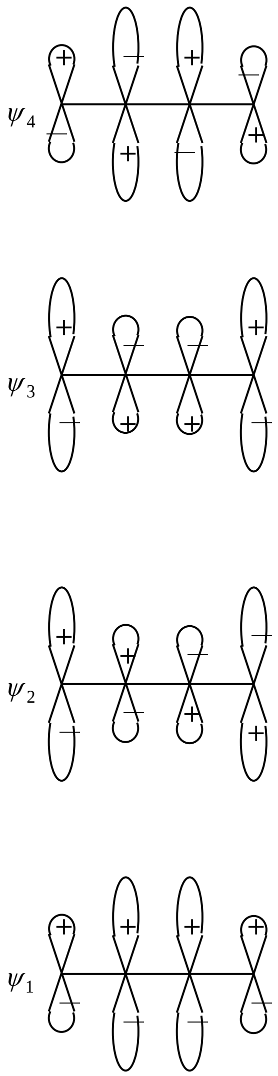
分子構造と吸収スペクトル　　シスピークの説明　　簡単のため、ブタジエンを例に説明　$V<0$

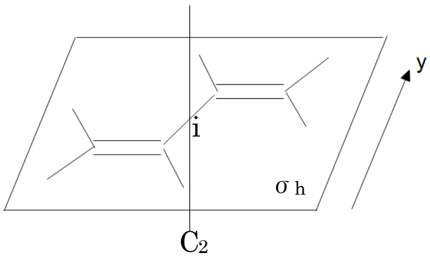
$$E-\frac{1+\sqrt{5}}{2}V \quad \psi_4=\sqrt{\frac{2}{5+\sqrt{5}}}\left\{\frac{1}{\sqrt{2}}(\phi_1-\phi_4)-\frac{1+\sqrt{5}}{2}\frac{1}{\sqrt{2}}(\phi_2-\phi_3)\right\}=0.371748(\phi_1-\phi_4)-0.601501(\phi_2-\phi_3)$$

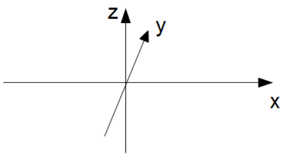
$$E+\frac{1-\sqrt{5}}{2}V \quad \psi_3=\sqrt{\frac{2}{5-\sqrt{5}}}\left\{\frac{1}{\sqrt{2}}(\phi_1+\phi_4)+\frac{1-\sqrt{5}}{2}\frac{1}{\sqrt{2}}(\phi_2+\phi_3)\right\}=0.601501(\phi_1+\phi_4)-0.371748(\phi_2+\phi_3)$$

$$E-\frac{1-\sqrt{5}}{2}V \quad \psi_2=\sqrt{\frac{2}{5-\sqrt{5}}}\left\{\frac{1}{\sqrt{2}}(\phi_1-\phi_4)-\frac{1-\sqrt{5}}{2}\frac{1}{\sqrt{2}}(\phi_2-\phi_3)\right\}=0.601501(\phi_1-\phi_4)+0.371748(\phi_2-\phi_3)$$

$$E+\frac{1+\sqrt{5}}{2}V \quad \psi_1=\sqrt{\frac{2}{5+\sqrt{5}}}\left\{\frac{1}{\sqrt{2}}(\phi_1+\phi_4)+\frac{1+\sqrt{5}}{2}\frac{1}{\sqrt{2}}(\phi_2+\phi_3)\right\}=0.371748(\phi_1+\phi_4)+0.601501(\phi_2+\phi_3)$$

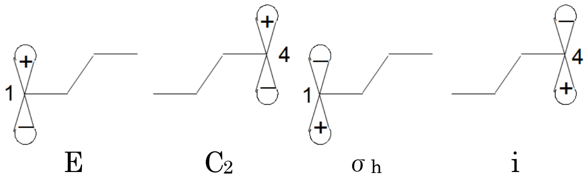




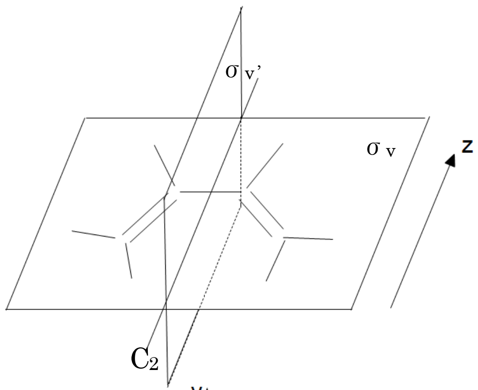


C_{2h}

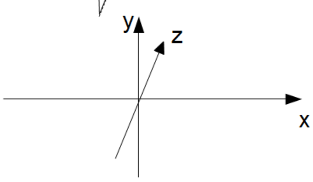
		E	$C_2(z)$	σ_h	i	
	A_g	1	1	1	1	
z	A_u	1	1	−1	−1	ϕ_1, ϕ_3
	B_g	1	−1	−1	1	ϕ_2, ϕ_4
x,y	B_u	1	−1	1	−1	



