



1. Symmetry, Group Theory, and Electronic Structure

2. Ground State Spectroscopic Methods

3. Excited State Spectroscopic Methods

3.1 Valence Electronic Spectroscopy

3.2 Core Electronic Spectroscopy

3.1 Valence Electronic Spectroscopy

Methods thus far did not strongly perturb chemical properties

- NMR, EPR, (Mössbauer), IR, and (Raman) → probes of ***ground state properties***
 - ΔE_{ex} too low to disturb molecular electron density distribution (ρ_e)
- benefits of such physical methods
 - perturbation is small → very accurately reflects actual molecular ground electronic state
 - effect is generally *spatially* localized → often easily simplified/interpreted/generalized
- disadvantages of such methods
 - perturbations of system are small → little about response to larger distortions (*i.e.*, actual chemistry!)
 - effects are spatially localized → longer-range interactions are not as influential
 - ultimately → ***chemistry = changes in electronic structure***

Spectroscopic probes of electronic structure provide direct insights into

- molecular bonding interactions → energetics of chemically-relevant processes
- split into two parts:
 - valence electronic spectroscopy (transitions involving valence electrons)
 - core electronic spectroscopy (transitions involving core electrons)

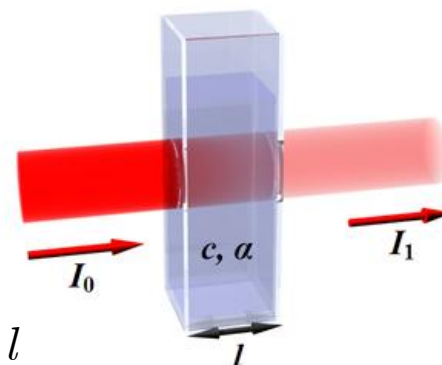
The Electronic Absorption Experiment

- direct absorption experiment → same as IR spectroscopy except
 - IR → intensity reported as “% transmittance”
 - Abs → intensity reported as “Absorbance” or optical density (OD)

$$A = \log\left(\frac{I_0}{I}\right) = \log\left(\frac{100}{\%T}\right) \quad \%T = \left(\frac{I}{I_0}\right) \times 100\%$$

- absorbance of a sample depends on
 - energy/wavelength of incident photons
 - interaction of molecule with photons
 - concentration of sample (c in M)
 - path length (l in cm)

$$A \nu = \underbrace{\epsilon \nu}_{\substack{\text{molar} \\ \text{absorbance} \\ \text{coefficient}}} \times c \times l$$



a.k.a. molar absorptivity,
molar extinction coefficient

- measured absorbance includes effects from light absorption, scattering, & luminescence
 - molar extinction coefficient → all that extinguishes the incident photon intensity
 - molar absorbance coefficient → only the part that is absorbed...

$$\sigma_{\text{scattering}} \propto \nu^4$$

bigger problem at higher energies ₃

Absorbance coefficients & oscillator strengths

- units $\rightarrow M^{-1}cm^{-1}$ (coefficients per absorbing molecule)
- relates to **oscillator strength (f)** of transition
 - oscillator strength = *intrinsic probability* of transition (no units!)
 - experimentally:

$$f_{\text{exp}} = 4.33 \times 10^{-9} \int \varepsilon \nu \, d\nu$$

total area under the experimental peak

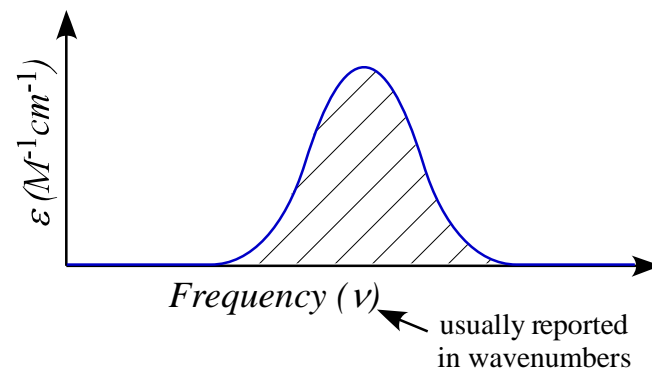
- theoretically:

$$f_{\text{theo}} = 1.085 \times 10^{-11} \nu \left\langle \Psi_g \left| \hat{M} \right| \Psi_e \right\rangle^2$$

where $\Psi_g = \psi_{orb} \psi_{spin}$ (total wavefunction)

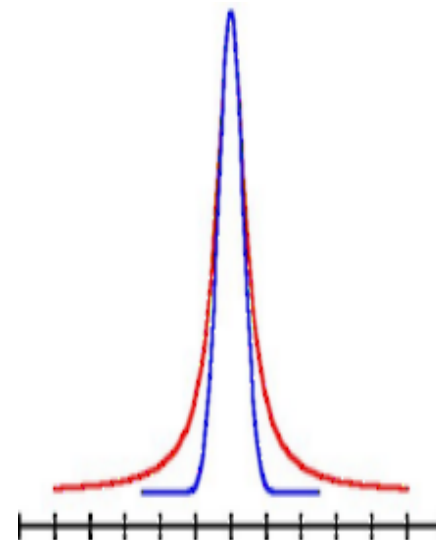
\hat{M} = transition moment operator (operates on orbital part)

$\hat{M} \approx \vec{\mu} = e\vec{r}$ (dominated by electric dipole operator)



Transition Bandshapes

- homogeneous broadening mechanisms
 - **Lorentzian bandshape**
 - inherent excited state lifetime (*natural* broadening)
 - collisional broadening (decreases lifetime)
- inhomogeneous broadening mechanisms
 - **Gaussian bandshape**
 - population of molecules with differing geometries
 - thermal variations (in source, sample, and/or detector)



