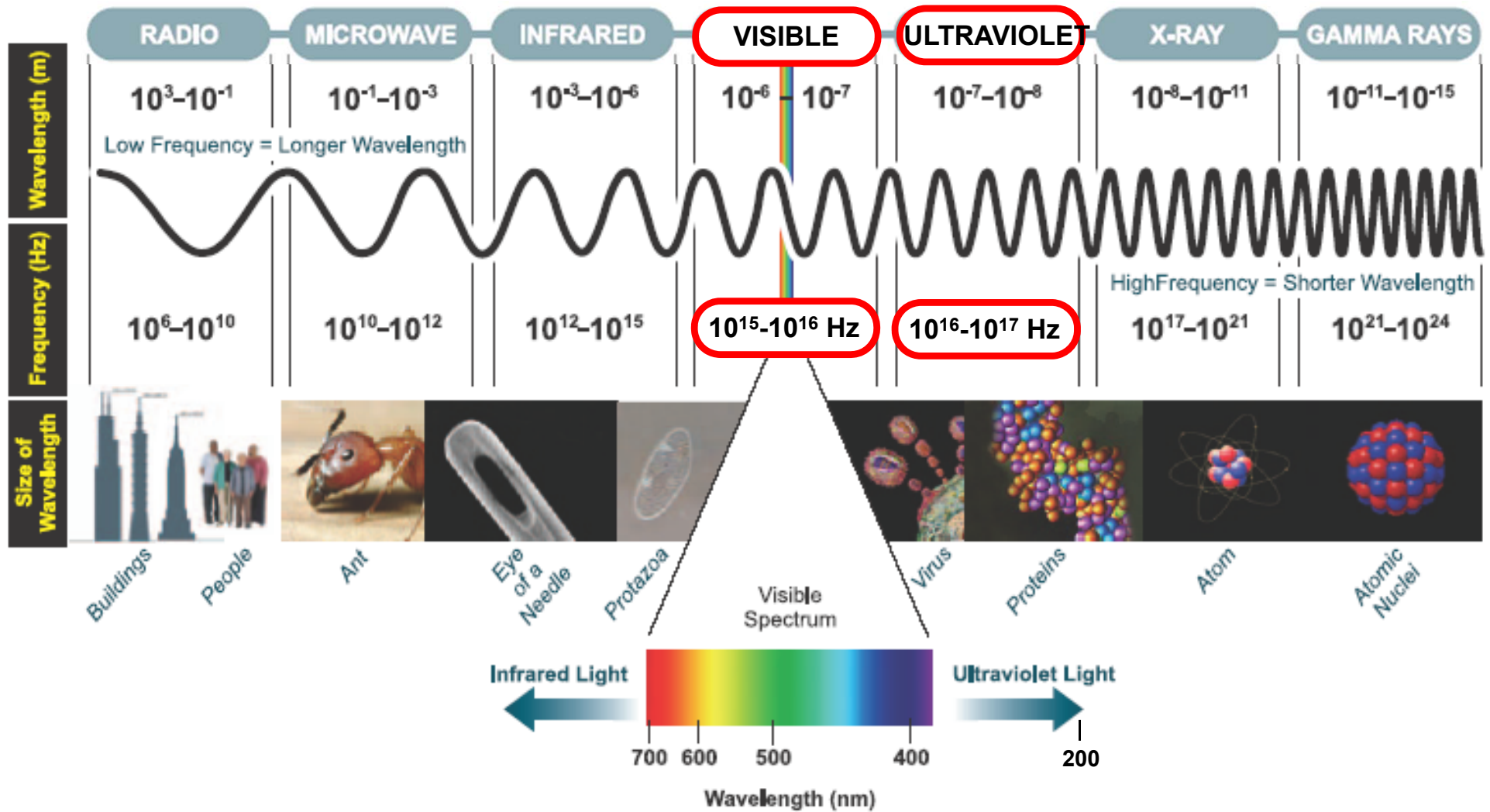


# UV-Vis spectroscopy

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# The electromagnetic spectrum



# UV-vis spectroscopy

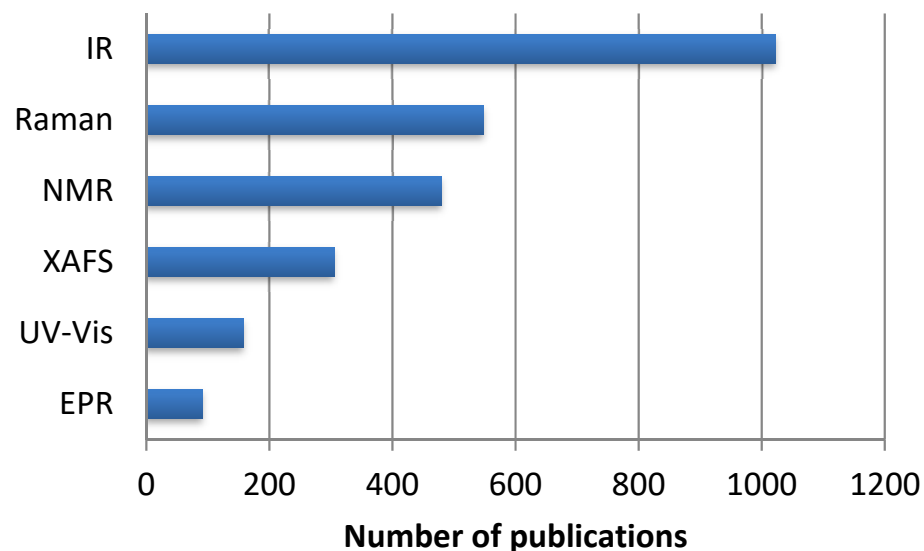
- Use of **ultraviolet** and **visible** radiation
- Electron excitation to excited electronic level (**electronic transitions**)
- Identifies functional groups ( $-(C=C)_n-$ ,  $-C=O$ ,  $-C=N$ , etc.)
- Access to molecular structure and oxidation state

## pros

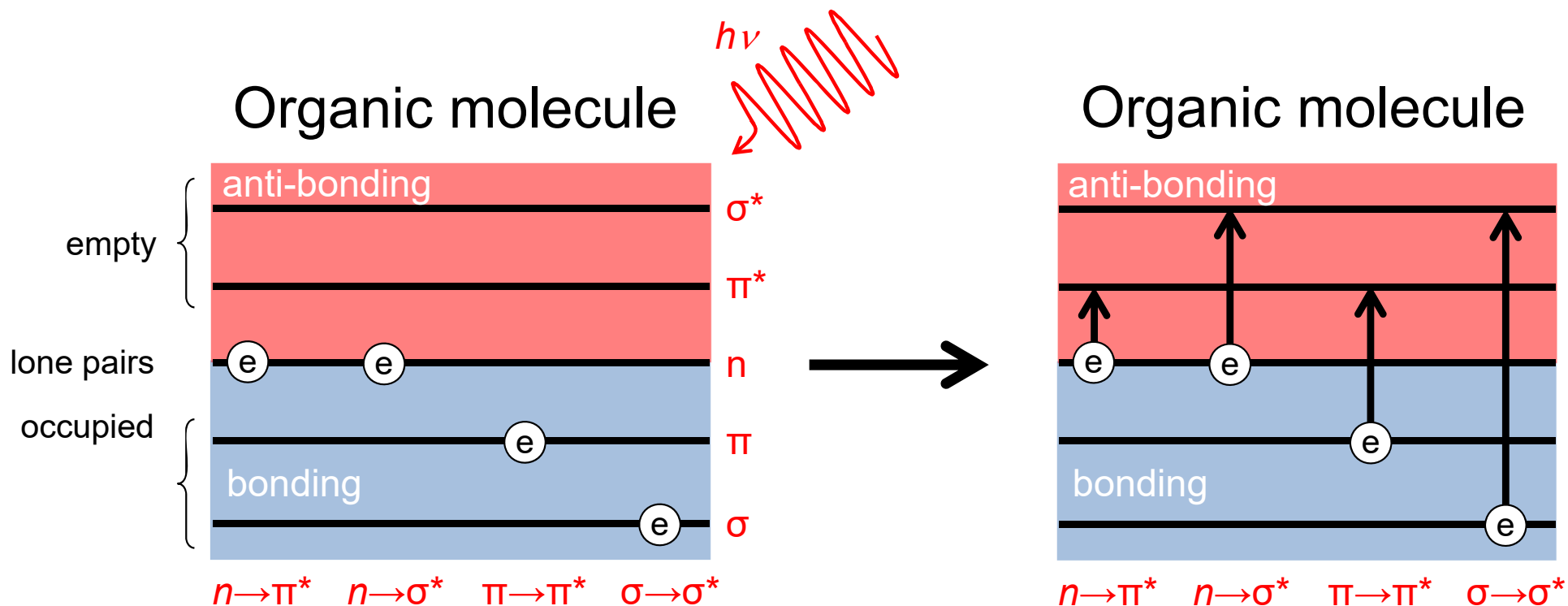
- economic
- non-invasive (fiber optics!)
- versatile (e.g. solid, liquid, gas)
- extremely sensitive (concentration)
- fast acquisition (but S/N!)

## cons

- no atomic resolution
- broad signals (spectral resolution, multiple overlapping components)



# Electronic transitions



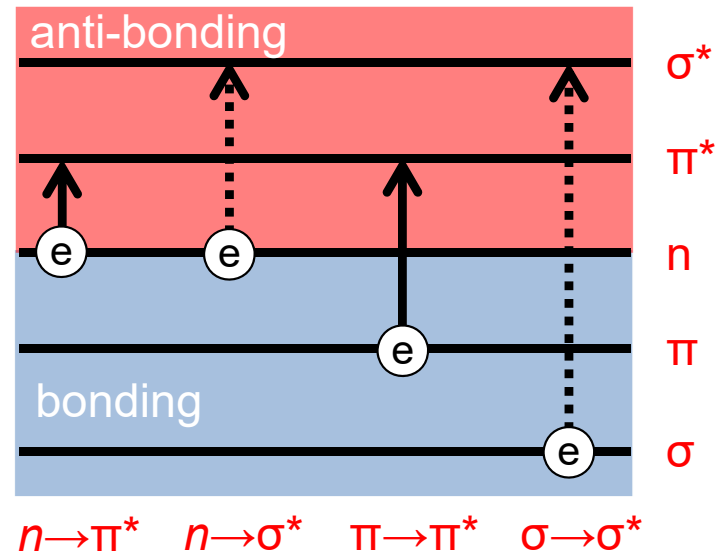
$$E = h\nu$$

$$\lambda = c/\nu$$

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**

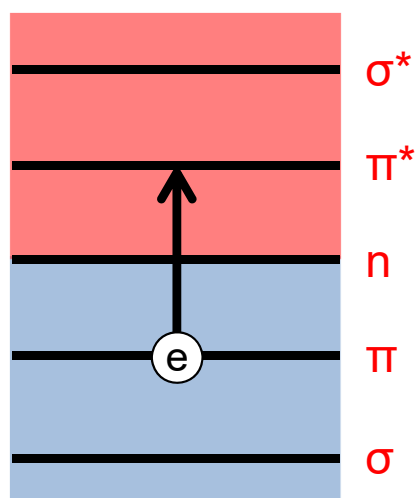
$\pi \rightarrow \pi^*$   
**200-700 nm, intense**

Condition to absorb light  
(200-800 nm):

