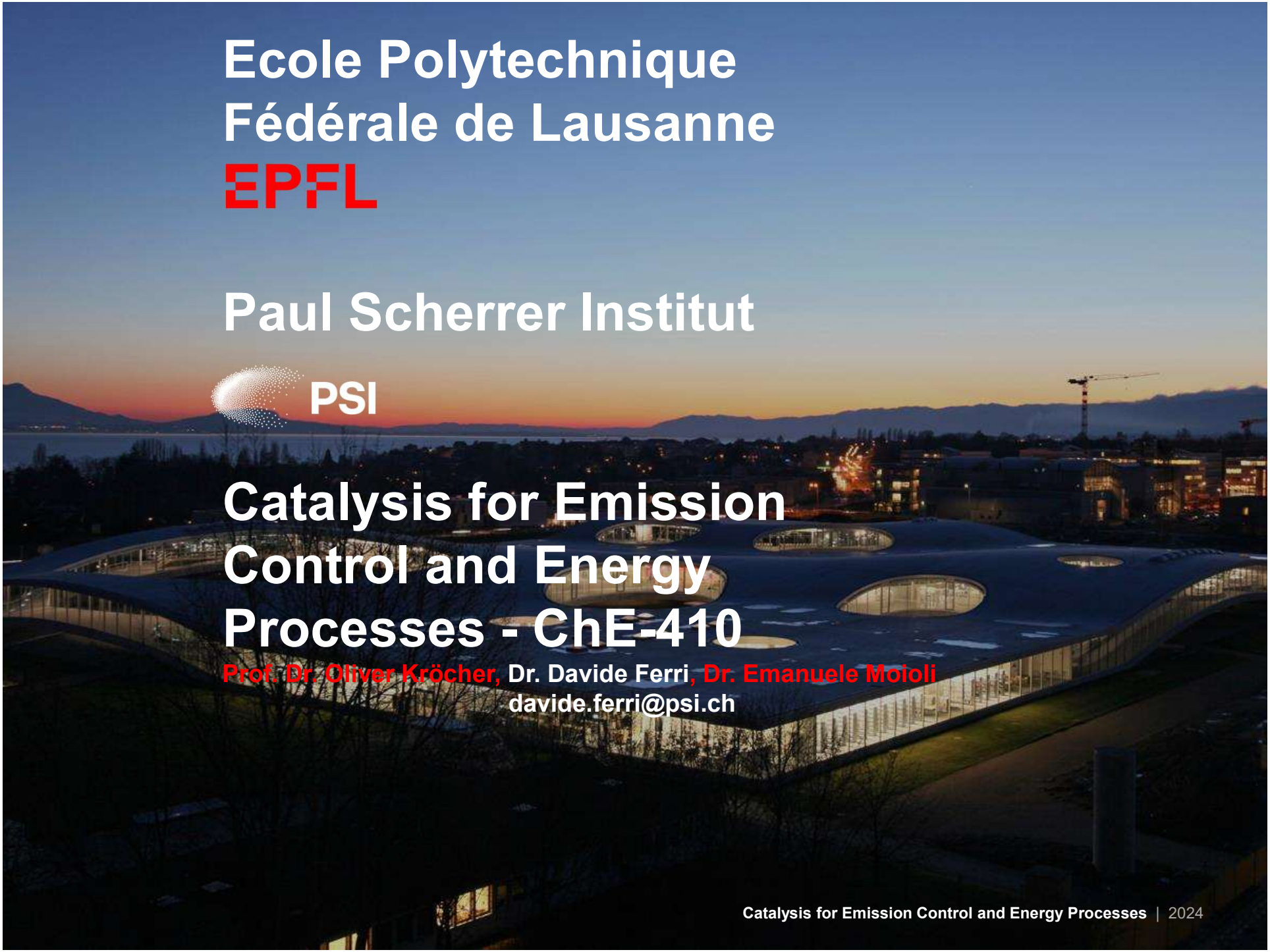


Ecole Polytechnique Fédérale de Lausanne

EPFL

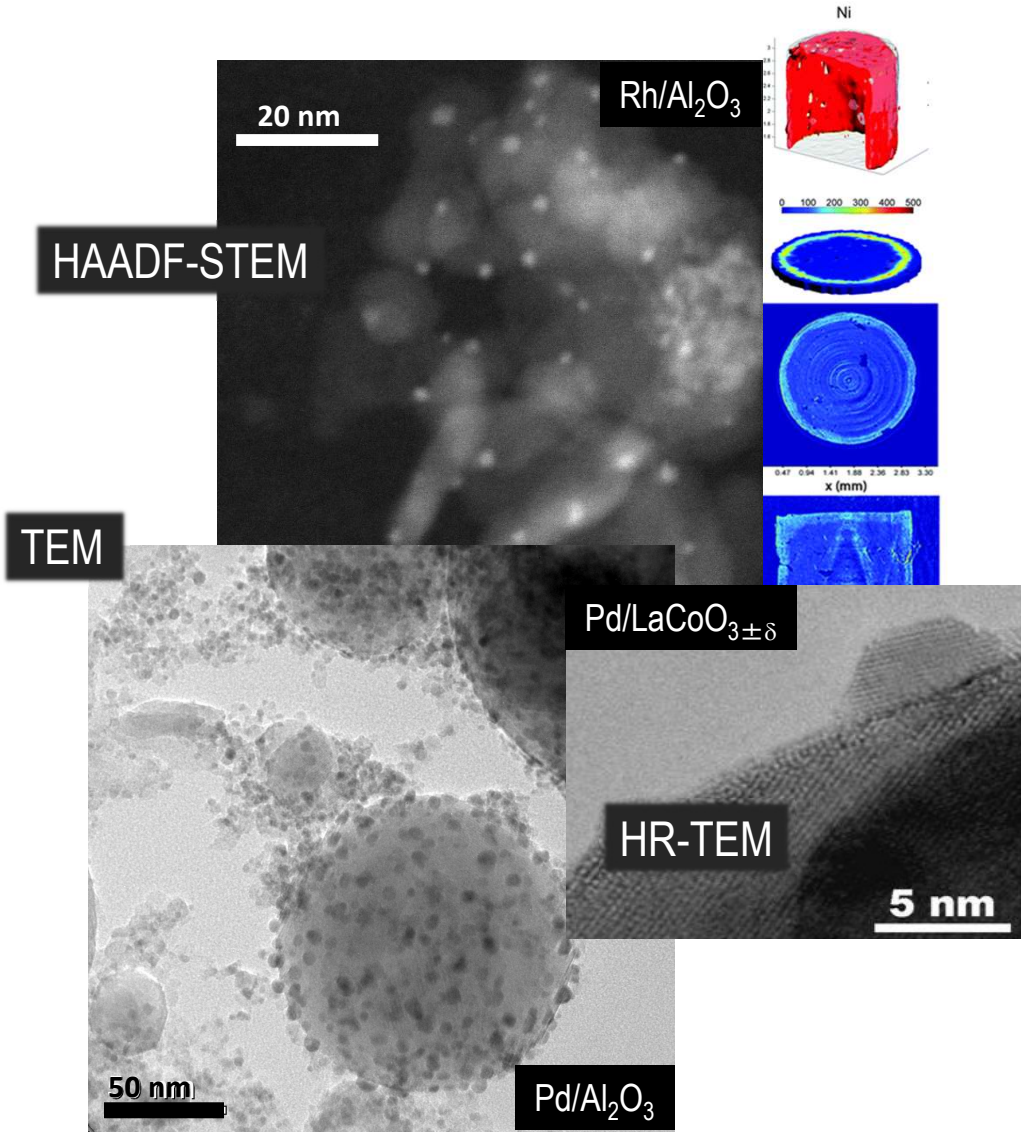
Paul Scherrer Institut

PSI

Catalysis for Emission Control and Energy Processes - ChE-410

Prof. Dr. Oliver Kröcher, Dr. Davide Ferri, Dr. Emanuele Moioli
davide.ferri@psi.ch

What is a catalyst?

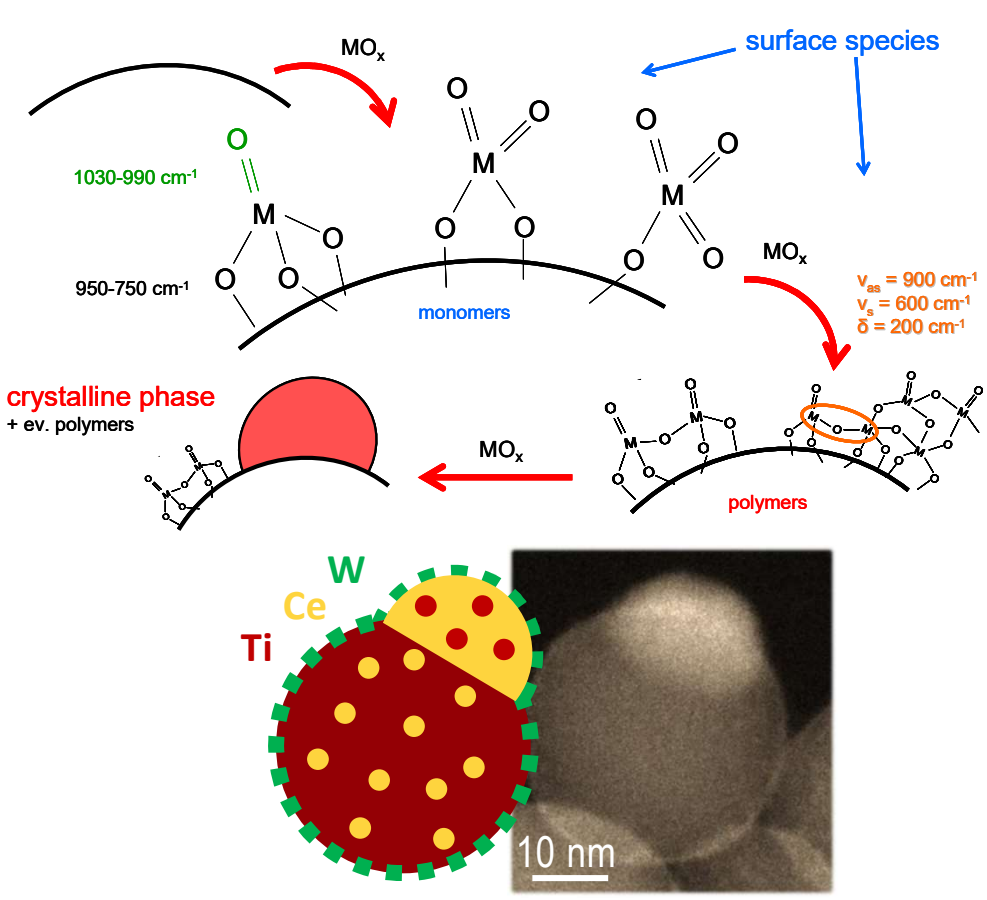


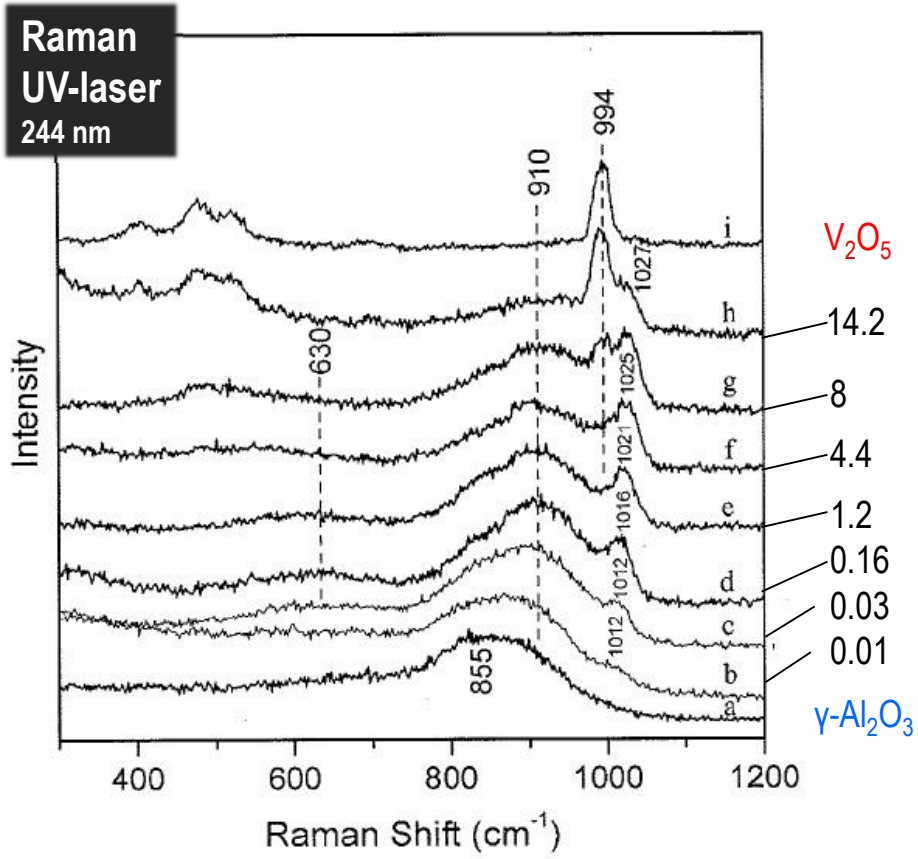
Catalyst structure, before, after and during catalytic process

- **Bulk & textural properties**
  - physico-chemical composition
  - phase composition
- **Particle properties**
  - density
  - particle size
  - mechanical properties
  - surface area and porosity
- **Surface properties**
  - morphology
  - structure
  - dispersion
  - acidity/basicity
- **Activity**

What is a catalyst?

- Not only PM nanoparticles! … monolayer (monomeric) & polymeric species

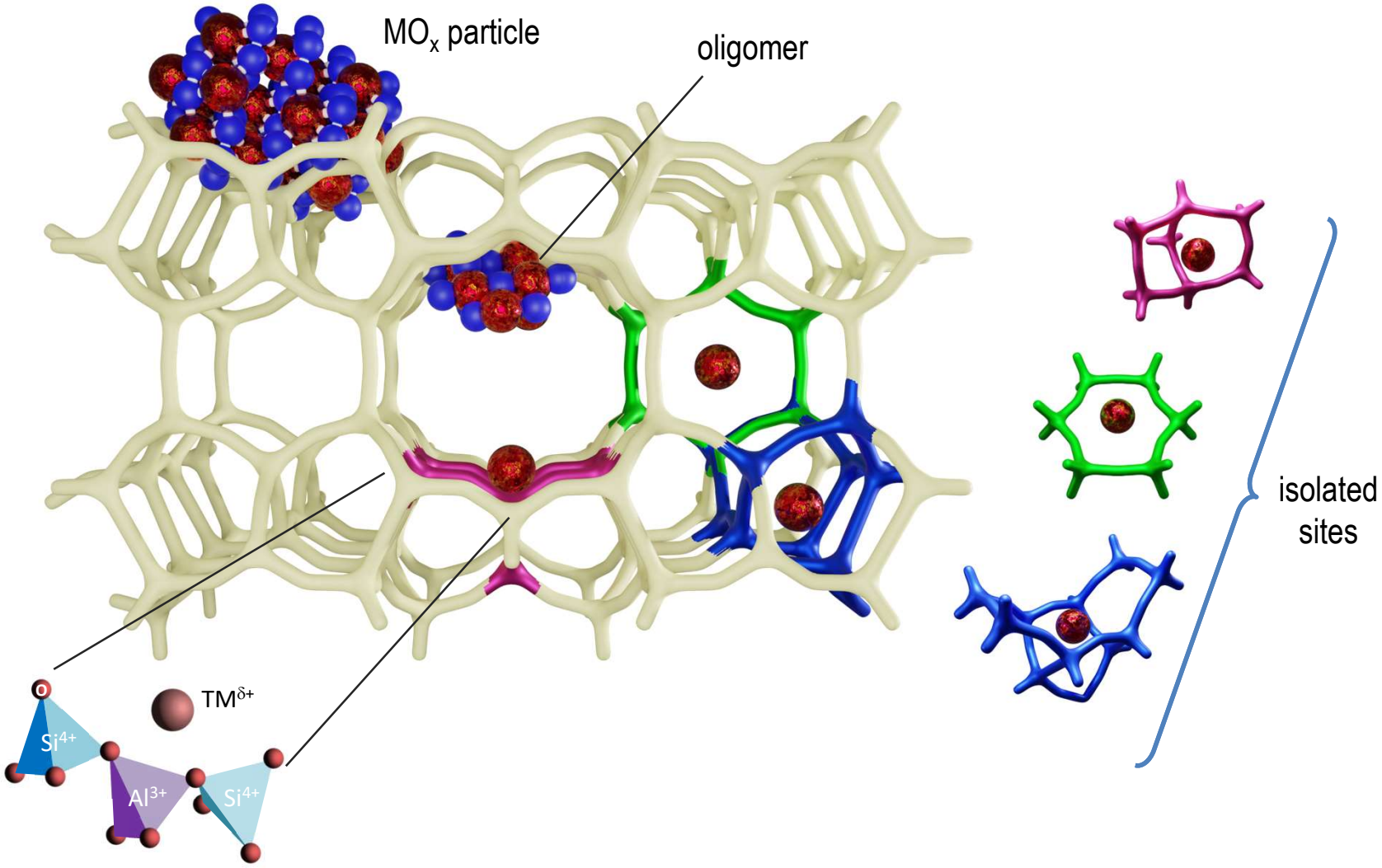




Wu et al., *J. Phys. Chem. B* 109 (2005) 2793

What is a catalyst?

- … or crystalline frameworks with/without additional active phase



courtesy Dr. Buttignol | PSI

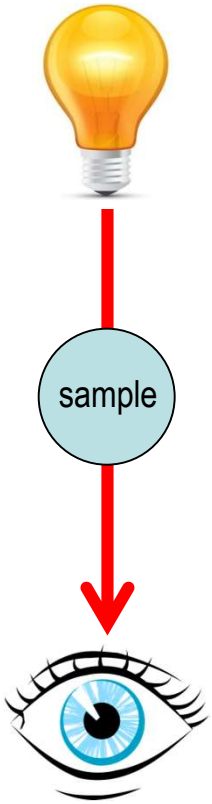
What can we characterize? How?

Surface area	Gas adsorption
Metal particle size	Selective gas adsorption (H_2, CO…), XRD, XAS
Dispersion	Selective gas adsorption, XRD, electron microscopy
Functional groups	Selective gas adsorption, IR, UV
Pore-size distribution	Gas adsorption, Hg porosimetry
Surface topography, distribution and shape of particles	Electron microscopy (TEM, SEM)
Phase composition and phase transformations	XRD, thermogravimetry, calorimetry
Chemical composition, bulk/surface	XPS, XRF
Nature of chemisorbed species	IR, UV, Raman
Reduction behaviour	Temperature Programmed Reduction (TPR)
Oxidation state, coordination state	XAS, XPS

adapted from Baiker et al., Characterization of heterogeneous catalysts, in Handbook of heat and mass transfer, Vol. 3, Gulf Publishing, Houston (1989) 3

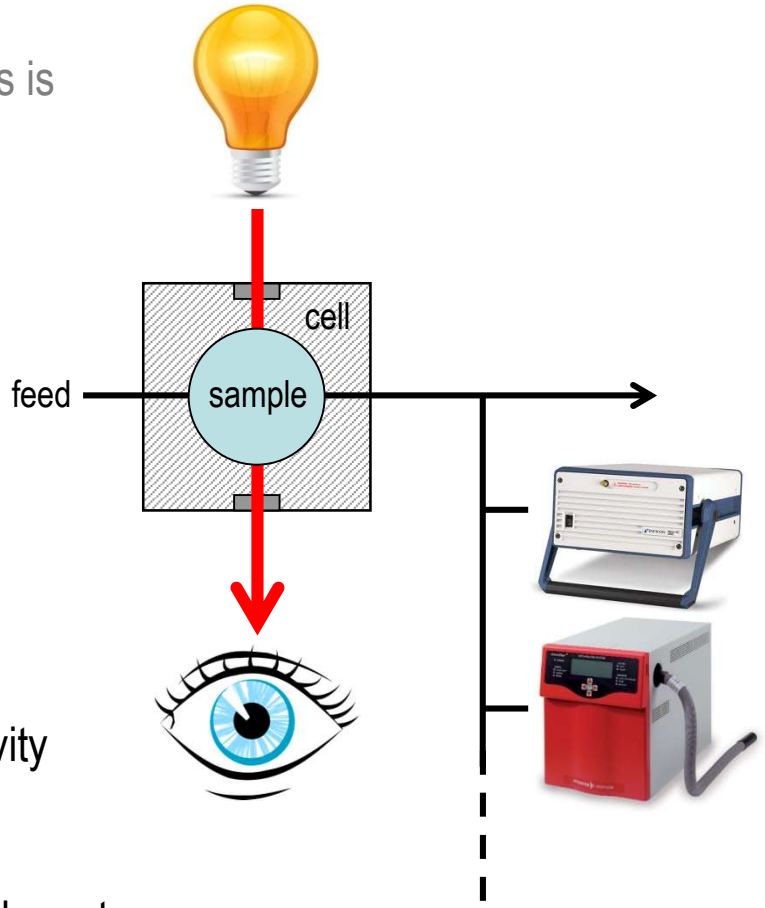
Definitions

- ***Ex situ*** methods
  - *pre-natal/post-mortem* structure of material as is
  - away from sorption/reaction conditions
  - typically, room temperature/pressure



Definitions

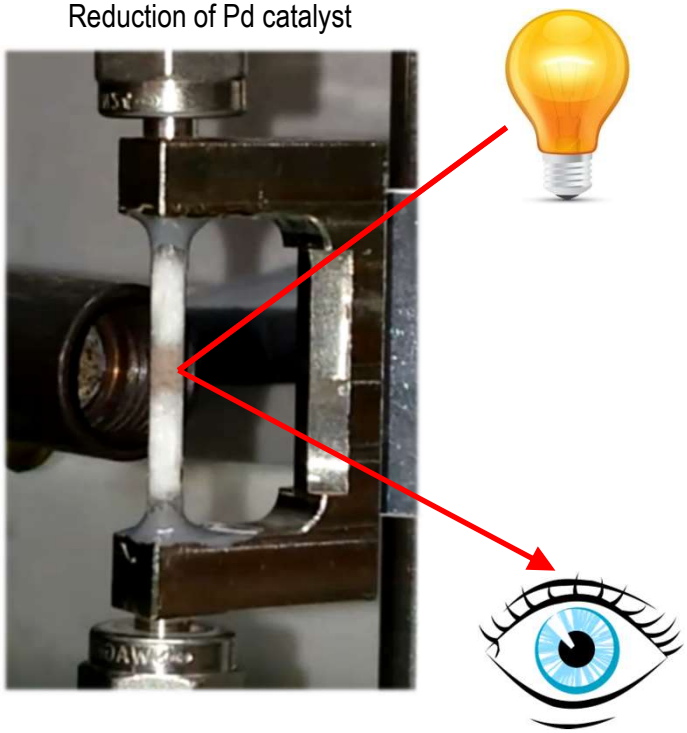
- *Ex situ* methods
  - *pre-natal/post-mortem* structure of material as is
  - away from sorption/reaction conditions
  - typically, room temperature/pressure
- ***In situ*** methods
  - defined sample environment
  - sorption/reaction in presence of reactants
  - relevant reaction conditions (T/P)
  - time-resolved
- ***Operando*** methods
  - synchronous measurement of activity/selectivity
  - structure-activity relationship
  - time-resolved
  - strict definition: cell design comparable to real reactor



Weckhuysen, *Chem. Commun.* (2002) 97; Banares, *Catal. Today* 100 (2005) 71; Banares et al., *Catal. Today* 113 (2006) 48
In situ spectroscopy of catalysts, Weckhuysen (Ed).; Am. Scientific Publishers, Stevenson Ranch, 2004

In situ/operando approach

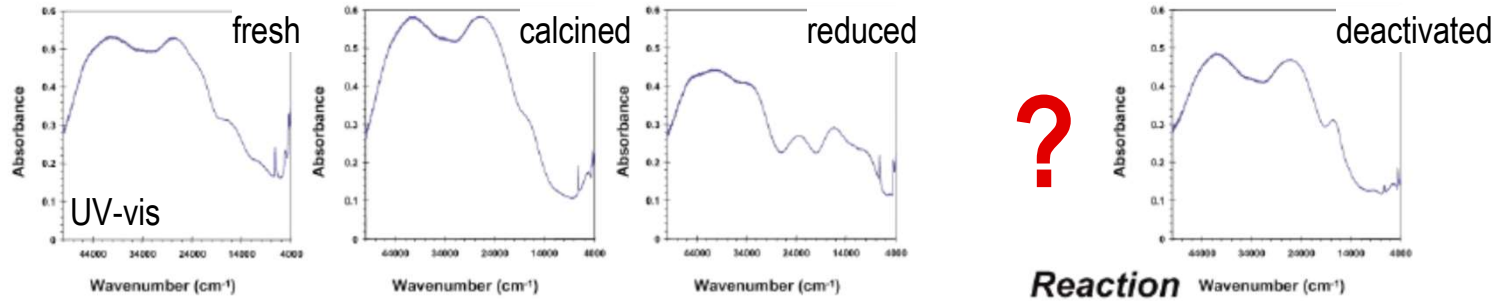
Reduction of Pd catalyst



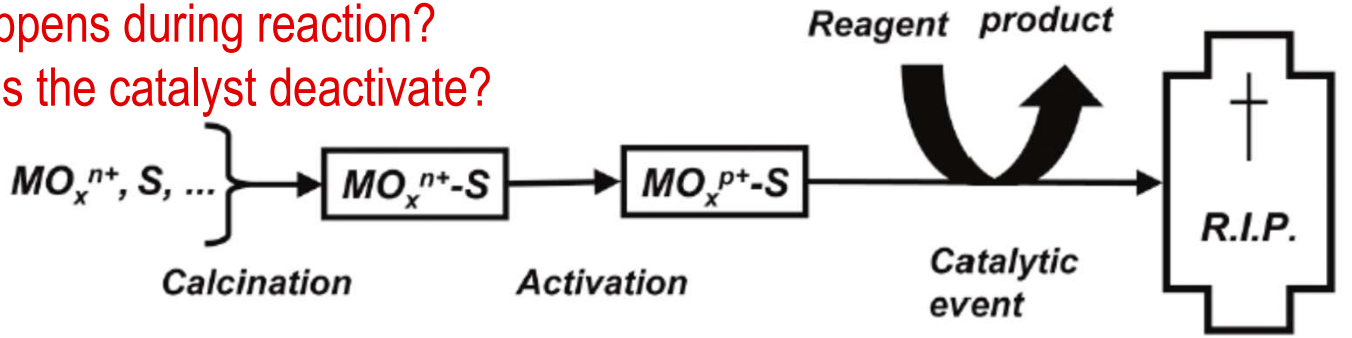
Boiling coffee with a mokka. A movie made with neutron images that shows the coffee making process.
Movie by A. Kaestner, Neutron imaging and activation group, PSI, Switzerland. The cold neutron imaging beam line ICON was used. The movie is four times faster than in real time.

