The Ultraviolet- Visible Spectroscopy

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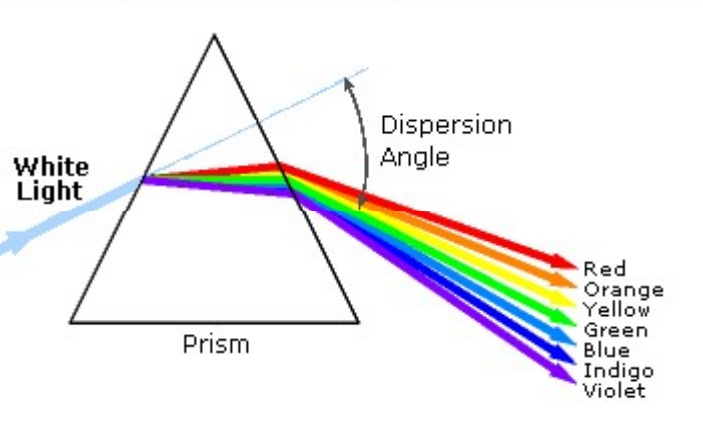
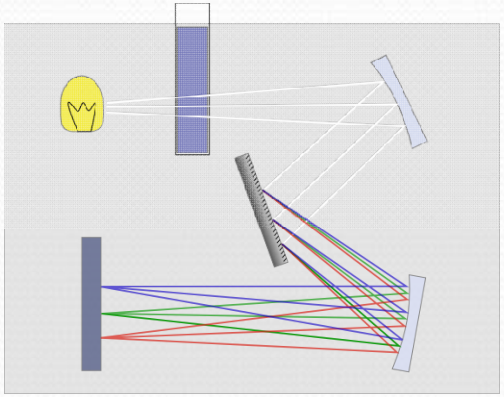
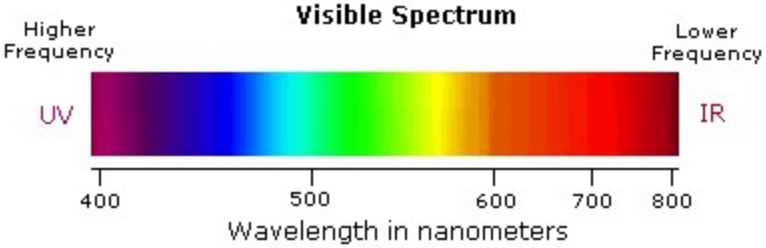
UV-Vis spectroscopy

Electronic absorption spectroscopy







- **Violet:** 400 - 420 nm
- **Indigo:** 420 - 440 nm
- **Blue:** 440 - 490 nm
- **Green:** 490 - 570 nm
- **Yellow:** 570 - 585 nm
- **Orange:** 585 - 620 nm
- **Red:** 620 - 780 nm

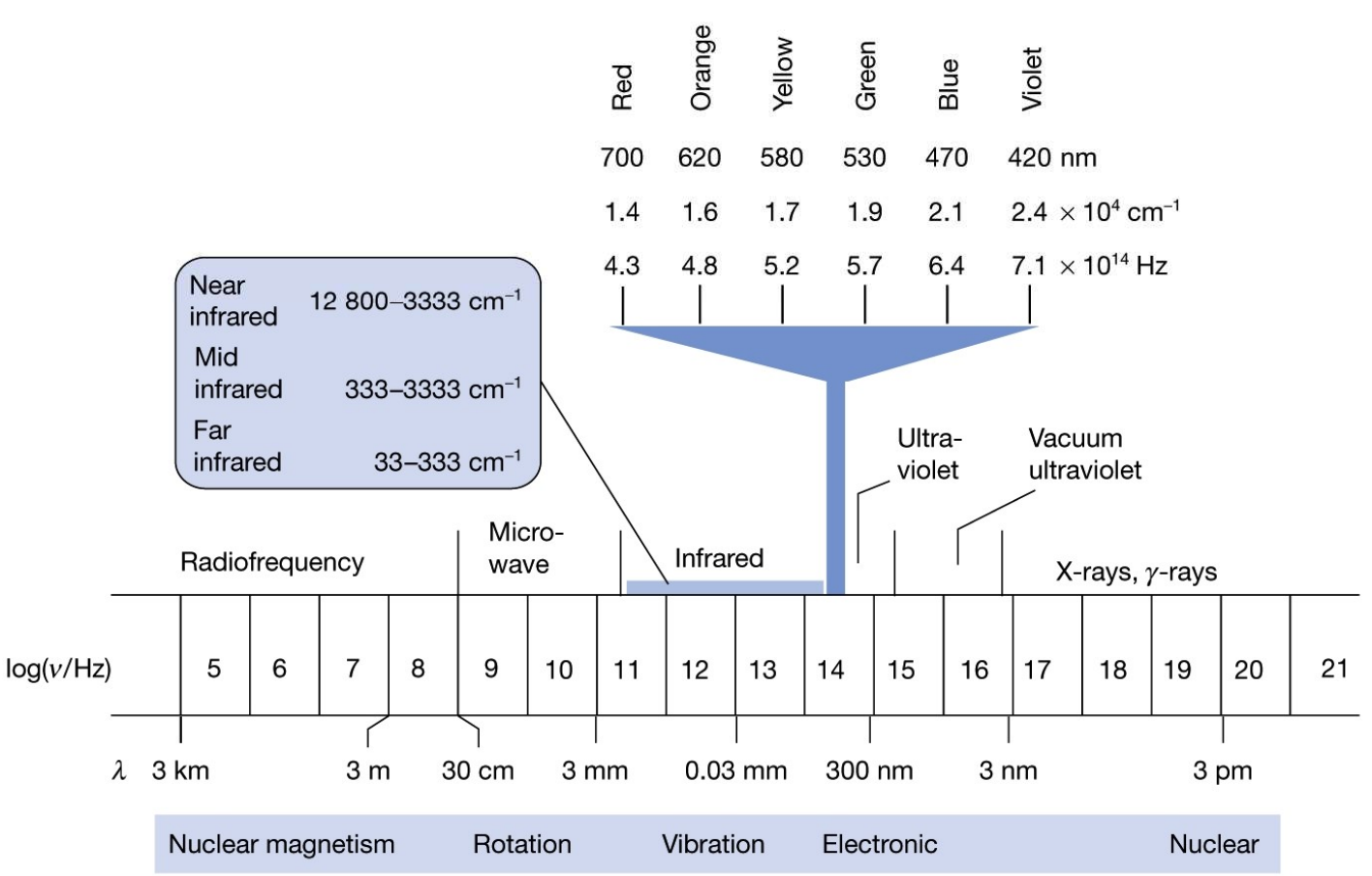
Outline of Presentation

- Introduction
- The absorption laws
- Principle: Electronic transitions
- Chromophore and Auxochrome
- Absorption and intensity shifts
- Types of absorption bands
- Effect of solvent
- Effect of conjugation
- Instrumentation
- Woodward-Fieser Rule
- Applications

