UV-Vis spectroscopy

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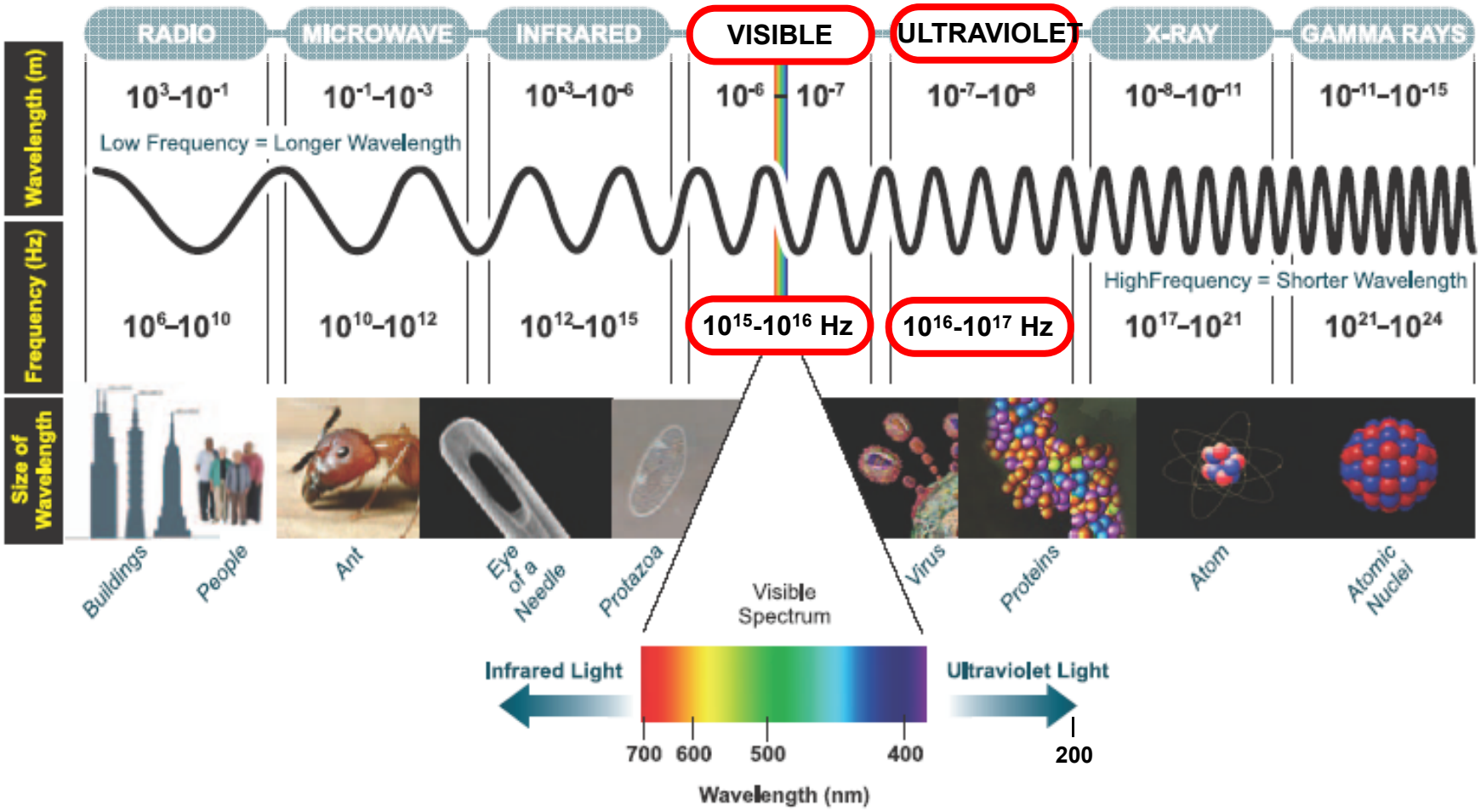
The electromagnetic spectrum



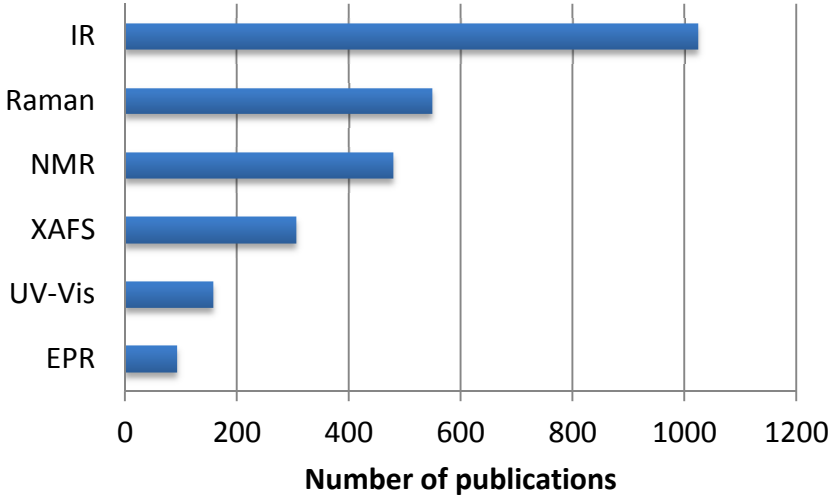
source: Andor.com

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

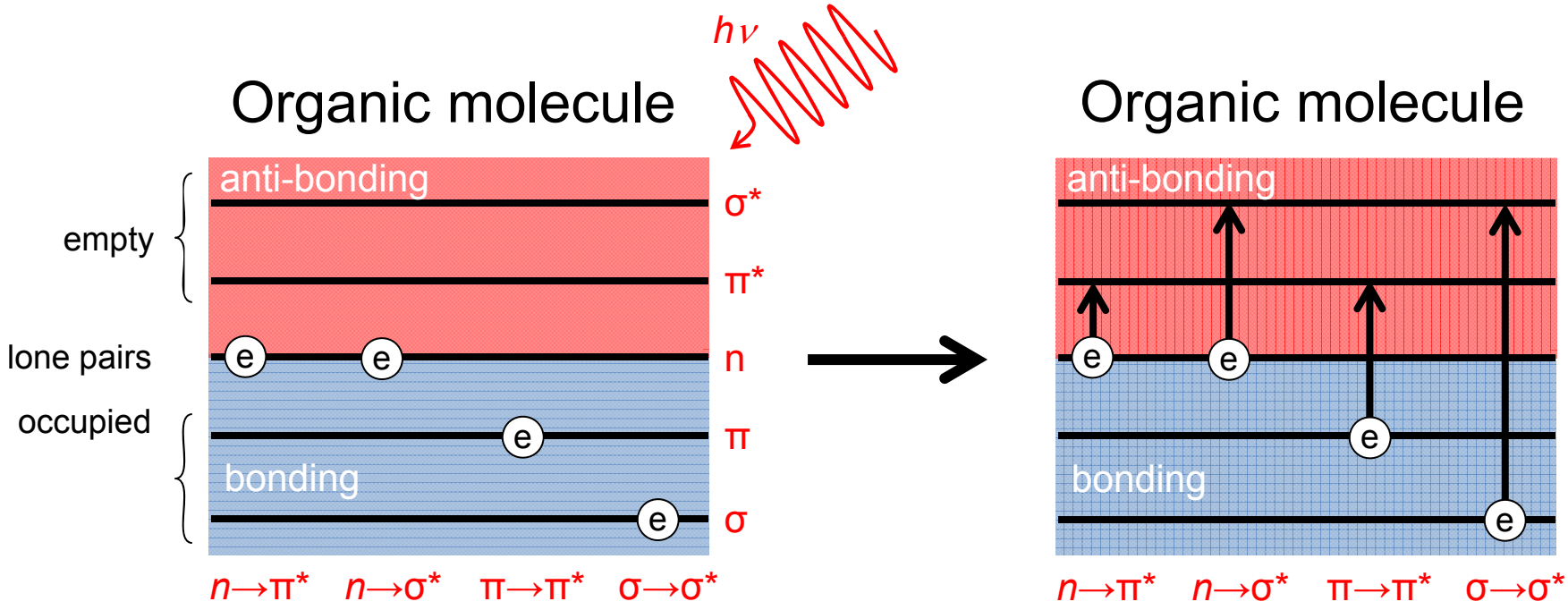
- economic
- non-invasive (fiber optics!)
- versatile (e.g. solid, liquid, gas)
- extremely sensitive (concentration)
- fast acquisition (but S/N!)



cons

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

Electronic transitions



$E = h\nu$

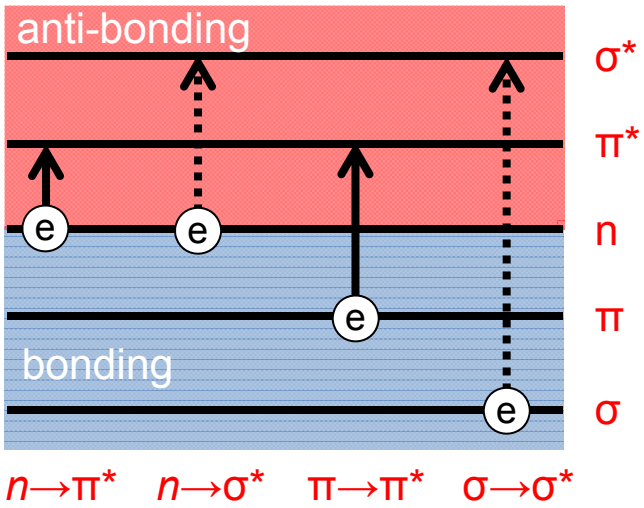
$\lambda = c/\nu$

high e^- jump $\rightarrow$ high E

high $E \rightarrow$ high ν

high $\nu \rightarrow$ low λ

Electronic transitions



σ→σ*
high *E*, low λ (<200 nm)

