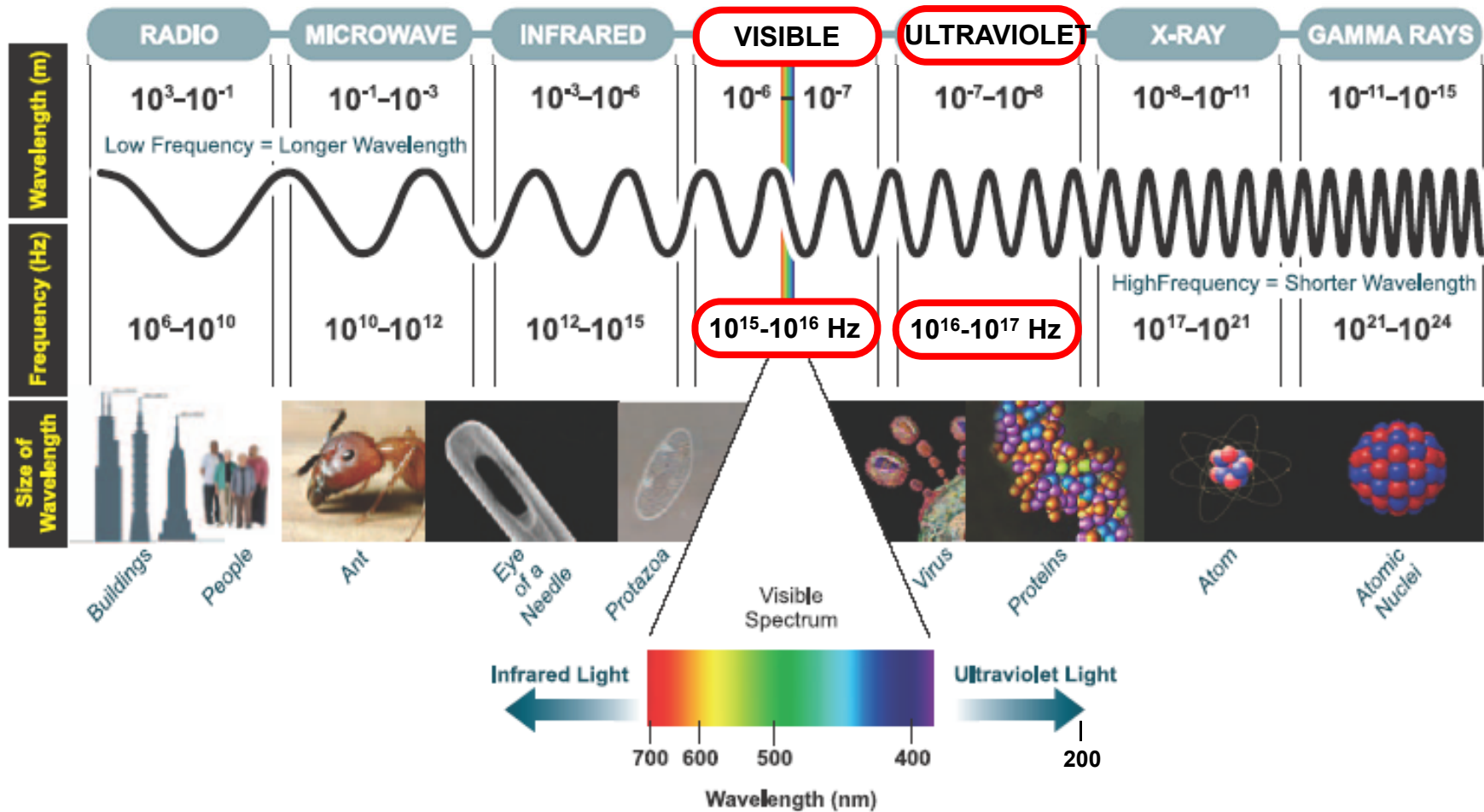


UV-Vis spectroscopy

Dr. Davide Ferri
Paul Scherrer Institut
 056 310 27 81
 davide.ferri@psi.ch

The electromagnetic spectrum



source: Andor.com

UV-vis spectroscopy

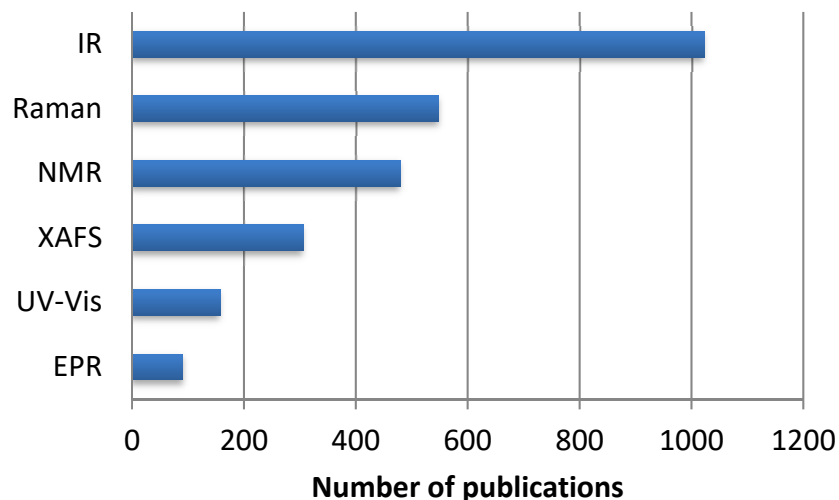
- Use of **ultraviolet** and **visible** radiation
- Electron excitation to excited electronic level (**electronic transitions**)
- Identifies functional groups ($-(C=C)_n-$, $-C=O$, $-C=N$, etc.)
- Access to molecular structure and oxidation state

pros

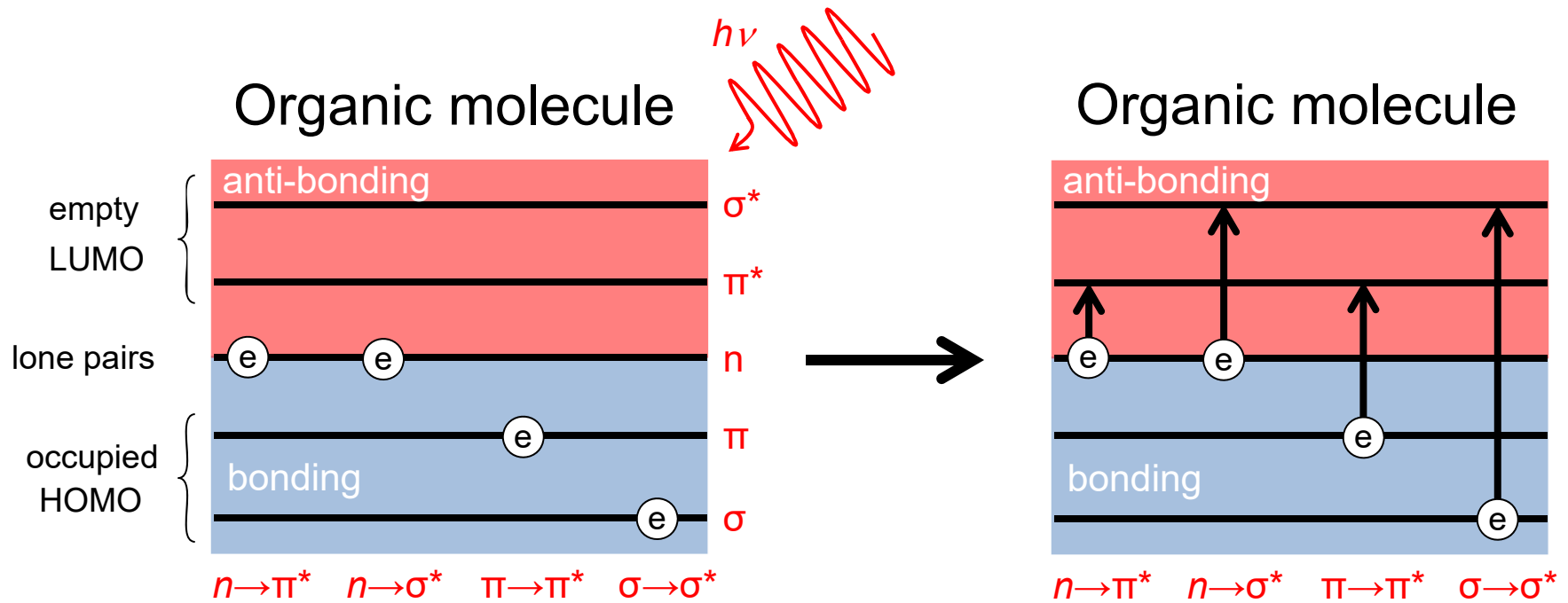
- economic
- non-invasive (fiber optics!)
- versatile (e.g. solid, liquid, gas)
- extremely sensitive (concentration)
- fast acquisition (but S/N!)

cons

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



Electronic transitions



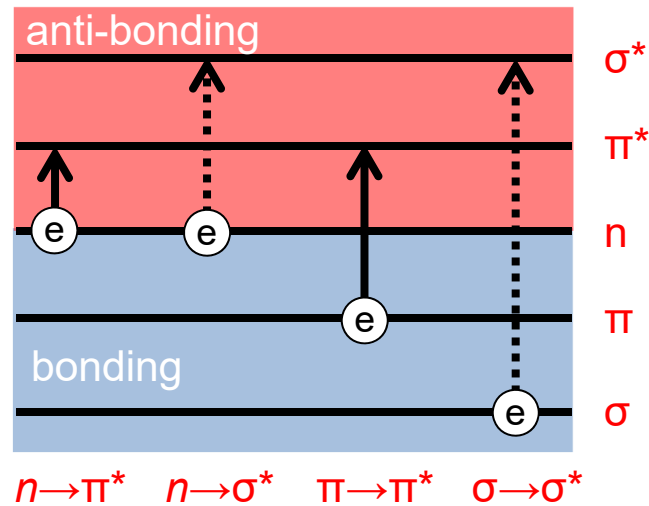
$$E = h\nu$$

$$\lambda = c/\nu$$

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

high $\nu \rightarrow$ low λ

Electronic transitions



$\sigma \rightarrow \sigma^*$
high E , low λ (<200 nm)

