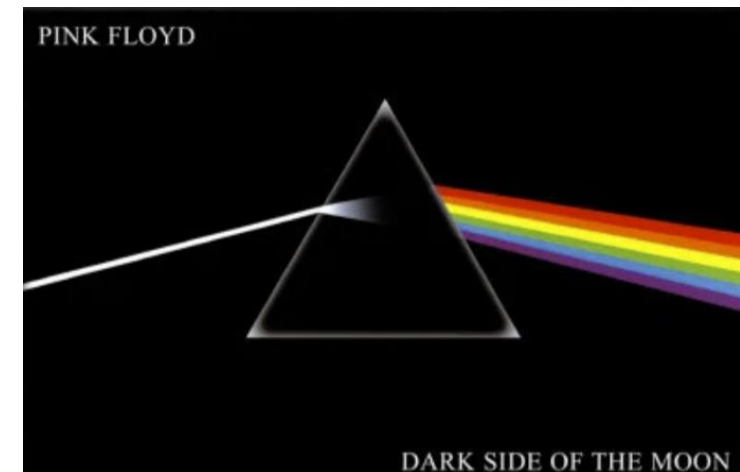
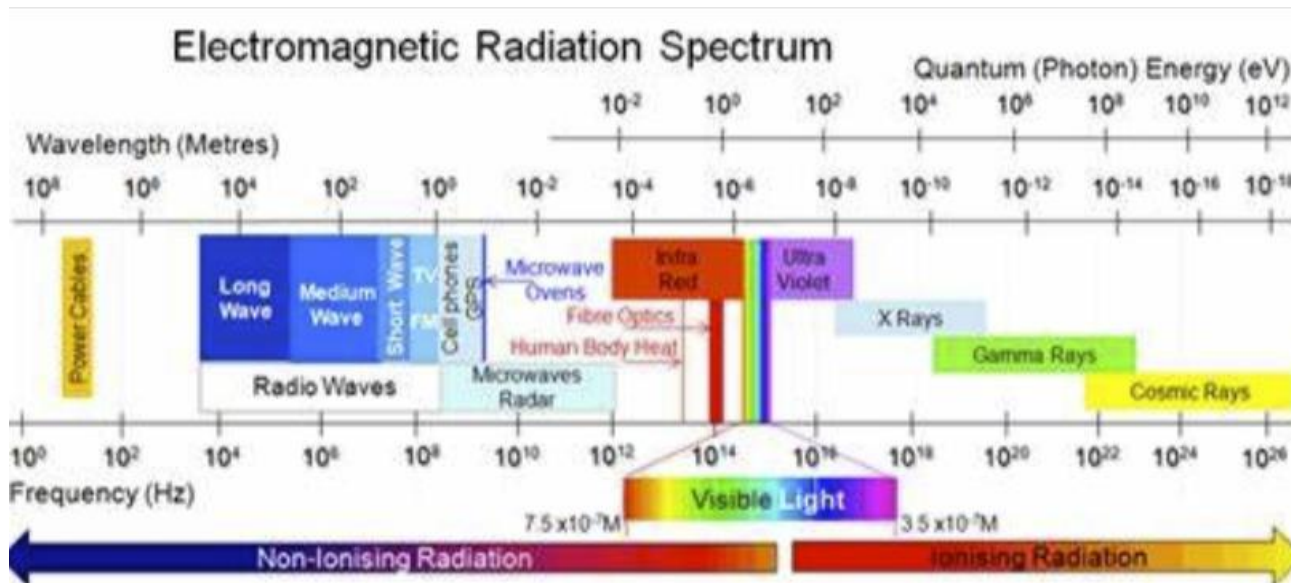


Electronic Spectroscopy

Electronic Transitions between Quantized Electronic Energy levels

Zeeman states	spin orientations (m_s)	EPR Spectroscopy	10^9 - 10^{11} Hz (microwaves)
Valence electron States (AO or MO)	orbital and spin angular momentum (L, S, J)	UVIS Spectroscopy (absorption/luminescence)	10^{14} - 10^{16} Hz (UVIS)
Inner-shell Electronic states	principal quantum number, orbital quantum number (n, L)	XPS, Auger-Spectroscopy EXAFS	10^{17} - 10^{19} Hz (X-rays)



Electronic Structure of Matter:

The H atom.

- Exact solutions to the Schrödinger-equation: quantized energy levels, characterized by numbers n , l , m_l and m_s , and wave functions $R_{nl}Y_{lm}$ where n is a natural number and $0 \leq l \leq n-1$.
- The Y_{lm} are the angular momentum eigenfunctions (spherical harmonics).
- The radial parts R_{nl} are obtained by the variable separation method.
- Spin is introduced via postulate of Goudsmit and Uhlenbeck: $S = 1/2$; $m_s = 1/2, -1/2$

• $n=1$: $R_{10}Y_{00}$

• $n=2$: $R_{20}Y_{20}$

• $n=3$: $R_{30}Y_{00}$

• $n=4$: $R_{40}Y_{00}$

$R_{21}Y_{10}$ $R_{21}Y_{11}$ $R_{21}Y_{1-1}$

$R_{31}Y_{10}$ $R_{31}Y_{11}$ $R_{31}Y_{1-1}$

$R_{41}Y_{10}$ $R_{41}Y_{11}$ $R_{41}Y_{1-1}$

$R_{32}Y_{20}$ $R_{32}Y_{21}$ $R_{32}Y_{2-1}$ $R_{32}Y_{22}$ $R_{32}Y_{2-2}$

$R_{42}Y_{20}$ $R_{42}Y_{21}$ $R_{42}Y_{2-1}$ $R_{42}Y_{22}$ $R_{42}Y_{2-2}$

$R_{43}Y_{30}$ $R_{43}Y_{31}$ $R_{43}Y_{3-1}$ $R_{43}Y_{32}$ $R_{43}Y_{3-2}$ $R_{43}Y_{33}$ $R_{43}Y_{3-3}$

$l = 0$: s electrons, $l = 1$: p-electrons, $l = 2$: d electrons, $l = 3$: f electrons

$$E = \frac{Z^2 m e^4}{8 \epsilon_0^2 h^2} \times \frac{1}{n^2}$$

Quantized energies depend only on n

Pauli principle: no two electrons within an atom can have the same set of quantum numbers.



Erwin Schrödinger
1887-1961
U. Zürich, Graz, Wien
Nobelprize 1933



Wolfgang Pauli
1900-1958
ETH Zürich
Nobelprize 1945

Radial parts of the electronic wave function

$$R_{10} = 2 \left(\frac{Z}{a_0} \right)^{\frac{3}{2}} e^{-Zr/a_0}$$

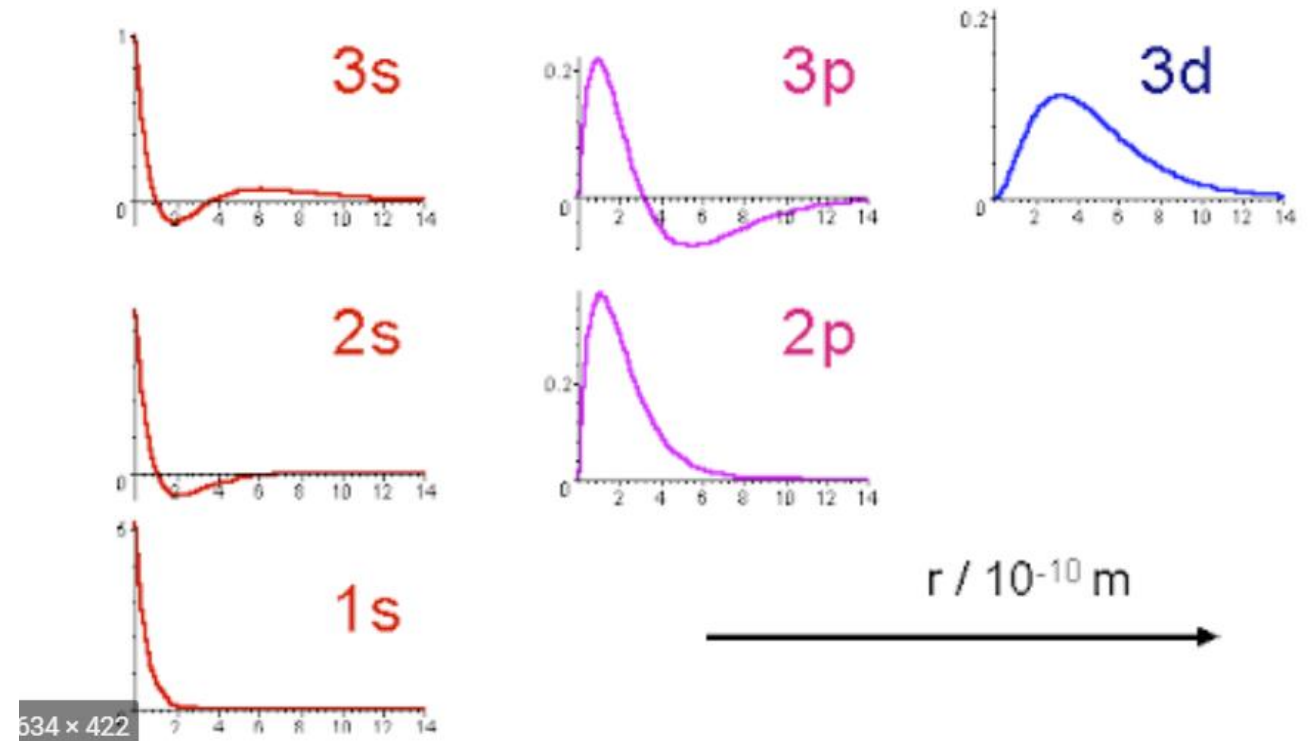
$$R_{21} = \frac{1}{\sqrt{3}} \left(\frac{Z}{2a_0} \right)^{\frac{3}{2}} \left(\frac{Zr}{a_0} \right) e^{-Zr/2a_0}$$

$$R_{20} = 2 \left(\frac{Z}{2a_0} \right)^{\frac{3}{2}} \left(1 - \frac{Zr}{2a_0} \right) e^{-Zr/2a_0}$$

$$R_{32} = \frac{2\sqrt{2}}{27\sqrt{5}} \left(\frac{Z}{3a_0} \right)^{\frac{3}{2}} \left(\frac{Zr}{a_0} \right)^2 e^{-Zr/3a_0}$$

$$R_{31} = \frac{4\sqrt{2}}{3} \left(\frac{Z}{3a_0} \right)^{\frac{3}{2}} \left(\frac{Zr}{a_0} \right) \left(1 - \frac{Zr}{6a_0} \right) e^{-Zr/3a_0}$$

$$R_{30} = 2 \left(\frac{Z}{3a_0} \right)^{\frac{3}{2}} \left(1 - \frac{2Zr}{3a_0} + \frac{2(Zr)^2}{27a_0^2} \right) e^{-Zr/3a_0}$$



Electronic Structure of Matter:

Many-electron atoms

inter-electronic interactions make exact solutions impossible. Only approximate solutions. The vectorial coupling of spin and angular momenta creates multiple electronic states with different strengths of inter-electronic repulsion → different energies for different states of L.

Russel-Saunders coupling: $\mathcal{L} = \sum \ell_i$
 Vector addition
 (1925)

$\mathcal{S} = \sum s_i$

where $L = \{ |l_1+l_2, l_1+l_2-1, l_1+l_2-2, \dots, |l_1-l_2| \}$
 where $S = \{ s_1+s_2, s_1+s_2-1, \dots, |s_1-s_2| \}$
 $J = \{ L+S, L+S-1, L+S-2, \dots, |L-S| \}$ $2J+1$ orientational states

Coupling of the angular momenta belonging to filled (sub-)shells always results in $S, L = 0$.

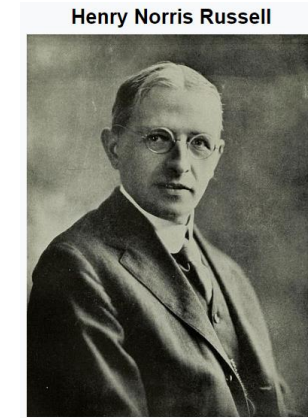
Terminology: use of term symbols $2S+1 \mathcal{L}_J$

For the symbol $\mathcal{L}$ we choose S, P, D, F, G, H, I
 characterizing L-values of 0, 1, 2, 3, 4, 5, 6

$2S+1$ is the orientational spin multiplicity

**Hund's rules regarding ground states
 (minimal interelectronic repulsion):**

- 1) Maximal S,
- 2) maximal L if various states with maximal S exist
- 3) minimal J (shell less than half-full);
 maximal J (shell more than half full)



Henry Norris Russell

1877-1957
 Princeton U.



Frederik Saunders
 1877-1963
 Syracuse U.

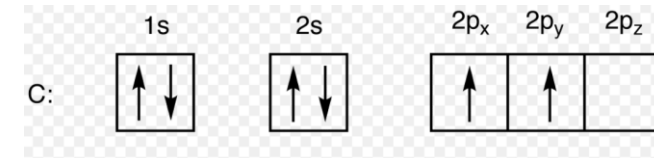


Friedrich Hund
 1896-1997
 U. Rostock, Leipzig,
 Jena, Frankfurt,
 Göttingen

Examples of ground state term symbols

- H atom: $1s^1$ $^2S_{1/2}$
- He atom: $1s^2$ 1S_0
- Li atom: $1s^2 2s^1$, $^2S_{1/2}$
- Be atom: $1s^2 2s^2$ 1S_0
- B atom: $1s^2 2s^2 2p^1$ $^2P_{1/2}, ^2P_{3/2}$
- C atom: $1s^2 2s^2 2p^2$ 3P_0
- N atom: $1s^2 2s^2 2p^3$ $^4S_{3/2}$
- O atom: $1s^2 2s^2 2p^4$ 3P_2
- F atom: $1s^2 2s^2 2p^5$ $^2P_{3/2}$
- Ne atom: $1s^2 2s^2 2p^6$ 1S_0

Example: Electronic states of the C-atom



Addition of orbital angular momenta of two electrons: $L = l_1 + l_2, l_1 + l_2 - 1, \dots, |l_1 - l_2| \rightarrow L = 2, 1, 0$

Addition of spin angular momenta of two electrons: $S = s_1 + s_2, s_1 + s_2 - 1, \dots, |s_1 - s_2| \rightarrow S = 1, 0$

$M_L = m_{l1} + m_{l2}$; $M_S = m_{s1} + m_{s2}$. Respecting the Pauli Principle we arrive at the following mother states:

M_L	M_S	1	0	-1
2			<u>$1^+ 1^-$</u>	
1		$1^+ 0^+$	<u>$1^+ 0^-$</u> , $0^+ 1^-$	$1^- 0^-$
0		$1^+ -1^+$	$-1^+ 1^-$, <u>$1^+ -1^-$</u> , $0^+ 0^-$	$1^- -1^-$
-1		$-1^+ 0^+$	<u>$0^+ -1^-$</u> , $-1^+ 0^-$	$-1^- 0^-$
-2			<u>$-1^+ -1^-$</u>	

Mother states L, total degeneracy $(2S+1)(2L+1)$

$L = 2$; 1D , 5-fold degenerate, $J=2$

$L = 1$; 3P , 3×3 -fold degenerate, $J = 2, 1, 0$

$L = 0$; 1S , non-degenerate, $J = 0$

Result: $^1D_{2L}, ^3P_2, ^3P_1, ^3P_0, ^1S_0$

Hund's rules: ground state is 3P_0

Spin-orbit coupling

- Vectorial coupling:

$$\mathcal{J} = \mathcal{L} + \mathcal{S} \text{ vector operators}$$

$$\mathcal{J}^2 = (\mathcal{L} + \mathcal{S})^2 = \mathcal{L}^2 + \mathcal{S}^2 + 2\mathcal{L}\mathcal{S}$$

$$\mathcal{L}\mathcal{S} |L, S, J, m_J\rangle = \frac{1}{2} (\mathcal{J}^2 - \mathcal{L}^2 - \mathcal{S}^2) |L, S, J, m_J\rangle$$

$$\mathcal{L}\mathcal{S} |L, S, J, m_J\rangle = \frac{1}{2} \hbar^2 (J(J+1) - L(L+1) - S(S+1)) |L, S, J, m_J\rangle$$

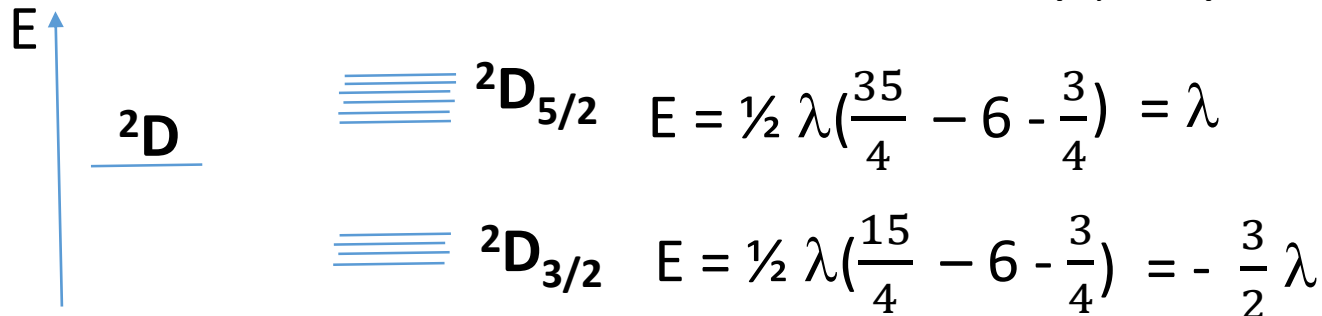
Spin orbit coupling Hamiltonian: $\mathcal{H}_{LS} = \lambda \mathcal{L}\mathcal{S}$
 λ : spin-orbit coupling constant

$\lambda > 0$ if shell is less than half filled
 $\lambda < 0$ if shell is more than half filled

Eigenvalues:

$$E_{LS} = \lambda \frac{1}{2} \hbar^2 (J(J+1) - L(L+1) - S(S+1))$$

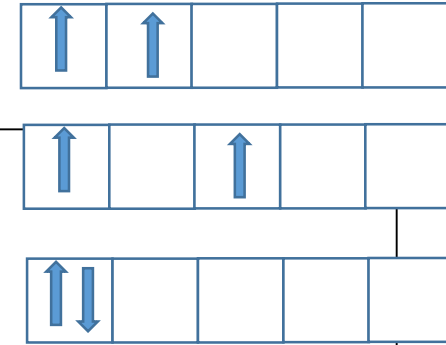
Example d^1 (Ti^{3+} , V^{4+}): Termsymbols $^2D_{3/2}$, $^2D_{5/2}$



Hund's rules regarding ground states (minimal interelectronic repulsion):

- 1) Maximal S,
- 2) maximal L if various states with maximal S exist
- 3) minimal J (shell less than half-full);
 maximal J (shell more than half full)

