application of Group theory in chemistry

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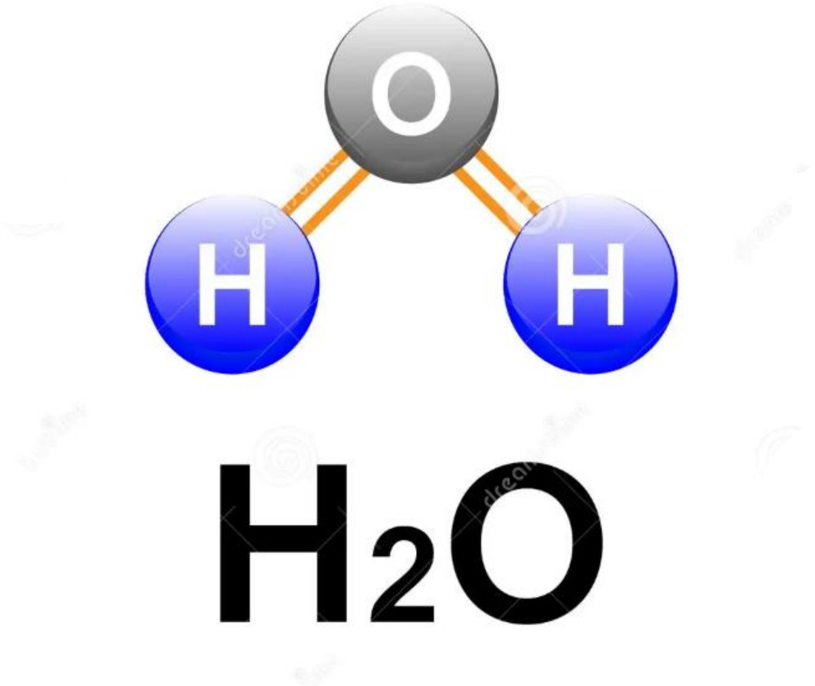
Viberation mode of a molecular

1. Bending：bond angle change
2. Stretching ： bond length change

- symmetry stretch
- asymmetric stretch



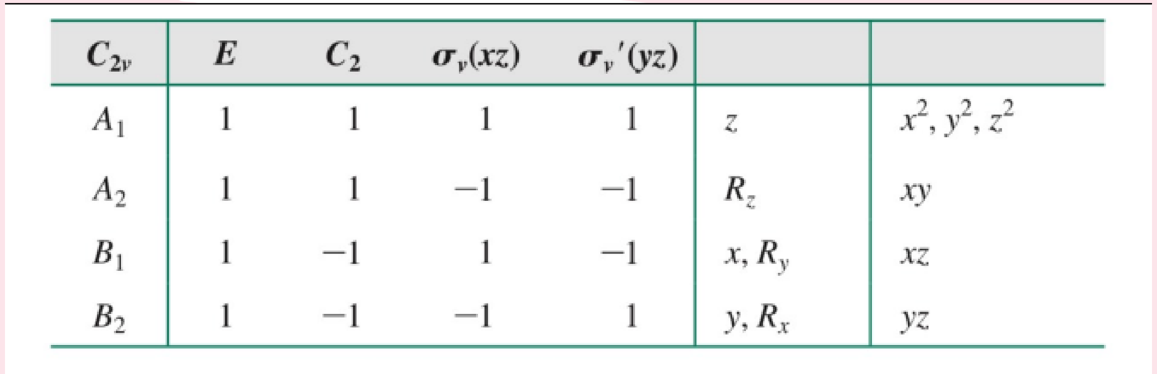
Character table of C_{2V}

Symmetry operation:

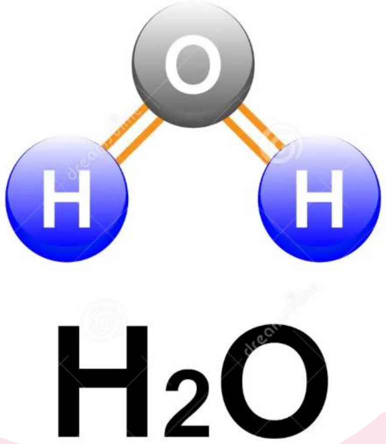
E: each lignad will have E

C_n : rotate the molecular by (360/n)°

σ_V : reflection plane(parallel to principle axis)

