Chapter 1

Ultraviolet/ Visible Spectroscopy
Introduction of Spectroscopy

• The structure of new compounds that are isolated from natural sources or prepared in the lab must be determined (and/or verified).
  – Chemical analysis (Classical methods)
  – Spectroscopy (Modern techniques)

• Spectroscopic techniques are non-destructive and generally require small amounts of sample.
# Types of Energy in Each Region of the Electromagnetic Spectrum

<table>
<thead>
<tr>
<th>Region of Spectrum</th>
<th>Energy Transitions</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-rays</td>
<td>Bond Breaking</td>
</tr>
<tr>
<td>Ultraviolet/Visible</td>
<td>Electronic</td>
</tr>
<tr>
<td>Infrared</td>
<td>Vibrational</td>
</tr>
<tr>
<td>Microwave</td>
<td>Rotational</td>
</tr>
<tr>
<td>Radiofrequencies</td>
<td>Nuclear Spin (Nuclear Magnetic Resonance)</td>
</tr>
<tr>
<td></td>
<td>Electron Spin (Electron Spin Resonance)</td>
</tr>
</tbody>
</table>
部分电磁波的波段分布示意图

高 ——— 频率（ν） ——— 低
高 ——— 能量 ——— 低

X-RAY 紫外 红外 微波 电磁 辐射

紫外 可见 中红外 核磁共振

200 nm ← 400 nm ← 800 nm 2.5μ ← 15μ
蓝 红

短 ———— 波长 ———— 长

部分电磁波的波段分布示意图
Four common spectroscopic techniques used to determine structure:

- Ultraviolet Spectroscopy
- Infrared Spectroscopy (IR)
- Nuclear Magnetic Resonance Spectroscopy (NMR)
- Mass Spectrometry (MS or Mass Spec)
• Ultraviolet Spectroscopy
  – Observes electronic transitions
  • Provides information on the electronic bonding in a molecule
• **Infrared spectroscopy:**
  – Used to determine the functional groups present in a molecule

• **Mass spectrometry**
  – Breaks molecule into fragments
    • Analysis of the masses of the fragments gives MW and clues to the structure of the molecule
• **Nuclear Magnetic Resonance Spectroscopy**
  
  – Observes the chemical environment of the hydrogen (or carbon) atoms in the molecule

  • Helps provide evidence for the structure of the carbon skeleton and/or the alkyl groups present

\[ ^1H \text{ NMR of } \text{CH}_3\text{CH}_2\text{OH} \]

\[ ^{13}C \text{ NMR of } \text{CH}_3\text{CH}_2\text{OH} \]
1.1 Principle of UV Light Absorption

**Ultraviolet light**: wavelengths between 190 and 400 nm

**Visible light**: wavelengths between 400 and 800 nm

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

\[ \pi \rightarrow \pi^* \]

- Chromophores:
  - Alkene: \( \lambda_{\text{max}} \approx 175 \)
  - Alkyne: \( \lambda_{\text{max}} \approx 170 \)
  - Carbonyl compounds: \( \lambda_{\text{max}} \approx 188 \)
There are several types of electronic transitions available to a molecule including:

\( \sigma \text{ to } \sigma^* \) (alkenes)
\( \pi \text{ to } \pi^* \) (alkenes, carbonyl compounds, alkynes, azo compounds)
\( n \text{ to } \sigma^* \) (oxygen, nitrogen, sulfur, and halogen compounds)
\( n \text{ to } \pi^* \) (carbonyl compounds)
Spectrometer

Polychromatic source

Lens

Sample

Photodiode array

Grating

Multichannel photodiode array
Ultraviolet/Visible Spectroscopy

Hewlett-Packard 8452a
Diode Array Spectrophotometer
1.2 Electronic Excitations
Vibrational levels

Electronic ground state

Electronic excited state

Vibrational levels

Vibrational levels

Electronic ground state
1.3 The Origin of UV Band Structure

A UV Absorption Band at Room Temperature (A) and at Lowered Temperature (B)
1.4 the absorption law—the Beer-Lambert Law

\[ \log \frac{I_0}{I} = \varepsilon l c \]