Selection rules in electronic absorption

- orbital/state symmetry considerations $\Gamma_{\Psi_g} \times \Gamma_{\hat{M}} \times \Gamma_{\Psi_e} \equiv A_{1g}$ in O_h
 - ED component of Γ_M always ungerade
 - GS and ES must have opposite inversion symmetry
 - leads to *parity* or *Laporte* selection rule
 - parity allowed transitions ($g \rightarrow u, u \rightarrow g$): $s \leftrightarrow p, p \leftrightarrow d, d \leftrightarrow f, \dots$
 - parity forbidden transitions ($g \rightarrow g, u \rightarrow u$): $s \leftrightarrow s, p \leftrightarrow p, d \leftrightarrow d, f \leftrightarrow f, s \leftrightarrow d, \dots$
 - all LF transitions are technically forbidden (unless *inversion* symmetry is broken)
 - $g \times u \times g \mapsto u$ (forbidden)
 - $g \times u \times u \mapsto g$ (may be allowed)
- spin considerations
 - photon can interact with either *orbital part* (Abs) or *electron spin* (EPR)
 - interaction with both is essentially a two-electron transition (forbidden)
 - selection rule for Abs is therefore $\rightarrow \Delta S = 0$

Trends in transition metal ion absorption intensities

Transition type	$\epsilon_{(max)}$	f	Bandshape
$d-d$, spin forbidden, parity forbidden (O_h)	0.1	$\sim 10^{-7}$	<i>sharper</i>
$d-d$, spin forbidden, parity allowed (T_d)	1	$\sim 10^{-6}$	↓
$d-d$, spin allowed, parity forbidden (O_h)	10	$\sim 10^{-4} - 10^{-5}$	
$d-d$, spin allowed, parity allowed (T_d)	100	$\sim 10^{-3} - 10^{-4}$	↓
Charge Transfer, spin allowed, parity allowed	10,000	$\sim 10^{-1}$	

- point groups without inversion symmetry:
- point groups with inversion symmetry:

$T_d, D_{nd}, C_{nv}, C_n, S_{2n+2}, C_{(2n+1)h}$

$O_h, D_{nh}, S_{2n}, C_{(2n)h}$

Why are LF transitions observed?

- technically forbidden, so how can they be observed?
 - need mechanism to get around the problem
 - mix other components into the wavefunction
- two approaches:
 - **static distortions** break inversion symmetry (no longer g or u)
 - **dynamic distortions** break local symmetry \rightarrow **vibronic coupling**
 - both mechanisms lower symmetry and allow mixing of wavefunctions
 - for LF \rightarrow mix in small amount of *ungerade* wavefunction yielding $g \rightarrow u$ (allowed)

$$\begin{array}{l}
 \Psi_1 = |\Gamma_1^g\rangle + \lambda |\Gamma_1^u\rangle \\
 \Psi_2 = |\Gamma_2^g\rangle + \lambda' |\Gamma_2^u\rangle
 \end{array}
 \left| \begin{array}{l}
 \Psi_1 \rightarrow \Psi_2 \text{ allowed due to} \\
 \lambda |\Gamma_1^u\rangle \rightarrow \lambda' |\Gamma_2^g\rangle
 \end{array} \right.
 \begin{array}{l}
 |\Gamma_1^g\rangle \rightarrow \lambda' |\Gamma_2^u\rangle \\
 \lambda |\Gamma_1^u\rangle \rightarrow |\Gamma_2^g\rangle
 \end{array}$$

Breaking parity symmetry → “intensity borrowing” from CI

- mixing of wavefunctions is perturbation:
 - symmetry determined by *geometric distortion*
- calculated oscillator strength for this situation...
 - for $\epsilon_u > 10,000 M^{-1} cm^{-1}$ at $E_u > 40,000 cm^{-1}$ and mixing of only 1-2%...

$$|\Psi'_e\rangle = |\Psi_e\rangle + \frac{\langle \Psi_e | \hat{H}_{dist} | \Psi_u \rangle}{E_e - E_u} |\Psi_u\rangle$$

$$f_{d-d} \approx 10^{-3} - 10^{-4} (\epsilon_{d-d} \approx 100 M^{-1} cm^{-1}) \text{ static}$$

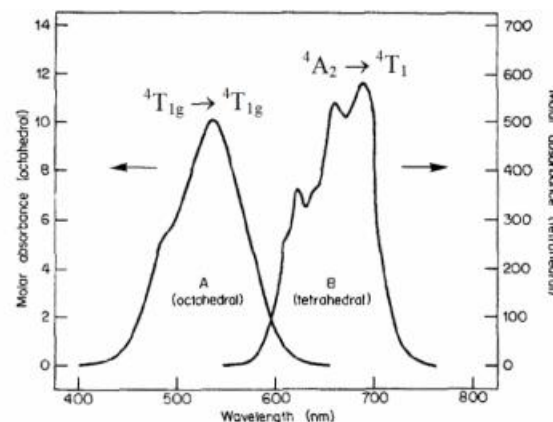
$$f_{d-d} \approx 10^{-4} - 10^{-5} (\epsilon_{d-d} \approx 10 M^{-1} cm^{-1}) \text{ dynamic}$$

$$f_{g \rightarrow e} = 0 + \frac{E_e}{E_u} \left[\frac{\langle \Psi_e | \hat{H}_{dist} | \Psi_u \rangle}{E_e - E_u} \right]^2 f_u$$

- example of static mechanism: T_d complexes...

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	$(x, y, z), (xy, xz, yz)$

- what can d orbitals mix with?



The visible spectra of $[Co(H_2O)_6]^{2+}$ (curve A) and $[CoCl_4]^{2-}$ (curve B). The molar absorbance scale at the left applies to curve A, and that at the right applies to curve B.

