



Aplicação de simetria para a visualização dos orbitais moleculares de moléculas pequenas e compostos de coordenação

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Aula 3 - Moléculas lineares

Diatômicas heteronucleares - $C_{\infty v}$

Diatômicas homonucleares - $D_{\infty h}$

Termos espectroscópicos para moléculas

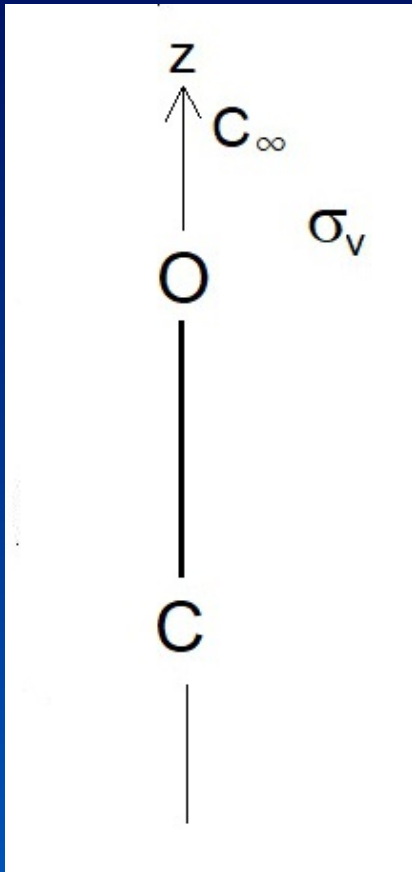


Sociedade Brasileira de Química

11 a 15 de março de 2024

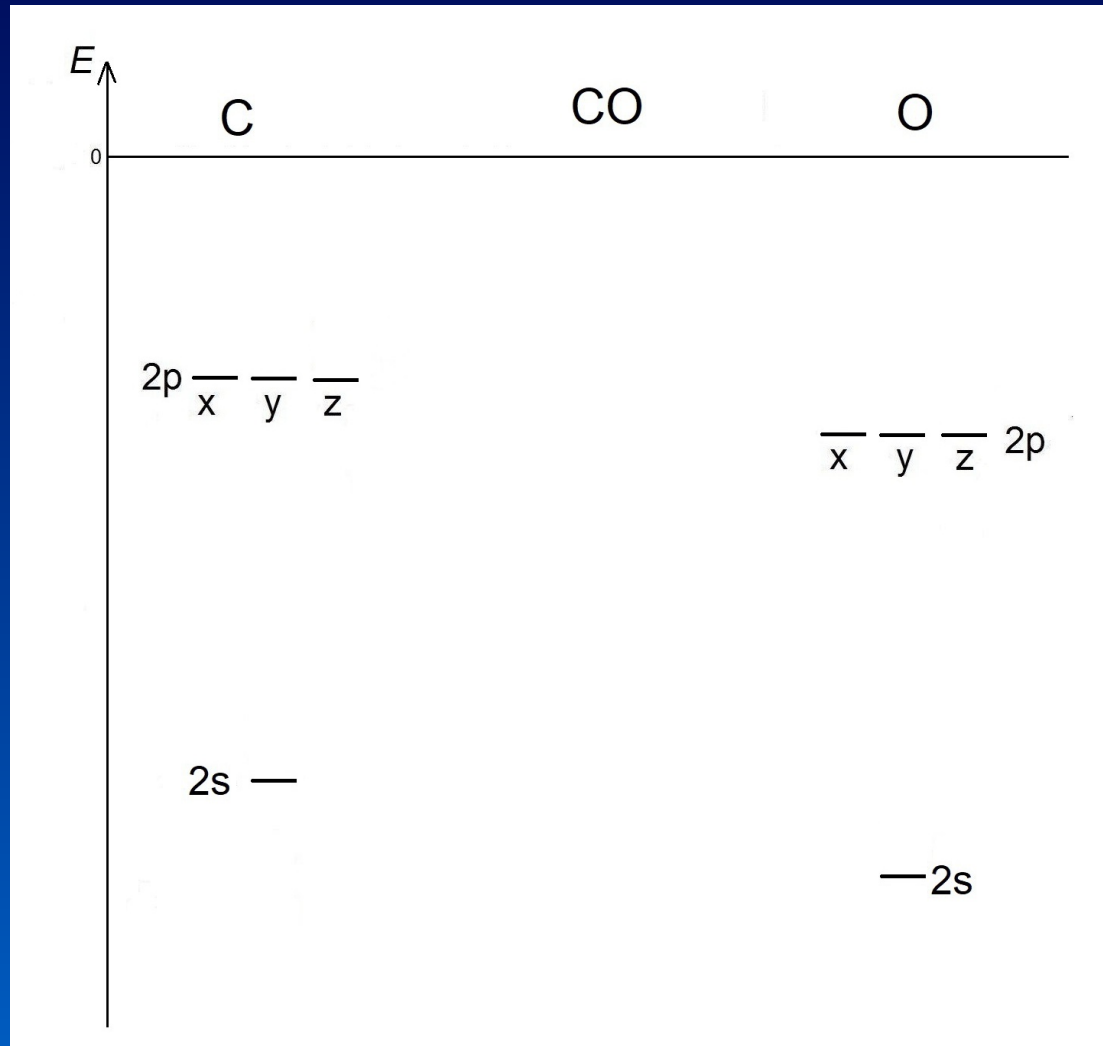
Diatômicas heteronucleares - $C_{\infty v}$

CO - $C_{\infty v}$



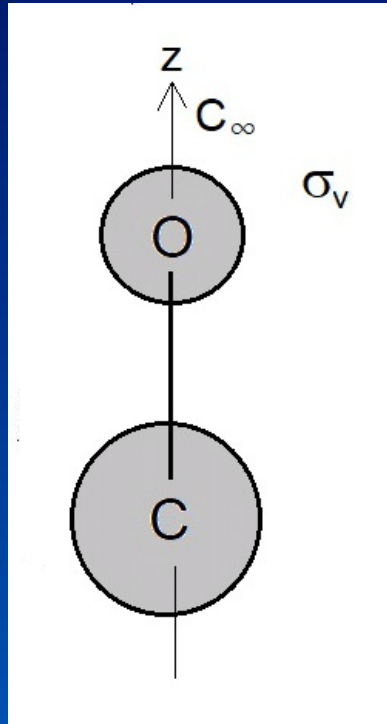
$C_{\infty v}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$
Σ^+	1	1	1
Σ^-	1	1	-1
Π	2	$2\cos\varphi$	0
Δ	2	$2\cos 2\varphi$	0
Φ	2	$2\cos 3\varphi$	0

CO - $C_{\infty v}$



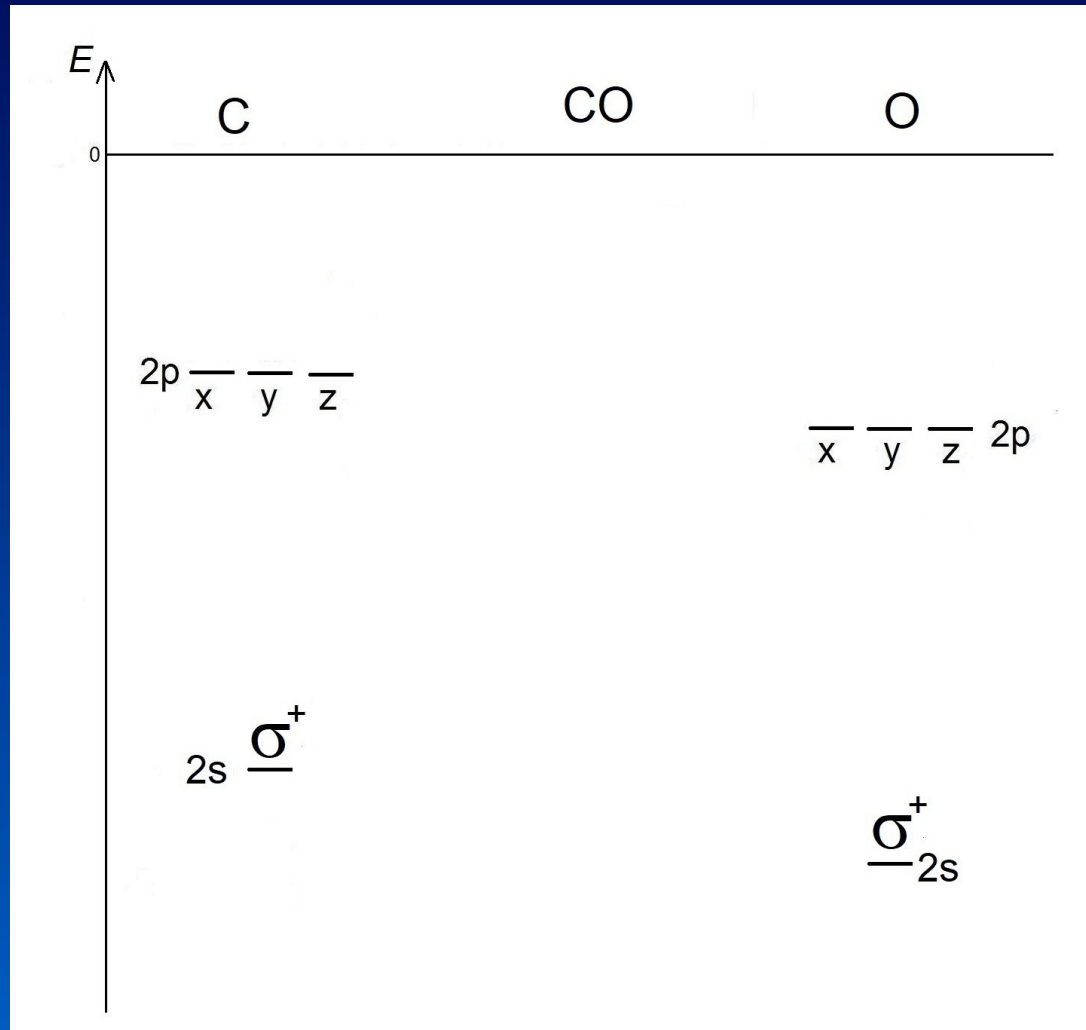
CO - $C_{\infty v}$

Orbitais 2s -independentes



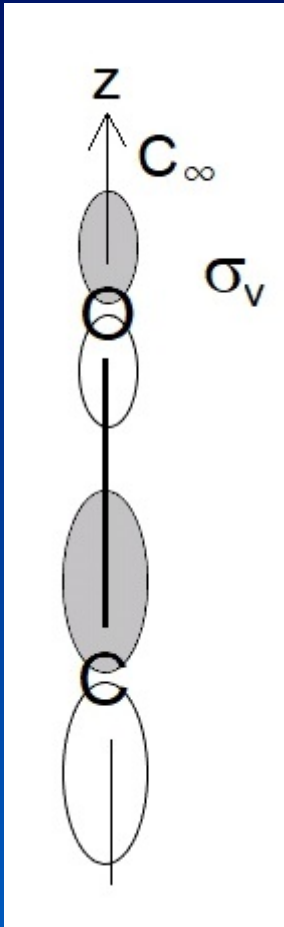
$C_{\infty v}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	
Σ^+	1	1	1	
Σ^-	1	1	-1	
Π	2	$2\cos\varphi$	0	
Δ	2	$2\cos 2\varphi$	0	
Φ	2	$2\cos 3\varphi$	0	
<hr/>				
2s(C)	1	1	1	Σ^+
2s(O)	1	1	1	Σ^+

CO - C_{∞v}



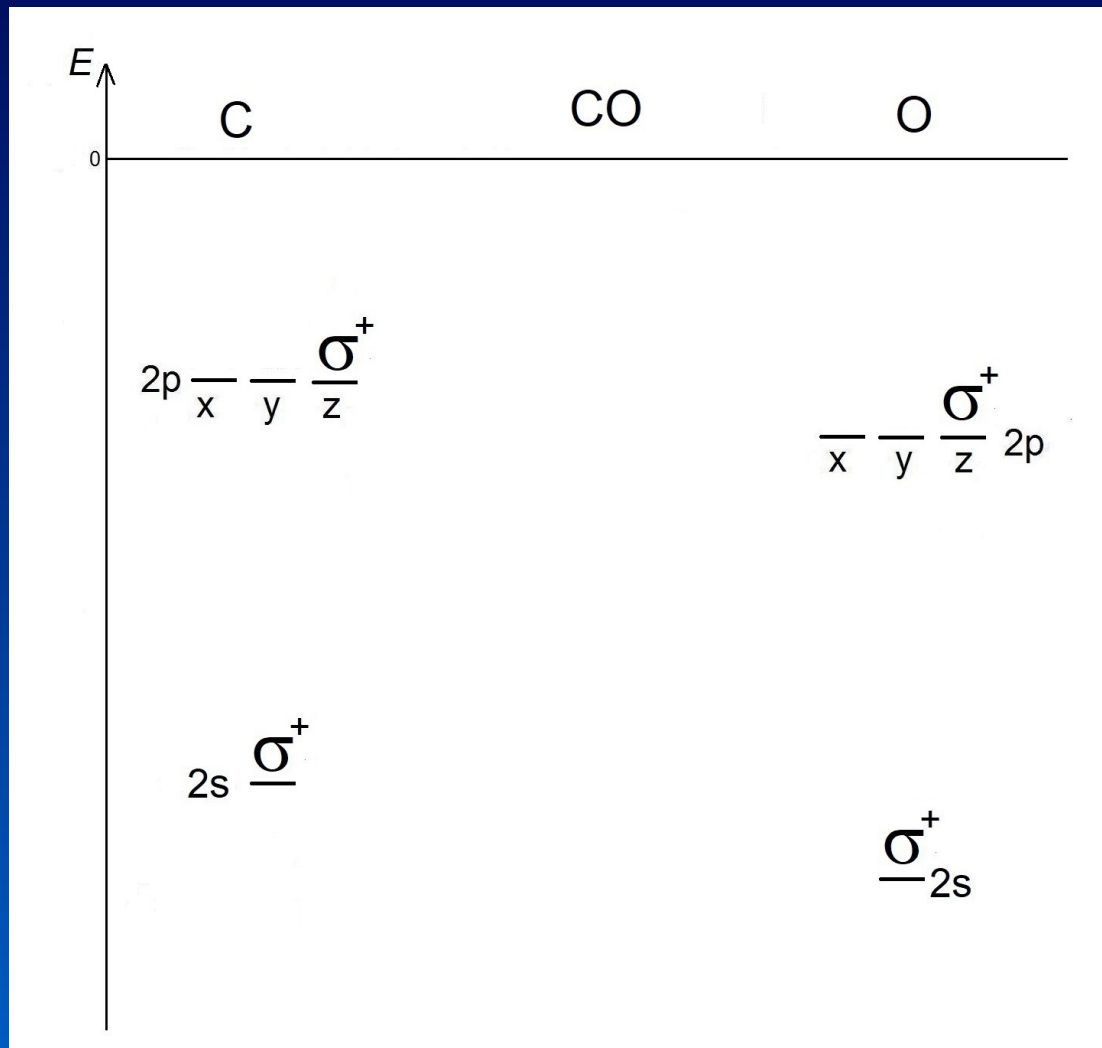
CO - $C_{\infty v}$

Orbitais $2p_z$ - independentes



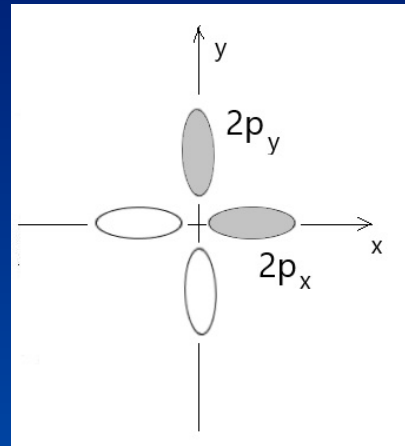
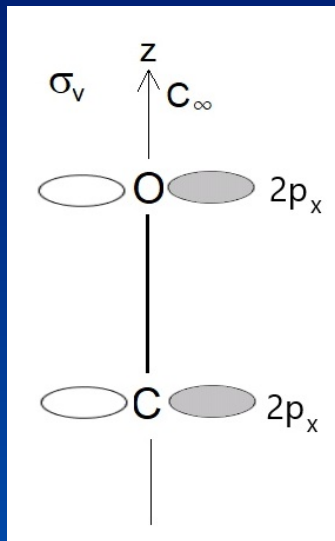
$C_{\infty v}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	
Σ^+	1	1	1	
Σ^-	1	1	-1	
Π	2	$2\cos\varphi$	0	
Δ	2	$2\cos 2\varphi$	0	
Φ	2	$2\cos 3\varphi$	0	
<hr/>				
$2p_z(C)$	1	1	1	Σ^+
$2p_z(O)$	1	1	1	Σ^+

CO - $C_{\infty v}$



CO - $C_{\infty v}$

Orbitais do carbono ou do oxigênio
 $2p_x$ e $2p_y$ - inseparáveis



Escolhendo $\varphi = 90^\circ$

$$C_{\infty}^{\varphi} = C_4$$

$$p_x \rightarrow p_y$$

$$p_y \rightarrow -p_x$$

CO - $C_{\infty v}$

Orbitais do carbono $2p_x$ e $2p_y$ -inseparáveis

$C_{\infty v}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	φ	$2\cos\varphi$	$2\cos2\varphi$	$2\cos3\varphi$
Σ^+	1	1	1	90°	0	-2	0
Σ^-	1	1	-1	180°	-2	2	-2
Π	2	$2\cos\varphi$	0	45°	$\sqrt{2}$	0	$-\sqrt{2}$
Δ	2	$2\cos2\varphi$	0				
Φ	2	$2\cos3\varphi$	0				

CO - C_{∞v}

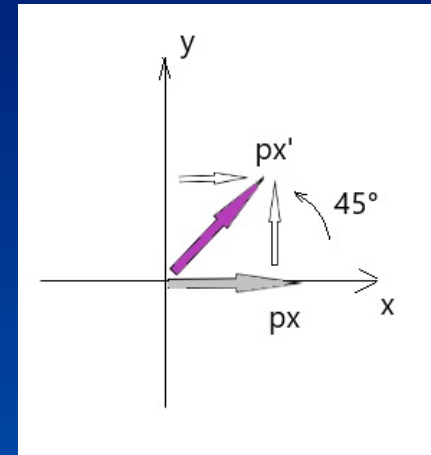
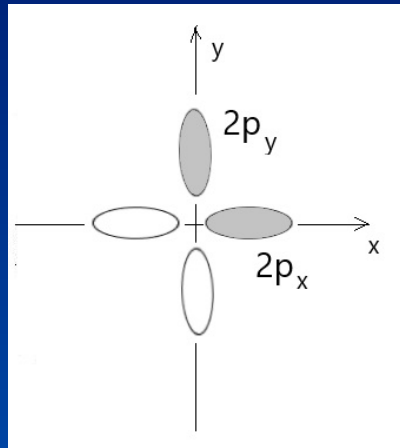
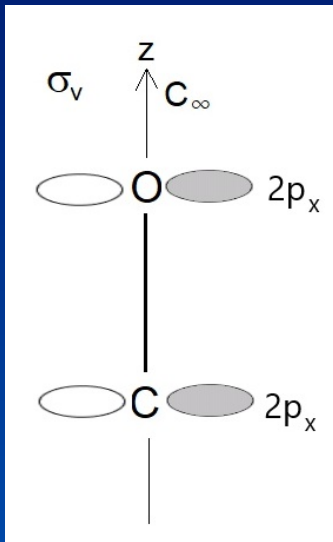
Orbitais do carbono 2p_x e 2p_y -inseparáveis

Escolhendo $\varphi = 45^\circ$

C _{∞v}	E	2C _∞ ^φ	∞σ _v	φ	2cosφ	2cos2φ	2cos3φ
Σ ⁺	1	1	1	90°	0	-2	0
Σ ⁻	1	1	-1	180°	-2	2	-2
Π	2	√2	0	45°	√2	0	-√2
Δ	2	0	0				
Φ	2	-√2	0				

CO - $C_{\infty v}$

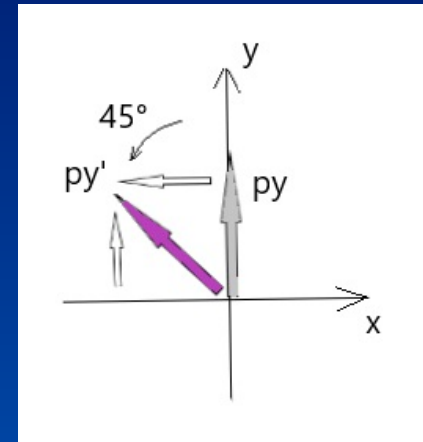
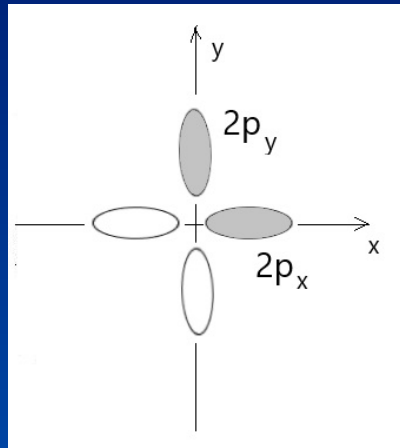
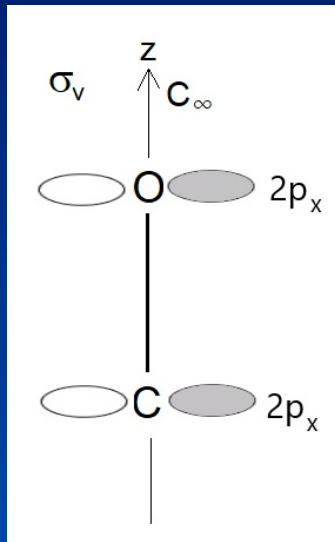
Orbitais do carbono ou do oxigênio
 $2p_x$ e $2p_y$ - inseparáveis
Escolhendo $\phi = 45^\circ$



$$\begin{aligned} (C_8)p_x &\rightarrow p_x' = \cos(45^\circ)p_x + \text{sen}(45^\circ)p_y \\ &= (\sqrt{2}/2)p_x + (\sqrt{2}/2)p_y \end{aligned}$$

CO - $C_{\infty v}$

Orbitais do carbono ou do oxigênio
 $2p_x$ e $2p_y$ - inseparáveis
Escolhendo $\varphi = 45^\circ$



$$\begin{aligned} (C_8)p_y &\rightarrow p_{y'} = -\text{sen}(45^\circ)p_x + \text{cos}(45^\circ)p_y \\ &= -(\sqrt{2}/2)p_x + (\sqrt{2}/2)p_y \end{aligned}$$

CO - $C_{\infty v}$

Orbitais do carbono ou do oxigênio

$2p_x$ e $2p_y$ - inseparáveis

Escolhendo $\phi = 45^\circ$

$$\begin{aligned} (C_8)p_x &\rightarrow p_x' = (\sqrt{2}/2)p_x + (\sqrt{2}/2)p_y \\ (C_8)p_y &\rightarrow p_y' = -(\sqrt{2}/2)p_x + (\sqrt{2}/2)p_y \end{aligned}$$

	$2p_x$	$2p_y$		$2p_x$	$2p_y$
$2p_x$	1	0	C_8	$\sqrt{2}/2$	$\sqrt{2}/2$
$2p_y$	0	1	\rightarrow	$-\sqrt{2}/2$	$\sqrt{2}/2$

$$\chi = \sqrt{2}$$

CO - C_{∞v}

Orbitais do carbono 2p_x e 2p_y -inseparáveis

Orbitais do carbono ou do oxigênio

2p_x e 2p_y - inseparáveis (φ = 45°)

