Chapter 4
Basics of Absorption Spectroscopy

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Course Name: Spectroscopy & Materials Analysis

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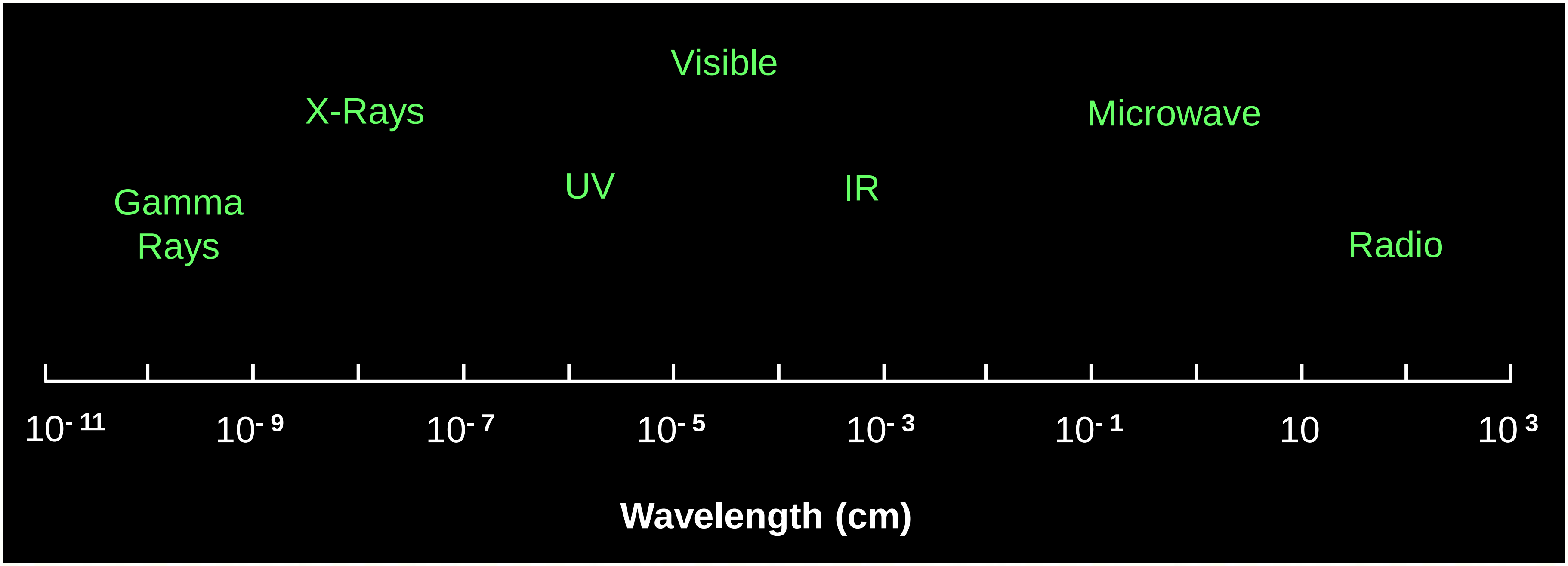
Spectroscopic Information

In spectroscopy, transitions between different energy levels within atoms and molecules are recorded and then used to give information on chemical structure. Energy levels are discrete. The transitions obey selection rules.

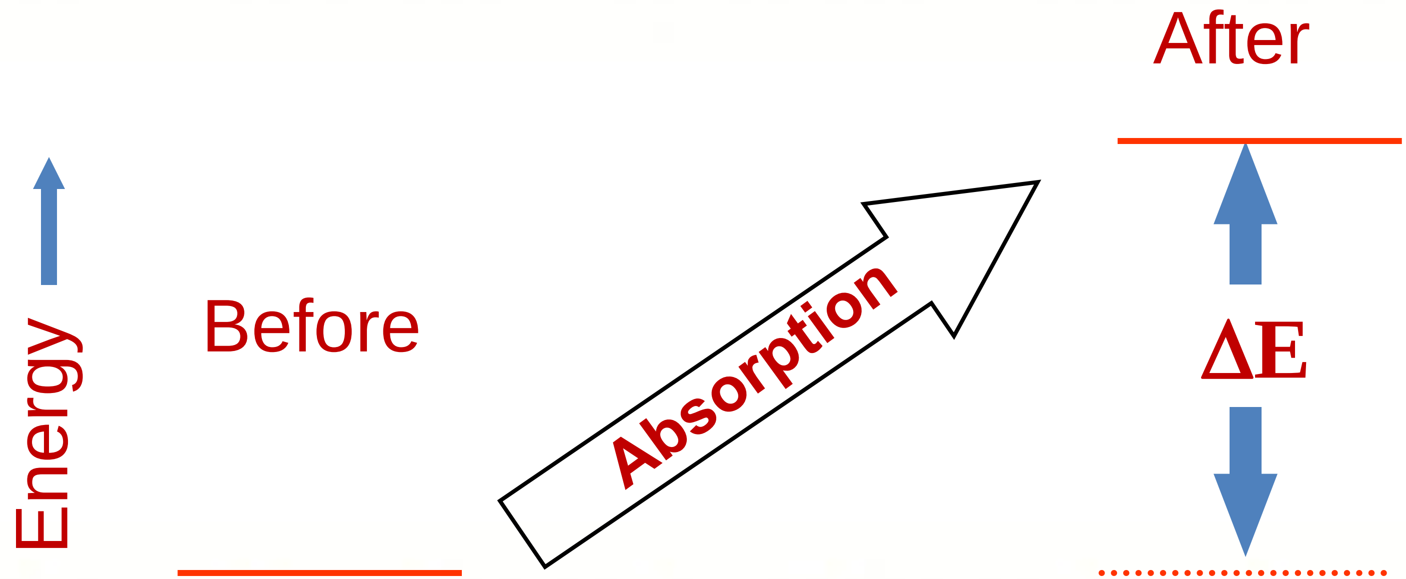
UV and Visible region is Used

The range of energies that can be used for spectroscopy is very large and spans a large proportion of the electromagnetic spectrum.



Typical Transitions

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.