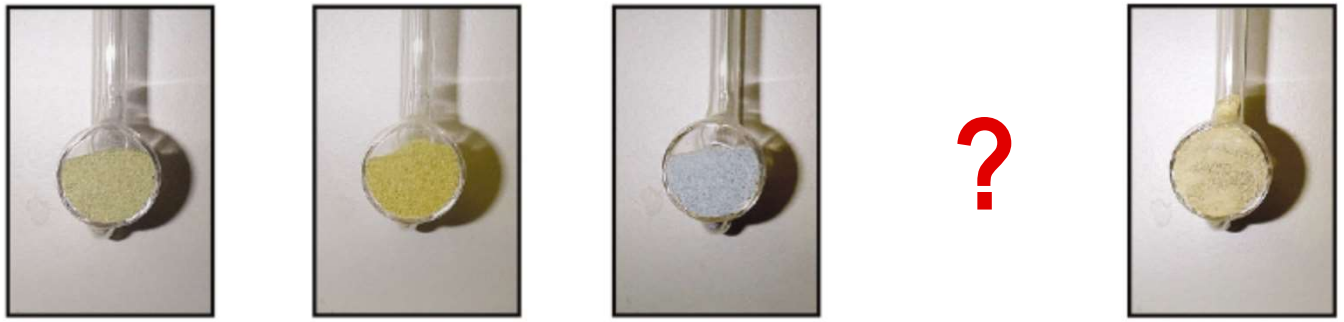
Do we really need in situ/operando?

The life time of a catalyst | 8 wt% CrO_3/Al_2O_3



what happens during reaction?
why does the catalyst deactivate?





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

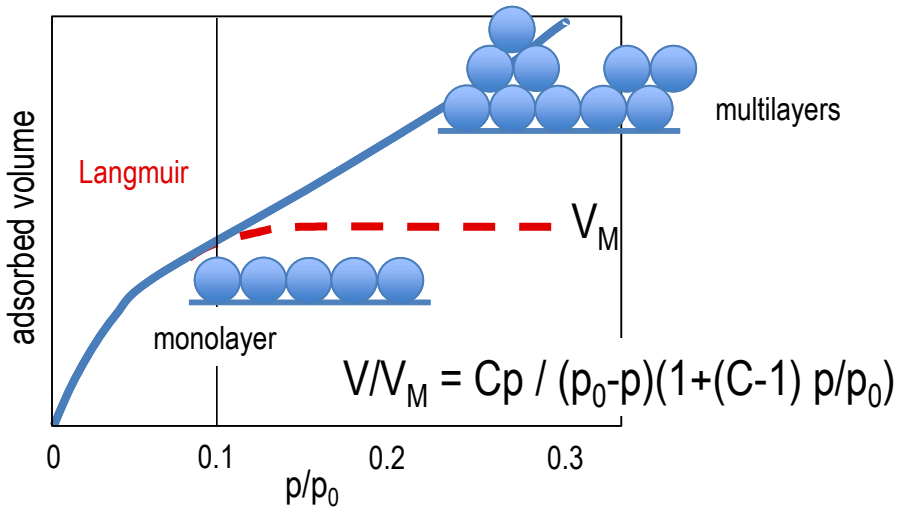
N_2 physisorption

- **Determination of specific surface area**

The Langmuir equation

$V/V_M = Kp/p_0 / (1+Kp/p_0)$ for low p

- localized adsorption – no interaction in adsorbate layer
- equivalent adsorption+desorption rates – dynamic equilibrium
- ads. enthalpy is ΔH_1 for first monolayer, approaches ΔH_c for other layers. ΔH_1 equivalent for all adsorption centres
- evaporation and condensation conditions are identical after the monolayer

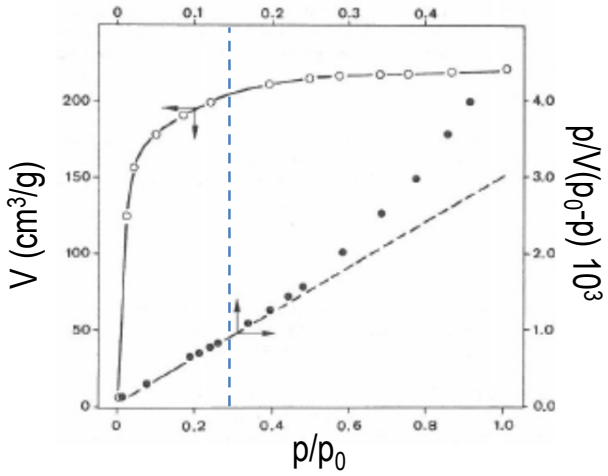


The **B**runauer-**E**mmet-**T**eller equation

$p/V(p_0-p) = 1/\mathbf{V_M}C + ((C-1) / \mathbf{V_M}C)\ p/p_0$

for $0.1<p/p_0<0.3$

C contains heats of ads. (ΔH_1) and condensation (ΔH_C); C characteristic of adsorbate-adsorbent interaction



$S_{BET}=V_M N_A A_M/V_{mol}$

A_M= 0.106 nm^2 (N_2)

N_2 physisorption

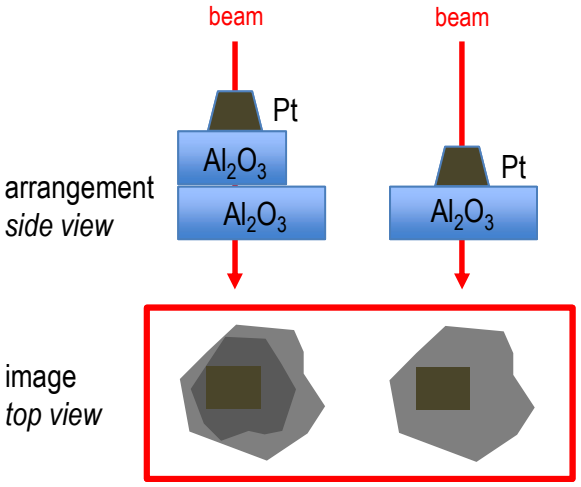
- **Determination of specific surface area**

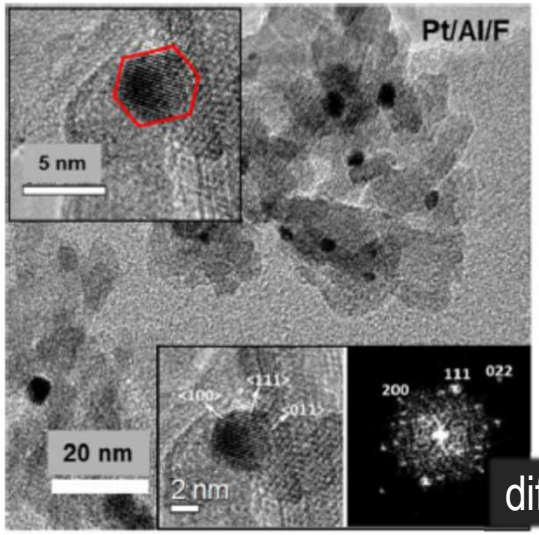
Material	SSA / m^2/g	use
Metal organic framework (MOF)	> 1000	sorbent, catalysis
Activated carbon	500-1000	support
Silica-alumina, zeolites	200-500	cracking
$CoMo/Al_2O_3$	200-300	hydrotreating
Ni/Al_2O_3	250	hydrogenation
$Pt/Pd/Rh/Al_2O_3/CeO_2/ZrO_2$	50-200	automotive
$Fe\text{-}Al_2O_3\text{-}K_2O$	10	NH_3 synthesis
V_2O_5	1	partial oxidation
Pt gauze	0.01	NH_3 oxidation

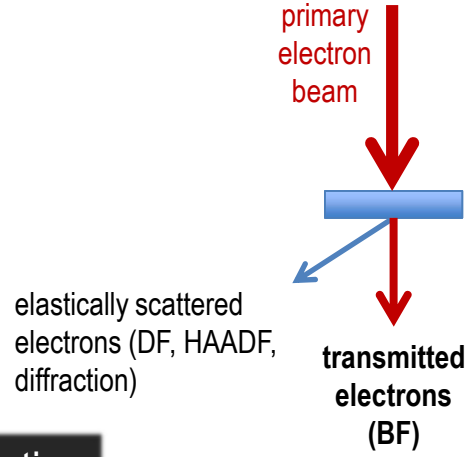
Electron microscopy

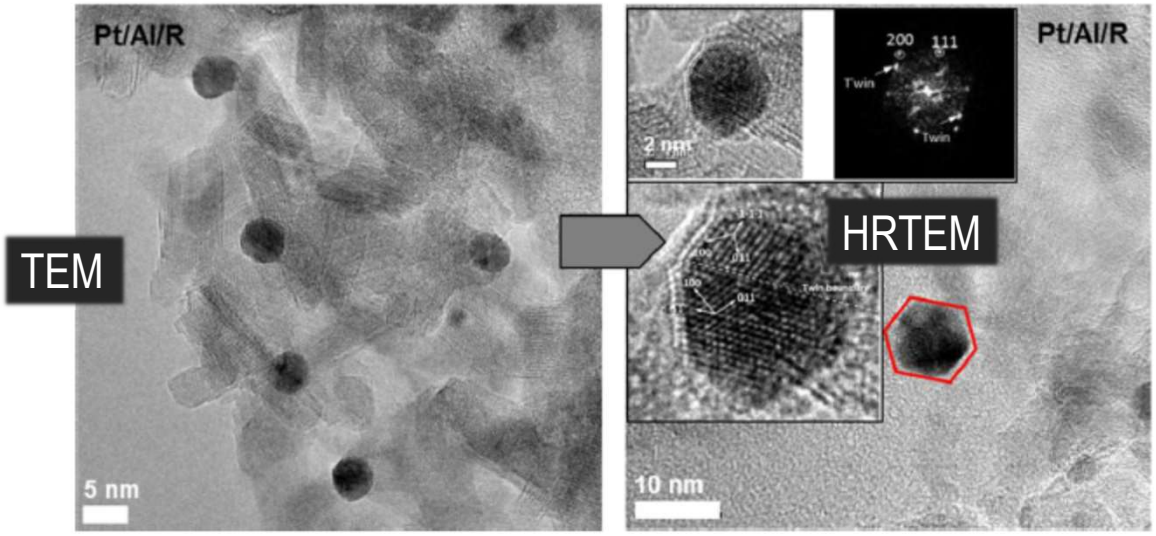
Information relevant to catalysis:

- Particle size
- Particle size distribution
- Morphology
- Imaging (diffraction, Z and thickness contrast)
- Structure (electron diffraction)
- Composition (EDX, EELS)
- Chemical (EELS)



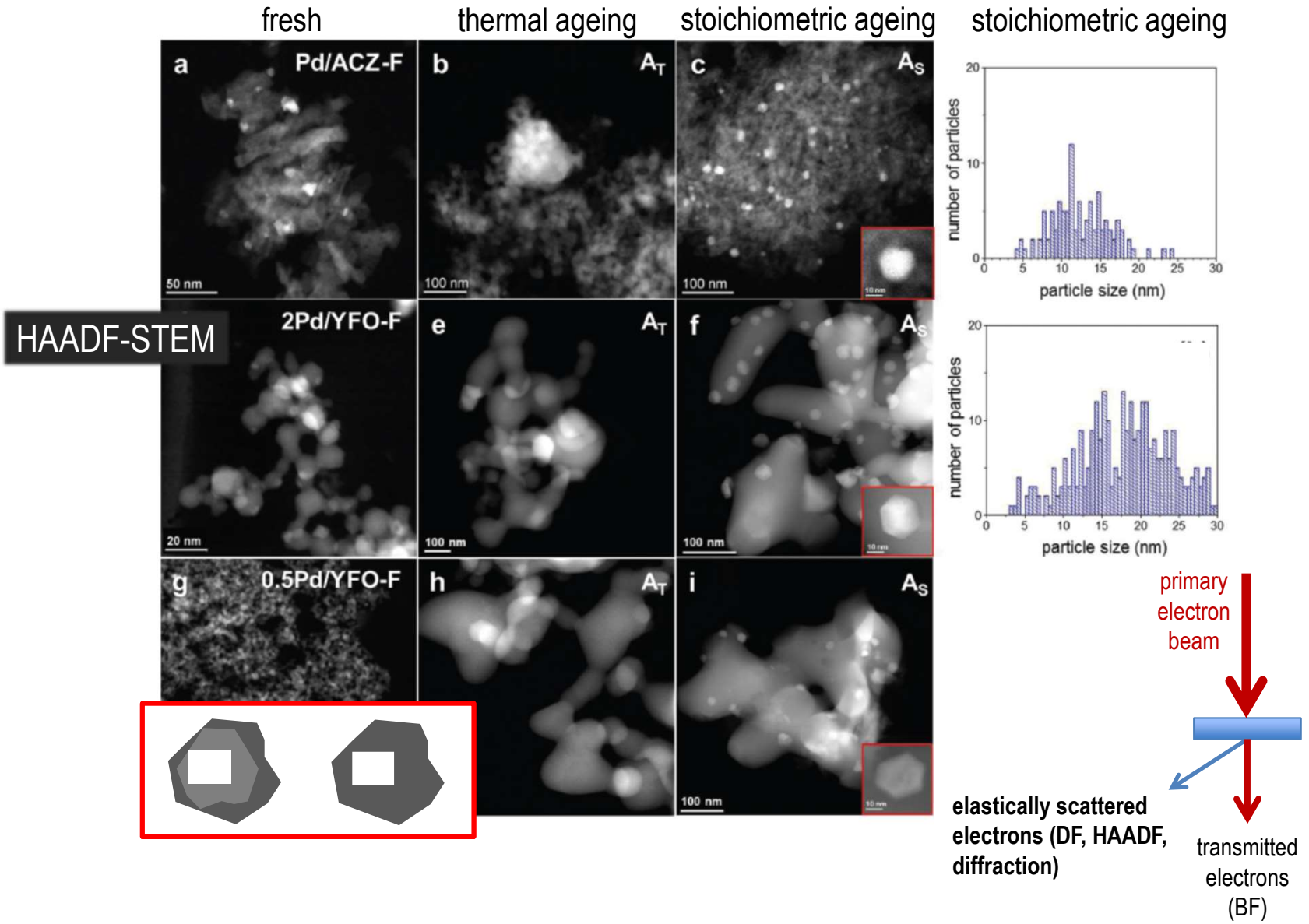






Matam et al., Appl. Catal. B 129 (2013) 214

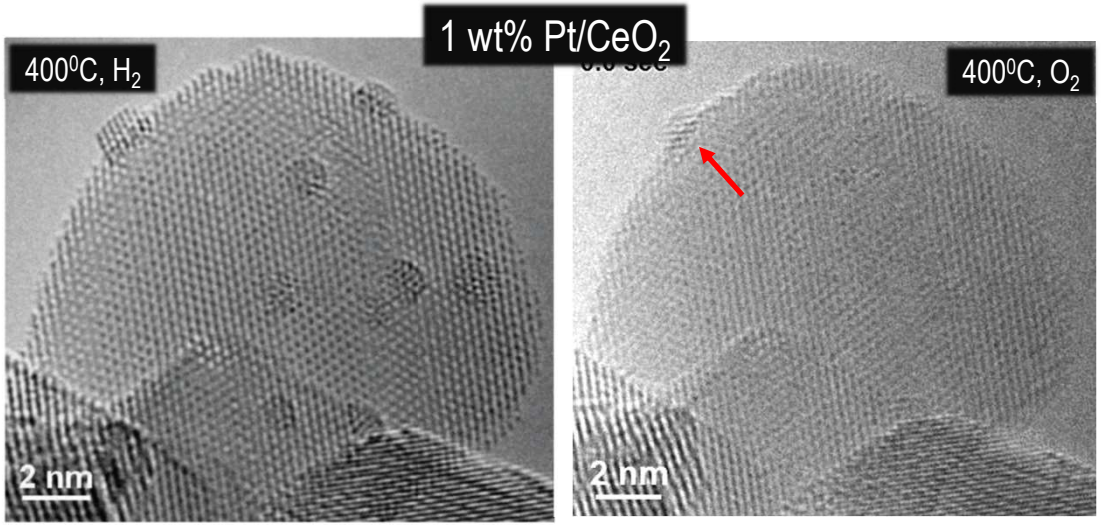
Electron microscopy



Lu et al., Catal. Sci. Technol. 4 (2014) 2687

Electron microscopy

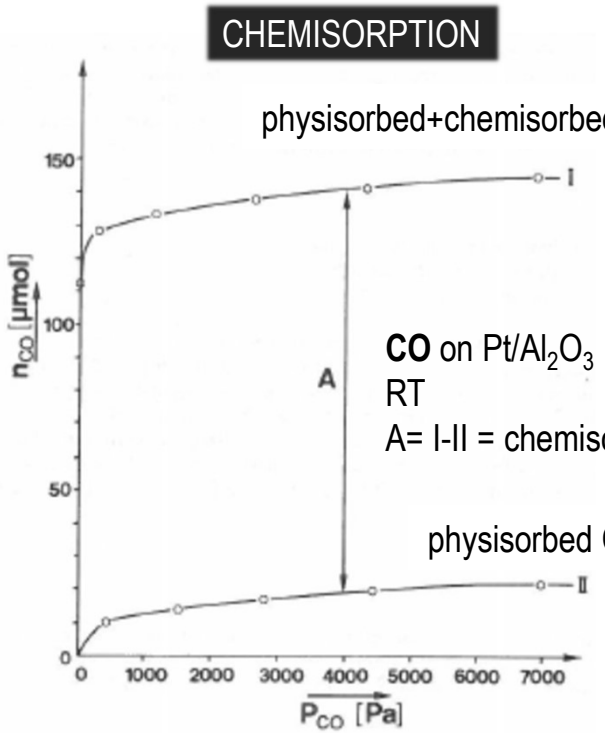
- **Environmental TEM | ETEM**



Gänzler et al., Angew. Chemie Int. Ed. 56 (2017) 13078

Metal surface area - Dispersion

- The fraction of **active** atoms in surface position
- High dispersion: atomically dispersed sites or small crystallites
- Selective coverage of one component of the solid by a *monolayer* of adsorbate
- Measure: chemisorption, but also X-ray diffraction (XRD) and electron microscopy (EM)



accessible surface atoms

$$N_S = V_M N_A X_M / V_{mol}$$

V_M, volume of chemisorbed monolayer; V_{mol}, molar volume of adsorbate; N_A, Avogadro number; X, *stoichiometric factor*

metal surface area

$$S_M = N_S / \Theta$$

Θ, atoms per unit surface area [1 - 1.6×10^{19} atoms/m^2]

degree of dispersion

$$D = N_S / N_T$$

N_T, total amount of atoms

particle size

$$D = 5 \times 10^{10}\ \rho_S W / N_A \rho_m d$$

ρ_m, atomic density; W, mol. weight; ρ_S, surface site density; d, particle diameter

Perez et al., J. Catal. 79 (1983) 240

Metal surface area - Dispersion

- Comparison of methods and limitations

- **Pitfalls of chemisorption**
  Overestimation of D and particle size

- X must be known
  - H_2, (almost) no problem; X=1:1 (H-metal) dissociative adsorption
  - CO, uncertain or variable with particle size
    - CO ads. by FTIR helps

- Simultaneous adsorption on metal **and** support
  - Ex.: CO adsorption on Pt/CeO_2

- Spill-over
  - Migration of H atoms to the support (visible from Temp. Program. Reduction, TPR)

- Phase formation (hydride…)

- **Disadvantages of XRD and EM**

- Calculation of metal surface area from size is not accurate

- Monolayer dispersion not detected

- Small (<2-3 nm) particles not visible by diffraction

- Shape (typically spherical) needs to be assumed in the calculation and is not always clear from EM

- Distribution of shape and size can exist

- Encapsulation, accessibility of atoms

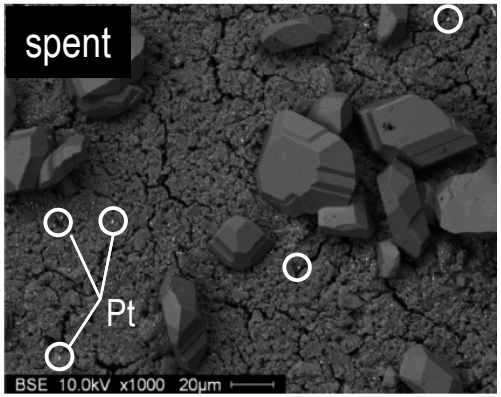
Scanning Electron Microscopy - SEM

Detection of
- secondary electrons (low E)
- back-scattered electrons (chemical composition)

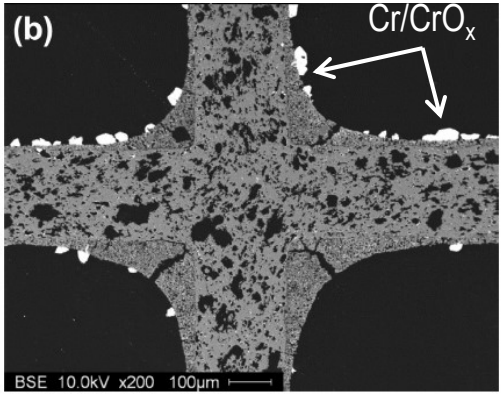
Determination of
- morphology
- surface topology
- particles of heavy elements

Combination with EDX
Mapping

poisoned Pt/Al_2O_3

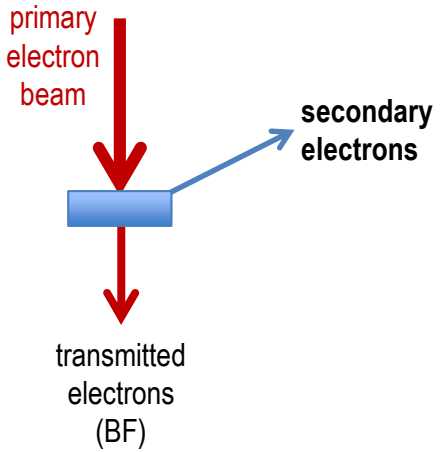


top view



cross section view

Large Cr containing deposits



Keav et al., *Appl. Catal. A* 469 (2014) 259

Scanning Electron Microscopy - SEM

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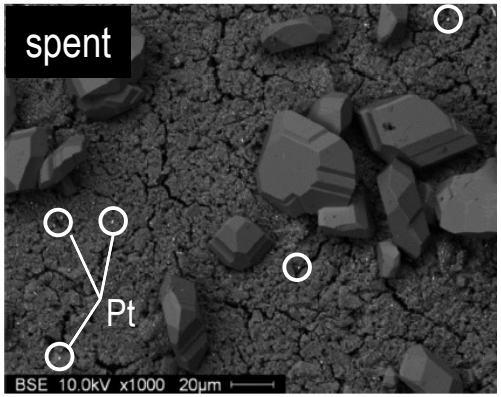
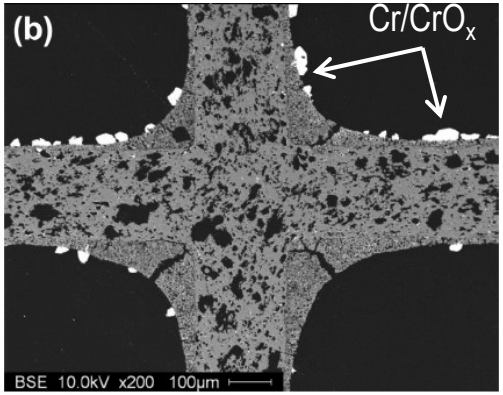
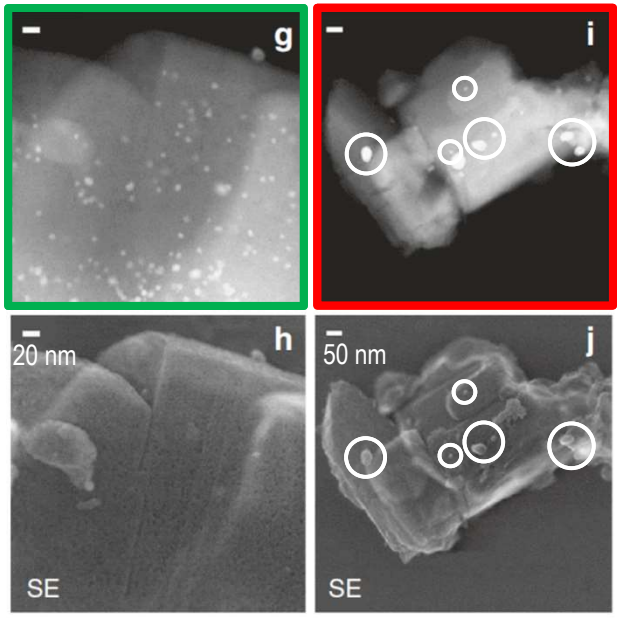


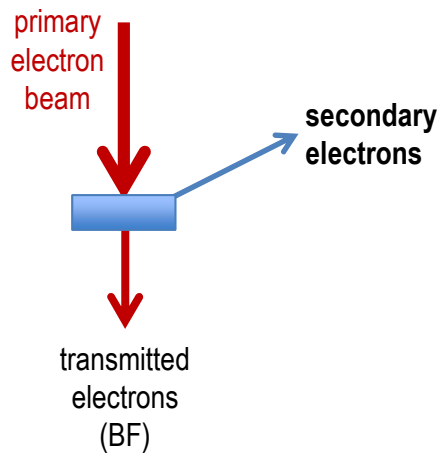
top view



cross section view

Pd exchanged ZSM-5





Pd particles inside ZSM-5

Pd particles outside ZSM-5

Keav et al., *Appl. Catal. A* 469 (2014) 259

Infrared spectroscopy

- Use of infrared radiation
- Excitation of vibrational and rotational modes (vibrational transitions)
- Identifies functional groups (-(C=C)n-, -C=O, -C=N, etc.)
- Access to molecular structure, interactions and lattice vibrations of solids (e.g. O-H, M-O)
- Use of probe molecules to characterize solid surfaces

pros

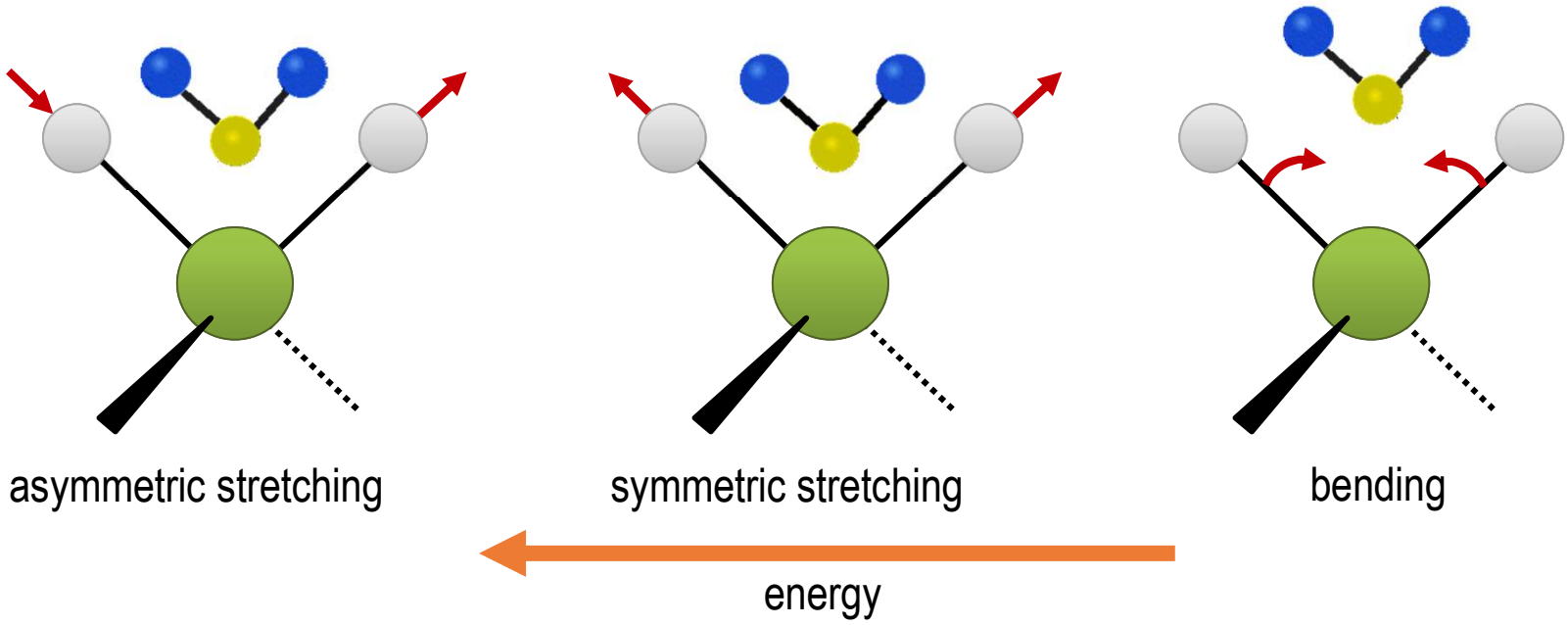
- economic
- non-invasive
- versatile (e.g. solid, liquid, gas and interfaces)
- very sensitive (concentration)
- fast acquisition (down to ns!)

cons

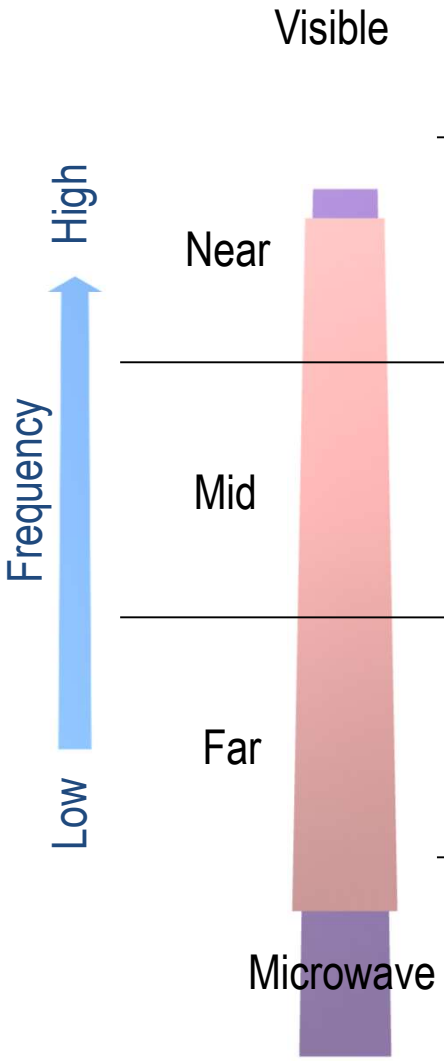
- no atomic resolution

Vibrational spectroscopy

- **Interaction with matter**
  - energy causes vibration of molecular bonds
  - energy is absorbed in correspondence of vibrational modes
  - an absorption band is generated
  - absorption occurs at charactestic values of functional groups and bonds



The IR spectral region



	λ [μm]	ν [cm^{-1}]	E [kJ/mol]	
Near	0.78-2.5	12800-4000	150-50	overtone, combination vibrations
Mid	2.5-25	4000-400	50-5	fundamental vibrations
Far	25-1000	400-10	5-0.1	fundamental vibrations of heavy elements, lattice vibrations

Infrared spectroscopy

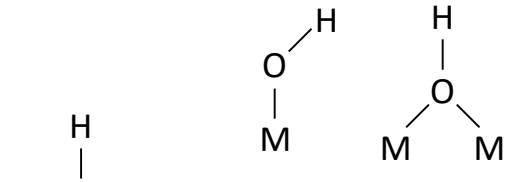
- ‘Quality control’: identification of compounds according to their fingerprint spectrum
  - also inorganic materials, e.g. metal oxides
  - ex situ, but also after degassing in cell (vacuum)

- Identification of surface sites | Detailed characterization of surface
  - use of molecular probes
  - in situ experiments, controlled dosage of probe

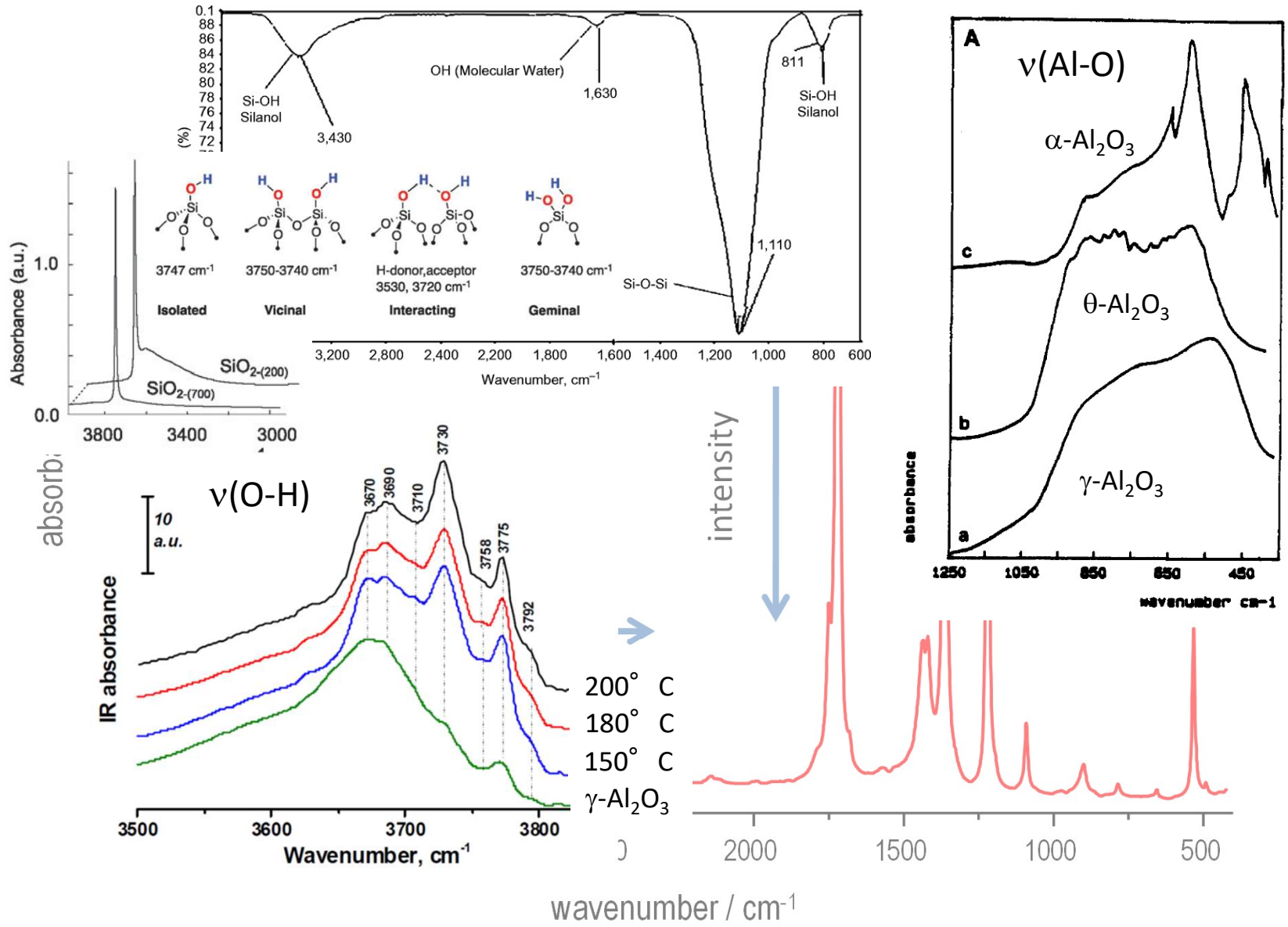
- Identification of surface sites under reaction conditions
  - in situ/operando experiments to obtain molecular reaction mechanism, exposure to reaction conditions

Information on materials

- The spectrum contains information on
  - terminal O-H bonds | 3800-3600 cm^{-1}
  - bridge hydroxyls | Brønsted acidity
  - H-bonded hydroxyls
  - M-O and M=O bonds, bulk and surface
    - fundamental (n) and overtone (2 × n) modes
  - other groups, e.g. C-H, carbonates, carboxylates…



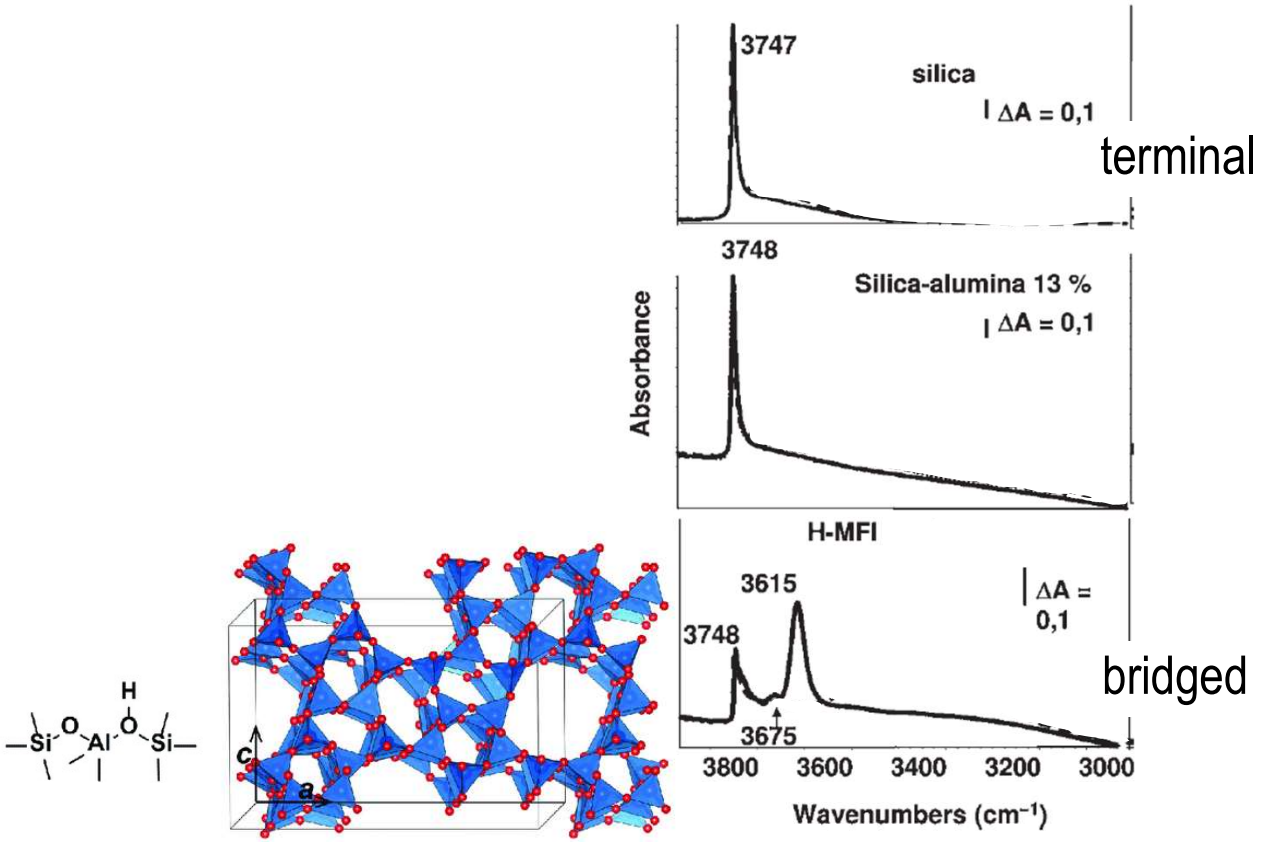
Information on materials



Morterra, Catal. Today 27 (1996) 497

Information on materials

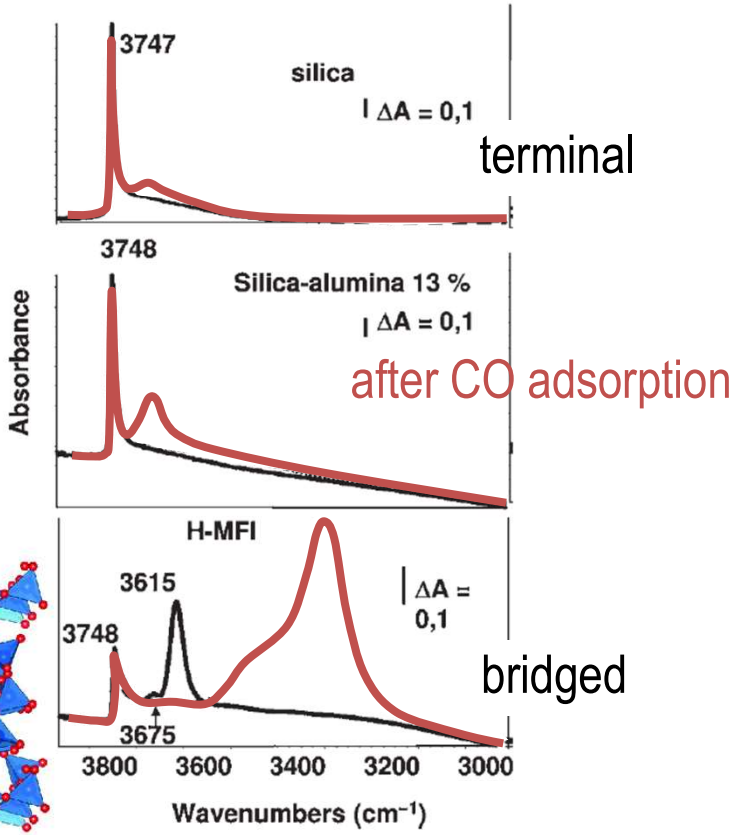
- Perturbation of hydroxyl groups

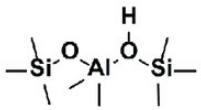


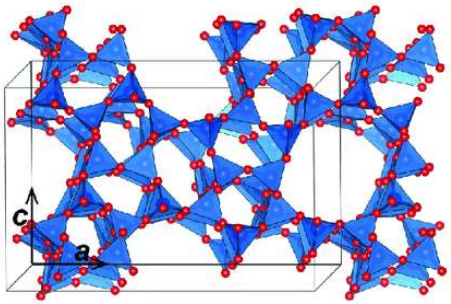
Busca, in Metal Oxide Catalysis, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim (2009) 95 | Uslamin, Zeolite-based catalysis for sustainable aromatics production, Technische Universiteit Eindhoven (2019)

Information on materials

- Perturbation of hydroxyl groups
  - adsorption of probe molecule



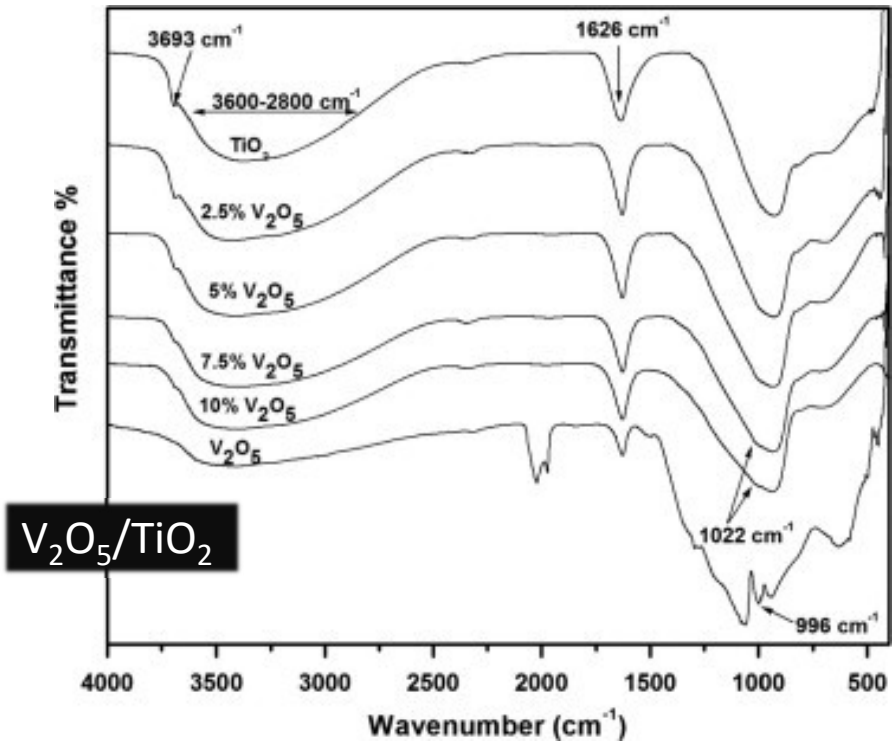




Busca, in Metal Oxide Catalysis, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim (2009) 95 | Uslamin, Zeolite-based catalysis for sustainable aromatics production, Technische Universiteit Eindhoven (2019)

The mid IR spectrum

- **FTIR not suitable to characterize supported metal oxides**
  - Spectra dominated by the features of the metal oxide support up to unrealistic loadings of the active metal oxide → **Raman**



Sethi et al., *J. Photochem. Photobiol. B* 144 (2015) 68

Selection rule

$$\left(\frac{\partial \mu}{\partial Q}\right) \neq 0$$

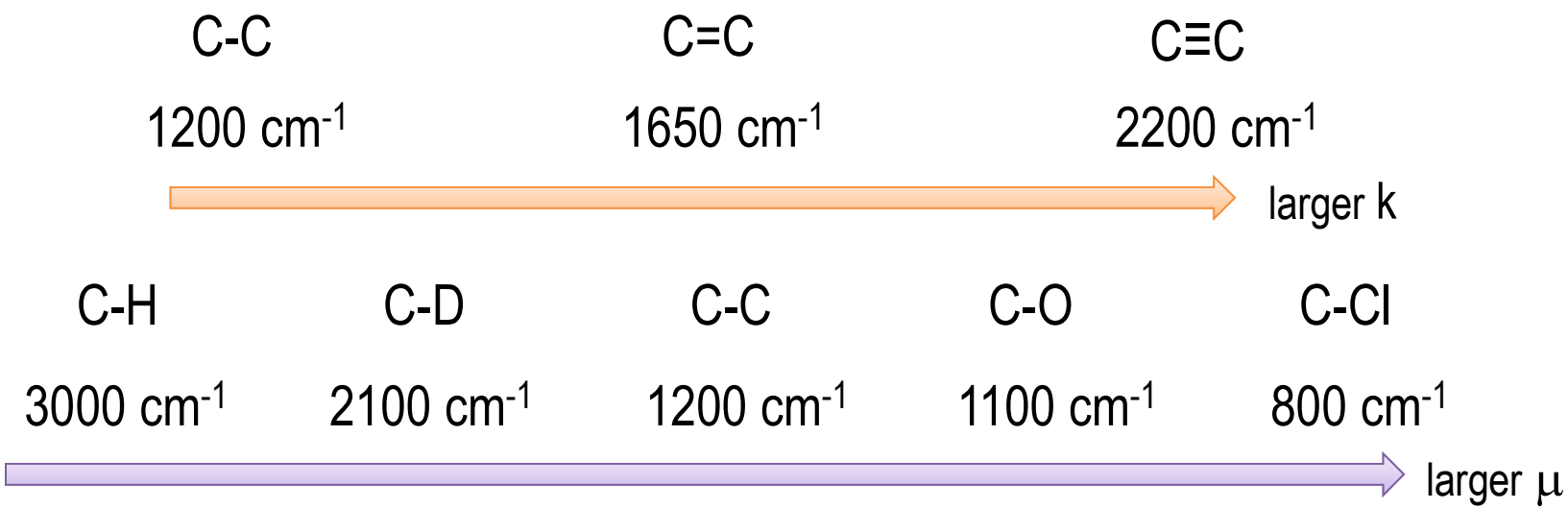
Molecular dipole moment μ must change due to vibration or rotation along its coordinate (normal mode or normal coordinate, ***Q***)

Q Are these molecules infrared active or inactive?

O=O H-Cl Ar

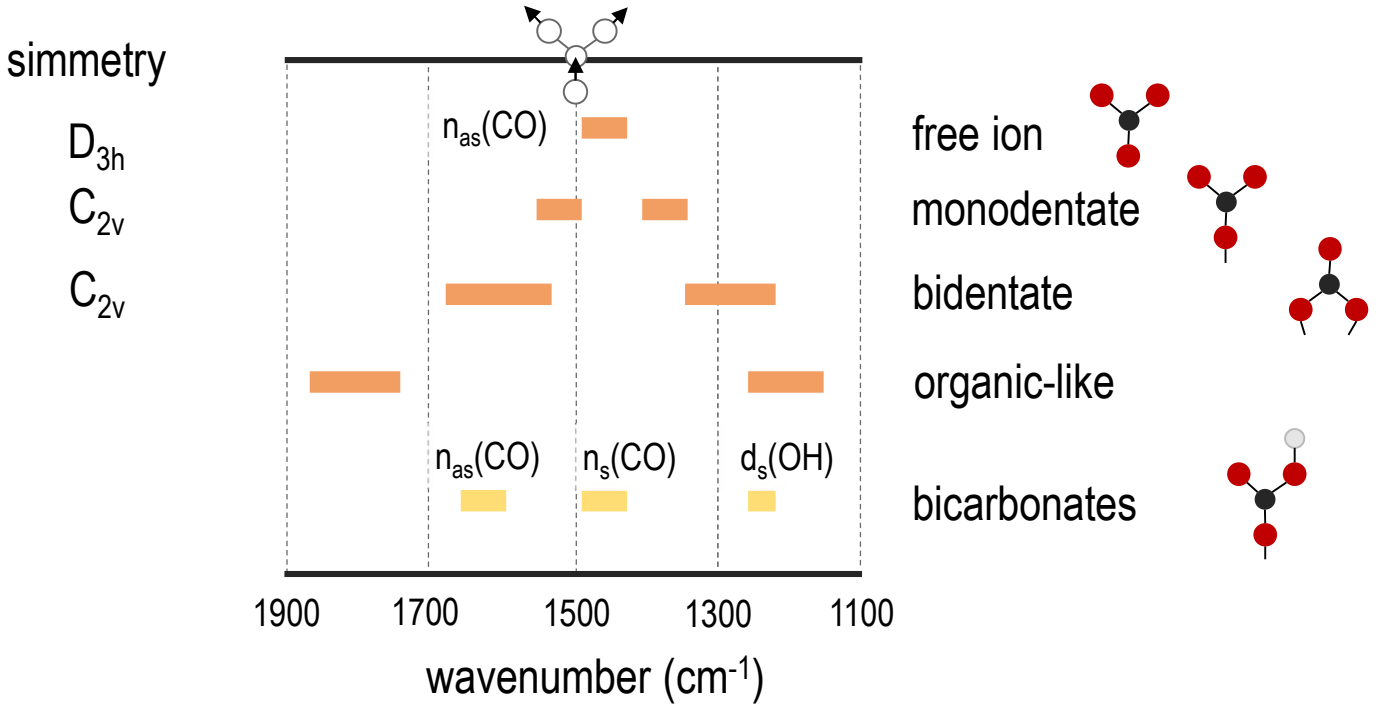
Energy of IR signals

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$



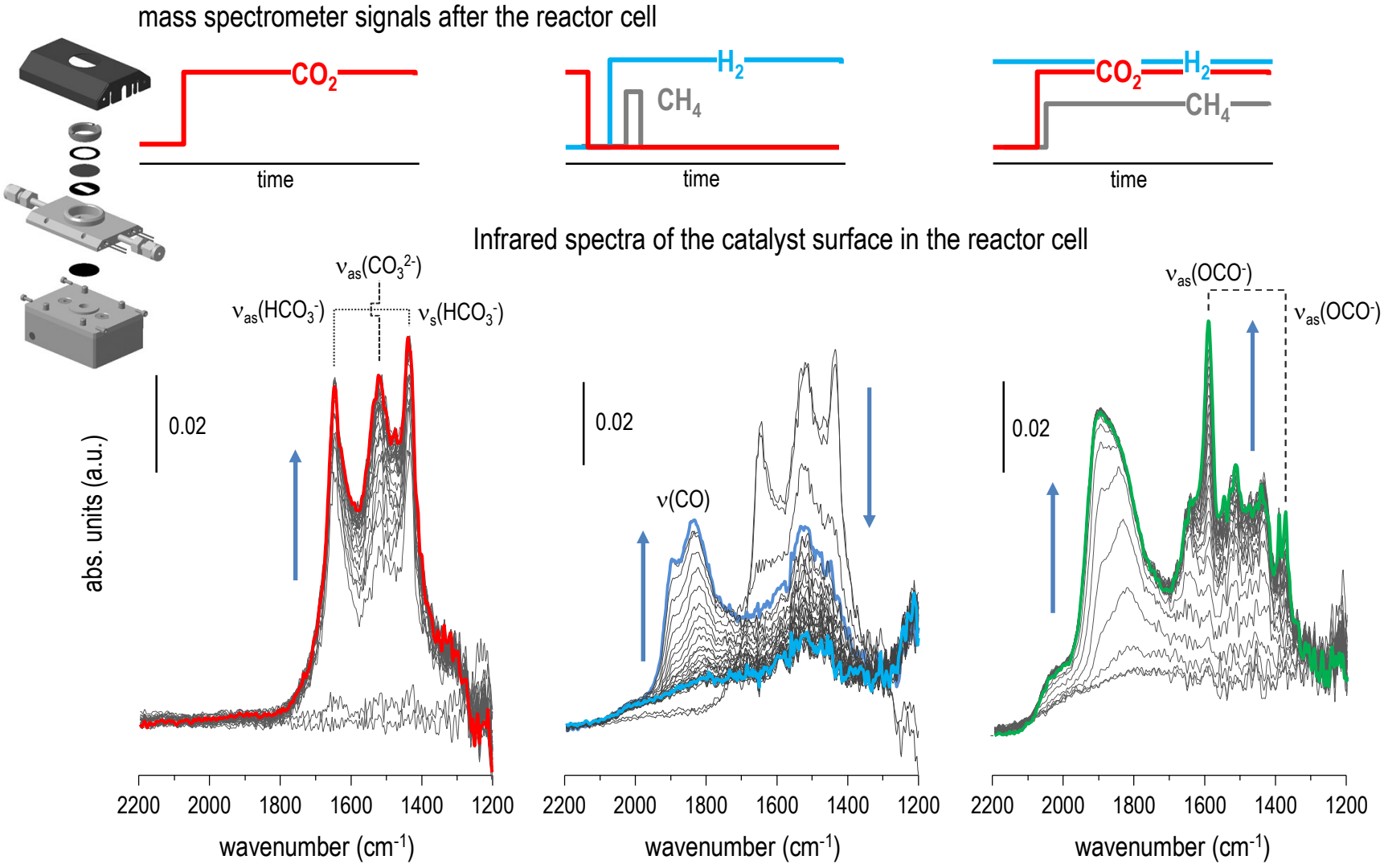
Adsorbates

- The carbonate ion



Morterra, Catal. Today 27 (1996) 497

Adsorbates



1.6. wt% Pd/Al_2O_3; red. 573 K, 30 min; 548 K

Probe molecules

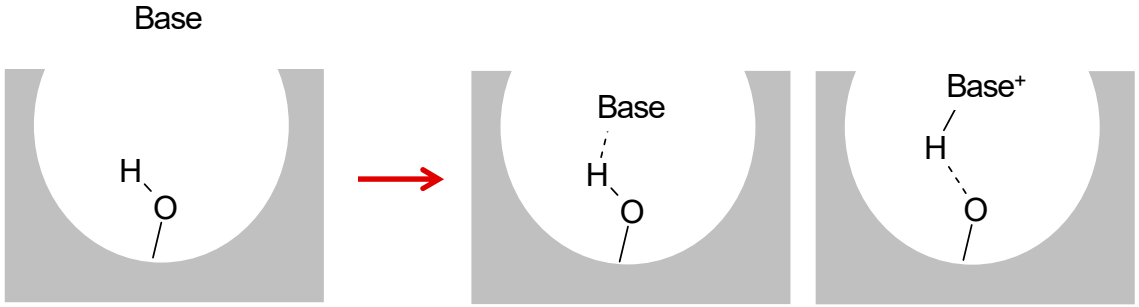
- **Quality and quantity of acid sites**
- **Criteria**
- unequivocal analysis of intermolecular interaction
- selective interaction with acidic or basic sites
- sufficient accuracy in frequency shift determination
- high (and available) extinction coefficients of adsorbed probe
- appropriate acid (base) strength to induce interaction - Hard–Soft classification of sites and probes
- high specificity (allow discrimination between sites with different strength) - Use different molecules !
- small molecular size - Use different molecules !
- low reactivity under exp. Conditions
- …

