Electronic Structure and Spectroscopy of TM Complexes

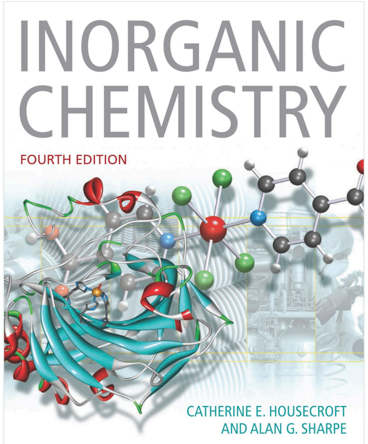
Books for this Topic

- Harris & Bertolucci, “Symmetry and Spectroscopy, An Introduction to Vibrational and Electronic Spectroscopy”
- Cotton, “Chemical Applications of Group Theory”
- Housecroft & Sharpe, “Inorganic Chemistry”, 3rd Edition, Chapter 21.
- Solomon & Lever, “Inorganic Electronic Structure and Spectroscopy” see Volume 1, Chapter 3 - by Hitchman and Riley.
- Cotton & Walton, “Multiple Bonds between Metal Atoms”, 2nd Edition, Chapter 10. [Last section.]

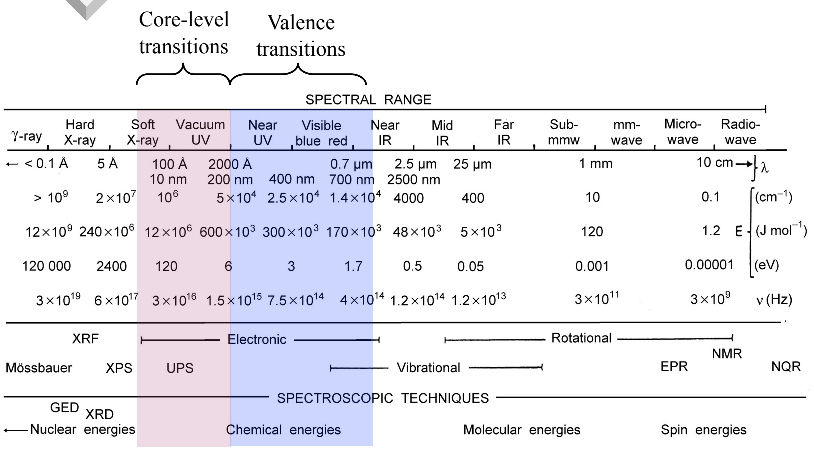
Required Reading: *Acc. Chem. Res.*, **2000**, *33*, 483-90.

Good Undergraduate Background Text

- Housecroft & Sharpe, “Inorganic Chemistry”, 4th Edition, Chapters 19 and 20.
- We cover more, but this chapter fills in almost everything I haven’t done in detail.
- Alternative: Shriver & Atkins, Chapter 19.



Spectroscopy: The Big Picture

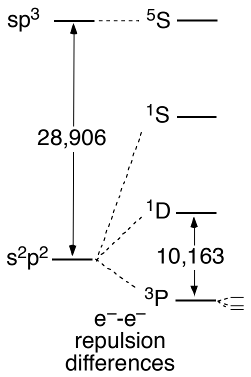


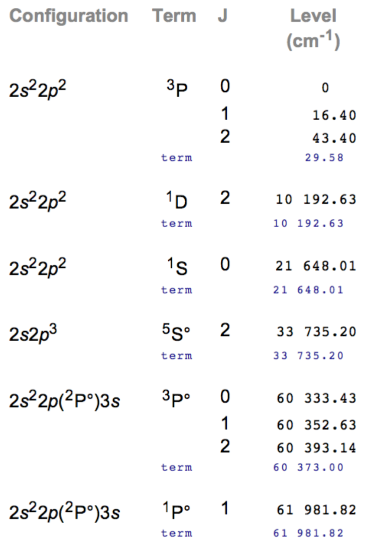
Electronic Energy Scales - The Hierarchical Approach

- The largest energy level splittings in atoms and molecules due to principal quantum number changes (and concomitant differences in screening). This underlies our familiar focus on valence vs. core-levels.
- Energy level splittings between different *l* levels (e.g., between *s*, *p*, *d*… electrons) are often comparable to bonding effects – evident in both the concept of "hybrid orbitals" and in mixed orbital parentage of molecular orbitals.
- In T.M. complexes, *e⁻-e⁻* repulsion *differences* are often comparable to M-L bonding energies. A big part of ligand-field theory deals with the complications that arise from the competition between these energetic effects.

Carbon: Atomic Energy Levels

Experimental atomic energy levels (cm-1).

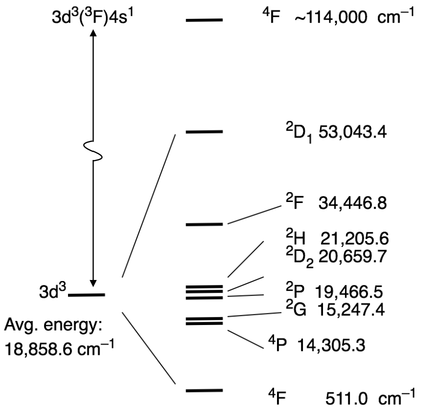


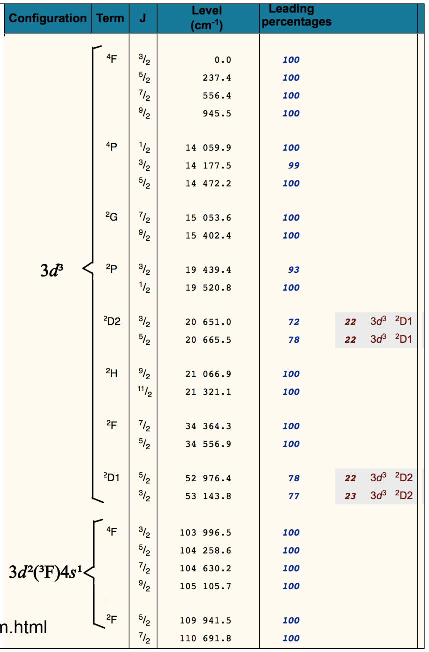


Configuration	Term	J	Level (cm-1)
$2s^22p^2$	^{3}P	0	0
		1	16.40
		2	43.40
	term		29.58
$2s^22p^2$	^{1}D	2	10 192.63
	term		10 192.63
$2s^22p^2$	^{1}S	0	21 648.01
	term		21 648.01
$2s2p^3$	^{5}S°	2	33 735.20
	term		33 735.20
$2s^22p(^2P°)3s$	^{3}P°	0	60 333.43
		1	60 352.63
		2	60 393.14
	term		60 373.00
$2s^22p(^2P°)3s$	^{1}P°	1	61 981.82
	term		61 981.82

http://physics.nist.gov/PhysRefData/ASD/index.html

Cr(III): Electronic Energy Levels





Configuration	Term	J	Level (cm-1)	Leading percentages			
$3d^3$	^{4}F	3/2	0.0	100			
		5/2	237.4	100			
		7/2	556.4	100			
		9/2	945.5	100			
	^{4}P	1/2	14 059.9	100			
		3/2	14 177.5	99			
		5/2	14 472.2	100			
	^{2}G	7/2	15 053.6	100			
		9/2	15 402.4	100			
	^{2}P	3/2	19 439.4	93			
		1/2	19 520.8	100			
	^{2}D2	3/2	20 651.0	72	22	$3d^3$	^{2}D1
		5/2	20 665.5	78	22	$3d^3$	^{2}D1
	^{2}H	9/2	21 066.9	100			
		11/2	21 321.1	100			
	^{2}F	7/2	34 364.3	100			
		5/2	34 556.9	100			
	^{2}D1	5/2	52 976.4	78	22	$3d^3$	^{2}D2
		3/2	53 143.8	77	23	$3d^3$	^{2}D2
$3d^2(^3F)4s^1$	^{4}F	3/2	103 996.5	100			
		5/2	104 258.6	100			
		7/2	104 630.2	100			
		9/2	105 105.7	100			
	^{2}F	5/2	109 941.5	100			
		7/2	110 691.8	100			

https://physics.nist.gov/PhysRefData/ASD/levels_form.html

Background Topics

- MO theory of transition metals: Octahedral coordination,
- σ-donors (all ligands)
- π-donors (halides, amides, alkoxides, thiolates, …)
- π-acceptors (CO, NO+, CN-, CNR)

Bonding and Electronic Structure

- Molecular orbital picture for Lewis acid-base interaction
- d-orbitals - acceptor orbitals on transition metals
- MO picture for octahedral complexes
- Low-spin vs. high-spin complexes; ligand-field splitting vs. pairing energy