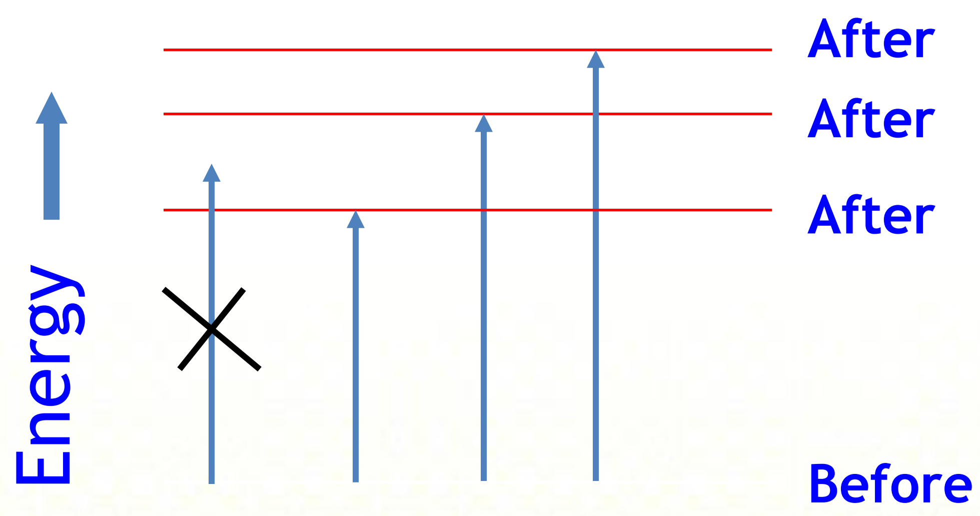


Absorption: Rapid process (10^{-15}s)

All Transitions are not Allowed

Absorption can only occur when the energy of the radiation (calculated from the frequency or wavelength) matches the energy gap.

If there are several different upper levels (and there usually are) then several transitions will be observed.



For current purposes we look only at:

UV/visible (highest energy)

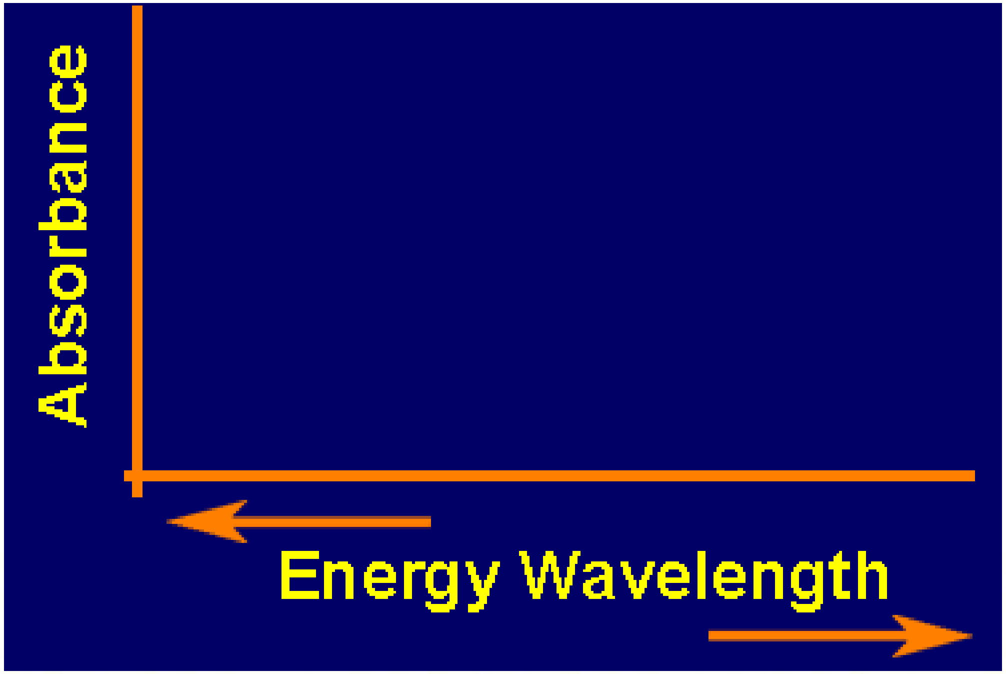
Infra red (intermediate)

Radio frequency (lowest energy).

