UV-Vis spectroscopy
The electromagnetic spectrum

**Visible**
- Frequency: $10^{15} - 10^{16}$ Hz

**Ultraviolet**
- Frequency: $10^{16} - 10^{17}$ Hz

source: Andor.com
UV-vis spectroscopy

- Use of ultraviolet and visible radiation
- Electron excitation to excited electronic level (electronic transitions)
- Identifies functional groups (-(C=C)_n-, -C=O, -C=N, etc.)
- Access to molecular structure and oxidation state

**Pros**
- Economic
- Non-invasive (fiber optics!)
- Versatile (e.g., solid, liquid, gas)
- Extremely sensitive (concentration)
- Fast acquisition (but S/N!)

**Cons**
- No atomic resolution
- Broad signals (spectral resolution, multiple overlapping components)
Electronic transitions

Organic molecule

- empty
- lone pairs
- occupied

bonding

$E = h \nu$

high e\(^{-}\) jump $\rightarrow$ high $E$

high $E$ $\rightarrow$ high $\nu$

$\lambda = c / \nu$

high $\nu$ $\rightarrow$ low $\lambda$
Electronic transitions

Condition to absorb light (200-800 nm):

- $\pi$ and/or $n$ orbitals

$\pi \rightarrow \pi^*$
200-700 nm, intense

$\sigma \rightarrow \sigma^*$
high $E$, low $\lambda$ (<200 nm)

$n \rightarrow \sigma^*$
150-250 nm, weak

$n \rightarrow \pi^*$
200-700 nm, weak
The UV spectrum

The UV spectrum shows a peak at 217 nm, indicating no visible light absorption.

The UV spectrum is characterized by vibrational, rotational, and electronic energy transitions. The signal envelope is shown for the CH₃-CH=O molecule.

How many signals do you expect from CH₃-CH=O?
The UV spectrum

- Conjugation effect

(delocalisation)

\[
\begin{array}{cccc}
\lambda_{\text{max}} & \lambda & \nu & E \\
171 & 217 & 258 & \\
\end{array}
\]

\[
\begin{array}{ccc}
\text{C}_2\text{H}_4 & \text{C}_4\text{H}_6 & \text{C}_6\text{H}_8 \\
\text{π}^* & \text{π} & e \\
\text{π} & e & \\
\end{array}
\]
**The UV spectrum**

- **Conjugation effect:** β-carotene

![UV spectrum diagram](image)
The UV spectrum

- Complementary colours

If a colour is absorbed by white light, what the eye detects by mixing all other wavelengths is its complementary colour.
Inorganic compounds

- UV-vis spectra of transition metal complexes originate from

  - **Electronic \(d-d\) transitions**

  - Degenerate \(d\)-orbitals
  - TM + ligand
  - \(e_g\) to \(t_{2g}\)
  - \(\Delta\)
  - \(d_\sigma\)
  - \(d_\pi\)
**Inorganic compounds**

- **Crystal field theory (CFT) - electrostatic model**
  - same electronic structure of central ion as in isolated ion
  - perturbation only by negative charges of ligand
  - ionic bonds

\[ \Delta = \text{crystal field splitting} \]
**Inorganic compounds**

- **d-d transitions**: \( \text{Cu(H}_2\text{O)}_6^{2+} \)

Yellow light is absorbed and the Cu\(^{2+} \) solution is coloured in blue (ca. 800 nm).

- The greater \( \Delta \), the greater the \( E \) needed to promote the e\(^- \), and the shorter \( \lambda \).

- \( \Delta \) depends on the nature of ligand, \( \Delta_{\text{NH}_3} > \Delta_{\text{H}_2\text{O}} \)
Inorganic compounds

- \( \text{TM(H}_2\text{O)}_6^{n+} \)

