UV-VIS Absorption spectroscopy
(Electronic spectroscopy)

The earliest method of molecular spectroscopy!

Quantitative analysis: concentration determination.

Qualitative analysis: identification of molecule properties
(electronic transitions of molecules ↔ UV-Vis absorption)
Quantitative Analysis

UV-Vis spectroscopy is used more for **routine analytical determinations**.

**Beer-Lambert law:**

\[ A = \varepsilon \cdot b \cdot c \]

Parameters:

- \( A \) - absorbance, \( A = \log(\frac{I_o}{I_1}) \)
- \( I \) - light intensity
- \( \varepsilon \) - molar absorption coefficient (L·mol\(^{-1}\)·cm\(^{-1}\)),
- \( b \) - sample pathlength (usually 1 cm),
- \( c \) - concentration (mol/L).

\[ I_1 = I_o e^{-\varepsilon bc} \]

\[ \ln(\frac{I_o}{I_1}) = \varepsilon bc \]
Conceptual Basis of Beer’s Law:

- Light of a particular wavelength enters the ‘sample’.
- Light *scatters* from particles in solution reducing light transmission
- Light is *absorbed* by molecules/particles and remitted at different wavelengths, reducing light transmission

\[
\frac{dI}{I} = -\varepsilon c dl
\]

\[
\int_{I_o}^{I} \frac{dI}{I} = -\int_{0}^{I} \varepsilon c db
\]

\[
\ln \frac{I}{I_o} = -\varepsilon cb
\]

\[
A = \ln \frac{I_o}{I}
\]

\[
A = \varepsilon cb
\]
The amount of absorbed radiation may be measured in different ways:

If all the light is absorbed, then percent transmittance is zero, and absorption is infinite.

If all the light passes through a solution without any absorption, then absorbance is zero, and percent transmittance is 100%.
Molar absorptivity is a constant for a particular substance (at a wavelength!).

\[ \varepsilon = f(\text{subst}, \lambda) \]
Absorption spectrum \((A = f(\lambda))\) represents the dependence of absorbance from wavelength.

From the absorption spectrum can be determined:
- the position of the absorption maxima \(\lambda_{\text{max}}\)
- the intensity of the absorption maxima \(A\)
For concentration determinations the calibration curve (already existing or determined in the laboratory) can be used.

According to the Beer-Lambert Law, absorbance is proportional to concentration.

To build a calibration curve:
- record the absorption spectra for different knowns concentrations of a substance
- determine the absorbance (maximum of absorption band) for each spectra
- plotted the absorbance versus concentration $A = f(c)$ to produce a calibration ‘curve’
- obtain equation of straight line ($y = mx$) from line of ‘best fit’

To determine an unknown concentration:
- record the absorption spectra for unknown concentration of same substance
- use for calibration curve.
- use obtained equation to calculate the concentration.
The Beer-Lambert law is additive:

Absorbance of a mixture, at a certain wavelength, is the sum of each component absorbance at the considered wavelength: \( A_{\text{tot}} = A_1 + A_2 + A_3 + \ldots \)

To determining the concentration of a mixture of two or more substances, UV-Vis absorption spectra of each component is needed (for a known concentration).

Usually, the number of wavelength used to determine the absorbances is equal with the number of the constituents from mixture. One option is to choose those wavelengths at which each component has the maximum of absorption.

In order to determine the concentrations of each component of the mixture \((c_{Mx}, c_{Ny})\) the values of molar absorptivities of the two substances M, N must be calculated (using Beer-Lambert law) from the UV-Vis absorption spectrum of each component recorded for known concentrations \((c_M, c_N)\).

\[
\begin{align*}
A_{\lambda_1}^{(M+N)} &= A_{\lambda_1}^{Mx} + A_{\lambda_1}^{Ny} \\
A_{\lambda_2}^{(M+N)} &= A_{\lambda_2}^{Mx} + A_{\lambda_2}^{Ny}
\end{align*}
\]

\[
\begin{align*}
A_{\lambda_1}^{(M+N)} &= \varepsilon_{\lambda_1}^M b c_{Mx} + \varepsilon_{\lambda_1}^N b c_{Ny} \\
A_{\lambda_2}^{(M+N)} &= \varepsilon_{\lambda_2}^M b c_{Mx} + \varepsilon_{\lambda_2}^N b c_{Ny}
\end{align*}
\]

\[
\begin{align*}
\varepsilon_M &= \frac{A_\lambda^M}{b \cdot c_M} \\
\varepsilon_N &= \frac{A_\lambda^N}{b \cdot c_N}
\end{align*}
\]

By solving the system, the concentrations \((c_{Mx}, c_{Ny})\) of the two components of the mixture can be determined.
Absorption curve is influenced by:

- **Temperature** (at higher temperatures monomers are predominant)

- **Concentration** (at higher concentrations dimers/polymers are predominant)

- **pH** (influence the balance between ionized and non-ionized forms)

*Isosbestic point* is the intersection of all absorption curves of a solution at different pH's.
Limits to Beer’s Law: High Concentration and Chemical Deviations

- high concentration:
  - particles too close
  - average distance between ions and molecules are diminished
  - affect the charge distribution and extent of absorption.
  - cause deviations from linear relationship.

The Beer-Lambert Law breaks down for solutions of higher concentration!

A<1 for accurate results!

If A > 1:
- Dilute the sample
- Use a narrower cuvette

dimension of usually cuvettes:
  1 mm,
  1 cm,
  10 cm.

