

Other Crystal Fields

- We can deduce the CFT splitting of d orbitals in virtually any ligand field by
 - Noting the direct product listings in the appropriate character table to determine the ways in which the d orbital degeneracies are lifted
 - Carrying out an analysis of the metal-ligand interelectronic repulsions produced by the complex's geometry.
- Sometimes useful to begin with either the octahedral or tetrahedral results and consider the effects brought about by distorting the perfect geometry to bring about the new configuration.
 - The results for the perfect and distorted geometries can be correlated through descent in symmetry, using the appropriate correlation tables.
 - Can take this approach with distortions produced by ligand substitution or by intermolecular associations, if descent in symmetry involves a group-subgroup relationship.

Jahn-Teller Theorem

A Fundamental Cause of Distortion

- The Jahn-Teller theorem requires that *for any nonlinear molecular system in a degenerate electronic state a distortion will occur so as to lower the symmetry and remove the degeneracy.*
 - The theorem does not predict the exact nature of the distortion.
 - However, *if the system is centrosymmetric, inversion symmetry will be preserved.*
- A Jahn-Teller distortion results in partial or complete lifting of the degeneracies among some orbitals.
 - In so doing, electrons may occupy lower-energy orbitals, resulting in a lower overall energy state for the system.
 - The “perfect” geometries really cannot exist as stable species for certain electronic configurations, since the distorted molecule is the energetically preferred structure.
 - ☞ Describing certain complexes as octahedral, tetrahedral, or square planar is often really an approximation of their true structure.

Degenerate and Non-degenerate d^n Ground States

- ☞ Only non-degenerate states are immune to Jahn-Teller Distortion.

Degeneracy	d^n Configuration	$t_{2g}e_g$ Configuration
Triply degenerate	d^1	t_{2g}^1
	d^2	t_{2g}^2
	d^4 low spin	t_{2g}^4
	d^5 low spin	t_{2g}^5
	d^6 high spin	$t_{2g}^4 e_g^2$
	d^7 high spin	$t_{2g}^5 e_g^2$
Doubly degenerate	d^4 high spin	$t_{2g}^3 e_g^1$
	d^7 low spin	$t_{2g}^6 e_g^1$
	d^9	$t_{2g}^6 e_g^3$
Non-degenerate	d^3	t_{2g}^3
	d^5 high spin	$t_{2g}^3 e_g^2$
	d^6 low spin	t_{2g}^6
	d^8	$t_{2g}^6 e_g^2$
	d^{10}	$t_{2g}^6 e_g^4$

Strong and Weak Jahn Teller Distortions of ML_6

- Distortions will be more pronounced for the doubly degenerate configurations, which have an imbalance in the filling of the e_g level.
- Lesser distortions result from triply degenerate states, which have an imbalance in the distribution among t_{2g} orbitals.
- The difference can be understood by considering shielding effects and the orientations of the t_{2g} and e_g orbitals.

Shielding Effects and Distortion for d^9

$$d^9 = t_{2g}^6 e_g^3 = t_{2g}^6 [(d_{x^2-y^2})^2 (d_{z^2})^1] \text{ and } t_{2g}^6 [(d_{x^2-y^2})^1 (d_{z^2})^2]$$

- $t_{2g}^6 [(d_{x^2-y^2})^2 (d_{z^2})^1]$: The pair of electrons in the $d_{x^2-y^2}$ orbital would more effectively shield ligands in the xy plane from the metal ion's charge than the single electron in the d_{z^2} orbital would shield ligands along the z axis.
 - If this were to occur, the ligands along z would be **more strongly** attracted to the central metal ion and their M-L bond lengths would be **shortened** relative to those in the xy plane.
- $t_{2g}^6 [(d_{x^2-y^2})^1 (d_{z^2})^2]$: The single electron in the $d_{x^2-y^2}$ orbital would less effectively shield ligands in the xy plane from the metal ion's charge than the pair of electrons in the d_{z^2} orbital would shield ligands along the z axis.
 - If this were to occur, the ligands along z would be **less strongly** attracted to the central metal ion and their M-L bond lengths would be **lengthened** relative to those in the xy plane.

