# 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)
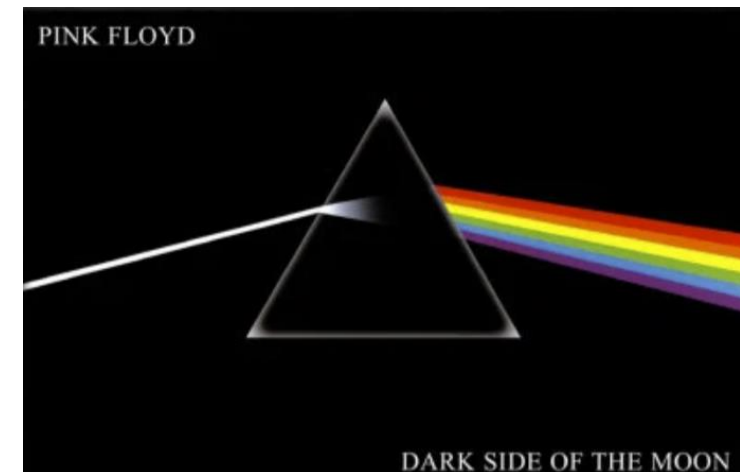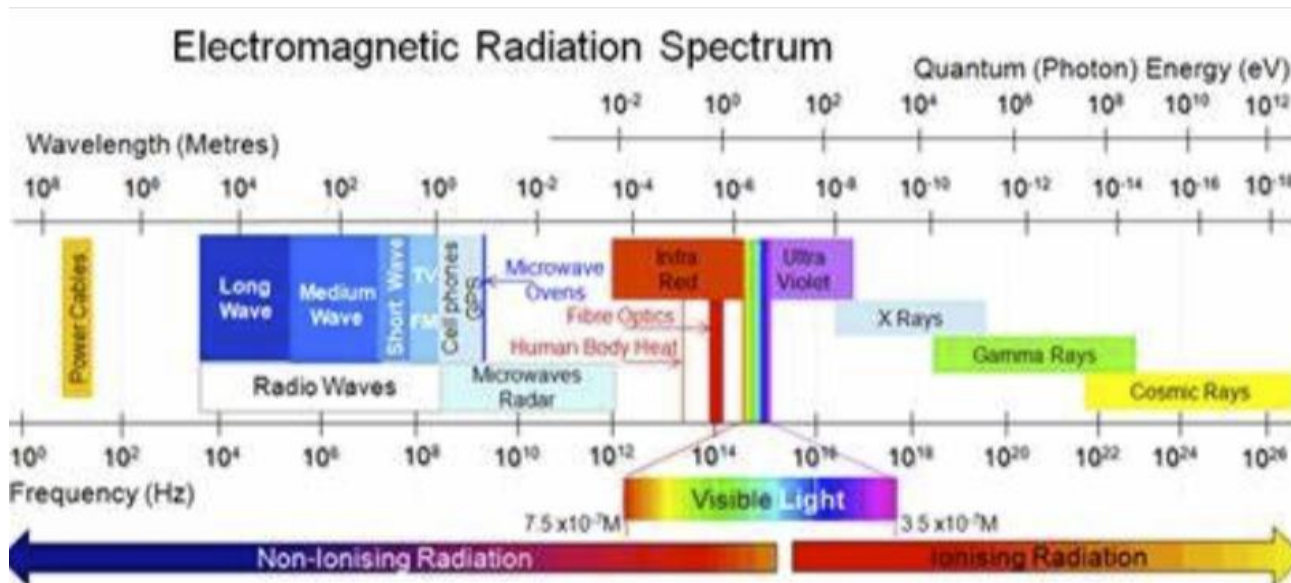
Electronic Structure of Matter:
The H atom.

- 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 $0 \le l \le n-1$.

- 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 = ½,-½

- n=1: $R_{10}Y_{00}$

- n=2: $R_{20}Y_{20}$ $R_{21}Y_{10}$ $R_{21}Y_{11}$ $R_{21}Y_{1-1}$

- n=3: $R_{30}Y_{00}$ $R_{31}Y_{10}$ $R_{31}Y_{11}$ $R_{31}Y_{1-1}$ $R_{32}Y_{20}$ $R_{32}Y_{21}$ $R_{32}Y_{2-1}$ $R_{32}Y_{22}$ $R_{32}Y_{2-2}$

- n=4: $R_{40}Y_{00}$ $R_{41}Y_{10}$ $R_{41}Y_{11}$ $R_{41}Y_{1-1}$ $R_{42}Y_{20}$ $R_{42}Y_{21}$ $R_{42}Y_{2-1}$ $R_{42}Y_{22}$ $R_{42}Y_{2-2}$

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

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

$$E = \frac{Z^2\, m\, e^4}{8\, \varepsilon_0^{\,2} h^2} \times \frac{1}{n^2}$$ **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

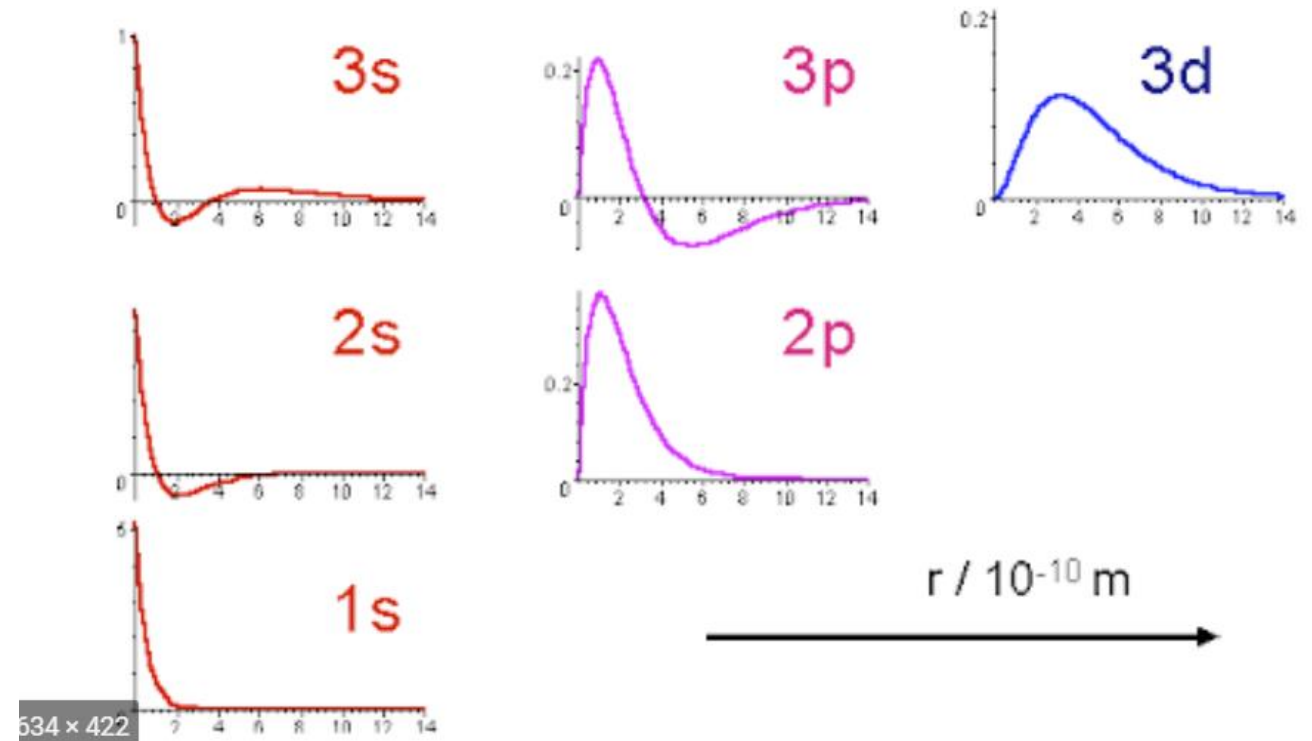$$R_{10} = 2\left(\frac{Z}{a_0}\right)^{\frac{3}{2}} e^{-Zr/a_0}$$

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

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

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

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

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

3s 3p 3d
2s 2p
1s

r / 10^{-10} m

Electronic Structure of Matter:
Many-electron atoms

Henry Norris Russell
1877-1957
Princeton U.

Frederik Saunders
1877-1963
Syracuse U.

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

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: $\mathcal{L} = \sum \boldsymbol{\ell}_i$

Vector addition
(1925)

$$\mathcal{S} = \sum \boldsymbol{s}_i$$

where $L = \{ l_1+l_2, l_1+l_2-1, l_1+l_2-2, ... l_1-l_2 \}$

where $S = \{ s_1+s_2, s_1+s_2-1, , s_1+s_2-2, ... s_1-s_2 \}$

$J = \{ L+S, L+S-1, L+S-2, ...|L-S| \}$ $2J+1$ orientational states

Coupling of the angular momenta belonging to filled (sub-)shells always results in S, L = 0.
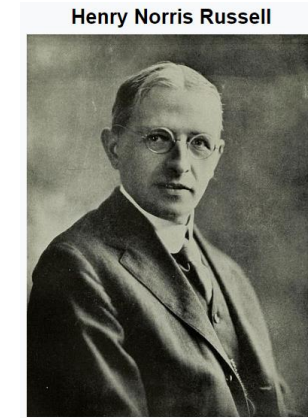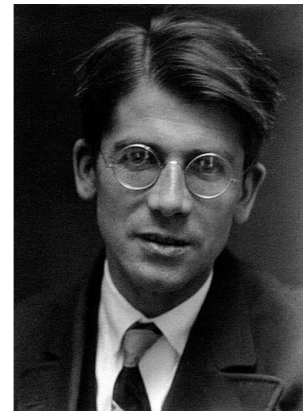
Terminology: use of term symbols $^{2S+1}\mathcal{L}_J$

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 (mimimal 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)

Examples of ground state term symbols

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

Example: Electronic states of the C-atom
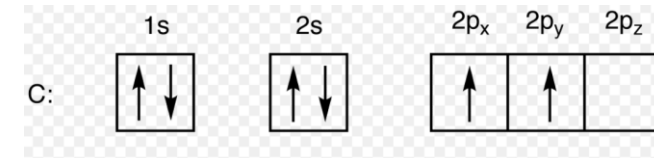
Addition of orbital angular momenta of two electrons: $L = l_1+l_2, l_1+l_2-1, ...l_1-l_2$ -> L = 2, 1, 0
Addition of spin angular momenta of two electrons: $S = s_1+s_2, s_1+s_2-1, ...s_1-s_2$ -> S = 1,0
$M_L = m_{l1}+m_{l2}$; $M_S = m_{s1}+m_{s2}$. **Respecting the Pauli Principle we arrive at the following mother states:**

M_L \ M_S	1	0	-1
2		1^+1^-	
1	1^+0^+	$1^+0^-, 0^+1^-$	1^-0^-
0	1^+-1^+	$-1^+1^-, \underline{1^+-1^-}, 0^+0^-$	1^--1^-
-1	-1^+0^+	$\underline{0^+-1^-}, -1^+0^-$	-1^-0^-
-2		$\underline{-1^+-1^-}$	

Mother states L, total degeneracy (2S+1)(2L+1)
L = 2; $\underline{^1D}$, 5-fold degenerate, J=2
L= 1; ^3P, 3×3-fold degenerate, J = 2,1,0
L= 0; ^1S, non-degenerate, J = 0

Result: $\underline{^1D_2}$, $^3P_2$, $^3P_1$, $^3P_0$ $^1S_0$
Hund's rules: ground state is $^3P_0$

Spin-orbit coupling

- Vectorial coupling:

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

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

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

$\mathcal{L}\mathcal{S}|L,S,J,m_J\rangle = \frac{1}{2}\hbar^2(J(J+1) - L(L+1) - S(S+1))|L,S,J,m_J\rangle$
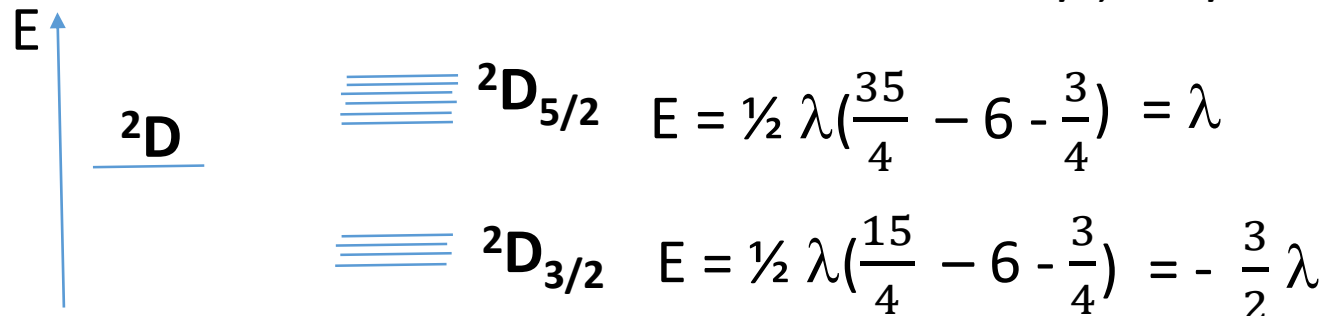
Spin orbit coupling Hamiltonian: $\mathcal{H}_{LS} = \lambda\,\mathcal{L}\,\mathcal{S}$

λ: **spin-orbit coupling constant**

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

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

Eigenvalues:

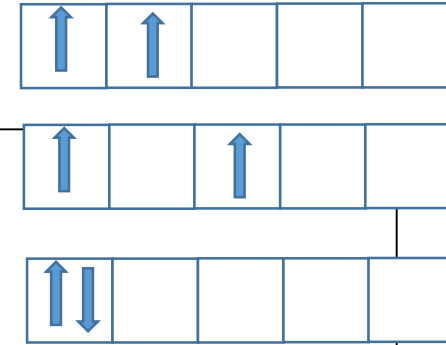$E_{LS} = \lambda\,\frac{1}{2}\,\hbar^2(J(J+1) - L(L+1) - S(S+1))$

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

E

^2D

$^2D_{5/2}$ $E = \frac{1}{2}\lambda(\frac{35}{4} - 6 - \frac{3}{4}) = \lambda$

$^2D_{3/2}$ $E = \frac{1}{2}\lambda(\frac{15}{4} - 6 - \frac{3}{4}) = -\frac{3}{2}\lambda$

Hund's rules regarding ground states (mimimal 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: Ti^{2+}, V^{3+}, Cr^{4+}, Mn^{5+}: 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 d^2 ions
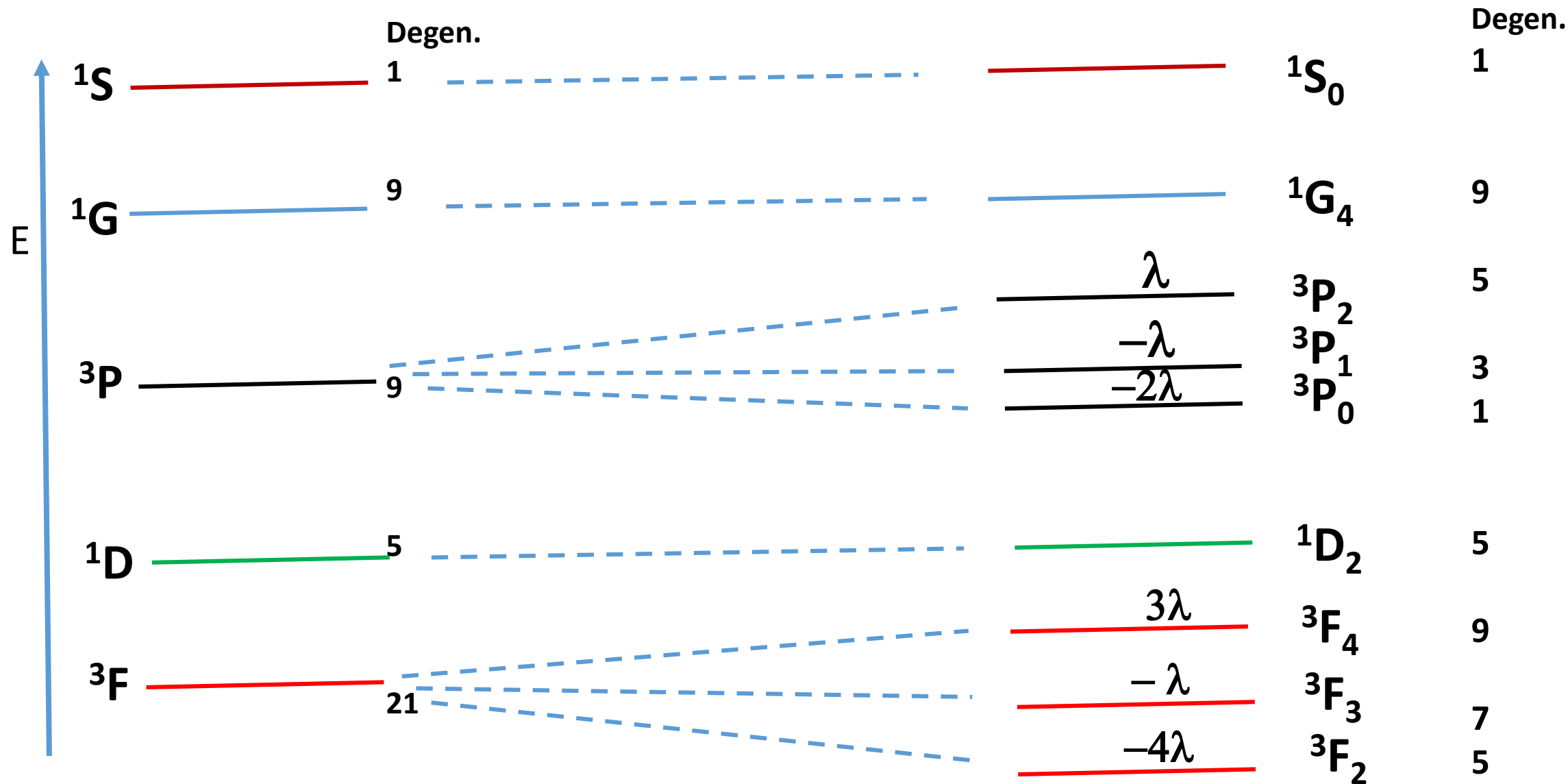
Electronic Structure of Transition Metal Complexes:

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

$d_{x^2-y^2}$ d_{z^2} d_{yz} d_{xz} d_{xy}
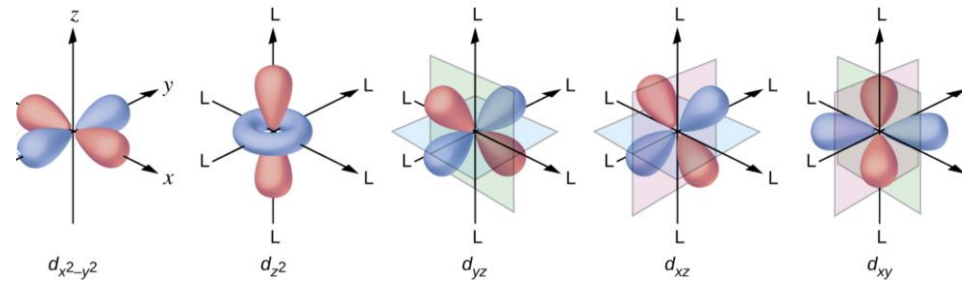
1. The situation for the free metal ions

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)**

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

Ti^{3+} (d^1): states $^2D_{3/2}$ and $^2D_{5/2}$

V^{3+} (d^2) states $^3F_2$, ^1D, ^3P, ^1G, ^1S

Cr^{3+} (d^3): states $^4F_{3/2}$, ^4P, ^2P, ^2F, ^2G, ^2H, ^2D

Mn^{3+} (d^4): states $^5D_0$, ^3H, ^3G, ^3F, ^3D, ^1I

Mn^{2+} (d^5): states $^6S_{5/2}$, ^4G, ^4D, ^4F, ^2I,

Fe^{2+} (d^6): states $^5D_4$, ^3H, ^3G, ^3F, ^3D, ^1I

Co^{2+} (d^7): states $^4F_{9/2}$, ^4P, ^2P, ^2F, ^2G, ^2H, ^2D

Ni^{2+} (d^8): states $^3F_4$, ^1G, ^1D, ^3P, ^1S

Cu^{2+} (d^9): states $^2D_{5/2}$ and $^2D_{3/2}$

„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)

Ligands approach metal

d_{z2} d_{x2-y2}

d-orbitals pointing directly at axis are affected most by electrostatic interaction

d_{xy} d_{yz} d_{xz}

d-orbitals not pointing directly at axis are least affected (stabilized) by electrostatic interaction

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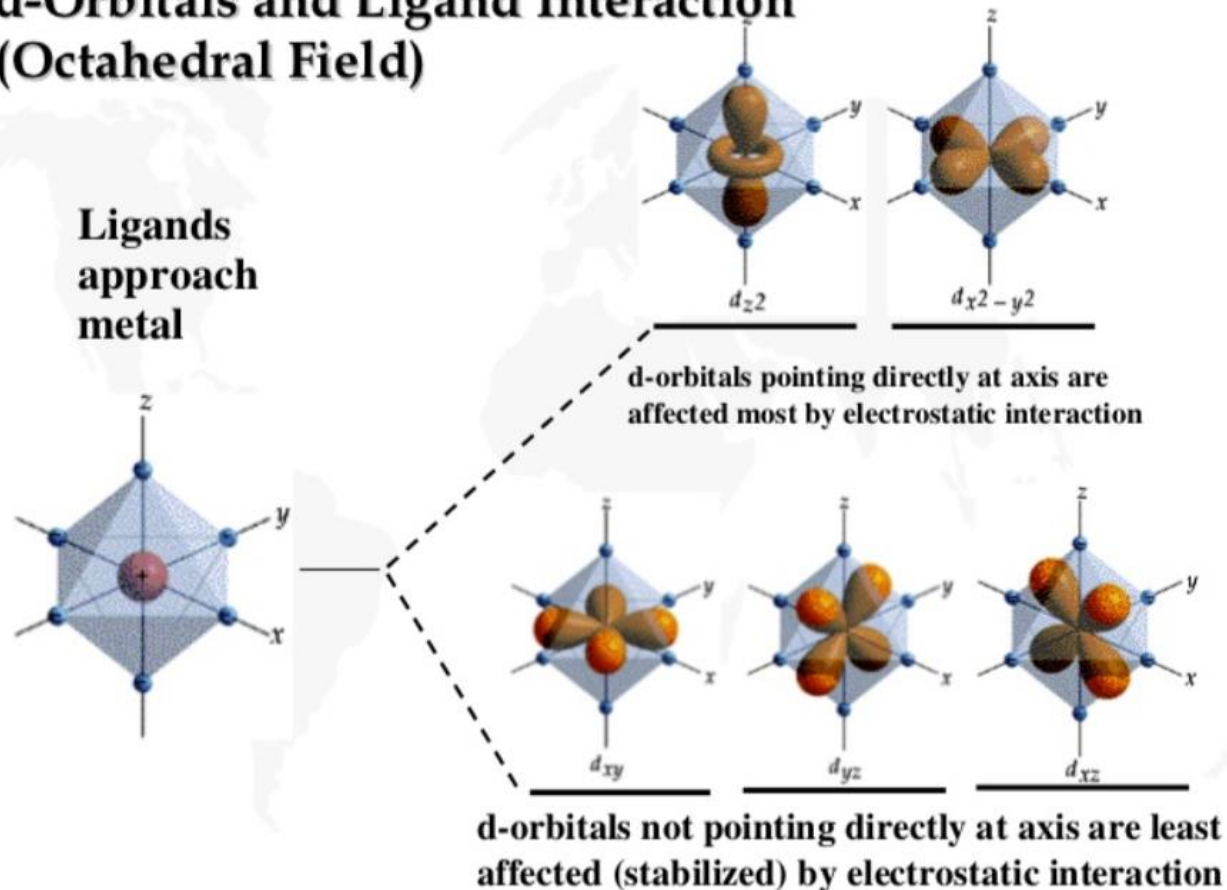
The simplest case: electron configuration d^1: Ti^{3+}, V^{4+}, Mn^{6+}
In an octahedral coordination environment

Free ion term symbol ^2D

General form of the wave function: ψ = R(r)Θ(θ) Φ(φ) φ(s)
Parts R(r) and φ(s) have no orientation dependence
Orientation dependence of part Θ(θ) can be disregarded by choice of coordinate system

Only orientation dependence of Φ(φ) 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.
Φ(φ) = 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

$$\begin{pmatrix} \exp +2i\phi \\ \exp +i\phi \\ \exp \ 0\phi \\ \exp -i\phi \\ \exp -2i\phi \end{pmatrix} \xrightarrow[\text{by } \alpha]{\text{Rotate}} \begin{pmatrix} \exp +2i(\phi+\alpha) \\ \exp +i(\phi+\alpha) \\ \exp \ 0(\phi+\alpha) \\ \exp -i(\phi+\alpha) \\ \exp -2i(\phi+\alpha) \end{pmatrix} = \begin{pmatrix} exp2i\alpha & 0 & 0 & 0 & 0 \\ 0 & expi\alpha & 0 & 0 & 0 \\ 0 & 0 & exp0\alpha & 0 & 0 \\ 0 & 0 & 0 & exp-i\alpha & 0 \\ 0 & 0 & 0 & 0 & exp-2i\alpha \end{pmatrix} \begin{pmatrix} \exp +2i\phi \\ \exp +i\phi \\ \exp \ 0\phi \\ \exp -i\phi \\ \exp -2i\phi \end{pmatrix}$$

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

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

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

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

Proof: **Substituting x = exp(iα) the summation reads**:

$\sum_{k=0}^{2L} (x)^k = x^{2L} + x^{2L-1} + \ldots\ldots + 1 \qquad$ We multiply both sides by **x-1**

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

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

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

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

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

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

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 $\psi(x,y,z) = \psi(-x,-y,-z)$

e_g orbitals — 3d_{z²}, 3d_{x²-y²}

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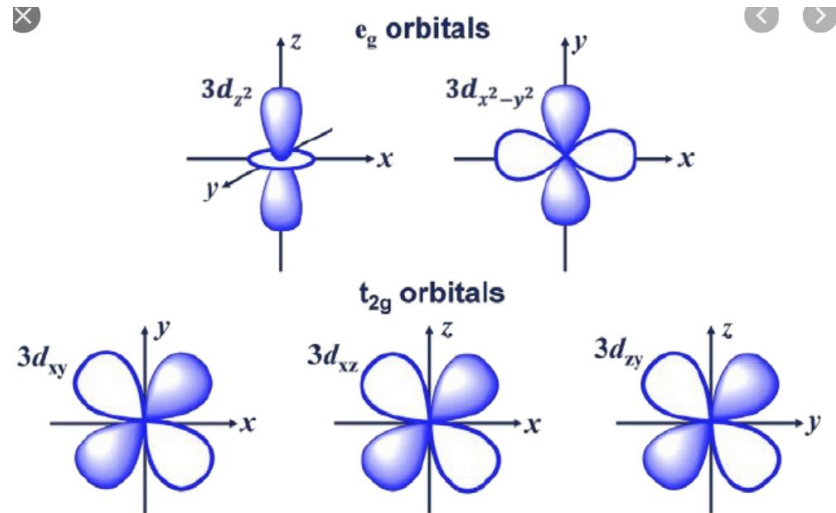
O (432)	E	$8C_3$	$3C_2$	$6C_4$	$6C_2'$	
A_1	1	1	1	1	1	$x^2+y^2+z^2$
A_2	1	1	1	−1	−1	
E	2	−1	2	0	0	$(2z^2-x^2-y^2, \sqrt{3}(x^2-y^2))$
T_1	3	0	−1	1	−1	(x,y,z) (R_x, R_y, R_z)
T_2	3	0	−1	−1	1	(xy, xz, yz)

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'

Developing the irreducible representation using the decomposition formula

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

$$a_l = \frac{1}{h}\sum_R \chi_T(R)\,\chi^{(l')}(R) = \frac{1}{h}\sum_c \chi_T(c)\,g(c)\,\chi^{(l')}(c) =$$

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

$$\chi_T(E) = 5$$

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

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

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

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

$$a_{A1} = \frac{1}{24}(5×1×1 + (-1)×6×1 + (-1)×8×1 + 1×6×1 + 1×3×1) = 0$$

$$a_{A2} = \frac{1}{24}(5×1×1 + (-1)×6×(-1) + (-1)×8×1 + 1×6×(-1) + 1×3×1) = 0$$

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

$$a_{T1} = \frac{1}{24}(5×1×3 + (-1)×6×1 + (-1)×8×0 + 1×6×(-1) + 1×3×(-1) = 0$$

$$a_{T2} = \frac{1}{24}(5×1×3 + (-1)×6×(-1) + (-1)×8×0 + 1×6×1 + 1×3×(-1) = 1$$

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

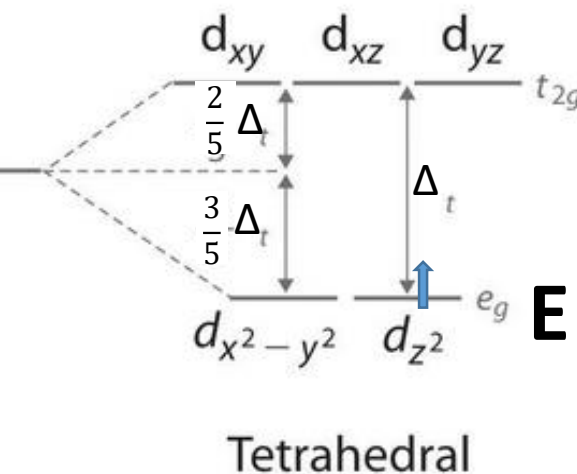# This corresponds to the known result we can already arrive at by inspection.

Negative charges distributed uniformly over surface of a sphere

Negative charges located at vertices of an octahedron

Metal cation, M^{n+}

E

e_g — $d_{x^2-y^2}$ d_{z^2}

Δ_o

$\frac{3}{5}\Delta_o$

$\frac{2}{5}\Delta_o$

t_{2g} — d_{xy} d_{xz} d_{yz}

e_g

Δ_o

t_{2g}

Electrostatic attractions (+/−) considered

(a)
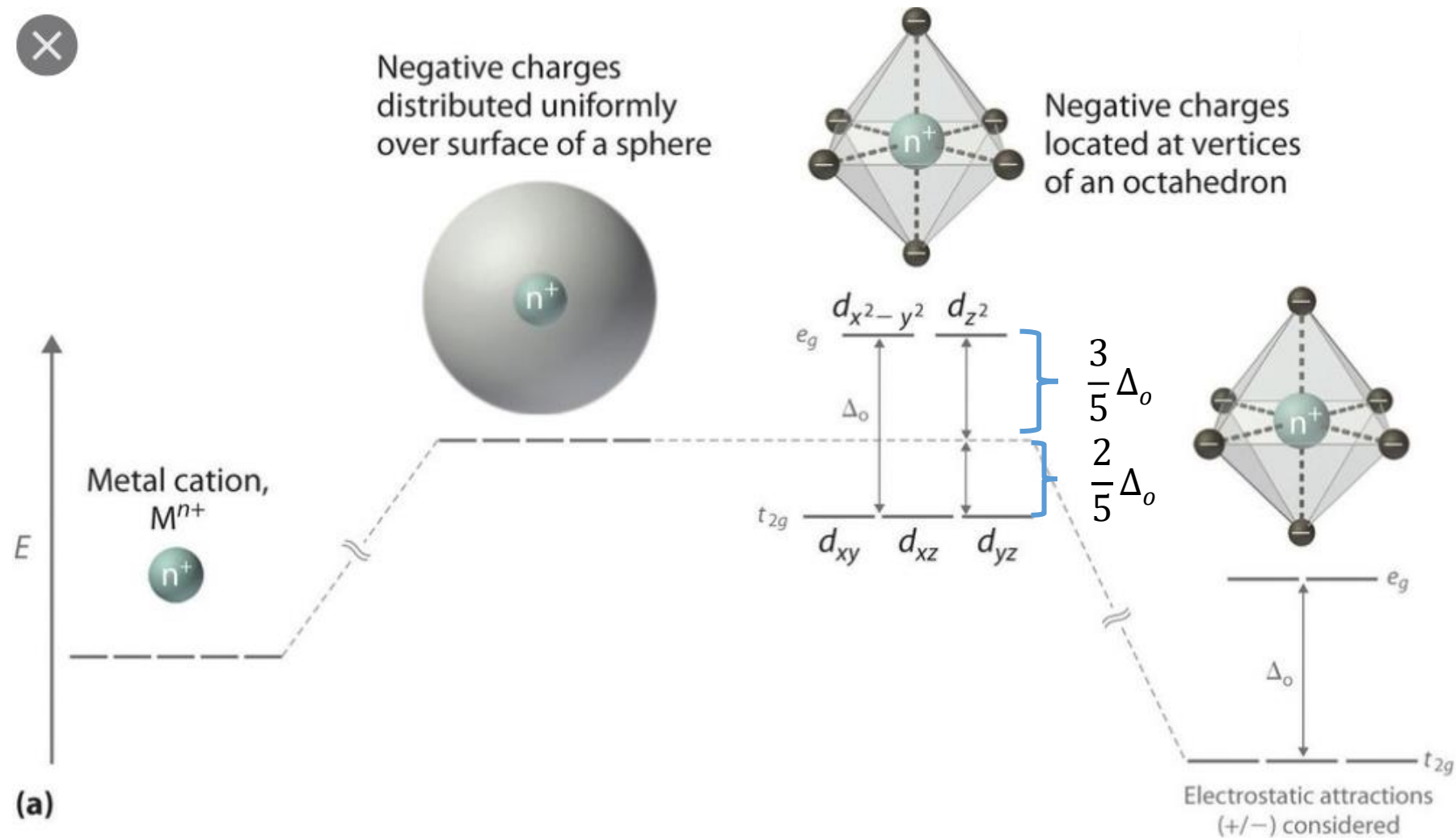
Octahedral versus Tetrahedral Coordination and d^1 vs. d^9