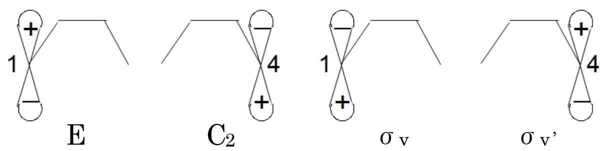
i　について　g, u
C_2について　A, B
σ_vについて　1, 2



C_{2v}

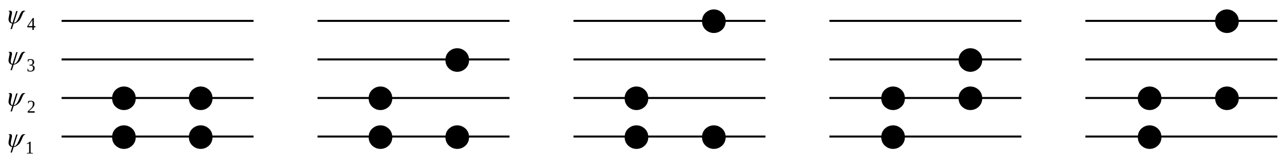


		E	$C_2(z)$	$\sigma_v(xz)$	$\sigma_v'(yz)$
z	A_1	1	1	1	1
	A_2	1	1	−1	−1　ϕ_2, ϕ_4
x	B_1	1	−1	1	−1
y	B_2	1	−1	−1	1　ϕ_1, ϕ_3

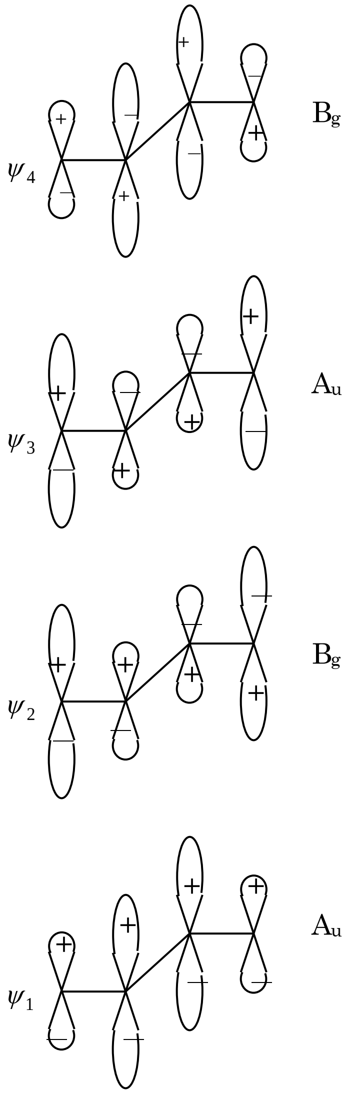


電子配置

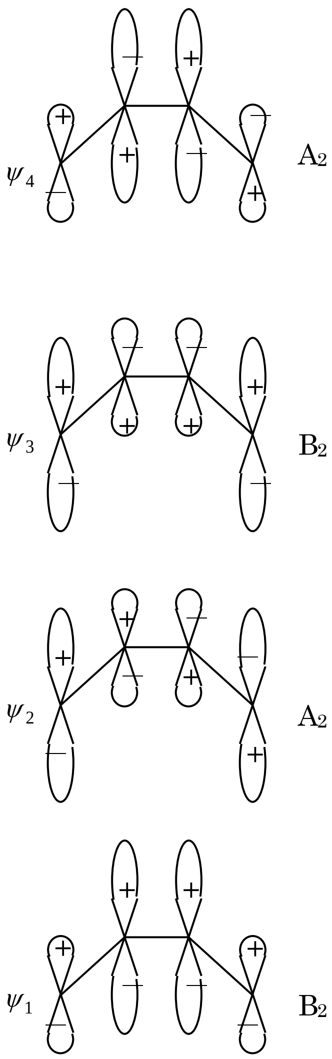
基底状態　　　　　励起状態



$\Psi_0 = \psi_1{}^2\psi_2{}^2$　　$\Psi_{2,3} = \psi_1{}^2\psi_2\psi_3$　　$\Psi_{2,4} = \psi_1{}^2\psi_2\psi_4$　　$\Psi_{1,3} = \psi_1\psi_2{}^2\psi_3$　　$\Psi_{1,4} = \psi_1\psi_2{}^2\psi_4$