Vibronic coupling → dynamic mixing

- for centrosymmetric complexes – involves electronic + vibrational excitation
- transition probability integral: $\langle \Psi_g | \hat{M} | \Psi_e \rangle$

$$|\Psi_g\rangle = \psi_{elec} \psi_{vib} \equiv \text{vibronic wavefunction}$$

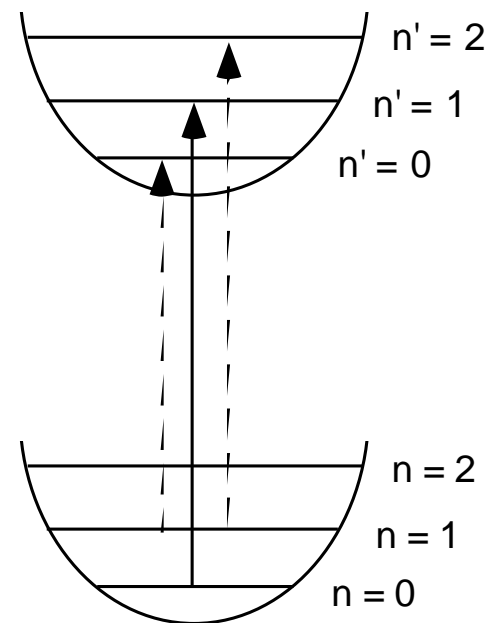
- selection rule is therefore

$$\Gamma \psi_g^{elec} \times \Gamma \psi_g^{vib} \times \Gamma \hat{M} \times \Gamma \psi_e^{elec} \times \Gamma \psi_e^{vib} \approx A_{1g}$$

$$\Gamma_g \times A_{1g} \times \Gamma_u \times \Gamma_g \times \underbrace{\Gamma \psi_e^{vib}} \approx A_{1g}$$

must have ungerade symmetry

- ligand field transitions in centrosymmetric complexes can therefore gain intensity ONLY by mixing with ungerade vibrational modes...
- e.g., the ${}^4A_{2g} \rightarrow {}^2T_{1g}$ transition in ReCl_6^{2-} (d^3)



**vibronic coupling
vs.
spin-orbit coupling**

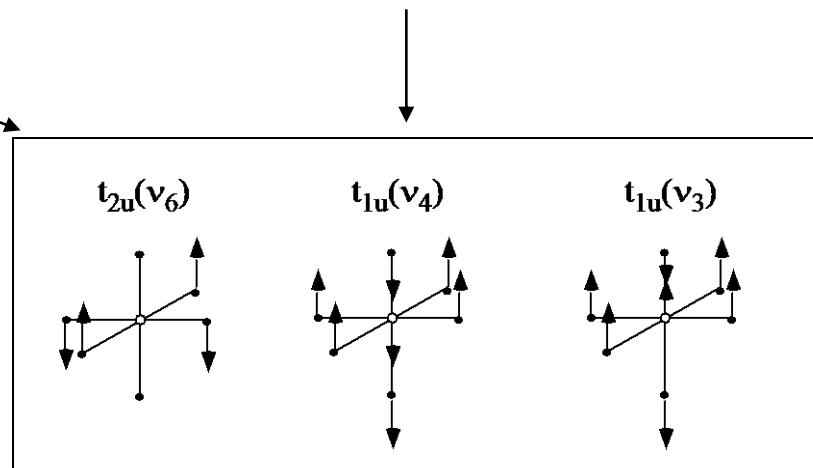
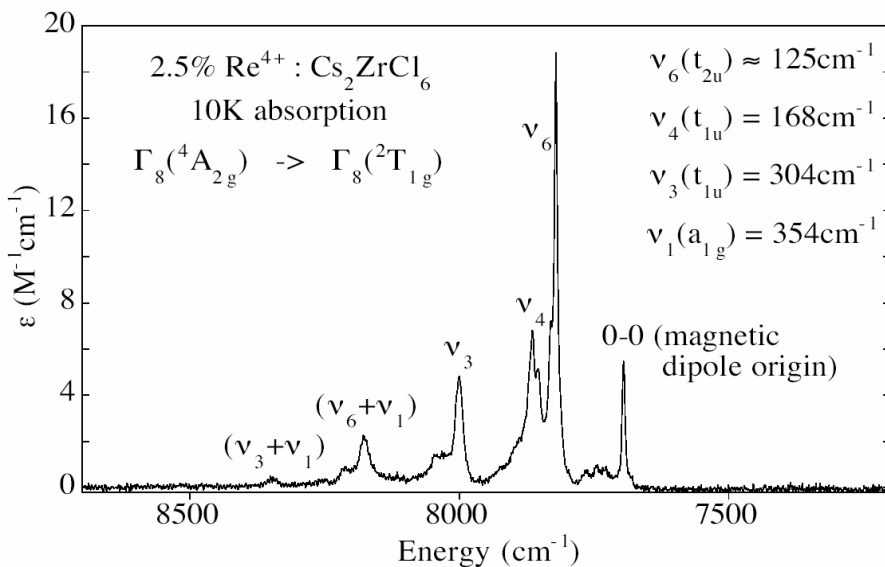
3.1.1 Electronic Absorption Spectroscopy

- the ${}^4A_{2g} \rightarrow {}^2T_{1g}$ transition in $\text{ReCl}_6^{2-} (d^3)$

