UV-VIS Spectroscopy

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Basics of UV Light Absorption

Ultraviolet/visible spectroscopy involves the absorption of ultraviolet/visible light by a molecule causing the promotion of an electron from a ground electronic state to an excited electronic state.

- Ultraviolet/Visible light:
  - wavelengths (l) between 190 and 800 nm
• **Types of Transitions**
  - There are several types of electronic transitions available to a molecule including:
    - s to s* (alkanes)
    - s to p* (carbonyl compounds)
    - p to p* (alkenes, carbonyl compounds, alkynes, azo compounds)
    - h to s* (oxygen, nitrogen, sulfur, and halogen compounds)
    - h to p* (carbonyl compounds)

• Transitions from the highest occupied molecular orbital (HOMO) to the lowest occupied molecular orbital (LUMO) require the least amount of energy and are therefore usually the most important.

• Not all transitions that are possible will be observed. Some electronic transitions are “forbidden” by certain selection rules. However, even forbidden transitions can be observed, but these are usually not very intense.
Peak Broadening

- UV absorptions are generally broad because vibrational and rotational levels are "superimposed" on top of the electronic levels.

![Diagram showing electron and vibrational levels]

- Figure 2. Peak broadening.

- For this reason, the wavelength of maximum absorption ($\lambda_{max}$) is usually reported.

Terminology

- The following definitions are useful in a discussion of UV/Vis spectroscopy.
- **chromophore** Any group of atoms that absorbs light whether or not a color is thereby produced.
- **auxochrome** A group which extends the conjugation of a chromophore by sharing of nonbonding electrons.
- **bathochromic shift** The shift of absorption to a longer wavelength.
- **hypsochromic shift** The shift of absorption to a shorter wavelength.
- **hyperchromic effect** An increase in absorption intensity.
- **hypochromic effect** A decrease in absorption intensity.
Law of light absorption

- **Beer-Lambert Law**
  - The ultraviolet spectra of compounds are usually obtained by passing light of a given wavelength (monochromatic light) through a dilute solution of the substance in a non-absorbing solvent.
  - The intensity of the absorption band is measured by the percent of the incident light that passes through the sample:
    - \( \% \text{ Transmittance} = \left( \frac{I}{I_0} \right) \times 100\% \)
    - where:
      - \( I \) = intensity of transmitted light
      - \( I_0 \) = intensity of incident light

- Because light absorption is a function of the concentration of the absorbing molecules, a more precise way of reporting intensity of absorption is by use of the Beer-Lambert Law:
  - \( \text{Absorbance} = -\log \left( \frac{I}{I_0} \right) = ecl \)
  - where:
    - \( e \) = molar absorptivity
    - \( c \) = molar concentration of solute
    - \( l \) = length of sample cell (cm)
Measurement of spectrum

- The UV spectrum is usually taken on a very dilute solution (1 mg in 100 ml of solvent). A portion of this solution is transferred to a silica cell. A matched cell containing pure solvent is prepared, and each cell is placed in the appropriate place in the spectrometer. This is so arranged that two equal beams of light are passed, one through the solution of the sample, one through the pure solvent. The intensities of the transmitted light are then compared over the whole wavelength range of the instrument. The spectrum is plotted automatically as a log10(I0/I) ordinate and I abscissa. For publication and comparisons these are often converted to an e vs. I or log(e) vs. I plot. The I unit is almost always in nanometers (nm).
- In general, organic compounds will have molar absorptivities (e) of around 10,000. Therefore, in order to obtain solutions that will have a maximum absorbance of 1, it is most likely that the concentration of the starting solution (the stock) to be 1 x 10^-4 M.