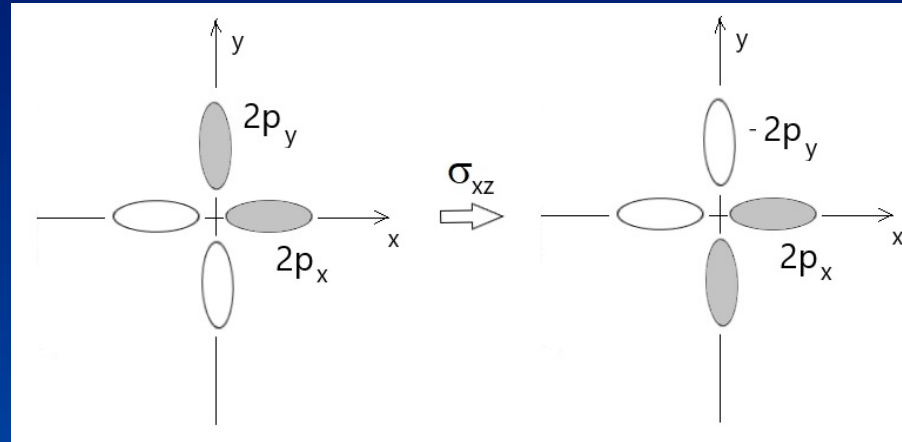
C _{∞v}	E	2C _∞ ^φ	∞σ _v	φ	2cosφ	2cos2φ	2cos3φ
Σ ⁺	1	1	1	90°	0	-2	0
Σ ⁻	1	1	-1	180°	-2	2	-2
Π	2	√2	0	45°	√2	0	-√2
Δ	2	0	0				
Φ	2	-√2	0				
<hr/>							
(p _x ,p _y) _C	2	√2					
(p _x ,p _y) _O	2	√2					

CO - $C_{\infty v}$

Orbitais do carbono ou do oxigênio

$2p_x$ e $2p_y$ - inseparáveis

Escolhendo $\varphi = 45^\circ$



$$\begin{array}{cc}
 & \begin{array}{c} 2p_x \\ 2p_y \end{array} \\
 \begin{array}{c} 2p_x \\ 2p_y \end{array} & \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array}
 \end{array}
 \xrightarrow{\sigma_{xz}}
 \begin{array}{cc}
 & \begin{array}{c} 2p_x \\ 2p_y \end{array} \\
 \begin{array}{c} 2p_x \\ 2p_y \end{array} & \begin{array}{cc} 1 & 0 \\ 0 & -1 \end{array}
 \end{array}
 \chi = 0$$

CO - C_{∞v}

Orbitais do carbono 2p_x e 2p_y -inseparáveis

Orbitais do carbono ou do oxigênio

2p_x e 2p_y - inseparáveis (φ = 45°)

C _{∞v}	E	2C _∞ ^φ	∞σ _v	φ	2cosφ	2cos2φ	2cos3φ
Σ ⁺	1	1	1	90°	0	-2	0
Σ ⁻	1	1	-1	180°	-2	2	-2
Π	2	√2	0	45°	√2	0	-√2
Δ	2	0	0				
Φ	2	-√2	0				
<hr/>							
(p _x ,p _y) _C	2	√2	0				
(p _x ,p _y) _O	2	√2	0				

CO - C_{∞v}

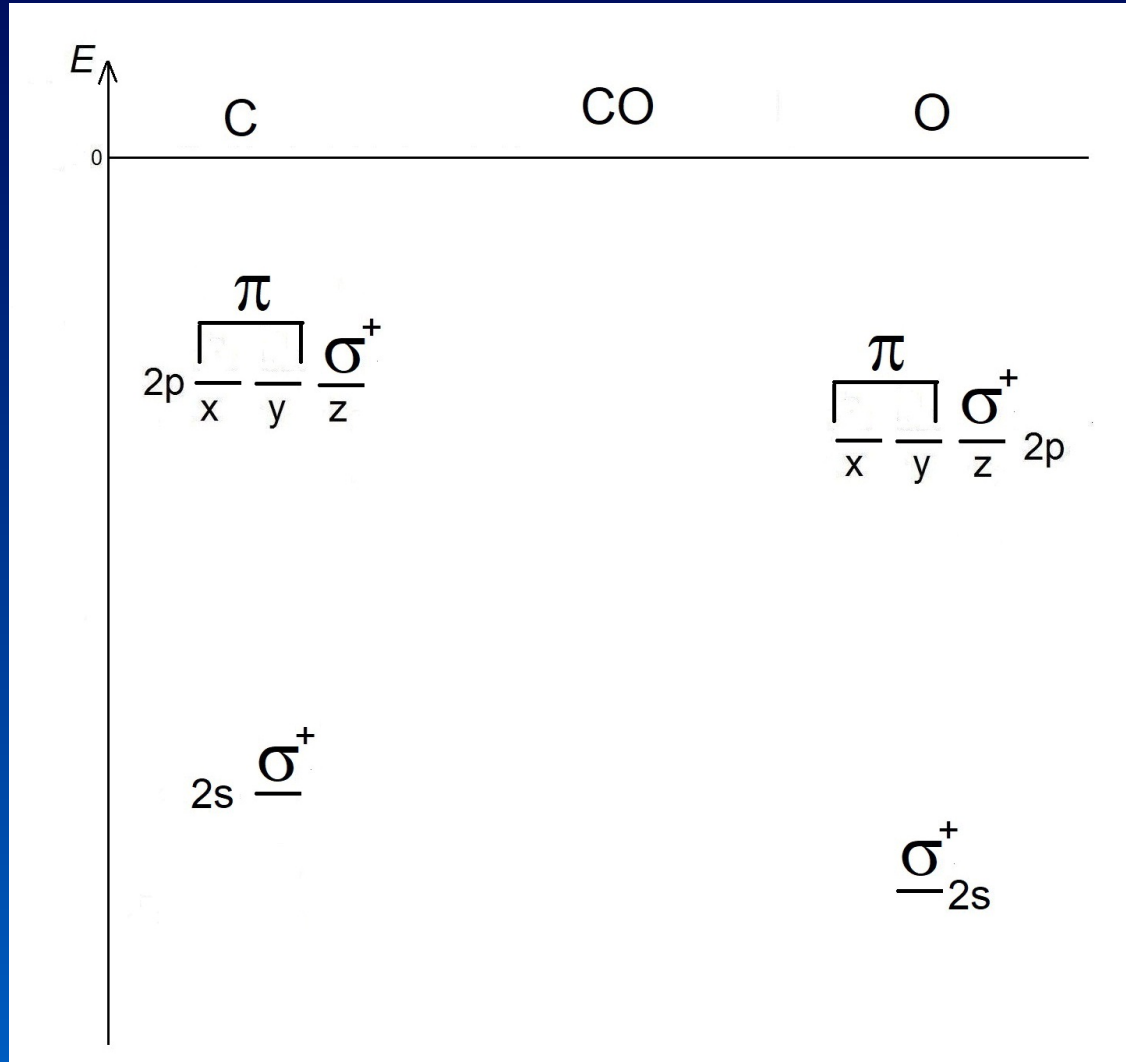
Orbitais do carbono 2p_x e 2p_y -inseparáveis

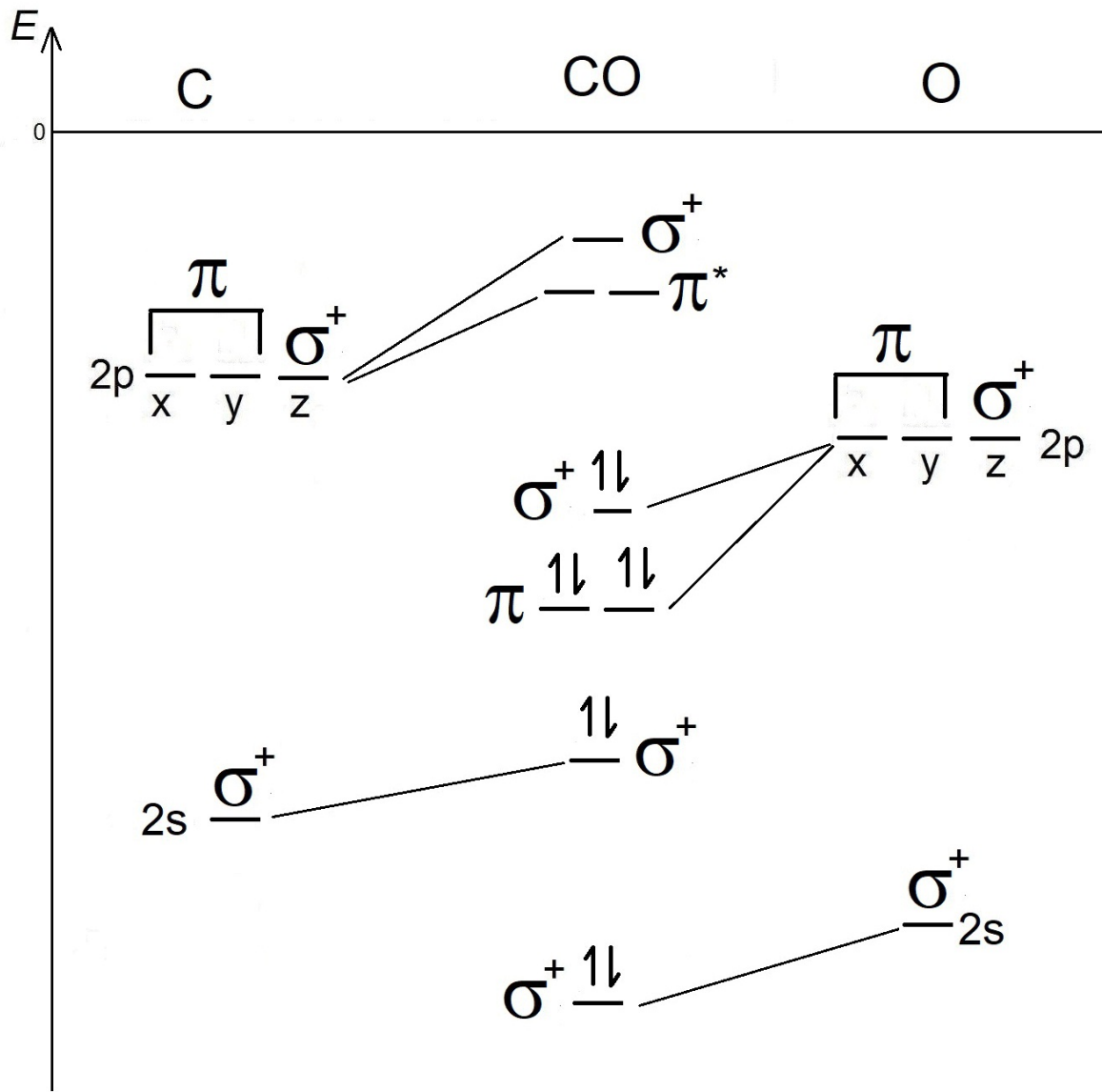
Orbitais do carbono ou do oxigênio

2p_x e 2p_y - inseparáveis (φ = 45°)

C _{∞v}	E	2C _∞ ^φ	∞σ _v		φ	2cosφ	2cos2φ	2cos3φ
Σ ⁺	1	1	1		90°	0	-2	0
Σ ⁻	1	1	-1		180°	-2	2	-2
Π	2	√2	0		45°	√2	0	-√2
Δ	2	0	0					
Φ	2	-√2	0					
<hr/>								
(p _x ,p _y) _C	2	√2	0	Π				
(p _x ,p _y) _O	2	√2	0	Π				

CO - C_{∞v}





Espectros de fotoelétron - CO

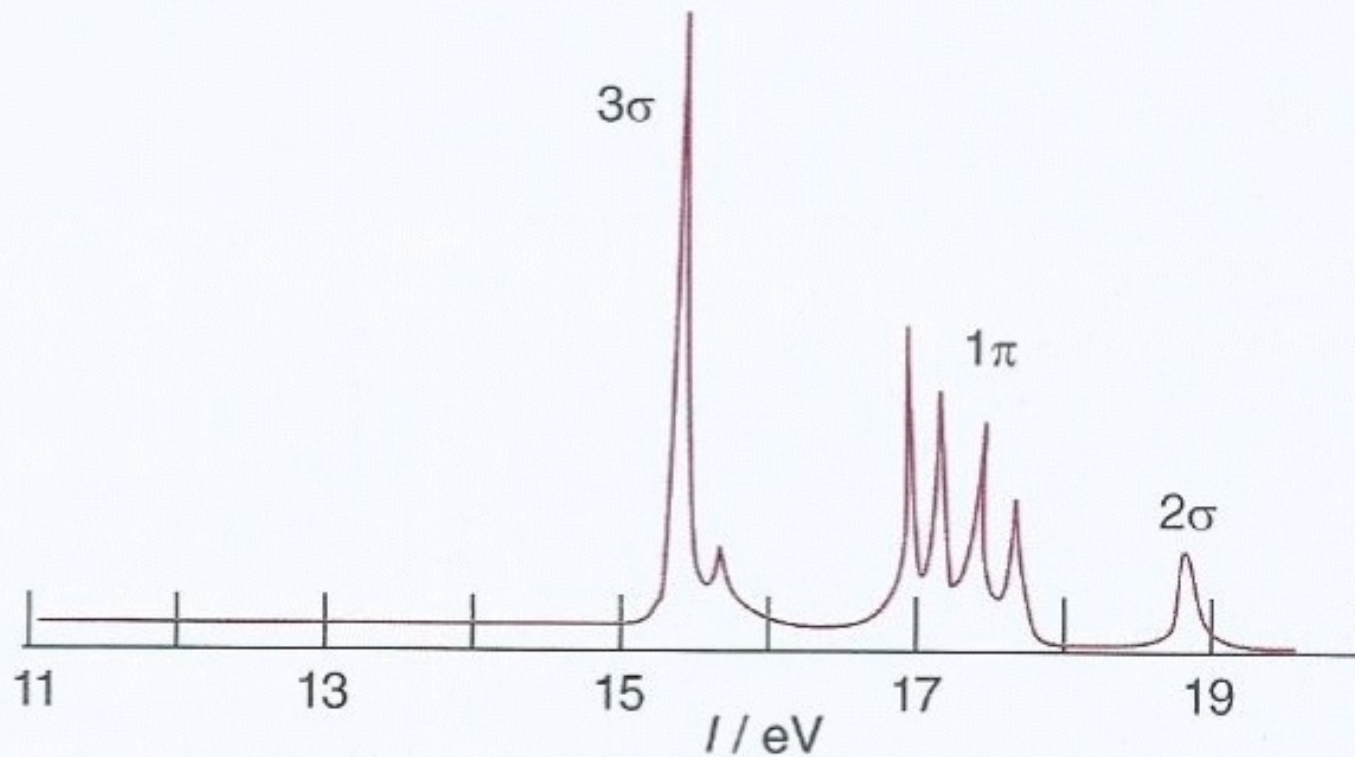
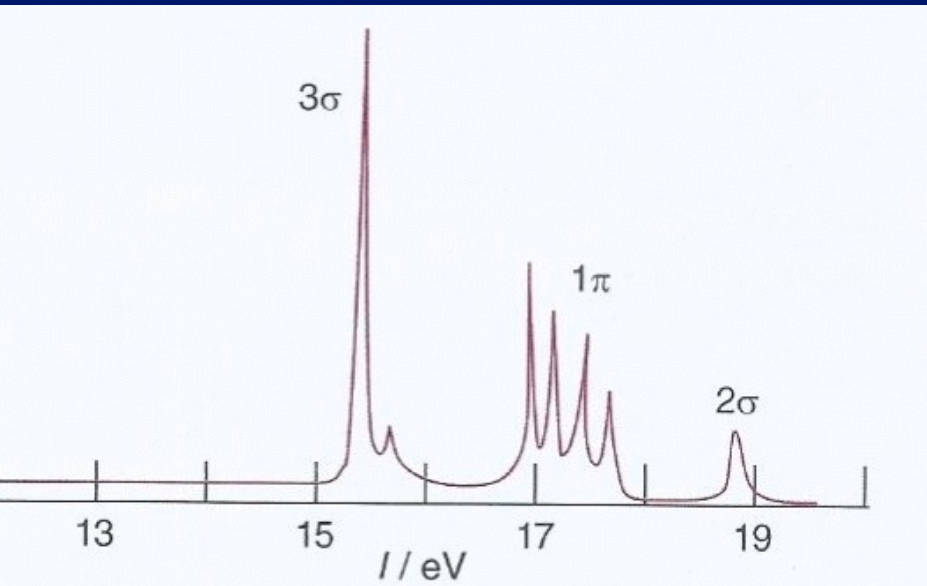


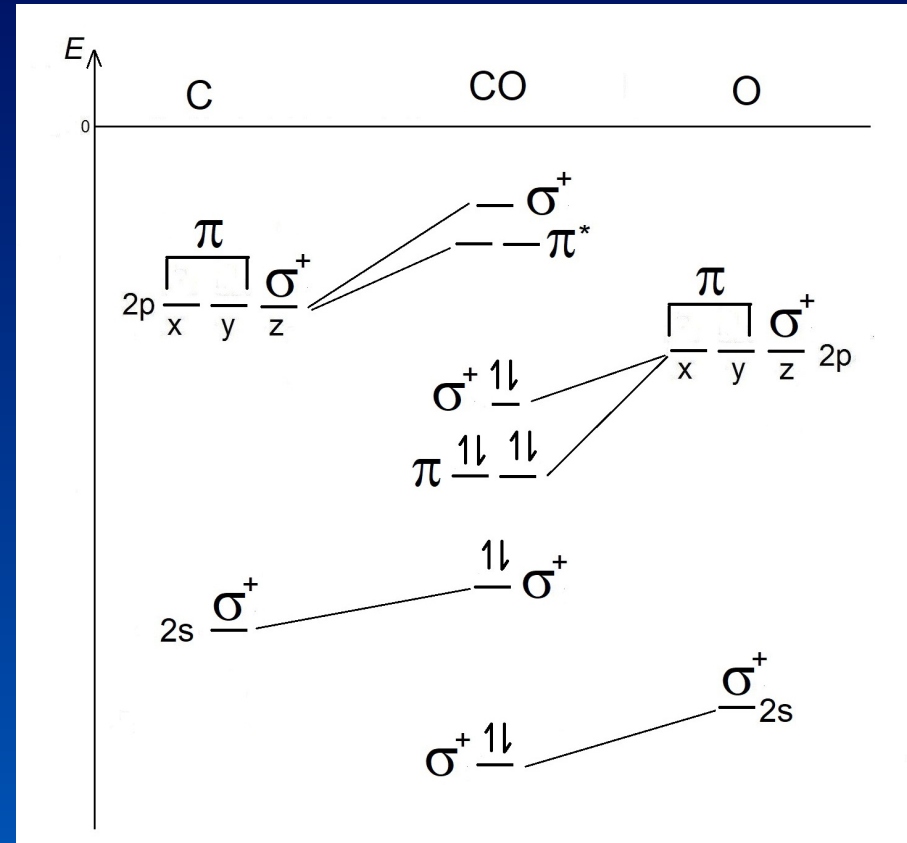
Fig. 2.37 The ultraviolet photoelectron spectrum of CO obtained using 21 eV radiation.

Espectros de fotoelétron - CO



Ultraviolet photoelectron spectrum of CO obtained using

Ke, J.; Armstrong, F.; *Inorganic Chemistry*, 6a ed., Oxford University Press, 2014. pg 63.



Diatômicas homonucleares - $D_{\infty h}$

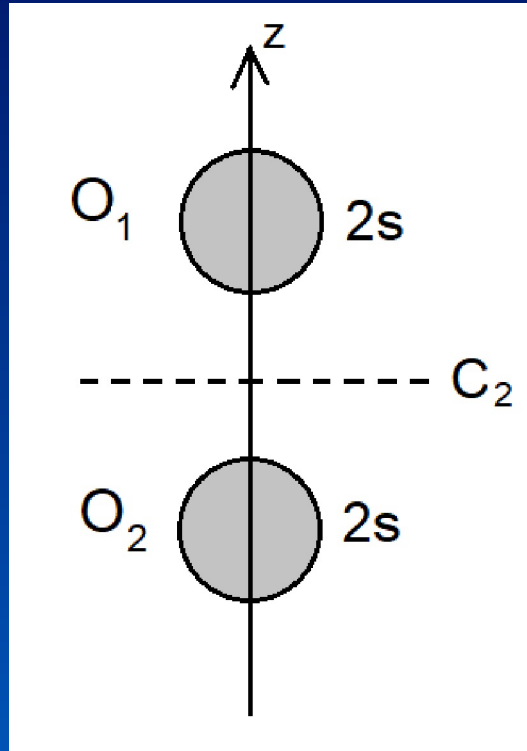
$D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
Σ_{g}^{+}	1	1	1	1	1	1
Σ_{g}^{-}	1	1	-1	1	1	-1
Π_{g}	2	$2\cos\varphi$	0	2	$-2\cos\varphi$	0
Δ_{g}	2	$2\cos 2\varphi$	0	2	$2\cos 2\varphi$	0
Σ_{u}^{+}	1	1	1	-1	-1	-1
Σ_{u}^{-}	1	1	-1	-1	-1	1
Π_{u}	2	$2\cos\varphi$	0	-2	$2\cos\varphi$	0
Δ_{u}	2	$2\cos 2\varphi$	0	-2	$-2\cos 2\varphi$	0

Dioxigênio - O₂



Orbitais 2s - inseparáveis



Dioxigênio - O₂ - D_{∞h}

D _{∞h}	E	2C _∞ ^φ	∞σ _v	i	2S _∞ ^φ	∞C ₂
Σ_{g}^{+}	1	1	1	1	1	1
Σ_{g}^{-}	1	1	-1	1	1	-1
Π_{g}	2	2cosφ	0	2	-2cosφ	0
Δ_{g}	2	2cos2φ	0	2	2cos2φ	0
Σ_{u}^{+}	1	1	1	-1	-1	-1
Σ_{u}^{-}	1	1	-1	-1	-1	1
Π_{u}	2	2cosφ	0	-2	2cosφ	0
Δ_{u}	2	2cos2φ	0	-2	-2cos2φ	0

2s(O ₁ ,O ₂)	2	2	2
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$O_2 - D_{\infty h}$