- \( I_o \) = the intensities of the incident light
- \( I \) = the intensities of the transmitted light
- \( l \) = the path length of the absorbing in centimetres
- \( c \) = the concentration in moles per litre
- \( \log_{10} \left( \frac{I_0}{I} \right) \) is called the absorbance or optical density;
- \( \varepsilon \) is known as the molar extinction coefficient
1.5 Presentation of Spectra

Ultraviolet Spectrum of Benzoic Acid in Cyclohexane

\[ \lambda_{\text{max}} = 230\, \text{nm}; \quad \log \varepsilon = 4.2 \]

\[
\begin{array}{cc}
272 & 3.1 \\
282 & 2.9 \\
\end{array}
\]
1.6 Choice of Solvents

Some solvents used in ultraviolet spectroscopy

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Minimum wavelength for 1 cm cell, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetonitrile</td>
<td>190</td>
</tr>
<tr>
<td>Water</td>
<td>191</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>195</td>
</tr>
<tr>
<td>Hexane</td>
<td>201</td>
</tr>
<tr>
<td>Methanol</td>
<td>203</td>
</tr>
<tr>
<td>Ethanol</td>
<td>204</td>
</tr>
<tr>
<td>Ether</td>
<td>215</td>
</tr>
<tr>
<td>Methylene dichloride</td>
<td>220</td>
</tr>
<tr>
<td>Chloroform</td>
<td>237</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>257</td>
</tr>
</tbody>
</table>
The first criterion for solvent

- A good solvent should not absorb ultraviolet radiation in the same region as the substance whose spectrum is being determined.
- Usually solvents which do not contain conjugated systems are most suitable for this purpose, although they vary as to the shortest wavelength at which they remain transparent to ultraviolet radiation.
- The solvents most commonly used are water, 95% ethanol, and n-hexane.
A second criterion (the effect of a solvent on the fine structure of an absorption band)

Ultraviolet Spectra of Phenol in Ethanol and in Isooctane
Large energy lowering caused by solvent interaction

The effect of a polar solvent on a transition
A third property of a solvent

The ability of a solvent to influence the wavelength of ultraviolet light which will be absorbed.

- Polar solvents may not form hydrogen bonds as readily with excited states as with ground states of polar solvents. Transitions of the $n \rightarrow \pi^*$ type are shifted to shorter wavelengths by polar solvents.

- On the other hand, in some cases the excited states may form stronger hydrogen bonds than the corresponding ground state. In such cases, a polar solvent would shift an absorption to longer wavelength, since the energy of the electronic transition would be decreased. Transitions of the $\pi \rightarrow \pi^*$ type are shifted to longer wavelengths by polar solvents.
Solvent Shifts on the Transition in Acetone

$n \rightarrow \pi^*$

<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>$\lambda_{\text{max}}, \text{nm}$</td>
<td>264.5</td>
<td>270</td>
<td>272</td>
<td>277</td>
<td>279</td>
</tr>
</tbody>
</table>
1.7 the Effect of Conjugation

Ultraviolet Spectra of Dimethylpolyenes, $\text{CH}_3(\text{CH}=\text{CH})_n\text{CH}_3$ ;
A, $n=3$; B, $n=4$; C, $n=5$
Conjugation of two chromophores not only results in a bathochromic shift, but it also increases the intensity of the absorption.

The Effect of Conjugation on Electronic Transitions

<table>
<thead>
<tr>
<th>Alkenes</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene</td>
<td>175</td>
<td>15,000</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>217</td>
<td>21,000</td>
</tr>
<tr>
<td>1,3,5-Hexatriene</td>
<td>258</td>
<td>35,000</td>
</tr>
<tr>
<td>$\beta$-Carotene (11 double bonds)</td>
<td>465</td>
<td>125,000</td>
</tr>
<tr>
<td>Ketones</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone $\pi \rightarrow \pi^*$</td>
<td>189</td>
<td>900</td>
</tr>
<tr>
<td></td>
<td>$n \rightarrow \pi^*$</td>
<td>280</td>
</tr>
<tr>
<td>3-Buten-2-one</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>213</td>
</tr>
<tr>
<td></td>
<td>$n \rightarrow \pi^*$</td>
<td>320</td>
</tr>
</tbody>
</table>
The Effect of a Polar Solvent on an n* Transition
1.8 the Effect of Conjugation on Alkenes