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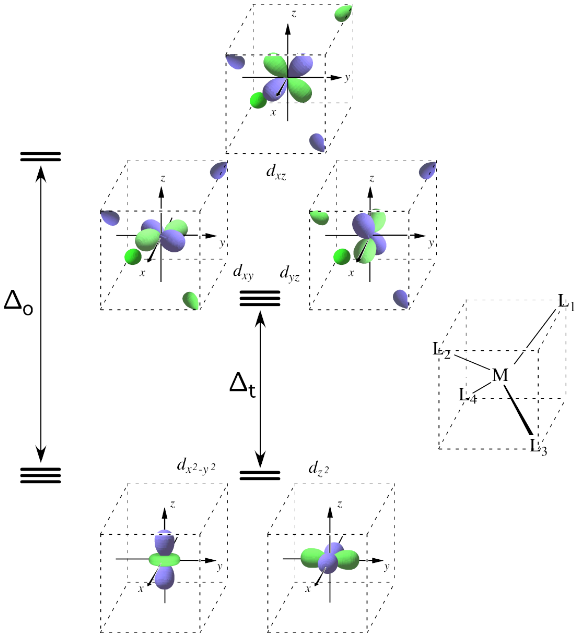
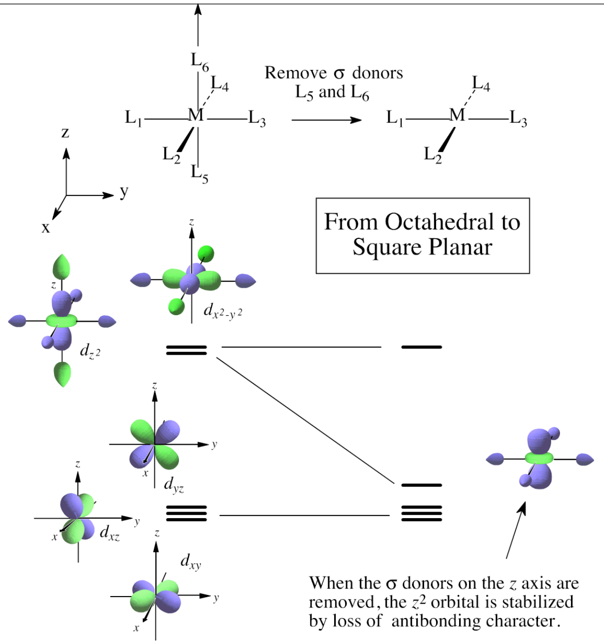
Metal-Ligand bonding

- Concepts of “hardness” and “softness” already discussed (qualitatively). (Pearson’s 1963 JACS paper introducing these concepts is posted in the web site “handouts” section.)
- Intro to Ligand fields - an MO scheme for a “typical” octahedral transition metal complex.

Contrast between octahedral & tetrahedral LF splitting





Remove σ donors L_5 and L_6

From Octahedral to Square Planar

When the σ donors on the z axis are removed, the z^2 orbital is stabilized by loss of antibonding character.

Background Topics - increasing Δ_o

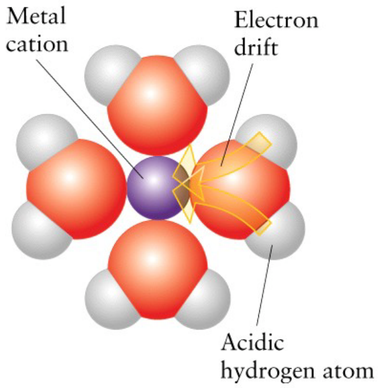
- Spectrochemical Series:

  $NO^+ > CR_3^- > CO \geq PF_3 \geq CN^- > NO_2 > NH_3 >$
  $H_2O > OH^- > F^- > S^{2-} > Cl^- > Br^- > I^-$

  the series represents the confluence of several trends in electronegativity (greater), σ-donation (weaker), and decreasing/increasing π-donation/acceptance
- Metal trends:

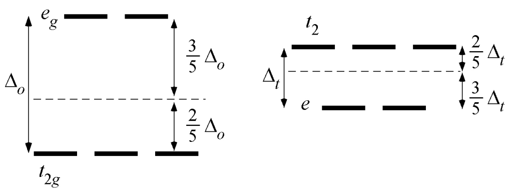
  $Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Cr^{3+} < V^{3+} < Co^{3+} < Mn^{4+} < Rh^{3+} < Pd^{4+} < Ir^{3+} < Re^{4+} < Pt^{4+}$

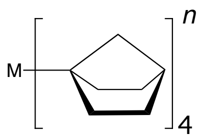
Hydrolysis constants of Metal ion complexes give acidic solutions



pK_a's for $[M(H_2O)_6]^{n+}$	
$[Fe(H_2O)_6]^{3+}$	2.46
$[Cr(H_2O)_6]^{3+}$	3.89
$[Al(H_2O)_6]^{3+}$	4.85
$[Fe(H_2O)_6]^{2+}$	5.89
$[Cu(H_2O)_6]^{3+}$	7.49
$[Ni(H_2O)_6]^{2+}$	9.03

Spectrochemical Series for Ligands applies to all geometries





M	n	$\mu_{eff}(\mu_B)$
Co	0	1.89
Co	-1	3.18
Co	+1	~0
Fe	0	~0
Mn	+1	3.78
Mn	0	high-spin

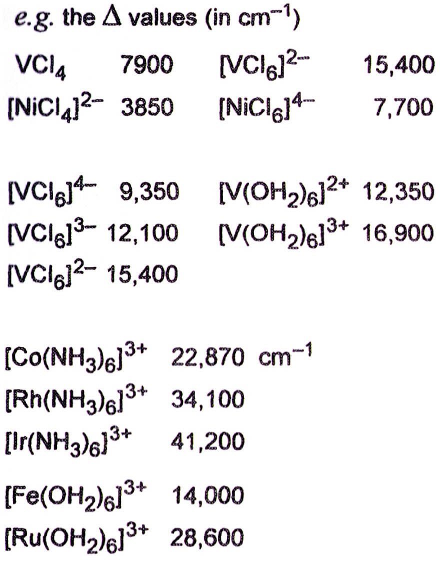
- Tetrahedral complexes are almost never low-spin; *rare* exceptions occur at the highest end of the series.

Examples of two trends

Complex	**Δ_o (10 Dq)**	**Ox. State**
$[Co(H_2O)_6]^{2+}$	**9,000**	**Co(II)**
$[Co(H_2O)_6]^{3+}$	**18,000**	**Co(III)**
$[Co(NH_3)_6]^{2+}$	**12,000**	**Co(II)**
$[Co(NH_3)_6]^{3+}$	**22,870**	**Co(III)**
$[CoF_6]^{3-}$	**13,000**	**Co(III)**
$[Co(CN)_6]^{3-}$	**32,000**	**Co(III)**

Energy scale discussion

More Examples



e.g. the Δ values (in cm^{-1})

VCl_4	7900	$[VCl_6]^{2-}$	15,400
$[NiCl_4]^{2-}$	3850	$[NiCl_6]^{4-}$	7,700

$[VCl_6]^{4-}$	9,350	$[V(OH_2)_6]^{2+}$	12,350
$[VCl_6]^{3-}$	12,100	$[V(OH_2)_6]^{3+}$	16,900
$[VCl_6]^{2-}$	15,400		

$[Co(NH_3)_6]^{3+}$	22,870 cm^{-1}
$[Rh(NH_3)_6]^{3+}$	34,100
$[Ir(NH_3)_6]^{3+}$	41,200
$[Fe(OH_2)_6]^{3+}$	14,000
$[Ru(OH_2)_6]^{3+}$	28,600

Background Topics - more on bonding

- Other geometries:

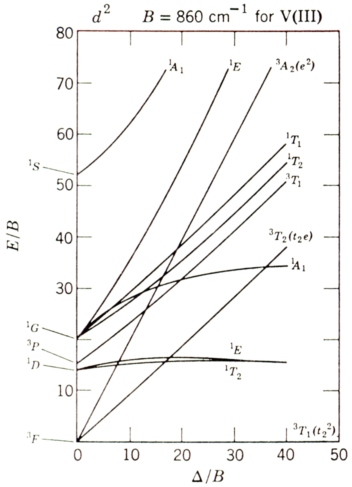
  e.g., tetrahedral, trigonal bipyramid, square planar
- Simple VB theory:

  In spectroscopy, the Pauling-style VB approach is nearly useless, but it provides a handy way to simplify bonding in parts of the molecule where details of electronic structure are not important to the task at hand (example: where is the d^2sp^3 hybridization scheme a useful concept for octahedral complexes?)

Background Topics - the role of e^-–e^- repulsion

Illustrative Questions:

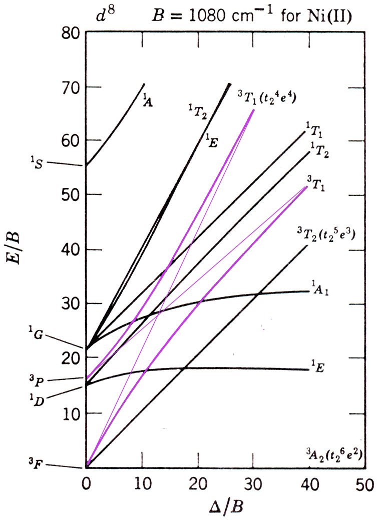
- What is the (specific) origin of the energy difference between the ^3F and ^1G atomic states?
- In the *strong-field limit*, what is the origin of the splittings between the $^3A_{2g}$, ^1E_g, and $^1A_{1g}$ ligand field states from the e_g^2 configuration?



