UV-Vis spectroscopy

Basic theory

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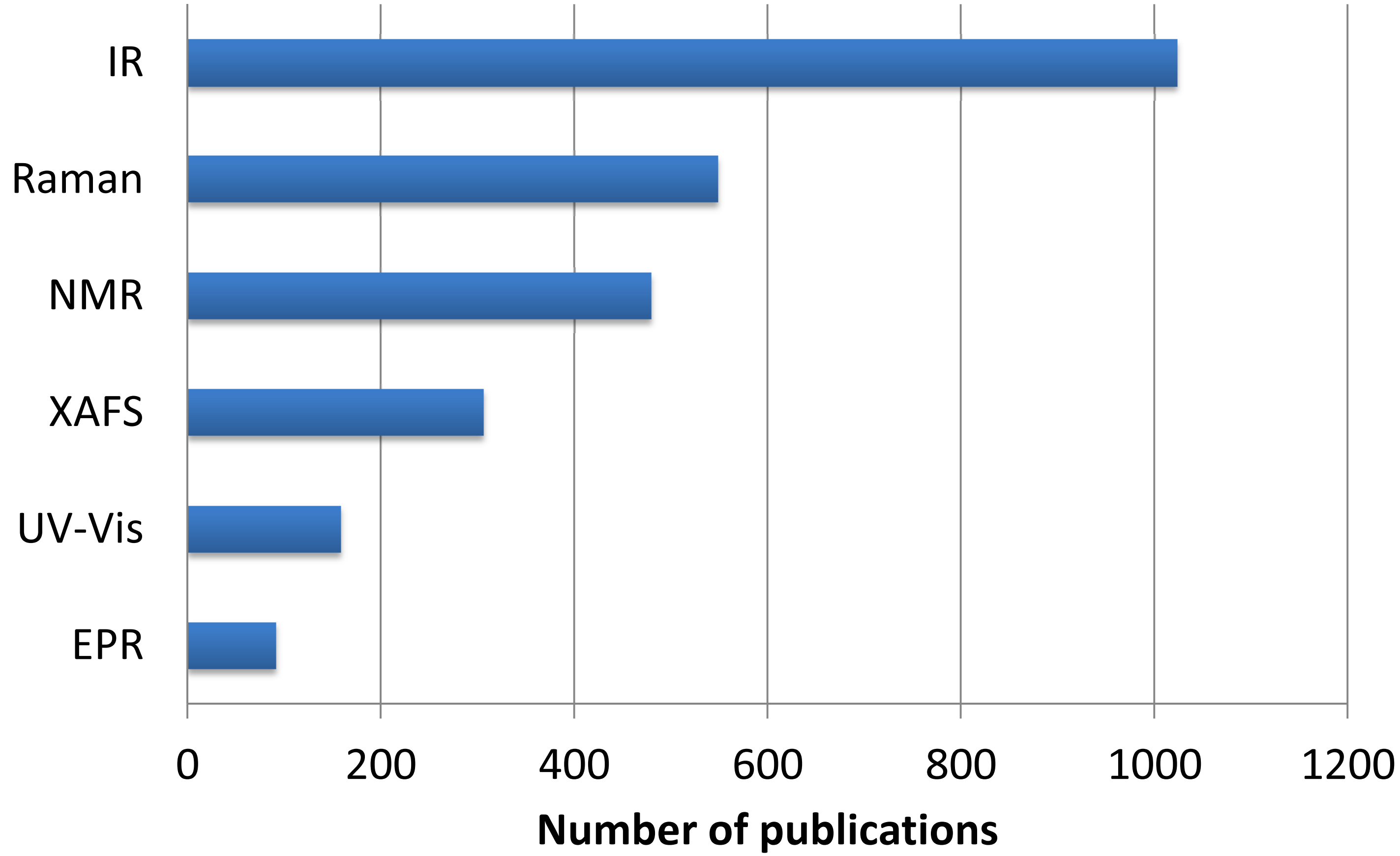
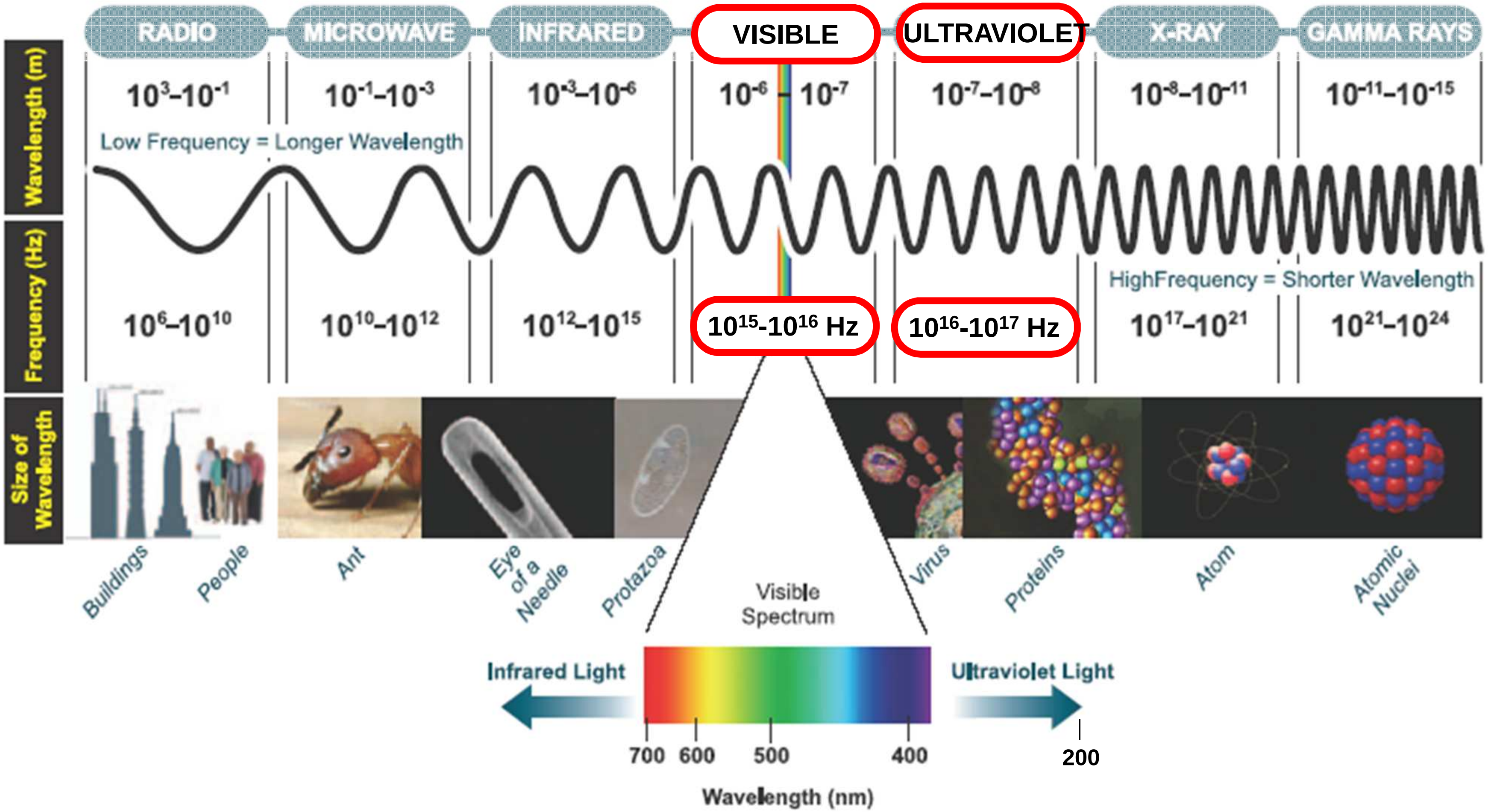
Importance of UV-Vis in catalysis



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

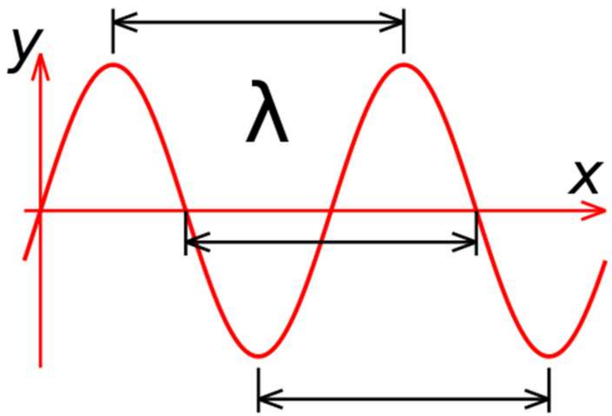
The electromagnetic spectrum



source: Andor.com

The ‘energy’ unit

- Typically, the wavelength (nm) is used
- the distance over which the wave's shape repeats



x nm = 10’000’000 / x cm^{-1}
y cm^{-1} = 10’000’000 / y nm

Is UV-vis spectroscopy popular?

pros

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

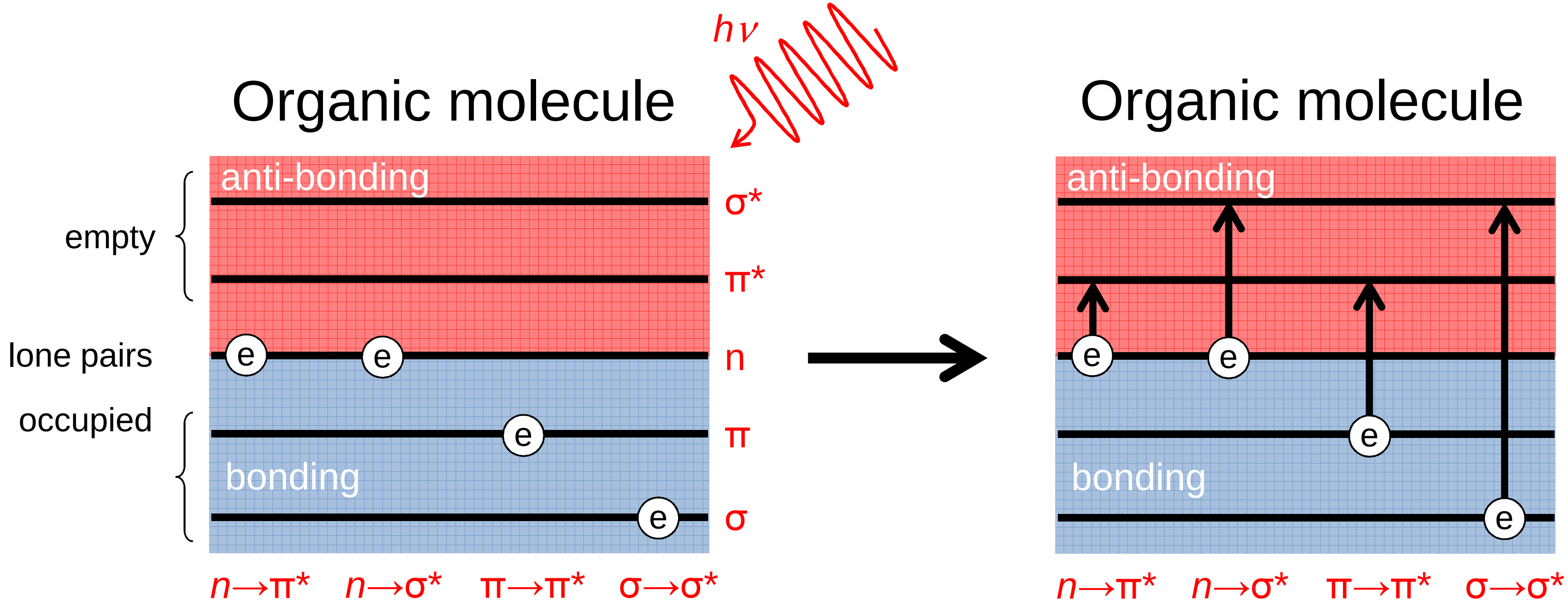
cons

- 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)$_n$-, -C=O, -C=N, etc.)
- Access to molecular structure and oxidation state

