

5.04, Principles of Inorganic Chemistry II
 MIT Department of Chemistry
Lecture 31: Electronic Selection Rules

Selection rules for electronic transitions determine whether a transition is allowed or forbidden. The integrated intensity or oscillator strength, f , of an absorption band is related to the transition moment integral, M ,

$$f = 4.315 \times 10^{-4} \int \epsilon dv = 1.085 \times 10^{11} \nu \left| \langle \psi_{gs} | M | \psi_{es} \rangle \right|^2$$

molar absorptivity coefficient

$$\text{where } M = \vec{\mu} \cdot \left(-e \sum_i \mathbf{r}_i \right) \quad \therefore M \text{ transforms as } x, y, z$$

↑
electric polarization

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electric dipole moment

The Born-Oppenheimer principle allows wavefunction to be separated into electronic and vibronic components... $\Psi = \psi_{es} \psi_v$

$$\Psi = \psi_{es} \psi_v$$

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spin electronic vibrational

Thus the transition moment integral becomes

$$M = \langle \psi_v | \psi_v \rangle \langle \psi_e | \hat{\mu} | \psi_e' \rangle \langle \psi_s | \psi_s' \rangle$$

This integral must be non zero for the transition to be allowed. Ignoring the vibronic component of the wave function, M will be non zero iff

$$\langle \psi_e | \hat{\mu} | \psi_e' \rangle \text{ and } \langle \psi_s | \psi_s' \rangle \text{ are } \neq 0$$

For $\langle \psi_s | \psi_s' \rangle \neq 0$... $\psi_s = \psi_s'$ thus the spin selection rule establishes that only transitions between states of the same spin ($\Delta S = 0$) will be allowed.

The orbital or Laporte selection rule states that $\langle \psi_e | \hat{\mu} | \psi_e' \rangle \neq 0$ for an allowed transition. This integral will be non-zero iff the direct product contains the total symmetric representation (i.e. function must be even over all space)

$$\Gamma(\psi_e') \times \Gamma(\hat{\mu}) \times \Gamma(\psi_e) \text{ must contain } a_{1(g)}$$

↑
transforms as x, y, z

Ligand Field or dd transitions:

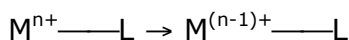
For d - orbitals... $\psi(\text{qs})$ and $\psi'(\text{es})$ will be of g symmetry.
 \hat{u} transforms as u

Hence transition moment integral transforms as $g \times u \times g = u$... can't be totally symmetric. Hence d-orbitals are formally forbidden. This is why they are weak:

$$\epsilon \sim 10^{-2} \text{ to } 10^2 \text{ M}^{-1}\text{cm}^{-1}$$

Charge Transfer transitions: two types, ligand-to-metal charge transfer (LMCT) and metal-to-ligand charge transfer (MLCT).

LMCT transition promotes an electron from a ligand-based orbital (primarily of p-character, and hence u symmetry) to an orbital that is primarily metal-based (of g symmetry)...



hence M transforms as $g \times u \times u \rightarrow g$. These transitions are therefore much stronger than d-d with $\epsilon \sim 5000 - 50000 \text{ M}^{-1}\text{cm}^{-1}$.

Consider MO diagram of ML_6 (O_h) complex with π -donating ligands:

ground state $\rightarrow a_{1g}$
 $\hat{u} \rightarrow t_{1u}$

$$M = \Gamma(\psi(\text{es})) \times t_{1u} \times a_{1g} = \Gamma(\psi(\text{es})) \times t_{1u}$$

will be non-zero if totally symmetric...

$L(\sigma) \rightarrow e_g$ ($\text{M-L}\sigma^*$):

$t_{1u}(\sigma) \rightarrow e_g$ ← allowed
 $e_g(\sigma) \rightarrow e_g$ allowed →
 $a_{1g}(\sigma) \rightarrow e_g$ allowed →

$L(\pi) \rightarrow e_g$ ($\text{M-L}\sigma^*$):

$t_{1g}(\pi) \rightarrow e_g$
 $t_{2u}(\pi) \rightarrow e_g$
 $t_{1u}(\pi) \rightarrow e_g$
 $t_{2g}(\pi) \rightarrow e_g$

can convince oneself pretty quickly that $\Gamma(\psi(\text{es})) \times t_{1u}$ will contain a_{1g} iff $\Gamma(\psi(\text{es})) = t_{1u}$.

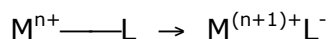
allowed transitions are ones that contain t_{1u}

Consider the following data for LMCT transitions:

Complex	E(LMCT) / cm ⁻¹	Complex	E(LMCT) / cm ⁻¹
OsCl ₆ ²⁻	24 - 30,000	OsCl ₆ ³⁻	35,500
OsBr ₆ ²⁻	17 - 25,000	--	--
OsI ₆ ²⁻	12 - 18,000	OsI ₆ ³⁻	19,100

As move from Cl⁻ → I⁻, halide more easily oxidized (lower E_N)... for LMCT, transition will therefore shift to lower energy. Similarly Os^{IV} is more easily reduced than Os^{III}, hence OsX₆²⁻ have lower energy LMCTs (as compared to OsX₆³⁻)

MLCT transitions promote an electron from metal-based orbital to ligand π* orbital. Again, p character introduced into transition. For same reasons as LMCT, MLCTs possess ε ~ 5000 - 50,000 M⁻¹cm⁻¹,



Allowed transitions for a ML₆ (L = π acceptor) complex are:

