ULTRA VIOLET SPECTROSCOPY

BY

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In spectroscopy, transitions between different energy levels within atoms and molecules are recorded and then used to give information on chemical structure.
UV Spectroscopy

• UV & electronic transitions
• Usable ranges & observations
• Selection rules
• Band Structure
• Instrumentation & Spectra
• Beer-Lambert Law
• Application of UV-spec
UV Spectroscopy

I. Introduction
   A. UV radiation and Electronic Excitations
      1. The difference in energy between molecular bonding, non-bonding and anti-bonding orbital's ranges from 125-650 kJ/mole
      2. This energy corresponds to EM radiation in the ultraviolet (UV) region, 100-400 nm, and visible (VIS) regions 400-800 nm of the spectrum
      3. For comparison, recall the EMR spectrum:

      4. Using IR we observed vibrational transitions with energies of 8-40 kJ/mol at wavelengths of 2500-15,000 nm
      5. For purposes of our discussion, we will refer to UV and VIS spectroscopy as UV
UV Spectroscopy

I. Introduction

B. The Spectroscopic Process

1. In UV spectroscopy, the sample is irradiated with the broad spectrum of the UV radiation.

2. If a particular electronic transition matches the energy of a certain band of UV, it will be absorbed.
3. The remaining UV light passes through the sample and is observed.
4. From this residual radiation a spectrum is obtained with “gaps” at these discrete energies – this is called an absorption spectrum.

Where has the energy that was within the photons gone to?
In a typical experiment, the molecules or atoms start at lower energy and go to a higher energy level upon absorption of radiation of appropriate wavelength.
Electronic Transitions

HOMO

LUMO
I. Introduction
   Selection Rules
   1. Not all transitions that are possible are observed.

   2. For an electron to transition, certain quantum mechanical constraints apply – these are called “selection rules”.

   3. For example, an electron can change its spin quantum number during a transition – these are “forbidden”
   Other examples include:
   • the number of electrons that can be excited at one time
   • symmetry properties of the molecule
   • symmetry of the electronic states

   4. To further complicate matters, “forbidden” transitions are sometimes observed.
1. UV tends to give wide i.e. broad, overlapping bands; as the electronic excitation is associated with vibrational and rotational excitation which cannot be resolved.

2. It would seem that since the electronic energy levels of a pure sample of molecules would be quantized, fine, discrete bands would be observed – for atomic spectra, this is the case.

3. This effect will impact the wavelength at which a transition is observed – very similar to the effect of H-bonding on the O-H vibrational energy levels in neat samples.
UV Spectroscopy

Instrumentation and Spectra

1. The construction of a traditional UV-VIS spectrometer is very similar to an IR, as similar functions – sample handling, irradiation, detection and output are required.

2. Here is a simple schematic that covers most modern UV spectrometers:

\[
\log \left( \frac{I_0}{I} \right) = A
\]

UV-VIS sources → monochromator/beam splitter optics → sample → detector → reference

\[ \lambda, \text{ nm} \]

200 → 700
3. Two sources are required to scan the entire UV-VIS band:
   • Deuterium lamp – covers the UV – 200-330
   • Tungsten lamp – covers 330-700

4. As with the dispersive IR, the lamps illuminate the entire band of UV or visible light; the monochromator (grating or prism) gradually changes the small bands of radiation sent to the beam splitter.

5. The beam splitter sends a separate band to a cell containing the sample solution and a reference solution.

6. The detector measures the difference between the transmitted light through the sample ($I$) vs. the incident light ($I_0$) and sends this information to the recorder.

7. As with dispersive IR, time is required to cover the entire UV-VIS band due to the mechanism of changing wavelengths.
B. Instrumentation – Sample Handling

1. Virtually all UV spectra are recorded solution-phase.

2. Cells can be made of plastic, glass or quartz.

3. Only quartz is transparent in the full 200-700 nm range; plastic and glass are only suitable for visible spectra.

4. Concentration is empirically determined.

A typical sample cell (commonly called a cuvet):
5. Solvents must be transparent in the region to be observed; the wavelength a solvent is no longer transparent is referred to as the cutoff.

6. Since spectra are only obtained up to 200 nm, solvents typically only need to lack conjugated $\pi$ systems or carbonyls.