Electronic transitions



$$E = h\nu$$

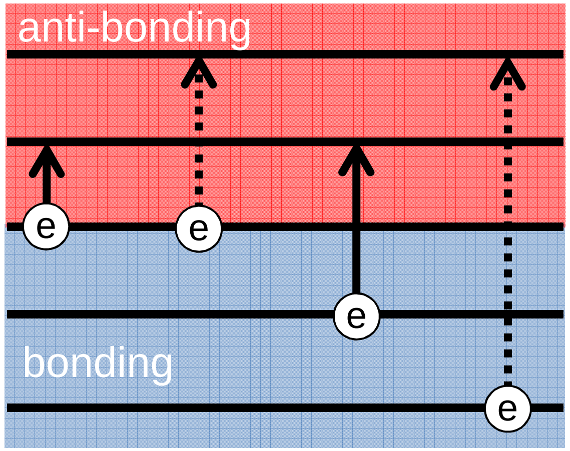
$$\lambda = c / \nu$$

high e^- jump → high E

high E → high ν

high ν → low λ

Electronic transitions



σ→σ*
high *E*, low *λ* (<200 nm)

n→σ*
150-250 nm, weak

n→π*
200-700 nm, weak

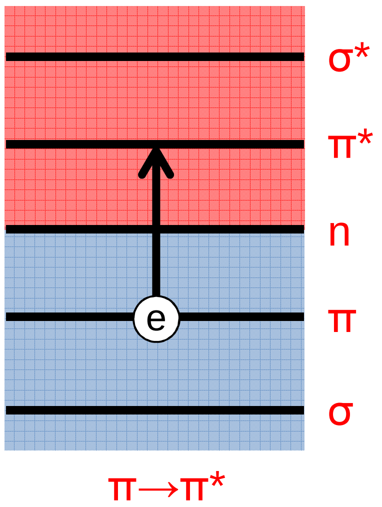
π→π*
200-700 nm, intense

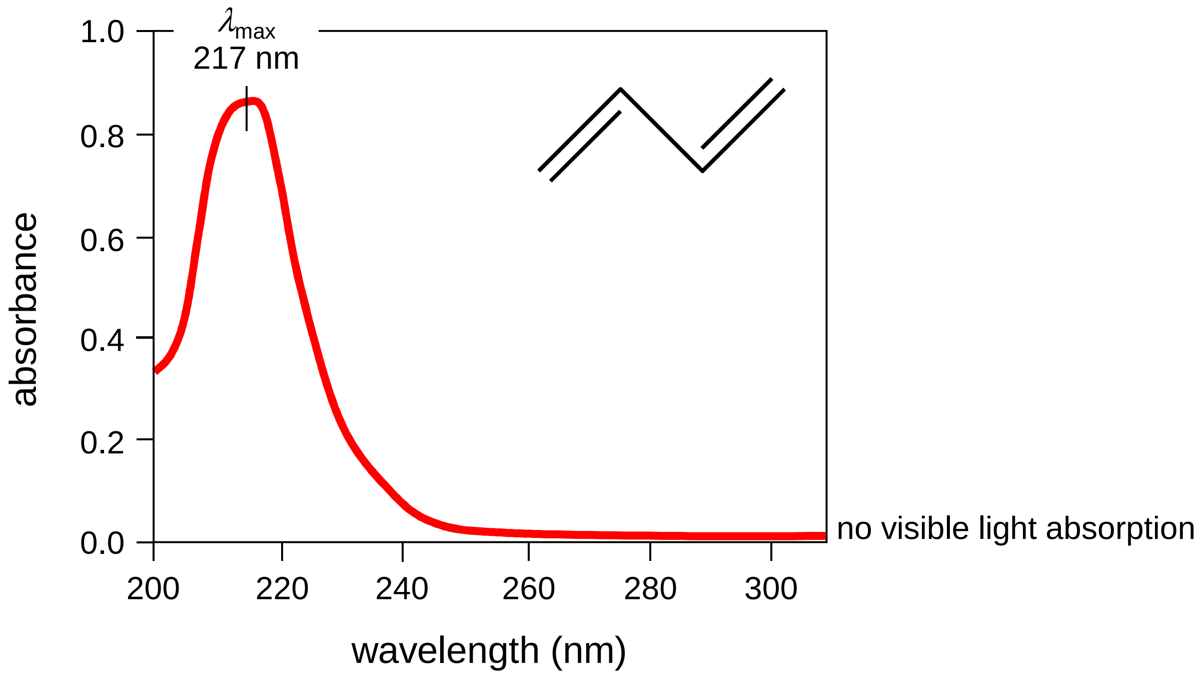
Condition to absorb light (200-800 nm):

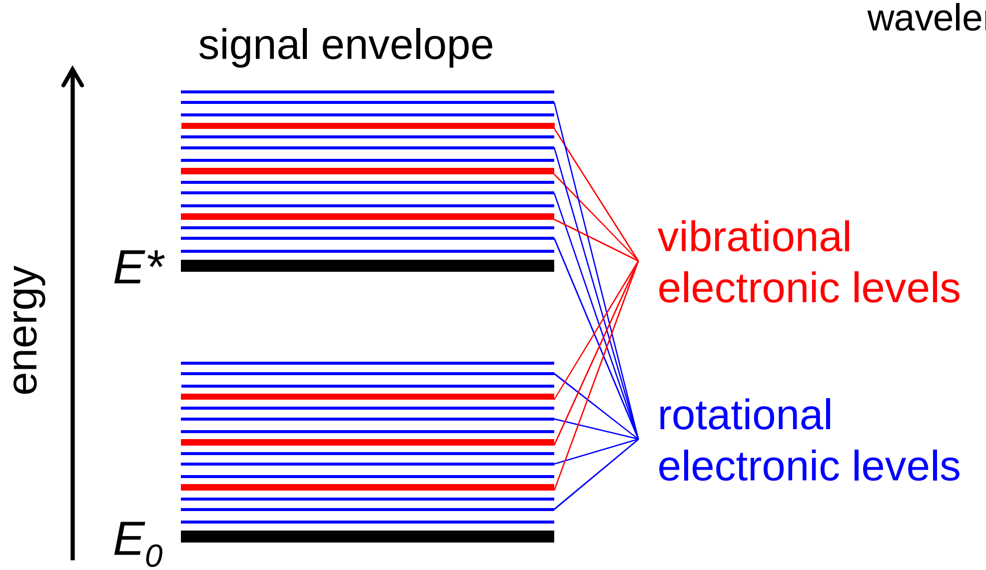
π and/or *n* orbitals

CHROMOPHORE

The UV spectrum

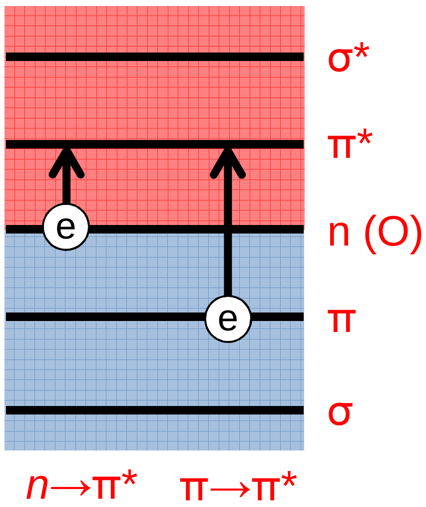


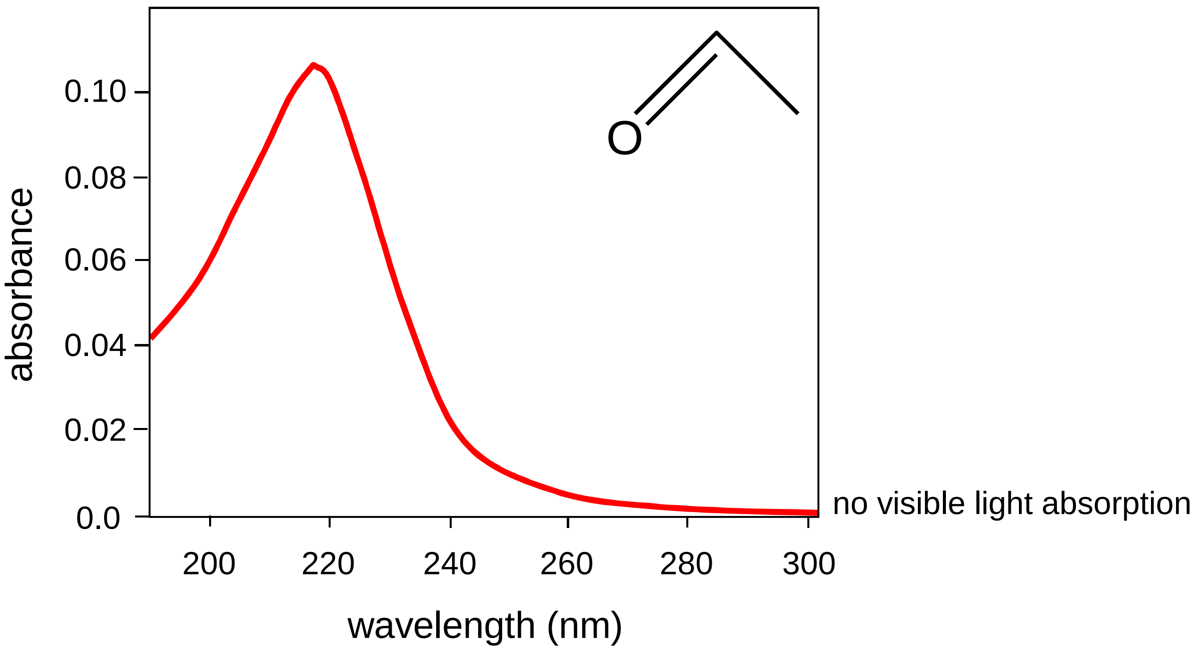




Q How many signals do you expect from CH_3-CH=O?

