrias de Grupos Pontuais

1. Grupos especiais: a) moléculas lineares: $C_{\infty v}$, $D_{\infty h}$
b) eixos múltiplos de ordem elevada: O_h, T_d, T, T_h, I, I_h

↓

2. Não possui eixos de rotação própria ou imprópria: C_1, C_s, C_i

↓

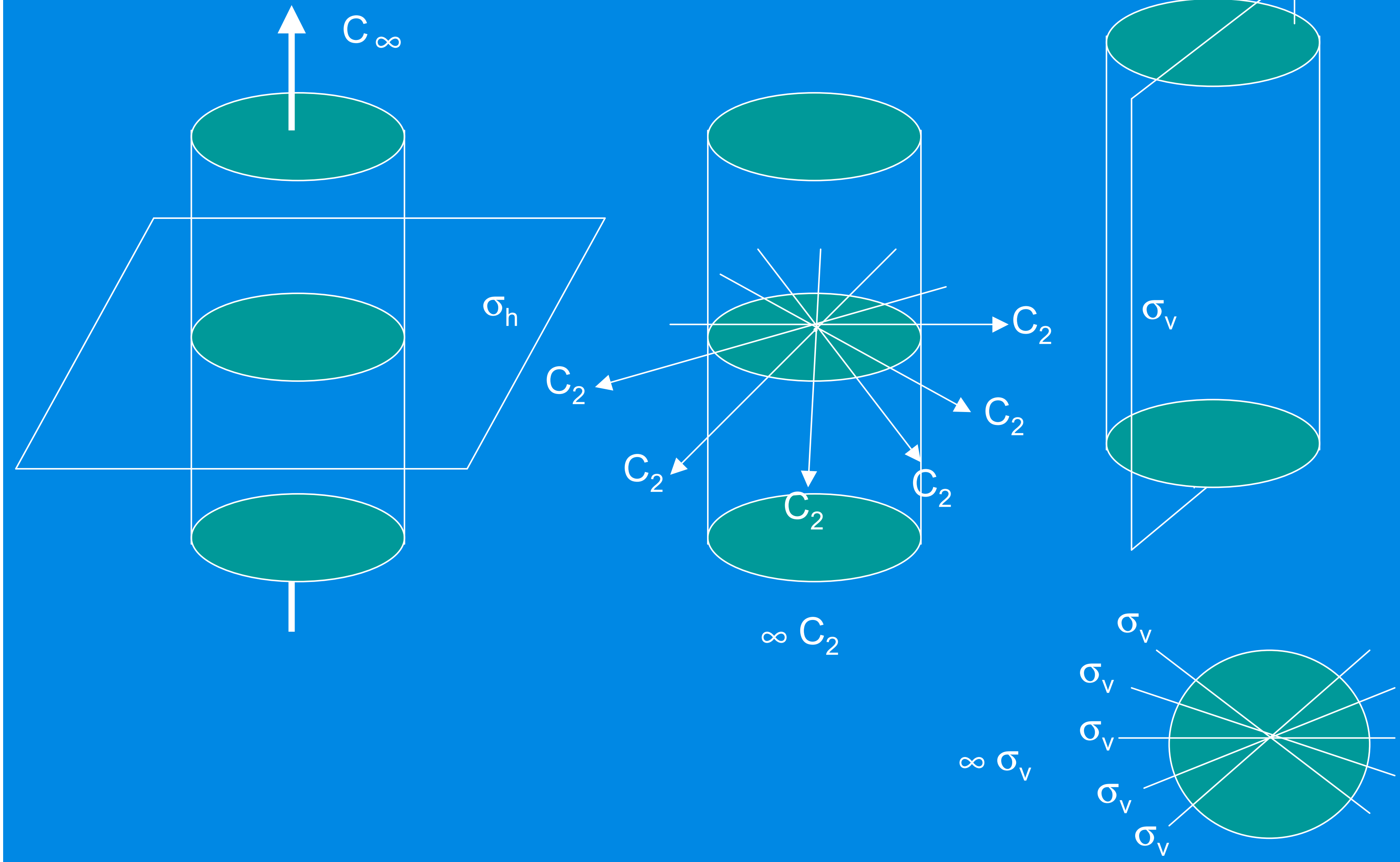
3. Sómente eixo de rotação imprópria (n par): S_n n=2, 4, 6