The d² ions: Ti²⁺, V³⁺, Cr⁴⁺, Mn⁵⁺: 2 electrons in 5 orbitals



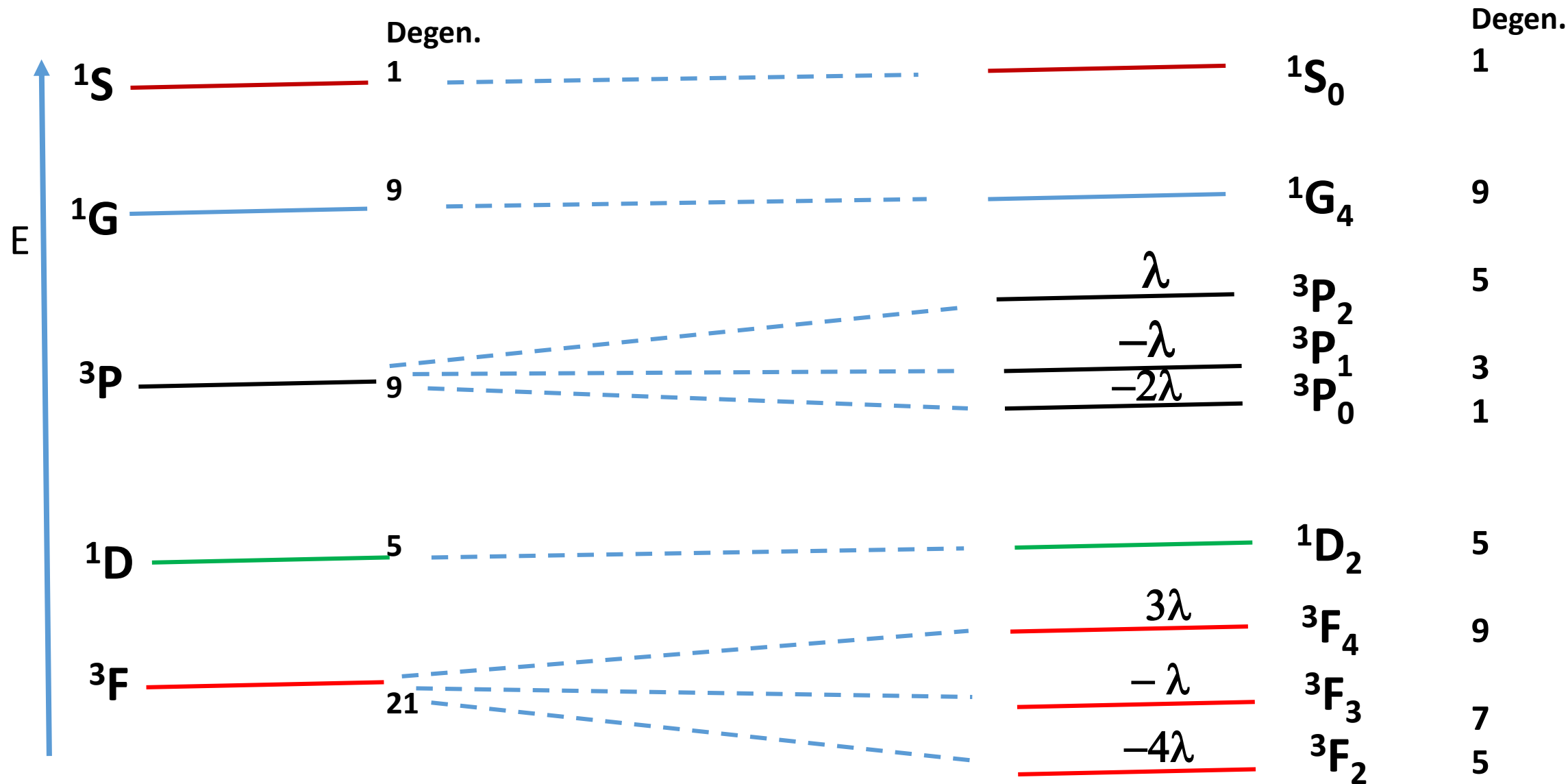
M _L M _S	1	0	-1
4		2 ⁺ 2 ⁻	
3	2 ⁺ 1 ⁺	2 ⁺ 1 ⁻ , 1 ⁺ 2 ⁻	2 ⁻ 1 ⁻
2	2 ⁺ 0 ⁺	2 ⁺ 0 ⁻ , 0 ⁺ 2 ⁻ , 1 ⁺ 1 ⁻	2 ⁻ 0 ⁻
1	2 ⁺ -1 ⁺ , 1 ⁺ 0 ⁺	2 ⁺ -1 ⁻ , 2 ⁻ -1 ⁺ , 1 ⁺ 0 ⁻ , 0 ⁺ 1 ⁻	2 ⁻ 1 ⁻ , 1 ⁻ 0 ⁻
0	2 ⁺ -2 ⁺ 1 ⁺ -1 ⁺	2 ⁺ -2 ⁻ , -2 ⁺ 2 ⁻ , -1 ⁺ 1 ⁻ , 1 ⁺ -1 ⁻ , 0 ⁺ 0 ⁻	-2 ⁻ 2 ⁻ , 1 ⁻ -1 ⁻
-1	-2 ⁺ 1 ⁺ -1 ⁺ 0 ⁺	-2 ⁺ 1 ⁻ , -2 ⁻ 1 ⁺ , 0 ⁺ -1 ⁻ , -1 ⁺ 0 ⁻	-2 ⁺ 1 ⁺ -1 ⁻ 0 ⁻
-2	-2 ⁺ 0 ⁺	-2 ⁻ 0 ⁺ , -2 ⁺ 0 ⁻ -1 ⁺ -1 ⁻	-2 ⁻ 0 ⁻
-3	-2 ⁺ -1 ⁺	-2 ⁺ -1 ⁻ , -2 ⁻ 1 ⁺	-2 ⁻ -1 ⁻
-4		-2 ⁺ -2 ⁻	

etc: 45 permutations
Consistent with Pauli

Mother States: ¹G, ³F, ¹D, ³P, and ¹S

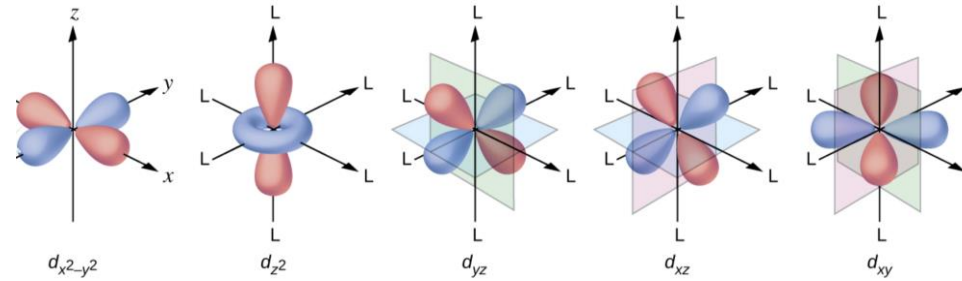
In total there are 45 distinct states, having degeneracies 9, 3x7 = 21, 5, 3x3 = 9, and 1

Partial removal of degeneracy due to spin-orbit coupling: the case of d² ions



Electronic Structure of Transition Metal Complexes:

Principal Effect: in transition metal ions the degeneracy of the open-shell d-electrons is removed by electrostatic repulsion effects by the electrons of surrounding ligands. The effect depends on how the ligands are oriented relative to the d-orbitals. The symmetry aspects of this problem make it an important application field of group theory



1. The situation for the free metal ions

Aside from the electronic ground state there are the various possible excited electronic states, whose term symbols can be worked out obeying the Clebsch-Gordan rules, (not discussed here):

Examples: **(electronic ground states in red)**

Ti³⁺ (d¹): states **²D_{3/2}** and ²D_{5/2}

V³⁺ (d²) states **³F₂**, ¹D, ³P, ¹G, ¹S

Cr³⁺ (d³): states **⁴F_{3/2}**, ⁴P, ²P, ²F, ²G, ²H, ²D

Mn³⁺ (d⁴): states **⁵D₀**, ³H, ³G, ³F, ³D, ¹I

Mn²⁺ (d⁵): states **⁶S_{5/2}**, ⁴G, ⁴D, ⁴F, ²I,

Fe²⁺ (d⁶): states **⁵D₄**, ³H, ³G, ³F, ³D, ¹I

Co²⁺ (d⁷): states **⁴F_{9/2}**, ⁴P, ²P, ²F, ²G, ²H, ²D

Ni²⁺ (d⁸): states **³F₄**, ¹G, ¹D, ³P, ¹S

Cu²⁺ (d⁹): states **²D_{5/2}** and ²D_{3/2}

22	23	24	25	26	27	28	29
Ti	V	Cr	Mn	Fe	Co	Ni	Cu

„Hole formalism“



Alfred Clebsch, 1833–1872

U. Gießen, Göttingen



Paul Gordan, 1837–1912

U. Erlangen

2. The situation in the metal complexes (Crystal field theory)

Besides the Coulombic attraction between the central metal atom and the negatively charged (or polarized) ligands, there is an electrostatic repulsion between the d-electrons situated on the central metal ions and the ligands in their coordination environment. The strength of the repulsion depends on the mutual orientation of the ligands relative to the d-orbitals. This produces energy level differences which correspond to the electromagnetic wavelengths in the UVIS region. Responsible for the colored appearance of many transition metal salts and complexes.

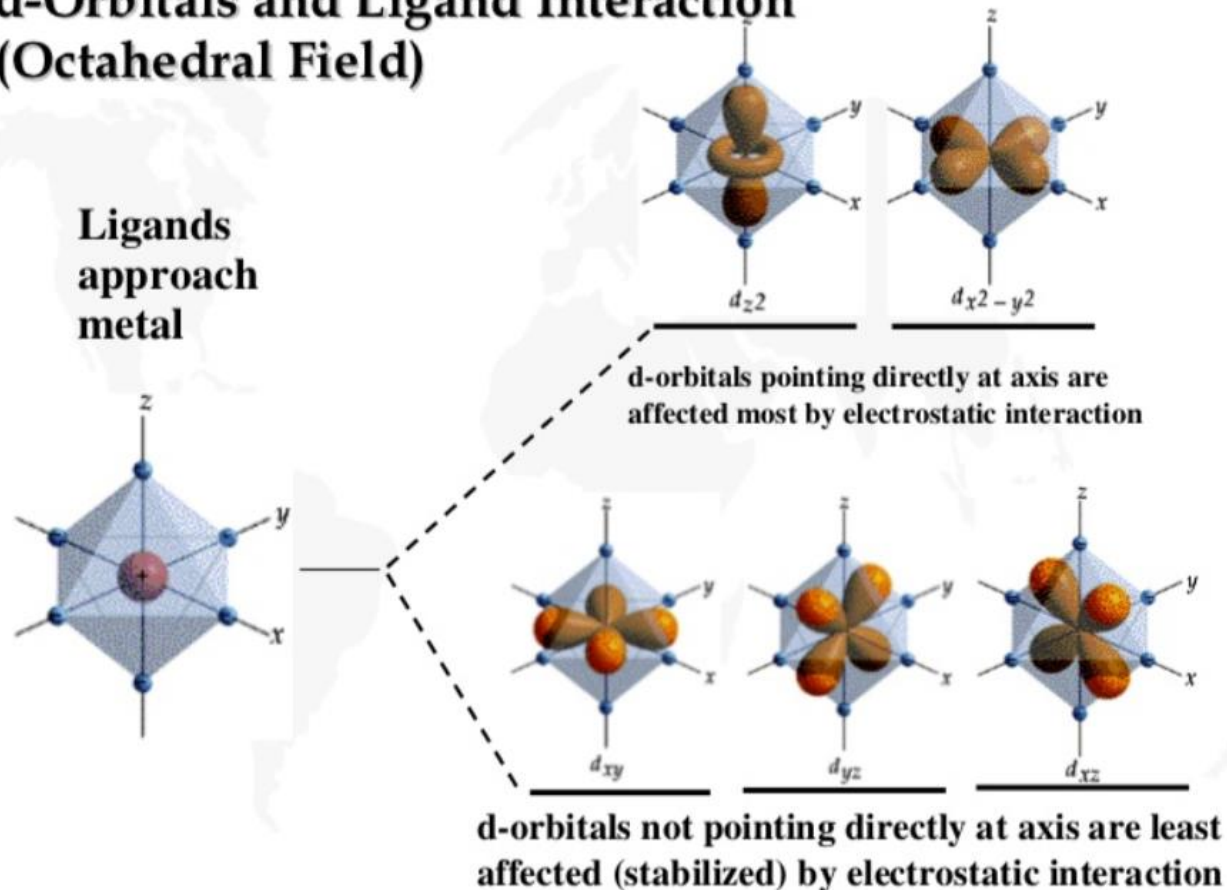
d-Orbitals and Ligand Interaction (Octahedral Field)

The symmetry – related aspects of this Problem can be addressed by the group theory formalism: Qualitative assesment of optical absorption spectra in terms of:

- 1) the number of differentiable energy levels (extent of degeneracy removal)
- 2) Coordination preferences of the ions
- 3) Transition probabilities and selection rules
- 4) Transition linewidths and intensities

Limitations:

- 1) Qualitative – no exact calculations
- 2) No exact information about energy ordering
- 3) Spin-orbit coupling effects are neglected (require an extension of the theory, (Double group, and experimental study by EPR).



The simplest case: electron configuration d^1 : Ti^{3+} , V^{4+} , Mn^{6+}
In an octahedral coordination environment

Free ion term symbol 2D

General form of the wave function: $\psi = R(r)\Theta(\theta) \Phi(\phi) \varphi(s)$

Parts $R(r)$ and $\varphi(s)$ have no orientation dependence

Orientation dependence of part $\Theta(\theta)$ can be disregarded by choice of coordinate system

Only orientation dependence of $\Phi(\phi)$ must be considered. The five wavefunctions differ with respect to the orientational quantum number m_l : 2, 1, 0, -1, -2 (because $l = 2$ for d-electrons).

Thus, the basis relevant to this problem is 5-dimensional, consisting of the five orthogonal d-wavefunctions.

$$\Phi(\phi) = \exp im_l \phi$$

For each group considered, we have 5×5 matrices to describe the symmetry operations. Again, all that matters are the characters of these symmetry operations

Again, the symmetry operation is described by a matrix multiplying a 5-dimensional vector

Transformation matrix – rotation by α

$$\begin{pmatrix} \exp + 2i\phi \\ \exp + i\phi \\ \exp \quad 0\phi \\ \exp - i\phi \\ \exp - 2i\phi \end{pmatrix} \xrightarrow[\text{by } \alpha]{\text{Rotate}} \begin{pmatrix} \exp + 2i(\phi + \alpha) \\ \exp + i(\phi + \alpha) \\ \exp \quad 0(\phi + \alpha) \\ \exp - i(\phi + \alpha) \\ \exp - 2i(\phi + \alpha) \end{pmatrix} = \begin{pmatrix} \exp 2i\alpha & 0 & 0 & 0 & 0 \\ 0 & \exp i\alpha & 0 & 0 & 0 \\ 0 & 0 & \exp 0\alpha & 0 & 0 \\ 0 & 0 & 0 & \exp - i\alpha & 0 \\ 0 & 0 & 0 & 0 & \exp - 2i\alpha \end{pmatrix} \begin{pmatrix} \exp + 2i\phi \\ \exp + i\phi \\ \exp \quad 0\phi \\ \exp - i\phi \\ \exp - 2i\phi \end{pmatrix}$$

Thus, our representation of the group is the set of 5-dimensional transformation matrices for all the symmetry operations that occur in the group. This representation is generally reducible, and the characters characterizing the symmetry operations are again denoted χ_T .

$$\chi_T = \exp(2i\alpha) + \exp(i\alpha) + \exp(0\alpha) + \exp(-i\alpha) + \exp(-2i\alpha)$$

This is the relevant formula for $L = 2$ (a single d-electron). For other electronic states with different L values our Representation is $2L+1$ – dimensional, and the trace will have $2L+1$ summation terms, with m_L values ranging from L , $L-1$,.....to $-L$. The above formula then turns into

$$\chi_T = \exp(Li\alpha) + \exp((L - 1)i\alpha) + \dots + \exp(-Li\alpha) \text{ (there are } 2L+1 \text{ terms)}$$

This summation can be written as: $\chi_T = \exp(-Li\alpha) \sum_{k=0}^{2L} (\exp(i\alpha))^k$

A

For the summation we may write: $\sum_{k=0}^{2L} (\exp(i\alpha))^k = \frac{\exp(i\alpha(2L+1)) - 1}{\exp(i\alpha) - 1}$

Proof: Substituting $x = \exp(i\alpha)$ the summation reads:

$$\sum_{k=0}^{2L} (x)^k = x^{2L} + x^{2L-1} + \dots + 1 \quad \text{We multiply both sides by } x-1$$

$$(x-1) \sum_{k=0}^{2L} (x)^k = x^{2L+1} + x^{2L} + \dots + x - x^{2L} - x^{2L-1} - \dots - 1$$

$$(x-1) \sum_{k=0}^{2L} (x)^k = x^{2L+1} - 1$$

$$\sum_{k=0}^{2L} (x)^k = \frac{x^{2L+1} - 1}{(x-1)}$$

Re-substituting $x = \exp(i\alpha)$, we see that $\sum_{k=0}^{2L} (\exp(i\alpha))^k = \frac{\exp(i\alpha(2L+1)) - 1}{\exp(i\alpha) - 1}$

Using this result in A we get $\chi_T = \exp(-Li\alpha) \sum_{k=0}^{2L} (\exp(i\alpha))^k = \exp(-Li\alpha) \frac{\exp(i\alpha(2L+1)) - 1}{\exp(i\alpha) - 1}$

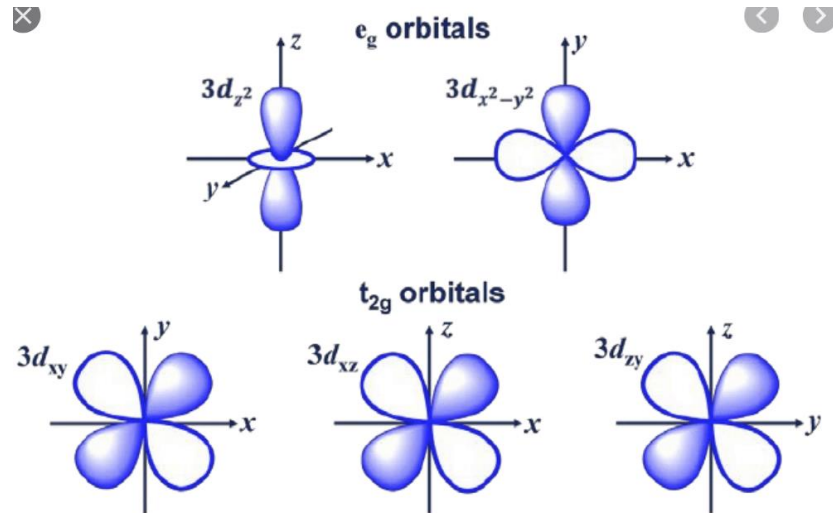
$$\chi_T = \frac{\exp(i\alpha(L+1)) - \exp(-iL\alpha)}{\exp(i\alpha) - 1} = \frac{\exp(i\alpha(L+1/2)) \exp(\frac{i\alpha}{2}) - \exp(-iL\alpha)}{\exp(i\alpha) - 1} = \frac{\exp(i\alpha(L+\frac{1}{2})) - \exp(-i\alpha(L+\frac{1}{2}))}{\exp(\frac{i\alpha}{2}) - \exp(-\frac{i\alpha}{2})}$$

Our result corresponds to:

$$\chi_T = \frac{\sin(L + \frac{1}{2})\alpha}{\sin \alpha/2}$$

Irreducible representations of the electronic states in octahedral complexes

Relevant group: O_h , but can be simplified to O , because both groups differ only in the existence of a center of inversion, Which is absent in the group O . In the group O_h there exist irreducible representations of both types g and u. However, d-orbitals always belong to a g-representation. Their wave function is always of the form $\psi(x,y,z) = \psi(-x,-y,-z)$



O (432)	E	$8C_3$	$3C_2$	$6C_4$	$6C'_2$	
A_1	1	1	1	1	1	$x^2 + y^2 + z^2$
A_2	1	1	1	-1	-1	
E	2	-1	2	0	0	$(2z^2 - x^2 - y^2, \sqrt{3}(x^2 - y^2))$
T_1	3	0	-1	1	-1	(x, y, z) (R_x, R_y, R_z)
T_2	3	0	-1	-1	1	(xy, xz, yz)

Character table for point group O_h

O_h	E	$8C_3$	$6C_2$	$6C_4$	$3C_2 = (C_4)^2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	linear functions, rotations	quadratic functions	cubic functions
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	-	(xz, yz, xy)	-
A_{1u}	+1	+1	+1	+1	+1	-1	-1	-1	-1	-1	-	-	-
A_{2u}	+1	+1	-1	-1	+1	-1	+1	-1	-1	+1	-	-	xyz
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)	-	$(x^3, y^3, z^3) [x(z^2 + y^2), y(z^2 + x^2), z(x^2 + y^2)]$
T_{2u}	+3	0	+1	-1	-1	-3	+1	0	+1	-1	-	-	$[x(z^2 - y^2), y(z^2 - x^2), z(x^2 - y^2)]$

Irreducible Representations of the d^1 electronic states (L=2) for the group O

Characters of the reducible representation for the five classes E, C_3 , C_4 , C_2 , C_2'

$$\chi_T = \frac{\sin(L + \frac{1}{2})\alpha}{\sin \alpha/2}$$

$$\chi_T(E) = 5$$

$$\chi_T(C_4) = \frac{\sin 5\pi/4}{\sin \pi/4} = -1$$

$$\chi_T(C_3) = \frac{\sin 5\pi/3}{\sin \pi/3} = -1$$

$$\chi_T(C_2) = \frac{\sin 5\pi/2}{\sin \pi/2} = 1$$

$$\chi_T(C_2') = \frac{\sin 5\pi/2}{\sin \pi/2} = 1$$

Developing the irreducible representation using the decomposition formula

$$a_i = \frac{1}{h} \sum_R \chi_T(R) \chi^{(i)}(R) = \frac{1}{h} \sum_c \chi_T(c) g(c) \chi^{(i)}(c) =$$

where the $g(c)$ are the number of operations belonging to the same class

$$a_{A_1} = \frac{1}{24} (5 \times 1 \times 1 + (-1) \times 6 \times 1 + (-1) \times 8 \times 1 + 1 \times 6 \times 1 + 1 \times 3 \times 1) = 0$$

$$a_{A_2} = \frac{1}{24} (5 \times 1 \times 1 + (-1) \times 6 \times (-1) + (-1) \times 8 \times 1 + 1 \times 6 \times (-1) + 1 \times 3 \times 1) = 0$$