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

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

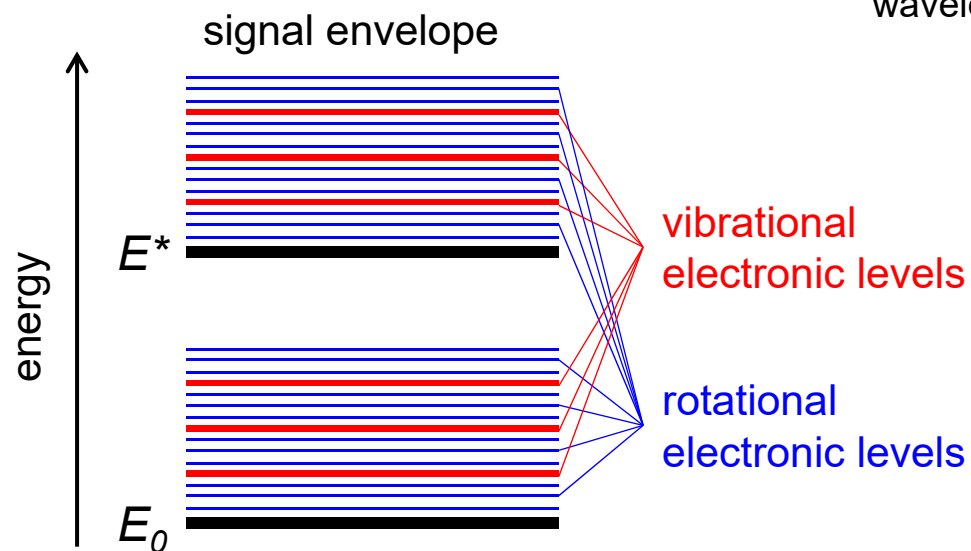
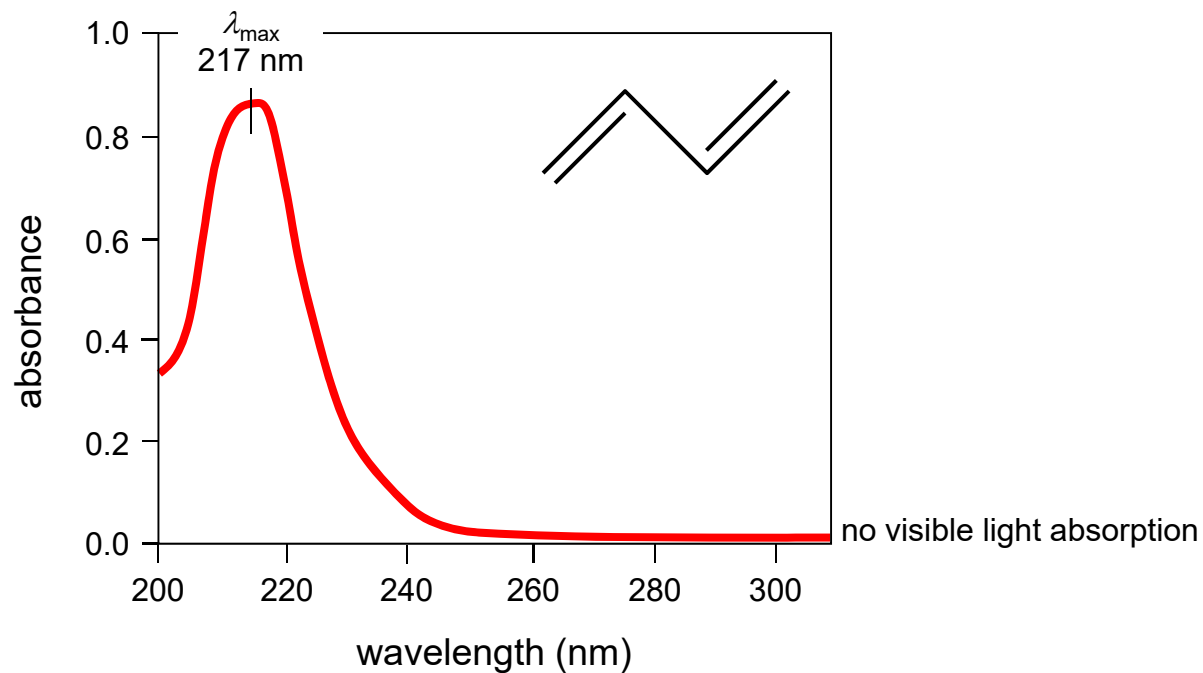
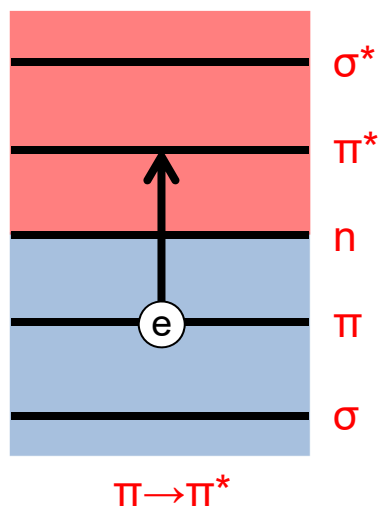
$\pi \rightarrow \pi^*$
200-700 nm, intense

Condition to absorb light
(200-800 nm):

π and/or n orbitals

CHROMOPHORE

The UV spectrum



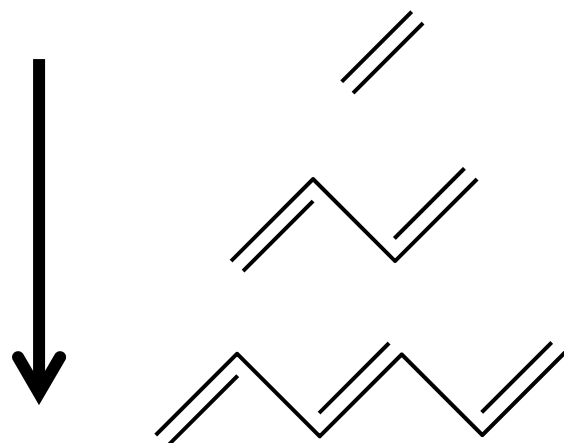
Q

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

The UV spectrum

■ Conjugation effect

delocalisation



λ_{\max}

171

217

258

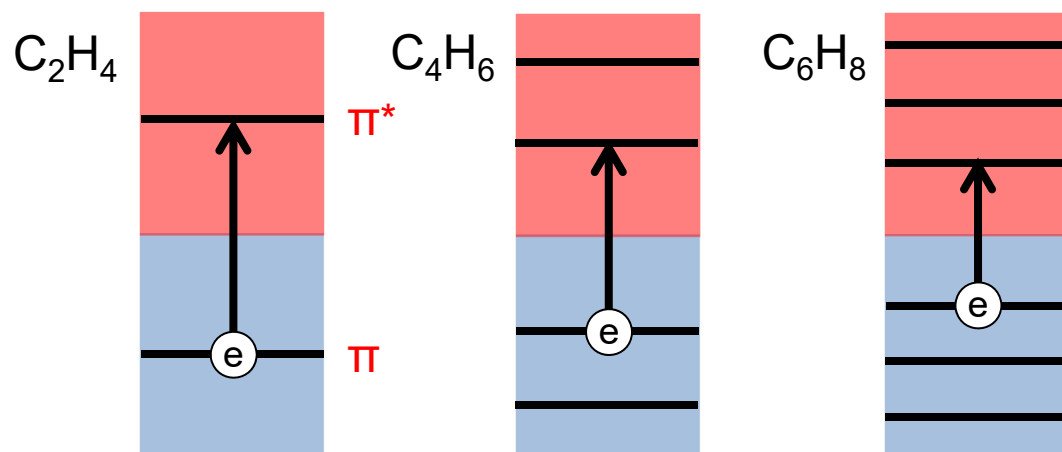
λ



ν

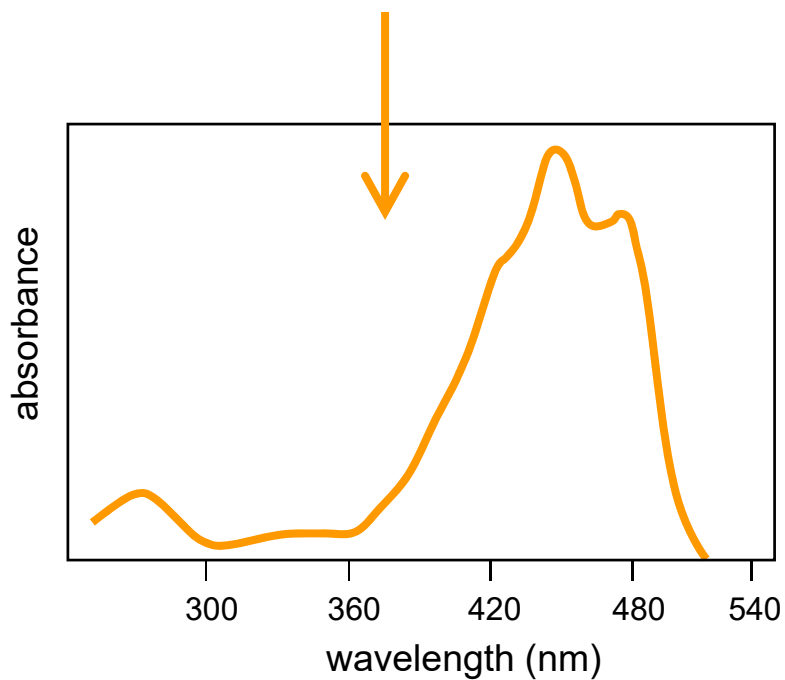
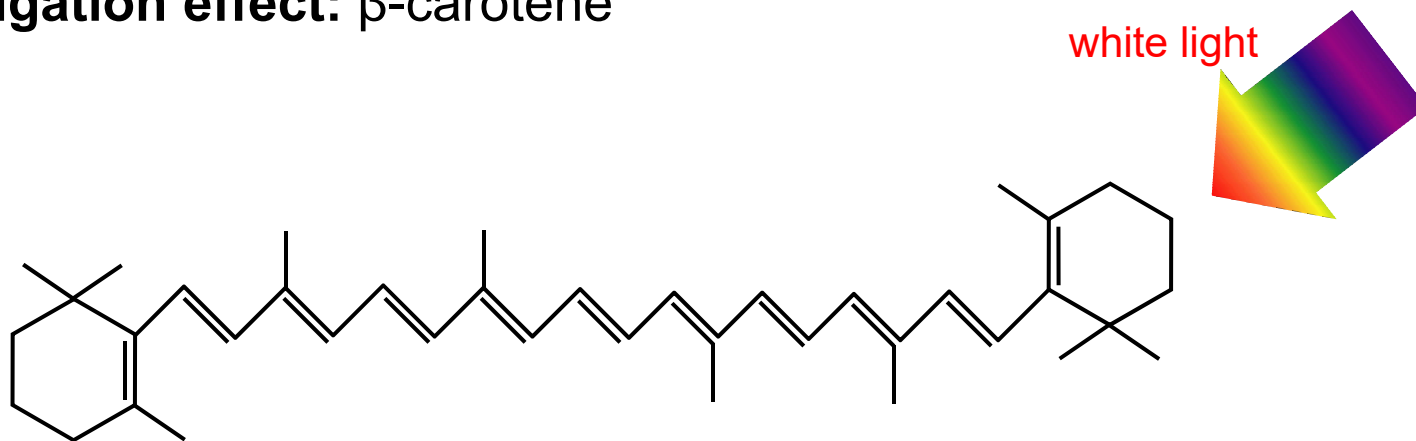