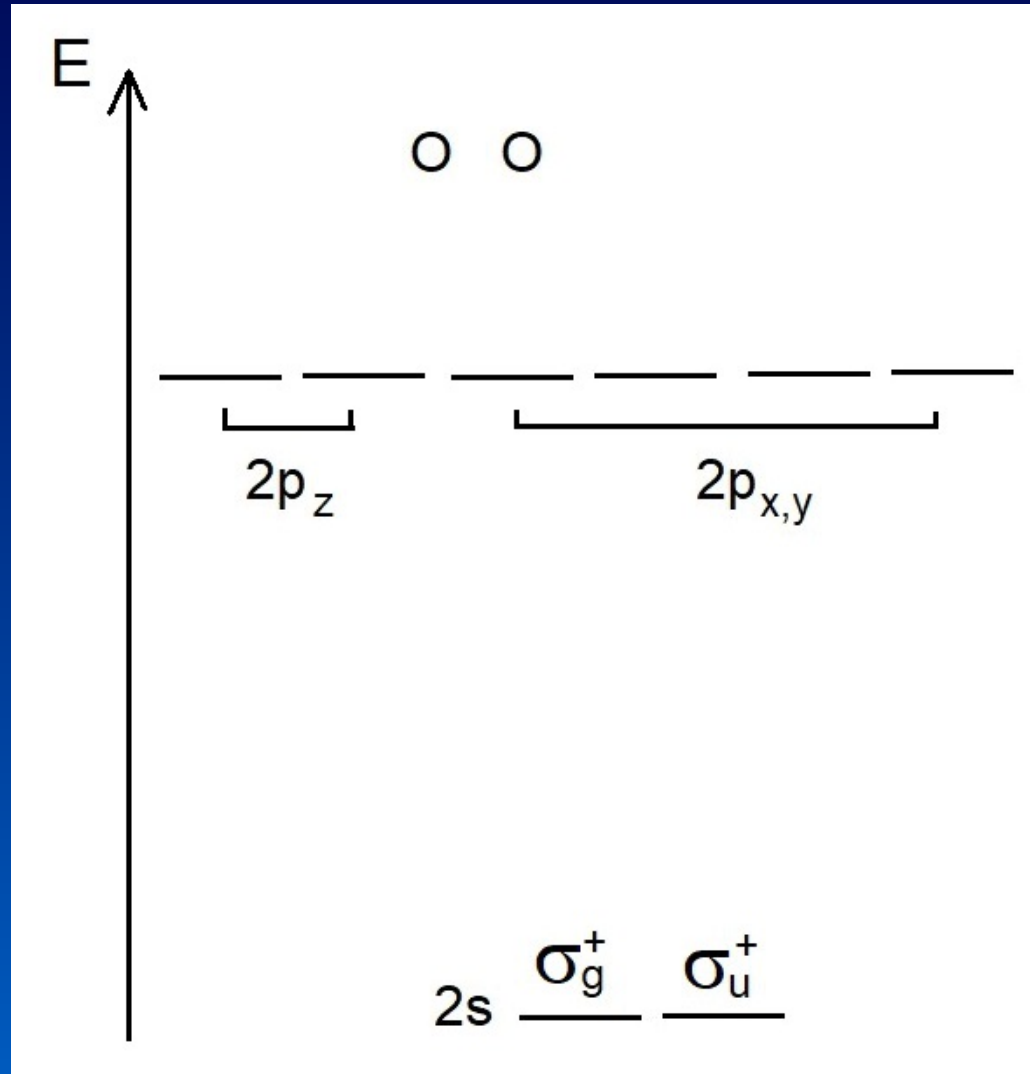
Orbitais 2s - inseparáveis

	$2s(O_1)$	$2s(O_2)$			$2s(O_1)$	$2s(O_2)$
$2s(O_1)$	1	0	i, C_2	$2s(O_1)$	0	1
$2s(O_2)$	0	1	\rightarrow	$2s(O_2)$	1	0
			S_{∞}			
	$\chi = 2$				$\chi = 0$	

Dioxiênio - O₂ - D_{∞h}

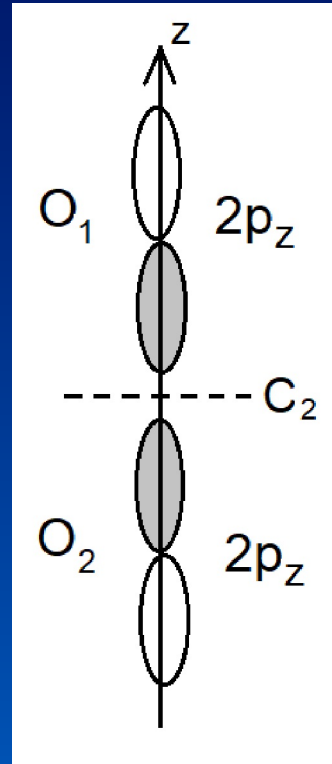
D _{∞h}	E	2C _∞ ^φ	∞σ _v	i	2S _∞ ^φ	∞C ₂
Σ _g ⁺	1	1	1	1	1	1
Σ _g ⁻	1	1	-1	1	1	-1
Π _g	2	2cosφ	0	2	-2cosφ	0
Δ _g	2	2cos2φ	0	2	2cos2φ	0
Σ _u ⁺	1	1	1	-1	-1	-1
Σ _u ⁻	1	1	-1	-1	-1	1
Π _u	2	2cosφ	0	-2	2cosφ	0
Δ _u	2	2cos2φ	0	-2	-2cos2φ	0
2s(O ₁ ,O ₂)	2	2	2	0	0	0
					Σ _g ⁺ ⊕ Σ _u ⁺	

$O_2 - D_{\infty h}$



$O_2 - D_{\infty h}$

Orbitais $2p_z$ - inseparáveis



$O_2 - D_{\infty h}$

Orbitais $2p_z$ - INSEPARÁVEIS

	$2p_z(O_1)$	$2p_z(O_2)$			$2p_z(O_1)$	$2p_z(O_2)$
$2p_z(O_1)$	1	0	E, C_{∞}	$2p_z(O_1)$	1	0
$2p_z(O_2)$	0	1	\rightarrow	$2p_z(O_2)$	0	1
			σ_v			

$$\chi = 2$$

Dioxiênio - O₂ - D_{∞h}

D _{∞h}	E	2C _∞ ^φ	∞σ _v	i	2S _∞ ^φ	∞C ₂
Σ_{g}^{+}	1	1	1	1	1	1
Σ_{g}^{-}	1	1	-1	1	1	-1
Π_{g}	2	2cosφ	0	2	-2cosφ	0
Δ_{g}	2	2cos2φ	0	2	2cos2φ	0
Σ_{u}^{+}	1	1	1	-1	-1	-1
Σ_{u}^{-}	1	1	-1	-1	-1	1
Π_{u}	2	2cosφ	0	-2	2cosφ	0
Δ_{u}	2	2cos2φ	0	-2	-2cos2φ	0

2p _z (O ₁ ,O ₂)	2	2	2
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$O_2 - D_{\infty h}$

Orbitais $2p_z$ - INSEPARÁVEIS

$$\begin{array}{cc} & \begin{array}{cc} 2p_z(O_1) & 2p_z(O_2) \end{array} \\ \begin{array}{c} 2p_z(O_1) \\ 2p_z(O_2) \end{array} & \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \end{array}$$

$$\chi = 2$$

i, C_2
 \rightarrow
 S_{∞}

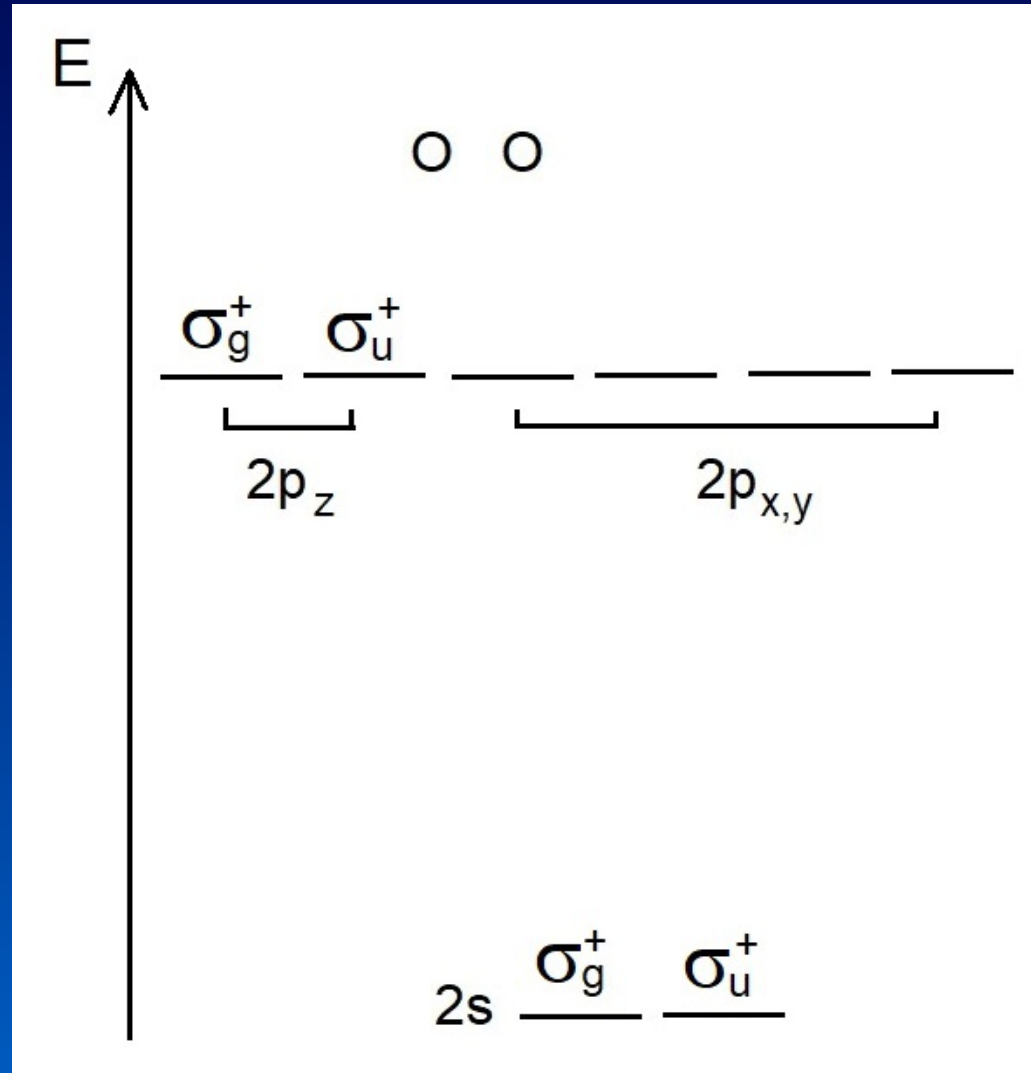
$$\begin{array}{cc} & \begin{array}{cc} 2p_z(O_1) & 2p_z(O_2) \end{array} \\ \begin{array}{c} 2p_z(O_1) \\ 2p_z(O_2) \end{array} & \begin{array}{cc} 0 & 1 \\ 1 & 0 \end{array} \end{array}$$

$$\chi = 0$$

Dioxiênio - O₂ - D_{∞h}

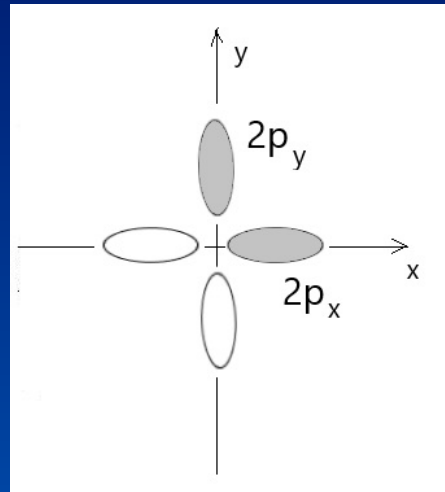
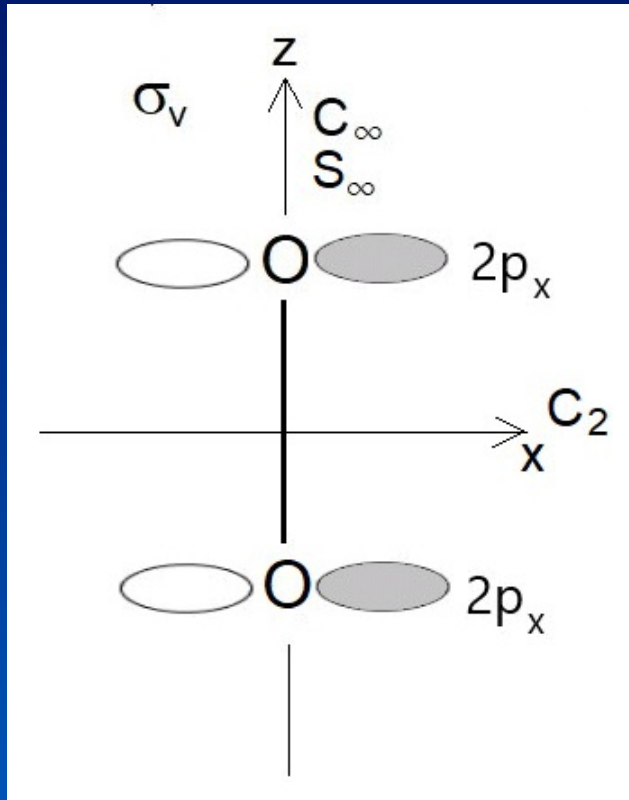
D _{∞h}	E	2C _∞ ^φ	∞σ _v	i	2S _∞ ^φ	∞C ₂
Σ _g ⁺	1	1	1	1	1	1
Σ _g ⁻	1	1	-1	1	1	-1
Π _g	2	2cosφ	0	2	-2cosφ	0
Δ _g	2	2cos2φ	0	2	2cos2φ	0
Σ _u ⁺	1	1	1	-1	-1	-1
Σ _u ⁻	1	1	-1	-1	-1	1
Π _u	2	2cosφ	0	-2	2cosφ	0
Δ _u	2	2cos2φ	0	-2	-2cos2φ	0
2p _z (O ₁ ,O ₂)	2	2	2	0	0	0
					Σ _g ⁺ ⊕ Σ _u ⁺	

$O_2 - D_{\infty h}$



$O_2 - D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios -inseparáveis



Escolhendo $\varphi = 90^\circ$

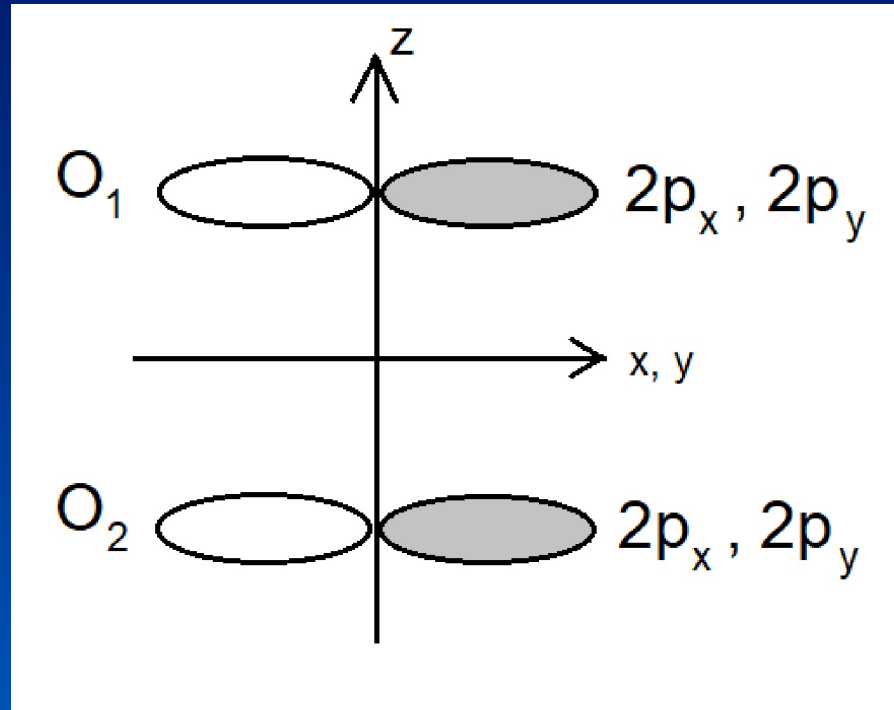
$$C_{\infty}^{\varphi} = C_4$$

$$p_x \rightarrow p_y$$

$$p_y \rightarrow -p_x$$

$O_2 - D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios, inseparáveis



$D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
Σ_{g}^{+}	1	1	1	1	1	1
Σ_{g}^{-}	1	1	-1	1	1	-1
Π_g	2	$2\cos\varphi$	0	2	$-2\cos\varphi$	0
Δ_g	2	$2\cos 2\varphi$	0	2	$2\cos 2\varphi$	0
Σ_u^{+}	1	1	1	-1	-1	-1
Σ_u^{-}	1	1	-1	-1	-1	1
Π_u	2	$2\cos\varphi$	0	-2	$2\cos\varphi$	0
Δ_u	2	$2\cos 2\varphi$	0	-2	$-2\cos 2\varphi$	0

Escolhendo $\varphi = 90^{\circ}$ $\cos\varphi = 0$ $\cos 2\varphi = -1$

$D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
Σ_{g}^{+}	1	1	1	1	1	1
Σ_{g}^{-}	1	1	-1	1	1	-1
Π_g	2	0	0	2	0	0
Δ_g	2	-2	0	2	-2	0
Σ_{u}^{+}	1	1	1	-1	-1	-1
Σ_{u}^{-}	1	1	-1	-1	-1	1
Π_u	2	0	0	-2	0	0
Δ_u	2	-2	0	-2	2	0

Escolhendo $\varphi = 90^{\circ}$ $\cos\varphi = 0$ $\cos 2\varphi = -1$

$O_2 - D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios - INSEPARÁVEIS

	$2p_x^1$	$2p_y^1$	$2p_x^2$	$2p_y^2$		$2p_x^1$	$2p_y^1$	$2p_x^2$	$2p_y^2$	
$2p_x^1$	1	0	0	0	$C_{\infty}^{\varphi=90^\circ}$ \rightarrow	$2p_x^1$	0	1	0	0
$2p_y^1$	0	1	0	0		$2p_y^1$	-1	0	0	0
$2p_x^2$	0	0	1	0		$2p_x^2$	0	0	0	1
$2p_y^2$	0	0	0	1		$2p_y^2$	0	0	-1	0
				$\chi = 4$					$\chi = 0$	

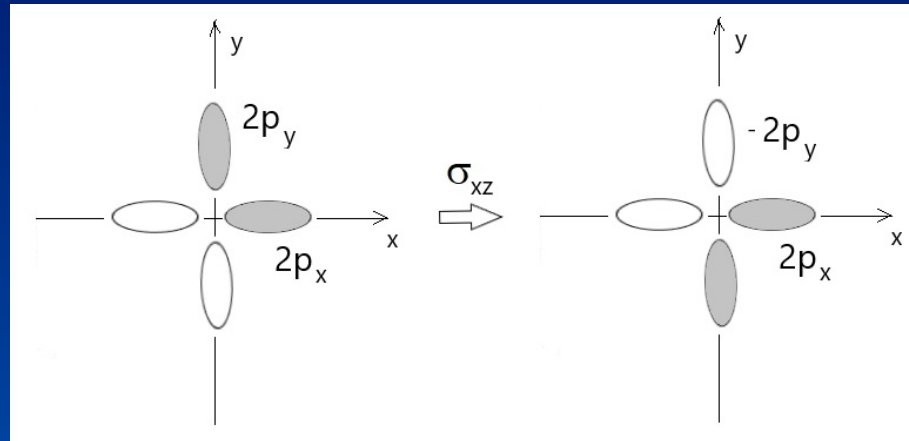
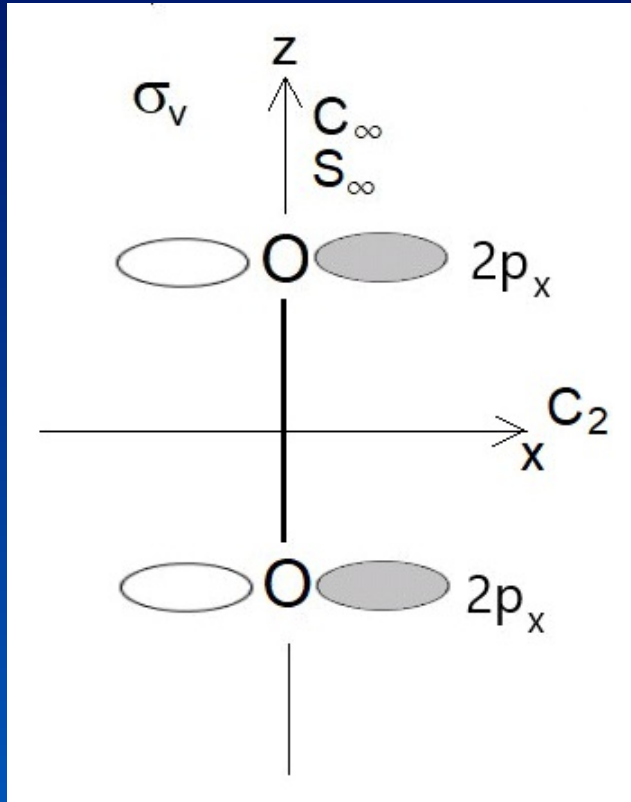
Dioxiênio - O₂ - D_{∞h}

D _{∞h}	E	2C _∞ ^φ	∞σ _v	i	2S _∞ ^φ	∞C ₂
Σ _g ⁺	1	1	1	1	1	1
Σ _g ⁻	1	1	-1	1	1	-1
Π _g	2	0	0	2	0	0
Δ _g	2	-2	0	2	-2	0
Σ _u ⁺	1	1	1	-1	-1	-1
Σ _u ⁻	1	1	-1	-1	-1	1
Π _u	2	0	0	-2	0	0
Δ _u	2	-2	0	-2	2	0

2p_{x,y}(O₁,O₂) 4 0

$O_2 - D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios -inseparáveis



$O_2 - D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios - INSEPARÁVEIS

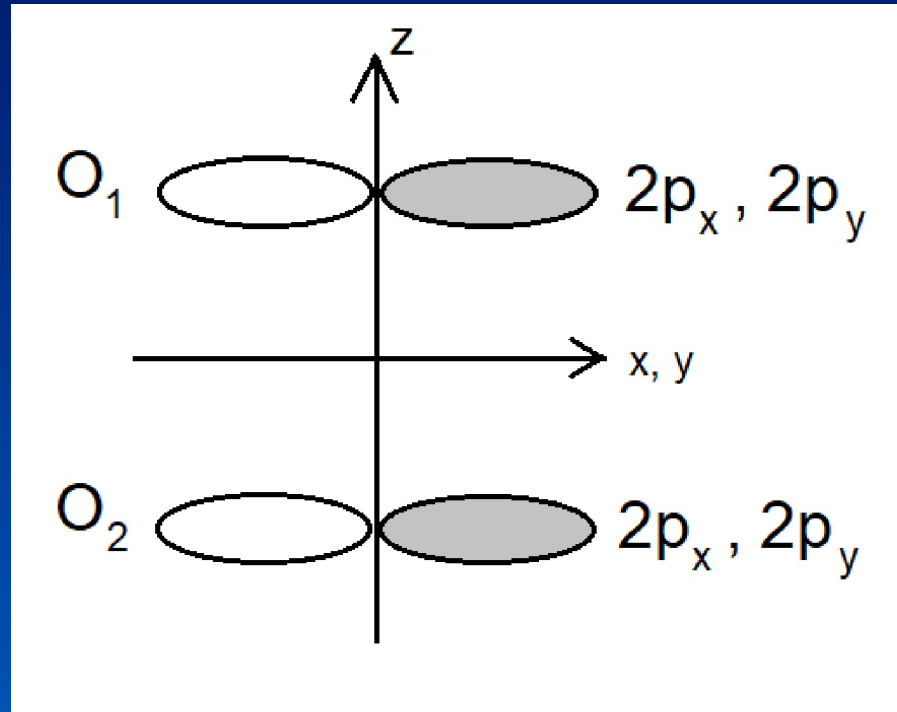
	$2p_x^1$	$2p_y^1$	$2p_x^2$	$2p_y^2$		$2p_x^1$	$2p_y^1$	$2p_x^2$	$2p_y^2$	
$2p_x^1$	1	0	0	0	$\sigma_v^{(xz)}$ →	$2p_x^1$	1	0	0	0
$2p_y^1$	0	1	0	0		$2p_y^1$	0	-1	0	0
$2p_x^2$	0	0	1	0		$2p_x^2$	0	0	1	0
$2p_y^2$	0	0	0	1		$2p_y^2$	0	0	0	-1
			$\chi = 4$					$\chi = 0$		