- Examples
  - acidity of zeolite with different channel sizes
  - acid sites located in all channels
  - use of pyridine (smaller channels) and picoline (larger channels or surface only)

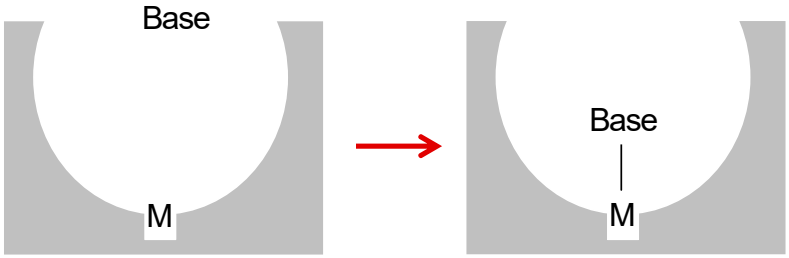
Probe molecules

- **Acid sites**

Brønsted sites (protic)

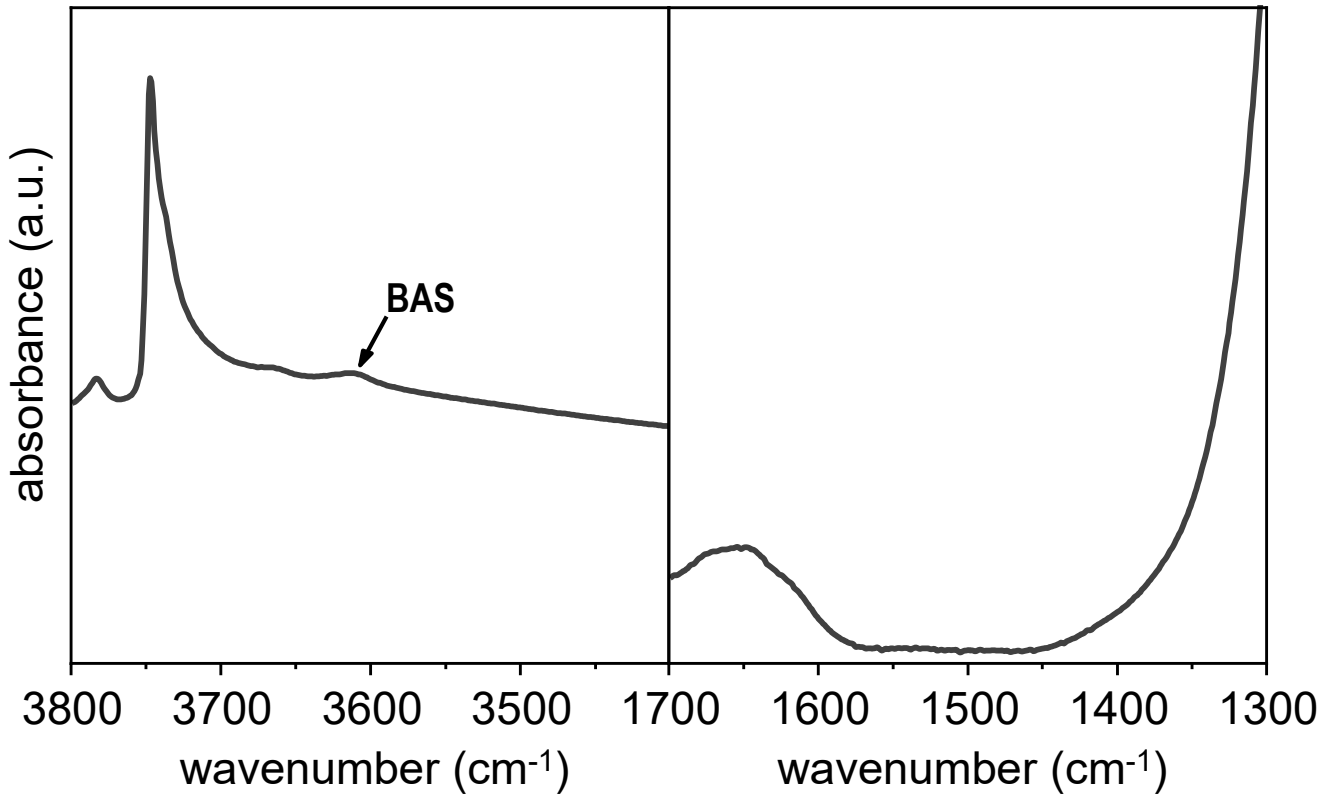


Lewis sites (aprotic)



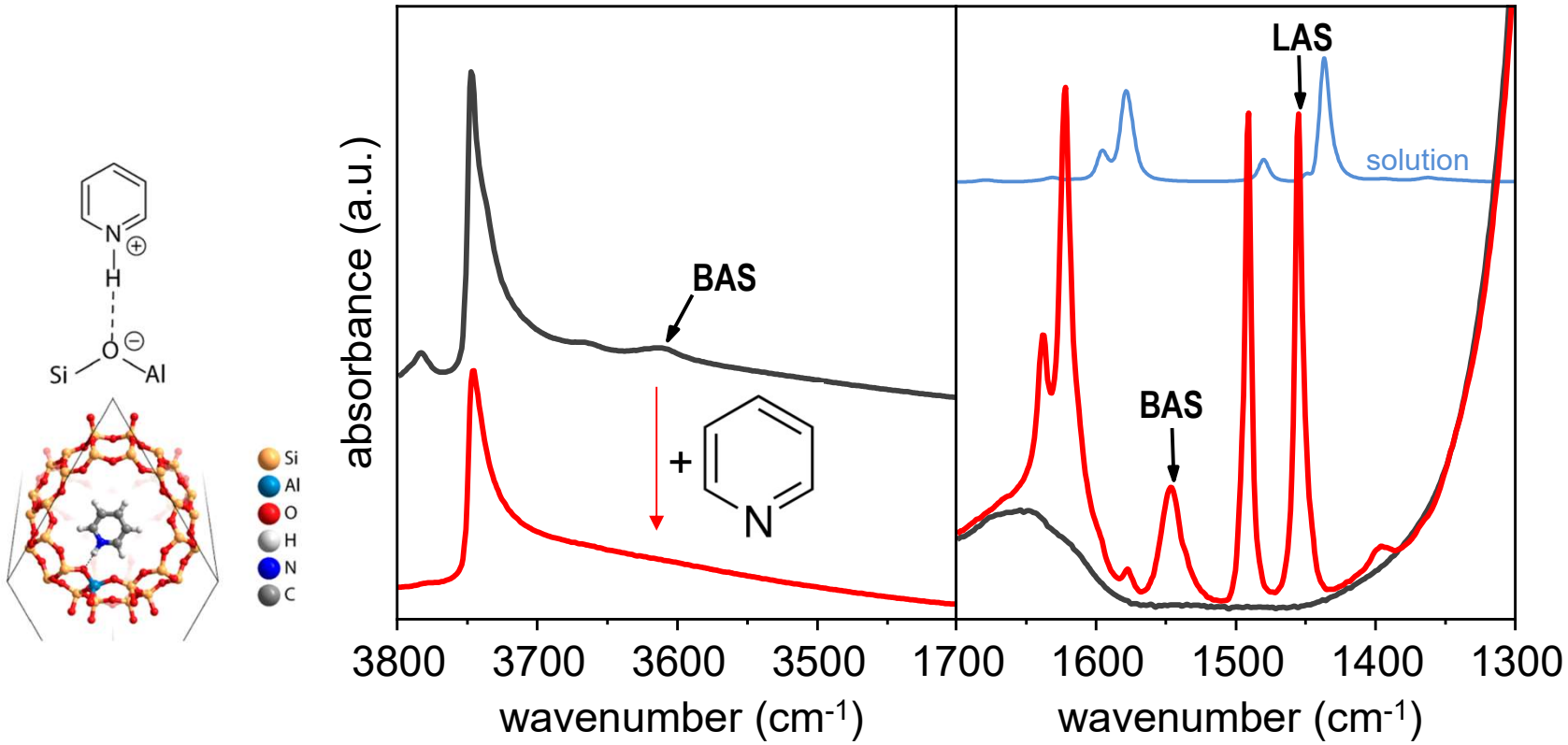
Probe molecules

- **Pyridine: acid sites**



Probe molecules

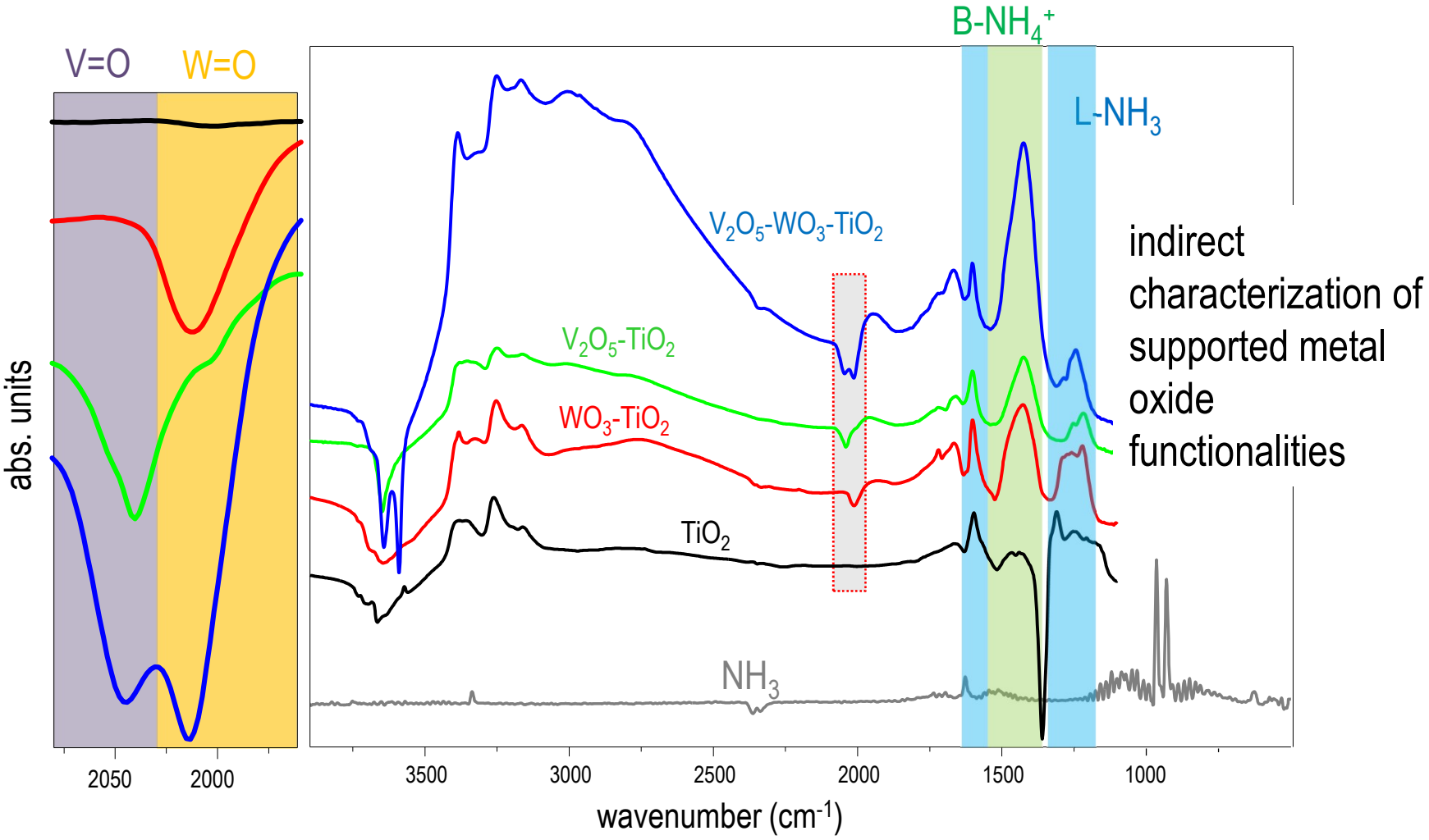
- **Pyridine: acid sites**



Liu et al., J. Phys. Chem. C 121 (2017) 23520

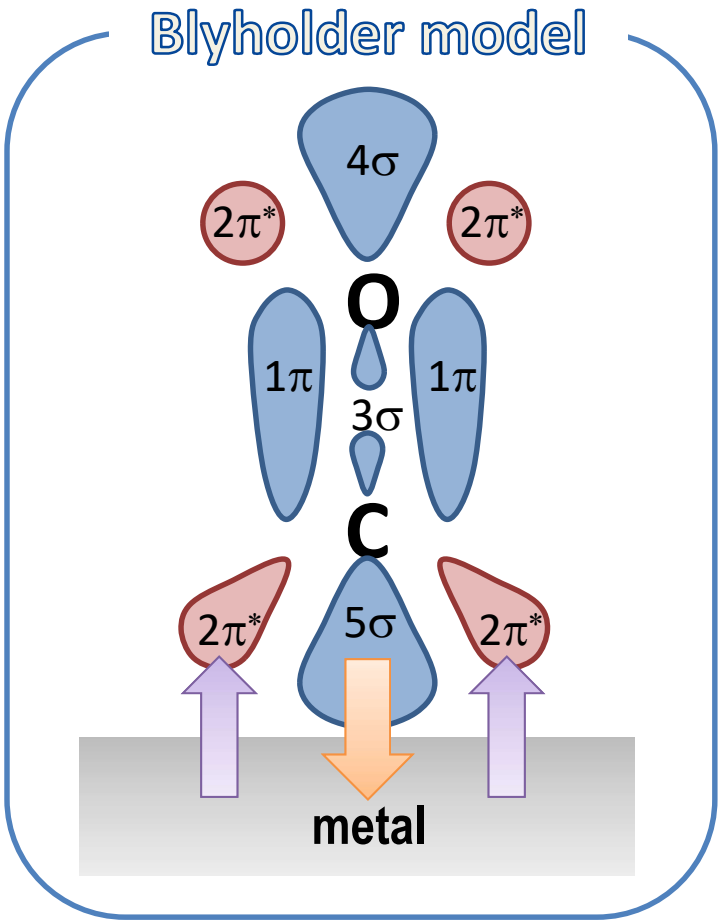
Probe molecules

- **Ammonia: acid sites and more…**



Probe molecules

- **Carbon monoxide (CO)**
  - Widely used as a *sensor* to investigate the electronic state of catalytic active sites



Donation

CO donates electrons from the s orbital to metal

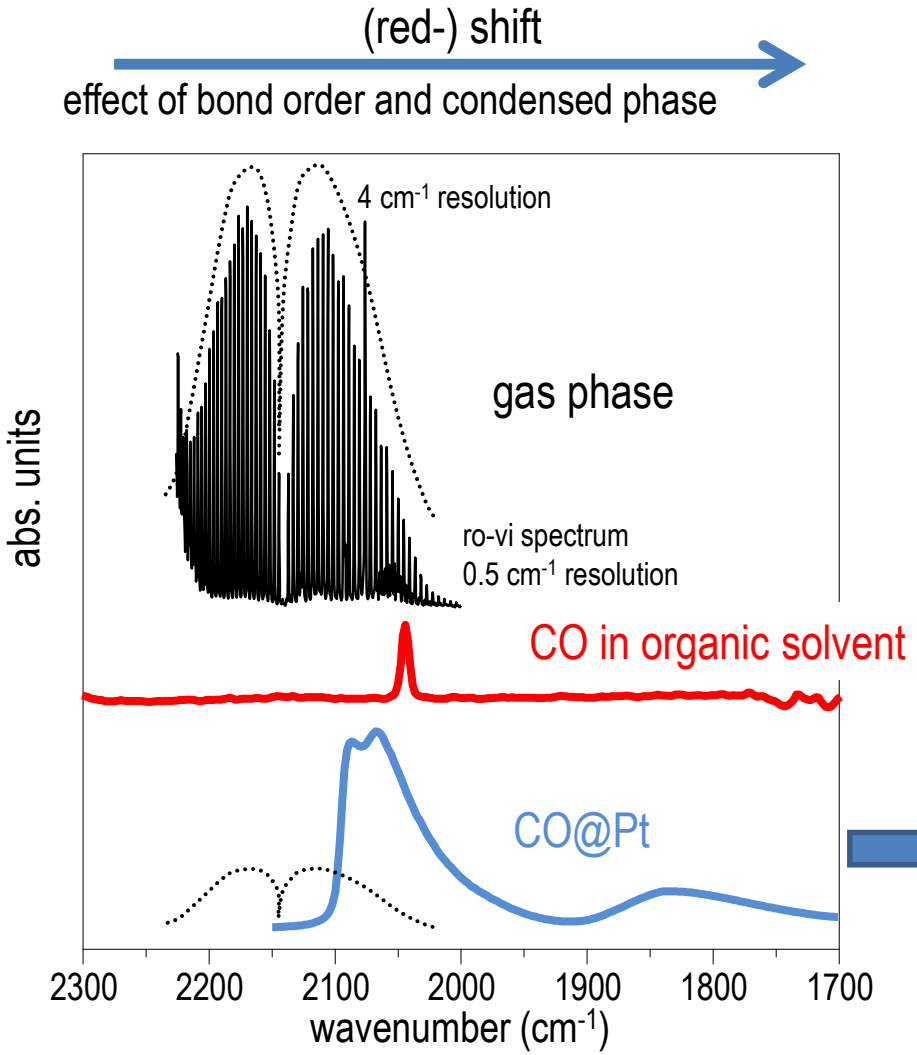
Back-donation (BD)

Metal donates back electrons to the anti-bonding π orbital of CO

- Low coverage: n_{CO} depends on the geometry of **adsorption site** (face order: **terrace – corner – edge**) – **BD is strong**
- High coverage: n_{CO} depends on **dipole-dipole interactions** – **BD is weak**

Probe molecules

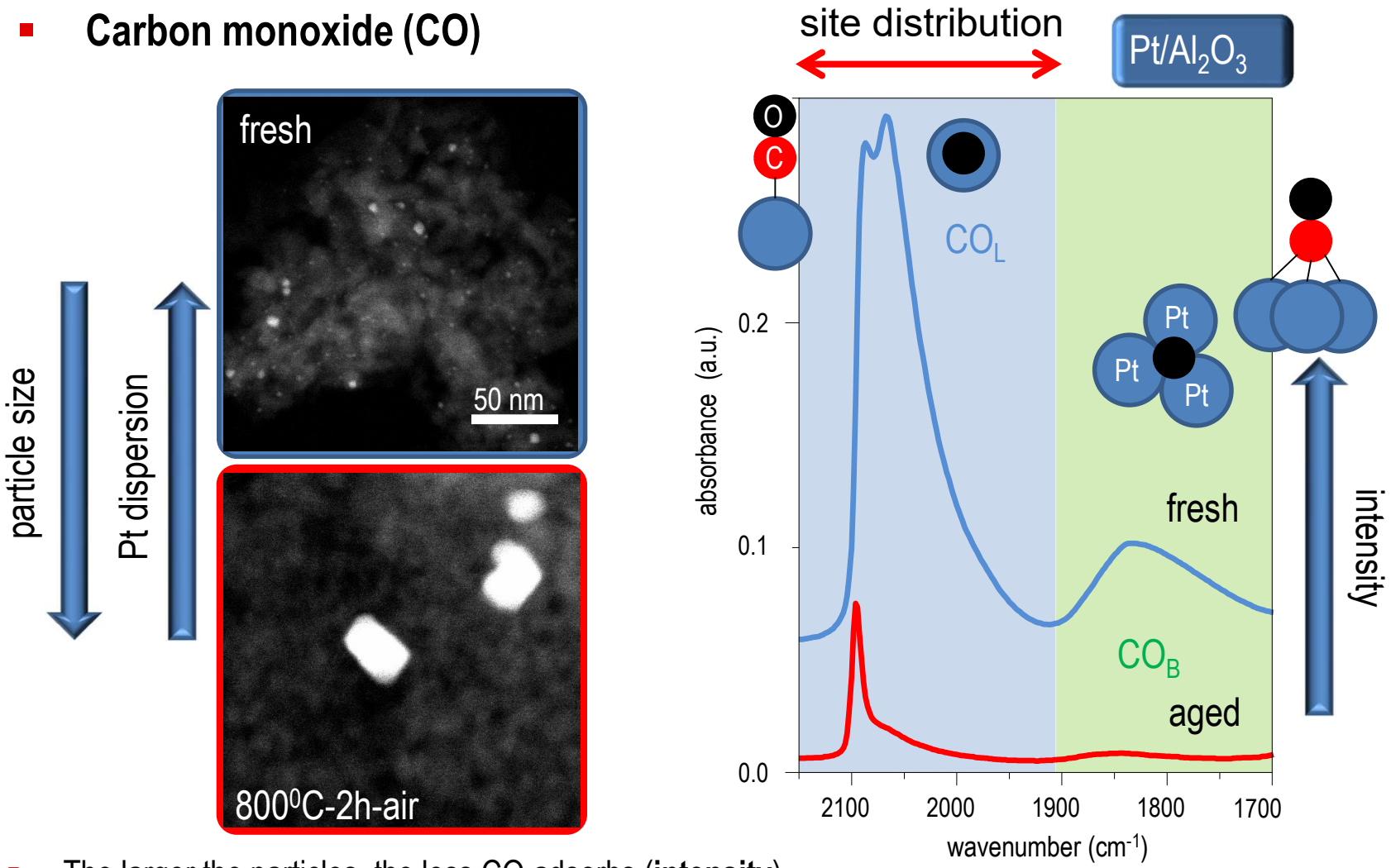
- **Carbon monoxide (CO)**



Adsorbate
assignments on powders by comparison with reference UHV studies (single crystals)

Probe molecules

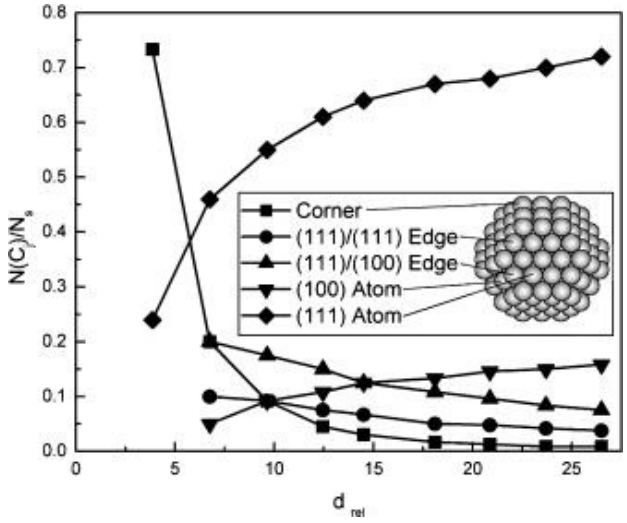
- **Carbon monoxide (CO)**

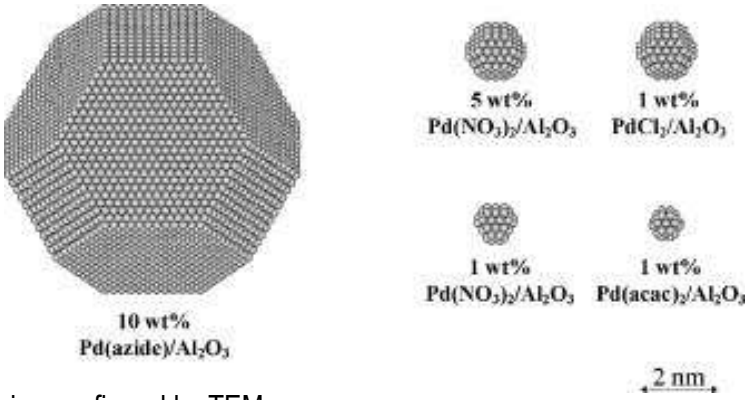


- The larger the particles, the less CO adsorbs (**intensity**)
- The larger the particles, the less defects available (**nr. of signals**)