The UV spectrum

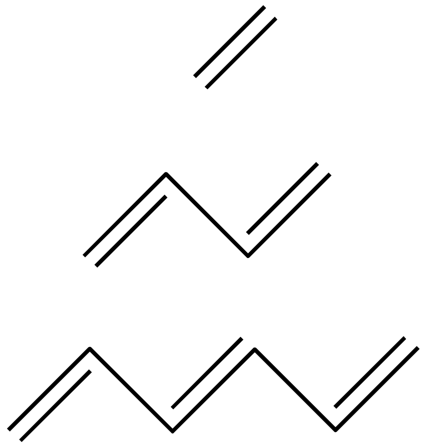




The UV spectrum

- **Conjugation effect**

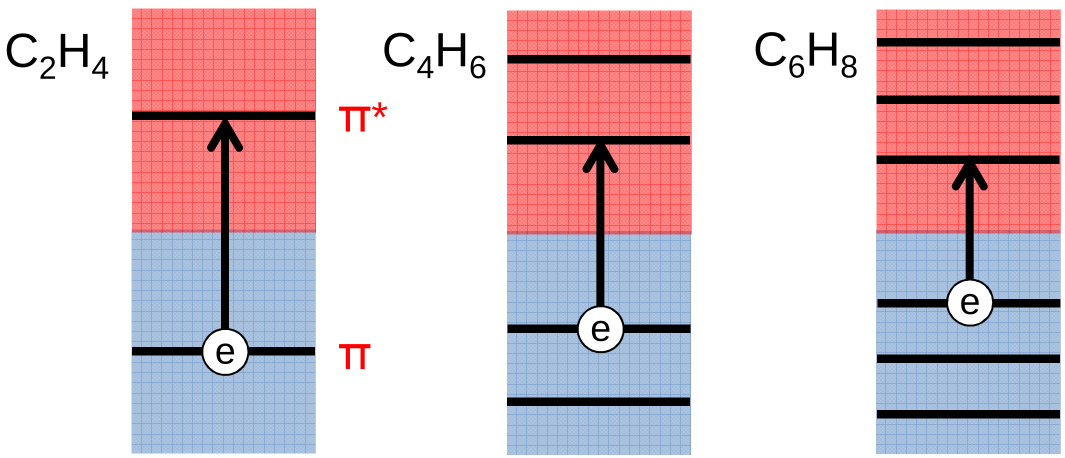
delocalisation λ_{max} λ ν E



171

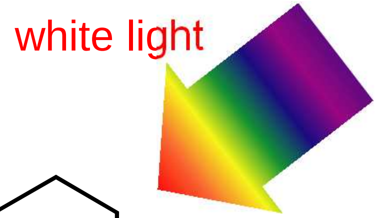
217

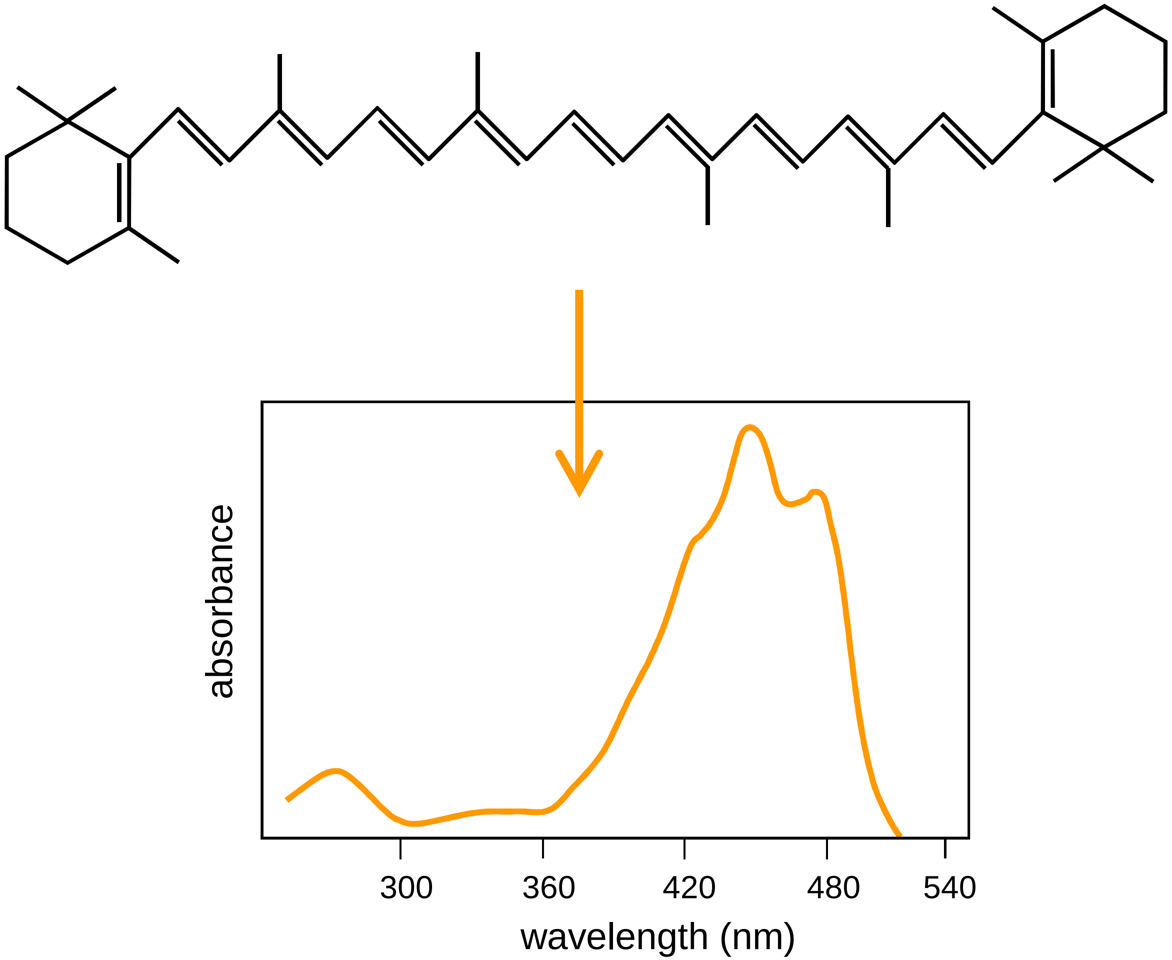
258



The UV spectrum

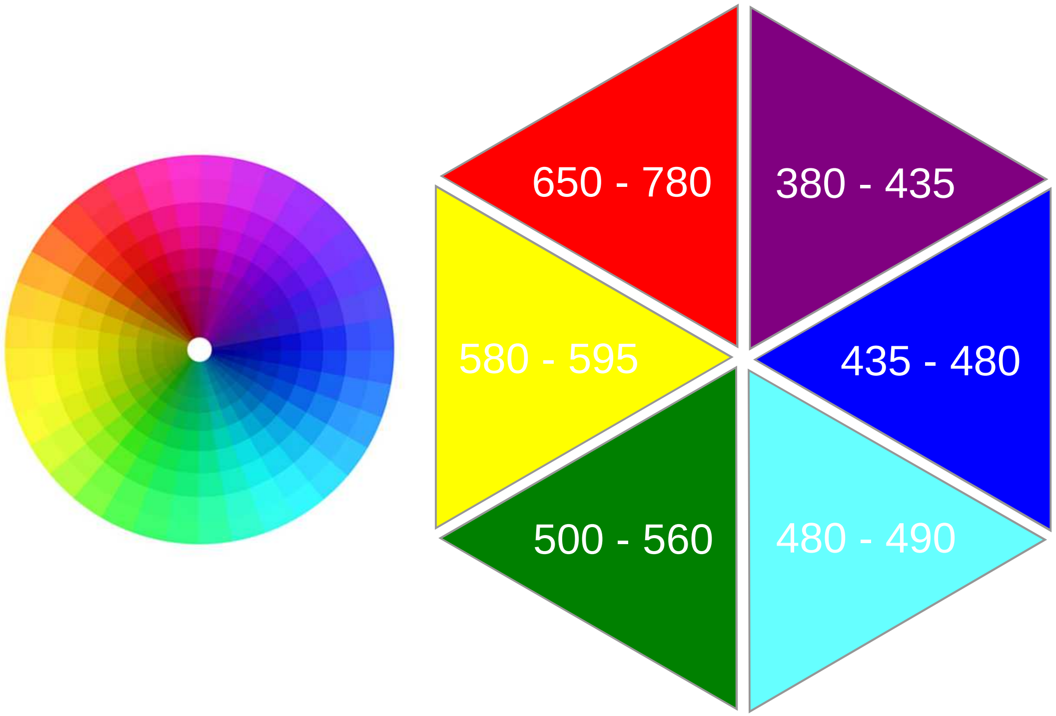
- **Conjugation effect:** β-carotene





The UV spectrum

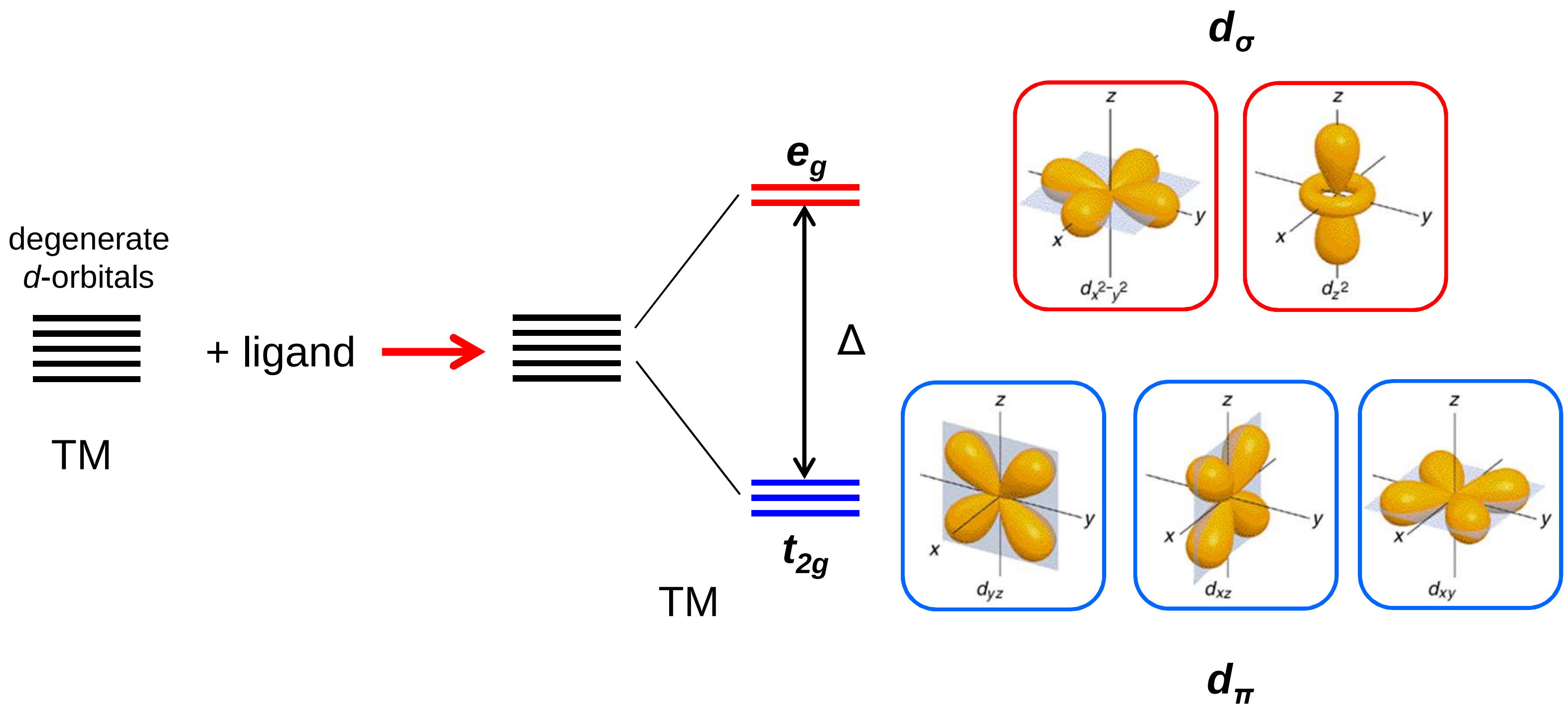
- **Complementary colours**



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

Inorganic compounds

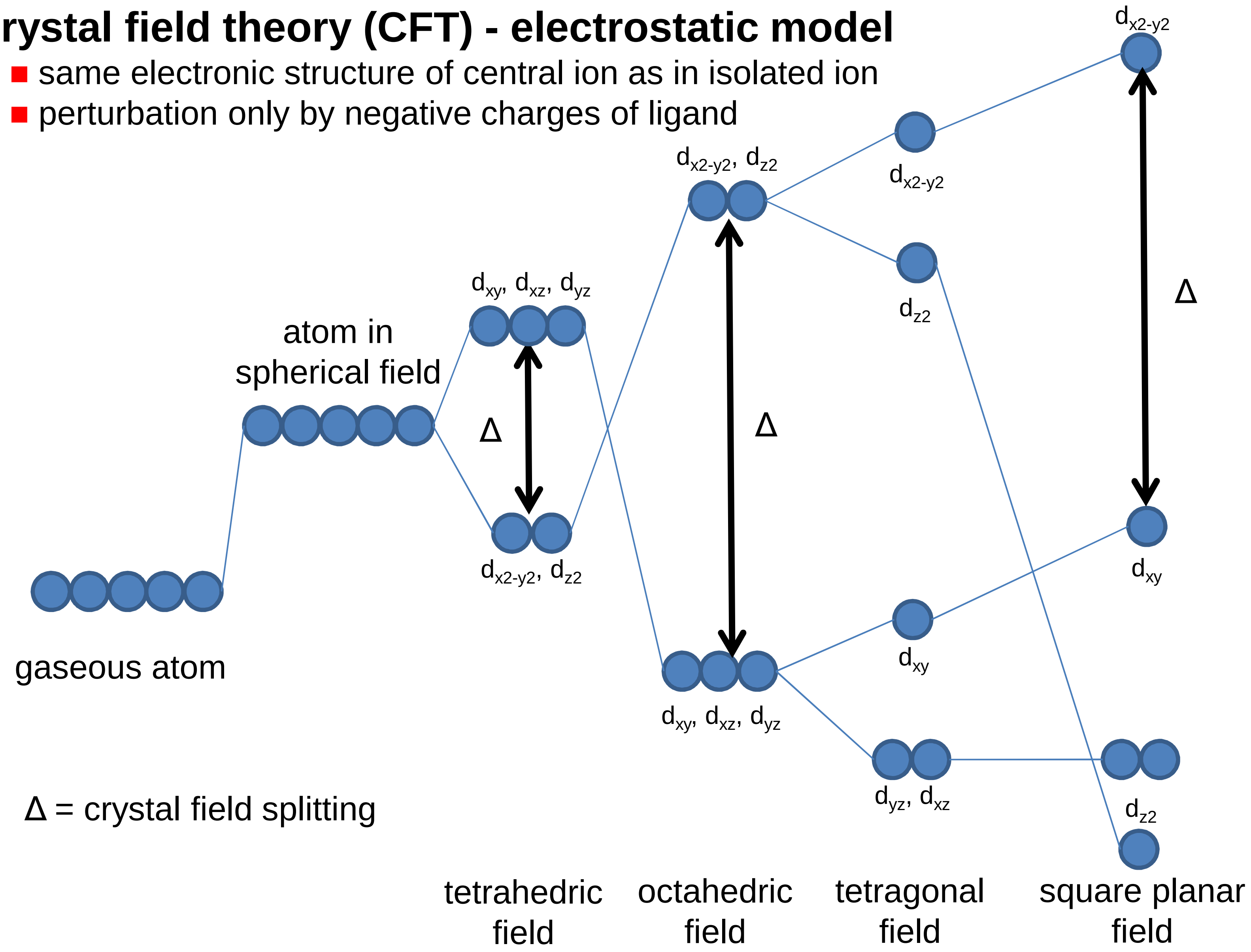
- UV-vis spectra of transition metal complexes originate from
  - **Electronic *d-d* transitions**