Background Topics - the noncrossing rule

Illustrative Issues:

- What is the strength of the mixing between the $^3F(^3T_{1g})$ and $^3P(^3T_{1g})$ atomic states?
- In the *strong-field limit*, exactly how much of the two $^3F(^3T_{1g})$ and $^3P(^3T_{1g})$ states contribute to the two molecular $^3T_{1g}$ states?



Physical Background - Symmetry Review

- In the handout, "**Transitions Between Stationary States (Adapted from *Harris* and *Bertolucci*, p. 130)**", an expression for the probability that a system in its ground state, ψ_0 can be stimulated by radiation into an excited state, ψ_1, is derived:

$$\Psi(\mathbf{r},t) = c_0(t)\Psi_0(\mathbf{r},t) + c_1(t)\Psi_1(\mathbf{r},t)$$

$$\boxed{\frac{d\left(c_1{}^*c_1\right)}{dt} \propto \mathcal{E}_0^2\left(\mu_{01}^{x\;2} + \mu_{01}^{y\;2} + \mu_{01}^{z\;2}\right)} \text{ assuming } c_0(0) = 1 \text{ and } c_1(0) = 0.$$

$\mathcal{E}_0^2$ is proportional to the light intensity and

$$\boxed{\mu_{01}^{x,y,z} = e\int \psi_1^* \begin{Bmatrix} x \\ y \\ z \end{Bmatrix} \psi_0\, d\tau} \text{ are the transition moment integrals.}$$

- This expression applies to an integral over all wavelengths of incident light (in the dipole approximation) and was the form used to evaluate whether an electron transition was symmetry allowed.

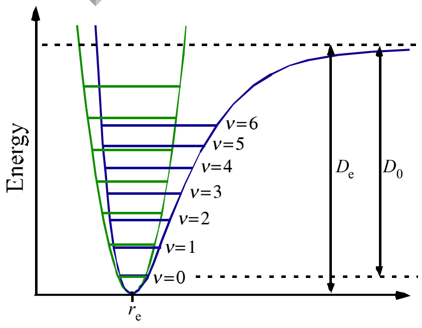
Allowedness

- In group theory, prescription for deciding whether a transition is dipole-allowed is straightforward:
  - If the ground and excited states respectively belong to the Γ_0 and Γ_1 representations of the point group of the molecule in question, then a transition is dipole-allowed if and only if

$$\Gamma_0 \otimes \Gamma_1 \text{ contains } \begin{cases} \Gamma_x & \text{for } x\text{-polarized light} \\ \Gamma_y & \text{for } y\text{-polarized light} \\ \Gamma_z & \text{for } z\text{-polarized light} \end{cases}$$

  - Spin doesn't change: $\Delta S = 0$. For states where large spin-orbit mixing is possible (large ζ and/or small ΔE between mixed states), the rule is weakened.

Harmonic vs. Real Potentials



Internuclear Separation (r)

- Harmonic oscillators have equally spaced levels

$$E_i(n) = (n_i + \tfrac{1}{2})h\nu_i$$

for the i^{th} vibrational mode

- Real oscillators exhibit *anharmonicity*

Solutions for the Morse Potential →

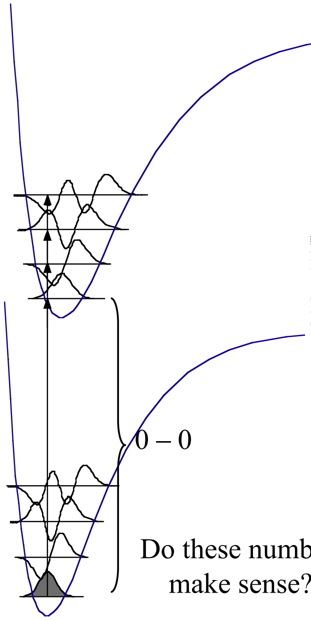
$$V(r) = D_e\left(1 - e^{-a(r-r_e)}\right)^2 \quad a = \sqrt{k_e/2D_e}$$

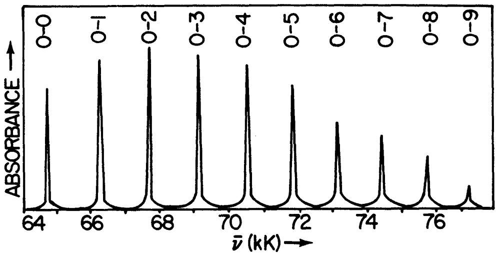
$$E_i(n) = \left(n_i + \tfrac{1}{2}\right)h\nu_0 - \left(n_i + \tfrac{1}{2}\right)^2 \left(h\nu_0\right)^2 / 4D_e$$

$$\frac{E_i(n)}{hc} = \left(n_i + \tfrac{1}{2}\right)\omega_e - \left(n_i + \tfrac{1}{2}\right)^2 \omega_e x_e$$

$$E_i(n+1) - E_i(n) = h\nu_0 - \left(n_i + \tfrac{1}{2}\right)\left(h\nu_0\right)^2 / 2D_e$$

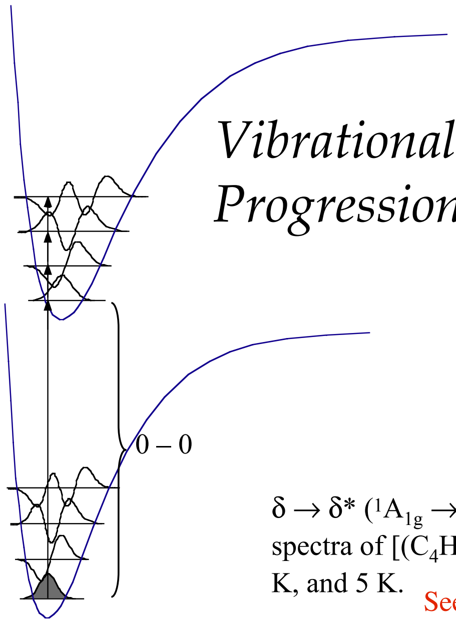
Vibrational Progressions



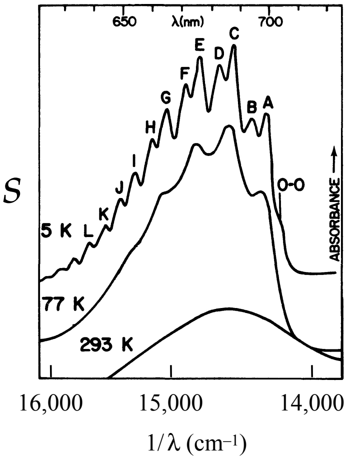


Schematic ${}^1\Sigma^+ \rightarrow {}^1\Pi$ electronic absorption spectrum of CO showing vibronic transitions to higher energy than the pure electronic 0-0 transition.

Do these numbers make sense? → $\bar{\omega}_e = 1516 \text{ cm}^{-1}$ $\omega_e x_e = 17.25 \text{ cm}^{-1}$



Vibrational Progressions



$\delta \rightarrow \delta^*$ ($^1A_{1g} \rightarrow {}^1A_{2u}$) *z*-polarized absorption spectra of $[(C_4H_9)_4N]_2[Re_2Cl_8]$ at 293 K, 77 K, and 5 K. See prob. 5.56, *H & B*, pp. 413-4.

LMCT and MLCT Transitions

Ligand-to-Metal Charge Transfer (LMCT)

a) intramolecular e⁻ transfer from ligand-based orbitals to metal-based orbitals $M^{n+}—L^- \rightarrow M^{(n-1)+}—L$

b) ε values are 5,000-50,000 $M^{-1}cm^{-1}$ (very intense)

c) since we are "oxidizing" the ligand and "reducing" the metal, LMCTs are favored with

  a) easily oxidized ligands (π-donors) Low I. E. ($I^- < Br^- < Cl^- < F^-$)

  b) easily reduced metals (i.e. high oxidation states)

Metal-to-Ligand Charge Transfer (MLCT) – less common

a) intramolecular e⁻ transfer from metal-based orbitals to ligand-based orbitals $M—L \rightarrow M^+—L^-$

b) Intensities similar to LMCT

Types of Transitions: d-d

a) intramolecular e⁻ transfer within the *d*-orbital manifold

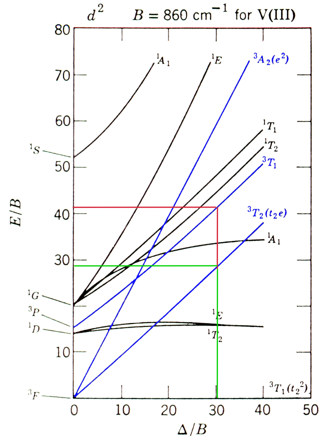
b) Values for ε vary: up to 1,000 M^{-1} cm^{-1} (moderately intense) for spin-allowed transitions in non-centrosymmetric molecules; ~10 $M^{-1}cm^{-1}$ for spin-allowed transitions in centrosymmetric molecules (weak); ~10^{-1} $M^{-1}cm^{-1}$ for spin-forbidden transitions in centrosymmetric molecules (very weak).

c) 1-e⁻ transitions much more intense (2-e⁻ transitions typically 10^{-2} times weaker)

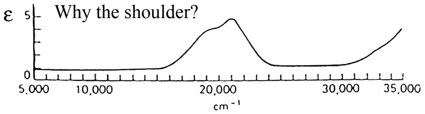
d) Shoulders and/or broad peaks expected where Jahn-Teller distortions apply.

