UV-Vis spectroscopy
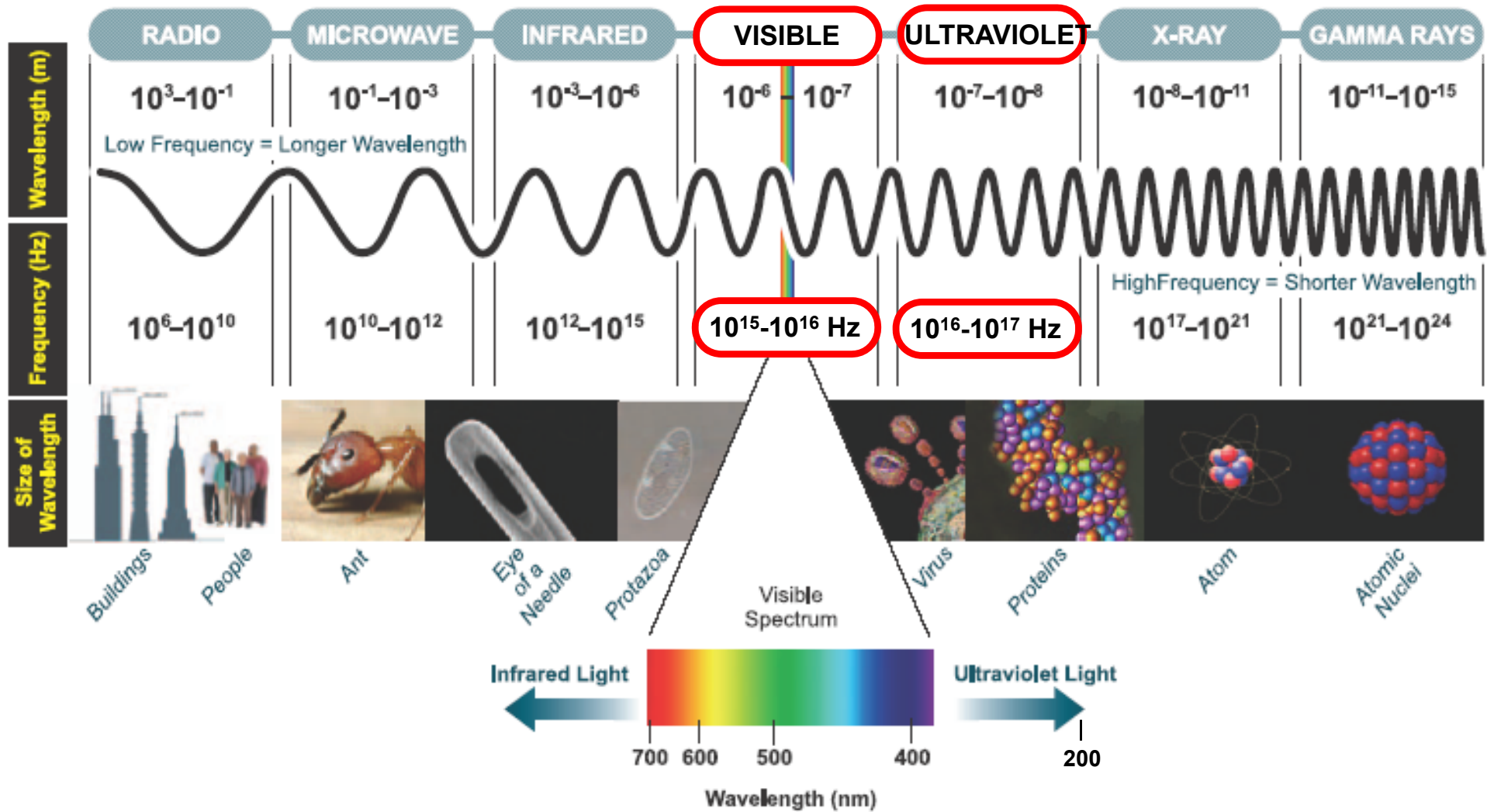
Dr. Davide Ferri
Paul Scherrer Institut
☎ 056 310 27 81
✉ davide.ferri@psi.ch

The electromagnetic spectrum

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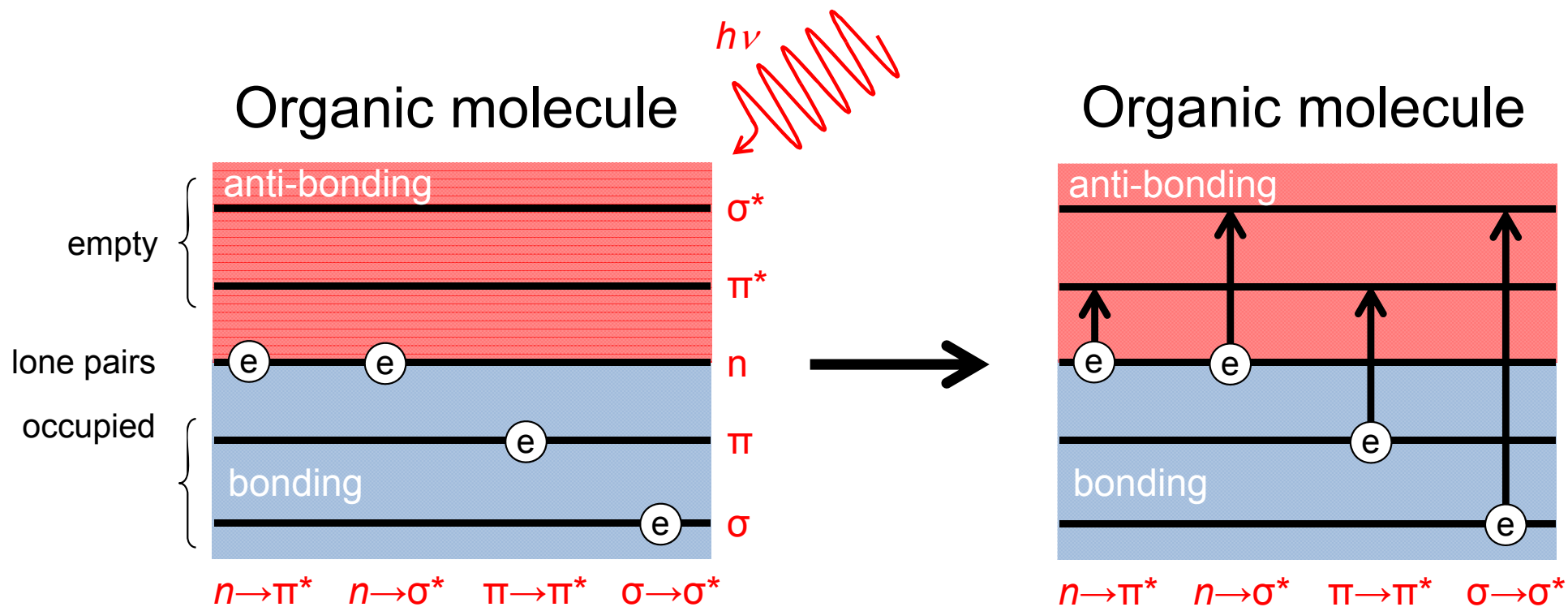
- economic
- non-invasive (fiber optics!)
- versatile (e.g. solid, liquid, gas)
- extremely sensitive (concentration)
- fast acquisition (but S/N!)

cons

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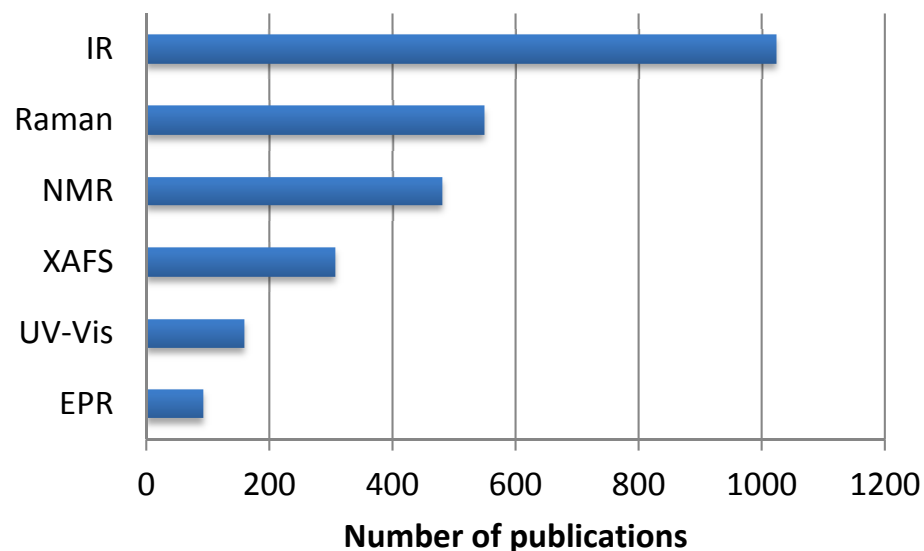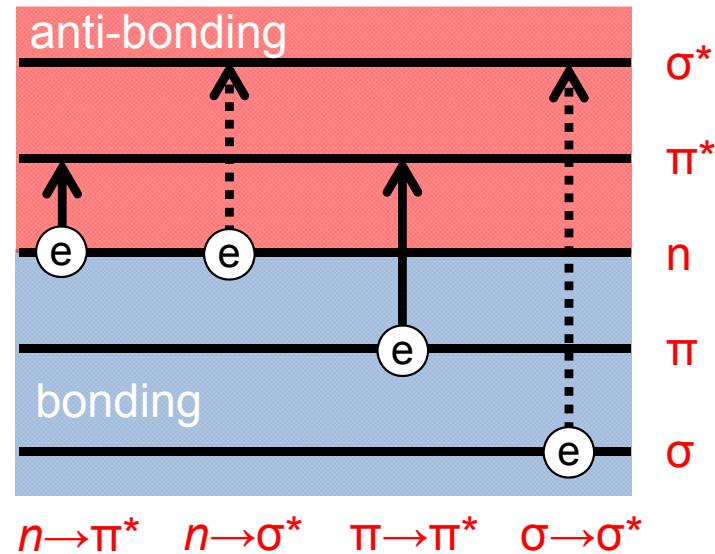
Electronic transitions

Electronic transitions

σ→σ*
high *E*, low λ (<200 nm)

n→σ*
150-250 nm, weak

n→π*
200-700 nm, weak

π→π*
200-700 nm, intense

Condition to absorb light
(200-800 nm):

π and/or *n* orbitals

CHROMOPHORE

The UV spectrum

σ^*

π^*

n

π

σ

$\pi \rightarrow \pi^*$

λ_{max}
217 nm

absorbance

1.0

0.8

0.6

0.4

0.2

0.0

200   220   240   260   280   300

wavelength (nm)