Common solvents and cutoffs:

- acetonitrile: 190 nm
- chloroform: 240 nm
- cyclohexane: 195 nm
- 1,4-dioxane: 215 nm
- 95% ethanol: 205 nm
- n-hexane: 201 nm
- methanol: 205 nm
- isooctane: 195 nm
- water: 190 nm
7. Additionally solvents must preserve the fine structure (where it is actually observed in UV)
UV Spectroscopy

The Spectrum

1. The x-axis of the spectrum is in wavelength; 200-400 nm for UV, 200-800 nm for UV-VIS determination.

2. Due to the lack of any fine structure, spectra are rarely shown in their raw form, rather, the peak maxima are simply reported as a numerical list of “\( \lambda \text{ max} \)” values.

\[ \lambda_{\text{max}} = 206 \text{ nm} \\
\lambda_{\text{max}} = 252 \text{ nm} \\
\lambda_{\text{max}} = 317 \text{ nm} \\
\lambda_{\text{max}} = 376 \text{ nm} \]
A. Introduction

Observed electronic transitions

1. The lowest energy transition (and most often obs. by UV) is typically that of an electron in the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO).

2. There are three kinds of electrons present in molecules as
   a) \( \sigma \)-electrons – present in \( \sigma \)-bonds.
   b) \( \pi \)-electrons - present in \( \pi \)-bonds.
   c) ‘n’-nonbonding electrons- present as unshared electrons.

3. Sigma and pi electrons have corresponding higher energy antibonding molecular orbitals (\( \sigma^* \) \( \pi^* \)), but there is no higher energy antibonding molecular orbital for non bonding electrons.
4. From the molecular orbital diagram, there are several possible electronic transitions that can occur, each of a different relative energy:

- $\sigma \rightarrow \sigma^*$ : alkanes
- $\sigma \rightarrow \pi^*$ : carbonyls
- $\pi \rightarrow \pi^*$ : unsaturated cmpds.
- $n \rightarrow \sigma^*$ : O, N, S, halogens
- $n \rightarrow \pi^*$ : carbonyls
5. Although the UV spectrum extends below 100 nm (high energy), oxygen in the atmosphere is not transparent below 200 nm.

6. Special equipment to study vacuum or far UV is required.

7. Routine organic UV spectra are typically collected from 200-800 nm.

8. This limits the transitions that can be observed:

<table>
<thead>
<tr>
<th>Transition</th>
<th>Molecule Type</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma \rightarrow \sigma^*$</td>
<td>alkanes</td>
<td>150</td>
</tr>
<tr>
<td>$\sigma \rightarrow \pi^*$</td>
<td>carbonyls</td>
<td>170</td>
</tr>
<tr>
<td>$\pi \rightarrow \pi^*$</td>
<td>unsaturated cmpds.</td>
<td>180</td>
</tr>
<tr>
<td>$\pi \rightarrow \pi^*$</td>
<td>unsaturated cmpds.</td>
<td>180</td>
</tr>
<tr>
<td>$n \rightarrow \sigma^*$</td>
<td>O, N, S, halogens</td>
<td>190</td>
</tr>
<tr>
<td>$n \rightarrow \pi^*$</td>
<td>carbonyls</td>
<td>300</td>
</tr>
</tbody>
</table>
UV Spectroscopy

B. Instrumentation and Spectra

The Spectrum

1. The *y-axis* of the spectrum is **absorbance, A**.

2. From the spectrometers point of view, absorbance is the inverse of transmittance: 
   \[ A = \log_{10} \left( \frac{I_0}{I} \right) \]

3. From an experimental point of view, three other considerations must be made:
   i. a longer **path length, l** through the sample will cause more UV light to be absorbed – linear effect
   ii. the greater the **concentration, c** of the sample, the more UV light will be absorbed – linear effect
   iii. some electronic transitions are more effective at the absorption of photon than others – **molar absorptivity, e** this may vary by orders of magnitude.
4. These effects are combined into the

**Beer-Lambert Law:** \( A = e \cdot C \cdot l \)

i. For most UV spectrometers, \( l \) would remain constant (standard cells are typically 1 cm in path length).

ii. Concentration is typically varied depending on the strength of absorption observed or expected – typically dilute – sub .001 M.

iii. Molar absorptivities vary by orders of magnitude:

- values of \( 10^4 \text{-} 10^6 \) are termed high intensity absorptions
- values of \( 10^3 \text{-} 10^4 \) are termed low intensity absorptions
- values of 0 to \( 10^3 \) are the absorptions of forbidden transitions

A **is unitless**, so the units for \( e \) are \( \text{cm}^{-1} \cdot \text{M}^{-1} \) and are rarely expressed
C. Practical application of UV spectroscopy

1. UV was the first organic spectral method, however, it is rarely used as a **primary** method for structure determination.

