UV-Vis spectroscopy

Basic theory
Importance of UV-Vis in catalysis

Number of publications containing *in situ*, *catalysis*, and respective method
Source: ISI Web of Knowledge (Sept. 2008)
The electromagnetic spectrum

source: Andor.com
Typically, the wavelength (nm) is used
the distance over which the wave's shape repeats

\[ x \text{ nm} = 10'000'000 / x \text{ cm}^{-1} \]
\[ y \text{ cm}^{-1} = 10'000'000 / y \text{ nm} \]
Is UV-vis spectroscopy popular?

pros
- economic
- non-invasive (fiber optics allowed)
- versatile (e.g. solid, liquid, gas)
- extremely sensitive (concentration)

cons
- Broad signals (resolution)
- Time resolution (S/N)
What is UV-vis spectroscopy?

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

Organic molecule

Empty states

Lone pairs

Occupied states

$E = h\nu$

$\lambda = c/\nu$

High $e^-$ jump $\rightarrow$ high $E$

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

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

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

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

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

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

Condition to absorb light (200-800 nm):
\[ \pi \] and/or \( n \) orbitals

**CHROMOPHORE**
The UV spectrum

λ\text{max} = 217 nm

no visible light absorption

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

$n \rightarrow \pi^*$  $\pi \rightarrow \pi^*$

$\sigma^*$  $\pi^*$  $n (O)$  $\pi$

absorbance

wavelength (nm)
	no visible light absorption
The UV spectrum

- **Conjugation effect**

  delocalisation

  $\lambda_{\text{max}}$  $\lambda$  $\nu$  $E$

  171  217  258

**Conjugation**

- $\text{C}_2\text{H}_4$
- $\text{C}_4\text{H}_6$
- $\text{C}_6\text{H}_8$
The UV spectrum

- **Conjugation effect:** β-carotene

![Chemical structure of β-carotene](image)

![UV spectrum graph](image)

- **White light**
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

  ![Diagram showing electronic transitions in transition metal complexes](image)

  - Degenerate $d$-orbitals
  - Transition metal (TM) + ligand
  - $e_g$ to $t_{2g}$ transition
  - Energy difference $\Delta$
  - $d_{\sigma}$ and $d_{\pi}$ orbitals

- ...
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

\[
\Delta = \text{crystal field splitting}
\]

- Atom in spherical field
- Gaseous atom
- \(d_{xy}, d_{xz}, d_{yz}\)
- \(d_{x^2-y^2}, d_{z^2}\)
- \(d_{xy}, d_{xz}, d_{yz}\)
- \(d_{x^2-y^2}, d_{z^2}\)
- \(d_{xy}\)
- \(d_{xy}, d_{xz}, d_{yz}\)
- \(d_{y^2}, d_{xz}\)
- \(d_{yz}\)
- \(d_{x^2-y^2}, d_{z^2}\)
- \(\Delta\)
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

- **TM(H₂O)₆ⁿ⁺**

<table>
<thead>
<tr>
<th>elec. config. TM</th>
<th>gas complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>3d⁴</td>
<td>Cr(H₂O)₆³⁺</td>
</tr>
<tr>
<td>3d⁵</td>
<td>Mn(H₂O)₆²⁺</td>
</tr>
<tr>
<td>3d⁶</td>
<td>V⁴⁺</td>
</tr>
<tr>
<td>3d⁷</td>
<td>Cu(H₂O)₆²⁺</td>
</tr>
<tr>
<td>3d⁸</td>
<td>Ti(H₂O)₆³⁺</td>
</tr>
<tr>
<td>3d⁹</td>
<td>Ti(H₂O)₆³⁺</td>
</tr>
</tbody>
</table>

$d$-$d$ transitions: $\epsilon_{\text{max}} = 1 - 100 \text{ Lmol}^{-1}\text{cm}^{-1}$, 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

- **d-d transitions**: selection rules

- **Spin rule**: \( \Delta S = 0 \)
  - On promotion, no change of spin

- **Laporte's rule**: \( \Delta l = \pm 1 \)
  - \( d-d \) transition of complexes with center of symmetry are forbidden

- Because of selection rules, colours are faint (\( \varepsilon = 20 \text{ Lmol}^{-1}\text{cm}^{-1} \)).
Inorganic compounds

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

  - 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

back donation!!!

CO adsorption on precious metals
UV-Vis spectroscopy

Instrumentation
Examples for catalysis

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Instrumentation

- **Dispersive instruments**

  Measurement geometry:
  - transmission
  - diffuse reflectance

  ![Diagram of a double beam spectrometer](image1.png)

  ![Diagram of a single beam spectrometer](image2.png)
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, BaSO$_4$, 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⁺⁺/Al₂O₃**

![Table showing coordination geometry and oxidation state of various compounds with their absorption bands and colors.]

- Cr⁶⁺ (250, 370 nm)
- Reduction in CO atmosphere

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Examples

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

Weckhuysen et al., Catal. Today \textbf{49} (1999) 441
Examples

- Determination of oxidation state: 0.2 wt% Cr\textsuperscript{n+}/SiO\textsubscript{2}

* decomposition into pure components (including noise)

Examples

- Determination of oxidation state: 0.5 wt% Cr\textsuperscript{n+}/SiO\textsubscript{2}

DRUV, 350°C, 2% isobutane-N\textsubscript{2}

pure components

Examples

- **Determination of oxidation state: 4 wt% Cr\(^{n+}/\text{Al}_2\text{O}_3**

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**K-M intensity**

- **Hydrated** calcined 550°C reduced 550°C
- **C\(_3\)H\(_8\)**, 21 sec
- **C\(_3\)H\(_8\)**, 6 min

**K-M intensity**

- **Cr\(^{6+}\)**
- **Cr\(^{3+}\)**

**Wavenumber (cm\(^{-1}\))**

- **Calc. 850°C, O\(_2\)**
- **He**
- **C\(_3\)H\(_8\)**, 21 sec
- **C\(_3\)H\(_8\)**, 6 min

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**in situ DRS**

- 20 scans, 50 msec

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Examples

- Comparison of techniques: x wt% Cr\textsuperscript{n+}/support

Examples

- Reactivity of V/TiO₂ after oxidative treatment

Brückner et al., Catal. Today 113 (2006) 16
Examples

- Reactivity of V/TiO$_2$ after oxidative treatment

UV-vis: V$^{5+}$ CT (UV)
V$^{4+}$ d-d transitions (vis)

Examples

- Determination of speciation: Fe species in Fe-ZSM5

hydrated samples
- isolated Fe$^{3+}$
- oligomeric Fe$_x$O$_y$
- extended F$_2$O$_3$-like clusters

calcination @ 600°C