☞ **Can't tell which distortion will occur.**

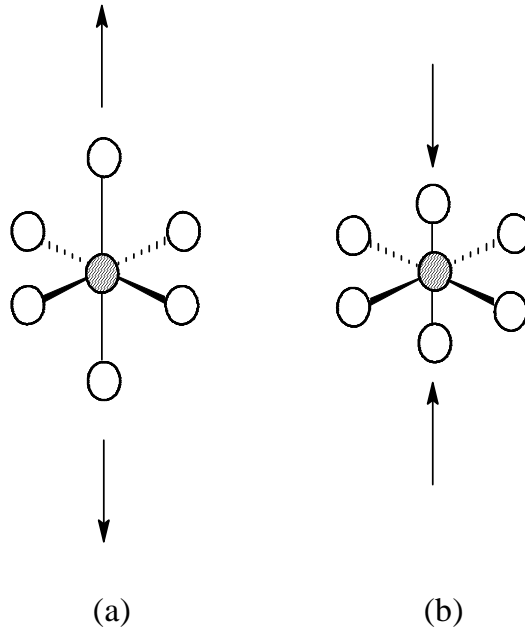
- Shielding effects are less pronounced for triply degenerate configurations, because the orbitals' lobes are oriented between the ligands.
 - Thus, the resulting distortions are not as severe.

Tetragonal Distortion

- Although the exact nature of the resulting distortion cannot be predicted from the Jahn-Teller theorem, the foregoing analysis of the d^9 case suggests that a *tetragonal distortion* might result.
 - A tetragonal distortion to an octahedron results from any change in geometry that preserves a C_4 axis.
 - Tetragonal distortion occurs whenever two *trans* related ligands are differentiated from the remaining four.
- Jahn-Teller tetragonal distortions must result in a centrosymmetric group (e.g., D_{4h}).
- Tetragonal distortions to non-centrosymmetric groups (e.g., C_{4v}) are possible, but not by the Jahn-Teller effect.

Jahn-Teller Tetragonal Distortions

- A tetragonal distortion would occur if the M-L bonds of two ligands lying along the z axis were either stretched or compressed equally while maintaining equivalence among the four remaining ligands in the xy plane.



- By either process, the symmetry would descend from O_h to D_{4h} .
 - The descent in symmetry causes a partial lifting of the degeneracies among the d orbitals in the octahedral field.

Splitting of d Orbital Degeneracies – $O_h \rightarrow D_{4h}$

- From the correlation table that links the groups O_h and D_{4h} (Appendix B) we see that the two e_g orbitals of the octahedral field become nondegenerate as a_{1g} and b_{1g} in the tetragonal field.
- From the direct product listings in the D_{4h} character table (Appendix A) we see

$$a_{1g} = d_{2z^2-x^2-y^2} (= d_{z^2})$$
$$b_{1g} = d_{x^2-y^2}$$

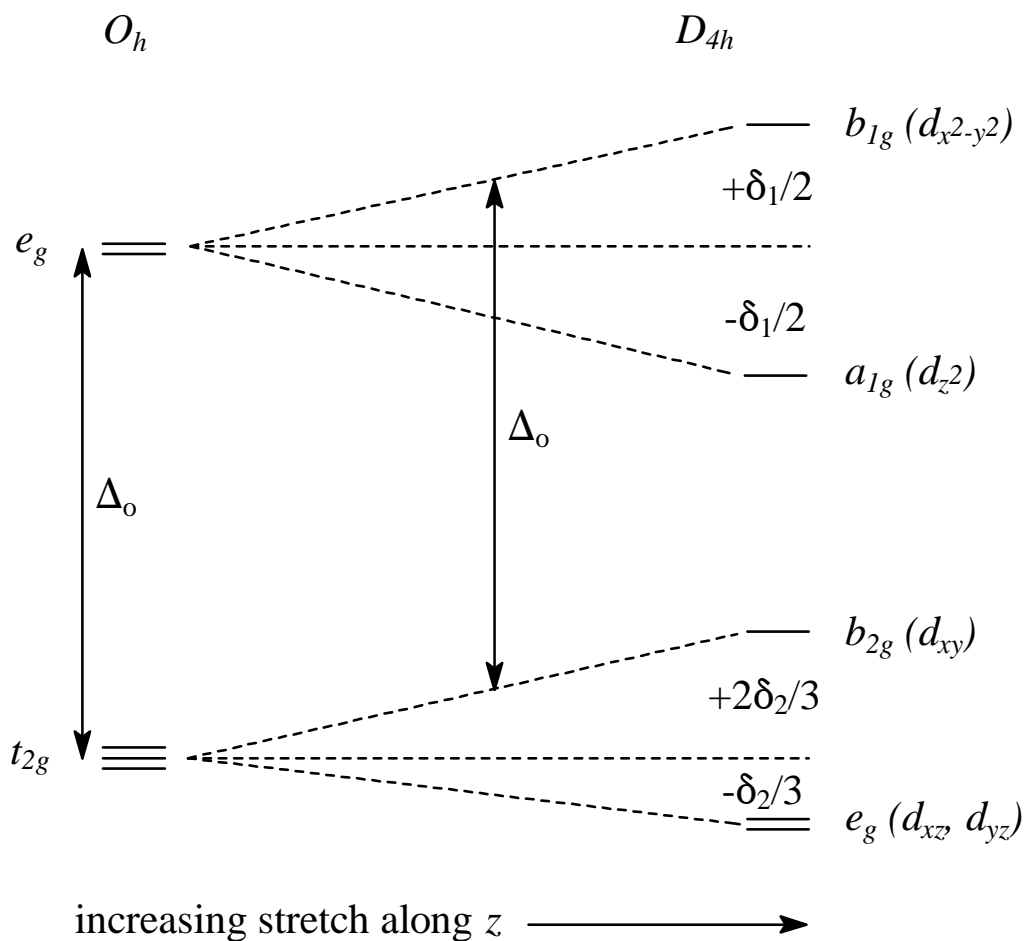
- From the correlation table we also see that the degeneracy among the t_{2g} orbitals in O_h is partially lifted to become b_{2g} and e_g in the D_{4h} tetragonal field.
- From the direct product listings in the D_{4h} character table we see