2. It is **most useful in combination with NMR and IR data** to elucidate unique electronic features.

3. Determination of sterochemistry (cis and trans): A trans isomer usually has a greater $\lambda_{\text{max}}$ and $\varepsilon_{\text{max}}$ value than the corresponding cis isomer. Thus UV spectra is useful to distinguish between cis and trans isomer.

4. The strength of Hydrogen bond can be calculated by running the UV spectrum in different solvents like polar and non-polar.
1. Remember the electrons present in organic molecules are involved in covalent bonds or lone pairs of electrons on atoms such as O or N.

2. Since similar functional groups will have electrons capable of discrete classes of transitions, the characteristic energy of these energies is more representative of the functional group than the electrons.

3. A functional group capable of having characteristic electronic transitions is called a chromophore (color loving).

4. Structural or electronic changes in the chromophore can be quantified and used to predict shifts in the observed electronic transitions.

5. Chromophore are compounds containing unsaturation i.e. Alkenes, Alkynes, Azo compounds, Nitriles, Nitro compounds etc.
1. **Alkanes** – only possess s-bonds and no lone pairs of electrons, so only the high energy $\sigma \rightarrow \sigma^*$ transition is observed in the far UV.

This transition is destructive to the molecule, causing cleavage of the $\sigma$ bond.

![Diagram of Alkanes with $\sigma$ and $\sigma^*$ transitions]
2. **Alcohols, ethers, amines and sulfur compounds** – in the cases of simple, aliphatic examples of these compounds the $n \rightarrow \sigma^*$ is the most often observed transition; like the alkane $\sigma \rightarrow \sigma^*$ it is most often at shorter wavelength than 200 nm.

Note how this transition occurs from the HOMO to the LUMO.
3. **Alkenes and Alkynes** – in the case of isolated examples of these compounds *the $\pi \rightarrow \pi^*$ is observed* at 175 and 170 nm, respectively.

Even though this transition is of lower energy than $\sigma \rightarrow \sigma^*$, it is still in the far UV – however, the transition energy is sensitive to substitution.
4. **Carbonyls** – unsaturated systems incorporating N or O can undergo $n \rightarrow \pi^*$ transitions (~285 nm) in addition to $\pi \rightarrow \pi^*$. Despite the fact this transition is forbidden by the selection rules ($e = 15$), it is the most often observed and studied transition for carbonyls.

**This transition is also sensitive to substituents on the carbonyl**

Similar to alkenes and alkynes, **non-substituted carbonyls undergo the $\pi \rightarrow \pi^*$ transition in the vacuum UV** (190 nm, $e = 900$); sensitive to substitution effects.
4. Carbonyls – $n \rightarrow \pi^*$ transitions ($\sim$285 nm); $\pi \rightarrow \pi^*$ (188 nm)

$\sigma_{CO}$ transitions omitted for clarity

It has been determined from spectral studies, that carbonyl oxygen more approximates sp rather than sp$^2$. 
**General** – from our brief study of these general chromophores, only the weak $n \rightarrow \pi^*$ transition occurs in the routinely observed UV region.

The attachment of substituent groups (other than H) can shift the energy of the transition.

**Substituent's that increase the intensity and often wavelength of an absorption are called Auxochrome.**

Common auxochromes include alkyl, hydroxyl, alkoxy and amino groups and the halogens
General – Substituents may have any of four effects on a chromophore

i. Bathochromic shift (red shift) – a shift to longer wavelength.

ii. Hypsochromic shift (blue shift) – shift to shorter wavelength.

iii. Hyperchromic effect – an increase in intensity.

iv. Hypochromic effect – a decrease in intensity.
UV Spectroscopy

Substituent Effects

1. **Conjugation** – most efficient means of bringing about a bathochromic and hyperchromic shift of an unsaturated chromophore:

<table>
<thead>
<tr>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>175</td>
<td>15,000</td>
</tr>
<tr>
<td>217</td>
<td>21,000</td>
</tr>
<tr>
<td>258</td>
<td>35,000</td>
</tr>
<tr>
<td>465</td>
<td>125,000</td>
</tr>
</tbody>
</table>

$n \rightarrow \pi^*$

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>280</td>
<td>12</td>
</tr>
<tr>
<td>280</td>
<td>27</td>
</tr>
<tr>
<td>213</td>
<td>7,100</td>
</tr>
</tbody>
</table>

$\pi \rightarrow \pi^*$

<table>
<thead>
<tr>
<th>$\lambda$ (nm)</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>189</td>
<td>900</td>
</tr>
</tbody>
</table>

$\beta$-carotene
Conjugation – Alkenes

The observed shifts from conjugation imply that an increase in conjugation decreases the energy required for electronic excitation.

From molecular orbital (MO) theory two atomic p orbitals, \( f_1 \) and \( f_2 \) from two sp\(^2\) hybrid carbons combine to form two MOs \( Y_1 \) and \( Y_2^* \) in ethylene.

\[ \Psi_2^* \]

\[ \phi_1 \]

\[ \psi_1 \]

\[ \pi \]

\[ \phi_2 \]
UV Spectroscopy

Conjugation – Alkenes

When we consider **butadiene**, we are now mixing 4 p orbitals giving 4 MOs of an energetically symmetrical distribution compared to ethylene.

\[ \Psi_1 \quad \Psi_2 \quad \Psi_3 \quad \Psi_4 \]

\[ \Delta E \text{ for the HOMO } \rightarrow \text{ LUMO transition is reduced} \]
Extending this effect out to longer conjugated systems the energy gap becomes progressively smaller:

- Ethylene
- Butadiene
- Hexatriene
- Octatetraene

Lower energy = Longer wavelengths
Conjugation – Alkenes

Methyl groups also cause a bathochromic shift, even though they are devoid of $\pi$- or $n$-electrons. This effect is thought to be through what is termed “Hyperconjugation” or sigma bond resonance.
The effect of substituent groups can be reliably quantified from empirical observation of known conjugated structures and applied to new systems.

This quantification is referred to as the Woodward-Fieser Rules which we will apply to two specific chromophores:

1. Conjugated dienes
2. Conjugated dienones

\[ \lambda_{\text{max}} = 239 \text{ nm} \]
Structure Determination

Dienes

**Woodward-Fieser Rules**
Woodward and the Fiesers performed extensive studies of terpene and steroidal alkenes and noted similar substituents and structural features would predictably lead to an empirical prediction of the wavelength for the lowest energy $\pi \rightarrow \pi^*$ electronic transition.

The general approach for calculating $\lambda_{\text{max}}$ value is to begin with an absorption wavelength for the parent chromophore and add a value of each substituent attached to the conjugated system.
UV Spectroscopy

Woodward-Fieser Rules - Dienes

The rules begin with a base value for $\lambda_{\text{max}}$ of the chromophore being observed:

\[
\text{acyclic butadiene} = 215 \text{ nm}
\]

The incremental contribution of substituents is added to this base value from the group tables:

<table>
<thead>
<tr>
<th>Group</th>
<th>Increment (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extended conjugation</td>
<td>+30</td>
</tr>
<tr>
<td>Homoannular component</td>
<td>+39</td>
</tr>
<tr>
<td>Each exo-cyclic C=C</td>
<td>+5</td>
</tr>
<tr>
<td>Alkyl</td>
<td>+5</td>
</tr>
<tr>
<td>-OCOCH$_3$</td>
<td>+0</td>
</tr>
<tr>
<td>-OR</td>
<td>+6</td>
</tr>
<tr>
<td>-SR</td>
<td>+30</td>
</tr>
<tr>
<td>-Cl, -Br</td>
<td>+5</td>
</tr>
<tr>
<td>-NR$_2$</td>
<td>+60</td>
</tr>
</tbody>
</table>
For example:

Isoprene - acyclic butadiene = 215 nm
one alkyl subs. + 5 nm 220 nm
Experimental value 220 nm

Allylidene-cyclohexane
- acyclic butadiene = 215 nm
one exocyclic C=C + 5 nm 230 nm
2 alkyl subs. +10 nm 237 nm
Experimental value 237 nm
Woodward-Fieser Rules – Cyclic Dienes

There are two major types of cyclic dienes, with two different base values:

**Heteroannular diene** is the cyclic diene in which the two double bonds in conjugation are present in two different rings.