n→σ*
150-250 nm, weak

n→π*
200-700 nm, weak

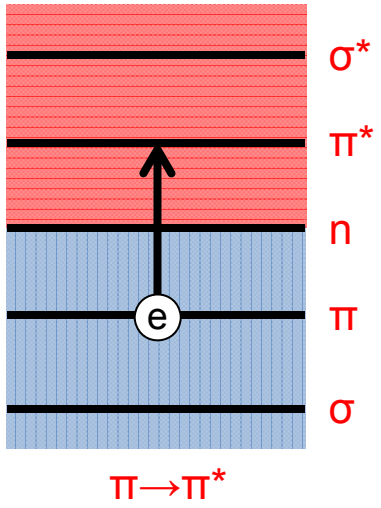
π→π*
200-700 nm, intense

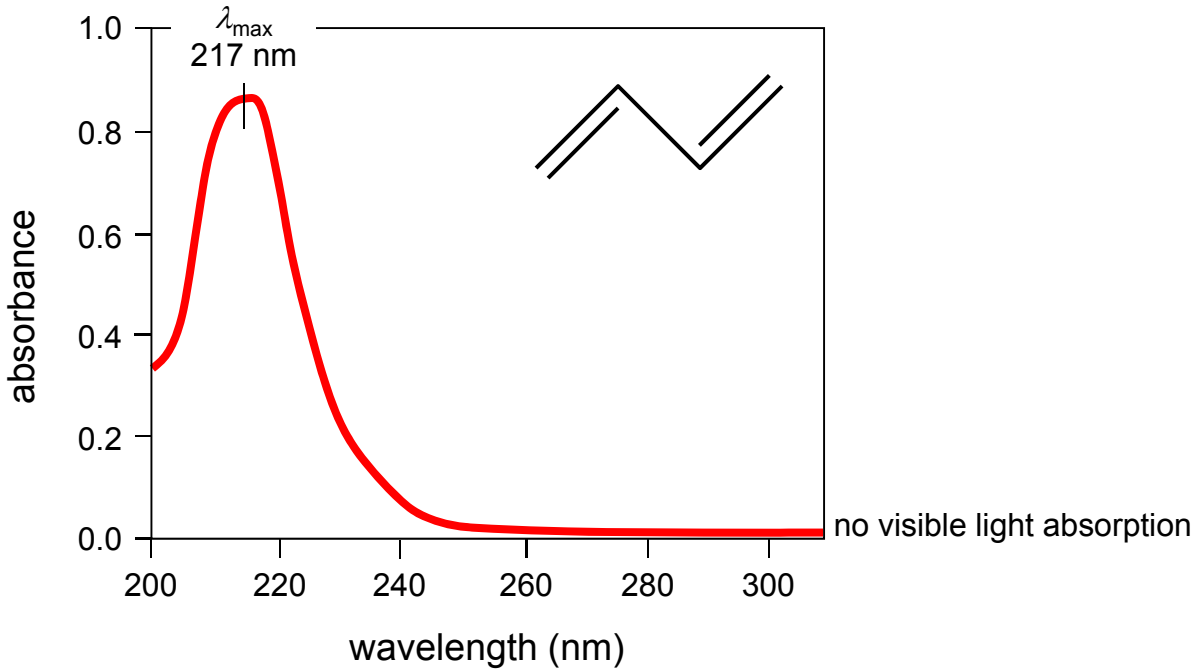
Condition to absorb light (200-800 nm):

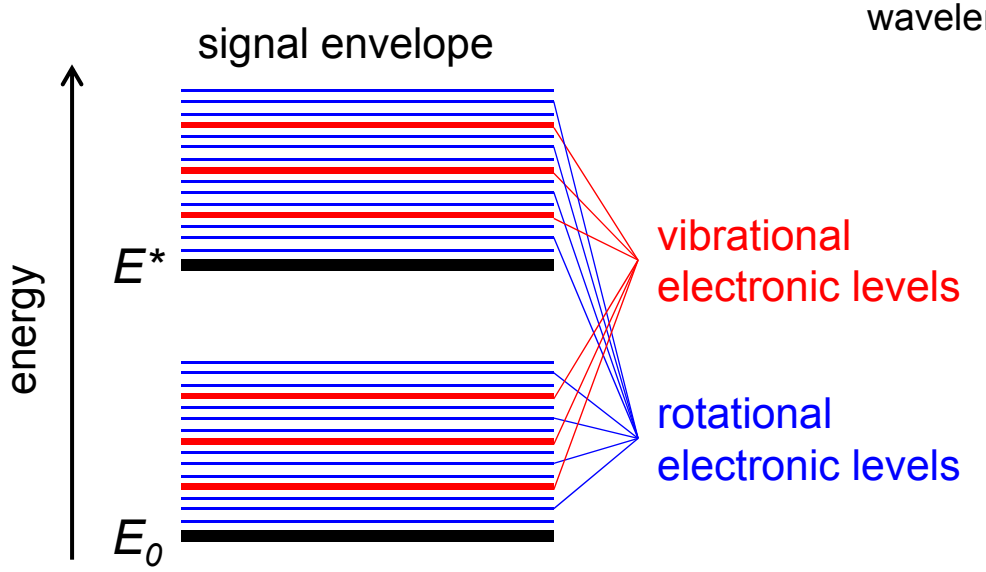
π and/or *n* orbitals

CHROMOPHORE

The UV spectrum



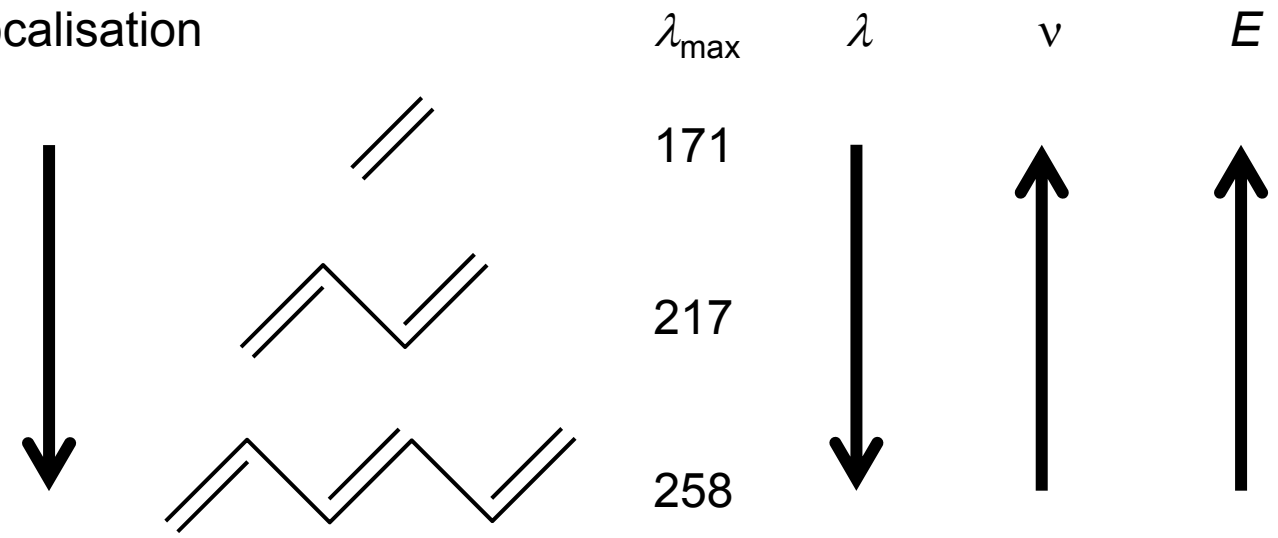


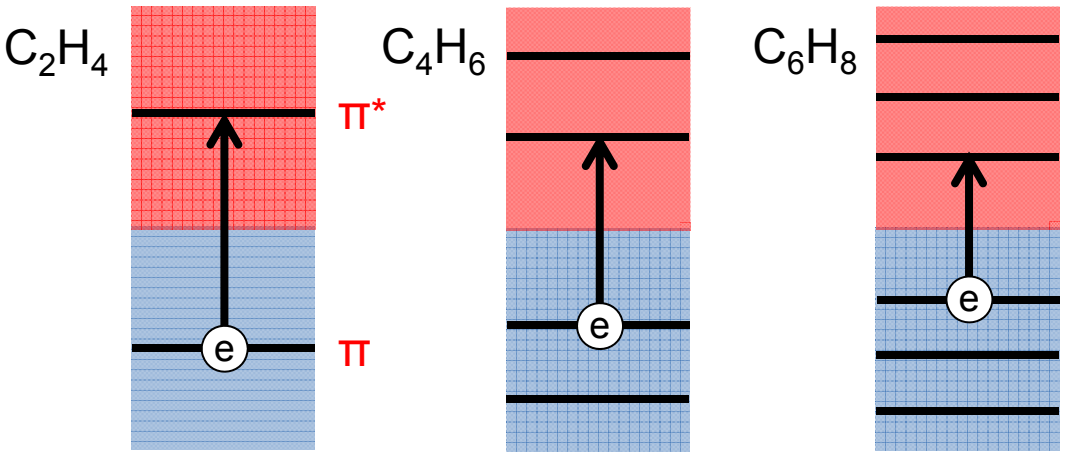


Q How many signals do you expect from CH_3-CH=O?