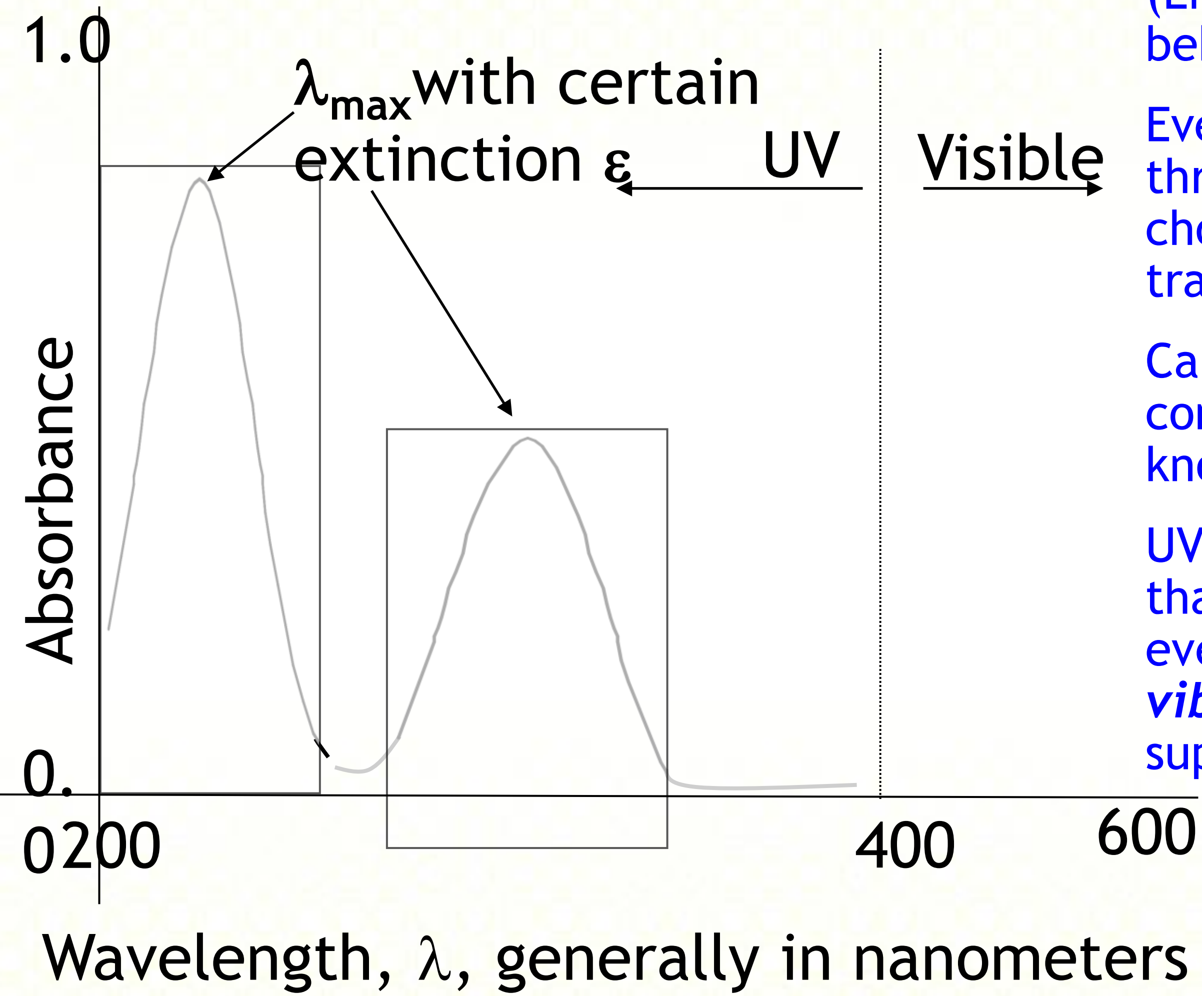
But in all cases :

Typical Absorption Spectra

To record a spectrum, sweep through the appropriate range of energies and look for absorption at particular values.



An Electronic/UV-Vis Spectrum



Make solution of concentration low enough that A≤ 1

(Ensures Linear Beer's law behavior)

Even though a dual beam goes through a solvent blank, choose solvents that are UV transparent.

Can extract the ε value if conc. (M) and b (cm) are known

UV bands are much broader than the photonic transition event. This is because ***vibration levels*** are superimposed on UV.

Significance of UV-Vis Spectrum

Absorption gives peaks, when these have been measured this gives the energy gaps within the sample. These can then be related to structure.

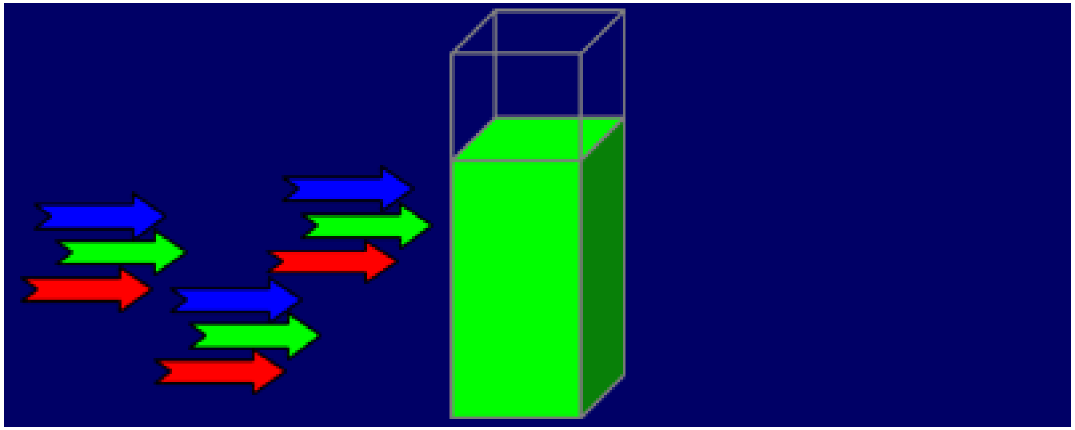
Interpretation depends on the energy range investigated.

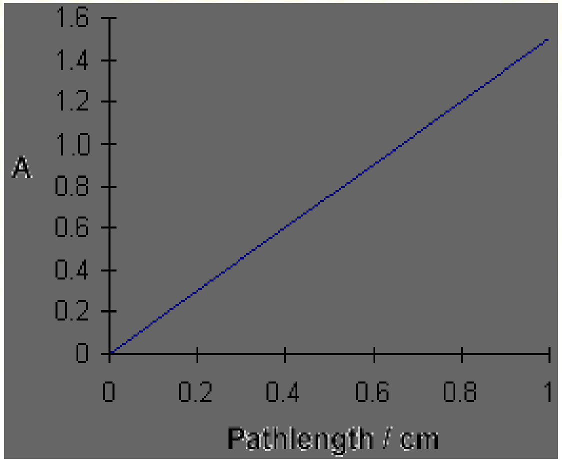
UV/visible Spectroscopy

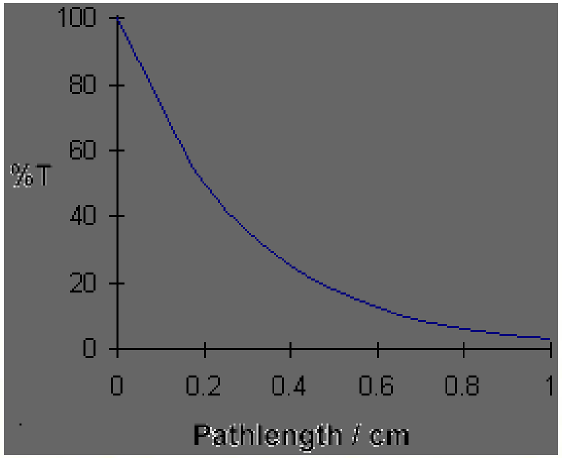
Chemical compounds are colored because they absorb visible light.