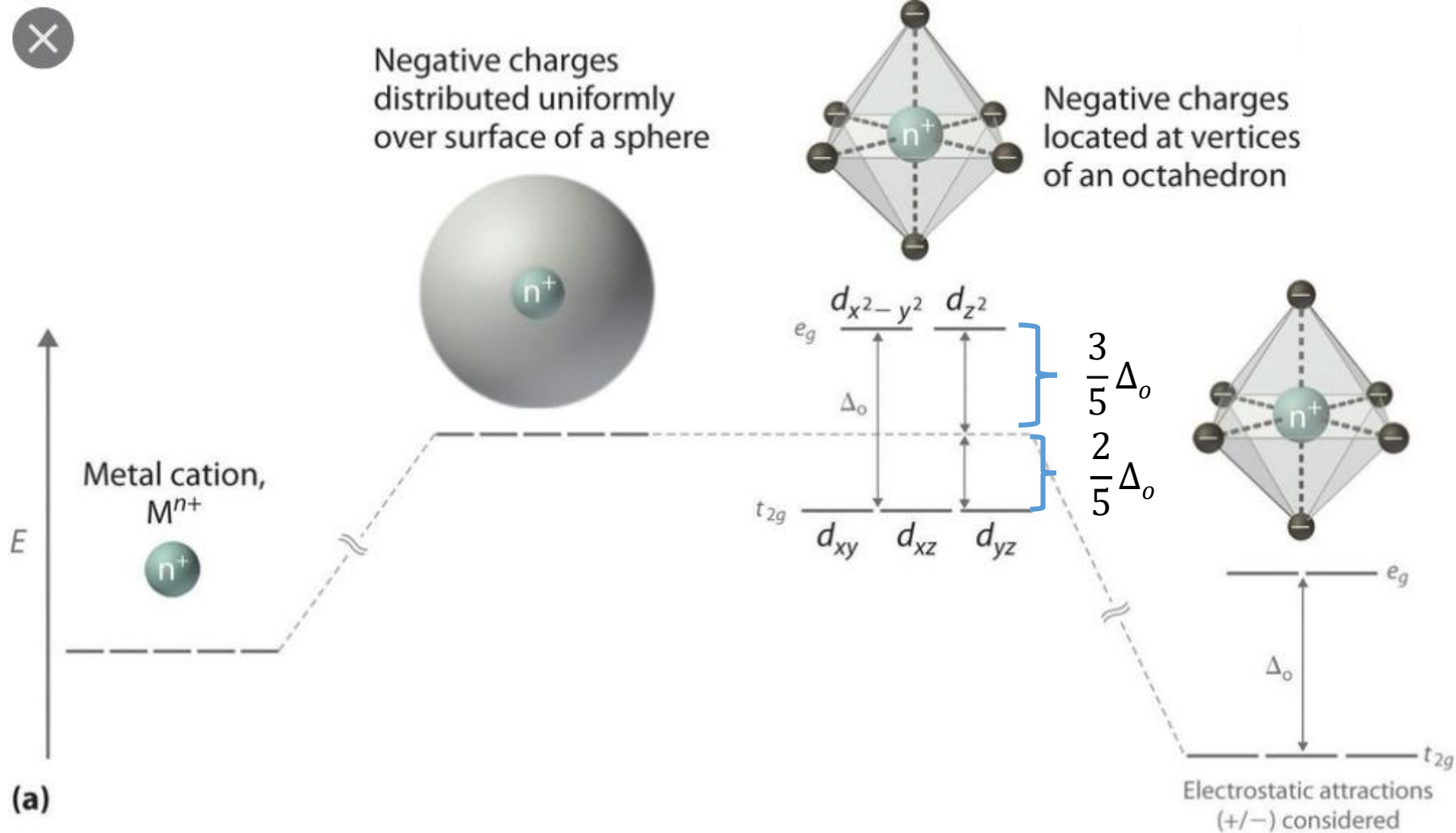
$$a_E = \frac{1}{24} (5 \times 1 \times 2 + (-1) \times 6 \times 0 + (-1) \times 8 \times (-1) + 1 \times 6 \times 0 + 1 \times 3 \times 2) = 1$$

$$a_{T_1} = \frac{1}{24} (5 \times 1 \times 3 + (-1) \times 6 \times 1 + (-1) \times 8 \times 0 + 1 \times 6 \times (-1) + 1 \times 3 \times (-1)) = 0$$

$$a_{T_2} = \frac{1}{24} (5 \times 1 \times 3 + (-1) \times 6 \times (-1) + (-1) \times 8 \times 0 + 1 \times 6 \times 1 + 1 \times 3 \times (-1)) = 1$$

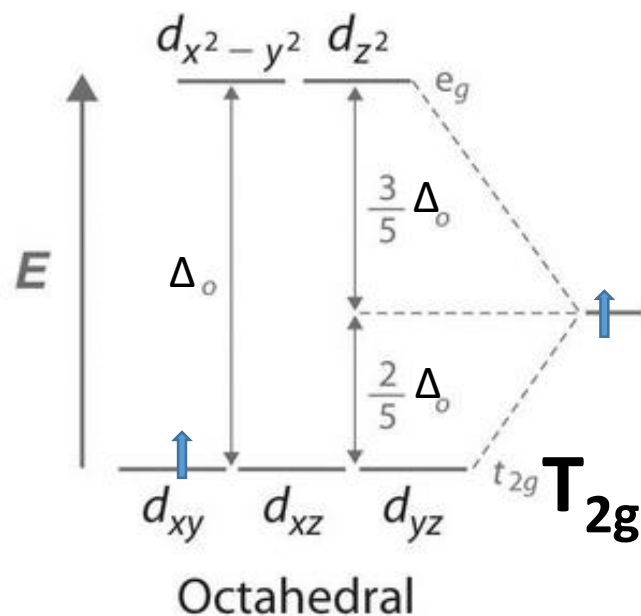
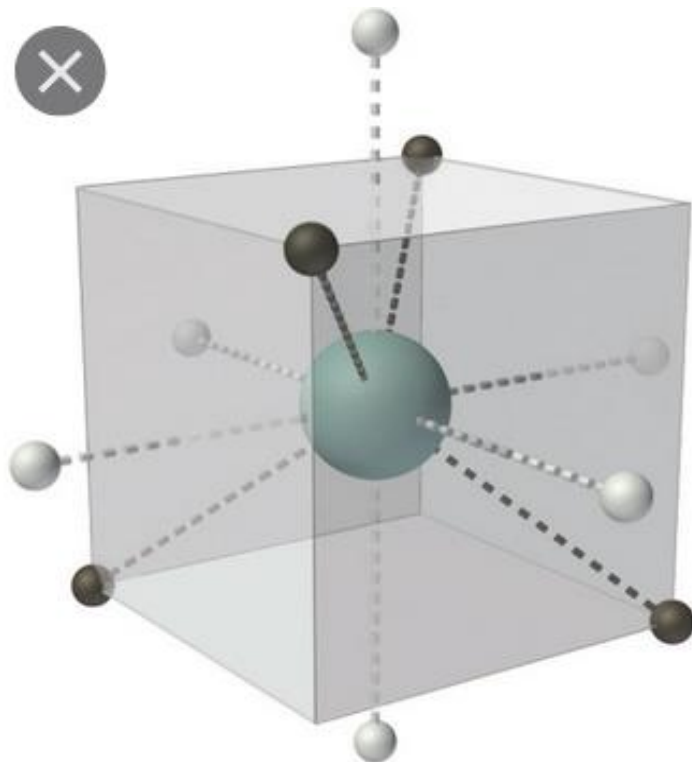
$$\Gamma(d^1_{Oh}) = E_g + T_{2g}$$

This corresponds to the known result we can already arrive at by inspection.

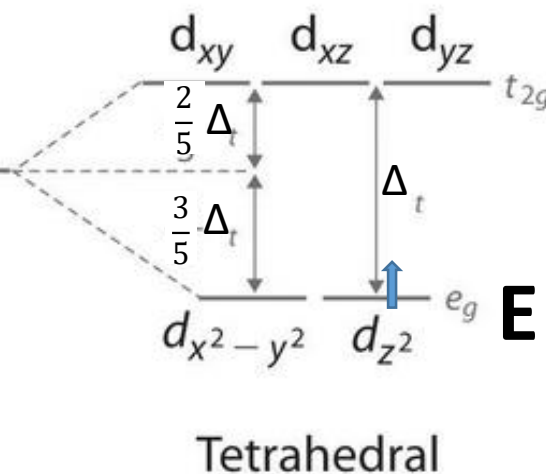


Octahedral versus Tetrahedral Coordination and d^1 vs. d^9

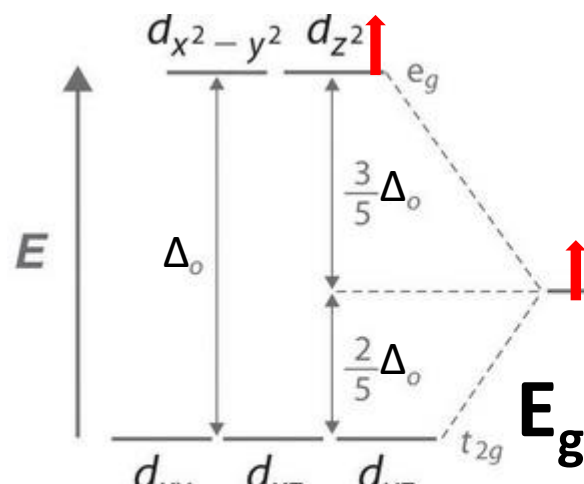
single electron vs single hole



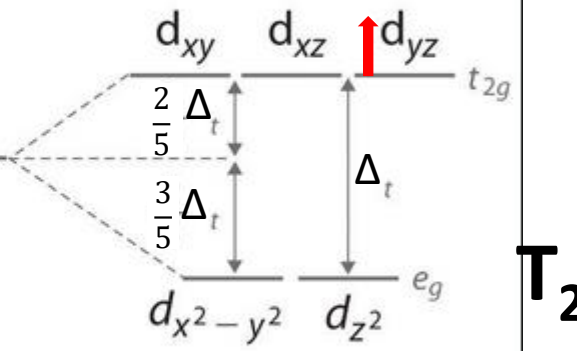
d^1



Coord	$\text{Ti}^{3+}d^1$	$\text{Cu}^{2+}d^9$
Octah.	T_{2g}	E_g
Tetrah.	E	T_2

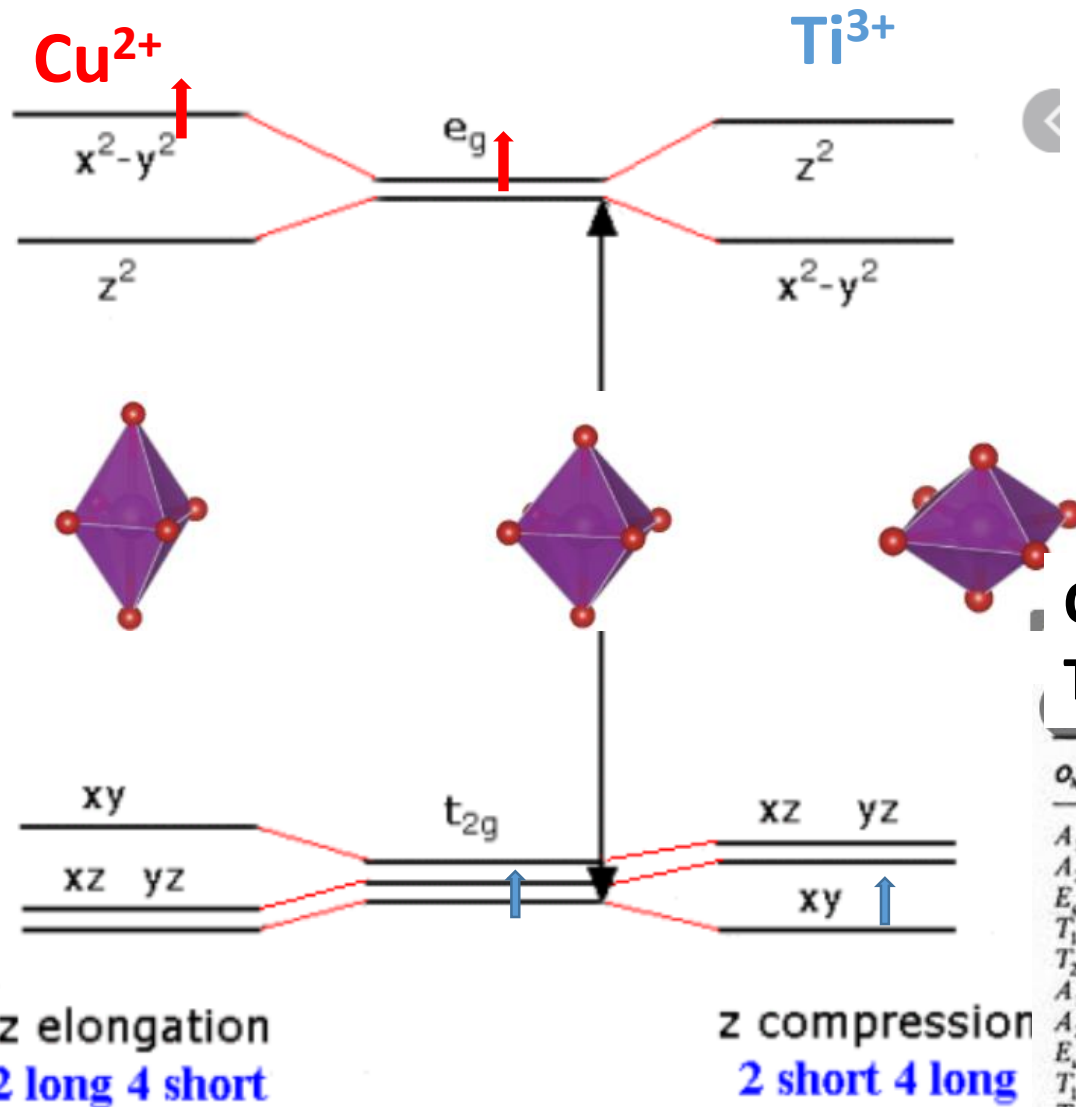


d^9



Jahn-Teller Effect

Degenerate ground states suffer geometric distortions that remove the degeneracy lowering the overall energy of the complex. Here $O_h \rightarrow D_{4h}$ distortion



Hermann Arthur Jahn
1907-1979
U. Southampton



Edward Teller
1908-2003
U. Chicago, Los Alamos, Florida Inst. Technol, LLNL, UCD, UCB

Correlation table of Terms generated by symmetry reduction

O_h	O	T_d	D_{4h}	D_{2d}	C_{4v}	C_{2v}	D_{3d}	D_3	C_{2h}
A_{1g}	A_1	A_1	A_{1g}	A_1	A_1	A_1	A_{1g}	A_1	A_g
A_{2g}	A_2	A_2	B_{1g}	B_1	B_1	A_2	A_{2g}	A_2	B_g
E_g	E	E	$A_{1g} + B_{1g}$	$A_1 + B_1$	$A_1 + B_1$	$A_1 + A_2$	E_g	E	$A_g + B_g$
T_{1g}	T_1	T_1	$A_{2g} + E_g$	$A_2 + E$	$A_2 + E$	$A_2 + B_1 + B_2$	$A_{2g} + E_g$	$A_2 + E$	$A_g + 2B_g$
T_{2g}	T_2	T_2	$B_{2g} + E_g$	$B_2 + E$	$B_2 + E$	$A_1 + B_1 + B_2$	$A_{1g} + E_g$	$A_1 + E$	$2A_g + B_g$
A_{1u}	A_1	A_2	B_{1u}	B_1	A_2	A_2	A_{1u}	A_1	A_u
A_{2u}	A_2	A_1	B_{1u}	A_1	B_2	A_1	A_{2u}	A_2	B_u
E_u	E	E	$A_{1u} + B_{1u}$	$A_1 + B_1$	$A_2 + B_2$	$A_1 + A_2$	E_u	E	$A_u + B_u$
T_{1u}	T_1	T_2	$A_{2u} + E_u$	$B_2 + E$	$A_1 + E$	$A_1 + B_1 + B_2$	$A_{2u} + E_u$	$A_2 + E$	$A_u + 2B_u$
T_{2u}	T_2	T_1	$B_{2u} + E_u$	$A_2 + E$	$B_1 + E$	$A_2 + B_1 + B_2$	$A_{1u} + E_u$	$A_1 + E$	$2A_u + B_u$

Systems d^2 (V^{3+} , Cr^{4+} , Mn^{5+}) and d^8 (Ni^{2+}) in octahedral crystal field

Inspection no longer possible, group theory needed. There are two principal effects

- 1) Intra-atomic interelectronic repulsion
- 2) Interelectronic repulsion d-electrons/ ligand electrons.

Different cases to be distinguished:

Weak ligand field case: Mother states still dominate, ligand field makes a perturbation

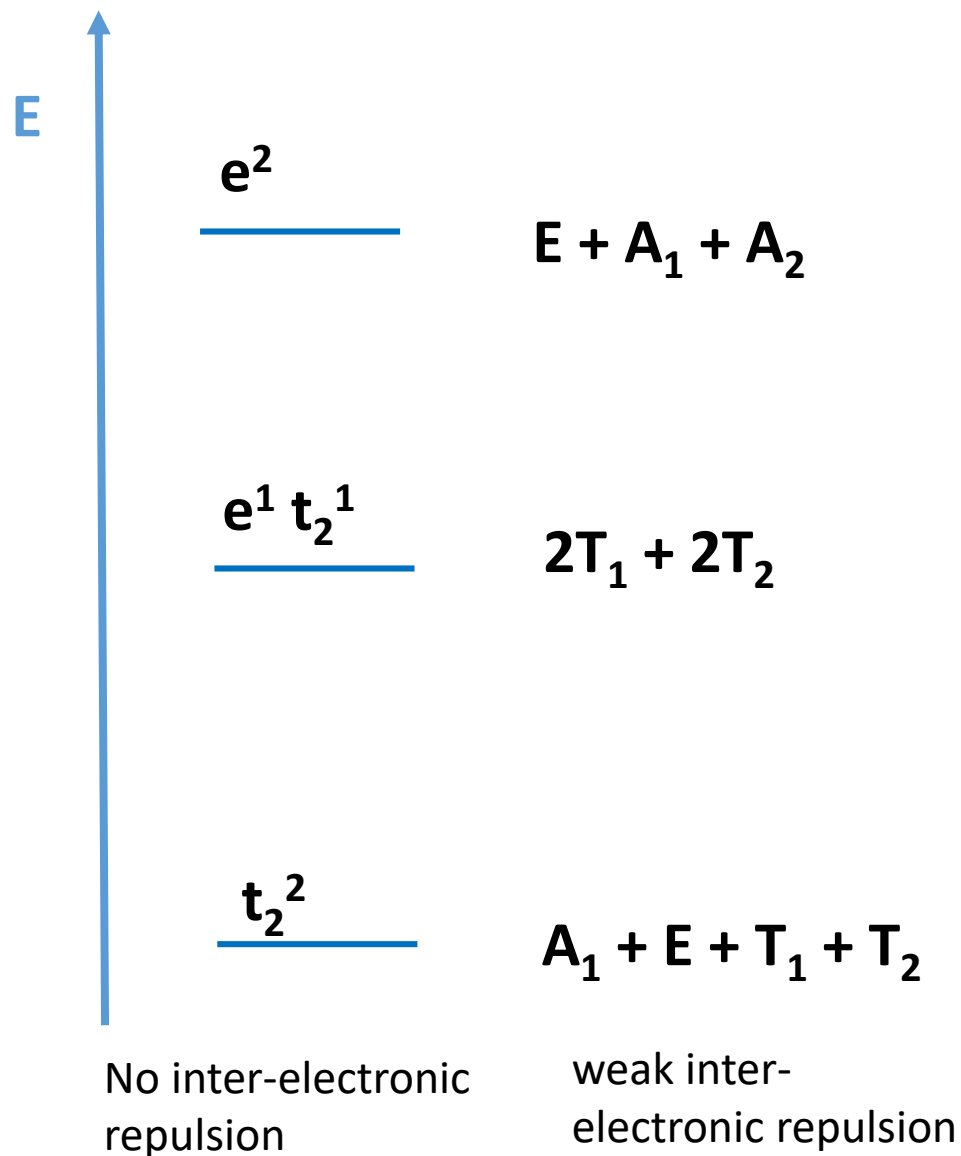
Extremely strong field case: intra-atomic repulsion is neglected

Strong-field case: Intra-atomic repulsion is a perturbation to the extremely strong field case

Weak field case: Spin multiplicity of the mother state is preserved.