Introduction

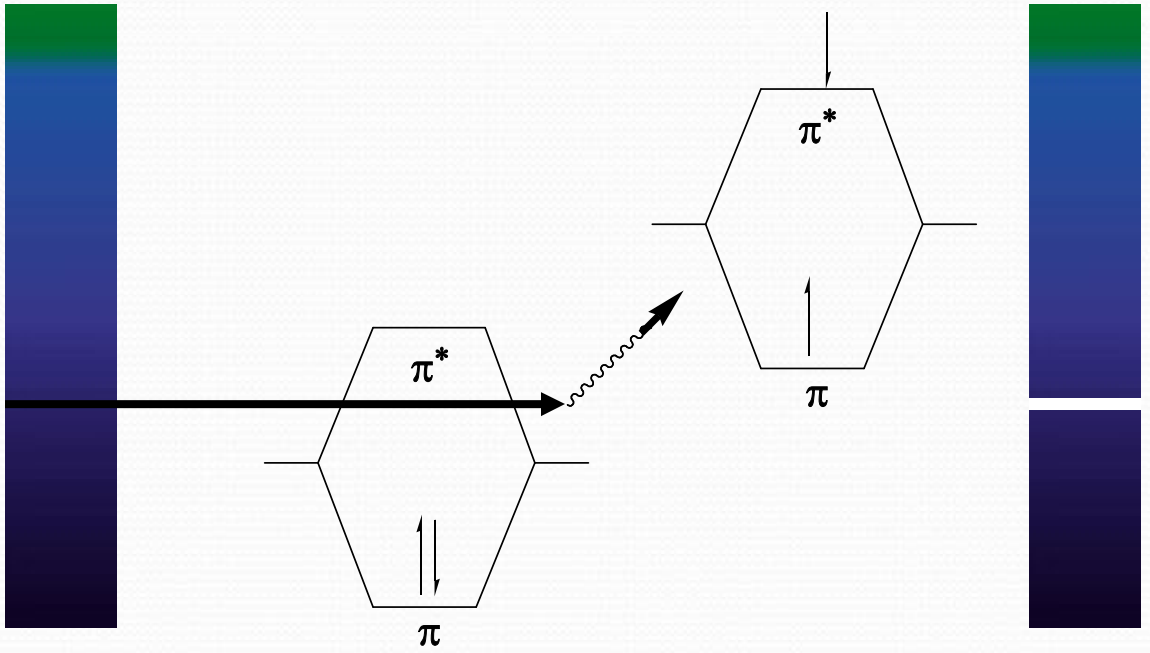
- This is the earliest method of molecular spectroscopy.
- A phenomenon of interaction of molecules with ultraviolet and visible lights.
- Absorption of photon results in electronic transition of a molecule, and electrons are promoted from ground state (HOMO) to higher electronic states (LUMO).
- Ultraviolet radiation stimulates molecular vibrations and electronic transitions.
- Absorption spectroscopy from 160 nm to 780 nm
- Measurement absorption or transmittance
- Identification of inorganic and organic species