↓ eixo C_n

não possui $nC_2 \perp C_n$:
- σ_h → C_{nh}
- σ_v → C_{nv}
- ñ σ → C_n

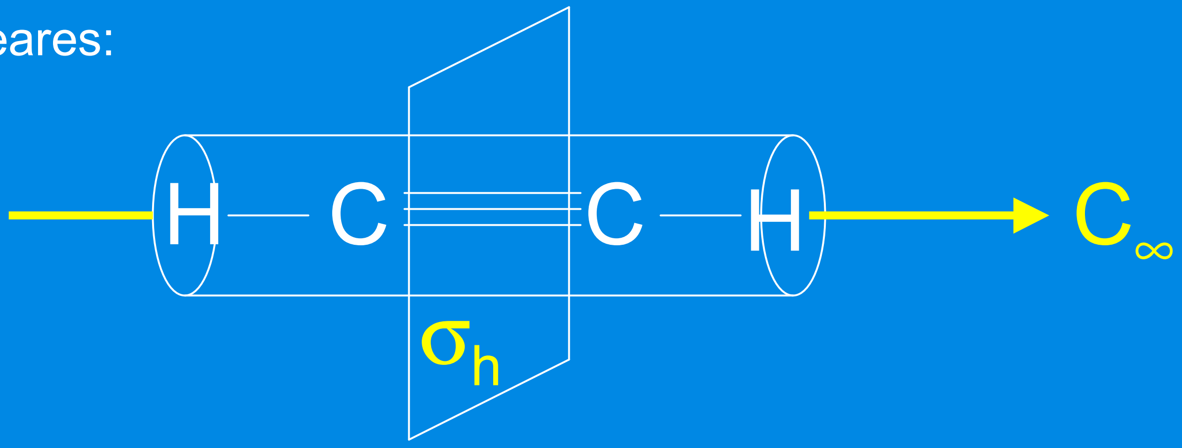
possui $nC_2 \perp C_n$:
- σ_h → D_{nh}
- σ_v → D_{nd}
- ñ σ → D_n

Molécula linear



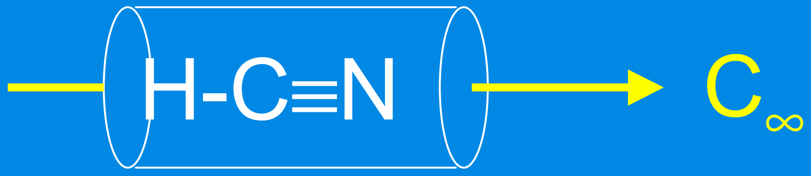
1a. Moléculas lineares:

H-C≡C-H



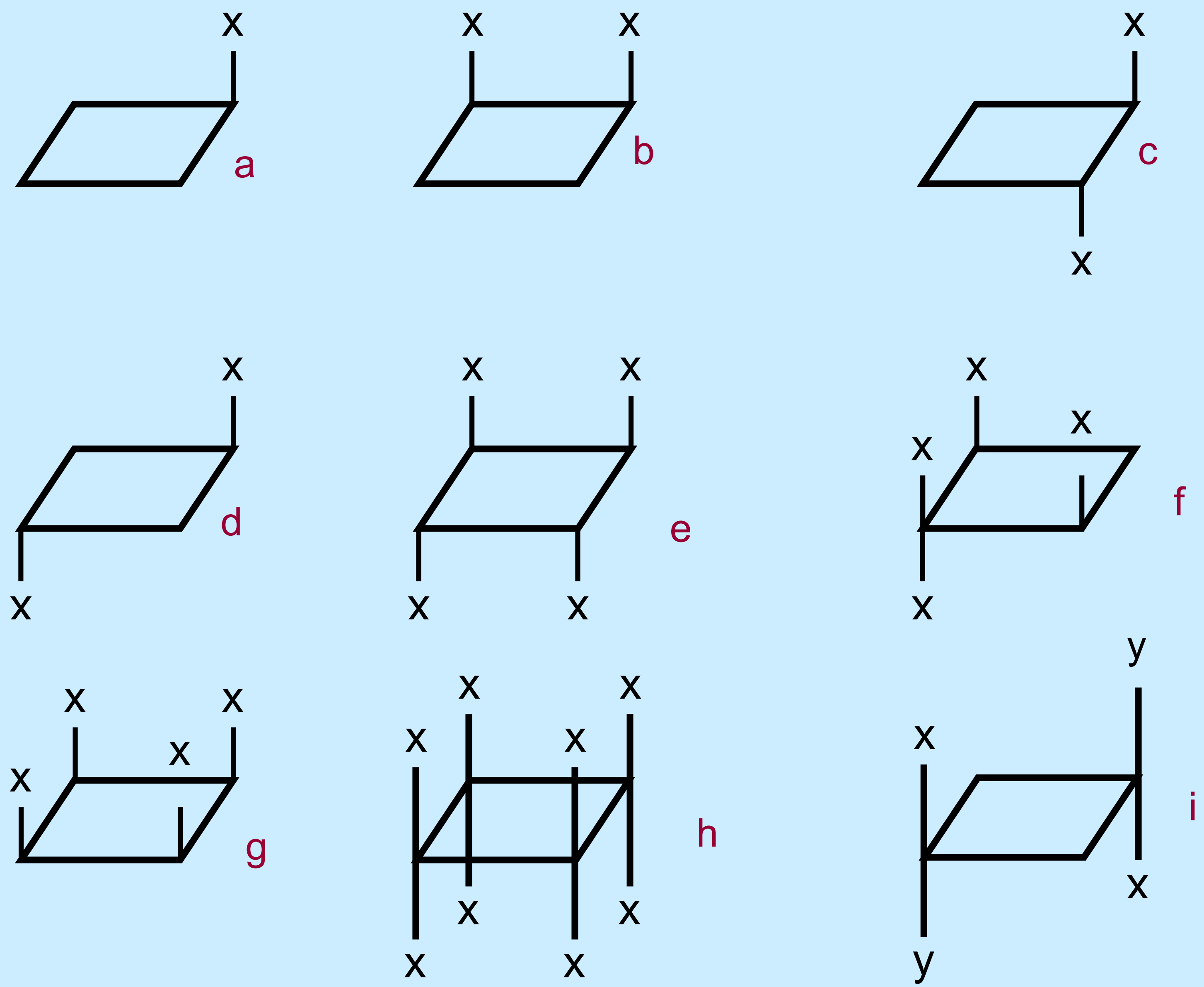
$C_\infty \perp \sigma_h \rightarrow D_{\infty h}$

H-C≡N

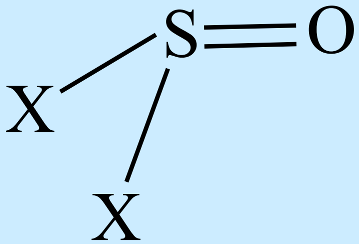


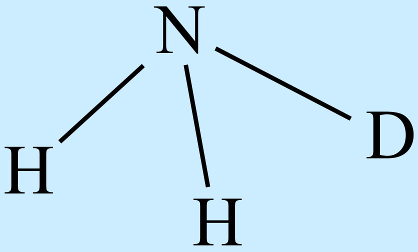
Não possui $\sigma_h \rightarrow C_{\infty v}$

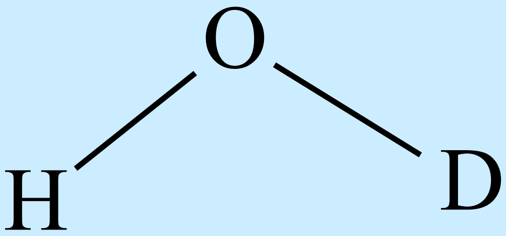
Determinar a simetria de grupo pontual das moleculas abaixo