The UV spectrum

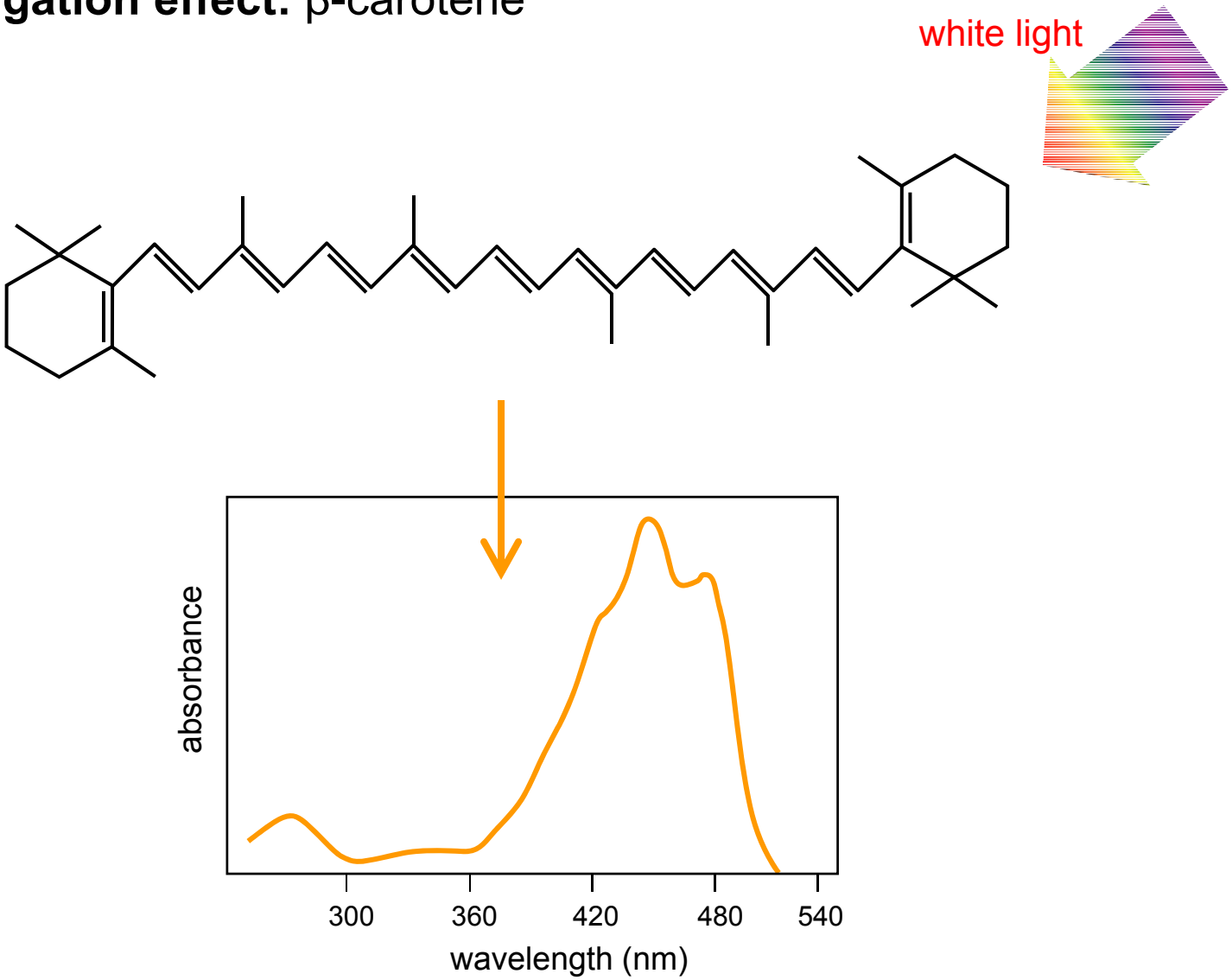
- **Conjugation effect**





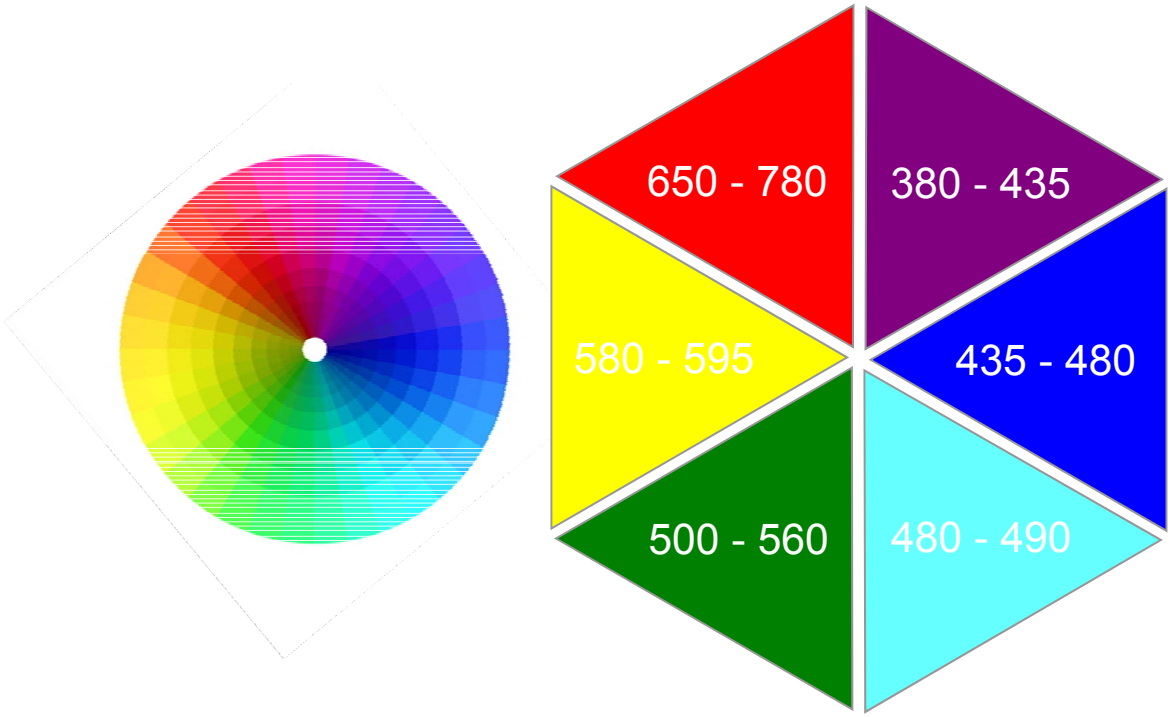
The UV spectrum

- **Conjugation effect:** β-carotene



The UV spectrum

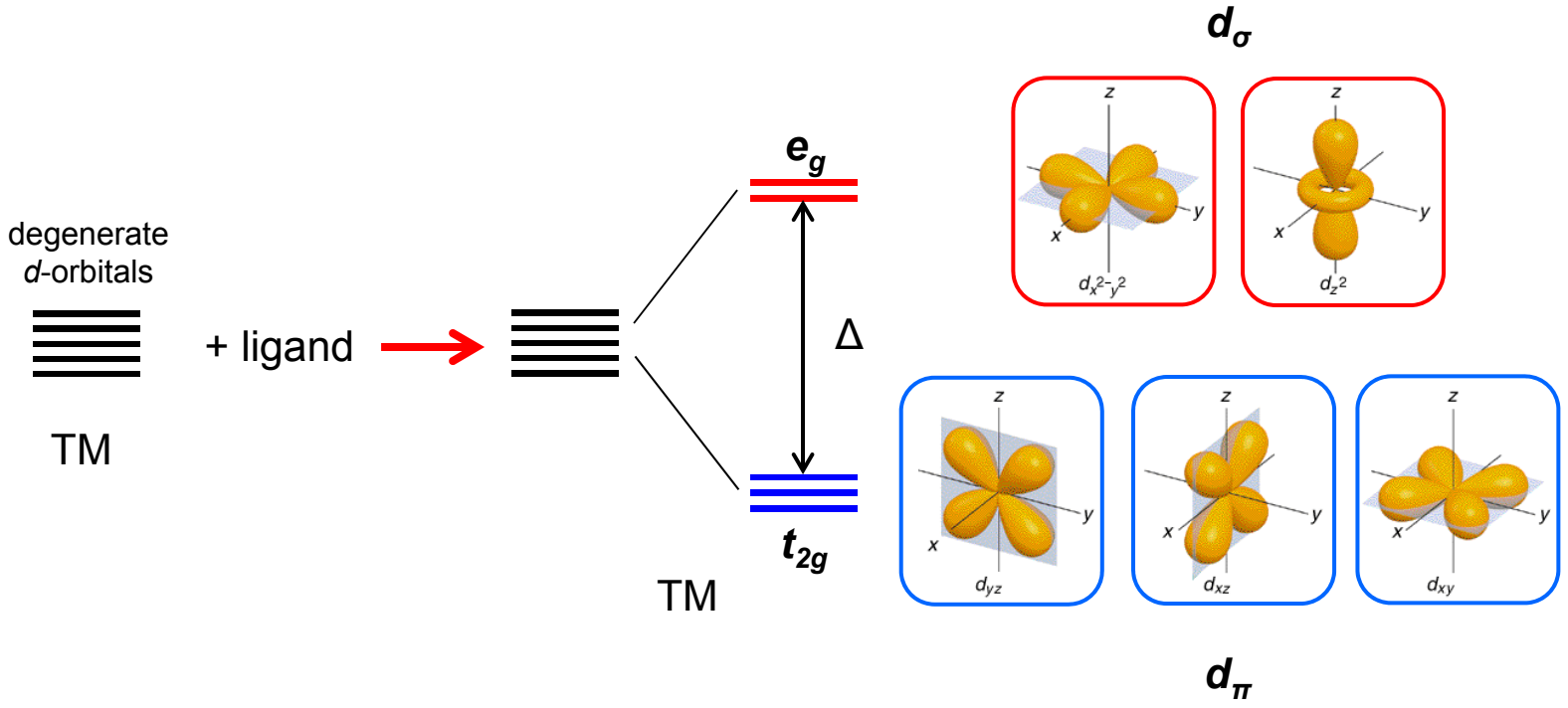
- **Complementary colours**



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

Inorganic compounds

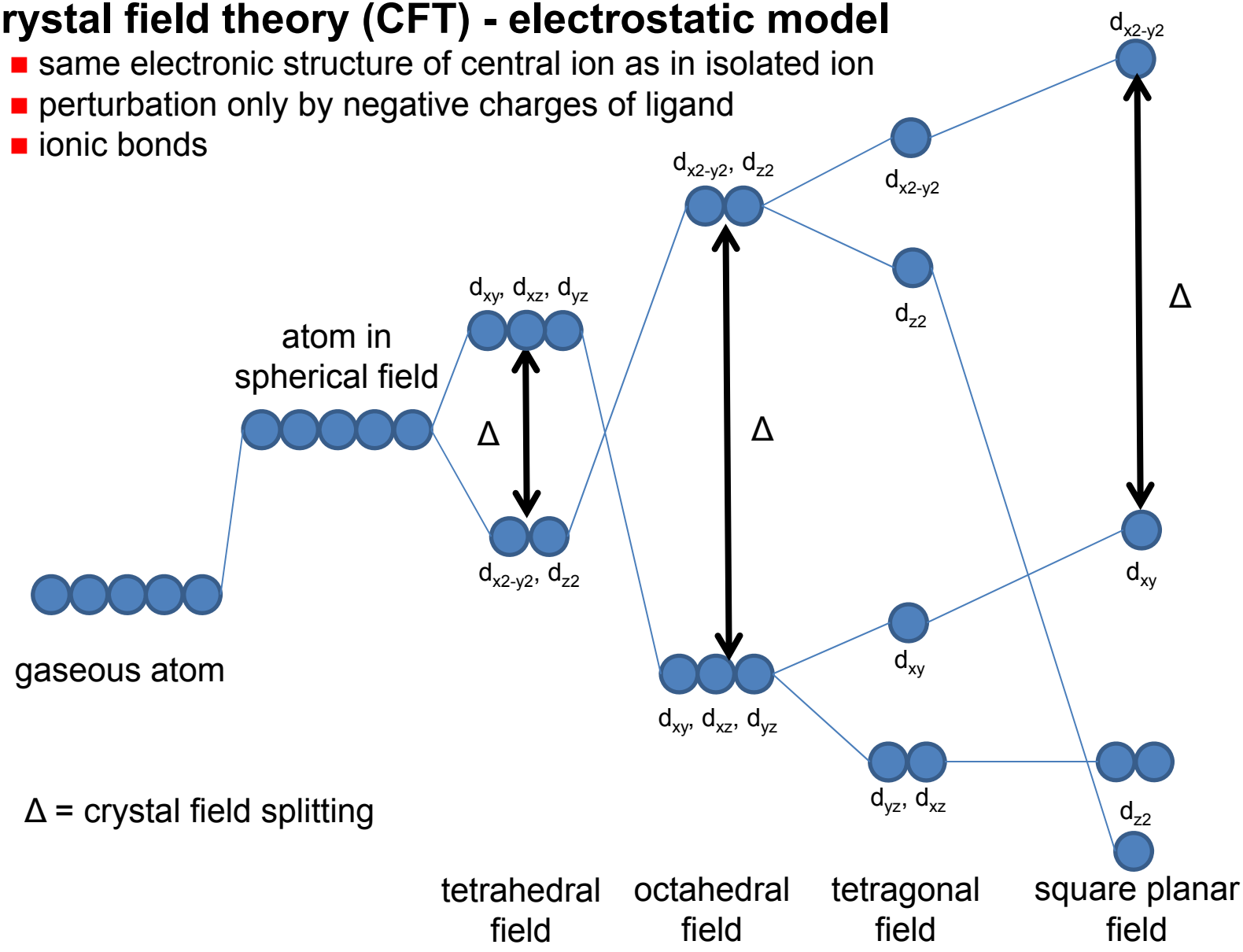
- UV-vis spectra of transition metal complexes originate from
  - **Electronic *d-d* transitions**