$$b_{2g} = d_{xy}$$
$$e_g = (d_{xz} \text{ and } d_{yz})$$

Relative Energies of d Orbitals in D_{4h}

- The relative energy ordering of the orbitals depends on the direction and magnitude of the tetragonal distortion.
- A distortion in which the two M-L bonds along z are progressively stretched is an interesting case to consider, because at its limit the two ligands would be removed, resulting in a square planar ML_4 complex.
- Moving the two ligands away from the central metal ion lowers the repulsions between ligand electrons and the metal electrons in d orbitals that have substantial electron distribution along z .
 - Thus the energies of the d_{xz} , d_{yz} , and d_{z^2} orbitals are lowered.
- If we assume that the stretch along z is accompanied by a counterbalancing contraction in the xy plane, so as to maintain the overall energy of the system, then the orbitals with substantial electron distribution in the xy plane will experience increased repulsions.
 - Thus, the d_{xy} and $d_{x^2-y^2}$ orbitals rise in energy.

Orbital Splitting from Stretching Tetragonal Distortion



- The upper e_g orbitals of the perfect octahedron split equally by an amount δ_1 , with the $d_{x^2-y^2}$ orbital (b_{1g} in D_{4h}) rising by $+\delta_1/2$ and the d_{z^2} orbital (a_{1g} in D_{4h}) falling by $-\delta_1/2$.
- The lower t_{2g} orbitals of the perfect octahedron split by an amount δ_2 , with the d_{xy} orbital (b_{2g} in D_{4h}) rising by $+2\delta_2/3$, and the degenerate d_{xz} and d_{yz} orbitals (e_g in D_{4h}) falling by $-\delta_2/3$.

Magnitudes of the δ_1 and δ_2 Splittings

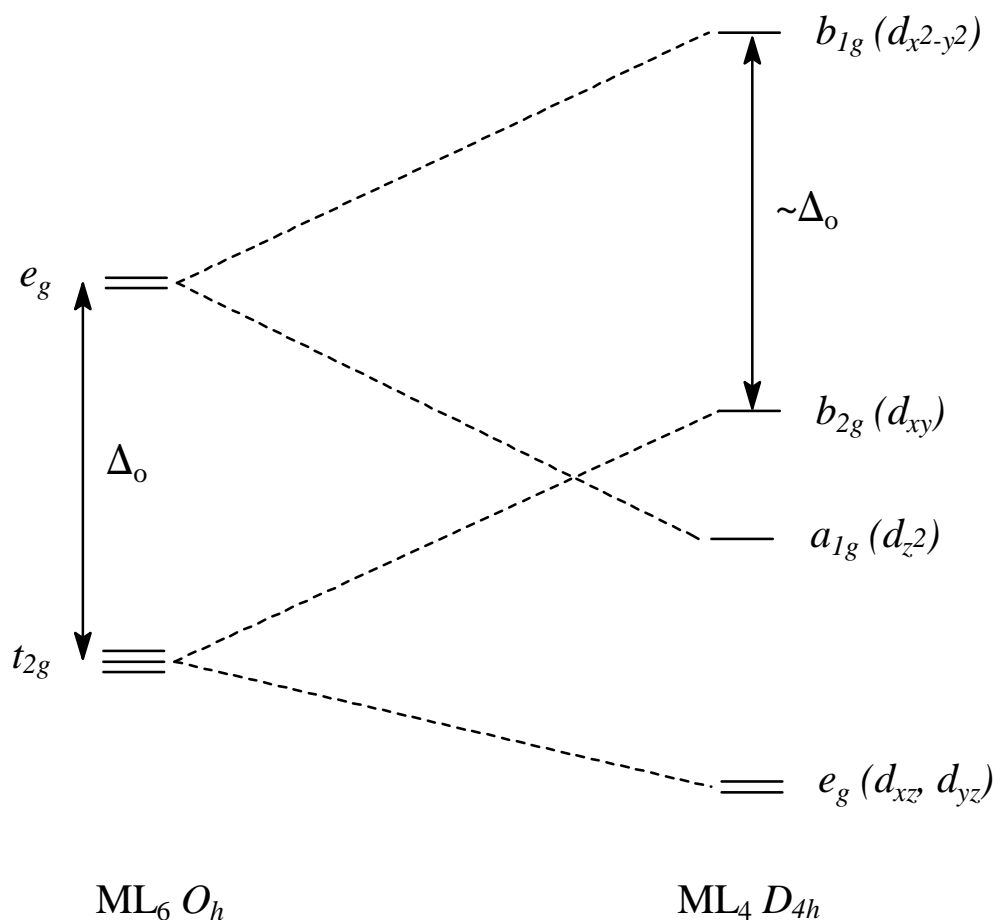
- Both the δ_1 and δ_2 splittings, which are very small compared to Δ_o , maintain the barycenters defined by the e_g and t_{2g} levels of the undistorted octahedron.
 - The energy gap δ_1 is larger than that of δ_2 , because the $d_{x^2-y^2}$ and d_{z^2} orbitals are directed at ligands.
 - The distortion has the same effect on the energies of both the $d_{x^2-y^2}$ and d_{xy} orbitals; i.e. $\delta_1/2 = 2\delta_2/3$.
 - ☞ As a result, their energies rise in parallel, maintaining a separation equal to the Δ_o of the undistorted octahedral field.