Dioxiênio - O₂ - D_{∞h}

D _{∞h}	E	2C _∞ ^φ	∞σ _v	i	2S _∞ ^φ	∞C ₂
Σ _g ⁺	1	1	1	1	1	1
Σ _g ⁻	1	1	-1	1	1	-1
Π _g	2	0	0	2	0	0
Δ _g	2	-2	0	2	-2	0
Σ _u ⁺	1	1	1	-1	-1	-1
Σ _u ⁻	1	1	-1	-1	-1	1
Π _u	2	0	0	-2	0	0
Δ _u	2	-2	0	-2	2	0
<hr/>						
2p _{x,y} (O ₁ ,O ₂)	4	0	0			

$O_2 - D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios, inseparáveis



Orbitais $2p_x$ e $2p_y$ dos d

$O_2 - D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios - INSEPARÁVEIS

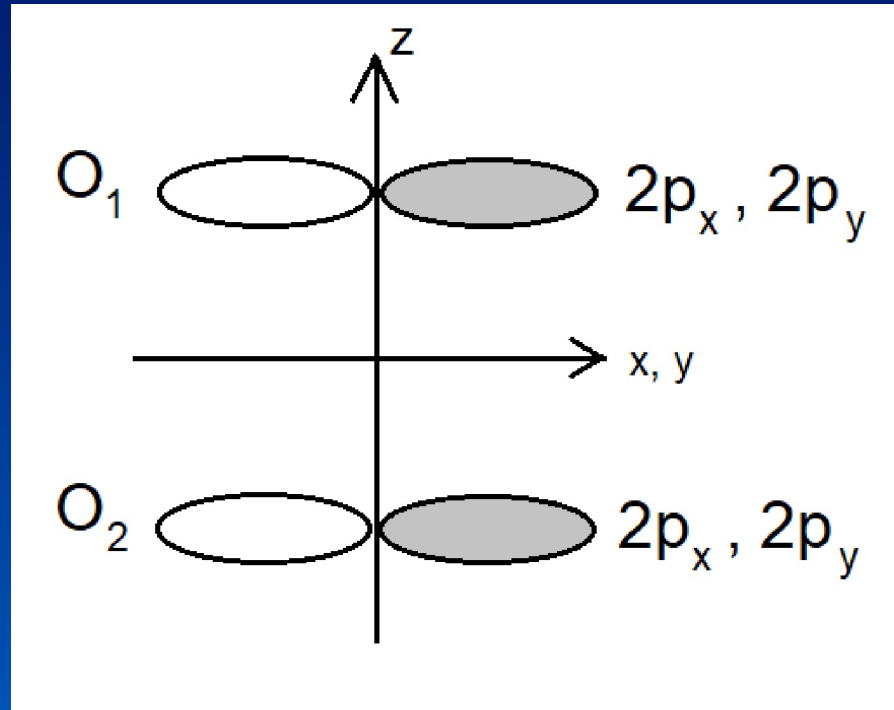
	$2p_x^1$	$2p_y^1$	$2p_x^2$	$2p_y^2$		$2p_x^1$	$2p_y^1$	$2p_x^2$	$2p_y^2$	
$2p_x^1$	1	0	0	0	i →	$2p_x^1$	0	0	-1	0
$2p_y^1$	0	1	0	0		$2p_y^1$	0	0	0	-1
$2p_x^2$	0	0	1	0		$2p_x^2$	-1	0	0	0
$2p_y^2$	0	0	0	1		$2p_y^2$	0	-1	0	0
			$\chi = 4$					$\chi = 0$		

Dioxiênio - O₂ - D_{∞h}

D _{∞h}	E	2C _∞ ^φ	∞σ _v	i	2S _∞ ^φ	∞C ₂
Σ _g ⁺	1	1	1	1	1	1
Σ _g ⁻	1	1	-1	1	1	-1
Π _g	2	0	0	2	0	0
Δ _g	2	-2	0	2	-2	0
Σ _u ⁺	1	1	1	-1	-1	-1
Σ _u ⁻	1	1	-1	-1	-1	1
Π _u	2	0	0	-2	0	0
Δ _u	2	-2	0	-2	2	0
<hr/>						
2p _{x,y} (O ₁ ,O ₂)	4	0	0	0		

$O_2 - D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios, inseparáveis



$O_2 - D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios - INSEPARÁVEIS

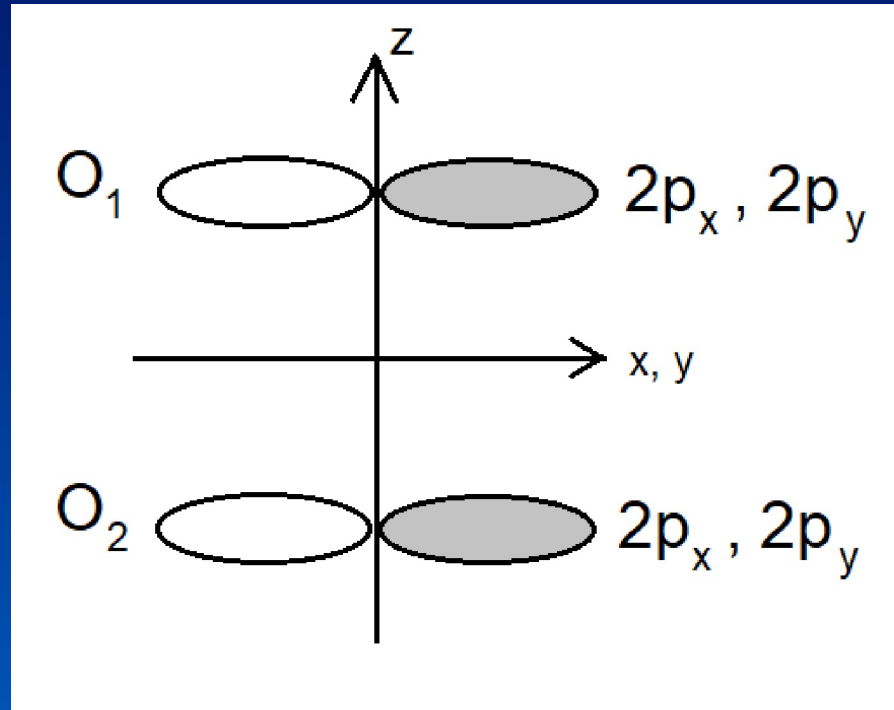
	$2p_x^1$	$2p_y^1$	$2p_x^2$	$2p_y^2$		$2p_x^1$	$2p_y^1$	$2p_x^2$	$2p_y^2$	
$2p_x^1$	1	0	0	0	$S_{\infty}^{\varphi=90^\circ}$ →	$2p_x^1$	0	0	0	1
$2p_y^1$	0	1	0	0		$2p_y^1$	0	0	-1	0
$2p_x^2$	0	0	1	0		$2p_x^2$	0	1	0	0
$2p_y^2$	0	0	0	1		$2p_y^2$	-1	0	0	0
			$\chi = 4$						$\chi = 0$	

Dioxiênio - O₂ - D_{∞h}

D _{∞h}	E	2C _∞ ^φ	∞σ _v	i	2S _∞ ^φ	∞C ₂
Σ _g ⁺	1	1	1	1	1	1
Σ _g ⁻	1	1	-1	1	1	-1
Π _g	2	0	0	2	0	0
Δ _g	2	-2	0	2	-2	0
Σ _u ⁺	1	1	1	-1	-1	-1
Σ _u ⁻	1	1	-1	-1	-1	1
Π _u	2	0	0	-2	0	0
Δ _u	2	-2	0	-2	2	0
<hr/>						
2p _{x,y} (O ₁ ,O ₂)	4	0	0	0	0	0

$O_2 - D_{\infty h}$

Orbitais $2p_x$ e $2p_y$ dos dois oxigênios, inseparáveis



$O_2 - D_{\infty h}$

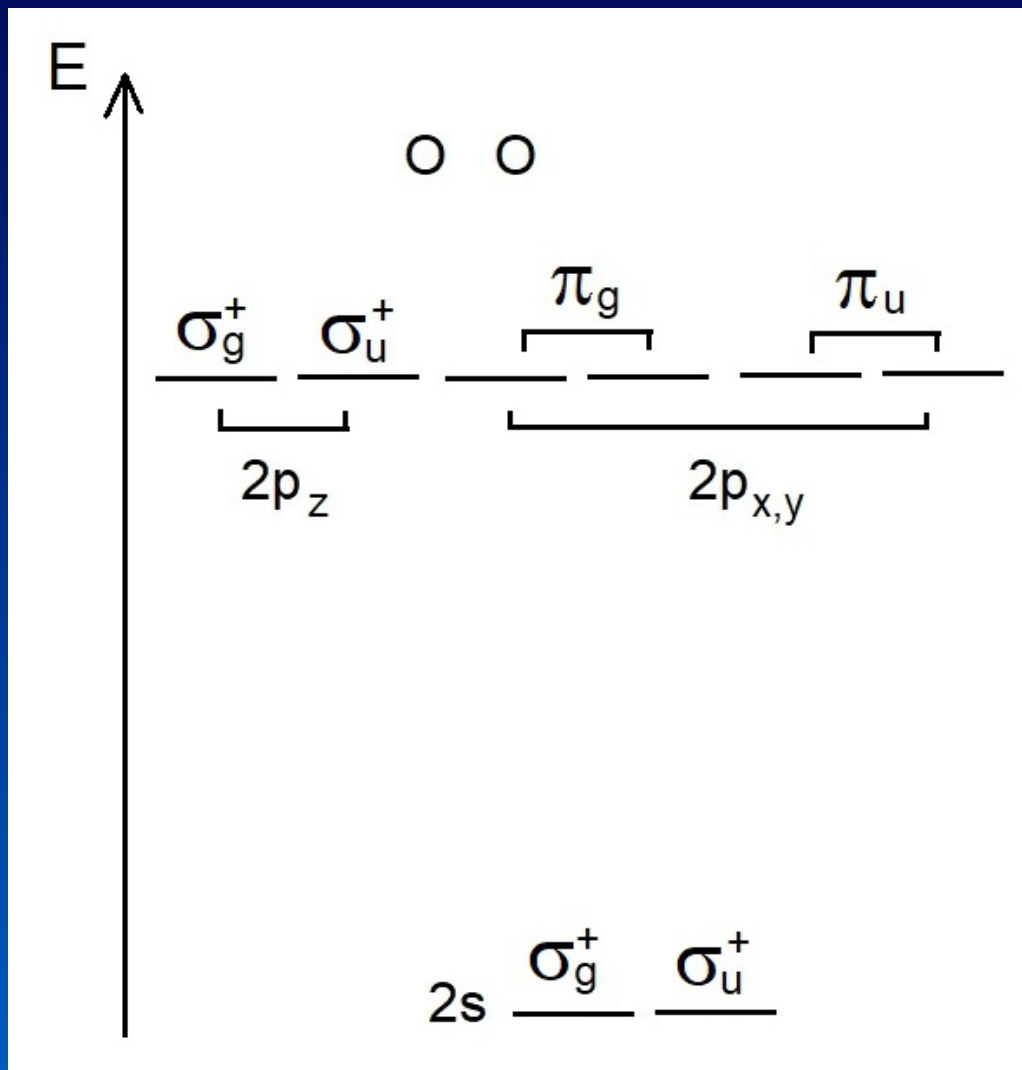
Orbitais $2p_x$ e $2p_y$ dos dois oxigênios - INSEPARÁVEIS

	$2p_x^1$	$2p_y^1$	$2p_x^2$	$2p_y^2$		$2p_x^1$	$2p_y^1$	$2p_x^2$	$2p_y^2$	
$2p_x^1$	1	0	0	0	C_2^x →	$2p_x^1$	0	0	1	0
$2p_y^1$	0	1	0	0		$2p_y^1$	0	0	0	-1
$2p_x^2$	0	0	1	0		$2p_x^2$	1	0	0	0
$2p_y^2$	0	0	0	1		$2p_y^2$	0	-1	0	0
				$\chi = 4$					$\chi = 0$	

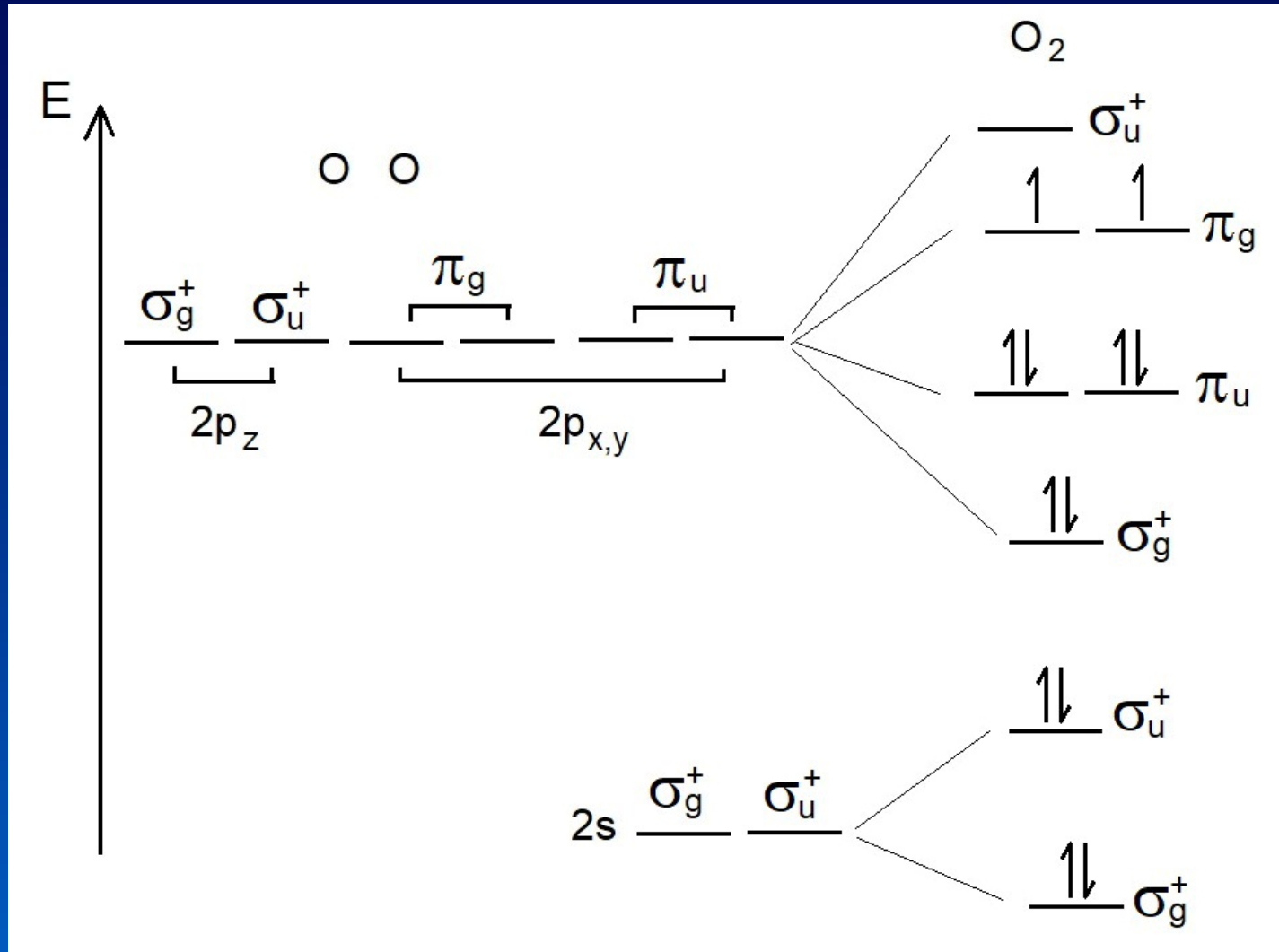
Dioxiênio - O₂ - D_{∞h}

D _{∞h}	E	2C _∞ ^φ	∞σ _v	i	2S _∞ ^φ	∞C ₂
Σ _g ⁺	1	1	1	1	1	1
Σ _g ⁻	1	1	-1	1	1	-1
Π _g	2	0	0	2	0	0
Δ _g	2	-2	0	2	-2	0
Σ _u ⁺	1	1	1	-1	-1	-1
Σ _u ⁻	1	1	-1	-1	-1	1
Π _u	2	0	0	-2	0	0
Δ _u	2	-2	0	-2	2	0
2p _{x,y} (O ₁ ,O ₂)	4	0	0	0	0	0
						Π _g ⊕ Π _u

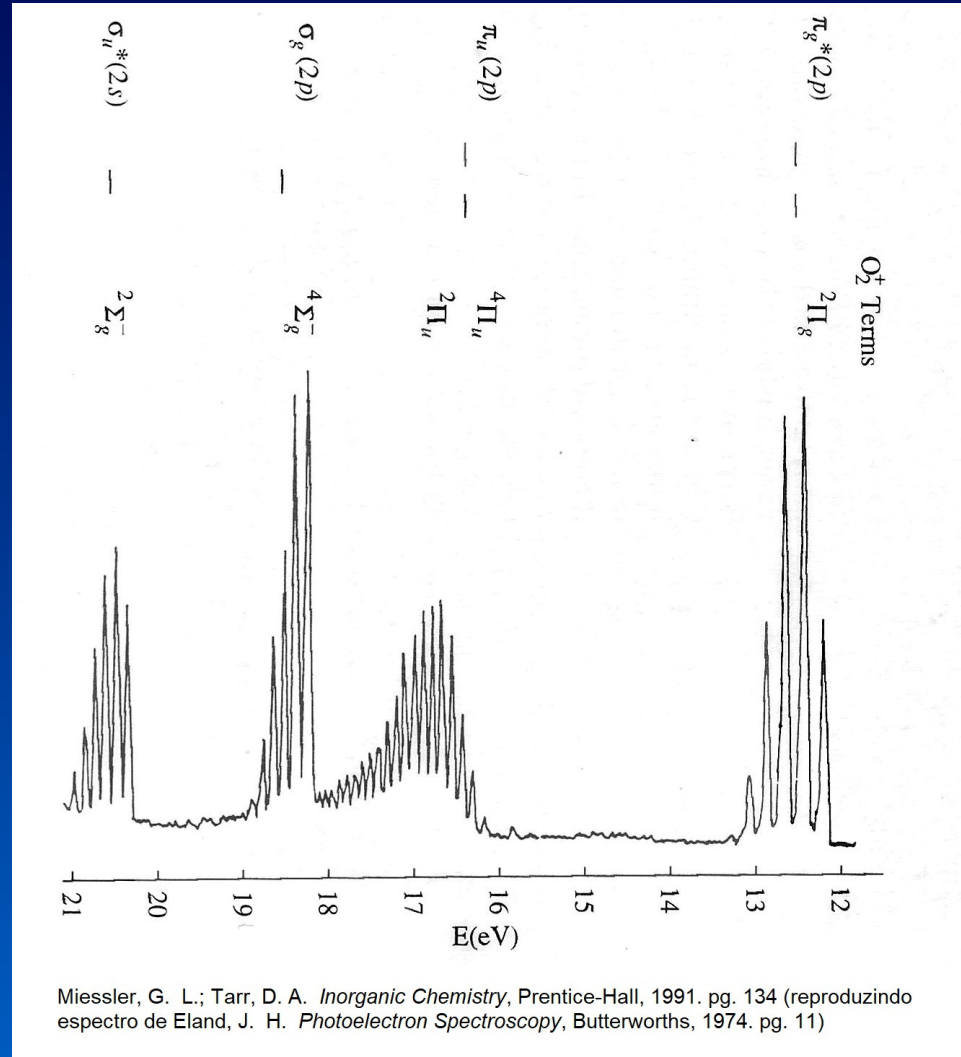
$O_2 - D_{\infty h}$



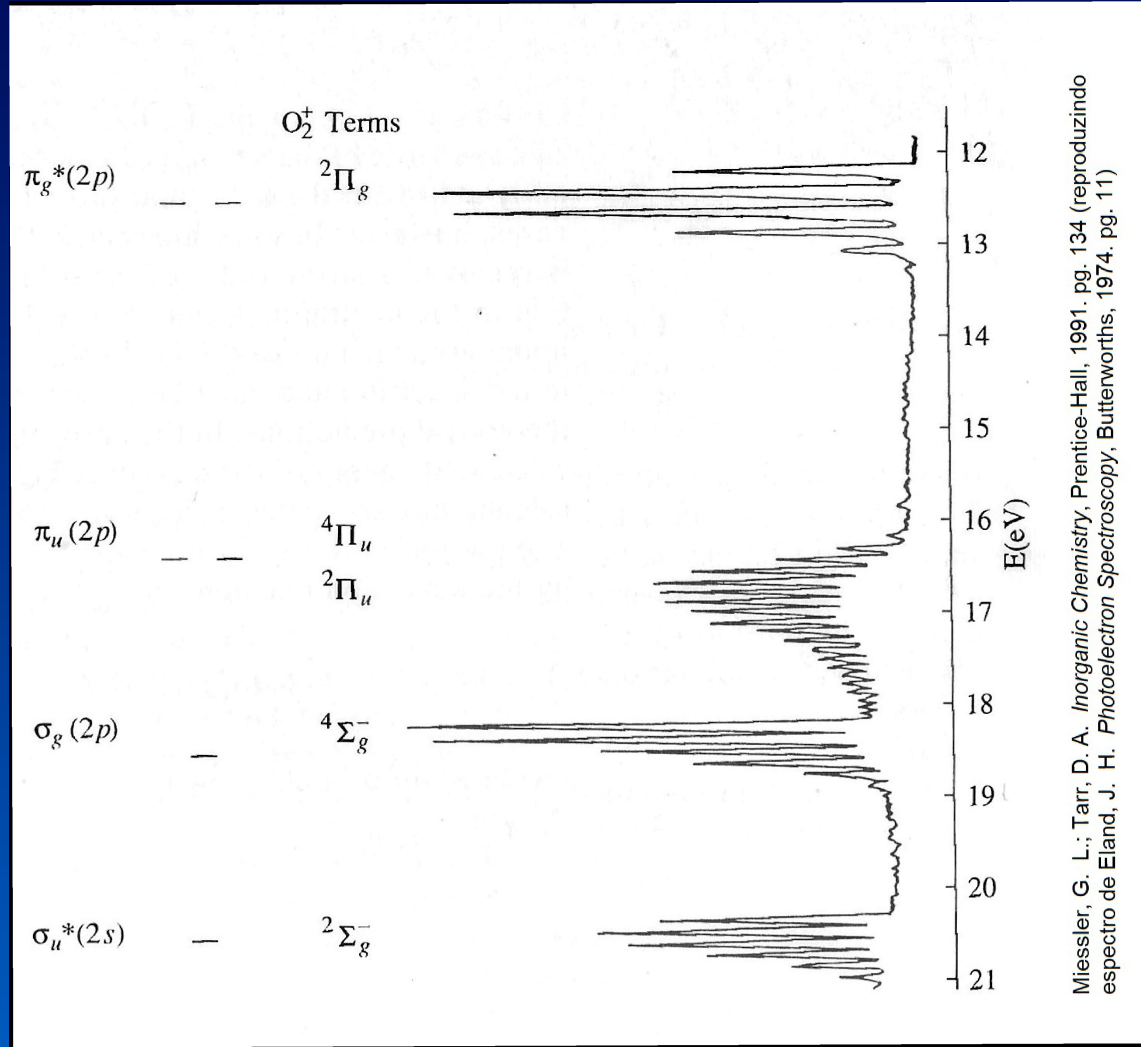
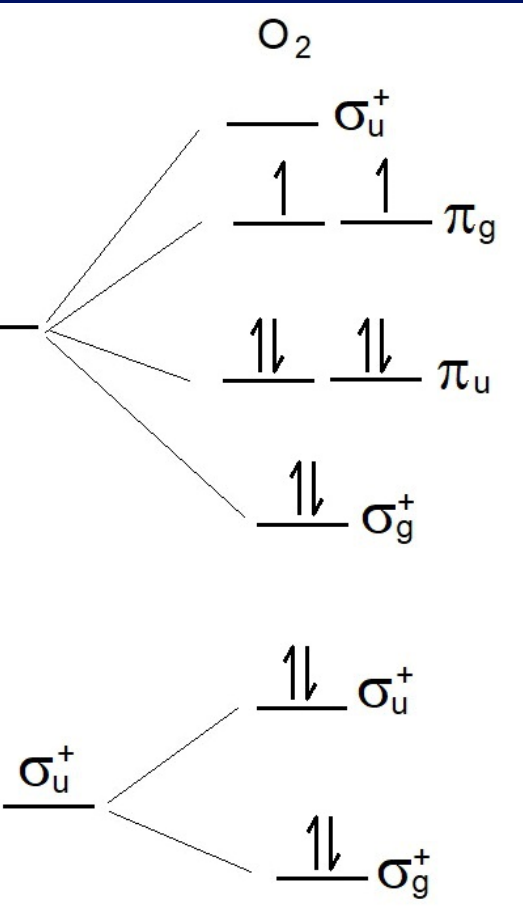
$O_2 - D_{\infty h}$



