UV-Vis spectroscopy
The electromagnetic spectrum

- **Visible** (10^15 - 10^16 Hz)
- **Ultraviolet** (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=\text{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**
  - Anti-bonding

- **Lone pairs**
  - Presence of electrons

- **Occupied**
  - Bonding

\[ E = h \nu \]

\[ \lambda = \frac{c}{\nu} \]

- High electron jump → High \( E \)
- High \( E \) → High \( \nu \)
- High \( \nu \) → Low \( \lambda \)
Electronic transitions

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

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

Condition to absorb light (200-800 nm):

\[ n \rightarrow \pi^* \]
200-700 nm, weak

\[ \pi \rightarrow \pi^* \]
200-700 nm, intense

\[ \sigma \rightarrow \pi^* \]
\( \pi \) and/or \( n \) orbitals

\textit{CHROMOPHORE}
The UV spectrum

The UV spectrum shows a peak at 217 nm, indicating no visible light absorption. The spectrum includes energy levels for rotational and vibrational electronic states, with transitions from $\pi \rightarrow \pi^*$.

**Question:** How many signals do you expect from CH$_3$-CH=O?
The UV spectrum

- Conjugation effect
  - delocalisation

\[ \text{\textcolor{red}{\lambda_{\text{max}}}} \quad \text{\textcolor{blue}{\lambda}} \quad \text{\textcolor{green}{\nu}} \quad \text{\textcolor{purple}{E}} \]

\[ \begin{align*}
171 & \\
217 & \\
258 & 
\end{align*} \]

\[
\text{C}_2\text{H}_4 \quad \text{C}_4\text{H}_6 \quad \text{C}_6\text{H}_8
\]

- Conjugation effect
  - delocalisation

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\]
The UV spectrum

- **Conjugation effect:** β-carotene

![UV spectrum diagram]
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**

\[ \text{degenerate } d\text{-orbitals} \quad + \quad \text{ligand} \quad \rightarrow \quad \begin{array}{c}
\text{TM} \\
\text{TM}
\end{array} \]

\[ \begin{array}{c}
e_g \\
t_{2g}
\end{array} \quad \Delta \quad \begin{array}{c}
d_\sigma \\
d_\pi
\end{array} \]
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

- Inorganic compounds
  - tetrahedric field
  - octahedric field
  - tetragonal field
  - square planar field

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

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

- Yellow light is absorbed and the \( \text{Cu}^{2+} \) solution is coloured in blue (ca. 800 nm)
- The greater \( \Delta \), the greater the \( E \) needed to promote the \( \text{e}^- \), and the shorter \( \lambda \)
- \( \Delta \) depends on the nature of ligand, \( \Delta_{\text{NH}_3} > \Delta_{\text{H}_2\text{O}} \)
# Inorganic compounds

**TM(H₂O)₆ⁿ⁺**

<table>
<thead>
<tr>
<th>elec. config. TM</th>
<th>gas complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>3d⁰</td>
<td>Ti(H₂O)₆³⁺</td>
</tr>
<tr>
<td>3d¹</td>
<td>Ti(H₂O)₆³⁺</td>
</tr>
<tr>
<td>3d²</td>
<td>Cr(H₂O)₆³⁺</td>
</tr>
<tr>
<td>3d³</td>
<td>Cr(H₂O)₆²⁺</td>
</tr>
<tr>
<td>3d⁴</td>
<td>Mn(H₂O)₆²⁺</td>
</tr>
<tr>
<td>3d⁵</td>
<td>Cu(H₂O)₆²⁺</td>
</tr>
<tr>
<td>3d⁶, 3d⁷, 3d⁸</td>
<td></td>
</tr>
<tr>
<td>3d⁹</td>
<td></td>
</tr>
</tbody>
</table>

**d-d transitions:** $\varepsilon_{\text{max}} = 1 - 100 \text{ Lmol}^{-1}\text{cm}^{-1}$, weak
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
    - Degenerate $d$-orbitals
      - Transition metal $+\,$ ligand
      - $e_g \rightarrow t_{2g}$
      - $\Delta$
    - $d_{xz}$, $d_{yz}$, $d_{xy}$ orbitals
  - 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

- CT much weaker than covalent forces

- **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 (laso $d^0$)
    - M-L strengthened
  - **MLCT**
    - ligands with low lying $\pi^*$ orbitals (CO, CN⁻, SCN⁻)
    - low oxidation state (high energy $d$ orbitals)
    - M-L strengthened, $\pi$ bond of L weakened

