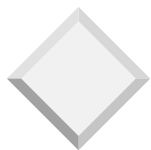## Electronic-Vibrational Coupling

---

Colors of Co(III) solutions

Solutions are ordered according to the ligand spectrochemical series: (a) CN^-, (b) NO_2^-, (c) phen, (d) en, (e) NH_3, (f) gly, (g) H_2O, (h) ox^{2-}, (i) CO_3^{2-}.

Vibronic Coupling

★ Because they have $g-g$ character, the $d\text{-}d$ transitions of complexes of the transition metals are "forbidden" (LaPorte forbidden).

★ Complexes with noncentrosymmetric coordination geometries (e.g., tetrahedral) have more intense $d\text{-}d$ spectra.

★ Spectra in centrosymmetric (e.g., octahedral) complexes "acquire intensity" via <u>vibronic coupling</u>.

The total molecular wavefunction can usually be approximated as a product of electronic, vibrational, and rotational parts:

$$\mathcal{H}\,\Psi$$

It is good first approximation to assume that electronic, vibrational, and rotational motion can be separated:

$$\mathcal{H} \approx \mathcal{H}_{elec.} + \mathcal{H}_{vib.} + \mathcal{H}_{rot.}$$

In this approximation, the wavefunction is a product:

$$\Psi = \psi_{elec.}\psi_{vib.}\psi_{rot.}$$

$$\mathcal{H}\,\Psi = \psi_{vib.}\psi_{rot.}\left(\mathcal{H}_{elec.}\psi_{elec.}\right) +$$

$$+\psi_{elec.}\psi_{rot.}\left(\mathcal{H}_{vib.}\psi_{vib.}\right) + \psi_{elec.}\psi_{vib.}\left(\mathcal{H}_{rot.}\psi_{rot.}\right)$$

$$\mathcal{H}\,\Psi = \left(E_{elec.} + E_{vib.} + E_{rot.}\right)\Psi$$

However, the "separability" is not exact.

More accurately, $\mathcal{H} \approx \mathcal{H}_{elec.} + \mathcal{H}_{vib.} + \mathcal{H}_{rot.} + \mathcal{H}_{elec\text{-}vib}$

Including the effects of coupling demands a modified wavefunction. In the simplest approximation, $\psi_{elec.}$ and $\psi_{vib.}$ not separable.

$\therefore$ Consider the product, $\psi_{elec.}\psi_{vib.}$, for examining selection rules:

$$\int \psi_{elec.}^{gnd}\psi_{vib.}^{gnd}\,\hat{\mathbf{d}}\,\psi_{elec.}^{ex}\psi_{vib.}^{ex}\,d\tau \overset{?}{=} 0$$

$\psi_{vib.}^{gnd}$ generally belongs to totally symmetric rep. (otherwise, "hot bands" are involved). $\therefore$ consider,

$$\int \psi_{elec.}^{gnd}\,\hat{\mathbf{d}}\,\psi_{elec.}^{ex}\psi_{vib.}^{ex}\,d\tau \overset{?}{=} 0$$

Vibronic Coupling in [trans-Co(en)$_2$Cl$_2$]$^+$

- Spectra: Fig. 9.13 in Cotton - (solution spectrum is nearly indistinguishable from [*trans*-Co(NH$_3$)$_4$Cl$_2$]$^+$)
- Virtual D$_{4h}$ symmetry, d^6, low-spin
- In approximate O$_h$ symmetry, ground state configuration is $(t_{2g})^6$, $^1A_{1g}$ state.
- Dipole allowed transitions? Lowest energy singlets? See Tanabe-Sugano diagram.
- O$_h$ to D$_{4h}$ correlations?
- Vibrations of the [*trans*-CoCl$_2$N$_4$] grouping

D_{4h}	E	$2C_4$	$C_2(C_4^2)$	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
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	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	

Dichroism of [trans-CoCl$_2$(en)$_2$]$^+$
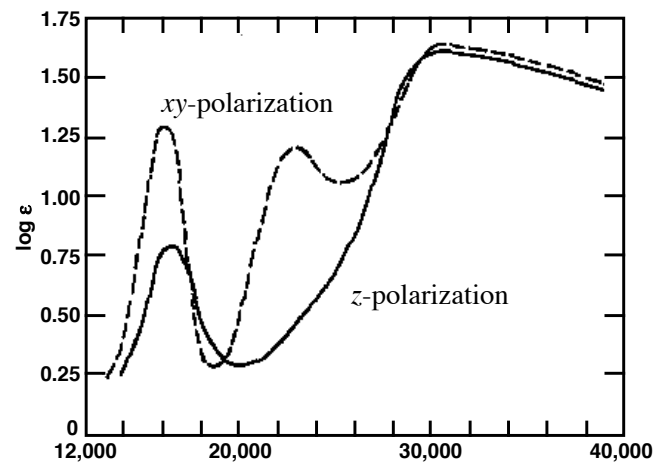
Fig. 9.13 in Cotton