	$\underline{L}$		
1S	0		$\longrightarrow$ 1A_1
1G	4	$\chi_T = \frac{\sin(L+\frac{1}{2})\alpha}{\sin \alpha/2}$	$\longrightarrow$ $^1E + ^1T_1 + ^1T_2 + ^1A_1$
3P	1		$\longrightarrow$ 3T_1
1D	2		$\longrightarrow$ $^1E + ^1T_2$
3F_2	3		$\longrightarrow$ $^3T_1 + ^3T_2 + ^3A_2$

The extremely strong-field and the strong field cases for d^2



O <i>h=24</i>	E	8 C_3	3 C_2	6 C_4	6 C_2'
A_1	1	1	1	1	1
A_2	1	1	1	-1	-1
E	2	-1	2	0	0
T_1	3	0	-1	1	-1
T_2	3	0	-1	-1	1

Interelectronic repulsion via direct product formation

E x E	4	1	4	0	0
T_2 x E	6	0	-2	0	0
T_2 x T_2	9	0	1	1	1

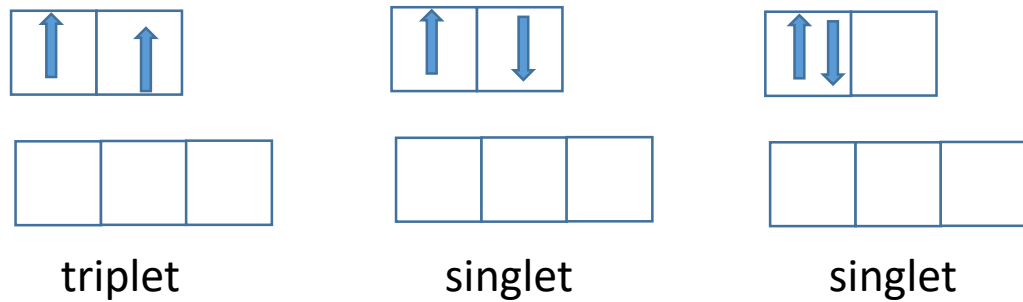


Decomposition formula

Irreducible representations

Assigning spin multiplicities by the method of descending symmetry

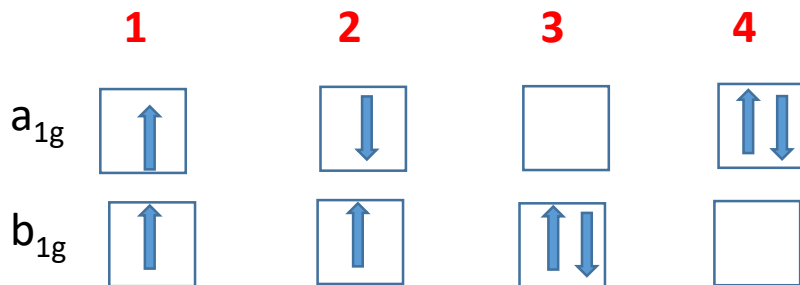
Consider the case of d^2 in octahedral ligand field.
For the e_g^2 state the distribution possibilities are:



Inter-electronic repulsion produces the states $E + A_1 + A_2$
But we do not know their spin multiplicities
Solution: lower the symmetry : $O_h \rightarrow D_{4h}$

The correlation table tells us
 $A_{1g} \rightarrow A_{1g}$
 $A_{2g} \rightarrow B_{1g}$
 $E_g \rightarrow A_{1g} + B_{1g}$

In the reduced symmetry, the two e_g orbitals have different energies. Now the distribution possibilities are:



Only distribution **1** produces a triplet back-correlation to O_h

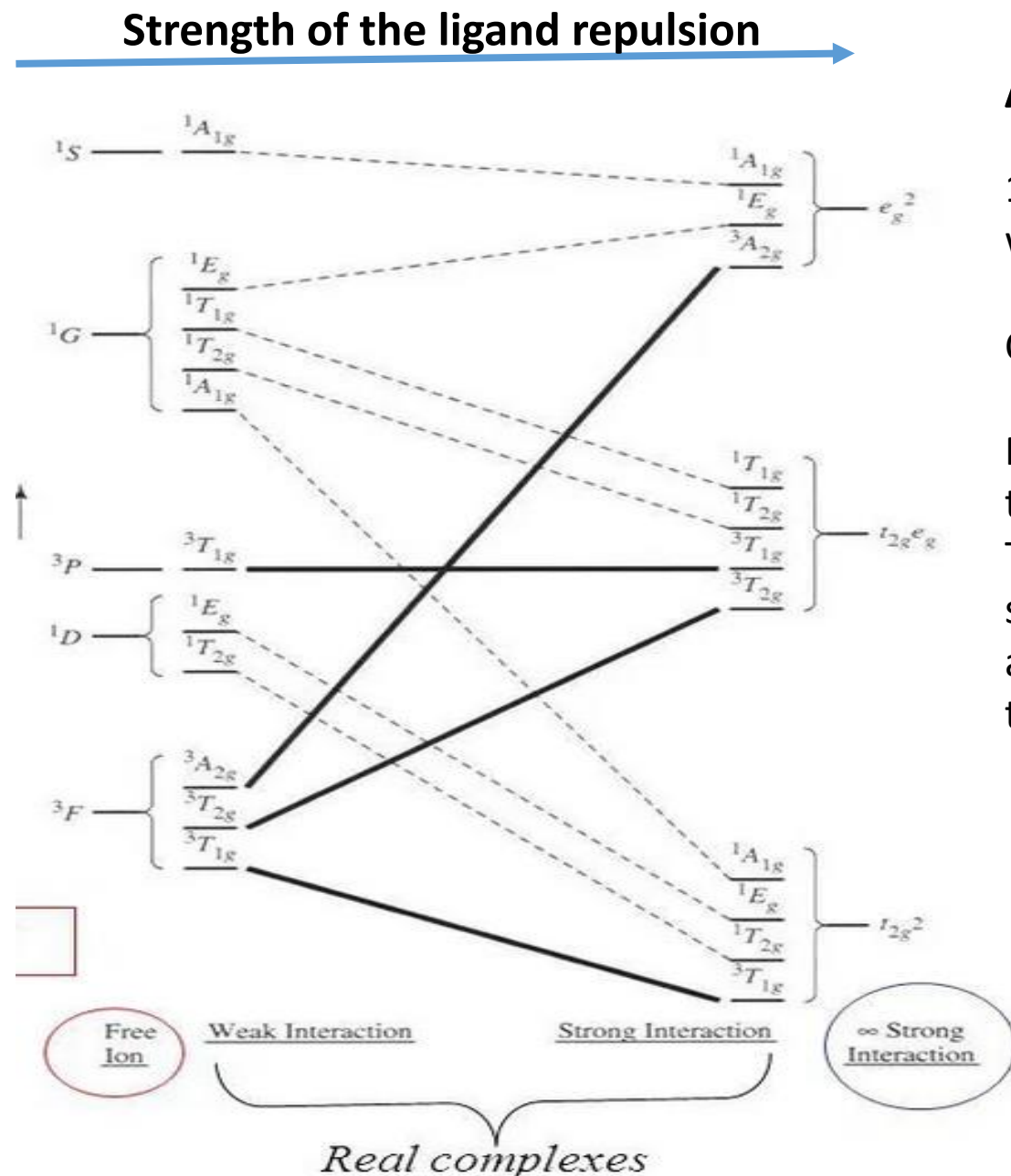
1	$a_{1g} \times b_{1g} = B_{1g}$	triplet $\rightarrow$	${}^3A_{2g}$
2	$a_{1g} \times b_{1g} = B_{1g}$	singlet $\rightarrow$	1E_g
3	$b_{1g} \times b_{1g} = A_{1g}$	singlet $\rightarrow$	1E_g
4	$a_{1g} \times a_{1g} = A_{1g}$	singlet $\rightarrow$	${}^1A_{1g}$

This procedure has told us that the E_g state is a singlet and the A_{2g} state is a triplet. The cases $e_g t_{2g}$ and t_{2g}^2 can be treated in the same way:

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

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

Orgel diagrams: Plot of Energy versus ligand field strength Δ

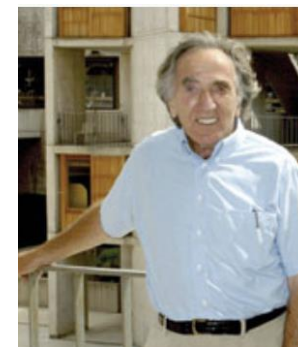


Assembling the Orgel diagram

1:1 Correspondence of weak-field and strong-field states.

Connect state by lines

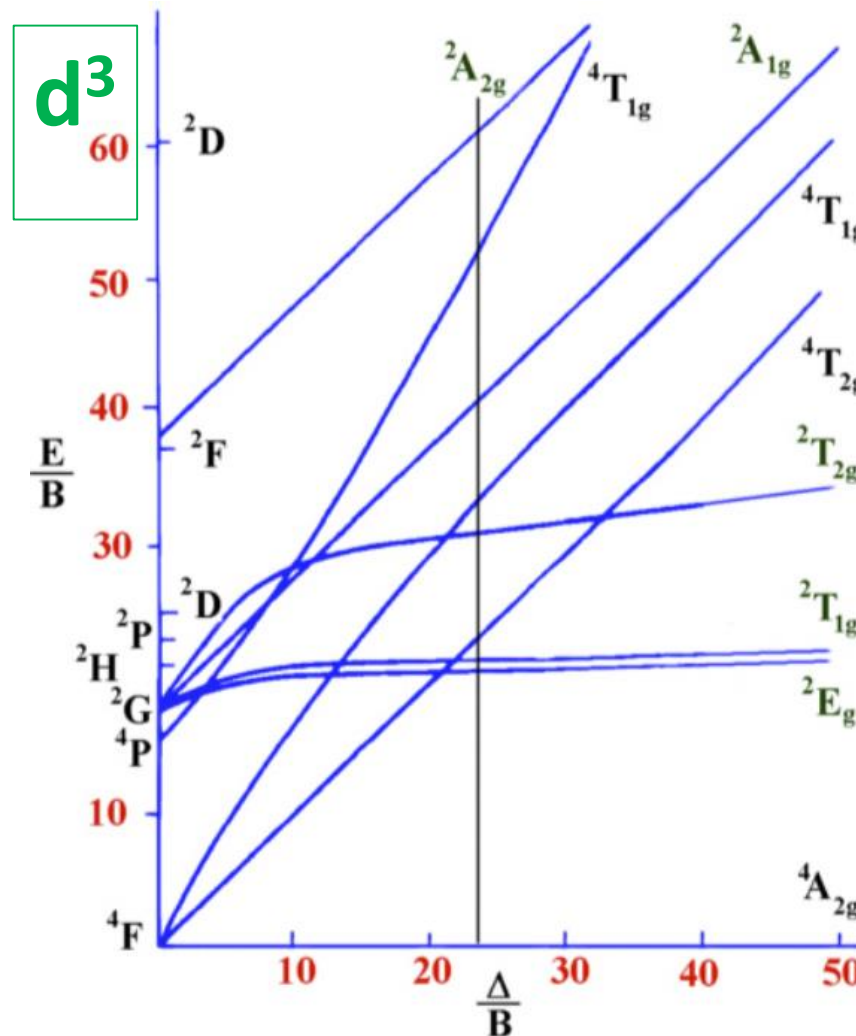
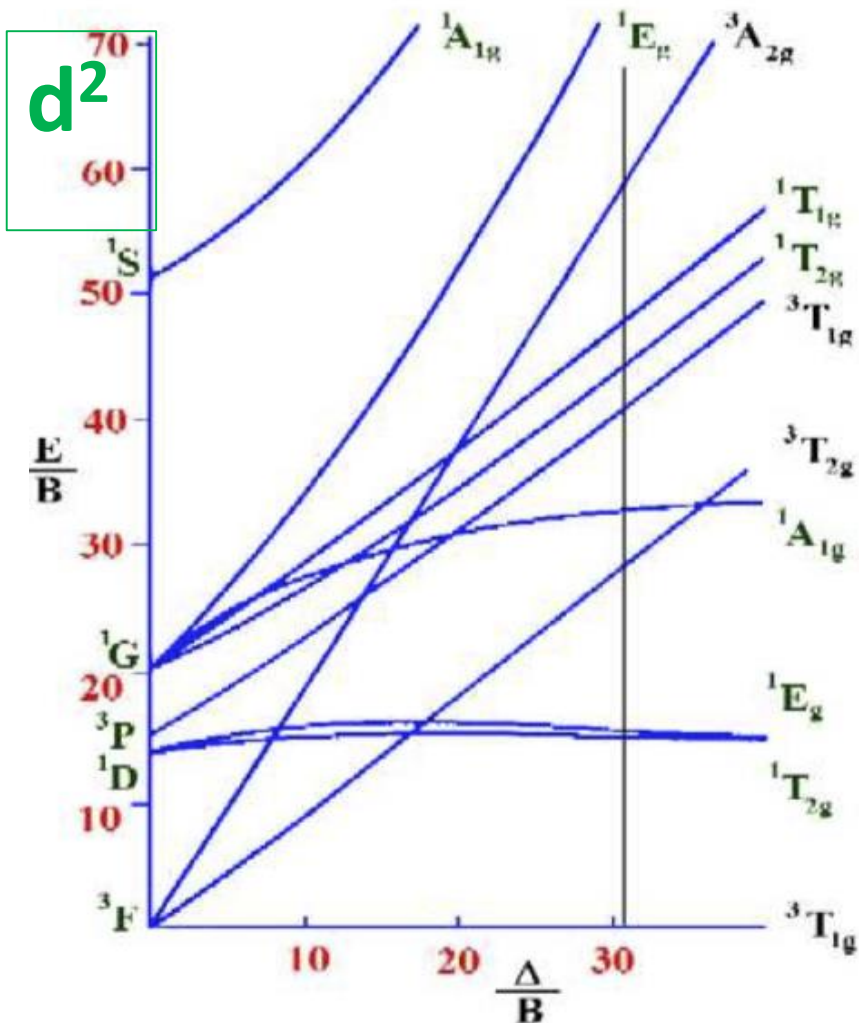
Non-crossing rule for state belonging to the same irreducible representation. They characterize the same relative symmetry of ligands relative to d-orbitals and thus respond to a change in Δ in the same direction.



Leslie Orgel
1927-2007
U. Cambridge,
Salk Inst. San
Diego

Tanabe-Sugano diagrams:

Plot of E/B versus Δ/B , where B = energy of interelectronic repulsion
(Racah parameter) weak field $\rightarrow$ strong field
Abcissa is identical with the energy of the electronic ground state

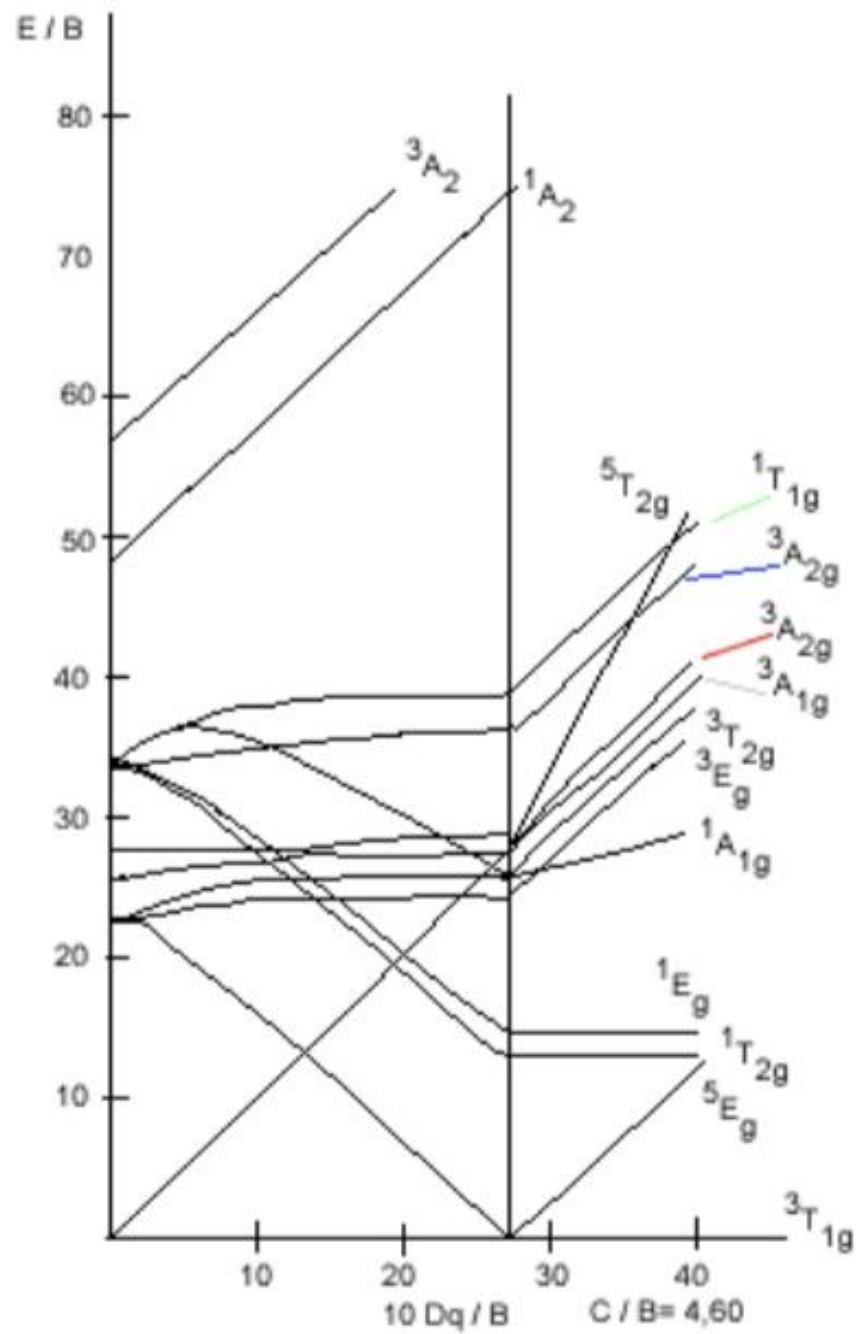


Giulio Racah
1909-1965
Hebrew. U
Jerusalem

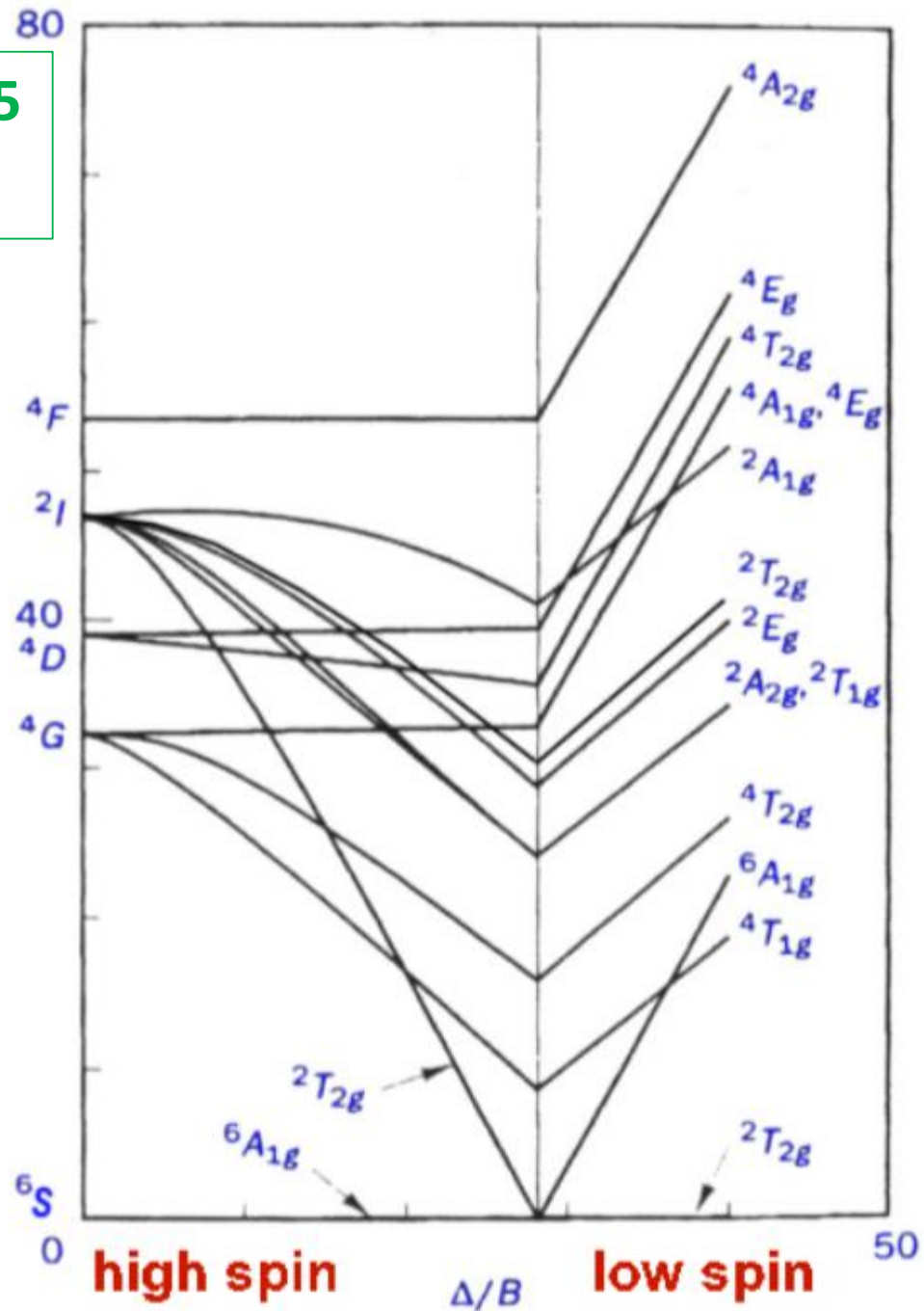


Satoru
Sugane,
1928-
U. Tokyo,
Himeji Inst.