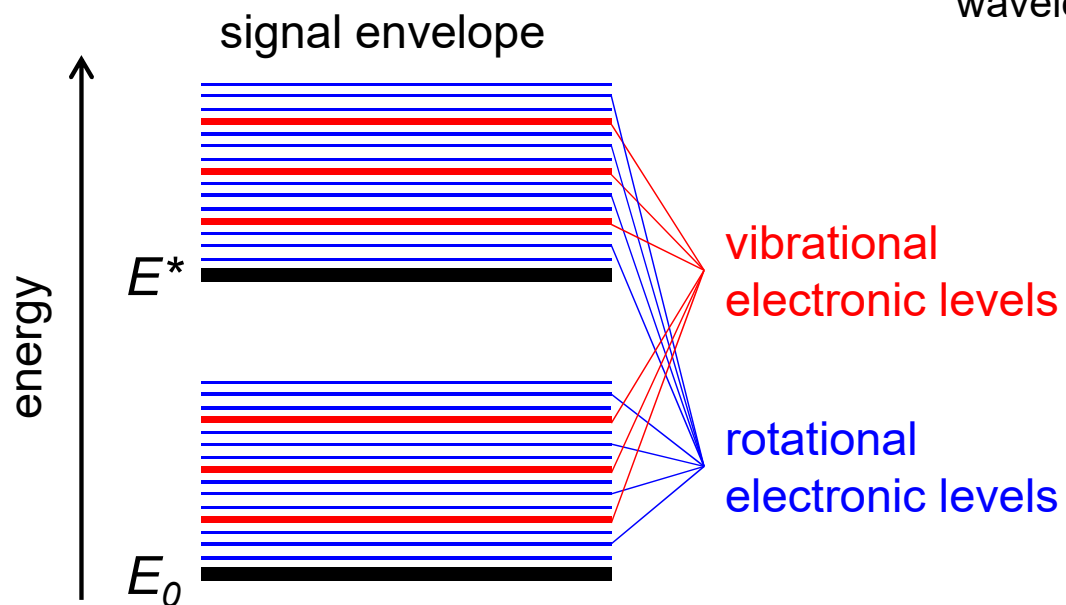
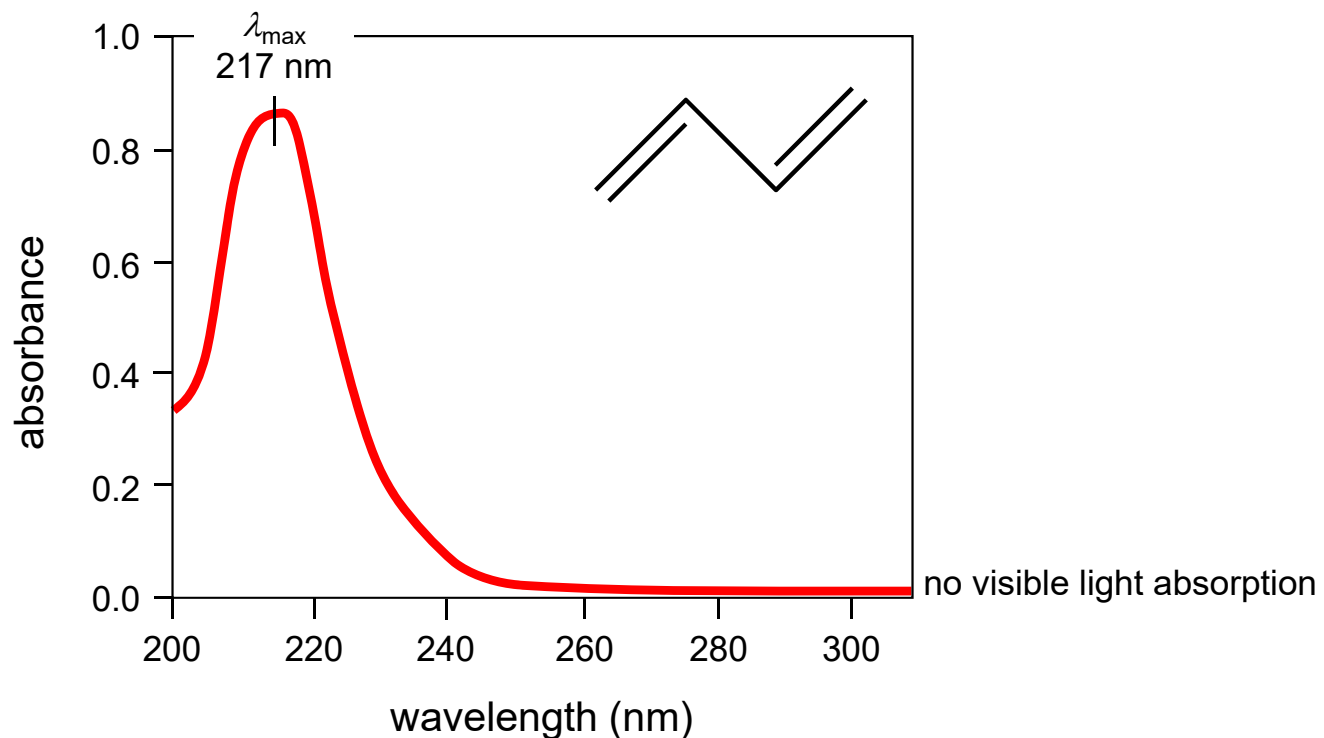
$\pi$  and/or  $n$  orbitals

**CHROMOPHORE**

# The UV spectrum



$\pi \rightarrow \pi^*$



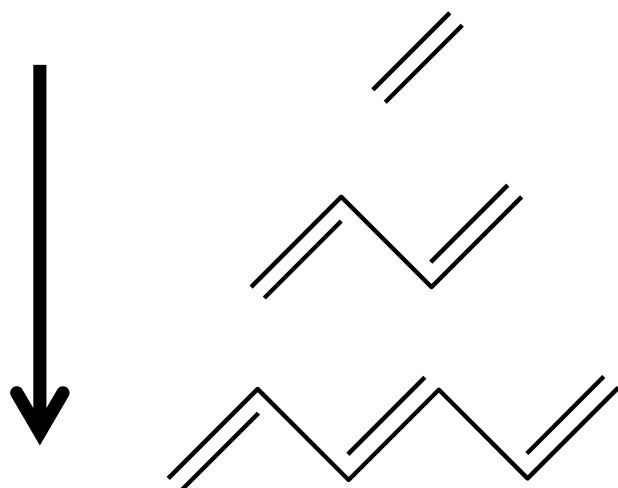
Q

How many signals do you expect from  $\text{CH}_3\text{-CH=O}$ ?

# The UV spectrum

## ■ Conjugation effect

delocalisation



$\lambda_{\max}$

171

217

258

$\lambda$



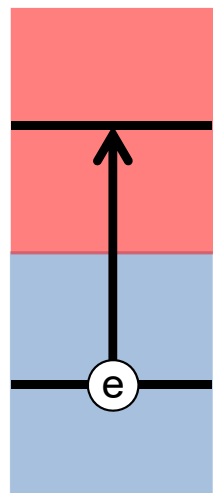
$\nu$



$E$



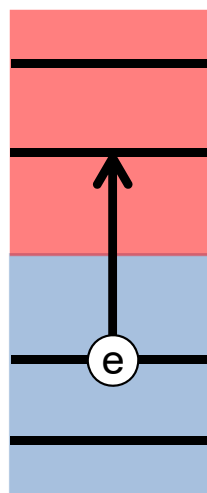
$C_2H_4$



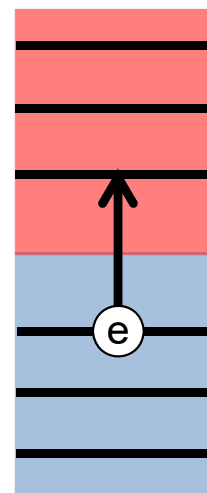
$C_4H_6$

$\pi^*$

$\pi$

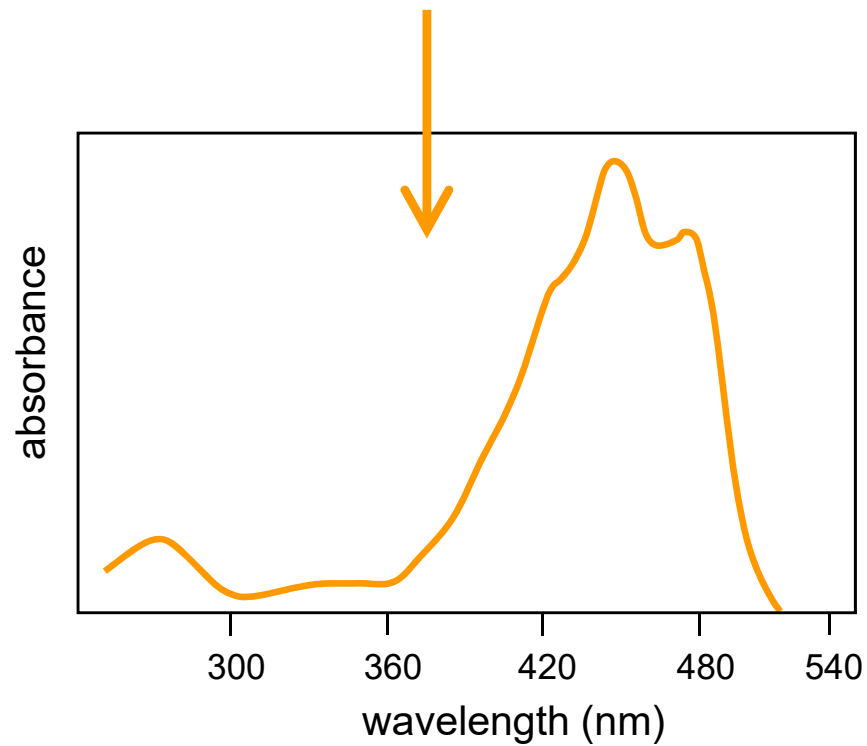
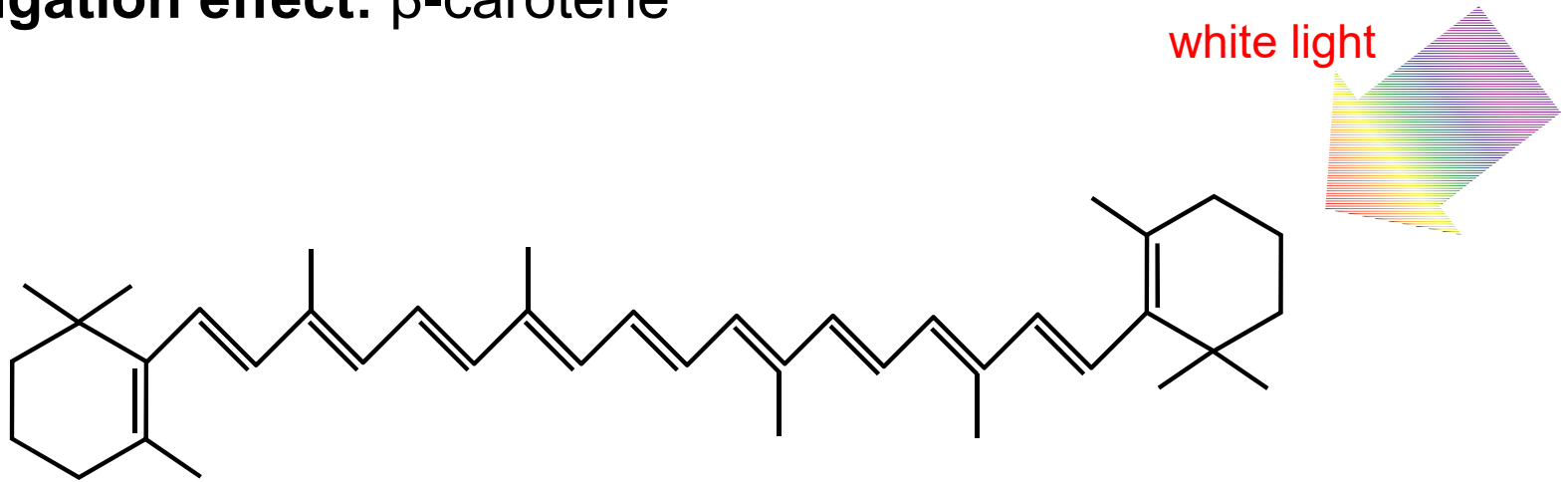


$C_6H_8$



# The UV spectrum

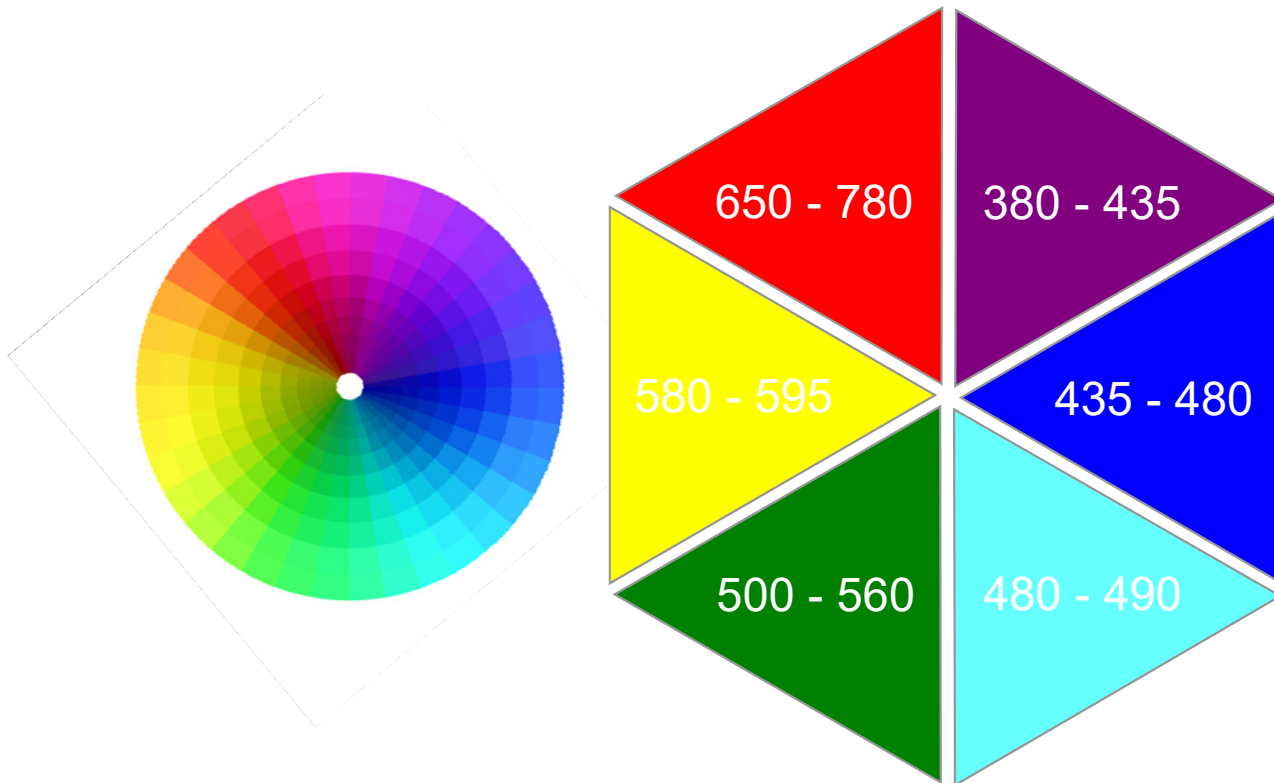
## ■ Conjugation effect: $\beta$ -carotene





