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M. SC. Chemistry Semester –II
Inorganic Chemistry

Microstates and their significance, Ligand field excited states

I

UV- Visible Wavelength region;

λ=	200	300	400	500	600	700	800	900 nm
1/ λ=	50,000	33,333	25,000	20,000	16,667	14,286	12,500	11,111 cm^{-1}
E=	6.20	4.13	3.10	2.48	2.06	1.77	1.55	1.33 eV

$E = h(c/\lambda) \quad 1240/\lambda \text{ nm})$

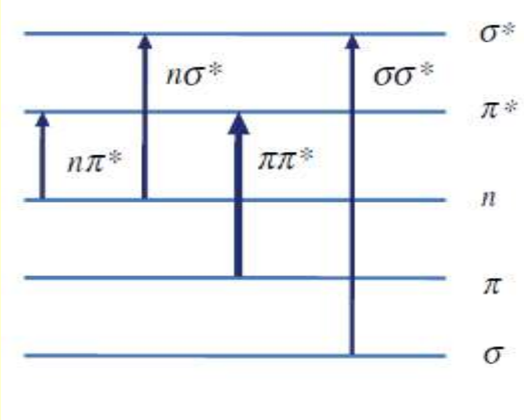
Molecule

hν

Organic Molecule

- Radiation may be absorbed or reflected from molecule.
- Reorganization of electron density

Electronic transition



Inorganic Molecule

- Radiation may be absorbed or reflected from the molecule.
- Reorganization of electron density
- d–d electron transition
- Charge transfer transition
- Inter–electronic repulsion with in the electrons.

Microstate

1. Microstate for d orbitals

$$=[4l+2]!/N\,![4l+2-N]\,!$$

2. Microstates for given Terms F terms :

$$= [2L+1][2S+1]$$

3. Microstate from given J values

$$= [2J+1]$$

4. Microstates for 't_{2g} e_g orbital electrons

$$= (2d)\,!/\,[N\,!\,(2d-N]\,!$$

microstates for d^2 configurations and their terms

$$= [4x2+2]!/2\,![4x2+2-2]! = 45$$

d^2	$\longrightarrow$	^3F	+ ^1D	+ ^3P	+ ^1G	+ ^1S
45		21	5	9	9	1

Terms = [2L+1][2S+1]

What is Significance of Microstate ?

Calculate the microstates for d^1 configuration and arrange the two electrons in d orbital indistinguishable ways equal to calculated values of microstates

Microstate for d^1

$= [(4l+2)!]/N!([(4l+2 - N)]!$

L values for d is = 2 ;

N- number of electrons = 1

∴ Microstate

∴ $= [(4 \times 2+2)!]/2!([(4 \times 2+2 - 1)]!$

∴ Microstate for d^2 = $10!/1! \times 9!$

∴ Microstate for d^2 = $10 \times 9!/9!$

∴ Microstate for d^2 = 10

m_l =2	1	0	-1	-2	M_L	M_S	Total microstate
↑					2	1/2	1
	↑				1	1/2	1
		↑			0	1/2	1
			↑		-1	1/2	1
				↑	-2	1/2	1
↓					2	-1/2	1
	↓				1	-1/2	1
		↓			0	-1/2	1
			↓		-1	-1/2	1
				↓	-2	-1/2	1
		Total microstate					10

Microstates for d^2 = 45

m_l =2	1	0	-1	-2	M_L	M_S	Total nos. microstate
↑	↑				3	**1, 0,0,-1**	4
↑		↑			2	**1, 0,0,-1**	4
↑			↑		1	**1, 0,0,-1**	4
↑				↑	0	**1, 0,0,-1**	4
	↑	↑			1	**1, 0,0,-1**	4
	↑		↑		0	**1, 0,0,-1**	4
	↑			↑	-1	**1, 0,0,-1**	4
		↑	↑		-1	**1, 0,0,-1**	4
		↑		↑	-1	**1, 0,0,-1**	4
			↑	↑	-3	**1, 0,0,-1**	4
↑↓					4	**0**	1
	↑↓				2	**0**	1
		↑↓			0	**0**	1
			↑↓		-2	**0**	1
				↑↓	-4	**0**	1
Total arrangements of 2 electrons							45