- chemical interactions: dissociation or reaction with the solvent
- **non-monochromatic radiation**: deviation of calibration curve from linearity

- if a significant amount of the light passed through the sample contains wavelengths that have much lower extinction coefficients than the nominal one, the instrument will report an incorrectly low absorbance.
Limits to Beer’s Law: Experimental Deviations

- reflections, scattering, etc. modify the reported absorption.
UV-VIS Absorption: Instrumentation

Light Source

Deuterium Lamps—a truly continuous spectrum in the ultraviolet region is produced by electrical excitation of deuterium at low pressure. (160nm~375nm)

Tungsten Filament Lamps—the most common source of visible and near infrared radiation.
**Monochromator**

- The diffraction grating splits light into its component colours.

- The exit slit allows only light of a very narrow range of wavelengths into the rest of the spectrometer.

- By gradually rotating the diffraction grating, the light from the whole spectrum (a tiny part of the range at a time) reach into the rest of the instrument.
**Detector**

The **Photovoltaic Detector** measures the intensity of photons by means of the voltage developed across the semiconductor layer. Electrons, ejected by photons from the semiconductor, are collected by the silver layer. **The potential** depends on the number of photons hitting the detector.

![Diagram of Photovoltaic Detector](image)

The **Phototube Detector** is a vacuum tube with a cesium-coated photocathode. Photons of sufficiently high energy hitting the cathode can dislodge electrons, which are collected at the anode. Photon flux is measured by the **current flow** in the system.

![Diagram of Phototube Detector](image)
The **Photomultiplier Detector** consists of a photoemissive cathode coupled with a series of electron-multiplying dynode stages.

The primary electrons ejected from the photo-cathode are accelerated by an electric field so as to strike a small area on the first dynode.

The impinging electrons strike with enough energy to eject **two to five secondary electrons**, which are accelerated to the second dynode to eject still more electrons.

A photomultiplier may have 9 to 16 stages, and overall gain of $10^6$ to $10^9$ electrons per incident photon.
**Single and Double Beam Spectrometer**

- **Single-Beam:** There is only one light beam or optical path from the source through to the detector.

- **Double-Beam:** The light from the source, after passing through the monochromator, is split into two separate beams: one for the sample and the other for the reference.
Photodiode array (CCD) allow simultaneous detection of all wavelength. No monochromator is needed!
Sample cell

The sample and reference cells are small rectangular containers made by:
- glass (using over Visible region)
- quartz or fused silica (Using over 190 nm)

The cell are often designed so that the light beam travels a distance of 1 cm through the contents (1 mm for low volume).

The sample cell contains a solution of the substance - usually very dilute.

The solvent is chosen so that it doesn't absorb any significant amount of light in the wavelength range we are interested in (200 - 800 nm).

The reference cell just contains the pure solvent.
**Absorption** of electromagnetic radiation in the **UV-Vis** range:
- *change the distribution of electrons* in the molecule
- *electrons are promoted* from the ground state to an unoccupied orbital (excited electronic states)

- *electronic transition***

\[
\begin{align*}
250 \text{ nm} & = 40000 \text{ cm}^{-1} = 1.2 \times 10^{15} \text{ Hz} \\
400 \text{ nm} & = 25000 \text{ cm}^{-1} = 7.5 \times 10^{14} \text{ Hz} \\
750 \text{ nm} & = 13333 \text{ cm}^{-1} = 4 \times 10^{14} \text{ Hz}
\end{align*}
\]

*Internuclear distances* and *force constants* corresponding to the excited electronic states *differ* from those corresponding to ground electronic states!
All molecules give electronic spectra!
(contrary to vibrational and rotational spectroscopies)

UV-Vis absorptions features:

a. Transitions between electronic energy levels are induced by electromagnetic radiation in the UV-Visible region.

b. Within each electronic state are a series of vibrational and rotational levels.

c. The relative populations of the various states are governed by Boltzmann distributions:

\[
\frac{n_2}{n_1} = \exp \left[ -\frac{(E_2 - E_1)}{kT} \right]; \quad k = 1.38 \times 10^{-23} \text{ J/K};
\]

d. At room temperature nearly all molecules are in the vibrational ground state.

(e.g., at 298 K: for \(\Delta E = 10 \text{ kJ/mol} \rightarrow \frac{N_2}{N_1} = 0.0176\) )
Electronic transitions can occur to various vibrational-rotational states in the excited electronic state.

The spectrum for a given electronic transition should consist of a large number of closely spaced lines.

In practice, this is observed only in dilute gases or at very low temperatures.

In solution and at room temperature, the fine structure is lost due to collisions, environmental heterogeneity, Doppler shifts, etc.

The electronic energy can be modeled as a harmonic oscillator near the equilibrium bond distance.

On the timescale of the electronic transition the nuclei are fixed because the electronic transitions are very fast.

Franck-Condon Principle: electronic transitions are vertical!
UV-Vis spectroscopy is related with transitions between electronic energy levels of **molecular orbitals** → electronic transitions

*The frequency of absorbed light* (wave number, wavelength) *depends on the structure of the molecule and on its neighborhood.*

Different molecules absorb different wavelengths of radiation!

Because certain molecules absorb light in a characteristic way, this is useful to identify and quantify biological molecules.

Indigo carmine: synthetic dye (blue) used in textile industry.
Vibrational changes produce a “coarse structure” on the electronic transitions. Rotational changes produce a “fine structure” on the electronic transitions.
Shape of UV-VIS Bands

The vibrational fine structure disappear for solutions but can be observed for gases.

I  Gas phase, room temperature
II  In isopentane-methylcyclohexane matrix, 77K
III  In cyclohexane, room temperature
IV  In water, room temperature

ex. 1,2,4,5-tetrazine
Electronic transition

A diatomic molecule may simultaneously undergo electronic, vibrational and rotational transitions.