# The UV spectrum

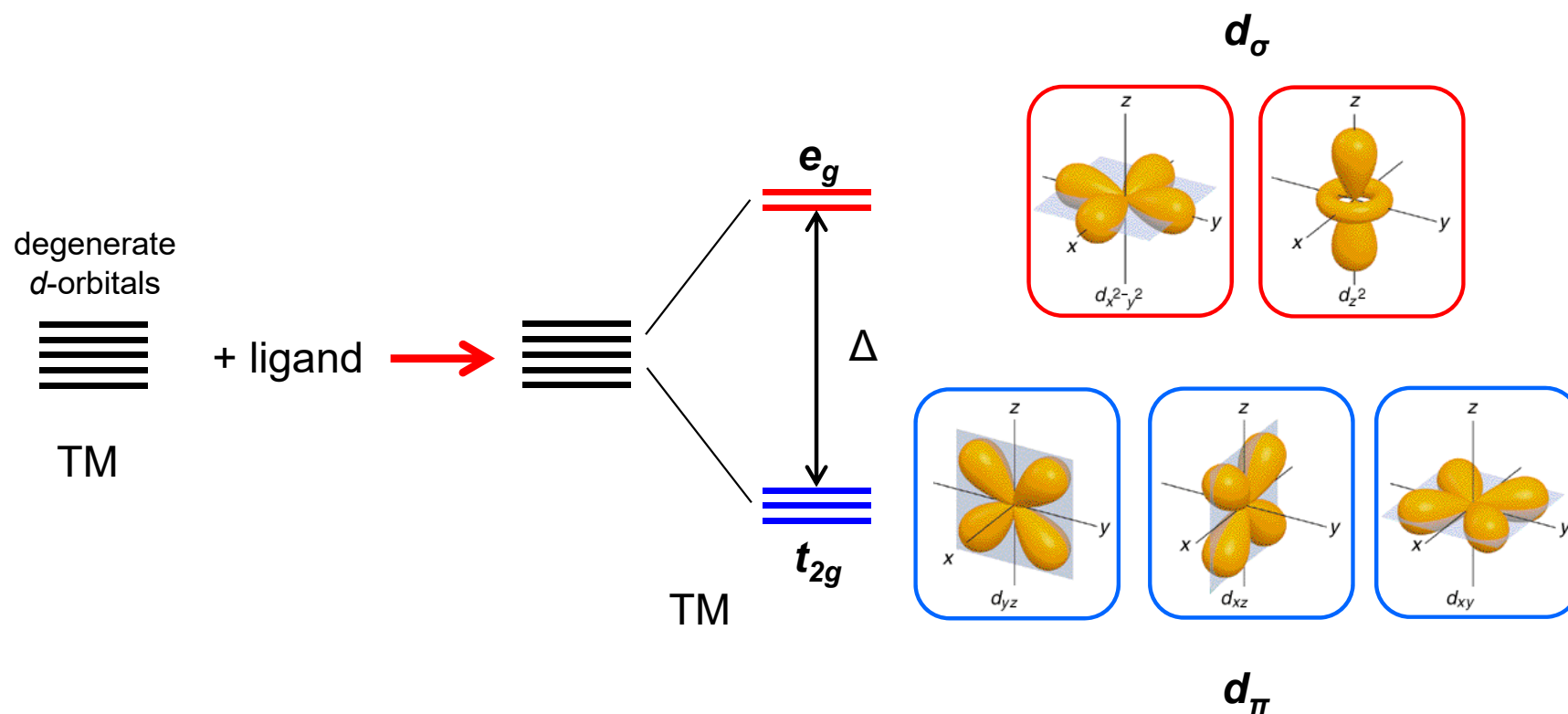
## ■ Complementary colours



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

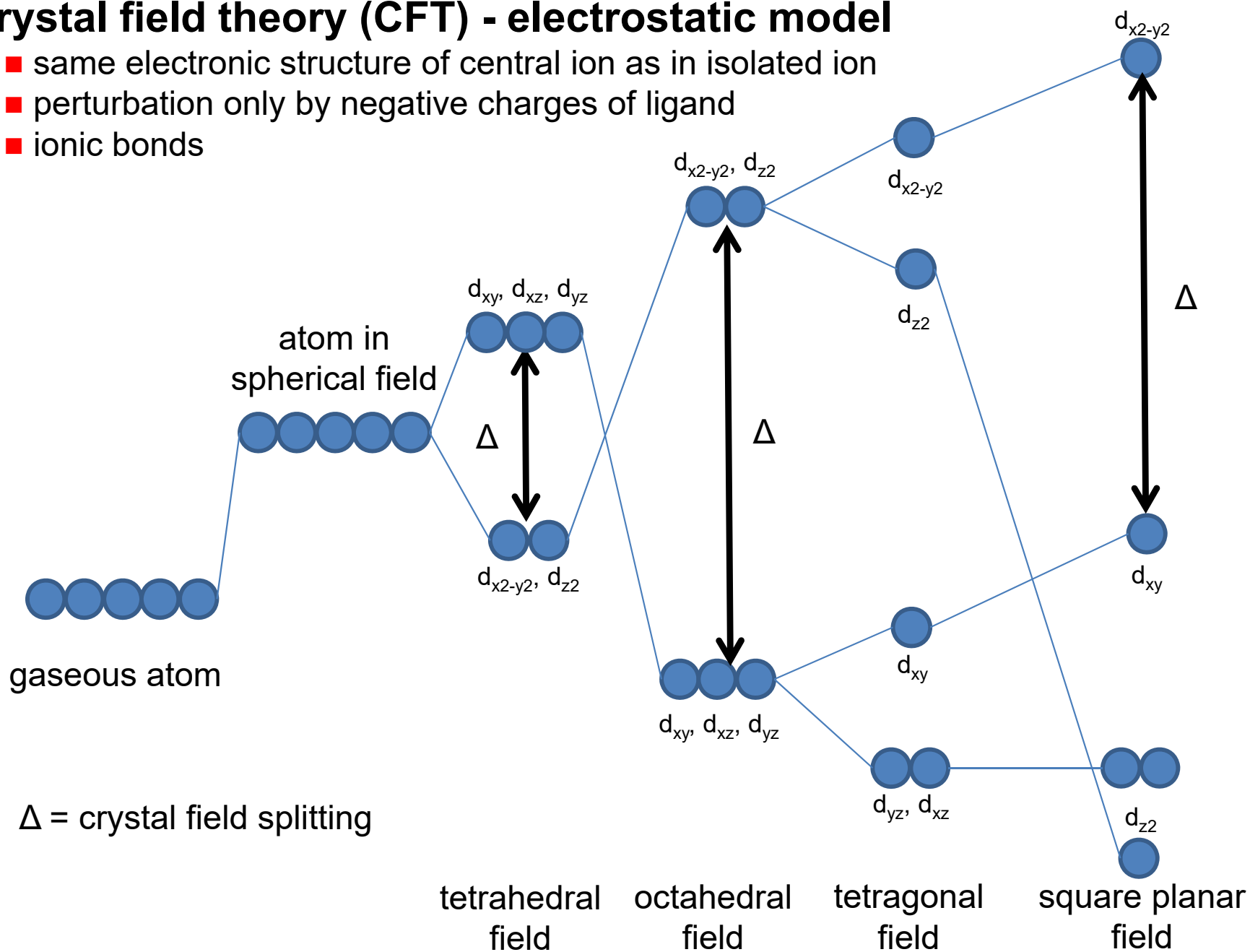


■ ...

# Inorganic compounds

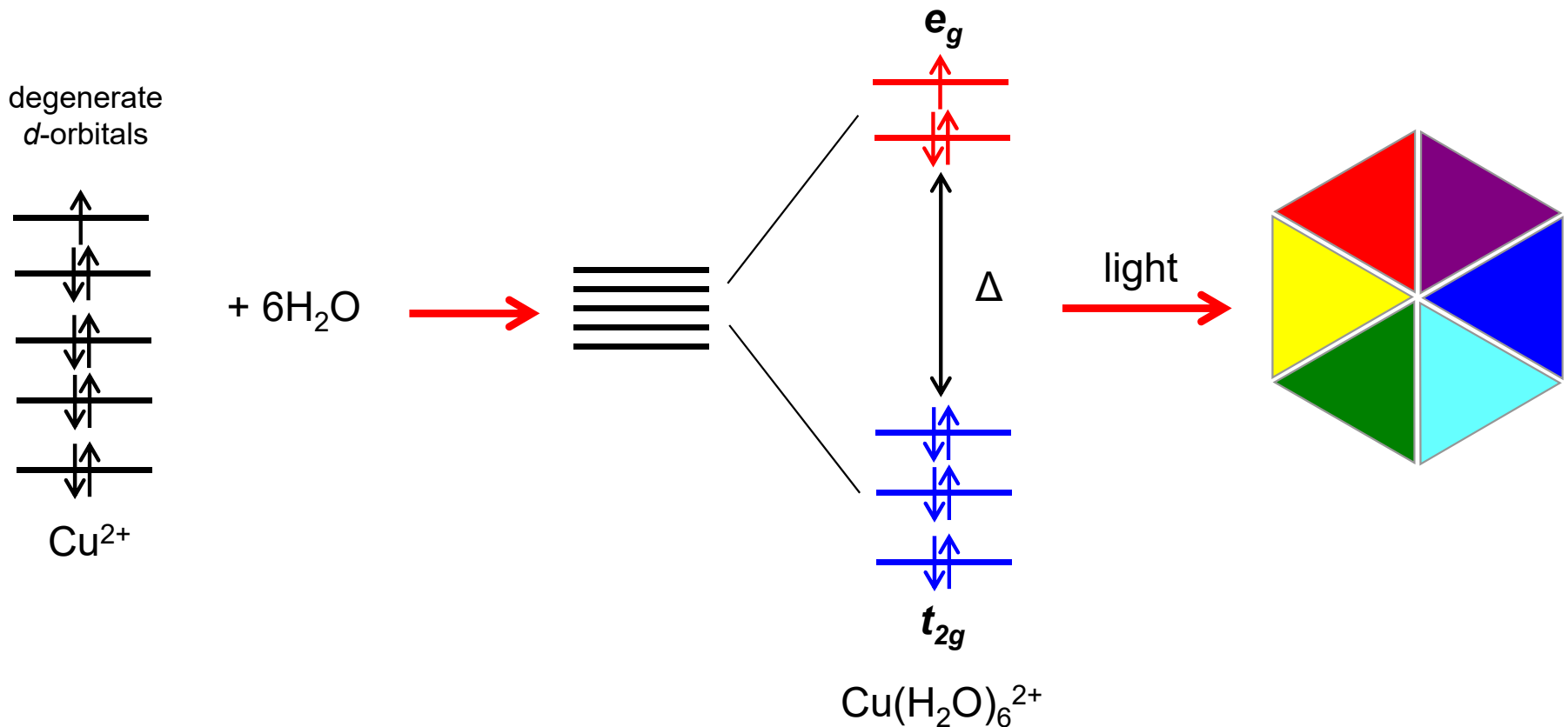
## ■ Crystal field theory (CFT) - electrostatic model

- same electronic structure of central ion as in isolated ion
- perturbation only by negative charges of ligand
- ionic bonds



# 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  $e^-$ , and the shorter  $\lambda$
- $\Delta$  depends on the nature of ligand,  $\Delta_{\text{NH}_3} > \Delta_{\text{H}_2\text{O}}$