single electron vs single hole

d^1

E

$d_{x^2-y^2}$ d_{z^2} e_g

Δ_o

$\frac{3}{5}\Delta_o$

$\frac{2}{5}\Delta_o$

d_{xy} d_{xz} d_{yz} t_{2g} **T$_{2g}$**

Octahedral

d_{xy} d_{xz} d_{yz} t_{2g}

$\frac{2}{5}\Delta_t$

$\frac{3}{5}\Delta_t$

Δ_t

$d_{x^2-y^2}$ d_{z^2} e_g **E**

Tetrahedral

d^9

E

$d_{x^2-y^2}$ d_{z^2} e_g

Δ_o

$\frac{3}{5}\Delta_o$

$\frac{2}{5}\Delta_o$

t_{2g} **E$_g$**

d_{xy} d_{xz} d_{yz} t_{2g}

$\frac{2}{5}\Delta_t$

$\frac{3}{5}\Delta_t$

Δ_t

$d_{x^2-y^2}$ d_{z^2} e_g **T$_2$**
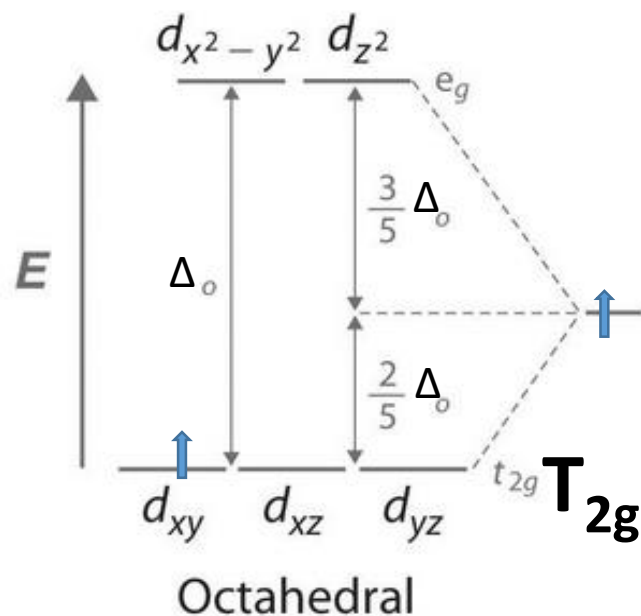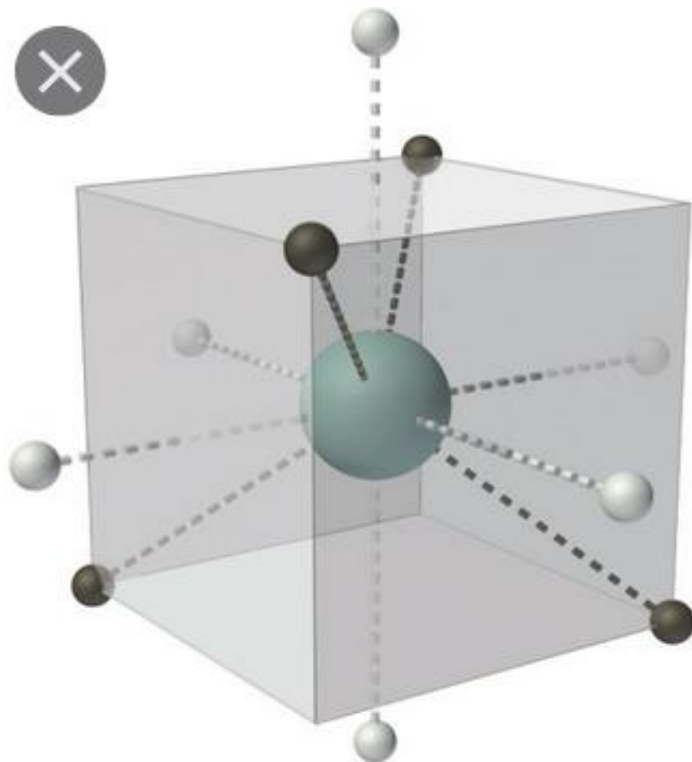
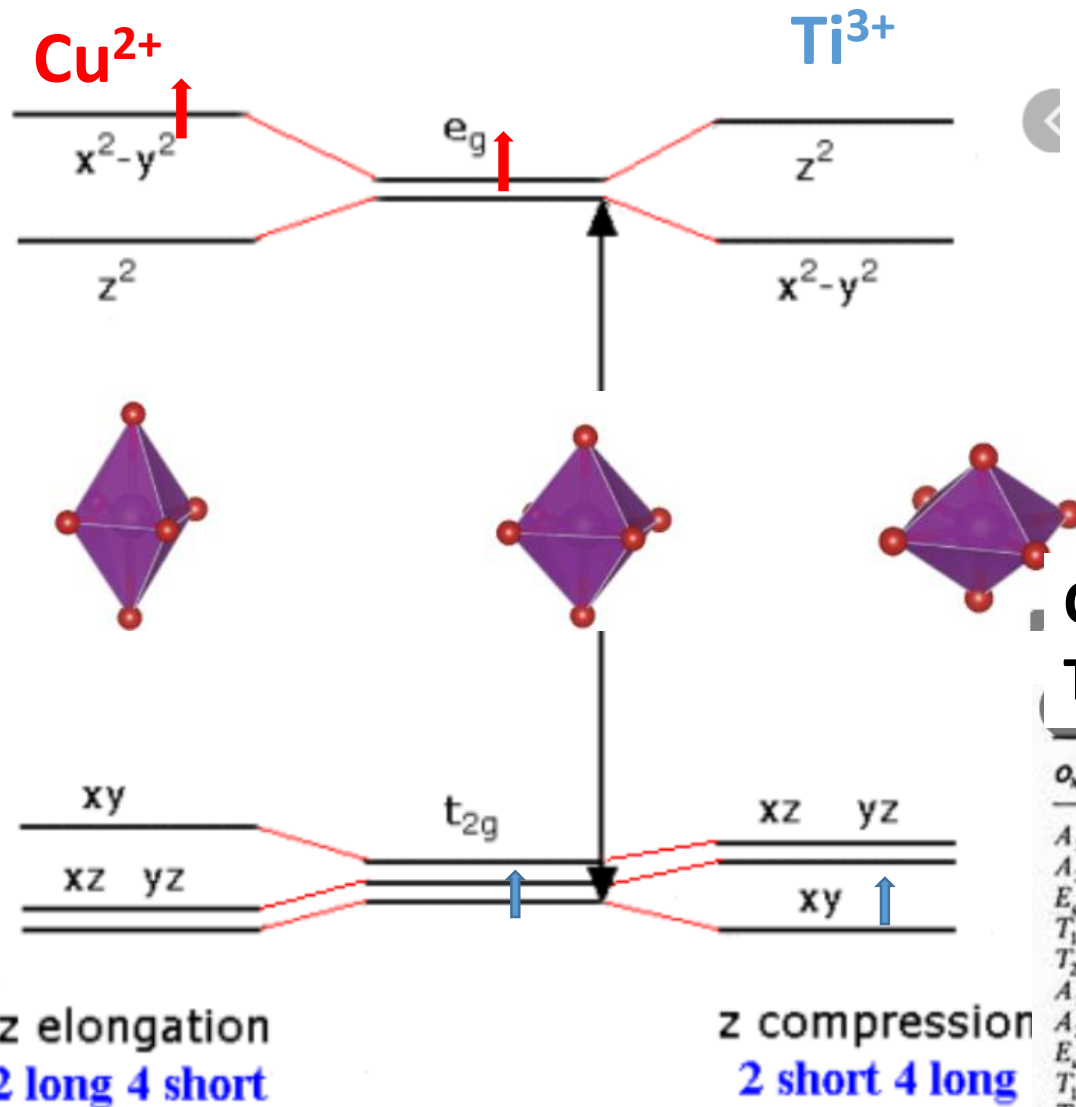| Coord	$Ti^{3+}d^1$	$Cu^{2+}d^9$
Octah.	T_{2g}	E_g
Tetrah.	E	T_2
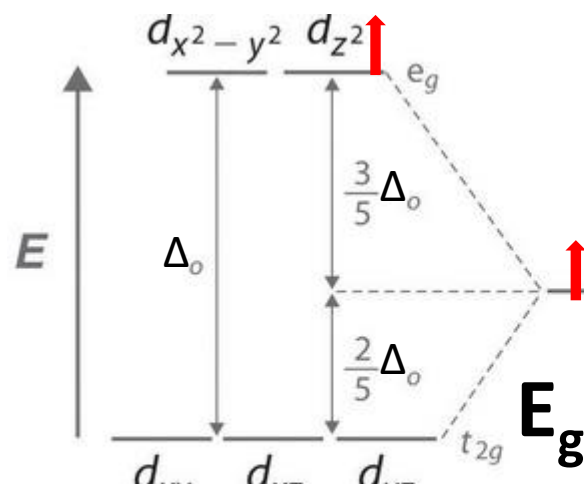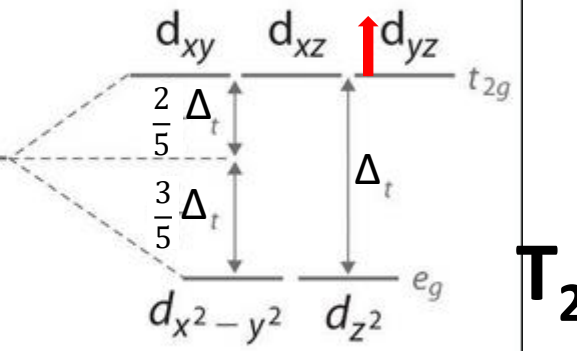
Jahn-Teller Effect

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

Cu²⁺

Ti³⁺

x^2-y^2

e_g

z^2

z^2

x^2-y^2

xy

t_{2g}

xz   yz

xz   yz

xz   yz

xy

z elongation
2 long 4 short

z compression
2 short 4 long

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	A_{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 d² (V³⁺, Cr⁴⁺ , Mn⁵⁺) and d⁸ (Ni²⁺) 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:

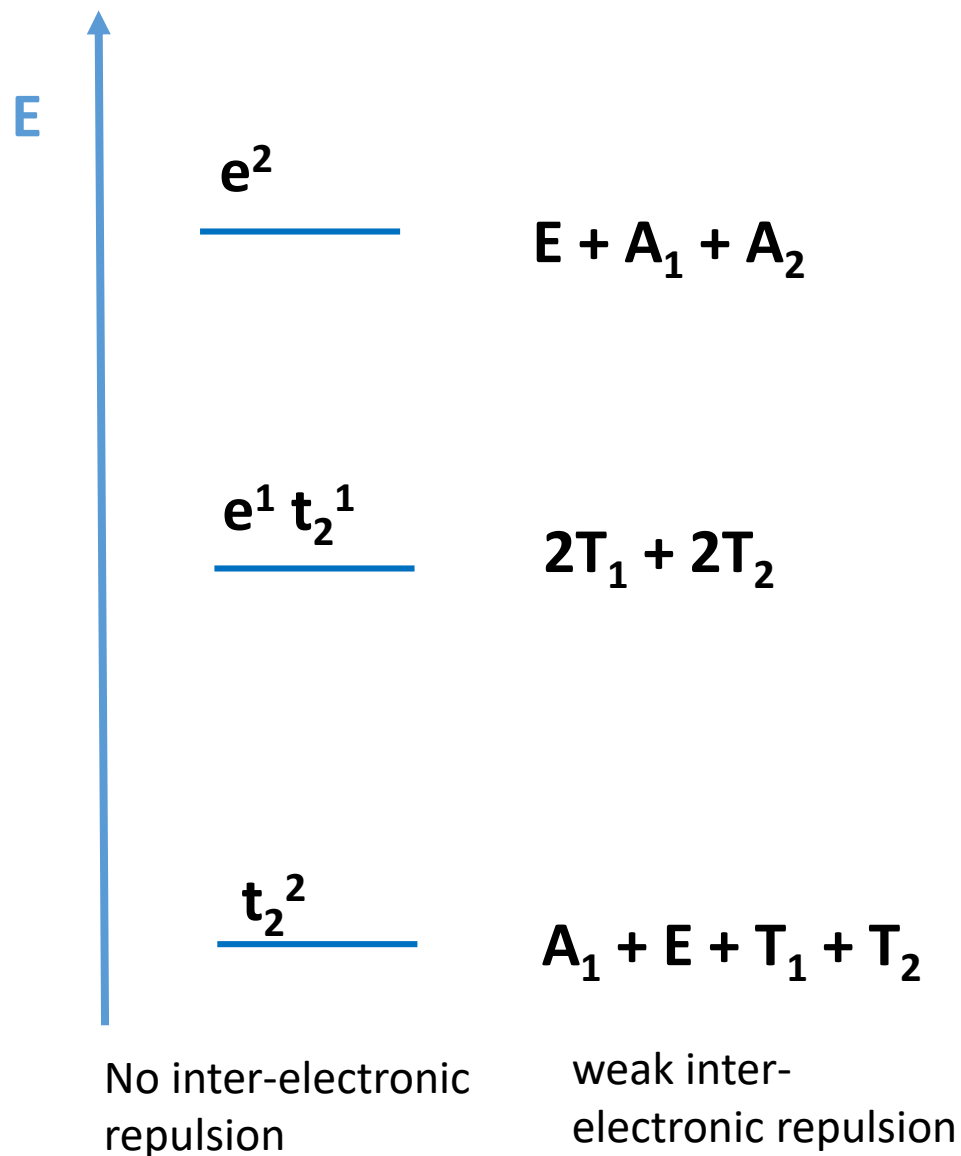**Weak ligand field case:** Mother states still dominate, ligand field makes a perturbation
Extremely strong field case: intra-atomic repulsion is neglected
Strong-field case: Intra-atomic repulsion is a perturbation to the extremely strong field case

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

$$\underline{L}$$

^1S	0
^1G	4
^3P	1
^1D	2
$^3F_2$	3

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

$^1A_1$

$^1E + {^1T_1} + {^1T_2} + {^1A_1}$

$^3T_1$

$^1E + {^1T_2}$

$^3T_1 + {^3T_2} + {^3A_2}$

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

E

e^2 — $E + A_1 + A_2$

$e^1 t_2^1$ — $2T_1 + 2T_2$

t_2^2 — $A_1 + E + T_1 + T_2$

No inter-electronic repulsion

weak inter-electronic repulsion

O $h=24$	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

$E \times E$	4	1	4	0	0
$T_2 \times E$	6	0	-2	0	0
$T_2 \times T_2$	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:

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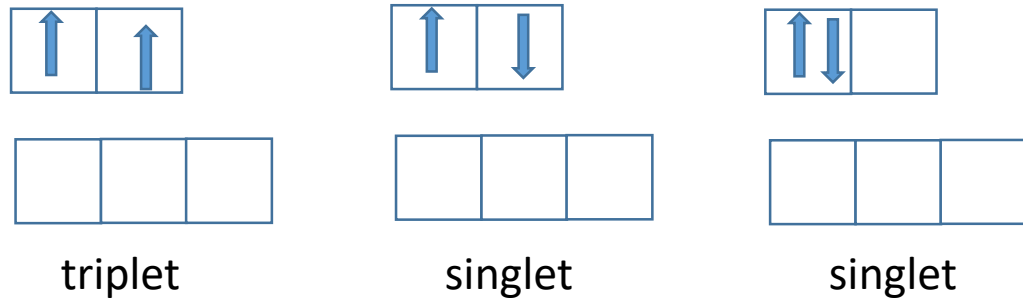
Inter-eletronic repulsion produces the states $\mathbf{E + A_1 + A_2}$
But we do not know their spin multiplicities
Solution: lower the symmetry : $O_h \to D_{4h}$

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

In the reduced symmetry, the two e_g orbitals have different energies. Now the distribution possibilities are:
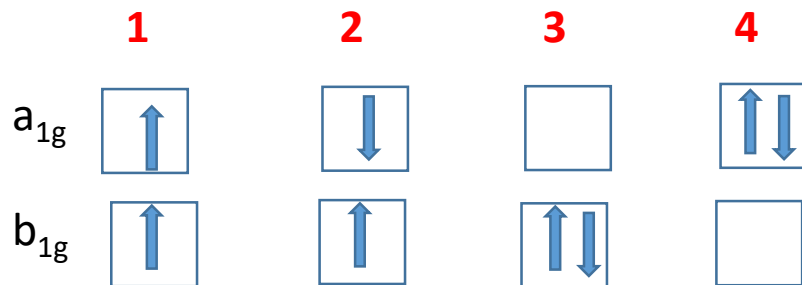
Only distribution **1** produces a triplet   back-correlation to O_h

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

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: $e_g t_{2g} \to {}^3T_{1g} + {}^3T_{2g} \to {}^1T_{1g} \to {}^1T_{1g}$
$t_{2g}^2 \to {}^1A_{1g} + E_g + T_{1g} + T_{2g}$

Orgel diagrams: Plot of Energy versus ligand field strength Δ
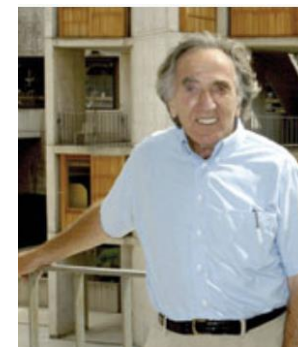
Strength of the ligand repulsion
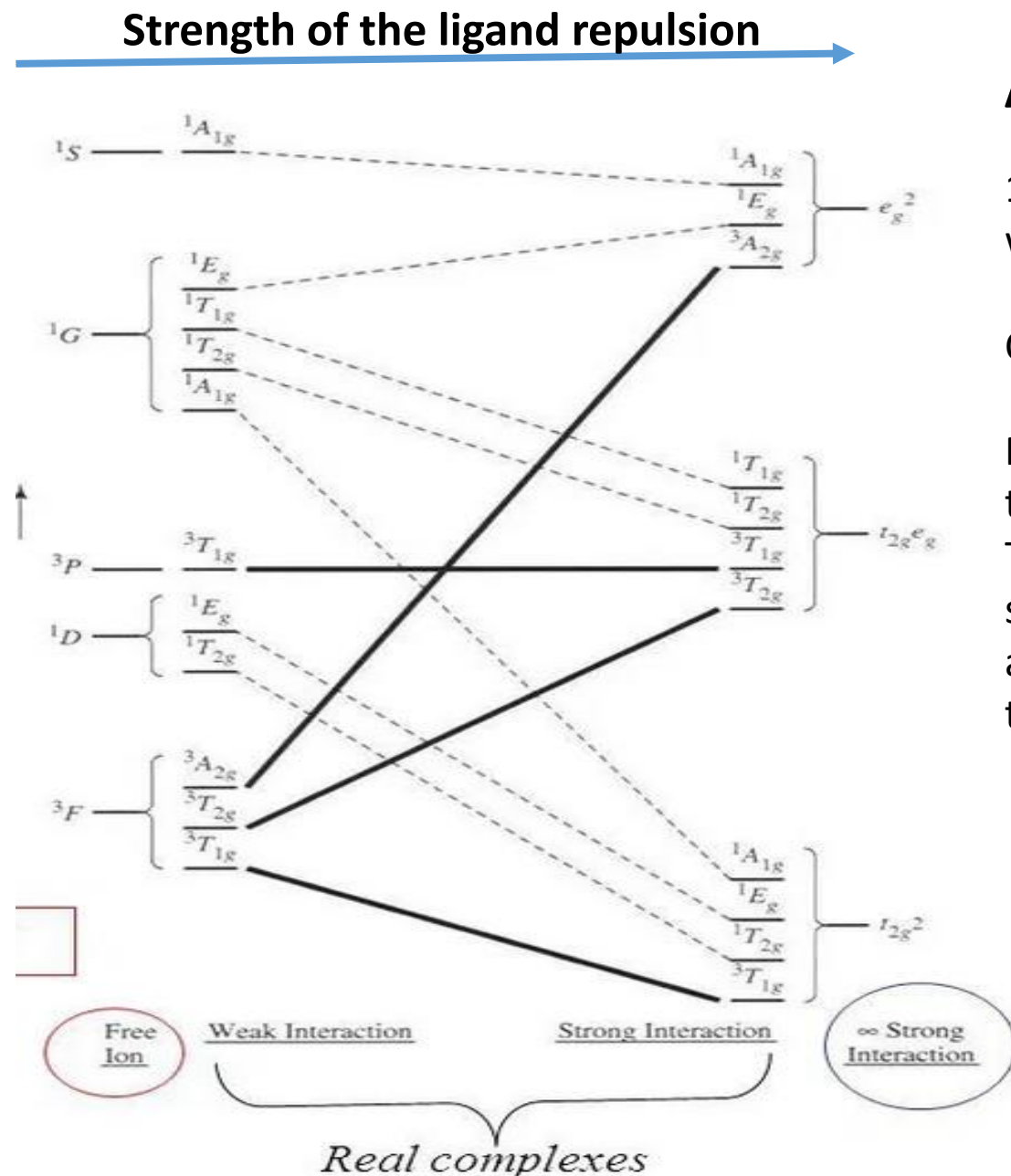
Assembling the Orgel diagram