  - …

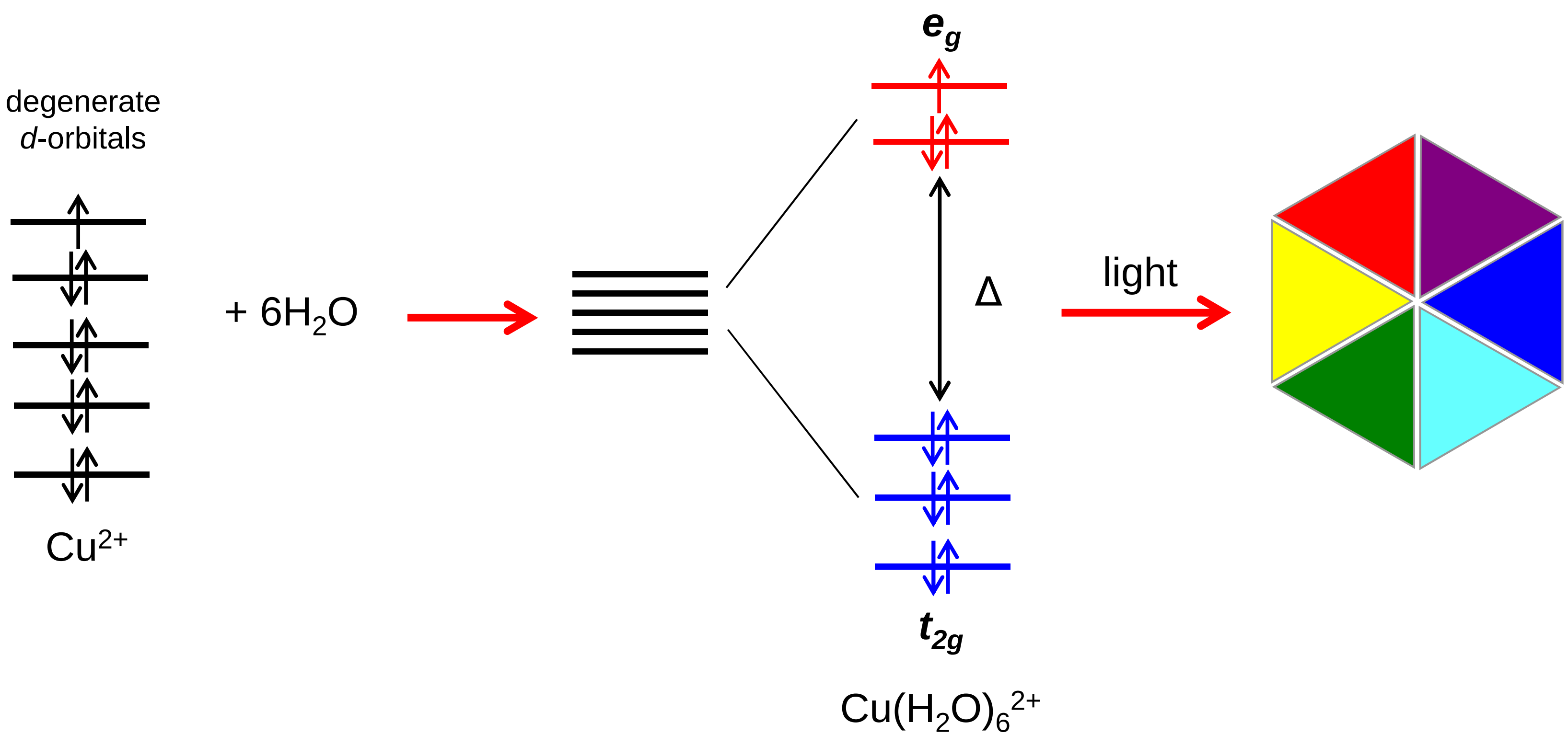
Inorganic compounds

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



Inorganic compounds

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

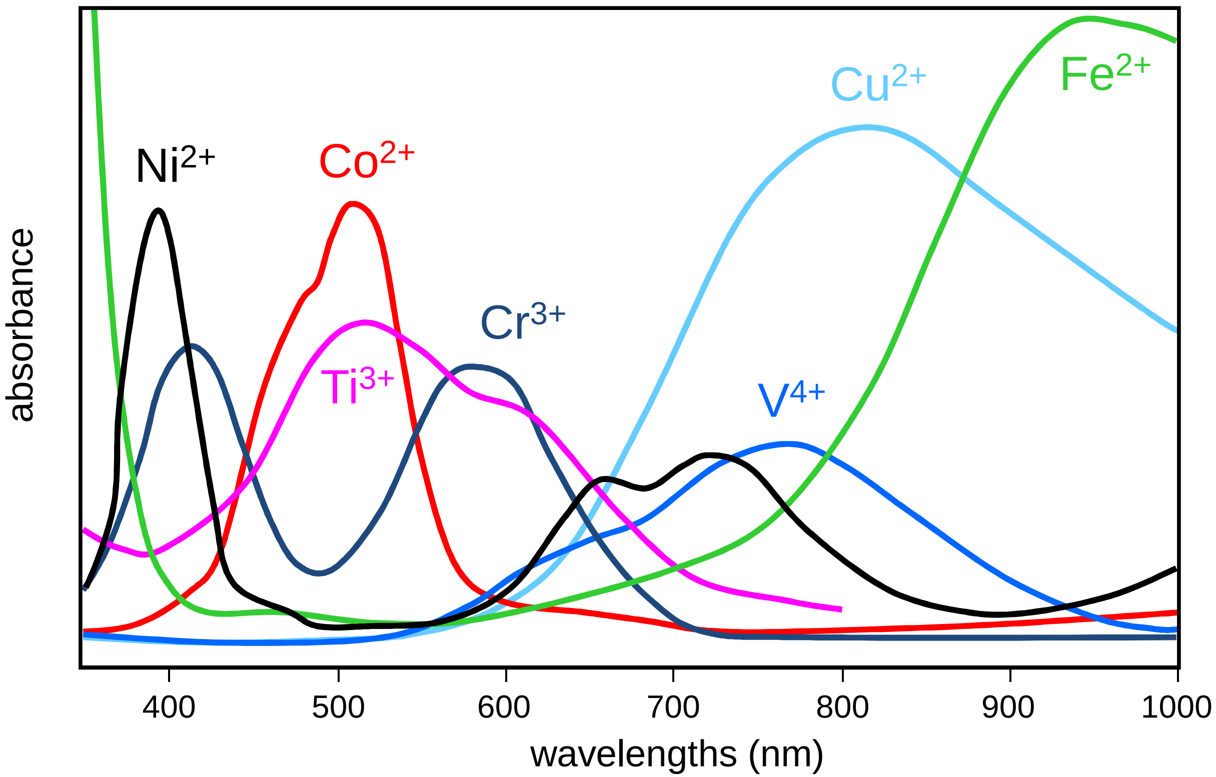


- Yellow light is absorbed and the Cu^{2+} solution is coloured in blue (ca. 800 nm)
- The greater Δ, the greater the *E* needed to promote the e^-, and the shorter λ
- Δ depends on the nature of ligand, $\Delta_{NH3} > \Delta_{H2O}$

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**

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

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

spin rule: $\Delta S = 0$

on promotion, no change of spin

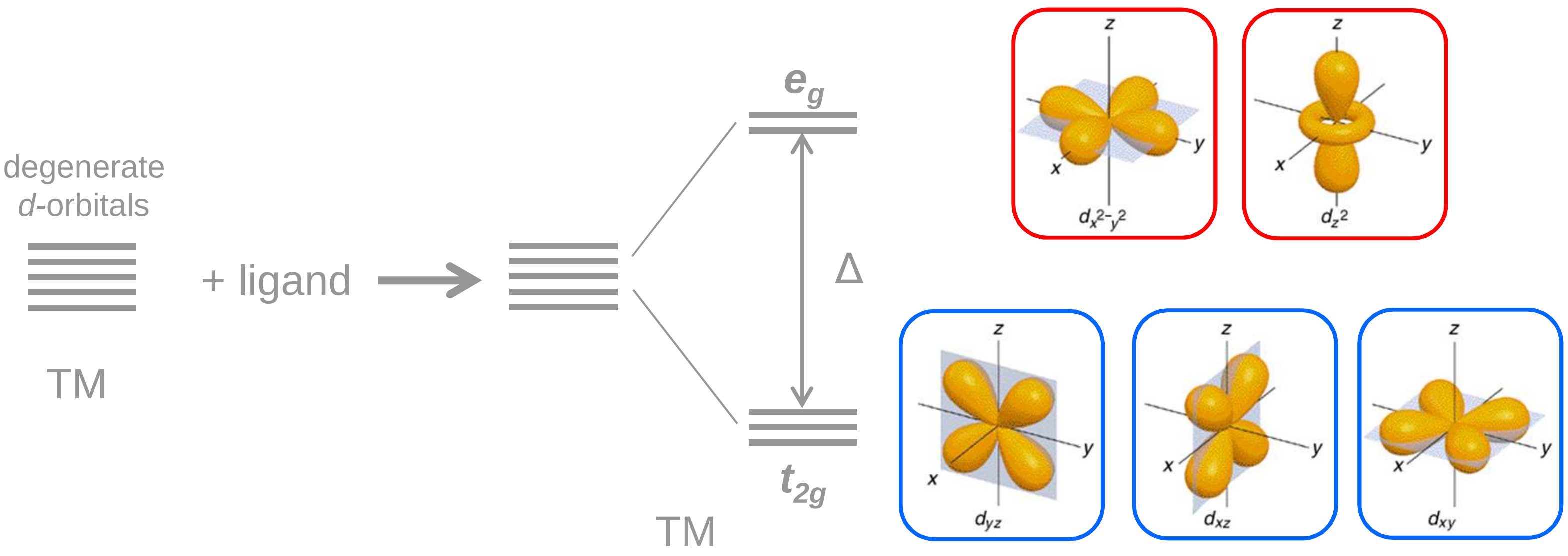
Laporte's rule: $\Delta l = \pm 1$

d-d transition of complexes with center of simmetry are forbidden

- Because of selection rules, colours are faint (ε= 20 $L mol^{-1} cm^{-1}$).