- electric dipole forbidden
- look for vibronic coupling...
- available vibrational modes can be determined (*vide supra*)

$$\begin{aligned} \Gamma_{\langle \Psi_g | \hat{M} | \Psi_e \rangle} &= \underbrace{\Gamma_{\psi_g^{elec}}}_{A_{1g}} \times \underbrace{\Gamma_{\psi_g^{vib}}}_{A_{1g}} \times \underbrace{\Gamma_{\hat{M}}}_{T_{1u}} \times \underbrace{\Gamma_{\psi_e^{elec}}}_{T_{1g}} \times \underbrace{\Gamma_{\psi_e^{vib}}}_{\Gamma_q} \\ &= A_{1g} \times A_{1g} \times T_{1u} \times T_{1g} \times \Gamma_q \\ &= A_{2g} + E_u + T_{1u} + T_{2u} \times \Gamma_q \end{aligned}$$

$$\Gamma_q = A_{1g} + E_g + T_{2g} + \boxed{2T_{1u} + T_{2u}}$$

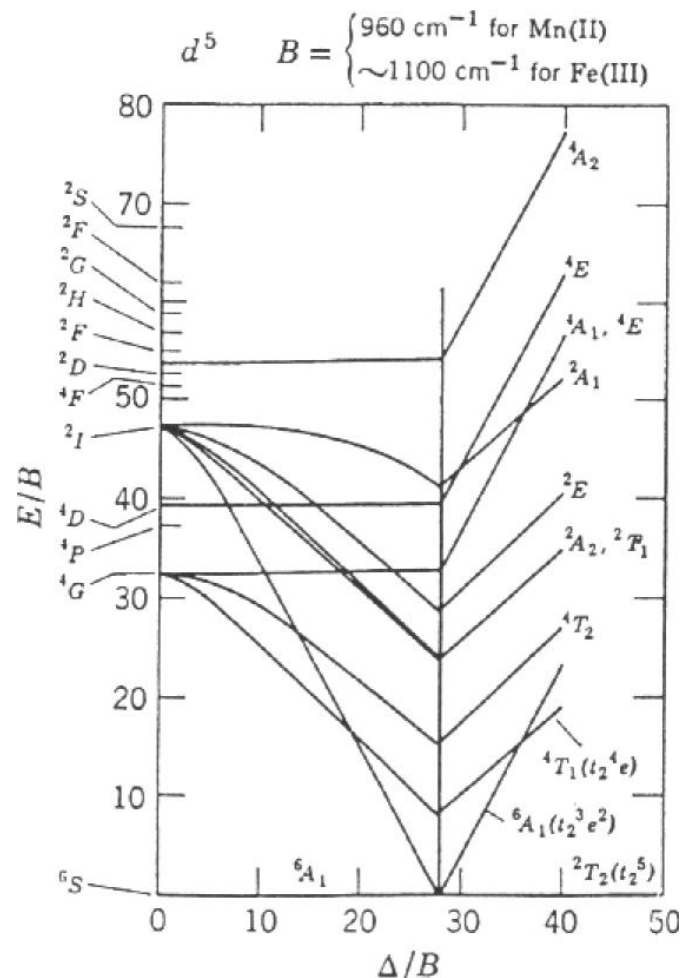


note that combination bands also include modes that are not technically of correct symmetry (A_{1g})

- combination band is of correct symmetry for vibronic coupling....

Analysis of LF States → Tanabe-Sugano Diagrams

- allows evaluation of O_h/T_d complexes
 - transitions involving $d-d$ states
 - includes effects from ligand field and electron-electron repulsion ($H_{LF} \sim H_{ee}$)
 - *does not include SOC*
 - *only indirectly includes covalency (B)*
- derived from ligand field matrices that allow for mixing of states due to $e-e$ repulsion and ligand field effects.



3.1.1 Electronic Absorption Spectroscopy

- example of ligand field matrices (for d^5 case)

Table A3-4 Energy Matrices for the Configuration d^5 in a Cubic Field (Tanabe and Sugano)

${}^2E(a^2D, b^2D, c^2D, a^2G, b^2G, {}^2H, {}^2I)$							
$t^4({}^1A_1)e$	$-10Dq - 4B + 12C$	$10B$	$6B$	$6\sqrt{3}B$	$6\sqrt{2}B$	$-2B$	$4B + 2C$
$t^4({}^1E)e$		$-10Dq - 13B + 9C$	$-3B$	$3\sqrt{3}B$	0	$2B + C$	$2B$
$t^3({}^2E)e^2({}^1A_1)$			$-4B + 10C$	0	0	$-3B$	$-6B$
$t^3({}^3E)e^2({}^3A_2)$				$-16B + 8C$	$2\sqrt{6}B$	$-3\sqrt{3}B$	$6\sqrt{3}B$
$t^3({}^2E)e^2({}^1E)$					$-12B + 8C$	0	$6\sqrt{2}B$
$t^2({}^1E)e^3$						$-10Dq - 13B + 9C$	$-10B$
$t^2({}^1A_1)e^3$							$-10Dq - 4B + 12C$
${}^2A_1(a^2F, b^2F, {}^2I)$							
$t^4({}^1E)e$		$-10Dq - 3B + 9C$		$-3\sqrt{2}B$		0	$6B + C$
$t^3({}^2E)e^2({}^1E)$				$-12B + 8C$		$-4\sqrt{3}B$	$3\sqrt{2}B$
$t^3({}^4A_2)e^2({}^3A_2)$						$-19B + 8C$	0
$t^2({}^1E)e^3$							$10Dq - 3B + 9C$
${}^2A_2({}^2F, {}^2I)$				${}^4T_1({}^4P, {}^4F, {}^4G)$			
$t^4({}^1E)e$	$-10Dq - 23B + 9C$	$3\sqrt{2}B$	$-2B + C$	$t^4({}^3T_1)e$	$-10Dq - 25B + 6C$	$-3\sqrt{2}B$	C
$t^3({}^2E)e^2({}^1E)$		$-12B + 8C$	$-3\sqrt{2}B$	$t^3({}^2T_2)e^2({}^3A_1)$		$-16B + 7C$	$-3\sqrt{2}B$
$t^2({}^1E)e^3$			$10Dq - 23B + 9C$	$t^2({}^3T_1)e^3$			$10Dq - 25B + 6C$
${}^4T_2({}^4E, {}^4G, {}^4D)$				${}^4E({}^4D, {}^4G)$			
$t^4({}^3T_1)e$	$-10Dq - 17B + 6C$	$\sqrt{6}B$	$4B + C$	$t^3({}^2E)e^2({}^3A_2)$		$-22B + 5C$	$-2\sqrt{3}B$
$t^3({}^2T_1)e^2({}^3A_2)$		$-22B + 5C$	$-\sqrt{6}B$	$t^3({}^4A_2)e^2({}^1E)$			$-21B + 5C$
$t^2({}^3T_1)e^3$			$-10Dq - 17B + 6C$				
${}^6A_1({}^6S)$		$t^3({}^4A_2)e^2({}^3A_2)$	$-35B$				
${}^4A_1({}^4G)$		$t^3({}^4A_2)e^2({}^3A_2)$	$-25B + 5C$				
${}^4A_2({}^4F)$		$t^3({}^4A_2)e^2({}^1A_1)$	$-13B + 7C$				