  - **…**

Inorganic compounds

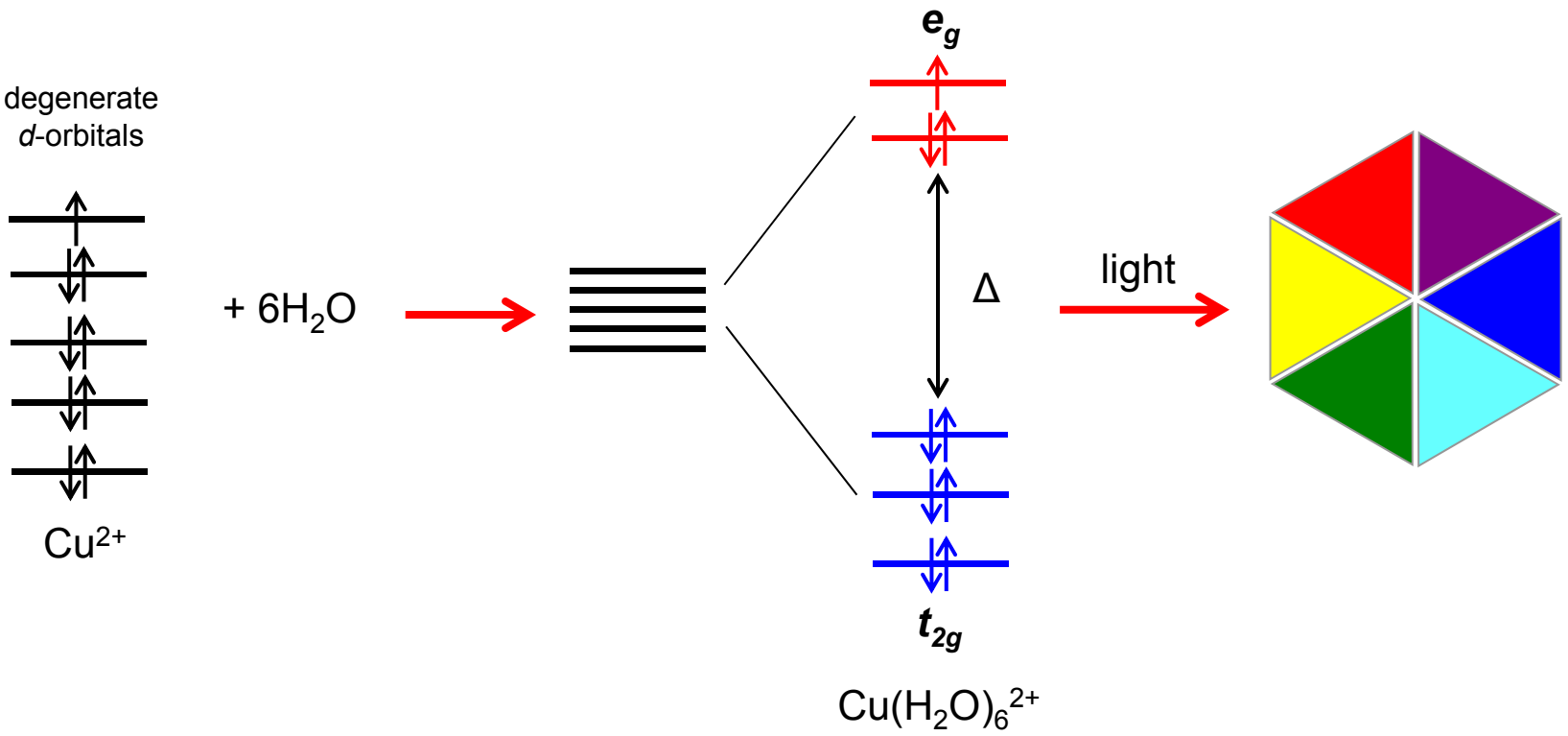
- **Crystal field theory (CFT) - electrostatic model**
  - same electronic structure of central ion as in isolated ion
  - perturbation only by negative charges of ligand
  - ionic bonds



Δ = crystal field splitting

Inorganic compounds

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

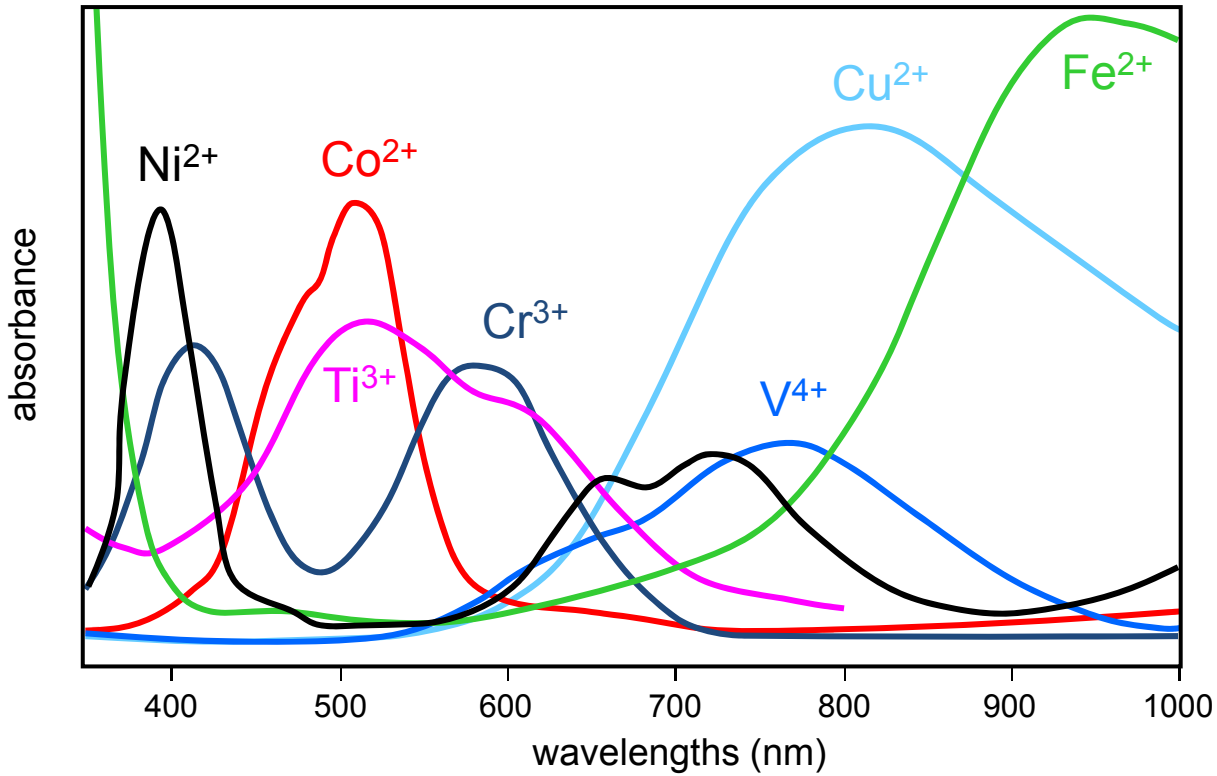


- Yellow light is absorbed and the Cu^{2+} solution is coloured in blue (ca. 800 nm)
- The greater Δ, the greater the *E* needed to promote the e^-, and the shorter λ
- Δ depends on the nature of ligand, $\Delta_{NH3} > \Delta_{H2O}$

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



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

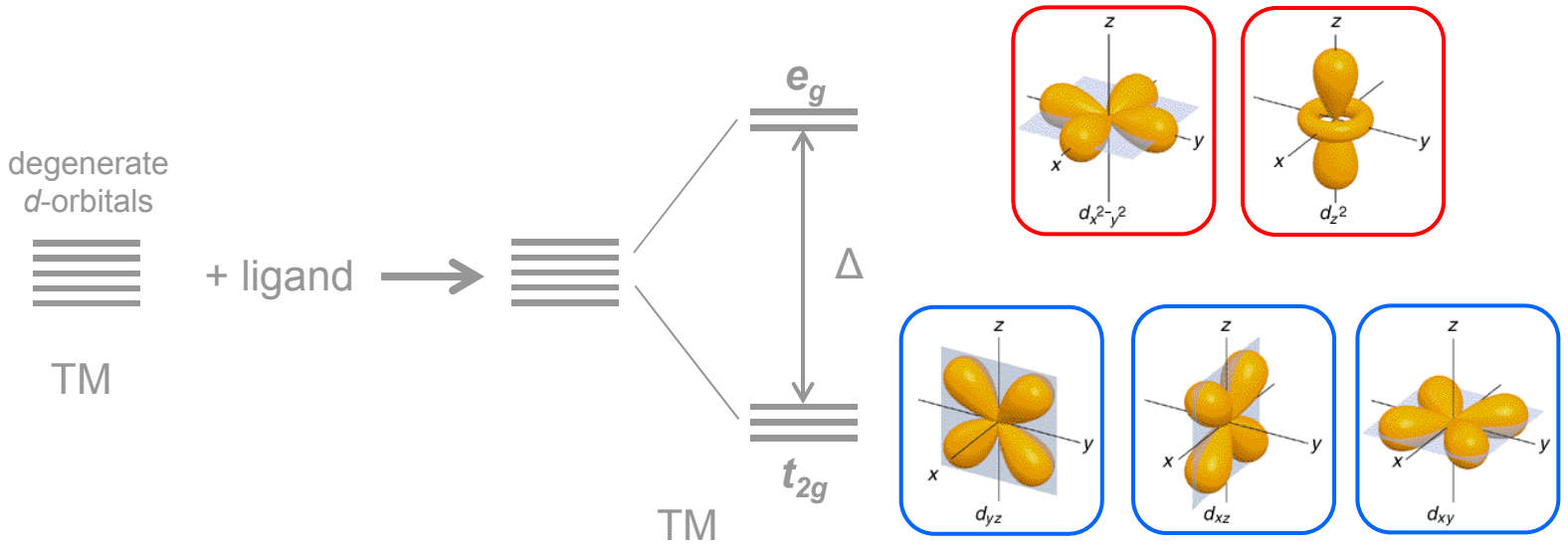
Inorganic compounds

- ***d-d* transitions:** factors governing magnitude of Δ
  - **Oxidation state of metal ion**
    - Δ increases with increasing ionic charge on metal ion
  - **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**