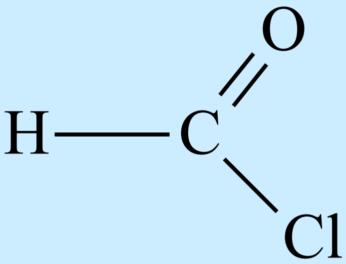


Determinar a simetria de grupo pontual das moleculas abaixo

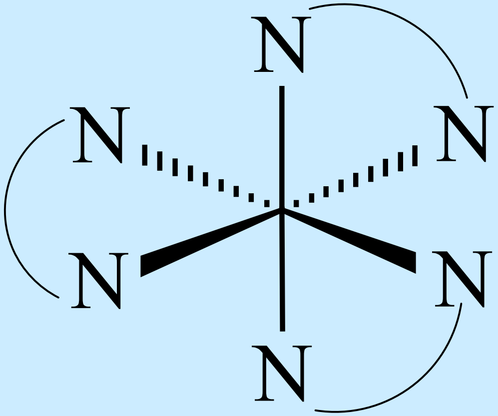


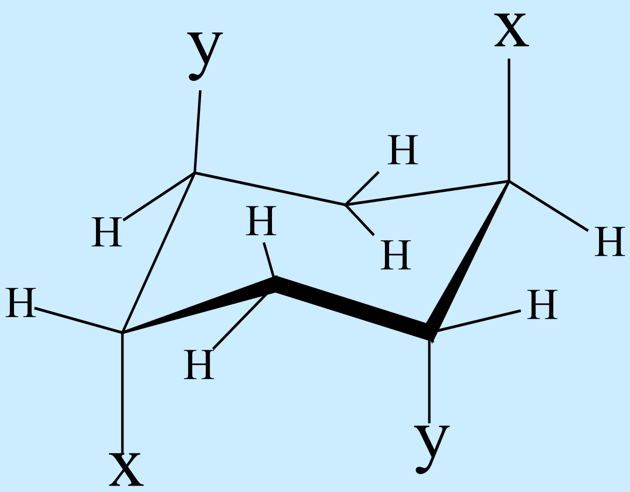


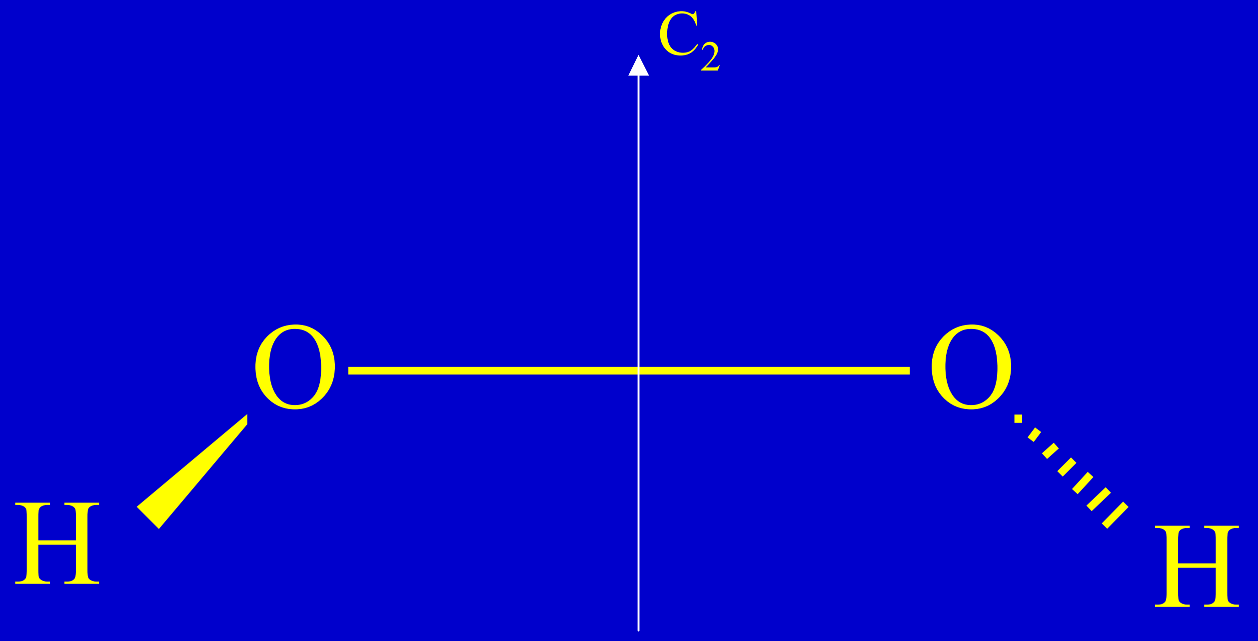




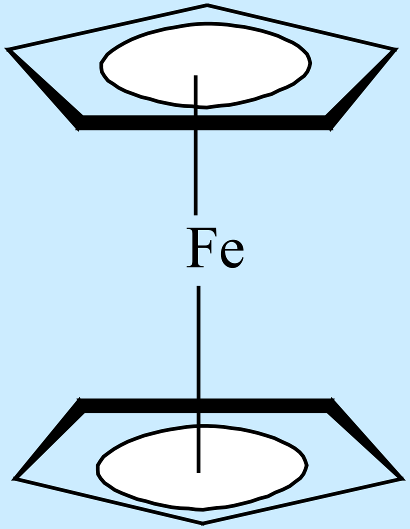
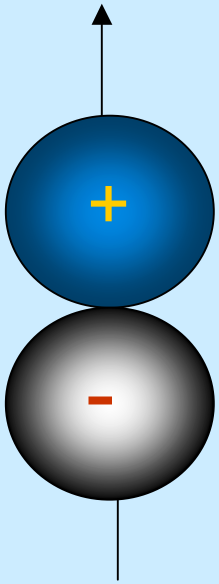
Determinar a simetria de grupo pontual das moleculas abaixo