UUU, UUD,UDU,DUU, UDD,DUD,DDU, DDD

d^3 configuration has 120 microstate

m_l =2	1	0	-1	-2	M_L	M_S	Total nos. microstate
↑	↑	↑			3	3/2, 3x(1/2), 3x(-1/2), -3/2	8
↑	↑		↑		2	3/2, 3x(1/2), 3x(-1/2), -3/2	8
↑	↑			↑	1	3/2, 3x(1/2), 3x(-1/2), -3/2	8
↑		↑	↑		1	3/2, 3x(1/2), 3x(-1/2), -3/2	8
↑		↑		↑	0	3/2, 3x(1/2), 3x(-1/2), -3/2	8
↑			↑	↑	-1	3/2, 3x(1/2), 3x(-1/2), -3/2	8
	↑	↑	↑		0	3/2, 3x(1/2), 3x(-1/2), -3/2	8
	↑	↑		↑	-1	3/2, 3x(1/2), 3x(-1/2), -3/2	8
	↑		↑	↑	-2	3/2, 3x(1/2), 3x(-1/2), -3/2	8
		↑	↑	↑	-3	3/2, 3x(1/2), 3x(-1/2), -3/2	8

↑	↑↓				4	**1/2, -1/2**	2
↑		↑↓			2	**1/2, -1/2**	2
↑			↑↓		0	**1/2, -1/2**	2
↑				↑↓	-2	**1/2, -1/2**	2
	↑	↑↓			1	**1/2, -1/2**	2
	↑		↑↓		-1	**1/2, -1/2**	2
	↑			↑↓	-3	**1/2, -1/2**	2
		↑	↑↓		-2	**1/2, -1/2**	2
		↑		↑↓	-4	**1/2, -1/2**	2
			↑	↑↓	-5	**1/2, -1/2**	2
↑↓	↓				5	**-1/2, 1/2**	2
↑↓		↓			4	**-1/2, 1/2**	2
↑↓			↓		3	**-1/2, 1/2**	2

↑↓				↓	2	**-1/2, 1/2**	2
	↑↓	↓			2	**-1/2, 1/2**	2
	↑↓		↓		1	**-1/2, 1/2**	2
	↑↓			↓	0	**-1/2, 1/2**	2
		↑↓	↓		-1	**-1/2, 1/2**	2
		↑↓		↓	-2	**-1/2, 1/2**	2
			↑↓	↓	-4	**-1/2, 1/2**	2
Total microstate or arrangement							120

Application of microstate :

It is used for determination of spin multiplicity of ligand field excited state for low spin complex

Problem : Calculate the microstates for t_{2g}^2 configuration in an octahedral environment and correlate it with ${}^aT_{1g} + {}^bT_{2g} + {}^cE_g + {}^dA_{1g}$ ligand field excited states by trial and error method, and find the values of a,b,c and d

$= (2d)!/[N!(2d-N)]!$

t_{2g}^2

$= (2x3)!/(2!(2x3-2)!$

$= 6!/2x1x4!$

$= 15$

$d^2 \rightarrow t_{2g}^2 = t_{2g}^1 X\ t_{2g}^1 = {}^aT_{1g} + {}^bT_{2g} + {}^cE_g + {}^dA_{1g} = 15$

Consider Possible spin multiplicities for two unpaired electrons are triplet & doublet