<table>
<thead>
<tr>
<th>elec. config. TM</th>
<th>Ti(H(_2\text{O})_6^{3+}</th>
<th>\text{Ti(H}_2\text{O)}_6^{3+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>gas complex</td>
<td>( t_{2g}^1 )</td>
<td>( t_{2g}^1 )</td>
</tr>
<tr>
<td></td>
<td>( t_{2g}^1 )</td>
<td>( t_{2g}^1 )</td>
</tr>
<tr>
<td></td>
<td>( t_{2g}^3 )</td>
<td>( t_{2g}^3 )</td>
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<td></td>
<td>( t_{2g}^3 )</td>
<td>( t_{2g}^3 )</td>
</tr>
<tr>
<td></td>
<td>( t_{2g}^3 e_g^1 )</td>
<td>( t_{2g}^3 e_g^1 )</td>
</tr>
<tr>
<td></td>
<td>( t_{2g}^3 e_g^2 )</td>
<td>( t_{2g}^3 e_g^2 )</td>
</tr>
<tr>
<td></td>
<td>( t_{2g}^6 e_g^3 )</td>
<td>( t_{2g}^6 e_g^3 )</td>
</tr>
</tbody>
</table>

\( d-d \) transitions: \( \epsilon_{\text{max}} = 1 - 100 \text{ Lmol}^{-1}\text{cm}^{-1} \), weak (selection rule: forbidden transition)
Inorganic compounds

- **d-d transitions**: factors governing magnitude of $\Delta$
  
  - **Oxidation state of metal ion**
    - $\Delta$ increases with increasing ionic charge on metal ion
  
  - **Nature of metal ion**
    - $\Delta$ increases in the order $3d < 4d < 5d$
  
  - **Number and geometry of ligands**
    - $\Delta$ for tetrahedral complexes is larger than for octahedral ones
  
  - **Nature of ligands**
    - spectrochemical series
      
      $I^- < Br^- < S^{2-} < SCN^- < Cl^- < NO_3^- < N_3^- < F^- < OH^- < C_2O_4^{2-} < H_2O < NCS^- < CH_3CN < py < NH_3 < en < bipy < phen < NO_2^- < PPh_3 < CN^- < CO$
Inorganic compounds

- UV-vis spectra of transition metal complexes originate from
  - Electronic $d-d$ transitions
  - Charge transfer

- Electronic $d-d$ transitions
  - Degenerate $d$-orbitals
  - $e_g$ to $t_{2g}$ transitions
  - Charge transfer

- Charge transfer
Inorganic compounds

Charge transfer complex

- no selection rules → intense colours ($\varepsilon = 50'000 \text{ Lmol}^{-1}\text{cm}^{-1}$, strong)

- Association of 2 or more molecules in which a fraction of electronic charge is transferred between the molecular entities. The resulting electrostatic attraction provides a stabilizing force for the molecular complex

- **Electron donor**: source molecule
  - **Electron acceptor**: receiving species

- **Ligand field theory** (LFT), based on MO
  - Metal-to-ligand transfer (MLCT)
  - Ligand-to-metal transfer (LMCT)
Inorganic compounds

- **Ligand field theory (LFT)**
  - involves AO of metal and ligand, therefore MO
  - what CFT indicates as possible electronic transitions ($t_{2g} \rightarrow e_g$) are now: $\pi_d \rightarrow \sigma_{dz^2}$ or $\pi_d \rightarrow \sigma_{dx^2-y^2}$

$\Delta = \text{crystal field splitting}$
Inorganic compounds

- **Ligand field theory (LFT)**
  - **LMCT**
    - ligand with high energy lone pair
    - or, metal with low lying empty orbitals
    - *high oxidation state* (also d°)
    - M-L strengthened
  
  - **MLCT**
    - ligands with low lying π* orbitals (CO, CN-, SCN-)
    - *low oxidation state* (high energy d orbitals)
    - M-L strengthened, π bond of L weakened

back donation!!!

CO adsorption on precious metals
Band gap

Analysis of semiconductors

TiO$_2$, 3.2 eV, 387 nm

Photocatalysis

- Reduction: $A^+ + e^- \rightarrow A^+$
- Oxidation: $B + h^+ \rightarrow B^-$

$\Delta$
Band gap

How to measure
- inflection point
- energy at exp. increase
- intercept energy axis
Metal colloids

- **Analysis of metals**
- **Localized plasmon resonance**
  - When
    - wavelength larger than metal particle
  - What
    - collective excitations of conduction electrons (plasmons)
  - limit: ca. 20-30 nm
  - $\lambda$ position depends on nature of metal
**Instrumentation**

- **Dispersive instruments**

  Measurement geometry:
  - transmission
  - diffuse reflectance

  ![Diagram of double beam spectrometer](double-beam.png)

  ![Diagram of single beam spectrometer](single-beam.png)

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In situ instrumentation

- Diffuse reflectance (DRUV)
  - time resolution (CCD camera)
  - coupling to reactors
  - 20% of light is collected
  - gas flows, pressure, vacuum
  - long meas. time
  - spectral collection (λ after λ)
  → different parts of spectrum do not represent same reaction time!!!

