UV-Vis Spectroscopy

Chem 744
Spring 2013
UV-Vis Spectroscopy

- Every organic molecule absorbs UV-visible light
- Energy of electronic transitions
- Saturated functionality not in region that is easily accessible (obscured by solvent and atmosphere)
- Conjugation
Basic Instrument Design

- Light source
- Sample cuvette
- Detector
- Aperture
- Diffraction grating
- Shutters
- Lens
- Sample
- Grating
- Slit
- 1024-element diode array
- Tungsten lamp
- Deuterium lamp

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Electronic Transitions

possible electronic transitions

\[ \Delta E = [E_{\text{excited}} - E_{\text{ground}}] = h\nu \]

- \( \sigma \rightarrow \sigma^* \): alkanes
- \( \sigma \rightarrow \pi^* \): carbonyls
- \( \pi \rightarrow \pi^* \): alkenes, carbonyls, alkynes, etc.
- \( n \rightarrow \sigma^* \): heteroatoms - O, N, S, X, etc.
- \( n \rightarrow \pi^* \): carbonyls
Beer-Lambert Law

\[ A = \log \left( \frac{I_0}{I_1} \right) = \varepsilon l c \]

- **A** is absorbance (no units)
- **\( \varepsilon \)** is the molar absorptivity or extinction coefficient (L mol\(^{-1}\) cm\(^{-1}\)) (how strongly it absorbs - intrinsic)
- **l** is the path length of the sample (cm)
- **c** is the concentration of the compound (mol L\(^{-1}\))
- **I\(_0\)** is the intensity of the incident light
- **I\(_1\)** is the intensity of the transmitted light
Organic Molecules UV-Vis Characteristics

- Most organic molecules absorb in UV region unless highly conjugated
- Most common detector for HPLC
  - best to have conjugated chromophore
- Spectra are broad (why?) making it useful for qualitative identification
- Can quantitate using Beer’s law analysis
Presentation of Spectra

- many vibrational bands - many slightly different absorbances
- Absorption of light occurs in $10^{-15}$ s, faster than vibrational changes
- Franck-Codon principle - absorption occurs via a vertical transition - all bond lengths, angles, conformations and solvation are conserved in the transition.

![Diagram showing absorption spectra with maxima at different wavelengths and terms for hyperchromic, bathochromic, hypochromic, and hypsochromic shifts.](https://example.com/diagram.png)
Presentation of Spectra

VIS-spectra in DMSO

$\varepsilon \,[l/mol \cdot cm]$
Measuring UV-Vis spectra <200 nm is impractical

- Quartz glass cutoff 210 nm
- Fused synthetic silica can get down to 190 nm

**Solvent Cutoffs**

<table>
<thead>
<tr>
<th>solvent</th>
<th>cut-off (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>205</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>210</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>210</td>
</tr>
<tr>
<td>diethyl ether</td>
<td>210</td>
</tr>
<tr>
<td>ethanol</td>
<td>210</td>
</tr>
<tr>
<td>methanol</td>
<td>210</td>
</tr>
<tr>
<td>dioxane</td>
<td>220</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>solvent</th>
<th>cut-off (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>220</td>
</tr>
<tr>
<td>dichloromethane</td>
<td>235</td>
</tr>
<tr>
<td>chloroform</td>
<td>245</td>
</tr>
<tr>
<td>carbon tet</td>
<td>265</td>
</tr>
<tr>
<td>benzene</td>
<td>280</td>
</tr>
<tr>
<td>acetone</td>
<td>300</td>
</tr>
</tbody>
</table>
Solvent effects on spectra

Solvent shifts on the $n \rightarrow \pi^*$ transition of acetone

<table>
<thead>
<tr>
<th>Solvent</th>
<th>H$_2$O</th>
<th>CH$_3$OH</th>
<th>C$_2$H$_5$OH</th>
<th>CHCl$_3$</th>
<th>C$<em>6$H$</em>{14}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_{max}$ (nm)</td>
<td>264.5</td>
<td>270</td>
<td>272</td>
<td>277</td>
<td>279</td>
</tr>
</tbody>
</table>
Selection Rules

- Not all transitions are observed
- Depends on symmetry and multiplicity
- “Forbidden Transitions” (e.g. n-π*) can be seen but are weak
- Molecular vibrations can disrupt the symmetry
Transitions

Figure 6.6 $\sigma \rightarrow \sigma^*$ transition.

Figure 6.7 $n \rightarrow \sigma^*$ transition.

Figure 6.8 $\pi \rightarrow \pi^*$ transition.