The Electromagnetic Spectrum



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

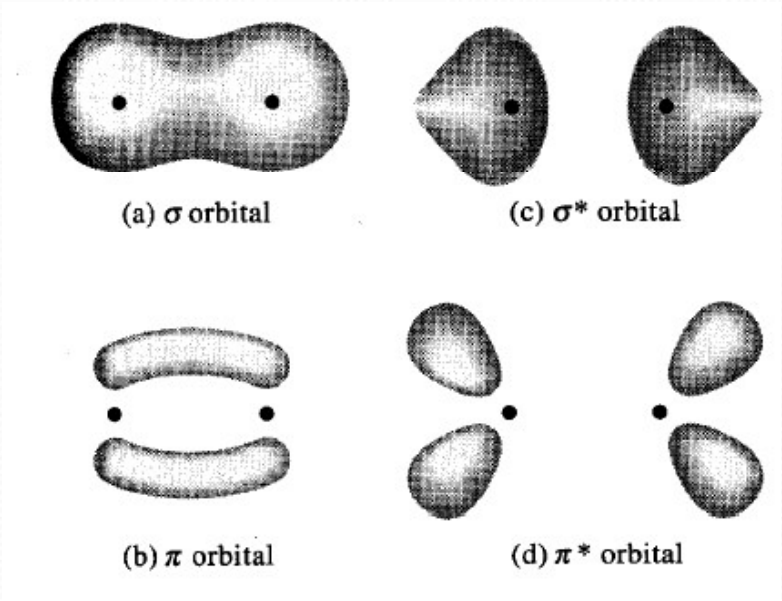


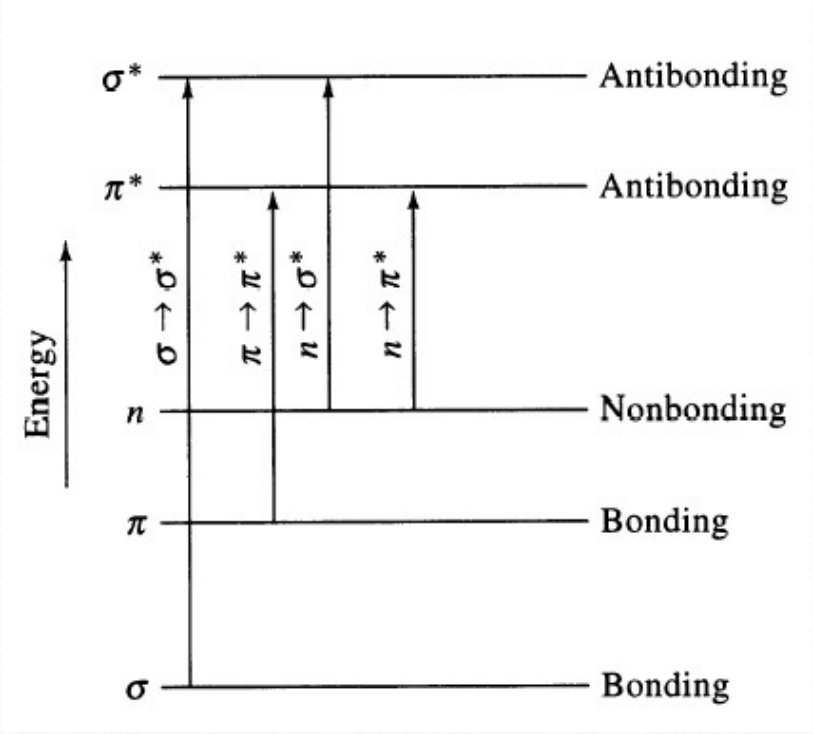
UV-Visible Spectroscopy

- Electronic transitions occur when the molecule absorbs energy
- Electrons in a molecule: σ, π and η electrons
- The difference in energy between molecular bonding, non-bonding and anti-bonding orbitals ranges from 125-650 kJ/mole
- This energy corresponds to EM radiation in the ultraviolet (UV) region, 100-350 nm, and visible (VIS) regions 350-700 nm of the spectrum

Electronic transitions

- Molecular Orbital Theory





electronic transitions

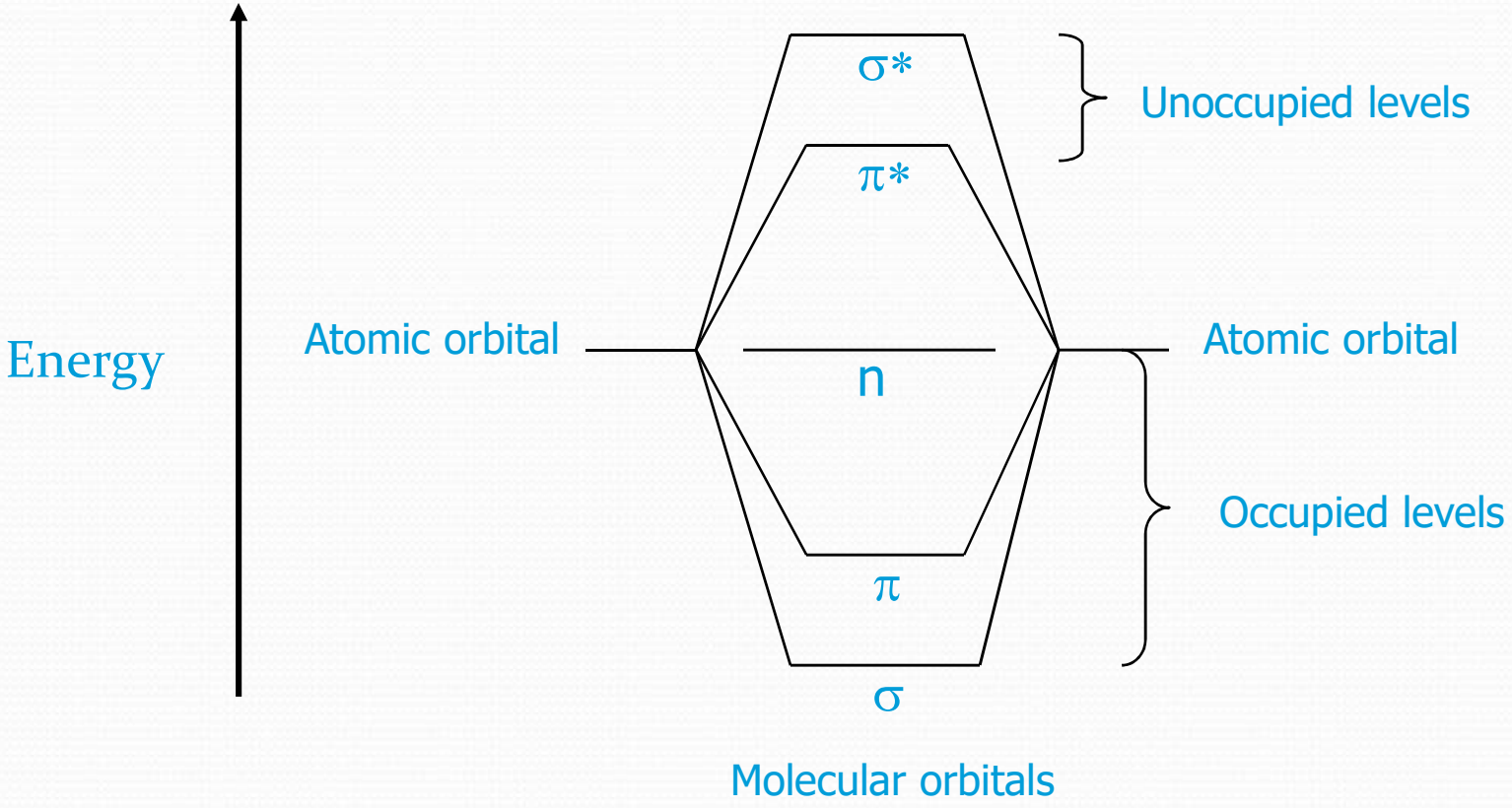
- The lowest energy transition (and most often obs. by UV) is typically that of an electron in the Highest Occupied Molecular Orbital (HOMO) to the Lowest Unoccupied Molecular Orbital (LUMO)

- For any bond (pair of electrons) in a molecule, the molecular orbitals are a mixture of the two contributing atomic orbitals; for every bonding orbital "created" from this mixing (s, p), there is a corresponding anti-bonding orbital of symmetrically higher energy (s^*, p^*)

- The lowest energy occupied orbitals are typically the s; likewise, the corresponding anti-bonding s^* orbital is of the highest energy

