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

<table>
<thead>
<tr>
<th>Type</th>
<th>Region</th>
<th>$\lambda$ (nm)</th>
<th>$\varepsilon$</th>
<th>Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma \rightarrow \sigma^*$</td>
<td>vacuum UV</td>
<td>&lt; 150 nm</td>
<td>weak (unlikely)</td>
<td>C-C ~135 nm, C-H ~125 nm</td>
</tr>
<tr>
<td>$n \rightarrow \sigma^*$</td>
<td>vacuum UV</td>
<td>150-250 nm</td>
<td>fairly weak</td>
<td>lone pairs, $\sigma$ bonds</td>
</tr>
<tr>
<td></td>
<td>near UV</td>
<td></td>
<td></td>
<td>ethers, sulfides...</td>
</tr>
<tr>
<td>$n \rightarrow \pi^*$</td>
<td>near UV</td>
<td>180-700 nm</td>
<td>moderate</td>
<td>lone pairs, $\pi$ bonds</td>
</tr>
<tr>
<td></td>
<td>visible</td>
<td></td>
<td>10-100 L/(mol cm)</td>
<td>carbonyls, nitroso,</td>
</tr>
<tr>
<td>$\pi \rightarrow \pi^*$</td>
<td>near UV</td>
<td>180-700 nm</td>
<td>strong</td>
<td>$\pi$ systems</td>
</tr>
<tr>
<td></td>
<td>visible</td>
<td></td>
<td>&gt; 1000 L/(mol cm)</td>
<td>multiple bonds, conjugation</td>
</tr>
</tbody>
</table>
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)
   - $E_2$ 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 $\pi^*$, 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
  - $I \prec Cl^{-} \prec H_{2}O \prec SCN^{-} \prec NH_{3} \prec CN^{-}$

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

- 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 $\varepsilon$)

  - 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)

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**Figure 16-9** Ultraviolet absorption spectra for 1,2,4,5-tetrasubstituted benzene in different environments: (a) in the vapor phase, (b) in benzene solution, and (c) in aqueous solution. (From T.F. Hayes, Chrom. Rev. 1969, 14, 199. With permission.)