Figure 6.9 Electronic transitions of the carbonyl group.
Nature of absorption

- Ethane - $\lambda_{\text{max}} = 135$ nm
Acetone - $\lambda_{\text{max}} = \sim 166 \text{ nm} \ (n-\sigma^*; \ \varepsilon = >10000)$

$\lambda_{\text{max}} = 188 \text{ nm} \ (\pi-\sigma^*; \ \varepsilon = 1860)$

$\lambda_{\text{max}} = 279 \text{ nm} \ (n-\pi^*; \ \varepsilon = 15)$
Tetraphenyldicyclopentadienone

\[ \pi \rightarrow \pi^* \quad 343 \text{ nm} \]

\[ \eta \rightarrow \pi^* \quad 512 \text{ nm} \]
Ethylene $\pi - \pi^*$ $\lambda_{\text{max}} = 165$ nm ($n-\sigma^*$ ; $\varepsilon = 16,000$)

- Substitution with an atom containing non-bonding electrons (–OH, OR, –NH2, –NHR, –SH, –SR, –Hal) results in a bathochromic shift $\rightarrow$ the non-bonding electrons interact with the $\pi$-orbitals of the double bond
- the energy difference between the HOMO and LUMO decreases
Conjugation

- Ethylene ($\lambda_{\text{max}} = 165 \text{ nm}$)
- 1,3-Butadiene ($\lambda_{\text{max}} = 217 \text{ nm}$)
- 1,3,5-Hexatriene ($\lambda_{\text{max}} = 258 \text{ nm}$)
Conjugation of two or more double bonds results in decreasing energy difference between the HOMO and LUMO.

\[ \lambda_{\text{max}} \]

\[
\begin{array}{cccccccc}
R - (\text{CH} = \text{CH})_n - R \\
\hline
R = \text{CH}_3 & & & & & & R = \text{C}_6\text{H}_5 & \\
\hline
n = 1 & \lambda_{\text{max}}^a & \varepsilon_{\text{max}} & \lambda_{\text{max}}^b & \varepsilon_{\text{max}} \\
1 & 174 & 24000 & 306 & 24000 \\
2 & 227 & 24000 & 334 & 48000 \\
3 & 275 & 30200 & 358 & 75000 \\
4 & 310 & 76500 & 384 & 86000 \\
5 & 342 & 122000 & 403 & 94000 \\
6 & 380 & 146500 & 420 & 113000 \\
\end{array}
\]
Empirical Rules

- Woodward (1942) as well as Fieser and Scott derived a set of empirical rules for the estimation of the long wavelength maxima in diens:

\[
\begin{align*}
\text{acyclic, transoid} & \quad 217 \text{ nm} \\
\text{cisoid (homoannular)} & \quad 253 \text{ nm} \\
\text{transoid (heteroannular)} & \quad 214 \text{ nm}
\end{align*}
\]

Increments:

- For each additional conjugated double bond: +30 nm
- For each exocyclic position of a double bond: +5 nm
- For each alkyl group: +5 nm
- For each of the following auxochromic groups:
  - O-alkyl: +6 nm
  - O-acyl: +0 nm
  - S-alkyl: +30 nm
  - N(alkyl)_2: +60 nm
  - Cl: +5 nm
  - Br: +5 nm
Woodward-Fieser Rules work well up to 4 double bonds

\[
\lambda_{\text{max}} = 114 + 5(\text{# alkyl substituents}) + n(48 - 1.7n) - 16.5(\text{# endo}) - 10(\text{# exo})
\]
Lycopene and beta-carotene

\[ \lambda_{\text{max}} = 114 + 5(\# \text{ alkyl substituents}) + n(48 - 1.7n) - 16.5(\# \text{ endo}) - 10(\# \text{ exo}) \]

\[ \lambda_{\text{max}} = 114 + 5(8) + 11(48 - 1.7 \times 11) - 0 - 0 = 476 \text{ nm} \]
\[ \lambda_{\text{max}} \text{ (actual)} = 474 \]

\[ \lambda_{\text{max}} = 114 + 5(10) + 11(48 - 1.7 \times 11) - 16.5(2) - 0 = 453.3 \text{ nm} \]
\[ \lambda_{\text{max}} \text{ (actual)} = 452 \]
Benzene

A) Energy diagram of the benzene $\pi$-orbitals

B) Energy term diagram:

I: $\lambda_{\text{max}}$ 256 nm, $^1A_{1g} \rightarrow ^1B_{2u}$ ($\alpha$-band)
II: $\lambda_{\text{max}}$ 203 nm, $^1A_{1g} \rightarrow ^1B_{1u}$ ($p$-band)
III: $\lambda_{\text{max}}$ 184 nm, $^1A_{1g} \rightarrow ^1E_{1u}$ ($\beta$-band)