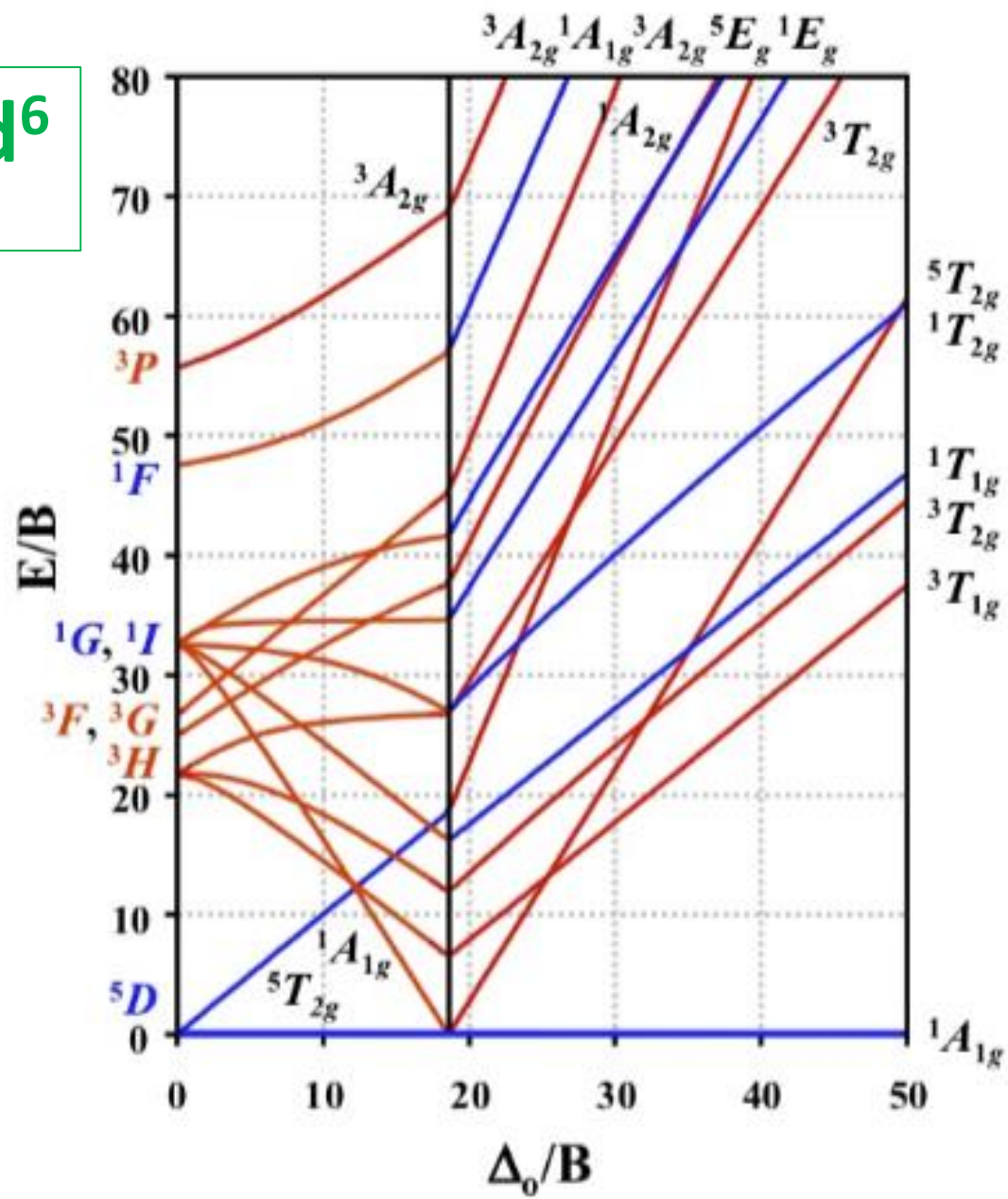
d^4



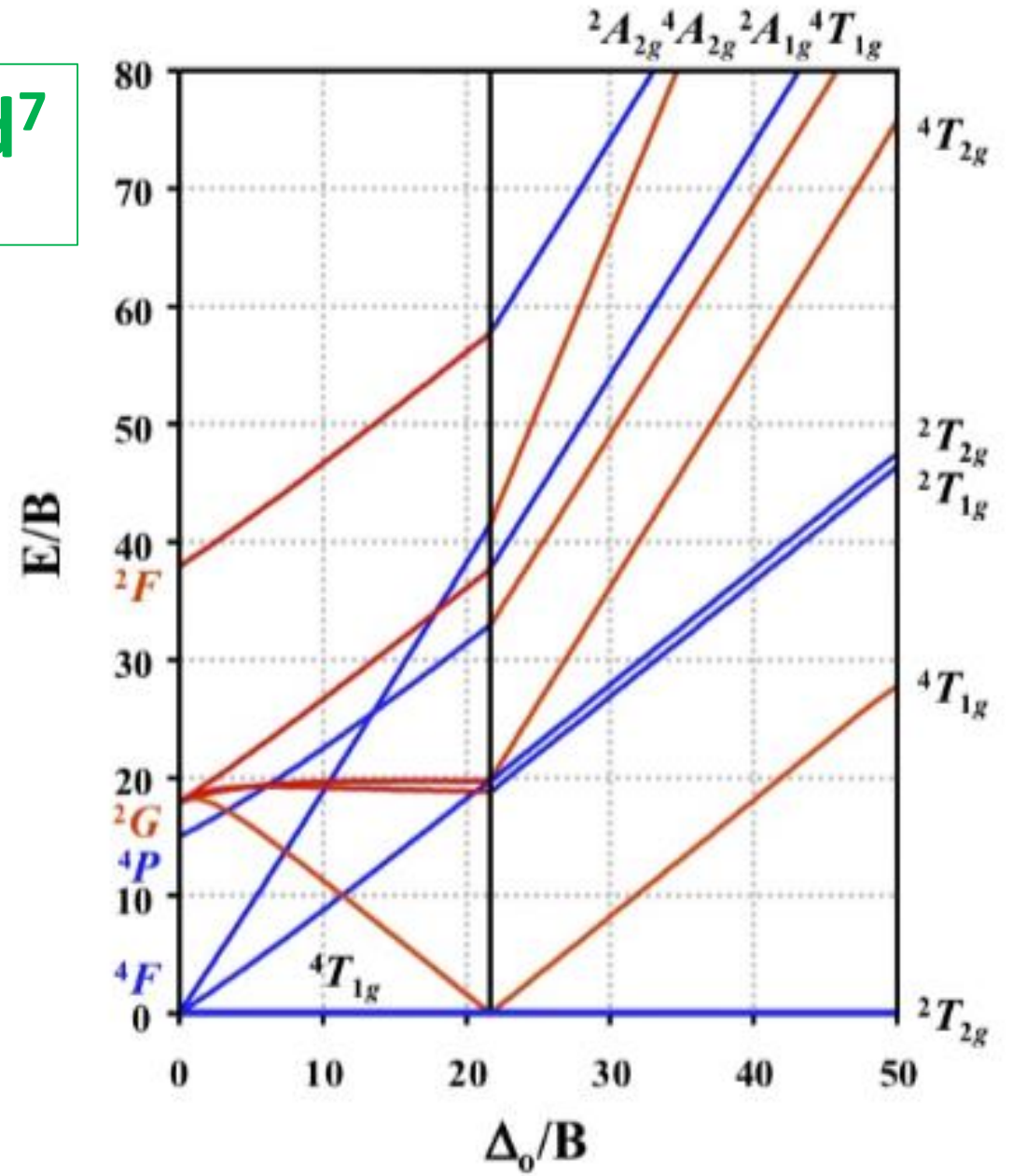
d^5

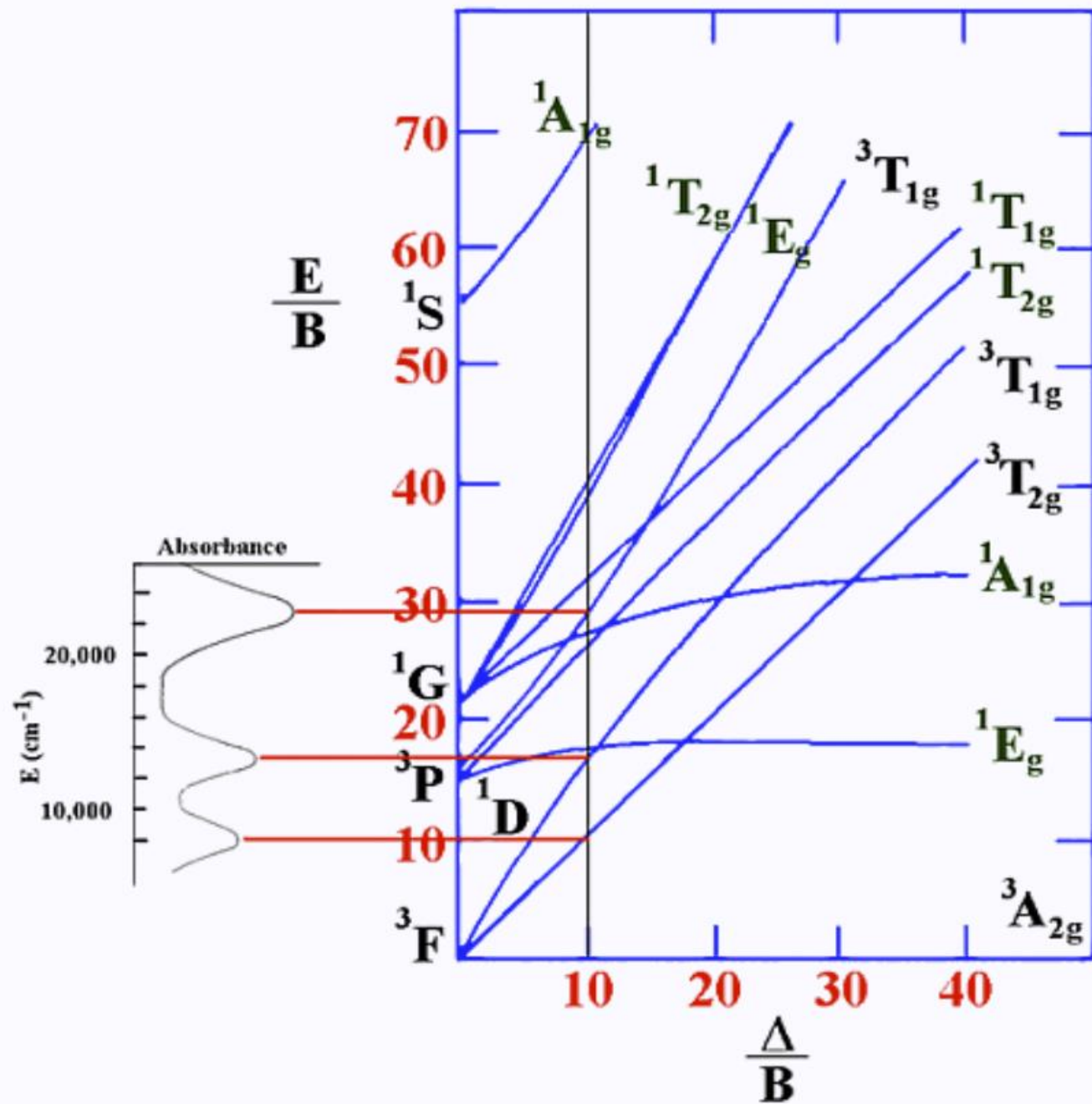


d^6



d^7





Spectroscopic Aspects:

Otto Laporte
1902-1971
U. Michigan



Basis for discussion: The Tanabe-Sugano Diagrams.

1. Only the electronic ground state is populated
2. Spin multiplicity is always conserved upon the transition
3. Selection rules:

These direct products must be analyzed

$$\left. \begin{array}{l} \Gamma_{\psi_g} \otimes \Gamma_x \otimes \Gamma_{\psi_e} \\ \Gamma_{\psi_g} \otimes \Gamma_y \otimes \Gamma_{\psi_e} \\ \Gamma_{\psi_g} \otimes \Gamma_z \otimes \Gamma_{\psi_e} \end{array} \right\}$$

For octahedral complexes x,y,z belong to the representation T_{1u} . While ψ_g and ψ_e always belong to a representation of type g. Transitions are forbidden (Laporte rule). True for all ligand fields with a center of symmetry

$$\text{Transition Moment Integral : } M = \langle \psi_g | \mu | \psi_e \rangle = \langle \psi_g | \mu_n + \mu_e | \psi_e \rangle$$

Wave function for the electronic ground state: $\psi_g = \psi(\text{el})_g \psi(\text{vib})_g = \psi_{sg} \psi(\text{orb})_g \psi(\text{vib})_g$

Wave function for the electronic excited state: $\psi_e = \psi(\text{el})_e \psi(\text{vib})_e = \psi_{se} \psi(\text{orb})_e \psi(\text{vib})_e$

Wave function contains **vibrational**, **orbital** and **spin** parts.

μ_n acts on vibrational part

μ_e acts on orbital part

zero due to orthog.

Franck-Condon factor

$$\begin{aligned} M &= \langle \psi_{sg} \psi(\text{orb})_g | \psi_{se} \psi(\text{orb})_e \rangle \langle \psi(\text{vib})_g | \mu_n | \psi(\text{vib})_e \rangle + \langle \psi(\text{vib})_g | \psi(\text{vib})_e \rangle \langle \psi_{sg} \psi(\text{orb})_g | \mu_e | \psi_{se} \psi(\text{orb})_e \rangle \\ M &= \langle \psi(\text{vib})_g | \psi(\text{vib})_e \rangle \langle \psi_{sg} \psi(\text{orb})_g | \mu_e | \psi_{se} \psi(\text{orb})_e \rangle = \langle \psi(\text{vib})_g | \psi(\text{vib})_e \rangle \langle \psi_{sg} | \psi_{se} \rangle \langle \psi(\text{orb})_g | \mu_e | \psi(\text{orb})_e \rangle \end{aligned}$$

$\langle \psi_{sg} | \psi_{se} \rangle = 0$ if the spin wave functions of ground and excited state are different. $\rightarrow$ spin multiplicity is conserved

$\langle \psi(\text{orb})_g | \mu_e | \psi(\text{orb})_e \rangle$ subject to orbital selection rule (group theory)

$\langle \psi(\text{vib})_g | \psi(\text{vib})_e \rangle$ non-zero because they refer to different electronic states.

Vibronic Coupling

Relaxation of the Laporte rule due to vibrational modes that break the inversion center. (vibronic coupling).
We can see this when we consider the vibrational part of the complete wavefunction

$$\begin{array}{l} \Gamma_{\psi_g} \otimes \Gamma_x \otimes \Gamma_{\psi_e} \\ \Gamma_{\psi_g} \otimes \Gamma_y \otimes \Gamma_{\psi_e} \\ \Gamma_{\psi_g} \otimes \Gamma_z \otimes \Gamma_{\psi_e} \end{array}$$

Wave function for the electronic **ground state**: $\psi_g = \psi(\text{el})_g \psi(\text{vib})_g$

Wave function for the electronic **excited state**: $\psi_e = \psi(\text{el})_e \psi(\text{vib})_e$

The transition moment Integral is given by:

$$M = \langle \psi_g | \mu | \psi_e \rangle = \langle \psi(\text{el})_g \psi(\text{vib})_g | \mu | \psi(\text{el})_e \psi(\text{vib})_e \rangle$$

Thus we must consider the 5-factor direct products of the type:

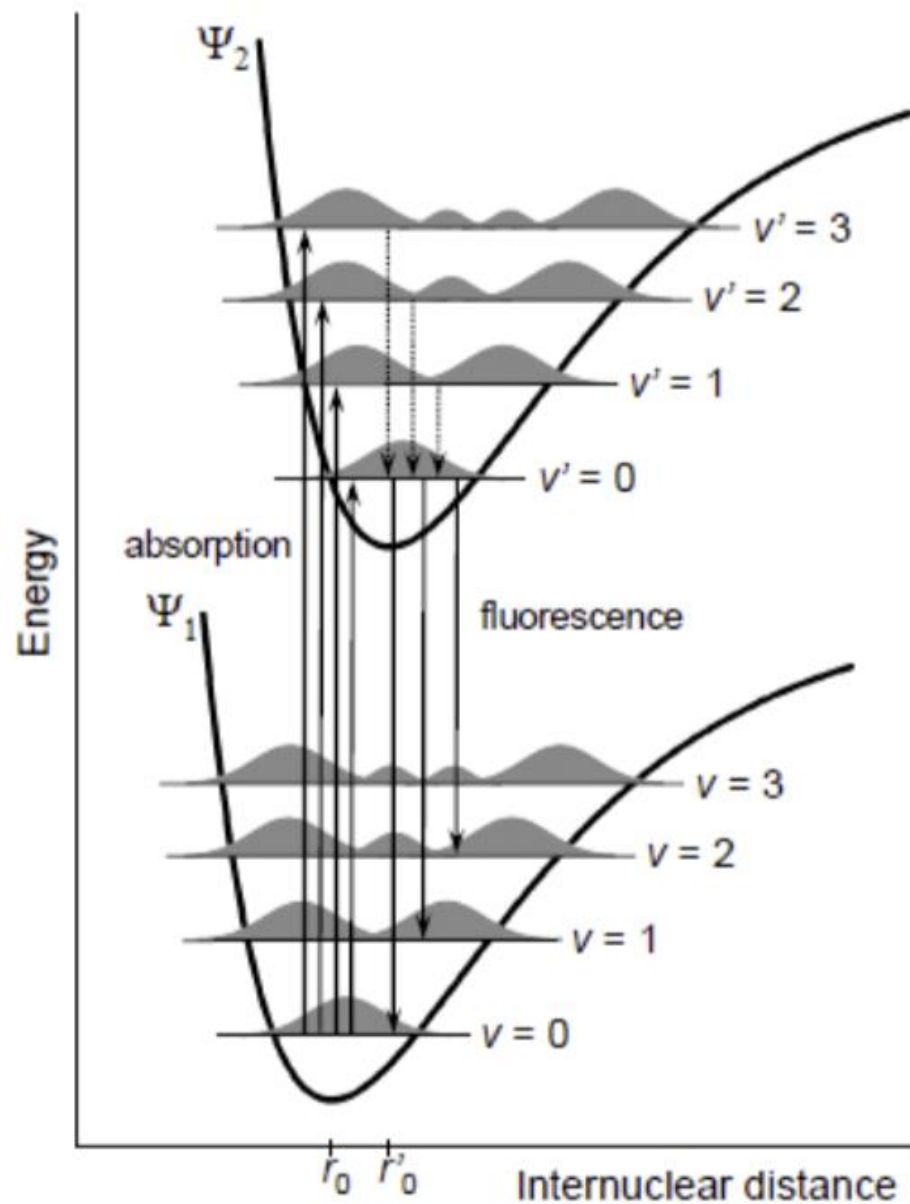
$$\Gamma_{\psi(\text{vib})g} \otimes \Gamma_{\psi(\text{el})g} \otimes \Gamma_{x,y,z} \otimes \Gamma_{\psi(\text{vib})e} \otimes \Gamma_{\psi(\text{el})e}$$

Where $\Gamma_{\psi(\text{vib})g} = A_1$ (vibrational ground state of the ground state electronic wave function)

If the electronic transition results in the population of the first excited vibrational level of the excited electronic State, $\Gamma_{\psi(\text{vib})e}$ is the same as the irreducible representation of the mode itself.