E



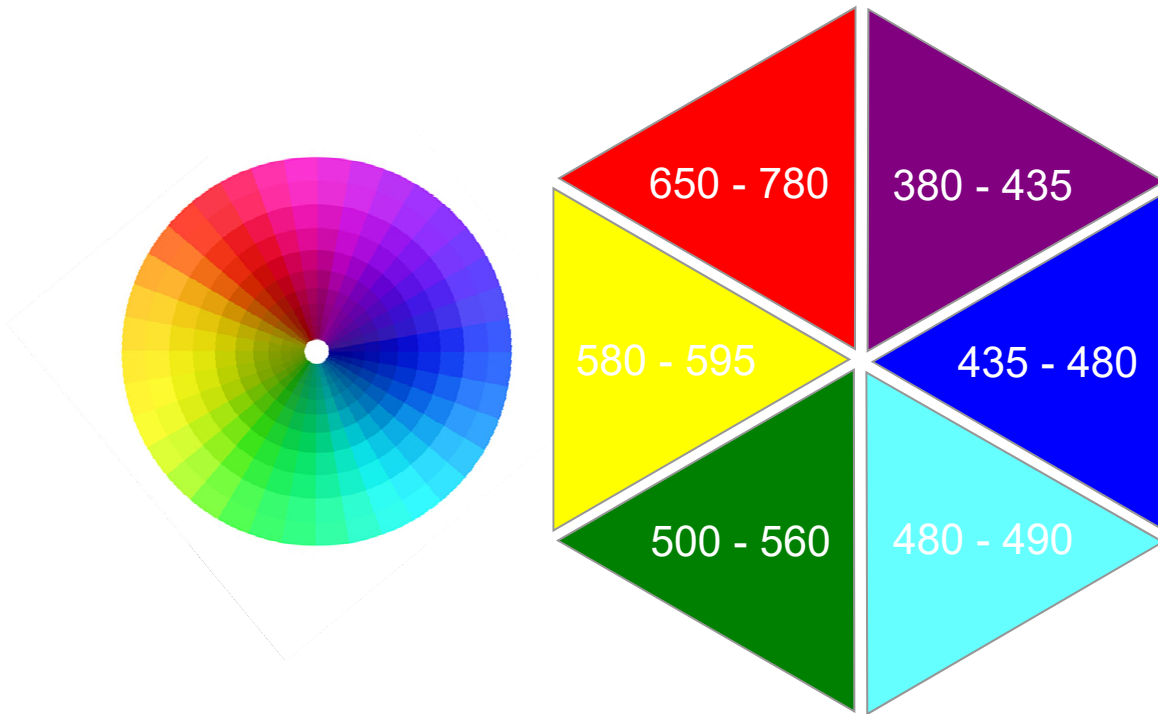
The UV spectrum

- Conjugation effect: β -carotene



The UV spectrum

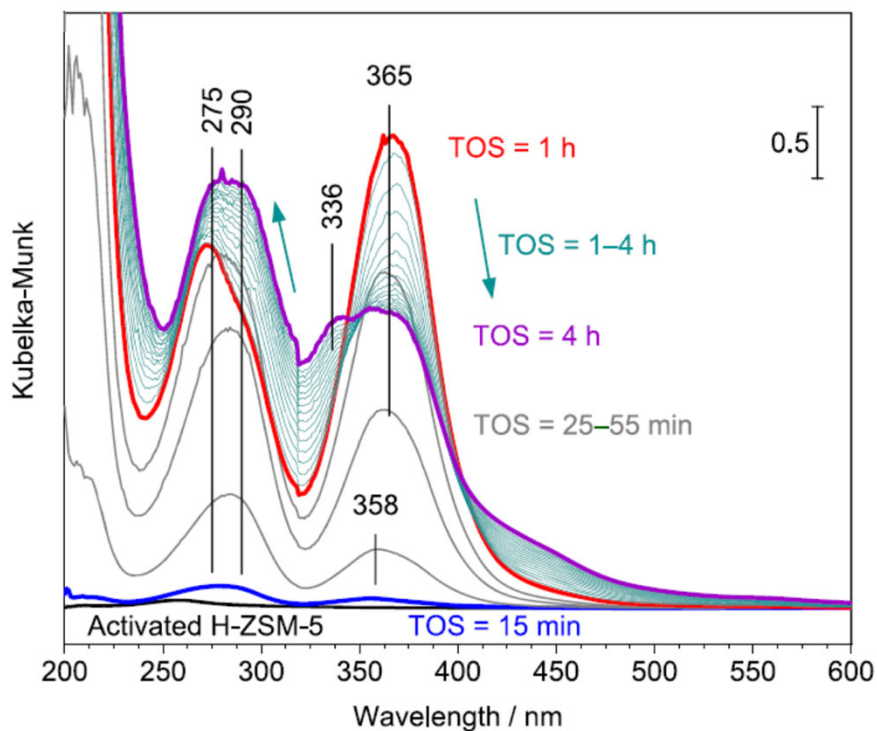
■ Complementary colours



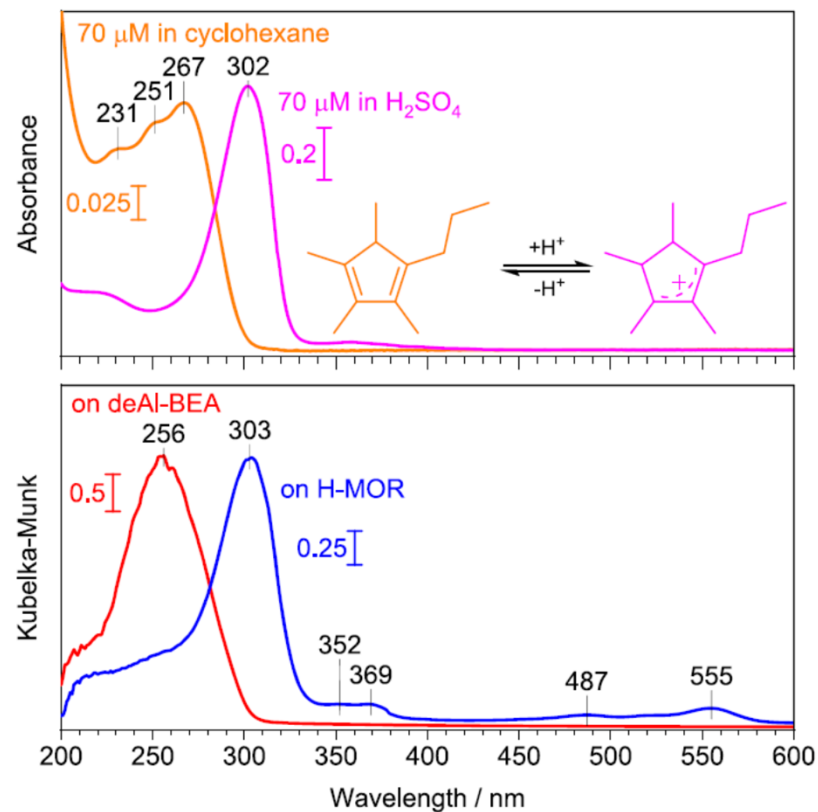
If a colour is absorbed by white light, what the eye detects by mixing all other wavelengths is its complementary colour

Examples

■ Methanol-to-olefins (MTO)



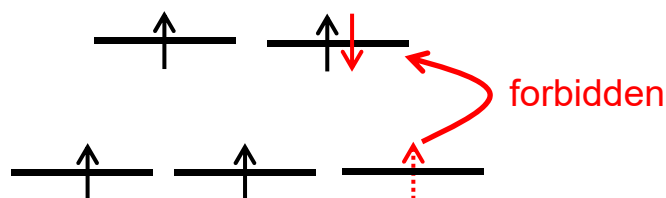
H-ZSM-5, 300°C, methanol feed



Selection rules

- **Spin selection rule**

- Transition to different spin state is **forbidden**



- **Symmetry selection rule (Laporte)**

- Only allowed transitions are those involving change in parity

$g \rightarrow u$ and $u \rightarrow g$, allowed

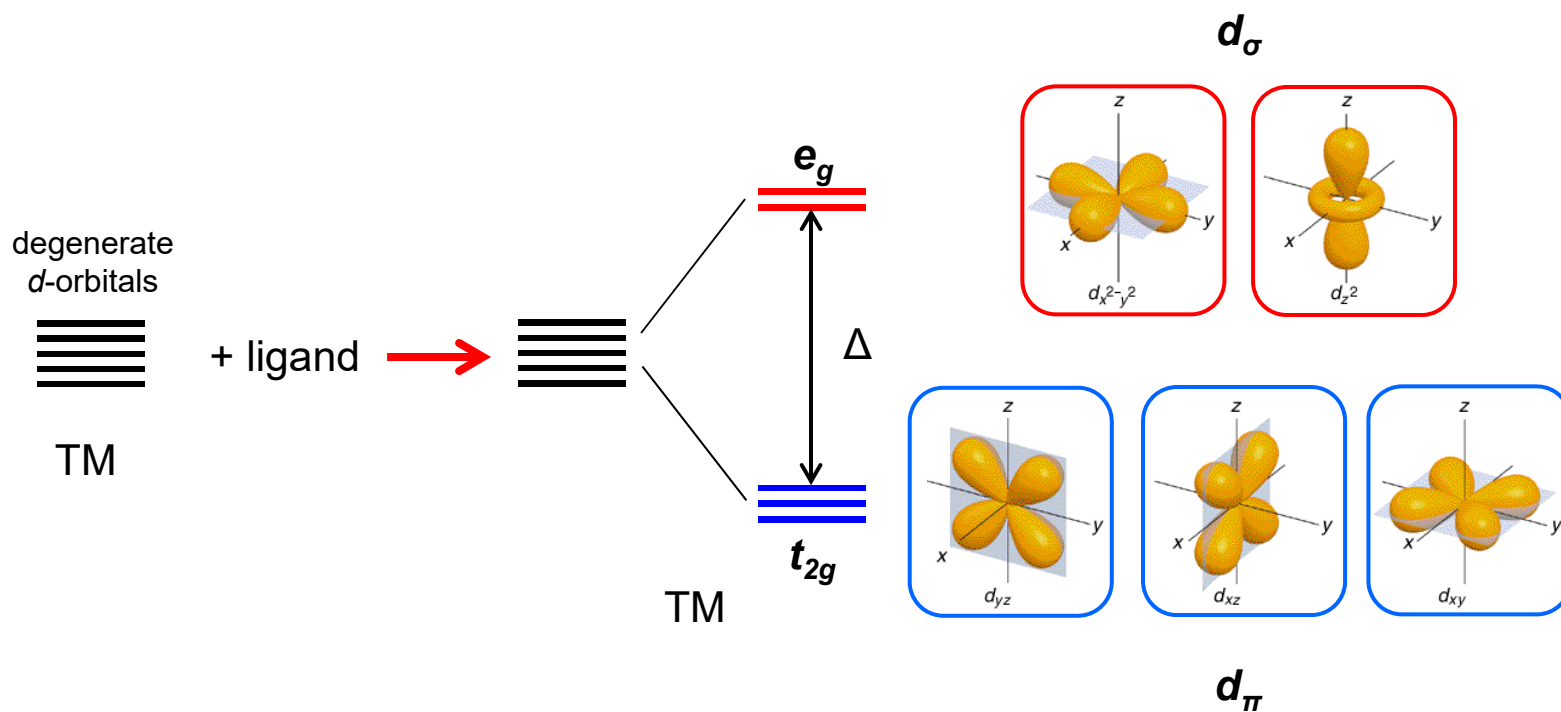
thus, $t_{2g} \rightarrow e_g$ is forbidden

- For molecules with center of inversion (centrosymmetric)
 $p \rightarrow p$ and $d \rightarrow d$ are **forbidden**

Inorganic compounds

- UV-vis spectra of transition metal complexes originate from

- Electronic *d-d* transitions

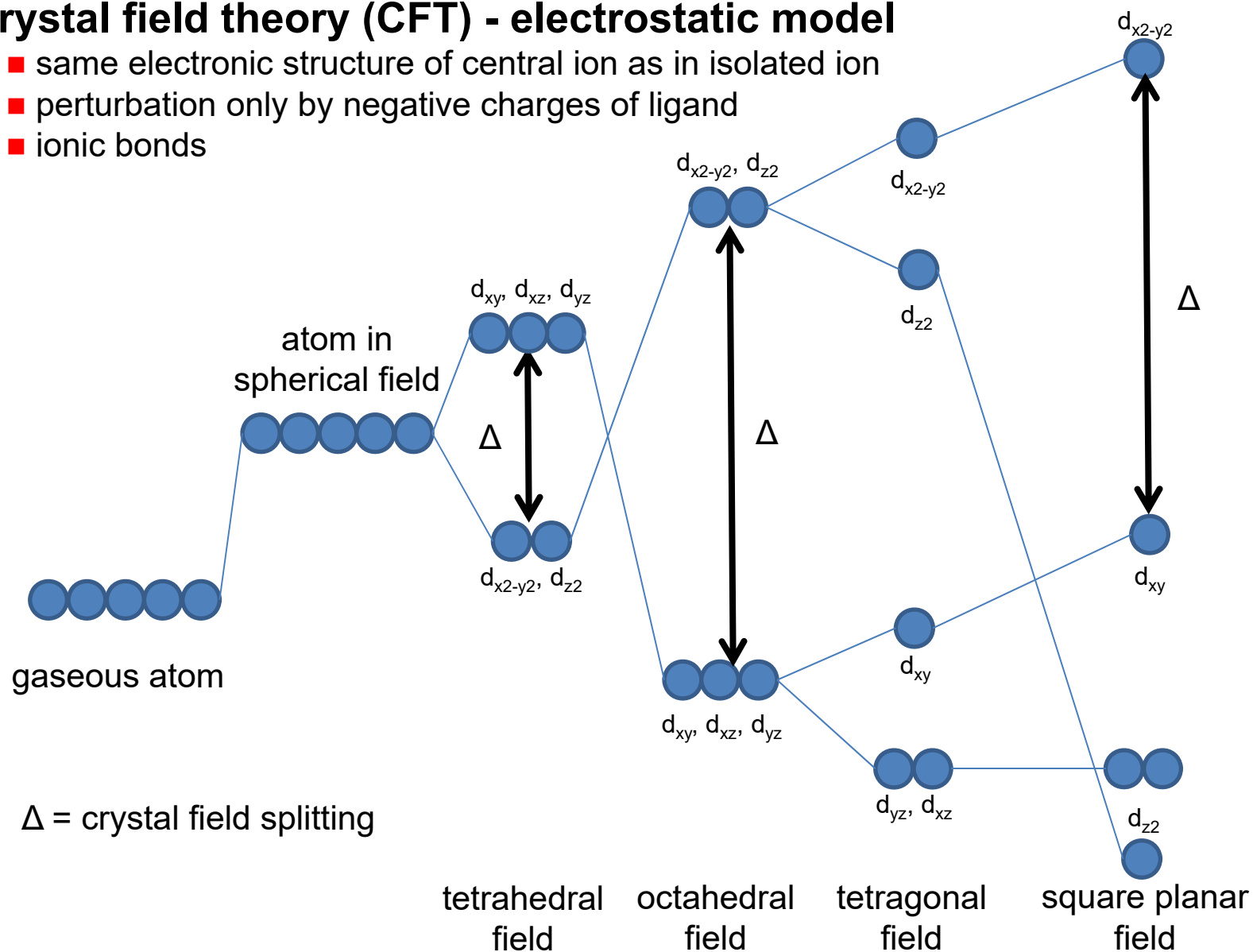


■ ...

