UV Spectroscopy:

Ultraviolet spectroscopy;
Infrared spectroscopy;
Nuclear magnetic resonance spectroscopy

General basis of spectroscopy:
- Shine light at a collection of molecules ⇒ monitor response ⇒ interpret in terms of molecular structure

Analogy with photography: measure reflection, monitor with dyes which change color depending on wavelength (color) and intensity of light reflected.

Spectroscopy: usually measure absorption of light energy, monitor change in intensity of light as passes through sample.
Different structure features (functional groups, pi bonds) cause absorption of different wavelengths of the light beam.

Interpretation:
- a. quantum mechanics
- b. empirical correlations--study many known structures, develop correlations or patterns.

Molecules can absorb (or emit) radiant energy in quanta of photons

\[ E = n \hbar \nu \]

- \( E \) = energy of light being absorbed
- \( n \) = integer (# of quanta)
- \( \hbar \) = Planck's constant
- \( \nu \) = frequency of light waves

\( \hbar \nu \) = energy of one quanta

Consider ELECTRONIC EXCITATION:

- Light is absorbed and an electron moves from one orbital to a higher energy orbital.

The energy transferred, \( \hbar \nu \), must exactly match the energy gap between orbitals.

What energies are we talking about? Consider formaldehyde (a fairly complicated case)
**Orbitals:**

2 (1s) atomic orbitals on C, O
2 C-H \( \sigma \) and 2 C-H \( \sigma^* \)
1 C-O \( \sigma \) and 1 C-O \( \sigma^* \)
1 C-O \( \pi \) and 1 C-O \( \pi^* \)
2 n-type on O

Total of 12 orbitals, 8 are filled

Energy can be absorbed to promote an electron to a higher, empty (or half filled) orbital.

Possible combination: \( n \rightarrow \pi^* \quad \pi \rightarrow \pi^* \quad n \rightarrow \sigma^* \quad \pi \rightarrow \sigma^* \quad \sigma \rightarrow \pi^* \quad \sigma \rightarrow \sigma^* \)

70-150 Kcal/mol
convenient range

>150 Kcal/mol
possible, but not common

What type of radiation for 70-150 Kcal/mol. Recall: \( \lambda = \frac{c}{\nu} \quad E = h\nu \)

150 kcal/mol = 195 nm (wavelength, \( \lambda \))
longer wavelength, lower energy per photon

<table>
<thead>
<tr>
<th>X-ray</th>
<th>ultraviolet</th>
<th>visible</th>
<th>infrared</th>
<th>microwave</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 nm</td>
<td>400 nm</td>
<td>800 nm</td>
<td>25000 nm</td>
<td>25 mm</td>
</tr>
<tr>
<td>70 kcal/mol</td>
<td>1 kcal/mol</td>
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Practical cut-off: vacuum UV / UV
180 nm
160 kcal/mol

So for organic structure analysis, convenient to use light of \( \lambda = 180-400 \text{ nm} \) (ultraviolet)
\( E = 160-70 \text{ Kcal/mol} \)

\( n \rightarrow \pi^* \quad \pi \rightarrow \pi^* \) only (others too high energy jump)

Mechanics:
**Experiment:**

systematically change $\lambda$ by rotating the prism, allow light of different $\lambda$ to pass through the sample.

Measure I, the intensity of transmitted light. Compare with incident intensity (before sample; reference beam)

Calculate: $A = \log_{10} \left( \frac{I}{I_0} \right) = \varepsilon dc$

$\varepsilon$ = extinction coefficient (characteristic of molecule)
$d$ = path length of sample cell in cm
$c$ = concentration of sample in moles/L

$\varepsilon$ depends on overlap of orbitals involved in the electron jump:
- $\pi \rightarrow \pi^*$ good overlap, high $\varepsilon$ (1000-10,000)
- $n \rightarrow \pi^*$ poor overlap, low $\varepsilon$ (10-100)

Can use for quantitative purposes: for pure compound, get $\varepsilon$.

if know $\varepsilon$, can measure amount (c) of cpn in a solution (measure A, d)

Consider the UV spectrum of ethylene:

two observations:

$\lambda_{\text{max}} = 180 \text{ nm} \quad \varepsilon = 12,000$

peak is broad. Why?

Each electronic state has a collection of vibrational states associated with it.
In promoting the electron, can arrive at several different vibrational levels of higher state.
The absorption is an envelope of all excitations, $E_0 \rightarrow E_1$ (at various vibrational levels).
Can observe vibrational "fine structure":

Consider the UV spectrum of ethylene at "high resolution"

Record $\varepsilon$ for $\lambda_{\text{max}}$. For simple spectra, characterize the molecule by $\varepsilon$ and $\lambda_{\text{max}}$ at longest $\lambda$ (lowest energy). For complete description, assign $\lambda_{\text{max}}$ and $\varepsilon$ to each significant maximum.

Now: consider 1,3-butadiene. Predict the UV spectrum. Two ethylenes? Same $\lambda_{\text{max}}$, twice the $\varepsilon$? No.
Consider 1,3,5-hexatriene: 6 p orbitals give 6 MOs

Lowest energy gap between filled and unfilled is $\pi_3$ and $\pi_4$
smaller compared to 1,3-butadiene
lowest energy $\lambda_{\text{max}}$ is 268 nm
What actually happens to the molecule after absorption of the photon: PHOTOCHEMISTRY

\[
\text{trans to cis 1,3-pentadiene}
\]

\[\text{retinaldehyde} \quad \text{retinol Vitamin A}\]
all trans retinal → cis-retinal

all trans retinal + opsins → rhodopsin

rhodopsin → cis-retinal

cis-retinal + opsins → all trans retinal