In general, even organic compounds that are colorless will absorb UV light.

Absorption of Visible Light

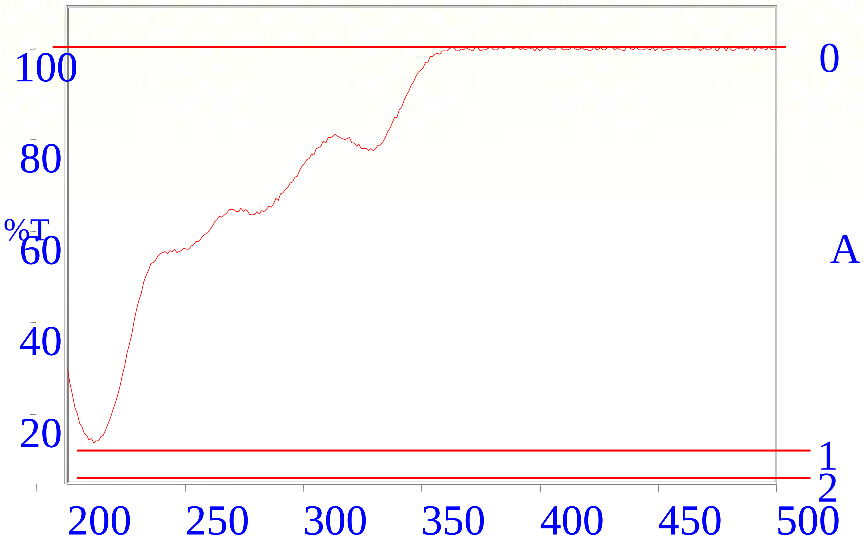




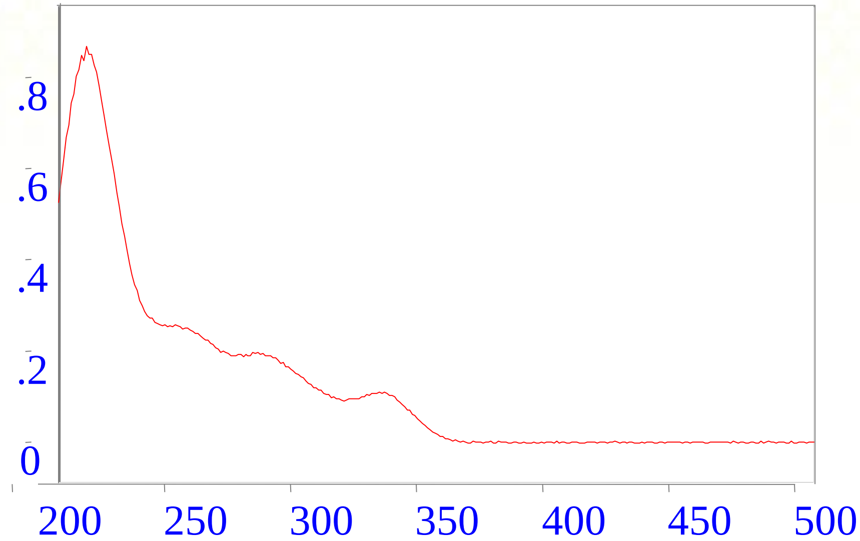


Where has the energy that was within the photons gone to ?

Absorbance & Transmittance Spectra



% Transmission Spectrum

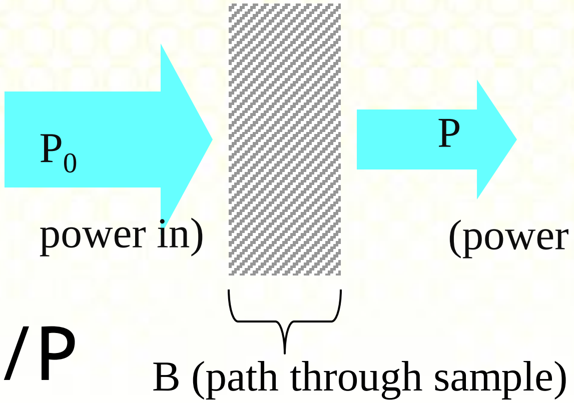


Absorbance Spectrum

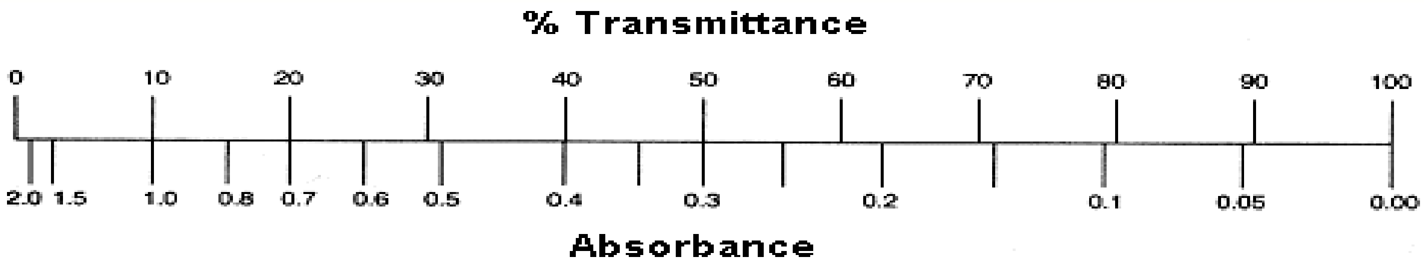
$$A = -\log T = abc$$

The Quantitative Picture

- Transmittance: $T = P/P_0$



- Absorbance: $A = -\log_{10} T = \log_{10} P_0/P$



- The Beer-Lambert Law (a.k.a. Beer's Law): $A = \varepsilon b c$

  Where the absorbance A has no units, since $A = \log_{10} P_0 / P$

  ε is the molar absorbtivity with units of $L\ mol^{-1}\ cm^{-1}$

  b is the path length of the sample in cm

  c is the concentration of the compound in solution, expressed in $mol\ L^{-1}$ (or M, molarity)