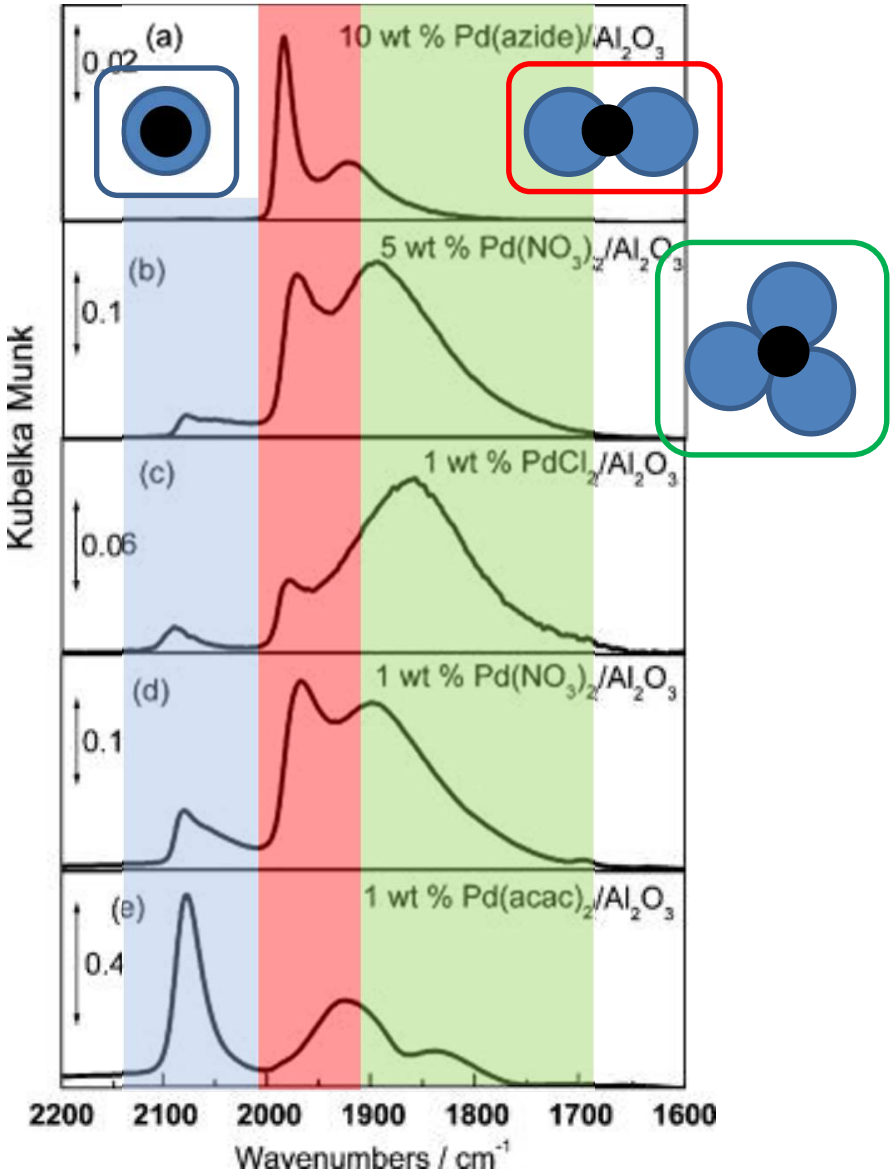
Probe molecules

- **Carbon monoxide (CO)**





size confirmed by TEM

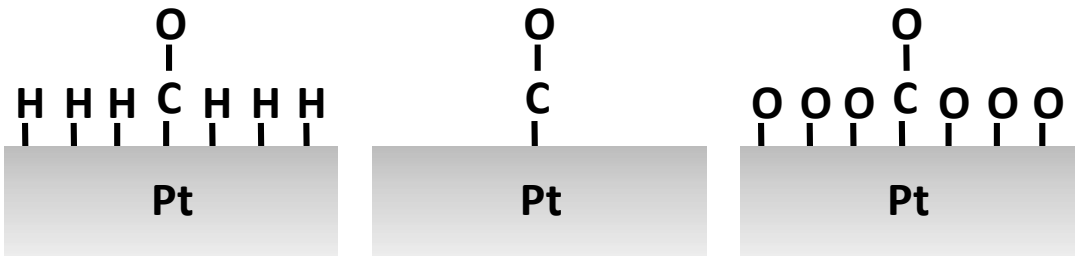


Lear et al., *J. Chem. Phys.* 123 (2005) 174706

Probe molecules

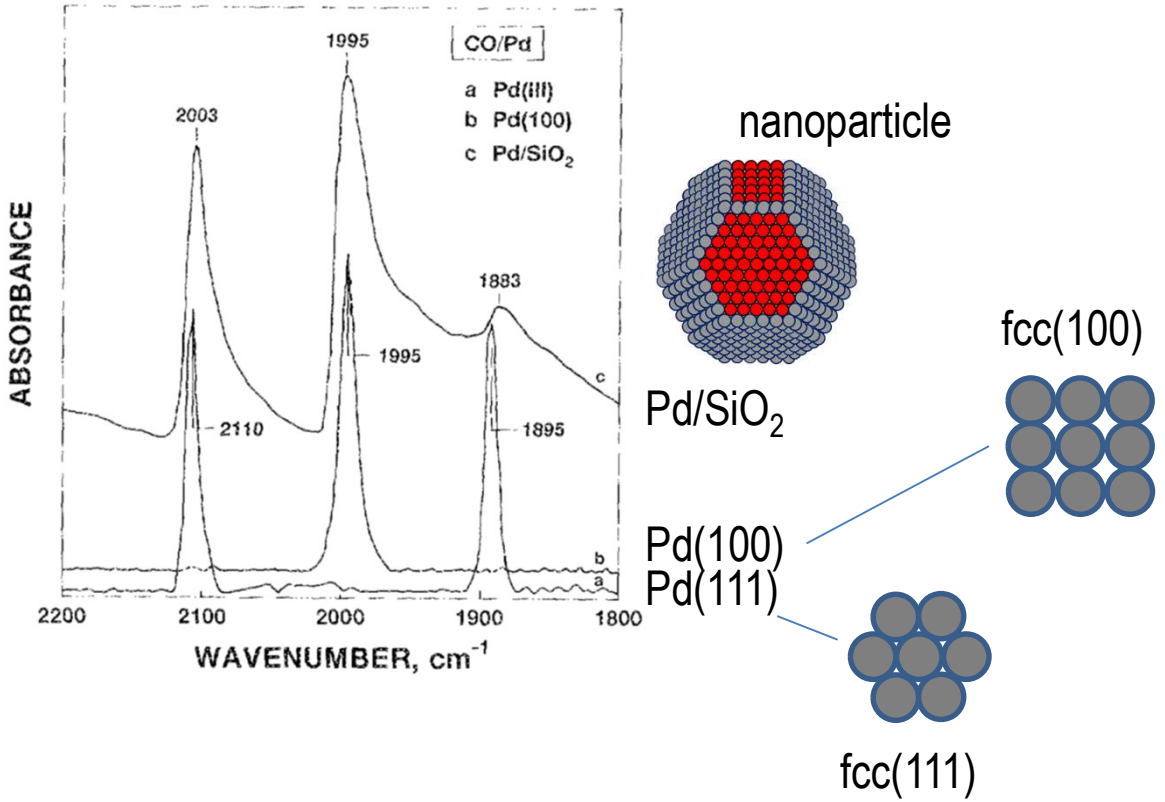
- **Carbon monoxide (CO)**

Q How does the CO stretching frequency shift when a Pt surface is covered with hydrogen or oxygen prior to CO adsorption?



Probe molecules

- **Rationalise results on powders**



Szanyi et al., J. Vac. Sci. Technol. A 11 (1993) 1969

Adsorbates

- **Orientation on surfaces**

Powders

- qualitative
- adsorption mode, coordination to surface (e.g., mono-, bidentate, bridging, tilted…)

Metallic surfaces (e.g. single crystals)

- more accurate
- surface selection rule
- orientation information from dynamic dipole moment direction
- group theory
- combination with theory (Density Functional Theory – DFT)

Adsorbates

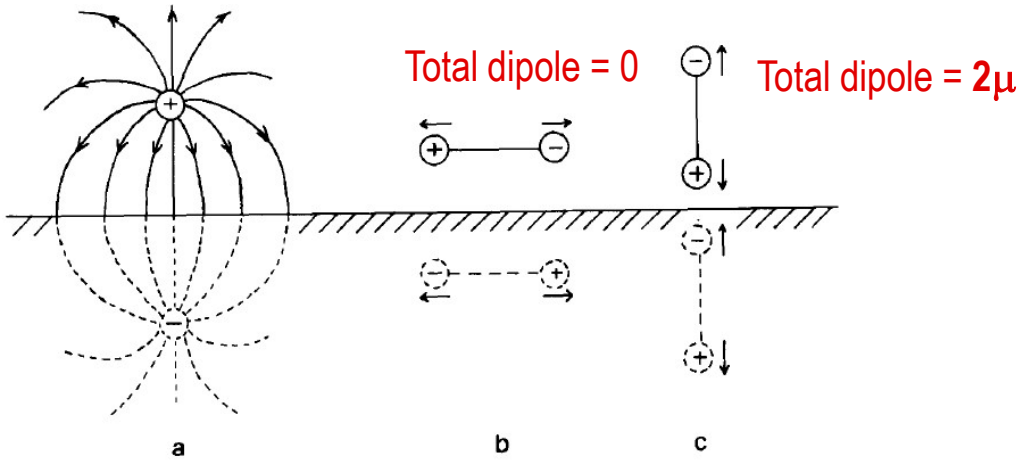
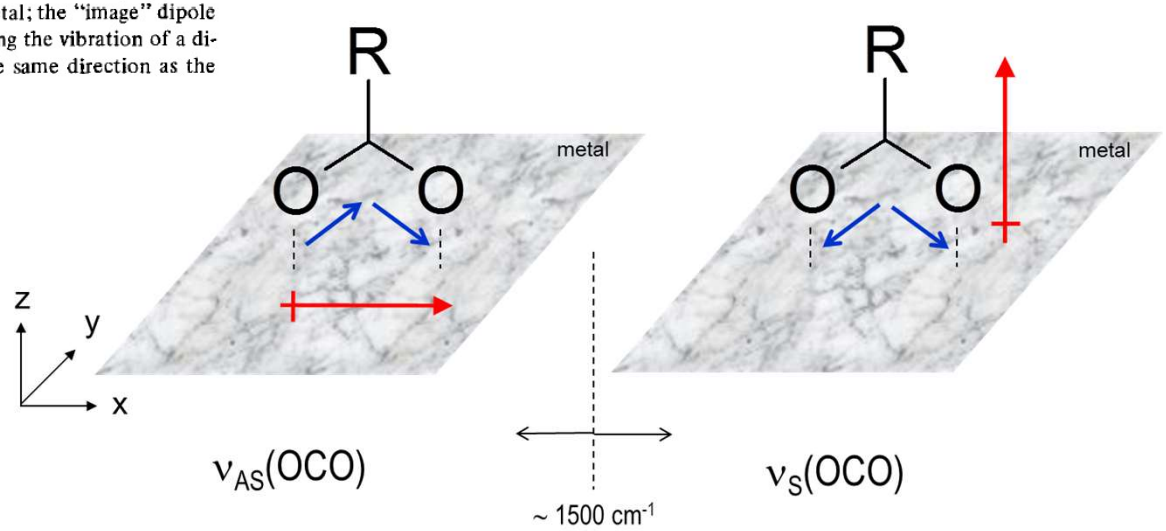


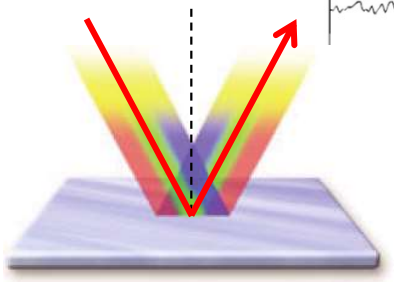
Fig. 1. (a) The lines of force and the electrical "image" resulting from a positive charge over the surface of a conductor (the metal surface is the upper line above the hatched area). (b) The changes during the vibration of a dipole parallel to the surface of the metal; the "image" dipole change is in the opposite direction to the original. (c) The changes during the vibration of a dipole perpendicular to the surface; the "image" dipole change is in the same direction as the original.

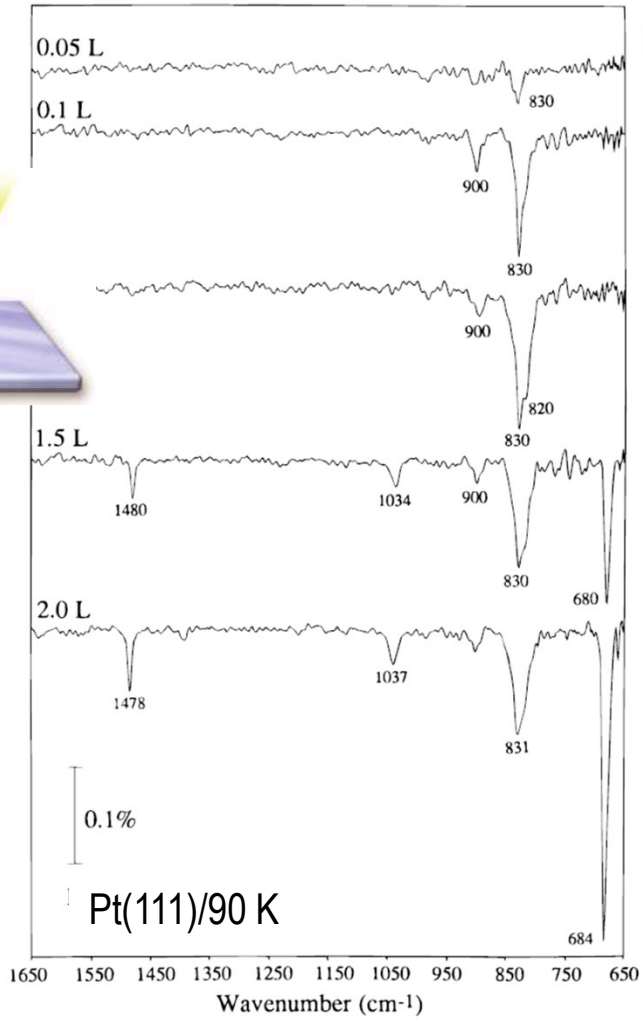
- **SURFACE selection rule**



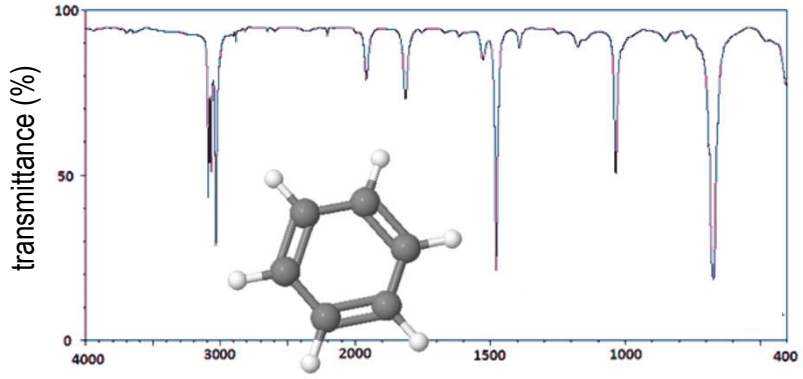
Pearce and Sheppard, Surf. Sci. 59 (1976) 205

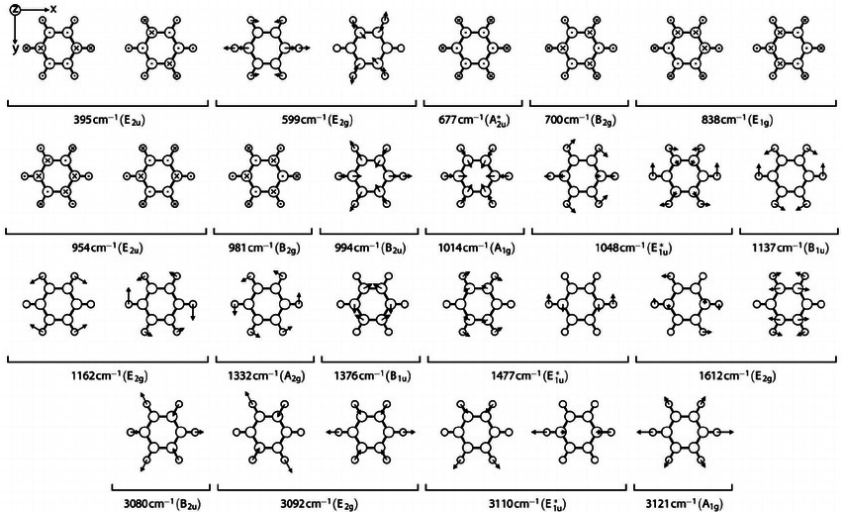
Adsorbates





L (Langmuir)= exposure of 10^{-6} Torr gas for 1 s

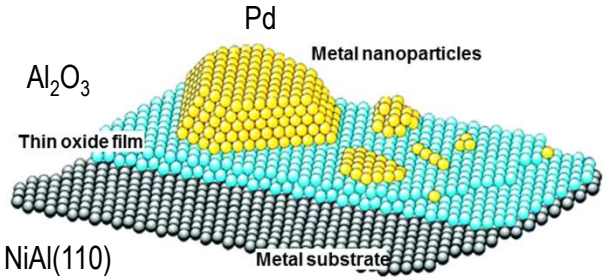




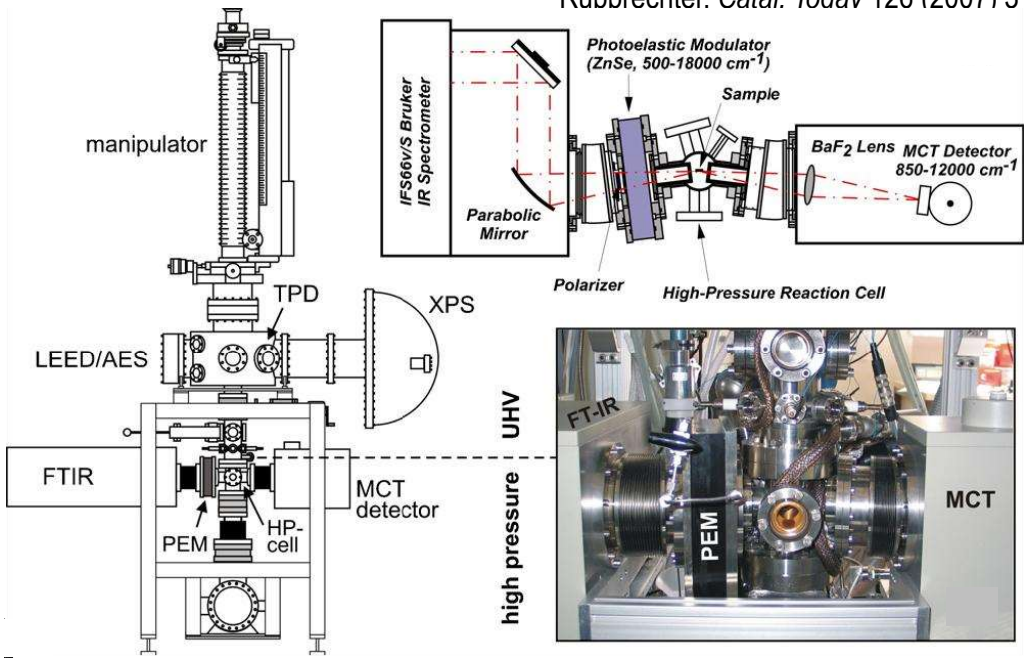
Haq et al., J. Phys. Chem. 100 (1996) 16957; Preuss et al., Phys. Rev. B 73 (2006) 155413

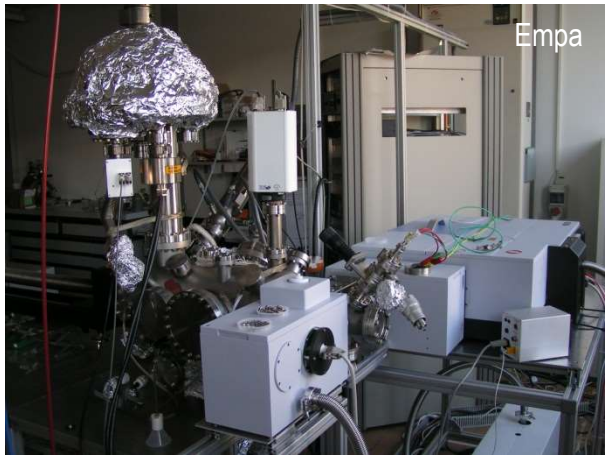
Reflection-Absorption

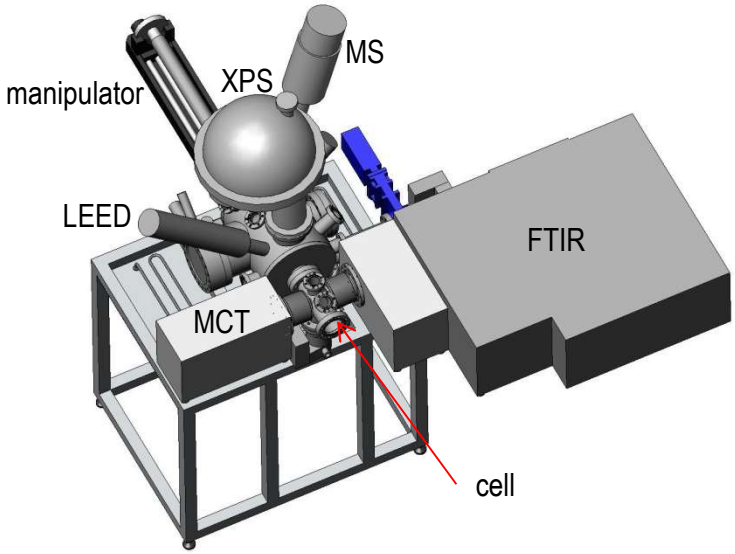
- **Model system investigation | UHV**
  - single crystals
  - well-defined nano-particles



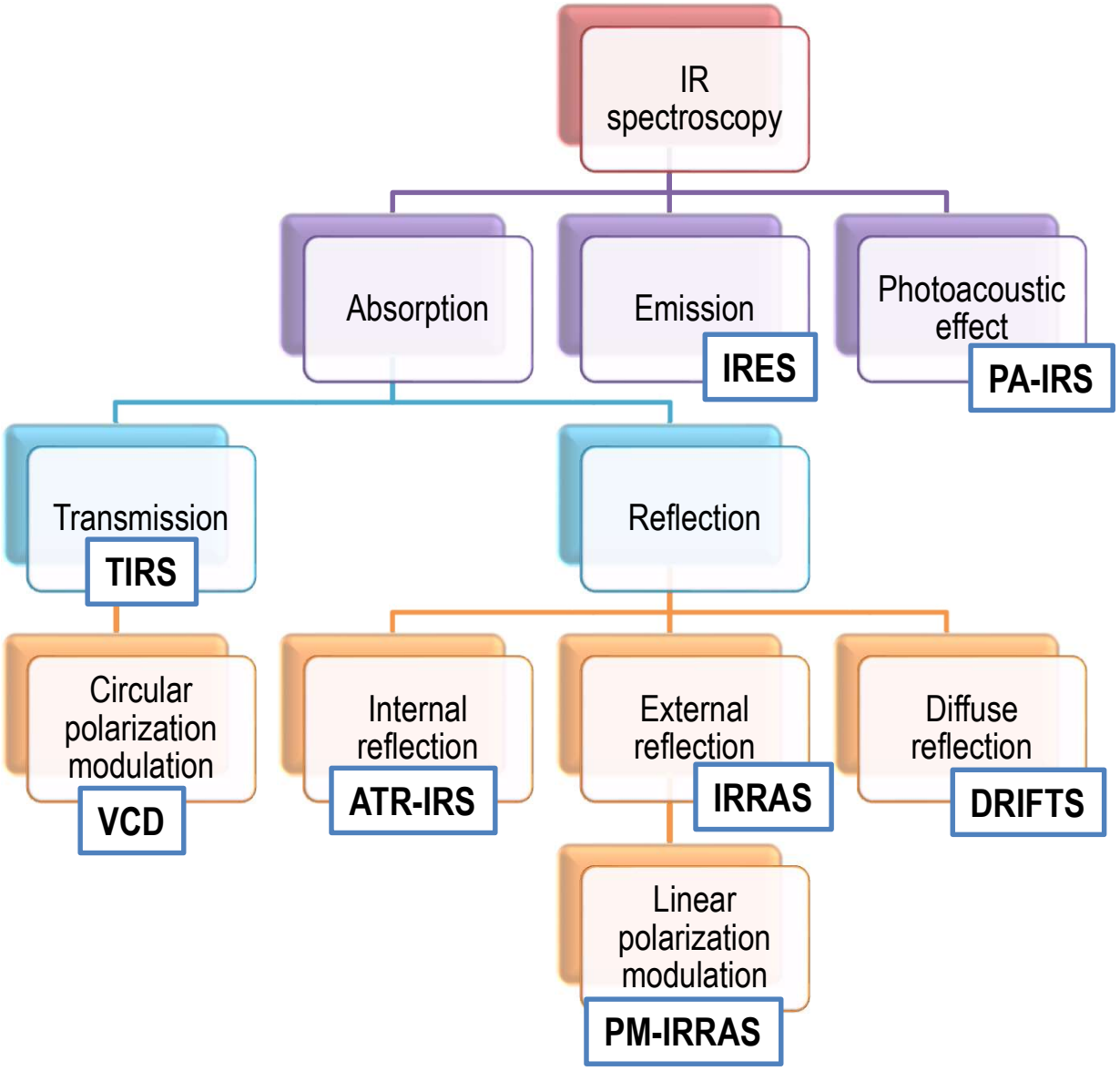
Rupprechter, *Catal. Today* 126 (2007) 3