Inorganic compounds

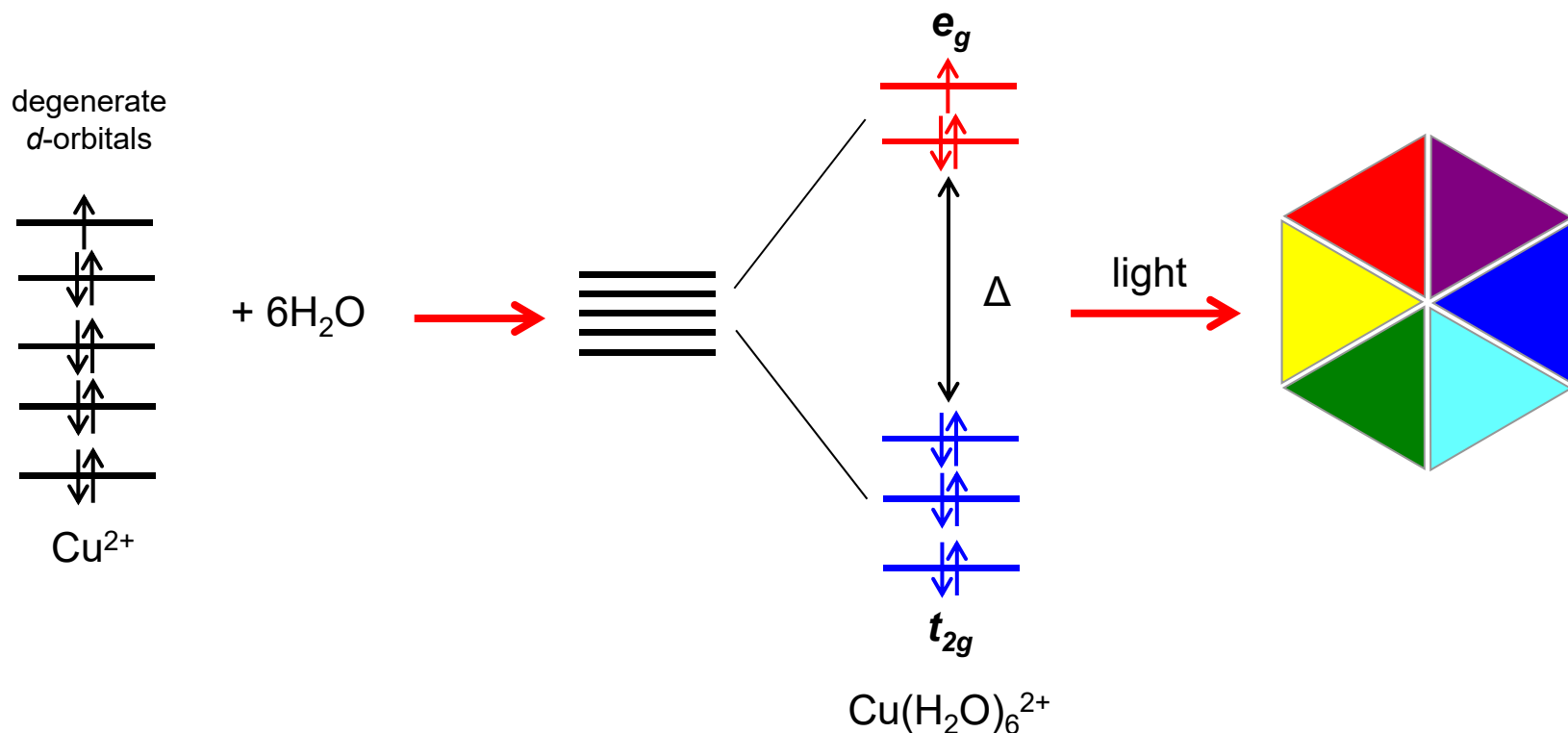
■ Crystal field theory (CFT) - electrostatic model

- 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 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, $\Delta_{\text{NH}_3} > \Delta_{\text{H}_2\text{O}}$

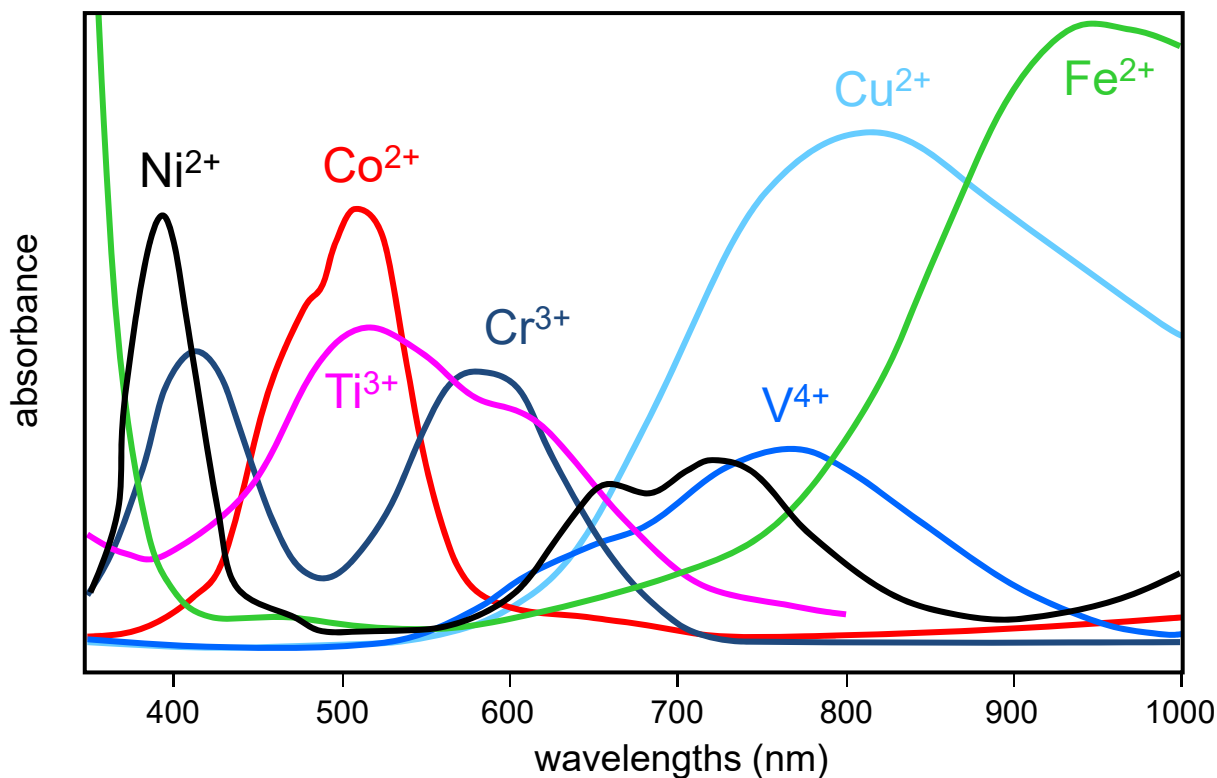
Inorganic compounds

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

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

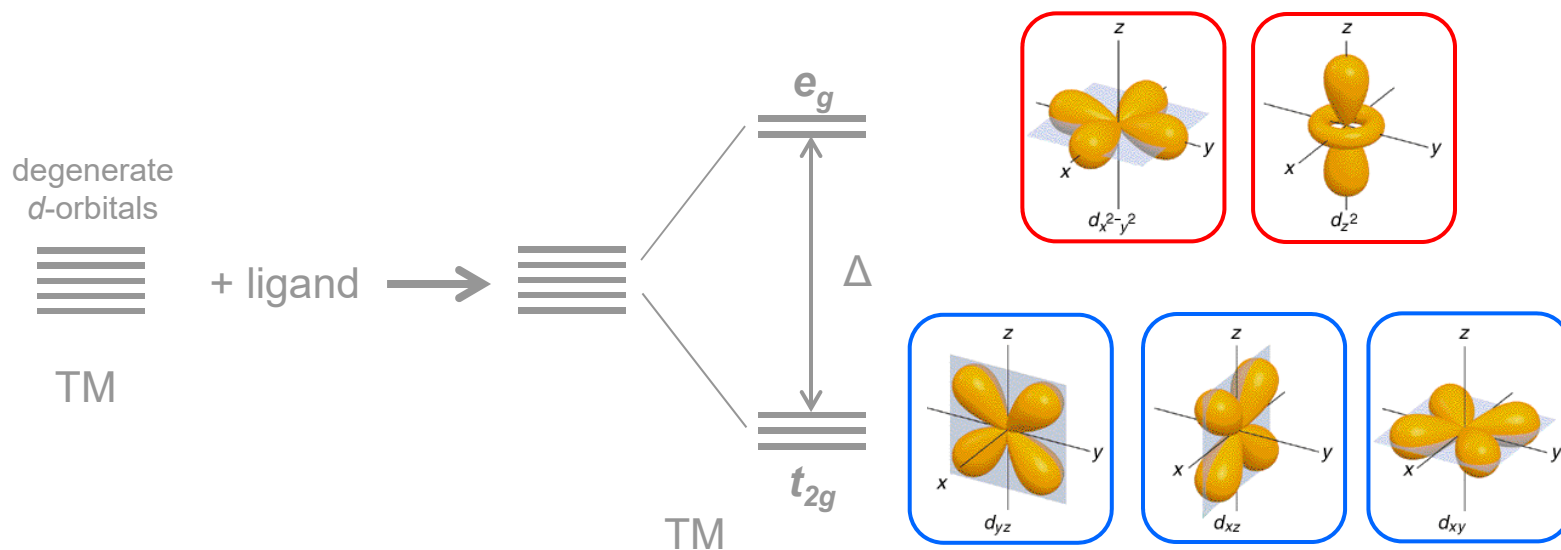
- ***d-d* transitions:** factors governing magnitude of Δ
 - **Oxidation state of metal ion**
 - Δ increases with increasing oxidation state
 - **Nature of metal ion**
 - Δ increases in the order $3d < 4d < 5d$
 - **Number and geometry of ligands**
 - Δ for tetrahedral complexes is larger than for octahedral 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