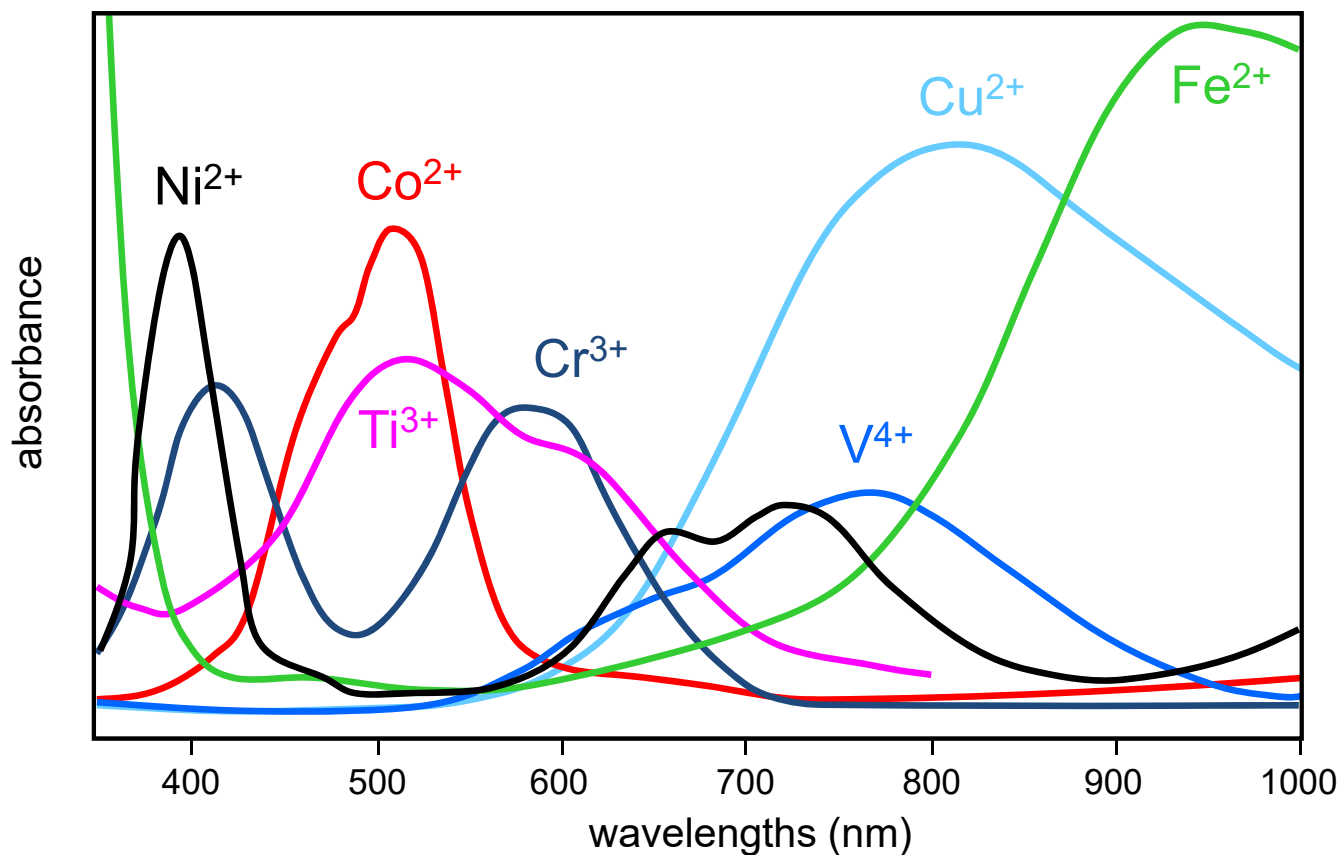
# Inorganic compounds

## ■ $\text{TM}(\text{H}_2\text{O})_6^{n+}$

elec. config. TM

gas complex

$3d^1$	$t_{2g}^1$	$\text{Ti}(\text{H}_2\text{O})_6^{3+}$
$3d^2$	$t_{2g}^2$	$\text{Ti}(\text{H}_2\text{O})_6^{3+}$
$3d^3$	$t_{2g}^3$	$\text{Cr}(\text{H}_2\text{O})_6^{3+}$
$3d^4$	$t_{2g}^3 e_g^1$	$\text{Cr}(\text{H}_2\text{O})_6^{2+}$
$3d^5$	$t_{2g}^3 e_g^2$	$\text{Mn}(\text{H}_2\text{O})_6^{2+}$
$3d^6$		
$3d^7$		
$3d^8$		
$3d^9$	$t_{2g}^6 e_g^3$	$\text{Cu}(\text{H}_2\text{O})_6^{2+}$



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

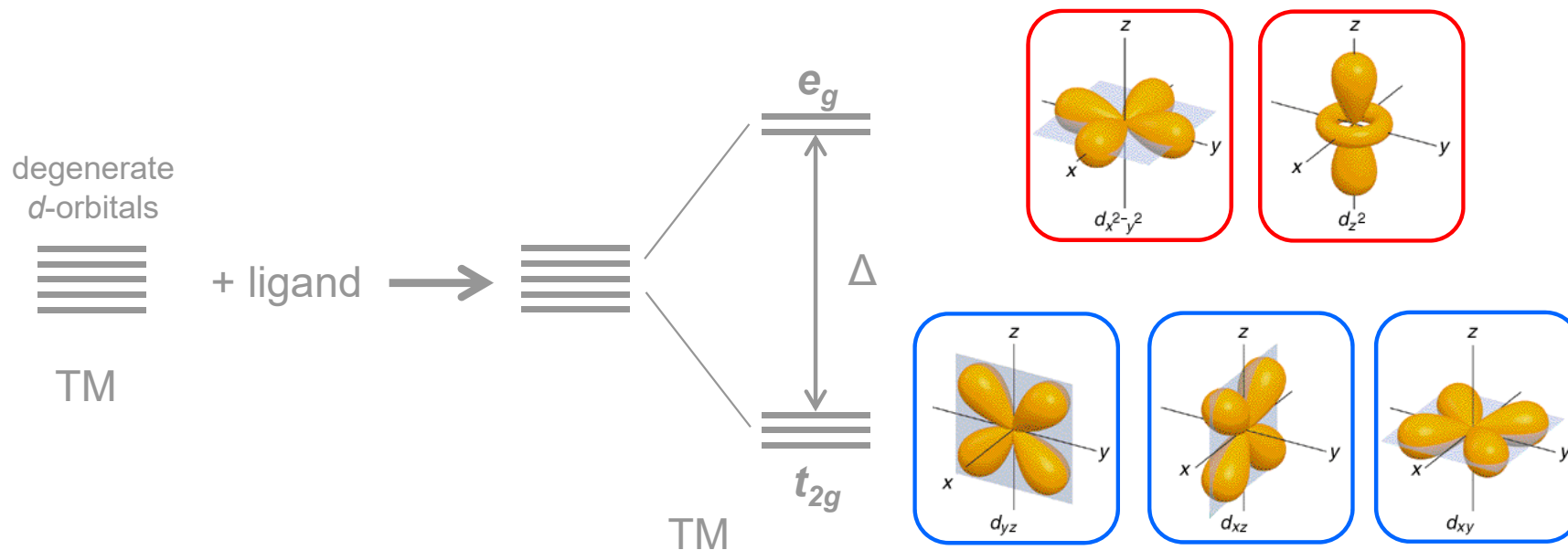
# Inorganic compounds

- ***d-d* transitions:** factors governing magnitude of  $\Delta$ 
  - **Oxidation state of metal ion**
    - $\Delta$  increases with increasing oxidation state
  - **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

# Inorganic compounds

## ■ Charge transfer complex

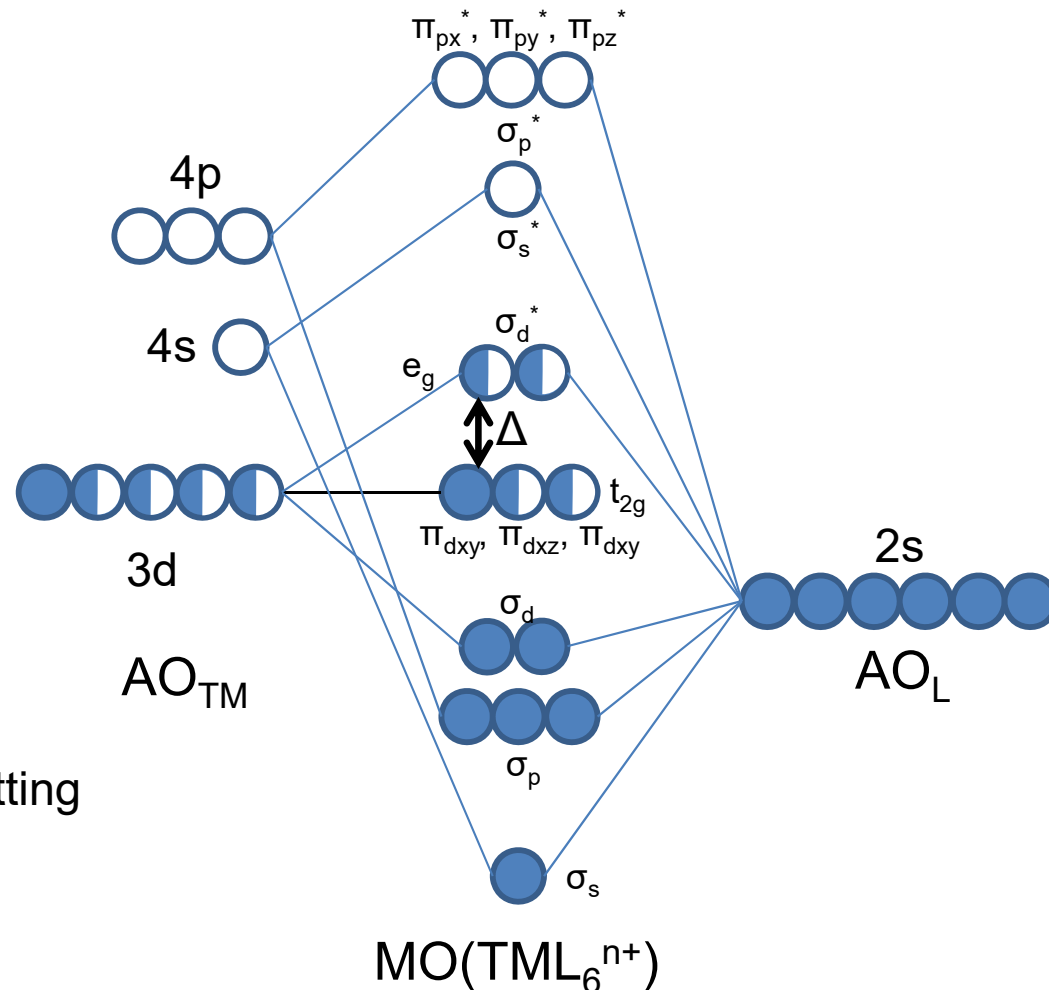
- no selection rules → intense colours ( $\epsilon = 50'000 \text{ Lmol}^{-1}\text{cm}^{-1}$ , **strong**)
- Association of 2 or more molecules in which a fraction of electronic charge is transferred between the molecular entities. The resulting electrostatic attraction provides a stabilizing force for 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  $\pi_d \rightarrow \sigma_{dx^2-y^2}^*$



$\Delta$  = crystal field splitting

# Inorganic compounds

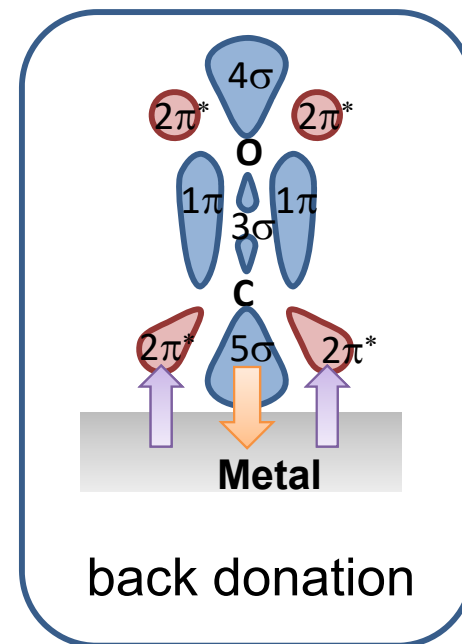
## ■ Ligand field theory (LFT)

### ■ LMCT

- ligand with high energy lone pair
- or, metal with low lying empty orbitals
- *high oxidation state* (also  $d^0$ )
- M-L strengthened

### ■ MLCT

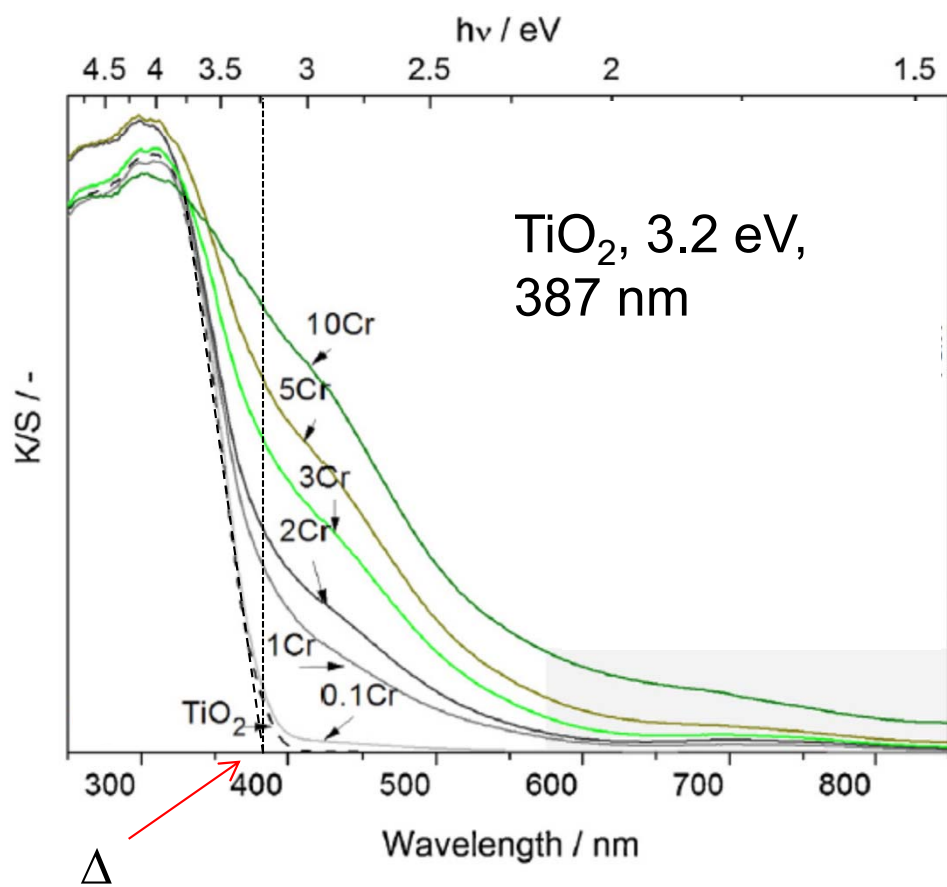
- ligands with low lying  $\pi^*$  orbitals (CO,  $\text{CN}^-$ ,  $\text{SCN}^-$ )
- *low oxidation state* (high energy d orbitals)
- M-L strengthened,  $\pi$  bond of L weakened