no visible light absorption

signal envelope

energy

E^*

E_0

vibrational
electronic levels

rotational
electronic levels
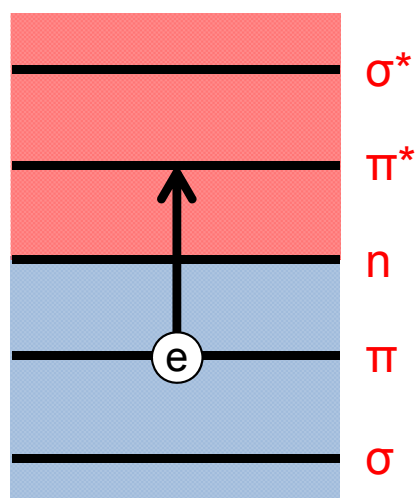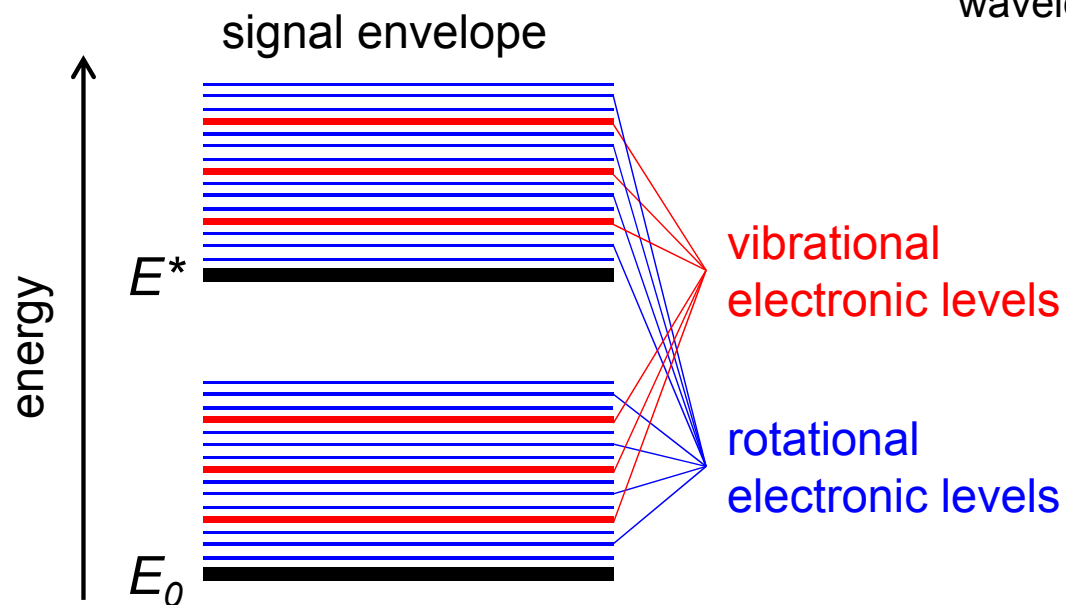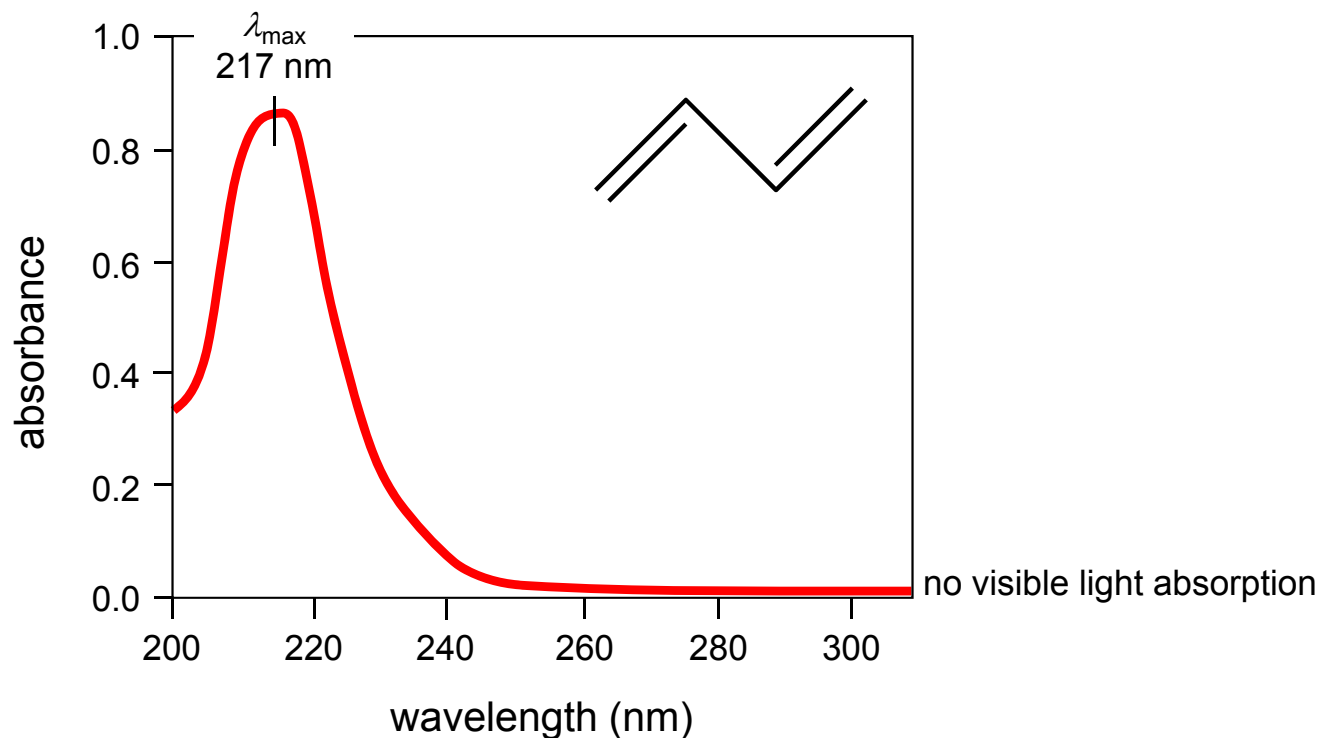
Q How many signals do you expect from $CH_3-CH=O$?

The UV spectrum

■ **Conjugation effect:** β-carotene
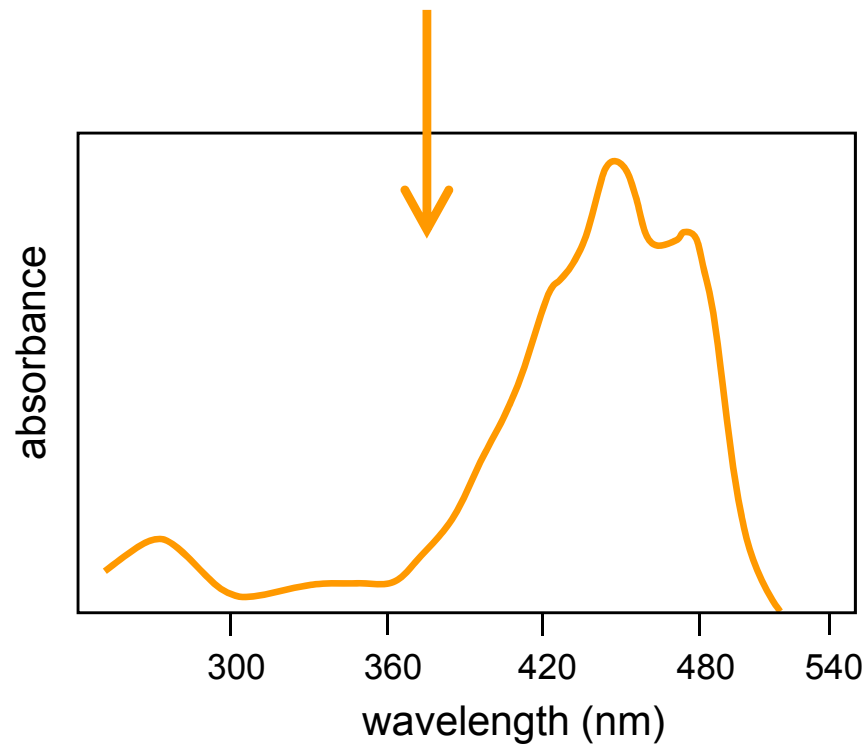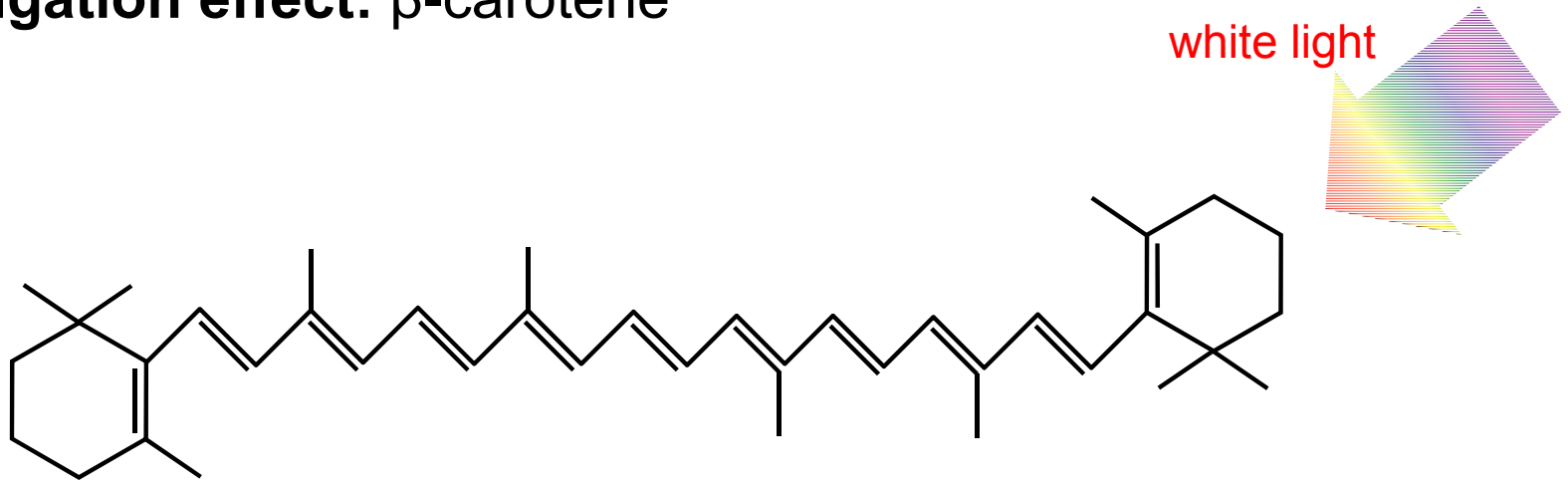
white light

The UV spectrum

- **Complementary colours**
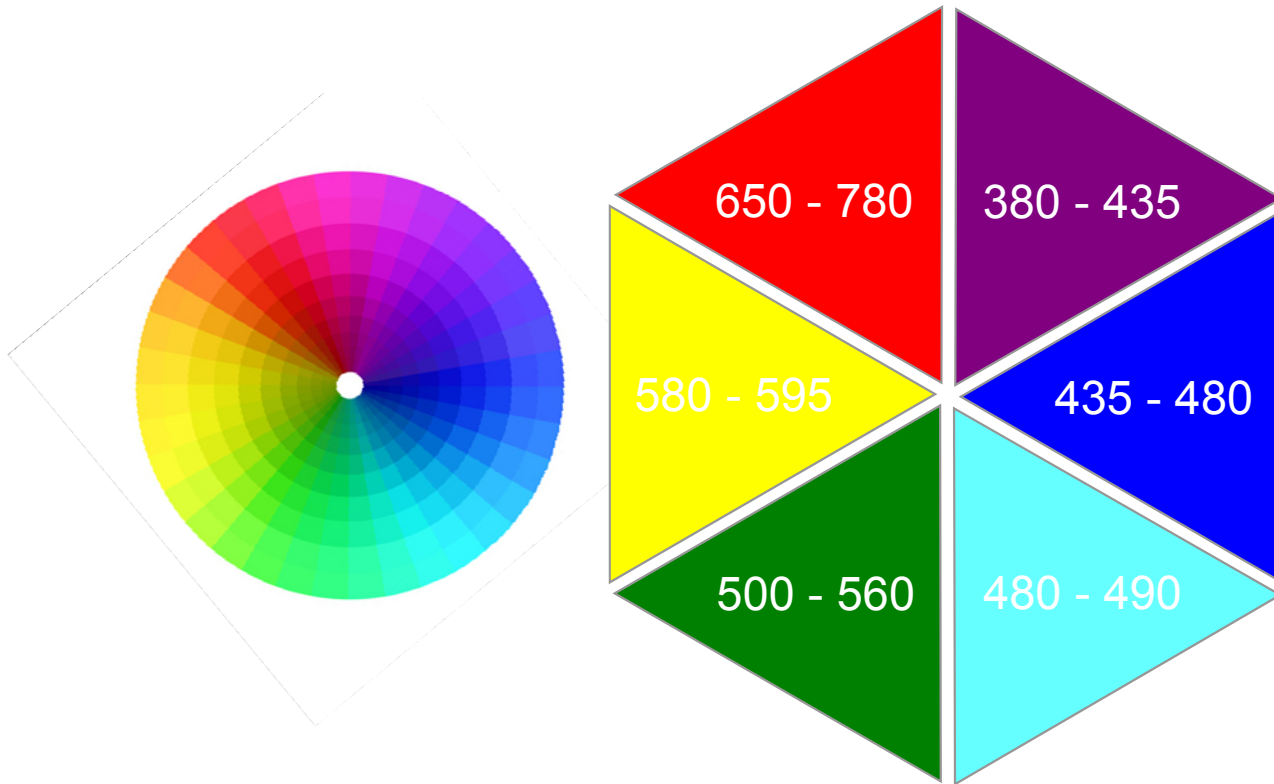
If a colour is absorbed by white light, what the eye detects by mixing all other wavelengths is its complementary colour