Inorganic compounds

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



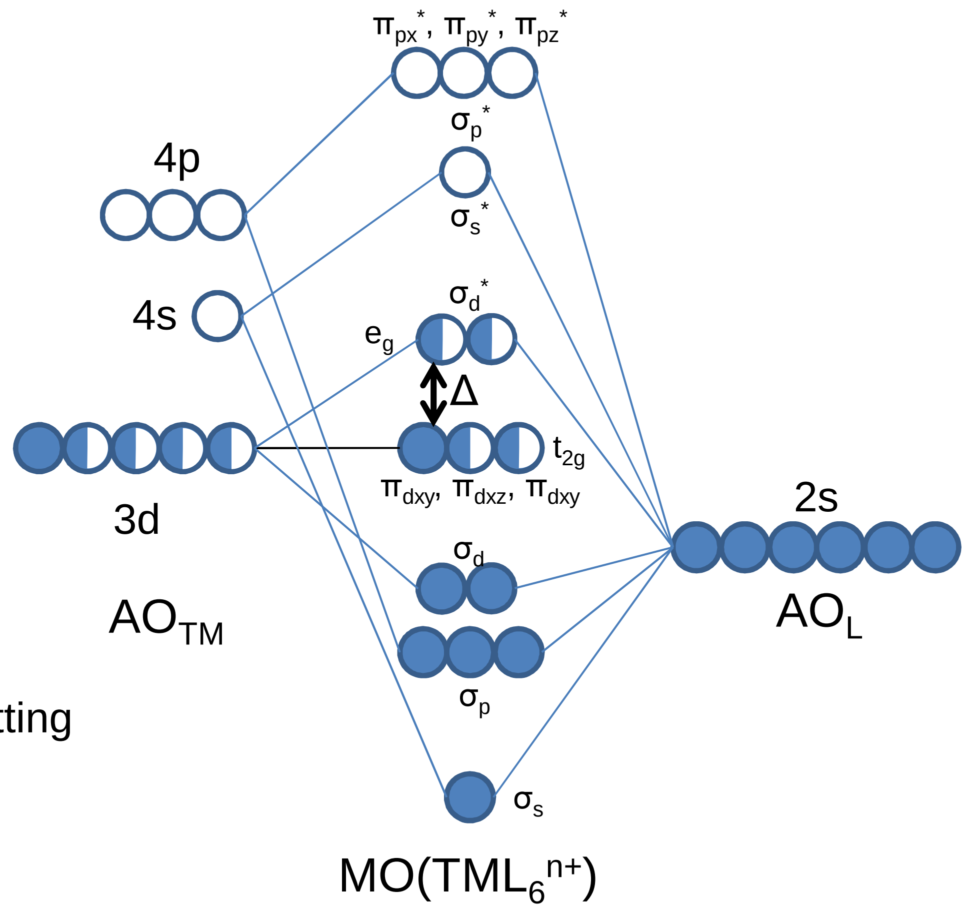
  - **Charge transfer**

Inorganic compounds

- **Charge transfer complex**
  - no selection rules → intense colours (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
  - 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

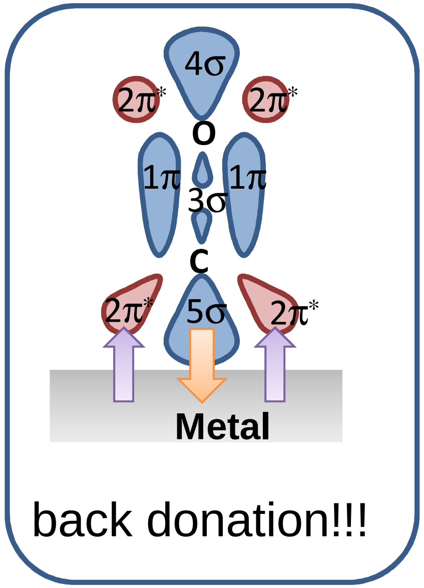
- **Ligand field theory (LFT)**
  - involves AO of metal and ligand, therefore MO
  - what CFT indicates as possible electronic transitions ($t_{2g}\rightarrow e_g$) are now: $\boldsymbol{\pi_d\rightarrow\sigma_{dz2}^*}$ or $\boldsymbol{\pi_d\rightarrow\sigma_{dx2-y2}^*}$



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 (laso 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

UV-Vis spectroscopy

Instrumentation
Examples for catalysis

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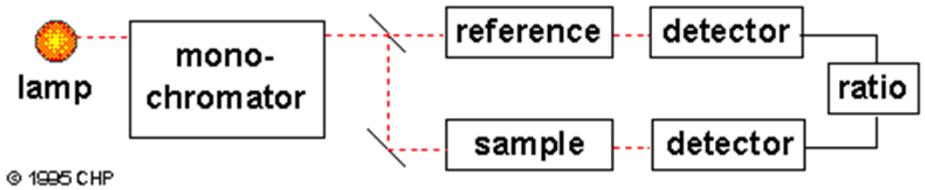
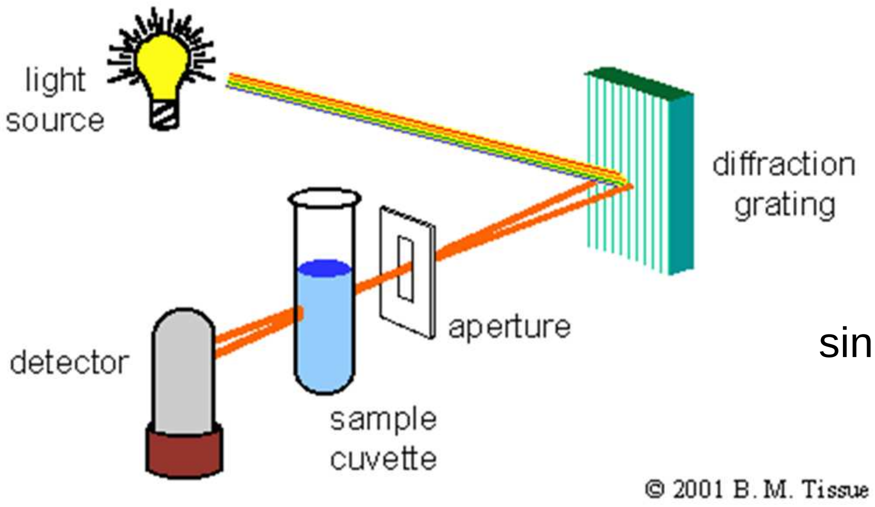
Instrumentation

- **Dispersive instruments**

Measurement geometry:
- transmission
- diffuse reflectance



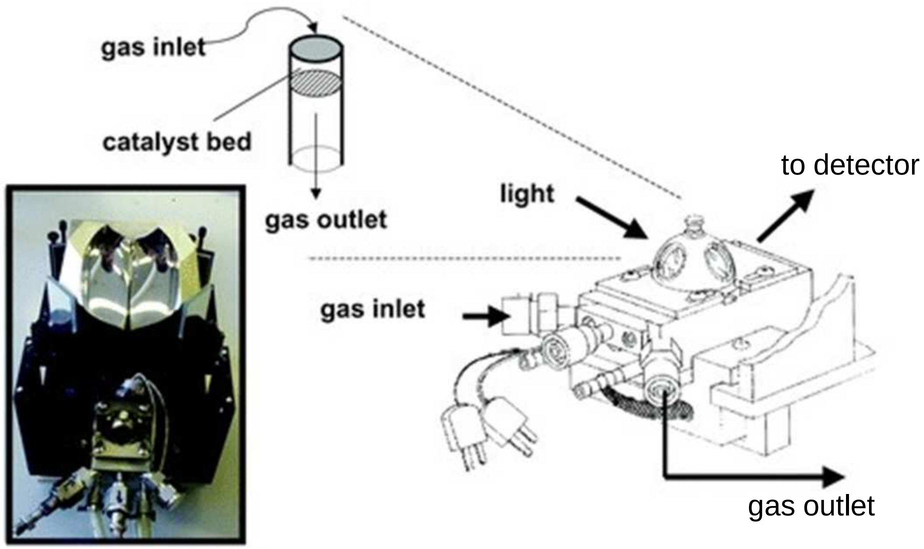
double beam spectrometer



single beam spectrometer

In situ instrumentation

■ Diffuse reflectance (DRUV)

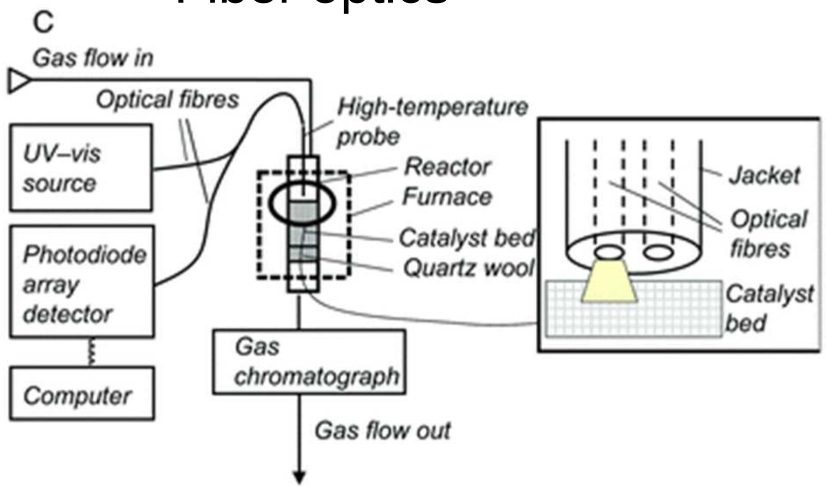


☑ - 20% of light is collected
- gas flows, pressure, vacuum

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

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

■ Fiber optics



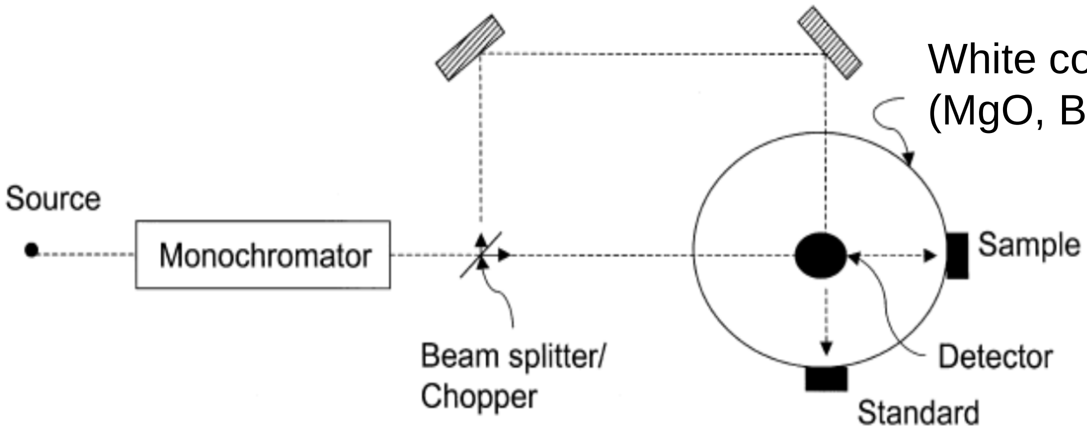
☑ - time resolution (CCD camera) [spectra colleted at once]
- coupling to reactors

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

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

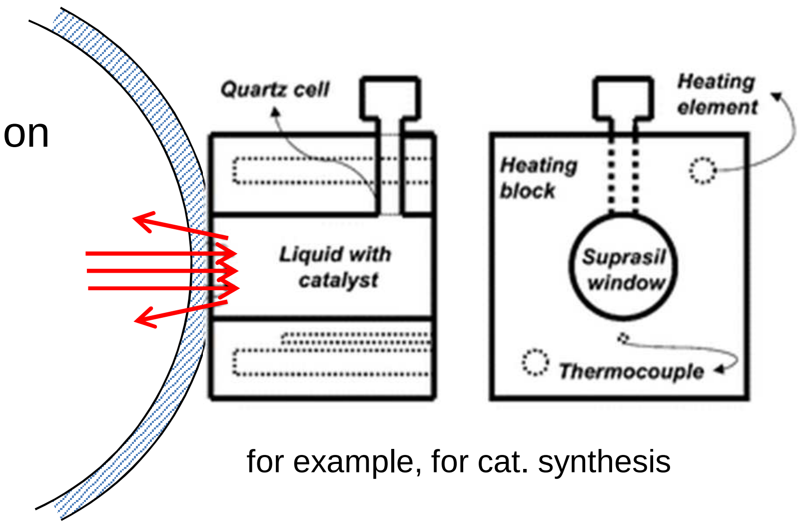
In situ instrumentation

- Integration sphere



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

integration
sphere



for example, for cat. synthesis

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

- only homemade cells

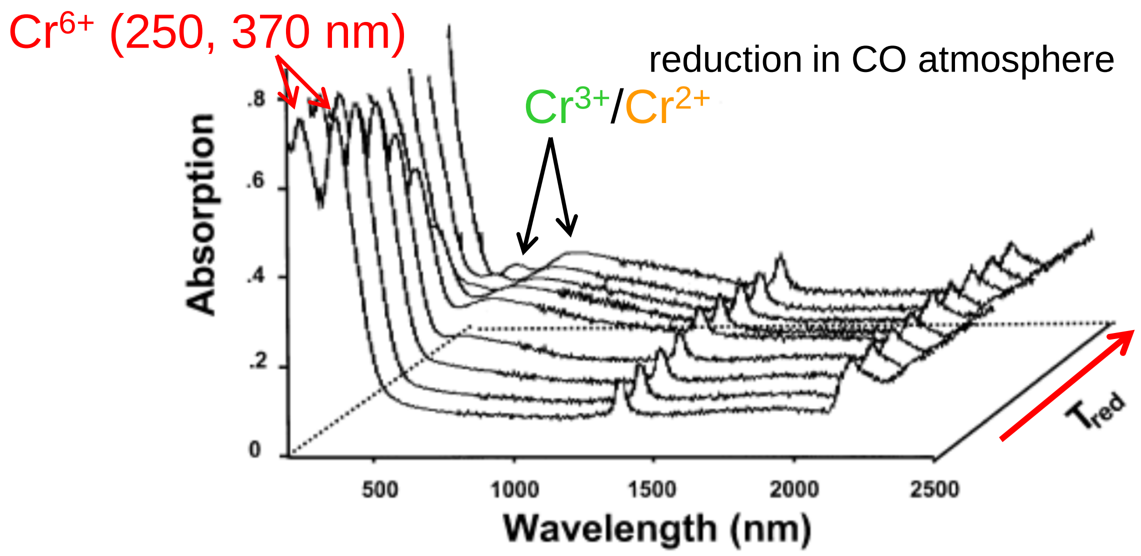
Weckhuysen, *Chem. Commun.* (2002) 97

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.