The **Born-Oppenheimer approximation** ("Since the energies of the various motions are very different, motions of a diatomic molecule may be considered as independent") allows us to express the **total molecular energy** as:

\[
E_{\text{tot}} = E_{\text{elec}} + E_{\text{vib}} + E_{\text{rot}}
\]

As a result of a transition, the change in the total energy of a molecule is:

\[
\Delta E_{\text{total}} = \Delta E_{\text{elec}} + \Delta E_{\text{vib}} + \Delta E_{\text{rot}}
\]

(the approximate orders of magnitude: \(\Delta E_{\text{elec}} \sim \Delta E_{\text{vib}} \cdot 10^3 \sim \Delta E_{\text{rot}} \cdot 10^6\))

For **vibrational transitions** between different electronic levels, there is **no rule for \(\Delta v\)**, so that every \(v'' \rightarrow v'\) transition has some probability, giving rise to many spectral lines.

**Absorption** spectra from the ground state are more likely: virtually all the molecules are in their lowest vibrational state \((v'' = 0)\), so that the only transitions we observe are \((0, 1), (0, 2), (0, 3)\) etc.
Each set of transitions in a band is called a $v'$ **progression**, since the value of $v'$ increases by unity for each line in the set.

The lines in a band are closer together at high frequencies because of the anharmonicity of the upper state vibrations, which causes vibration energy levels to converge.

In general, the spacing of vibrational energy levels in the two electronic states is different.

\[
\begin{align*}
v'' &\rightarrow \text{vibrational quantum number of ground electronic state (initial state)} \\
v' &\rightarrow \text{vibrational quantum number of excited electronic state (final state)}
\end{align*}
\]
Example:

The vibrational-electronic spectrum of I$_2$ in the region from 500-650 nm displays a large number of well-defined bands which, for the most part, correspond to 0 $\rightarrow$ v' transitions connecting the v" = 0 vibrational level of the ground electronic state to many different vibrational levels v' of the excited electronic state. Under the conditions of this experiment (i.e., low resolution), the rotational lines within each band are not resolved.

Each small peak, such as the (26,0) band labelled on the spectrum, corresponds to a transition between two vibrational levels and is called a band. Each band is comprised of several hundred lines, each of which involves different upper and lower rotational quantum numbers; as mentioned, these lines are not resolved in the present experiment. The region of maximum absorption in each band is caused by many of these lines falling together; it is called the band head. The set of all of these bands is referred to as the visible band system of I$_2$.

If the sample is hot, then excited vibrational levels of the ground state may be populated, and these also will absorb light.

The hot bands arising from absorption from v"=1 and v"=2 are shown very approximately on the absorption spectrum above.

At a point called the convergence limit, the spacing between bands decreases to zero.

Beyond this convergence limit, the spectrum is continuous because the excited state of the I$_2$ molecule is not bound.
Birge Sponer plot

The energy of a real molecule (anharmonic vibration) is:

\[ E_{\text{total}} = E_{\text{elec}} + \hbar c [(\nu + \frac{1}{2}) \bar{\nu}_e - x_e (\nu + \frac{1}{2})^2 \bar{\nu}_e] \]

The change in the total energy is:

\[ \Delta E_{\text{total}} = \Delta E_{\text{elec}} + \Delta E_{\text{vib}} \]

\[ \Delta E_{\text{total}} = E'_{\text{elec}} - E''_{\text{elec}} + \hbar c [(\nu' + \frac{1}{2}) \bar{\nu}'_e - x'_e (\nu' + \frac{1}{2})^2 \bar{\nu}'_e - (\nu'' + \frac{1}{2}) \bar{\nu}''_e - x''_e (\nu'' + \frac{1}{2})^2 \bar{\nu}''_e] \]

If a sufficient number (at least five) of lines can be resolved in the band, the values: \( x'_e, x''_e, \bar{\nu}'_e, \bar{\nu}''_e \) and \( (E'_{\text{elec}} - E''_{\text{elec}}) \) can be calculated.

\[ \text{X} - \text{electronic ground state} \quad (S_0), \]
\[ \text{b} - \text{electronic excited state} \quad (S_1), \]
\[ (\text{''}) - \text{lower state}; \]
\[ (\text{'}) - \text{higher state} \]
For a given electronic transition: \( E'_{\text{elec}} - E''_{\text{elec}} = \Delta E_{\text{elect}} = \text{constant}. \)

\[
\Delta E_{\text{total}} = \Delta E_{\text{elec}} + \hbar c \left[ (v' + \frac{1}{2}) \bar{v}'_e - x'_e (v' + \frac{1}{2})^2 \bar{v}'_e - (v'' + \frac{1}{2}) \bar{v}''_e - x''_e (v'' + \frac{1}{2})^2 \bar{v}''_e \right]
\]

Considering only the terms \( (G(v') = \Delta E_{\text{total}}/\hbar c) \) from a progression (ex. \( v'' = 0 \))

\[
G(v') = \frac{1}{\hbar c} \Delta E_{\text{elec}} + \left[ (v' + \frac{1}{2}) \bar{v}'_e - x'_e (v' + \frac{1}{2})^2 \bar{v}'_e - (\frac{1}{2}) \bar{v}''_e - x''_e (\frac{1}{2})^2 \bar{v}''_e \right]
\]

and makes the difference between two consecutive terms, will obtain an expression which is a first degree equation in \( (v'+1/2) \):

\[
\Delta G = G(v'+1) - G(v') = \bar{v}'_e - 2x'_e \bar{v}'_e (v' + \frac{1}{2}) = f(v' + \frac{1}{2})
\]
If we represent $\Delta G = f(v' + 1/2)$ will obtain the Birge-Sponer plot.

The slope of this line is equal to: $2x'_e \bar{v}'_e$

The y intercept represent $\bar{v}'_e$ (the vibrational frequency of harmonic oscillator).