Espectros de fotoelétron - O₂

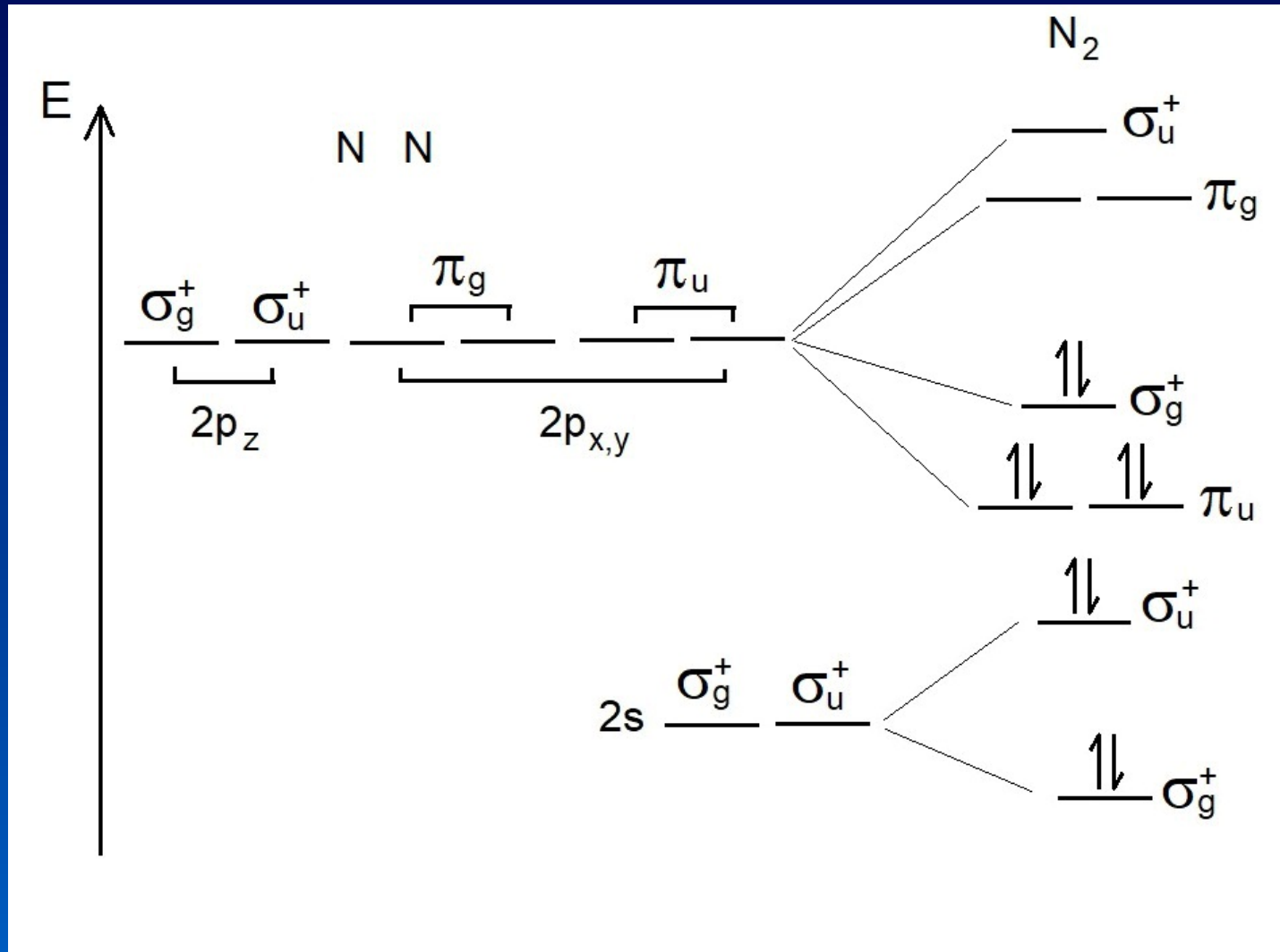


Espectros de fotoelétron - O₂

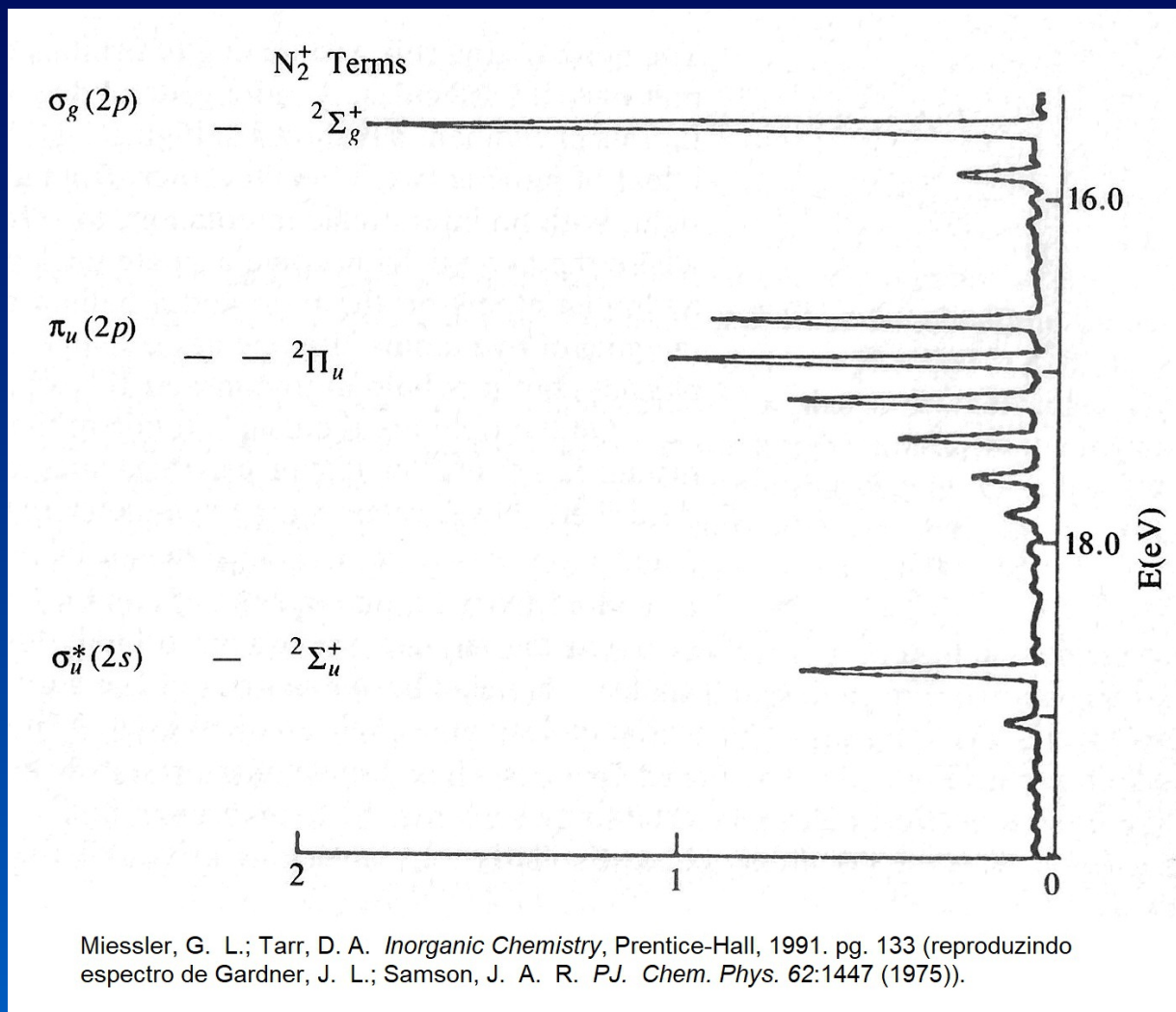


Miessler, G. L.; Tarr, D. A. *Inorganic Chemistry*, Prentice-Hall, 1991, pg. 134 (reproduzindo espectro de Eland, J. H. *Photoelectron Spectroscopy*, Butterworths, 1974, pg. 11)

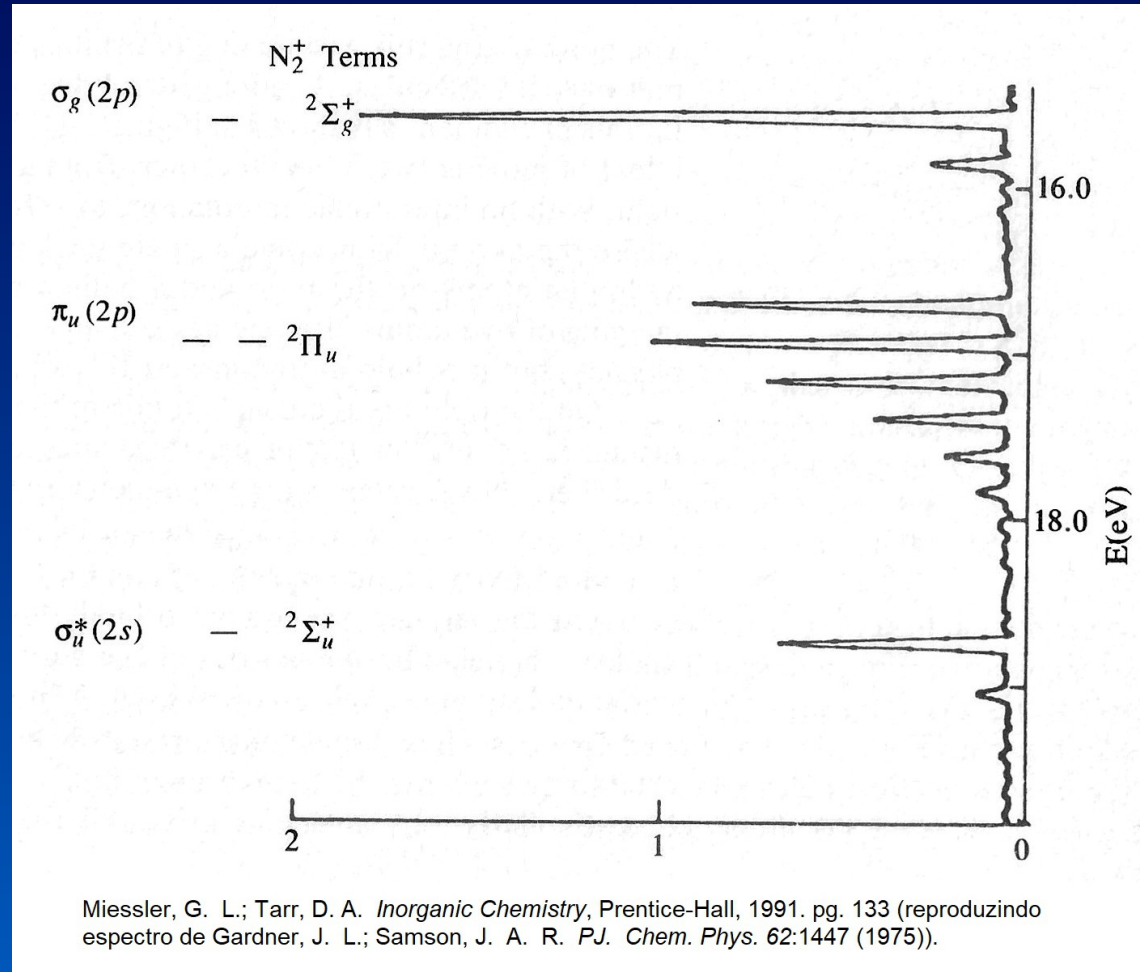
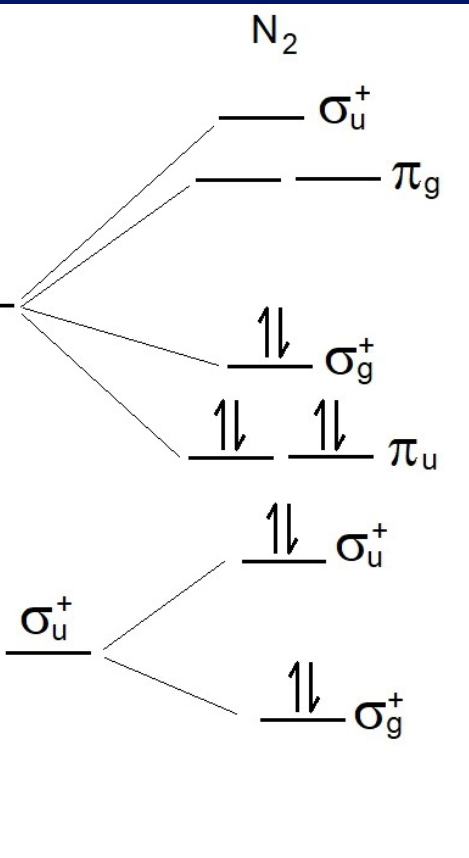
$N_2 - D_{\infty h}$



Espectro de fotoelétron - N₂

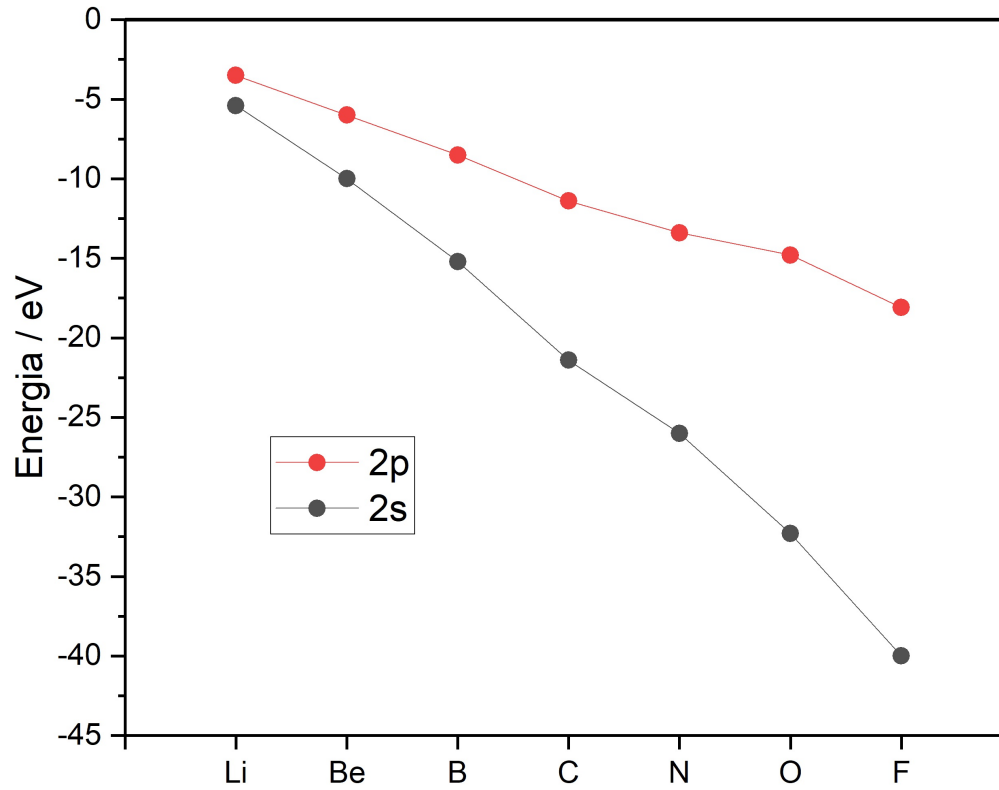


Espectro de fotoelétron - N₂

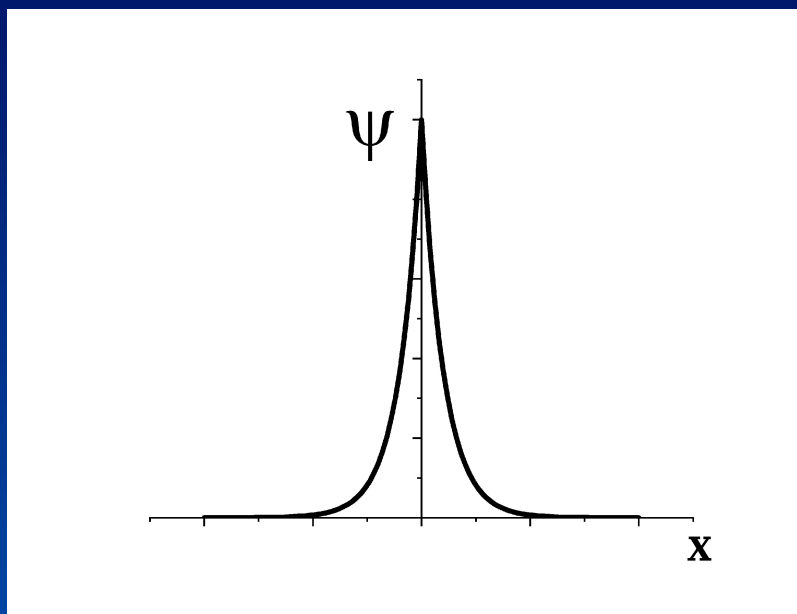


Miessler, G. L.; Tarr, D. A. *Inorganic Chemistry*, Prentice-Hall, 1991. pg. 133 (reproduzindo espectro de Gardner, J. L.; Samson, J. A. R. *PJ. Chem. Phys.* 62:1447 (1975)).