Preparing a sample

- Preparing A Sample
- The following steps can be followed to produce solutions that will give generally good results in the UV/Vis experiment. An example for 2-nitroaniline is worked out along the way.
- Prepare a concentrated solution that is about 1 x 10^-3 M. This solution is made concentrated so that you can weigh out a reasonable amount of material (like 13 mg as opposed to 1.3 mg). For 2-nitroaniline (MW = 138.13 g/mol), weigh out about 0.0138 g of material. In this example, 0.0132 g were obtained, and diluting this amount of material to 100 mL in water produces a 9.556 x 10^-4 M solution.
- Perform a 10:1 dilution to produce a solution roughly 1 x 10^-4 M. This will be the stock solution. For 2-nitroaniline, 10 mL of the concentrated solution was transferred to a new 100 mL volumetric flask, and diluted to 100 mL with water.
- Prepare several more solutions that are dilutions of the stock. For 2-nitroaniline, solutions that are 80%, 60%, 40%, and 20% of the stock concentration are prepared as listed below:
• concentration solution preparation
• $9.556 \times 10^{-5}$ M stock
• $7.654 \times 10^{-5}$ M stock
  - 20 mL of stock diluted to 25 mL
• $5.734 \times 10^{-5}$ M stock
  - 15 mL of stock diluted to 25 mL
• $3.822 \times 10^{-5}$ M stock
  - 10 mL of stock diluted to 25 mL
• $1.911 \times 10^{-5}$ M stock
  - 5 mL of stock diluted to 25 mL

http://www.chemistry.ccsu.edu/glagovich/teaching/316/index.html

Presentation of spectrum

The UV/Vis spectrum is plotted automatically as a $\log_{10}(I/I_o)$ (absorbance) ordinate and $\lambda$ (in nanometers) abscissa. An example spectrum is given below.
As you can see from the above spectrum, different concentrations of 2-nitroaniline will give spectra with differing absorbance values. This can make comparing one spectrum of 2-nitroaniline to another spectrum of 2-nitroaniline obtained by someone else difficult. Converting the above plot from an absorbance ordinate to an $e$ ordinate essentially removes concentration dependence from the presentation. The spectrum below illustrates this point. Notice that each spectrum taken at different concentrations are now essentially overlapping each other.

For publication purposes, UV/Vis spectra are often converted to a log($e$) vs. $l$ plot. This type of presentation will normalize the absorbance signals so that all are on a similar scale (essentially diminishing intense absorption signals and increasing weak absorption signals).
To determine the molar absorptivity (ε) for the compound in question, one can produce a Beer's Law plot. This plot shows the linear relationship between absorbance and concentration. The slope of the line is the molar absorptivity.

### Choice of solvent

- The table below gives a list of common solvents and the minimum wavelength from which they may be used in a 1 cm cell.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Minimum Wavelength (nm)</th>
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<tbody>
<tr>
<td>acetonitrile</td>
<td>190</td>
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<tr>
<td>water</td>
<td>191</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>195</td>
</tr>
<tr>
<td>hexane</td>
<td>195</td>
</tr>
<tr>
<td>methanol</td>
<td>201</td>
</tr>
<tr>
<td>ethanol</td>
<td>204</td>
</tr>
<tr>
<td>ether</td>
<td>215</td>
</tr>
<tr>
<td>methylene chloride</td>
<td>220</td>
</tr>
<tr>
<td>chloroform</td>
<td>237</td>
</tr>
<tr>
<td>carbon tetrachloride</td>
<td>257</td>
</tr>
</tbody>
</table>
Generalisations

• Generalizations Regarding $\lambda_{\text{max}}$
  • If the spectrum of a given compound exhibits an absorption band of very low intensity ($e = 10^{-100}$) in the 270-350 nm region, and no other absorptions above 200 nm, the compound contains a simple, non-conjugated chromophore containing $n$ electrons. The weak band is due to $h$ to $p^*$ transitions.
  • If the spectrum of a given compound exhibits many bands, some of which appear even in the visible region, the compound is likely to contain long-chain conjugated or polycyclic aromatic chromophore. If the compound is colored, there may be at least 4 to 5 conjugated chromophores and auxochromes. Exceptions: some nitro-, azo-, diazo-, and nitroso-compounds will absorb visible light.
• Generalizations Regarding $e_{\text{max}}$
  • An $e$ value between 10,000 and 20,000 generally represents a simple $a,b$-unsaturated ketone or diene.
  • Bands with $e$ values between 1,000 and 10,000 normally show the presence of an aromatic system. Substitution on the aromatic nucleus by a functional group which extends the length of the chromophore may give bands with $e > 10,000$ along with some which still have $e < 10,000$.
  • Bands with $e < 100$ represent $h$ to $p^*$ transitions.