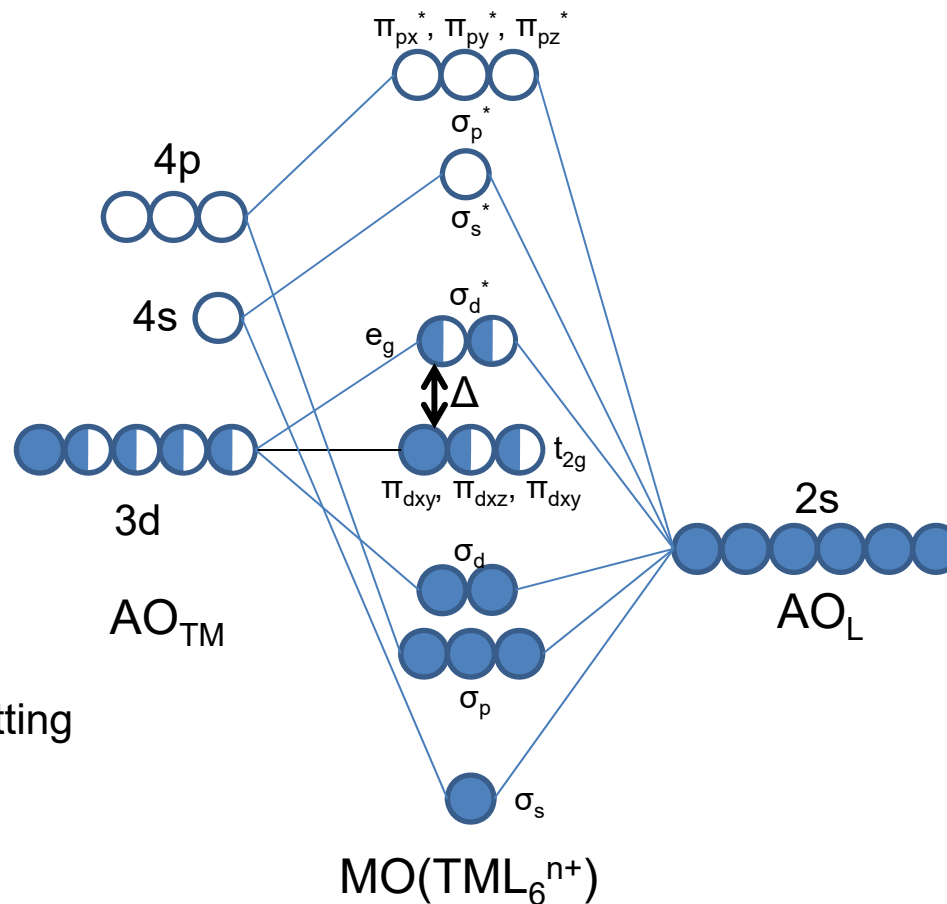
■ Charge transfer complex

- no selection rules → 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 $\pi_d \rightarrow \sigma_{dx^2-y^2}^*$



Δ = crystal field splitting

Inorganic compounds

■ Ligand field theory (LFT)

■ LMCT

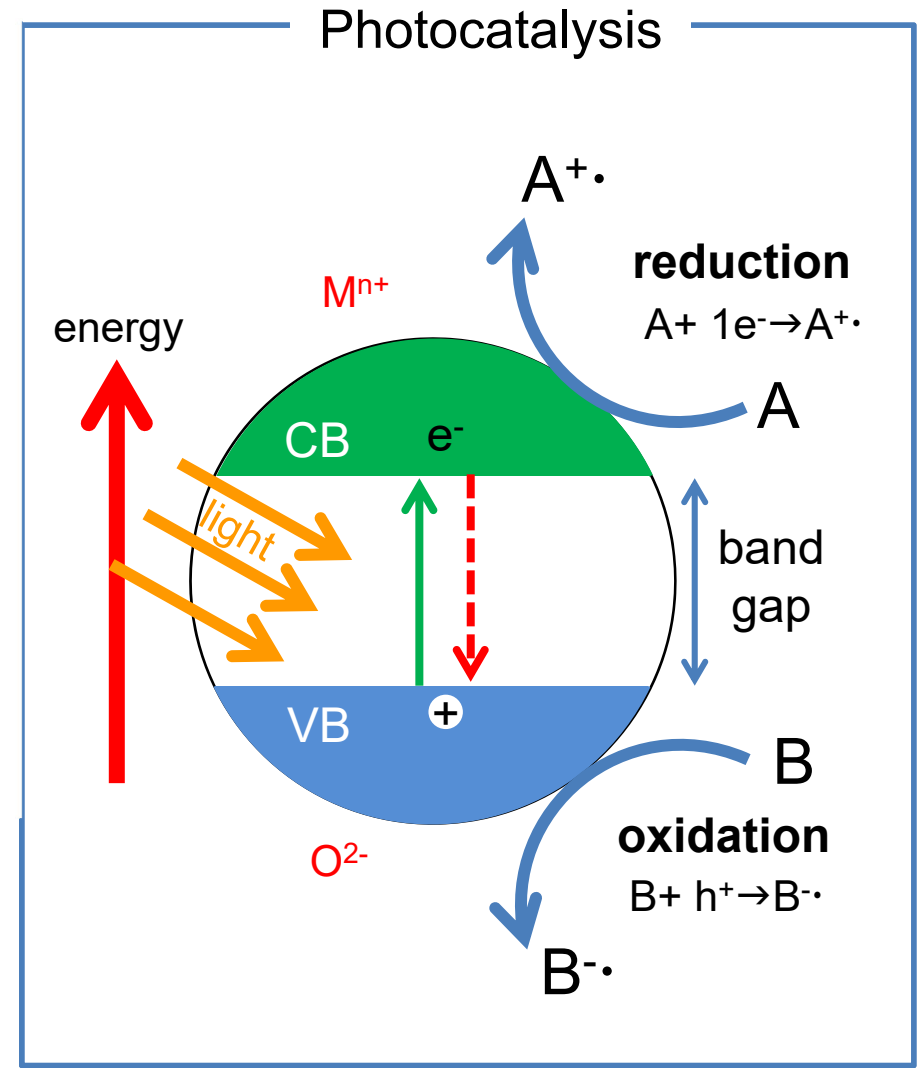
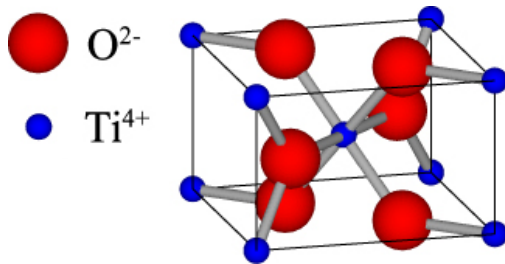
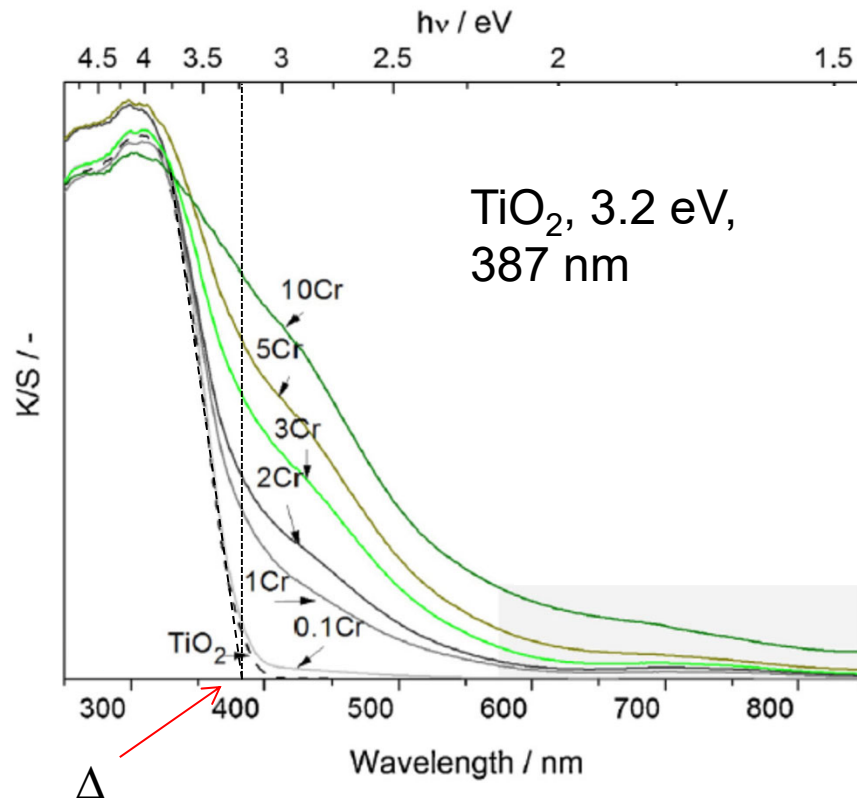
- ligand with high energy lone pair
- or, metal with low lying empty orbitals
- *high oxidation state* (also d^0)
- M-L strengthened

■ MLCT

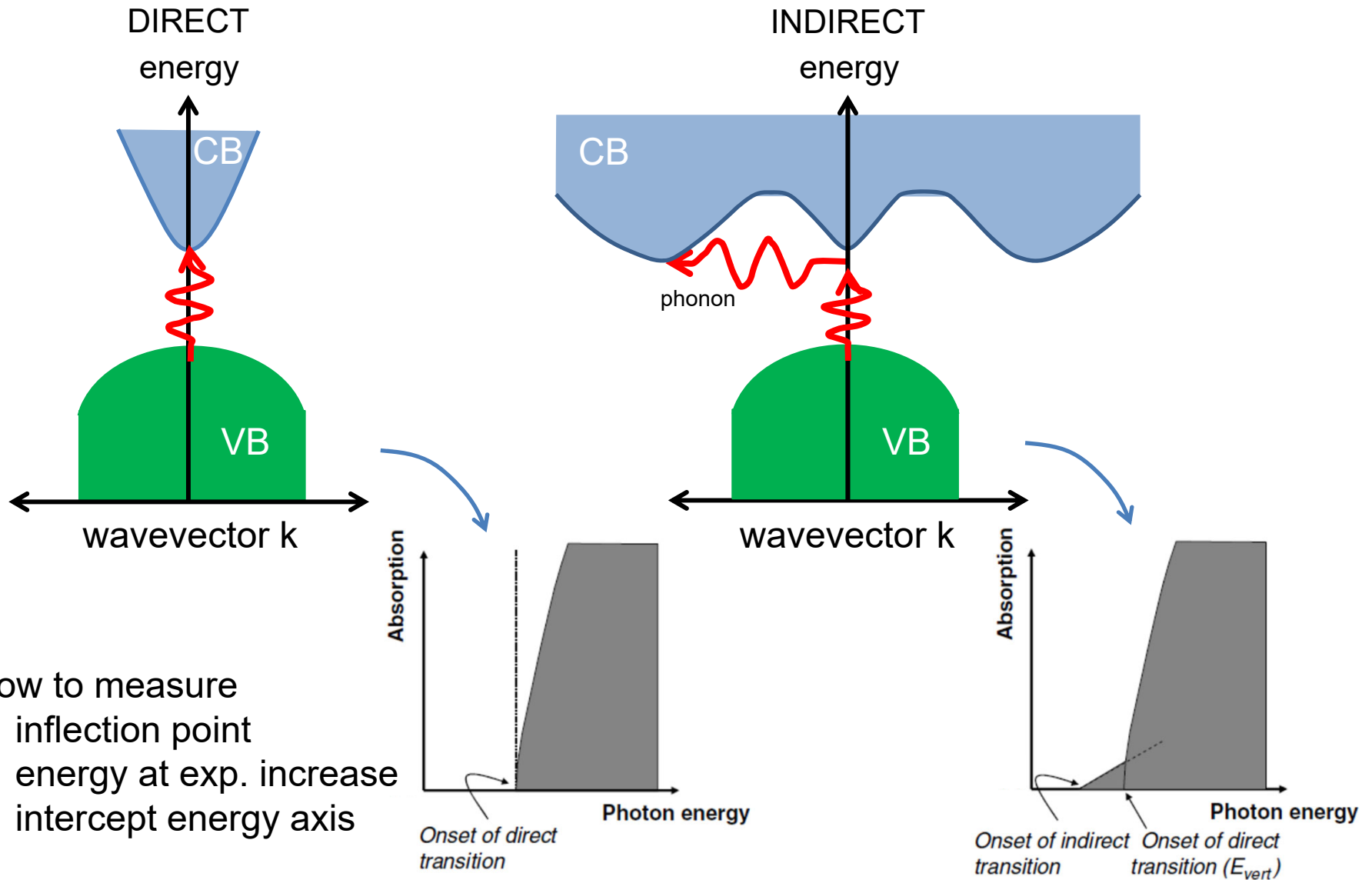
- ligands with low lying π^* orbitals (CO, CN⁻, SCN⁻)
- *low oxidation state* (high energy d orbitals)
- M-L strengthened, π bond of L weakened