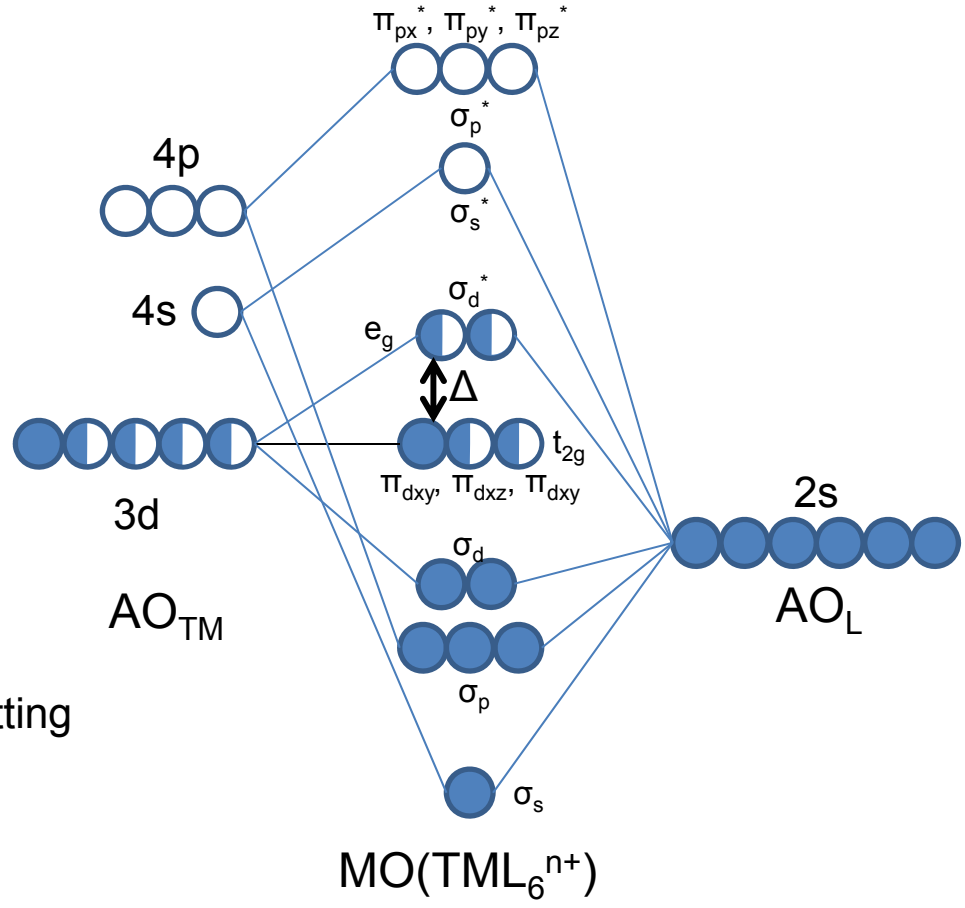
  - **Charge transfer**

Inorganic compounds

- **Charge transfer complex**
  - no selection rules → 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

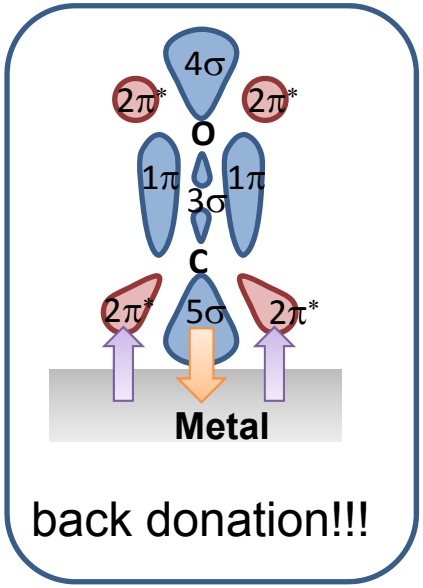
- **Ligand field theory (LFT)**
  - involves AO of metal and ligand, therefore MO
  - what CFT indicates as possible electronic transitions ($t_{2g} \rightarrow e_g$) are now: $\pi_d \rightarrow \sigma_{dz2}^*$ or $\pi_d \rightarrow \sigma_{dx2-y2}^*$



Δ = crystal field splitting

Inorganic compounds

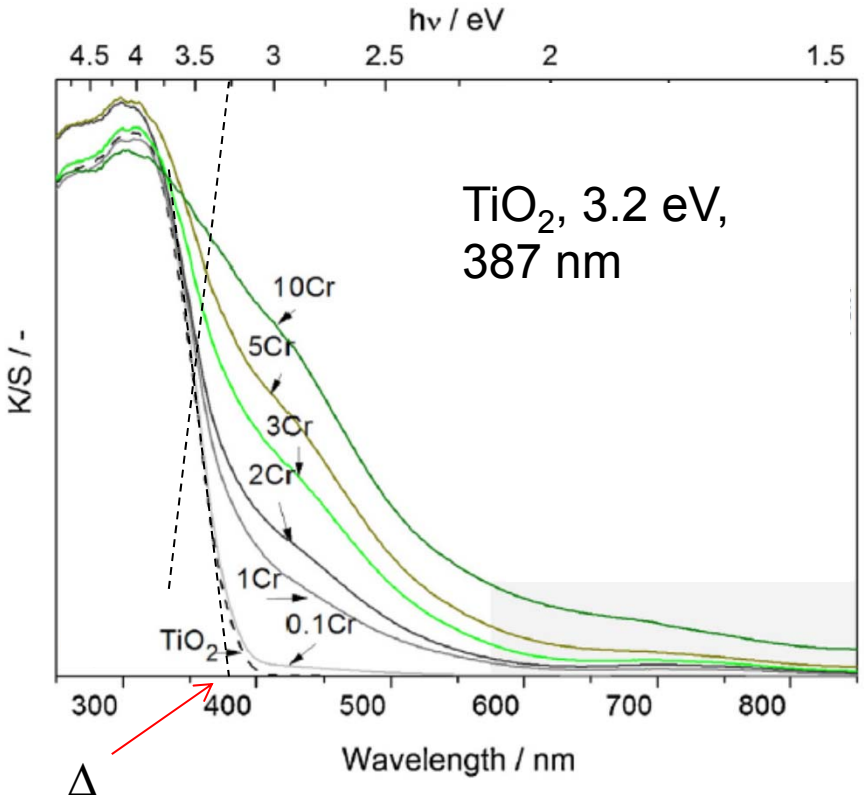
- **Ligand field theory (LFT)**
  - LMCT
    - ligand with high energy lone pair
    - or, metal with low lying empty orbitals
    - *high oxidation state* (also d^0)
    - M-L strengthened
  - MLCT
    - ligands with low lying π* orbitals (CO, CN^-, SCN^-)
    - *low oxidation state* (high energy d orbitals)
    - M-L strengthened, π bond of L weakened