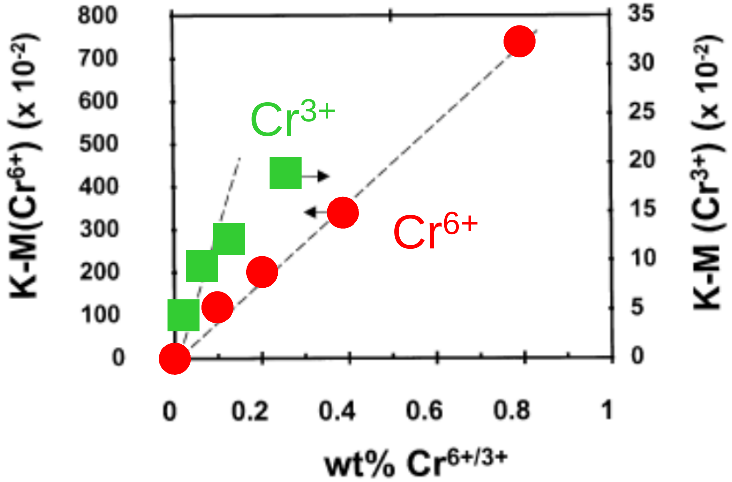


Weckhuysen et al., *Catal. Today* **49** (1999) 441

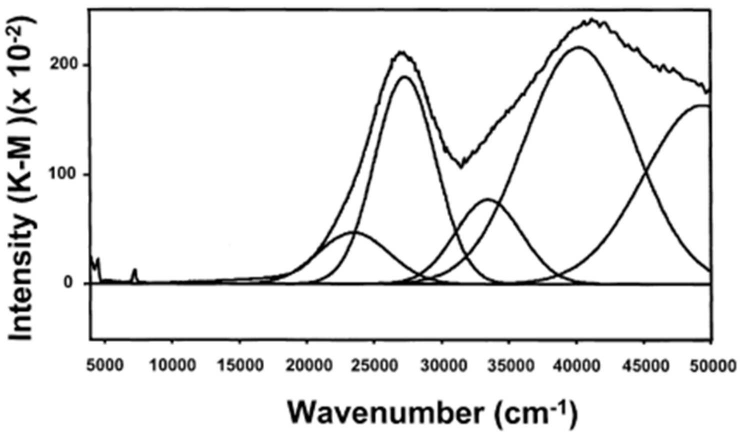
Examples

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

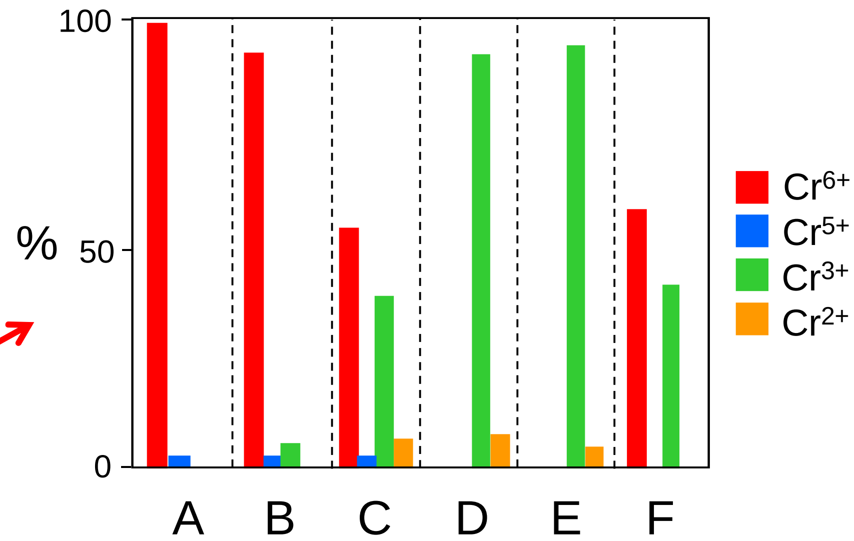
calibration



deconvolution



distribution of Cr^{n+}

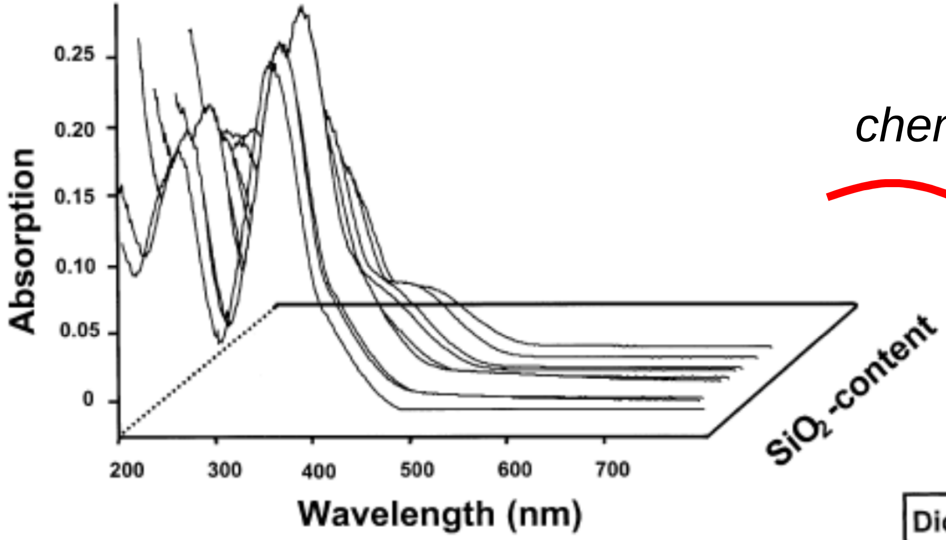


A: calc. 550℃
B: red. 200℃
C: red. 300℃
D: red. 400℃
E: red. 600℃
F: re-calc. 550℃

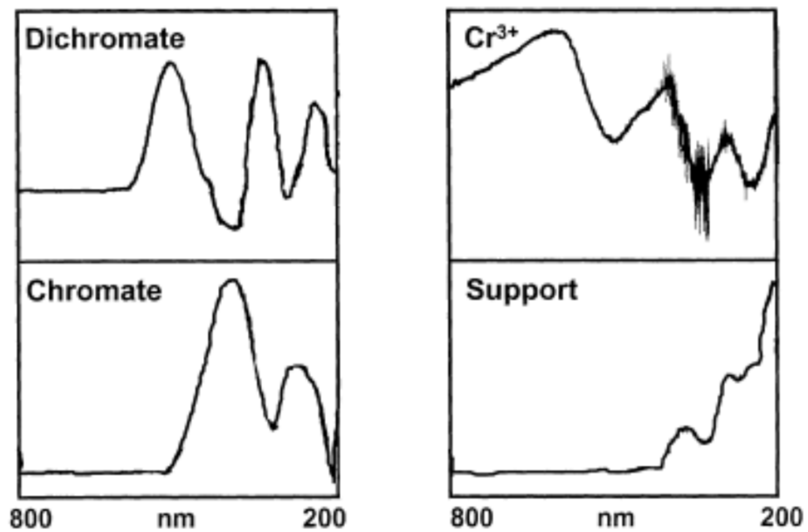
Weckhuysen et al., *Catal. Today* **49** (1999) 441

Examples

- **Determination of oxidation state: 0.2 wt% Cr^{n+}/SiO_2**



chemometrics * PCA, principal component analysis
FA, factor analysis
PLS, partial least squares
own routines…

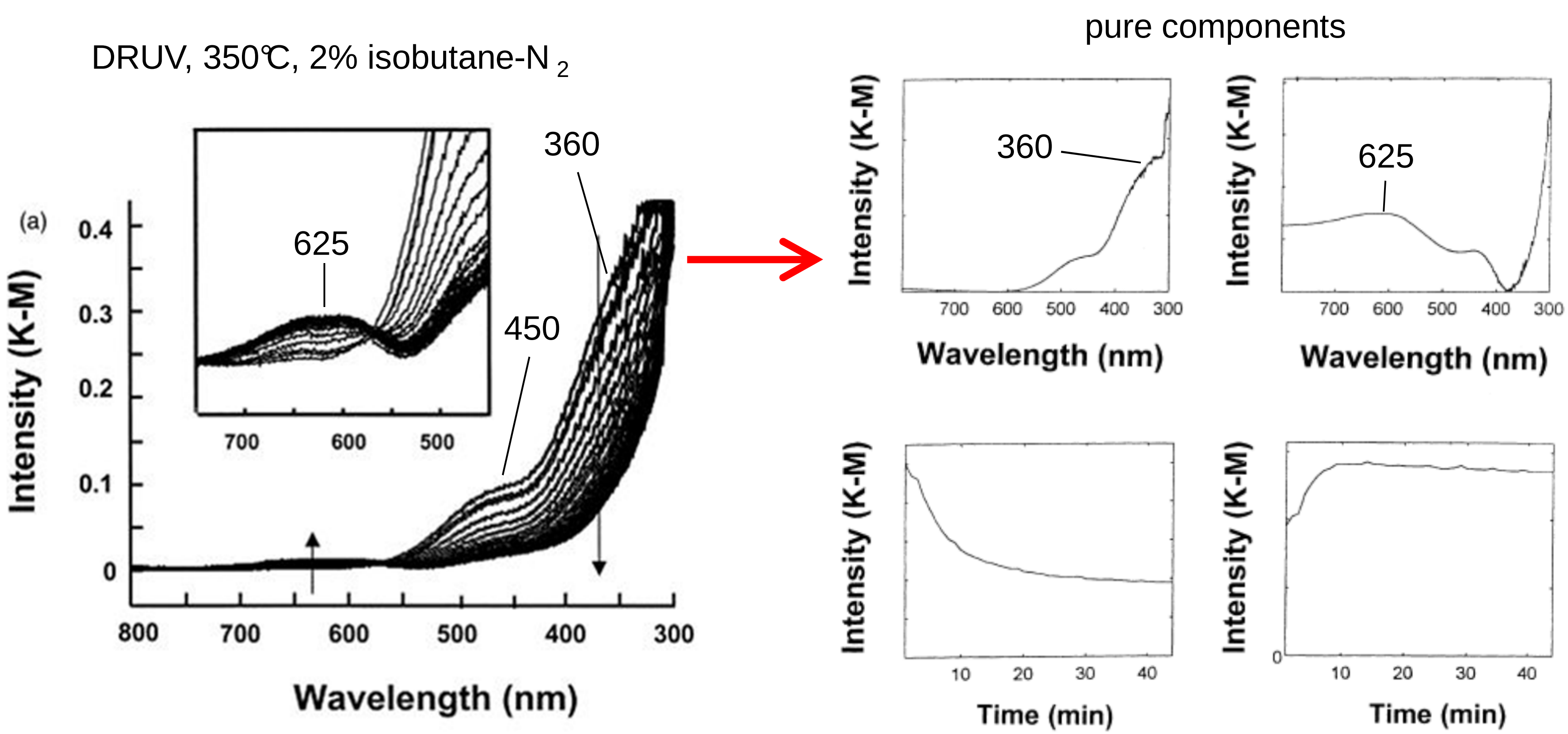


* decomposition into pure components (including noise)