Band gap

■ Analysis of semiconductors



Band gap



How to measure

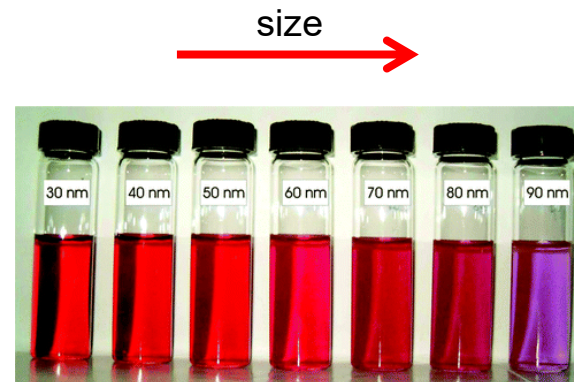
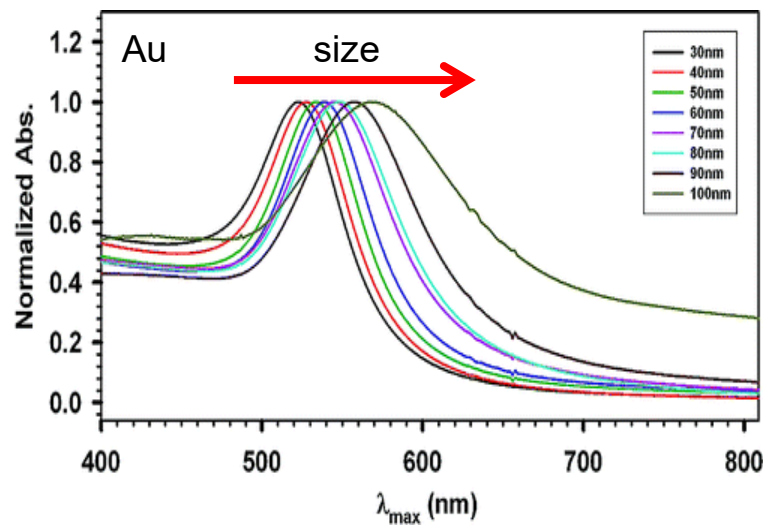
- inflection point
- energy at exp. increase
- intercept energy axis

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

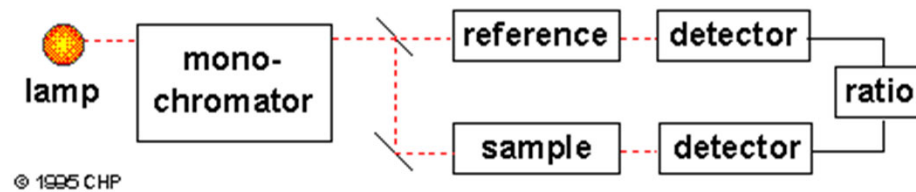


Instrumentation

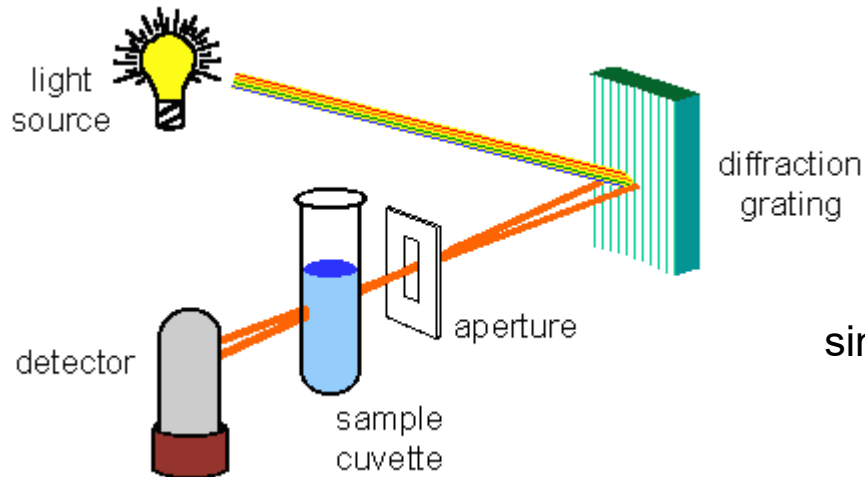
■ Dispersive instruments

Measurement geometry:

- transmission
- diffuse reflectance



double beam spectrometer

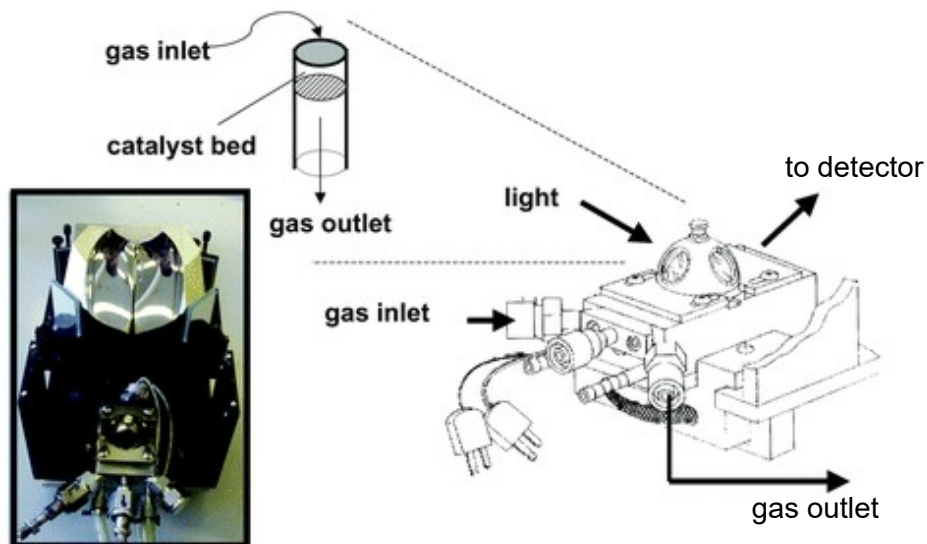


single beam spectrometer

© 2001 B. M. Tissue

In situ instrumentation

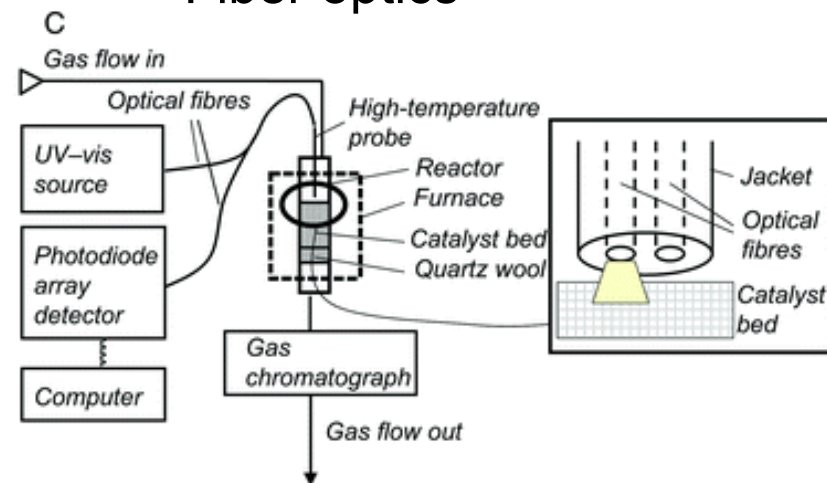
■ Diffuse reflectance (DRUV)



- ✓ - 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!!!

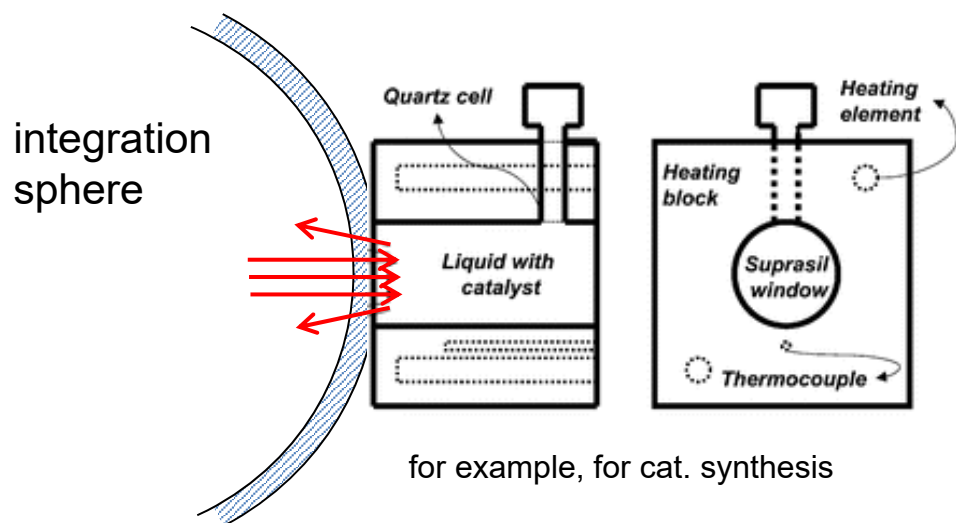
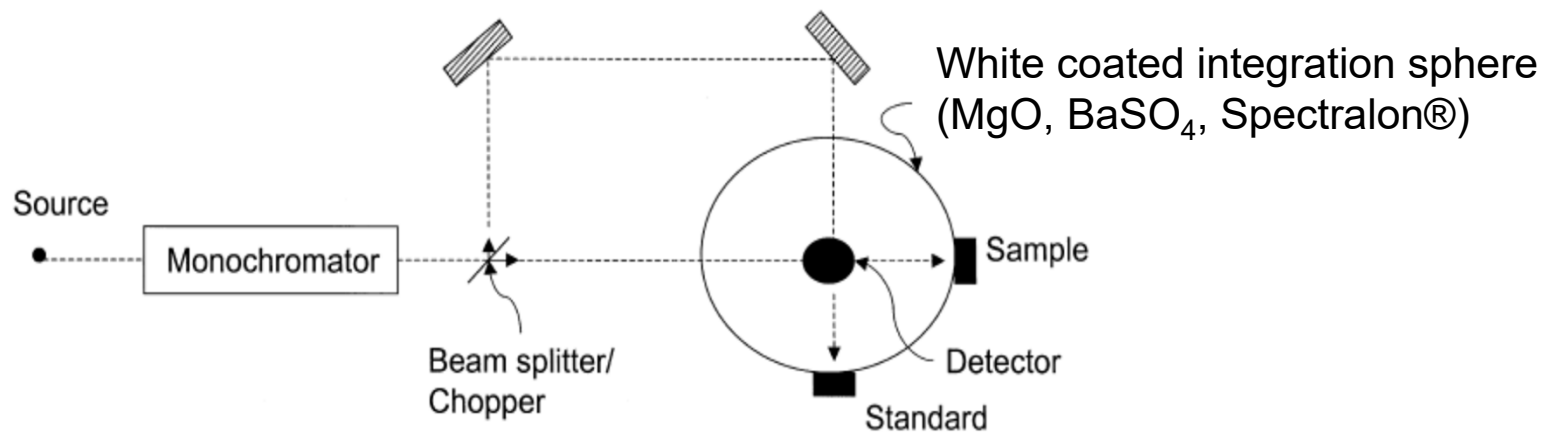
■ Fiber optics