Qualitative MO Diagram

z
y
x

L_6
L_4
L_1—M—L_3
L_2
L_5

(replace L_5 and L_6 with X_1 and X_2)

X_1
L_4
L_1—M—L_3
L_2
X_2

X_1 and X_2 lower in the spectrochemical series and are weaker σ donors. Antibonding z^2 orbital pushed up less by antibonding interaction with the X ligands.
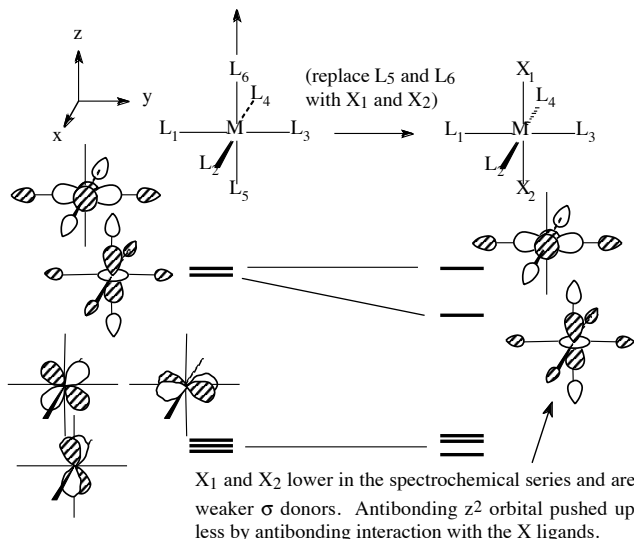
Configurations and States

b_{1g} $x^2 - y^2$

a_{1g} z^2

e_g (xz,yz)
b_{2g} xy

| A_{1g} | E_g | B_{2g} | E_g | A_{2g} |

$e_g \otimes a_{1g} = $ **E_g** $b_{2g} \otimes a_{1g} = $ **B_{2g}** $e_g \otimes b_{1g} = $ **E_g** $b_{2g} \otimes b_{1g} = $ **A_{2g}**
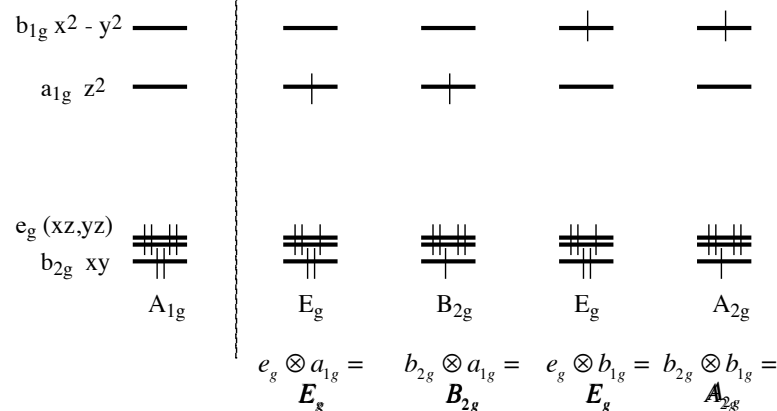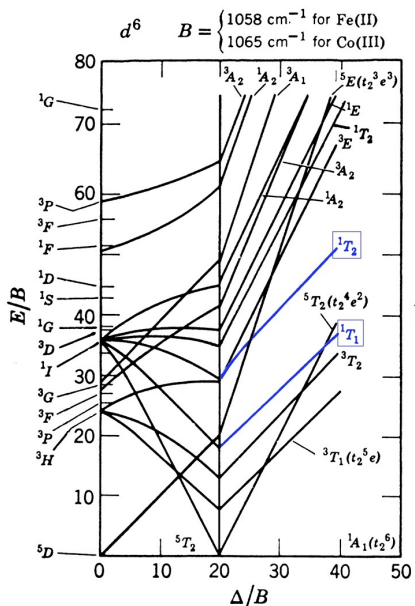
Tanabe-Sugano Diagram & State Symmetry Correlation

In O_h symmetry, two spin-allowed transitions are $^1A_{1g}$ to $^1T_{1g}$ and $^1T_{2g}$. When symmetry is lowered to D_{4h}, the excited states are split as:

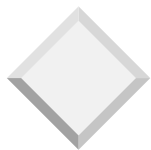$^1T_{1g} : {}^1A_{2g} + {}^1E_g$

$^1T_{2g} : {}^1B_{2g} + {}^1E_g$

d^6 $B = \begin{cases} 1058 \text{ cm}^{-1} \text{ for Fe(II)} \\ 1065 \text{ cm}^{-1} \text{ for Co(III)} \end{cases}$

Splitting of T_{1g} in O_h on lowering symmetry to D_{4h}

O	E	$8C_3$	$3C_2$ $(= C_4^2)$	$6C_4$	$6C_2$		
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		$(2z^2 - x^2 - y^2, x^2 - y^2)$
T_1	3	0	−1	1	−1	(R_x, R_y, R_z); (x, y, z)	
T_2	3	0	−1	−1	1		(xy, xz, yz)

D_4	E	$2C_4$	$C_2(C_4^2)$	$2C_2'$	$2C_2''$		
A_1	1	1	1	1	1		$x^2 + y^2, z^2$
A_2	1	1	1	−1	−1	z, R_z	
B_1	1	−1	1	1	−1		$x^2 - y^2$
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(x, y), (R_x, R_y)$	(xz, yz)
$T_1(O_h)$	3	1	−1	−1	−1		

Electronic Symmetries

	Electronic Transitions		
	$A_{1g} \to A_{1g}$	$A_{1g} \to B_{2g}$	$A_{1g} \to E_g$
$\psi_{elec.}^{gnd} z \, \psi_{elec.}^{ex}$			
$\psi_{elec.}^{gnd} (x,y) \psi_{elec.}^{ex}$			

D_{4h}	E	$2C_4$	$C_2(C_4^2)$	$2C_2'$	$2C_2''$	i	$2S_4$	σ_h	$2\sigma_v$	$2\sigma_d$		
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	R_z	
B_{1g}	1	−1	1	1	−1	1	−1	1	1	−1		x^2-y^2
B_{2g}	1	−1	1	−1	1	1	−1	1	−1	1		xy
E_g	2	0	−2	0	0	2	0	−2	0	0	(R_x, R_y)	(xz, yz)
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1		
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1	z	
B_{1u}	1	−1	1	1	−1	−1	1	−1	−1	1		
B_{2u}	1	−1	1	−1	1	−1	1	−1	1	−1		
E_u	2	0	−2	0	0	−2	0	2	0	0	(x, y)	
Γ_{all}	21	3	−3	−3	−1	−3	−1	5	5	3		
Γ_{t+r}	6	2	−2	−2	−2	0	0	0	0	0		
Γ_{vib}	15	1	−1	−1	1	−3	−1	5	5	3		

Vibrations of the *trans*-[CoCl$_2$N$_4$] group

– On p. 293 of Cotton's text, he gives
$2A_{1g}$, B_{1g}, B_{2g}, E_g, $2A_{2u}$, B_{1u}, $3E_u$

This should be
$2A_{1g}$, B_{1g}, B_{2g}, E_g, $2A_{2u}$, B_{2u}, $3E_u$

Allowedness w/ Vibronic Coupling

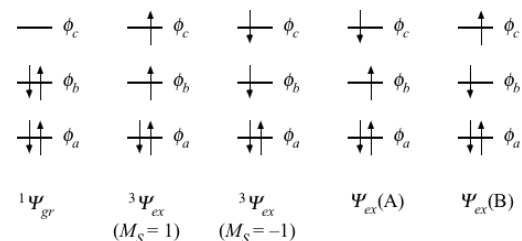| Electronic Transition	Polarization	
	z	(x,y)
$A_{1g} \to A_{2g}$	forbidden	allowed
$A_{1g} \to B_{2g}$	forbidden	allowed
$A_{1g} \to E_g$	allowed	allowed

Use info. with Qualitative Energy
Diagram to assign spectrum

Graphical Summary

O_h D_{4h}

- Because of the $O_h \rightarrow D_{4h}$ symmetry correlations, the specific configurations shown correspond to only the states shown - even in O_h.
- The dashed transitions are *dipole and vibronically forbidden* in z-polarization.
- The x,y-polarized transition at ~23,000 cm^{-1} is difficult to assign. The $^1B_{2g}$ state should be relatively favored by the weaker ligand field of the Cl ligands, but there is less e$^-$-e$^-$ repulsion in the $^1A_{2g}$ state.