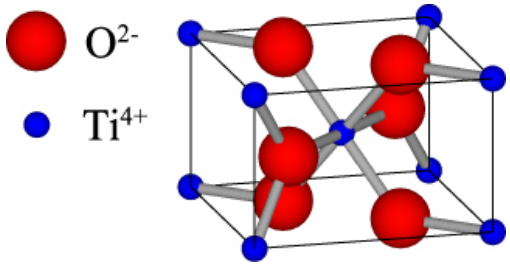


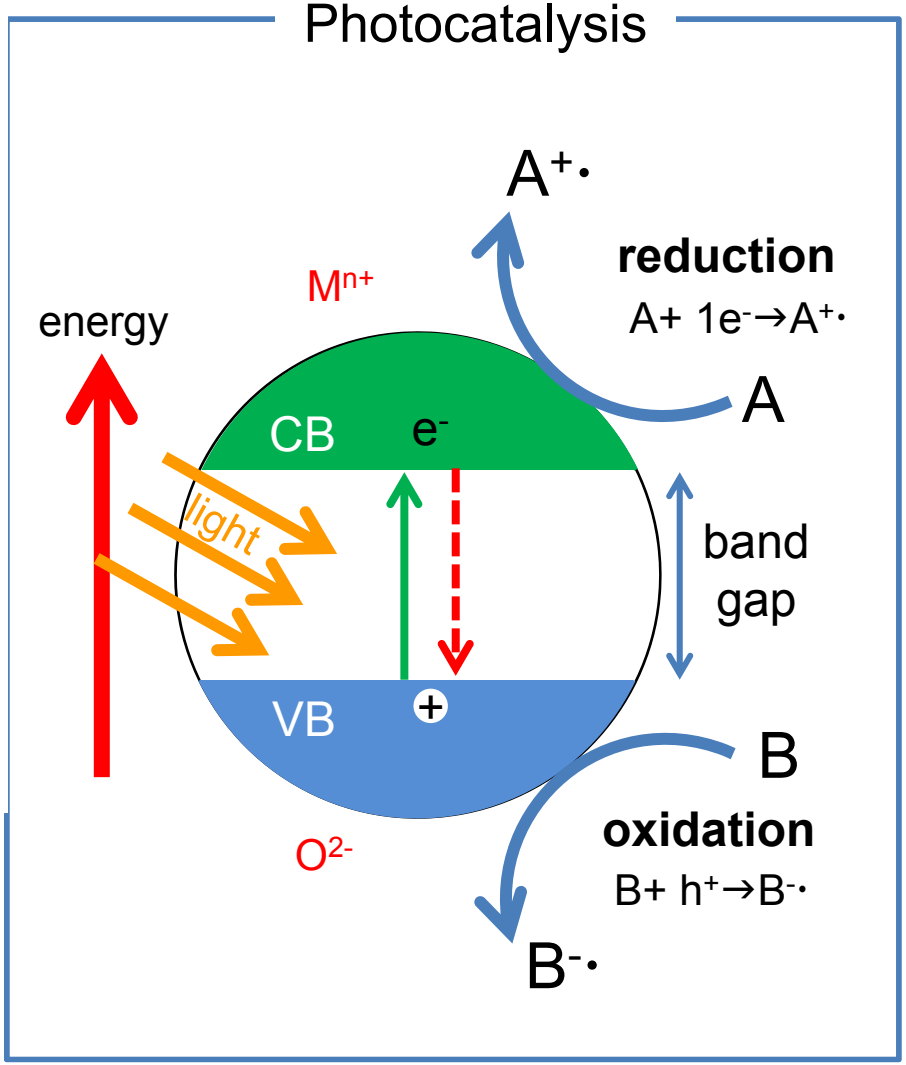
CO adsorption on precious metals

Band gap

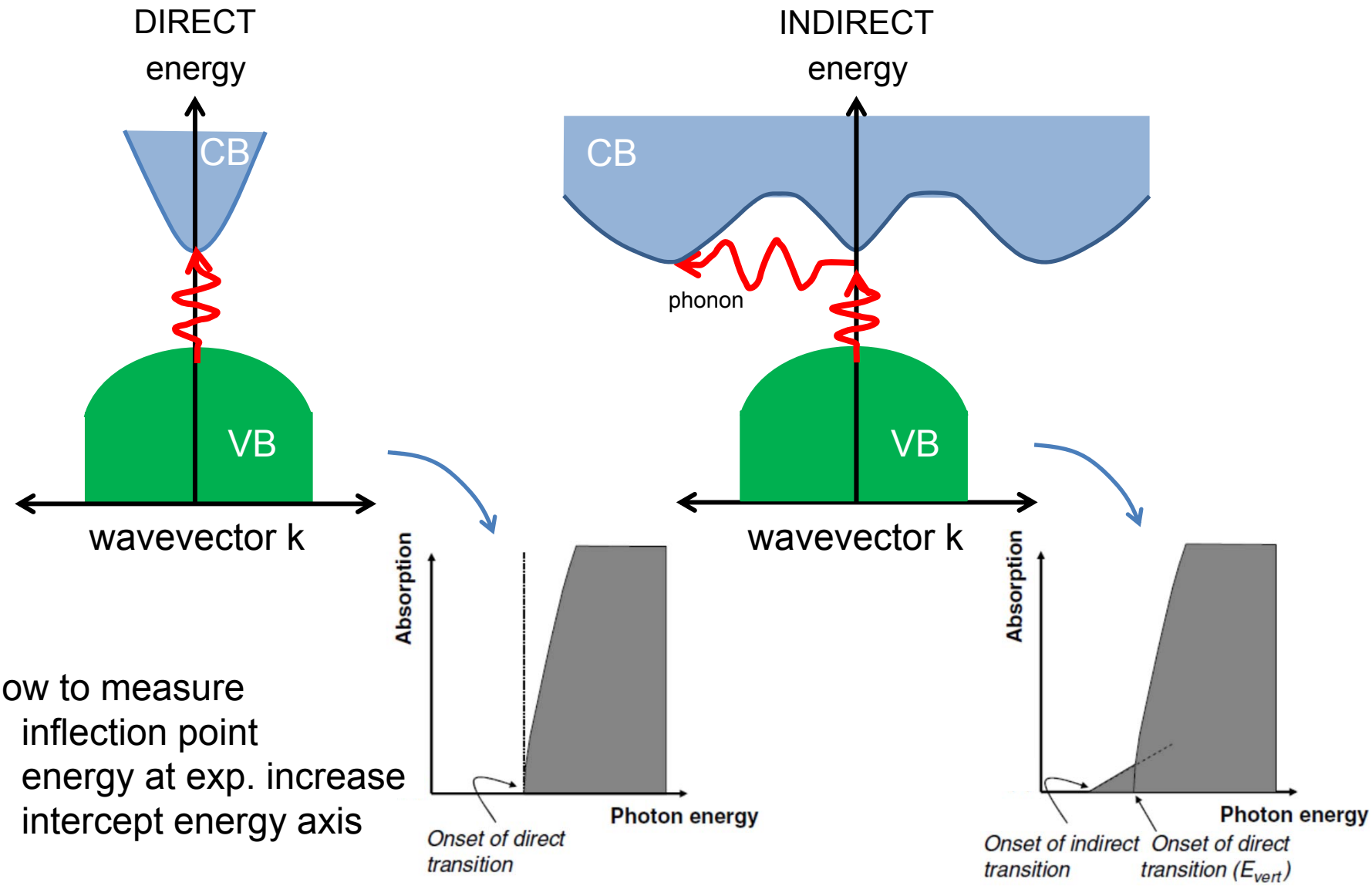
- **Analysis of semiconductors**







Band gap

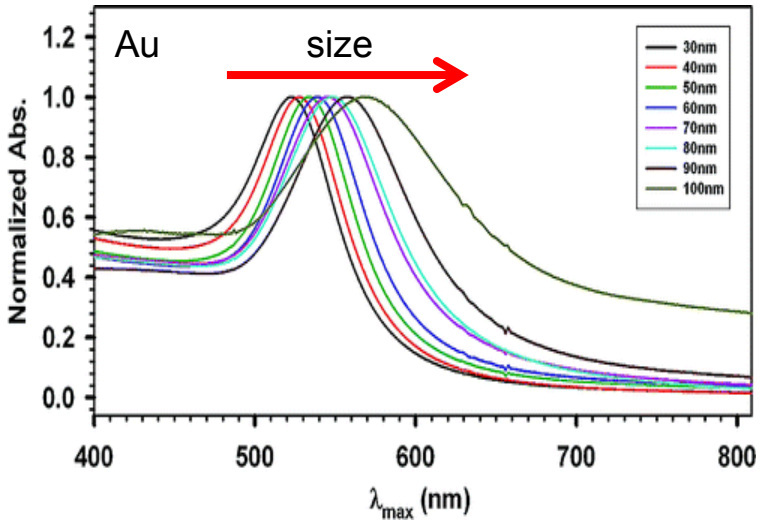


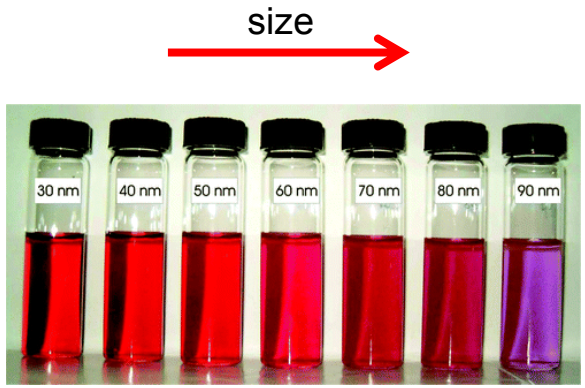
How to measure

- 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
  - λ position depends on nature of metal