3.1.1 Electronic Absorption Spectroscopy

- example of ligand field matrices (for d^5 case)...

Table A3-4 (Continued)

${}^2T_2(a^2F, b^2F, a^2G, b^2G, {}^2H, {}^2I, a^2D, b^2D, c^2D)$										
t^5	$-20Dq - 20B + 10C$	$3\sqrt{6}B$	$\sqrt{6}B$	0	$-2\sqrt{3}B$	$4B + 2C$	$2B$	0	0	0
$t^4({}^3T_1)e$		$-10Dq - 8B + 9C$	$3B$	$(\sqrt{6}/2)B$	$(-3\sqrt{2}/2)B$	$(3\sqrt{6}/2)B$	$(3\sqrt{6}/2)B$	0	$4B + C$	0
$t^4({}^1T_2)e$			$-10Dq - 18B + 9C$	$(3\sqrt{6}/2)B$	$(-3\sqrt{2}/2)B$	$(5\sqrt{6}/2)B$	$(-5\sqrt{6}/2)B$	C	0	0
$t^3({}^2T_1)e^2({}^3A_2)$				$-16B + 8C$	$2\sqrt{3}B$	0	0	$(-3\sqrt{6}/2)B$	$(-\sqrt{6}/2)B$	0
$t^3({}^2T_1)e^2({}^1E)$					$-12B + 8C$	$-10\sqrt{3}B$	0	$(3\sqrt{2}/2)B$	$(3\sqrt{2}/2)B$	$-2\sqrt{3}B$
$t^3({}^2T_2)e^2({}^1A_1)$						$2B + 12C$	0	$(-5\sqrt{6}/2)B$	$(-3\sqrt{6}/2)B$	$4B + 2C$
$t^3({}^2T_2)e^2({}^1E)$							$-6B + 10C$	$(-5\sqrt{6}/2)B$	$(3\sqrt{6}/2)B$	$2B$
$t^2({}^1T_2)e^3({}^2E)$								$10Dq - 18B + 9C$	$3B$	$-\sqrt{6}B$
$t^2({}^3T_2)e^3({}^2E)$									$10Dq - 8B + 9C$	$-3\sqrt{6}B$
te^4										$20Dq - 20B + 10C$
${}^2T_1(a^2P, a^2F, b^2F, a^2G, b^2G, {}^2H, {}^2I)$										
$t^4({}^3T_1)e$	$-10Dq - 22B + 9C$	$-3B$		$(-3\sqrt{2}/2)B$	$(3\sqrt{2}/2)B$	$(-3\sqrt{2}/2)B$	$(-3\sqrt{6}/2)B$	0		C
$t^4({}^1T_2)e$		$-10Dq - 8B + 9C$		$(-3\sqrt{2}/2)B$	$(3\sqrt{2}/2)B$	$(15\sqrt{2}/2)B$	$(5\sqrt{6}/2)B$	$4B + C$		0
$t^3({}^2T_1)e^2({}^1A_1)$			$-4B + 10C$	0	0	0	$10\sqrt{3}B$	$(3\sqrt{2}/2)B$		$(-3\sqrt{2}/2)B$
$t^3({}^2T_1)e^2({}^1E)$				$-12B + 8C$	0	0	0	$(-3\sqrt{2}/2)B$		$(-3\sqrt{2}/2)B$
$t^3({}^2T_2)e^2({}^3A_2)$					$-10B + 10C$	$-2\sqrt{3}B$		$(15\sqrt{2}/2)B$		$(-3\sqrt{2}/2)B$
$t^3({}^2T_2)e^2({}^1E)$						$-6B + 10C$		$(5\sqrt{6}/2)B$		$(-3\sqrt{6}/2)B$
$t^2({}^1T_2)e^3$								$10Dq - 8B + 9C$		$-3B$
$t^2({}^3T_1)e^3$										$10Dq - 22B + 9C$

Low-symmetry effects in Ligand Field States

- TS Diagrams are only for O_h / T_d symmetries – lower symmetry?
 - more possibilities for mixing (analysis of states is more complex)
 - easier to evaluate orbital splitting/mixing & then derive states
- single-crystal polarized Abs can be extremely useful in determining effects of low-symmetry splitting of states...
 - $O_h/T_d \rightarrow$ transition moment operator is *isotropic*
 - in lower symmetries – it rarely is