Formation of the Molecular Orbitals for Ethylene
Conjugation makes the energy lower
A Comparison of the $\pi \rightarrow \pi^*$ Energy Gap in a Series of Polyenes of Increasing Chain Length

The longer the conjugated system, the longer the wavelength of the absorption maximum.
the Appearance of the Spectra of some Polyenes
An extension of the length of the conjugated system

$\mathbf{B} = \text{-OH, -OR, -X, or -NH}_2$

$\Delta E_1 > \Delta E_2$

Energy Relationships of the New Molecular Orbitals and the Interacting $\pi$ System and its Auxochrome
Overlap of the electrons

Hyperconjugation

Quasi-resonance structures

The net effect is an extension of the $\pi$ system.
1.9 the Effect of conformation and Geometry on Polyene Spectra

- **All-trans** polyenes show only the $\Psi_2 \rightarrow \Psi_3^*$ transition.
- In polyenes with one or more *cis* double bonds, the $\Psi_2 \rightarrow \Psi_4^*$ transitions may become allowed — called “*cis band*”.
- Any molecule which retains a center of symmetry, even when possessing several *cis* double bonds, will not show the *cis* band.

<table>
<thead>
<tr>
<th>Conformation</th>
<th>$\psi_1$</th>
<th>$\psi_2$</th>
<th>$\psi_3^*$</th>
<th>$\psi_4^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>All-trans</td>
<td></td>
<td></td>
<td>230 nm (allowed)</td>
<td>175 nm (forbidden)</td>
</tr>
<tr>
<td>s-cis</td>
<td></td>
<td></td>
<td>271 nm (allowed)</td>
<td>175 nm (allowed)</td>
</tr>
</tbody>
</table>

- s-trans Conformation
- s-cis Conformation
Spectra of isomeric β-carotenes, showing the development of the cis band.
Empirical rules for calculating UV/Vis Absorptions

Woodward-Fieser Rules for Dienes

A. Woodward's Rules for Conjugated Carbonyl Compounds
B. Mono-Substituted Benzene Derivatives
C. Di-Substituted Benzene Derivatives
D. Benzoyl Derivatives
1.10 the Woodward-Fieser Rules for Dienes

Conjugated dienes

\[ \pi \rightarrow \pi^* \text{ transition} \quad \varepsilon = 20,000 \text{ to } 26,000 \quad \lambda = 217 \text{ to } 245 \text{nm} \]

Butadiene and many simple conjugated dienes exist in a planar \textit{s-trans} conformation.

Generally, alkyl substitution produces bathochromic shifts and hyperchromic effects.

With certain patterns of alkyl substitution, the wavelength increases, but the intensity decreases.
Cyclic dienes

The central bond is a part of the ring system, the diene chromophore is usually held rigidly in either the s-trans or the s-cis conformation.

**Homoannular Diene**
(s-cis)
less intense, $\varepsilon = 5,000 - 15,000$
$\lambda$ longer (273nm)

**Heteroannular Diene**
(s-trans)
more intense, $\varepsilon = 12,000 - 28,000$
$\lambda$ shorter (234nm)

The actual rules for predicting the absorption of open chain and six-membered ring diene were first made by Woodward in 1941. Since that time they have been modified by Fieser and Scott as a result of experience with a very large number of dienes and trienes.
**Rules for diene and triene absorption**

<table>
<thead>
<tr>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Value assigned to parent heteroannular or open diene</td>
<td>214 nm</td>
</tr>
<tr>
<td>Value assigned to parent homoannular diene</td>
<td>253 nm</td>
</tr>
<tr>
<td>Increment for</td>
<td></td>
</tr>
<tr>
<td>(a) each alkyl substituent or ring residue</td>
<td>5 nm</td>
</tr>
<tr>
<td>(b) the exocyclic double bond</td>
<td>5 nm</td>
</tr>
<tr>
<td>(c) a double-bond extension</td>
<td>30 nm</td>
</tr>
<tr>
<td>(d) auxochrome</td>
<td></td>
</tr>
<tr>
<td>— OCOCH₃</td>
<td>0 nm</td>
</tr>
<tr>
<td>— OR</td>
<td>6 nm</td>
</tr>
<tr>
<td>— SR</td>
<td>30 nm</td>
</tr>
<tr>
<td>— Cl, —Br</td>
<td>5 nm</td>
</tr>
<tr>
<td>— NR₂</td>
<td>60 nm</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>λ&lt;sub&gt;calc&lt;/sub&gt;</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>transoid: 214 nm</td>
<td></td>
</tr>
<tr>
<td>alkyl groups: 3 × 5 = 15</td>
<td>229 nm</td>
</tr>
<tr>
<td>observed: 217 nm</td>
<td></td>
</tr>
<tr>
<td>observed: 228 nm</td>
<td></td>
</tr>
</tbody>
</table>
Exocyclic Double Bond