$=[aX3] + [bX3] + [cX2] + [dX1] = 15$

$=[3X3] + [1X3] + [1X2] + [1X1] = 15$

${}^3T_{1g} + {}^1T_{2g} + 1E_g + {}^1A_{1g}$

Problem : Calculate the microstates for $t_{2g}^1\ e_g^1$ configuration in an octahedral environment and correlate it with its ligand field excited states by trial and error method, and find the values of a,b,c and d

$$= [(2d)!/[N!(2d-N)!]\,[(2d)!/[N!(2d-N)!]$$

$t_{2g}^1\ e_g^1$

$$= [(2\times3)!/(1!(2\times3-1)!]\,[(2\times2)!/(1!(2\times2-1)!]$$
$$= [6!/1!\times5!]\times[4!/1!\times3!]$$
$$= 6\times4$$
$$= 24$$

d^2 ➡ $= t_{2g}^1 \times e_g^1$ $= {}^aT_{1g} + {}^bT_{2g} + {}^cT_{1g} + {}^dT_{2g} = 24$

Consider Possible spin multiplicities for two electron are triplet & singlet

$$=[a\times3] + [b\times3] + [c\times3] + [d\times3] = 24$$

$$=[3\times3] + [3\times3] + [1\times3] + [1\times3] = 24$$

$$= {}^3T_{1g} + {}^3T_{2g} + {}^1T_{1g} + {}^1T_{2g}$$

Problem : Calculate the microstates for e_g^2 configuration in an octahedral environment and correlate it with its ligand field excited states by trial and error method, and find the values of a,b,c and d

$= (2d)!/[N!(2d-N]!$

e_g^2

$= (2x2)! / (2!(2x2-2)!$

$= 4!/2x2!$

$= 4x3x2/4$

$=6$

$= e_g^2 = eg^1 X\ eg^1 = {}^aA_{2g} + {}^bE_g + {}^cA_{1g} = 6$

Consider Possible spin multiplicities for two electron are triplet & singlet

$=[aX1] + [bX2] + [cX1] = 6$

$=[3X1] + [1X2] + [1X1] = 6$

${}^3A_{2g} + {}^1E_g + {}^1A_{1g}$

Splitting of spectroscopic terms in an octahedral environment :

Due to formation of complex between metal and ligand , the free ion terms are split into different sub levels . These sublevels are alaso called as crystal field terms or ligand field excited states.

High spin complexes :

- Ligand field excited states are generated due to Inter electronic repulsion , which is greater than Crystal field effect in high spin complexes

Electronic configuration Central metal ion in the complex → (**Inter electronic repulsions**) → Terms → (**Ligand field excited state**) → Sub levels

Degeneracy= 2l+1

Terms	Degeneracy	Sub levels
S	(1)	A_{1g}
P	(3)	T_{1g}
D	(5)	$T_{2g} + E_g$
F	(7)	$T_{1g} + T_{2g} + A_{2g}$
G	(9)	$A_{1g} + E_g + T_{1g} + T_{2g}$

What are the ligand field excited state for high spin d^2 configuration in an octahedral complexs ?

According to weak field approach/ high spin complex's d^2 configuration gives a free ion spectroscopic terms ,

In case of high complexes the parents terms spin multiplicity is labeled as it

d^2 → Terms	ligand field excited
^3F ------	$^3T_{1g} + {}^3T_{2g} + {}^3A_{2g}$
^1D --------	$^1T_{2g} + {}^1E_g$
^3P -------	$^3T_{1g}$
^1G --------	$^1T_{1g} + {}^1T_{2g} + {}^1A_{1g} + {}^1E_g$
^1S ---------	$^1A_{1g}$

Which of the ligand field state is ground level ?

A, E, T Symmetric Lable for configuration (Octahedral complex)