UV-Visible Spectroscopy

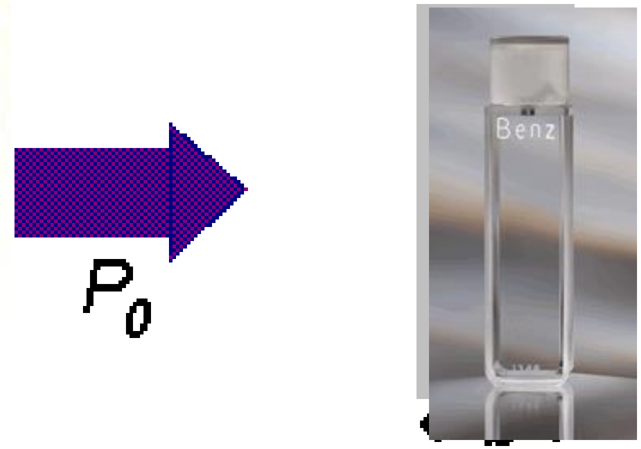
- ✓ Ultraviolet-visible spectroscopy involves the absorption of ultraviolet/visible light by a molecule causing the promotion of an electron from a ground electronic state to an excited electronic state.
- ✓ Ultraviolet/Visible light: wavelengths between 190 and 800 nm

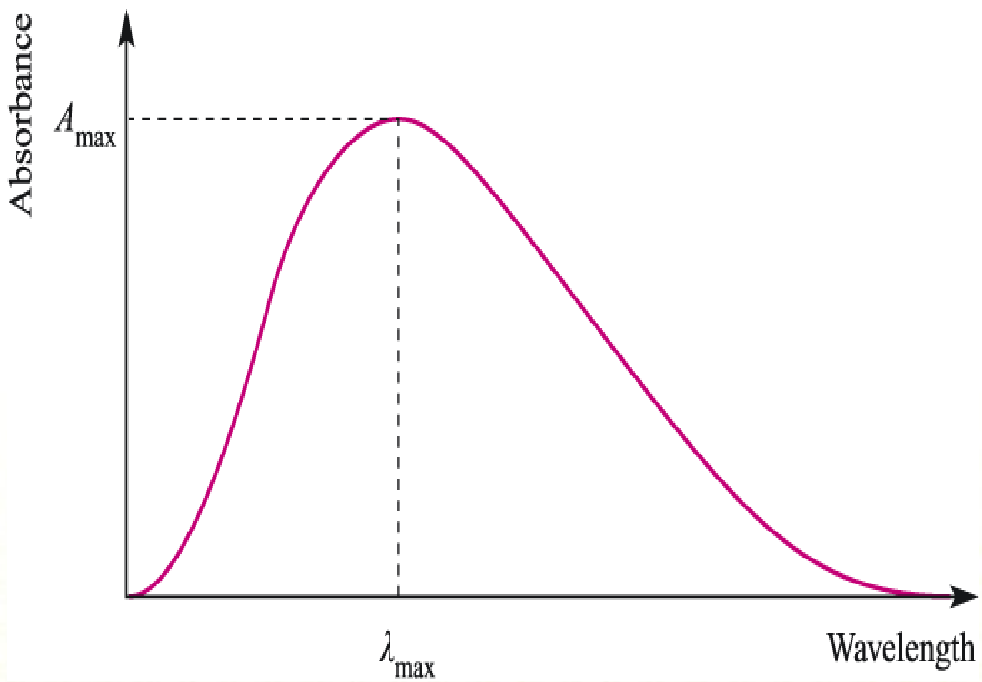
$$A = \log \frac{I_0}{I_t} = \varepsilon bl = -\log T$$

UV-Visible Spectrum

The two main properties of an absorbance peak are:

1. Absorption wavelength l_{max}
2. Absorption intensity A_{max}





Beer-Lambert Law:

$$\log(I_0/I) = \varepsilon bc$$

$$\varepsilon = A/cb$$

$$A = \varepsilon bc$$

$$A = \varepsilon c \text{ (when } b \text{ is 1 cm)}$$

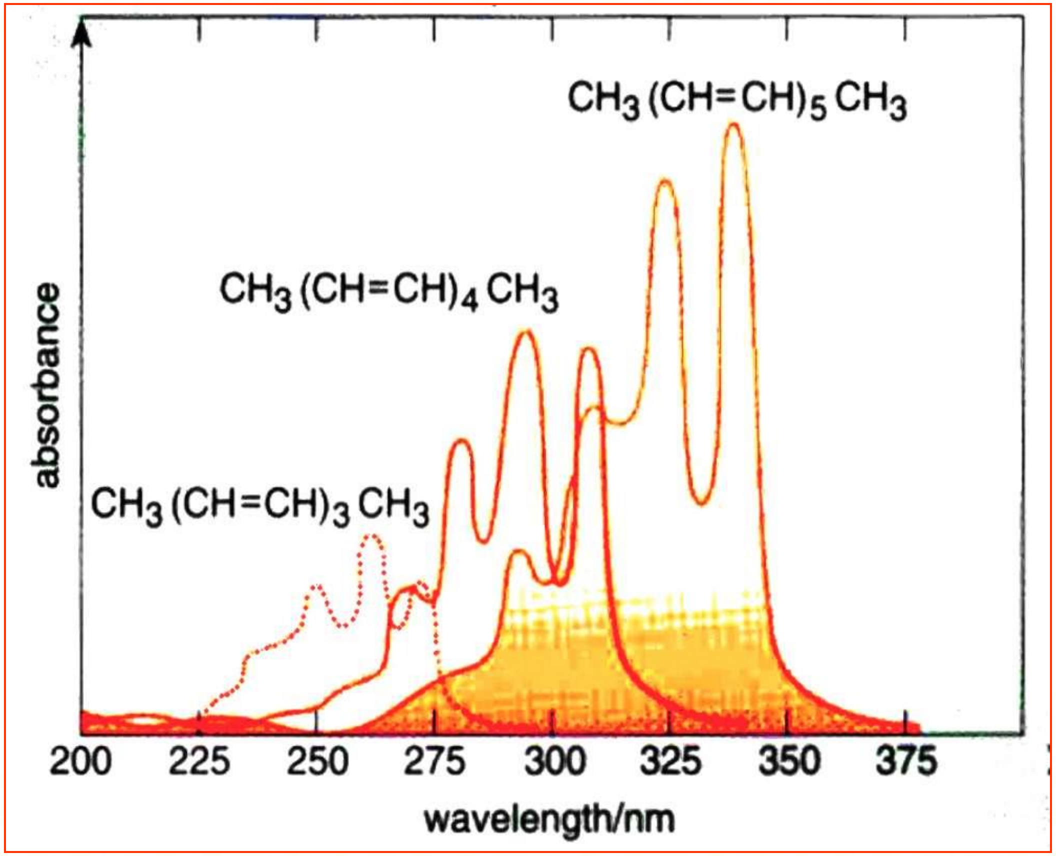
This overall change is typically due to promotion of a single electron from a lower to higher energy orbital. The energy of the transition depends on the gap between the two orbitals.