$O_h: E(^1T_{2g}) - E(^1T_{1g}) = 16B \approx 17000 \text{ cm}^{-1}$
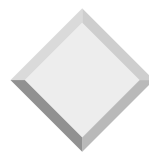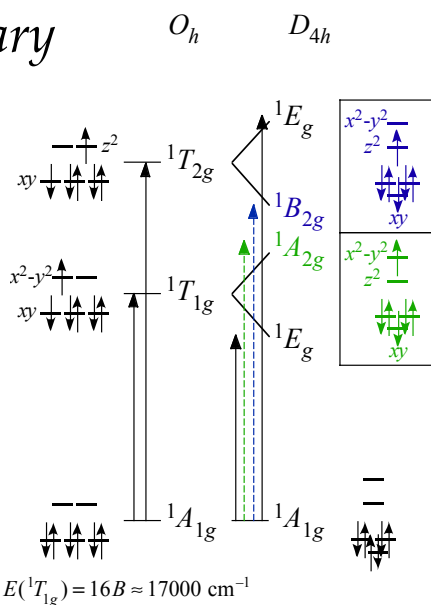
Graphical Tools for getting relative Energies of States

$^1\Psi_{gr}$ $^3\Psi_{ex}$ $^3\Psi_{ex}$ $\Psi_{ex}(A)$ $\Psi_{ex}(B)$
       $(M_S = 1)$ $(M_S = -1)$

$^3\Psi_{ex} = {}^1/_{\sqrt{2}}(\Psi_{ex}(A) + \Psi_{ex}(B))$
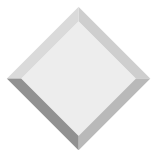$^1\Psi_{ex} = {}^1/_{\sqrt{2}}(\Psi_{ex}(A) - \Psi_{ex}(B))$
       $(M_S = 0)$

Energies of each configuration are given by counting the orbital energies, adding up the repulsions (J_{ij}) and subtracting the exchange "stabilizations" (K_{ij}) between like spins.

A Graphical Scheme for getting relative Energies of States

$E_{gr} = 2\varepsilon_a + 2\varepsilon_b + J_{a,a} + J_{b,b} + 4J_{a,b} - 2K_{a,b}$

$E_{ex}^{(3)} = 2\varepsilon_a + \varepsilon_b + \varepsilon_c + J_{a,a} + 2J_{a,b} + 2J_{a,c} + J_{b,c} - \left(K_{a,b} + K_{a,c}\right) - K_{b,c}$

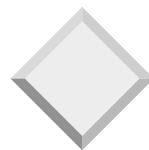$E_{ex}^A = 2\varepsilon_a + \varepsilon_b + \varepsilon_c + J_{a,a} + 2J_{a,b} + 2J_{a,c} + J_{b,c} - \left(K_{a,b} + K_{a,c}\right)$

$E_{ex}^B = 2\varepsilon_a + \varepsilon_b + \varepsilon_c + J_{a,a} + 2J_{a,b} + 2J_{a,c} + J_{b,c} - \left(K_{a,b} + K_{a,c}\right)$

$E_{ex}^{A+B} + E_{ex}^{A-B} = E_{ex}^A + E_{ex}^B$; but $E_{ex}^{A+B} = E_{ex}^{(3)}$ and $E_{ex}^{A-B} = E_{ex}^{(1)}$
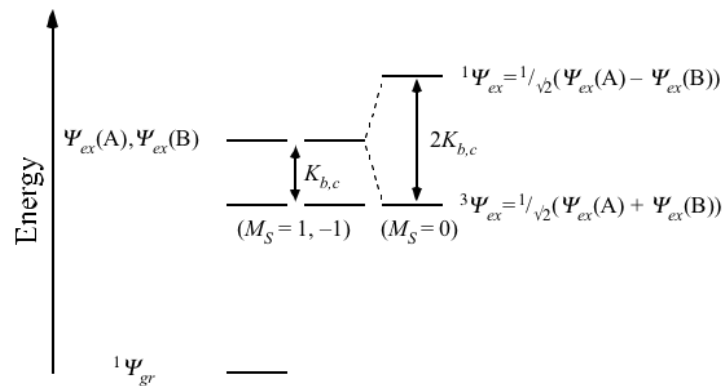
$\therefore E_{ex}^{(1)} = E_{ex}^A + E_{ex}^B - E_{ex}^{(3)}$

$E_{ex}^{(1)} = 2\varepsilon_a + \varepsilon_b + \varepsilon_c + J_{a,a} + 2J_{a,b} + 2J_{a,c} + J_{b,c} - \left(K_{a,b} + K_{a,c}\right) + K_{b,c}$