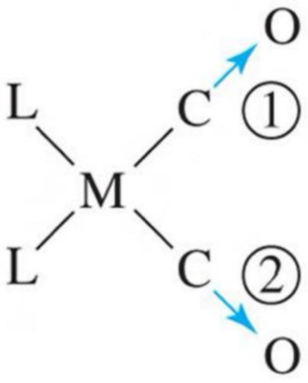


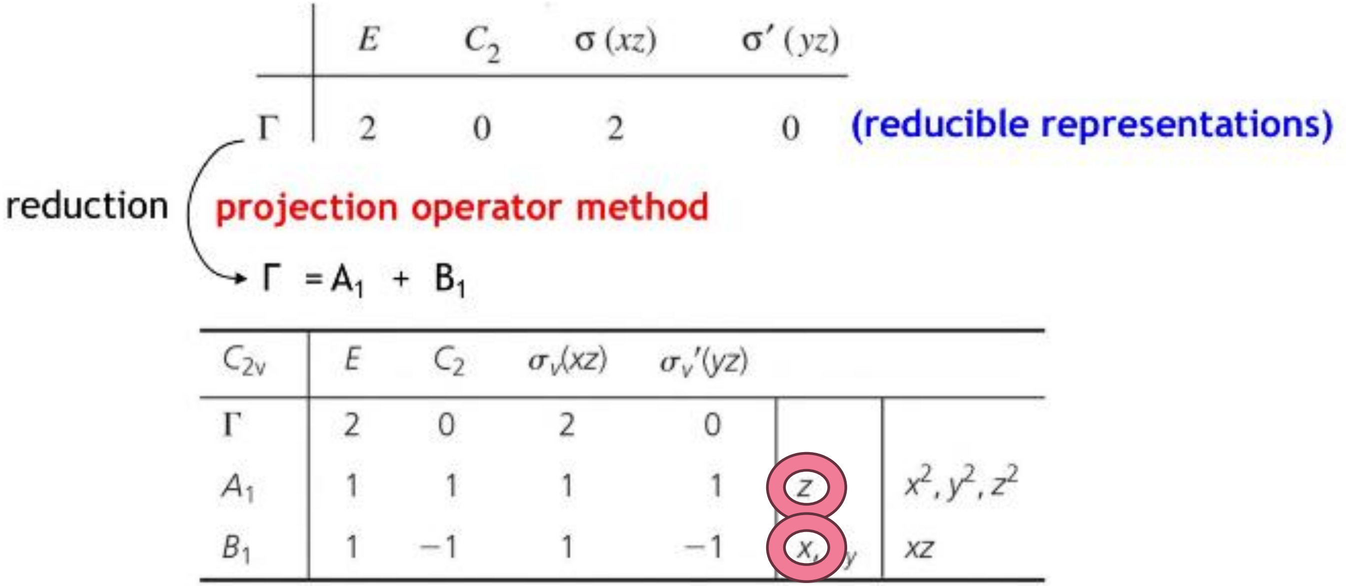
C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
A_1	1	1	1	1	z	x^2, y^2, z^2
A_2	1	1	−1	−1	R_z	xy
B_1	1	−1	1	−1	x, R_y	xz
B_2	1	−1	−1	1	y, R_x	yz



Difference of cis and trans $L_2(CO)_2$

- Seen CO as a point and do the symmetry operation of C_{2V} to find reducible representations
- Find which linear combination corresponding to reducible representations
- Identity how many IR active modes





	E	C_2	$\sigma\,(xz)$	$\sigma'\,(yz)$
Γ	2	0	2	0

(reducible representations)

reduction

projection operator method

$\Gamma = A_1 + B_1$

C_{2v}	E	C_2	$\sigma_v(xz)$	$\sigma_v'(yz)$		
Γ	2	0	2	0		
A_1	1	1	1	1	z	x^2, y^2, z^2
B_1	1	−1	1	−1	$x,\ _y$	xz