Basic d-d Spectra

All 6-coordinate

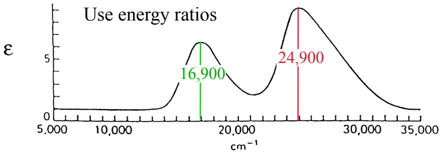


Aqueous $TiCl_3$ **$Ti^{3+}(d^1)$**



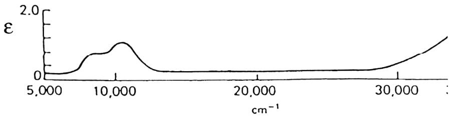
Why the shoulder?

Aqueous $V(ClO_4)_3$ **$V^{3+}(d^2)$**



Use energy ratios

Aqueous $Fe(ClO_4)_2$ **$Fe^{2+}(d^6)$**



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)

Atomic State splittings: All Operations

Carter, p. 205

$$\chi(E) = 2J+1$$

$$\chi(C_\alpha) = \frac{\sin[(J+1/2)\alpha]}{\sin(\alpha/2)}$$

$$\chi(i) = \pm(2J+1)$$

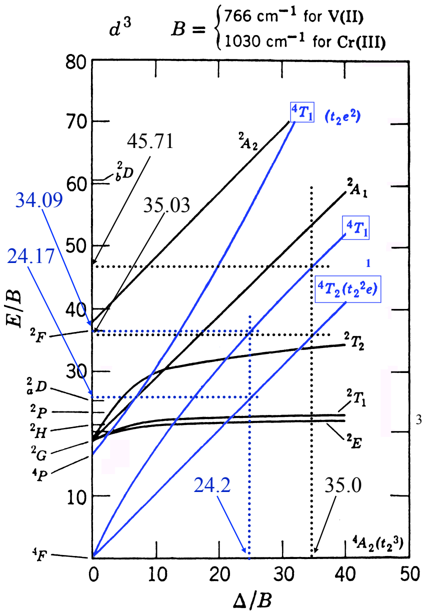
$$\chi(S_\alpha) = \pm\frac{\sin[(J+1/2)(\alpha+\pi)]}{\sin[(\alpha+\pi)/2]}$$

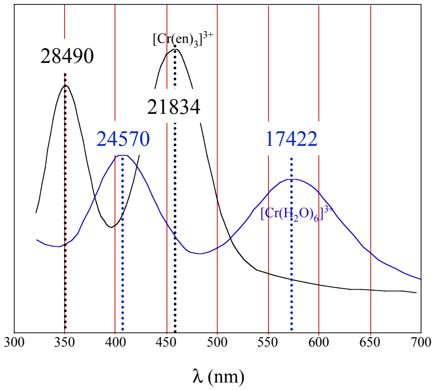
$$\chi(\sigma) = \pm\sin[(J+1/2)\pi]$$

- + signs apply for a *gerade* ***atomic state*** and – signs apply for an *ungerade* ***atomic state***, whether the point group under consideration has inversion symmetry or not. Examples: a ^3P state derived from either p^2 configuration ($u\times u$) or a d^2 configuration ($g\times g$) give g states. However, a ^2D state derived from a p^3 configuration ($u\times u\times u$) gives a u state, while a ^2D state derived from a d^3 configuration ($g\times g\times g$) gives a g state.
- The symbol J refers to the angular momentum quantum number of the state under consideration. In the Russell-Saunders scheme, J can be replaced by L when considering a spatial wave function.

See notes-11 from CHEM 673

Cr^{III} d-d spectra





Use energy ratios

$$\frac{24510}{17360} = 1.410 \qquad \frac{28490}{21834} = 1.305$$

http://wwwchem.uwimona.edu.jm:1104/lab_manuals/CrTSexptnu/CrexptJ.html

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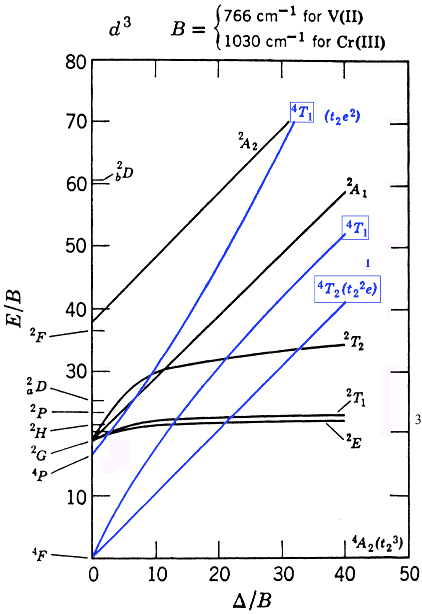
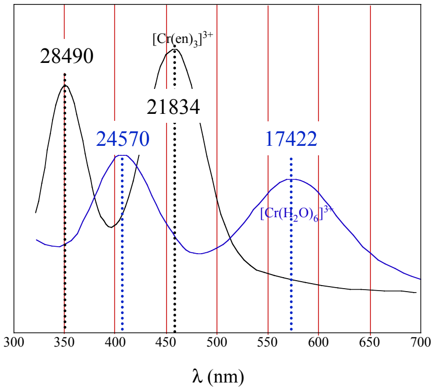
Cr^{III} d-d spectra





Use energy ratios

http://wwwchem.uwimona.edu.jm:1104/lab_manuals/CrTSexptnu/CrexptJ.html

Nephelauxetic Series

- Nephelauxetic Ligand Series: $F^- < H_2O < NH_3 <$ en $< [ox]^{2-} < [\underline{N}CS]^- < Cl^- < [CN]^- < Br^- < I^-$
- This series orders the extent to which ligands induce the nephelauxetic (cloud expanding) effect in coordination complexes in which they are bound. Quantitatively, this is measured in the extent to which electron-electron repulsion is reduced in the metal coordination complex vs. the free metal ions; i.e., in the ratio $(B_0 - B)/B_0$ where B is the measured empirical Racah parameter and B_0 is the free-ion value.
- Metal trends: $Mn^{2+} < Ni^{2+} \approx Co^{2+} < Mo^{2+} < Re^{4+} < Fe^{3+} < Ir^{3+} < Co^{3+} < V^{3+} < Mn^{4+}$

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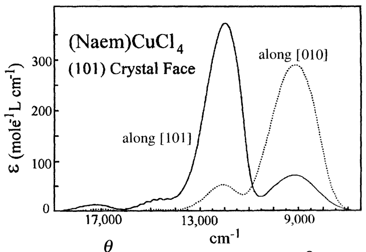
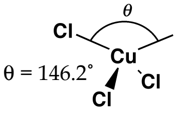
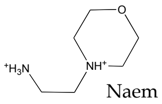
spectrum of (Naem)$CuCl_4$ at ~12 K







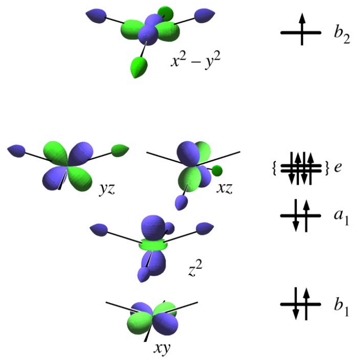
- Naem = [N-(2-ammonioethyl) morpholinium]$CuCl_4$
- Directions indicate the electric vector orientations.

McDonald, R.G., Riley, M.J., Hitchman, M.A., *Inorg. Chem.*, **1988,** *27,* 894. See also Solomon & Lever, "Inorg. Elec. Structure and Spec." Vol. 1, Chapter 3 - by Hitchman and Riley, p. 234.

Polarized Spectra, Example

- Both D_{4h} and D_{2d} $CuCl_4^{2-}$ ions are present, but the distorted tetrahedral ions give ~20 times more intense absorption.
- The [101] crystal axis is nearly parallel to the D_{2d} ions' S_4 axes.
- Can you assign the transitions?