$E_{ex}^{(1)} - E_{ex}^{(3)} = +2K_{b,c}$

A Graphical Scheme for getting relative Energies of States

Complex d-orbital J and K's

$J_{0,0}$	$A + 4B + 3C$
$J_{2,2} = J_{-2,-2} = J_{2,-2}$	$A + 4B + 2C$
$J_{2,1} = J_{-2,-1} = J_{2,-1} = J_{-2,1}$	$A - 2B + C$
$J_{2,0} = J_{-2,0}$	$A - 4B + C$
$J_{1,1} = J_{-1,-1} = J_{1,-1}$	$A + B + 2C$
$J_{1,0} = J_{-1,0}$	$A + 2B + C$
$K_{1,-1}$	$6B + 2C$
$K_{2,-2}$	C
$K_{2,1} = K_{-2,-1}$	$6B + C$
$K_{2,-1} = K_{-2,1}$	C
$K_{2,0} = K_{-2,0}$	$4B + C$
$K_{1,0} = K_{-1,0}$	$B + C$

$B \approx 650 - 1100 \text{ cm}^{-1}$ $C \approx 2500 - 5500 \text{ cm}^{-1}$

The Coulomb (J_{ij}) and exchange (K_{ij}) integrals shown here can often be used to calculate state energy differences.

For 1st row transition metals, Racah parameters B and C have typical ranges shown. (State energy differences don't involve A.)

Slater-Condon and Racah Parameters

The "Slater-Condon parameters" are defined by

$$F^k \equiv e^2 \int_0^\infty r_1^2 \left[\int_0^\infty r_2^2 \frac{r_<^k}{r_>^{k+1}} \left| R_{nl}(r_1) \right|^2 \left| R_{nl}(r_2) \right|^2 dr_2 \right] dr_1 \quad ; \quad \frac{r_<^k}{r_>^{k+1}} = \begin{cases} \dfrac{r_1^k}{r_2^{k+1}} & \text{if } r_2 > r_1 \\ \dfrac{r_2^k}{r_1^{k+1}} & \text{if } r_1 > r_2 \end{cases}$$

and (in the d-shell): $F_0 \equiv F^0$, $F_2 = \dfrac{F^2}{49}$, $F_4 = \dfrac{F^4}{441}$

The "Racah Parameters" are related to the Slater-Condon parameters by

$$A = F_0 - 49F_4$$
$$B = F_2 - 5F_4$$
$$C = 35F_4$$

Example: B parameter for V^{3+}

^3F state: $|^3F ; 3\ 1\rangle = |\ 2^+ 1^+\rangle$

$E(^3F) = 2h_d + J_{2,1} - K_{2,1}$
$= 2h_d + (A - 2B + C) - (6B + C)$
$= 2h_d + A - 8B$

^3P state:
$|^3P ; 1\ 1\rangle = \sqrt{3}/_5\ |1^+ 0^+\rangle - \sqrt{2}/_5\ |2^+ -1^+\rangle$
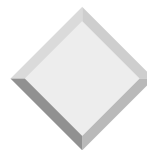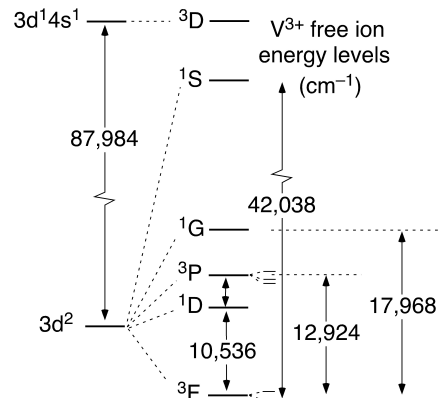$E(1^+ 0^+) = 2h_d + J_{1,0} - K_{1,0}$
$= 2h_d + (A + 2B + C) - (B + C)$
$= 2h_d + A + B$
$E(2^+ -1^+) = 2h_d + J_{2,-1} - K_{2,-1}$
$= 2h_d + (A - 2B + C) - C$
$= 2h_d + A - 2B$
$E(^3P) = E(1^+ 0^+) + E(2^+ -1^+) - E(^3F)$
$= 2h_d + A + 7B$

$E(^3P) - E(^3F) = 15B = 12{,}924 \text{ cm}^{-1}$
$B = 861.7 \text{ cm}^{-1}$

$3d^1 4s^1$ —— ^3D —— V^{3+} free ion energy levels (cm^{-1})