Difference of cis and trans $L_2(CO)_2$

- Using same method ,we can also get IR active of trans $L_2(CO)_2$ (D_{2h})
- one C-O stretching band $\longrightarrow$ trans $L_2(CO)_2$
- two C-O stretching band $\longrightarrow$ cis $L_2(CO)_2$

Introduction to d-orbital

In QM, d orbitals arise as solutions to the Schrödinger equation for the hydrogen atom or hydrogen-like systems. These orbitals correspond to:

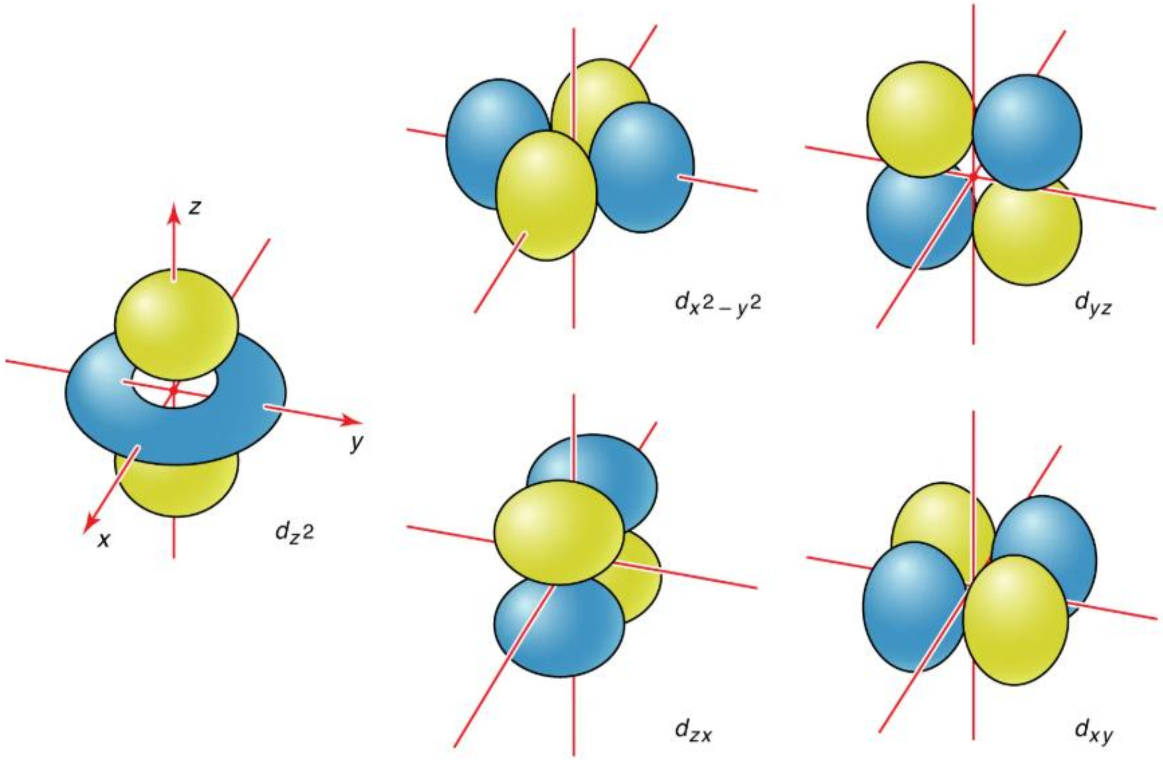
$$\psi_{n,l,m}(r,\theta,\phi) = R_{n,l}(r) \cdot Y_l^m(\theta,\phi)$$