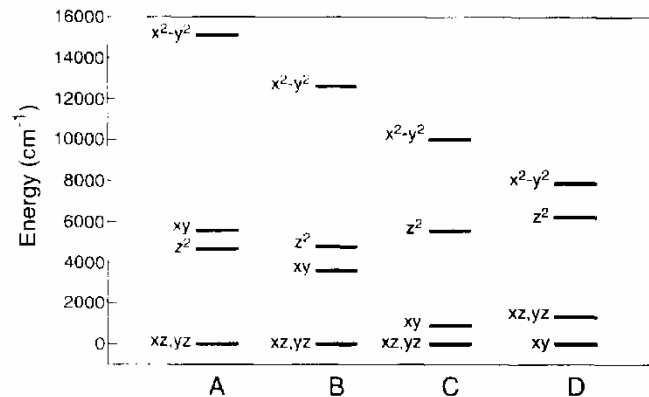
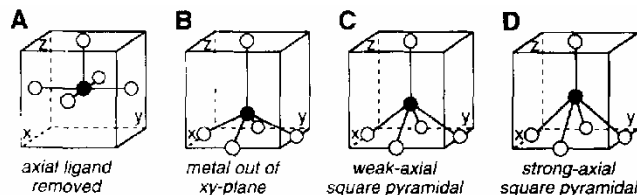
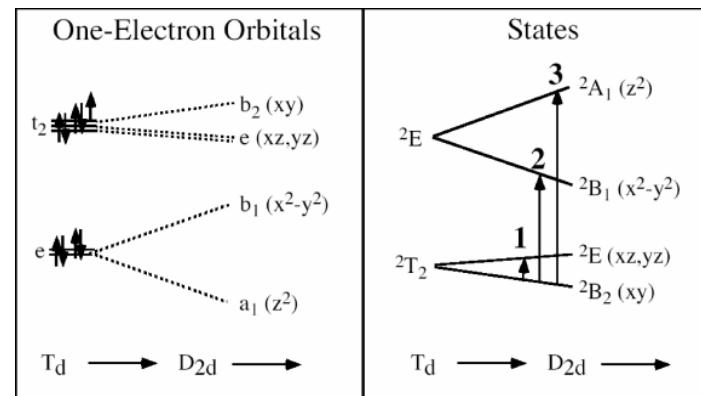


Fig. 12. Calculated energy level diagrams for a five-coordinate Fe^{2+} square pyramidal site, moving the metal out of the equatorial plane. d-orbital energy splittings of a square pyramidal Fe^{2+} center with five O-type ligands and the metal pulled out of the equatorial plane by: A, 0° (removal of one ligand from a pure octahedron); B, 10° ; C, 15° ; D, 17.5° (resulting in a strong-axial system). All orbital wave functions are written in a tetragonal basis set.

3.1.1 Electronic Absorption Spectroscopy

- e.g., D_{2d} distorted $[\text{CuCl}_4]^{2-}$
 - why does it distort?
 - what is the effect of the distortion on the electronic structure of the complex?
 - what is the effect of the spectroscopy?



$$\langle \Psi_g | \hat{M} | \Psi_e \rangle \approx \langle \Psi_g | \hat{\mu} | \Psi_e \rangle$$

$$\Gamma_{\hat{\mu}_{x,y}} = E \quad \Gamma_{\hat{\mu}_z} = B_2$$

$$(1) \quad \langle \Psi_g | \hat{\mu}_{(x,y)} | \Psi_e \rangle \mapsto B_2 \times E \times E \mapsto A_1 + \dots$$

$$\langle \Psi_g | \hat{\mu}_{(z)} | \Psi_e \rangle \mapsto B_2 \times B_2 \times E \mapsto E$$

$$(2) \quad \langle \Psi_g | \hat{\mu}_{(x,y)} | \Psi_e \rangle \mapsto B_2 \times E \times B_1 \mapsto E$$

$$\langle \Psi_g | \hat{\mu}_{(z)} | \Psi_e \rangle \mapsto B_2 \times B_2 \times B_1 \mapsto B_1$$

$$(3) \quad \langle \Psi_g | \hat{\mu}_{(x,y)} | \Psi_e \rangle \mapsto B_2 \times E \times A_1 \mapsto E$$

$$\langle \Psi_g | \hat{\mu}_{(z)} | \Psi_e \rangle \mapsto B_2 \times B_2 \times A_1 \mapsto A_1$$

D_{2d}	E	$2S_4$	$C_2(z)$	$2C'_2$	$2\sigma_d$	
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	x^2-y^2
B_2	+1	-1	+1	-1	+1	z, xy
E	+2	0	-2	0	0	$(x, y), (R_x, R_y), (xz, yz)$

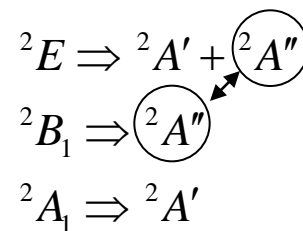
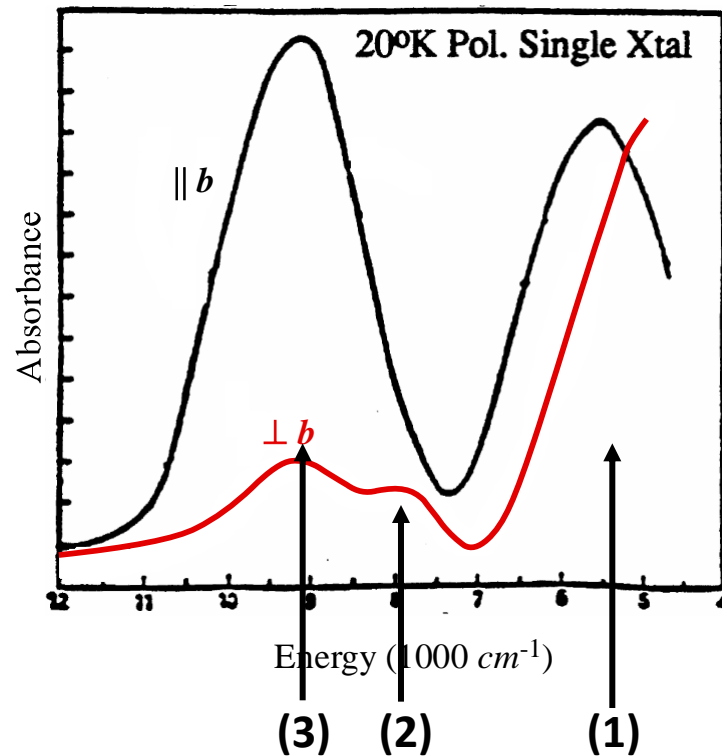
1 will be (x,y)-polarized and **3** will be z-polarized