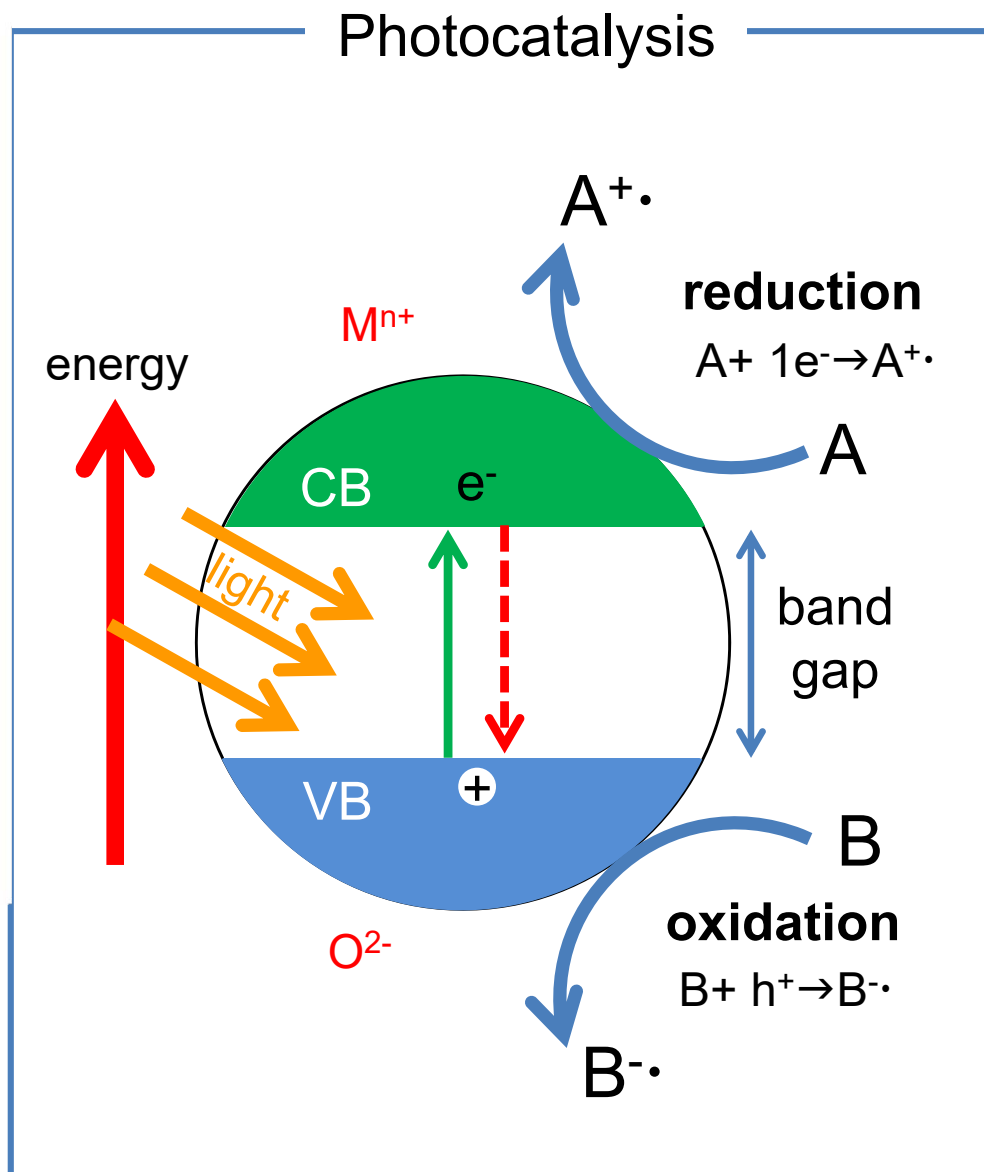
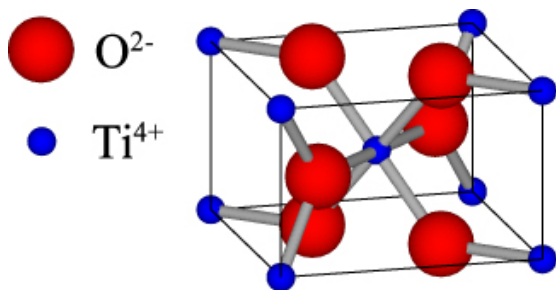
CO adsorption on  
precious metals

# Band gap

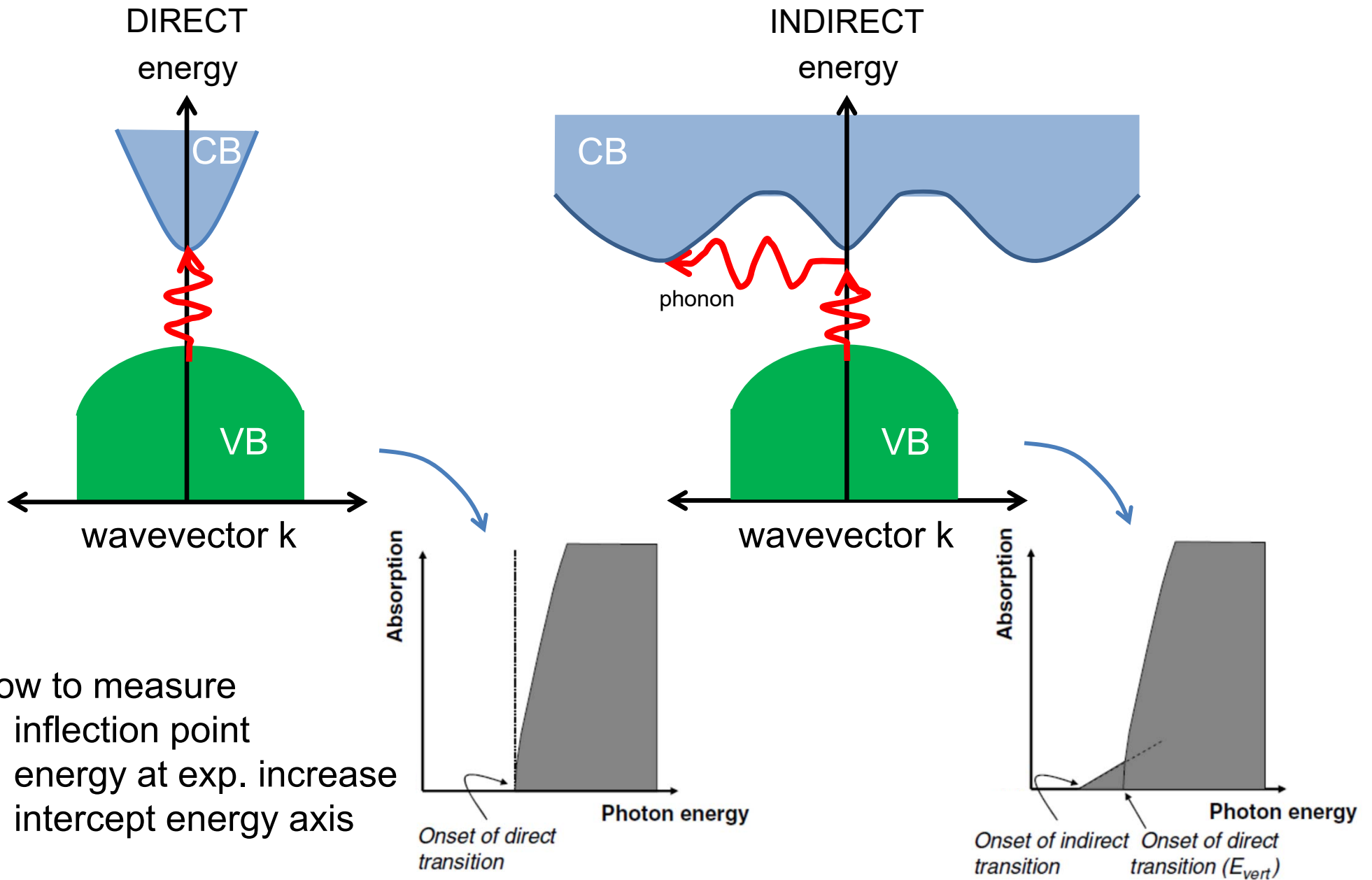
## ■ Analysis of semiconductors



$\text{TiO}_2$ , 3.2 eV,  
387 nm



# Band gap



How to measure

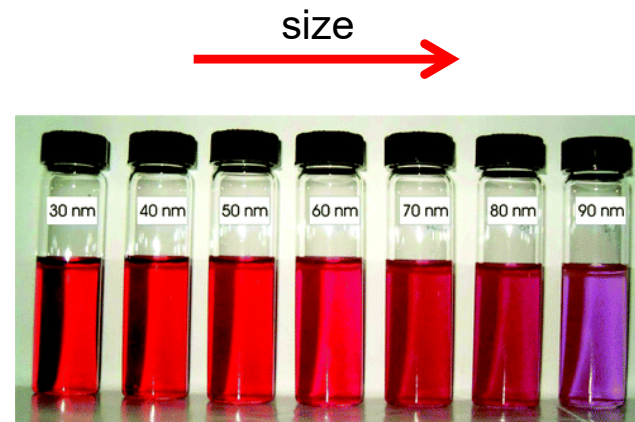
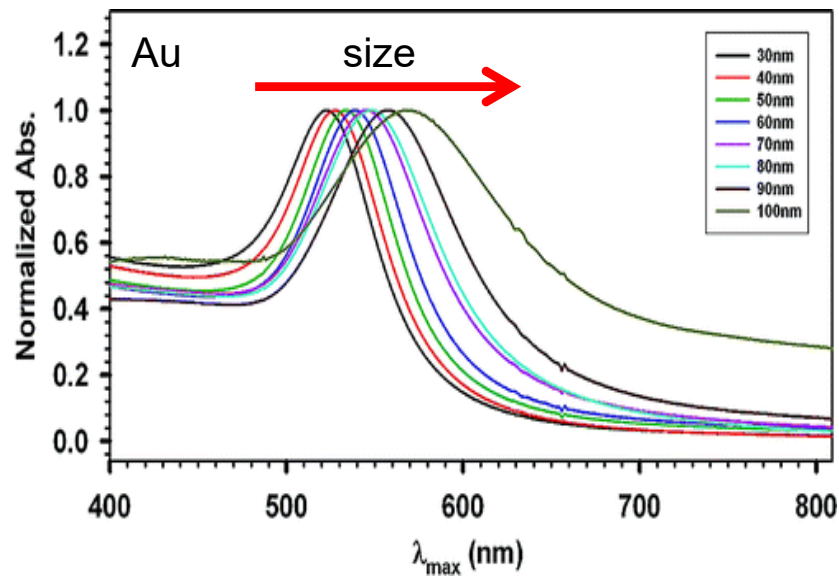
- inflection point
- energy at exp. increase
- intercept energy axis

# 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

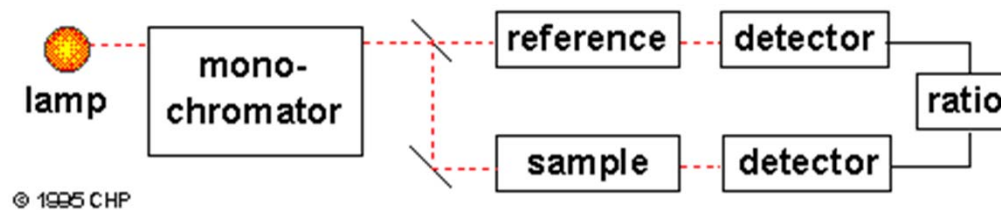


# Instrumentation

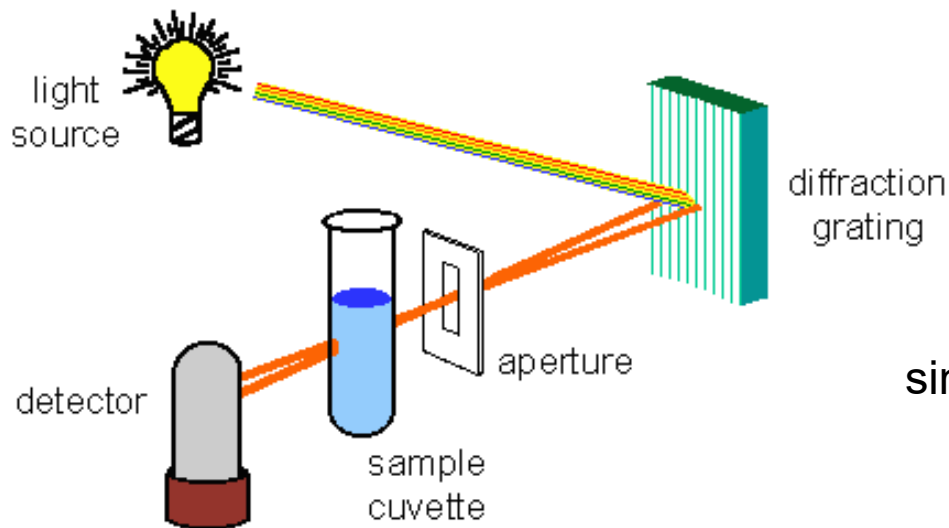
## ■ Dispersive instruments

Measurement geometry:

- transmission
- diffuse reflectance



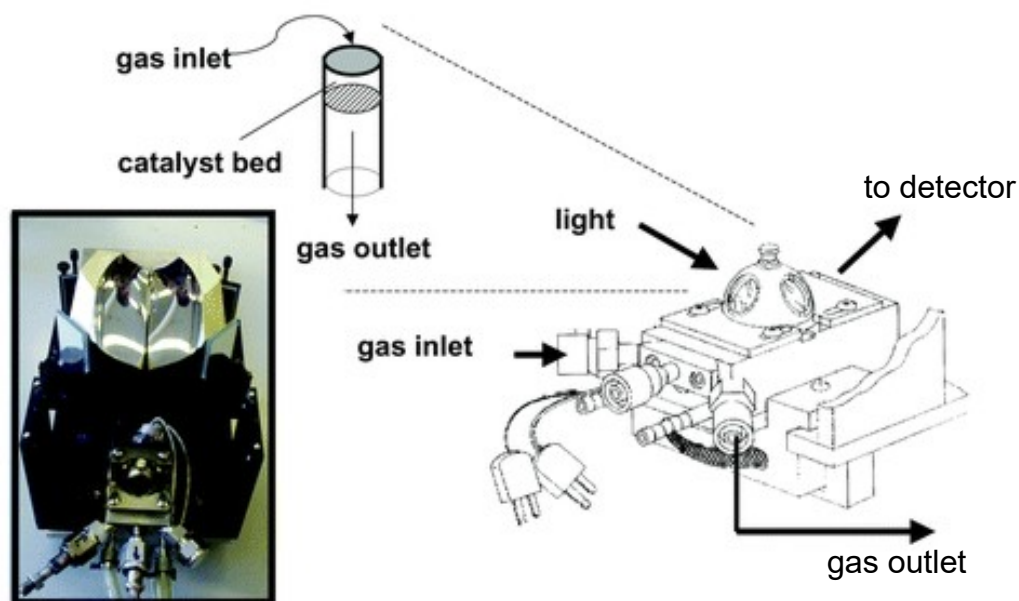
double beam spectrometer



single beam spectrometer

# In situ instrumentation

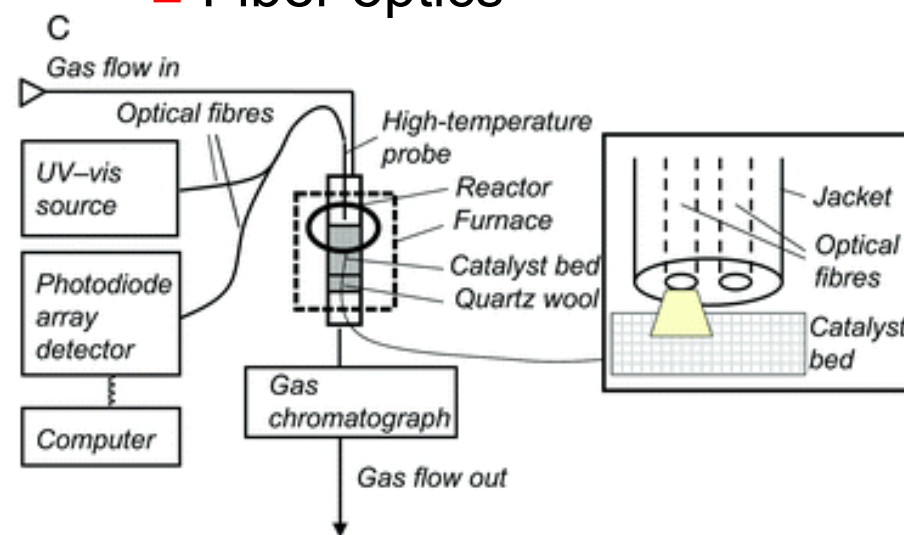
## ■ Diffuse reflectance (DRUV)



- ✓ - 20% of light is collected
- gas flows, pressure, vacuum

- ✗ - long meas. time
- spectral collection ( $\lambda$  after  $\lambda$ )
- different parts of spectrum do not represent same reaction time!!!

## ■ Fiber optics

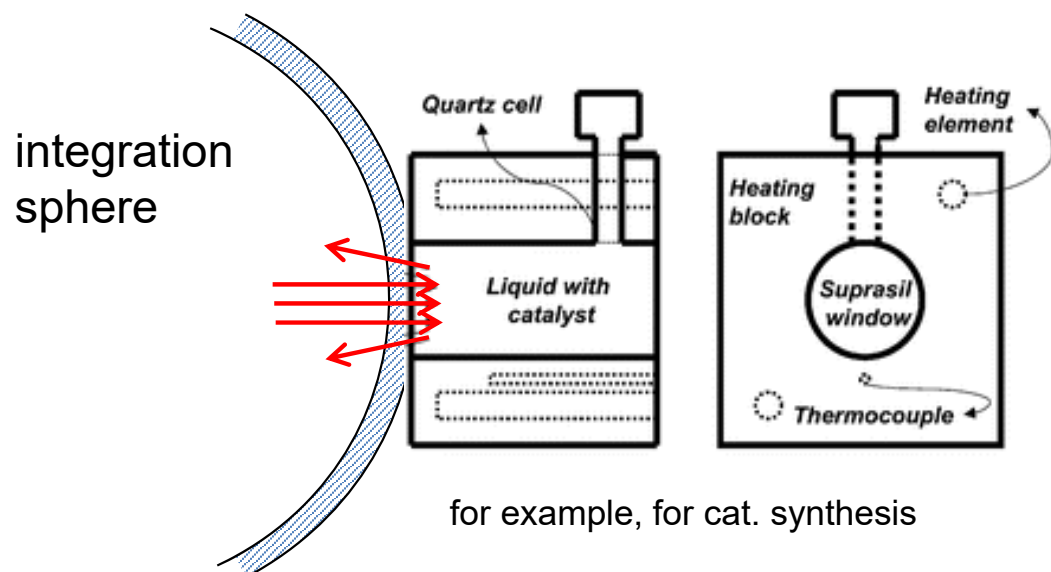
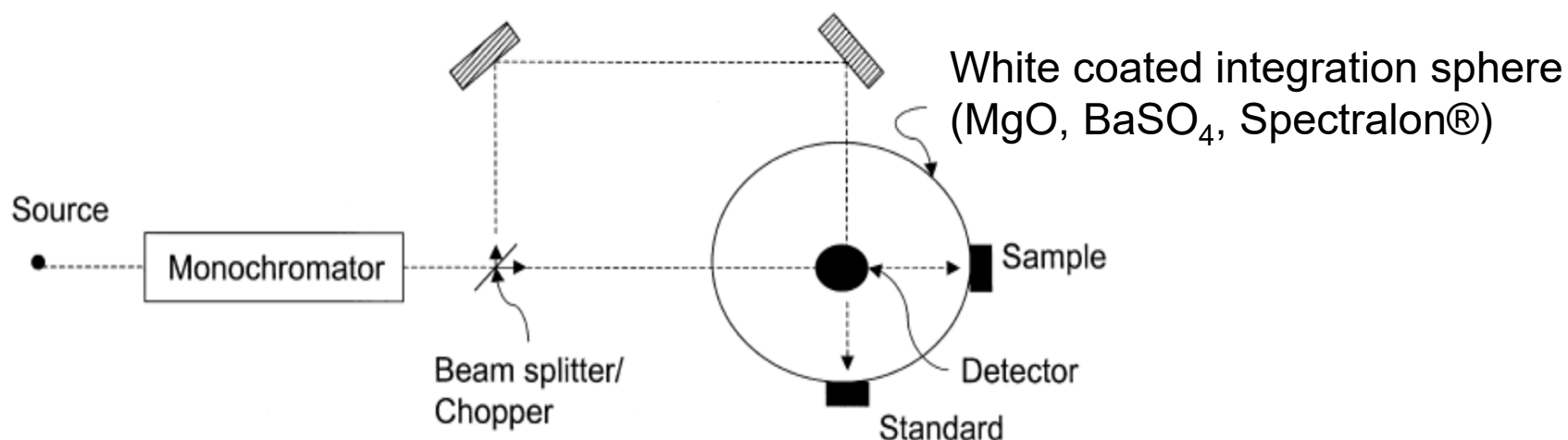


- ✓ - time resolution (CCD camera)  
[spectra collected at once]
- coupling to reactors

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

# In situ instrumentation

## ■ Integration sphere



for example, for cat. synthesis

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

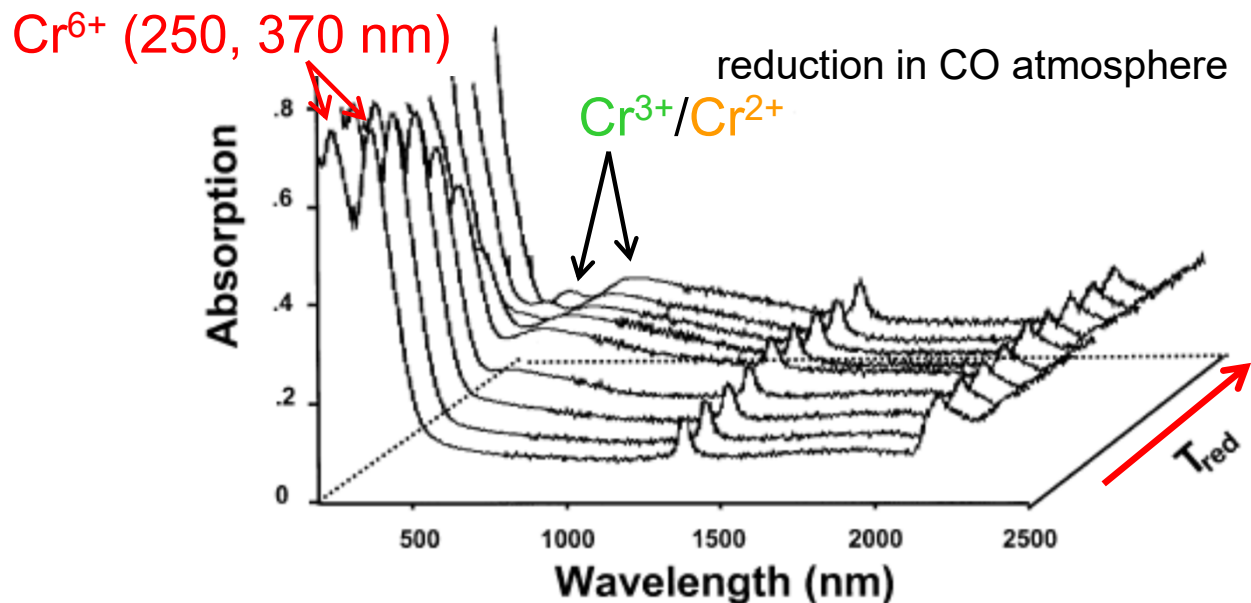


# Examples

## ■ Determination of oxidation state: 0.1 wt% Cr<sup>n+</sup>/Al<sub>2</sub>O<sub>3</sub>

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

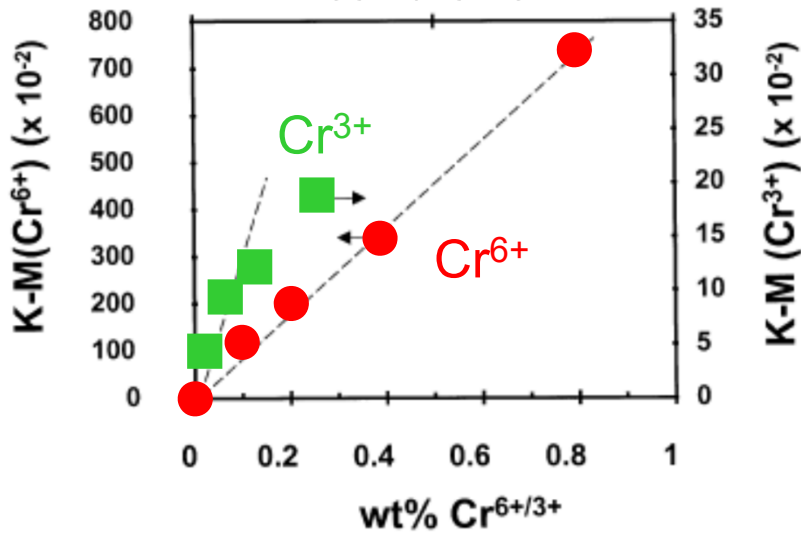
<sup>a</sup>s: strong; m: medium; w: weak; vw: very weak; sh: shoulder; br: broad.