D_{2d}



D_{2d}	E	$2S_4$	$C_2(S_4^2)$	$2C_2'$	$2\sigma_d$		
A_1	1	1	1	1	1		$x^2+y^2,\ z^2$
A_2	1	1	1	–1	–1	R_z	
B_1	1	–1	1	1	–1		xy
B_2	1	–1	1	–1	1	z	x^2-y^2
E	2	0	–2	0	0	$(x, y)\ (R_x, R_y)$	(xz, yz)

(for *this* coordinate system)

Vibronic Coupling

- Because they have $g-g$ character, the *d-d* transitions of complexes of the transition metals are "forbidden" (LaPorte forbidden).
- Complexes with noncentrosymmetric coordination geometries (e.g., tetrahedral) have more intense *d-d* spectra.
- Spectra in centrosymmetric (e.g., octahedral) complexes "acquire intensity" via vibronic coupling.

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:

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

$\psi^{gnd}_{vib.}$ generally belongs to totally symmetric rep.

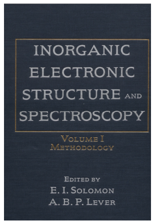
(otherwise, "hot bands" are involved). $\therefore$ consider,

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

D_{4h} $CuCl_4^{2-}$

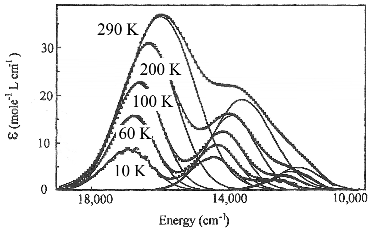
- T-dependence of band positions *and* intensities is different for bands centered at ~16,500 cm^{-1} and 14,000 cm^{-1} (at 290 K).
- Explain!

Solomon & Lever, “Inorg. Elec. Structure and Spec.” Vol. 1, Chapter 3 - by Hitchman and Riley, p. 246.

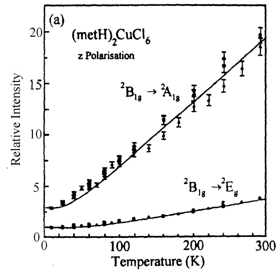

INORGANIC ELECTRONIC STRUCTURE AND SPECTROSCOPY

VOLUME I METHODOLOGY

EDITED BY E. I. SOLOMON A. B. P. LEVER



Temperature dependence of the spectrum of the planar $CuCl_4^{2-}$ ion in *z* polarization. In order of increasing intensity, the spectra were measured at 10, 60, 100, 200, and 290 K.



D_{4h}

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_{tot}	15	1	–1	–3	–1	–3	–1	5	3	1		
Γ_{vib}	9	–1	1	–1	1	–3	–1	5	3	1		
$\Gamma_{stretch}$	4	0	0	2	0	0	0	4	2	0		

$\Gamma_{vib} = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u$ $\Gamma_{stretch} = A_{1g} + B_{1g} + E_u$

Source of broadening and shifting of absorption peaks

Solomon & Lever, “Inorg. Elec. Structure and Spec.” Vol. 1, Chapter 3 - by Hitchman and Riley, p. 222.

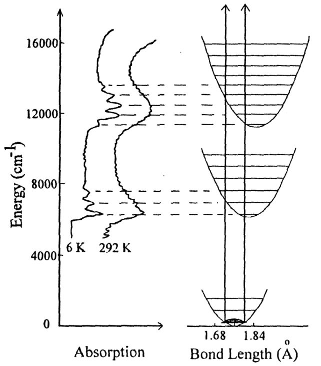


Figure 2. Correlation of the *d–d* bands observed for K_3NiO_2 with the energy levels of the totally symmetric stretching mode in the ground state and excited state potential surfaces. The spectrum is the sum of the *xy* and *z* spectra of the linear complex and the spectra are rather noisy because of the extremely small size of the crystal (adapted from reference 17 with permission).

Source of broadening and shifting of absorption peaks

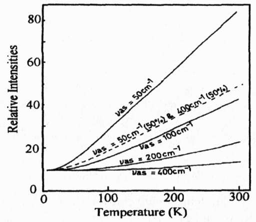


Figure 3. Effect of the energy of the intensity-inducing vibration upon the temperature dependence of a vibronically-allowed band.

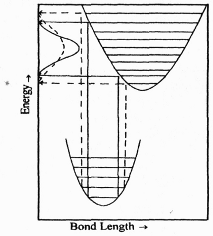


Figure 4. Mechanism by which the thermal population of higher vibrational levels of the α_1 metal–ligand stretching vibration influences the bandwidth of an electronic transition.

Solomon & Lever, "Inorg. Elec. Structure and Spec." Vol. 1, Chapter 3 - by Hitchman and Riley, p. 225.

Narrow lines and hot bands in UCl_6^{2-}

U(IV): $6p^6 5f^2 6d^0$

$^3H_4$ ground state

Solomon & Lever, "Inorg. Elec. Structure and Spec." Vol. 1, Chapter 3 - by Hitchman and Riley, p. 239.

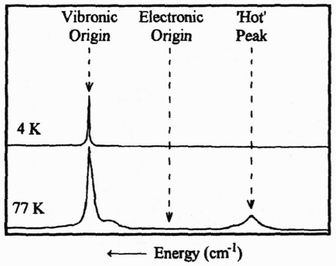


Figure 15. Transition to one of the $^3H_6$ levels of the UCl_6^{2-} ion illustrating the appearance of a hot peak at higher temperature (adapted from reference 21 with permission).

spectrum of the centrosymmetric UCl_6^{2-} ion at 4 K and 77 K, part of which is shown in Figure 15.[21] The pronounced peak present at both temperatures is a vibronic origin due to electronic excitation plus a quantum of the *u* metal–ligand vibration of energy 93 cm^{-1}. The weak peak appearing 93 cm^{-1} below the electronic origin at 77 K is the hot transition from the $v = 1$ vibrational level of the ground state to the $v = 0$ level of the excited state. The parity-forbidden transition of the electronic origin itself is too weak to be observed.

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*Dichroism of [*trans-*$CoCl_2(en)_2]^+$*

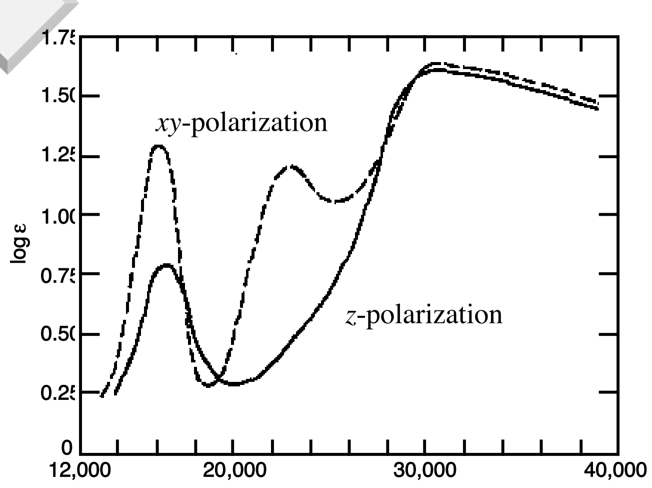


Fig. 9.13 in Cotton

Facts of the [*trans*-$CoCl_2(en)_2]^+$ case.

- Spectrum: Fig. 9.13 in Cotton (from S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, *25,* 127, **1952**).
- The solution spectrum is virtually identical with [*trans*-$CoCl_2(NH_3)_4]^+$ ∴ Virtual D_{4h} symmetry is a reasonable assumption.
- Both Cotton and, following him, Harris and Bertolucci, have made an error in the analysis of this case which leads to some wrong/problematic predictions.

Vibronic Coupling in [*trans*-$CoCl_2(en)_2]^+$

- Virtual D_{4h} symmetry, d^6, low-spin
- The Co^{III} ion is 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*-$CoCl_2N_4$] grouping

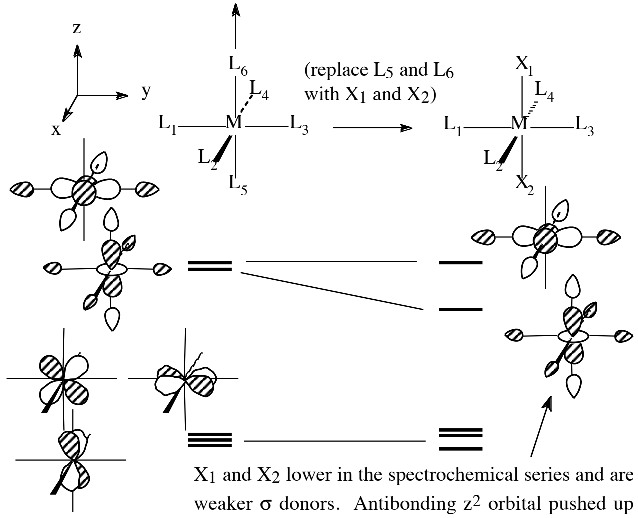
Vibrations of the *trans*-[$CoCl_2N_4$] group

