DETERMINACIÓN DE ESTRUCTURAS ORGÁNICAS
(ORGANIC SPECTROSCOPY)

UV/VIS SPECTROSCOPY

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The nature of light

- Light exhibits dualistic properties:
  - Depending on the type of experiment performed it behaves as either a wave or particle
  - Light as a wave: electromagnetic wave
  - Light as a particle: photons

- What are waves?
  - A traveling disturbance that transports energy but not matter
  - With light energy is transported by oscillating electric and magnetic fields
Electronic Excitation by UV/Vis Spectroscopy:

- **X-ray:** core electron excitation
- **UV:** valance electronic excitation
- **IR:** molecular vibrations
- **Radio waves:** Nuclear spin states (in a magnetic field)

![Electromagnetic spectrum diagram](image)
The electromagnetic spectrum and nature of the light.

The wavelength and amount of light that a compound absorbs depends on its molecular structure and the concentration of the compound used.

The concentration dependence follows Beer’s Law.

\[ A = \varepsilon b c \]

Where \( A \) is absorbance (no units, since \( A = \log \frac{I_0}{I} \))

\( \varepsilon \) is the molar absorptivity with units of \( \text{L mol}^{-1} \text{ cm}^{-1} \)

\( b \) is the path length of the sample - that is, the path length of the cuvette in which the sample is contained (typically in cm).

\( c \) is the concentration of the compound in solution, expressed in mol L\(^{-1} \)
Molecules have quantized energy levels: ex. electronic energy levels.

\[ \Delta E = h\nu \]

Each electronic energy level (configuration) has many vibrational energy levels.
Absorptions having $\lambda_{max} < 200$ nm are difficult to observe because everything (including quartz glass and air) absorbs in this spectral region.
Example: ethylene absorbs at longer wavelengths:

$$\lambda_{\text{max}} = 165 \text{ nm} \ \varepsilon = 10,000$$
The \( n \rightarrow \pi^* \) transition is at even lower wavelengths but is not as strong as \( p \rightarrow \pi^* \) transitions. It is said to be “forbidden.”

Example:

Acetone: \( n-\sigma^* \quad \lambda_{\text{max}} = 188 \text{ nm} \quad ; \quad \varepsilon = 1860 \)

\( n-\pi^* \quad \lambda_{\text{max}} = 279 \text{ nm} \quad ; \quad \varepsilon = 15 \)
\[ \begin{align*} 
\text{C} - & \text{C} \quad \sigma \rightarrow \sigma^* \quad 135 \text{ nm} \\
\text{C} = & \text{C} \quad \pi \rightarrow \pi^* \quad 165 \text{ nm} \\
\text{C} - & \text{H} \quad \text{n} \rightarrow \sigma^* \quad 183 \text{ nm} \quad \text{weak} \\
\text{C} = & \text{O} \quad \pi \rightarrow \pi^* \quad 150 \text{ nm} \\
\text{C} = & \text{O} \quad \text{n} \rightarrow \sigma^* \quad 188 \text{ nm} \\
\text{C} = & \text{O} \quad \text{n} \rightarrow \pi^* \quad 279 \text{ nm} \quad \text{weak} 
\end{align*} \]
Conjugated systems:

Preferred transition is between Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO).

Note: Additional conjugation (double bonds) lowers the HOMO-LUMO energy gap:
Example:

1,3 butadiene: \( \lambda_{\text{max}} = 217 \text{ nm} \) ; \( \varepsilon = 21,000 \)
1,3,5-hexatriene \( \lambda_{\text{max}} = 258 \text{ nm} \) ; \( \varepsilon = 35,000 \)
Similar structures have similar UV spectra:

\[ \lambda_{\text{max}} = 238, 305 \text{ nm} \]

\[ \lambda_{\text{max}} = 240, 311 \text{ nm} \]

\[ \lambda_{\text{max}} = 173, 192 \text{ nm} \]
**Woodward-Fieser Rules for Dienes**

<table>
<thead>
<tr>
<th>Homoannular</th>
<th>Heteroannular</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parent</td>
<td>Parent</td>
</tr>
<tr>
<td>$\lambda = 253$ nm</td>
<td>$\lambda = 214$ nm</td>
</tr>
</tbody>
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For more than 4 conjugated double bonds:

$$\lambda_{\text{max}} = 114 + 5(\# \text{ of alkyl groups}) + n(48.0-1.7n)$$
Examples

Parent: (heteroannular)
3 alkyls (exocyclic)
TOTAL
(Actual = 235 nm)

Parent: (homooannular)
3 alkyls (exocyclic)
TOTAL
(Actual = 275 nm)

Parent: (5-member ring ketone)
(alpha hydroxyl)
(beta alkyl - note part of ring)
Total:
\[ \lambda_{\text{max}} = 114 + 5(8) + 11(48.0 - 1.7 \times 11) = 476 \text{ nm} \]

\[ \lambda_{\text{max}}(\text{Actual}) = 474. \]