

Classes of Electronic Transitions

I. Transitions involving σ , π , and non-bonded e^-

- Molecular orbital picture
 - typically involve either delocalized electrons or electrons in unshared pairs.
 - Chromophore**
 - Different compounds have different MO diagrams

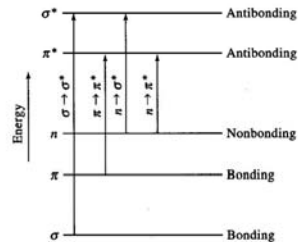


Figure 14-3 Electronic molecular energy levels.

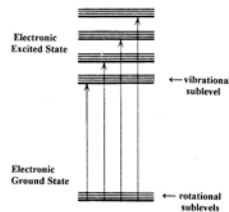


Figure 5.9 An electronic transition occurs over a 1

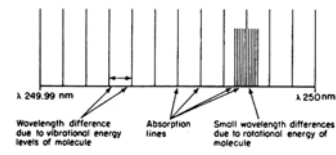


Figure 5.10 Illustration of a UV absorption band greatly expanded.

Classes of Electronic Transitions

Type	Region	λ (nm)	ϵ	Groups
$\sigma \rightarrow \sigma^*$	vacuum UV	< 150 nm	weak (unlikely)	C-C ~135 nm C-H ~125 nm
$n \rightarrow \sigma^*$	vacuum UV near UV	150-250 nm	fairly weak	lone pairs, σ bonds aldehydes, amines, ethers, sulfides...
$n \rightarrow \pi^*$	near UV visible	180-700 nm	moderate 10-100 L/(mol cm)	lone pairs, π bonds carbonyls, nitroso,
$\pi \rightarrow \pi^*$	near UV visible	180-700 nm	strong > 1000 L/(mol cm)	π systems multiple bonds, conjugation

Classes of Electronic Transitions: Influences on σ , π , n

- $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ are the most analytically useful
 - accessible wavelengths, strong absorbance
- 1. Auxochromes: saturated group with nonbonding electrons
 - Tends to stabilize π^* , decreasing $n \rightarrow \pi^*$ energy
- 2. Solvent Effects
- 3. Multiple Chromophores: If separated by > 2 single bonds, absorbance sums
- 4. Conjugation (aliphatic): Delocalized electrons
 - decreases (stabilizes) π^* , decreasing $\pi \rightarrow \pi^*$ energy
- 5. Aromatics: Three bands due to $\pi \rightarrow \pi^*$ transitions
 - Absorption band (highest energy)
 - E_2 Band (intermediate energy)
 - B Band (lowest energy)
 - Substituents cause band position to change depending on electron donating/withdrawing character.
 - Greater delocalization in aromatic system leads to stabilized π^* , and longer wavelength

Classes of Electronic Transitions

- **II. Transitions involving d and f electrons**
 - Transition metals (d), Lanthanides and Actinides (f)
- **Transition Metals:** electronic transitions between partially filled d-orbitals
 - Typically broad absorption bands
 - Energetics depend on:
 - identity of metal
 - complexation (shape and ligand identity)
 - Described by crystal-field theory and ligand-field theory
 - Complexation results in splitting (Δ) of d-orbital energies

Classes of Electronic Transitions

- Identity of ligand plays major role in Δ
 - Crystal Field (electrostatics) and Ligand Field (MO-like) theories
 - $I < Cl < H_2O < SCN^- < NH_3 < CN^-$

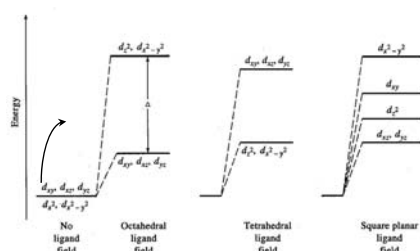
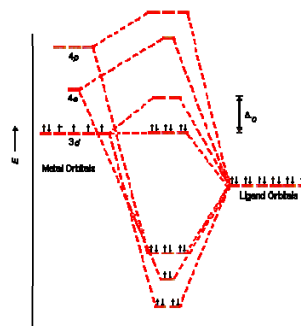


Figure 14-9 Effect of ligand field on d -orbital energies.



<http://chemed.chem.purdue.edu/genchem/topicreview/bp/ch12/ligand.php>

- Lanthanides and Actinides: f -electrons
 - Narrow lines - shielded f -orbitals
 - little environmental (ligand) dependence

Classes of Electronic Transitions

- **III. Charge-Transfer Transitions**
- Absorption of photon induces transfer of electron from one component to another
 - Requires electron donor and electron acceptor
 - Lewis acid/base phenomenon
 - can be metal-ligand or organic
 - Typically strong absorbance (large ϵ)
- **Application of UV-VIS to non (or weakly) absorbing species**
 - DO SOME CHEMISTRY!
 - Add complexing or color forming reagent
 - can also add stability
 - Need to be sure chemistry is understood to position equilibrium for maximum sensitivity

Experimental Observations

- Monitor electronic transitions of outermost (bonding/valence) e^-
 - Not enough energy to affect core e^-
- Bandshapes:
 - Influenced by concentration, intermolecular interaction, temperature...
 - Anything that affects the orbital energy
 - Resolution of spectrometer also plays a role
- Position: depends on “strength” of electronic interaction
 - UV – Strong
 - Vis - Less Strong
 - Impacted by *auxochrome*
 - Bathochromic (red) vs hypsochromic (blue)

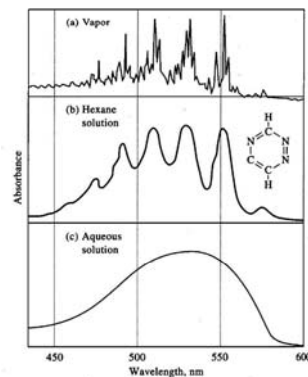


Figure 14-5 Ultraviolet absorption spectra for 1,2,4,5-tetrazine (a) in the vapor phase, (b) in hexane solution, and (c) in aqueous solution. (From S. F. Mason, J. Chem. Soc. 1959, 1265. With permission.)