- 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

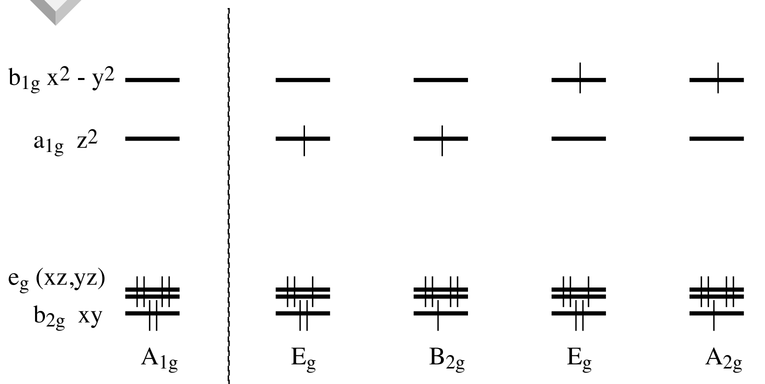
$2A_{1g}, B_{1g}, B_{2g}, E_g, 2A_{2u}, B_{2u}, 3E_u$

Qualitative MO Diagram



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



$e_g \otimes a_{1g} =$ $\boldsymbol{E_g}$ $b_{2g} \otimes a_{1g} =$ $\boldsymbol{B_{2g}}$ $e_g \otimes b_{1g} =$ $\boldsymbol{E_g}$ $b_{2g} \otimes b_{1g} =$ A_{2g}

Electronic Symmetries

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

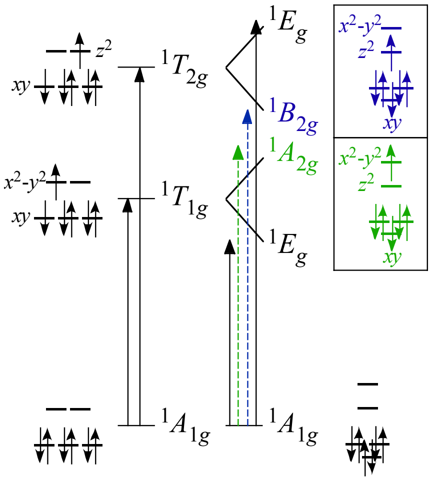
Allowedness w/ Vibronic Coupling

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

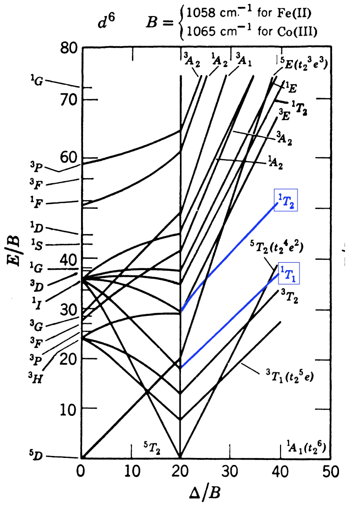
- Because of the $O_h \rightarrowtail D_{4h}$ symmetry correlations, the specific configurations shown correspond to only the states shown - even in O_h .
- The dashed transitions are *dipole and vibronically forbidden* in z-polarization.
- The x,y-polarized transition at ~23,000 cm^{-1} is difficult 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.



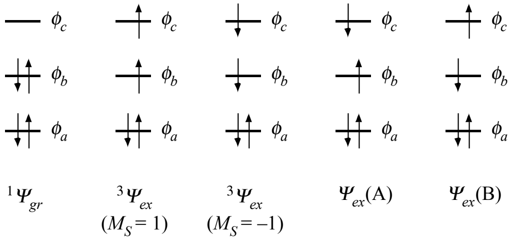
$$O_h\text{: } E(^1T_{2g}) - E(^1T_{1g}) = 16B \approx 17000 \text{ cm}^{-1}$$

Beyond just Symmetry

- Information about e-e repulsion can be obtained from the O_h Tanabe-Sugano diagram.



Graphical Tools for getting relative Energies of States



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

$^1\Psi_{ex} = {}^1/_{\sqrt{2}}(\Psi_{ex}(\mathrm{A}) - \Psi_{ex}(\mathrm{B}))$

$(M_S = 0)$

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

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

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

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

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

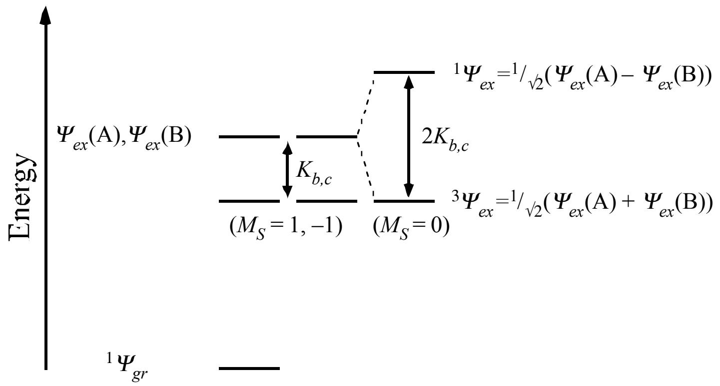
$$E_{ex}^{A+B} + E_{ex}^{A-B} = E_{ex}^{A} + E_{ex}^{B} \;\; ; \text{ but } E_{ex}^{A+B} = E_{ex}^{(3)} \text{ and } E_{ex}^{A-B} = E_{ex}^{(1)}$$

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

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

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

A Graphical Scheme for getting relative Energies of States



Some Coulomb and Exchange Integrals

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

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

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

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

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

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

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:

$|^3P\,;1\ 1\rangle=\sqrt{3/5}\,|1^+0^+\rangle-\sqrt{2/5}\,|2^+-1^+\rangle$

$E(1^+0^+)=2h_d+J_{1,0}-K_{1,0}$

$=2h_d+(A+2B+C)-(B+C)$

$=2h_d+A+B$

$E(2^+-1^+)=2h_d+J_{2,-1}-K_{2,-1}$

$=2h_d+(A-2B+C)-C$

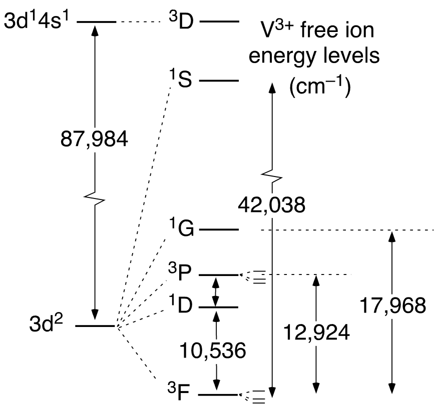
$=2h_d+A-2B$

$E(^3P)=E(1^+0^+)+E(2^+-1^+)-E(^3F)$

$=2h_d+A+7B$

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

$B=861.7\ \text{cm}^{-1}$



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 $\lambda=3,+$ $\lambda=1,-$	$3F_0+5F_2+3F_4$ $\pm(193F_2^2-1650F_2F_4$ $+8325F_4^2)^{1/2}$	$3A-3B+5C$ $\pm(193B^2+8BC+4C^2)^{1/2}$

*Condon and Shortley, *The Theory of Atomic Spectra*, p. 202, p. 206.

Tanabe-Sugano ΔE's and the Scheme

Worked out details: singlet states example for the high-field limit for the d⁶ case.

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

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

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

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

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

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

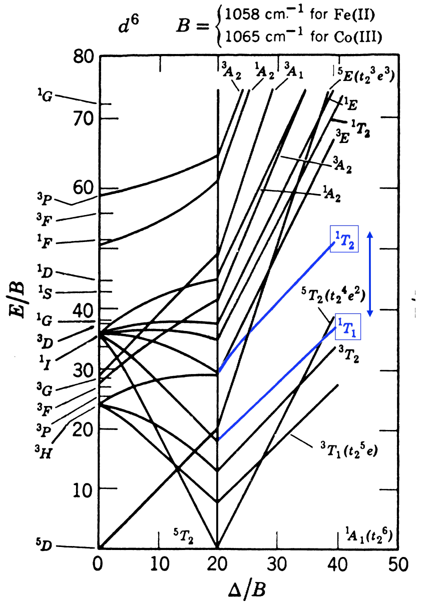
Note: The exchange contributions are positive because these are the singlet states - see the diagram - back six slides!

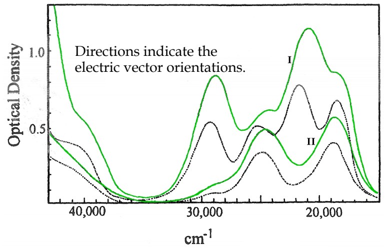
Beyond just Symmetry

- Information about e-e repulsion can be obtained from the O_h Tanabe-Sugano diagram.