The x intercept represent the number of vibrational levels from the electronic excited state: $v'_{\text{max}}$

If the terms from a series are used, the values corresponding to ("') state will be obtained.

The area below Birge-Sponer line represent the dissociation energy $D_0$. 

$D_e$ energy is the maximum value of $G(v)$:

$$D_e = G_{\text{max}}(v) = \frac{\bar{v}_e^2}{4 \cdot \bar{v}_e \cdot x_e}$$
Example:
The vibrational energy levels of HgH converge rapidly and successive intervals are: (from 0→1): 1203.7, 965.6, 632.4, 172 cm\(^{-1}\).

Estimate the dissociation energy

\[ \Delta G = f\left(\nu' + \frac{1}{2}\right) = \bar{\nu}'_e - 2x'_e \bar{\nu}'_e \left(\nu' + \frac{1}{2}\right) \]
Vibrational band analysis: the Deslandres table

In order to draw Birge-Sponer line the Deslandres table could be used. The Deslandres table contain vibrational wavenumbers of electronic transitions and the differences between them.

The differences between rows and columns is constant, and correspond to the energy difference between a particular pair of vibrational levels in either the upper state (rows) or the lower state (columns):

<table>
<thead>
<tr>
<th>$v''$</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v' = 0$</td>
<td>64748</td>
<td>62605</td>
<td>60488</td>
<td>58398</td>
</tr>
<tr>
<td>$v' = 1 - 0$</td>
<td>1480</td>
<td>1480</td>
<td>1480</td>
<td>1480</td>
</tr>
<tr>
<td>$v' = 2 - 1$</td>
<td>1440</td>
<td>1440</td>
<td>1440</td>
<td>1440</td>
</tr>
<tr>
<td>$v' = 3 - 2$</td>
<td>1402</td>
<td>1402</td>
<td>1402</td>
<td>1402</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$v'' + 1/2$</th>
<th>$\lambda$ [Å]</th>
<th>$\nu$ [cm$^{-1}$]</th>
<th>$\Delta G(v''+1/2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5</td>
<td>5145</td>
<td>19436</td>
<td>213</td>
</tr>
<tr>
<td>1.5</td>
<td>5202</td>
<td>19222</td>
<td>208</td>
</tr>
<tr>
<td>2.0</td>
<td>5259</td>
<td>19015</td>
<td>215</td>
</tr>
<tr>
<td>3.0</td>
<td>5319</td>
<td>18800</td>
<td>205</td>
</tr>
<tr>
<td>4.0</td>
<td>5378</td>
<td>18594</td>
<td>212</td>
</tr>
<tr>
<td>5.0</td>
<td>5440</td>
<td>18382</td>
<td>203</td>
</tr>
<tr>
<td>6.0</td>
<td>5501</td>
<td>18179</td>
<td>211</td>
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<tr>
<td>7.0</td>
<td>5565</td>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>17.5</td>
<td>6255</td>
<td>15988</td>
<td>190</td>
</tr>
</tbody>
</table>
Intensity of vibrational-electronic transitions (vibronic):
The vibrational lines in a progression are not of the same intensity. Intensities of the vibrational bands are determined by three factors:

(1) The intrinsic strength of the transition
(2) The populations of the levels involved.
(3) The overlap of the vibrational wavefunctions (the Franck-Condon factor).

**Franck-Condon Factors**

- The intensity of a transition from one electronic state to another is related to the **Franck-Condon factor (FCF)**.

\[ I \propto FCF = |S_{nm}|^2 \]

- The quantity \( S_{nm} \) is the overlap integral between the ground and excited state wavefunctions.

\[ S_{nm} = \int_{-\infty}^{\infty} \psi_n^*(x) \psi_m(x) \, dx \]
**The Franck-Condon principle:** “Since electronic transitions occur very rapidly (≈ $10^{-15}$ s), vibration and rotation of the molecule do not change the internuclear distance appreciably during the transition”.

The intensity of a transition is greatest for the largest of the vibrational wavefunctions.

**Franck-Condon principle** → explains the intensity of vibronic transitions

An electronic transition occur without changing the position of nuclei in the molecule.

In view of the Franck-Condon principle, electronic transitions occur “vertically” on a potential energy diagram.

When the nucleus realigns itself with the new electronic configuration, the theory states that it must undergo a vibration.
(1) If the internuclear distances in the upper and lower states are equal \( r_e'' \approx r_e' \), the most probable transition is \((0, 0)\) (left). However, there is a non-zero probability of \((1, 0), (2, 0), (3, 0)\) etc. transitions. The successive lines will therefore have rapidly diminishing intensities.

(2) If the excited electronic state has a slightly larger nuclear separation than the ground state \((r_e' > r_e'')\), the most probable (and thus most intense) transition is \((2, 0)\) (center). The intensities of the neighbouring transitions are lower.

(3) When the excited electronic state has a considerably larger nuclear separation than the ground state \((r_e' > > r_e'')\) (right), the vibrational state to which the transition takes place has a high \(v'\) value. Further, transitions can occur to levels where the molecule has energy in excess of its dissociation energy.

From such states the molecule will dissociate without any vibrations and, since the fragments which are formed may take up any value of kinetic energy, the transitions are not quantized and a continuum results.
**Types of electronic transitions:**

A. Transitions involving electrons $\pi$, $\sigma$ and $n$

B. Transitions involving charge transfer

C. Transitions involving electrons d and f

---

**A. Organics:** Involving $\pi$, $\sigma$, $n$ electrons

- **Saturated compounds**
  - $\sigma \rightarrow \sigma^*$ (<150 nm), $n \rightarrow \sigma^*$ (<250 nm): deep UV

- **Double bonds/unsaturated systems**
  - less energy to $\pi^*$
  - $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$ transitions: (200-700 nm)

**B. Metal-ligand complexes: charge transfer transition**

- Electron moves between ligand and metal.
- One must act as donor and other as acceptor.