Constraints: n≥3 and L=2

So m= -2,-1,0,1,2 $\longrightarrow$ d orbital has 5 degeneracy

d-orbital diagram

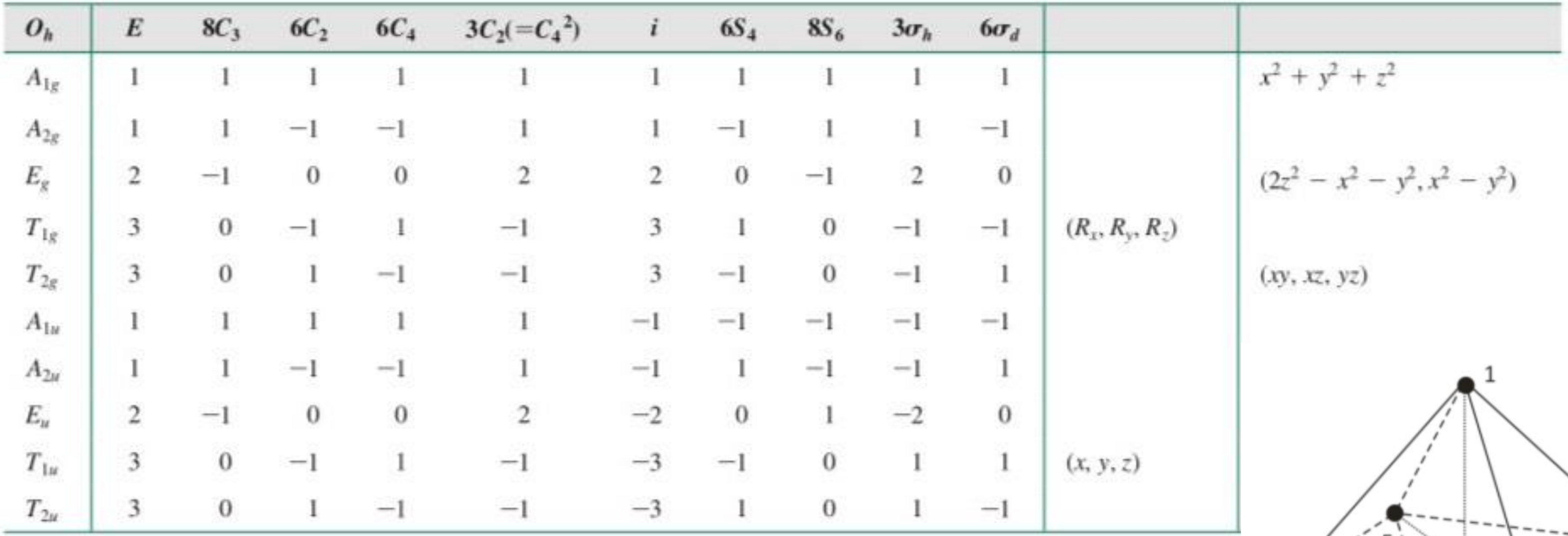
d_{z^2}	$Y_2^0 \propto 3\cos^2\theta - 1$
$d_{x^2-y^2}$	$\propto \cos 2\phi \cdot \sin^2\theta$
d_{xy}	$\propto \sin 2\phi \cdot \sin^2\theta$
d_{xz}	$\propto \cos\phi \cdot \sin\theta \cdot \cos\theta$
d_{yz}	$\propto \sin\phi \cdot \sin\theta \cdot \cos\theta$



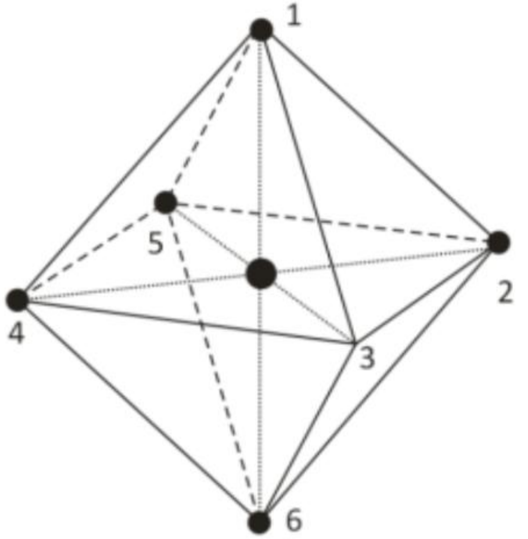
Construct MO diagram of octahedral complex