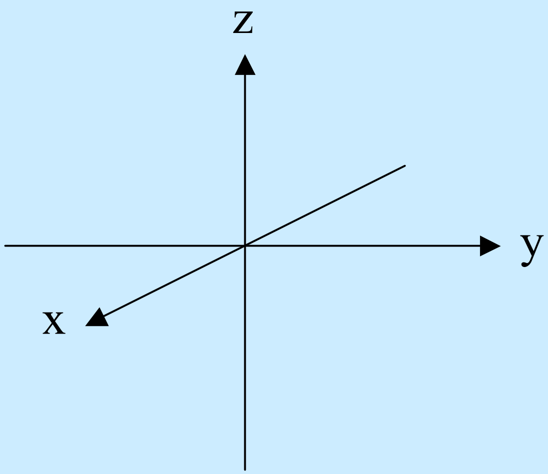




Simetria de grupo pontual C_2


Fe

+
-

Representação matricial das Operações de Simetria



Considerando a coordenada ao lado, vamos efetuar as operações:

$E(x,y,z) \rightarrow (x,y,z)$
$\sigma_h^{xy}(x,y,z) \rightarrow (x,y,-z)$
$i(x,y,z) \rightarrow (-x,-y,-z)$
$C_2^{z}(x,y,z) \rightarrow (-x,-y,z)$

$$\begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{vmatrix} \begin{vmatrix} x \\ y \\ z \end{vmatrix} = \begin{vmatrix} -x \\ -y \\ -z \end{vmatrix}$$

i

$$\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \begin{vmatrix} x \\ y \\ z \end{vmatrix} = \begin{vmatrix} x \\ y \\ z \end{vmatrix}$$

E

$$\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{vmatrix} \begin{vmatrix} x \\ y \\ z \end{vmatrix} = \begin{vmatrix} x \\ y \\ -z \end{vmatrix}$$

σ_h^{xy}

$$\begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \begin{vmatrix} x \\ y \\ z \end{vmatrix} = \begin{vmatrix} -x \\ -y \\ z \end{vmatrix}$$

C_2^z

Multiplicação das operações de simetria

$$\underset{i}{\begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{vmatrix}} \underset{i}{\begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{vmatrix}} = \underset{E}{\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}}$$

$$\underset{\sigma_h^{xy}}{\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{vmatrix}} \underset{\sigma_h^{xy}}{\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{vmatrix}} = \underset{E}{\begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}}$$

$$\begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{vmatrix} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