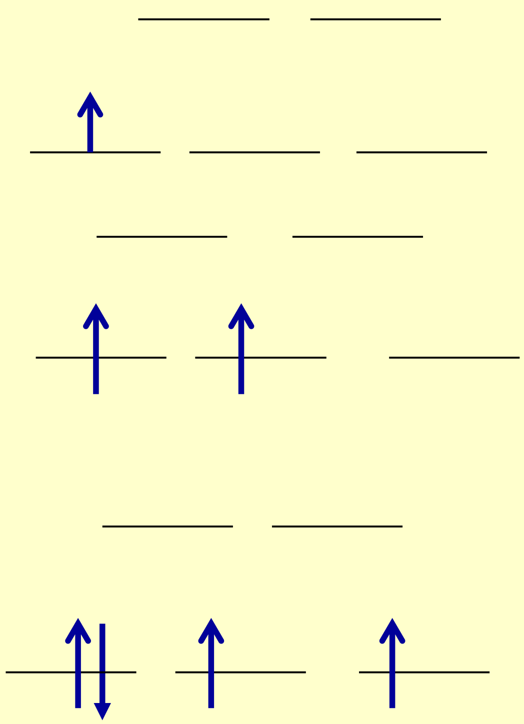
- T – designates a TRIPLY degenerate states is asymmetrically occupied electron state.

- E– designates a DOUBLY degenerate state are asymmetrically occupied electron state.

d^1

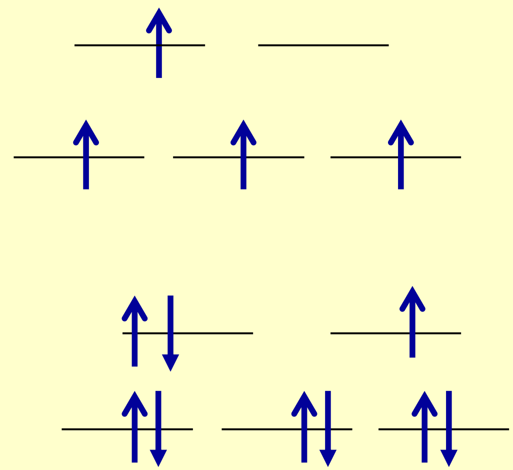
d^2

d^4



d^4(high spin)

d^9(high spin)



- E– designates a DOUBLY degenerate asymmetrically occupied state.

Strong field ligand complexes of d^2 configuration gives following possible excited states

$d^2 \rightarrow t_{2g}^2 = t_{2g}^1 \times t_{2g}^1 = {}^aT_{1g} + {}^bT_{2g} + {}^cE_g + {}^dA_{1g} = 15$

=[3X3] + [1X3] + [1X2] + [1X1] = 15

$^3T_{1g} + {}^1T_{2g} + {}^1E_g + {}^1A_{1g}$

$t_{2g}^1 e_g^1 = t_{2g}^1 \times e_g^1$

$= {}^aT_{1g} + {}^bT_{2g} + {}^cT_{1g} + {}^dT_{2g} = 24$

=[3X3] + [3X3] + [1X3] + [1X3] = 24

$= {}^3T_{1g} + {}^3T_{2g} + {}^1T_{1g} + {}^1T_{2g}$

$e_g^2 = e_g^1 \times e_g^1$

$= {}^aA_{2g} + {}^bE_g + {}^cA_{1g} = 6$

=[3X1] + [1X2] + [1X1] = 6

$= {}^3A_{2g} + {}^1E_g + {}^1A_{1g}$

Apply spin free & spin paired treatment for every configurations

Direct product of group theoretical representation

for Oh, Td

$E \times E = A_1 + A_2 + E$

$T \times T = A_1 + E + T_1 + T_2$

$E \times T = T_1 + T_2$

Possible excited states for d^1 to d^{10} configuration in an low spin octahedral complexes

Ti(III) complex

	Excited state configuration	Ligand field states
d^1	t_{2g}^{1}	$^{2}T_{2g}$
	e_g^{1}	$^{2}E_g$

V(III) complex

	Excited state configuration	Ligand field states
d^2	t_{2g}^{2}	$^{3}T_{1g} + {}^{1}T_{2g} + {}^{1}E_g + {}^{1}A_{1g}$
	$t_{2g}^{1}e_g^{1}$	$^{3}T_{1g} + {}^{3}T_{2g} + {}^{1}T_{1g} + {}^{1}T_{2g}$
	e_g^{2}	$^{3}A_{2g} + {}^{1}E_g + {}^{1}A_{1g}$