- Seen six ligand as points and do the symmetry operation of O_h to find reducible representations
- Find which linear combination corresponding to reducible representations
- Combine ligand orbital with metal orbital

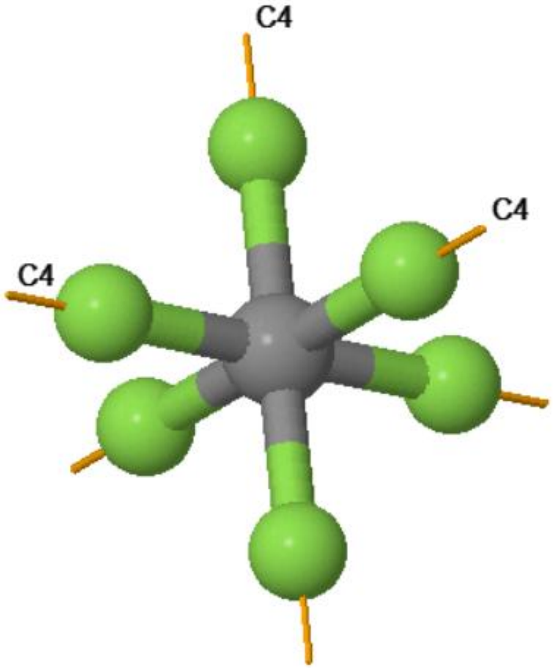
Character table of O_h

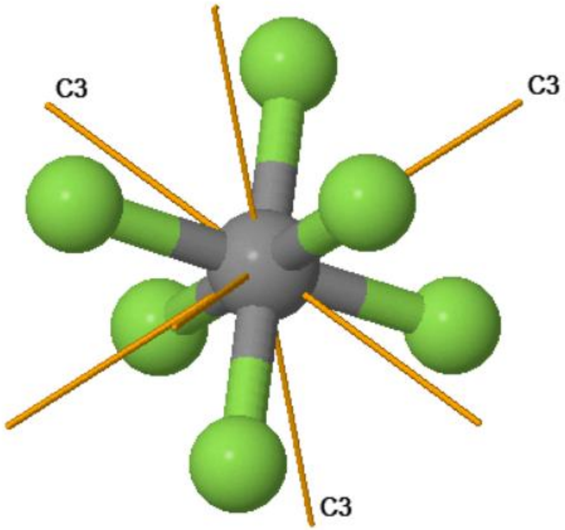


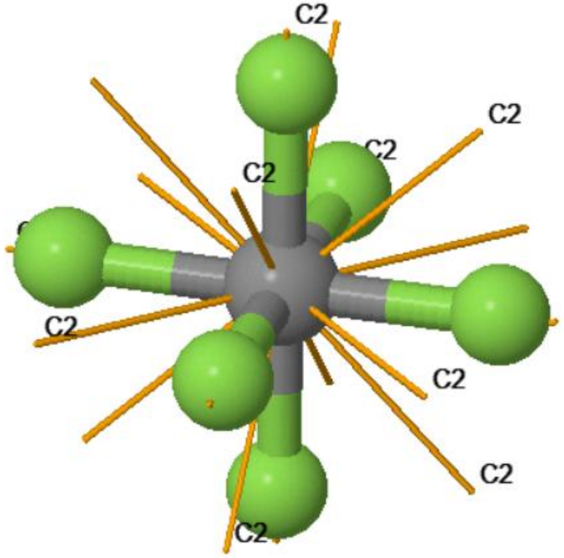
O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$		
A_{1g}	1	1	1	1	1	1	1	1	1	1		$x^2 + y^2 + z^2$
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1		
E_g	2	−1	0	0	2	2	0	−1	2	0		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1	(R_x, R_y, R_z)	
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1		(xy, xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	−1	−1	1	−1	1	−1	−1	1		
E_u	2	−1	0	0	2	−2	0	1	−2	0		
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1	(x, y, z)	
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1		