Inorganic compounds

- UV-vis spectra of transition metal complexes originate from

  - **Electronic *d-d* transitions**

  - …
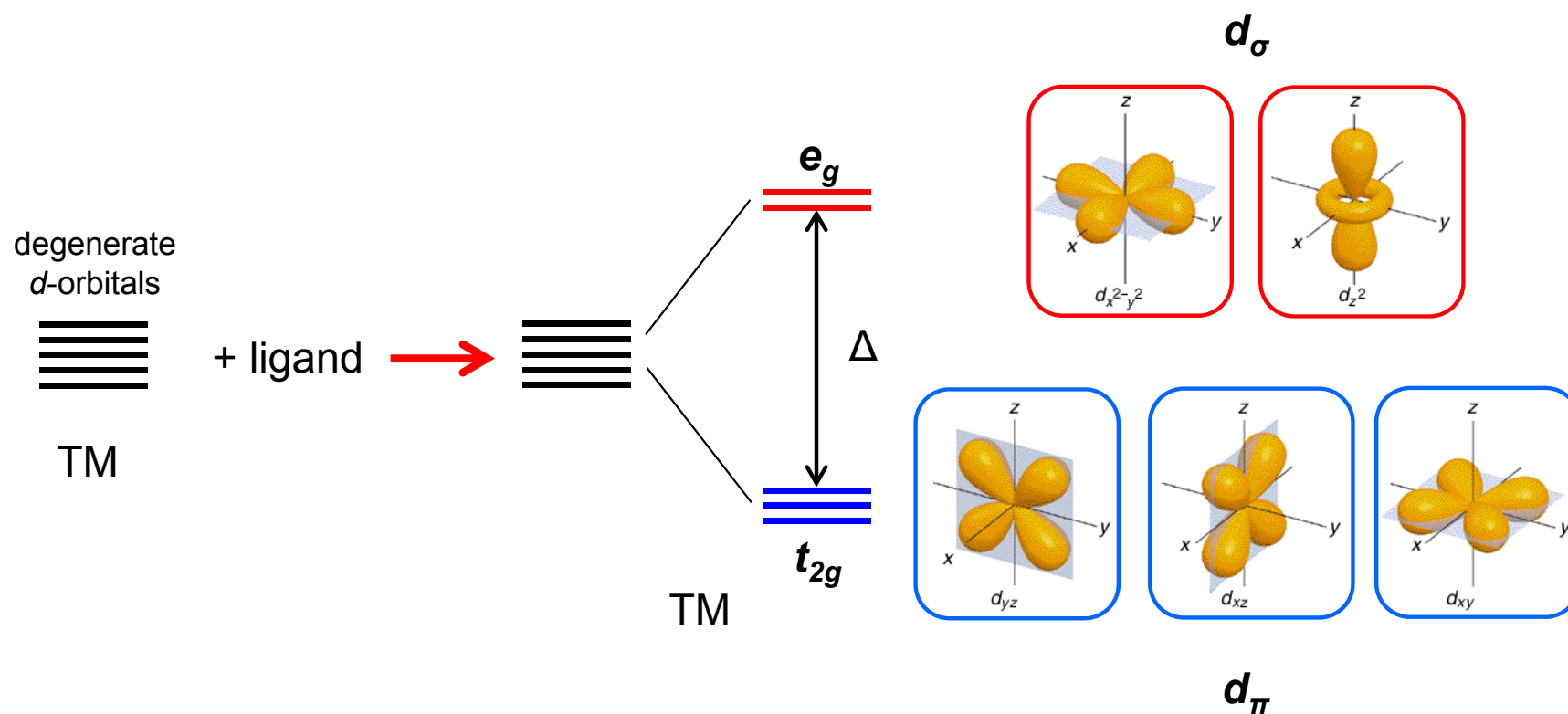
Inorganic compounds

- **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

Δ = crystal field splitting
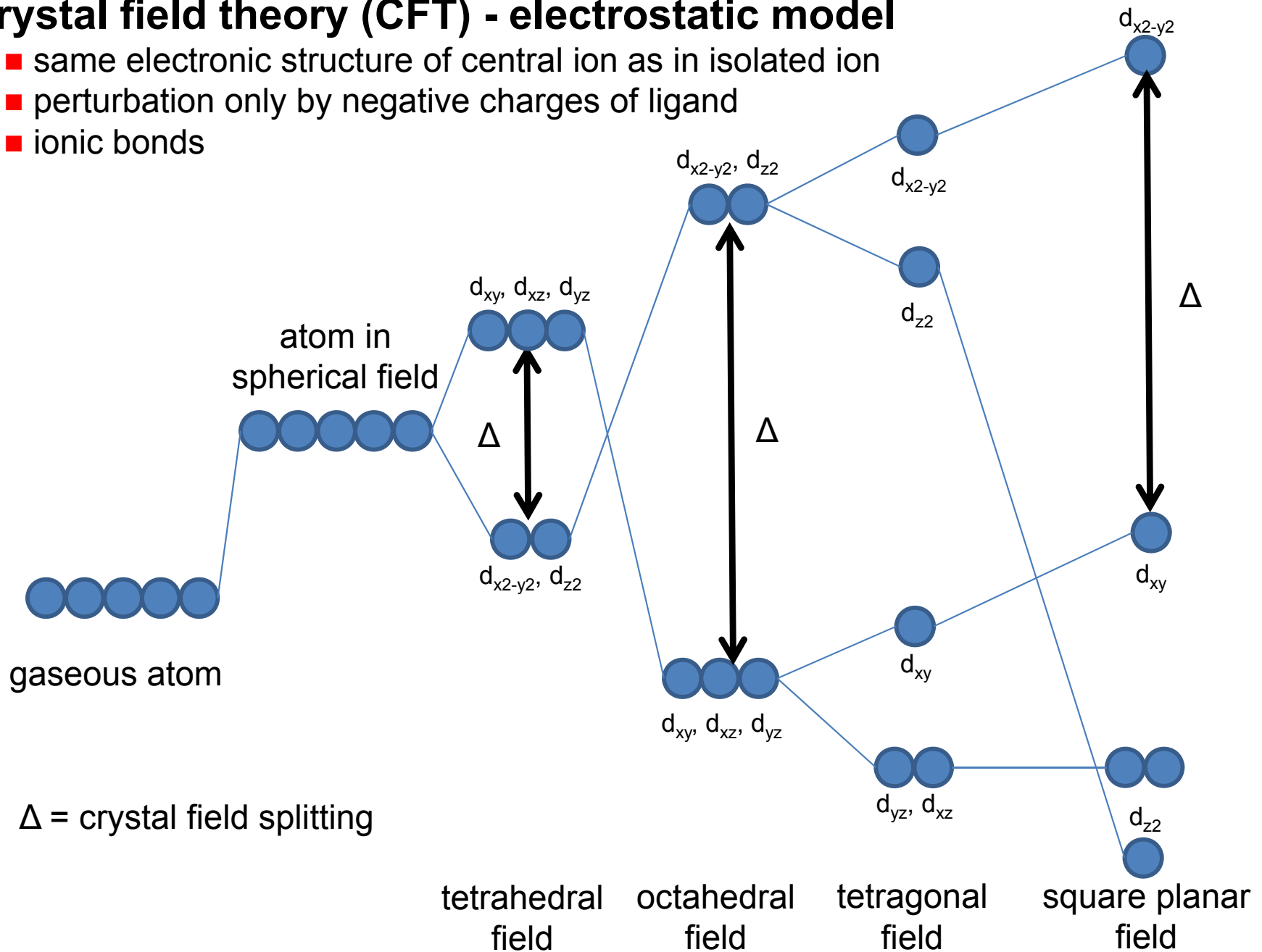
Inorganic compounds

■ **d-d transitions:** $Cu(H_2O)_6^{2+}$

degenerate
d-orbitals

e_g

+ $6H_2O$

Δ

light

Cu^{2+}

t_{2g}

$Cu(H_2O)_6^{2+}$
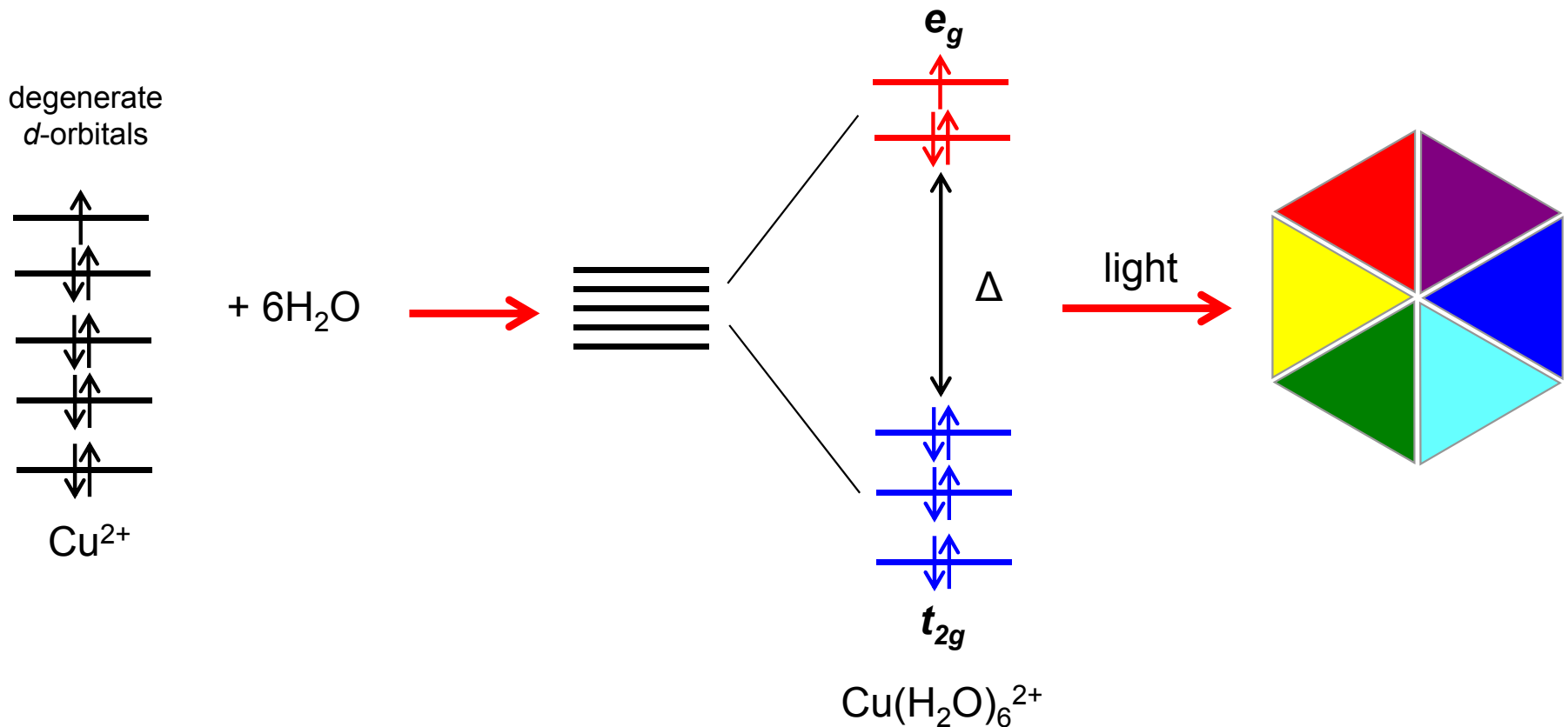
■ Yellow light is absorbed and the Cu^{2+} solution is coloured in blue (ca. 800 nm)
■ The greater Δ, the greater the E needed to promote the e$^-$, and the shorter λ
■ Δ depends on the nature of ligand, $\Delta_{NH3} > \Delta_{H2O}$