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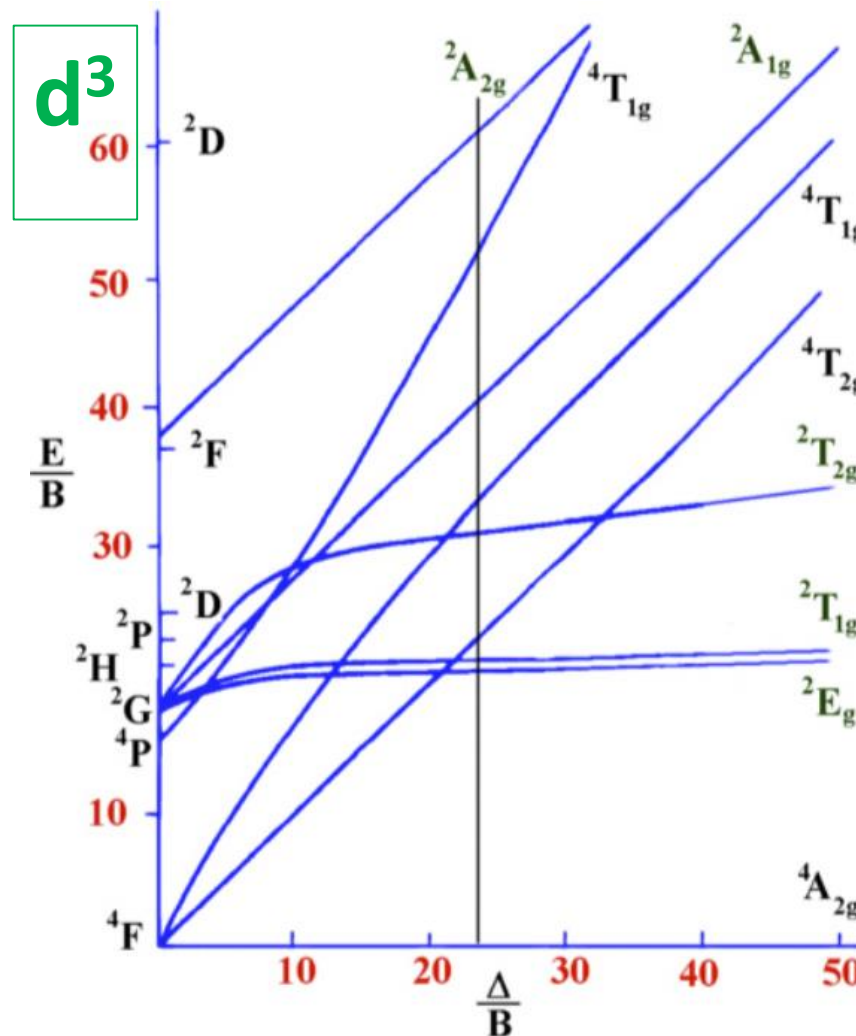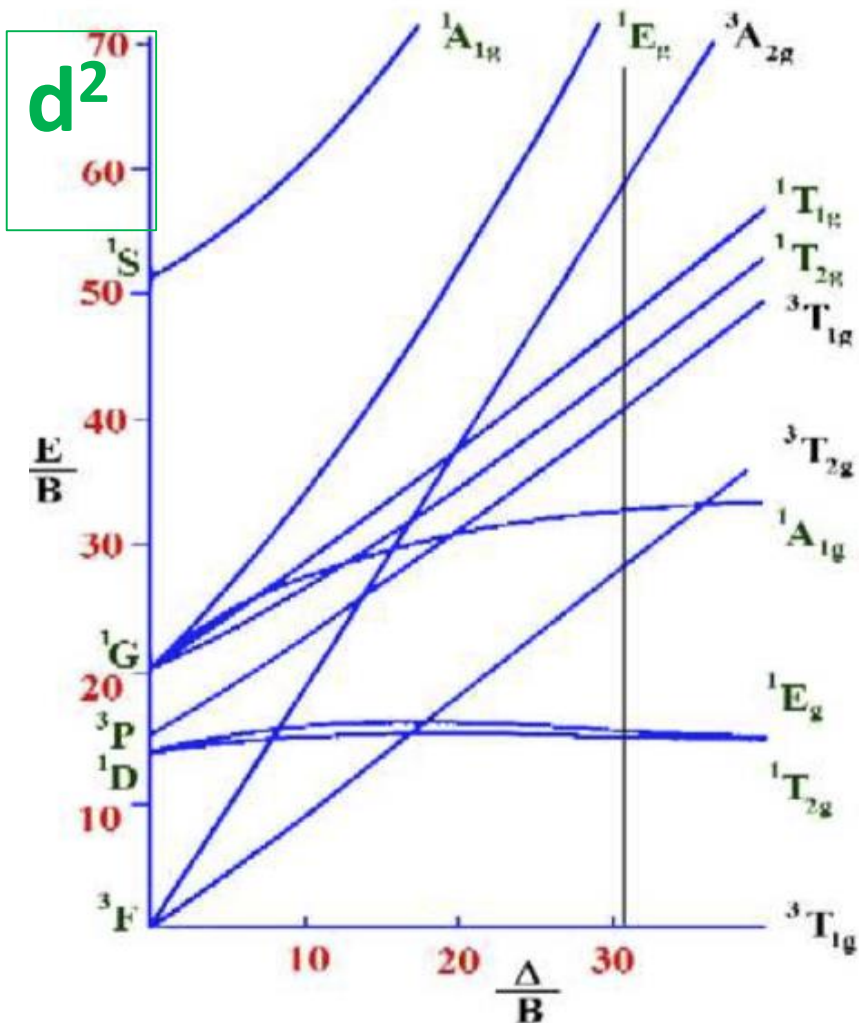
Leslie Orgel
1927-2007
U. Cambridge,
Salk Inst. San
Diego

Tanabe-Sugano diagrams:

Plot of E/B versus Δ/B, where B = energy of interelectronic repulsion
(Racah parameter) weak field -> strong field
Abscissa is identical with the energy of the electronic ground state
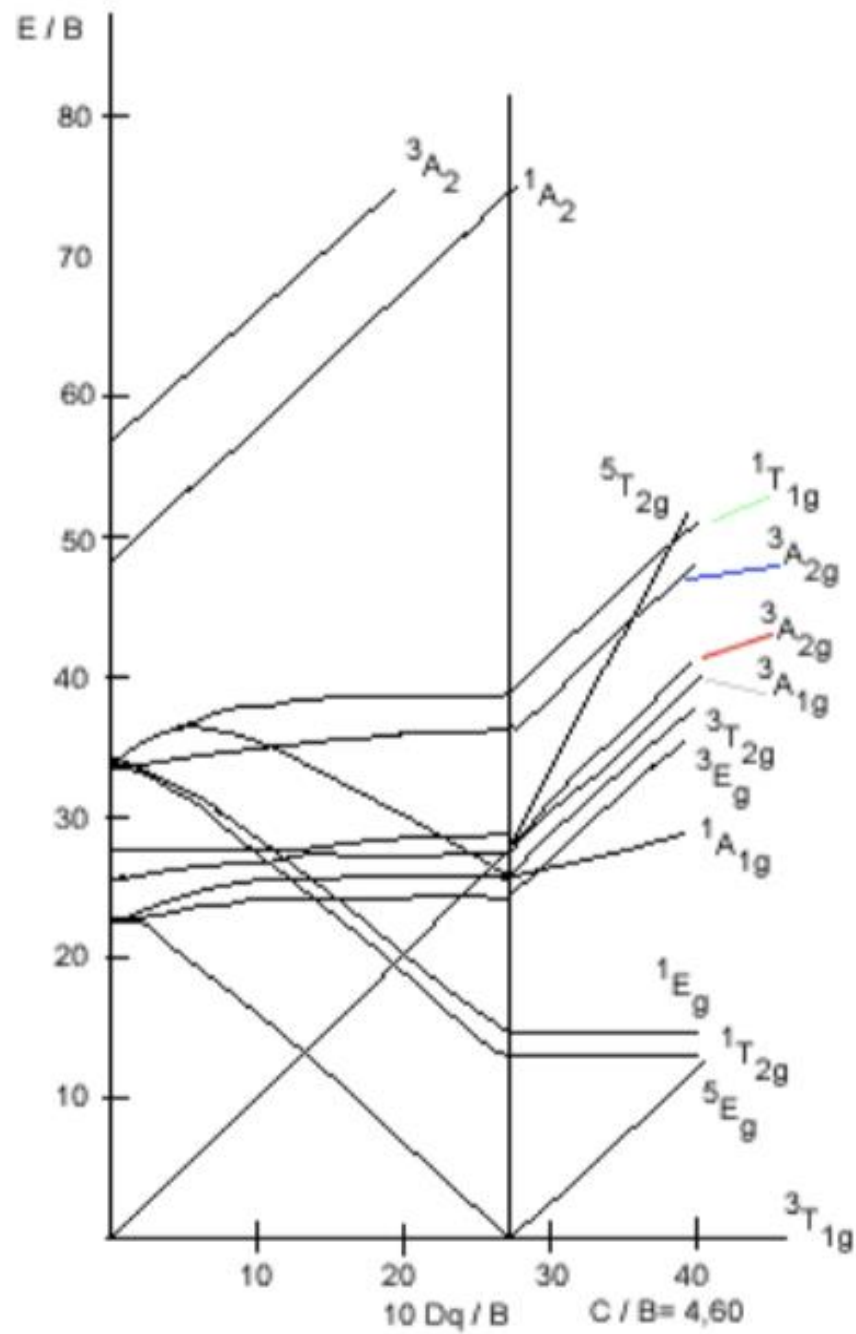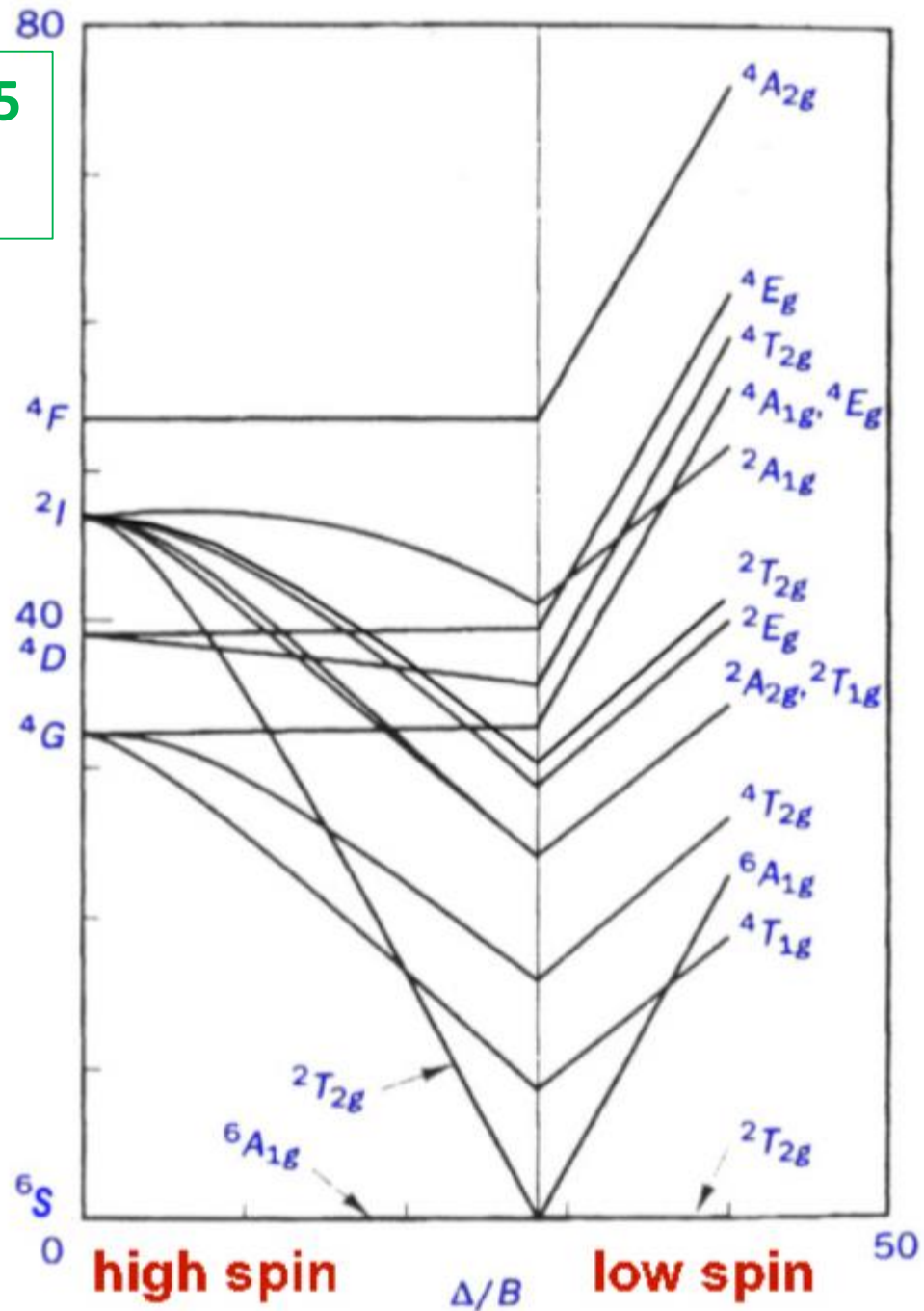

Giulio Racah
1909-1965
Hebrew. U
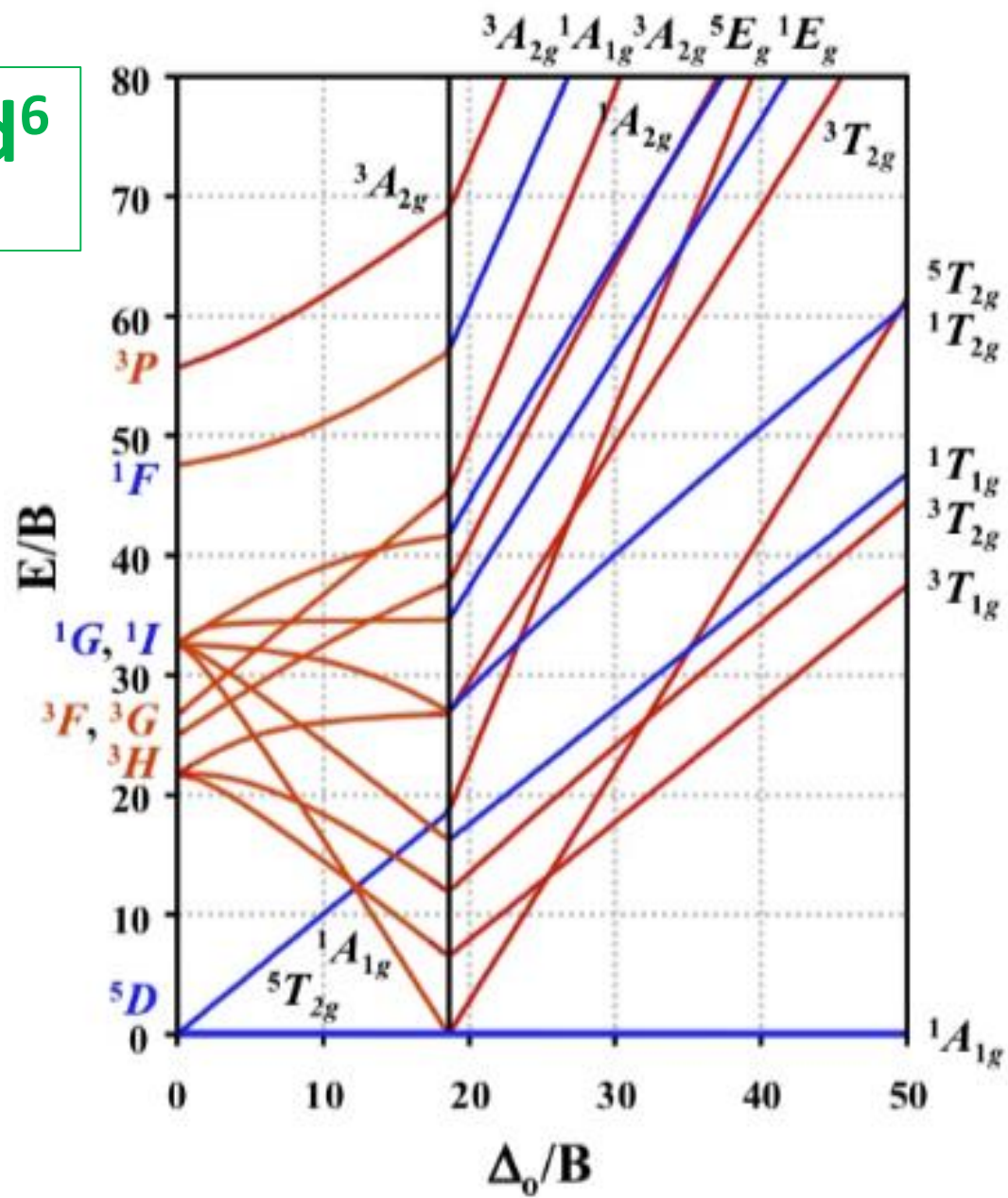Jerusalem