In the high-field limit

$E(^{1}T_{2g}) - E(^{1}T_{1g}) = 16B$



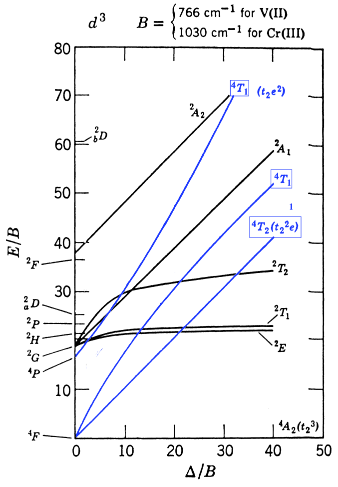


Polarized absorption spectra of the prominent crystal face of [***trans***-Cr(en)$_2$F$_2$]ClO$_4$ with the electric vector along the two extinction directions (I and II) **at 295 K and 4K.**

Dubicki, L., Hitchman, M.A., Day, P., *Inorg. Chem.*, **1970,** *9,* 188.

Polarized Spectra, Dichroism of [trans-CrF$_2$(en)$_2$]$^+$

- [*trans*-CrF$_2$(en)$_2$]$^+$ has virtual D_{4h} symmetry.
- For two directions of the electric vector (for which spectra are shown), some bands are completely absent (extinction directions). Which molecular axis (axes?) correspond to direction I? Direction II?
- Can you assign the transitions?



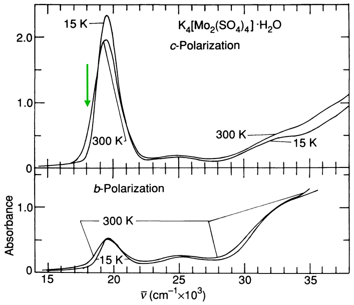
Vibrations of the *trans*-[CrF$_2$N$_4$] group

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

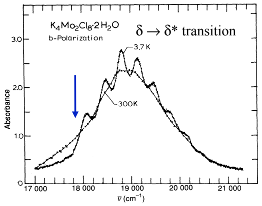
This should be

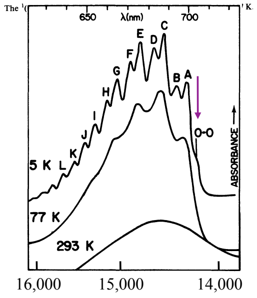
$2A_{1g}, B_{1g}, B_{2g}, E_g, 2A_{2u}, B_{2u}, 3E_u$

Quadruply Bonded Systems



Polarized crystal spectra of $K_4[Mo_2(SO_4)_4] \cdot 2H_2O$.





δ → δ* ($^1A_{1g} \rightarrow {^1A_{2u}}$) z-polarized spectra of $[(C_4H_9)_4N]_2[Re_2Cl_8]$ at 293 K, 77 K, and 5 K.

See Cotton & Walton, Ch. 10

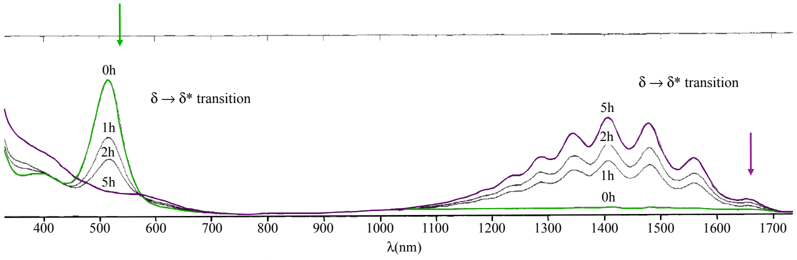
Required Reading: *Acc. Chem. Res.*, **2000**, *33*, 483-90.

$[Mo_2Cl_8]^{4-}$
~18-20 × 10³ cm⁻¹

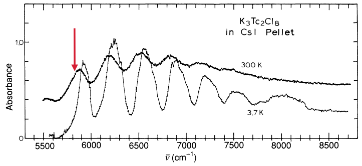
$[Mo_2(SO_4)_4]^{4-}$
~18 × 10³ cm⁻¹

$[Re_2Cl_8]^{2-}$
14 × 10³ cm⁻¹

Quadruply Bonded Systems



re 1. Electronic absorption spectral changes during 254-nm irradiation of $K_4Mo_2(SO_4)_4$ in 5 M D_2SO_4 solution.



The δ → δ* transition in the $[Tc_2Cl_8]^{3-}$ ion at 300 K and 3.7 K.

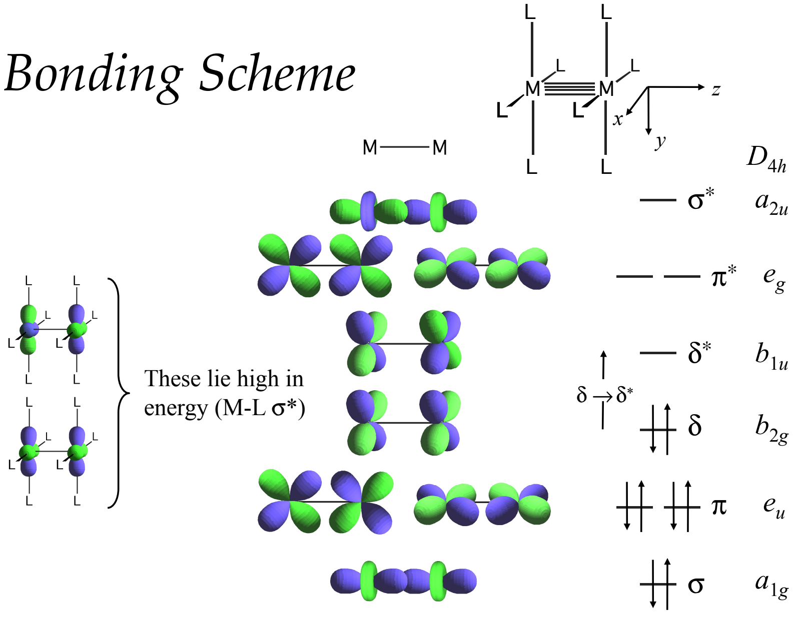
$[Mo_2(SO_4)_4]^{4-}$
~18 × 10³ cm⁻¹

$[Mo_2(SO_4)_4]^{3-}$
~6 × 10³ cm⁻¹

$[Tc_2Cl_8]^{3-}$
~5.8 × 10³ cm⁻¹

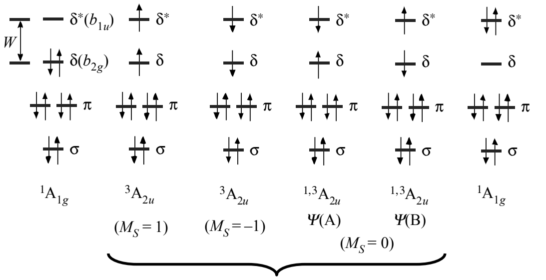
Why are these so much lower in frequency (energy)?

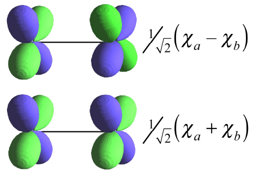
Bonding Scheme



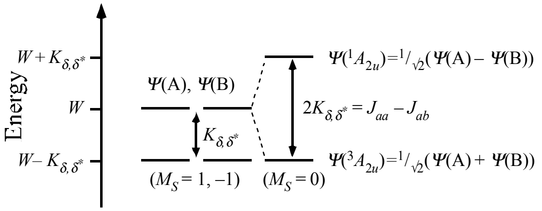
These lie high in energy (M-L σ*)

δ² configuration

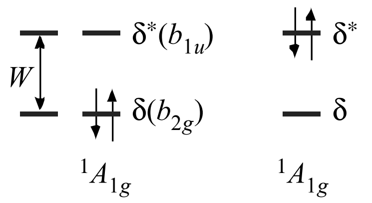




Triplet and singlet excited state ($^{1,3}A_{2u}$) energies:



δ^2-δ^{*2} ${}^1A_{1g}$ *state configuration interaction*



$$\begin{array}{c|cc|l} & |\delta\delta\rangle & |\delta^*\delta^*\rangle & \\ \langle\delta\delta| & -E & K_{\delta\delta^*} & \\ \langle\delta^*\delta^*| & K_{\delta\delta^*} & 2W-E & =0 \end{array}$$

The δ orbital energy has been chosen as the zero of energy.

$$E = W \pm \sqrt{W^2 + K_{\delta\delta^*}^2}$$

Both configurations have ${}^1A_{1g}$ symmetry and since W is modest, the δ^{*2} configuration contributes significantly to the ground state.

$$\Psi_{\delta\delta} = \delta(1)\delta(2)\left(\frac{\alpha_1\beta_2-\beta_1\alpha_2}{\sqrt{2}}\right) \; ; \; \Psi_{\delta^*\delta^*} = \delta^*(1)\delta^*(2)\left(\frac{\alpha_1\beta_2-\beta_1\alpha_2}{\sqrt{2}}\right)$$

$$\int \Psi_{\delta\delta}\mathcal{H}\Psi_{\delta^*\delta^*}d\tau = \int \delta(1)\delta(2)\frac{1}{r_{12}}\delta^*(1)\delta^*(2)d\tau = K_{\delta\delta^*} = \frac{1}{2}\left[J_{aa} - J_{ab}\right]$$

δ^2-δ^{*2} ${}^1A_{1g}$ *state configuration interaction*

The lower energy solution is the ground state, $\Psi_{gr} = c_{\delta\delta}\Psi_{\delta\delta} + c_{\delta^*\delta^*}\Psi_{\delta^*\delta^*}$.