^1S ——

87,984

42,038

^1G ——

^3P ——

^1D —— 17,968

$3d^2$ —— 12,924

10,536

^3F ——

Energies of d^2 and d^3 Terms

N	Term Symbol	Slater–Condon Expression	Racah Expression
d^2	^3F	$F_0 - 8F_2 - 9F_4$	$A - 8B$
	^3P	$F_0 + 7F_2 - 84F_4$	$A + 7B$
	^1G	$F_0 + 4F_2 + F_4$	$A + 4B + 2C$
	^1D	$F_0 - 3F_2 + 36F_4$	$A - 3B + 2C$
	^1S	$F_0 + 14F_2 - 126F_4$	$A + 14B + 7C$
d^3	^4F	$3F_0 - 15F_2 - 72F_4$	$3A - 15B$
	^4P	$3F_0 - 147F_4$	$3A$
	^2H	$3F_0 - 6F_2 - 12F_4$	$3A - 6B + 3C$
	^2P	$3F_0 - 6F_2 - 12F_4$	$3A - 6B + 3C$
	^2G	$3F_0 - 11F_2 + 13F_4$	$3A - 11B + 3C$
	^2F	$3F_0 + 9F_2 - 87F_4$	$3A + 9B + 3C$
	^2D $\lambda = 3, +$ $\lambda = 1, -$	$3F_0 + 5F_2 + 3F_4$ $\pm (193F_2^2 - 1650F_2F_4 + 8325F_4^2)^{1/2}$	$3A - 3B + 5C$ $\pm (193B^2 + 8BC + 4C^2)^{1/2}$

Tanabe-Sugano ΔE's and the Scheme

Worked out details: singlet states example for the high-field limit for the d^6 case.

$$^1A_{1g}:\ 6\varepsilon_{t_{2g}} + 3J_{xy,xy} + 12J_{xy,xz} - 6K_{xy,xz}$$

$$^1T_{1g}:\ 5\varepsilon_{t_{2g}} + \varepsilon_{e_g} + 2J_{xy,xy} + J_{x^2-y^2,xy} + 12J_{xy,xz} - 6K_{xy,xz} + K_{x^2-y^2,xy}$$

$$^1T_{2g}:\ 5\varepsilon_{t_{2g}} + \varepsilon_{e_g} + 2J_{xy,xy} + J_{xy,z^2} + 8J_{xy,xz} + 4J_{xz,z^2} - 4K_{xy,xz} - 2K_{xz,z^2} + K_{xy,z^2}$$

$$E(^1T_{2g}) - E(^1T_{1g}) =$$

$$\left(J_{xy,z^2} - J_{x^2-y^2,xy}\right) + 4\left(J_{xz,z^2} - J_{xy,xz}\right) + 2\left(K_{xy,xz} - K_{xz,z^2}\right) + \left(K_{xy,z^2} - K_{x^2-y^2,xy}\right)$$

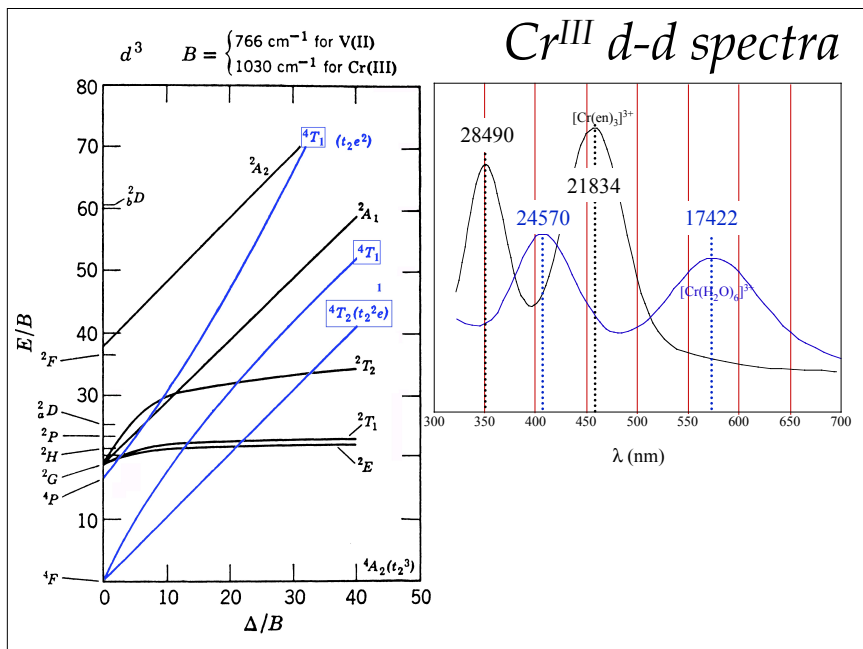$$= -8B + 4(4B) + 2(3B - B) + (4B - 0) = 16B$$

Note: The exchange contributions are <u>positive</u> because these are the <u>singlet</u> states - see the diagram - back four slides!