**C. Inorganics: d-d transition**

- Additionally, transitions between d orbitals split by presence of ligand field.
- Usually in visible.
Wavelengths below 200 nm are absorbed by air therefore, can not be registered with a ordinary UV-Vis spectrometer.

"Vacuum UV" all parts must be maintained in a vacuum. The vacuum UV absorption are caused by $\sigma \rightarrow \sigma^*$ transitions.

These transitions correspond to simple bonds and are common to all molecules.

$\pi \rightarrow \pi^*$ transitions depend on the conjugation, so it can reach the visible region of radiation, causing the color of substances.
Molecular orbital theory (MO):

An *atomic orbital* is the space within which an electron belonging to the orbital spends 95% of its time.

In *molecular orbital theory* orbitals embrace two or more nuclei.

Electrons in a molecule are not tied to a particular atom, they are "scattered" throughout the entire molecule.
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 (σ, π), there is a corresponding anti-bonding orbital of symmetrically higher energy (σ*, π*).

- **σ-orbitals**: typically are the lowest energy occupied orbitals; the corresponding anti-bonding (σ*) orbital is of the highest energy.

- **π-orbitals** are of somewhat higher energy, and their complementary anti-bonding orbital (π*) somewhat lower in energy than σ*.

- **n-orbitals**: non-bonding electrons lie at the energy of the original atomic orbital, most often this energy is higher than π or σ (since no bond is formed, there is no benefit in energy).
Molecular orbital wavefunction is a linear combination of atomic orbital wavefunctions.

For bonding orbitals the interference between the two atomic orbitals are constructive. For unbonding orbitals the interference between the two atomic orbitals are destructive.

Ex: Hydrogen molecule:

The sum: \( \psi_{\text{H}_2}^+ = \psi_{1s} + \psi_{1s} \)

This bonding orbital (called 1s\(\sigma\), as it is produced from two s atomic orbitals) is a simple symmetrical ellipsoid. It does not change sign upon inversion about the centre of symmetry, which is marked by the subscript \(g\) (\(gerade = \text{even}\)). The orbital is thus known as 1s\(\sigma\)\(_g\).

The difference: \( \psi_{\text{H}_2}^- = \psi_{1s} - \psi_{1s} \)

In this antibonding orbital (called 1s\(\sigma^*\)) the charge is concentrated outside the nuclei, which repel one another. This orbital does change sign upon inversion, which is marked by the subscript \(u\) (\(ungerade = \text{odd}\)). It is thus known as 1s\(\sigma^*\)u\(_u\).
formation of $\sigma_g$ and $\sigma_u^*$ orbitals from two atomic $2p_z$ orbitals

formation of $\pi_g$ and $\pi_u^*$ orbitals from two atomic $2p_y$ orbitals
Transitions involving electrons $\pi$, $\sigma$ and $n$

$\sigma \rightarrow \sigma^*$ transitions

The energy of this transitions is big. The corresponding maxima does not appear in specific UV-Vis spectra (200 - 700 nm). (UV absorption!)

Ex: CH$_4$ (only C-H bond) allows only $\sigma \rightarrow \sigma^*$ transition. The maximal of absorption is at 125 nm.

$n \rightarrow \sigma^*$ transitions

Saturated compounds containing atoms with unpaired electrons (nonbonding electrons) allows $n \rightarrow \sigma^*$ transitions. The energy necessary for those transitions is less than the energy needed for $\sigma \rightarrow \sigma^*$ transitions. Transitions may be initiated by radiation in the wavelength 150-250 nm.

The number of organic functional groups which have the maximum of absorption in UV region is small.
\[ n \rightarrow \pi^* \text{ and } \pi \rightarrow \pi^* \text{ transitions} \]

Most absorption bands of organic compounds are due to electronic transitions from fundamental levels \( n \) or \( \pi \) on the excited levels \( \pi^* \). Absorption bands for these transitions fall in the 200 nm - 700 nm region. These transitions require the presence, in the molecule, of an unsaturated group which has \( \pi \) electrons.

\( n \rightarrow \pi^* \) transitions have low molar absorptivity (\( \varepsilon \sim 10 - 100 \text{ L/mol} \cdot \text{cm} \)).
\( \pi \rightarrow \pi^* \) transitions have high molar absorptivity (\( \varepsilon \sim 1.000 - 10.000 \text{ L/mol} \cdot \text{cm} \)).

The solvent could influence the positions of absorption bands.

With increasing polarity \( n \rightarrow \pi^* \) transitions are shifted to lower wavelengths (blue shift). This shift is due to unpaired electrons (orbital energy decreases \( n \)).

With increasing polarity \( \pi \rightarrow \pi^* \) transitions are often (not always) shifted to higher wavelengths (red shift). This is caused by attractive polarization forces between the solvent and absorbent, which determine the decrease of ground and excited states energy. This decrease is greater for excited state than for fundamental state, so the difference in energy between the two levels decreases, resulting in a shift of the absorption band to higher wave numbers (red shift).

This effect also influences \( n \rightarrow \pi^* \) transitions but is covered by the blue shift due to unpaired electrons.
**Charge-transfer transitions**

These electronic transitions usually appear in light absorption of inorganic molecules.

For a molecule to allow a charge-transfer transition must have a component (atom, group) able to donate an electron and another component must be able to accept an electron.

The absorption of radiation involves an electron transfer from an orbital of a donor to an orbital associated with an acceptor.

Charge-transfer transitions have high molar absorptivity ($\varepsilon > 10,000$ l/mol·cm).

Charge transfer transitions are common in metal-ligand complexes.

→ Typical metal-ligand transition: an electron from an orbital of the metal is transferred to a $\pi^*$ orbital of the ligand.

→ If the metal has an empty d orbital, it is possible a transfer from ligand to metal.
**d-d transitions**

d-d transitions correspond to the transition of an electron from a metal d orbital to another metal d orbital.

Problem: → d orbitals have the symmetry g (even)
→ d-d transition is forbidden "symmetry forbidden".

**Vibronic coupling:** some vibration can remove the center of symmetry of the molecule.
→ d-d transitions are "weakly allowed".

The intensity of d-d transitions is very low, because d-d transitions are forbidden.

Molar absorptivity is under 100 L/mol·cm.

<table>
<thead>
<tr>
<th>type of transition</th>
<th>Molar absorptivity ε (L/mol·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>π-π*</td>
<td>thousands</td>
</tr>
<tr>
<td>σ- σ*</td>
<td>hundred - thousands</td>
</tr>
<tr>
<td>d-d</td>
<td>10-100</td>
</tr>
<tr>
<td>charge transfer</td>
<td>&gt;10,000</td>
</tr>
</tbody>
</table>
The wavelength of light absorbed is that having the energy required to move an electron from a lower energy level to a higher energy level.

Figure 2
Electronic transitions in formaldehyde
Transitions involving $\pi$ and $n$ orbitals ($n = \text{non-bonding}$) are important because they can be used to identify conjugate systems, which have strong absorption.

The lowest energy transition is that between the HOMO (Highest occupied molecular orbital) and LUMO (Lowest unoccupied molecular orbital) orbitals.

The absorption of electromagnetic radiation extracts an electron from the HOMO and transfers it on the LUMO, creating an excited state.
The color arises when a molecule absorbs certain wavelengths of visible light and transmits or reflects others.

Absorption spectrum consists of absorption bands corresponding to structural groups of molecules (chromophores).

**Chromophores**: atom groups acting as a light absorber!

The chromophore is a region in the molecule where the energy difference between two different molecular orbitals falls within the range of the visible spectrum.

Visible light that hits the chromophore can be absorbed by exciting an electron from its ground state into an excited state.
In the absorption spectrum of molecules that contain more chromophores, the following changes can occur due to *interaction of the chromophores*:

- Hypsochromic shift \((\lambda_{\text{max}} \downarrow)\)
- Bathochromic shift \((\lambda_{\text{max}} \uparrow)\)
- Hypochromic effect (abs. \(\downarrow\))
- Hyperchromic effect (abs. \(\uparrow\))
**The color of a substance:**
- *the transmitted color* not the absorbed color
- the color that remains after subtracting from the incident light the absorbed light.

<table>
<thead>
<tr>
<th>Absorbed Light</th>
<th>Observed (transmitted) color</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Wavelength nm</strong></td>
<td><strong>Corresponding color</strong></td>
</tr>
<tr>
<td>400</td>
<td>violet</td>
</tr>
<tr>
<td>425</td>
<td>indigo blue</td>
</tr>
<tr>
<td>450</td>
<td>blue</td>
</tr>
<tr>
<td>490</td>
<td>blue-green</td>
</tr>
<tr>
<td>510</td>
<td>green</td>
</tr>
<tr>
<td>530</td>
<td>yellow-green</td>
</tr>
<tr>
<td>550</td>
<td>yellow</td>
</tr>
<tr>
<td>590</td>
<td>orange</td>
</tr>
<tr>
<td>640</td>
<td>red</td>
</tr>
<tr>
<td>730</td>
<td>purple</td>
</tr>
</tbody>
</table>

![Diagram illustrating the absorption of light by different colors](image-url)
The color we see in ink, dyes, flowers, etc. is due to conjugation of organic molecules!

If the system is conjugated, the gap between HOMO and LUMO became lower, so the frequency of radiation absorbed is smaller (the wavelength of radiation absorbed is greater).

**Conjugated molecules** are those in which there is an alternation of single and double bonds along a chain of carbon atoms.
When two isolated double bonds are brought into conjugation, both levels are shifted to give bonding and antibonding orbitals.

The effect of conjugation is that the LUMO $\pi^*$ orbital is shifted downwards, and the $n \rightarrow \pi^*$ absorption shifts to lower energy (longer wavelengths).

Repeated conjugation increases this effect.

Absorption by a C=C double bond excites a $\pi$ electron into an antibonding $\pi^*$ orbital. The chromophore activity is due to an $\pi \rightarrow \pi^*$ transition, corresponding to absorption at 180 nm.

When the double bond is part of a conjugated chain, the energies of the molecular orbitals lie closer together, and the $\pi \rightarrow \pi^*$ transition moves to longer wavelengths (lower energy). It may even lie in the visible region if the conjugated system is long enough.
An important example is the photochemical mechanism of vision. The retina of the eye contains “visual purple”, a combination of a protein with 11-cis-retinal, which acts as a chromophore and is a receptor of photons entering the eye.

11-cis-retinal itself absorbs at 380 nm, but in combination with the protein the absorption maximum shifts to ca. 500 nm and tails into the blue.

The conjugated double bonds are responsible for the ability of the molecule to absorb over the entire visible region. They play another important role: in its electronically excited state the conjugated chain can isomerize by twisting about an excited C=C bond, forming 11-trans-retinal.