Type transition

\[ \sigma \rightarrow \sigma^* \]

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>$\lambda_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkanes</td>
<td>~ 150</td>
</tr>
</tbody>
</table>
### π to π*

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>$\lambda_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>alkenes</td>
<td>~ 175</td>
</tr>
<tr>
<td>alkynes</td>
<td>~ 170</td>
</tr>
<tr>
<td>carbonyls</td>
<td>~ 188</td>
</tr>
</tbody>
</table>

### $n \rightarrow \sigma^*$

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>$\lambda_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>alcohols, ethers</td>
<td>~ 185</td>
</tr>
<tr>
<td>amines</td>
<td>~ 195</td>
</tr>
<tr>
<td>sulfur compounds</td>
<td>~ 195</td>
</tr>
</tbody>
</table>
\begin{align*}
N & \rightarrow \pi^* \\
\text{Chromophore} & \quad \lambda_{\text{max}} & \quad \log(\varepsilon) \\
\text{carbonyls} & \quad \sim 285 & \\
\end{align*}

\begin{tabular}{|l|c|c|}
\hline
Chromophore & Transition & $\lambda_{\text{max}}$ & log($\varepsilon$) \\
\hline
nitrile & $\eta$ to $\pi^*$ & 160 & <1.0 \\
alkyne & $\pi$ to $\pi^*$ & 170 & 3.0 \\
alkene & $\pi$ to $\pi^*$ & 175 & 3.0 \\
alcohol & $\eta$ to $\sigma^*$ & 180 & 2.5 \\
ether & $\eta$ to $\sigma^*$ & 180 & 3.5 \\
ketone & $\pi$ to $\pi^*$ & 180 & 3.0 \\
& $\eta$ to $\pi^*$ & 280 & 1.5 \\
aldehyde & $\pi$ to $\pi^*$ & 190 & 2.0 \\
& $\eta$ to $\pi^*$ & 290 & 1.0 \\
amine & $\eta$ to $\sigma^*$ & 190 & 3.5 \\
acid & $\eta$ to $\pi^*$ & 205 & 1.5 \\
ester & $\eta$ to $\pi^*$ & 205 & 1.5 \\
amide & $\eta$ to $\pi^*$ & 210 & 1.5 \\
thiol & $\eta$ to $\sigma^*$ & 210 & 3.0 \\
nitro & $\eta$ to $\pi^*$ & 271 & <1.0 \\
azo & $\eta$ to $\pi^*$ & 340 & <1.0 \\
\hline
\end{tabular}
Empirical Rules for Calculating Uv/Vis Absorptions

<table>
<thead>
<tr>
<th>Parent</th>
<th>Homoannular (cisoid)</th>
<th>Heteroannular (transoid)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\lambda = 253$ nm</td>
<td>$\lambda = 214$ nm</td>
</tr>
<tr>
<td>Increments for:</td>
<td></td>
<td>$= 217$ (acyclic)</td>
</tr>
<tr>
<td>Double bond extending conjugation</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Alkyl substituent or ring residue</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>Exocyclic double bond</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

Polar groupings:

<table>
<thead>
<tr>
<th>Polar grouping</th>
<th>Homoannular</th>
<th>Heteroannular</th>
</tr>
</thead>
<tbody>
<tr>
<td>-OC(O)CH$_3$</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>-OR</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>-Cl, -Br</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>-NR$_2$</td>
<td>60</td>
<td>60</td>
</tr>
<tr>
<td>-SR</td>
<td>30</td>
<td>30</td>
</tr>
</tbody>
</table>
Example 1:

![Diagram of transoid structure]