transoid: 214 nm
ring residues: $3 \times 5 = 15$
exocyclic double bond: 5
observed: 234 nm
observed: 235 nm

cisoid: 253 nm
ring residues: $3 \times 5 = 15$
exocyclic double bond: 5
observed: 273 nm
observed: 275 nm
cisoid: 253 nm
ring residues: \(5 \times 5 = 25\)
double bonds extending
  conjugation: \(2 \times 30 = 60\)
  exocyclic double bonds: \(3 \times 5 = 15\)
CH\(_3\)COO–: 0
observed: \(353\) nm

\[\text{355 nm}\]

The Woodward-Fieser rules work well for polyenes with from one to four conjugated double bonds.
1.11 The Fieser-Kuhn Rules for polyenes

\[ \beta\text{-Carotene, 11 Double Bonds} \]
\[ \lambda_{\text{max}} = 452 \text{ nm (hexane)}, \, \varepsilon = 15.2 \times 10^4 \]

\[ \text{Lycopene, 13 Double Bonds (11 Conjugated)} \]
\[ \lambda_{\text{max}} = 474 \text{ nm (hexane)}, \, \varepsilon = 18.6 \times 10^4 \]
Empirical Rules for Polyens

\[
\lambda_{\text{max}} \ (\text{hexane}) = 114 + 5M + n(48.0 - 1.7n) - 16.5R_{\text{endo}} - 10R_{\text{exo}} \\
\varepsilon_{\text{max}} \ (\text{hexane}) = 1.74 \times 10^4 n
\]

where:

\[
\begin{align*}
M & \quad = \text{the number of alkyl substituents} \\
n & \quad = \text{the number of conjugated double bonds} \\
R_{\text{endo}} & \quad = \text{the number of rings with endocyclic double bonds} \\
R_{\text{exo}} & \quad = \text{the number of rings with exocyclic double bonds}
\end{align*}
\]

For example, β-Carotene:

\[
\begin{align*}
M & \quad = 10 \\
n & \quad = 11 \\
R_{\text{endo}} & \quad = 2 \\
R_{\text{exo}} & \quad = 0
\end{align*}
\]

Therefore:

\[
\lambda_{\text{max}} = 453.3 \quad \varepsilon_{\text{max}} = 19.1 \times 10^4
\]
1.12 carbonyl compounds; enones

Two principal uv transition:

Substitution by an auxochrome with a lone pair of electrons, such as –NR₂, –OH, –OR, –NH₂, or –X, as in amides, acids, esters, or acid chlorides, gives a pronounced hypsochromic effect on the n→π* transition and lesser bathochromic effect on the π→π* transition. (resonance interaction)
the Hypsocromic Effect of Lone Pair Auxochromes on the n→π* Transition of a Carbonyl Group

<table>
<thead>
<tr>
<th>Structure</th>
<th>λ_{max} (nm)</th>
<th>ε_{max}</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃=C=O</td>
<td>293</td>
<td>12</td>
<td>Hexane</td>
</tr>
<tr>
<td>CH₃=C=CH₃</td>
<td>279</td>
<td>15</td>
<td>Hexane</td>
</tr>
<tr>
<td>CH₃=C=Cl</td>
<td>235</td>
<td>53</td>
<td>Hexane</td>
</tr>
<tr>
<td>CH₃=C=NH₂</td>
<td>214</td>
<td>-</td>
<td>Water</td>
</tr>
<tr>
<td>CH₃=C=OCH₂CH₃</td>
<td>204</td>
<td>60</td>
<td>Water</td>
</tr>
</tbody>
</table>