- ✓ - 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



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

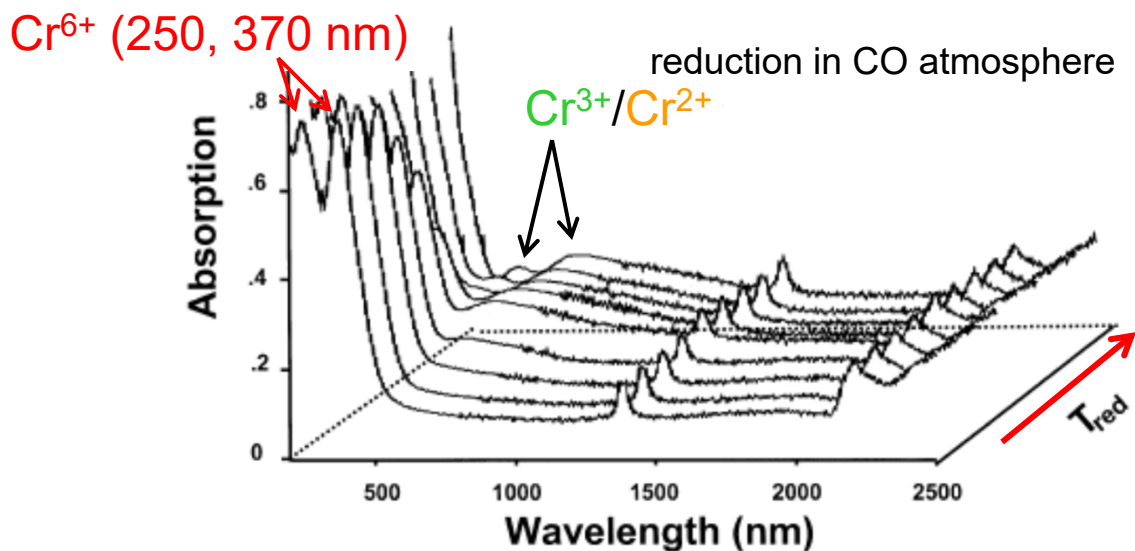
for example, for cat. synthesis

Examples

■ Determination of oxidation state: 0.1 wt% Crⁿ⁺/Al₂O₃

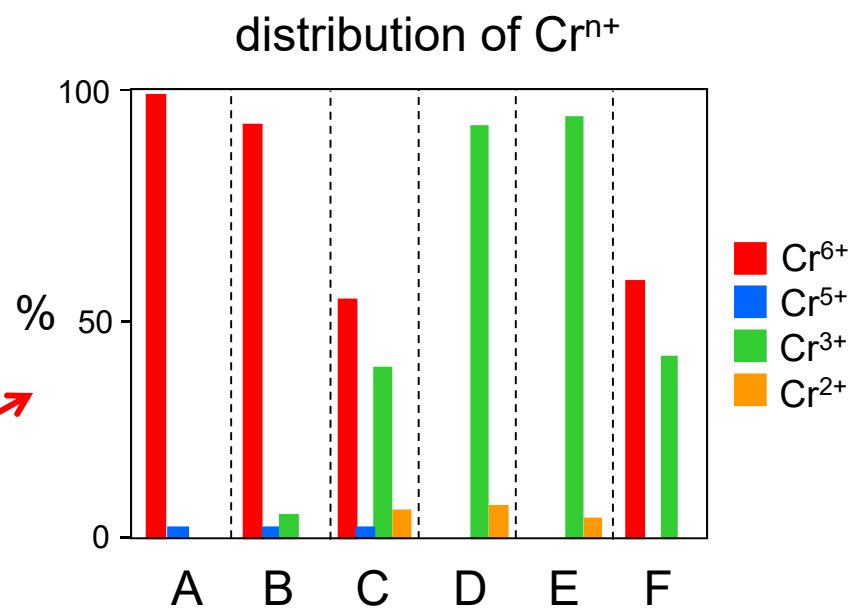
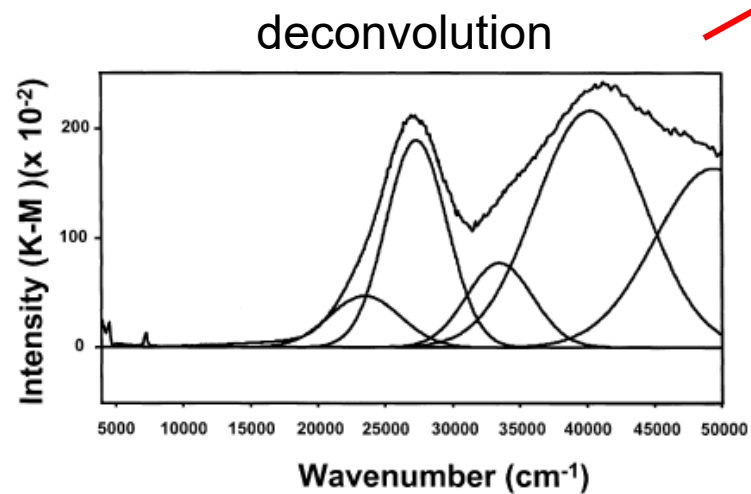
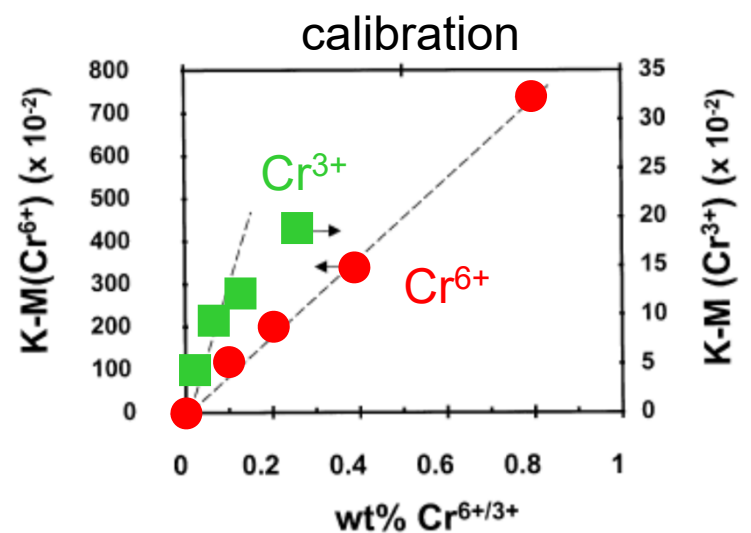
Compound	Coordination geometry and oxidation state	Absorption bands (nm) ^a	Color
K ₂ CrO ₄ (solution)	T _d , Cr ⁶⁺	440 (sh, vw), 370 (s), 275 (s)	Yellow
K ₂ CrO ₄ (solid)	T _d , Cr ⁶⁺	459 (s), 340 (s), 265 (s), 229 (s)	Yellow
K ₂ Cr ₂ O ₇ (solution)	T _d , Cr ⁶⁺	440 (w), 352 (s), 255 (s)	Orange
K ₂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

^as: strong; m: medium; w: weak; vw: very weak; sh: shoulder; br: broad.



Examples

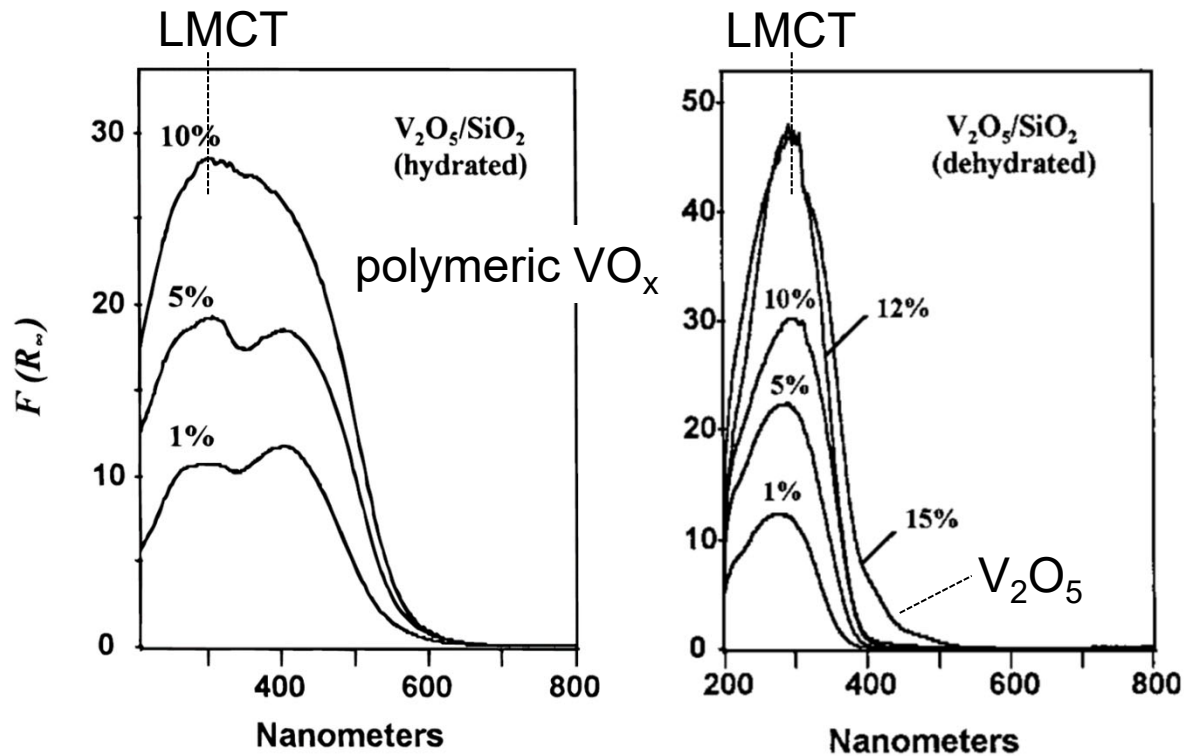
■ Determination of oxidation state: 0.1 wt% Crⁿ⁺/Al₂O₃



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

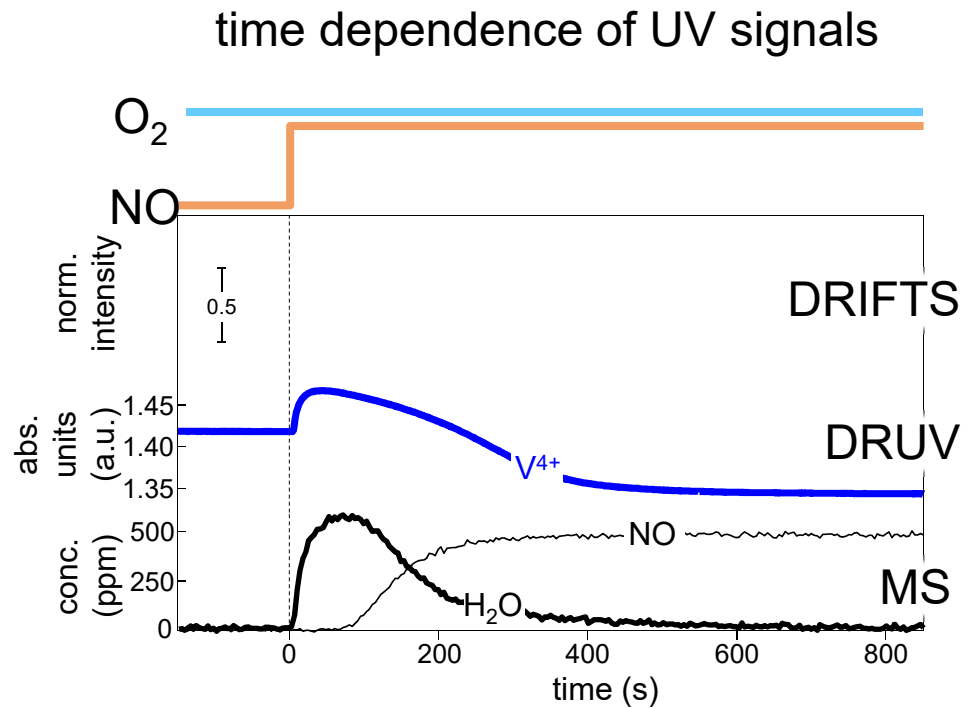
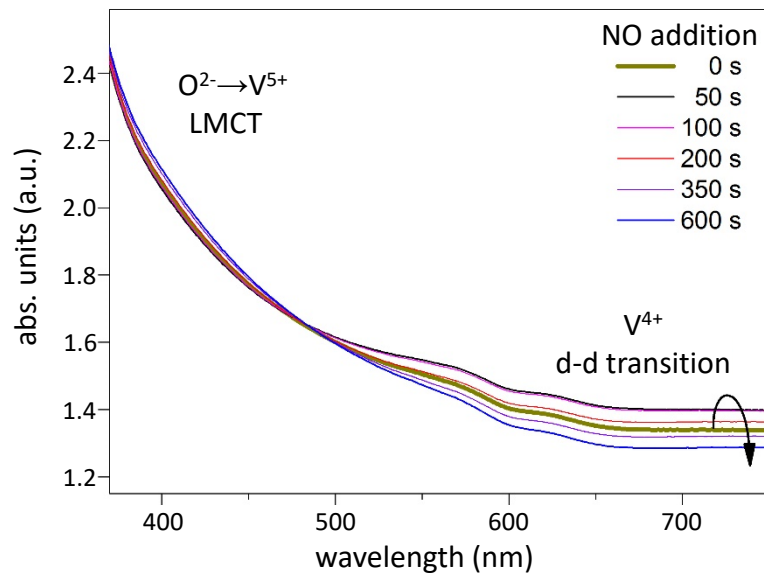
Examples