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

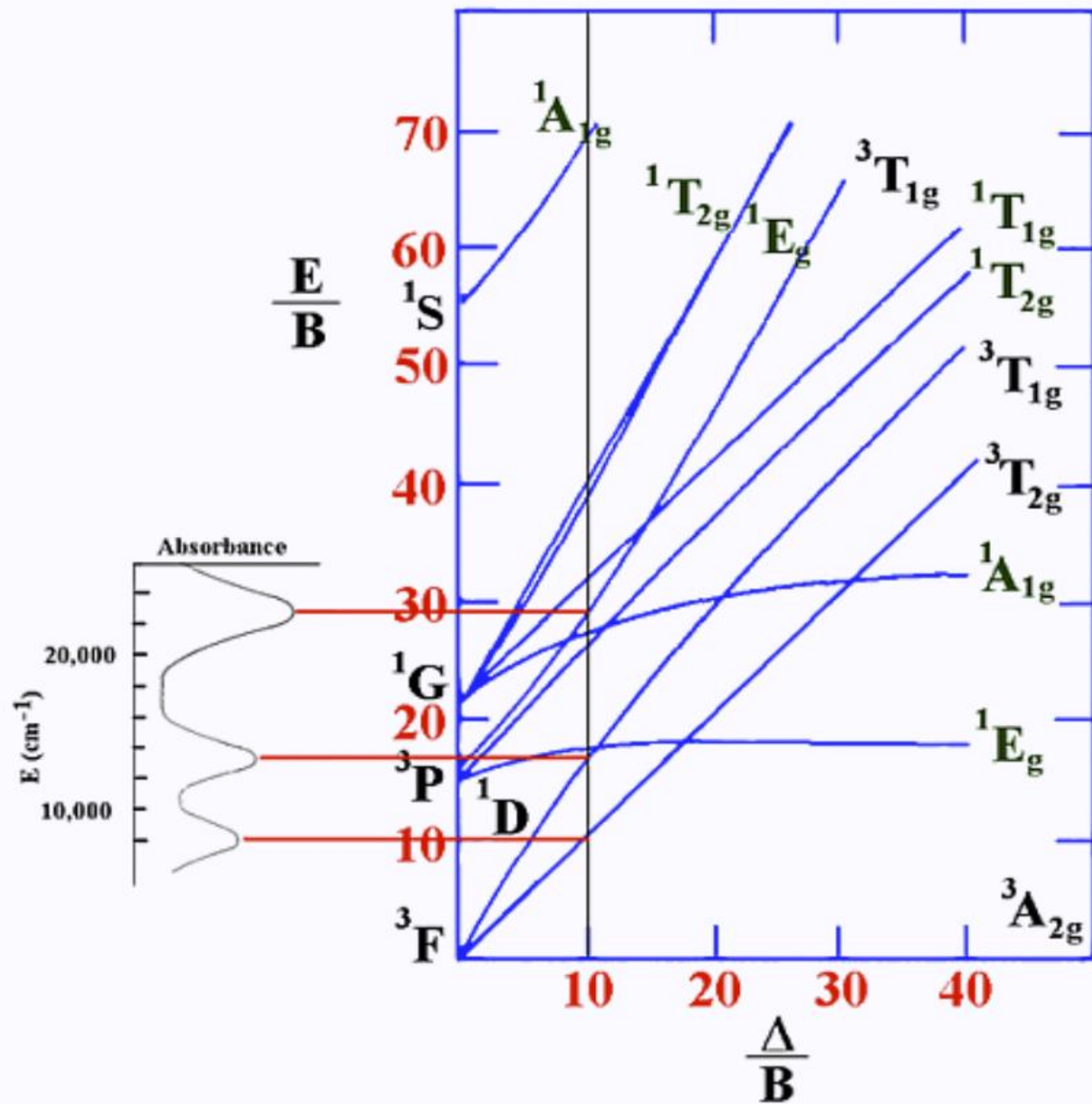d⁴ diagram (left): E/B versus 10 Dq/B, C/B = 4.60. Terms labeled: ³A₂, ¹A₂, ⁵T₂g, ¹T₁g, ³A₂g, ³A₂g, ³A₁g, ³T₂g, ³Eg, ¹A₁g, ¹Eg, ¹T₂g, ⁵Eg, ³T₁g.

d⁵ diagram (right): E/B versus Δ/B, high spin — low spin. Terms: ⁴A₂g, ⁴Eg, ⁴T₂g, ⁴A₁g ⁴Eg, ²A₁g, ²T₂g, ²Eg, ²A₂g ²T₁g, ⁴T₂g, ⁶A₁g, ⁴T₁g, ²T₂g, ⁶A₁g, ²T₂g. Free-ion terms: ⁴F, ²I, ⁴D, ⁴G, ⁶S.

d⁶ (left diagram)

Top labels: $^3A_{2g}$ $^1A_{1g}$ $^3A_{2g}$ ^5E_g ^1E_g

Left axis labels: ^3P, ^1F, $^1G, ^1I$, $^3F, ^3G$, ^3H, ^5D

Internal labels: $^3A_{2g}$, $^1A_{2g}$, $^3T_{2g}$, $^5T_{2g}$, $^1A_{1g}$

Right axis labels: $^5T_{2g}$, $^1T_{2g}$, $^1T_{1g}$, $^3T_{2g}$, $^3T_{1g}$, $^1A_{1g}$

Y-axis: E/B (0 to 80)
X-axis: Δ_o/B (0 to 50)

d⁷ (right diagram)

Top labels: $^2A_{2g}$ $^4A_{2g}$ $^2A_{1g}$ $^4T_{1g}$

Left axis labels: ^2F, ^2G, ^4P, ^4F

Internal label: $^4T_{1g}$

Right axis labels: $^4T_{2g}$, $^2T_{2g}$, $^2T_{1g}$, $^4T_{1g}$, $^2T_{2g}$

Y-axis: E/B (0 to 80)
X-axis: Δ_o/B (0 to 50)

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

$$\Gamma_{\psi g} \otimes \Gamma_x \otimes \Gamma_{\psi e}$$
$$\Gamma_{\psi g} \otimes \Gamma_y \otimes \Gamma_{\psi e}$$
$$\Gamma_{\psi g} \otimes \Gamma_z \otimes \Gamma_{\psi e}$$

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

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**: $\psi_g = \psi(el)_g \, \psi(vib)_g = \psi_{sg} \, \psi(orb)_g \, \psi(vib)_g$
Wave function for the electronic **excited state**: $\psi_e = \psi(el)_e \, \psi(vib)_e = \psi_{se} \, \psi(orb)_e \, \psi(vib)_e$

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

$M = \langle \psi_{sg} \, \psi(orb)_g \, | \, \psi_{se} \, \psi(orb)_e \rangle \langle \psi(vib)_g \, |\mu_n| \, \psi(vib)_e \rangle + \langle \psi(vib)_g | \, \psi(vib)_e \rangle \, \langle \psi_{sg} \, \psi(orb)_g \, |\mu_e| \, \psi_{se} \, \psi(orb)_e \rangle$

$M = \langle \psi(vib)_g | \, \psi(vib)_e \rangle \, \langle \psi_{sg} \, \psi(orb)_g \, |\mu_e| \, \psi_{se} \, \psi(orb)_e \rangle = \langle \psi(vib)_g | \, \psi(vib)_e \rangle \, \langle \psi_{sg} | \psi_{se} \rangle \langle \psi(orb)_g |\mu_e| \psi(orb)_e \rangle$

$\langle \psi_{sg} | \psi_{se} \rangle = 0$ if the spin wave functions of ground and excited state are different. -> spin multiplicity is conserved
$\langle \psi(orb)_g |\mu_e| \psi(orb)_e$ subject to orbital selection rule (group theory)
$\langle \psi(vib)_g | \, \psi(vib)_e \rangle$ 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

$$\Gamma_{\psi g} \otimes \Gamma_x \otimes \Gamma_{\psi e}$$
$$\Gamma_{\psi g} \otimes \Gamma_y \otimes \Gamma_{\psi e}$$
$$\Gamma_{\psi g} \otimes \Gamma_z \otimes \Gamma_{\psi e}$$

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

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

The transition moment Integral is given by:

M = $< \psi_g\, |\mu|\, \psi_e > = < \psi(el)_g\, \psi(vib)_g\, |\mu|\, \psi(el)_e\, \psi(vib)_e >$

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

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

Where $\Gamma_{\psi(vib)g}$ = 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, $\Gamma_{\psi(vib)e}$ 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)
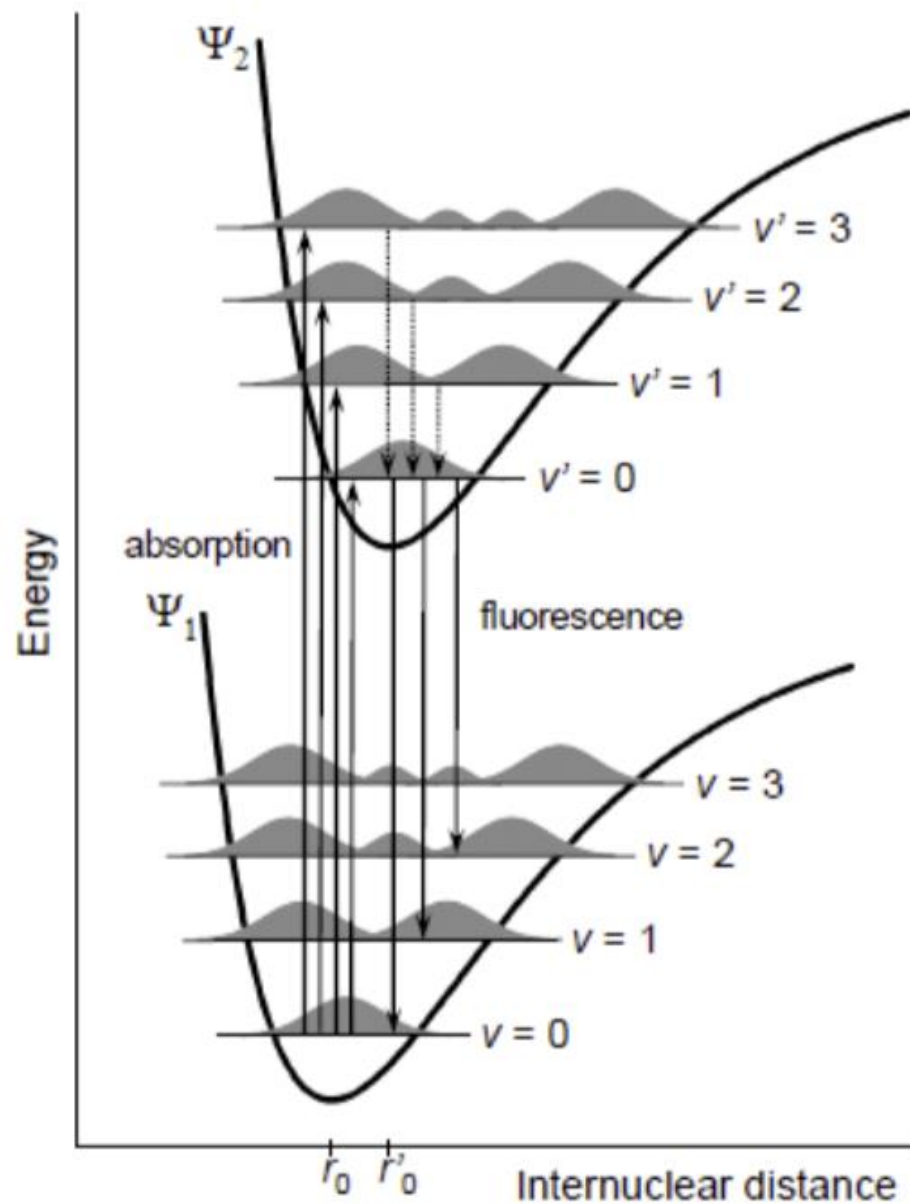
1. Optical transition is much faster than vibrational motion
2. Internuclear distance in the optical excited state is larger than in the ground state

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

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

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

v_1, A_{1g} v_2, E_g v_3, T_{1u}

v_4, T_{1u} v_5, T_{2g} v_6, T_{2u}
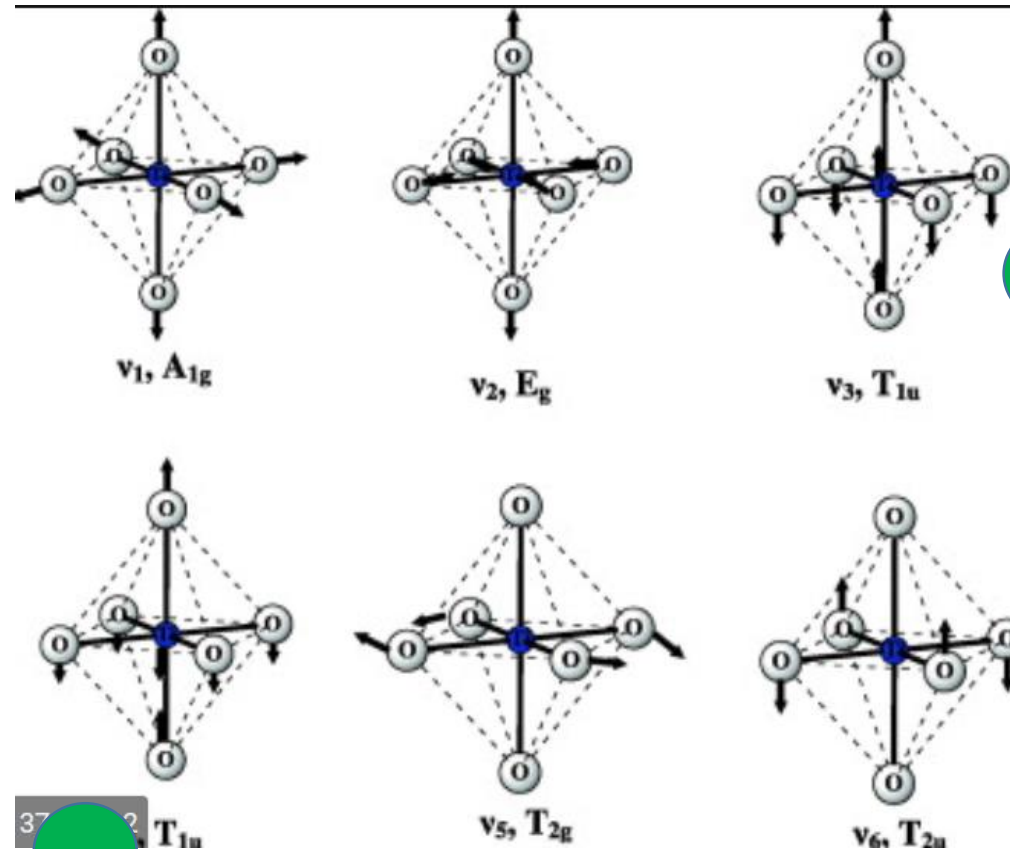
Electronic transitions are much faster than the vibrational motion. From the viewpoint of electronic spectroscopy the sample is a collection of molecules in different stages of vibrational motion. If the vibrational analysis produces normal modes of type u (it always does), the Laporte rule is relaxed, because the sample always contains molecules whose center of symmetry is broken by the vibrational motion.