Tetragonal Compression Jahn-Teller Distortion

- If we carry out the opposite tetragonal distortion (compression along z), the octahedral degeneracies will be lifted in the same manner, as required by symmetry, but the ordering of the orbitals across both the δ_1 and δ_2 gaps will be reversed.
 - The energy of the $d_{x^2-y^2}$ orbital (b_{1g}) will fall by $-\delta_1/2$, and the energy of the orbital d_{z^2} (a_{1g}) will rise by $+\delta_1/2$.
 - The energy of the d_{xy} (b_{2g}) orbital will fall by $-2\delta_2/3$, and the energy of the d_{xz} and d_{yz} (e_g) orbitals will rise by $+\delta_2/3$.
- In this case, the energy of the d_{xy} (b_{2g}) and $d_{x^2-y^2}$ (b_{1g}) orbitals will fall equally with increasing compression along z (i.e., $-\delta_1/2 = -2\delta_2/3$), maintaining a separation equal to Δ_o .

Square Planar ML_4 Complexes

- If we imagine continuing the stretching of M-L bonds along z , the orbital splittings will become progressively greater, producing successively larger values of δ_1 and δ_2 .
- Eventually the two ligands will be removed, resulting in a square planar ML_4 complex.
- At some point before this extreme the a_{1g} (d_{z^2}) level may cross and fall below the b_{2g} (d_{xy}) level, resulting in the following splitting scheme.¹



¹The ordering of the lower four d orbitals probably varies among square planar complexes and has been the subject of much debate. See A. B. P. Lever, *Inorganic Electron Spectroscopy*, 2nd ed., Elsevier, Amsterdam, 1984, p. 537ff. and references therein.

ML₄ (D_{4h}) vs. ML₄ (T_d)

- Most square planar complexes are d^8 and less often d^9 .
- In virtually all d^8 cases a low spin configuration is observed, leaving the upper b_{1g} ($d_{x^2-y^2}$) level vacant in the ground state.
 - This is expected, because square planar geometry in first-row transition metal ions is usually forced by strong field ligands.
 - Strong field ligands produce a large Δ_o value.
 - The energy gap between the b_{2g} (d_{xy}) and b_{1g} ($d_{x^2-y^2}$) levels is equivalent to Δ_o .
 - ☞ A large Δ_o value favors pairing in the b_{2g} (d_{xy}) level, a low-spin diamagnetic configuration for d^8 .
- Tetrahedral d^8 is a high-spin paramagnetic configuration $e^4t_2^4$.
 - ☞ ML₄ (D_{4h}) and ML₄ (T_d) can be distinguished by magnetic susceptibility measurements.
- Ni²⁺ ion tends to form square planar, diamagnetic complexes with strong-field ligands (e.g., [Ni(CN)₄]²⁻), but tends to form tetrahedral, paramagnetic complexes with the weaker-field ligands (e.g., [NiCl₄]²⁻).
- With second and third row transition metal ions the Δ_o energies are inherently larger, and square planar geometry can occur even with relatively weak field ligands (e.g., square planar [PtCl₄]²⁻).