C_{2h}



C_{2v}

	C_{2h}		C_{2v}
Ψ_0	$A_u{}^2B_g{}^2 = A_g$	Ψ_0	$B_2{}^2A_2{}^2 = A_1$
$\Psi_{2,3}$	$A_u{}^2B_gA_u = B_u$	$\Psi_{2,3}$	$B_2{}^2A_2B_2 = B_1$
$\Psi_{2,4}$	$A_u{}^2B_gB_g = A_g$	$\Psi_{2,4}$	$B_2{}^2A_2A_2 = A_1$
$\Psi_{1,3}$	$A_uB_g{}^2A_u = A_g$	$\Psi_{1,3}$	$B_2A_2{}^2B_2 = A_1$
$\Psi_{1,4}$	$A_uB_g{}^2B_g = B_u$	$\Psi_{1,4}$	$B_2A_2{}^2A_2 = B_1$

C_{2h}

$$\boldsymbol{m}(\Psi_0 \to \Psi_{2,3}) = e\left\{ \left\langle \Psi_{2,3} \middle| x \middle| \Psi_0 \right\rangle + \left\langle \Psi_{2,3} \middle| y \middle| \Psi_0 \right\rangle + \left\langle \Psi_{2,3} \middle| z \middle| \Psi_0 \right\rangle \right\} \neq 0$$

x, y許容　$B_u \cdot B_u \cdot A_g = A_g$　$B_u \cdot B_u \cdot A_g = A_g$　$B_u \cdot A_u \cdot A_g = B_g$

$$\boldsymbol{m}(\Psi_0 \to \Psi_{2,4}) = e\left\{ \left\langle \Psi_{2,4} \middle| x \middle| \Psi_0 \right\rangle + \left\langle \Psi_{2,4} \middle| y \middle| \Psi_0 \right\rangle + \left\langle \Psi_{2,4} \middle| z \middle| \Psi_0 \right\rangle \right\} = 0$$

禁制　$A_g \cdot B_u \cdot A_g = B_u$　$A_g \cdot B_u \cdot A_g = B_u$　$A_g \cdot A_u \cdot A_g = A_u$

$$\boldsymbol{m}(\Psi_0 \to \Psi_{1,3}) = 0$$

$$\boldsymbol{m}(\Psi_0 \to \Psi_{1,4}) \neq 0$$

C_{2v}

$$\boldsymbol{m}(\Psi_0 \to \Psi_{2,3}) = e\left\{ \left\langle \Psi_{2,3} \middle| x \middle| \Psi_0 \right\rangle + \left\langle \Psi_{2,3} \middle| y \middle| \Psi_0 \right\rangle + \left\langle \Psi_{2,3} \middle| z \middle| \Psi_0 \right\rangle \right\} \neq 0$$

x許容　$B_1 \cdot B_1 \cdot A_1 = A_1$　$B_1 \cdot B_2 \cdot A_1 = A_2$　$B_1 \cdot A_1 \cdot A_1 = B_1$

$$\boldsymbol{m}(\Psi_0 \to \Psi_{2,4}) = e\left\{ \left\langle \Psi_{2,4} \middle| x \middle| \Psi_0 \right\rangle + \left\langle \Psi_{2,4} \middle| y \middle| \Psi_0 \right\rangle + \left\langle \Psi_{2,4} \middle| z \middle| \Psi_0 \right\rangle \right\} \neq 0$$

z許容　$A_1 \cdot B_1 \cdot A_1 = B_1$　$A_1 \cdot B_2 \cdot A_1 = B_2$　$A_1 \cdot A_1 \cdot A_1 = A_1$

$$\boldsymbol{m}(\Psi_0 \to \Psi_{1,3}) \neq 0$$

$$\boldsymbol{m}(\Psi_0 \to \Psi_{1,4}) \neq 0$$

直観的説明