Spectroscopic observables:

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

Range of transition energies = width of the spectrum
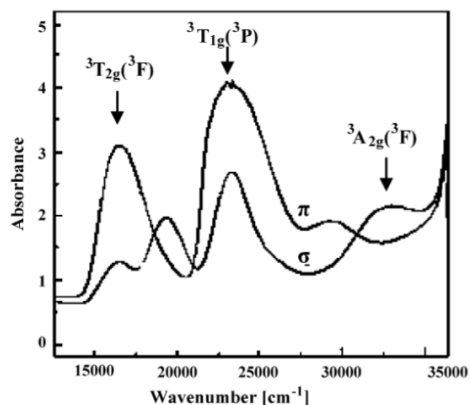
Fig. 1. Polarized absorption spectra of $Cs_3 VCl_2(H_2O)_4$ at 80 K [9].
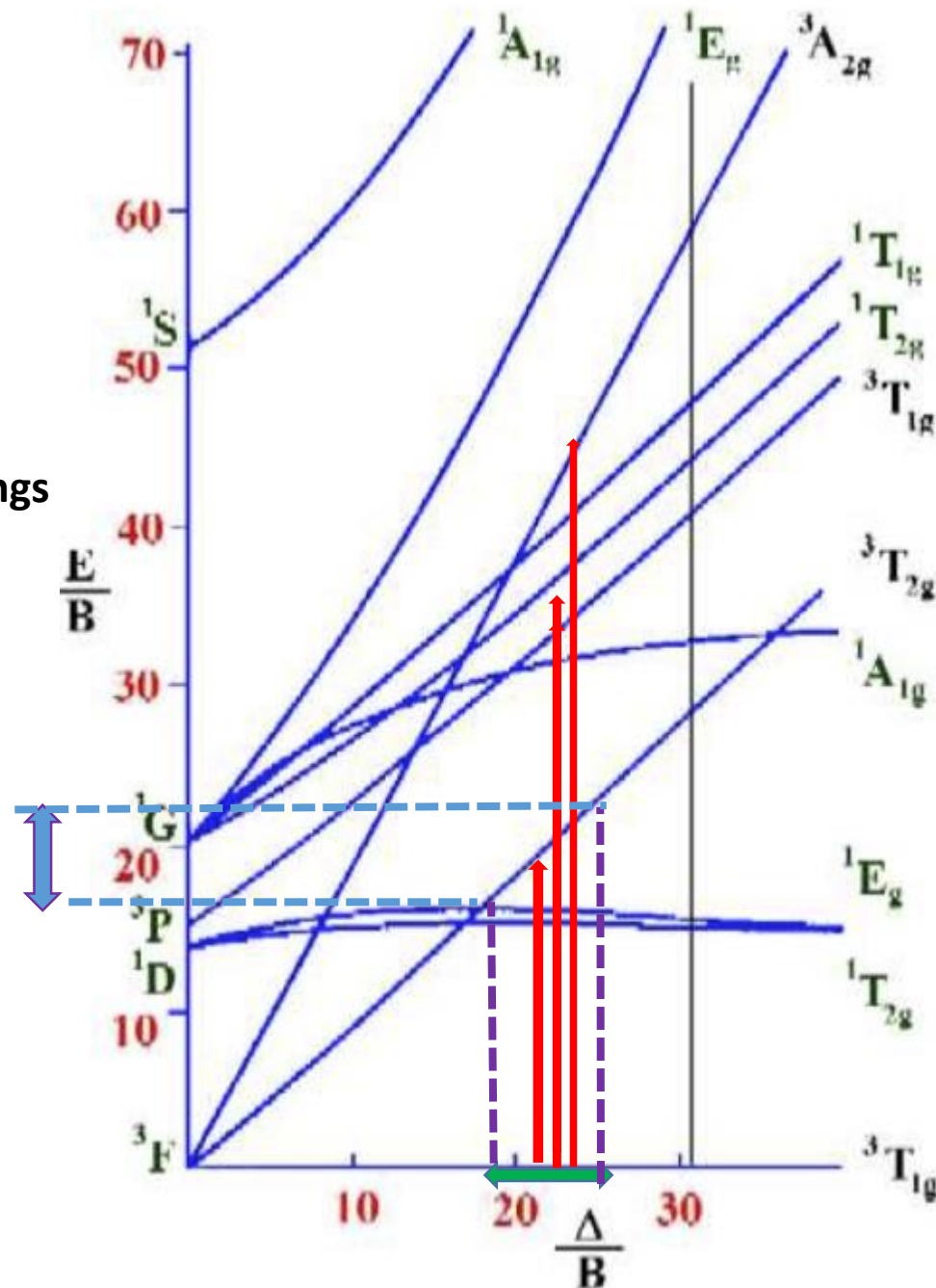
Spectrum for d^2 ions in an octahedral ligand field

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

Linewidths of the transitions ~ inclination in the TS-diagram

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

A walk through the first transition metal series

d^1 Ti^{3+} V^{4+} Cr^{5+} Mn^{6+}

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

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

Jahn-Teller distortions will always occur,
Strongly distorted V4+: „vanadyl" VO^{2+}
Δ increases with increasing charge of the central ion:

a: $Ba_3(PO_4)_2$:Mn^{5+} phosphor, b: undoped $BaSO_4$ crystal
c: $BaSO_4$:Mn^{6+} crystal, d: $BaSO_4$:(Mn^{6+}, Mn^{5+}) crystal
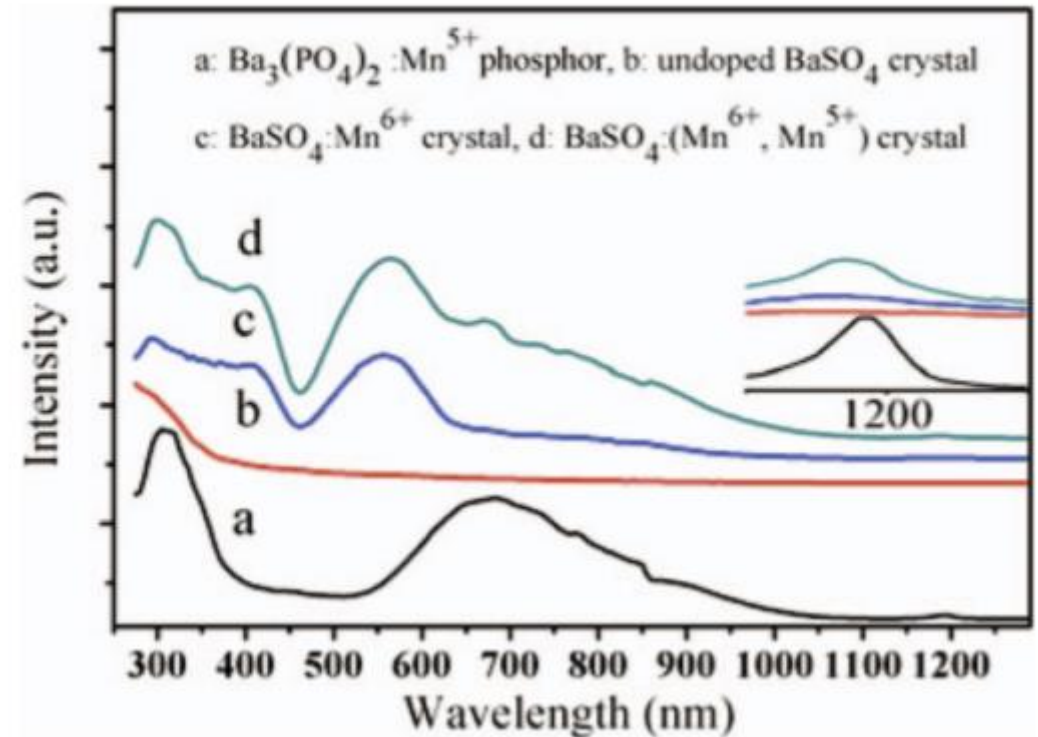
d² **Ti²⁺ V³⁺ Cr⁴⁺ Mn⁵⁺**

Octahedral LF:
$^3T_{1g}$ -> $^3T_{2g}$
$^3T_{1g}$ -> $^3T_{1g}$
$^3T_{1g}$ -> $^3A_{2g}$
J-T distortions

Range of transition energies = width of the spectrum
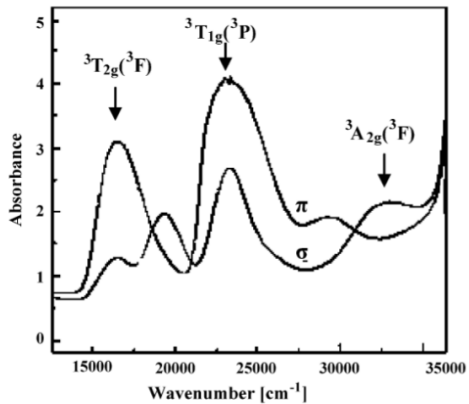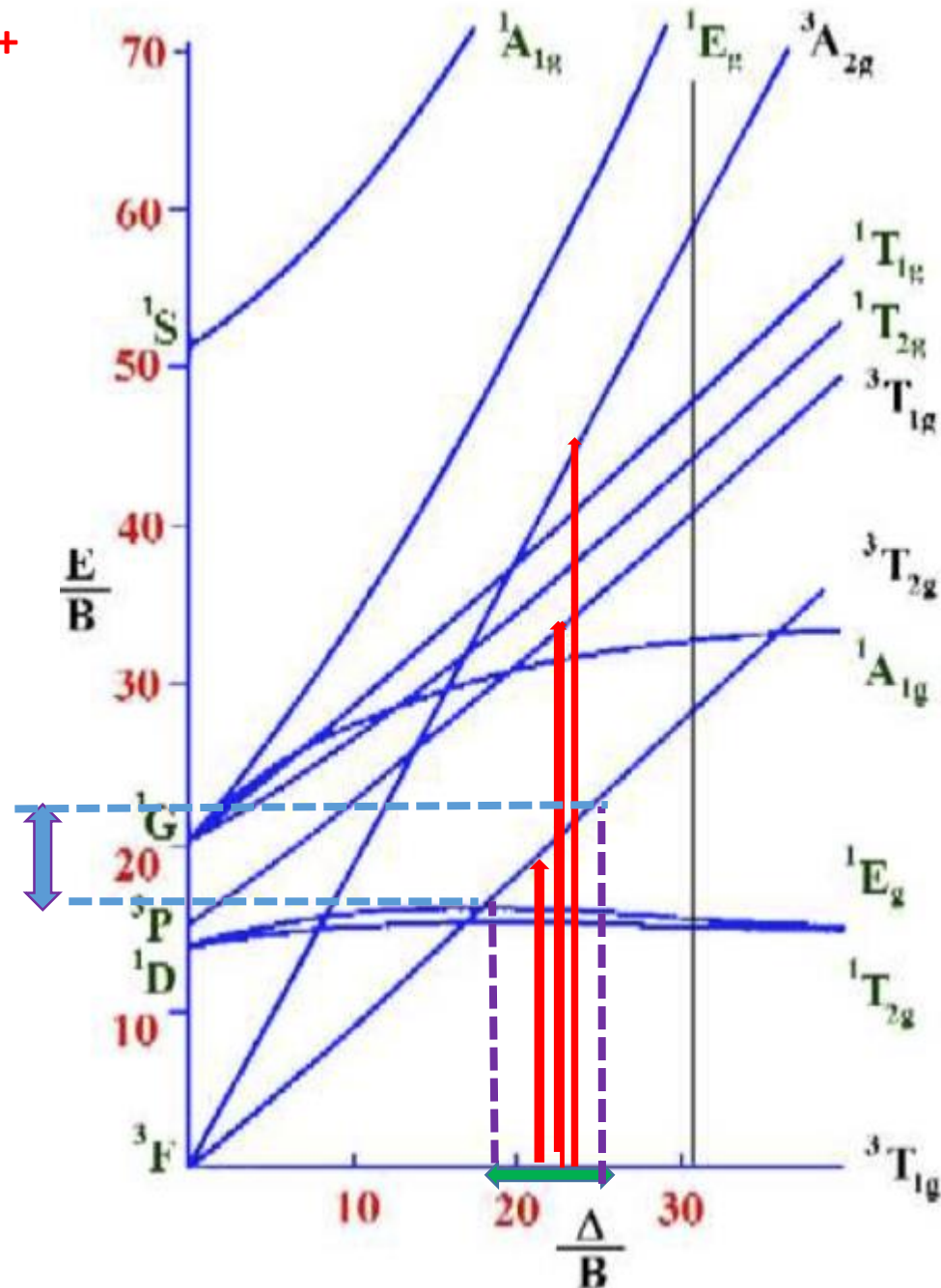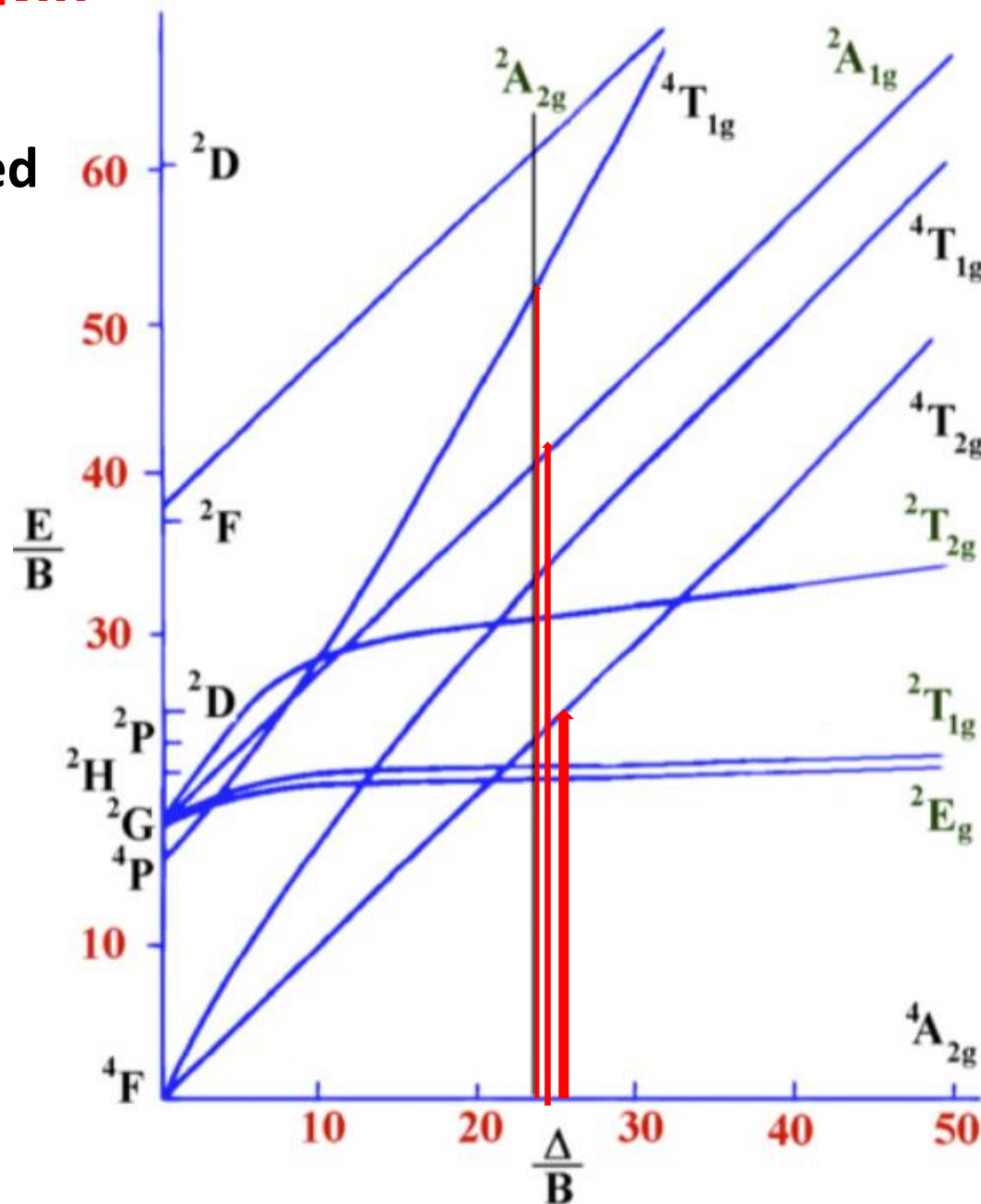
Fig. 1. Polarized absorption spectra of $Cs_3VCl_2(H_2O)_4$ at 80 K [9].

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

Linewidths of the transitions ~ inclination in the TS-diagram

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

d³ **V²⁺ Cr³⁺ Mn⁴⁺**

Octahedral LF:
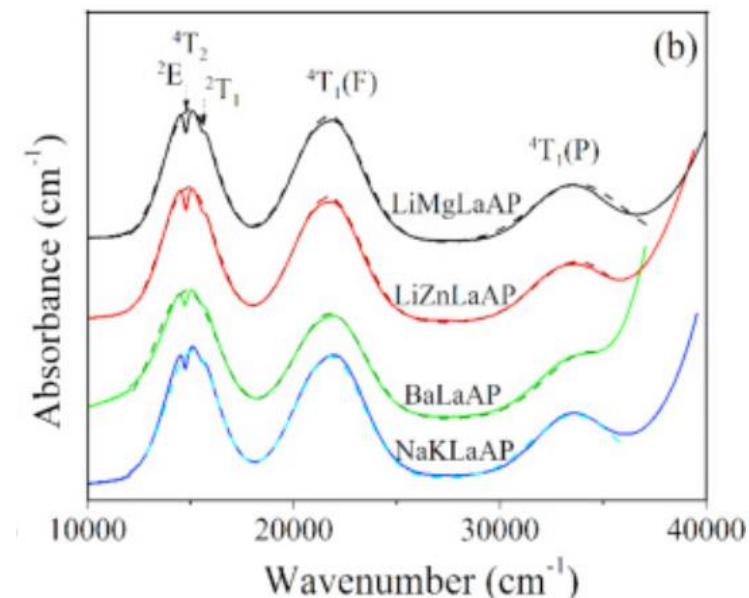**strongly preferred**
No J-T distortion

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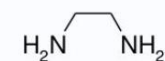

Cr³⁺ absorption in phosphate glasses

- **Spectrochemical Series: An order of ligand field strength based on experiment:**
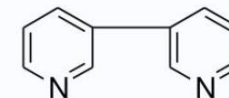
Weak Field I⁻ < Br⁻< S²⁻< SCN⁻< Cl⁻<
NO₃⁻< F⁻ < C₂O₄²⁻< H₂O< NCS⁻<
CH₃CN< NH₃< en < bipy< phen<
NO₂⁻< PPh₃< CN⁻< CO **Strong Field**