Cr(III) complex

	Excited state configuration		Ligand field states	
d^3	→	t_{2g}^3	→	$^4A_{2g} + {}^2E_g + {}^2T_{1g} + {}^2T_{2g}$
	→	$t_{2g}^2 e_g^1$	→	$^4T_{1g} + {}^4T_{2g} + {}^2T_{1g} + {}^2T_{2g} + {}^2E_g + {}^2A_{1g} + {}^2A_{2g}$
	→	$t_{2g}^1 e_g^2$	→	$^4T_{1g} + {}^2T_{1g} + {}^2T_{2g}$
	→	e_g^3	→	^2E_g

d^4 → Excited state configuration → Ligand field states

Excited state configuration	Ligand field states
t_{2g}^4	$^3T_{1g} + {}^1T_{2g} + {}^1E_g + {}^1A_{1g}$
$t_{2g}^3\, e_g^1$	$^5E_g + {}^3T_{1g} + {}^3T_{2g} + {}^3A_{1g} + {}^3A_{2g}$
$t_{2g}^2\, e_g^2$	$^5T_{1g} + {}^3T_{1g} + {}^3T_{2g} + {}^3A_{1g} + {}^3A_{2g} + {}^1T_{1g} + {}^1T_{2g} + {}^1A_{1g} + {}^1A_{2g}$
$t_{2g}^1 e_g^3$	$^3T_{1g} + {}^3T_{2g} + {}^1E_g + {}^1A_{1g}$
e_g^4	$^1A_{1g}$

Mn(II) complex

d^5	Excited state configuration	Ligand field states
	t_{2g}^5 →	$^2T_{2g}$
	$t_{2g}^4 e_g^1$ →	$^4T_{1g} + {}^4T_{2g} + {}^2T_{1g} + {}^2T_{2g} + {}^2E_g + {}^2A_{1g} + {}^2A_{2g}$
	$t_{2g}^3 e_g^2$ →	$^6A_{1g} + {}^4T_{1g} + {}^4T_{2g} + {}^4E_g + {}^4A_{1g} + {}^4A_{2g} + {}^2T_{1g} + {}^2T_{2g} + {}^2E_g + {}^2A_{1g} + {}^2A_{2g}$
	$T_{2g}^2 e_g^3$ →	$^4T_{1g} + {}^4T_{2g} + {}^2T_{1g} + {}^2T_{2g} + {}^2E_g + {}^2A_{1g} + {}^2A_{2g}$
	$T_{2g}^1 e_g^4$ →	$^2T_{1g}$

Excited state configuration

Ligand field states

Fe(II) complex

$d^6 \rightarrow t_{2g}^6 \rightarrow {}^1A_{1g}$

$\rightarrow t_{2g}^5 e_g^1 \rightarrow {}^3T_{1g} + {}^3T_{2g} + {}^1T_{1g} + {}^1T_{2g}$

$\rightarrow t_{2g}^4 e_g^2 \rightarrow {}^5T_{1g} + {}^3A_{1g} + {}^3A_{2g} + {}^3E_g + {}^3T_{2g} + {}^3T_{2g} + {}^1T_{1g} + {}^1T_{2g} + {}^1A_{1g} + {}^1A_{2g}$

$\rightarrow t_{2g}^3 e_g^3 \rightarrow {}^5E_g + {}^3A_{1g} + {}^3A_{2g} + {}^3E_g + {}^3T_{1g} + {}^3T_{2g} + {}^1T_{1g} + {}^1T_{2g} + {}^1A_{1g} + {}^1A_{2g}$

$\rightarrow t_{2g}^2 e_g^4 \rightarrow + {}^3T_{1g} + {}^1T_{2g} + {}^1E_{1g} + {}^1A_{1g}$