$$C_2^z \quad C_2^z \quad E$$

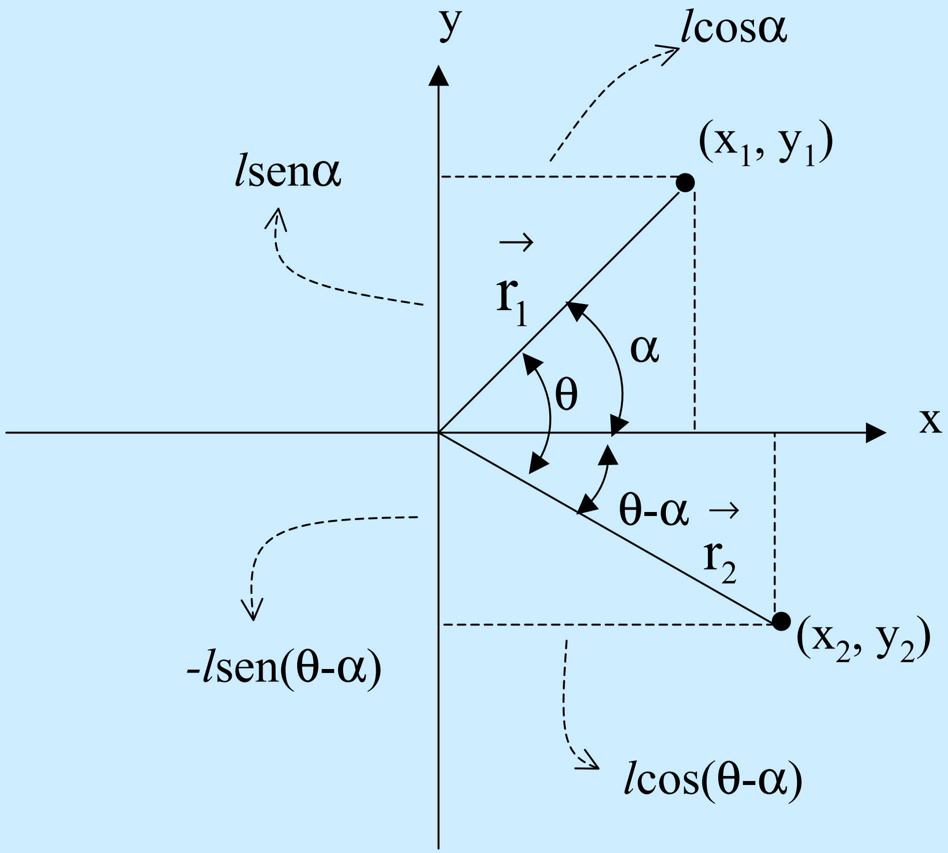
$$\begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{vmatrix} = \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{vmatrix}$$

$$C_2^z \quad i \quad \sigma_h^{xy}$$

$$\begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{vmatrix} = \begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{vmatrix}$$

$$C_2^z \quad \sigma_h^{xy} \quad i$$

Rotação propria C_n



Considerandop a rotação do vetor r_1 na figura acima por um angulo θ para dar o vetor r_2:

$x_1 = l\cos\alpha$, $y_1 = l\text{sen}\alpha$; $x_2 = l\cos(\theta-\alpha)$, $y_2 = -l\text{sen}(\theta-\alpha)$

Lembrando que: $\cos(\theta-\alpha) = \cos\theta.\cos\alpha + \text{sen}\theta.\text{sen}\alpha$

$\text{sen}(\theta-\alpha) = \text{sen}\theta.\cos\alpha - \cos\theta.\text{sen}\alpha$

$$\left.\begin{aligned} x_2 &= l\cos\theta.\cos\alpha + l\mathrm{sen}\theta.\mathrm{sen}\alpha \\ y_2 &= -l\mathrm{sen}\theta.\cos\alpha + l\cos\theta.\mathrm{sen}\alpha \end{aligned}\right\} \quad \text{como} \quad x_1 = l\cos\alpha \,,\; y_1 = l\mathrm{sen}\alpha$$

$$x_2 = x_1\cos\theta + y_1\mathrm{sen}\theta$$

$$y_2 = -\, x_1\cos\alpha + y_1\cos\theta$$

$$\underbrace{\begin{vmatrix} \cos\theta & \mathrm{sen}\theta \\ -\cos\alpha & \cos\theta \end{vmatrix}}_{C_n} \begin{vmatrix} x_1 \\ y_1 \end{vmatrix} = \begin{vmatrix} x_2 \\ y_2 \end{vmatrix}$$

Tabela de Mutiplicação

	E	C_2^z	σ_h^{xy}	i
E	E	C_2^z	σ_h^{xy}	i
C_2^z	C_2^z	E	i	C_2^z
σ_h^{xy}	σ_h^{xy}	i	E	σ_h^{xy}
i	i	σ_h^{xy}	C_2^z	E

E
C_2^z
σ_h^{xy}
i

Formam um grupo

Tabela de caracteres

	E	C_2	i	σ_h
Γ_1	1	1	1	1
Γ_2	1	-1	1	-1
Γ_3	1	1	-1	-1
Γ_4	1	-1	-1	1

$\Gamma_1, \Gamma_2, \Gamma_3, \Gamma_4$ Forma um conjunto de representações irredutiveis.