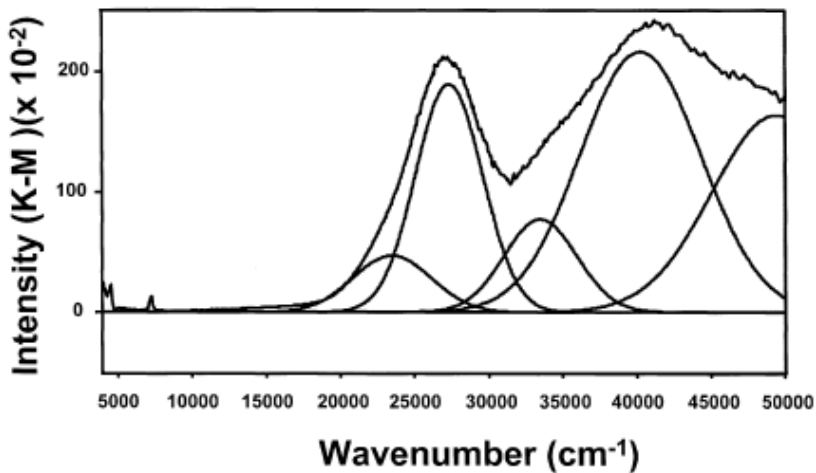
# Examples

## ■ Determination of oxidation state: 0.1 wt% Cr<sup>n+</sup>/Al<sub>2</sub>O<sub>3</sub>

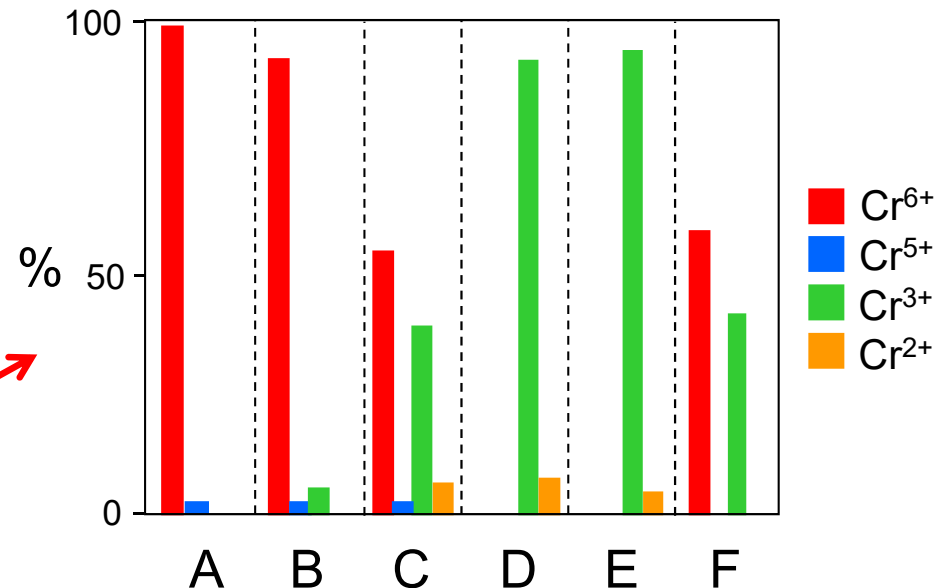
calibration



deconvolution



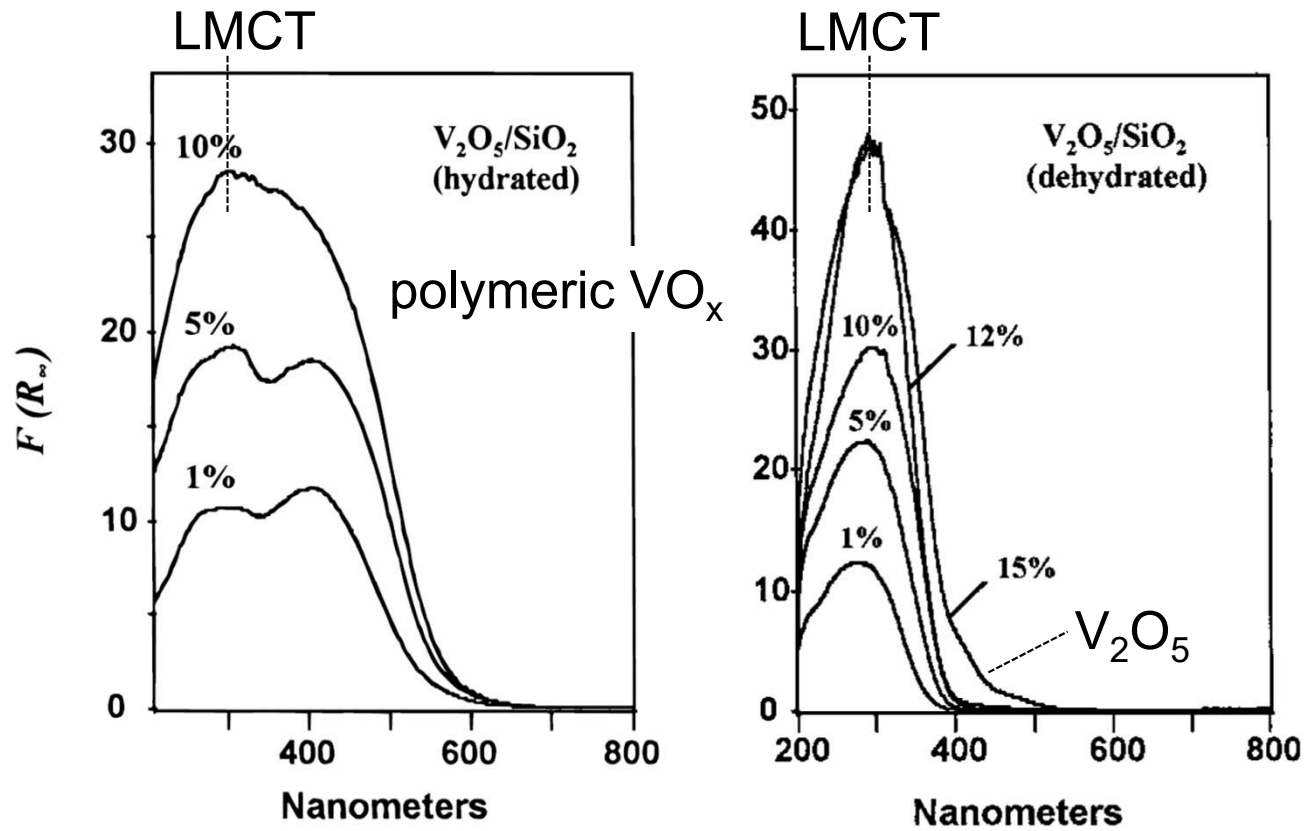
distribution of Cr<sup>n+</sup>



- 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

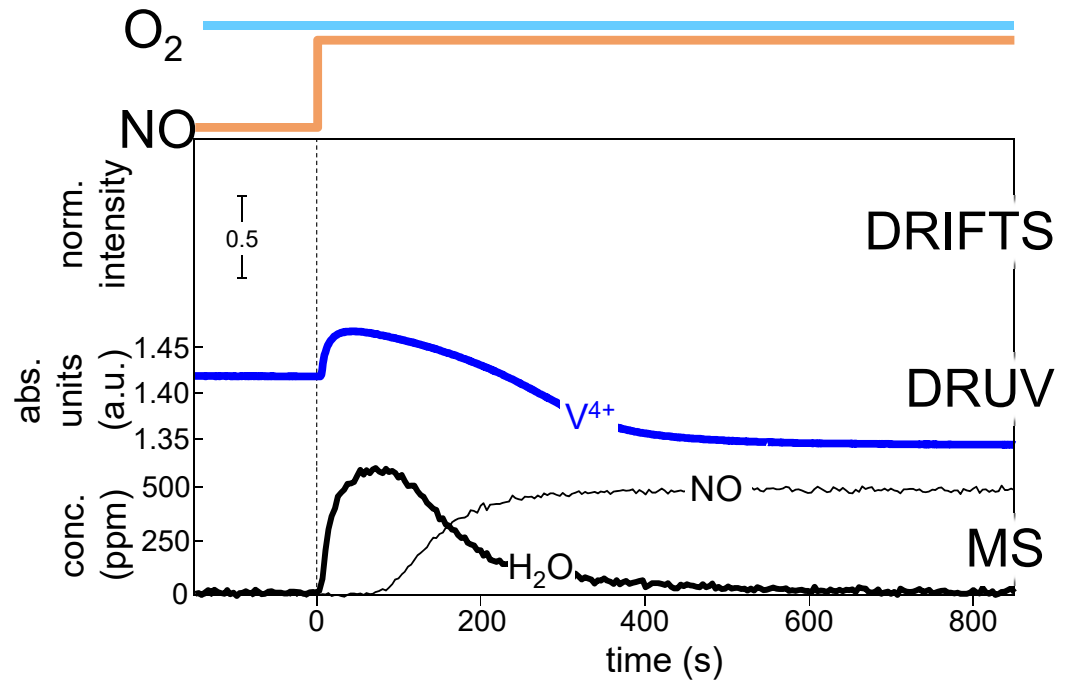
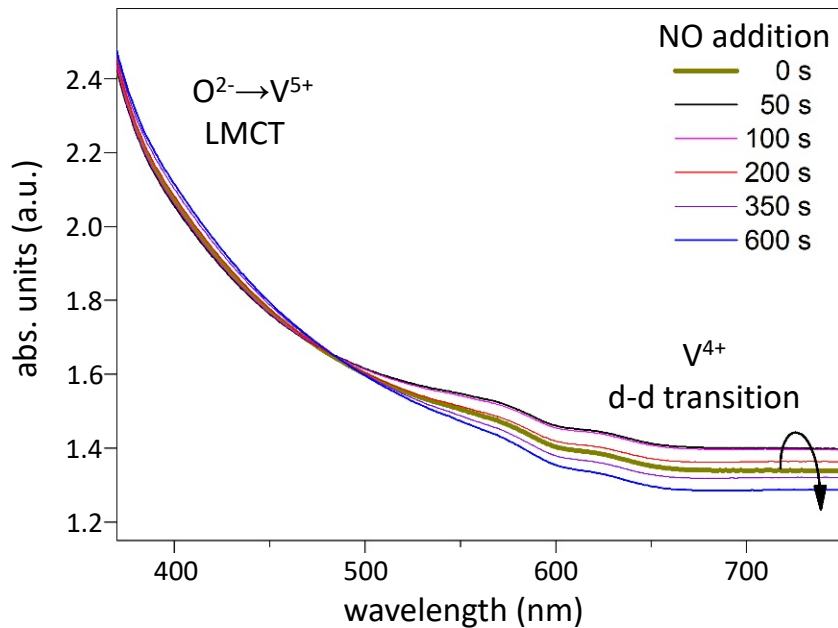
# Examples