In organic compounds which have only single bonds between the atoms the excitation energy is very high- lies in deep UV.

If we have a highly conjugated molecule the energy separation between the orbitals is smaller.

Excitation of the electron thus has a proportionately smaller effect and requires less energy- energy gap may lie in the visible region.

With increasing conjugation, the decreasing energy gap is reflected by absorption at longer wavelengths.



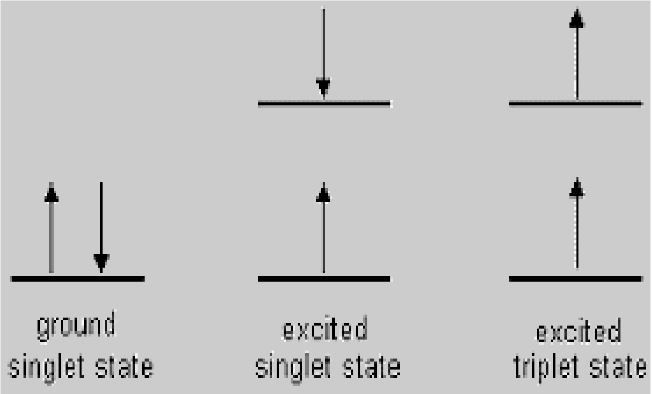
Selection Rules

There are three selection rules that determine the feasibility of allowed transitions:

1. Spin selection rule: $\Delta S = 0$

allowed transitions: singlet $\rightarrow$ singlet or triplet $\rightarrow$ triplet
forbidden transitions: singlet $\rightarrow$ triplet or triplet $\rightarrow$ singlet

Changes in spin multiplicity are forbidden



Selection Rules

2. Laporte selection rule: there must be a change in the parity (symmetry) of the complex

Laporte-allowed transitions: $g \rightarrow u$

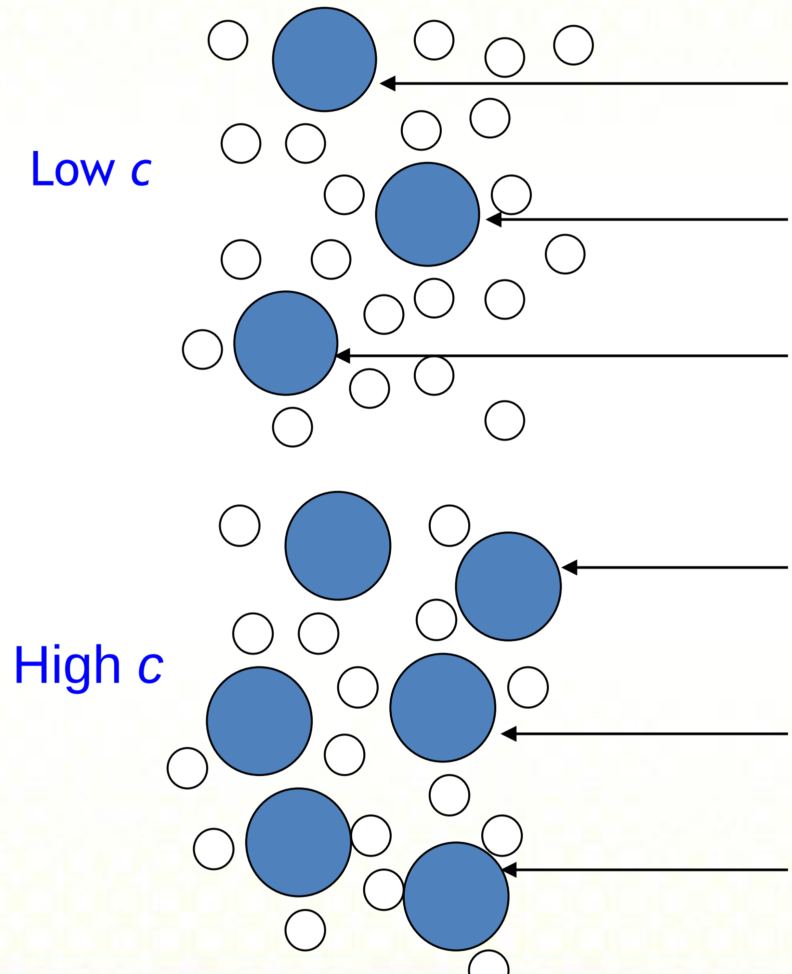
Laporte-forbidden transitions: $g \rightarrow g$ *or* $u \rightarrow u$