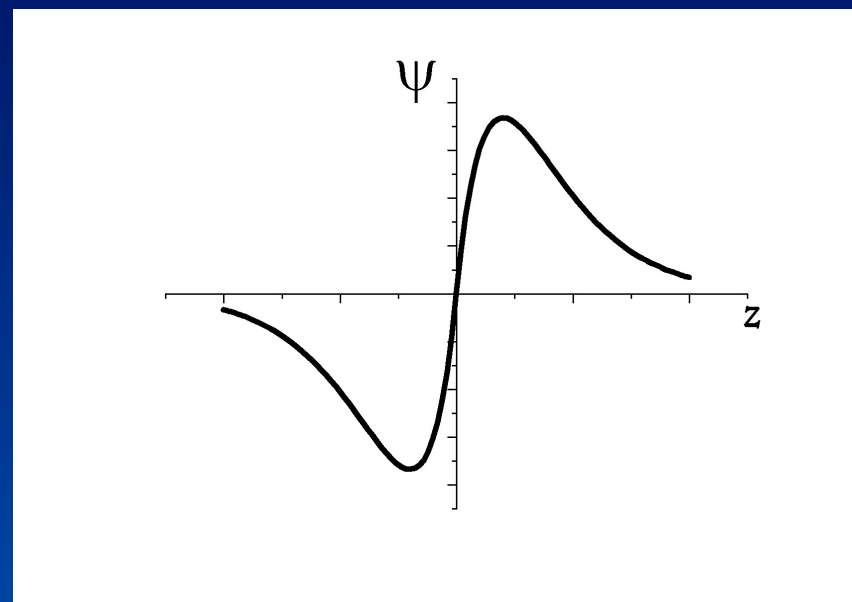
Energias dos orbitais atômicos



Funções de onda dos orbitais atômicos

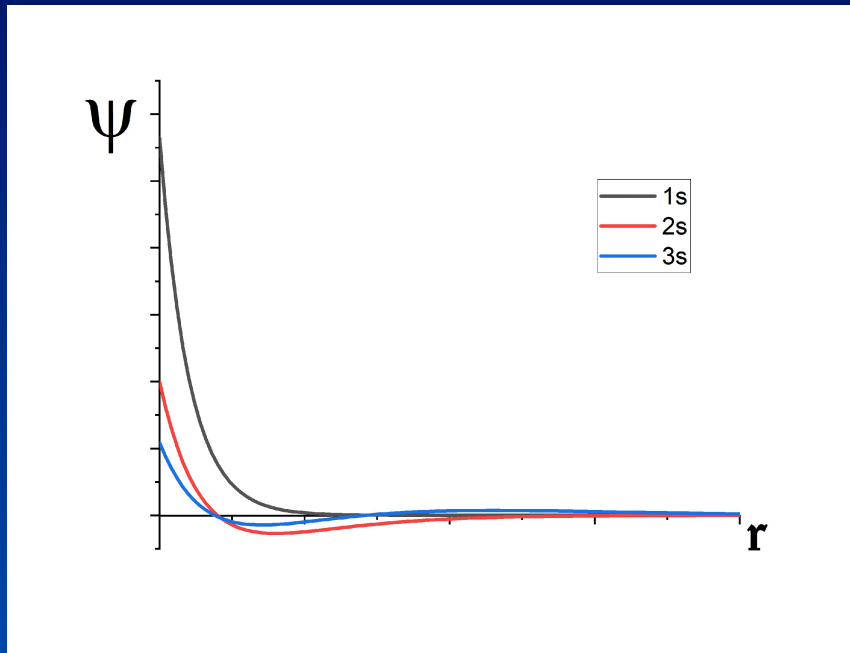


1s

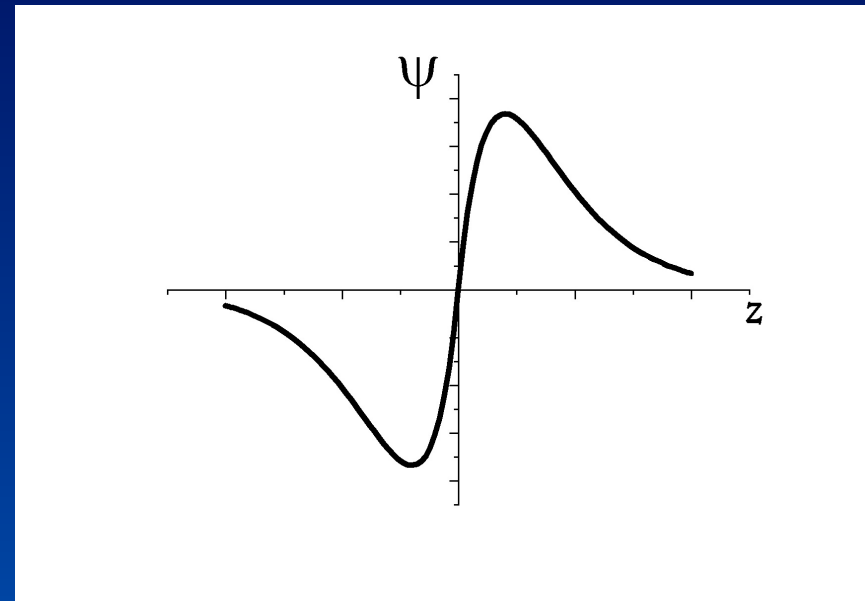


2p

Funções de onda dos orbitais atômicos



1s, 2s, 3s



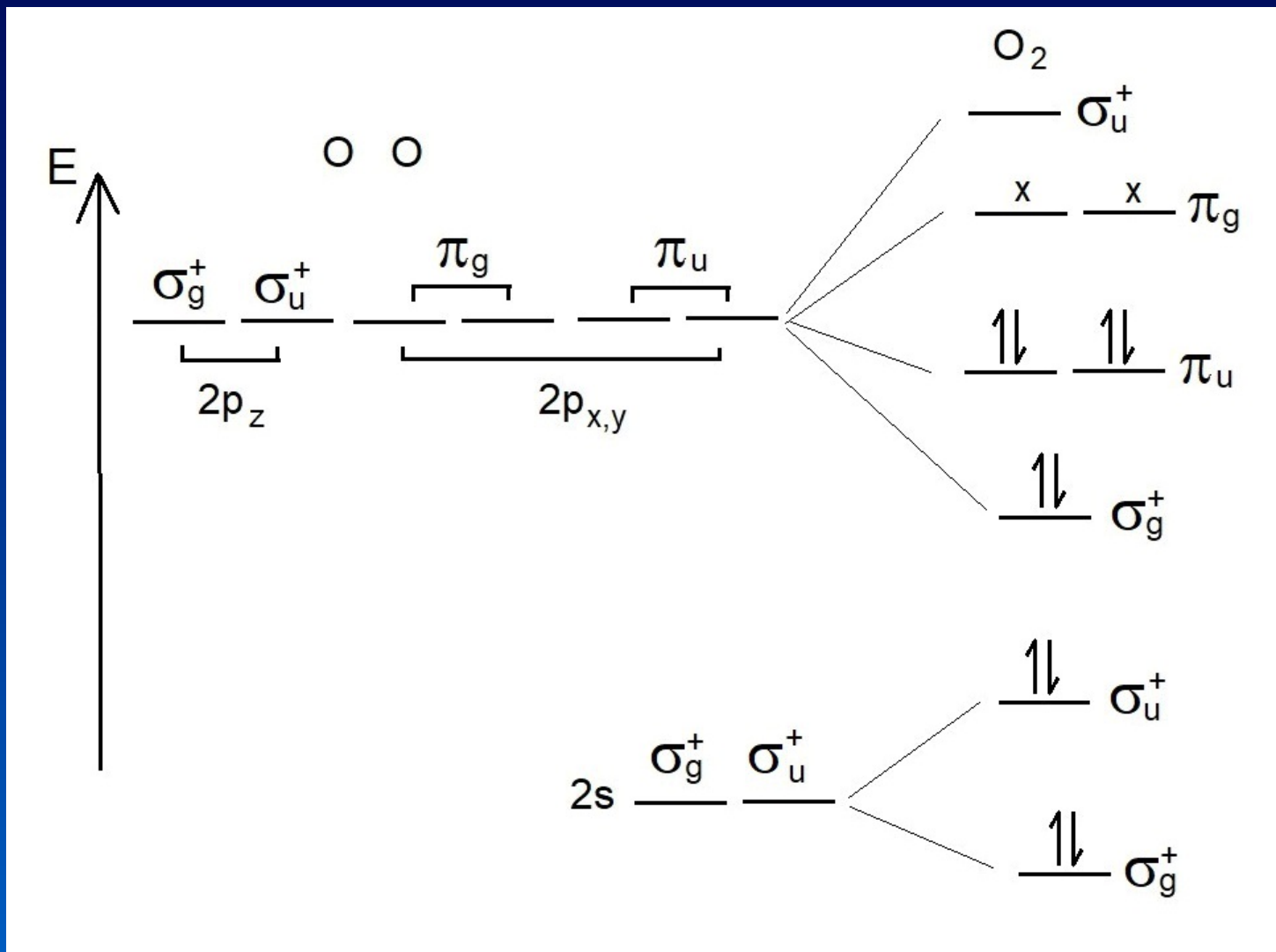
2p

Termos espectroscópicos para moléculas

Termos espectroscópicos para moléculas

dioxigênio - O₂

O₂ - D_{∞h}



$D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
Σ_{g}^{+}	1	1	1	1	1	1
Σ_{g}^{-}	1	1	-1	1	1	-1
Π_{g}	2	0	0	2	0	0
Δ_{g}	2	-2	0	2	-2	0
Σ_{u}^{+}	1	1	1	-1	-1	-1
Σ_{u}^{-}	1	1	-1	-1	-1	1
Π_{u}	2	0	0	-2	0	0
Δ_{u}	2	-2	0	-2	2	0

Escolhendo $\varphi = 90^{\circ}$ $\cos\varphi = 0$ $\cos 2\varphi = -1$

$D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
Σ_{g}^{+}	1	1	1	1	1	1
Σ_{g}^{-}	1	1	-1	1	1	-1
Π_{g}	2	0	0	2	0	0
Δ_{g}	2	-2	0	2	-2	0
Σ_{u}^{+}	1	1	1	-1	-1	-1
Σ_{u}^{-}	1	1	-1	-1	-1	1
Π_{u}	2	0	0	-2	0	0
Δ_{u}	2	-2	0	-2	2	0
$\Pi_{g} \otimes \Pi_{g}$	4	0	0	4	0	0
					$\Sigma_{g}^{+} \oplus \Sigma_{g}^{-} \oplus \Delta_{g}$	

$O_2 - D_{\infty h}$

Determinando os singletos e tripletos

- Uma vez que os elétrons estão em orbitais degenerados, temos as possibilidades:

Π_g		Σ_{ms}
<u>x</u>	<u>x</u>	1, 0, 0, -1
<u>xx</u>	<u> </u>	0
<u> </u>	<u>xx</u>	0

triplete = 1, 0, -1
 singleto = 0

6 microestados

$$\Pi_g \otimes \Pi_g = {}^a\Sigma_g^+ + {}^b\Sigma_g^- + {}^c\Delta_g$$

$$a + b + 2c = 6$$

(a, b, c) só podem ser 1 ou 3

Soluções possíveis:

$$(3, 1, 1) = {}^3\Sigma_g^+ + {}^1\Sigma_g^- + {}^1\Delta_g$$

ou

$$(1, 3, 1) = {}^1\Sigma_g^+ + {}^3\Sigma_g^- + {}^1\Delta_g$$

$O_2 - D_{\infty h}$

Determinando os singletos e tripletos

Para decidir entre as duas soluções possíveis

$${}^3\Sigma_g^+ + {}^1\Sigma_g^- + {}^1\Delta_g \quad \text{ou} \quad {}^1\Sigma_g^+ + {}^3\Sigma_g^- + {}^1\Delta_g$$

precisamos saber quais desses termos são simétricos ou antissimétricos

$O_2 - D_{\infty h}$

Determinando os singletos e tripletos

Para o caso do produto direto entre duas representações irredutíveis iguais, as componentes das representações simétricas (χ^+) e antissimétricas (χ^-) são dadas por:

$$\text{caracteres } \chi^+ = (1/2) \{[\chi(R)]^2 + \chi(R^2)\}$$

$$\text{caracteres } \chi^- = (1/2) \{[\chi(R)]^2 - \chi(R^2)\}$$

R^2 é o resultado da aplicação de uma mesma operação de simetria duas vezes. Assim, no $D_{\infty h}$ teremos:

R	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
R^2	E	—	E	E	—	E

$O_2 - D_{\infty h}$

Determinando os singletos e tripletos

$$\text{caracteres } \chi^+ = (1/2) \{[\chi(R)]^2 + \chi(R^2)\}$$

$$\text{caracteres } \chi^- = (1/2) \{[\chi(R)]^2 - \chi(R^2)\}$$

$\chi(R^2)$ é o caracter da operação de simetria resultante.

Assim, como para a operação E no Π_g temos

$$\chi(E) = \chi(R^2) = 2$$

R	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
R^2	E	—	E	E	—	E
$\chi(R^2)$	2	—	2	2	—	2

$O_2 - D_{\infty h}$

Determinando os singletos e tripletos

$$\text{caracteres } \chi^+ = (1/2) \{[\chi(R)]^2 + \chi(R^2)\}$$

$$\text{caracteres } \chi^- = (1/2) \{[\chi(R)]^2 - \chi(R^2)\}$$

$[\chi(R)]^2$ é o quadrado do caracter de cada operação de simetria. Assim, para o Π_g no $D_{\infty h}$ teremos:

	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
Π_g	2	$2\cos\varphi$	0	2	$-2\cos\varphi$	0
$[\chi(R)]^2$	4	—	0	4	—	0

$O_2 - D_{\infty h}$

Determinando os singletos e tripletos

$$\text{caracteres } \chi^+ = (1/2) \{[\chi(R)]^2 + \chi(R^2)\}$$

$$\text{caracteres } \chi^- = (1/2) \{[\chi(R)]^2 - \chi(R^2)\}$$

Dessa forma, para o Π_g no $D_{\infty h}$ teremos:

	E	$2C_{\infty}^{\phi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\phi}$	∞C_2
$[\chi(R)]^2$	4	—	0	4	—	0
$\chi(R^2)$	2	—	2	2	—	2
$\chi^+ =$	3	—	1	3	—	1
$\chi^- =$	1	—	-1	1	—	-1

$O_2 - D_{\infty h}$

Determinando os singletos e tripletos

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
Σ_{g}^{+}	1	1	1	1	1	1
Δ_{g}	2	$2\cos 2\varphi$	0	2	$2\cos 2\varphi$	0
$\chi^{+} =$	3	—	1	3	—	1
Σ_{g}^{-}	1	1	-1	1	1	-1
$\chi^{-} =$	1	—	-1	1	—	-1

Representações simétricas

Representações antissimétricas

$O_2 - D_{\infty h}$

Determinando os singletos e tripletos

- Como os elétrons possuem spin fracionário eles são férmions.
- Para os férmions, $\psi_{\text{orbital}}\psi_{\text{spin}}$ tem que ser uma função antissimétrica com relação à permutação dos elétrons.

$$\begin{array}{l} \Sigma_{\text{g}}^{+} \text{ (simétrica)} \quad \times \quad \psi_{\text{spin}} \text{ (antissimétrica)} \\ \Sigma_{\text{g}}^{-} \text{ (antissimétrica)} \quad \times \quad \psi_{\text{spin}} \text{ (simétrica)} \\ \Delta_{\text{g}} \text{ (simétrica)} \quad \times \quad \psi_{\text{spin}} \text{ (antissimétrica)} \end{array}$$

$O_2 - D_{\infty h}$

Determinando os singletos e tripletos

- Como os elétrons possuem spin fracionários eles são férmions.

- Para os férmions, $\psi_{\text{orbital}}\psi_{\text{spin}}$ tem que ser uma função antissimétrica com relação à permutação dos elétrons.

$$\begin{array}{ll} \Sigma_{\text{g}}^{+} \text{ (simétrica)} & \times [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \\ \Sigma_{\text{g}}^{-} \text{ (antissimétrica)} & \times \psi_{\text{spin}} \text{ (simétrica)} \\ \Delta_{\text{g}} \text{ (simétrica)} & \times [\alpha(1)\beta(2) - \alpha(2)\beta(1)] \end{array}$$

$O_2 - D_{\infty h}$

Determinando os singletos e tripletos

- Como a função de spin antissimétrica

$$[\alpha(1)\beta(2) - \alpha(2)\beta(1)]$$

corresponde a uma única possibilidade, trata-se de um singlete.

Σ_{σ}^+ (simétrica) \times singlete

Σ_{σ}^- (antissimétrica) $\times \psi_{\text{spin}}$ (simétrica)

Δ_{σ} (simétrica) \times singlete

$O_2 - D_{\infty h}$

Determinando os singletos e tripletos

$$\psi_{\text{spin}} (\text{simétrica}) = [\alpha(1)\alpha(2)] + [\beta(1)\beta(2)] + [\alpha(1)\beta(2) + \alpha(2)\beta(1)]$$

TRIPLETO

$O_2 - D_{\infty h}$

Determinando os singletos e tripletos

$$\begin{array}{l} \Sigma_{\sigma_g}^+ \text{ (simétrica)} \quad \times \text{ singleto} = {}^1\Sigma_{\sigma_g}^+ \\ \Sigma_{\sigma_g}^- \text{ (antissimétrica)} \quad \times \text{ tripleto} = {}^3\Sigma_{\sigma_g}^- \\ \Delta_{\sigma_g} \text{ (simétrica)} \quad \times \text{ singleto} = {}^1\Delta_{\sigma_g} \end{array}$$

$O_2 - D_{\infty h}$

Determinando os singletos e tripletos

Assim, entre as duas soluções possíveis

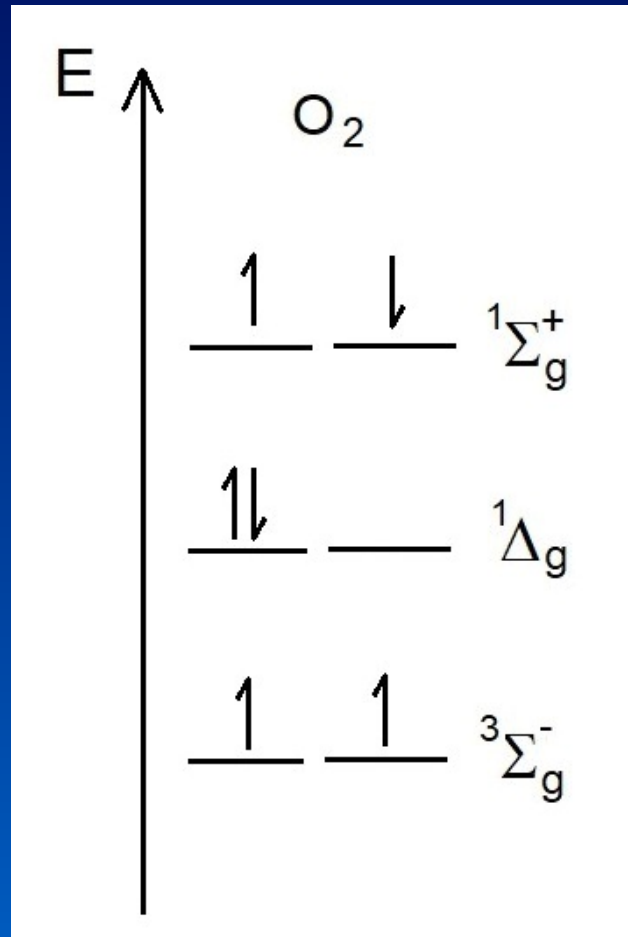
$${}^3\Sigma_g^+ + {}^1\Sigma_g^- + {}^1\Delta_g \quad \text{ou} \quad {}^1\Sigma_g^+ + {}^3\Sigma_g^- + {}^1\Delta_g$$

a solução correta é

$${}^1\Sigma_g^+ \quad {}^3\Sigma_g^- \quad {}^1\Delta_g$$

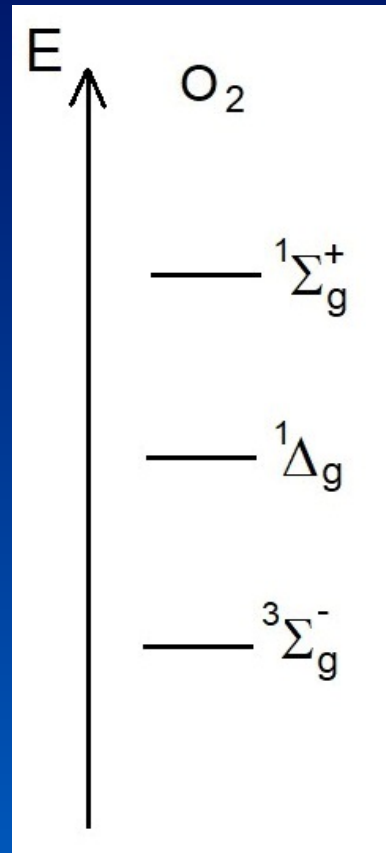
$O_2 - D_{\infty h}$

Níveis de energia da molécula



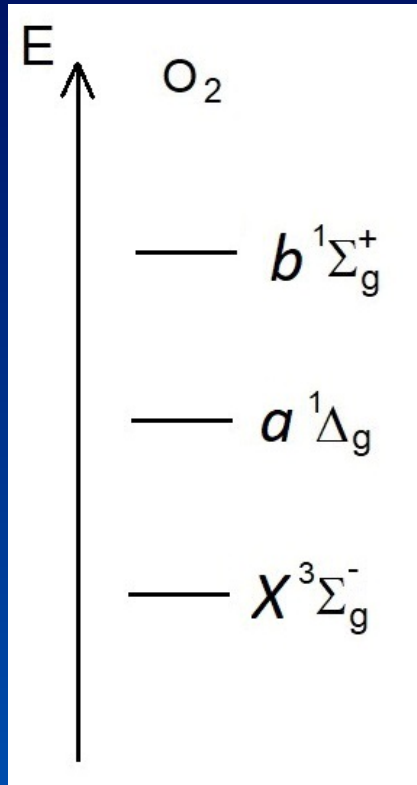
$O_2 - D_{\infty h}$

Níveis de energia da molécula



$O_2 - D_{\infty h}$

Níveis de energia da molécula



Energia da transição 0-0

cm^{-1}	nm	
13120	762	$b^1\Sigma_{g}^+$
7882	1268	$a^1\Delta_{g}$
0	0	$X^3\Sigma_{g}^+$

Regras para nomear os níveis de energia das moléculas diatômicas^{1,2}

- O estado fundamental é sempre indicado como X
- Utilizam-se as letras $A, B, C \dots$ para os estados excitados de mesma multiplicidade de spin que o estado fundamental, em ordem ascendente de energia.
- Utilizam-se as letras $a, b, c \dots$ para os estados excitados com multiplicidade de spin diferente do estado fundamental.
- Nas moléculas poliatômicas não lineares, utiliza-se um til (\sim) sobre a letra para evitar confusão com os rótulos de simetria.

1. Bernath, P. F., *Spectra of Atoms and Molecules*, 3^a ed., Oxford University Press, 2016. pg. 344.

2. Cohen, E. R. *et al.*, eds., *Grandezas, Unidades de Símbolos em Físico-Química*, 3^a ed., IUPAC-SBQ, 2018. pg. 35.

$O_2 - D_{\infty h}$

Energia da transição 0-0

cm^{-1}	nm	
13120	762	$b \ ^1\Sigma_{g}^+$
7882	1268	$a \ ^1\Delta_{g}$
0	0	$X \ ^3\Sigma_{g}^+$

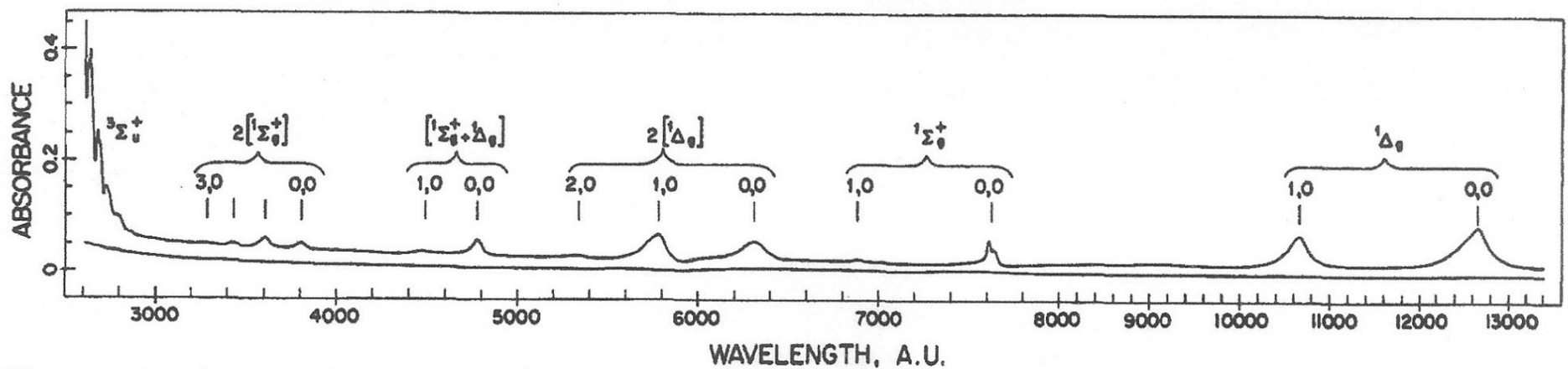
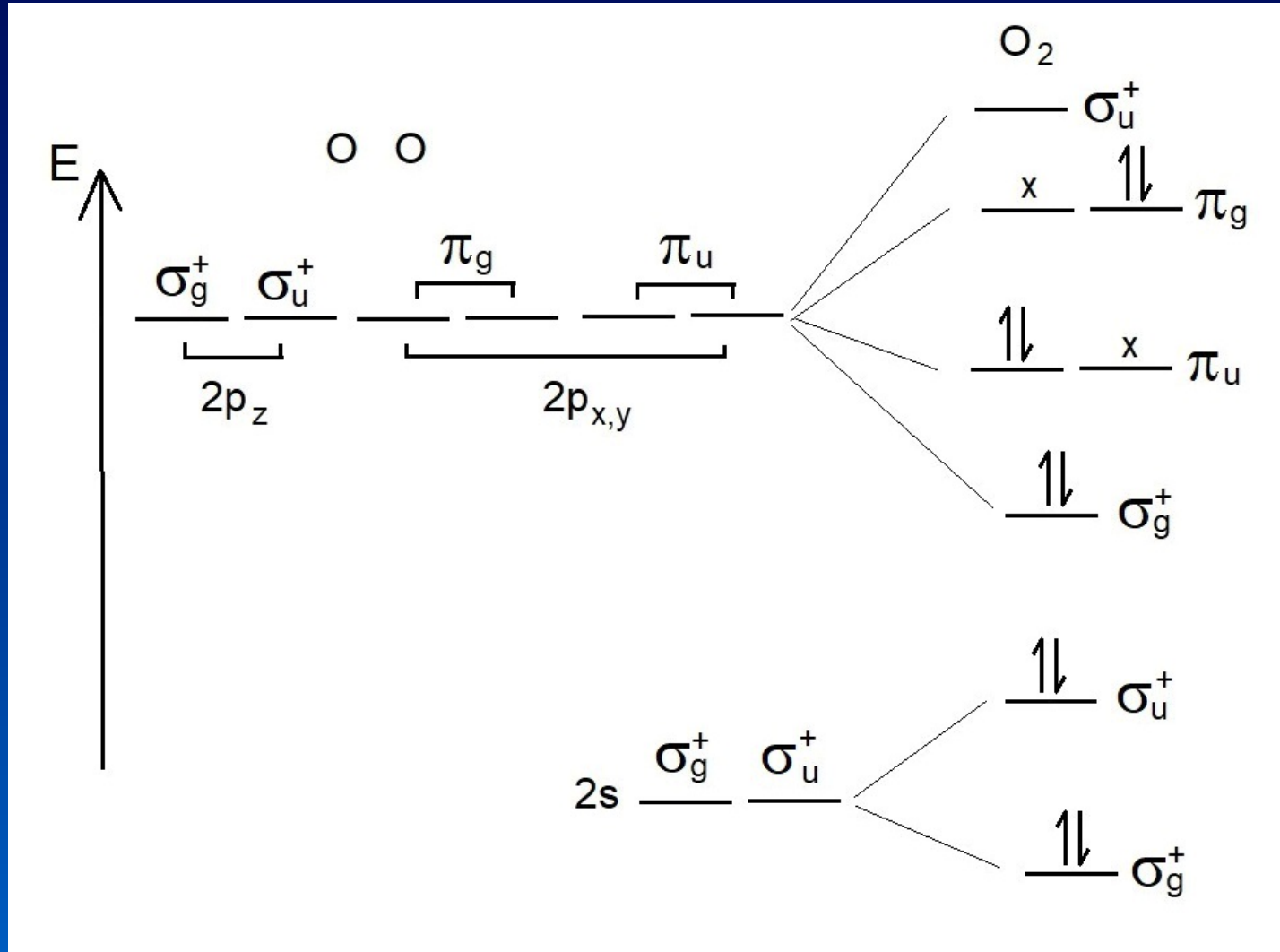


Figure 7. Complete absorption spectrum from 2600 to 13,400 Å of gaseous molecular oxygen at 150 atm in a 6.5-cm cell at 20°. Bands labeled according to upper electronic state by energy convention, with vibronic components.

