Spectrophotometry

- Procedure that use light to measure chemical concentration
  - Properties of Light
  - Interaction of light with matte
  - Atom & Light Energy
Properties of Light

- **Electric field**
- **Magnetic field**
- **Wave length** ($\lambda$): crest to crest distance between waves
- **Frequency** ($\nu$, s$^{-1}$): number of complete oscillations that the wave makes each second
  
  $1$ oscillation/second = Hertz (Hz)

- **Speed of light** ($c$): $2.998 \times 10^8$ m/s

- **Energy** ($E$) carried by each photon:
  
  $E = h \times \nu$

  - $h$: Planck’s constant ($6.63 \times 10^{-34}$ J.s)
  - $\nu$: Frequency (s$^{-1}$)

What happens when light strikes a sample?

- Some light is transmitted through the sample
- Some light is absorbed by the material
- Some light is reflected at each surface
- Some light is scattered to the side

**Beer-Lambert’s Law**

$$A = \varepsilon \times l \times c$$

- $A$: Absorbance of radiation
- $\varepsilon$: Molar extinction coefficient or molar absorptivity (M$^{-1}$·cm$^{-1}$)
- $l$: Path length (cm)
- $c$: Concentration (M)
Interaction of radiation with matter

Electromagnetic spectrum

Ground State of an electron is the state of lowest energy for that electron.

Atm: Building block of a matter (protons, neutrons, electrons)
When an electron temporarily occupies an energy state greater than its ground state, it is in an excited state. Electrons do not stay in excited states for very long - they soon return to their ground states, emitting a photon with the same energy as the one that was absorbed.

Electronic transitions

- Types of absorbing electrons in organic molecule
  - Electrons that participate directly in bond formation between atoms
  - Non-bonding or unshared electrons that are localized about such atoms as oxygen, the halogens, sulfur, and nitrogen

- Types of transitions
  - $\sigma \rightarrow \sigma^*$
  - $\pi \rightarrow \pi^*$
  - $n \rightarrow \sigma^*$
  - $n \rightarrow \pi^*$
Review- Quantum numbers

- Principal quantum number (n)
  - Defines the size and the energy of an orbital (n=1, 2, 3, etc)
    - n=1 (ground state)
    - n>1 (excited state)
- Angular quantum number (l)
  - Defines the shape of the orbital (l=0 to n-1)
    - l=0 (s), l=1 (p), l=2 (d), l=3 (f), l=4 (g)
- Magnetic quantum number (m)
  - Defines the orientation of the orbital (m=-1 to +1)
- Spin magnetic quantum number (m_s)
  - Defines the direction of an electron (m_s=-1/2 or +1/2)
    - +1/2 for spin up
    - -1/2 for spin down

Review-Electron configuration

- Orbital with the lowest energy is filled first (1s orbital), orbital in the second shell (n=2) is filled next and so on…
  - C 1s^2 2s^2 2p^2
    - 1st shell has 1 orbital (1s)
    - 2nd shell has 4 orbital (1s and 3p)
- Molecular Orbital (interaction between atomic orbitals creates a bonding and antibonding molecular orbitals)
  - H_2
  - O_2
Energy Absorption & Bonding

- A = absorbance
- F = fluorescence
- P = phosphorescence
- IC = internal conversion
- ISC = intersystem crossing
- R = vibrational relaxation

Electronic Molecular Energy Levels

The most applications of absorption spectroscopy to organic compounds are based upon transitions for n or π electrons to the π* excited state. Both transitions require the presence of unsaturated functional groups to provide the π orbitals.
Difference between two types of transitions: $\pi \rightarrow \pi^*$ & $n \rightarrow \pi^*$

- Molar absorptivity for peak associated with $n \rightarrow \pi^*$ transition are low (10 to 100 $M^{-1}.cm^{-1}$). For $\pi \rightarrow \pi^*$ transition, $\varepsilon$ range from 1000 to 10000 $M^{-1}.cm^{-1}$.