The primary step in vision is photon absorption followed by isomerization, which triggers a nerve impulse to the brain.
Chromophores have well-known absorption maxima:

<table>
<thead>
<tr>
<th>Chromophore</th>
<th>Example</th>
<th>Excitation</th>
<th>$\lambda_{\text{max}}, \text{nm}$</th>
<th>$\varepsilon$</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C</td>
<td>Ethene</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>171</td>
<td>15,000</td>
<td>hexane</td>
</tr>
<tr>
<td>C≡C</td>
<td>1-Hexyne</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>180</td>
<td>10,000</td>
<td>hexane</td>
</tr>
<tr>
<td>C=O</td>
<td>Ethanal</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>290</td>
<td>15</td>
<td>hexane</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\pi \rightarrow \pi^*$</td>
<td>180</td>
<td>10,000</td>
<td>hexane</td>
</tr>
<tr>
<td>N=O</td>
<td>Nitromethane</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>275</td>
<td>17</td>
<td>ethanol</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\pi \rightarrow \pi^*$</td>
<td>200</td>
<td>5,000</td>
<td>ethanol</td>
</tr>
<tr>
<td>C-X</td>
<td>Methyl bromide</td>
<td>$n \rightarrow \sigma^*$</td>
<td>205</td>
<td>200</td>
<td>hexane</td>
</tr>
<tr>
<td>X=Br</td>
<td>Methyl iodide</td>
<td>$n \rightarrow \sigma^*$</td>
<td>255</td>
<td>360</td>
<td>hexane</td>
</tr>
</tbody>
</table>

**Diagram:**

- C=C: 175-215 nm
- C≡C: 175-215 nm
- C=O: 270 nm
- H/C=O: 290 nm
- -OH: 186 nm
- N≡N: 345 nm
- O: 200, 268 nm
<table>
<thead>
<tr>
<th>Chromophore</th>
<th>Compound</th>
<th>Transition</th>
<th>$\lambda_{\text{max}}$ [nm]</th>
<th>$\epsilon_{\text{max}}$</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>CH$_3$-CH$_3$</td>
<td>$\sigma \rightarrow \sigma^*$</td>
<td>135</td>
<td>strong</td>
<td>gas</td>
</tr>
<tr>
<td>C-H</td>
<td>CH$_4$</td>
<td>$\sigma \rightarrow \sigma^*$</td>
<td>122</td>
<td>strong</td>
<td>gas</td>
</tr>
<tr>
<td>C-O</td>
<td>CH$_3$OH</td>
<td>n $\rightarrow \sigma^*$</td>
<td>177</td>
<td>200</td>
<td>hexane</td>
</tr>
<tr>
<td></td>
<td>CH$_3$-O-CH$_3$</td>
<td>n $\rightarrow \sigma^*$</td>
<td>184</td>
<td>2500</td>
<td>gas</td>
</tr>
<tr>
<td>C-N</td>
<td>(C$_2$H$_5$)$_2$NH</td>
<td>n $\rightarrow \sigma^*$</td>
<td>193</td>
<td>2500</td>
<td>hexane</td>
</tr>
<tr>
<td></td>
<td>(CH$_3$)$_2$N</td>
<td>n $\rightarrow \sigma^*$</td>
<td>199</td>
<td>4000</td>
<td>hexane</td>
</tr>
<tr>
<td>C-S</td>
<td>CH$_3$-SH</td>
<td>n $\rightarrow \sigma^*$</td>
<td>195</td>
<td>1800</td>
<td>gas</td>
</tr>
<tr>
<td></td>
<td>CH$_3$-S-CH$_2$</td>
<td>n $\rightarrow \sigma^*$</td>
<td>235</td>
<td>1800</td>
<td>gas</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_5$-S-C$_2$H$_5$</td>
<td>n $\rightarrow \sigma^*$</td>
<td>194</td>
<td>4500</td>
<td>gas</td>
</tr>
<tr>
<td>S-S</td>
<td>C$_2$H$_5$-S-S-C$_2$H$_5$</td>
<td>n $\rightarrow \sigma^*$</td>
<td>225</td>
<td>1800</td>
<td>gas</td>
</tr>
<tr>
<td></td>
<td>C$_2$H$_5$-S-C$_2$H$_5$</td>
<td>n $\rightarrow \sigma^*$</td>
<td>250</td>
<td>380</td>
<td></td>
</tr>
<tr>
<td>C-Cl</td>
<td>CH$_2$Cl</td>
<td>n $\rightarrow \sigma^*$</td>
<td>173</td>
<td>200</td>
<td>hexane</td>
</tr>
<tr>
<td>C-Br</td>
<td>n-C$_3$H$_7$Br</td>
<td>n $\rightarrow \sigma^*$</td>
<td>208</td>
<td>300</td>
<td>hexane</td>
</tr>
<tr>
<td>C-I</td>
<td>CH$_3$I</td>
<td>n $\rightarrow \sigma^*$</td>
<td>259</td>
<td>400</td>
<td>hexane</td>
</tr>
<tr>
<td>C=C</td>
<td>CH$_2$=CH$_2$</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>162.5</td>
<td>15000</td>
<td>heptane</td>
</tr>
<tr>
<td></td>
<td>(CH$_3$)$_2$C=CH$_2$</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>196.5</td>
<td>11500</td>
<td>heptane</td>
</tr>
<tr>
<td>C=O</td>
<td>(CH$_3$)$_2$C=O</td>
<td>n $\rightarrow \sigma^*$</td>
<td>166</td>
<td>16000</td>
<td>gas</td>
</tr>
<tr>
<td></td>
<td>(CH$_3$)$_2$C=O</td>
<td>$\pi \rightarrow \pi^*$</td>
<td>189</td>
<td>900</td>
<td>hexane</td>
</tr>
<tr>
<td></td>
<td></td>
<td>n $\rightarrow \pi^*$</td>
<td>279</td>
<td>15</td>
<td>hexane</td>
</tr>
<tr>
<td>CH$_3$-C-OH</td>
<td>n $\rightarrow \pi^*$</td>
<td>200</td>
<td>50</td>
<td>gas</td>
<td></td>
</tr>
<tr>
<td>CH$_3$-O-C$_2$H$_5$</td>
<td>n $\rightarrow \pi^*$</td>
<td>210</td>
<td>50</td>
<td>gas</td>
<td></td>
</tr>
<tr>
<td>CH$_3$-C-ONa</td>
<td>n $\rightarrow \pi^*$</td>
<td>210</td>
<td>150</td>
<td>water</td>
<td></td>
</tr>
<tr>
<td>CH$_3$-C-NH$_2$</td>
<td>n $\rightarrow \pi^*$</td>
<td>220</td>
<td>63</td>
<td>water</td>
<td></td>
</tr>
<tr>
<td>CH$_2$=C=O</td>
<td>191</td>
<td>15200</td>
<td>acetonitrile</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=N</td>
<td>H$_2$N-C=NH$_2$-HCl</td>
<td>265</td>
<td>15</td>
<td>water</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(CH$_3$)$_2$C=NO</td>
<td>193</td>
<td>2000</td>
<td>ethanol</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(CH$_3$)$_2$C=NONa</td>
<td>265</td>
<td>200</td>
<td>ethanol</td>
<td></td>
</tr>
<tr>
<td>N=N</td>
<td>CH$_3$-N=N=CH$_3$</td>
<td>340</td>
<td>16</td>
<td>ethanol</td>
<td></td>
</tr>
</tbody>
</table>
The color of conjugated systems