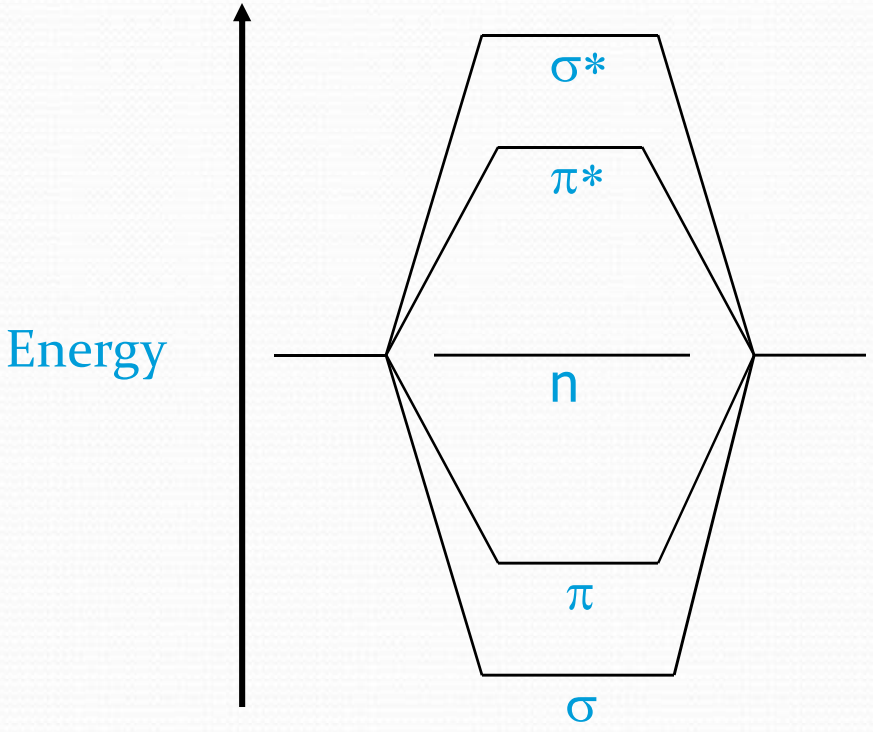
- p-orbitals are of somewhat higher energy, and their complementary anti-bonding orbital somewhat lower in energy than s*.

- Unshared pairs lie at the energy of the original atomic orbital, most often this energy is higher than p or s (since no bond is formed, there is no benefit in energy)



Graphical Representation of Electronic Transitions

Types of Electronic Transitions

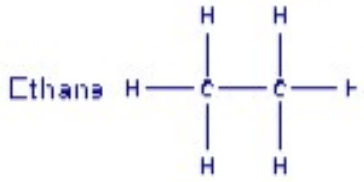
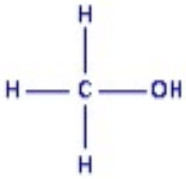
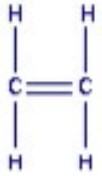
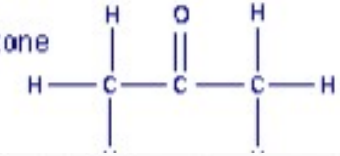


σ	$\rightarrow$	σ^*	alkanes
σ	$\rightarrow$	π^*	carbonyls
π	$\rightarrow$	π^*	unsaturated cmpds.
n	$\rightarrow$	σ^*	O, N, S, halogens
n	$\rightarrow$	π^*	carbonyls

- Although the UV spectrum extends below 100 nm (high energy), oxygen in the atmosphere is not transparent below 200 nm
- Special equipment to study vacuum or far UV is required
- Routine organic UV spectra are typically collected from 200-700 nm
- This limits the transitions that can be observed:

$\sigma \longrightarrow \sigma^*$	alkanes	150 nm	
$\sigma \longrightarrow \pi^*$	carbonyls	170 nm	
$\pi \longrightarrow \pi^*$	unsaturated cmpds.	180 nm	√ - if conjugated!
n $\longrightarrow \sigma^*$	O, N, S, halogens	190 nm	
n $\longrightarrow \pi^*$	carbonyls	300 nm	√

Examples of Transitions and resulting λmax

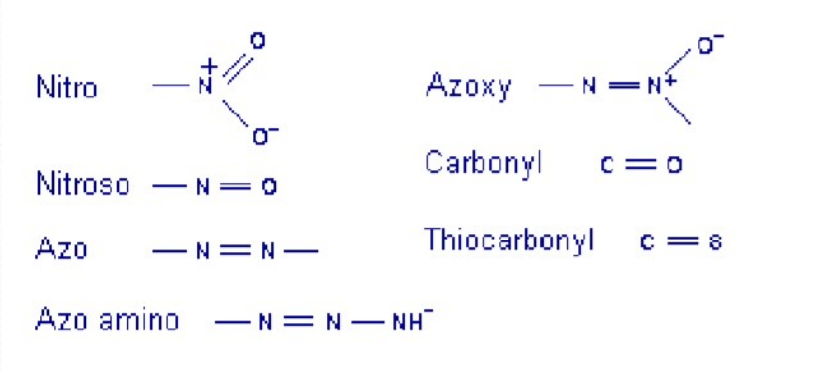
Molecule	Transition	λ_{max} (nm)
Ethane 	$\sigma \rightarrow \sigma^*$	135
Methanol 	$\sigma \rightarrow \sigma^*$ $\eta \rightarrow \sigma^*$	150 183
Ethylene 	$\pi \rightarrow \pi^*$	175
Benzene 	$\pi \rightarrow \pi^*$	254
Acetone 	$\eta \rightarrow \pi^*$	290

Selection Rules

- Not all transitions that are possible are observed
- For an electron to transition, certain quantum mechanical constraints apply – these are called "selection rules"
- For example, an electron cannot 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
- To further complicate matters, "forbidden" transitions are sometimes observed (albeit at low intensity) due to other factors

The Chromophore

A **chromophore** (literally color-bearing) group is a functional group, not conjugated with another group, which exhibits a characteristic absorption spectrum in the ultraviolet or visible region. Some of the more important chromophoric groups are:



If any of the simple chromophores is conjugated with another (of the same type or different type) a multiple chromophore is formed having a new absorption band which is more intense and at a longer wavelength that the strong bands of the simple chromophores.

This displacement of an absorption maximum towards a longer wavelength (i.e. from blue to red) is termed a **bathochromic shift**. The displacement of an absorption maximum from the red to ultraviolet is termed a **hypsochromic shift**.