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

Examples

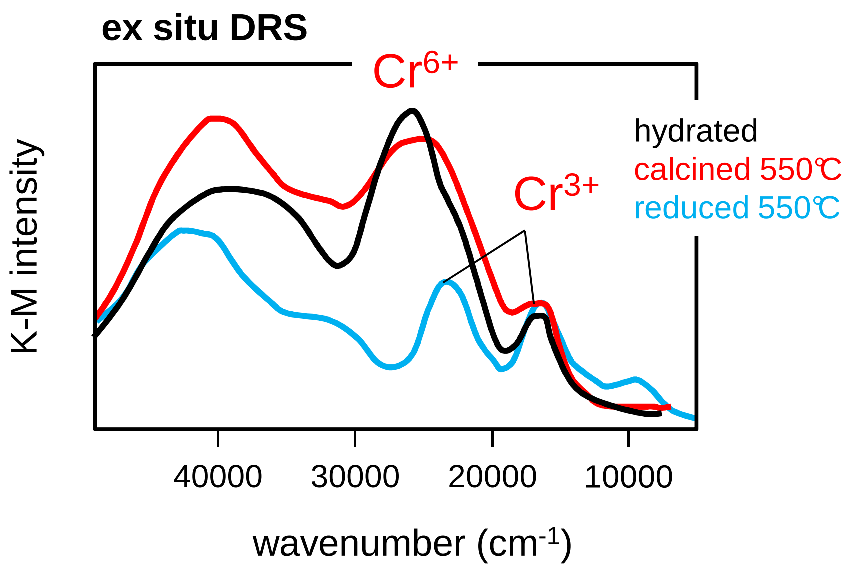
- **Determination of oxidation state: 0.5 wt% Cr^{n+}/SiO_2**