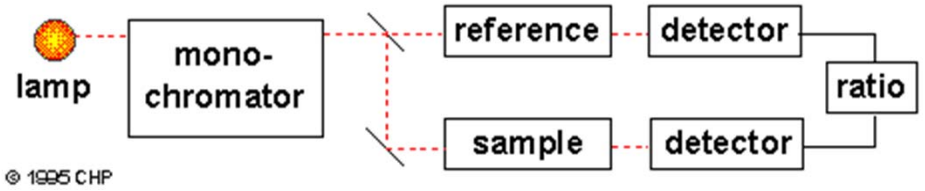




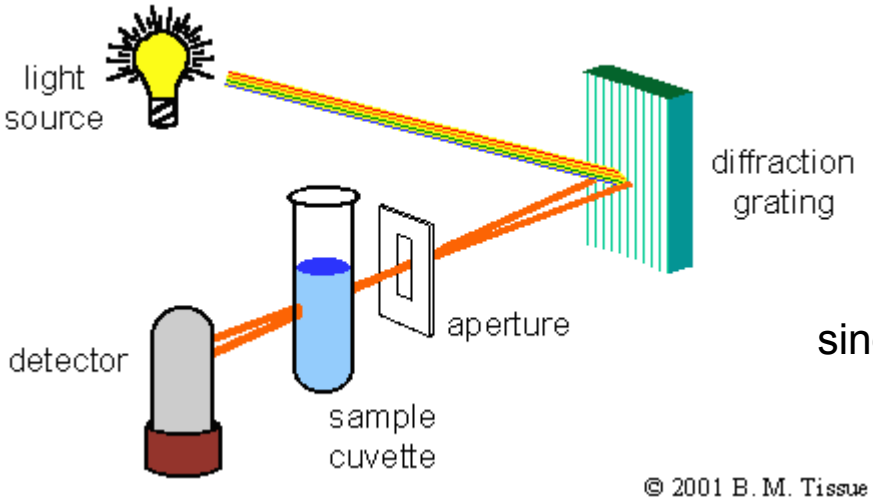
Instrumentation

- **Dispersive instruments**

Measurement geometry:
- transmission
- diffuse reflectance



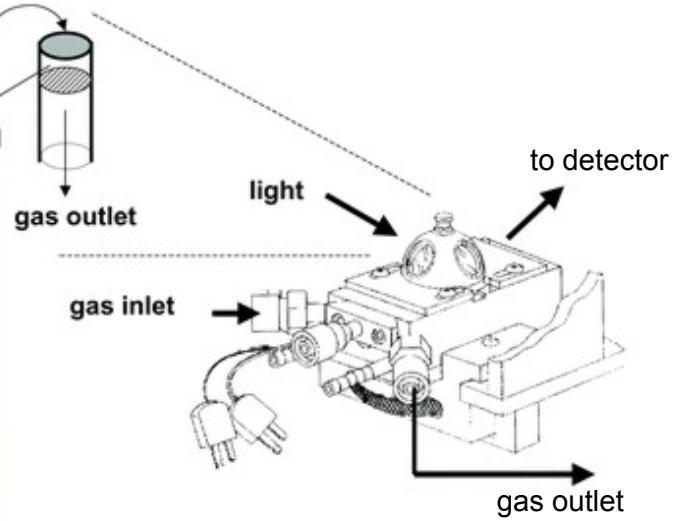
double beam spectrometer



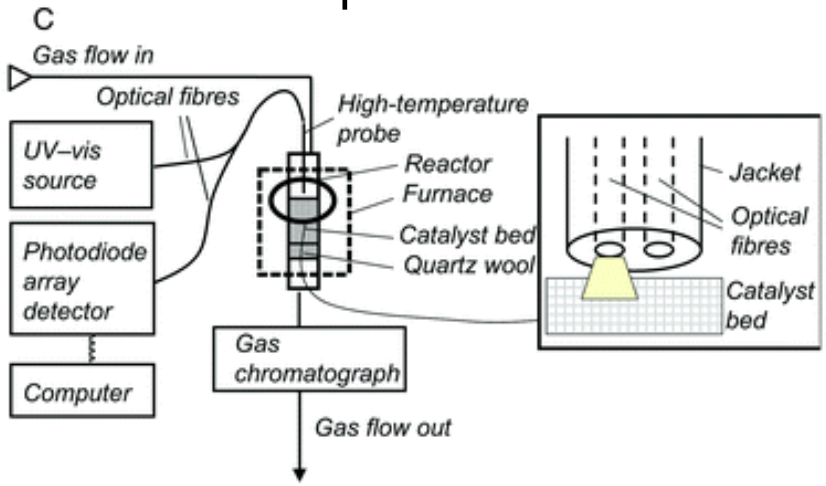
single beam spectrometer

In situ instrumentation

- Diffuse reflectance (DRUV)



- Fiber optics



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

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

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

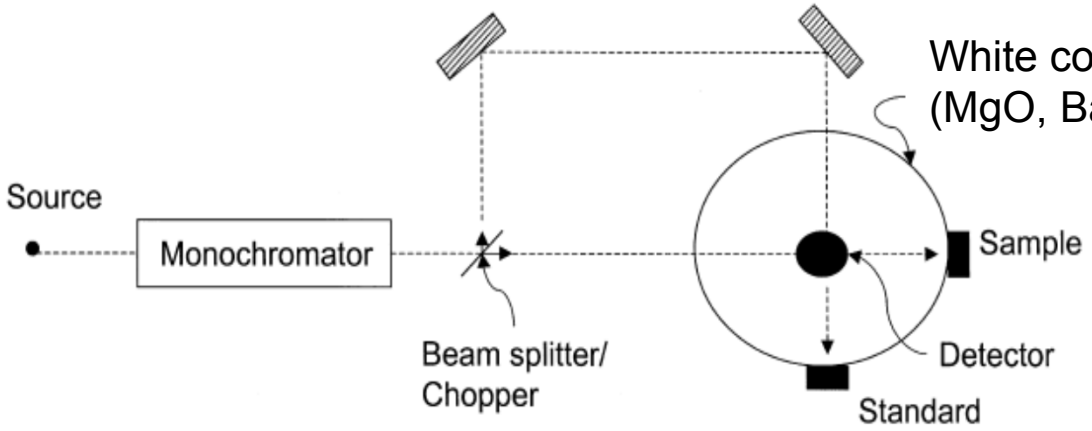
☒ - long meas. time
- spectral collection (λ after λ)

$\longrightarrow$ different parts of spectrum do not represent same reaction time!!!

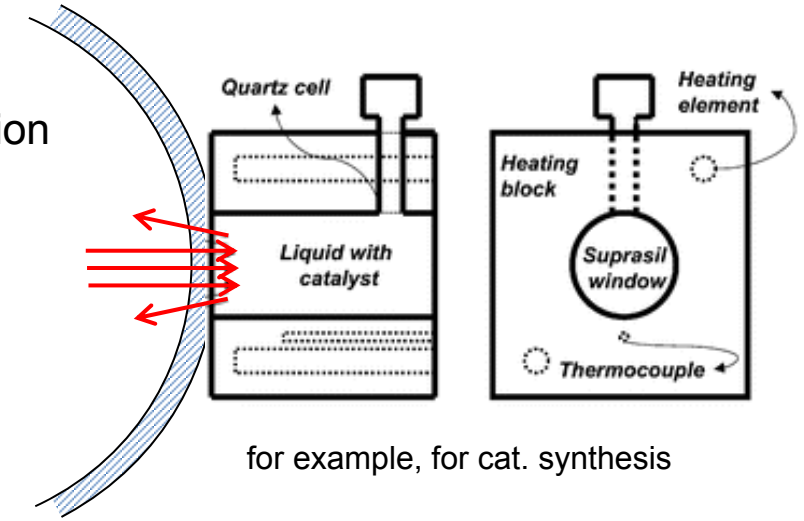
Weckhuysen, *Chem. Commun.* (2002) 97

In situ instrumentation

- Integration sphere



integration sphere



for example, for cat. synthesis

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

- only homemade cells

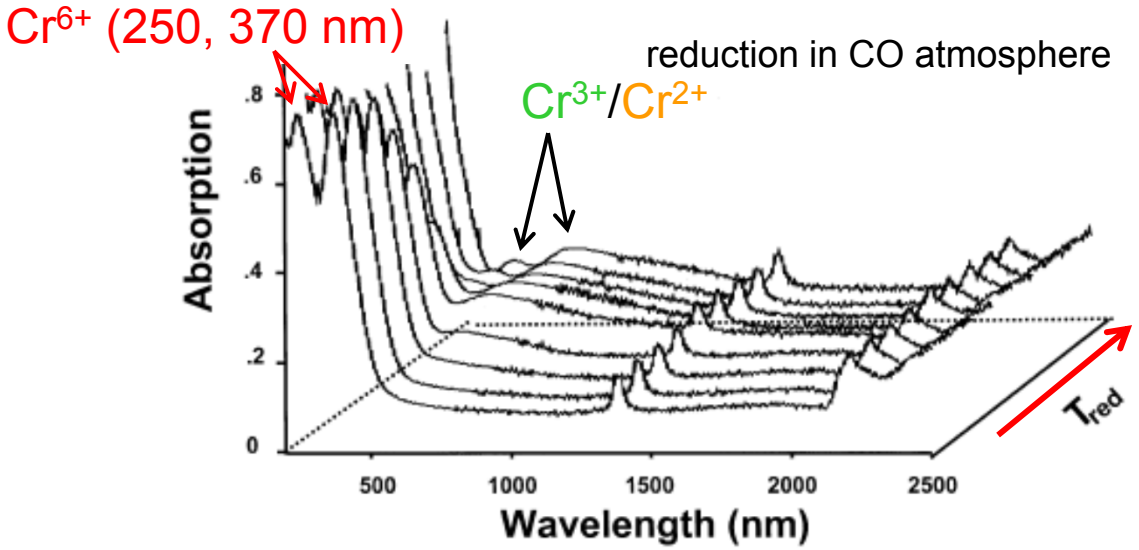
Weckhuysen, *Chem. Commun.* (2002) 97

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

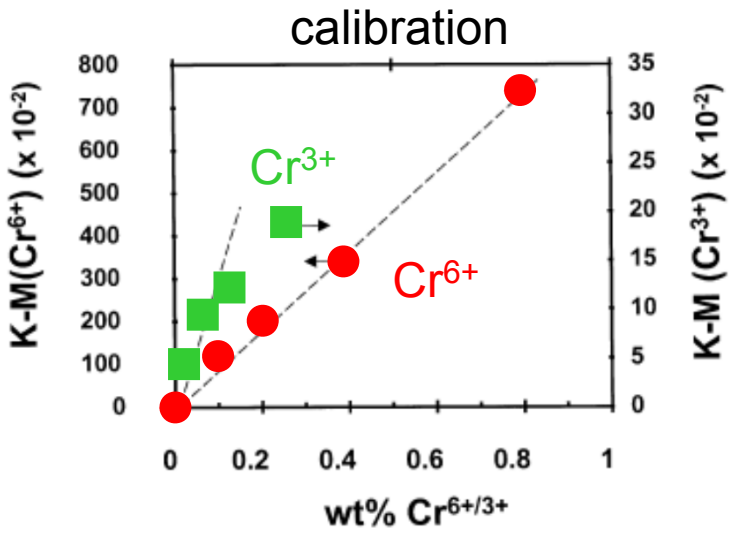
[a]s: strong; m: medium; w: weak; vw: very weak; sh: shoulder; br: broad.

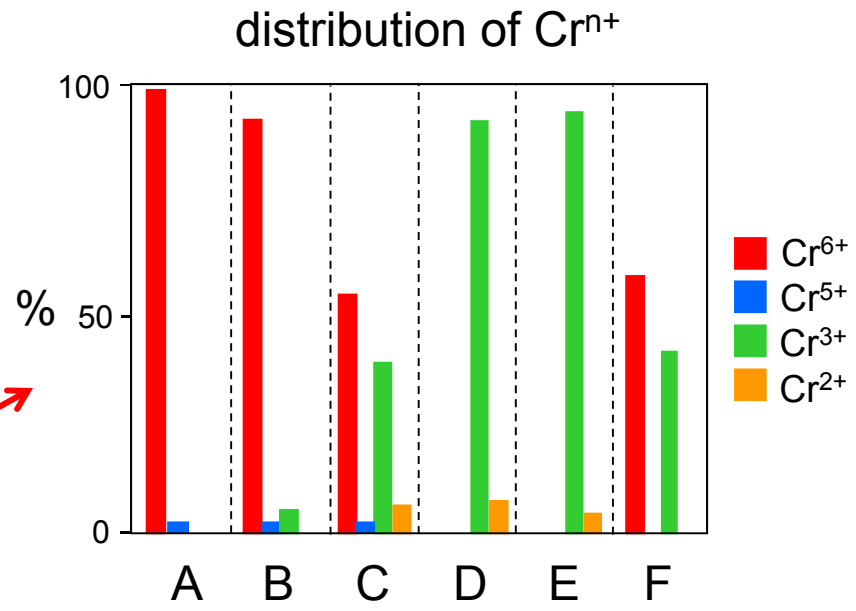


Weckhuysen et al., *Catal. Today* **49** (1999) 441

Examples

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

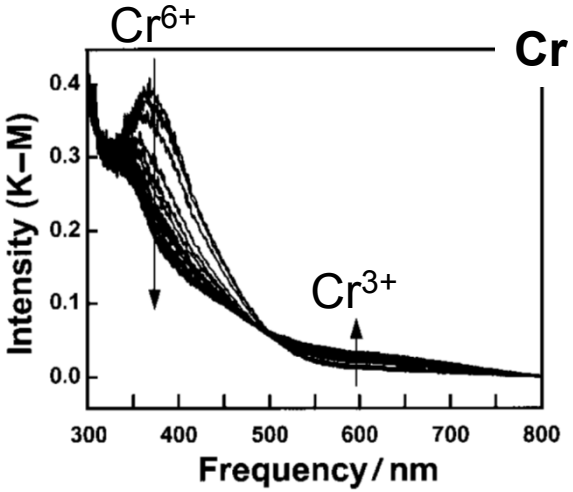




A: calc. 550°C
B: red. 200°C
C: red. 300°C
D: red. 400°C
E: red. 600°C
F: re-calc. 550°C