Inorganic compounds

■ $TM(H_2O)_6^{n+}$

elec. config. TM

gas	complex	
$3d^1$	t_{2g}^1	$Ti(H_2O)_6^{3+}$
$3d^2$	t_{2g}^1	$Ti(H_2O)_6^{3+}$
$3d^3$	t_{2g}^3	$Cr(H_2O)_6^{3+}$
$3d^4$	$t_{2g}^3e_g^1$	$Cr(H_2O)_6^{2+}$
$3d^5$	$t_{2g}^3e_g^2$	$Mn(H_2O)_6^{2+}$
$3d^6$		
$3d^7$		
$3d^8$		
$3d^9$	$t_{2g}^6e_g^3$	$Cu(H_2O)_6^{2+}$

absorbance

Ni^{2+} Co^{2+} Cu^{2+} Fe^{2+} Cr^{3+} Ti^{3+} V^{4+}

wavelengths (nm)
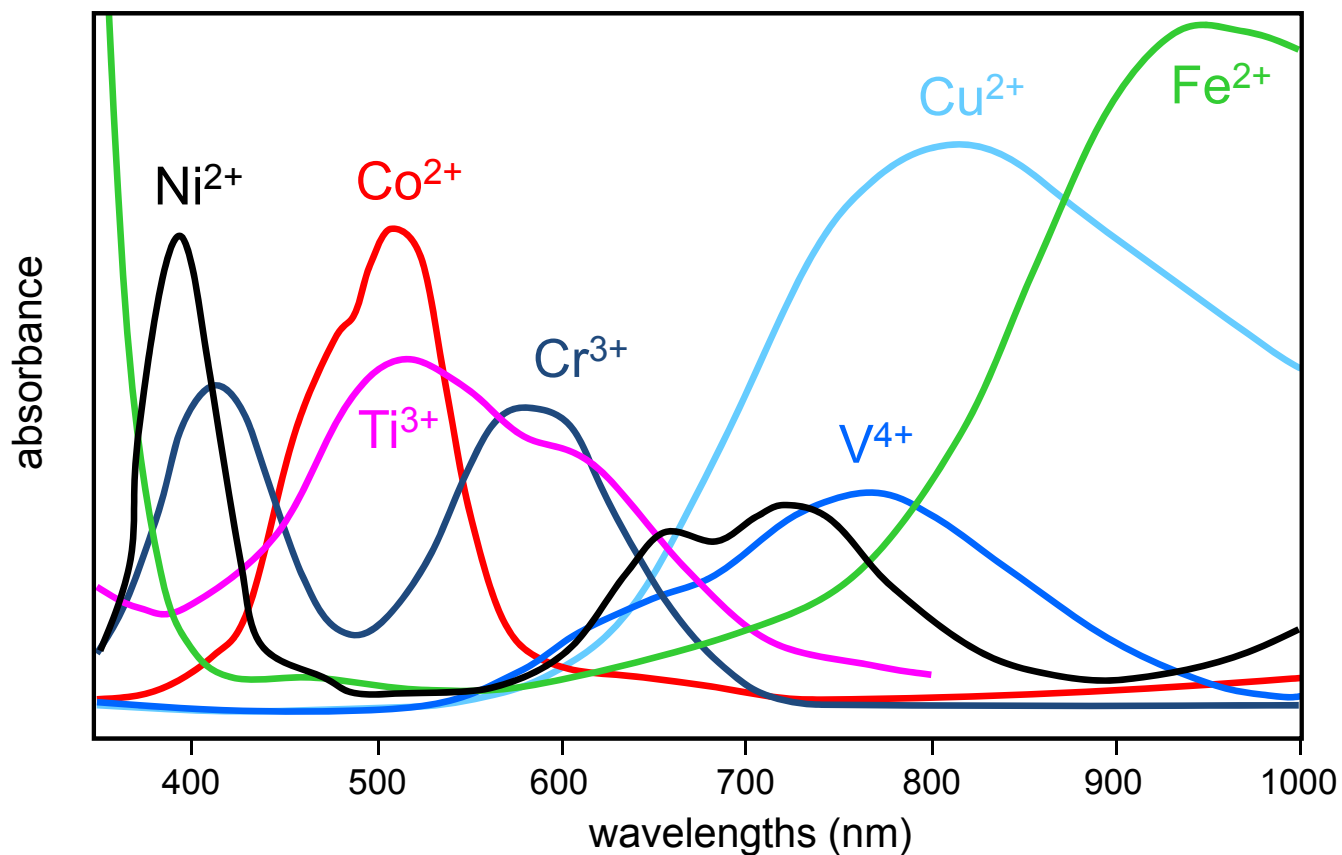
d-d transitions: ε_{max} = 1 - 100 Lmol^{-1}cm^{-1}, **weak** (selection rule: forbidden transition)

Inorganic compounds

- *d-d* **transitions:** factors governing magnitude of Δ

  - **Oxidation state of metal ion**
    - Δ increases with increasing oxidation state

  - **Nature of metal ion**
    - Δ increases in the order 3d < 4d < 5d

  - **Number and geometry of ligands**
    - Δ 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**
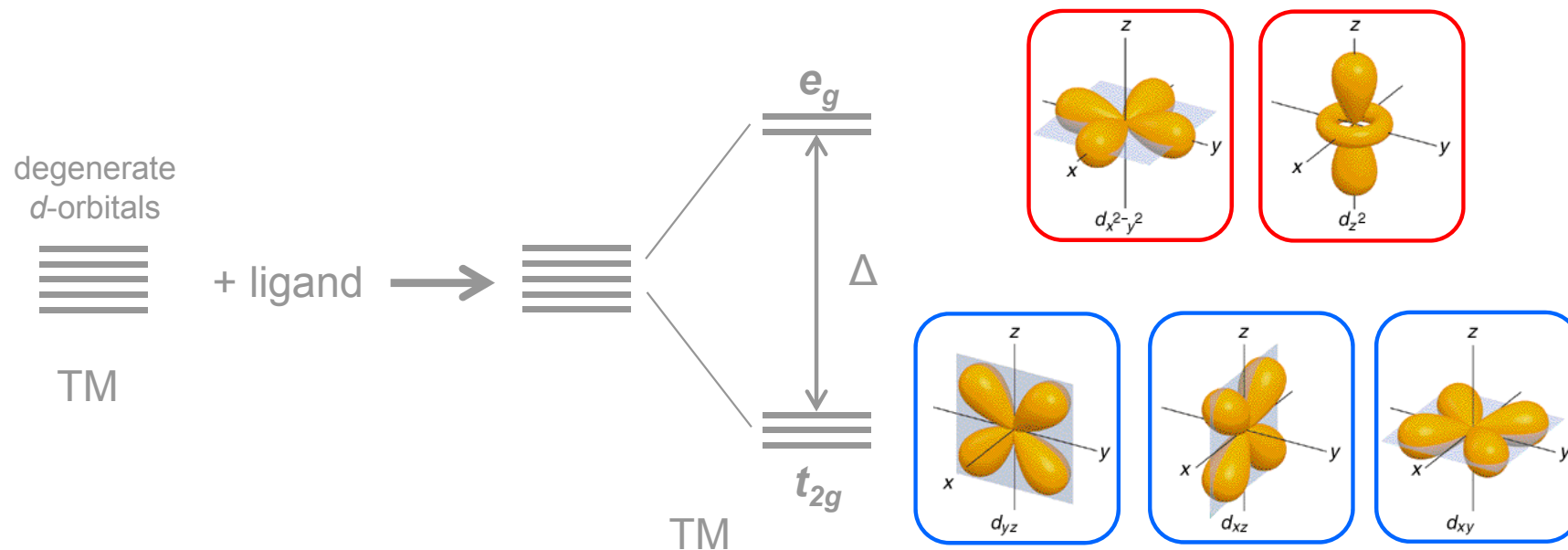
- **Charge transfer**

Inorganic compounds

■ **Charge transfer complex**

   ■ no selection rules $\rightarrow$ intense colours (ε= 50'000 Lmol^{-1}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: $\pi_d \rightarrow \sigma_{dz2}^*$ or $\pi_d \rightarrow \sigma_{dx2-y2}^*$

$\pi_{px}^*, \pi_{py}^*, \pi_{pz}^*$

σ_p^*

4p

σ_s^*

4s

σ_d^*

e_g

Δ

3d

t_{2g}

$\pi_{dxy}, \pi_{dxz}, \pi_{dxy}$

2s

AO_{TM}

σ_d

AO_L

σ_p

Δ = crystal field splitting

σ_s

$MO(TML_6^{n+})$
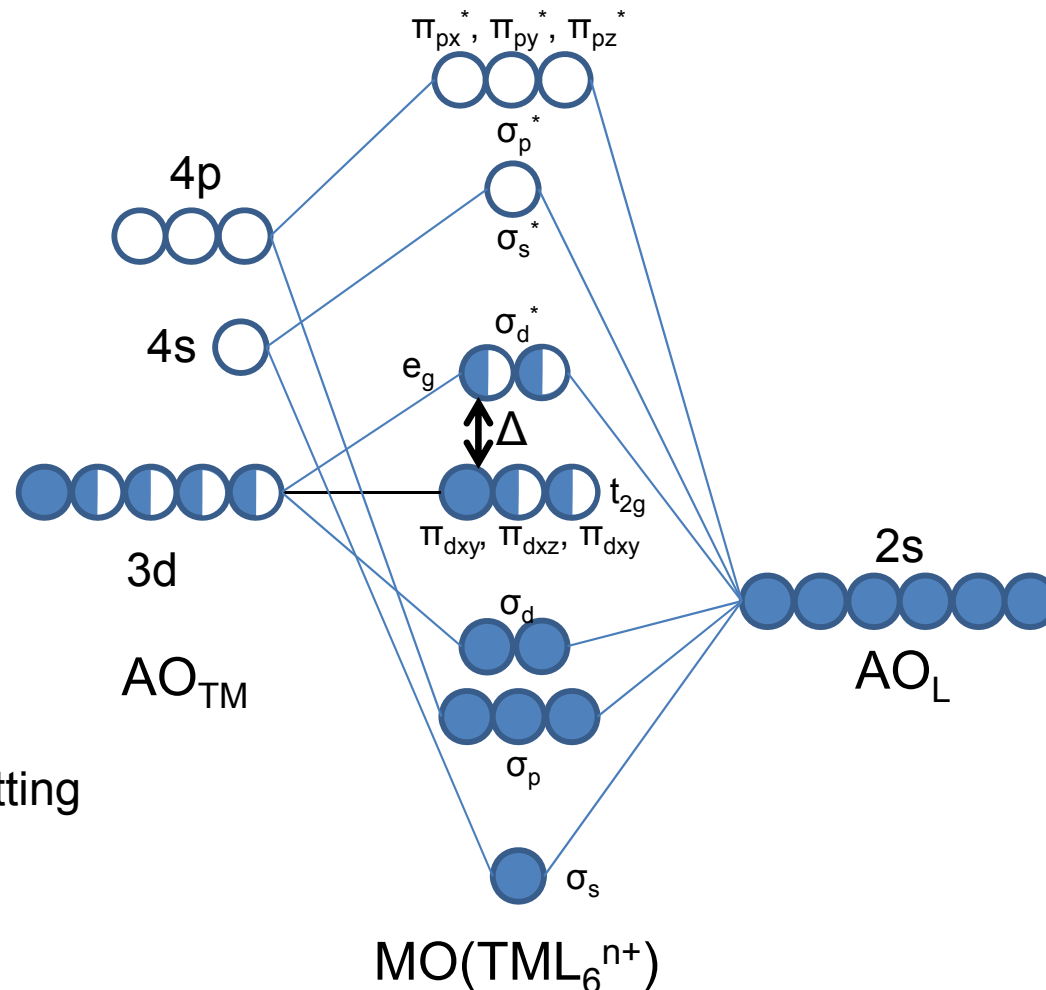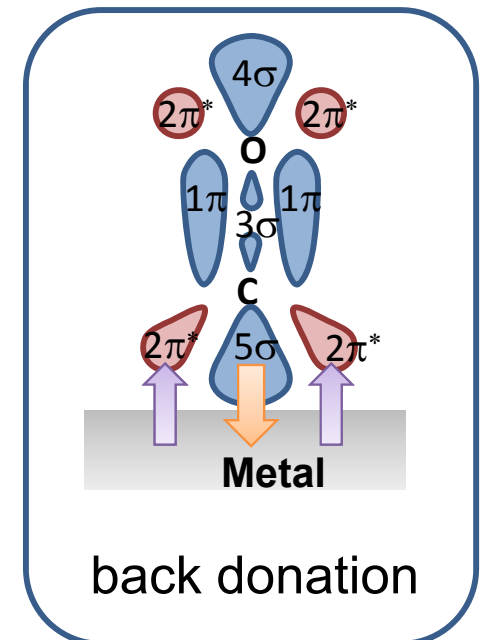
Inorganic compounds