Ethylenediamine (en)   2,2'-bipyridine (bipy)   1.10 - penanthroline (phen)
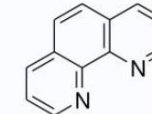
d⁴ d^4 | Cr²⁺ Mn³⁺ Cr^{2+} Mn^{3+}
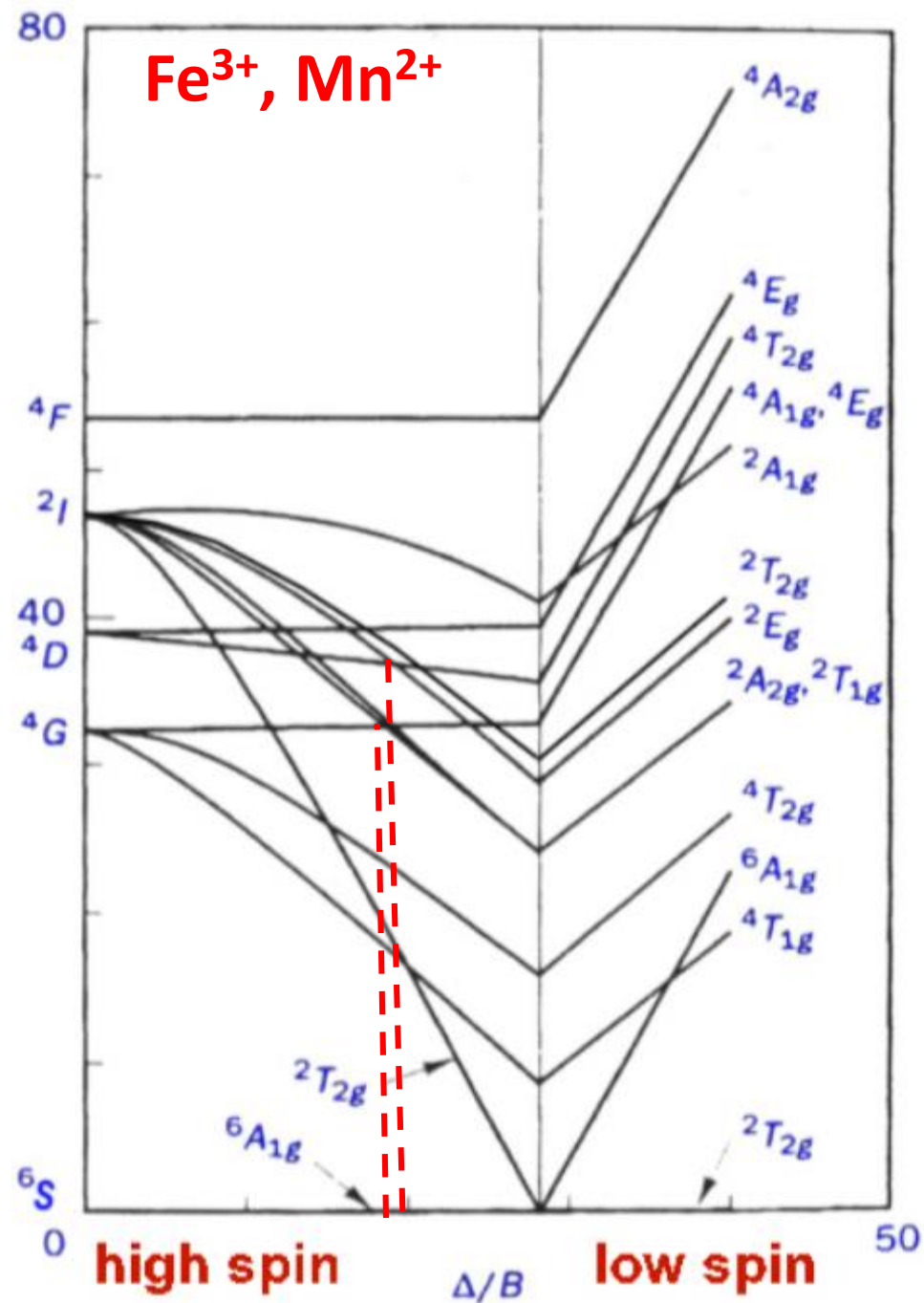
$^5E_g \rightarrow {}^5T_{2g}$

J-T distortion

high spin   low-spin
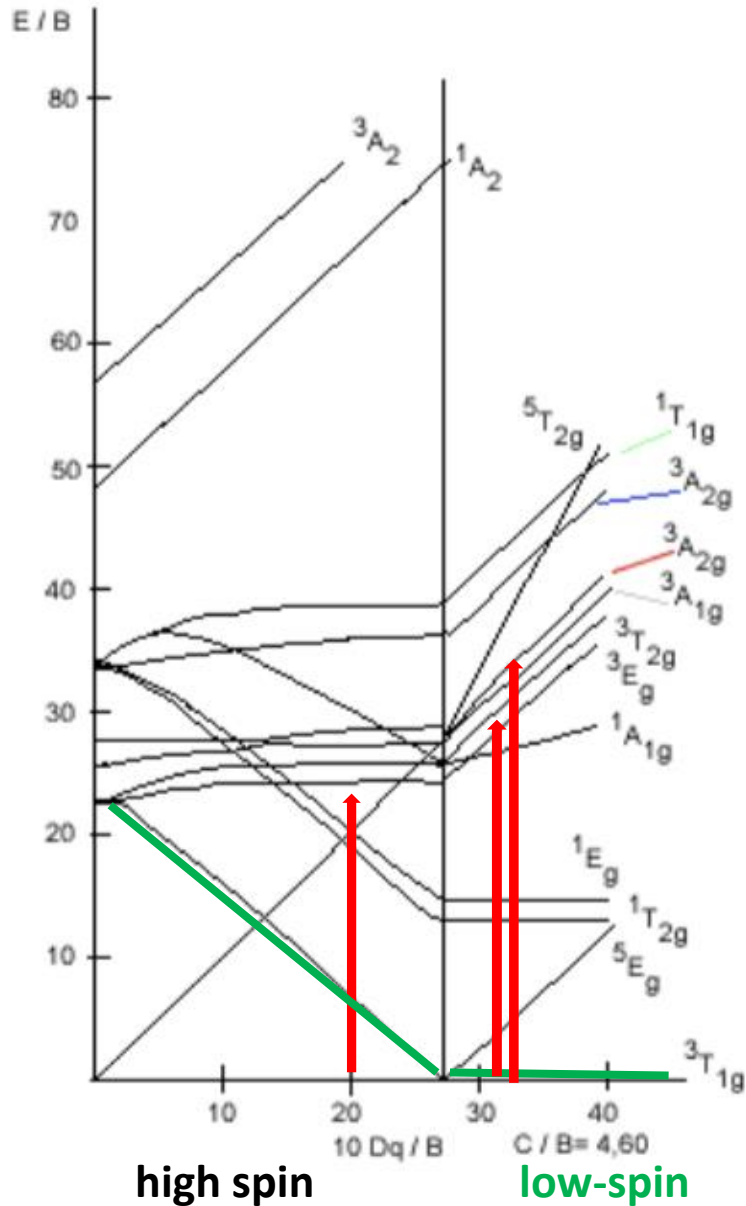
Absorption spectrum of Mn-containing phosphate glass

$T = 300K$

- - - - S7
.... S8
——— S9

Mn^{3+}

Mn^{2+}

O_2-atmosphere
N_2-atmosphere

d⁵

Fe^{3+}, Mn^{2+}

$^4A_{2g}$
^4E_g
$^4T_{2g}$
$^4A_{1g}$, ^4E_g
$^2A_{1g}$
$^2T_{2g}$
^2E_g
$^2A_{2g}$, $^2T_{1g}$
$^4T_{2g}$
$^6A_{1g}$
$^4T_{1g}$
$^2T_{2g}$
$^2T_{2g}$

^4F
^2I
^4D
^4G
^6S

$^6A_{1g}$
$^2T_{2g}$

high spin — low spin

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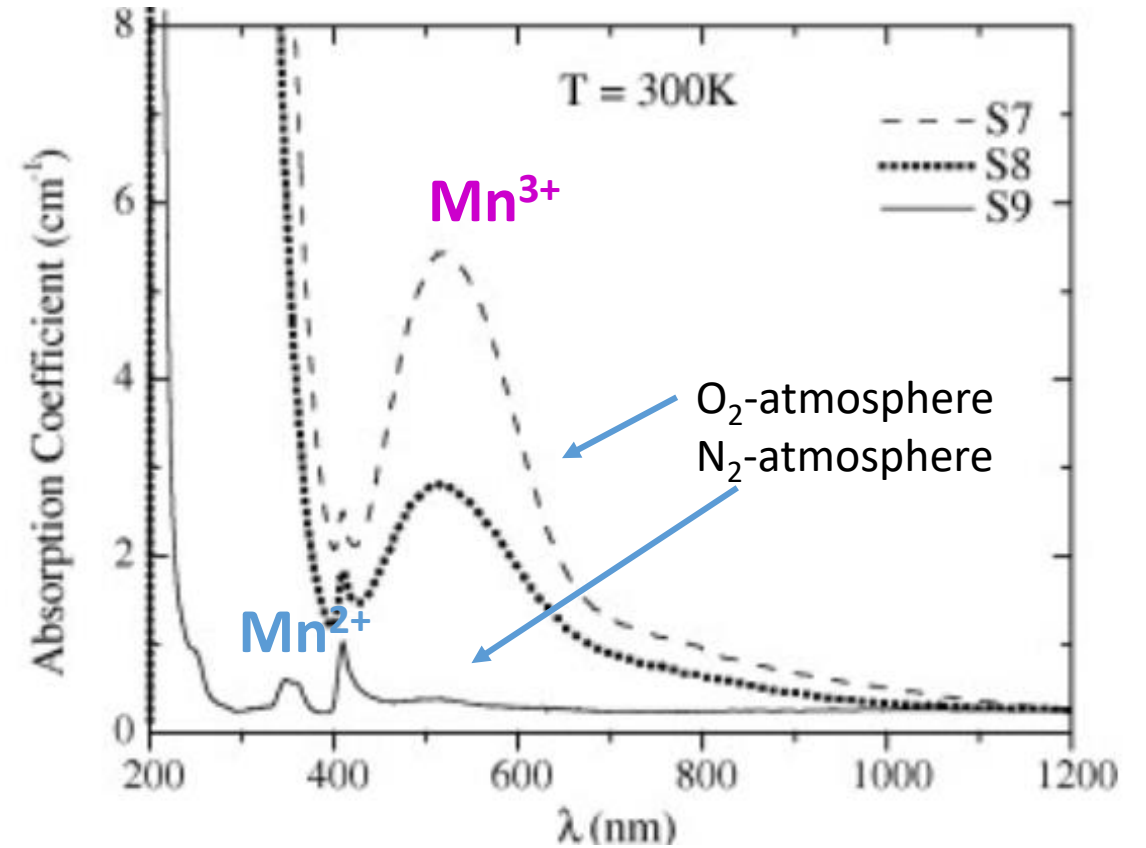
High-spin ground state $^6A_{1g}$:
No spin-allowed transitions
Weak forbidden transitions
Mn^{2+} complexes are colorless

Molar absorptivity

$^4A_{1g}$ ^4E_g $\big\}$ (^4G)
$^4E_g(^4D)$
$^4T_{1g}(^4P)$
$^4T_{1g}(^4G)$
$^4T_{2g}(^4G)$
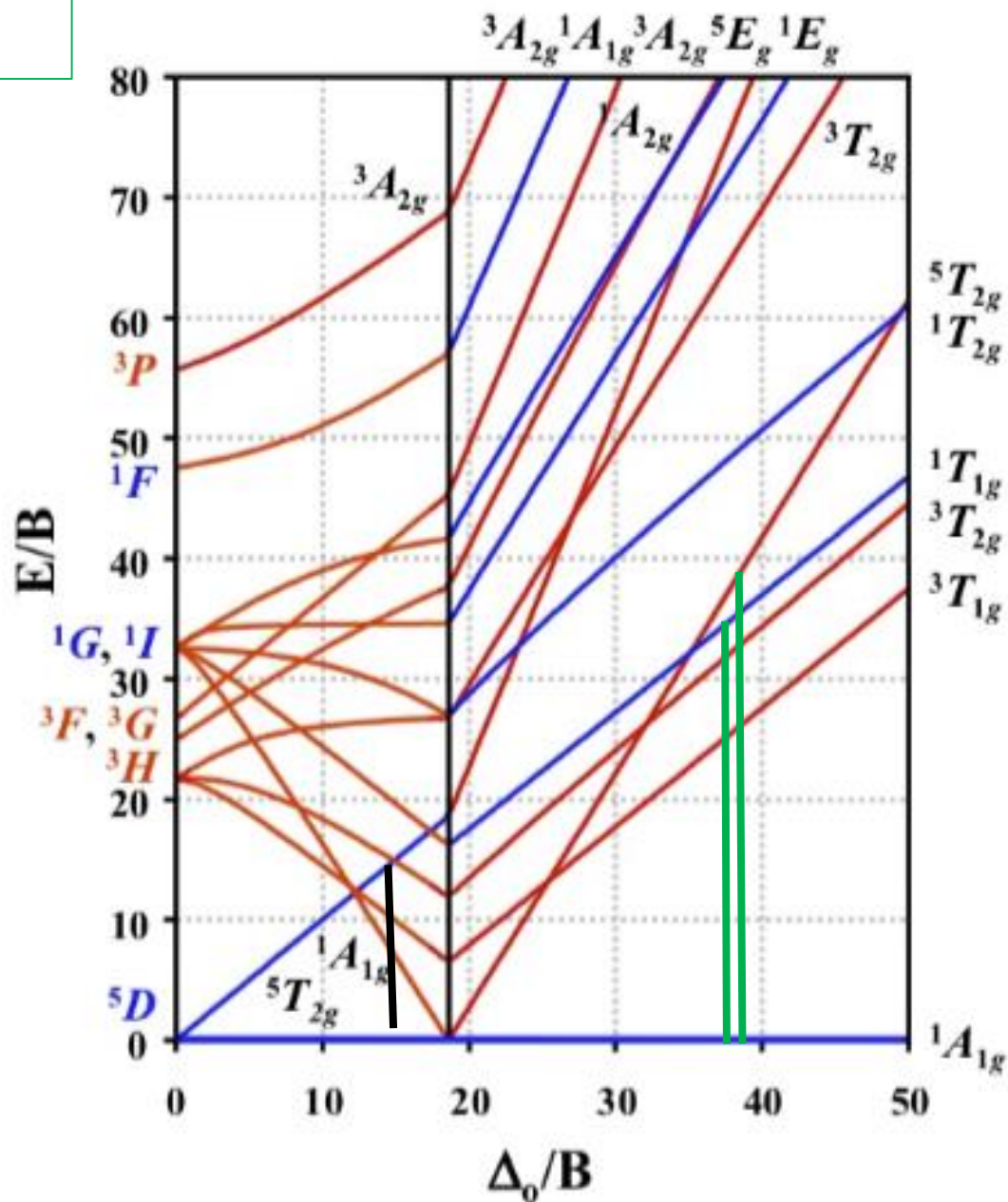$^4T_{2g}(^4D)$

$\bar{v}$ (cm^{-1} × 10^{-3})
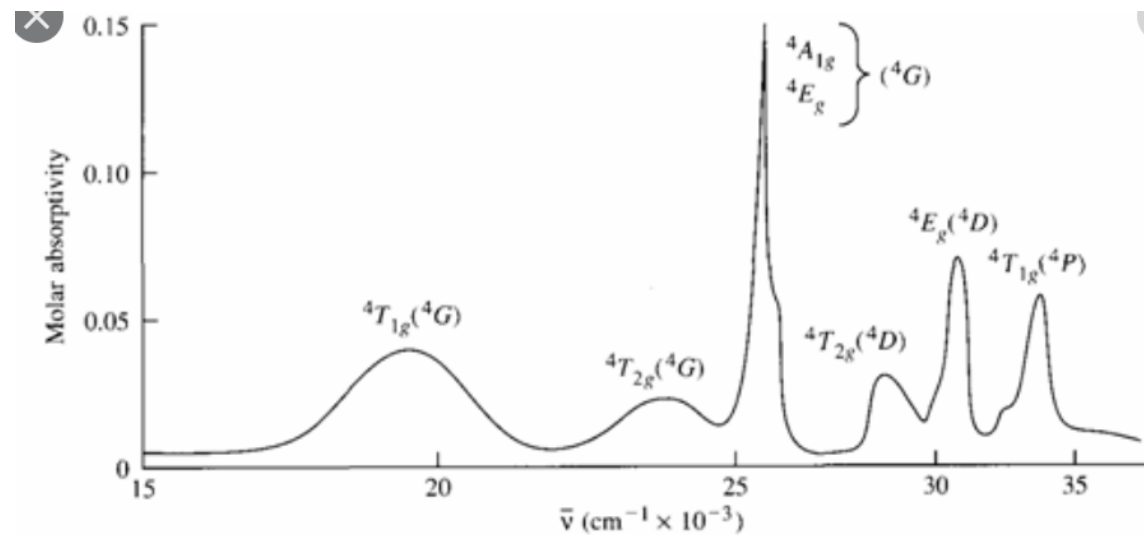
Fig. 11.41 Absorption spectrum for octahedral MnF$_2$. Note the narrow lines. [From Lever, A. B. P. *Inorganic Electronic Spectroscopy*; 2nd ed.; Elsevier: New York, 1986; p 451. Used with permission.]

d⁶

d^6

Fe²⁺, Co³⁺

High-spin: $^5T_{2g} \rightarrow {}^5E_g$ J-T effect
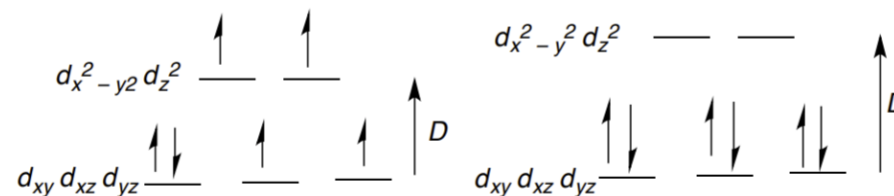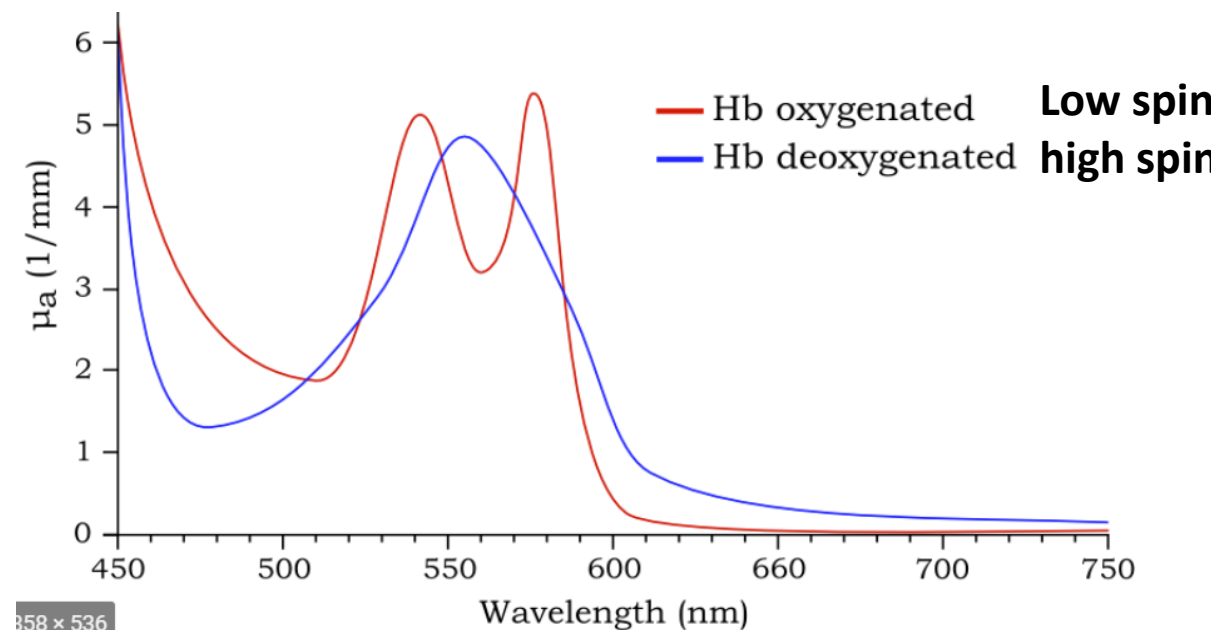
Low-spin: $^1A_{1g} \rightarrow {}^1T_{1g}$ No J-T effect