Sampling techniques



TIRS: transmission infrared spectroscopy

IRES: infrared emission spectroscopy

PA-IRS: photoacoustic infrared spectroscopy

VCD: vibrational circular dichroism

ATR-IRS: attenuated total reflection infrared spectroscopy

IRRAS: infrared reflection-absorption spectroscopy (also **RAIRS**)

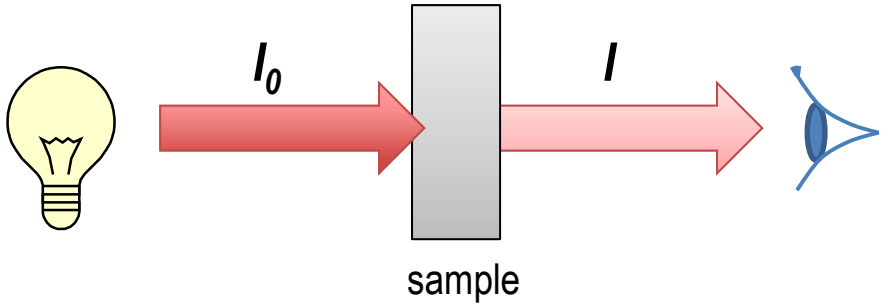
PM-IRRAS: polarization-modulation IRRAS

DRIFTS: diffuse reflectance infrared Fourier transform spectroscopy

courtesy prof. Urakawa | TU Delft

Transmission IR spectroscopy

- **‚Straight' IR light absorption**
  - **For solid-gas interfaces**



  - Popular for detections of gas and liquid samples
  - Solids have to be diluted or shaped in a very thin film
  - Quantification is more straightforward than other IR techniques

- **In heterogeneous catalysis**
  - Popular for *in situ* investigations
  - Typically a very thin self-supporting catalyst disk is used
  - Powder sample can also be dispersed on IR transparent grid (W)
  - Mass transfer can be an issue

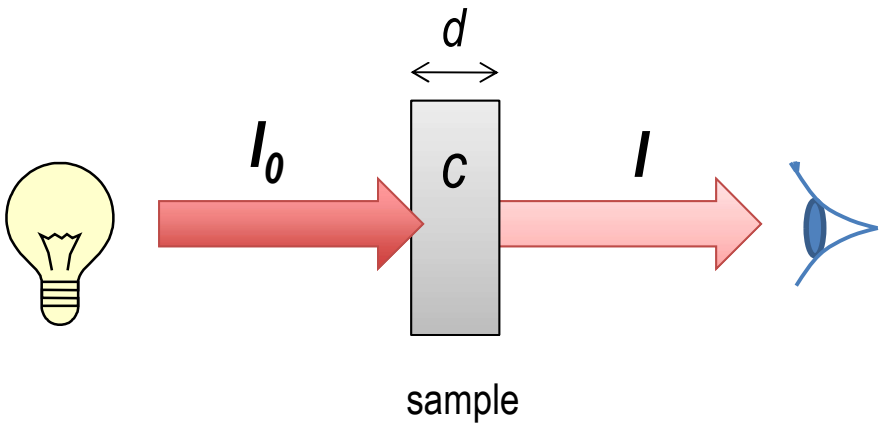
Transmission IR spectroscopy

- **Quantification: most straightforward than other techniques**

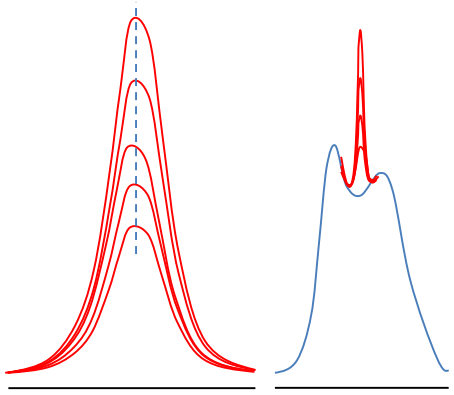
Lambert-Beer law

$$T = \frac{I}{I_0}$$

$$A = -\log(T) = -\log(\frac{I}{I_0}) = \varepsilon c d$$

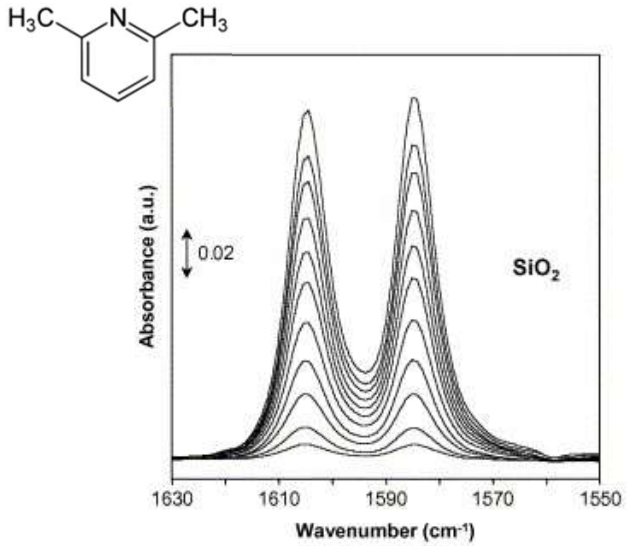


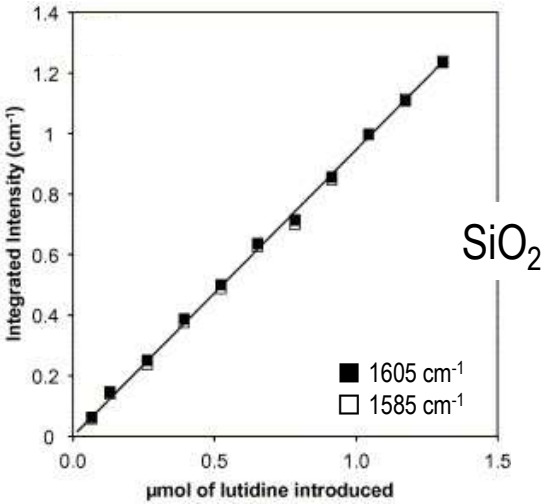
…but, validity:
isolated signal

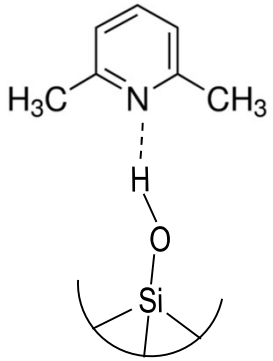


T: transmittance, **A**: absorbance, **e**: molar absorption (extinction) coefficient, **c**: concentration, **d**: path length

Molar absorption coefficient - Adsorbates







$$A = \varepsilon \ell \frac{n}{S\ell}$$

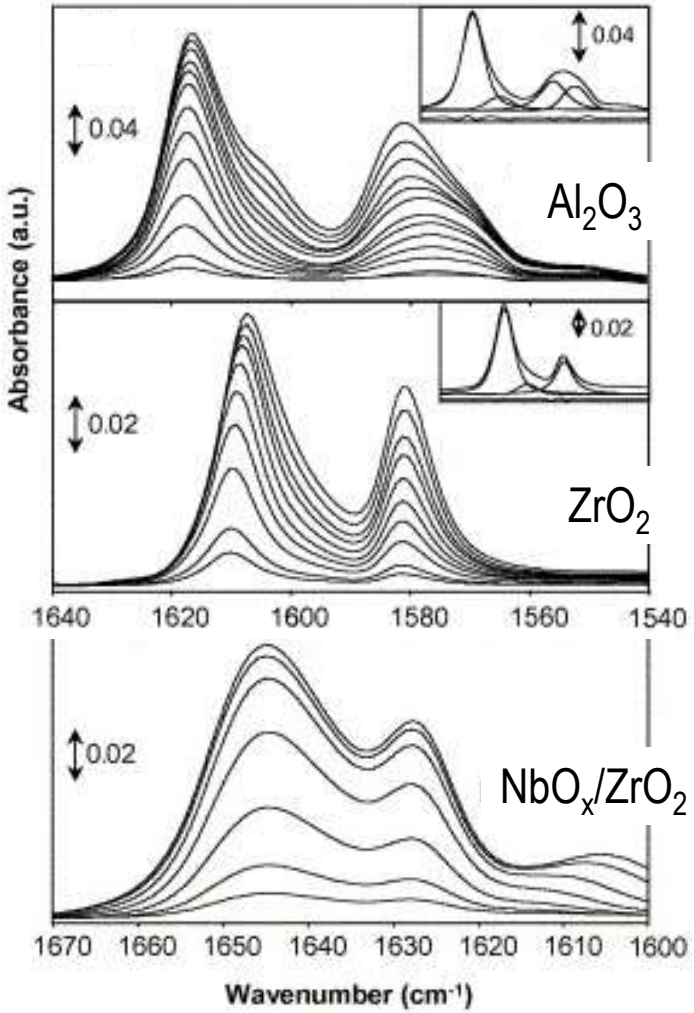
$$A = \frac{\varepsilon n}{S}$$

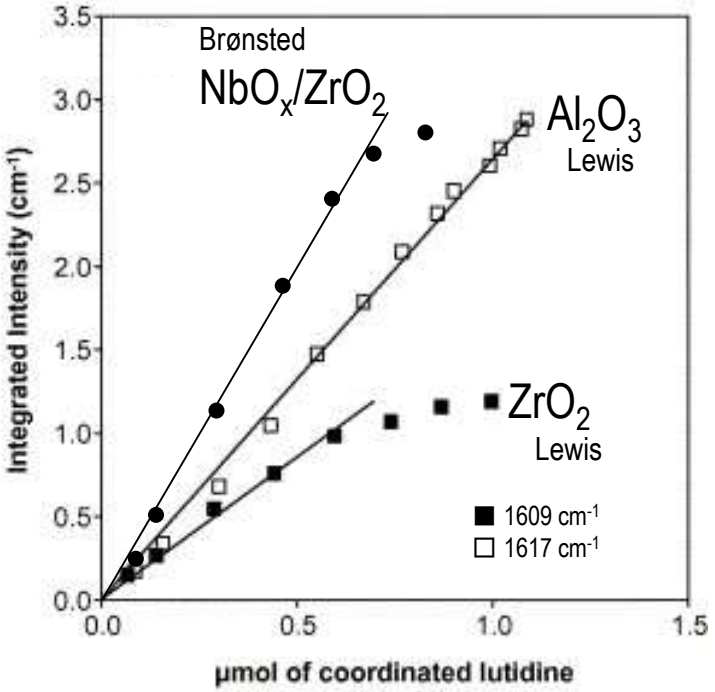
$$\varepsilon = \frac{SA}{n}$$

ε, integrated molar absorption coefficient
ℓ, disc thickness (optical path)
n, amount of adsorbed molecule
S, disc area

T. Onfroy et al., Micropor. Mesopor. Mater. 82 (2005) 99

Molar absorption coefficient - Adsorbates





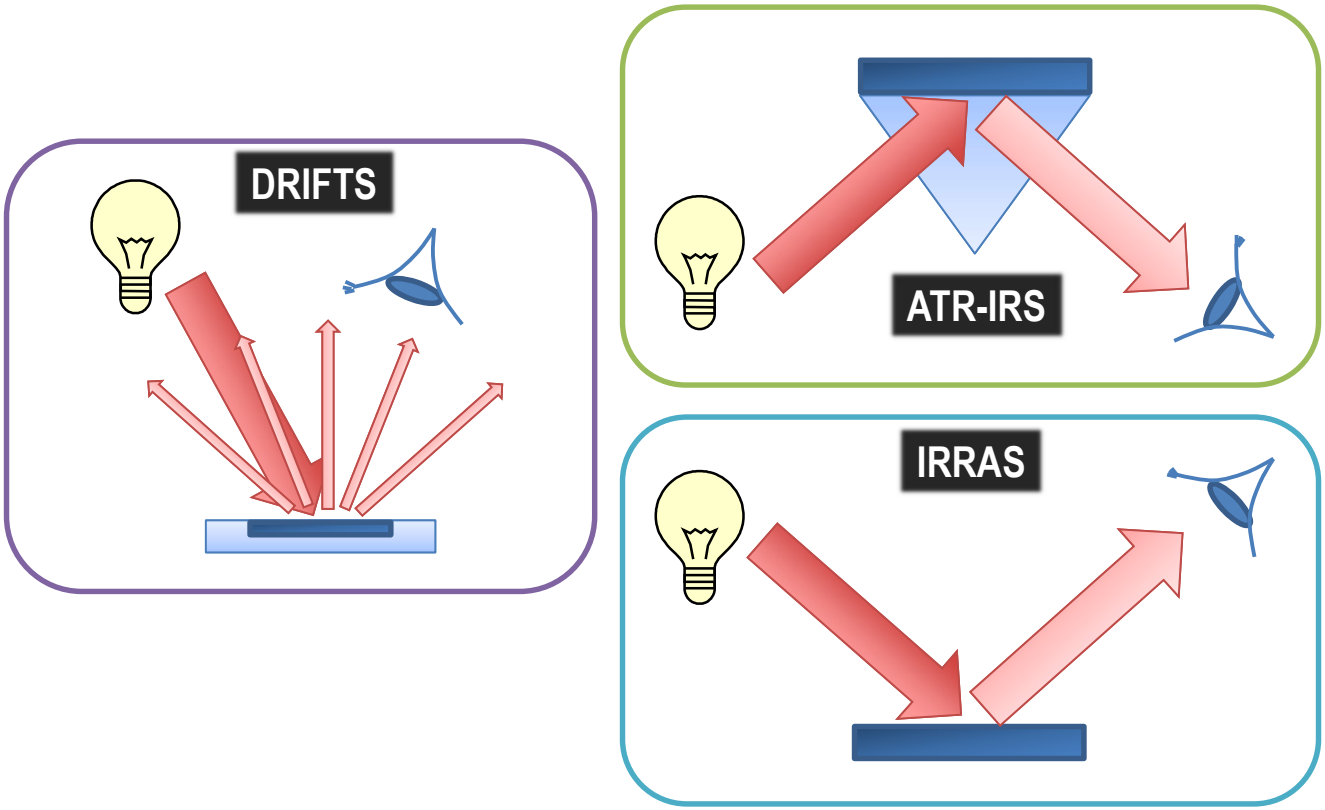
	H-bond	coordination	protonation
SiO_2	$\varepsilon_{1585} = 1.9$		
	$\varepsilon_{1605} = 1.9$		
Al_2O_3		$\varepsilon_{1617} = 5.3$	
ZrO_2		$\varepsilon_{1609} = 3.4$	
NbO_x/ZrO_2			$\varepsilon_{1644+1628} = 7.3$
Average	$\varepsilon_{1585} = 1.9$	$\varepsilon_{Lewis} = 4.35$	$\varepsilon_{Brønsted} = 6.8$
	$\varepsilon_{1605} = 1.9$		
ε= cm µmol^{-1}			

T. Onfroy et al., Micropor. Mesopor. Mater. 82 (2005) 99

Reflection techniques

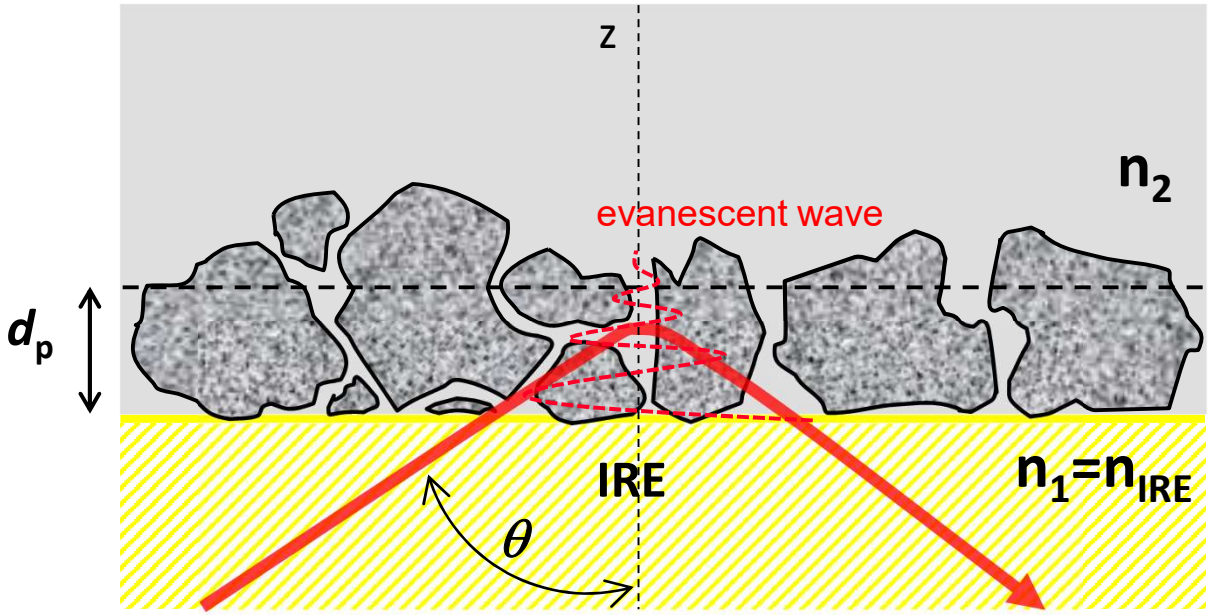
Aim for heterogeneous catalysis studies

study events occurring at interfaces and maximize signals related to catalysts and active species on surfaces, especially during reaction



Attenuated total reflection

- **How does it work?**
  - Light travels through a waveguide



$$d_p = \frac{\lambda_1}{2\pi\sqrt{\sin^2\theta - n_{21}^2}}$$

θ : angle of incidence

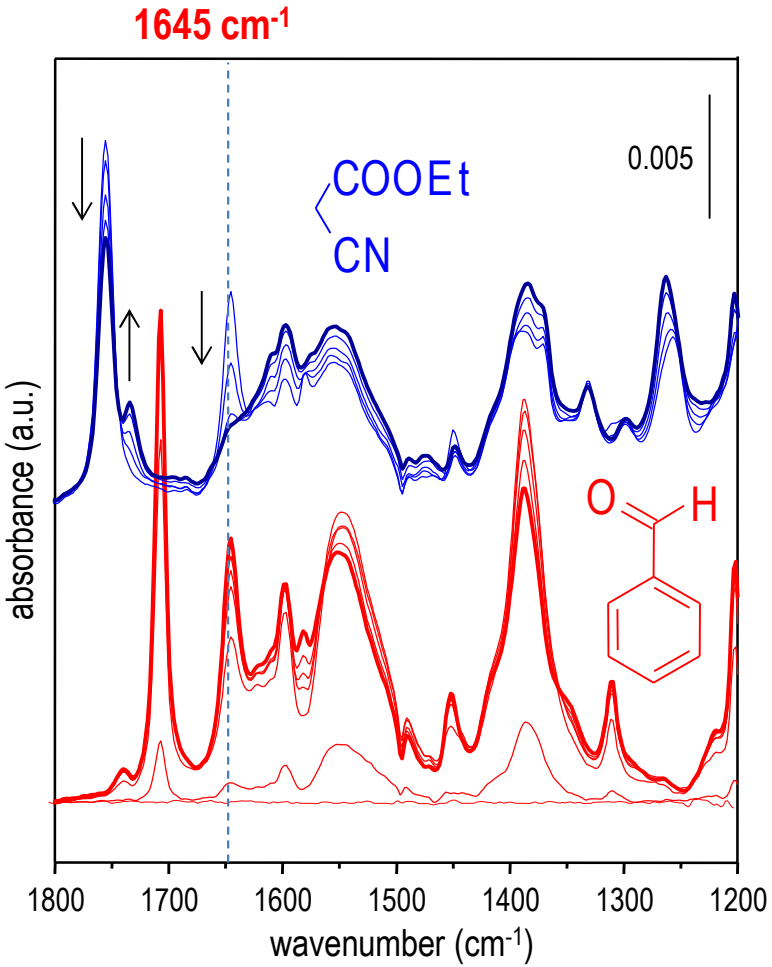
$$\lambda_1 = \frac{\lambda}{n_1} \qquad n_{21} = \frac{n_2}{n_1}$$

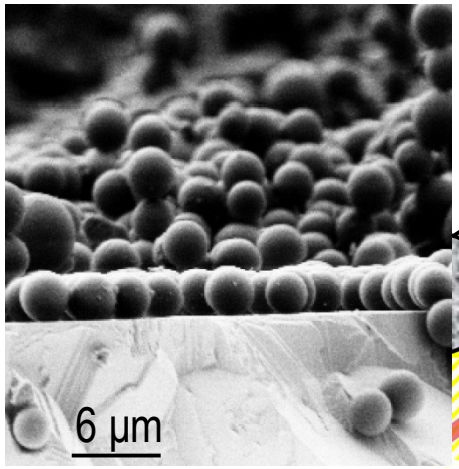
d_p: penetration depth; defined as the distance from interface where the electric field has decayed to 1/e of its value E_0 at the interface

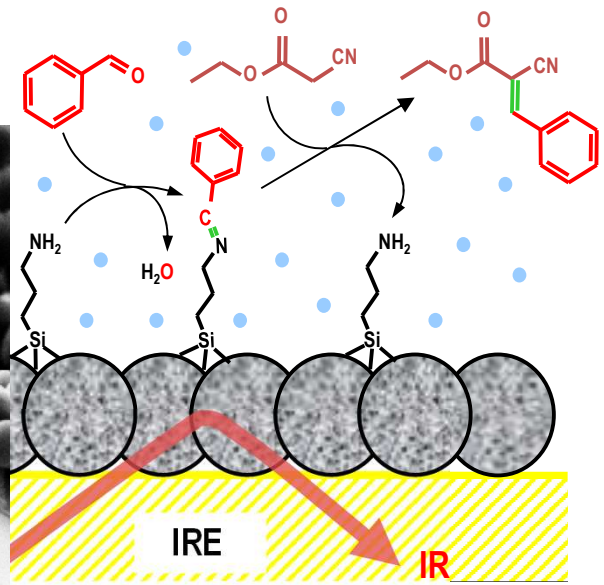
- Very powerful method for investigations of (catalytic) **solid-liquid interfaces**

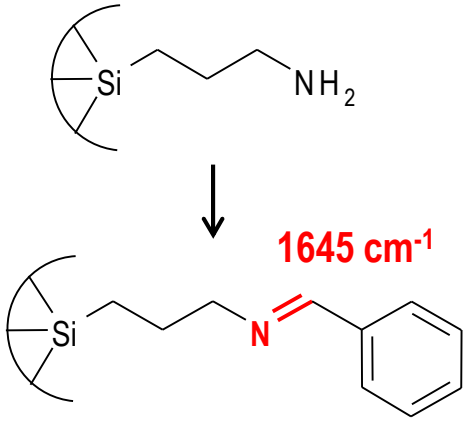
Attenuated total reflection

- Knoevenagel condensation





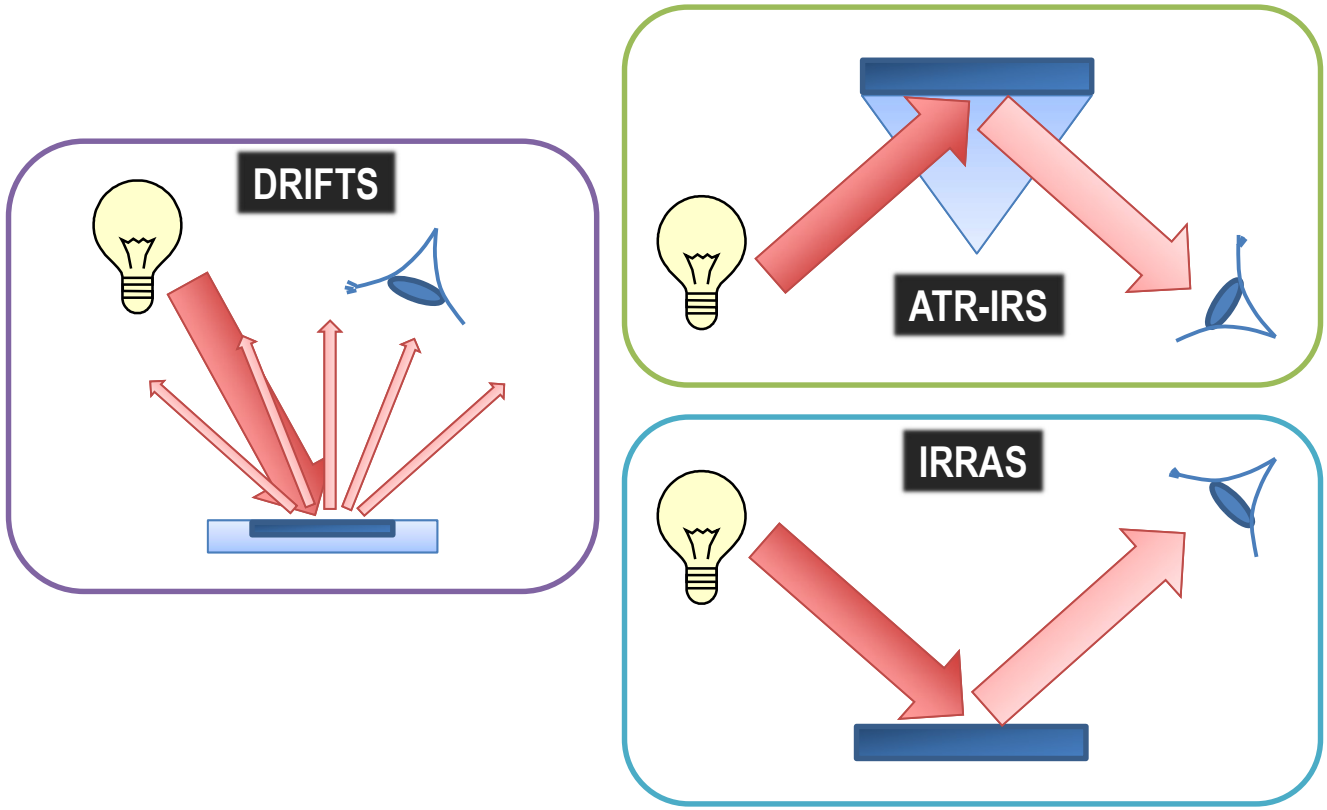




Wirz et al., *Langmuir* 22 (2008) 3698

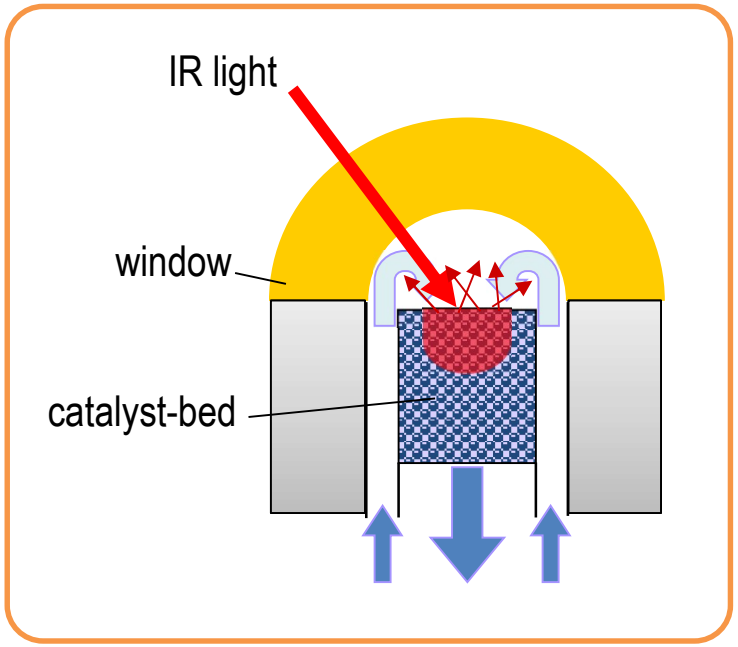
Reflection techniques

- **Aim for heterogeneous catalysis studies**
  study events occurring at interfaces and maximize signals related to catalysts and active species on surfaces, especially during reaction