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

Examples



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

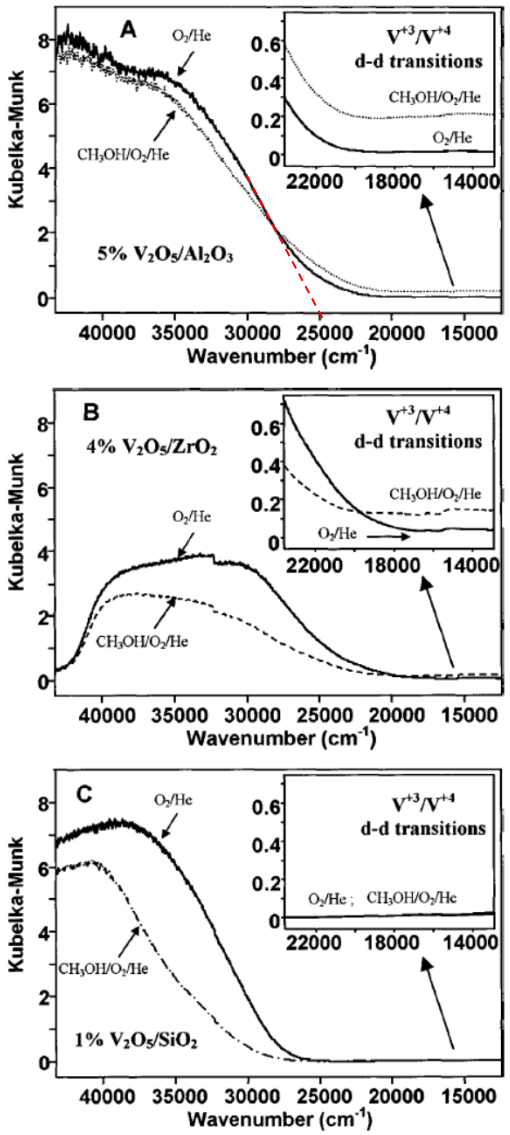


Table 1
UV-Vis DRS edge energies (V^{5+} LMCT band) during methanol oxidation at 230 °C.

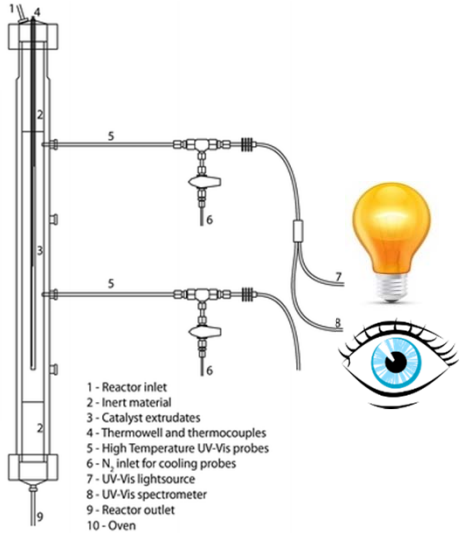
Catalyst	E_g (eV)		ΔE_g (eV)[a]
	O_2/He at 230 °C	CH_3OH/O_2/He at 230 °C	CH_3OH/O_2/He at 230 °C
1% V_2O_5/SiO_2	3.74	4.31	0.57
5% V_2O_5/Al_2O_3	3.61	3.65	0.04
4% V_2O_5/ZrO_2	3.14	3.29	0.15

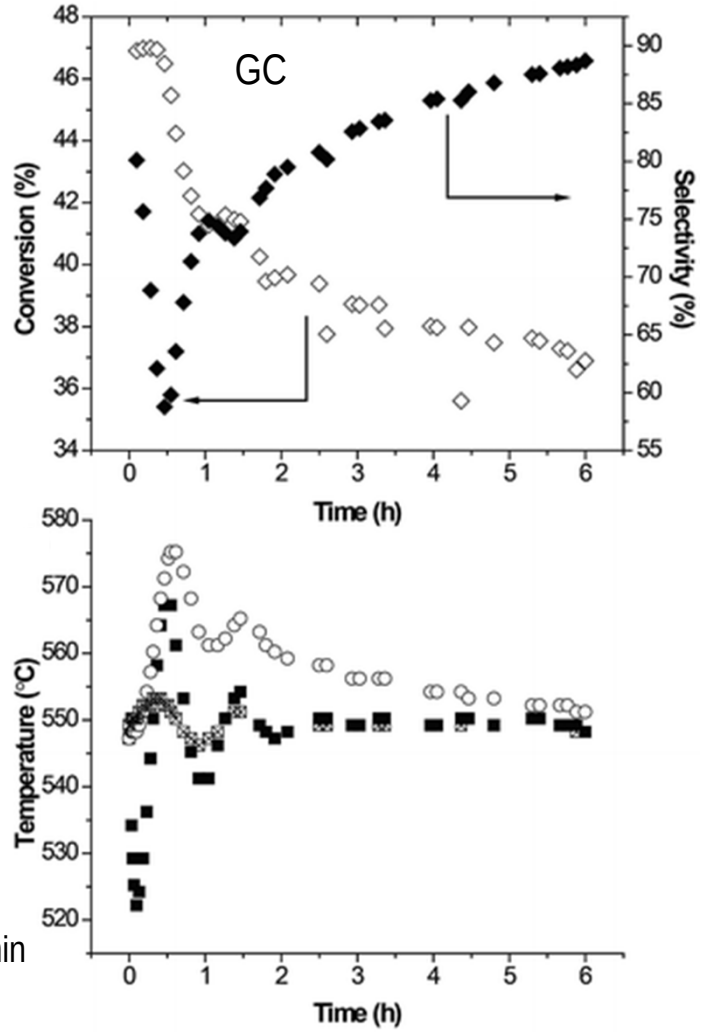
[a] $\Delta E_g = E_g(\text{rxn}) - E_g(O_2/\text{He})$.

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

Examples

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



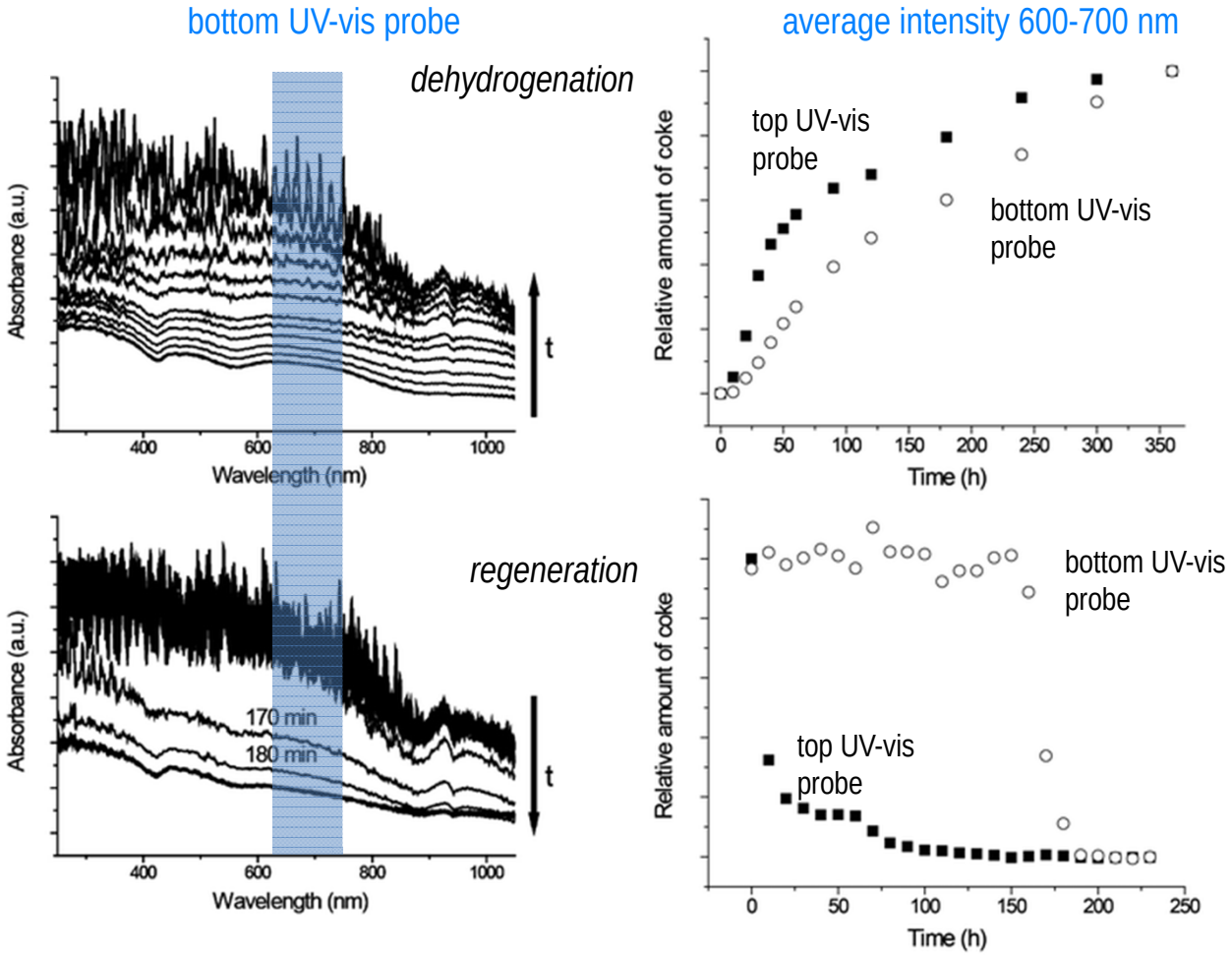


10 vol% C_3H_8, 90 vol% N_2, 5000 ml/min
20 wt% $Cr^{3+/6+}O_x/Al_2O_3$

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

Examples

- UV-vis probe in a pilot-scale reactor



- 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