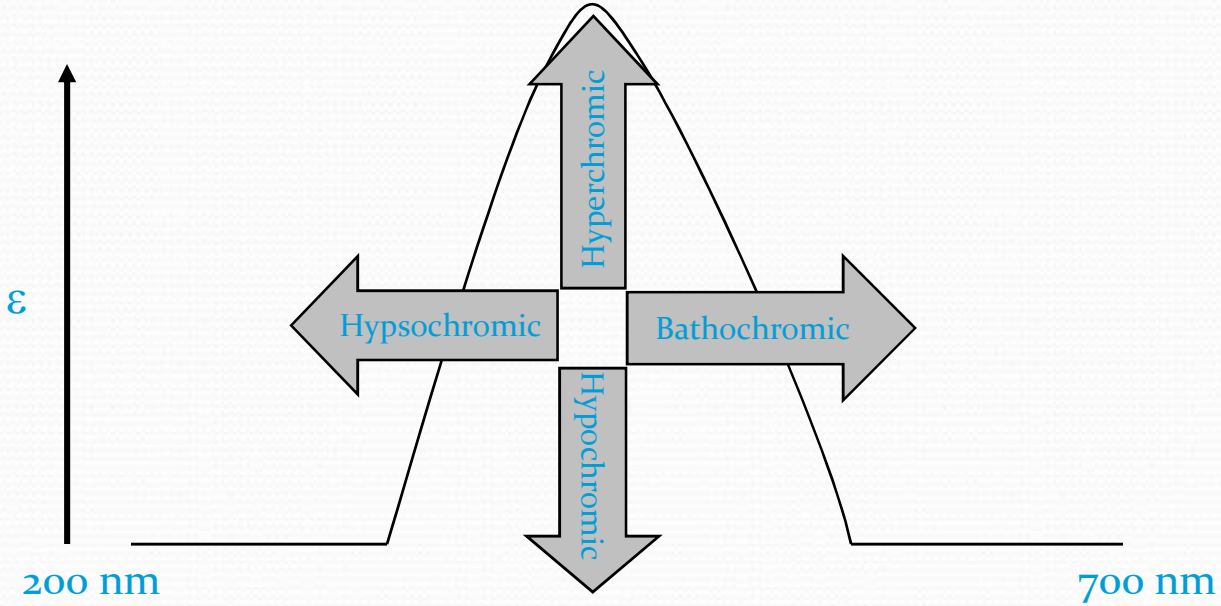
Auxochromes

- The color of a molecule may be intensified by groups called **auxochromes** which generally do not absorb significantly in the 200-800nm region, but will affect the spectrum of the chromophore to which it is attached. The most important auxochromic groups are OH, NH_2, CH_3 and NO_2 and their properties are acidic (phenolic) or basic.
- The actual effect of an auxochrome on a chromophore depends on the polarity of the auxochrome, e.g. groups like CH_3-, CH_3CH_2- and Cl- have very little effect, usually a small red shift of 5-10nm.
- Other groups such as -NH_2 and -NO_2 are very popular and completely alter the spectra of chromophores such as: BENZENE

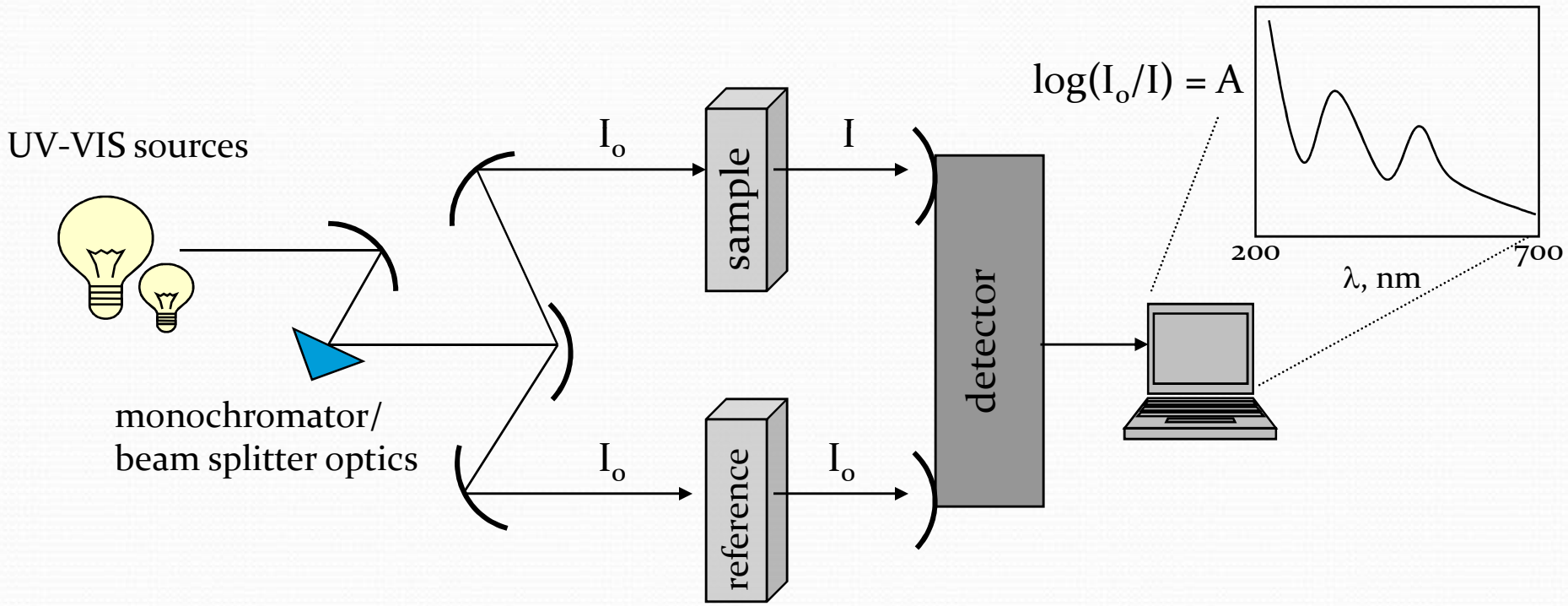
Absorption and Intensity Shifts

Substituents may have any of four effects on a chromophore

- Bathochromic shift (red shift) – a shift to longer l; lower energy
- Hypsochromic shift (blue shift) – shift to shorter l; higher energy
- Hyperchromic effect – an increase in intensity
- Hypochromic effect – a decrease in intensity