This shift is due primarily to the inductive effect of the oxygen, nitrogen, or halogen atoms. They withdraw electrons from the carbonyl carbon, causing the lone pair of electrons on oxygen to be held more firmly than would be the case in the absence of an inductive effect.
If the carbonyl group is a part of a conjugated system of double bonds, both the \( n \rightarrow \pi^* \) and the \( \pi \rightarrow \pi^* \) bands are shifted to longer wavelengths. The energy of the \( n \rightarrow \pi^* \) transition does not decrease as rapidly as that of the \( \pi \rightarrow \pi^* \) band, which is more intense. If the conjugated chain becomes long enough, the \( n \rightarrow \pi^* \) band becomes “buried” under the more intense \( \pi \rightarrow \pi^* \) band.
the Orbitals of an Enone System Compared to those of the Non-interacting Chromophores
1.13 Woodward’s Rules for Enones

- Conjugation of a double bond with a carbonyl group leads to absorption ($\varepsilon = 8,000$ to $20,000$), $\pi \rightarrow \pi^*$, at $220 \sim 250$ nm, predictable

- $n \rightarrow \pi^*$, at $310 \sim 330$ nm, much less intense ($\varepsilon = 50$ to $100$), not predictable
acyclic enone: 215nm
α-CH₃: 10
β-CH₃: 24
249nm
observed: 249nm

6-membered enone: 215nm
double bond extending conjugation: 30
homocyclic diene 39
δ-ring residue: 24
302nm
observed: 300nm

5-membered enone: 202nm
β-ring residue: 2×12= 24
exocyclic double bond: 5
231nm
observed: 226nm

5-membered enone: 202nm
α-Br: 25
β-ring residue: 2×12= 24
exocyclic double bond: 5
256nm
observed: 251nm
1.14 Solvent Shifts – a more detailed examination

1. In most $\pi \rightarrow \pi^*$ transitions

(bathochromic shift, lower energy)

the Effect of a Polar Solvent on a Transition
The ground state of the molecule is relatively non-polar, and the excited state is often more polar than the ground state. As a result, when a polar solvent is used, it interacts more strongly with the excited state than with the ground state, and the transition is shifted to longer wavelength.

In the ground state, the \( \pi \) electron density is equally distributed, and the nuclei of C are shielded.

In the \( \pi^* \) excited state, the electron is promoted, and the C becomes electron deficient.

The excited state interacts more strongly with polar or hydrogen bonding solvents.
2. In most $n \rightarrow \pi^*$ transitions
   (hypsochromic shift, higher energy)

- The ground state is more polar than the excited state.
- Hydrogen bonding solvents interact more strongly with unshared electron pairs in the ground state molecule.
1.15 Aromatic Compounds

Molecular Orbitals and Energy States for Benzene

184 and 202 nm primary bands
255nm secondary bands (fine-structure)
The second primary band (184 nm, \( \varepsilon = 47,000 \)) in vacuum ultraviolet region

The 202 nm band is much less intense (\( \varepsilon = 7,400 \)), it corresponds to a forbidden transition

The secondary band is the least intense of the benzene bands (\( \varepsilon = 230 \)). It corresponds to a symmetry forbidden electronic transition.

Ultraviolet Spectrum of Benzene
A. Substituents with Unshared Electrons

- The non-bonding electrons can increase the length of the π system though resonance.
- The more available these n-electrons are for interaction with the π system of the aromatic ring, the greater the shifts will be. (-NH₂, -OH, -OCH₃, -X)
- Interactions of this type between the n and π electrons usually cause shifts in the primary and secondary benzene absorption bands to longer wavelength.
- In addition, the presence of n-electrons in these compounds gives the possibility of n→π* transition.
If an \( n \)-electron is excited into the extended \( \pi^* \) chromophore, the atom from which it was removed becomes electron-deficient, while the \( \pi \) system of the aromatic ring acquires an extra electron. This causes a separation of charge in the molecule.

The extra electron in the ring is actually in a \( \pi^* \) orbital.

A charge transfer or an electron transfer excited state

With compounds which are acids or bases, pH changes can have a very significant effect on the positions of the primary and secondary bands.
B. Substituents capable of π-conjugation

Interaction of the benzene ring electrons and the π electrons of the substituent can also produce a new electron transfer band. This new band may be so intense as to obscure the secondary band of the benzene system.

Notice that the opposite polarity is induced; the ring becomes electron deficient.