The Laporte rule is relaxed because the electronic transition (which normally occurs from the vibrational ground level) is accompanied by vibrational transitions.

The reason for having the vibrational wave function of the electronic excited state represented by the one representing the vibrational mode itself lies in the fact that owing to the Franck Condon principle, a substantial fraction of the molecules end up in a vibrationally excited state with $n=1$ (or 3, etc)



1. Optical transition is much faster than vibrational motion
2. Internuclear distance in the optical excited state is larger than in the ground state



1. Upon electronic excitation the molecule ends up in various excited vibrational states.
2. Due to this fact, vibronic coupling is possible, relaxing the Laporte rule

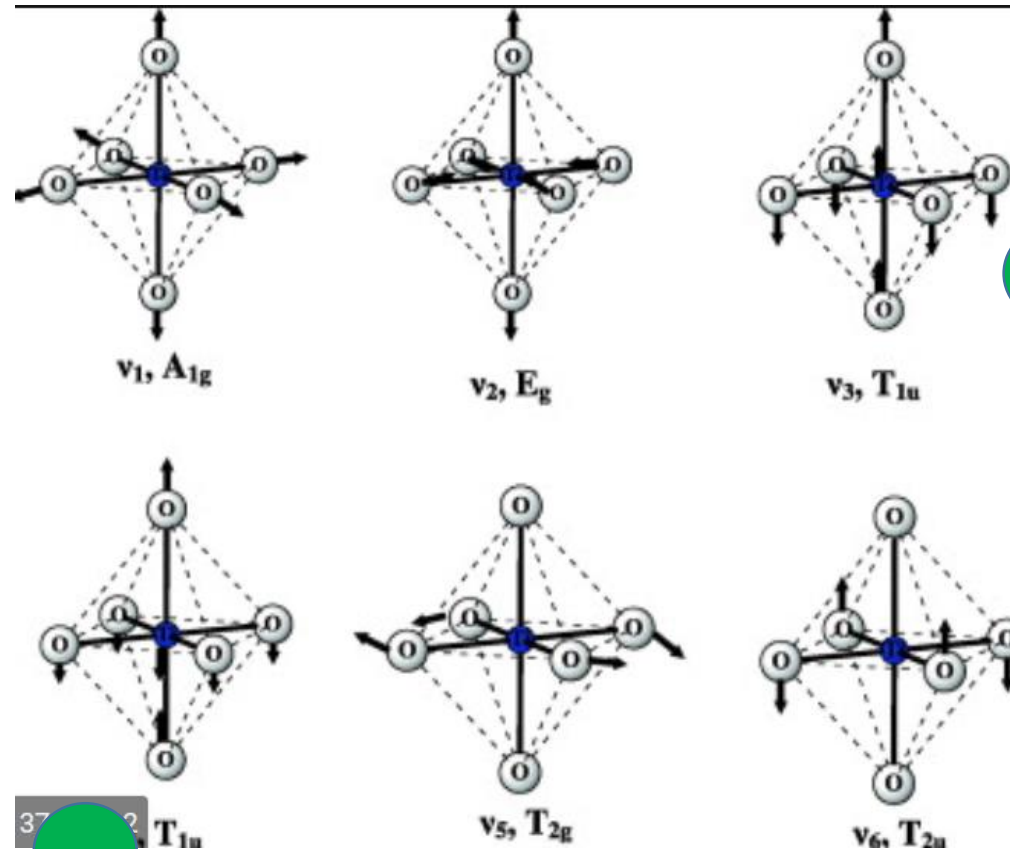


James Franck
1882-1964
U. Göttingen,
Johns Hopkins U.
U. Chicago,
Nobel Prize 1925



Edward Condon
1902-1974
US Government,
Washington U.,
U. Colorado, Boulder

To relax the Laporte rule, the vibrations have to be of type u



Electronic transitions are much faster than the vibrational motion. From the viewpoint of electronic spectroscopy the sample is a collection of molecules in different stages of vibrational motion. If the vibrational analysis produces normal modes of type u (it always does), the Laporte rule is relaxed, because the sample always contains molecules whose center of symmetry is broken by the vibrational motion.

Spectroscopic observables:

- 1) Frequency $\rightarrow \Delta$ (nature of the ligand/spectrochemical series)
 - 2) Linewidth $\rightarrow$ transition
- Assignments/unresolved splittings
- 3) Peak splittings $\rightarrow$ J.T. effects

Range of transition energies = width of the spectrum

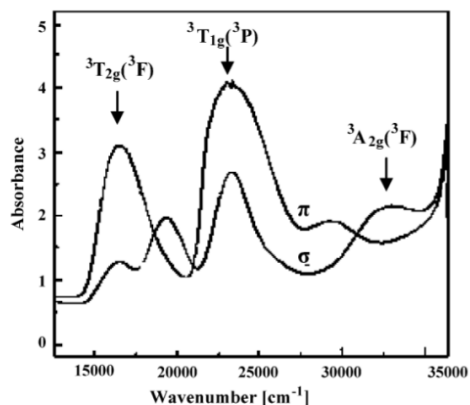
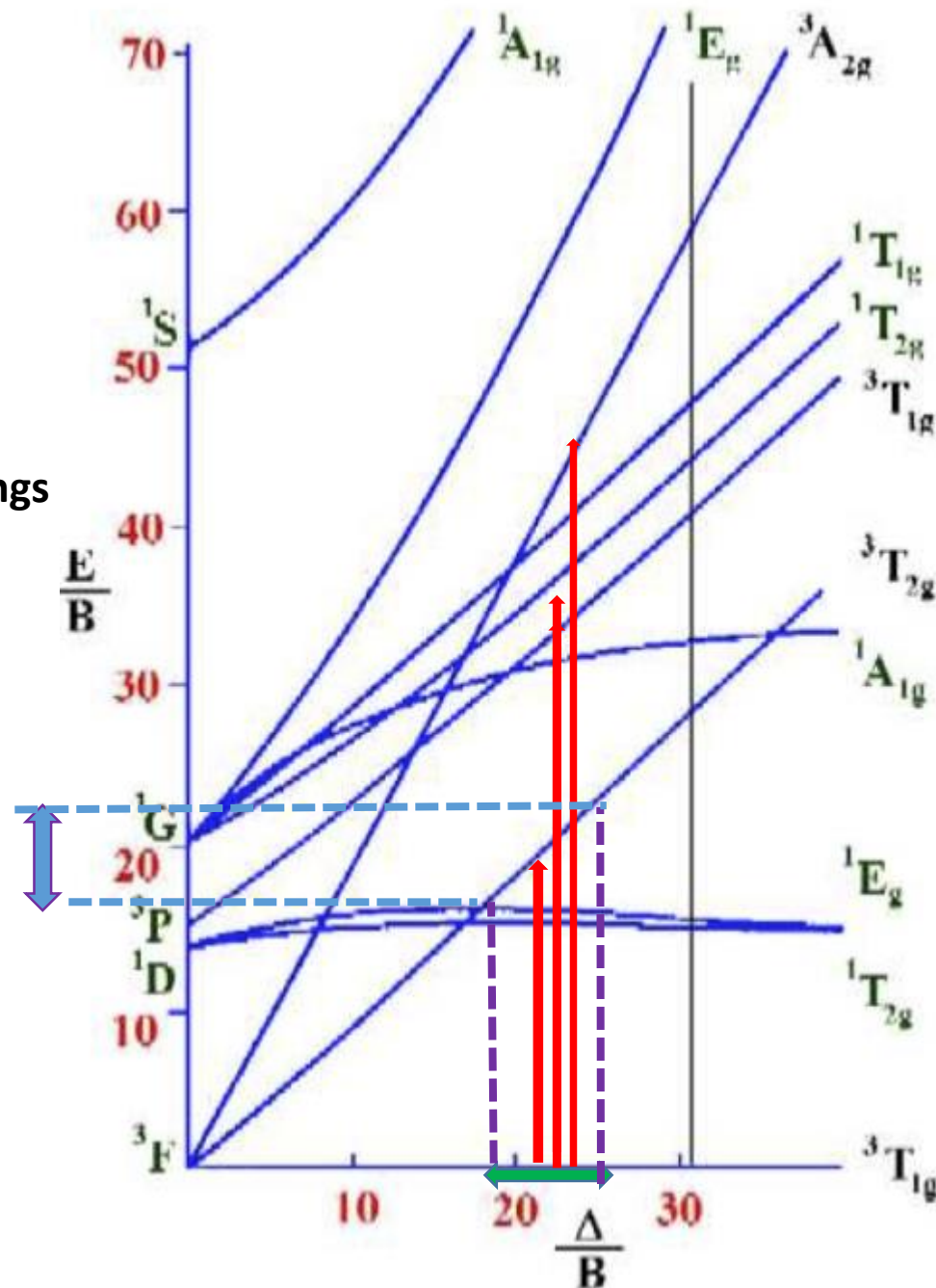


Fig. 1. Polarized absorption spectra of $\text{Cs}_3\text{VCl}_2(\text{H}_2\text{O})_4$ at 80 K [9].



Spectrum for d^2 ions in an octahedral ligand field



Distribution of ligand fields due to molecules in different stages of vibration



Linewidths of the transitions
~ inclination in the TS-diagram

$3T_{1g} \rightarrow 3A_{2g}$ very broad,
often not observed

A walk through the first transition metal series

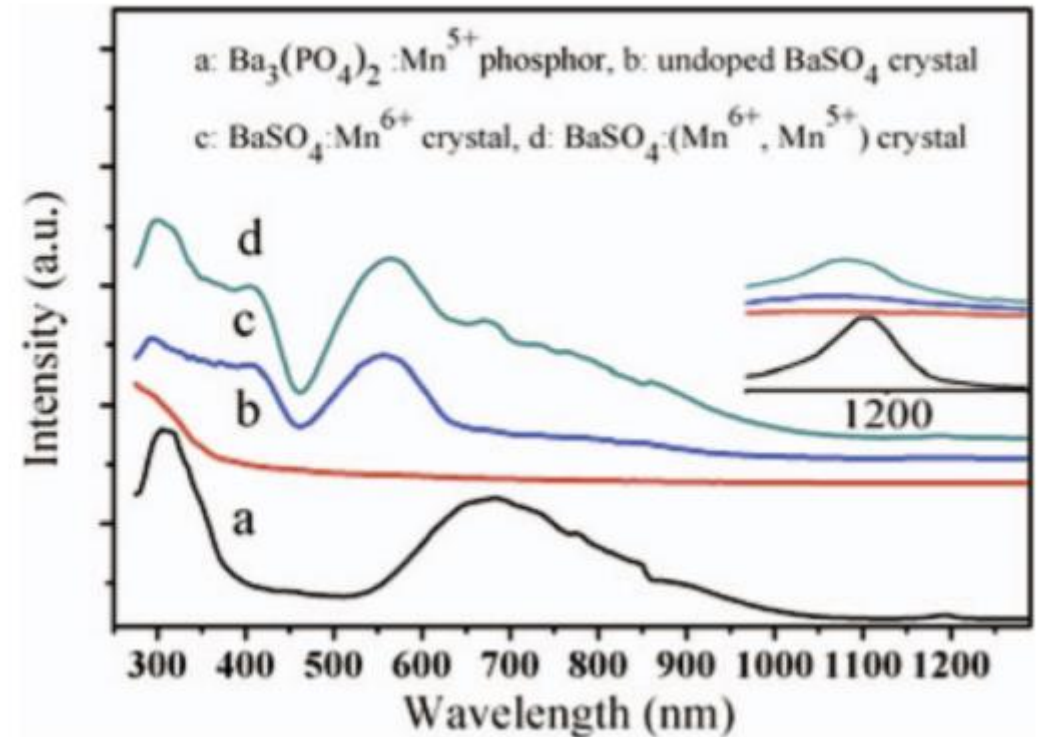
d¹

Ti³⁺ V⁴⁺ Cr⁵⁺ Mn⁶⁺

${}^2T_{2g} \rightarrow {}^2E_g$ octahedral

${}^2E \rightarrow {}^2T_2$ tetrahedral

Jahn-Teller distortions will always occur,
Strongly distorted V⁴⁺: „vanadyl“ VO²⁺
 Δ increases with increasing charge of the
central ion:



d² | **Ti²⁺ V³⁺ Cr⁴⁺ Mn⁵⁺**

$${}^3T_{1g} \rightarrow {}^3T_{2g}$$
$${}^3T_{1g} \rightarrow {}^3T_{1g}$$
$${}^3T_{1g} \rightarrow {}^3A_{2g}$$

Range of transition energies = width of the spectrum

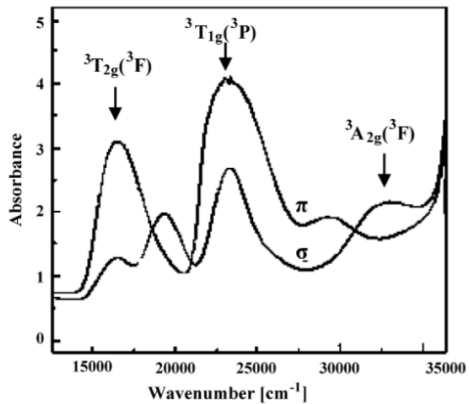
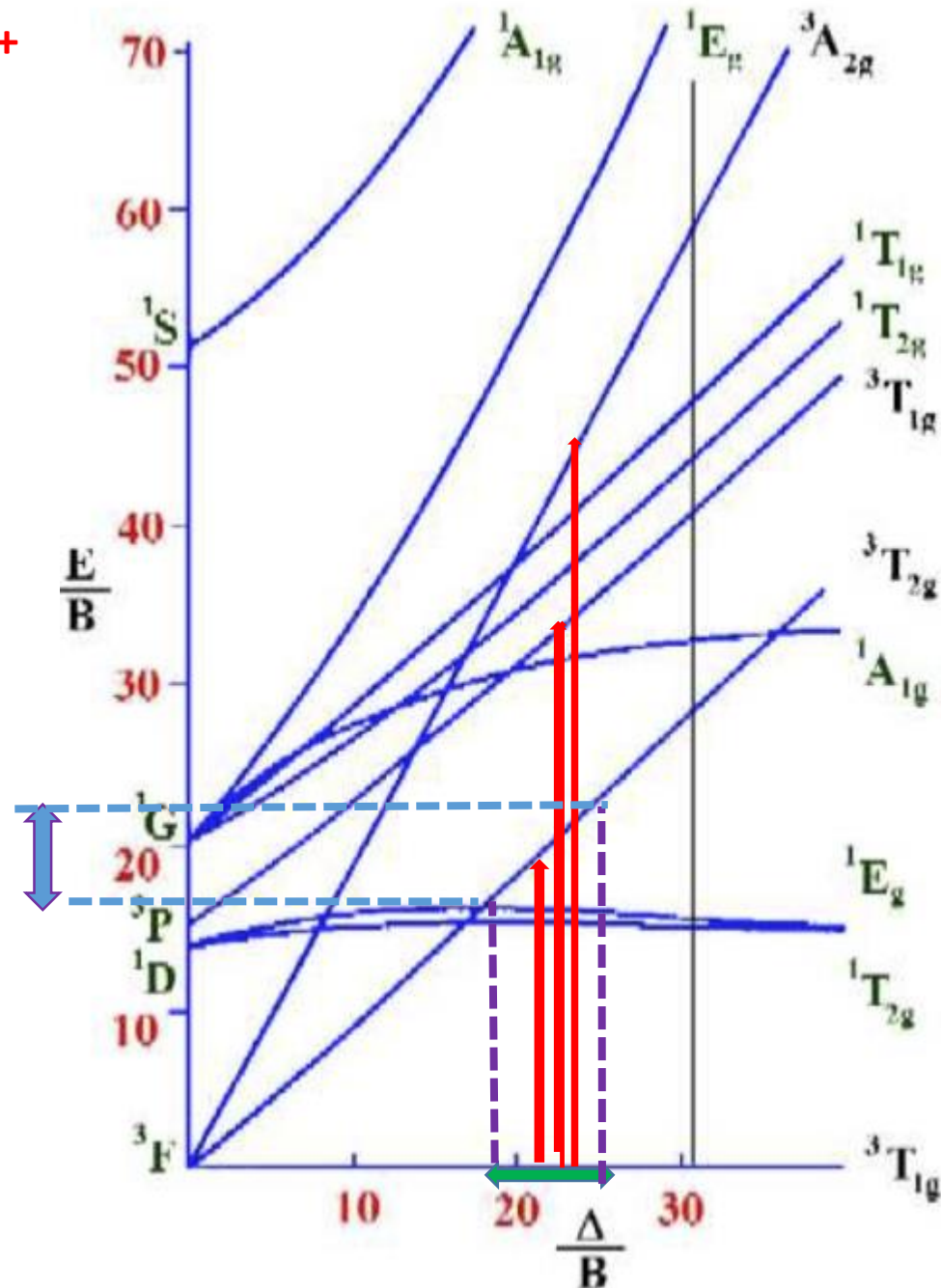


Fig. 1. Polarized absorption spectra of $\text{Cs}_3\text{VCl}_2(\text{H}_2\text{O})_4$ at 80 K [9].