The conjugation of double or triple bonds lead to increased absorptivity and determine the shift of $\lambda_{\text{max}}$ to higher wavelengths (bathochromic shift):

<table>
<thead>
<tr>
<th></th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{-C}=$</td>
<td>170</td>
<td>16 000</td>
</tr>
<tr>
<td>$\text{-C}=$</td>
<td>220</td>
<td>21 000</td>
</tr>
<tr>
<td>$\text{-C}=$</td>
<td>260</td>
<td>35 000</td>
</tr>
</tbody>
</table>

The word "conjugation" is derived from a Latin word that means "to link together". In organic chemistry, it is used to describe the situation that occurs when $\pi$ systems are "linked together".

An "isolated" $\pi$ system exists only between a single pair of adjacent atoms (e.g. $\text{C}=$),

An "extended" $\pi$ system exists over a longer series of atoms (e.g. $\text{C}=$-$\text{C}=$ or $\text{C}=$-$\text{C}=$-$\text{O}$ etc.).

An extended $\pi$ system results in an extension of the chemical reactivity.

A conjugated system requires that there is a continuous array of "$\pi$" orbitals that can align to produce a bonding overlap along the whole system. If a position in the chain does not provide a "$\pi$" orbital or if geometry prevents the correct alignment, then the conjugation is broken at that point.

The result of conjugation is that there are extra $\pi$ bonding interactions between the adjacent $\pi$ systems that results in an overall stabilisation of the system.
Conjugation = most efficient means of bringing about a bathochromic and hyperchromic shift of an unsaturated chromophore:

\[
\begin{array}{c}
H_2C=CH_2 \\
\cdots \\
\cdots \\
\beta\text{-carotene} \\
\end{array}
\]

\[
\begin{array}{c|c|c}
\lambda_{max} (nm) & \varepsilon \\
175 & 15,000 \\
217 & 21,000 \\
258 & 35,000 \\
465 & 125,000 \\
\end{array}
\]

\[
\begin{array}{c}
\begin{array}{c}
\text{\(n \rightarrow \pi^*\)} \\
\text{280} \\
\text{12} \\
\text{\(n \rightarrow \pi^*\)} \\
\text{280} \\
\text{27} \\
\text{\(\pi \rightarrow \pi^*\)} \\
\text{189} \\
\text{900} \\
\text{\(\pi \rightarrow \pi^*\)} \\
\text{213} \\
\text{7,100} \\
\end{array}
\end{array}
\]
Base value: 215 nm
2 additional conjugated double bonds: 60 nm
Exocyclic double bond: 5 nm
Homoannular diene system: 39 nm
C-substituent in β: 12 nm
3 additional C-substituents: 54 nm
Solvent correction: 0 nm

Estimated: 385 nm (ethanol)
Determined: 388 nm (ethanol)

Base value (homoannular): 253 nm
Additional conjugated double bond: 30 nm
Exocyclic double bond: 5 nm
3 C-substituents: 15 nm

Estimated: 303 nm
Determined: 306 nm
UV-Vis Selection rules:

1. Spin rule: Changes in spin multiplicity are forbidden
   Therefore, transitions between states with different multiplicity are forbidden

   allowed transitions: singlet → singlet or triplet → triplet
   forbidden transitions: singlet → triplet or triplet → singlet

Always there is a weak interaction between different wave functions due to the multiplicity spin-orbit coupling. Therefore the wave function corresponding to the singlet state containing a small fraction of the triplet wave function and vice versa. This leads to the occurrence of singlet-triplet transitions (intersystem crossing) with very low absorption coefficient, but still noticeable.
2. **Laporte rule**: In an electronic transition there must be a change in the parity (symmetry)

Therefore, a transition may be forbidden for symmetry reasons.

Electric dipole transition can occur only between states of opposite parity.

allowed transitions: \( g \rightarrow u \) or \( u \rightarrow g \)
forbidden transitions: \( g \rightarrow g \) or \( u \rightarrow u \)

\( g \) (gerade = even), \( u \) (ungerade = odd)

A symmetry forbidden transition may be observed due to vibronic coupling (result in a far from perfect symmetry).

Molar absorptivity is **very small** and the corresponding absorption bands have well-defined vibronic bands

Example: \( n \rightarrow \pi^* \) transitions of most solvents that can not form hydrogen bonds. \( (\varepsilon \sim 100\text{–}1000 \text{ L/mol} \cdot \text{cm}) \)