Khan, A.U.; Kasha, M.; *J. Amer. Chem. Soc.* 92:3293 (1970).

$O_2 - D_{\infty h}$ (estados excitados adicionais)



$D_{\infty h}$

$D_{\infty h}$	E	$2C_{\infty}^{\varphi}$	$\infty\sigma_v$	i	$2S_{\infty}^{\varphi}$	∞C_2
Σ_{g}^{+}	1	1	1	1	1	1
Σ_{g}^{-}	1	1	-1	1	1	-1
Π_{g}	2	0	0	2	0	0
Δ_{g}	2	-2	0	2	-2	0
Σ_{u}^{+}	1	1	1	-1	-1	-1
Σ_{u}^{-}	1	1	-1	-1	-1	1
Π_{u}	2	0	0	-2	0	0
Δ_{u}	2	-2	0	-2	2	0

$\Pi_{g} \otimes \Pi_{u}$	4	0	0	-4	0	0
					$\Sigma_{u}^{+} \oplus \Sigma_{u}^{-} \oplus \Delta_{u}$	

$O_2 - D_{\infty h}$

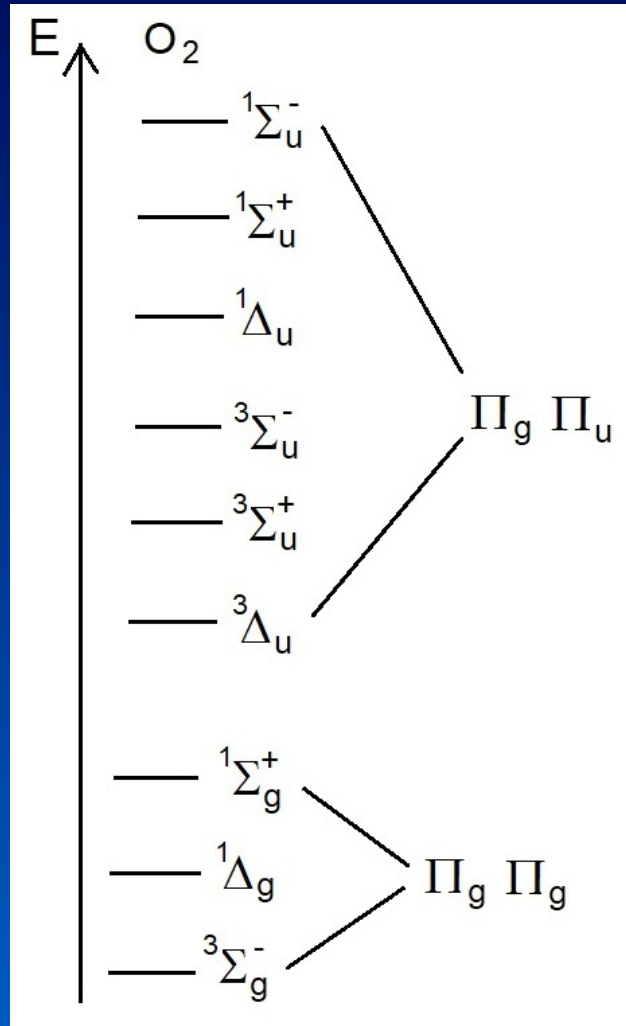
Determinando os singletos e tripletos

Nesse caso, como não se trata de um estado eletrônico degenerado, todos os termos apresentam as possibilidades singleto e tripleto.

$$\begin{array}{ccc} {}^1\Sigma_u^+ & {}^1\Sigma_u^- & {}^1\Delta_u \\ {}^3\Sigma_u^+ & {}^3\Sigma_u^- & {}^3\Delta_u \end{array}$$

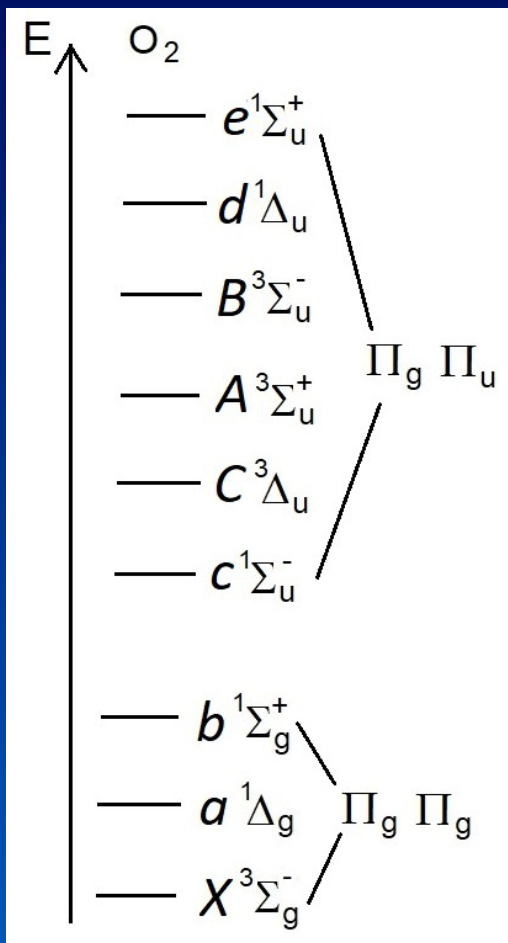
$O_2 - D_{\infty h}$

Níveis de energia incluindo estado excitado adicional



O₂ - D_{∞h}

Níveis de energia incluindo estado excitado adicional



Energia da transição 0-0

cm ⁻¹	nm	State
49358	203	B ³ Σ _u ⁻
35007	285	A ³ Σ _u ⁺
34319	291	C ³ Δ _u
32664	306	c ¹ Σ _u ⁻
13120	762	b ¹ Σ _g ⁺
7882	1268	a ¹ Δ _g
0	0	X ³ Σ _g ⁺

Descoberta depois das bandas A e B

Krupenie, P. H.; *J. Phys. Chem. Ref. Data* 1:423 (1972). Tabela 1, pg. 456-457.

$O_2 - D_{\infty h}$

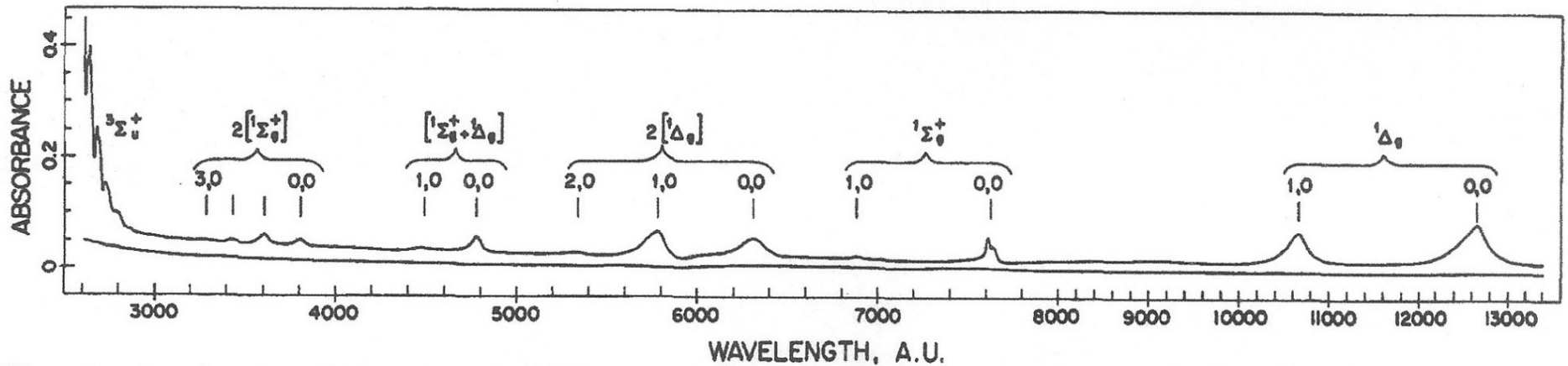


Figure 7. Complete absorption spectrum from 2600 to 13,400 Å of gaseous molecular oxygen at 150 atm in a 6.5-cm cell at 20°. Bands labeled according to upper electronic state by energy convention, with vibronic components.

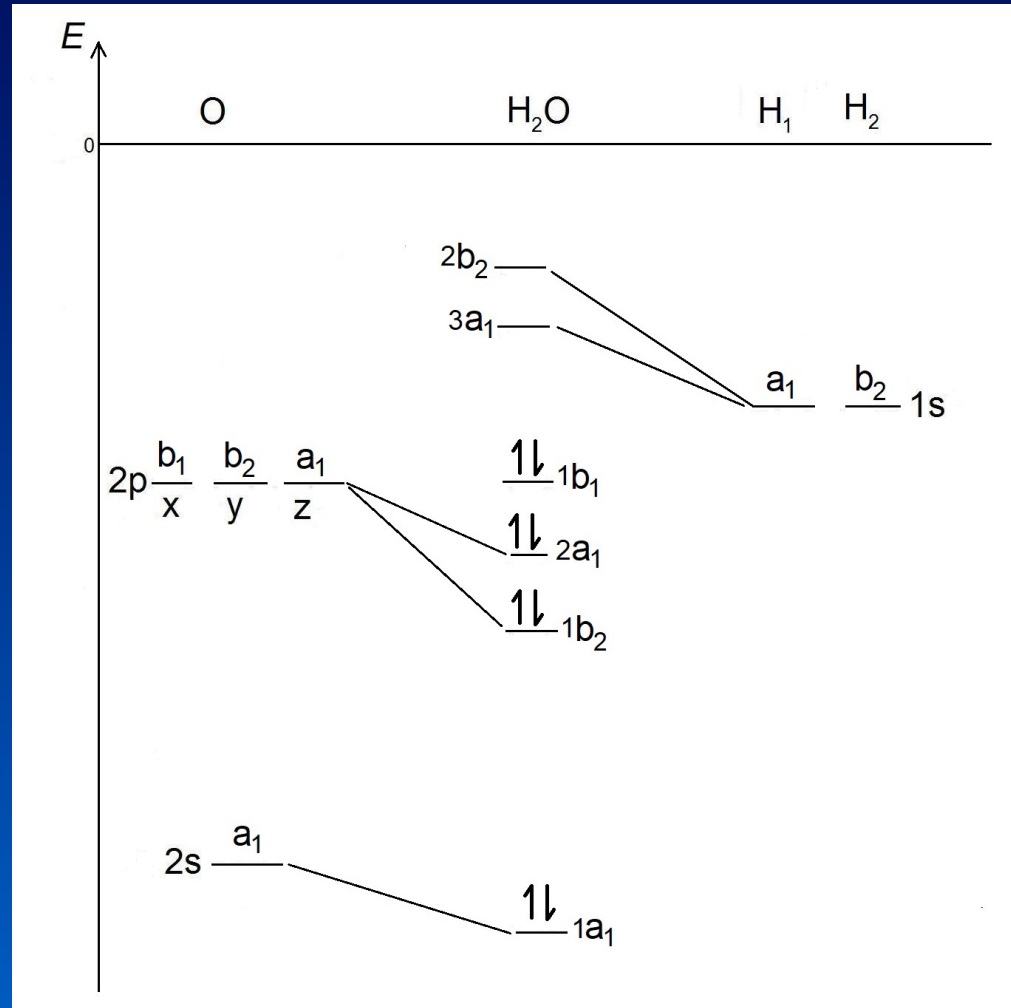
Khan, A.U.; Kasha, M.; *J. Amer. Chem. Soc.* 92:3293 (1970).

Termos espectroscópicos para moléculas

Água

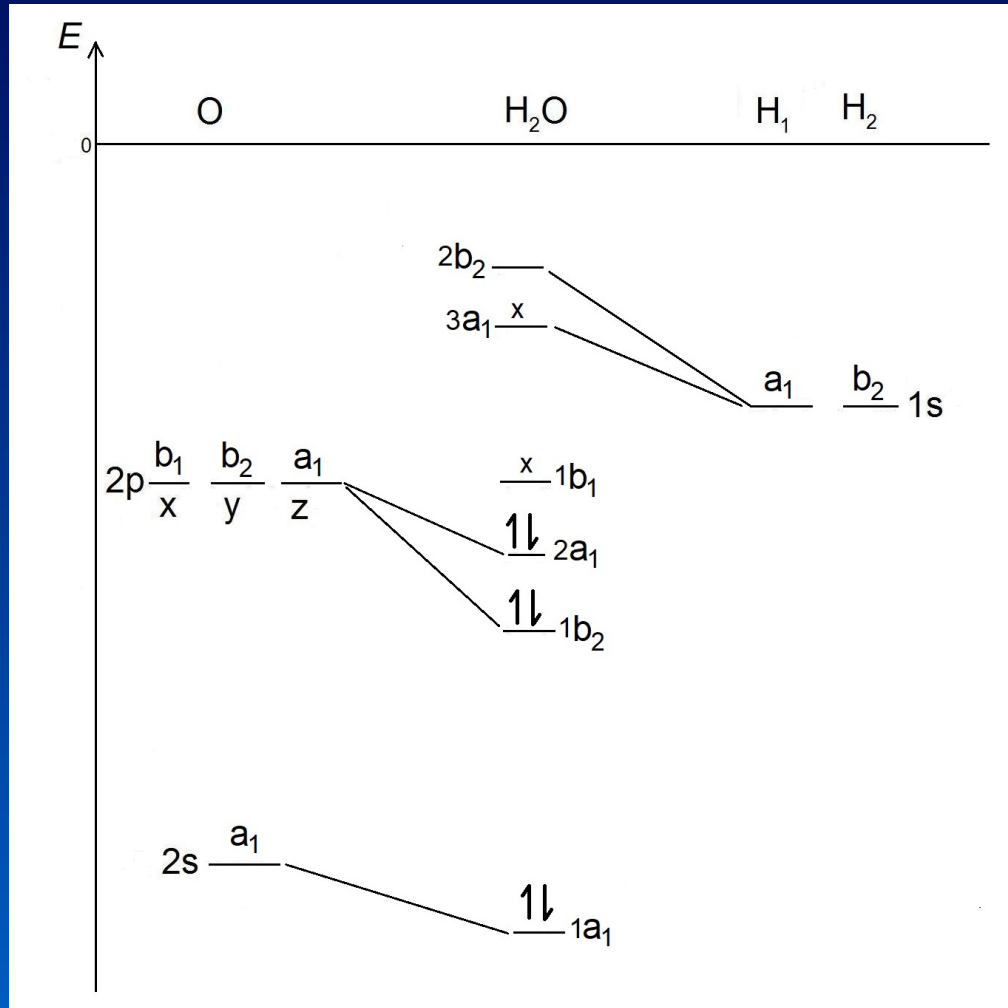
Água - C_{2v}

Diagrama de energia dos orbitais moleculares



Água - C_{2v}

Termos espectroscópicos para os estados excitados



Água - C_{2v}

C_{2v}	E	C_2	$\sigma_v^{(xz)}$	$\sigma'_v^{(yz)}$	
A_1	1	1	1	1	
A_2	1	1	-1	-1	
B_1	1	-1	1	-1	
B_2	1	-1	-1	1	
<hr/>					
$B_1 \otimes A_1$	1	-1	1	-1	B_1

Este estado excitado pode ser singlete ou tripleto



H₂O - C_{2v}

Níveis de energia da molécula

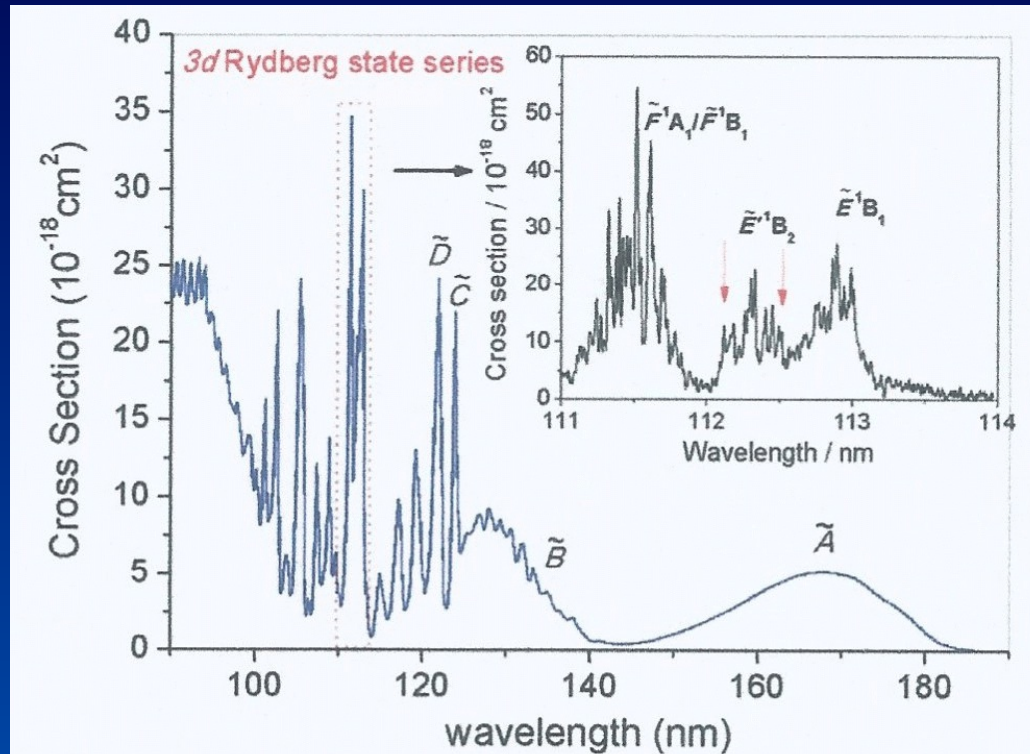
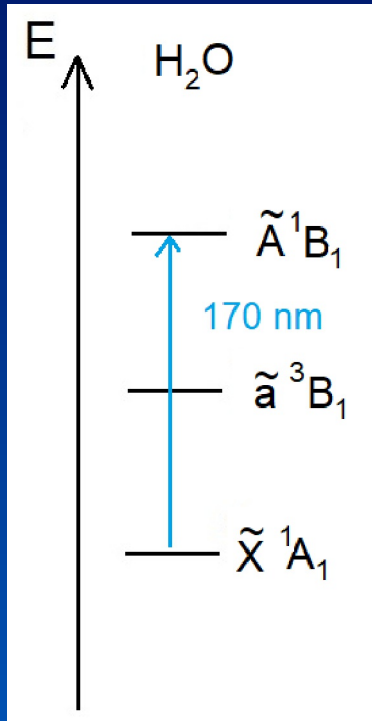
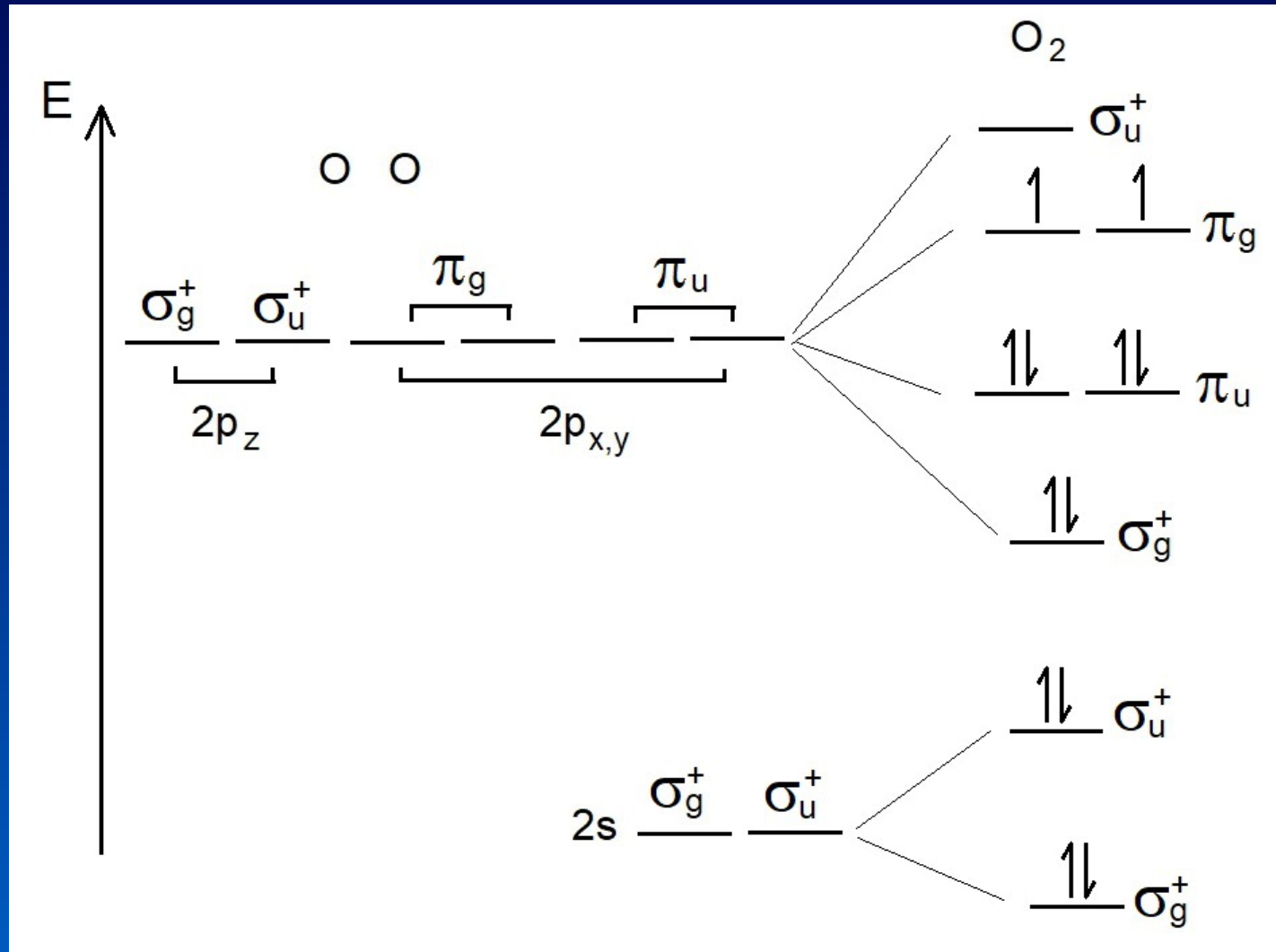


Figure 1. Absorption spectrum of a room temperature sample of H₂O vapor (adapted from ref 4). The spectrum around 114–111 nm with high resolution is adapted from ref 54. The excited electronic states have been marked in the figures. The photolysis wavelengths applied in this work are marked by red arrows.