Instrumentation and Spectra



Instrumentation

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

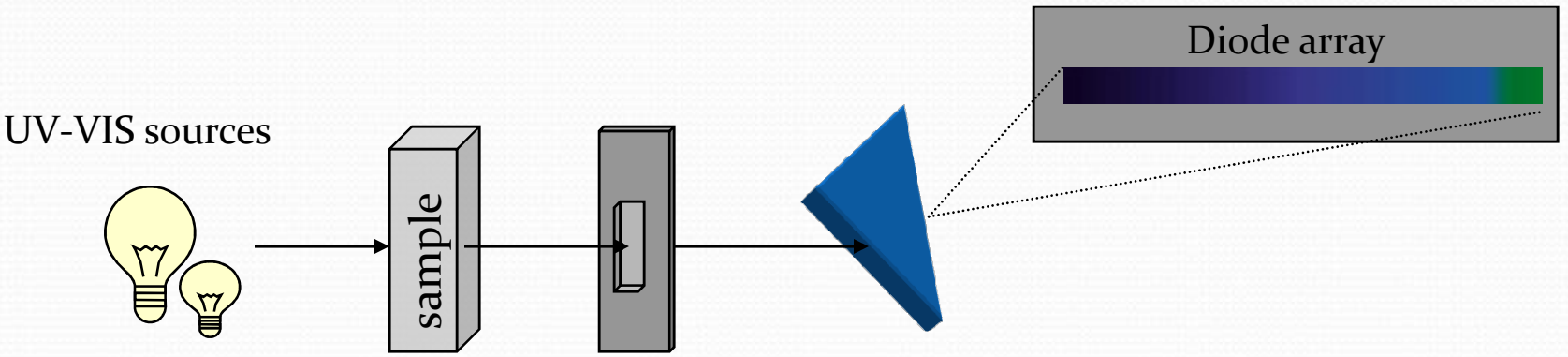
- As with the dispersive IR, the lamps illuminate the entire band of UV or visible light; the **monochromator** (grating or prism) gradually changes the small bands of radiation sent to the beam splitter

- The **beam splitter** sends a separate band to a cell containing the sample solution and a reference solution

- 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

- A recent improvement is the diode-array spectrophotometer - here a prism (dispersion device) breaks apart the full spectrum transmitted through the sample

- Each individual band of UV is detected by a individual diodes on a silicon wafer simultaneously – the obvious limitation is the size of the diode, so some loss of resolution over traditional instruments is observed



Instrumentation – Sample Handling

- Virtually all UV spectra are recorded solution-phase
- Cells can be made of plastic, glass or quartz
- Only quartz is transparent in the full 200-700 nm range; plastic and glass are only suitable for visible spectra
- Concentration (we will cover shortly) is empirically determined

A typical sample cell (commonly called a cuvette):

Instrumentation – Sample Handling

- Solvents must be transparent in the region to be observed; the wavelength where a solvent is no longer transparent is referred to as the cutoff

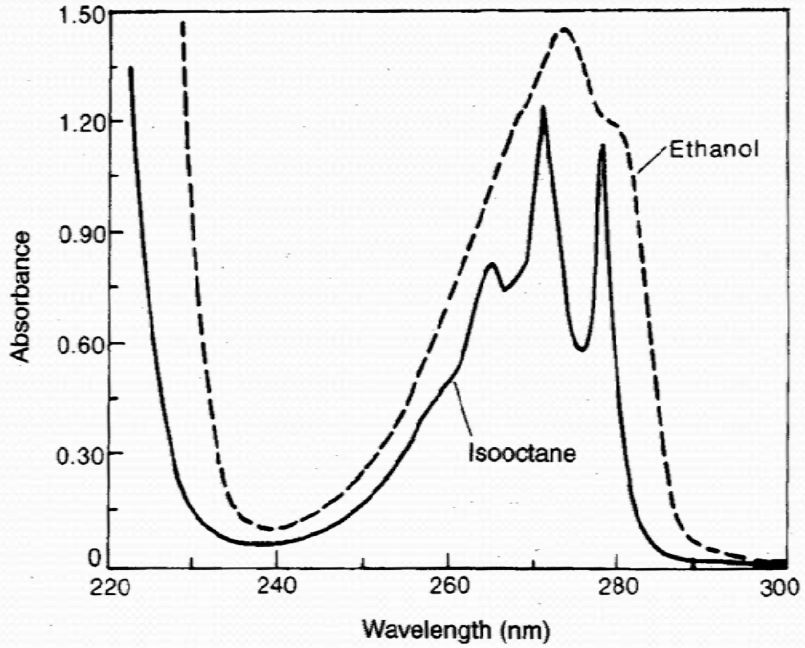
- Since spectra are only obtained up to 200 nm, solvents typically only need to lack conjugated p systems or carbonyls

Common solvents and cutoffs:

acetonitrile	190
chloroform	240
cyclohexane	195
1,4-dioxane	215
95% ethanol	205
n-hexane	201
methanol	205
isooctane	195
water	190

Instrumentation – Sample Handling

- Additionally solvents must preserve the fine structure (where it is actually observed in UV!) where possible
- H-bonding further complicates the effect of vibrational and rotational energy levels on electronic transitions, dipole-dipole interacts less so
- The more non-polar the solvent, the better (this is not always possible)