Co(II) complex

d^7

Excited state configuration → Ligand field states

$T_{2g}^{6}\, e_g^{1}$ → $^{2}E_g$

$t_{2g}^{5}\, e_g^{2}$ → $^{4}T_{1g} + {}^{2}T_{1g} + {}^{2}T_{2g}$

$t_{2g}^{4} e_g^{3}$ → $^{4}T_{1g} + {}^{4}T_{2g} + {}^{2}T_{1g} + {}^{2}T_{2g} + {}^{2}A_{1g} + {}^{2}A_{2g}$

$t_{2g}^{3} e_g^{4}$ → $^{4}A_{2g} + {}^{2}E_g + {}^{2}T_{1g} + {}^{2}T_{2g}$

d^8

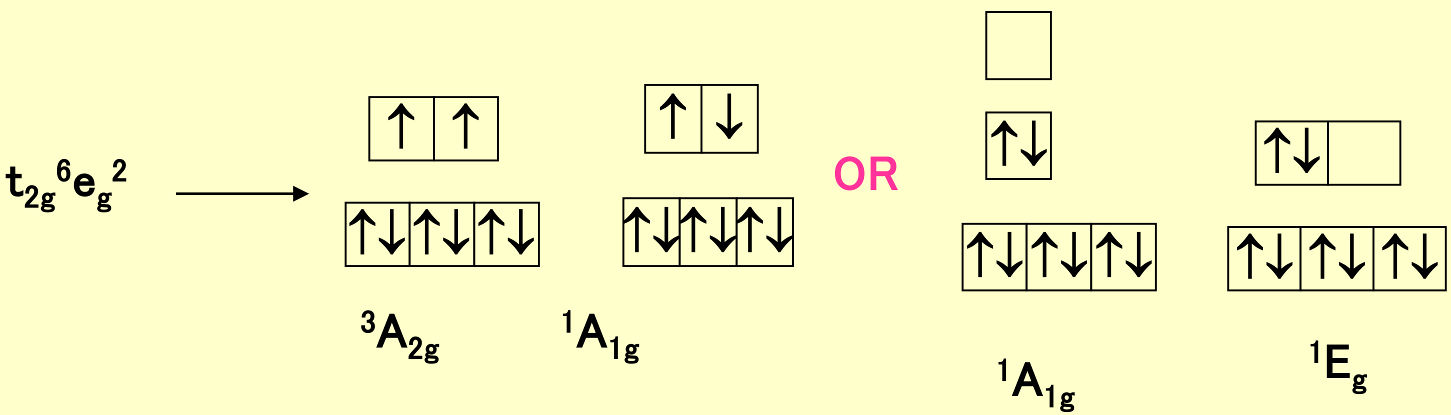
Ni(II) complex

Excited state configuration → Ligand field states

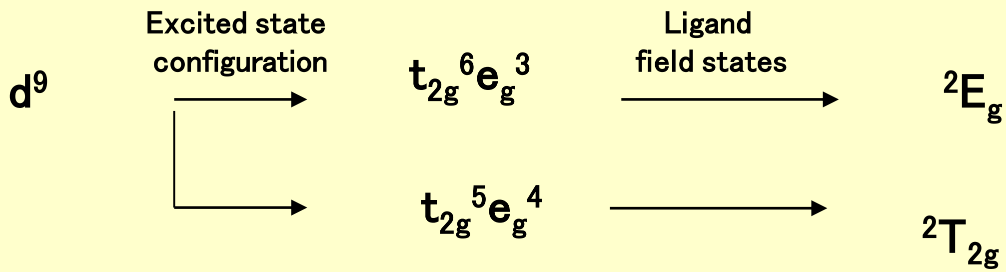
$t_{2g}^6 e_g^2$ → ${}^3A_{2g} + {}^1E_g + {}^1A_{1g}$

$t_{2g}^5 e_g^3$ → ${}^3T_{1g} + {}^3T_{2g} + {}^1T_{1g} + {}^1T_{2g}$

$t_{2g}^4 e_g^4$ → ${}^2T_{1g} + {}^1T_{2g} + {}^1E_g + {}^1A_{1g}$



Cu(II) complex



Thank You All