- **Ligand field theory (LFT)**

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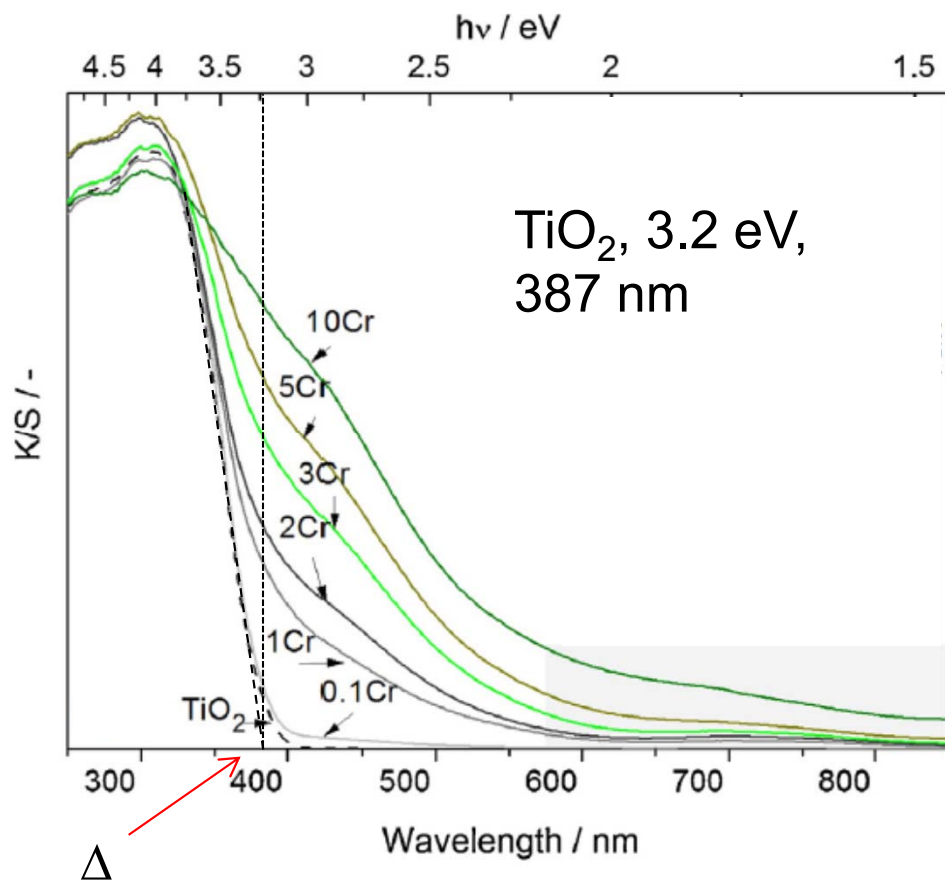   - *high oxidation state* (also d^0)
    - M-L strengthened

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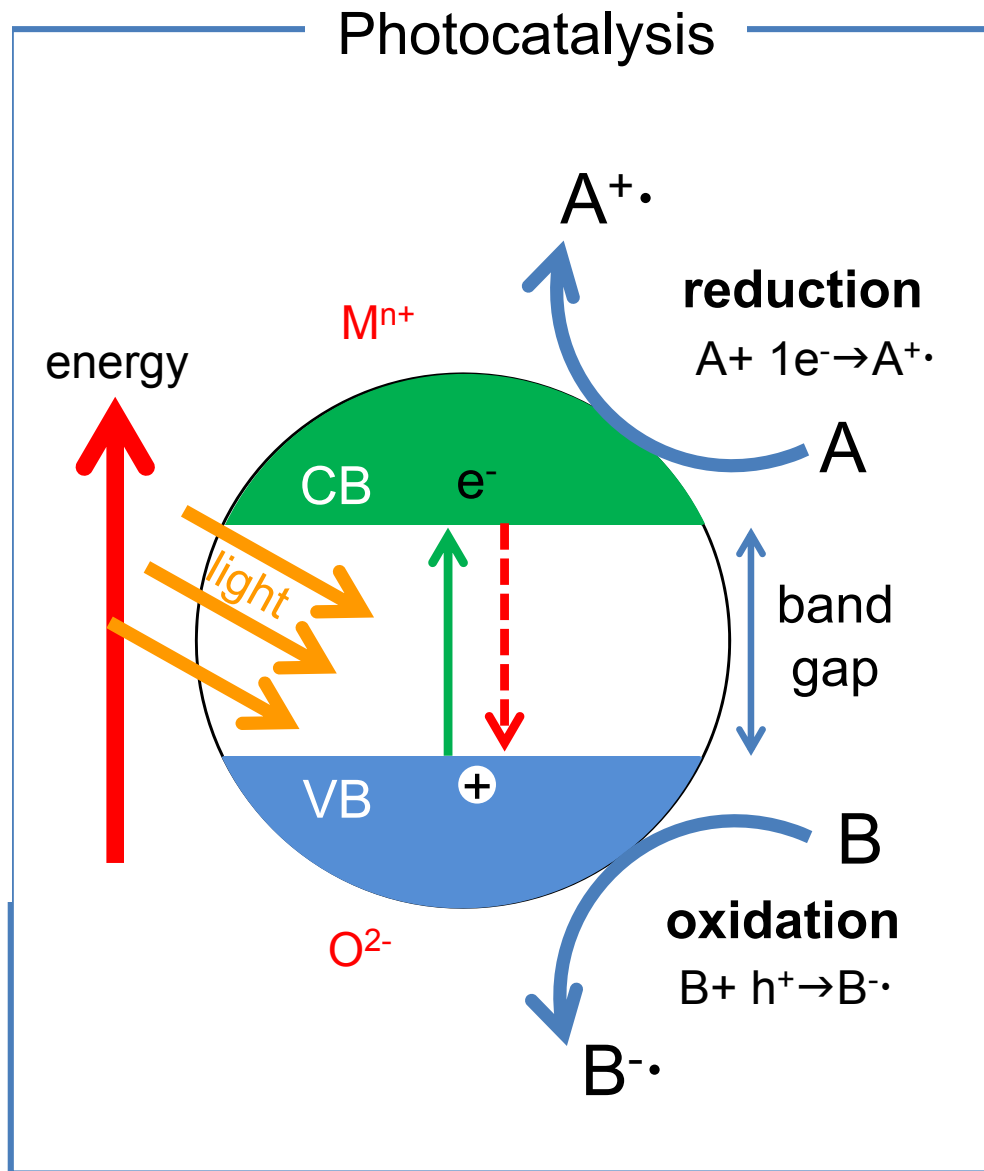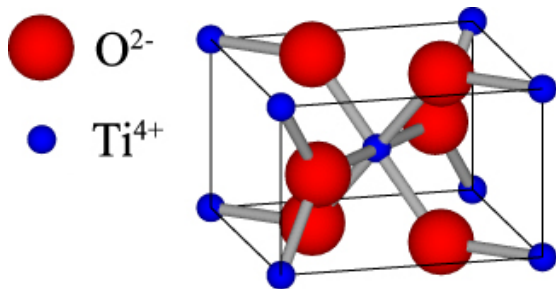   - M-L strengthened, π bond of L weakened

back donation

CO adsorption on precious metals

Band gap

■ **Analysis of semiconductors**

TiO$_2$, 3.2 eV, 387 nm

O^{2-}

Ti^{4+}

Photocatalysis

energy

M^{n+}

light

CB   e$^-$

band gap

VB   +

O^{2-}

A$^+$·

reduction

A+ 1e$^-$→A$^+$·

A

B

oxidation

B+ h$^+$→B$^-$·

B$^-$·

Band gap

DIRECT
energy

CB

VB

wavevector k

INDIRECT
energy

CB

phonon

VB

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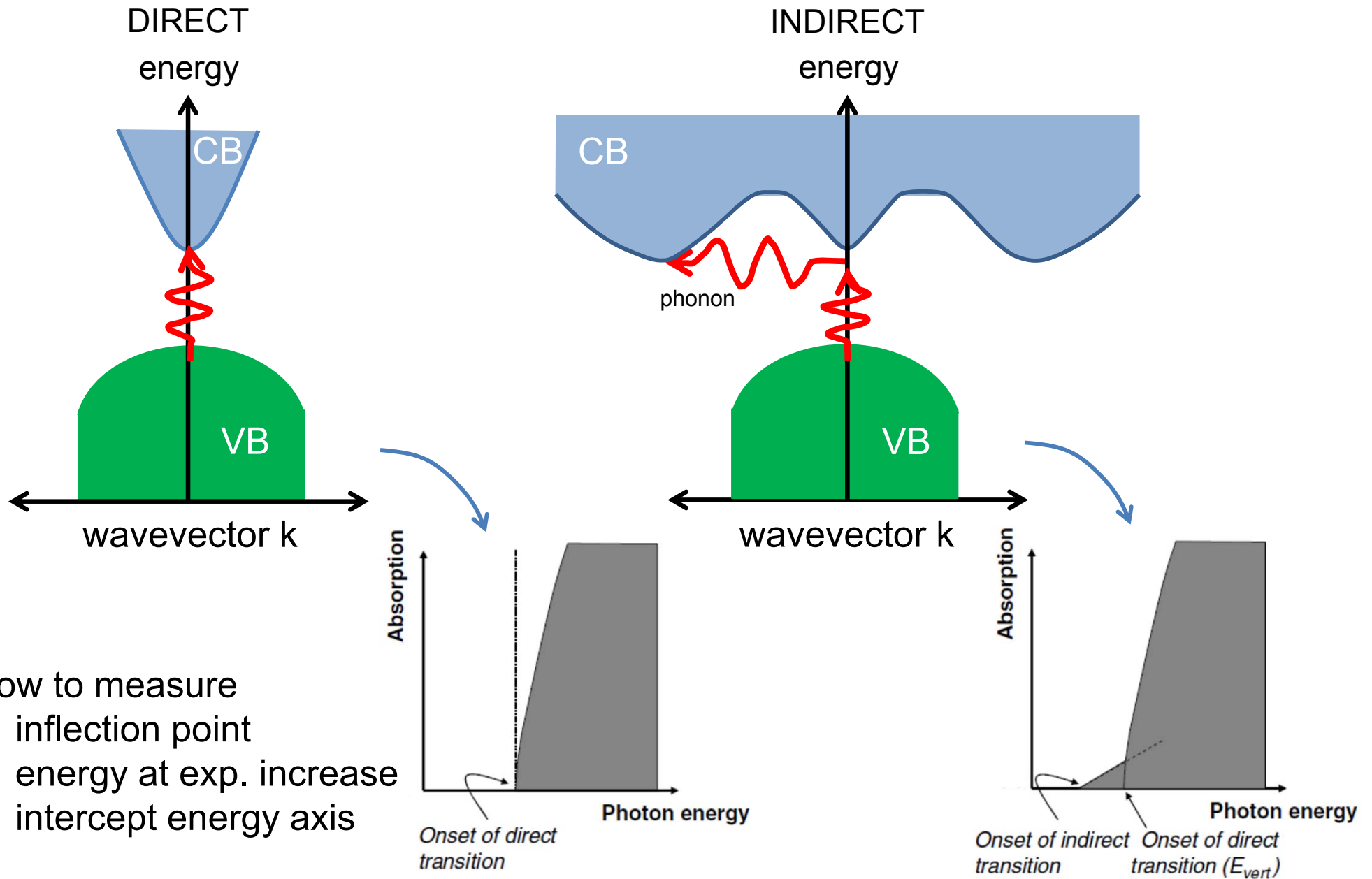
How to measure
- inflection point
- energy at exp. increase
- intercept energy axis

Absorption

Photon energy

Onset of direct
transition

Absorption

Photon energy

Onset of indirect   Onset of direct
transition   transition (E_{vert})