Some Coulomb and Exchange Integrals

Coulomb and Exchange Integrals	Racah Parameters
$J_{xy,xy} = J_{xz,xz} = J_{yz,yz} = J_{z^2,z^2} = J_{x^2-y^2,x^2-y^2}$	$A + 4B + 3C$
$J_{xz,yz} = J_{xy,yz} = J_{xy,xz} = J_{x^2-y^2,yz} = J_{x^2-y^2,xz}$	$A - 2B + C$
$J_{xy,z^2} = J_{x^2-y^2,z^2}$	$A - 4B + C$
$J_{yz,z^2} = J_{xz,z^2}$	$A + 2B + C$
$J_{x^2-y^2,xy}$	$A + 4B + C$
$K_{xy,xy} = K_{xz,yz} = K_{xy,xz} = K_{x^2-y^2,yz} = K_{x^2-y^2,xz}$	$3B + C$
$K_{xy,z^2} = K_{x^2-y^2,z^2}$	$4B + C$
$K_{yz,z^2} = K_{xz,z^2}$	$B + C$
$K_{x^2-y^2,xy}$	C
$\int \varphi_{xz}(1)\varphi_{xy}(2)\left(1/r_{12}\right)\varphi_{yz}(1)\varphi_{x^2-y^2}(2)d\tau_1 d\tau_2$	$-3B$
$B \approx 650 - 1100$ cm^{-1}	$C \approx 2500 - 5500$ cm^{-1}

The Coulomb (J_{ij}) and exchange (K_{ij}) integrals shown here can often be used to calculate state energy differences.

For 1st row transition metals, Racah parameters B and C have typical ranges shown. (State energy differences don't involve A.)

Cr^{III} d-d spectra

d^3 $B = \begin{cases} 766 \text{ cm}^{-1} \text{ for V(II)} \\ 1030 \text{ cm}^{-1} \text{ for Cr(III)} \end{cases}$

[Cr(en)$_3$]$^{3+}$ 28490   21834   24570   17422   [Cr(H$_2$O)$_6$]^{3}

Jahn-Teller Theorem

Nonlinear Molecules in orbitally degenerate states are inherently unstable with respect to distortion.

We can write the ground state electronic energy, $E_0(Q)$, as a series expansion in each normal coordinate, Q:

$$E_0(Q) = E_0^0 + E_0^1(Q)Q + E_0^2(Q)Q^2 + \dots$$

Q - belongs to non-totally symmetric rep.

Comments Regarding Stable Structures

- Movement of the nuclei along a non-totally symmetric normal coordinate represents an "instantaneous distortion" of the molecule.

- Normal coordinates are defined in terms of the molecular geometry as it exists in at least a local energy minimum as far as nuclear positions are concerned. At a local minimum,

$$E_0^1(0) = \left(\frac{\partial E}{\partial Q}\right)_0 = 0 \qquad \text{For \underline{stable} molecules.}$$

- What are the conditions under which the first term of the power series expansion is nonzero? In other words, when is the molecule is not stable with respect to distortion?
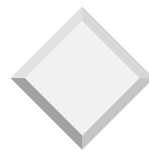
Symmetry Constraints on Structural Stability

Ground state energy, E, is given by: $E = \int \Psi_0^* \mathcal{H}\, \Psi_0\, d\tau$

Consider $\left(\dfrac{\partial E}{\partial Q}\right)_0$, where Q does *not* belong to the totally symmetric representation, Γ_{A_1}:

$$\left(\frac{\partial E}{\partial Q}\right)_0 = \int \left(\frac{\partial \Psi_0^*}{\partial Q}\right)_0 \mathcal{H}\, \Psi_0\, d\tau + \int \Psi_0^* \mathcal{H} \left(\frac{\partial \Psi_0}{\partial Q}\right)_0 d\tau$$

$$+ \int \Psi_0^* \left(\frac{\partial \mathcal{H}}{\partial Q}\right)_0 \Psi_0\, d\tau$$

The first two terms vanish, by symmetry.