**Diagram:**
- CO adsorption on precious metals
  - back donation!!!
Band gap

Analysis of semiconductors

TiO$_2$, 3.2 eV

Photocatalysis

A$^+$ → A$^+$

A$^+$ + 1e$^-$ → A$^+$

B$^-$→ B$^-$

B$^+$ + h$^+$ → B$^-$

Energy

Band gap

Reduction

Oxidation

Analysis of semiconductors

- TiO$_2$, 3.2 eV
Band gap

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

- Dispersive instruments

Measurement geometry:
- transmission
- diffuse reflectance

double beam spectrometer

single beam spectrometer
In situ instrumentation

- Diffuse reflectance (DRUV)
  - 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
  - time resolution (CCD camera)
    [spectra collected at once]
    - coupling to reactors
  - no NIR (no optical fiber > 1100 nm)
  - long term reproducibility (single beam)
  - Limited high temperature (ca. 600°C)

In situ instrumentation

- Integration sphere

White coated integration sphere (MgO, BaSO₄, Spectralon®)

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

for example, for cat. synthesis

Examples

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>Coordination geometry and oxidation state</th>
<th>Absorption bands (nm)\textsuperscript{a}</th>
<th>Color</th>
</tr>
</thead>
<tbody>
<tr>
<td>K\textsubscript{2}CrO\textsubscript{4} (solution)</td>
<td>T\textsubscript{d}, Cr\textsuperscript{6+}</td>
<td>440 (sh, vw), 370 (s), 275 (s)</td>
<td>Yellow</td>
</tr>
<tr>
<td>K\textsubscript{2}CrO\textsubscript{4} (solid)</td>
<td>T\textsubscript{d}, Cr\textsuperscript{6+}</td>
<td>459 (s), 340 (s), 265 (s), 229 (s)</td>
<td>Yellow</td>
</tr>
<tr>
<td>K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} (solution)</td>
<td>T\textsubscript{d}, Cr\textsuperscript{6+}</td>
<td>440 (w), 352 (s), 255 (s)</td>
<td>Orange</td>
</tr>
<tr>
<td>K\textsubscript{2}Cr\textsubscript{2}O\textsubscript{7} (solid)</td>
<td>T\textsubscript{d}, Cr\textsuperscript{6+}</td>
<td>526 (s, br), 332 (s), 262 (s), 229 (s)</td>
<td>Orange-red</td>
</tr>
<tr>
<td>Cr(NO\textsubscript{3})\textsubscript{3}-9H\textsubscript{2}O (solution)</td>
<td>O\textsubscript{h}, Cr\textsuperscript{3+}</td>
<td>575 (s), 410 (s), 303 (s)</td>
<td>Green</td>
</tr>
<tr>
<td>Cr(NO\textsubscript{3})\textsubscript{3}-9H\textsubscript{2}O (solid)</td>
<td>Dist O\textsubscript{h}, Cr\textsuperscript{3+}</td>
<td>575 (s), 410 (s), 304 (s), 263 (sh)</td>
<td>Green</td>
</tr>
<tr>
<td>Cr(H\textsubscript{2}O)\textsubscript{6}\textsuperscript{2+} (solution)</td>
<td>O\textsubscript{h}, Cr\textsuperscript{2+}</td>
<td>769 (s)</td>
<td>Blue</td>
</tr>
<tr>
<td>K\textsubscript{2}CrCl\textsubscript{4} (solid)</td>
<td>Distorted T\textsubscript{d}, Cr\textsuperscript{2+}</td>
<td>1430 (s)</td>
<td>Blue</td>
</tr>
<tr>
<td>Cr\textsubscript{2}O\textsubscript{3} (solid)</td>
<td>Distorted O\textsubscript{h}, Cr\textsuperscript{3+}</td>
<td>714 (sh), 645 (sh), 595 (s), 461 (s), 351 (s), 274 (s)</td>
<td>Green</td>
</tr>
</tbody>
</table>

\textsuperscript{a}s: strong; m: medium; w: weak; vw: very weak; sh: shoulder; br: broad.

Cr\textsuperscript{6+} (250, 370 nm)

Cr\textsuperscript{3+}/Cr\textsuperscript{2+}

reduction in CO atmosphere

**Examples**

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

**Calibration**

- \textbf{Cr\textsuperscript{6+}}
- \textbf{Cr\textsuperscript{3+}}

**Deconvolution**


- A: calc. 550° C
- B: red. 200° C
- C: red. 300° C
- D: red. 400° C
- E: red. 600° C
- F: re-calc. 550° C

**Distribution of Cr\textsuperscript{n+}**

Distribution bars for different reduction temperatures.
Examples

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

10 vol% \( \text{C}_3\text{H}_8 \), 90 vol% \( \text{N}_2 \), 5000 ml/min
20 wt% \( \text{Cr}^{3+/6+} \text{O}_x/\text{Al}_2\text{O}_3 \)

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