

















Types of El	ectronic Transitions in TM Complexes
d-d:	usually in the visible region relatively weak, $\mathcal{E} \sim 1 - 100$ if spin allowed < 0.1 if spin forbidden energy varies with $\Delta_o$ (or $\Delta_t$ )
LMCT:	Ligand to Metal Charge Transfer $\sigma_L \text{ or } \pi_L \xrightarrow{hv} d^*$ very intense, generally in UV or near UV
MLCT:	Metal to Ligand Charge Transfer d*— <sup>hυ</sup> →π <sub>L</sub> very intense (ε ~ 100 – 10,000) needs π-acceptor Ligand (CO, CN⁻, …
LL:	Ligand to Ligand $\pi_{L} \xrightarrow{h_{U}} \pi_{L}^{*}$ very intense ( $\varepsilon \sim 100 - 10,000$ )
Rydberg:	localized MO high energy, highly delocalized, deep UV











					d orbita	ls	: <b>z</b> <sup>2</sup> ,	x <sup>2</sup> .	·y²,	xy,	xz, yz	
	E	8C3	6C2	6C4	3C <sub>2</sub> =(C <sub>4</sub> ) <sup>2</sup>	i	6S4	8S6	3ơh	6σd	linear, rotations	quadratic
A1g	1	1	1	1	1	1	1	1	1	1		$x^{2}+y^{2}+z^{2}$
A <sub>2g</sub>	1	1	-1	-1	1	1	-1	1	1	-1		
Eg	2	-1	0	0	2	2	0	-1	2	0		(2z <sup>2</sup> -x <sup>2</sup> -y <sup>2</sup> , x <sup>2</sup> -y <sup>2</sup> )
T <sub>1g</sub>	3	0	-1	1	-1	3	1	0	-1	-1	(Rx, Ry, Rz)	
T <sub>2g</sub>	3	0	1	-1	-1	3	-1	0	-1	1		(xz, yz, xy)
A <sub>1u</sub>	1	1	1	1	1	-1	-1	-1	-1	-1		
A <sub>2</sub> u	1	1	-1	-1	1	-1	1	-1	-1	1		
Eu	2	-1	0	0	2	-2	0	1	-2	0		
T1u	3	0	-1	1	-1	-3	-1	0	1	1	(x. y. z)	
T <sub>2u</sub>	3	0	1	-1	-1	-3	1	0	1	-1		
ר: b	۲ł Du	ner It ti	e a her	re e a	only 5 are 6 qu	d- Ja	or dra	bita atic	als :s!	,	No ev 2z <sup>2</sup>	o d-orbital er $x^2 + y^2 +$ $-x^2 - y^2 \equiv 0$



linear
E 8C <sub>3</sub> 3C <sub>2</sub> 6S <sub>4</sub> 6σ <sub>d</sub> rotations quadratic
<b>A</b> <sub>1</sub> 1 1 1 1 1 $x^{2}+y^{2}+z^{2}$
A2 1 1 1 -1 -1
<b>E</b> 2 -1 2 0 0 $(2z^2-x^2-y^2, x^2-y^2)$
T <sub>1</sub> 3 0 -1 1 -1 (R <sub>x</sub> , R <sub>y</sub> , R <sub>z</sub> )
<b>T</b> <sub>2</sub> 3 0 -1 -1 1 (x, y, z) (xy, xz, yz)