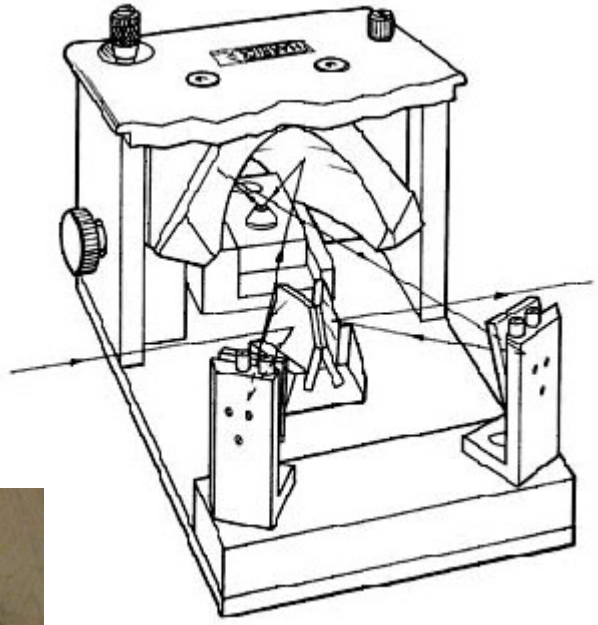
Diffuse reflectance

- Very popular for *in situ* measurements of physicochemical processes at **solid-gas interfaces** using realistic **powder catalysts**



IR light diffuses into the catalyst bed

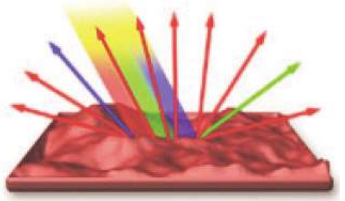
DRIFTS cell

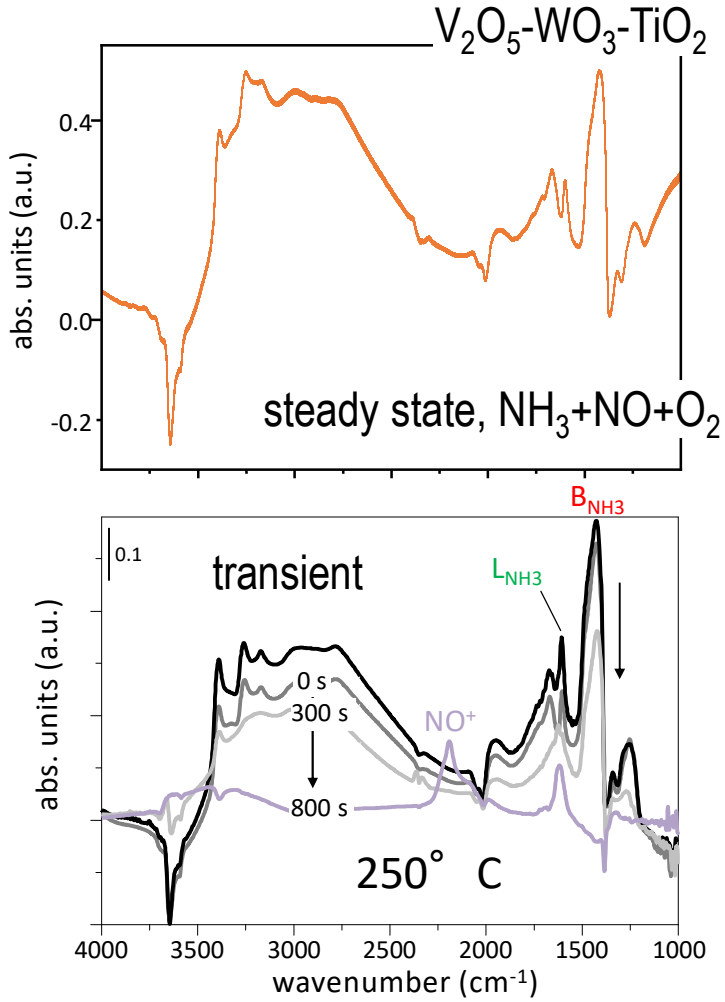


The Praying Mantis
(very popular, highly efficient light collection)

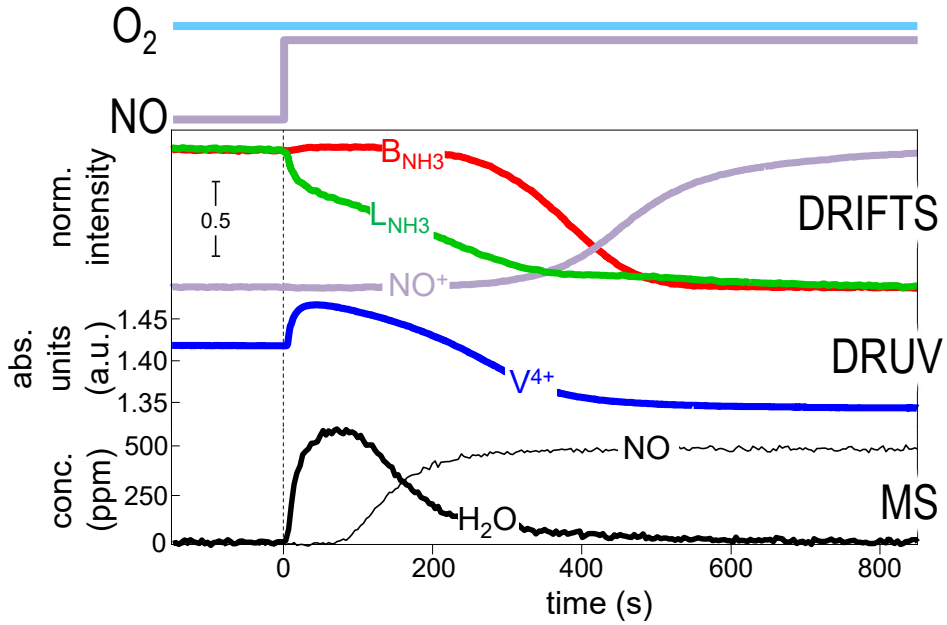
Diffuse reflectance

- **Selective catalytic reduction of NO by NH_3**





- Operando experiment
- Reactivity of Lewis acid sites L_{NH3} and Brönsted acid sites B_{NH3}
- Transient: NH_3 adsorption/desorption in O_2, then NO addition to consume surface bound species



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

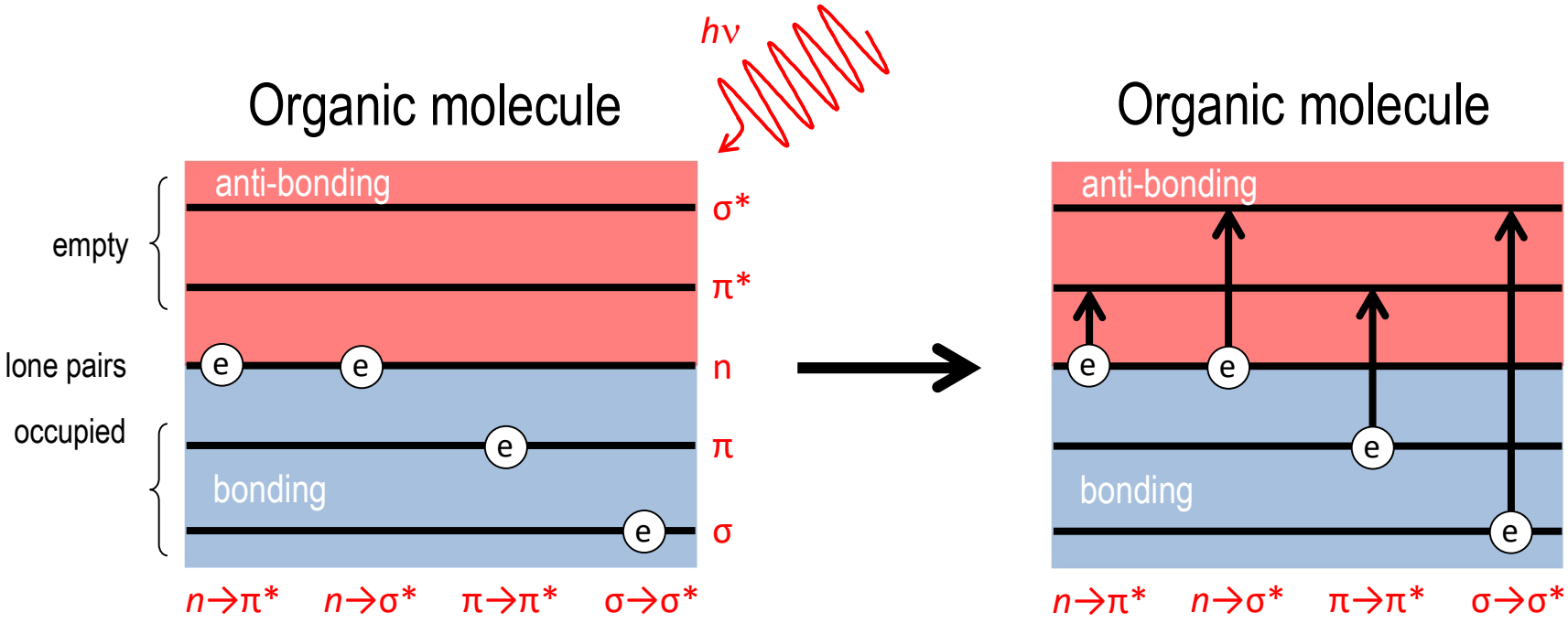
pros

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

cons

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

Electronic transitions



$E = h\nu$

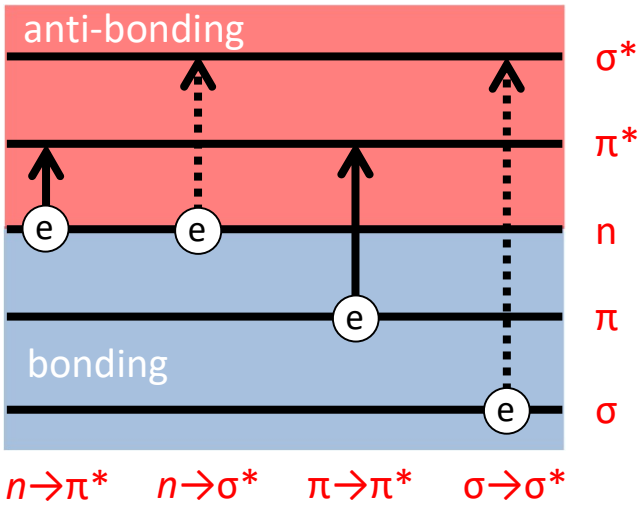
$\lambda = c/\nu$

high e^- jump $\longrightarrow$ high E

high $E \longrightarrow$ high ν

high $\nu \longrightarrow$ low λ

Electronic transitions



σ→σ*
high *E*, low λ (<200 nm)

n→σ*
150-250 nm, weak

n→π*
200-700 nm, weak

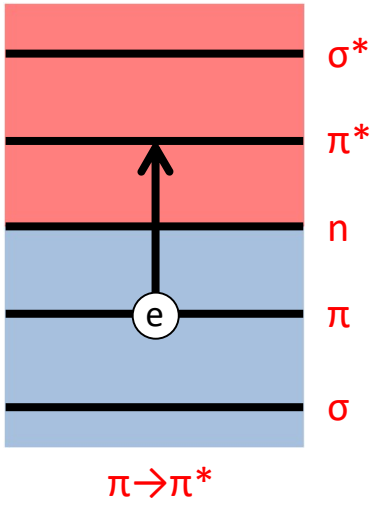
π→π*
200-700 nm, intense

Condition to absorb light (200-800 nm):

π and/or *n* orbitals

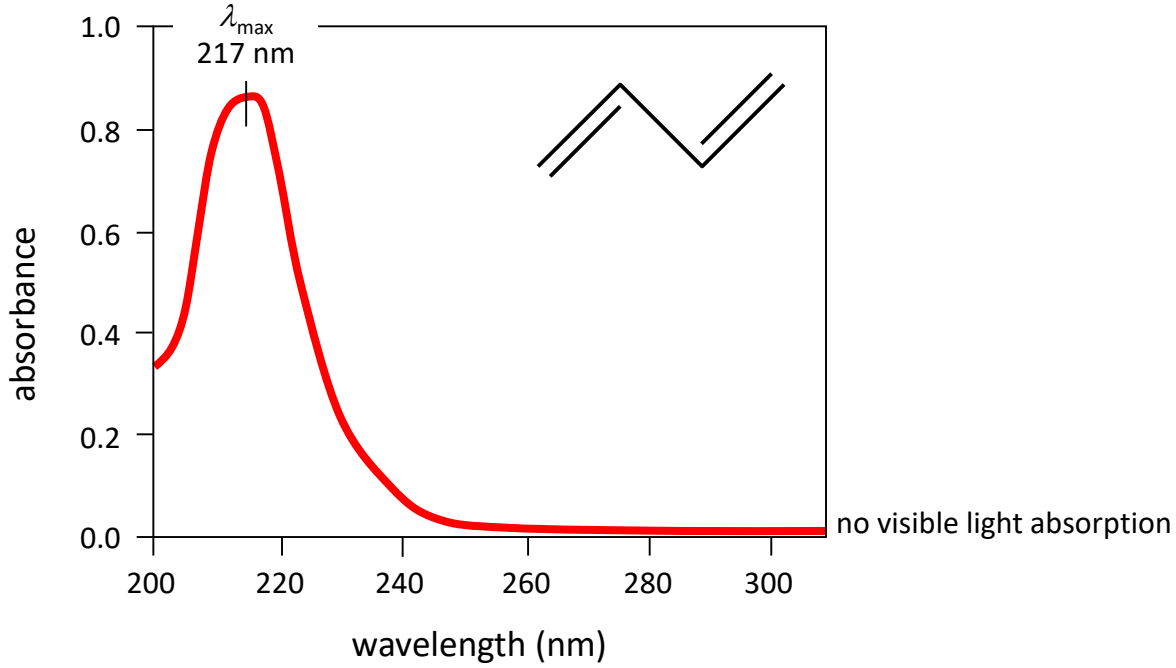
CHROMOPHORE

The UV-vis spectrum



π→π*

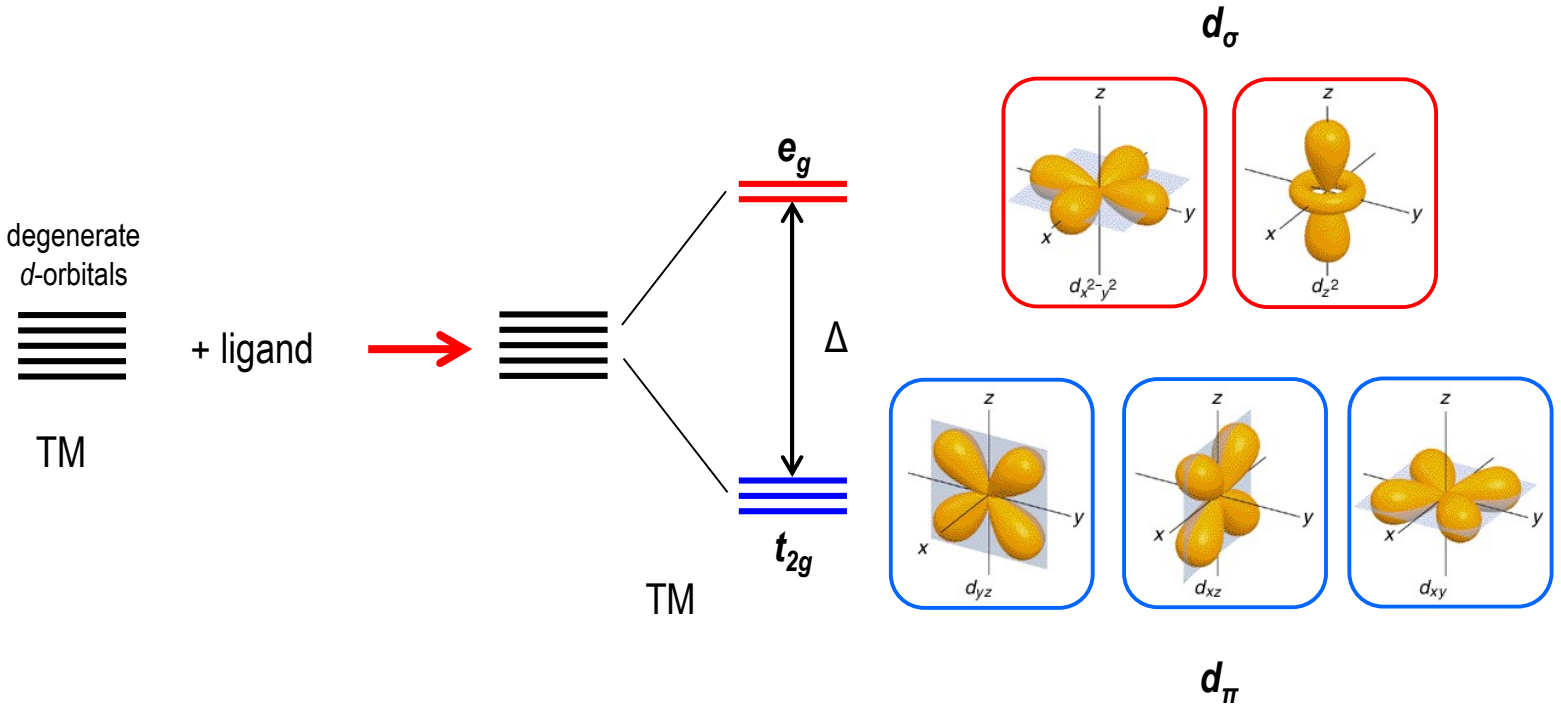
signal envelope



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

Inorganic compounds

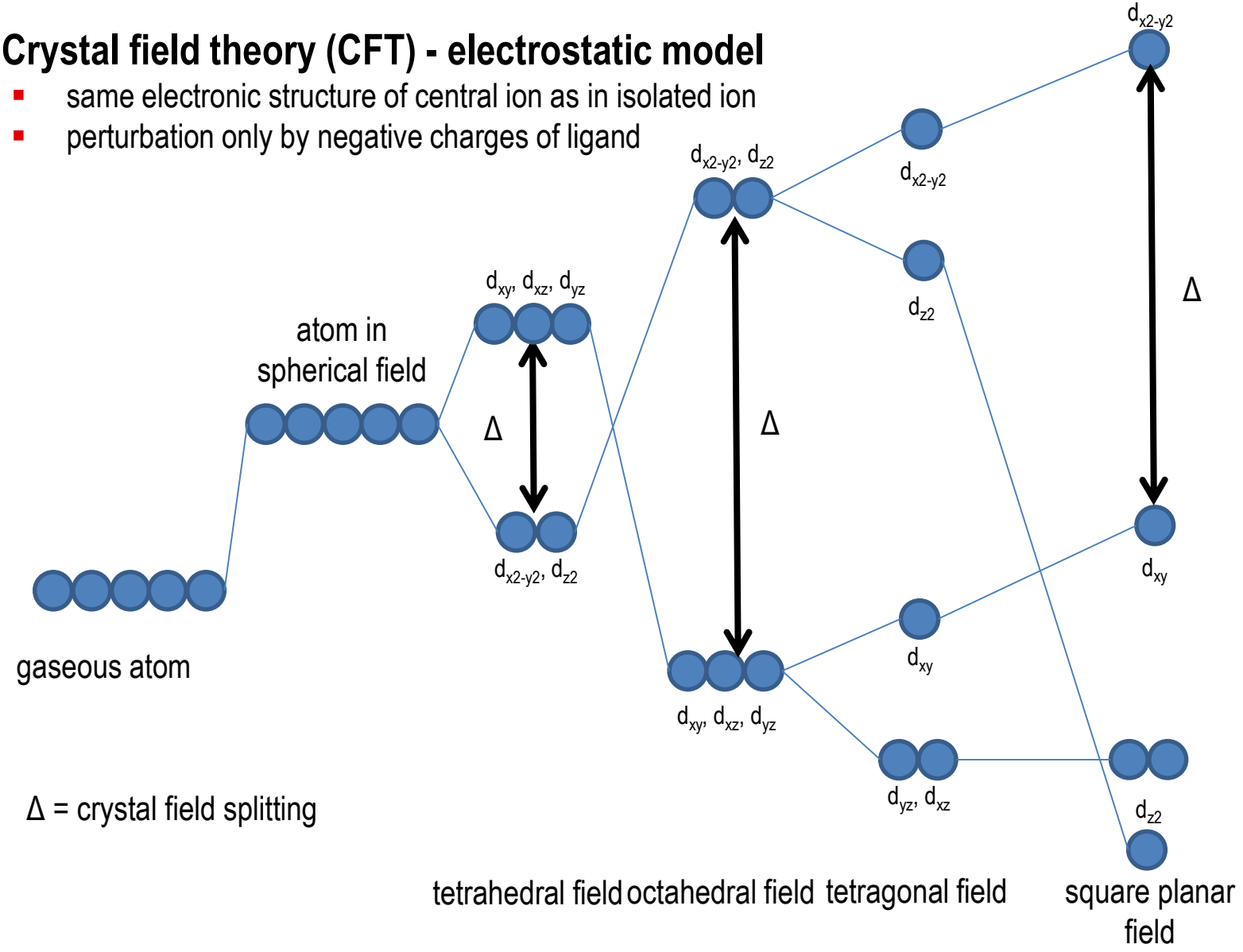
- UV-vis spectra of transition metal complexes originate from
  - **Electronic *d-d* transitions**



  - ...