Transoid: 217 nm
Alkyl groups or ring residues: \(3 \times 5 = 15\) nm
Calculated: 232 nm
Observed: 234 nm

Example 2:

![Diagram of cisoid structure]

Cisoid: 253 nm
Alkyl groups or ring residues: \(2 \times 5 = 10\) nm
Calculated: 263 nm
Observed: 256 nm

Transoid:

![Diagram of transoid structure with exocyclic double bond]

Alkyl groups or ring residues: \(3 \times 5 = 15\) nm
Exocyclic double bond: 5 nm
Calculated: 234 nm
Observed: 235 nm
**Woodward's Rules for Conjugated Carbonyl Compounds**

Cisoid: 253 nm
Alkyl groups or ring residues: \(4 \times 5 = 20\) nm
Exocyclic double bond: 5 nm
Calculated: 278 nm
Observed: 275 nm
Base values:

\[ X = R \]

Six-membered ring or acyclic parent enone \( \lambda = 215 \text{ nm} \)

Five-membered ring parent enone \( \lambda = 202 \text{ nm} \)

\( X = H \) \( \lambda = 208 \text{ nm} \)

\( X = \text{OH, OR} \) \( \lambda = 195 \text{ nm} \)

Increments for:

- Double bond extending conjugation \( \alpha \)
- Exocyclic double bond \( \beta \)
- Endocyclic double bond in a 5- or 7-membered ring for \( X = \text{OH, OR} \) \( \gamma \)
- Homocyclic diene component \( \delta \)
- Alkyl substituent or ring residue
  - \( \alpha \)
  - \( \beta \)
  - \( \gamma \) or higher

<table>
<thead>
<tr>
<th>Increment</th>
<th>Value</th>
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<tbody>
<tr>
<td>Double bond extending conjugation</td>
<td>30</td>
</tr>
<tr>
<td>Exocyclic double bond</td>
<td>5</td>
</tr>
<tr>
<td>Endocyclic double bond in a 5- or 7-membered ring for ( X = \text{OH, OR} )</td>
<td>5</td>
</tr>
<tr>
<td>Homocyclic diene component</td>
<td>39</td>
</tr>
<tr>
<td>Alkyl substituent or ring residue</td>
<td></td>
</tr>
<tr>
<td>( \alpha )</td>
<td>10</td>
</tr>
<tr>
<td>( \beta )</td>
<td>12</td>
</tr>
<tr>
<td>( \gamma ) or higher</td>
<td>18</td>
</tr>
</tbody>
</table>

Polar groupings:

- \( \text{OH} \)

<table>
<thead>
<tr>
<th>Increment</th>
<th>Value</th>
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</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>35</td>
</tr>
<tr>
<td>( \beta )</td>
<td>30</td>
</tr>
<tr>
<td>( \delta )</td>
<td>50</td>
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</table>

- \( \text{OC(O)CH}_3 \)

<table>
<thead>
<tr>
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<th>Value</th>
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</thead>
<tbody>
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<td>( \alpha, \beta, \gamma, \delta )</td>
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</tr>
</tbody>
</table>

- \( \text{OCH}_3 \)

<table>
<thead>
<tr>
<th>Increment</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>35</td>
</tr>
<tr>
<td>( \beta )</td>
<td>30</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>17</td>
</tr>
<tr>
<td>( \delta )</td>
<td>31</td>
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</table>

- \( \text{Cl} \)

<table>
<thead>
<tr>
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<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>15</td>
</tr>
<tr>
<td>( \beta, \gamma, \delta )</td>
<td>12</td>
</tr>
</tbody>
</table>

- \( \text{Br} \)

<table>
<thead>
<tr>
<th>Increment</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta )</td>
<td>30</td>
</tr>
<tr>
<td>( \alpha, \gamma, \delta )</td>
<td>25</td>
</tr>
</tbody>
</table>

- \( \text{NR}_2 \)

<table>
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<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \beta )</td>
<td>95</td>
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</table>
*Solvent shifts for various solvents:

<table>
<thead>
<tr>
<th>Solvent</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; shift (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>+ 8</td>
</tr>
<tr>
<td>chloroform</td>
<td>- 1</td>
</tr>
<tr>
<td>ether</td>
<td>- 7</td>
</tr>
<tr>
<td>ether</td>
<td>- 7</td>
</tr>
<tr>
<td>cyclohexane</td>
<td>- 11</td>
</tr>
<tr>
<td>dioxane</td>
<td>- 5</td>
</tr>
<tr>
<td>hexane</td>
<td>- 11</td>
</tr>
</tbody>
</table>

example

![Acyclic enone structure](image)

Acyclic enone: 215 nm
α-Alkyl groups or ring residues: 10 nm
β-Alkyl groups or ring residues: 2 x 12 = 24 nm
Calculated: 249 nm
Observed: 249 nm
Five-membered ring parent enone: 202 nm

β-Alkyl groups or ring residues: 2 x 12 = 24 nm
Exocyclic double bond: 5 nm
Calculated: 231 nm
Observed: 226 nm

Six-membered ring or alicyclic parent enone: 215 nm

Extended conjugation: 30 nm
Homocyclic diene component: 39 nm
δ-Alkyl groups or ring residues: 18 nm
Calculated: 302 nm
Observed: 300 nm
Five-membered ring parent enone: 202 nm

α-Br: 25 nm

β-Alkyl groups or ring residues: 2 x 12 = 24 nm

Exocyclic double bond: 5 nm

Calculated: 256 nm

Observed: 251 nm

Carboxylic acid: 195 nm

α-Alkyl groups or ring residues: 10 nm

β-Alkyl groups or ring residues: 12 nm

Calculated: 217 nm

Observed: 217 nm
Ester: 195 nm  
α-Alkyl groups or ring residues: 10 nm  
β-Alkyl groups or ring residues: 12 nm  
Endocyclic double bond in 7-membered ring: 5 nm  
Calculated: 222 nm  
Observed: 222 nm

Aldehyde: 208 nm  
α-Alkyl groups or ring residues: 10 nm  
β-Alkyl groups or ring residues: $2 \times 12 = 24$ nm  
Calculated: 242 nm  
Observed: 242 nm
Absorption for Mono-Substituted Benzene Derivatives

Absorption for Mono-Substituted Benzene Derivatives
<table>
<thead>
<tr>
<th>Substituent</th>
<th>E (≥30000)</th>
<th>K (~10000)</th>
<th>B (~300)</th>
<th>R (~50)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electronic Donating Substituents</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>none</td>
<td>184</td>
<td>204</td>
<td>254</td>
<td></td>
</tr>
<tr>
<td>-R</td>
<td>189</td>
<td>208</td>
<td>262</td>
<td></td>
</tr>
<tr>
<td>-OH</td>
<td>211</td>
<td>270</td>
<td></td>
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<tr>
<td>-OR</td>
<td>217</td>
<td>269</td>
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<td></td>
</tr>
<tr>
<td>-NH₂</td>
<td>230</td>
<td>280</td>
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<tr>
<td><strong>Electronic Withdrawing Substituents</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>-F</td>
<td>204</td>
<td>254</td>
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<td>-Cl</td>
<td>210</td>
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<tr>
<td>-Br</td>
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<tr>
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<td></td>
<td></td>
</tr>
<tr>
<td>-NH₃⁺</td>
<td>203</td>
<td>254</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**π-Conjugating Substituents**

<table>
<thead>
<tr>
<th>Substituent</th>
<th>E</th>
<th>K</th>
<th>B</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>-C=CH₂</td>
<td>248</td>
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<td>282</td>
<td></td>
</tr>
<tr>
<td>-CCH</td>
<td>202</td>
<td>248</td>
<td></td>
<td>278</td>
</tr>
<tr>
<td>-C₆H₅</td>
<td></td>
<td></td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>-CHO</td>
<td>242</td>
<td></td>
<td>280</td>
<td>328</td>
</tr>
<tr>
<td>-C(O)R</td>
<td>238</td>
<td></td>
<td>276</td>
<td>320</td>
</tr>
<tr>
<td>-CO₂H</td>
<td>226</td>
<td></td>
<td>272</td>
<td></td>
</tr>
<tr>
<td>-CN</td>
<td>224</td>
<td></td>
<td>271</td>
<td></td>
</tr>
<tr>
<td>-NO₂</td>
<td>252</td>
<td></td>
<td>280</td>
<td>330</td>
</tr>
</tbody>
</table>
In disubstituted benzenes, two situations are important:

1. When electronically complementary groups, such as amines and nitro, are situated para to each other, there is a pronounced shift to longer wavelength in the main absorption band.

2. Alternatively, when two groups are situated ortho or meta to each other or when the para disposed groups are not electronically complementary, then the observed spectrum is usually closer to that of the separate, noninteracting chromophores.

<table>
<thead>
<tr>
<th>R</th>
<th>R'</th>
<th>Orientation</th>
<th>$\lambda_{max}$</th>
<th>$\varepsilon_{max}$</th>
<th>$\lambda'_{max}$</th>
<th>$\varepsilon'_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-OH</td>
<td>-OH</td>
<td>ortho</td>
<td>214</td>
<td>6000</td>
<td>278</td>
<td>2630</td>
</tr>
<tr>
<td>-OR</td>
<td>-CHO</td>
<td>ortho</td>
<td>253</td>
<td>11000</td>
<td>319</td>
<td>4000</td>
</tr>
<tr>
<td>-NH$_2$</td>
<td>-NO$_2$</td>
<td>ortho</td>
<td>229</td>
<td>16000</td>
<td>275</td>
<td>5000</td>
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Benzoyl derivative

Base values:

R = alkyl or ring residue \( \lambda = 246 \text{ nm} \)
R = H \( \lambda = 250 \text{ nm} \)
R = OH, OR \( \lambda = 230 \text{ nm} \)

Increment for each substituent:

- **Alkyl or ring residue**
  - o,m
  - p
- **OH, -OR**
  - o,m
  - p
- **-O**
  - o,m
  - p
- **-Cl**
  - o,m
  - p
- **-Br**
  - o,m
  - p
- **-NH\textsubscript{2}**
  - o,m
  - p
- **-NHC(O)CH\textsubscript{3}**
  - o,m
  - p
- **-NHCH\textsubscript{3}**
  - p
- **-N(CH\textsubscript{3})\textsubscript{2}**
  - o,m
  - p

Increment for each substituent:

- **Alkyl or ring residue**
  - o,m
  - p
- **OH, -OR**
  - o,m
  - p
- **-O**
  - o,m
  - p
- **-Cl**
  - o,m
  - p
- **-Br**
  - o,m
  - p
- **-NH\textsubscript{2}**
  - o,m
  - p
- **-NHC(O)CH\textsubscript{3}**
  - o,m
  - p
- **-NHCH\textsubscript{3}**
  - p
- **-N(CH\textsubscript{3})\textsubscript{2}**
  - o,m
  - p
Parent chromophore: 246 nm
$\alpha$-Ring residue: 3 nm
$m$-Br: 2 nm
Calculated: 251 nm
Observed: 253 nm

Parent chromophore: 230 nm
$p$-OH: 25 nm
$m$-OH: $2 \times 7 = 14$ nm
Calculated: 269 nm
Observed: 270 nm
Which of the following isomers has the following spectral data?
IR: 3090, 2920, 1622, 1460, 1405, 1369, 705 cm⁻¹.
UV/Vis: λmax=235 nm (εmax=9500)

Which of the following isomers has the following spectral data?
IR: 3079, 2950, 1625, 1470, 1405, 1100, 810, 715 cm⁻¹.
UV/Vis: λmax=268 nm (εmax=11000)
What is the structure of the compound having the following spectral data?  
**MS:** M⁺=96  
IR: 3095, 2925, 2840, 2760, 1704, 1605, 825 cm⁻¹.  
UV/Vis: lmax=231 nm (emax=18000)