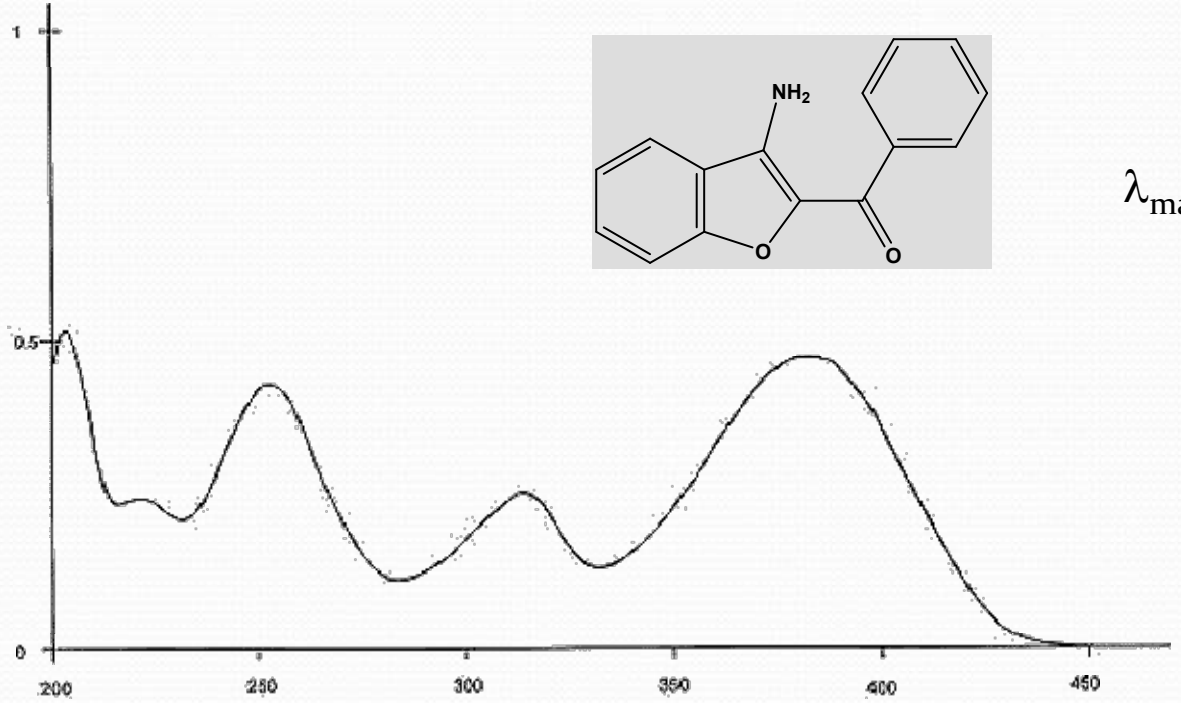


II. Instrumentation and Spectra

C. The Spectrum

1. The x-axis of the spectrum is in wavelength; 200-350 nm for UV, 200-700 for UV-VIS determinations

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 "lamba max" values or λ_{max}



λ_{max} = 206 nm
252
317
376

II. Instrumentation and Spectra

C. The Spectrum

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

2. From the spectrometers point of view, absorbance is the inverse of transmittance: $A = \log_{10} (I_0/I)$

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, ε this may vary by orders of magnitude…

II. Instrumentation and Spectra

C. The Spectrum

4. These effects are combined into the Beer-Lambert Law: $A = \varepsilon c l$

   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 10^4-10^6 10^4-10^6 are termed high intensity absorptions
   - values of 10^3-10^4 are termed low intensity absorptions
   - values of 0 to 10^3 are the absorptions of forbidden transitions

   A is unitless, so the units for ε are $cm^{-1} \cdot M^{-1}$ and are rarely expressed

5. Since path length and concentration effects can be easily factored out, absorbance simply becomes proportional to ε, and the y-axis is expressed as ε directly or as the logarithm of ε

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 that may be ambiguous in those methods

3. It can be used to assay (via l_{max} and molar absorptivity) the proper irradiation wavelengths for photochemical experiments, or the design of UV resistant paints and coatings

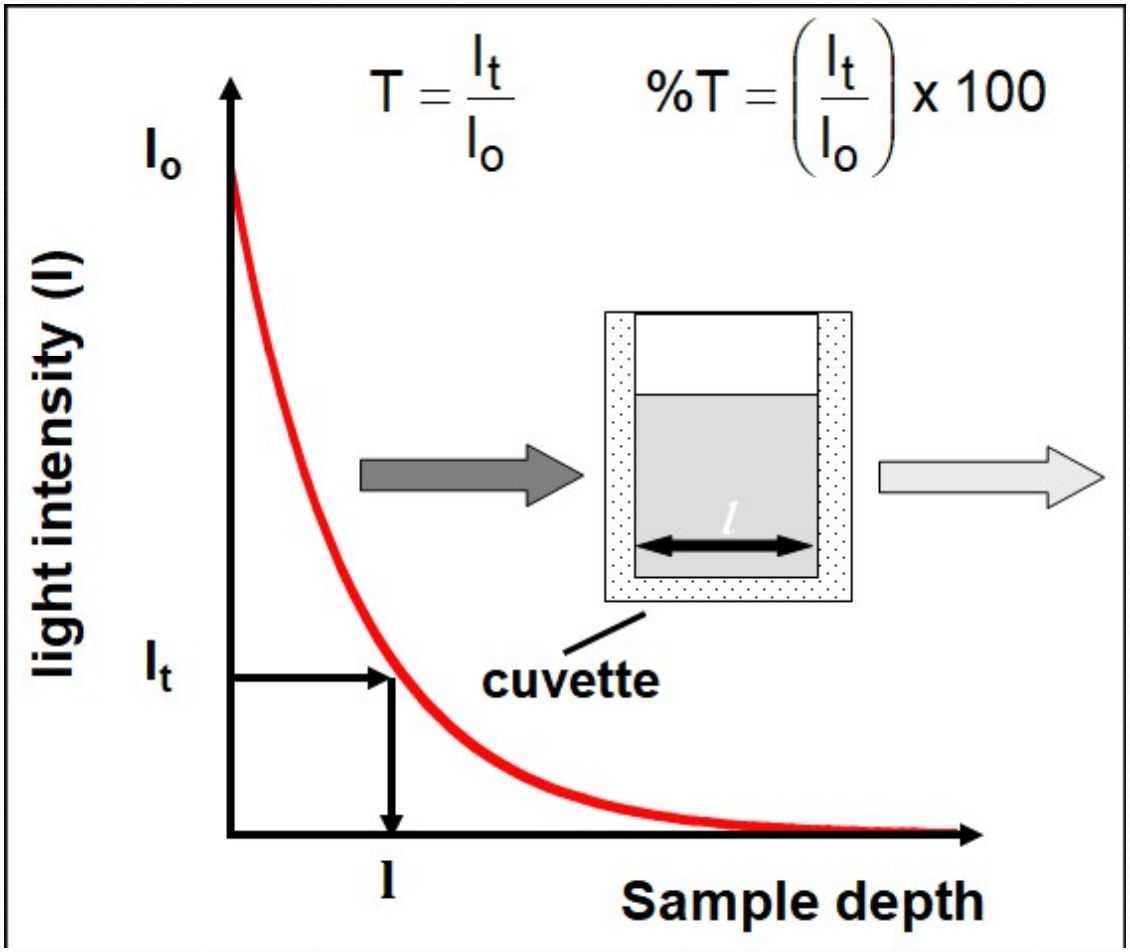
4. The most ubiquitous use of UV is as a detection device for HPLC; since UV is utilized for solution phase samples vs. a reference solvent this is easily incorporated into LC design