To get the coefficients plug the lower energy $E = W - \sqrt{W^2 + K_{\delta\delta^*}^2}$ into

$$\begin{bmatrix} -E & K_{\delta\delta^*} \\ K_{\delta\delta^*} & 2W-E \end{bmatrix}\begin{bmatrix} c_{\delta\delta} \\ c_{\delta^*\delta^*} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

$$\Rightarrow \begin{bmatrix} -W+\sqrt{W^2+K_{\delta\delta^*}^2} & K_{\delta\delta^*} \\ K_{\delta\delta^*} & W+\sqrt{W^2+K_{\delta\delta^*}^2} \end{bmatrix}\begin{bmatrix} c_{\delta\delta} \\ c_{\delta^*\delta^*} \end{bmatrix} = 0$$

This yields the ratio of the configurational mixing $\dfrac{c_{\delta^*\delta^*}}{c_{\delta\delta}} = \dfrac{W-\sqrt{W^2+K_{\delta\delta^*}^2}}{K_{\delta\delta^*}}$

In the limit of weak overlap, $K_{\delta\delta^*} \gg W$, $\dfrac{c_{\delta^*\delta^*}}{c_{\delta\delta}} \sim \left(\dfrac{W}{K_{\delta\delta^*}} - 1\right) \to -1$

In the limit of big overlap, $K_{\delta\delta^*} \ll W$, $\dfrac{c_{\delta^*\delta^*}}{c_{\delta\delta}} \sim \dfrac{-K_{\delta\delta^*}}{2W} \to 0$

δ^2-δ^{*2} ${}^1A_{1g}$ *states - the weak overlap limit*

In the **limit of weak overlap**, the configurational mixing becomes equal:

$$\Psi_{gr}({}^1A_{1g}) \to 1/\sqrt{2}\left(\Psi_{\delta\delta} - \Psi_{\delta^*\delta^*}\right).$$

Factoring the common spin part (keeping only the spatial part):

$$1/\sqrt{2}\left(\Psi_{\delta\delta} - \Psi_{\delta^*\delta^*}\right) = \frac{1}{\sqrt{2}}\left[\delta(1)\delta(2) - \delta^*(1)\delta^*(2)\right]\left(\frac{\alpha_1\beta_2-\beta_1\alpha_2}{\sqrt{2}}\right)$$

Concentrating on the spatial part:

$$\Psi_{\delta\delta} - \Psi_{\delta^*\delta^*} \sim \left(\chi_A(1)+\chi_B(1)\right)\left(\chi_A(2)+\chi_B(2)\right) - \left(\chi_A(1)-\chi_B(1)\right)\left(\chi_A(2)-\chi_B(2)\right)$$

$$\begin{aligned}\Psi_{\delta\delta} - \Psi_{\delta^*\delta^*} \sim &\left(\chi_A(1)\chi_B(2)+\chi_B(1)\chi_A(2)+\chi_A(1)\chi_A(2)+\chi_B(1)\chi_B(2)\right) \\ &+\left(\chi_A(1)\chi_B(2)+\chi_B(1)\chi_A(2)-\chi_A(1)\chi_A(2)-\chi_B(1)\chi_B(2)\right)\end{aligned}$$

Only the first terms survive, and we obtain the **valence bond wavefunction**:

$$\Psi_{gr}({}^1A_{1g}) \to 1/\sqrt{2}\left(\Psi_{\delta\delta} - \Psi_{\delta^*\delta^*}\right) = \frac{1}{\sqrt{2}}\left[\chi_A(1)\chi_B(2)+\chi_B(1)\chi_A(2)\right]\left(\frac{\alpha_1\beta_2-\beta_1\alpha_2}{\sqrt{2}}\right) \quad \text{(covalent)}$$

If one works through the excited ${}^1A_{1g}$ state, it is the ionic terms that survive:

$$\Psi_{ex}({}^1A_{1g}) \to 1/\sqrt{2}\left(\Psi_{\delta\delta} + \Psi_{\delta^*\delta^*}\right) = \frac{1}{\sqrt{2}}\left[\chi_A(1)\chi_A(2)+\chi_B(1)\chi_B(2)\right]\left(\frac{\alpha_1\beta_2-\beta_1\alpha_2}{\sqrt{2}}\right) \quad \text{(ionic)}$$

δ^2-δ^{*2}*: the* ${}^{1,3}A_{2u}$ *states*

The A_{2u} states can be written directly:

$$\Psi({}^3A_{2u}) = \frac{1}{\sqrt{2}}\left[\delta(1)\delta^*(2) - \delta(2)\delta^*(1)\right]\begin{cases} \alpha_1\alpha_2 \\ \dfrac{\alpha_1\beta_2+\beta_1\alpha_2}{\sqrt{2}} \\ \beta_1\beta_2 \end{cases}$$

$$\Psi({}^1A_{2u}) = \frac{1}{\sqrt{2}}\left[\delta(1)\delta^*(2) + \delta(2)\delta^*(1)\right]\left(\frac{\alpha_1\beta_2-\beta_1\alpha_2}{\sqrt{2}}\right)$$

Concentrating on the spatial parts:

$$\Psi({}^{1,3}A_{2u}) \sim \left(\chi_A(1)+\chi_B(1)\right)\left(\chi_A(2)-\chi_B(2)\right) \pm \left(\chi_A(1)+\chi_B(1)\right)\left(\chi_A(2)-\chi_B(2)\right)$$

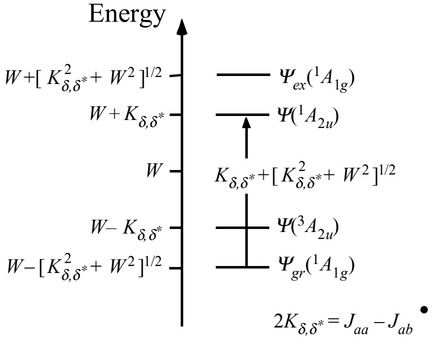
$-$: triplet
$+$: singlet

Only the covalent terms survive for the triplet; only the ionic terms survive for the singlet:

$$\Psi({}^3A_{2u}) = \frac{1}{\sqrt{2}}\left[\chi_A(1)\chi_B(2)-\chi_B(1)\chi_A(2)\right]\left(\frac{\alpha_1\beta_2+\beta_1\alpha_2}{\sqrt{2}}\right) \quad \text{(covalent)}$$

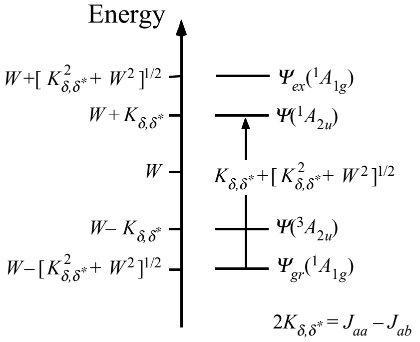
$$\Psi({}^1A_{2u}) = \frac{1}{\sqrt{2}}\left[\chi_A(1)\chi_A(2)-\chi_B(1)\chi_B(2)\right]\left(\frac{\alpha_1\beta_2-\beta_1\alpha_2}{\sqrt{2}}\right) \quad \text{(ionic)}$$

"$\delta \rightarrow \delta^*$ transition" in the δ^2 configuration



- The dipole-allowed transition is $^1A_{1g} \rightarrow {}^1A_{2u}$, which we've seen to be more complicated than the fairly simply described $^2B_{2g} \rightarrow {}^2A_{1u}$ transition for a δ^1 configuration.
- The ground state is more covalent, the excited state is more ionic (but nonpolar!).

"$\delta \rightarrow \delta^*$ transition" in the δ^2 configuration, cont.



The spectra we've seen in the previous slides indicate that δ bond is highly correlated, with the δ–δ* orbital splitting being perhaps slightly smaller than the e-e repulsion between pairs of electrons in the MOs in the quadruple bonds.

$\Delta E = K_{\delta,\delta^*} + \sqrt{W^2 + K^2_{\delta,\delta^*}}$. For the spectra we've seen, $\Delta E \simeq 3W$ (i.e., the transition energy for the δ^2 cases are about 3 times larger than for the δ^1 cases.) That corresponds to $W \simeq \frac{3}{4}K_{\delta,\delta^*} = \frac{3}{4}(J_{a,a} - J_{a,b})$.

δ^2-δ^{*2} $^1A_{1g}$ state configuration interaction

If we plug in $K_{\delta,\delta^*} \simeq \frac{4}{3}W$ into the expression for configurational mixing,

we obtain $\dfrac{c_{\delta^*\delta^*}}{c_{\delta\delta}} = \dfrac{W - \sqrt{W^2 + \frac{16}{9}W^2}}{\frac{4}{3}W} = -\dfrac{1}{2}$

This is also indicative of highly correlated bond, but one where overlap is still important.