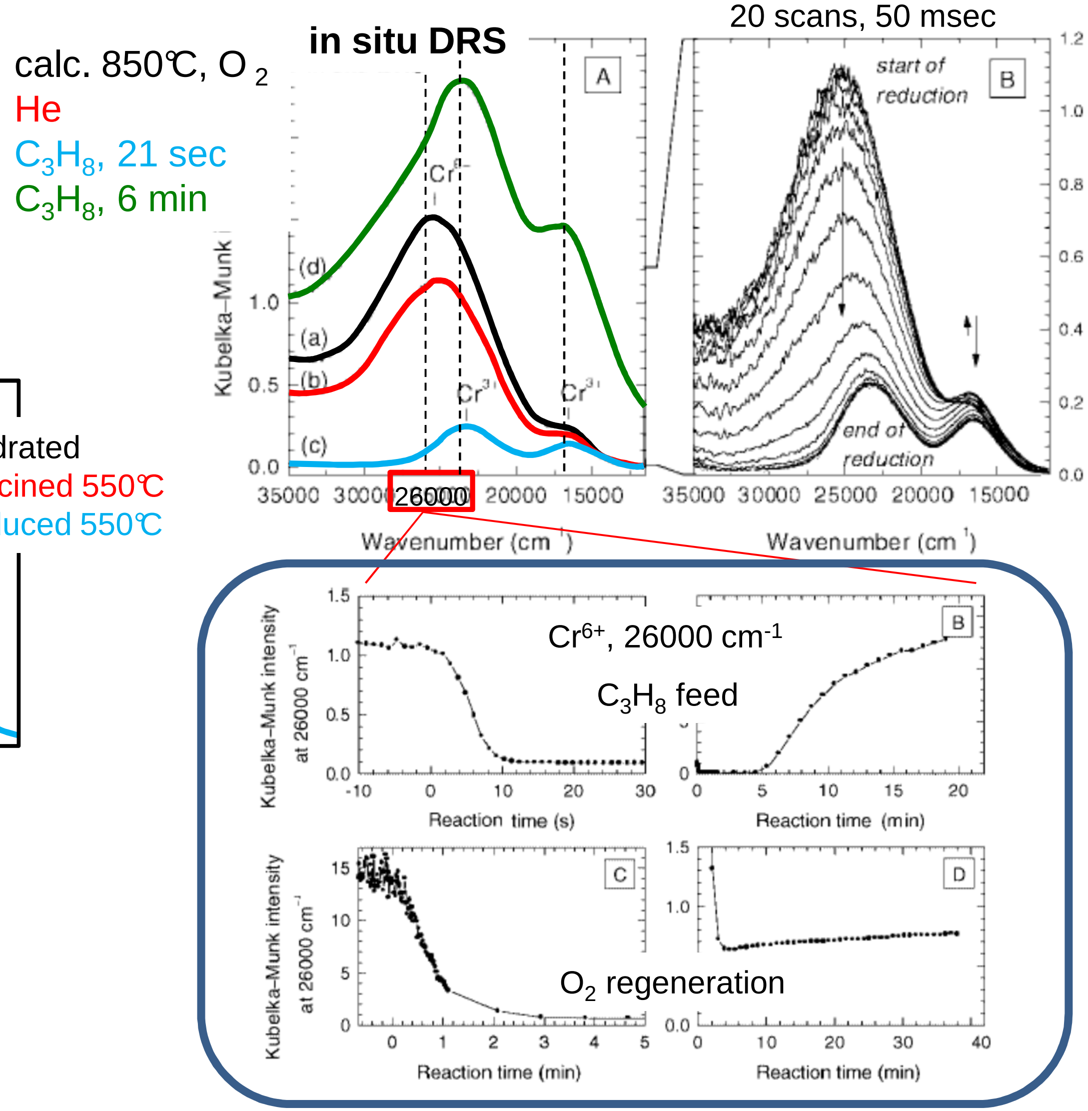


Weckhuysen et al., *Catal. Today* **49** (1999) 441

Examples

- **Determination of oxidation state: 4 wt% Cr^{n+}/Al_2O_3**



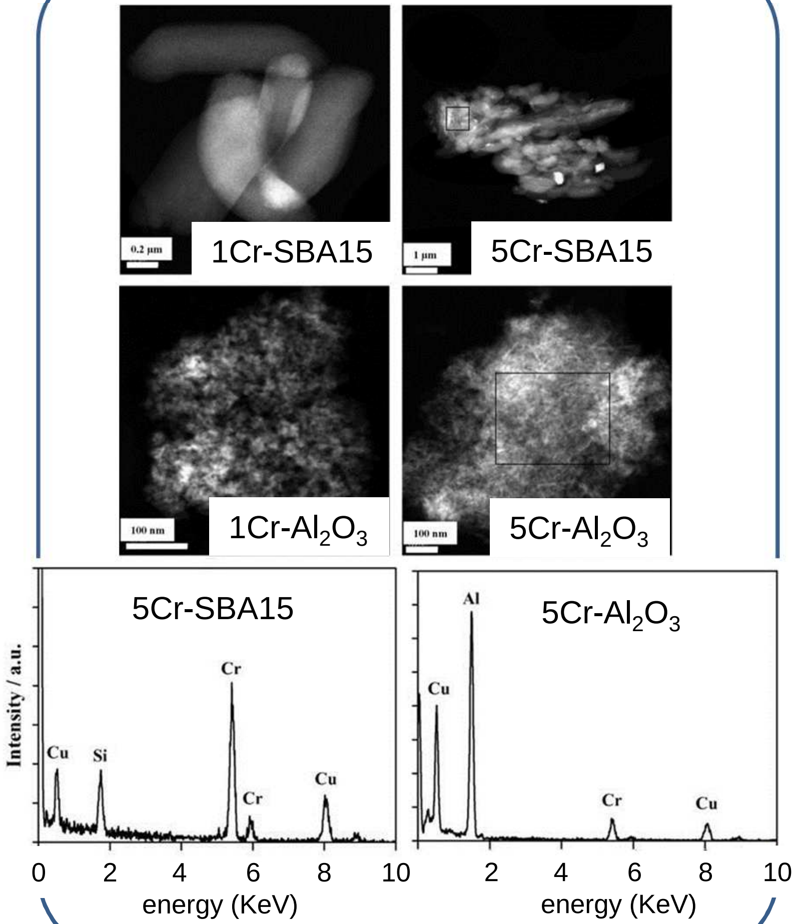


Puurunen et al., *J. Catal.* **210** (2002) 418

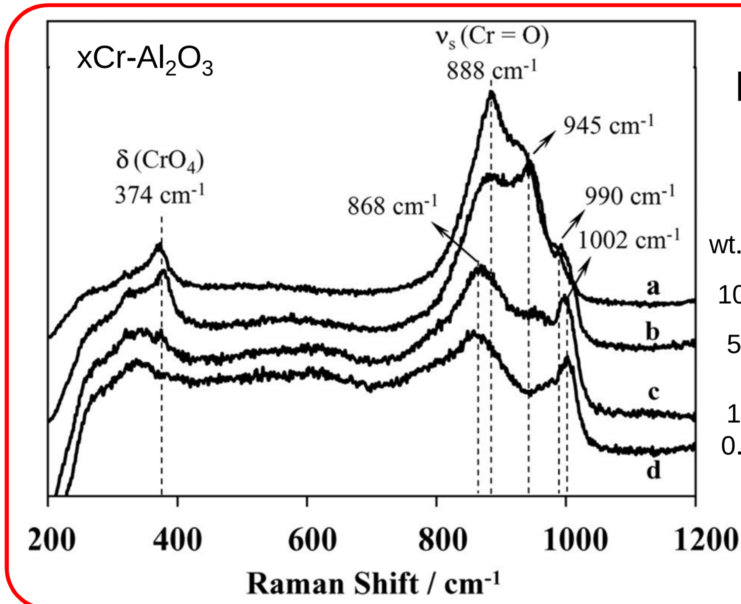
Examples

- **Comparison of techniques: x wt% Cr^{n+}/support**

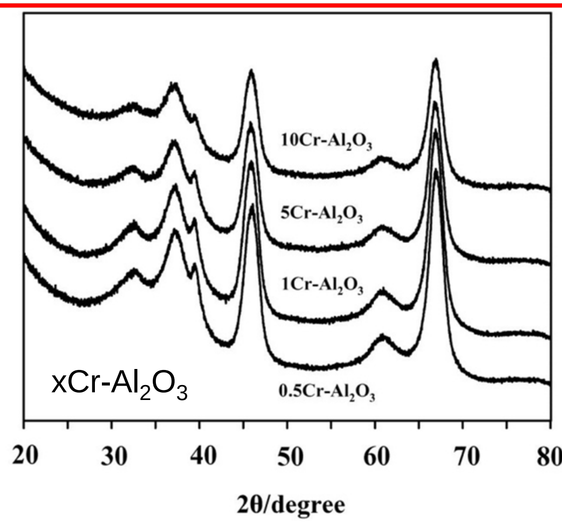
HAADF-STEM



Raman



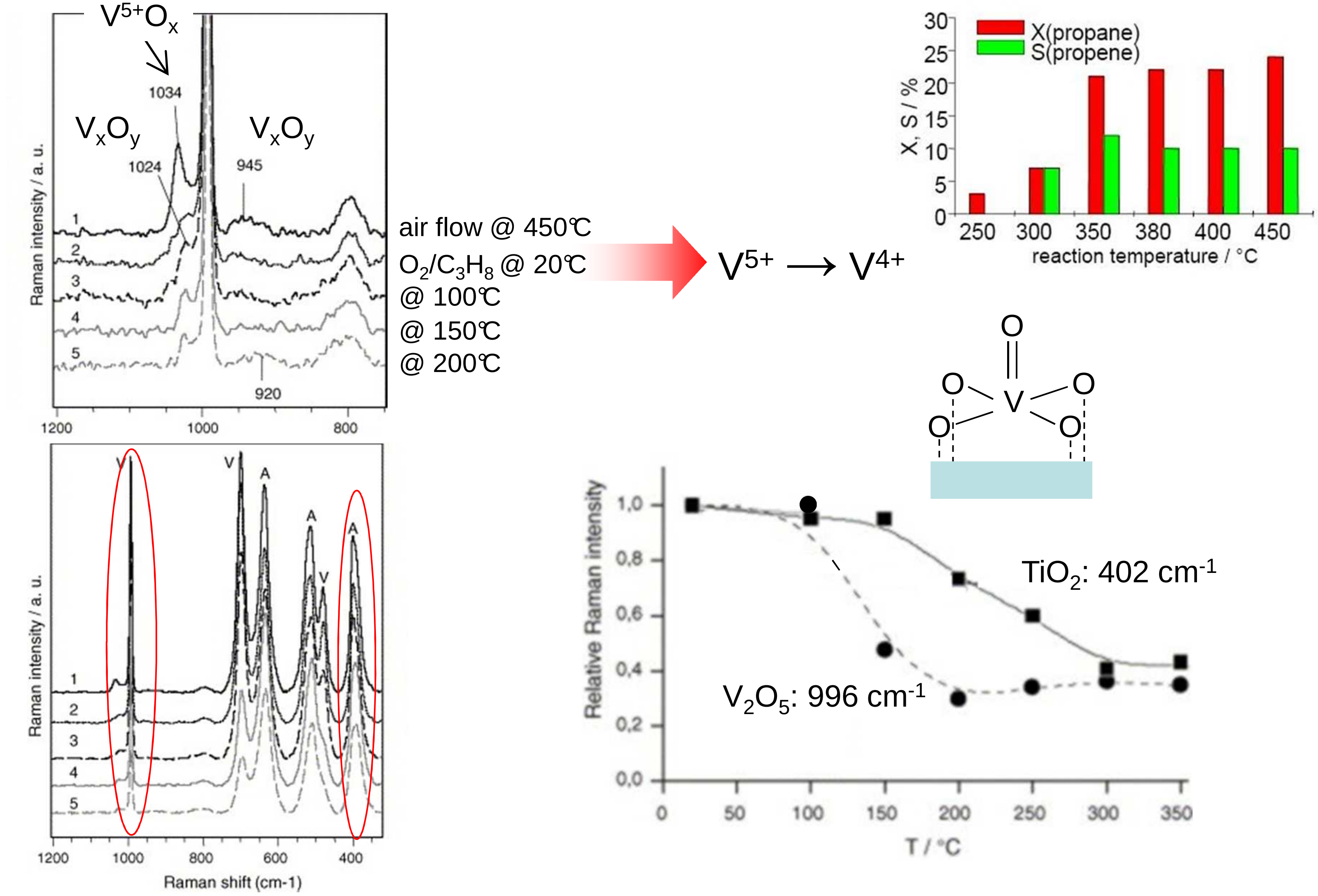
XRD



Santhosh Kumar et al., *J. Catal.* **261** (2009) 116

Examples

- Reactivity of V/TiO_2 after oxidative treatment



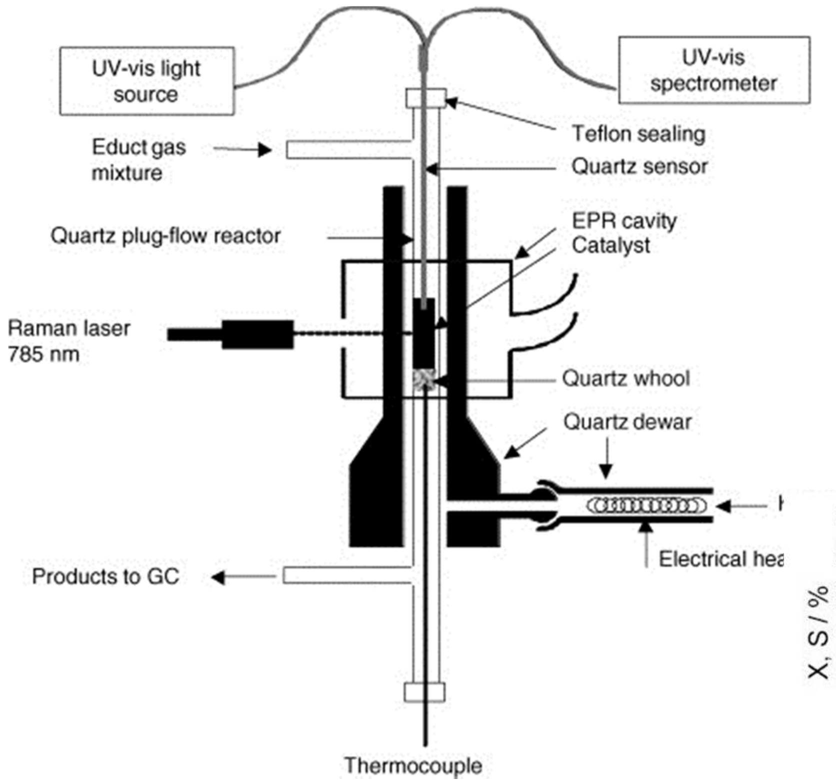
Brückner et al., *Catal. Today* **113** (2006) 16

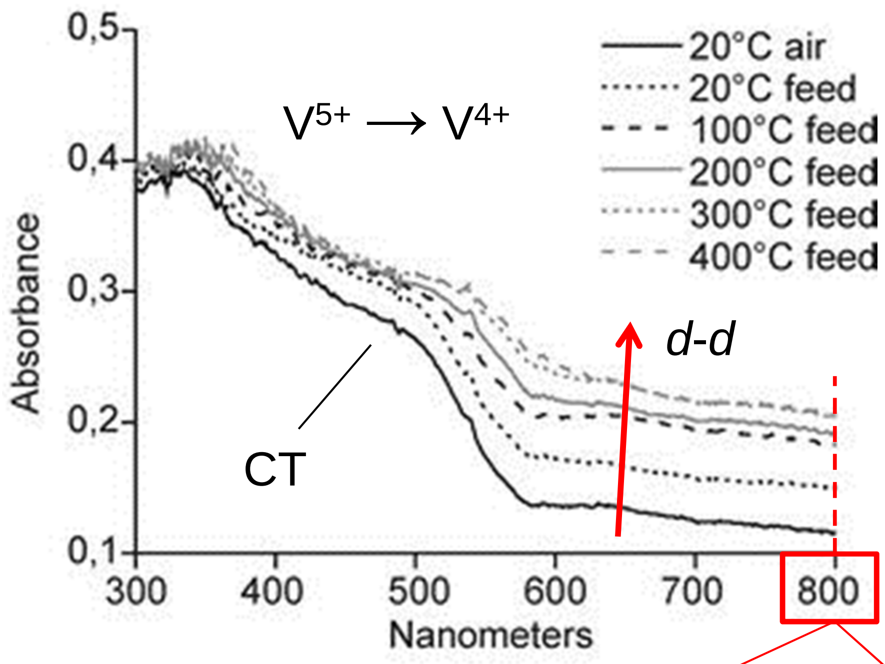
Examples

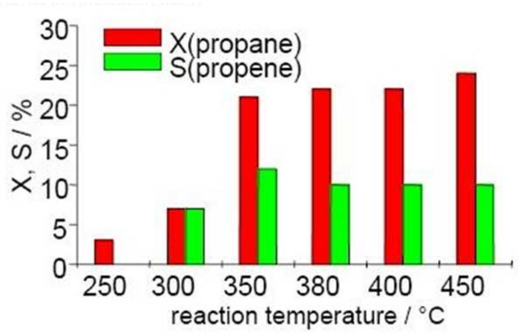
- Reactivity of V/TiO_2 after oxidative treatment

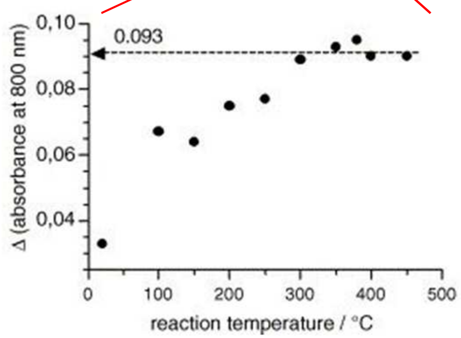
UV-vis: V^{5+} CT (UV)

V^{4+} d-d transitions (vis)







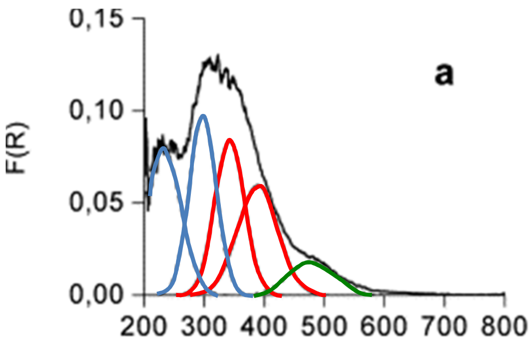


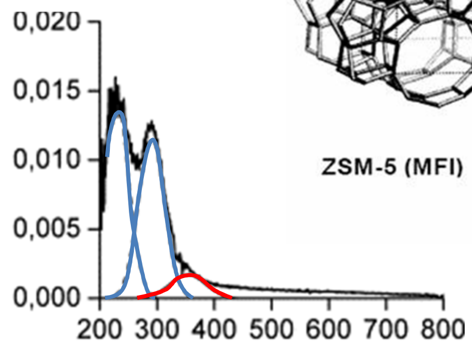
Brückner et al., *Catal. Today* **113** (2006) 16

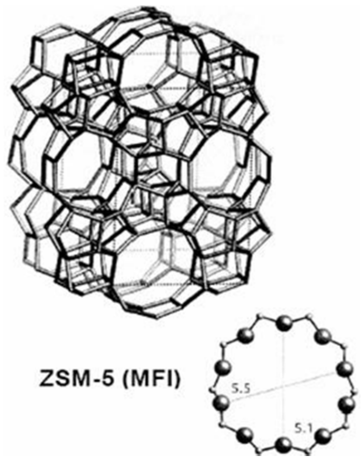
Examples

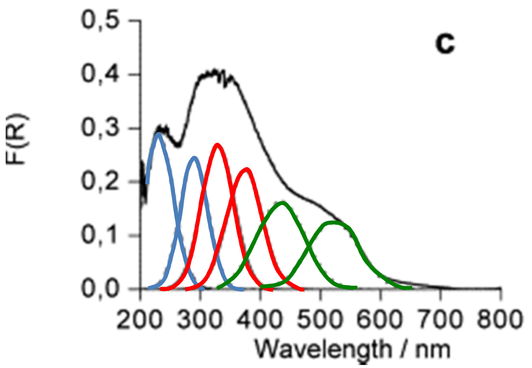
- **Determination of speciation: Fe species in Fe-ZSM5**

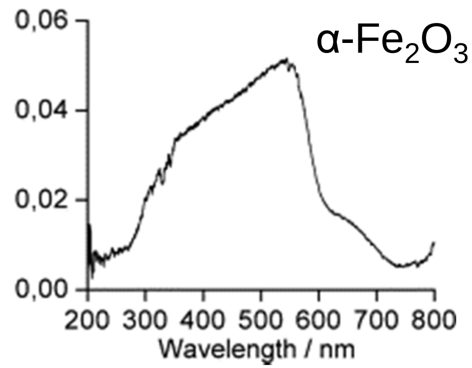
hydrated samples
isolated Fe^{3+}
oligomeric Fe_xO_y
extended F_2O_3-like clusters



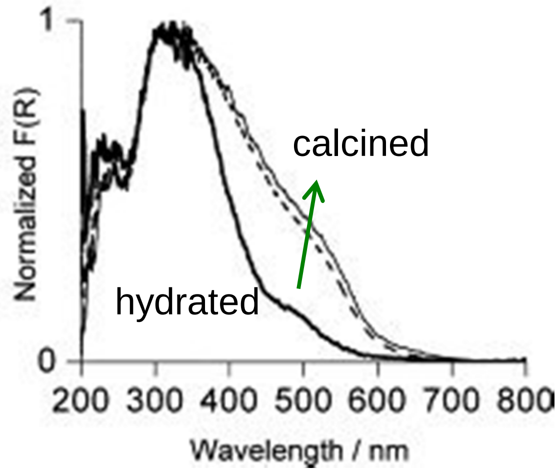








calcination @ 600℃



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