## ■ UV-vis of $V_2O_5$ - $SiO_2$



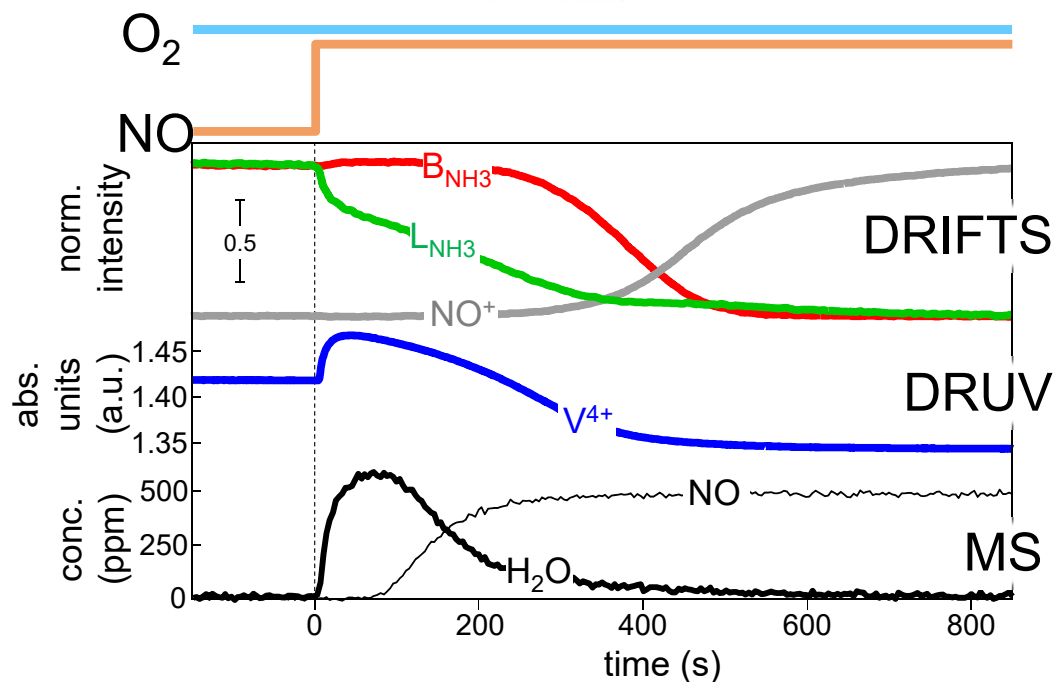
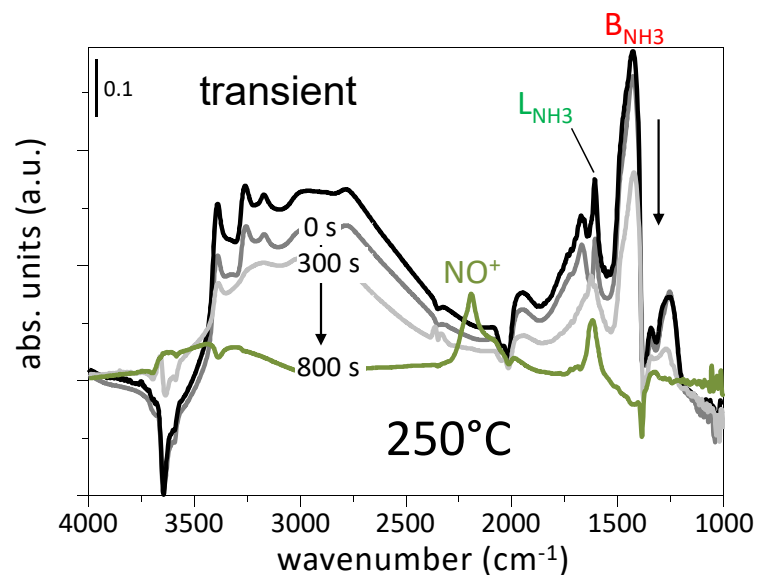
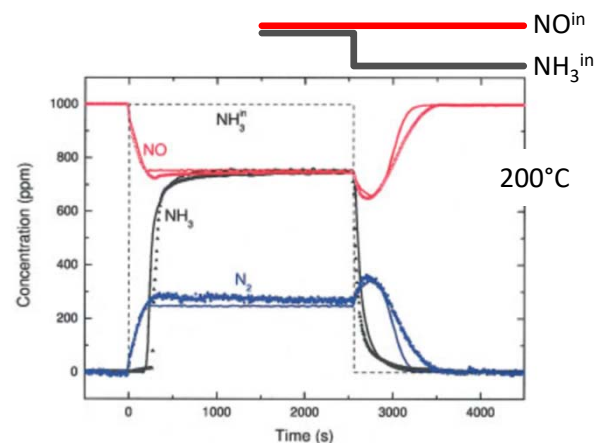
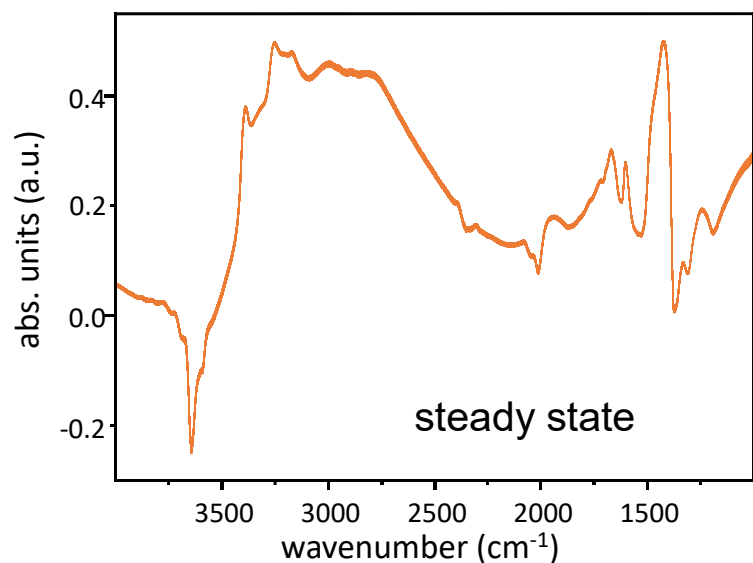
# Examples

- transient experiments vs steady state
- diffuse reflectance UV-vis of  $V_2O_5$ - $WO_3$ - $TiO_2$



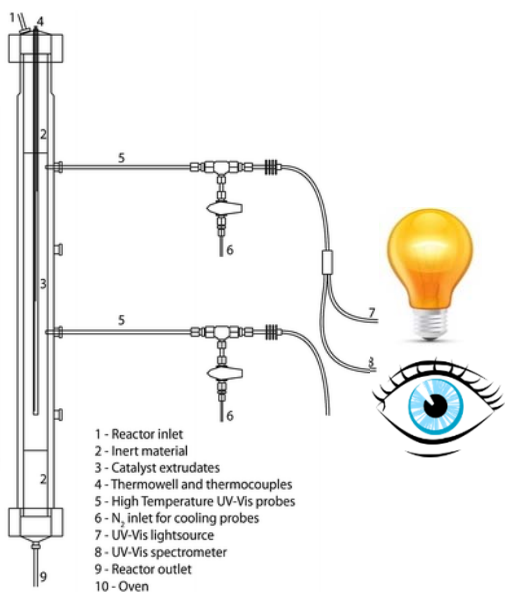
# Diffuse reflectance (DRIFTS)

## ■ transient experiments vs steady state

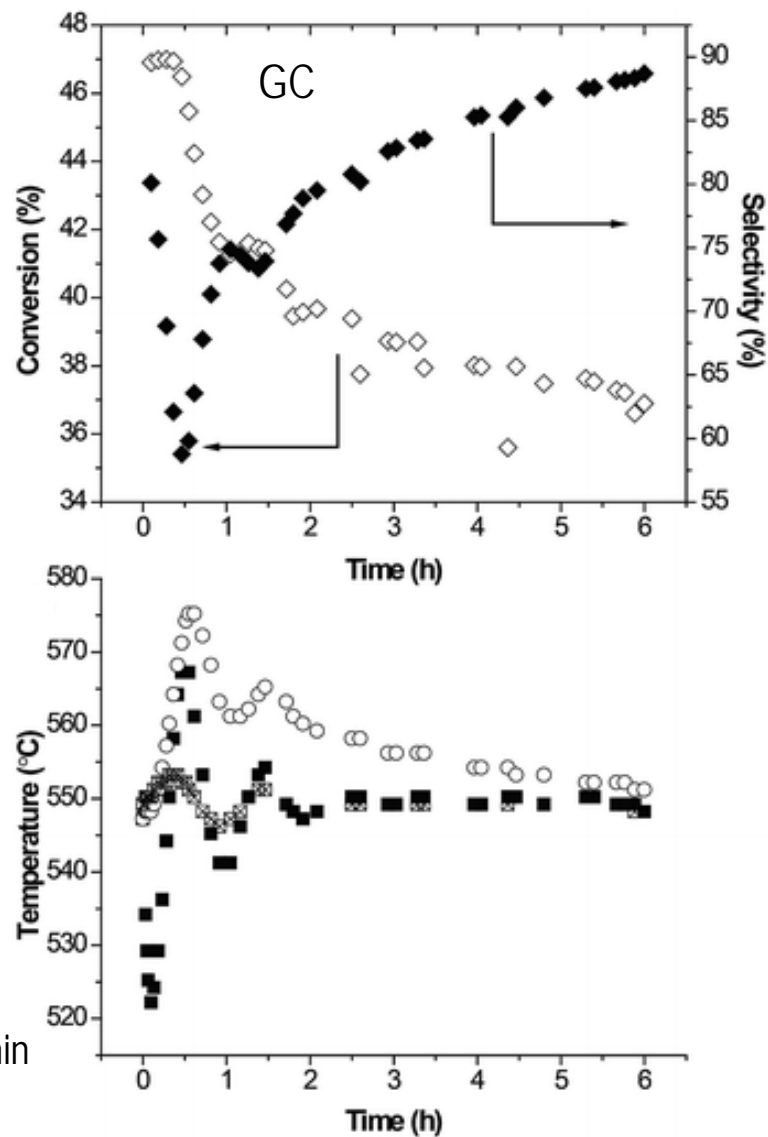


# Examples

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



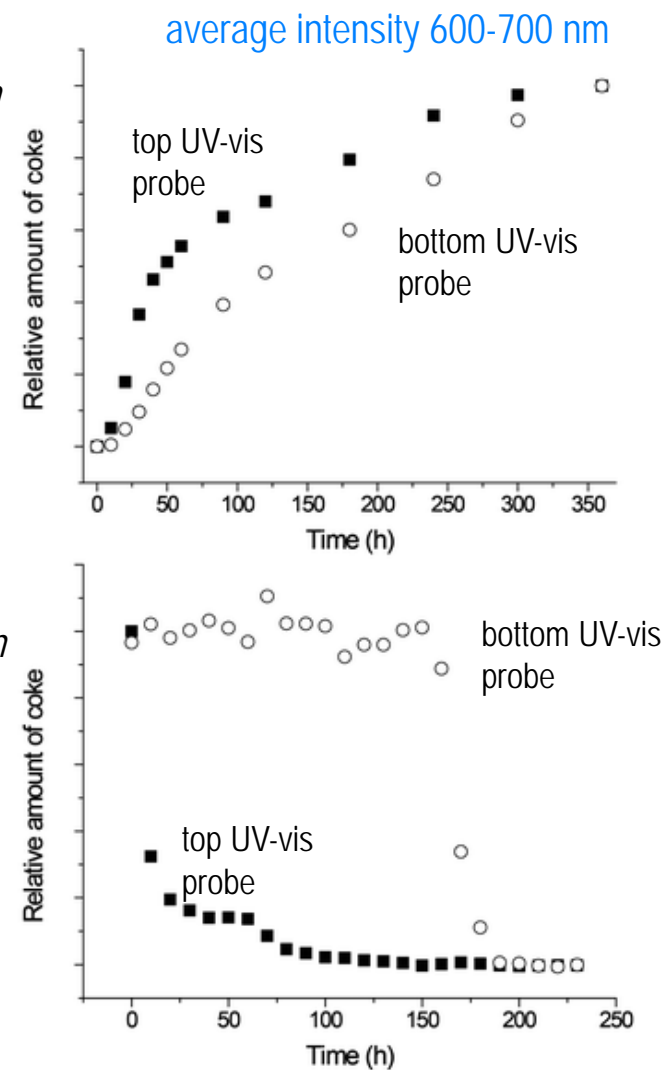
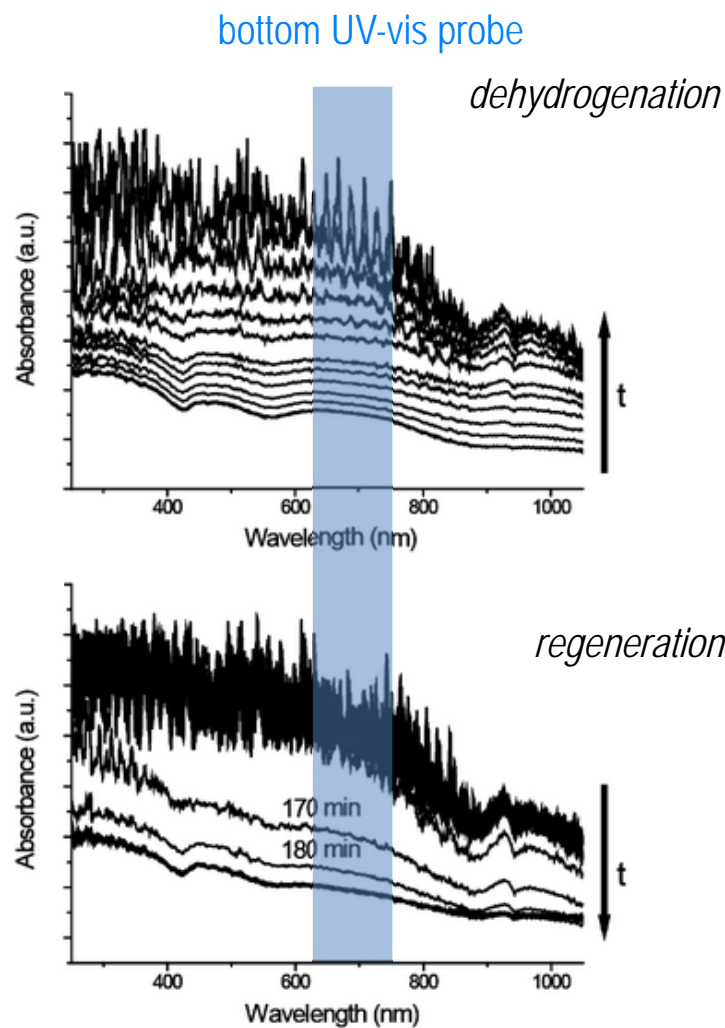
10 vol% C<sub>3</sub>H<sub>8</sub>, 90 vol% N<sub>2</sub>, 5000 ml/min  
20 wt% Cr<sup>3+/6+</sup>O<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub>





# 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