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

Spin Transition in hemoglobin upon binding to O₂

Low spin

high spin

d⁷ Co²⁺

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

E/B

^2F
^2G
^4P
^4F

$^4T_{2g}$
$^2T_{2g}$
$^2T_{1g}$
$^4T_{1g}$
$^4T_{1g}$
$^2T_{2g}$

Δ_o/B

Spectrochim. Acta 188 (2018), 507
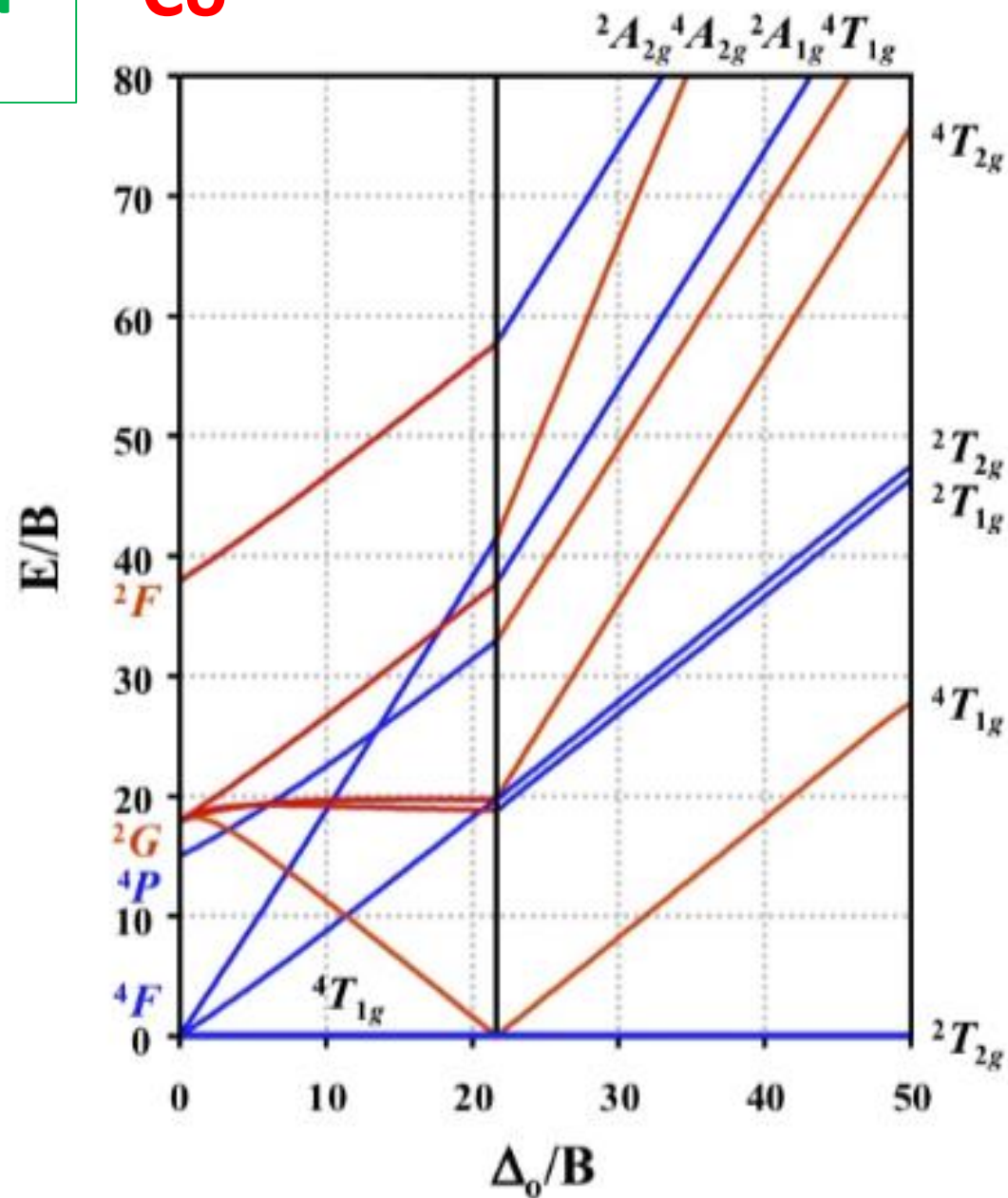
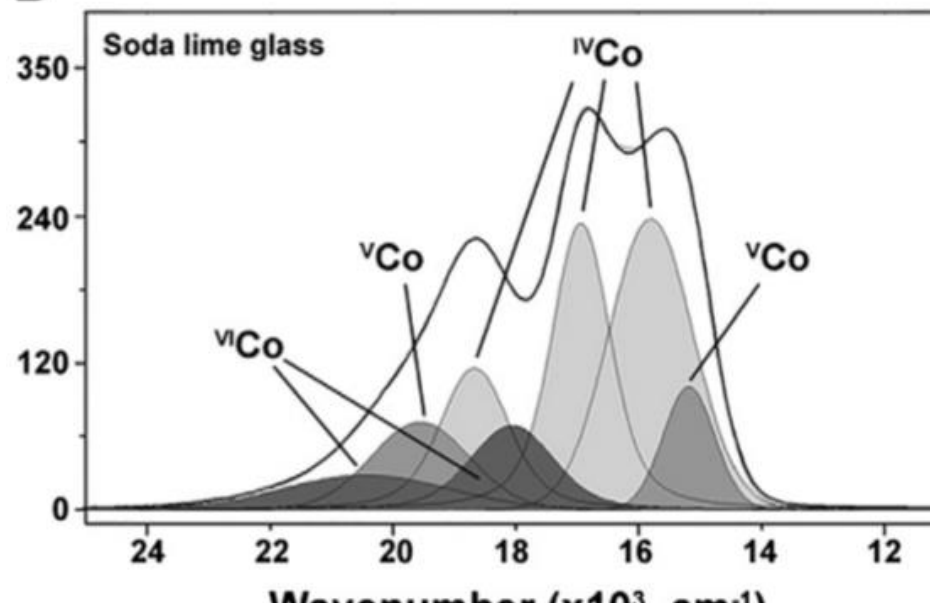**Co²⁺ in glasses: metal in tetrahedral and octahedral Coordination. Tetrahedral coordination gives rise to Intense blue color of Co in glasses.**

Table 1

Optical transitions of Co2+ 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_η	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

Soda lime glass

^{IV}Co
$^V Co$
$^V Co$
^{VI}Co

d⁸ — Ni^{2+}

Octahedral LF:

$^3A_{2g} \rightarrow\ ^3T_{2g}$ $^3A_{2g} \rightarrow\ ^3T_{1g}$ $^3A_{2g} \rightarrow\ ^3T_{1g}$
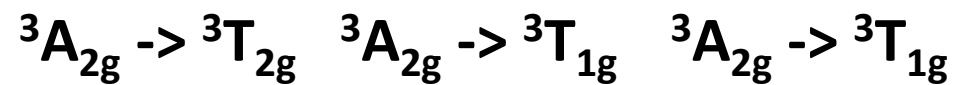
No J-T distortions
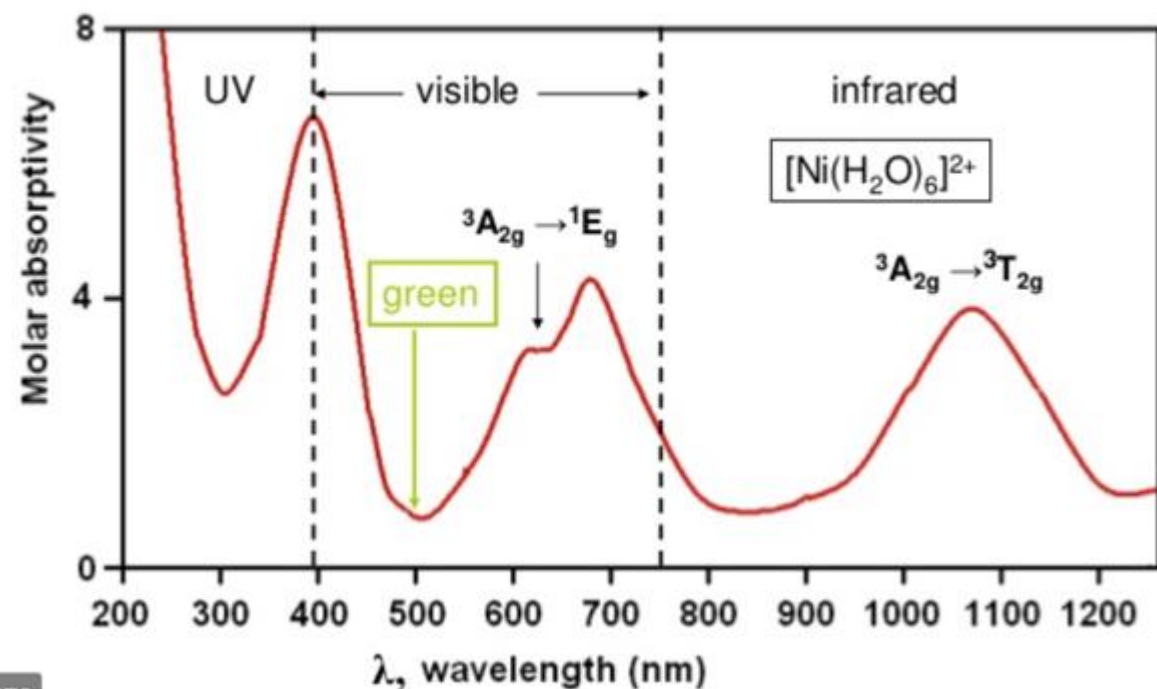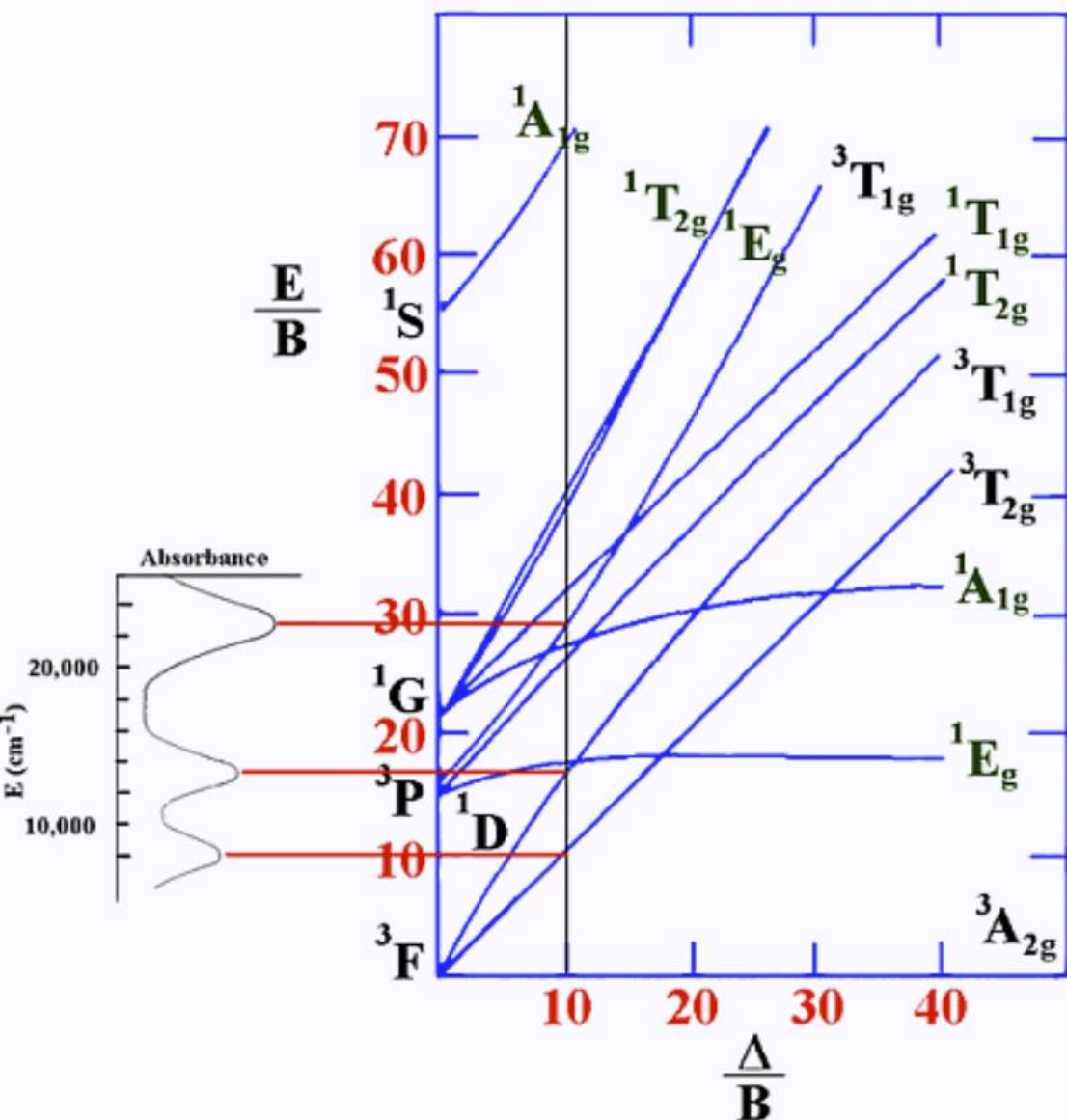
Table 2. Δ_o Values for Ni(II) Complexes: $[NiL_n]$

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^- < $ diethyldithio-carbamate$^-$ (**S**) $< OH^- < C_2O_4^{2-} < H_2O < SCN^-$ $< NH_3 \approx$ pyridine (**N**) $<$ ethylenediamine (**N**) $< NO_2^- \approx$ 2,2'-bipyridine (**N**) $<<$ **CN**$^-$

J.Chem. Ed. 75 (1998), 98

d⁹ **Cu²⁺**

$$^2T_{2g} \rightarrow {}^2E_g \quad \text{tetrahedral}$$
$$^2E \rightarrow {}^2T_2 \quad \text{octahedral}$$
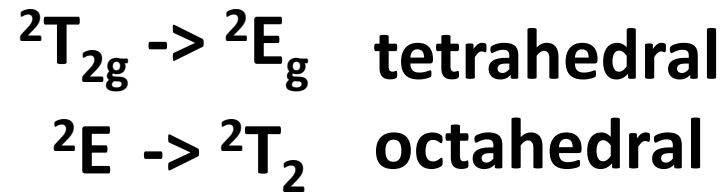
Very strong Jahn-Teller effects from
Octahedral coordination:

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)
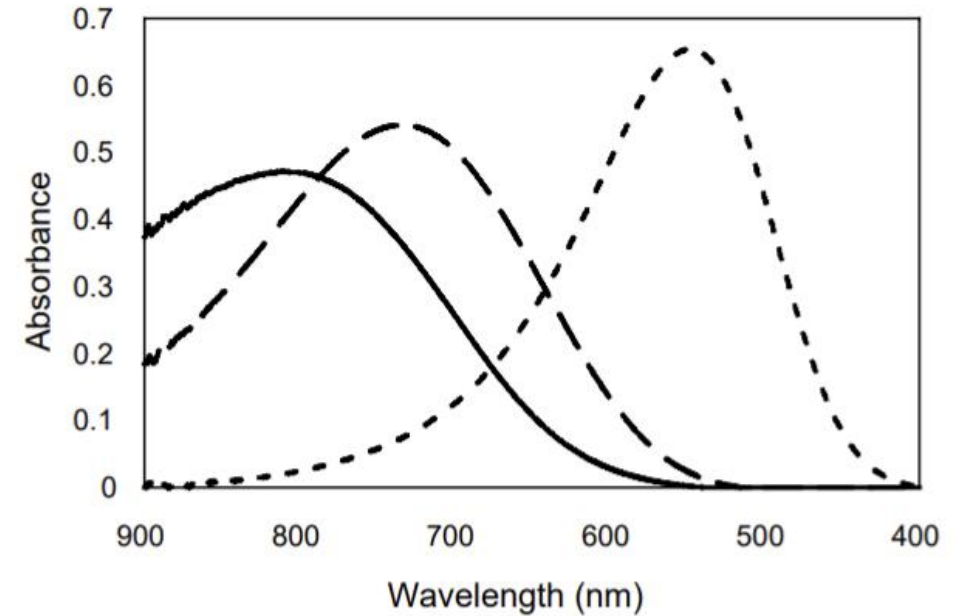
Band position very sensitive to ligands.

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

Ti^{3+} (d^1)
0.143 M $TiCl_3$

(F)

V^{3+} (d^2)
0.0472 M $V(ClO_4)_3/HClO_4$

Cr^{3+} (d^3)
0.00145 M $Cr(BF_4)_3$

(B)

Cr^{2+} (d^4)
0.10 M in 0.75 M H_2SO_4

Fe^{2+} (d^6)
0.077 M $Fe(ClO_4)_2$

(D)

Mn^{2+} (d^5)
0.36 M $Mn(ClO_4)_2$

Ni^{2+} (d^8)
0.0025 M $Ni(ClO_4)_2$

(H)

Cu^{2+} (d^9)
0.0030 M $Cu(ClO_4)_2$