■ UV-vis of V_2O_5 - SiO_2



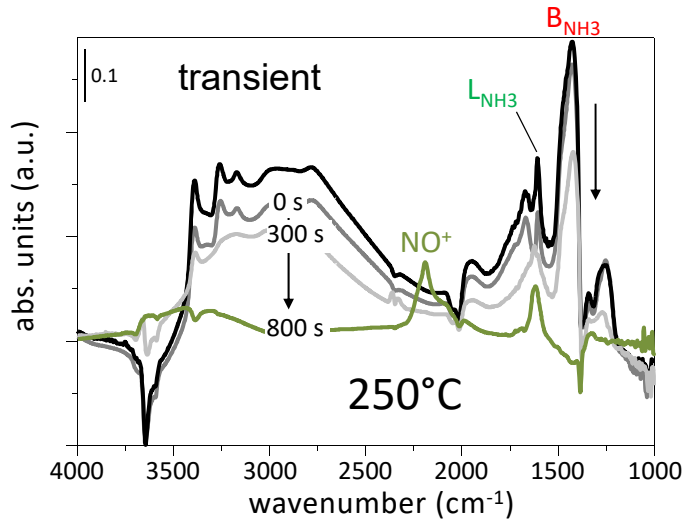
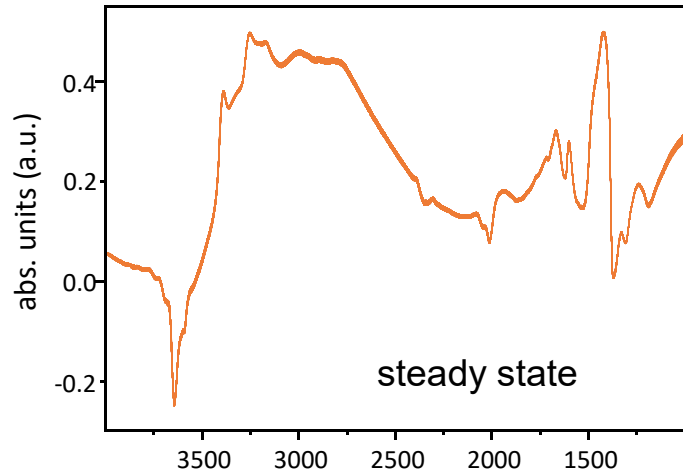
Examples

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

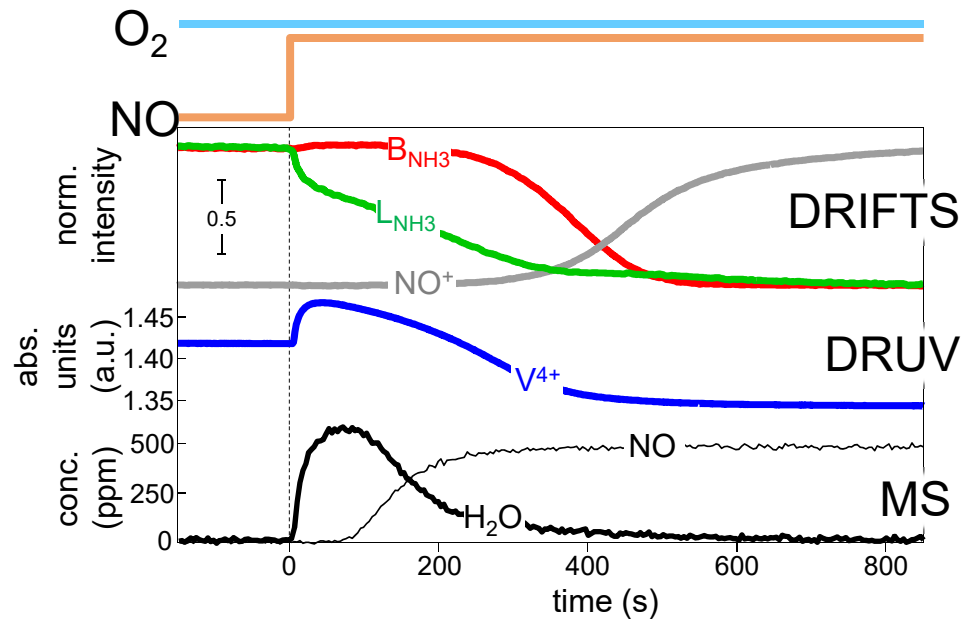


Examples

diffuse reflectance IR

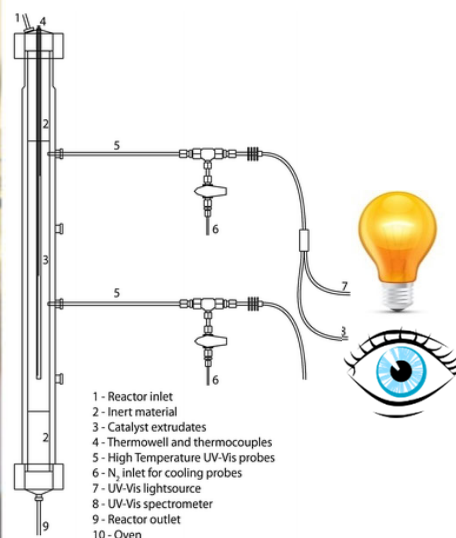


time dependence of UV and IR signals

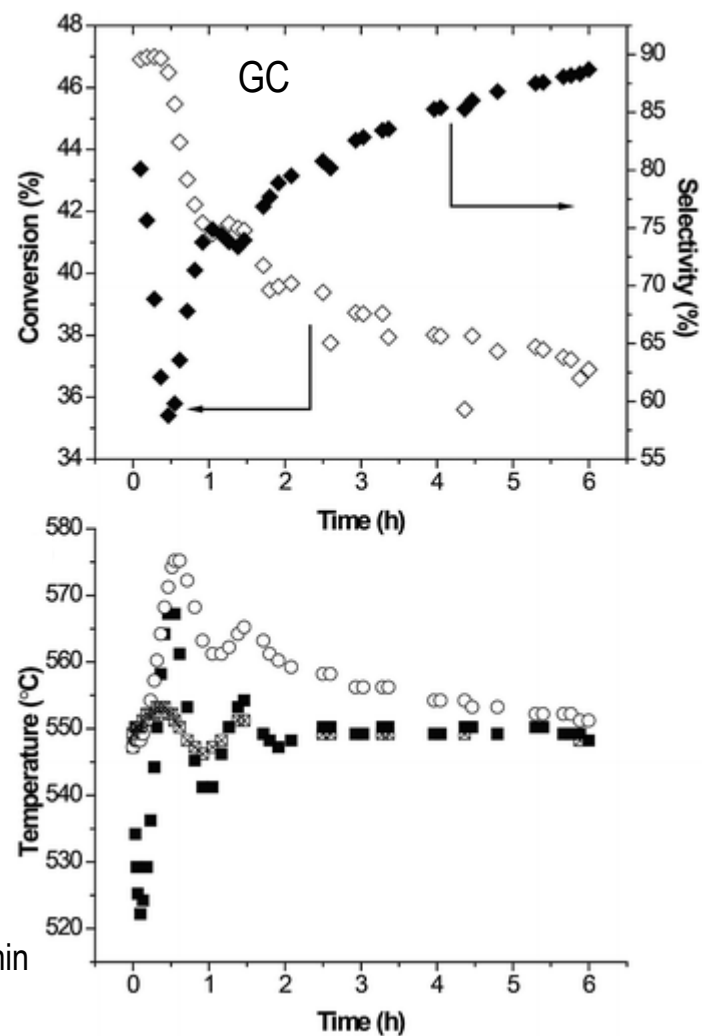


Examples

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

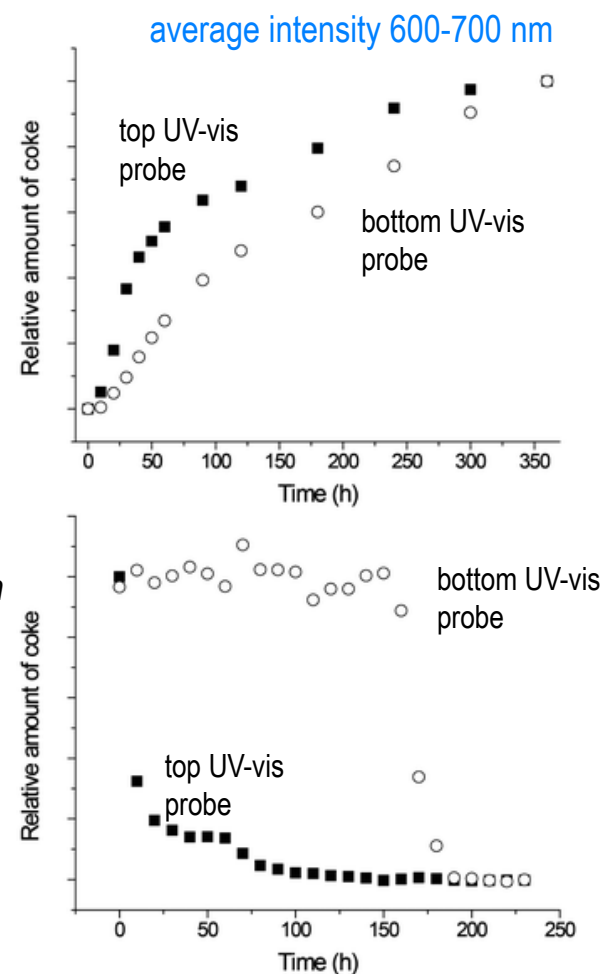
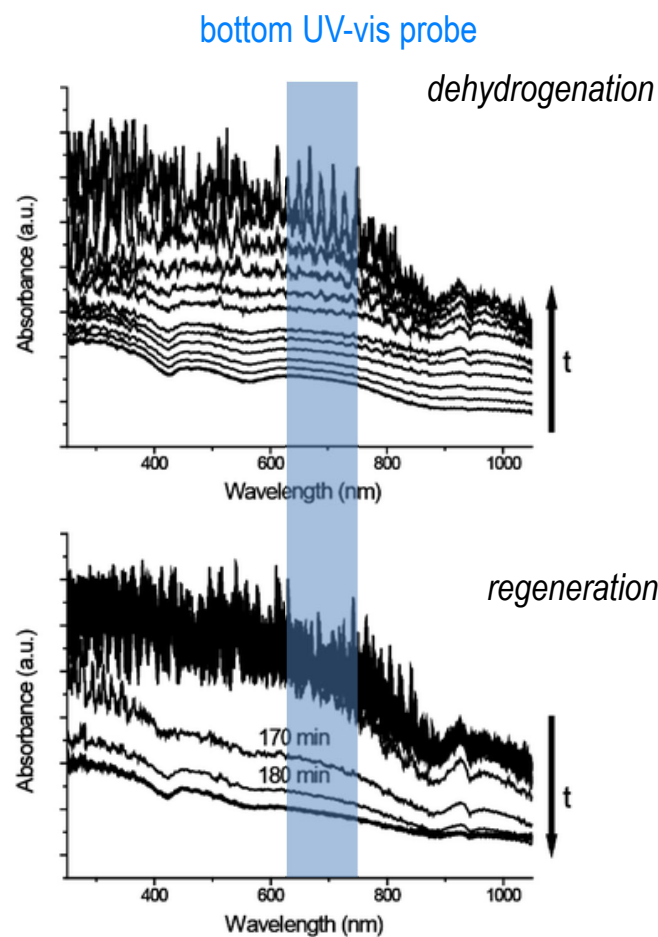


10 vol% C₃H₈, 90 vol% N₂, 5000 ml/min
20 wt% Cr^{3+/6+}O_x/Al₂O₃



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