Absorption spectrum of benzene

$\nu_A = 520 \text{ cm}^{-1}$

$\nu_B' = 923 \text{ cm}^{-1}$
Aromatic Substituent Effects

Long wavelength absorptions of some \textit{para}-disubstituted benzenes:

\begin{table}[h]
\begin{tabular}{|c|c|c|c|c|c|c|c|c|}
\hline
 & \textbf{$X^2 = H$} & \textbf{OH} & \textbf{NH$_2$} & \textbf{NO$_2$} \\
\hline
$X^1$ & $\lambda_{\text{max}}$ & log $\varepsilon$ & $\lambda_{\text{max}}$ & log $\varepsilon$ & $\lambda_{\text{max}}$ & log $\varepsilon$ & $\lambda_{\text{max}}$ & log $\varepsilon$ \\
\hline
H & 254 & 2.31 &  &  &  &  &  &  \\
OH & 270 & 3.16 & 293 & 3.43 &  &  &  &  \\
NH$_2$ & 280 & 3.16 & 294 & 3.30 & 315 & 3.30 &  &  \\
NO$_2$ & 269 & 3.89 & 310 & 4.00 & 375 & 4.20 & 267 & 4.16 \\
\hline
\end{tabular}
\end{table}

The strong bathochromic shift for 4-nitrophenol is due to a \textit{charge transfer absorption}:

\[
\begin{align*}
\begin{array}{c}
\text{N}^+ \quad \text{O}^-
\end{array}
\quad \quad \quad \quad \quad
\begin{array}{c}
\text{N}^+ \quad \text{O}^-
\end{array}
\end{align*}
\]

\[
\begin{align*}
\begin{array}{c}
\text{O}^- \quad \text{N}^+
\end{array}
\quad \quad \quad \quad \quad
\begin{array}{c}
\text{N}^+ \quad \text{O}^-\text{H}
\end{array}
\end{align*}
\]
Aromatic Substituent Effects

UV/vis spectra of ortho-, meta-, and para-nitrophenol:

A) in 10 mM HCl
B) in 5 mM NaOH

Note: the low energy charge transfer band is not only observed for the ortho and para isomer, but also for the meta isomer.
• As compared to benzene the HOMO and LUMO orbitals in condensed aromatic compounds are not degenerate
  → there are four different electronic transitions possible:

A) Orbital diagram  B) Term diagram  C) Electronic transitions (under consideration of configuration interaction)
Carbonyl Compounds

- Auxochromic substituents (−OH, OR, −NH₂, −NHR, −SH, −SR, −Hal) at the carbonyl group increase the energy of the π* orbital (π-donor), and decrease the n orbital energy (σ-acceptor)
  → the n,π* transitions are shifted to higher energy (shorter wavelength)
- Conjugation with a double bond has essentially no effect on the n-orbital energy, but increases the HOMO energy
  → the π,π* transition of enones with increasing chain length is shifted into the visible range
Carbonyl Compounds

C=O  aldehyde or ketone  \( n \rightarrow \sigma^* \) 166 nm  \( \varepsilon = 16,000 \)
\( \pi \rightarrow \pi^* \) 189 nm  \( \varepsilon = 900 \)
\( n \rightarrow \pi^* \) 166 nm  \( \varepsilon = 10\text{-}20 \)
# Carbonyl Compounds

## Table 9.5: Rules for Calculation of $\pi-\pi^*$ $\lambda_{\text{max}}$ (nm) for Conjugated Carbonyls

<table>
<thead>
<tr>
<th>Base Values</th>
<th>215</th>
<th>202</th>
<th>227</th>
<th>239</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X = H, 207$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$X = R, 215$</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>$X = OH, 193$</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>$X = OR, 193$</td>
<td></td>
<td></td>
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</tr>
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</table>

### Solvent Correction

<table>
<thead>
<tr>
<th>Solvent</th>
<th>nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O$</td>
<td>+8</td>
</tr>
<tr>
<td>EtOH</td>
<td>0</td>
</tr>
<tr>
<td>CHCl$_3$</td>
<td>-1</td>
</tr>
<tr>
<td>Dioxane</td>
<td>-5</td>
</tr>
<tr>
<td>Et$_2$O</td>
<td>-7</td>
</tr>
<tr>
<td>Hydrocarbon</td>
<td>-11</td>
</tr>
</tbody>
</table>

### Increments (nm)

<table>
<thead>
<tr>
<th>Groups</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$\delta$ and Higher</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extended Conjugation per C=C</td>
<td>+30</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Each exocyclic C=C</td>
<td>+5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Homoannular diene</td>
<td>+39</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Alkyl</td>
<td>+10</td>
<td>+12</td>
<td>+18</td>
<td>+18</td>
</tr>
<tr>
<td>OH</td>
<td>+35</td>
<td>+30</td>
<td>+6</td>
<td>+50</td>
</tr>
<tr>
<td>OAc</td>
<td>+6</td>
<td>+6</td>
<td>+6</td>
<td>+6</td>
</tr>
<tr>
<td>O–Alkyl</td>
<td>+35</td>
<td>+30</td>
<td>+17</td>
<td>+31</td>
</tr>
<tr>
<td>S–Alkyl</td>
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<td>+85</td>
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<td></td>
</tr>
<tr>
<td>N(Alkyl)$_2$</td>
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<td>+95</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>+15</td>
<td>+12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>+25</td>
<td>+30</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>