d Orbital Spli	ttings vs. Ligand	Field Symmetry					
O <sub>h</sub> (octahedral)	D <sub>4h</sub> (tetragon. elong.)	C <sub>4ν</sub> (sq. pyram.)					
e <sub>g</sub> z <sup>2</sup> , x <sup>2</sup> -y <sup>2</sup> t <sub>2g</sub> xy,xz,yz	b <sub>1g</sub> x <sup>2</sup> -y <sup>2</sup> a <sub>1g</sub> z <sup>2</sup> b <sub>2g</sub> xy e <sub>g</sub> xz, yz	b <sub>1</sub> x <sup>2</sup> -y <sup>2</sup> a <sub>1</sub> z <sup>2</sup> b <sub>2</sub> xy e xz, yz					
T <sub>d</sub> (tetrahedral)	D <sub>4h</sub> (sq. planar)	D <sub>3h</sub> (trig. bipyram.)					
<b>— — t</b> <sub>2</sub> xy,xz,yz <b>— e</b> z <sup>2</sup> , x <sup>2</sup> –y <sup>2</sup>	b <sub>1g</sub> x <sup>2</sup> -y <sup>2</sup> b <sub>2g</sub> xy a <sub>1g</sub> z <sup>2</sup> e <sub>g</sub> xz, yz xy, z <sup>2</sup> , (xz yz) energies can switch	— a' <sub>1</sub> z <sup>2</sup> — e' x <sup>2</sup> -y <sup>2</sup> , xy — e'' xz, yz					



















		Т	ABLE 9.1	7	100	
	CRYSTAL FIELD (All	AND NEPHELAU spin-paired; 10	Dq, B and	C in wave	FOR d <sup>6</sup> COI mumbers)	MPLEXES
	Complex	10 Dq	B	β	C	C/B(y
10Dq = ∆	Fe(o-phen)2+	13,110	602	0.68		10.00
	Fe(CN)4-	32,200	490	0.55		
	Fe(CNO)4-	27,000	410	0.46		
	Ru(HnO)2+	19,800	475	0.76		
	Ruen <sup>2+</sup>	28,100	420	0.68		
	Rudien2+	28,800	430	0.69		
	Co(CN)	32,200	400	0.36		
	Codtpa	14,200	400	0.36	1620	4.05
	Co(NHa)3+	22,870	615	0.56	3090	5.02
	Coen <sup>3+</sup>	23,160	590	0.53	2900	4.91
	Co(CNO)3-	26,100	450	0.405		
	Co(HrO)	20,760	510	0.46	4260	8.36
	Cooxa-	18,020	540	0.49		
	Rh(NHa)	34,000	430	0.60		
	Rh(SCN)	~20,300				18
	Rh(CN)a-	~ 45,500				
	RhF <sup>3</sup> -	23,300	460	0.64	~ 1850	4.0
	RhCla-	20,400	350	0.49		
	RhBra-	19,000	290	0.40		
	Rhdtpa	21,900	210	0.29		
	Ir(NH3)S+	41,200	470	0.71		
	IrCla-	25,000	300	0.46		
	Irens+	~ 41,400				
	ir(NHs)sHrO3+	40,400	550	0.83		
	Irdtps	26,700	160	0.24		
	Irdsepa	25,000	135	0.20		
	PrE-	33,000	380	0.53		































Origin of Forbidden Transition Intensities  
1. Spin Forbidden Transitions due to "Spin-Orbit Couple  
Angulan Momentum of "spinning" 
$$e^-$$
 can couple  
with Angulan Momentum of  $e^-$  "moving" in  
orbital. = Magnetic moment coupling  
 $\vec{J} = \vec{L} + \vec{S} = \text{constant}$   
 $\vec{f} = \vec{f}$   
 $f = constant$   
 $f$ 













Vibronic Coupling Selection Rules  

$$f \propto \left| \int \Psi_{el_{xs}}^{*} \Psi_{vib_{xs}}^{*} \widehat{M} \Psi_{el_{rs}} \Psi_{vib_{rs}} d\tau \right|^{2}$$

$$So, \ does \ \text{this integral (in red)} \neq 0 ?$$

$$\int_{xs}^{rel} \int_{xs}^{vib} x \widehat{M} \times \int_{rs}^{rel} \int_{rs}^{vib} \text{ contain } A_{rs} ?$$

$$\int_{xs}^{r} \int_{xs}^{r} \int_{rs}^{r} \int_{rs}^{r}$$







