3.1.1 Electronic Absorption Spectroscopy

• e.g., D_{2d} distorted $[\text{CuCl}_4]^{2-}$ (continued)

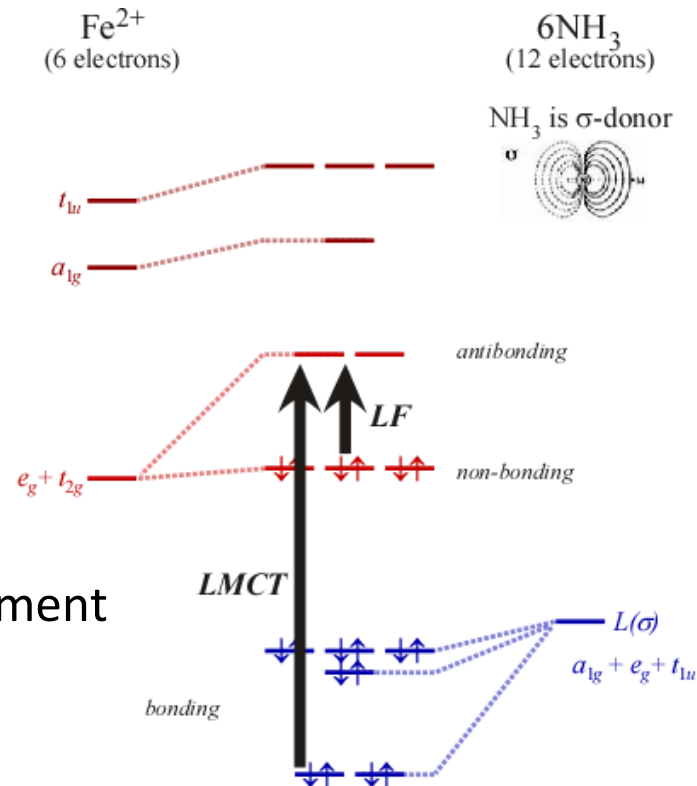
- crystals are orthorhombic
- site symmetry $\approx D_{2d}$ (strictly C_s)
- crystallizes as plates with ab face
 - $E \parallel b = (x,y)^2$
 - $E \parallel a = 0.638(z)^2 + 0.362(x,y)^2$
 - look along b -axis to determine polarization
- assignment of major components is easy... but some features don't make sense:
 - additional peak at $\sim 8000 \text{ cm}^{-1}$
 - peak at $\sim 5000 \text{ cm}^{-1}$ changes with polarization
 - why does this happen?
- site symmetry is actually C_s and NOT D_{2d}
 - 2E excited state (1) splits into ${}^2A'$ and ${}^2A''$ components, which causes splitting of 5000 cm^{-1} peak (by $\sim 1000 \text{ cm}^{-1}$)
 - forbidden 2B transforms to ${}^2A'' \rightarrow$ can now mix with one component of 2E (intensity at $\sim 8000 \text{ cm}^{-1}$) with intensity along the (x,y) direction

1 will be (x,y) -polarized and 2 will be z -polarized



Charge Transfer Transitions in TM Complexes

- CT transitions involve taking e^- from one atomic center to another:
 - both $L \rightarrow M$ (LMCT) & $M \rightarrow L$ (MLCT)
 - sometimes called redox transitions (involve e^- transfer)
- more intense than LF transitions
 - involve larger changes in electric dipole moment
 - interatomic transitions not parity forbidden
 - involve three possible terms...



$$\Psi_i = |L\rangle + \lambda |M\rangle$$

$$\Psi_f = |M\rangle - \lambda' |L\rangle$$

$$\left\| \begin{array}{l} LMCT \mapsto \langle \Psi_i | \hat{\mu} | \Psi_f \rangle = \mu_{if} = \lambda' \mu_{LL} - 2\lambda\lambda' \mu_{LM} + \lambda \mu_{MM} \end{array} \right.$$

depends on amount of ligand character in metal orbitals (β^2) ← **most important term: ligand-ligand overlap**
 ↑ **parity forbidden**
 ↑ **coefficient is very small**

3.1.1 Electronic Absorption Spectroscopy

- usual origin of low-energy CT transitions (*i.e.*, visible or near-UV)
 - LMCT → usually result from non-bonding (or weakly π -bonding) ligand orbitals
 - MLCT → usually result from transitions to weakly π -antibonding ligand orbitals (π^*)
 - ligand centered transitions → transitions that occur to/from the ligand
 - no direct participation from the metal
 - these are sometimes enhanced by the presence of the metal through indirect coupling
 - mostly occur when ligand involves π -bonding network

- intensities of CT transitions

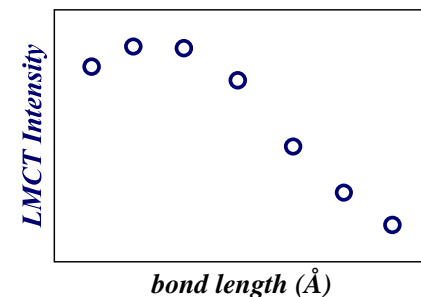
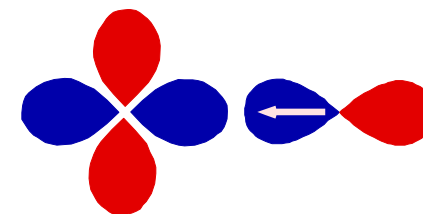
- intensity mechanism depends on LL overlap
- but intensity is generally directly dependent on metal-ligand covalency (*i.e.* M-L overlap)
- intensity reflects covalency of metal centre

$$\mu_{if} \sim \lambda' \mu_{LL}$$

↓
ligand character in
metal orbital!