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
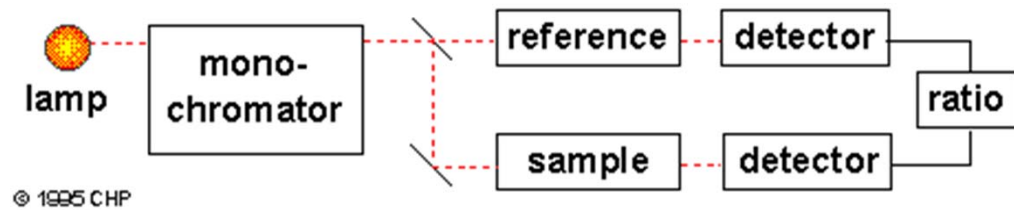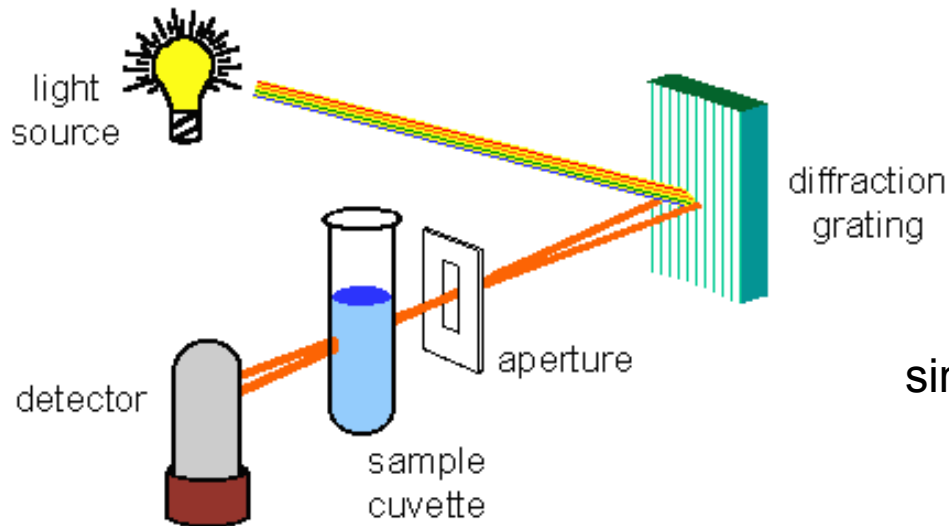 - λ position depends on nature of metal
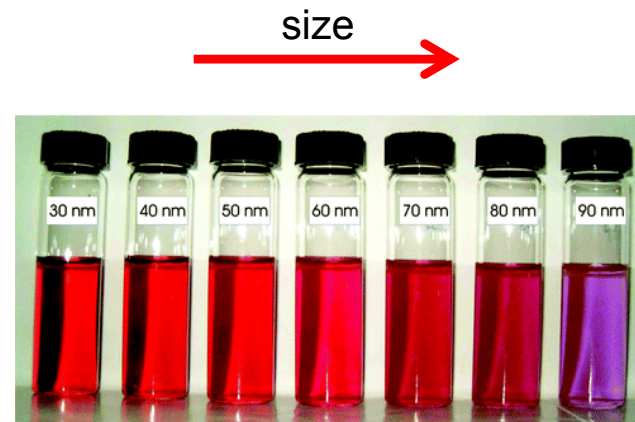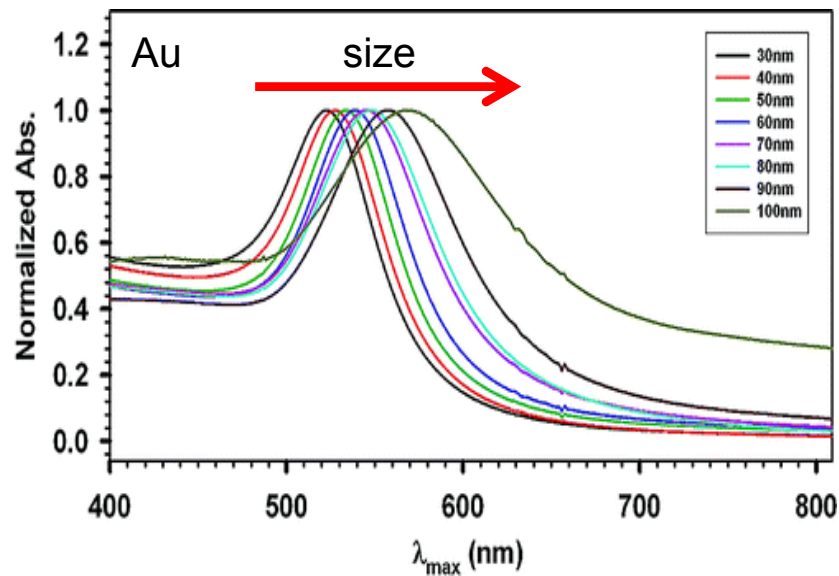
Instrumentation

- **Dispersive instruments**

Measurement geometry:
- transmission
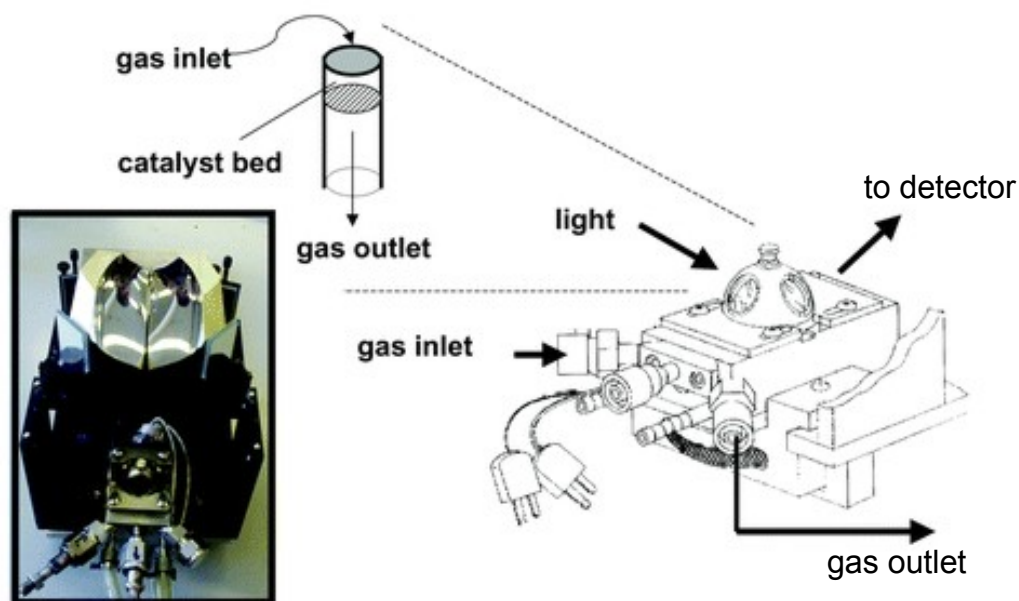- diffuse reflectance

double beam spectrometer
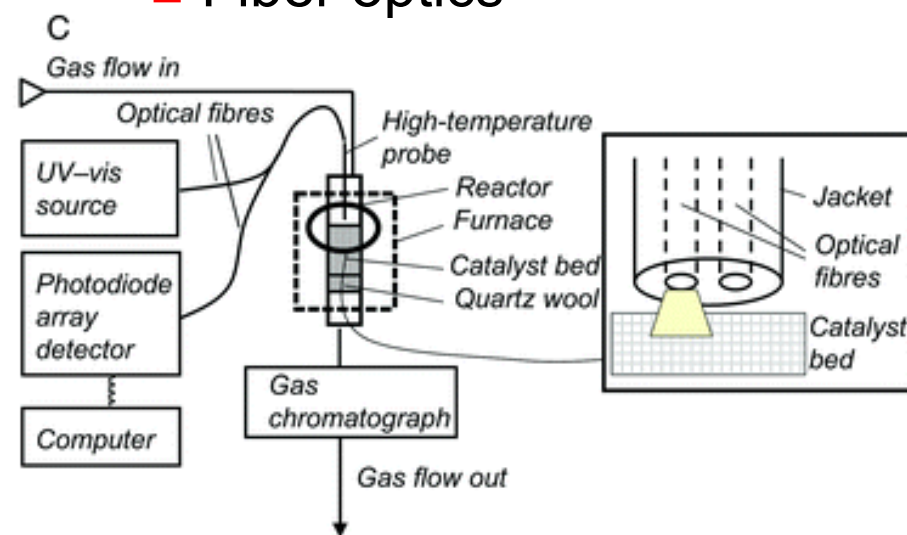

single beam spectrometer

In situ instrumentation

- ■ Diffuse reflectance (DRUV)

- ■ Fiber optics

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

☒ - long meas. time
- spectral collection (λ after λ)

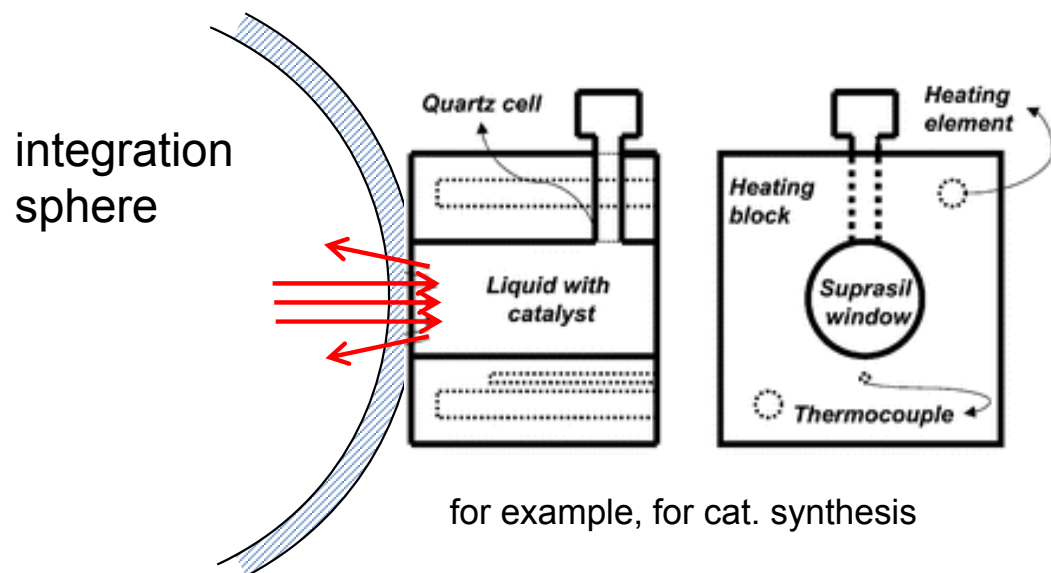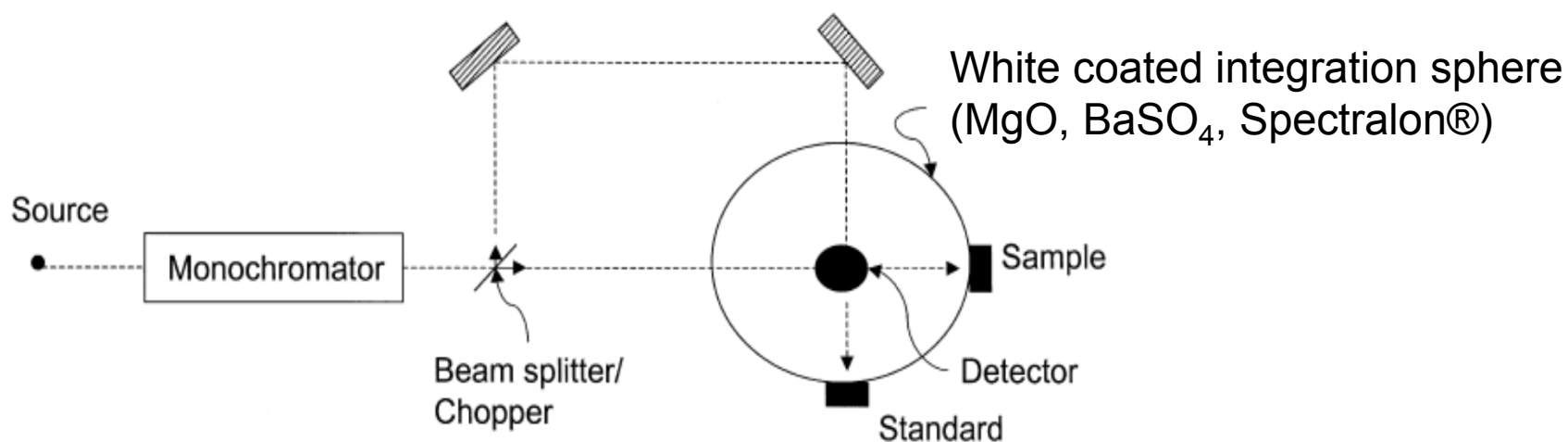→ different parts of spectrum do not represent same reaction time!!!