- Effect of solvent
  - Peaks associated with $n \rightarrow \pi^*$ transition are shifted to shorter wavelength (hypsochromic shift) with increasing polarity of solvent.
  - Peaks associated with $\pi \rightarrow \pi^*$ transition are shifted to longer wavelength (bathochromic shift) with increasing polarity of solvent.

Absorbance Spectra

- Nitrobenzene in aqueous solution
  - Heavily conjugated with 4 resonance forms

Graph from: Schwarzenbach et al., 1993
Terminology

- **Absorbance (A)** a measure of the amount of radiation that is absorbed
- **Band** Term to describe a uv-vis absorption which are typically broad.
- **Chromophore** Structural unit responsible for the absorption
- **Molar absorptivity ($\varepsilon$)**, absorbance of a sample of molar concentration in 1 cm cell.
- **Extinction coefficient** An alternative term for the molar absorptivity
- **Path length (l)** the length of the sample cell in cm
- **Beer-Lambert Law** $A = \varepsilon . l . c$ (c = concentration in moles / litre)
- $\lambda_{\text{max}}$ The wavelength at maximum absorbance
- $\varepsilon_{\text{max}}$ The molar absorbance at $\lambda_{\text{max}}$
- **HOMO** Highest Occupied Molecular Orbital
- **LUMO** Lowest Unoccupied Molecular Orbital

Bathochromic Shift

- **Ethylene**
  \[
  \begin{array}{c}
  \end{array}
  \]
  $\lambda_{\text{max}}$ 190 nm

- **Butadiene**
  \[
  \begin{array}{c}
  \end{array}
  \]
  220 nm

- **Benzene**
  \[
  \begin{array}{c}
  \end{array}
  \]
  255 nm

- **Nitrobenzene**
  \[
  \begin{array}{c}
  \end{array}
  \]
  270 nm
Conjugation

- Impact of double bonds in conjugation with aromatic ring
- More $\pi \rightarrow \pi^*$ transitions
- Example
  - Benzene
  - Styrene

From: Schwarzenbach et al., 1993

Heteroatoms

- Impact of heteroatoms
- $n \rightarrow \pi^*$ transitions
  - Longer $\lambda_{\text{max}}$
- Example
  - Trans-stilbene
  - Azobenzene

From: Schwarzenbach et al., 1993
Conjugation revisited

- Impact of increasing $\pi$
  - $\pi \rightarrow \pi^*$ transitions
    - $\lambda_{\text{max}}$ increases $\sim 30$ nm per
    - Bathochromic shift
  - Examples
    - Naphthalene
    - Anthracene
    - Phenanthrene

From: Schwarzenbach et al., 1993

- More Examples
  - Naphthacene
  - Benz(a)anthracene

From: Schwarzenbach et al., 1993
**Geometry**

- 1,2-Naphthoquinone
- 1,4-Naphthoquinone

From: Schwarzenbach et al., 1993
pH speciation: Acids

- Deprotonation leads to delocalization of negative charge
- Bathochromic shift
- Examples
  - 4-Nitrophenol
  - 4-Nitrophenolate

From: Schwarzenbach et al., 1993

pH Speciation: Bases

- Protonation causes loss of available “n” electrons
- Hypsochromic shift
- Examples
  - Aniline
  - Anilinium ion

From: Schwarzenbach et al., 1993
Background NOM

- Specific Absorbance of water samples from several Swiss lakes and rivers

![Absorbance Graph](image)

From: Schwarzenbach et al., 1993

S::CAN

- Field deployable diode array spectrophotometer in a probe-like configuration
  - Can be submerged in flowing water or fitted with a flow-through cell
  - Produces a full UV-Vis spectrum
  - Algorithms tailored to estimate other parameters
  - Good surrogate for DOC
    - especially when the character of the DOC is reasonably constant
  - A very good surrogate for THMFP, HAAFP
    - takes into account reactivity of DOC as well as amount of DOC
  - Oxidation processes (ozonation) disrupt relationships between UV and DOC or THMFP

Commercial field probe
Derivative Spectroscopy

- Derivatives can be used in various algorithms

Thomas & Burgess, 2007

To next lecture