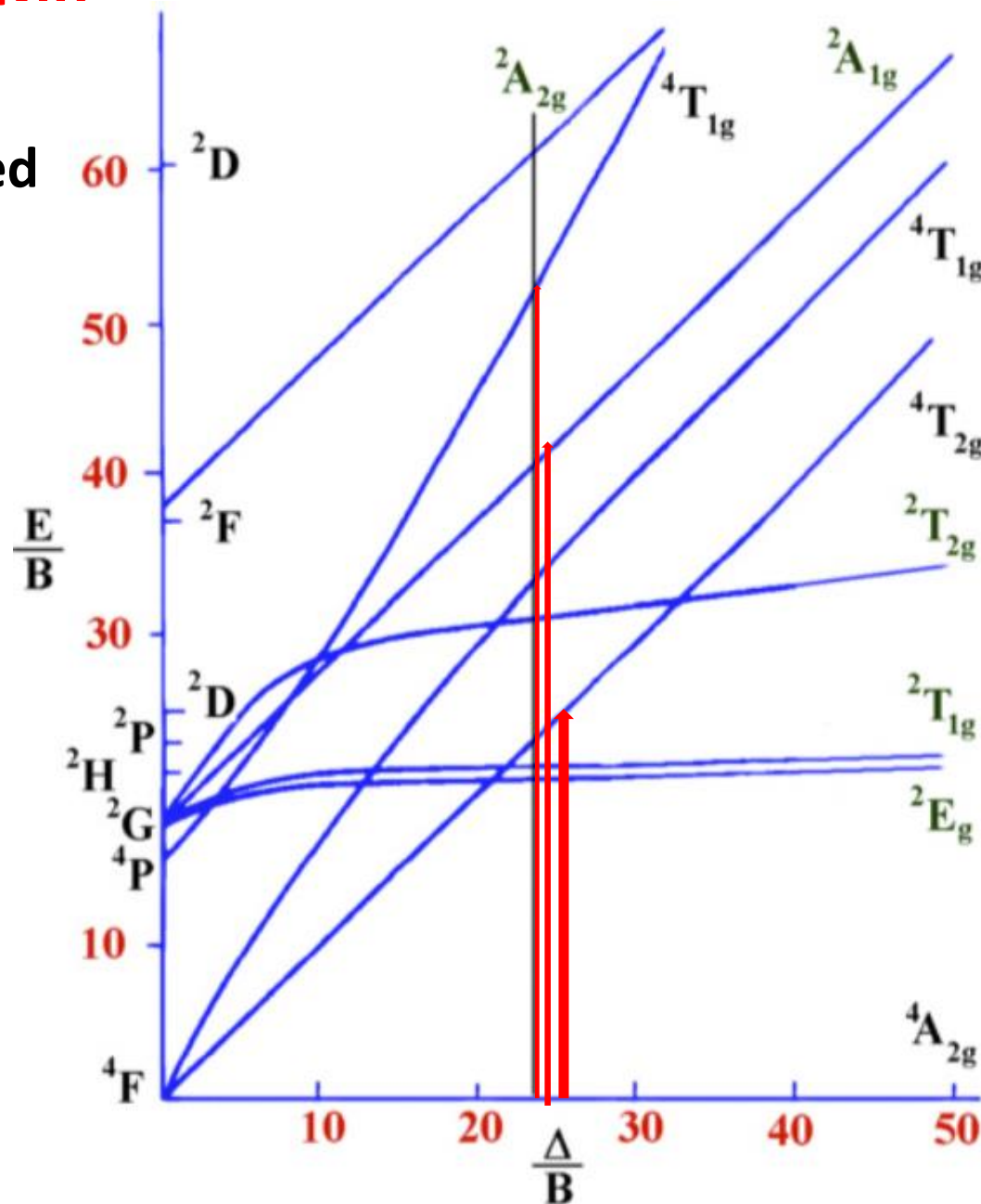
 Distribution of ligand fields due to molecules in different stages of vibration

 Linewidths of the transitions
~ inclination in the TS-diagram

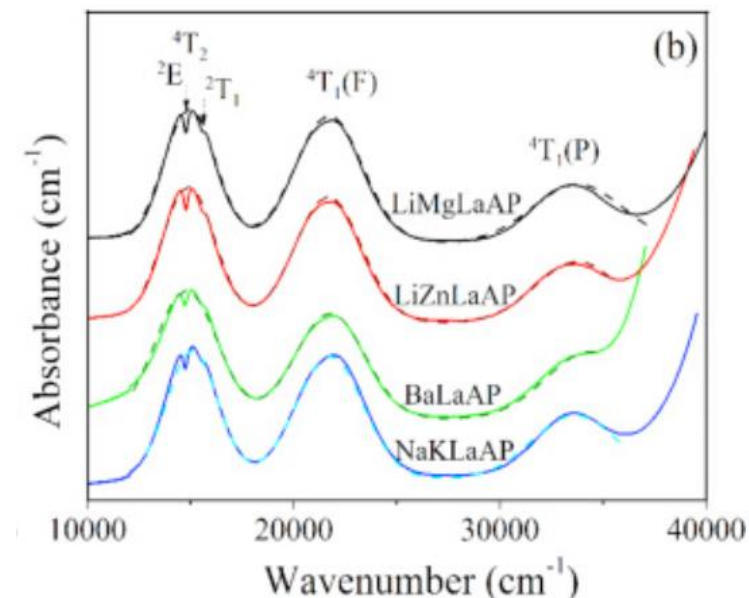
${}^3T_{1g} \rightarrow {}^3A_{2g}$ very broad,
often not observed

d^3 $V^{2+} Cr^{3+} Mn^{4+}$

Octahedral LF:
strongly preferred
No J-T distortion

 ${}^4A_{2g} \rightarrow {}^4T_{2g}$ ${}^4A_{2g} \rightarrow {}^4T_{1g}$ ${}^4A_{2g} \rightarrow {}^4T_{1g}$ 

Cr^{3+} absorption in phosphate glasses



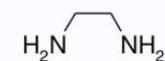
- Spectrochemical Series: An order of ligand field strength based on experiment:**

Weak Field $I^- < Br^- < S^{2-} < SCN^- < Cl^-$

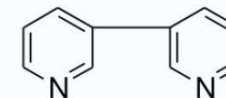
$NO_3^- < F^- < C_2O_4^{2-} < H_2O < NCS^-$

$CH_3CN < NH_3 < en < bipy < phen$

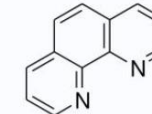
$NO_2^- < PPh_3 < CN^- < CO$ **Strong Field**



Ethylenediamine (en)



2,2'-bipyridine (bipy)

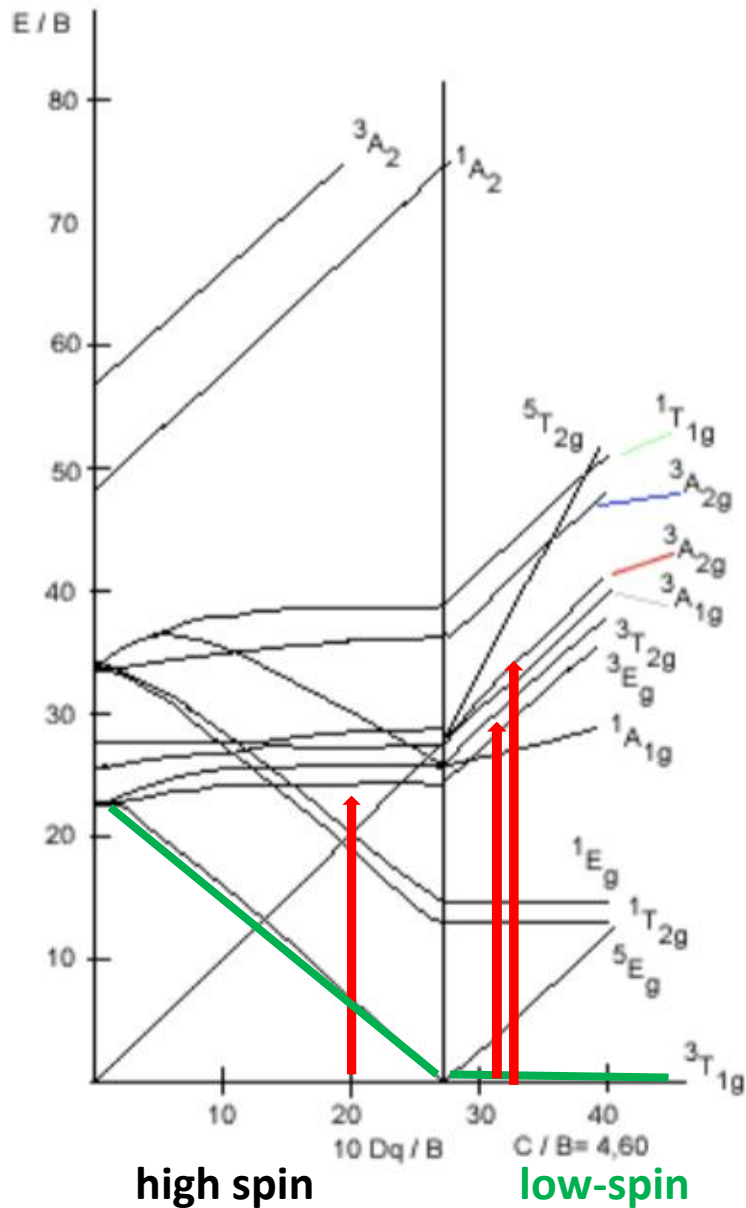


1.10 - phenanthroline (phen)

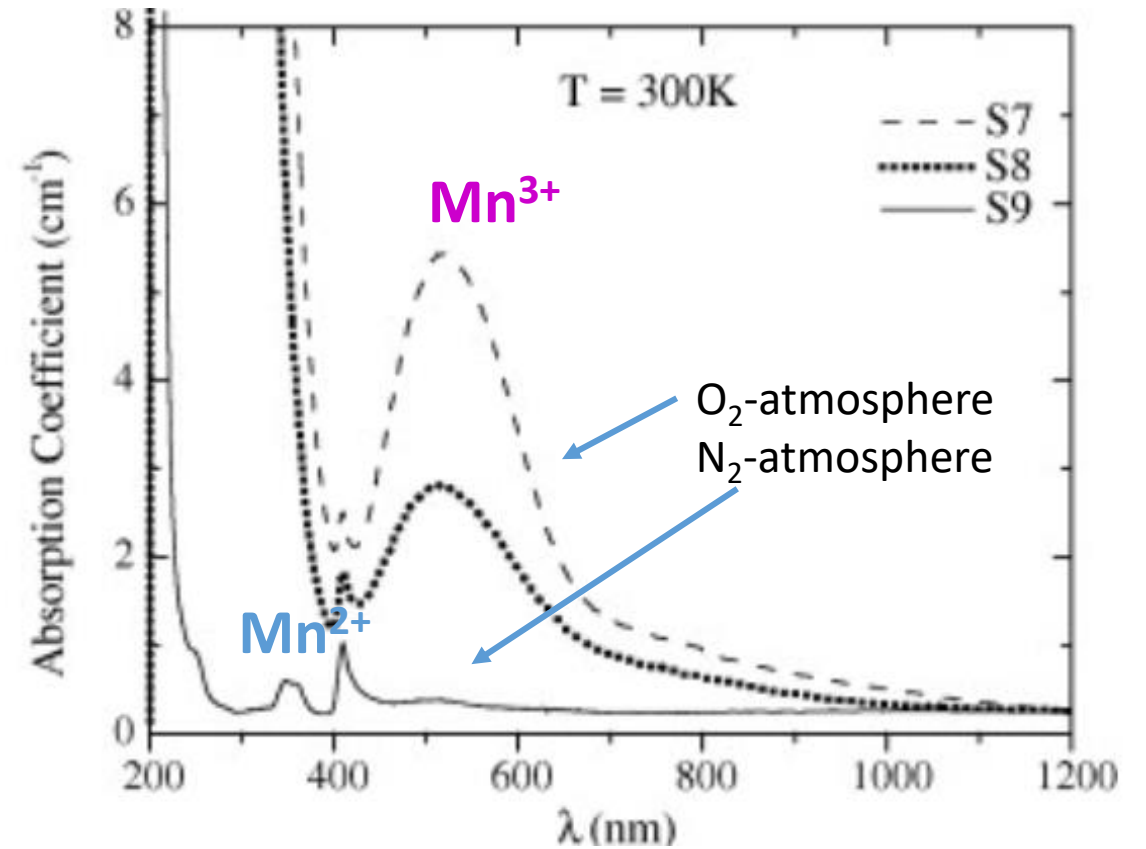
d^4

$\text{Cr}^{2+} \text{ Mn}^{3+}$

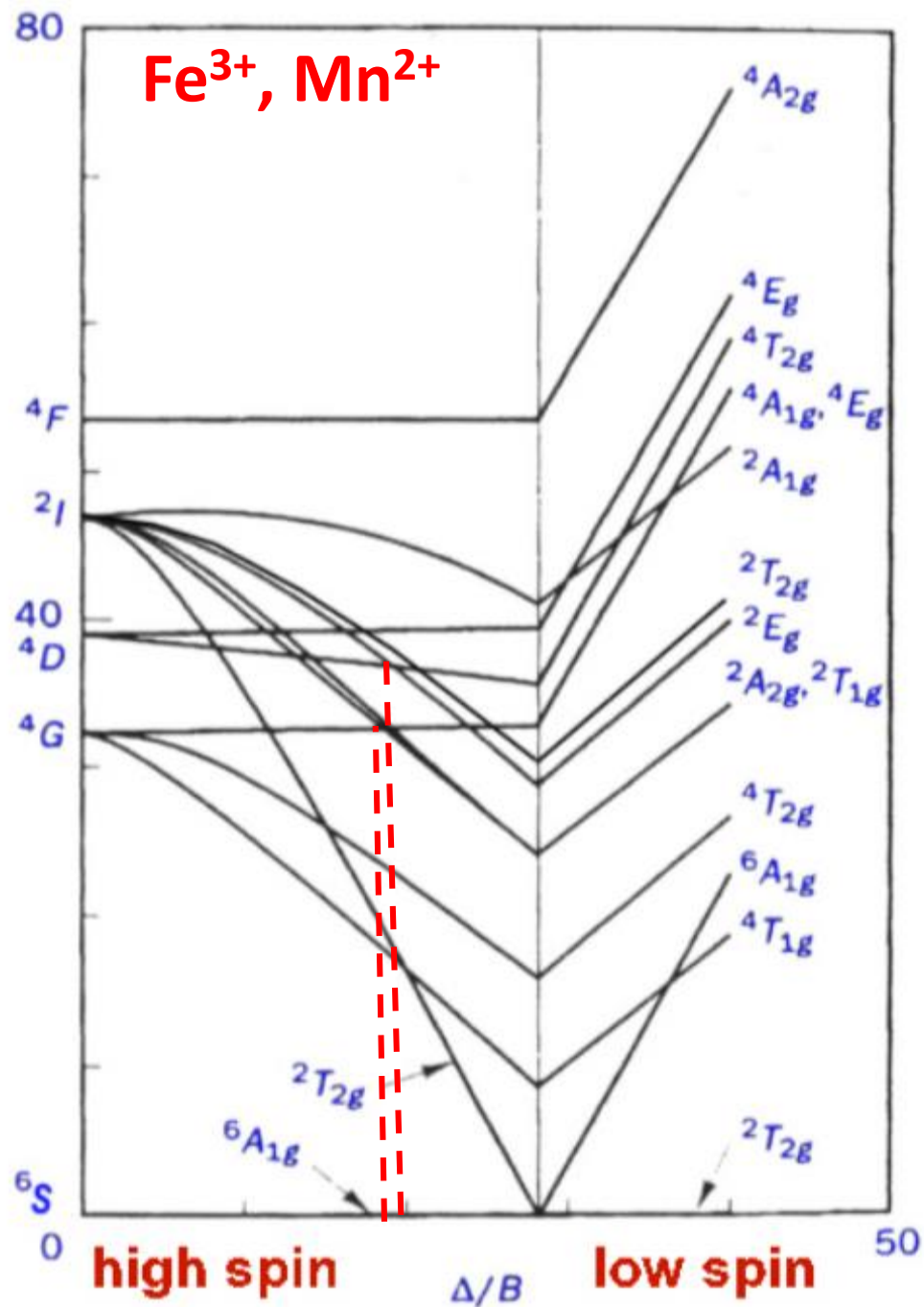
${}^5E_g \rightarrow {}^5T_{2g}$
J-T distortion



Absorption spectrum of Mn-containing phosphate glass



d^5



High-spin ground state $6A_{1g}$:
No spin-allowed transitions
Weak forbidden transitions
 Mn^{2+} complexes are colorless

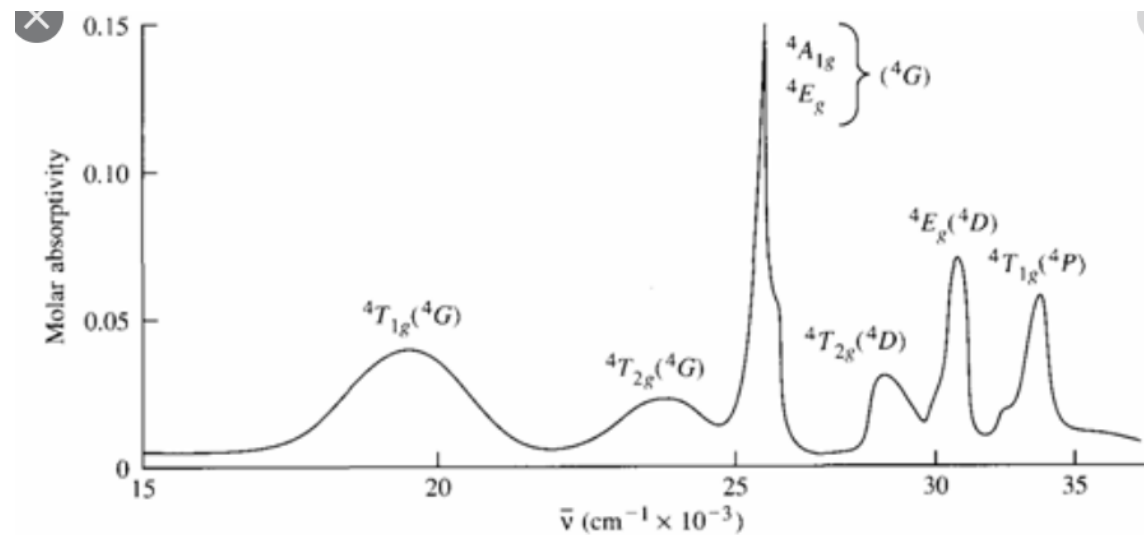
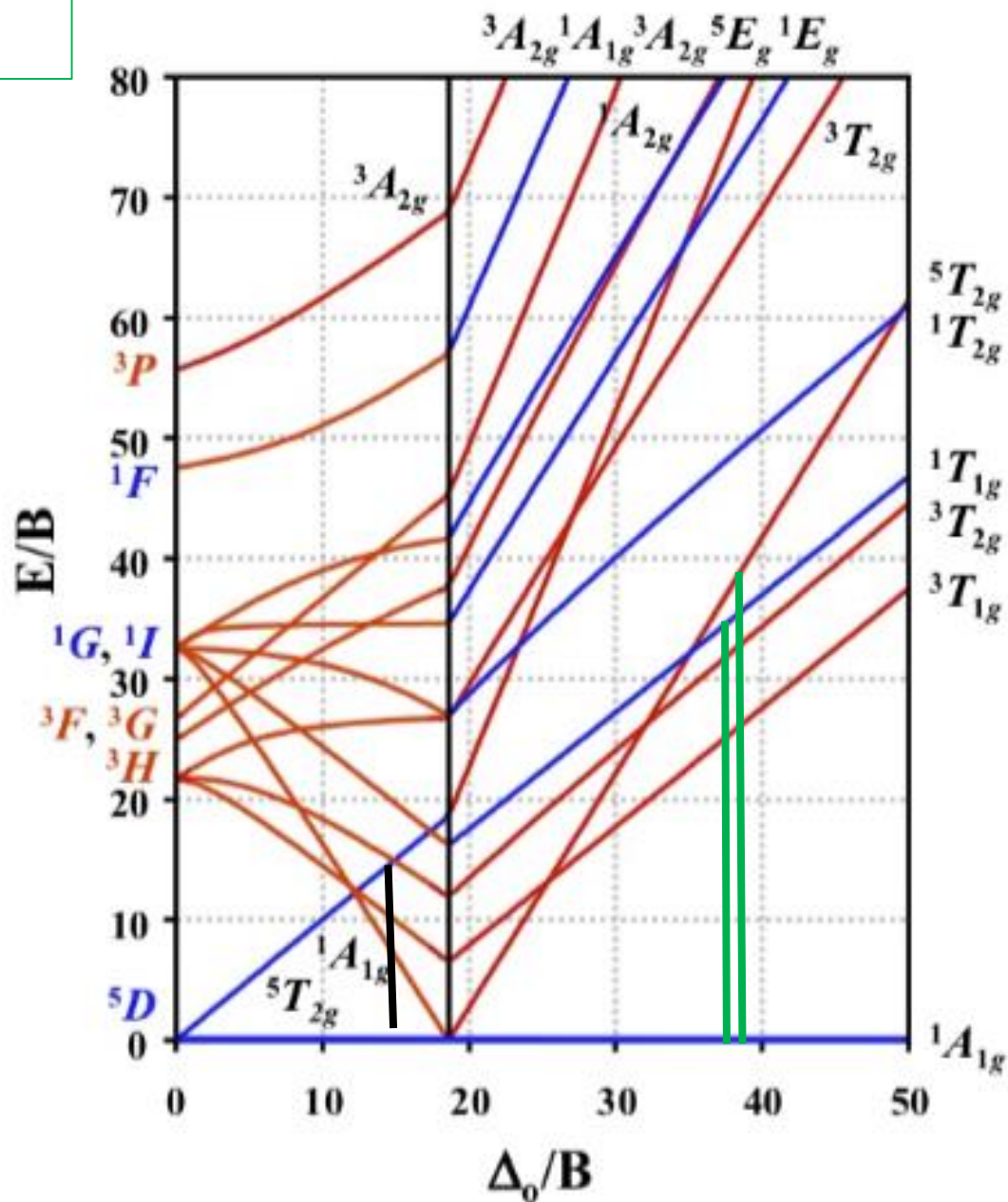


Fig. 11.41 Absorption spectrum for octahedral MnF_2 . Note the narrow lines. [From Lever, A. B. P. *Inorganic Electronic Spectroscopy*; 2nd ed.; Elsevier: New York, 1986; p 451. Used with permission.]