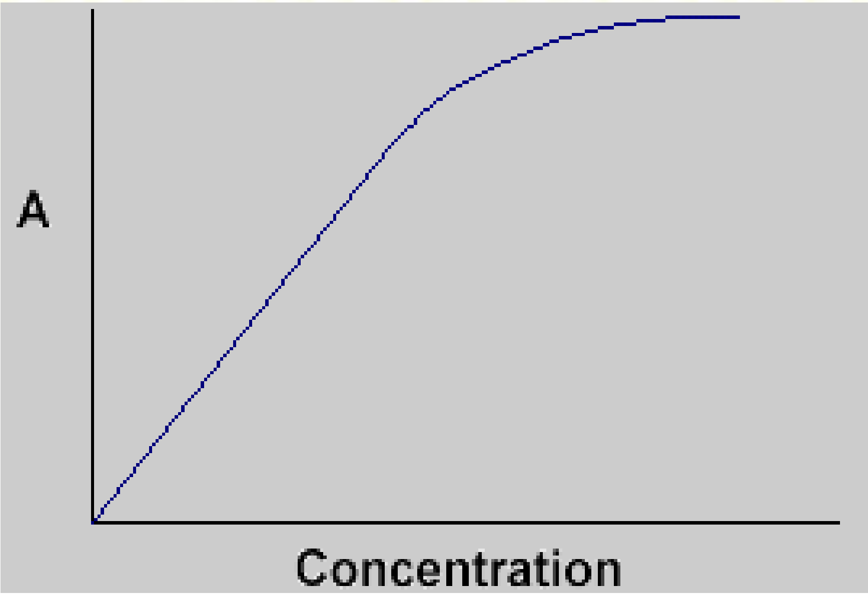
g stands for *gerade* – compound with a center of symmetry
u stands for *ungerade* – compound without a center of symmetry

3. Selection rule of $\Delta\ell = \pm 1$ (ℓ is the azimuthal or orbital quantum number, where ℓ = 0 (s orbital), 1 (p orbital), 2 (d orbital), etc.)

allowed transitions: s $\rightarrow$ p, p $\rightarrow$ d, d $\rightarrow$ f, etc.
forbidden transitions: s $\rightarrow$ s, d $\rightarrow$ d, p $\rightarrow$ f, etc.

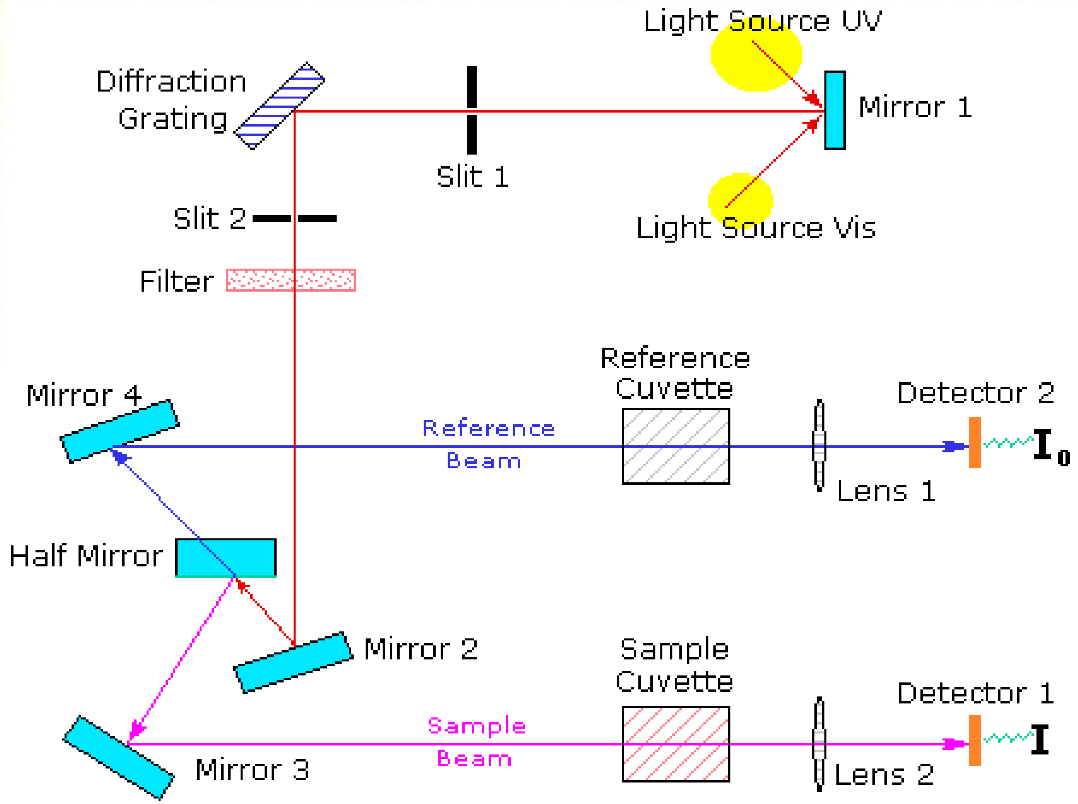
Deviations from the Beer-Lambert Law





The Beer-Lambert law assumes that all molecules contribute to the absorption and that no absorbing molecule is in the shadow of another

Measurement



- Scattering of light
  - Refraction at interfaces
  - Scatter in solution
    - Large molecules
    - Air bubbles
- Normalized by comparison to reference cell
  - Contains only solvent
    - Measurement for transmittance is compared to results from reference cell