- Fiber optics
  - no NIR (no optical fiber > 1100 nm)
  - long term reproducibility (single beam)
  - Limited high temperature (ca. 600°C)

In situ instrumentation

- Integration sphere

- > 95% light is collected
- high reflectivity
- wide range of $\lambda$
- only homemade cells

Examples

- Determination of oxidation state: 0.1 wt% $\text{Cr}^{n+}/\text{Al}_2\text{O}_3$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Coordination geometry and oxidation state</th>
<th>Absorption bands (nm)$^a$</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_2\text{CrO}_4$ (solution)</td>
<td>$T_d$, $\text{Cr}^{6+}$</td>
<td>440 (sh, vw), 370 (s), 275 (s)</td>
<td>Yellow</td>
</tr>
<tr>
<td>$K_2\text{CrO}_4$ (solid)</td>
<td>$T_d$, $\text{Cr}^{6+}$</td>
<td>459 (s), 340 (s), 265 (s), 229 (s)</td>
<td>Yellow</td>
</tr>
<tr>
<td>$K_2\text{Cr}_2\text{O}_7$ (solution)</td>
<td>$T_d$, $\text{Cr}^{6+}$</td>
<td>440 (w), 352 (s), 255 (s)</td>
<td>Orange</td>
</tr>
<tr>
<td>$K_2\text{Cr}_2\text{O}_7$ (solid)</td>
<td>$T_d$, $\text{Cr}^{6+}$</td>
<td>526 (s, br), 332 (s), 262 (s), 229 (s)</td>
<td>Orange-red</td>
</tr>
<tr>
<td>$\text{Cr(NO}_3)_2\cdot 9\text{H}_2\text{O}$ (solution)</td>
<td>$O_h$, $\text{Cr}^{3+}$</td>
<td>575 (s), 410 (s), 303 (s)</td>
<td>Green</td>
</tr>
<tr>
<td>$\text{Cr(NO}_3)_2\cdot 9\text{H}_2\text{O}$ (solid)</td>
<td>$\text{Dist O}_h$, $\text{Cr}^{3+}$</td>
<td>575 (s), 410 (s), 304 (s), 263 (sh)</td>
<td>Green</td>
</tr>
<tr>
<td>$\text{Cr(H}_2\text{O}_6)^{2+}$ (solution)</td>
<td>$O_h$, $\text{Cr}^{2+}$</td>
<td>769 (s)</td>
<td>Blue</td>
</tr>
<tr>
<td>$\text{Cr(H}_2\text{O}_6)^{2+}$ (solid)</td>
<td>Distorted $T_d$, $\text{Cr}^{2+}$</td>
<td>1430 (s)</td>
<td>Blue</td>
</tr>
<tr>
<td>$K_2\text{CrCl}_4$ (solid)</td>
<td>Distorted $T_d$, $\text{Cr}^{2+}$</td>
<td>714 (sh), 645 (sh), 595 (s), 461 (s), 351 (s), 274 (s)</td>
<td>Green</td>
</tr>
</tbody>
</table>

$^a$: s: strong; m: medium; w: weak; vw: very weak; sh: shoulder; br: broad.

$\text{Cr}^{6+}$ (250, 370 nm) reduction in CO atmosphere

$\text{Cr}^{3+}/\text{Cr}^{2+}$

Examples

- Determination of oxidation state: 0.1 wt% Cr\textsuperscript{n+}/Al\textsubscript{2}O\textsubscript{3}

![Calibration and deconvolution diagrams]

Weckhuysen et al., Catal. Today 49 (1999) 441
Examples

0.2 wt% Cr/SA, 500°C in 18 vol% n-butane in N₂

Examples

- UV-vis probe in a pilot-scale reactor: propane dehydrogenation

Examples

- UV-vis probe in a pilot-scale reactor

- Coke formation fast on top section of reactor
- Coke is combusted fast in top section of reactor

Weckhuysen et al., Chem. Commun. 49 (2013) 1518