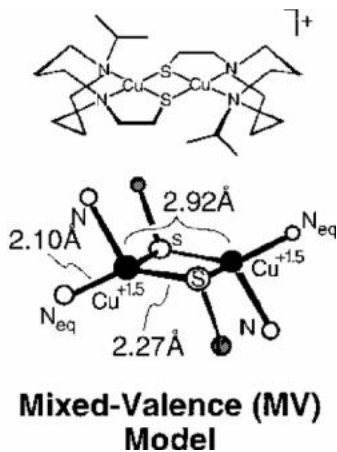
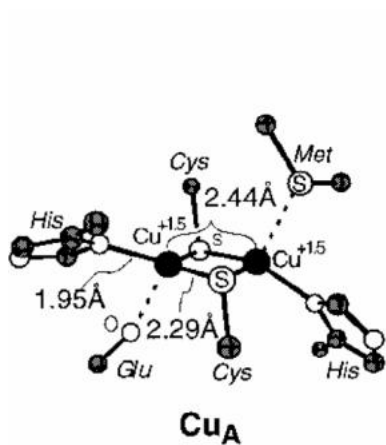
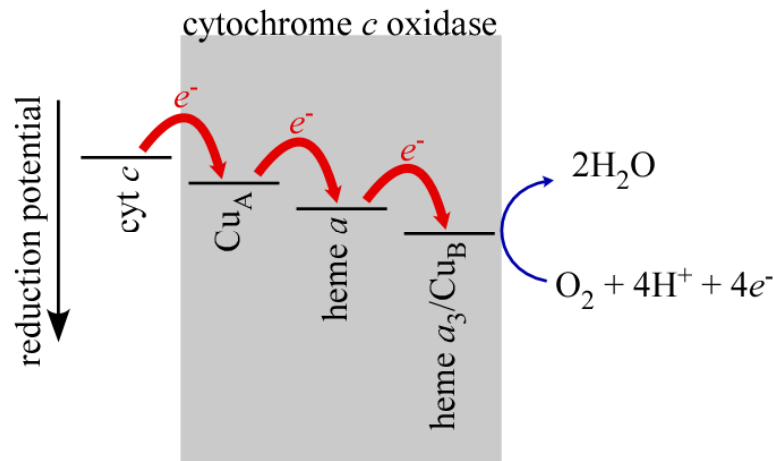
- transition energies of CT processes

- generally *very* complex (depends on many factors)
- since CT transitions involve e transfer → related to redox properties of donor/acceptor
- donor/acceptor orbital energies → from valence shell ionization energies (VSIE, H_{ij})
 - directly related to electronegativities → define “optical” electronegativities (C. K. Jørgensen)



3.1.1 Electronic Absorption Spectroscopy

- *e.g.*, Cu_A centre in cytochrome *c* oxidase
 - Cyt *c* Oxidase → terminal *oxidase* involved in aerobic respiration
 - role of Cu_A → electron conduit
 - electron acceptor from cytochrome *c*
 - electron donor to heme *a*
 - reduction potential must be accurately tuned for effective electron transport
 - potential must be "tuned" by the protein such that $E_{(cyt\ c)}^{0'} < E_{(Cu_A)}^{0'} < E_{(heme\ a)}^{0'}$
 - weaken axial ligands → less charge donation = more stable reduced site

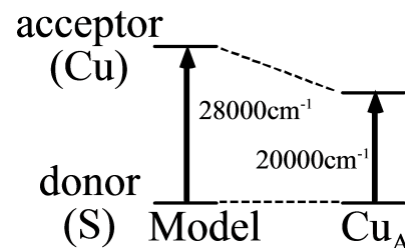
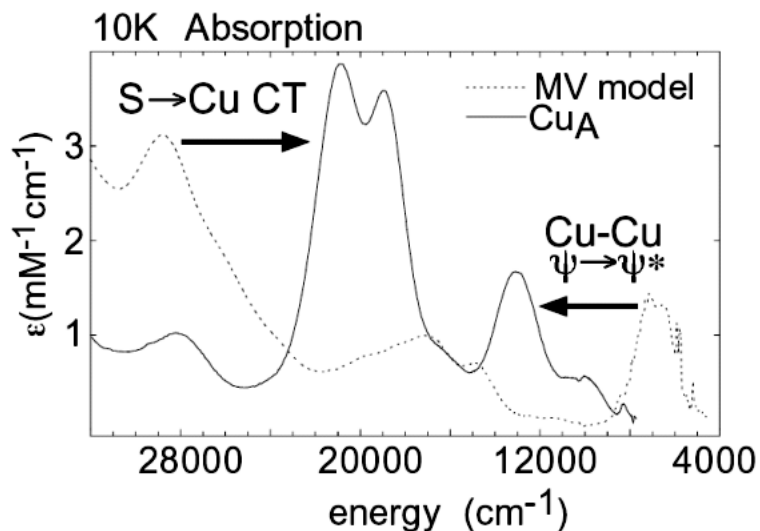


	Coord. number	$E^{0'}$ (mV vs NHE)
Model	4	-280
Cu _A	3 (+1)	+240

how is this manifested in the spectroscopy?

3.1.1 Electronic Absorption Spectroscopy

- S→Cu LMCT is much lower in energy for Cu_A centre



	CN	LMCT (cm ⁻¹)	E ⁰ (mV vs NHE)
Model	4	28000	-280
Cu _A	3 (+1)	20000	+240

- we also see a higher energy for the Cu $\Psi \rightarrow \Psi^*$
 - results from direct metal-metal overlap
 - yields better coupling for electron transfer
 - allows for faster/more efficient directional ET