☑ - time resolution (CCD camera)
[spectra colleted at once]
- coupling to reactors

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

Weckhuysen, *Chem. Commun.* (2002) 97

In situ instrumentation

■ Integration sphere

White coated integration sphere
(MgO, $BaSO_4$, Spectralon®)

Source

Monochromator

Beam splitter/
Chopper

Sample

Detector

Standard

integration
sphere

Quartz cell

Heating
block

Liquid with
catalyst

Heating
element

Suprasil
window

Thermocouple

- > 95% light is collected
- high reflectivity
- wide range of λ

- only homemade cells

for example, for cat. synthesis

Weckhuysen, *Chem. Commun.* (2002) 97

Examples

- **Determination of oxidation state: 0.1 wt% Cr^{n+}/Al_2O_3**

Compound	Coordination geometry and oxidation state	Absorption bands (nm)[a]	Color
K_2CrO_4 (solution)	T_d, Cr^{6+}	440 (sh, vw), 370 (s), 275 (s)	Yellow
K_2CrO_4 (solid)	T_d, Cr^{6+}	459 (s), 340 (s), 265 (s), 229 (s)	Yellow
$K_2Cr_2O_7$ (solution)	T_d, Cr^{6+}	440 (w), 352 (s), 255 (s)	Orange
$K_2Cr_2O_7$ (solid)	T_d, Cr^{6+}	526 (s, br), 332 (s), 262 (s), 229 (s)	Orange–red
$Cr(NO_3)_3 \cdot 9H_2O$ (solution)	O_h, Cr^{3+}	575 (s), 410 (s), 303 (s)	Green
$Cr(NO_3)_3 \cdot 9H_2O$ (solid)	Dist O_h, Cr^{3+}	575 (s), 410 (s), 304 (s), 263 (sh)	Green
$Cr(H_2O)_6^{2+}$ (solution)	O_h, Cr^{2+}	769 (s)	Blue
K_2CrCl_4 (solid)	Distorted T_d, Cr^{2+}	1430 (s)	Blue
Cr_2O_3 (solid)	Distorted O_h, Cr^{3+}	714 (sh), 645 (sh), 595 (s), 461 (s), 351 (s), 274 (s)	Green

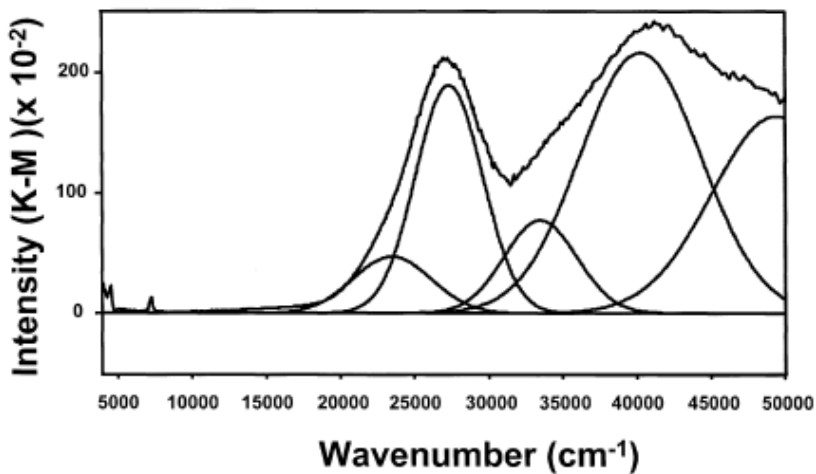[a] s: strong; m: medium; w: weak; vw: very weak; sh: shoulder; br: broad.

Cr^{6+} (250, 370 nm)

reduction in CO atmosphere

Cr^{3+}/Cr^{2+}

T_{red}

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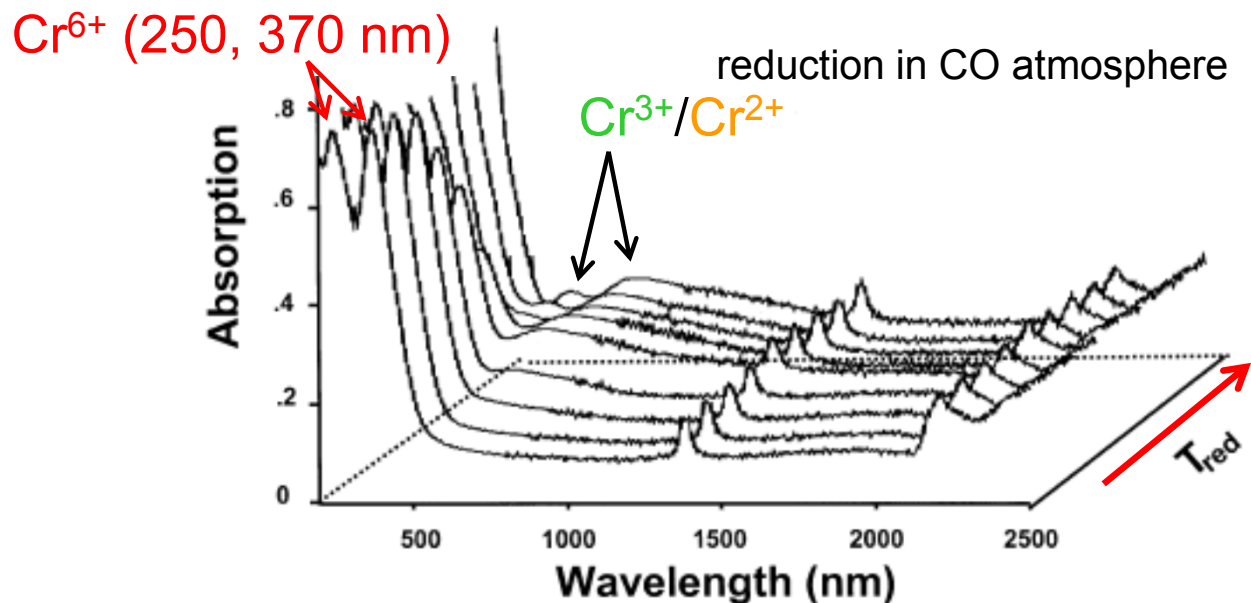
Examples

■ **Determination of oxidation state: 0.1 wt% Cr^{n+}/Al_2O_3**
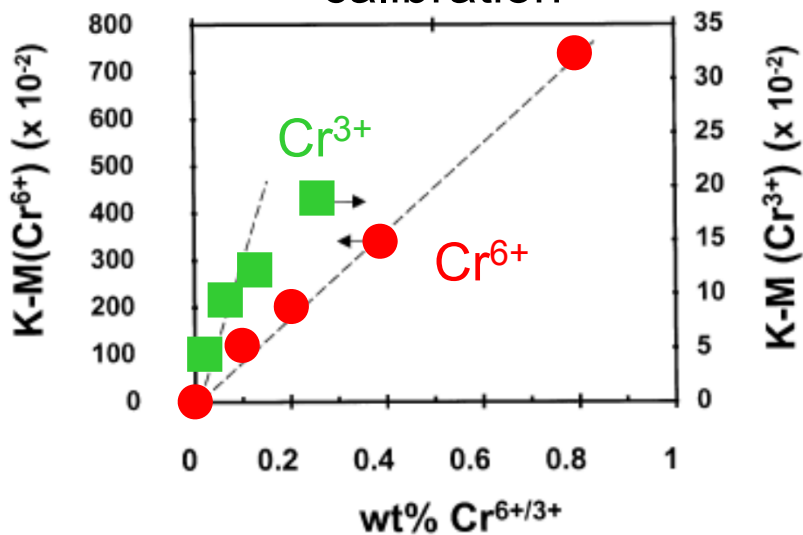
calibration

distribution of Cr^{n+}

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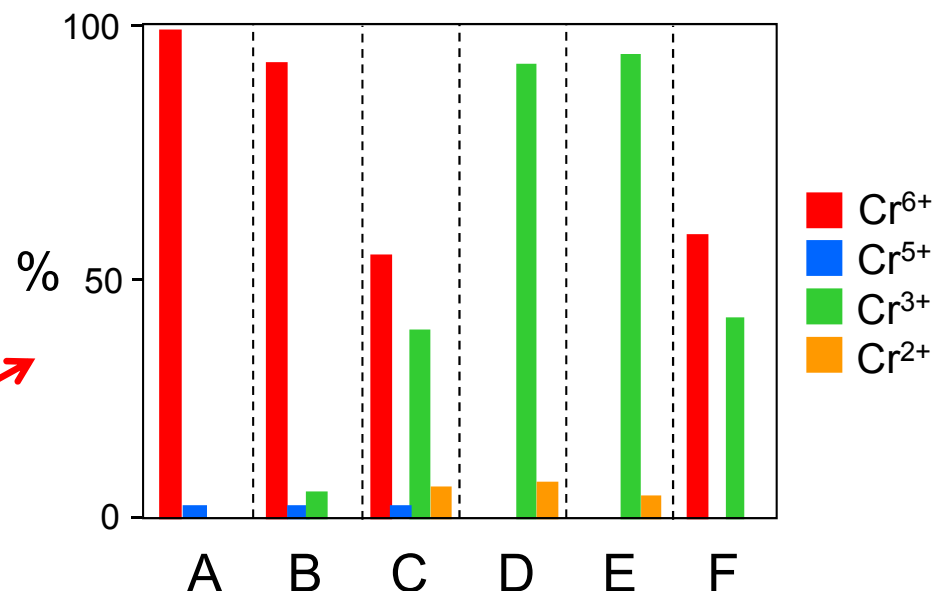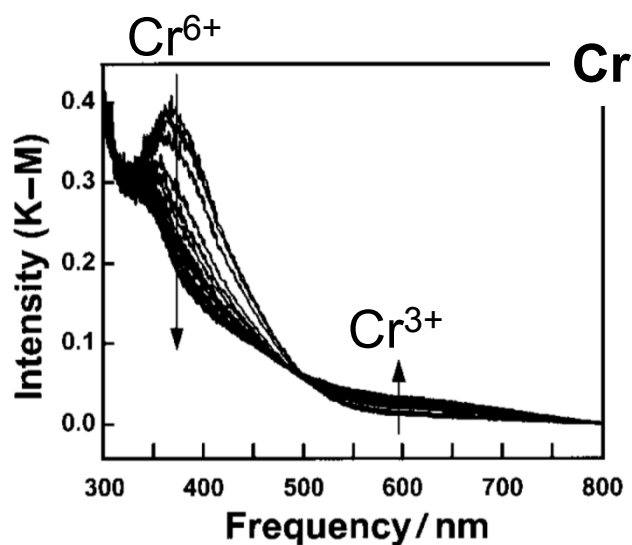
A: calc. 550°C
B: red. 200°C
C: red. 300°C
D: red. 400°C
E: red. 600°C
F: re-calc. 550°C

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

Examples

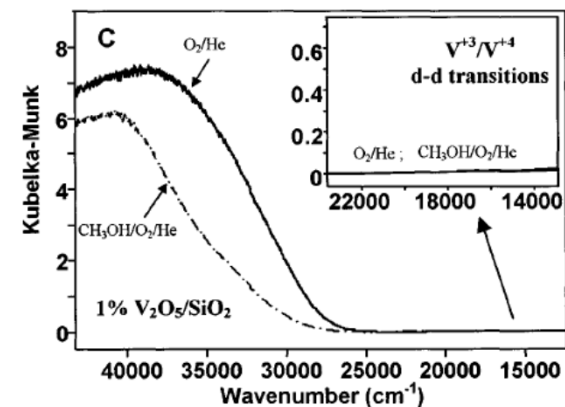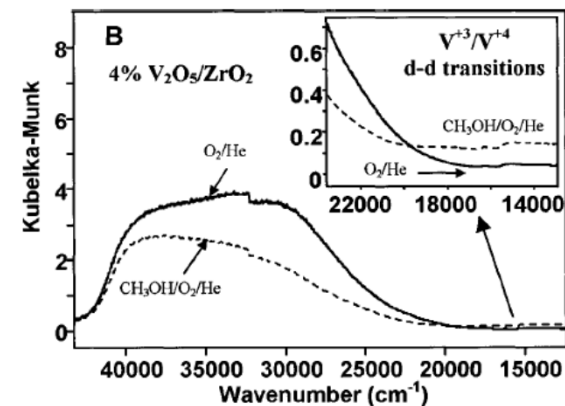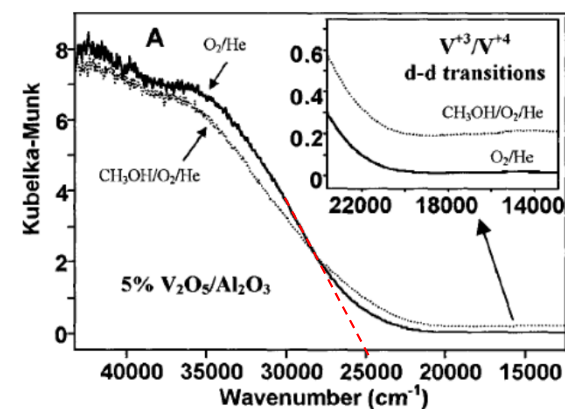