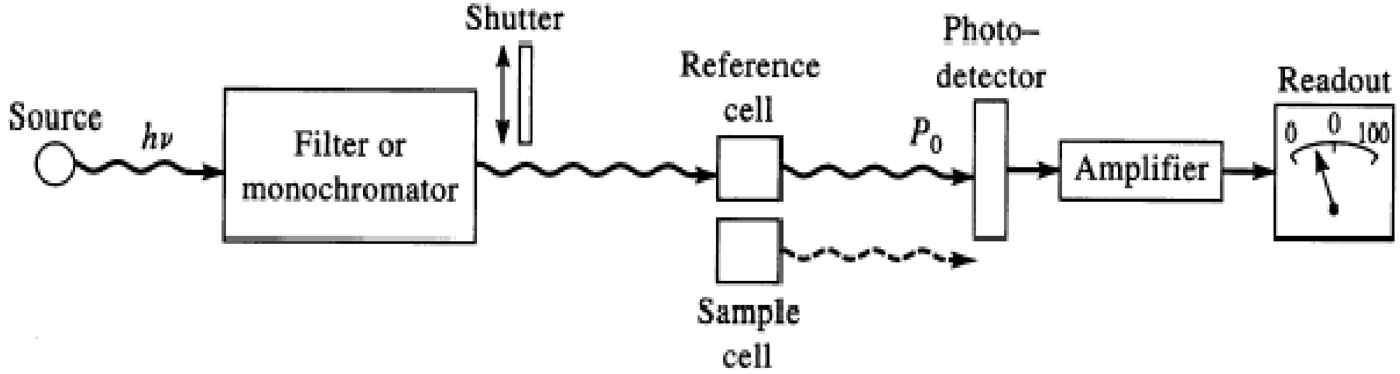
Noise

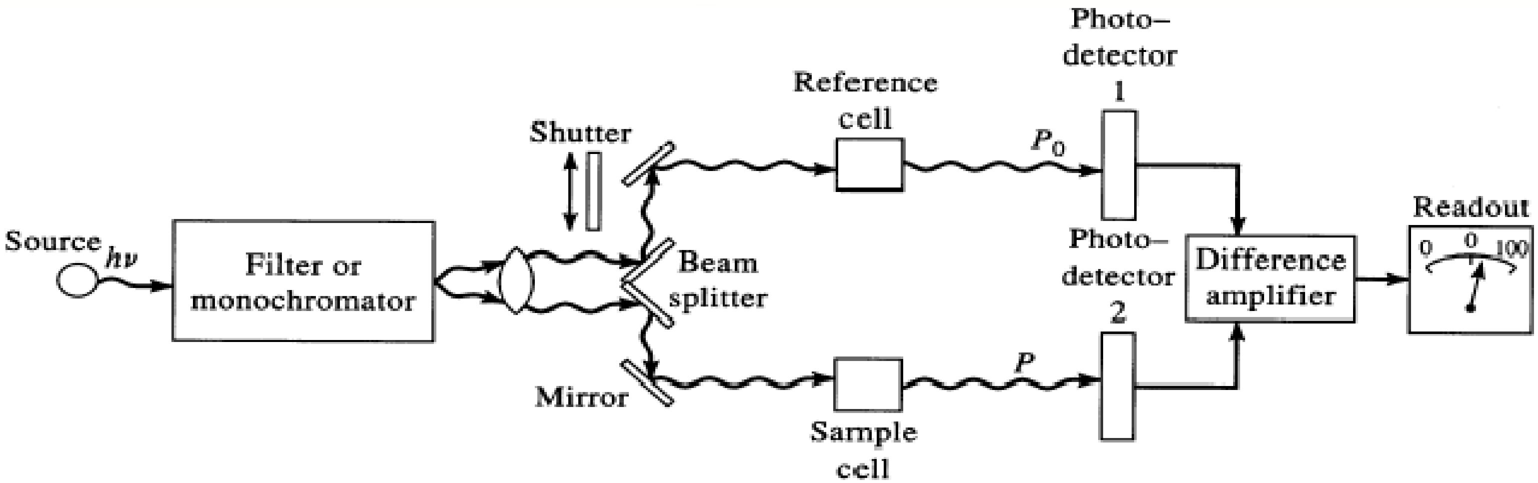
- Limited readout resolution
- Dark current and electronic noise
- Photon detector shot noise
- Cell position uncertainty
  - Changing samples
- Flicker

Instrumentation

- Light source
  - Deuterium and hydrogen lamps
  - W filament lamp
  - Xe arc lamps
- Sample containers
  - Cuvettes
    - Plastic
    - Glass
    - Quartz

Spectrometers





UV Spectrophotometer

Light Source

Visible Spectrophotometer

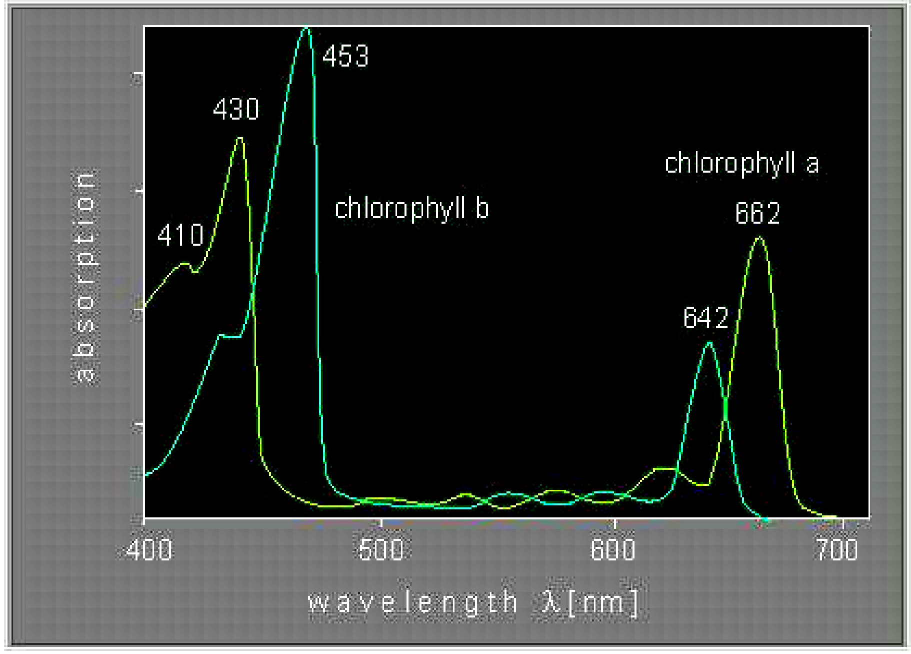
Tungsten Lamp

Application of UV-Visible Spectroscopy

- ✓ Identification of inorganic and organic species
- ✓ Widely used method
- ✓ Magnitude of molar absorptivities
- ✓ Absorbing species
- ✓ methods

Why are most plants are green & then red or yellow in the fall?

- ✓ Chlorophyll absorbs in the red and blue, and hence reflects in the green.
- ✓ Its absorption spectrum is due to electronic transitions



In the fall, trees produce carotenoids, which reflect yellow, and anthocyanins, which reflect orange and red.

Summary

✓ Absorption of UV-Vis radiation occurs *via* excitation of electrons from filled to unfilled orbitals called electronic transitions.

✓ Molecules and materials have characteristic absorption spectra related to their structure.

✓ The absorption can lead to coloured materials that we see.

✓ pH Indicators use the change in colour between the acid and alkali forms of the molecules.

Questions ?

Thank You