**Homoannular diene** is the cyclic diene in which both the conjugated double bonds are present in same ring.

**Heteroannular (transoid):**

\[
\begin{array}{c}
  \text{Heteroannular (transoid):} \\
  \text{e} = 5,000 - 15,000 \\
  \text{base } \lambda_{\text{max}} = 214 \text{ nm}
\end{array}
\]

**Homoannular (cisoid):**

\[
\begin{array}{c}
  \text{Homoannular (cisoid):} \\
  \text{e} = 12,000-28,000 \\
  \text{base } \lambda_{\text{max}} = 253 \text{ nm}
\end{array}
\]

The increment table is the same as for acyclic butadienes with a couple additions:

<table>
<thead>
<tr>
<th>Group</th>
<th>Increment (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Additional homoannular</td>
<td>+39</td>
</tr>
<tr>
<td>Where both types of diene are</td>
<td></td>
</tr>
<tr>
<td>present, the one with the</td>
<td></td>
</tr>
<tr>
<td>longer ( \lambda ) becomes</td>
<td></td>
</tr>
<tr>
<td>the base</td>
<td></td>
</tr>
</tbody>
</table>
Woodward-Fieser Rules – Cyclic Dienes

For example:

1,2,3,7,8,8a-hexahydro-8a-methylnaphthalene heteroannular diene = 215 nm

3 alkyl subs. (3 x 5) +15 nm

1 exo C=C + 5 nm 235 nm

Experimental value 235 nm
UV Spectroscopy

Woodward-Fieser Rules – Cyclic Dienes

heteroannular diene = 215 nm
4 alkyl subs. (4 x 5) + 20 nm
1 exo C=C  + 5 nm
240 nm

homoannular diene = 253 nm
4 alkyl subs. (4 x 5) + 20 nm
1 exo C=C  + 5 nm
278 nm
Three common errors:

This compound has three exocyclic double bonds; the indicated bond is exocyclic to two rings.

This is not a heteroannular diene; you would use the base value for an acyclic diene.

Likewise, this is not a homooannular diene; you would use the base value for an acyclic diene.
1. General Features

Carbonyls, as we have discussed, have two primary electronic transitions:

Remember, the \( \pi \rightarrow \pi^* \) transition is allowed and gives a high intensity, but lies outside the routine range of UV observation.

The \( n \rightarrow \pi^* \) transition is forbidden and gives a very low intensity, but can routinely be observed.
UV Spectroscopy

IV. Structure Determination
B. Enones

1. General Features
For auxochromic substitution on the carbonyl, pronounced hypsochromic shifts are observed for the n $\rightarrow$ $\pi^*$ transition ($\lambda_{\text{max}}$):

\[
\begin{align*}
\text{O} & \quad 293 \text{ nm} \\
\text{O} & \quad 279 \text{ nm} \\
\text{O} & \quad 235 \text{ nm} \\
\text{O} & \quad 214 \text{ nm} \\
\end{align*}
\]

This is explained by the inductive withdrawal of electrons by O, N or halogen from the carbonyl carbon – this causes the n-electrons on the carbonyl oxygen to be held more firmly.

\[
\begin{align*}
\text{O} & \quad 204 \text{ nm} \\
\end{align*}
\]

It is important to note this is different from the auxochromic effect on $\pi \rightarrow \pi^*$ which extends conjugation and causes a bathochromic shift.

\[
\begin{align*}
\text{O} & \quad 204 \text{ nm} \\
\end{align*}
\]

In most cases, this bathochromic shift is not enough to bring the $\pi \rightarrow \pi^*$ transition into the observed range.
UV Spectroscopy

IV. Structure Determination
   B. Enones
      1. General Features
         Conversely, if the C=O system is conjugated both the n $\rightarrow$ $\pi^*$ and $\pi$ $\rightarrow$ $\pi^*$ bands are bathochromically shifted.

         Here, several effects must be noted:
         i. the effect is more pronounced for $\pi$ $\rightarrow$ $\pi^*$

         ii. if the conjugated chain is long enough, the much higher intensity $\pi$ $\rightarrow$ $\pi^*$ band will overlap and drawn out the n $\rightarrow$ $\pi^*$ band.

         i. the shift of the n $\rightarrow$ $\pi^*$ transition is not as predictable.