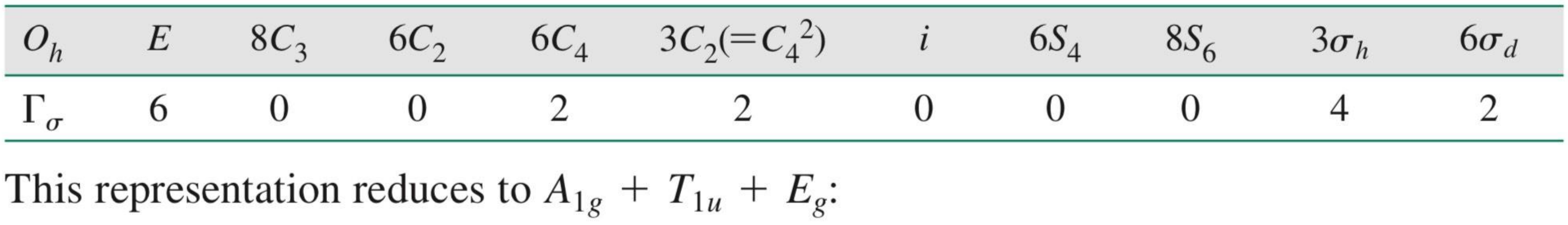


Character table of O_h







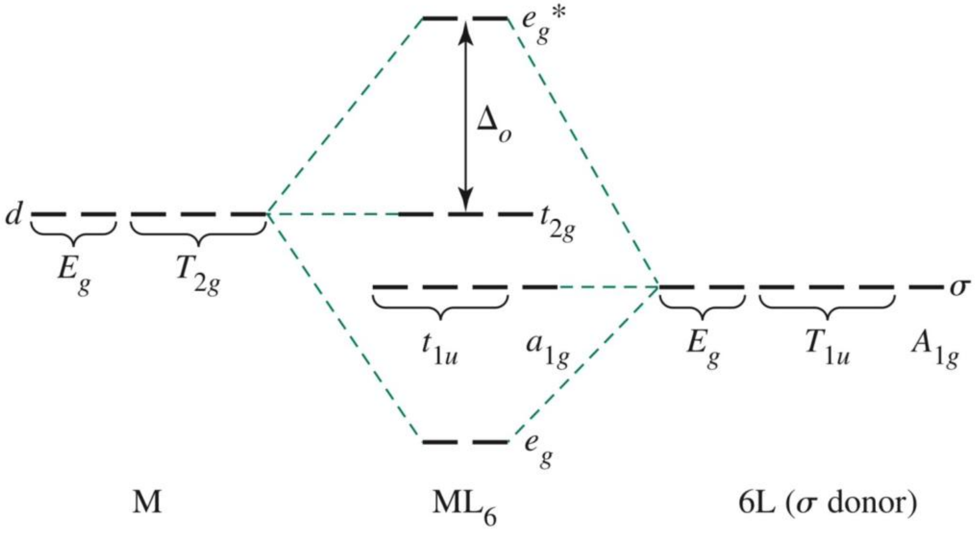


O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2(=C_4^2)$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
Γ_σ	6	0	0	2	2	0	0	0	4	2

This representation reduces to $A_{1g} + T_{1u} + E_g$:

MO of octahedral complex

- Electrons can transition between d orbitals($e_g^*$and t_{2g}), leading to different physical and chemical properties.



Why chemist using MO

1.Color and Light Absorption

- The energy gap between the split d orbitals (Δ_0) often corresponds to the energy of visible light.
- The complementary color is observed, giving rise to the vivid colors of many transition metal complexes.

2. Magnetic Properties

- This leads to paramagnetic (unpaired electrons) or diamagnetic (all paired) behavior.
- Depending on the magnitude of Δ_0 and electron pairing energy, electrons may either pair up in the lower orbitals or occupy higher orbitals singly

THANKS FOR LISTENING