The effect of acidity or basicity of the solution on such a chromophoric substituent group
C. Disubstituted benzene Derivatives

A. For para-, two possibilities:

1. Both groups are electron-releasing or electron-withdrawing, similar to monosubstituted benzenes;

2. One is electron-releasing while the other is electron-withdrawing, enhanced shifting (the magnitude of the shift of the primary band is greater than the sum of the shifts due to the individual group.)

\[
\begin{align*}
\text{resonance interactions}
\end{align*}
\]
# Empirical Rules for Benzoyl Derivatives

![Structural diagram of benzoyl derivative]

**Parent chromophore:**

<table>
<thead>
<tr>
<th>R</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkyl or ring residue</td>
<td>246</td>
</tr>
<tr>
<td>H</td>
<td>250</td>
</tr>
<tr>
<td>OH or OAlkyl</td>
<td>230</td>
</tr>
</tbody>
</table>

**Increment for each substituent:**

<table>
<thead>
<tr>
<th>Substituent</th>
<th>o-,m-</th>
<th>p-</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkyl or ring residue</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>O, OCH₃, or OAlkyl</td>
<td>7</td>
<td>25</td>
</tr>
<tr>
<td>O</td>
<td>11</td>
<td>20</td>
</tr>
<tr>
<td>P</td>
<td>78</td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>Br</td>
<td>2</td>
<td>15</td>
</tr>
<tr>
<td>NH₂</td>
<td>13</td>
<td>58</td>
</tr>
<tr>
<td>NHCOCOCH₃</td>
<td>20</td>
<td>45</td>
</tr>
<tr>
<td>NHCH₃</td>
<td>73</td>
<td></td>
</tr>
<tr>
<td>N(CH₃)₂</td>
<td>20</td>
<td>85</td>
</tr>
</tbody>
</table>
parent chromophore: 246nm

o-ring residue: 3

$m$-Br: \[ \frac{2}{251\text{nm}} \]

observed: 253nm

parent chromophore: 230nm

$m$-OH: \[ 2 \times 7 = 14 \]

$p$-OH: \[ \frac{25}{269\text{nm}} \]

observed: 270nm
Application of UV

1. To obtain the information of conjugation, $\varepsilon$

2. Qualification analysis

3. Quantitative analysis: $A = \varepsilon bc$
Example spectra
Example spectra
A practical guide: Exercises

What do you look for in an ultraviolet spectrum?

A single band of low intensity (10 to 100) in the region 250-360 nm, with no major absorption at shorter wavelengths (200-250 nm) $\rightarrow n\rightarrow\pi^*$

A simple, or unconjugated, chromophore (contains an O, N, or S):
C=O, C=N, N=N, -NO$_2$, -COOR, -COOH, or -CONH$_2$
Two bands of medium intensity ($\varepsilon=1,000$ to $10,000$), both with $\lambda_{\text{max}}$ above 200 nm

- A good deal of fine structure in the longer wavelength band (in non-polar solvents only).
- Substituent on the aromatic rings will increase the molar absorptivity above 10,000.
- In polynuclear aromatic substances, a third band will appear near 200 nm.

Bands of high intensity ($\varepsilon=10,000$ to $20,000$), above 210 nm

- The longer the length of the conjugated system, the longer the observed wavelength will be.
- For dienes, using the Woodwood-fieser rules
- More than four double bonds, using Fiese-Kuhn rules
Simple ketones, acids, esters, amides, and other compounds containing both $\pi$ system and unshared electron pairs, will show two absorptions:

\[ n \rightarrow \pi^* \] at longer wavelength (>300nm, low intensity)

\[ \pi \rightarrow \pi^* \] at shorter wavelength (<250nm, high intensity)

• With conjugation (enones), the $\lambda_{\text{max}}$ of the $\pi \rightarrow \pi^*$ band moves to longer wavelengths, Woodward’s rules

$\varepsilon$ above 10,000, bury the weaker $n \rightarrow \pi^*$ transition
• $\alpha,\beta$-unsaturated esters and acids, Nielsen’s rules

Compounds which are highly colored are likely to contain a long-chain conjugated system (4~5) or a polycyclic aromatic chromophore.
Homework and Course Requirements

- Comprehend the rationale Ultraviolet and visible spectra
- Master the fundamental type of electronic transition
- Master the major component parts and the demand of every part of visible ultraviolet spectrophotometer
- Finish Homework