$$\therefore \left(\frac{\partial E}{\partial Q}\right)_0 = \int \Psi_0^* \left(\frac{\partial \mathcal{H}}{\partial Q}\right)_0 \Psi_0\, d\tau \sim \Gamma_0 \otimes \Gamma_{\left(\frac{\partial \mathcal{H}}{\partial Q}\right)_0} \otimes \Gamma_0$$

$\mathcal{H}$ — belongs to totally symmetric representation;

$$\frac{\partial \mathcal{H}}{\partial Q} \text{ — belongs to } \Gamma_Q$$

$$\Rightarrow \left(\frac{\partial E}{\partial Q}\right)_0 \text{ will be } \textit{nonzero} \text{ iff } \left[\Gamma_0 \otimes \Gamma_0\right]^+ \text{ contains } \Gamma_Q$$

If the ground state is *non*degenerate, $\left[\Gamma_0 \otimes \Gamma_0\right]^+$
is the totally symmetric representation.

$$\therefore \left(\frac{\partial E}{\partial Q}\right)_0 = 0 \text{ if ground state is nondegenerate,}$$

(integrand will not belong to Γ_{A_1})

Summary: J-T active modes

If the ground state, Ψ_0, is <u>orbitally degenerate</u> and transforms as Γ_0, then then the molecule will distort to remove the degeneracy.

Possible symmetries of the distortion are found by taking the symmetric direct product:

$$[\Gamma_0 \otimes \Gamma_0]^+$$

(Totally symmetric modes are ignored.)

Examples

★ The best known J-T unstable molecules are $Cu^{II} d^9$ "octahedral" cases. What is the expected distortion coordinate?

★ "Tetrahedral" Cu^{II} complexes are common. Are they really tetrahedral?

★ Are octahedral Ni^{II} complexes J-T unstable, (*i*) in their ground states?, (*ii*) in excited states of the ground configuration?

★ Is cyclobutadiene J-T unstable, (*i*) in its ground state?, (*ii*) in excited states of the ground configuration?

★ What is the expected structure of the CrN_3^{6-} ion (in $Ca_3(CrN_3)$)?

★ Would an octahedral V^{III} complex be expected to exhibit a J-T distortion?

O	E	$8C_3$	$3C_2$ $(=C_4^2)$	$6C_4$	$6C_2$		
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		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	−1	1	−1	$(R_x,R_y,R_z);\ (x,y,z)$	
T_2	3	0	−1	−1	1		(xy,xz,yz)

D_4	E	$2C_4$	$C_2(C_4^2)$	$2C_2'$	$2C_2''$		
A_1	1	1	1	1	1		$x^2+y^2,\ z^2$
A_2	1	1	1	−1	−1	$z,\ R_z$	
B_1	1	−1	1	1	−1		x^2-y^2
B_2	1	−1	1	−1	1		xy
E	2	0	−2	0	0	$(x,y),\ (R_x,R_y)$	(xz,yz)

$[E \otimes E]^-$	1	1	1	−1	−1	$= A_2$
$[E \otimes E]^+$	3	−1	3	1	1	$= A_1 \oplus B_1 \oplus B_2$

Tetrahedral Group: T$_d$

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$		
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		$(2z^2-x^2-y^2, x^2-y^2)$
T_1	3	0	−1	1	−1	(R_x,R_y,R_z)	
T_2	3	0	−1	−1	1	(x,y,z)	(xy,xz,yz)

D$_{3h}$

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$		
A_1'	1	1	1	1	1	1		x^2+y^2,z^2
A_2'	1	1	−1	1	1	−1	R_z	
E'	2	−1	0	2	−1	0	(x,y)	(x^2-y^2,xy)
A_1''	1	1	1	−1	−1	−1		
A_2''	1	1	−1	−1	−1	1	z	
E''	2	−1	0	−2	1	0	(R_x,R_y)	(xz,yz)
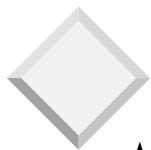
Examples - Some Answers

★ Cu^{II} d^9 "octahedral" cases:
$[E_g \otimes E_g]^+ = A_{1g} \oplus E_g$

★ Cu^{II} d^9 "tetrahedral" cases:
$[T_2 \otimes T_2]^+ = A_1 \oplus E \oplus T_2$

★ CrN_3^{6-} ion:
$[E'' \otimes E'']^+ = A_{1g} \oplus E'$

★ V^{III} complex:
Ground State is $[T_{2g} \otimes T_{2g}]^- = {}^3T_{1g}$
$[T_{1g} \otimes T_{1g}]^+ = A_{1g} \oplus E_g \oplus T_{2g}$