   UV is to HPLC what mass spectrometry (MS) will be to GC

UV-Visible Spectroscopy

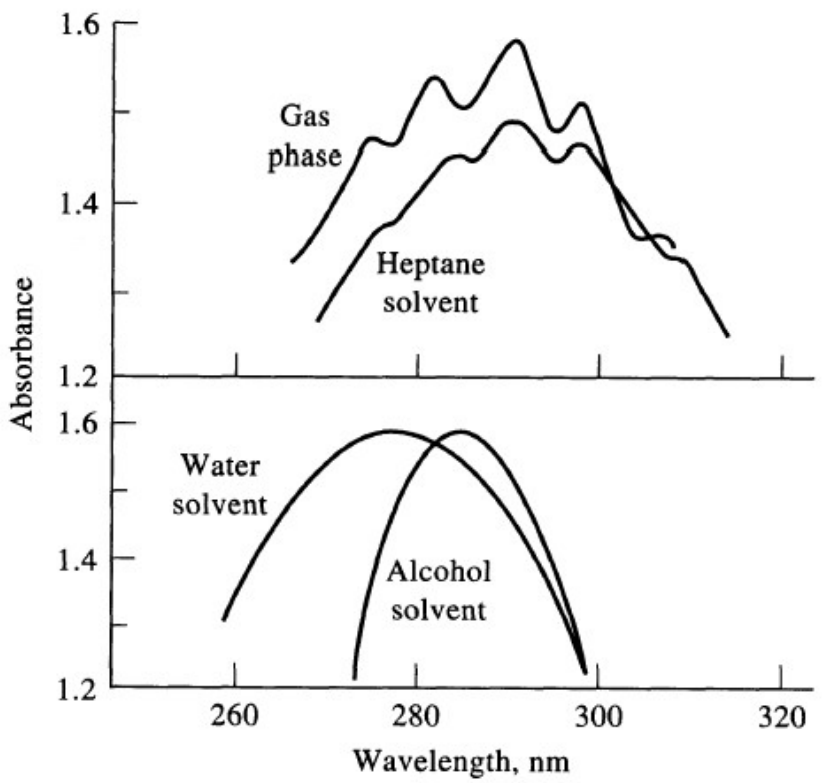
- **THE BEER-LAMBERT LAW**

- For a light absorbing medium, the light intensity falls exponentially with sample depth.
- For a light absorbing medium, the light intensity falls exponentially with increasing sample concentration.

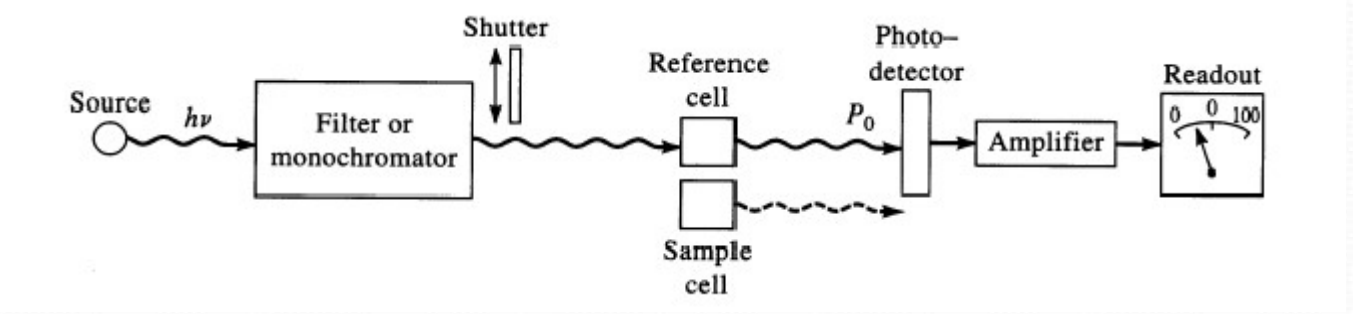


UV-Visible Spectroscopy

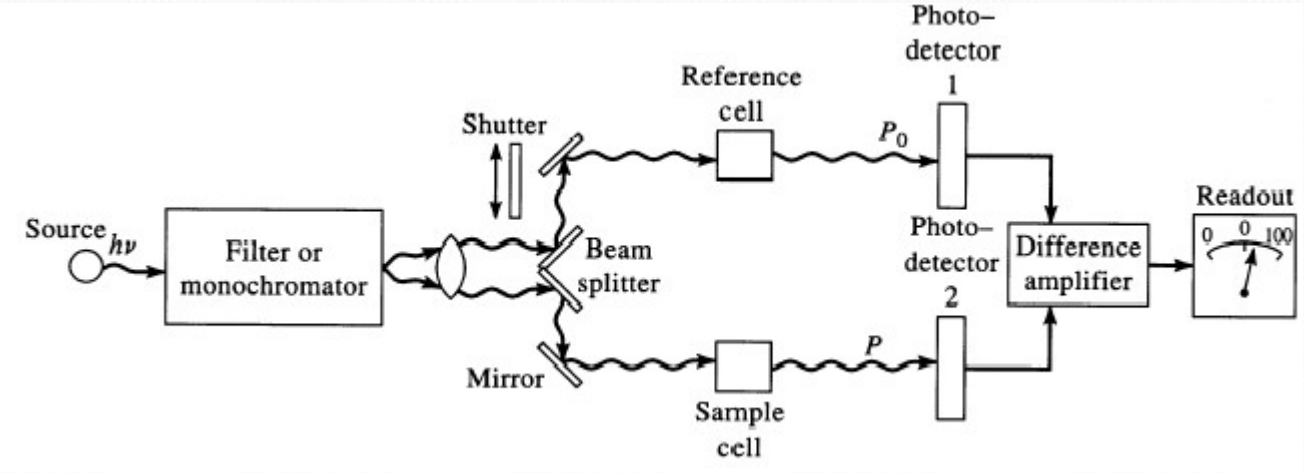
- **Beer-Lambert Law limitations**
  - Polychromatic Light
  - Equilibrium shift
  - Solvent
  - pH



Spectrometers



Single Beam



Double Beam

UV-Visible Instrumentation

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