Cr^{6+}

Cr

Cr^{3+}

0.2 wt% Cr/SA, 500°C in 18 vol% n-butane in N_2

Table 1

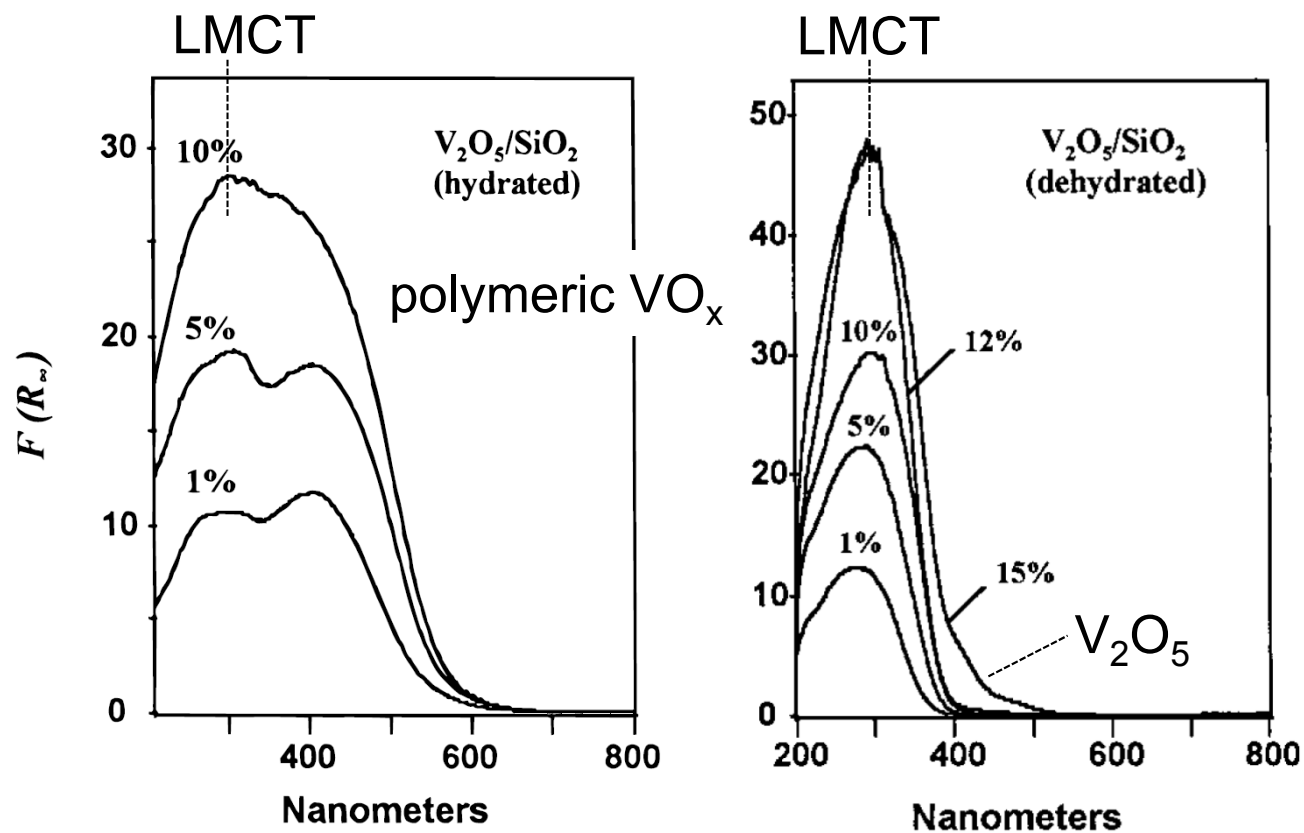UV-Vis DRS edge energies (V^{5+} LMCT band) during methanol oxidation at 230 °C.

Catalyst	E_g (eV)		ΔE_g (eV)[a]
	O_2/He at 230 °C	CH_3OH/O_2/He at 230 °C	CH_3OH/O_2/He at 230 °C
1% V_2O_5/SiO_2	3.74	4.31	0.57
5% V_2O_5/Al_2O_3	3.61	3.65	0.04
4% V_2O_5/ZrO_2	3.14	3.29	0.15

[a] $\Delta E_g = E_g(rxn) - E_g(O_2/He)$.

Weckhuysen et al., *J. Chem. Soc., Faraday Trans.*, **94** (1998) 2011
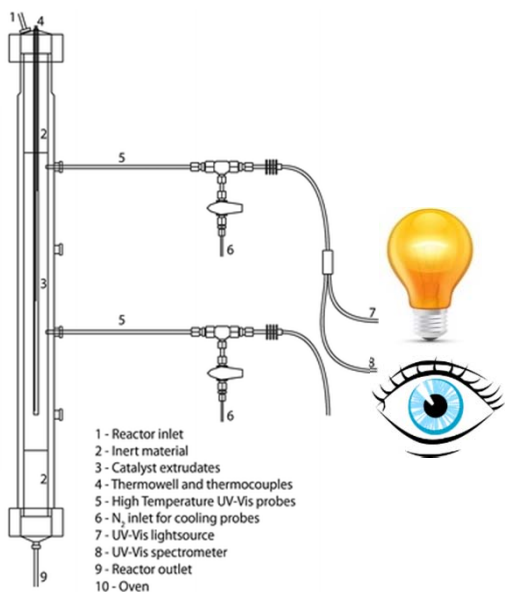Burcham et al., *Top. Catal.*, **11/12** (2000) 85
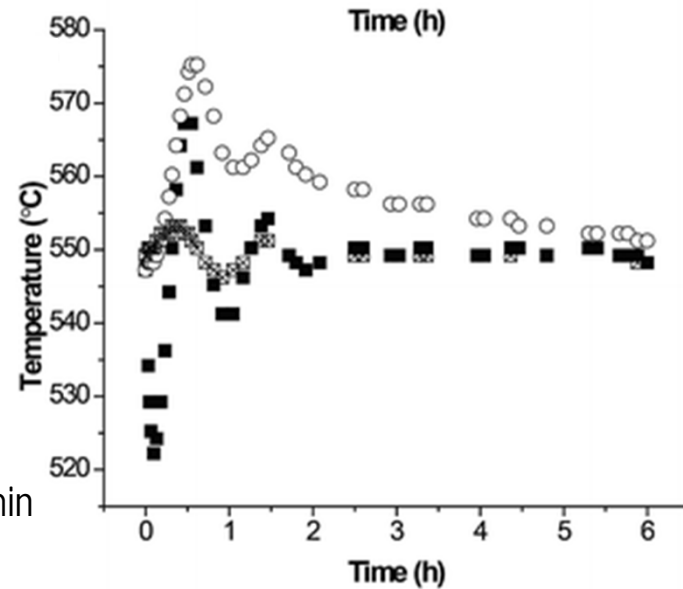
Examples

- UV-vis of V_2O_5-SiO_2

Examples

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

1 - Reactor inlet
2 - Inert material
3 - Catalyst extrudates
4 - Thermowell and thermocouples
5 - High Temperature UV-Vis probes
6 - N_2 inlet for cooling probes
7 - UV-Vis lightsource
8 - UV-Vis spectrometer
9 - Reactor outlet
10 - Oven

10 vol% C_3H_8, 90 vol% N_2, 5000 ml/min
20 wt% $Cr^{3+/6+}O_x/Al_2O_3$

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

Examples

- UV-vis probe in a pilot-scale reactor

bottom UV-vis probe

average intensity 600-700 nm
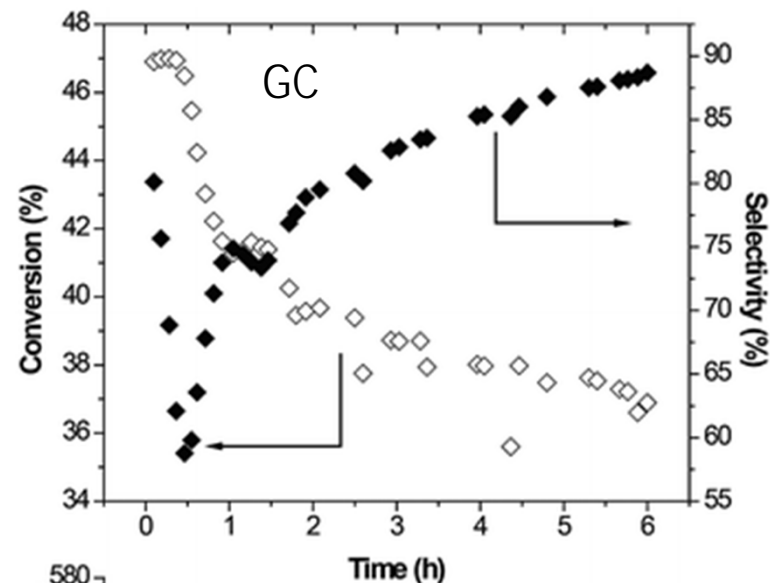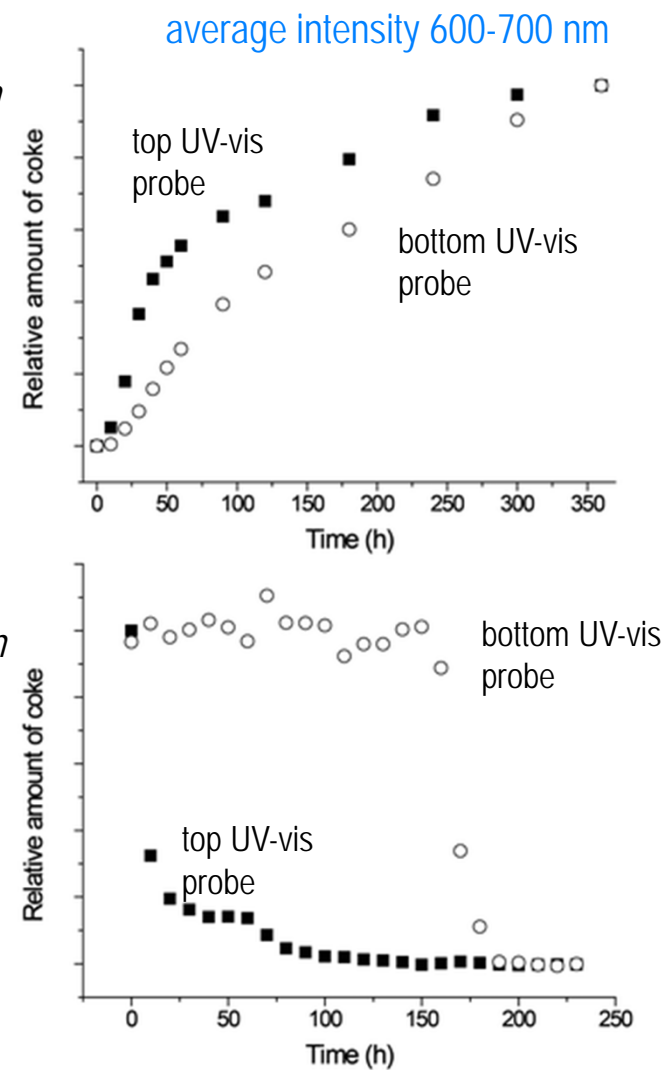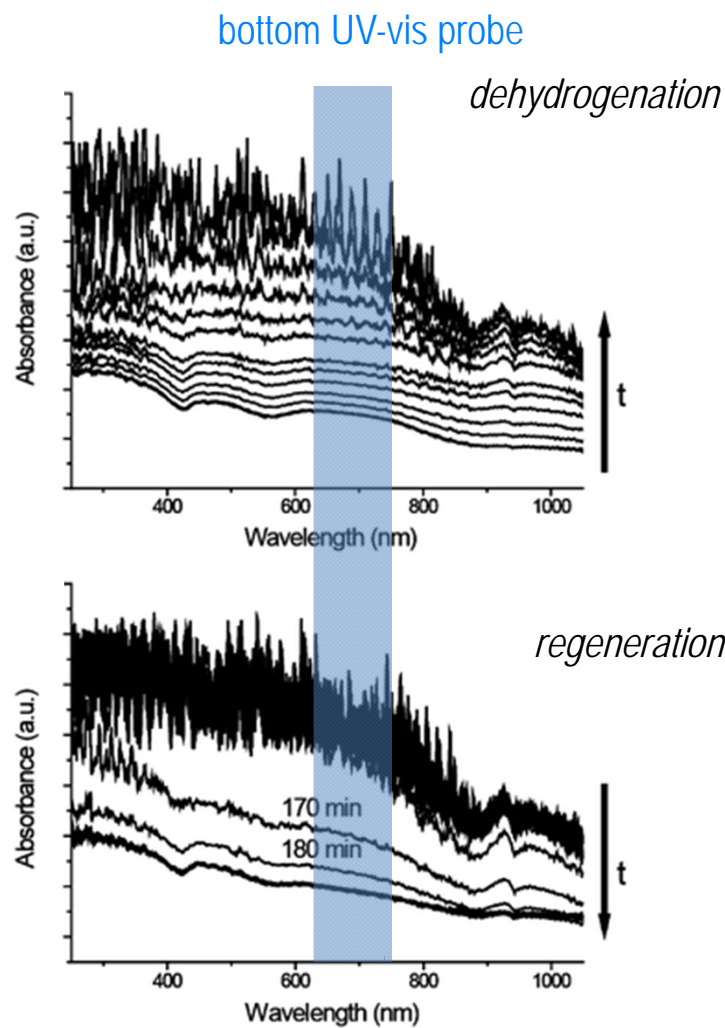
- Coke formation fast on top section of reactor
- Coke is combusted fast in top section of reactor

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