A tabela acima deve obeder as seguintes propriedades:

1. A soma dos quadrados das dimensões das representações irredutiveis, é igual ordem do grupo, isto é:

$$\sum l_i^2 = h$$

Exemplol: $(1)^2 + (1)^2 + (1)^2 + (1)^2 = 4$

2. A soma dos quadrados dos caracteres é igual a *h:*

$$\sum_R [\chi_i(R)]^2 = h,$$ onde $\chi_t(R)$ é o carater da representação

Exemplo: $(1)^2 + (1)^2 + (-1)^2 + (-1)^2 = 4$

3. $$\sum_R \chi_i(R)\chi_j(R) = 0$$ para $i \neq j$

Exemplo= $(1)(1) + (1)(1) + (1)(-1) + (1)(-1)= 0$ para Γ_1 e Γ_2

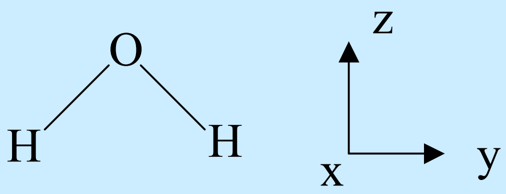
4. O número de representações irredutiveis, Γ, é igual ao número de classes no grupo

Tabela de caracteres para o grupo pontual C_{2h}

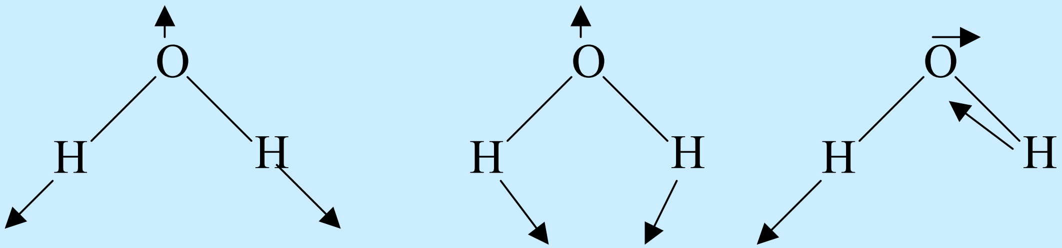
C_{2h}	E	C_2	i	σ_h
A_g	1	1	1	1
B_g	1	-1	1	-1
A_u	1	1	-1	-1
B_u	1	-1	-1	1