What is the structure of the compound having the following spectral data?  
**Formula:** C₈H₉NO₂  
IR: 3430, 3027, 2922, 1720, 1345, 1243, 840 cm⁻¹.  
UV/Vis: lmax=303 nm (emax=1200)

What is the structure of the compound having the following spectral data?  
**MS:** M⁺=96  
IR: 3072, 2950, 1715, 1460, 1372, 1220, 702 cm⁻¹.  
UV/Vis: lmax=226 nm (emax=18000)

- It is often difficult to extract a great deal of information from a UV spectrum used by itself. It should be clear by now that a UV spectrum is most useful when at least a general idea of the structure is already known; in this way, the various empirical rules can be applied. Nevertheless, several generalizations can serve to guide our use of UV data. These generalizations are a good deal more meaningful when combined with infrared and NMR data - which can, for instance, definitely identify carbonyl groups, double bonds, aromatic systems, nitro groups, nitriles, enones, and other important chromophores. In the absence of infrared or NMR data, the following observations should be taken only as guidelines.
A single band of low to medium intensity (e = 100 to 10,000) at wavelengths less than 220 nm usually indicates an h to s* transition. Amines, alcohols, ethers, and thiols are possibilities, provided that the nonbonded electrons are not included in a conjugated system. An exception to this generalization is that the h to p* transition of cyano groups appears in this region. However, this is a weak transition (e < 100), and the cyano group is easily identified in the infrared. Do not neglect to look for N-H, O-H, C-O, and S-H bands in the infrared spectrum.

- A single band of low intensity (e = 10 to 100) in the region 250 to 360 nm, with no major absorption at shorter wavelengths (200 to 250 nm), usually indicates an h to p* transition. Since the absorption does not occur at long wavelength, a simple, or unconjugated, chromophore is indicated, generally one which contains an O, N, or S atom. Examples of this may include C=O, C=N, N=N, -NO2, -CO2R, -CO2H, or -CONH2. Once again, infrared and NMR spectra should help a great deal.

- Two bands of medium intensity (e = 1,000 to 10,000), both with lmax above 200 nm, generally indicate the presence of an aromatic system. If an aromatic system is present, there may be a good deal of fine structure in the longer-wavelength band (in nonpolar solvents only). Substitution on the aromatic rings increases the molar absorptivity above 10,000, particularly if the substituent increases the length of the conjugated system.

- In polynuclear aromatic substances, a third band appears near 200 nm, a band which in simpler aromatics occurs below 200 nm, where it cannot be observed. Most polynuclear aromatics (and heterocyclic compounds) have very characteristic intensity and band-shape (fine-structure) patterns, and they may often be identified via comparison to spectra which are available in the literature.
• Bands of high intensity (e = 10,000 to 20,000) which appear above 210 nm generally represent either an a,b-unsaturated ketone (check the infrared spectrum), a diene, or a polyene. The greater the length of the conjugated system, the longer the observed wavelength. For dienes, the lmax may be calculated using the Woodward-Fieser Rules.

• Simple ketones, acids, esters, amides, and other compounds containing both p systems and unshared electron pairs show two absorptions: an h to p* transition at longer wavelengths (>300 nm, low intensity) and a p to p* transition at shorter wavelengths (<250 nm, high intensity). With conjugation (enones), the lmax of the p to p* band moves to longer wavelengths and can be predicted by Woodward's Rules. The e value usually rises above 10,000 with conjugation, and, as it is very intense, it may obscure or bury the weaker h to p* transition. For a,b-unsaturated esters and acids, Nielsen's Rules may be used to predict the position of lmax with increasing conjugation and substitution.

• Compounds which are highly colored (have absorption in the visible region) are likely to contain a long-chain conjugated system or a polycyclic aromatic chromophore. Benzenoid compounds may be colored if they have enough conjugating substituents. For nonaromatic systems, usually a minimum of four to five conjugated chromophores are required to produce absorption in the visible region. However, some simple nitro, azo, nitroso, a-diketo, polybromo, and polyido compounds may also exhibit color, as may many compounds with quinoid structures.