         For these reasons, empirical Woodward-Fieser rules for conjugated enones are for the higher intensity, allowed $\pi$ $\rightarrow$ $\pi^*$ transition.
IV. Structure Determination

B. Enones

1. General Features

These effects are apparent from the MO diagram for a conjugated enone:

\[
\begin{array}{c}
\text{\(\Psi_1\)} \\
\text{\(-\pi\)} \\
\text{\(-\pi^*\)} \\
\text{\(-\pi\)} \\
\text{\(-\pi^*\)}
\end{array}
\]

\[
\begin{array}{c}
\text{\(\Psi_2\)} \\
\text{\(-\pi\)} \\
\text{\(-\pi^*\)} \\
\text{\(-n\)} \\
\text{\(-\pi\)} \\
\text{\(-\pi^*\)}
\end{array}
\]

\[
\begin{array}{c}
\text{\(\Psi_3\)} \\
\text{\(-\pi\)} \\
\text{\(-\pi^*\)} \\
\text{\(-n\)} \\
\text{\(-\pi\)} \\
\text{\(-\pi^*\)}
\end{array}
\]

\[
\begin{array}{c}
\text{\(\Psi_4\)} \\
\text{\(-\pi\)} \\
\text{\(-\pi^*\)} \\
\text{\(-n\)} \\
\text{\(-\pi\)} \\
\text{\(-\pi^*\)}
\end{array}
\]
### Group Increment (nm)

<table>
<thead>
<tr>
<th>Group</th>
<th>Increment (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6-membered ring or acyclic enone</td>
<td>Base 215 nm</td>
</tr>
<tr>
<td>5-membered ring parent enone</td>
<td>Base 202 nm</td>
</tr>
<tr>
<td>Aldehyde</td>
<td>Base 207 nm</td>
</tr>
<tr>
<td>Double bond extending conjugation</td>
<td>30</td>
</tr>
<tr>
<td>Alkyl group or ring residue</td>
<td>$\alpha, \beta, \gamma,$ and higher 10, 12, 18</td>
</tr>
<tr>
<td>-OH</td>
<td>$\alpha, \beta, \gamma,$ and higher 35, 30, 18</td>
</tr>
<tr>
<td>-OR</td>
<td>$\alpha, \beta, \gamma, \delta$ 35, 30, 17, 31</td>
</tr>
<tr>
<td>-O(C=O)R</td>
<td>$\alpha, \beta, \gamma,$ 6</td>
</tr>
<tr>
<td>-Cl</td>
<td>$\alpha, \beta$ 15, 12</td>
</tr>
<tr>
<td>-Br</td>
<td>$\alpha, \beta$ 25, 30</td>
</tr>
<tr>
<td>-NR$_2$</td>
<td>$\beta$ 95</td>
</tr>
<tr>
<td>Exocyclic double bond</td>
<td>5</td>
</tr>
<tr>
<td>Homocyclic diene component</td>
<td>39</td>
</tr>
</tbody>
</table>
UV Spectroscopy

IV. Structure Determination
B. Enones

2. Woodward-Fieser Rules - Enones

Unlike conjugated alkenes, solvent does have an effect on $\lambda_{\text{max}}$

These effects are also described by the Woodward-Fieser rules.

<table>
<thead>
<tr>
<th>Solvent correction</th>
<th>Increment (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>+8</td>
</tr>
<tr>
<td>Ethanol, methanol</td>
<td>0</td>
</tr>
<tr>
<td>Chloroform</td>
<td>-1</td>
</tr>
<tr>
<td>Dioxane</td>
<td>-5</td>
</tr>
<tr>
<td>Ether</td>
<td>-7</td>
</tr>
<tr>
<td>Hydrocarbon</td>
<td>-11</td>
</tr>
</tbody>
</table>
IV. Structure Determination
B. Enones

2. Woodward-Fieser Rules - Enones

Some examples – keep in mind these are more complex than dienes

- cyclic enone = 215 nm
- 2 x b- alkyl subs. (2 x 12) +24 nm
- 239 nm

Experimental value 238 nm

- cyclic enone = 215 nm
- extended conj. +30 nm
- b-ring residue +12 nm
- d-ring residue +18 nm
- exocyclic double bond + 5 nm
- 280 nm

Experimental 280 nm
Thank you.....