d^6

$\text{Fe}^{2+}, \text{Co}^{3+}$



High-spin: $^5T_{2g} \rightarrow ^5E_g$

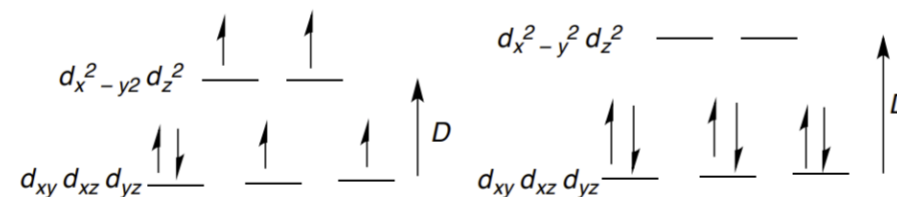
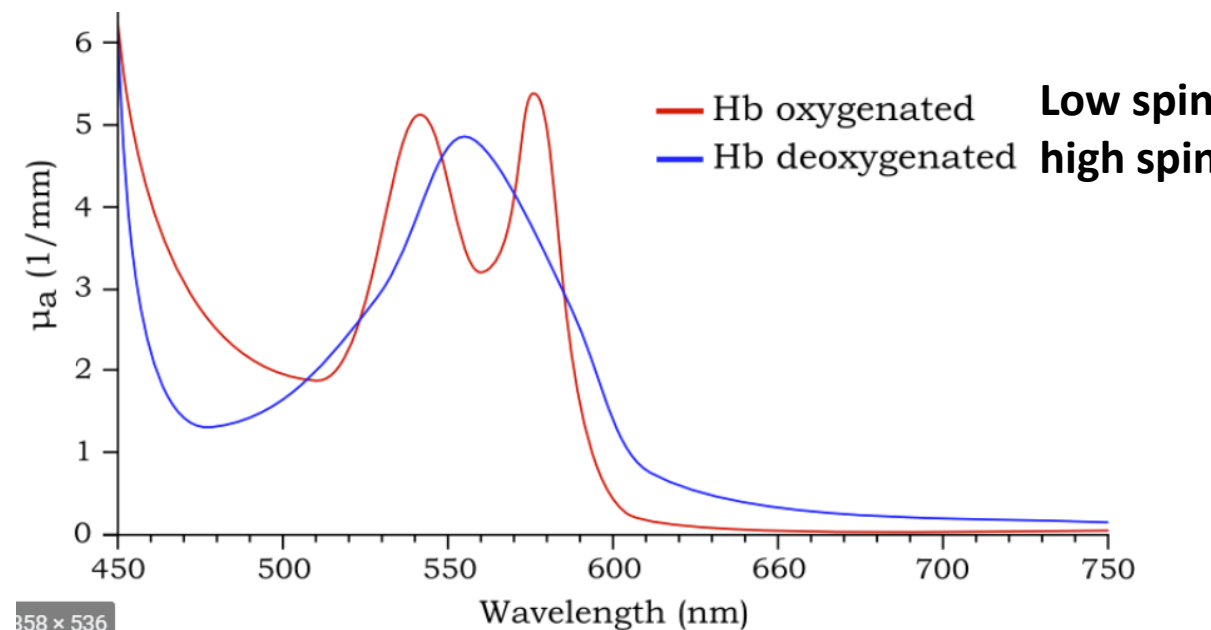
Low-spin: $^1A_{1g} \rightarrow ^1T_{1g}$

$^1A_{1g} \rightarrow ^1T_{2g}$

J-T effect

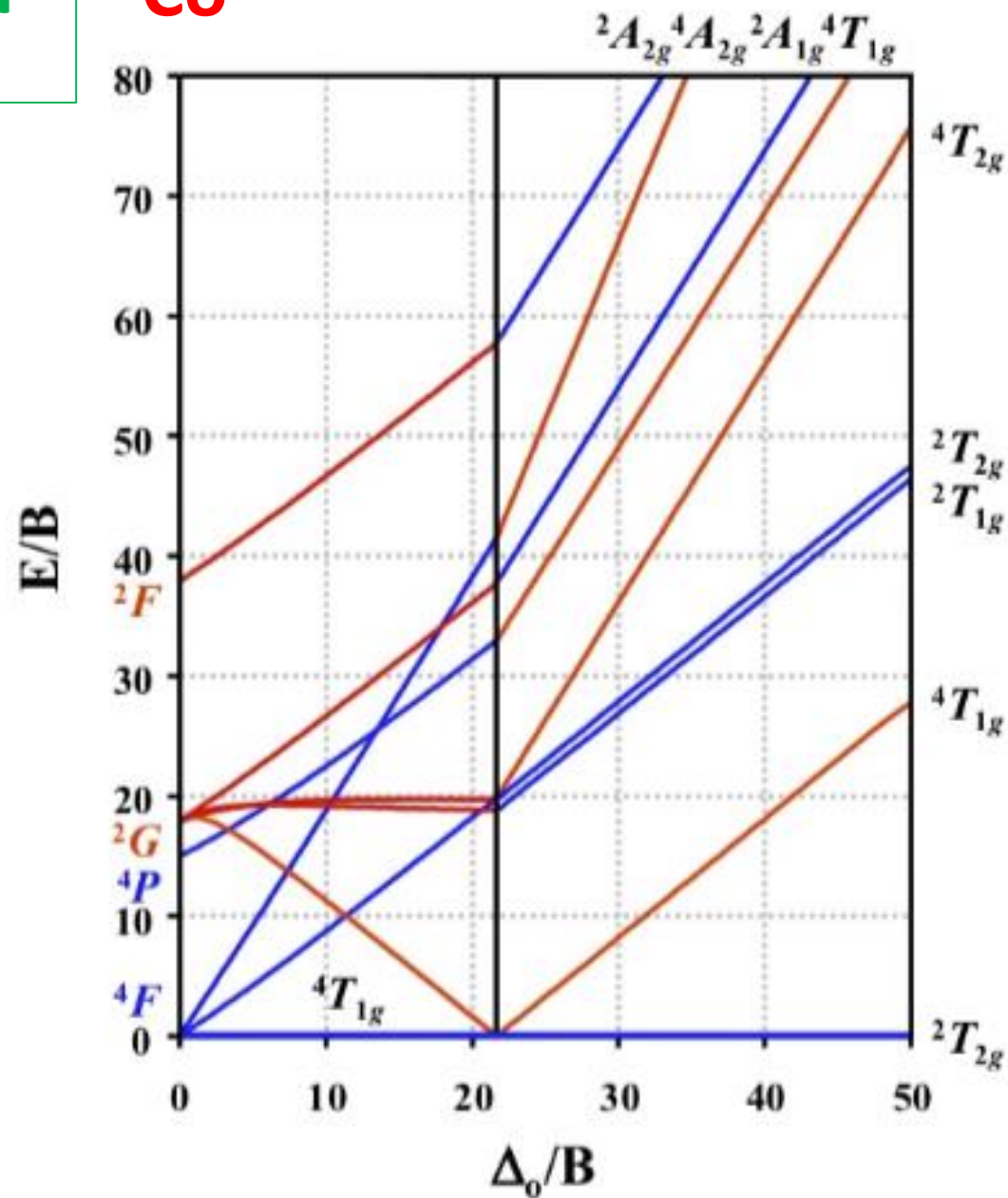
No J-T effect

Spin Transition in hemoglobin upon binding to O₂



d^7

Co^{2+}



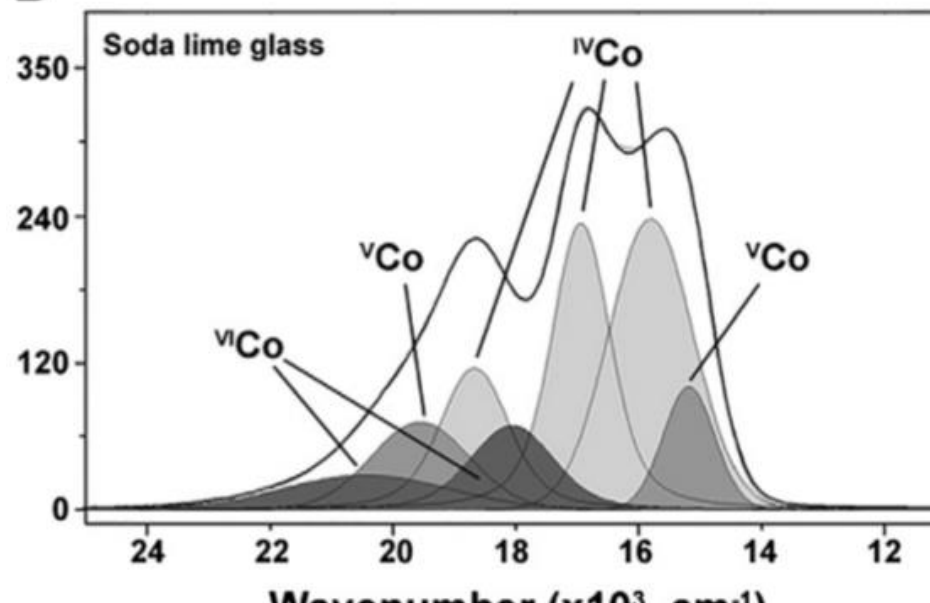
Co^{2+} in glasses: metal in tetrahedral and octahedral Coordination. Tetrahedral coordination gives rise to Intense blue color of Co in glasses.

TABLE 1

Optical transitions of Co^{2+} in tetrahedral (T_d) and octahedral (O_h) coordination.

Transition					Range (nm)
T_d	ν_1	$^4A_2(F)$	$\longrightarrow$	$^4T_2(F)$	1700–4000
	ν_2	$^4A_2(F)$	$\longrightarrow$	$^4T_1(^4F)$	1200–1800
	ν_3	$^4A_2(F)$	$\longrightarrow$	$^4T_1(^4P)$	540–640
O_h	ν_1	$^4T_{1g}(F)$	$\longrightarrow$	$^4T_{2g}(F)$	1333
	ν_2	$^4T_{1g}(F)$	$\longrightarrow$	$^4A_{2g}(F)$	606
	ν_3	$^4T_{1g}(F)$	$\longrightarrow$	$^4T_{1g}(P)$	555, 476–500

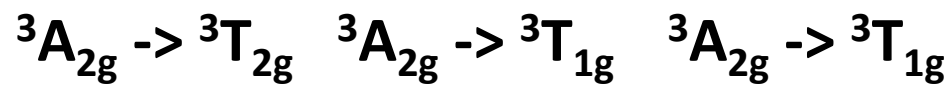
B



d^8

Ni^{2+}

Octahedral LF:



No J-T distortions

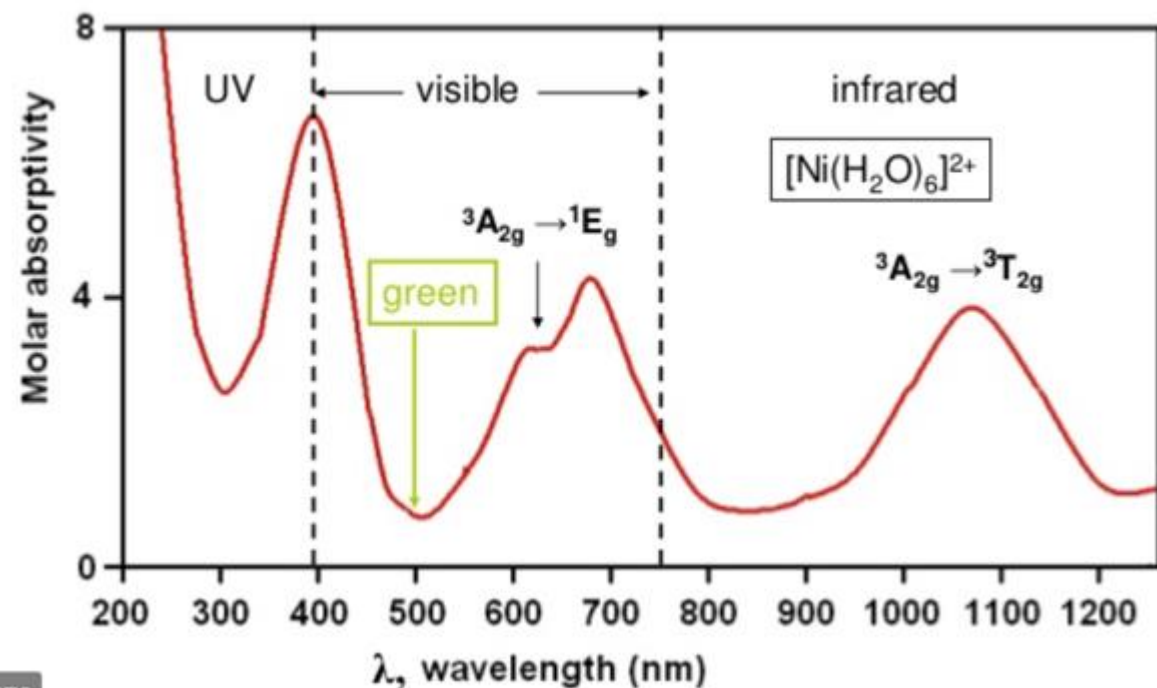
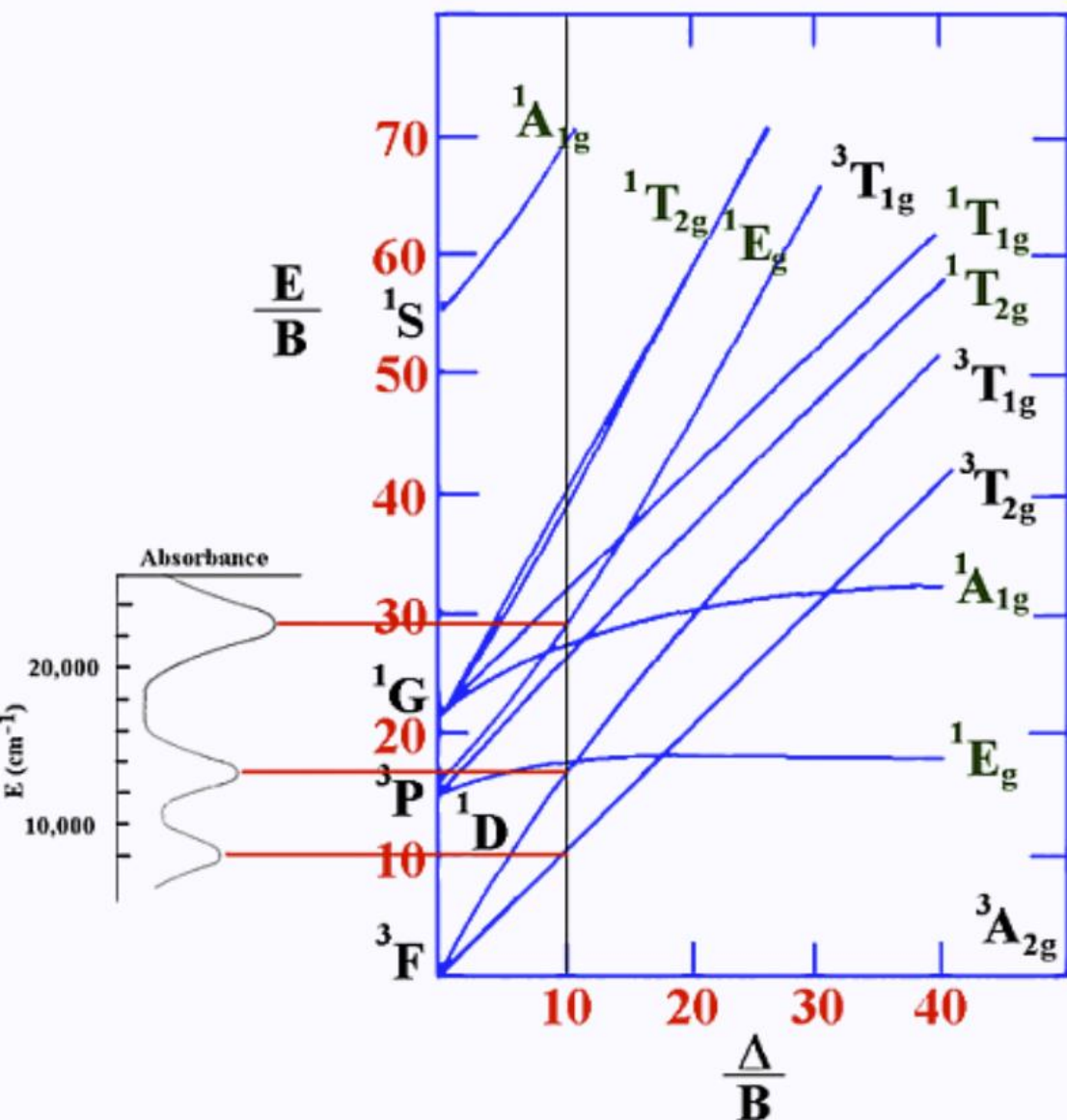
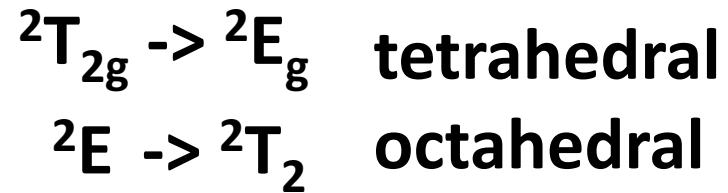


Table 2. Δ_o values for $Ni(II)$ complexes: $[NiL_n]^{2+}$

L	n	Donor Set	Δ_o (cm^{-1})
2,2'-Bipyridine	3	N_6	12 650
Ethylenediamine	3	N_6	11 700
Pyridine	6	N_6	10 150
Imidazole	6	N_6	10 150
NH_3	6	N_6	10 750
H_2O	6	O_6	8 500
Methanol	6	O_6	8 430
Pyridine N-oxide	6	O_6	8 400
Dimethylsulfoxide	6	O_6	7 730

$I^- < Br^- < Cl^- < NO_3^- < F^- < \text{diethyldithiocarbamate}^- (S) < OH^- < C_2O_4^{2-} < H_2O < SCN^- < NH_3 \approx \text{pyridine} (N) < \text{ethylenediamine} (N) < NO_2^- \approx 2,2'\text{-bipyridine} (N) \ll CN^-$

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Very strong Jahn-Teller effects from Octahedral coordination:

CuF₂: 4 ligands at 193 pm (in plane)
 2 ligands at 227 pm (along C₄)

CuBr₂: 4 ligands at 240 pm (in plane)
 2 ligands at 320 pm (along C₄)

Band position very sensitive to ligands.

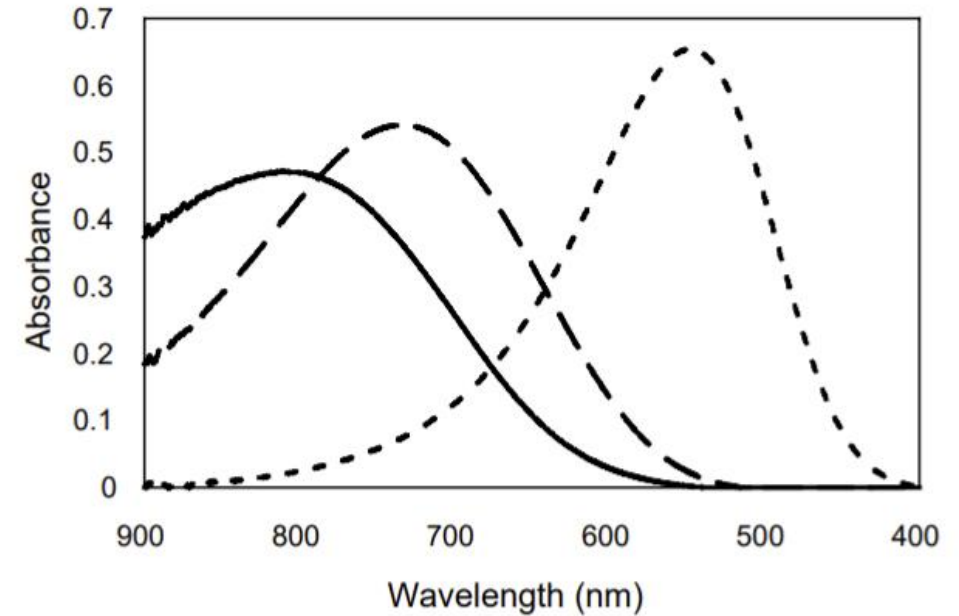


Figure 1. Spectra (absorbance vs. wavelength) for the species [Cu(H₂O)₆]²⁺ (—), [Cu(EDTA)]²⁻ (---), and [Cu(en)₂(H₂O)₂]²⁺ (- - - -).

Optical Spectra of the transition metal aquo complexes in solution