Desenhando os orbitais moleculares

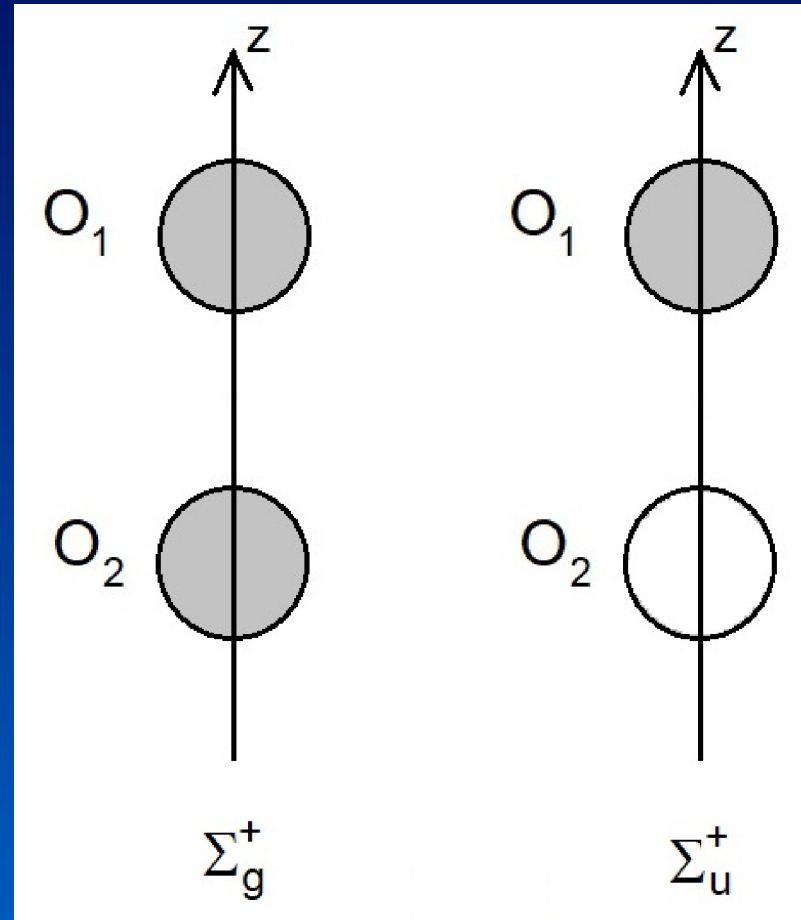
dioxigênio - O₂

$O_2 - D_{\infty h}$



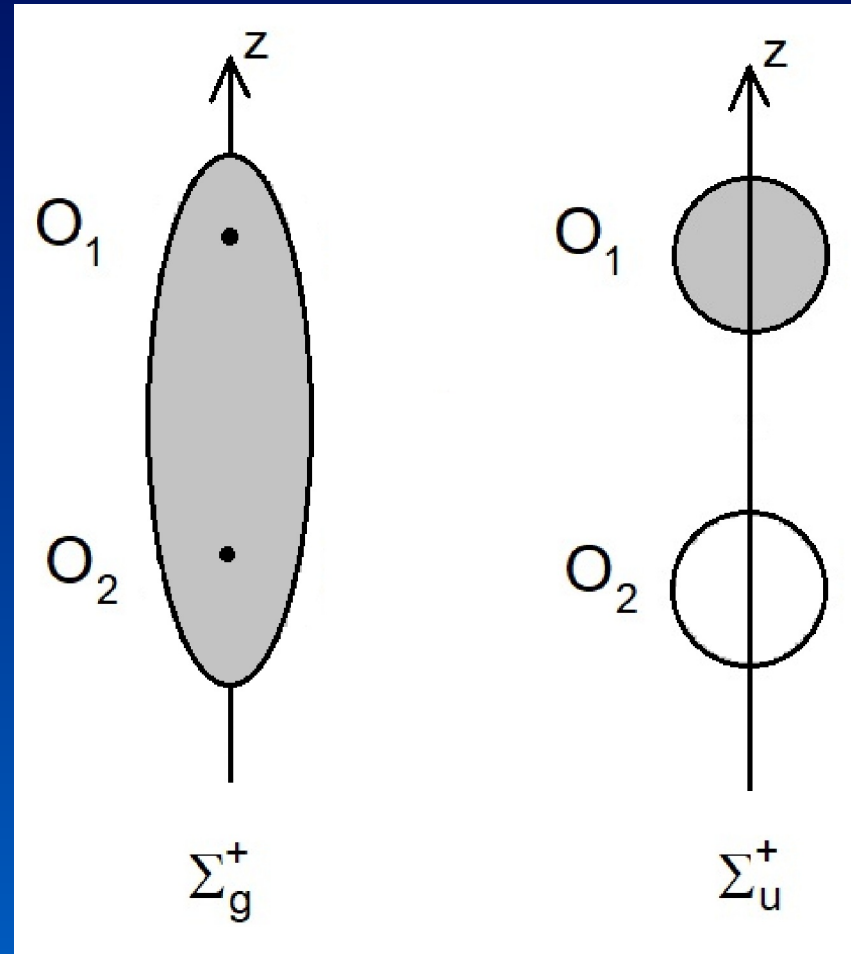
$O_2 - D_{\infty h}$

Os orbitais 2s podem formar uma combinação ligante e outra antiligante

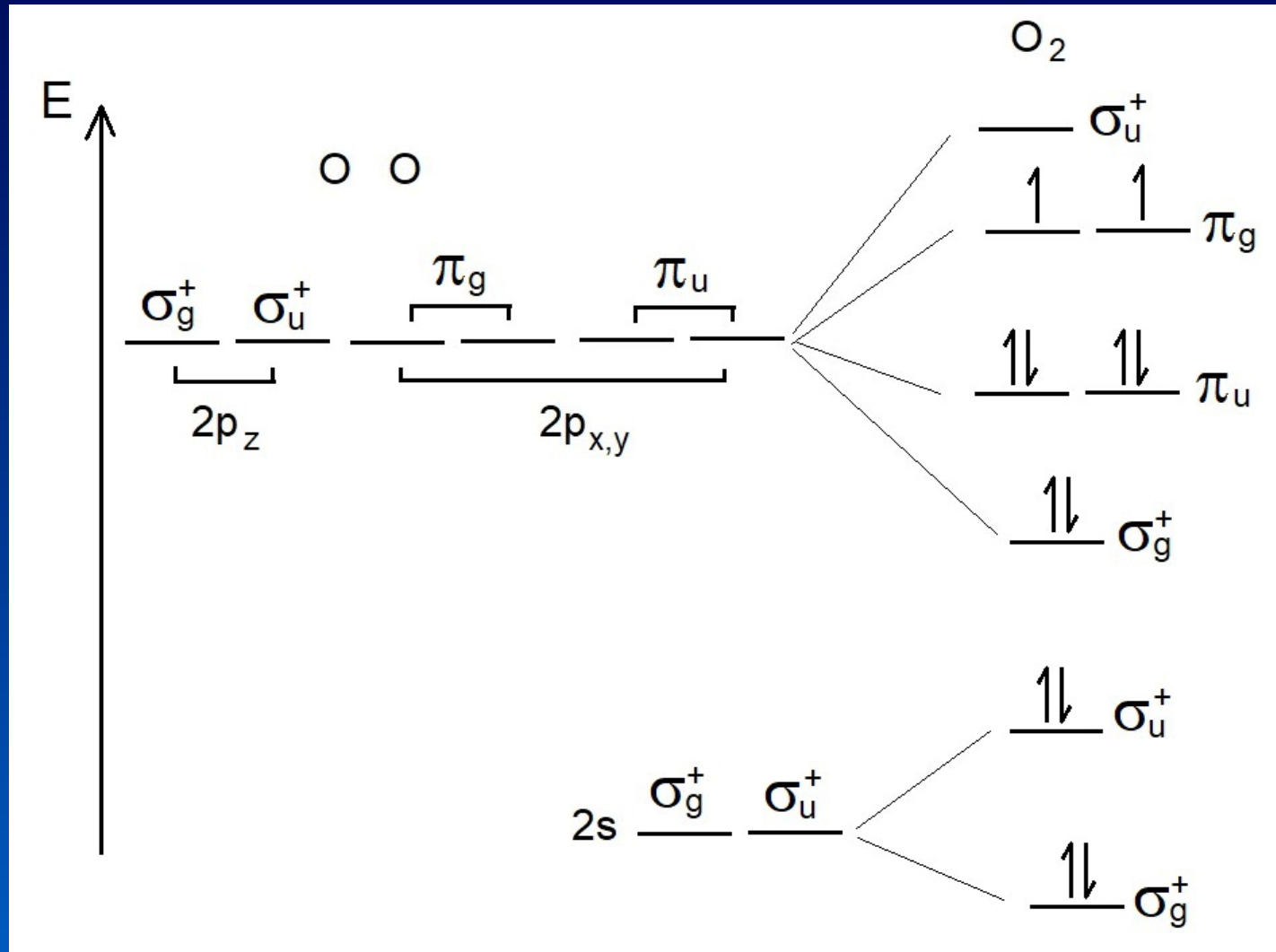


$O_2 - D_{\infty h}$

Os orbitais 2s podem formar uma combinação ligante e outra antiligante

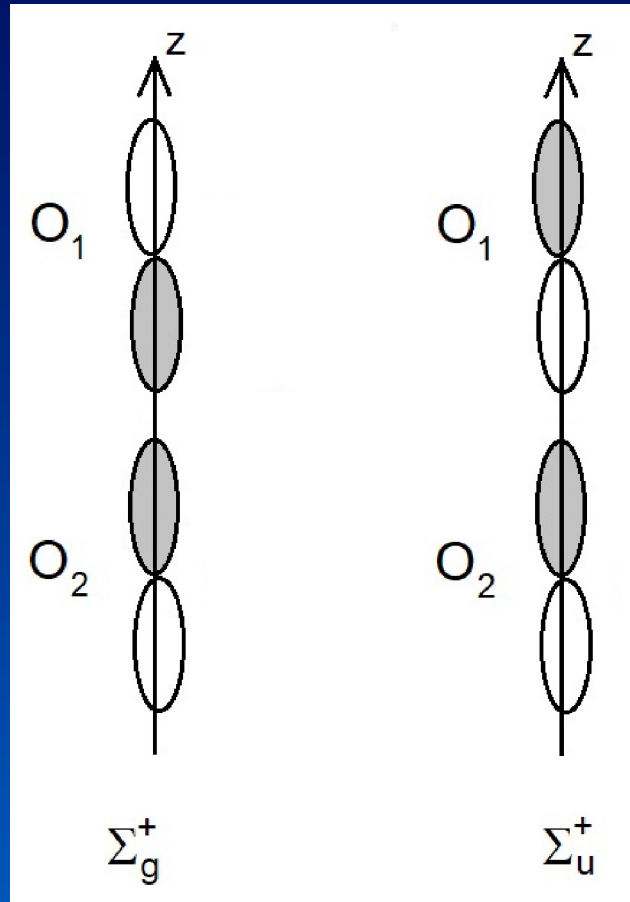


$O_2 - D_{\infty h}$



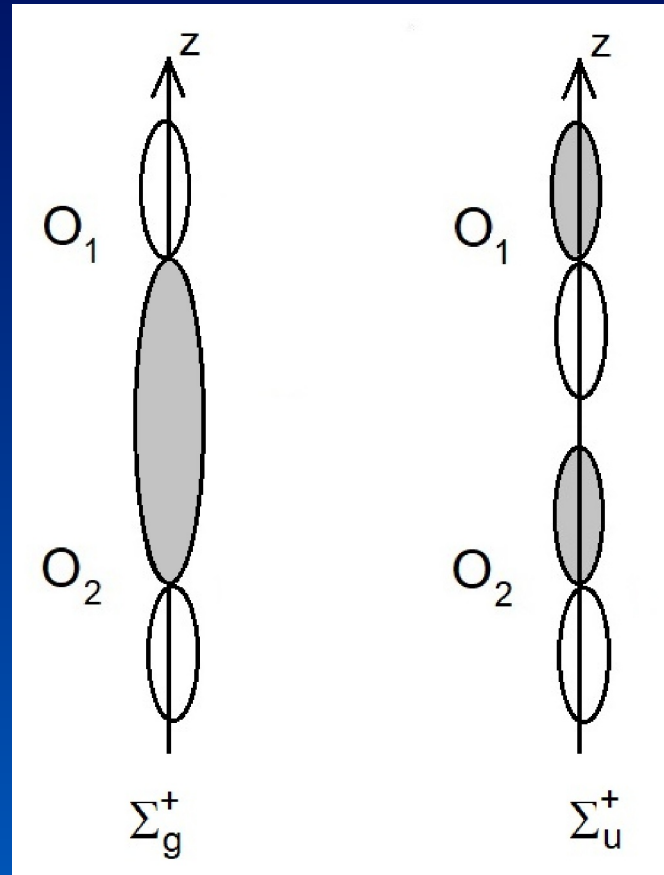
$O_2 - D_{\infty h}$

Os orbitais $2p_z$ também podem formar uma combinação σ ligante e antiligante

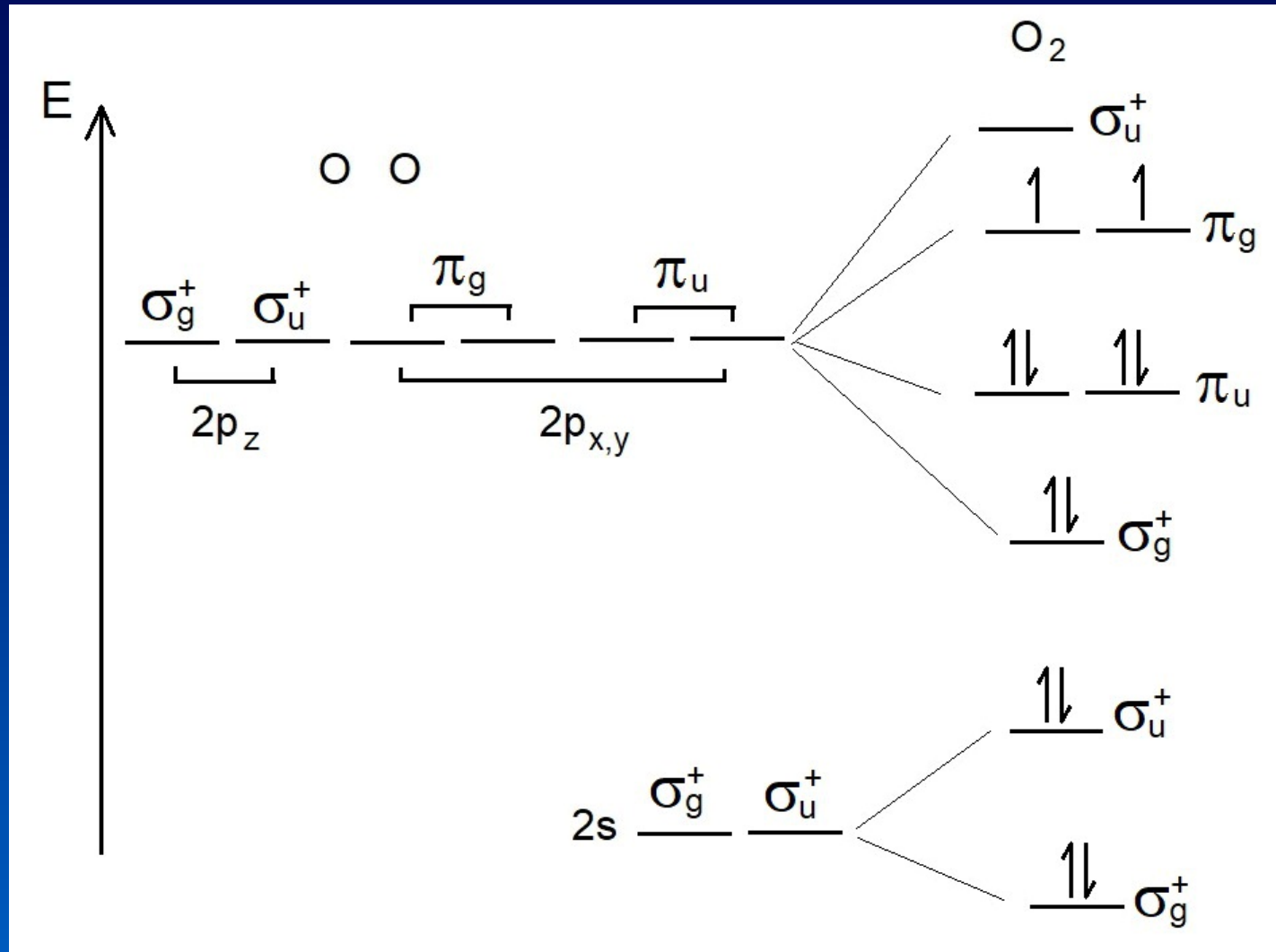


$O_2 - D_{\infty h}$

Os orbitais $2p_z$ também podem formar uma combinação σ ligante e antiligante

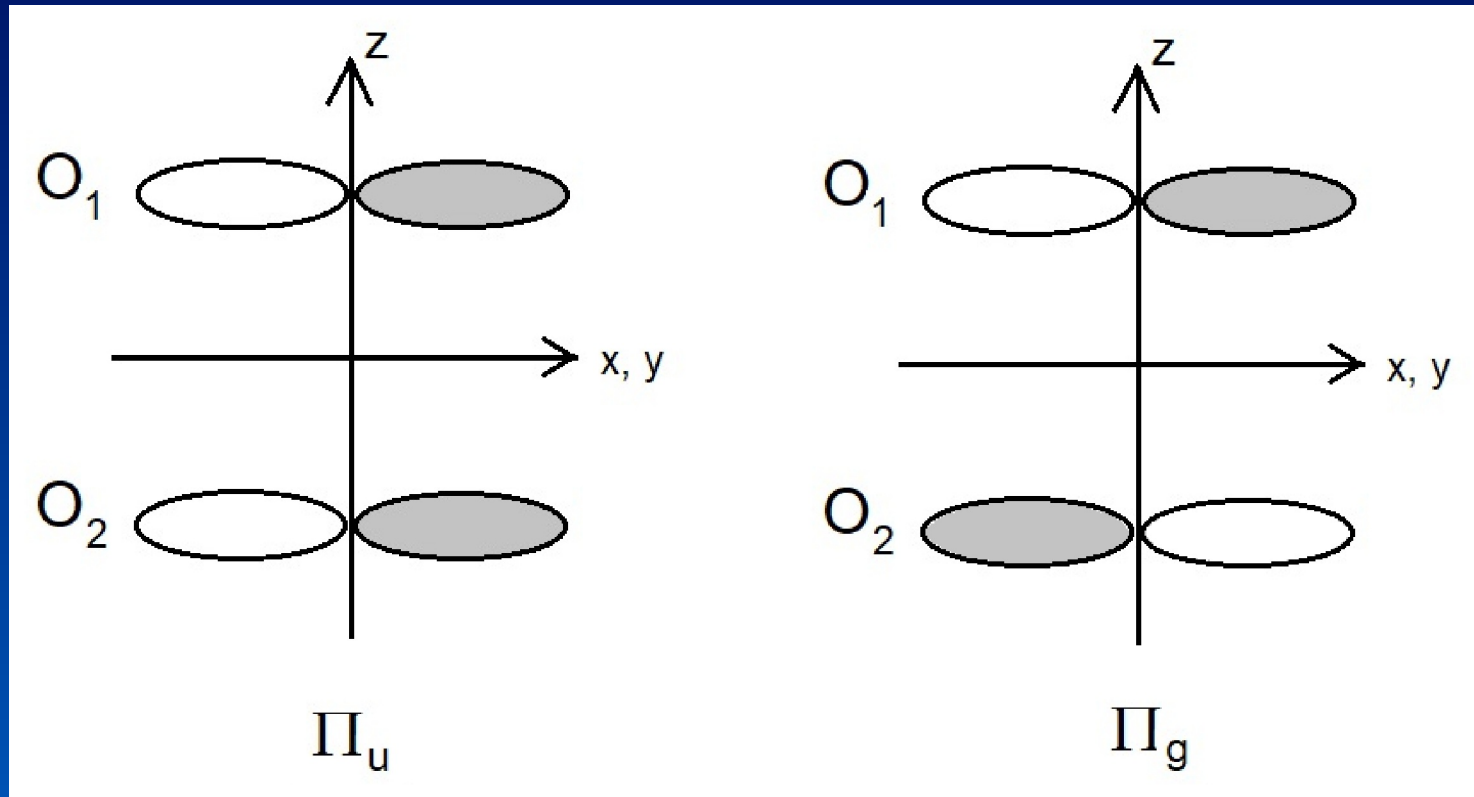


$O_2 - D_{\infty h}$



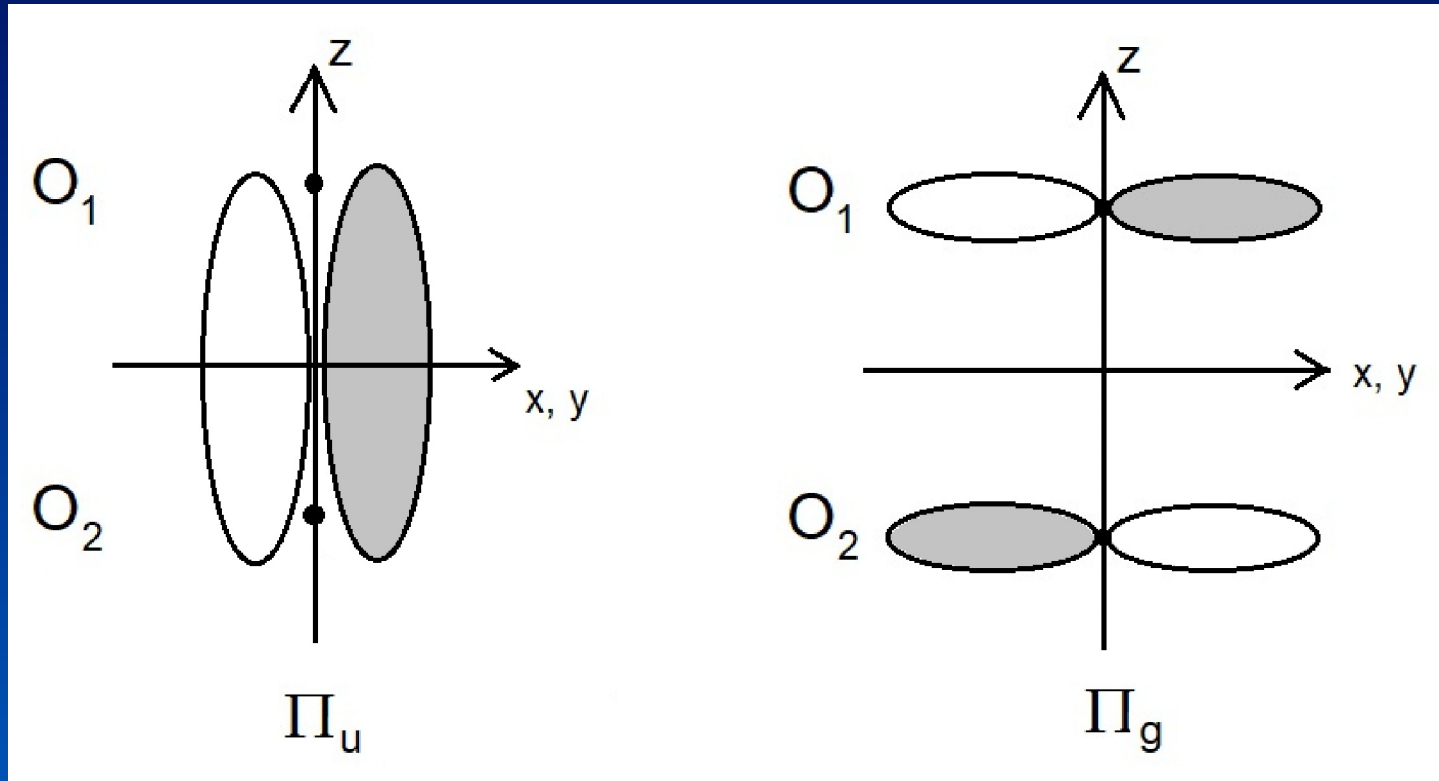
$O_2 - D_{\infty h}$

Os orbitais π (p_x, p_y) também formam combinações ligantes e antiligantes



$O_2 - D_{\infty h}$

Os orbitais π (p_x, p_y) também formam combinações ligantes e antiligantes



FIM DA AULA 3
