

## Classes of Electronic Transitions

### I. Transitions involving $\sigma$ , $\pi$ , and non-bonded $e^-$

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

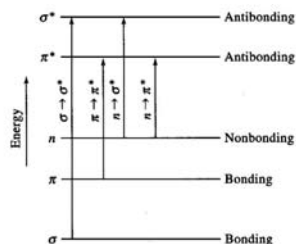


Figure 14-3 Electronic molecular energy levels.

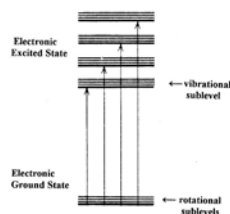


Figure 5.9 An electronic transition occurs over a 1

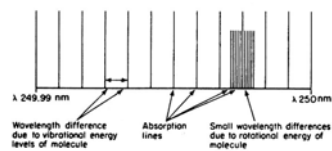


Figure 5.10 Illustration of a UV absorption band greatly expanded.

## Classes of Electronic Transitions

Type	Region	$\lambda$ (nm)	$\epsilon$	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, $\sigma$ bonds aldehydes, amines, ethers, sulfides...
$n \rightarrow \pi^*$	near UV visible	180-700 nm	moderate 10-100 L/(mol cm)	lone pairs, $\pi$ bonds carbonyls, nitroso,
$\pi \rightarrow \pi^*$	near UV visible	180-700 nm	strong > 1000 L/(mol cm)	$\pi$ systems multiple bonds, conjugation

## Classes of Electronic Transitions: Influences on $\sigma$ , $\pi$ , 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  $\pi^*$ , 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)  $\pi^*$ , decreasing  $\pi \rightarrow \pi^*$  energy
- 5. Aromatics: Three bands due to  $\pi \rightarrow \pi^*$  transitions
  - Absorption band (highest energy)
  - E<sub>2</sub> 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  $\pi^*$ , 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 ( $\Delta$ ) of d-orbital energies

## Classes of Electronic Transitions

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

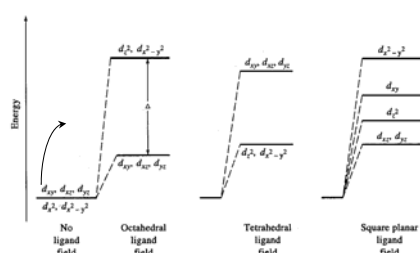
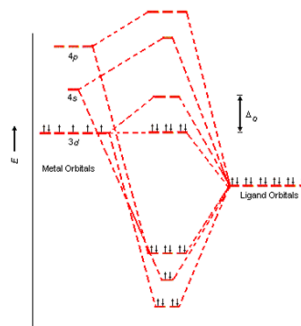


Figure 14-9 Effect of ligand field on  $d$ -orbital energies.



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

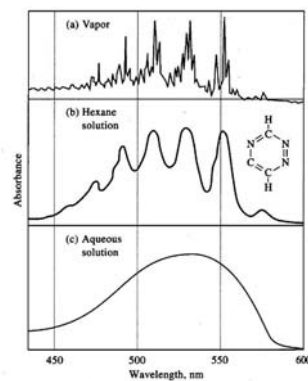
- Lanthanides and Actinides:  $f$ -electrons
  - Narrow lines - shielded  $f$ -orbitals
  - little environmental (ligand) dependence

## 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  $\epsilon$ )
- **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.)