Aplicações gerais da Teoria da Teoria de Grupo

Espectroscopia vibracional



grupo pontual C_{2v}

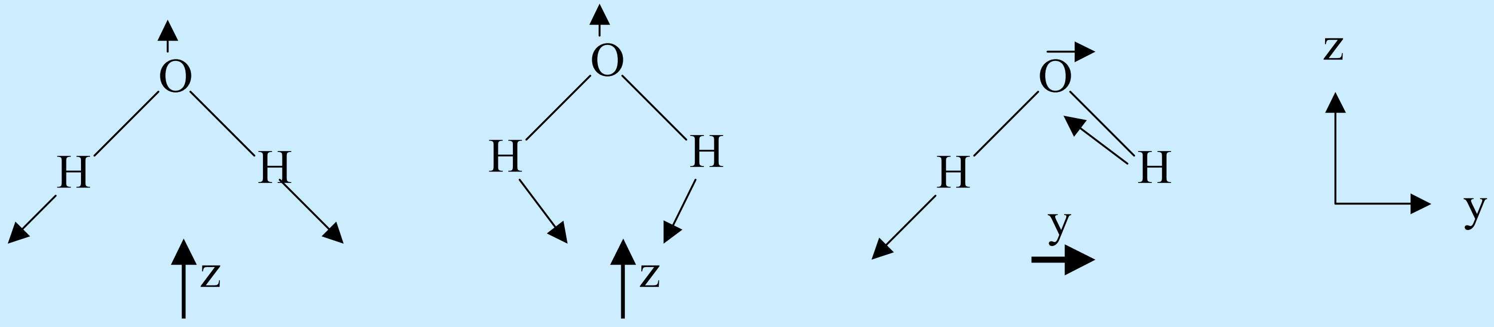


υ_1 υ_2 υ_3

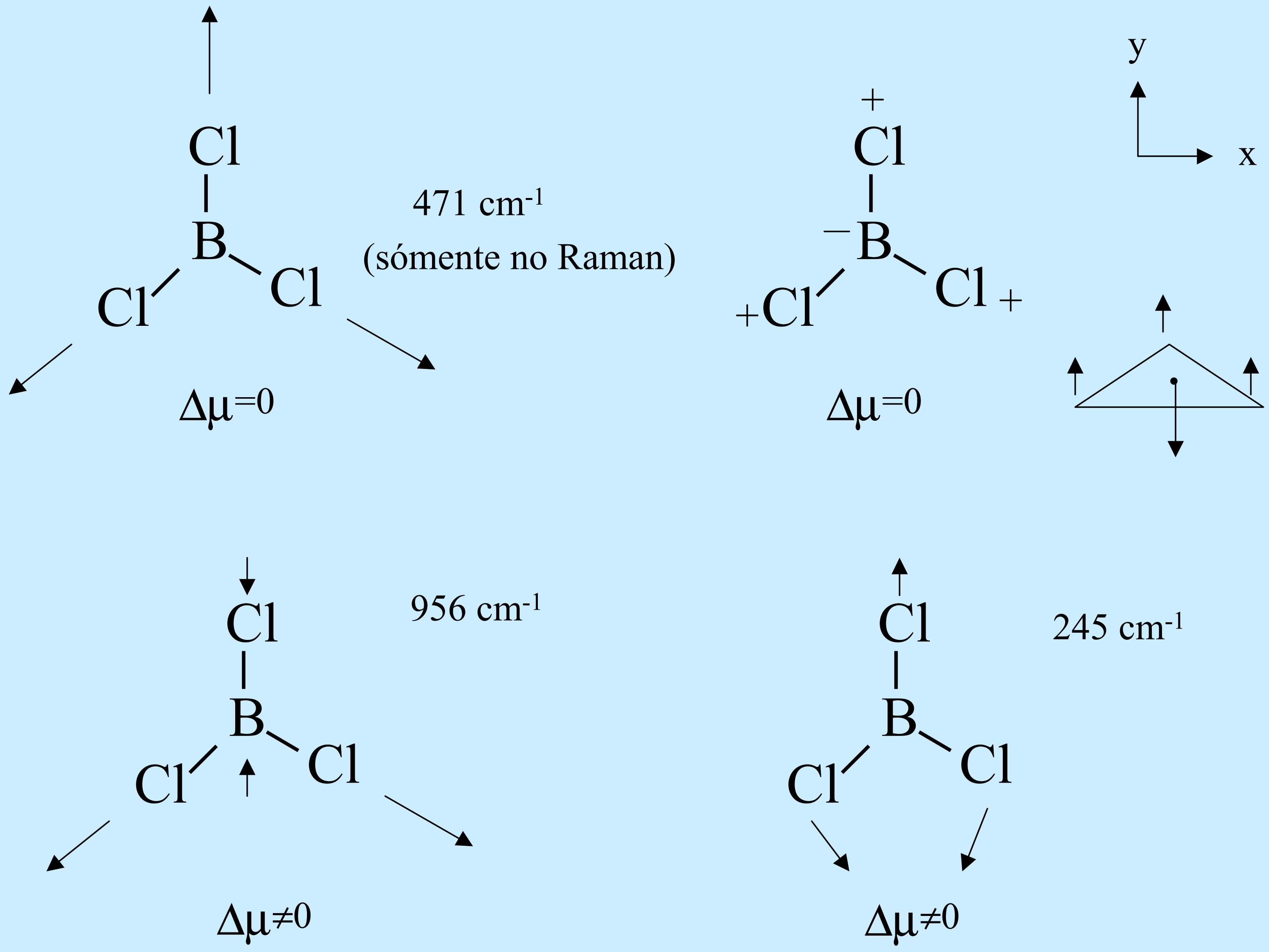
No modo vibracional ao lado o estiramento das ligações ocorrem em fase. A operação de simetria assumindo o valor 1 ou -1, conforme a mudança do sentido do vetor, temo:

	E	C_2	σ_v^{xz}	σ_z^{yz}
υ_1	1	1	1	1
υ_2	1	1	1	1
υ_3	1	-1	-1	1

C_{2v}	E	C_2	σ_v^{xz}	σ_z^{yz}
A_1	1	1	1	1
A_2	1	1	-1	-1
B_1	1	-1	1	-1
B_2	1	-1	-1	1



υ_1	υ_2	υ_3
A_1	A_1	B_2
estiramento simétrico	deformação	estiramento assimétrico


Cl
B
Cl
Cl
471 cm-1
(sómente no Raman)
Δμ=0
+
Cl
−B
+Cl
Cl +
Δμ=0
y
x
Cl
B
Cl
Cl
956 cm-1
Δμ≠0
Cl
B
Cl
Cl
245 cm-1
Δμ≠0