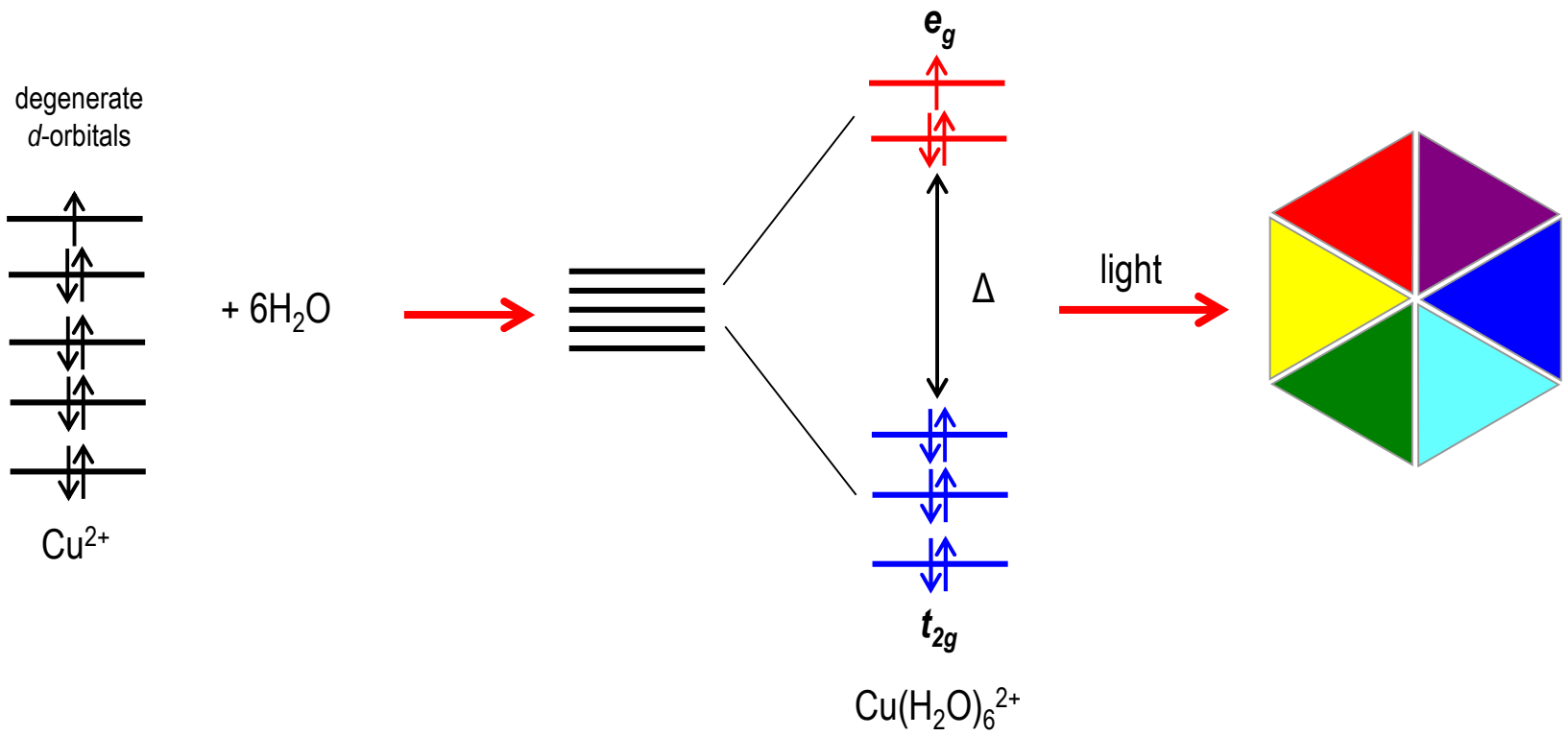
Inorganic compounds

- **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, $\Delta_{NH3} > \Delta_{H2O}$

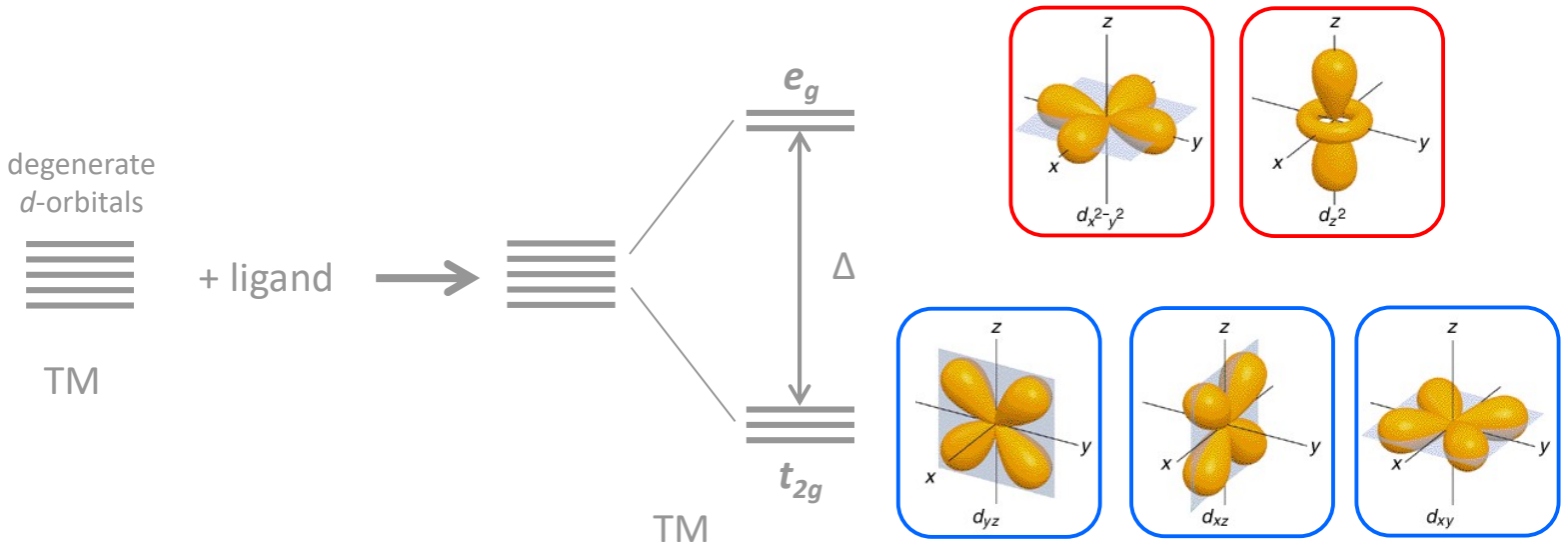
Inorganic compounds

- ***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 of ligands and geometry**
    - Δ depends on geometry of complex
  - **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



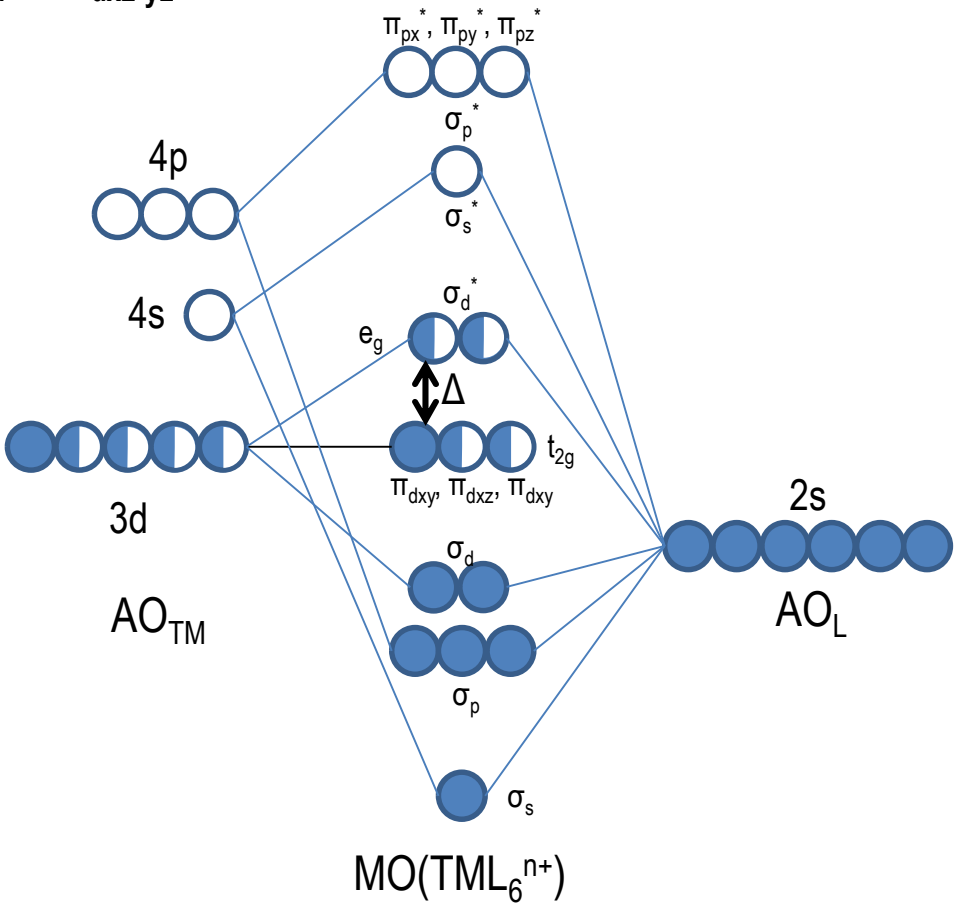
  - **Charge transfer**

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

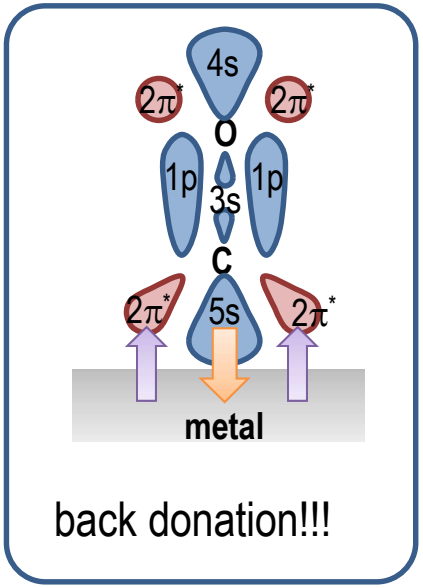
- **Ligand field theory (LFT)**
  - involves AO of metal and ligand, therefore MO
  - what CFT indicates as possible electronic transitions ($t_{2g} \rightarrow e_g$) are now:
    $\pi_d \rightarrow \sigma_{dz2}^*$ or $\pi_d \rightarrow \sigma_{dx2-y2}^*$



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
    - 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



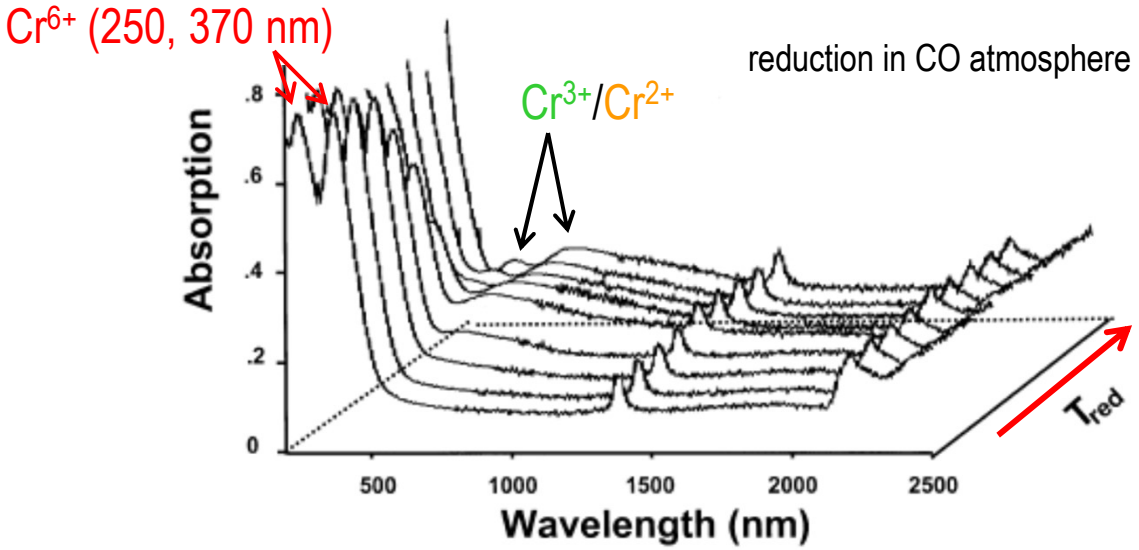
CO adsorption on precious metals

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

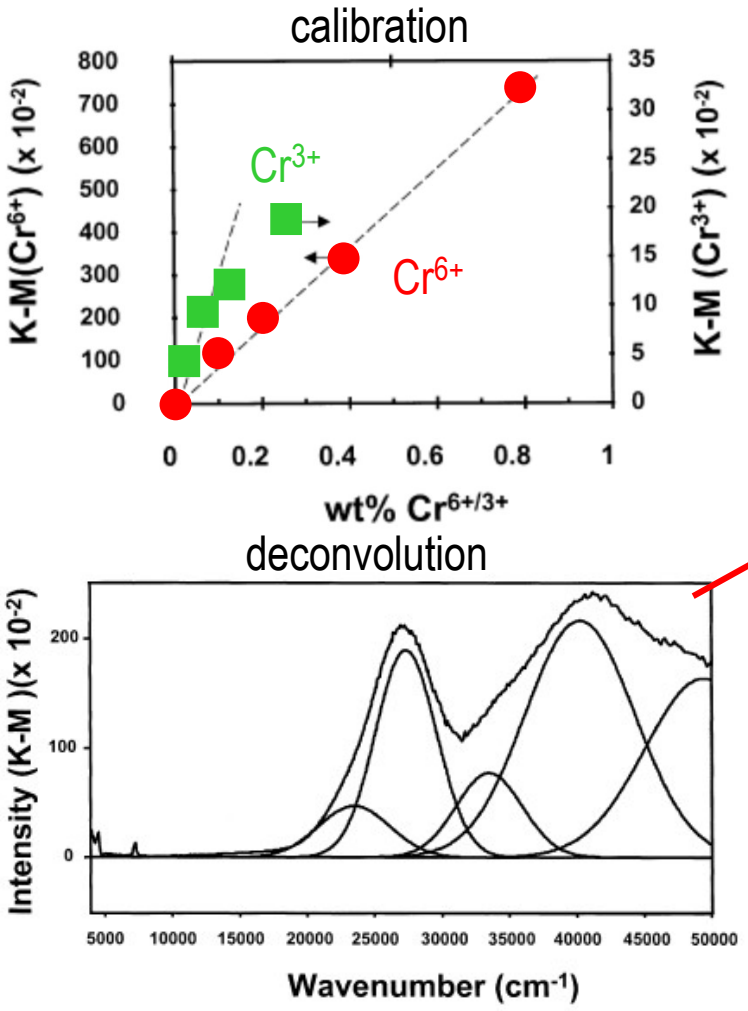
[a]s: strong; m: medium; w: weak; vw: very weak; sh: shoulder; br: broad.

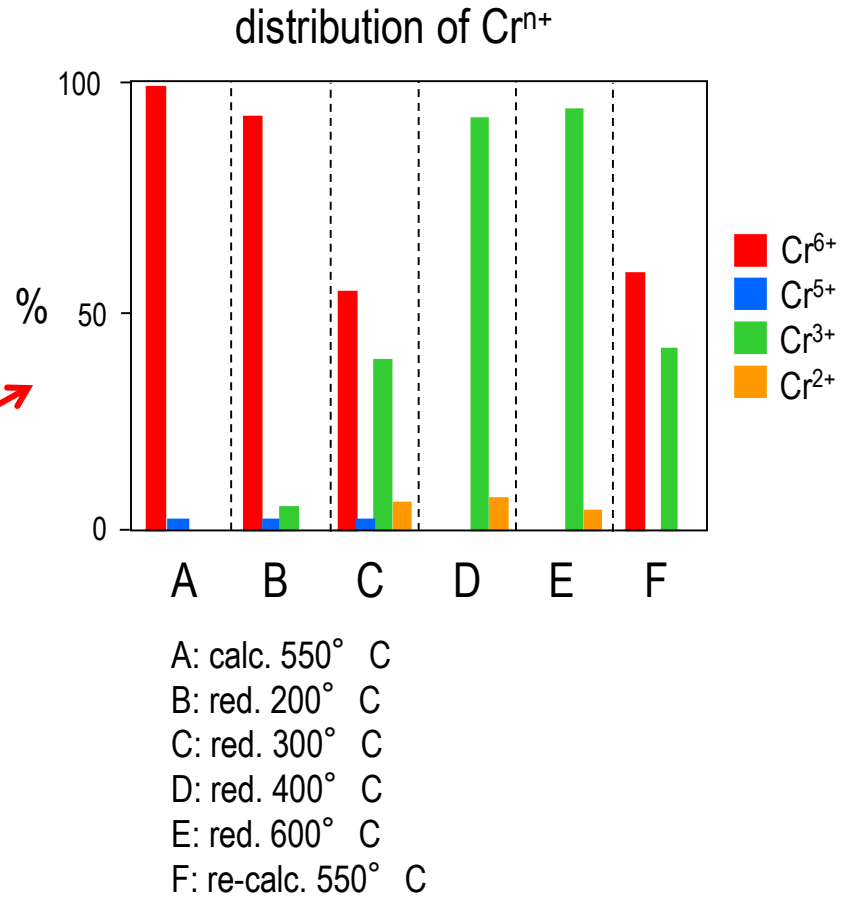


Weckhuysen et al., *Catal. Today* 49 (1999) 441

Examples

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



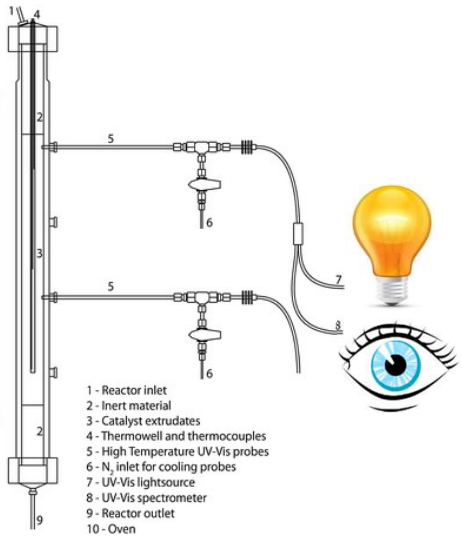


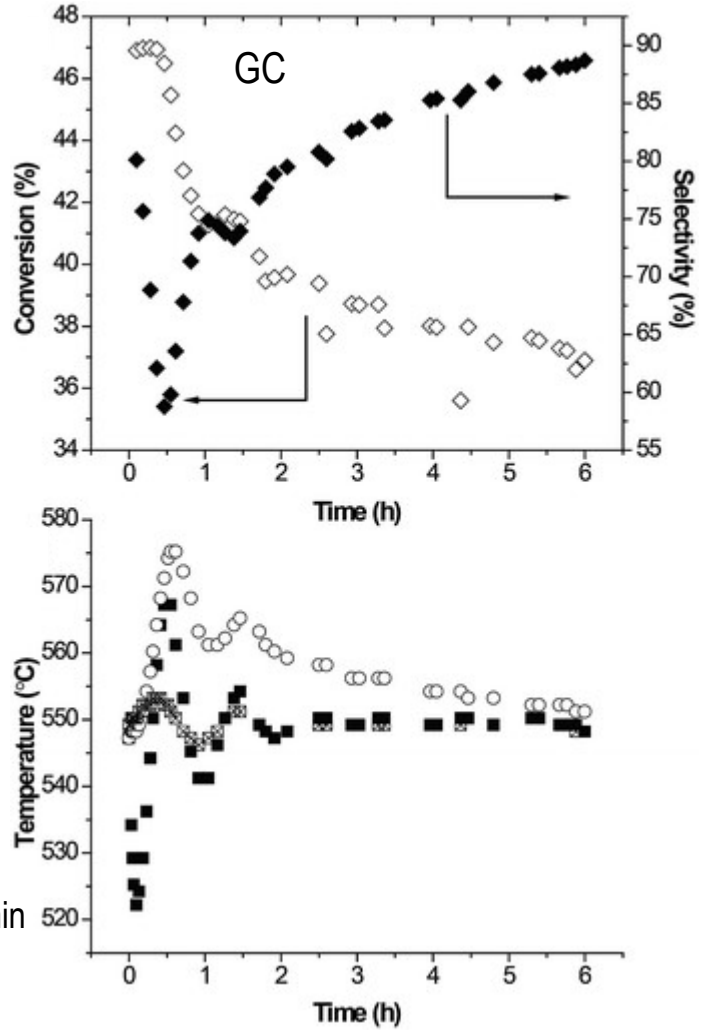
A: calc. 550° C
B: red. 200° C
C: red. 300° C
D: red. 400° C
E: red. 600° C
F: re-calc. 550° C

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

UV-vis probe in a pilot-scale reactor

- **Propane dehydrogenation**





10 vol% C_3H_8, 90 vol% N_2, 5000 ml/min

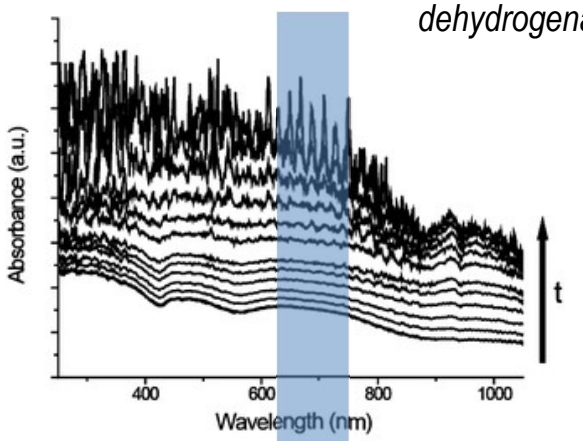
20 wt% $Cr^{3+/6+}O_x/Al_2O_3$

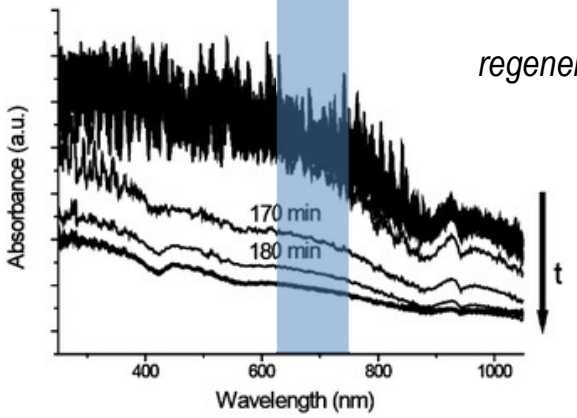
Weckhuysen et al., *Chem. Commun.* 49 (2013) 1518

UV-vis probe in a pilot-scale reactor

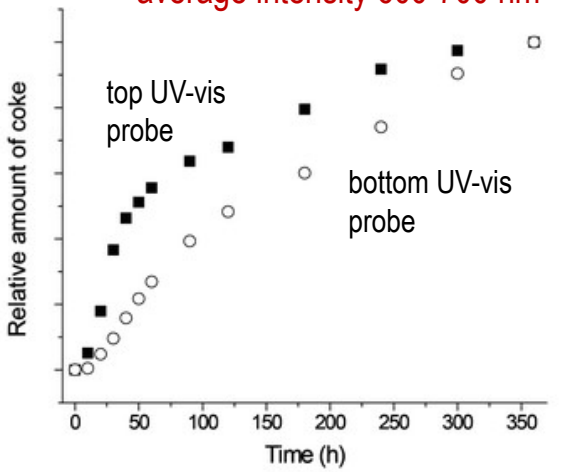
- **Propane dehydrogenation**

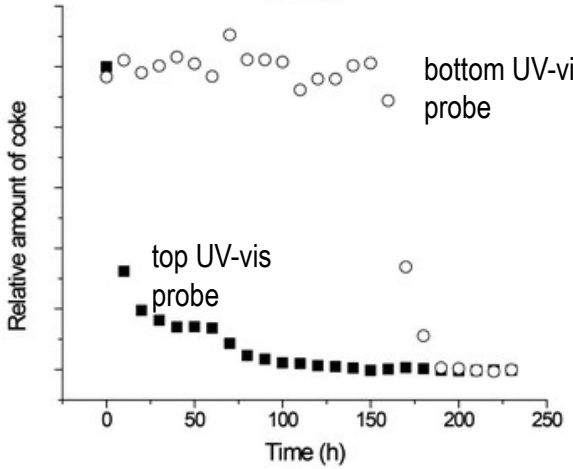
bottom UV-vis probe





average intensity 600-700 nm



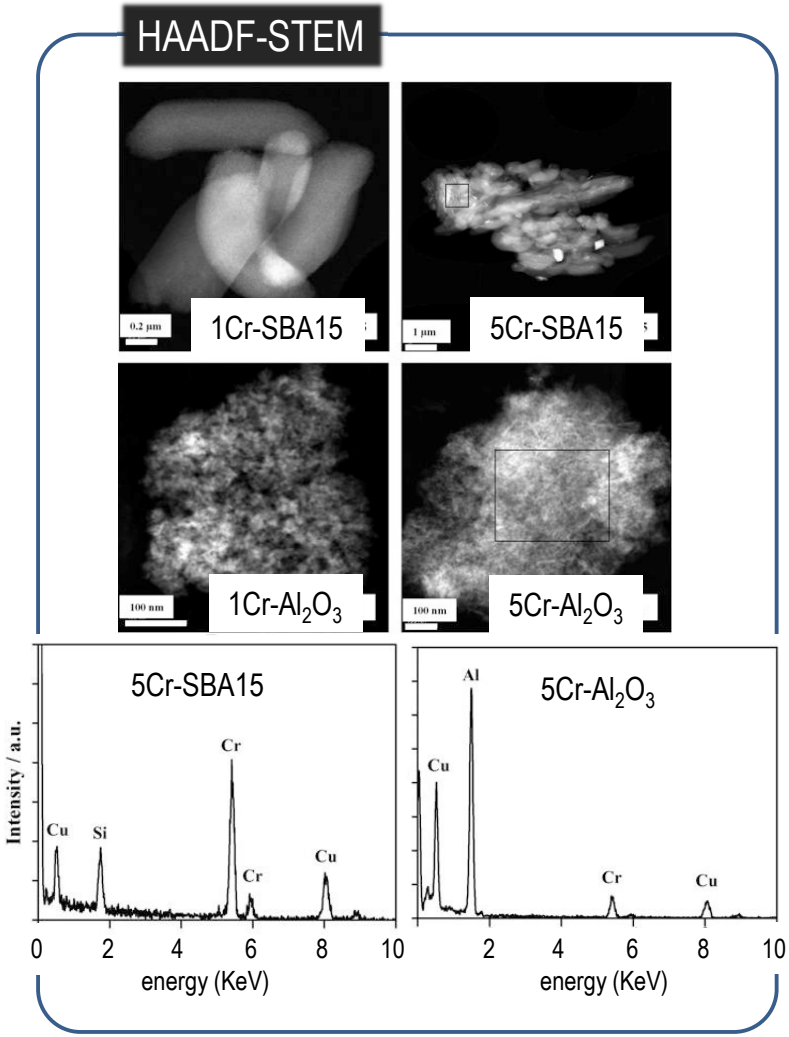


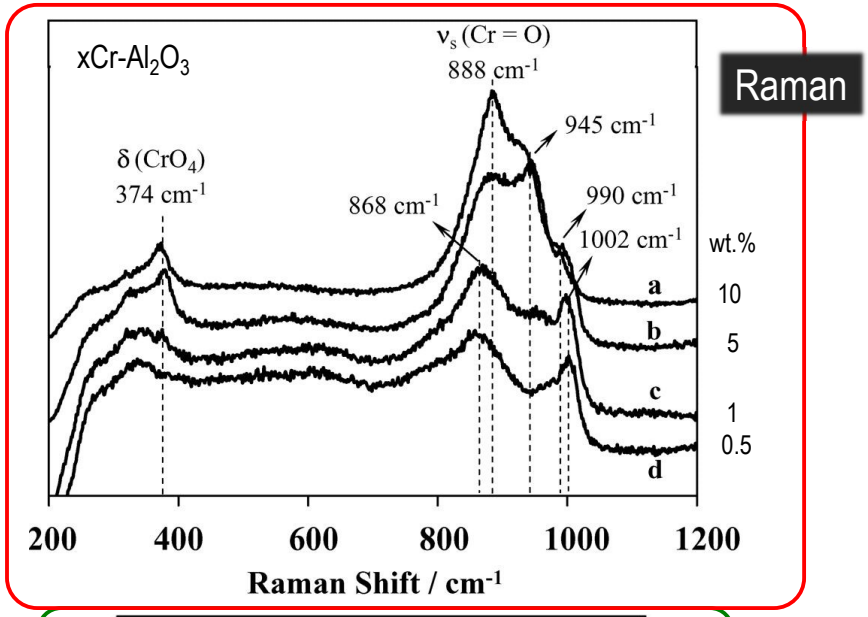
- Coke formation fast on top section of reactor
- Coke is combusted fast in top section of reactor

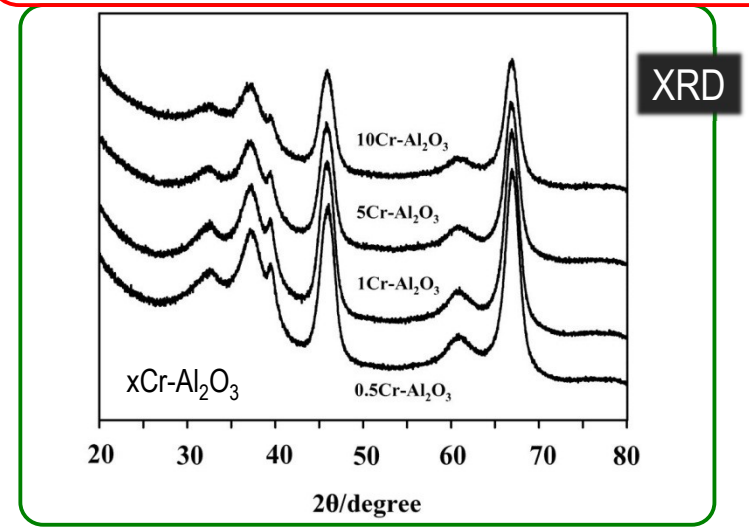
Weckhuysen et al., *Chem. Commun.* 49 (2013) 1518

Examples

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

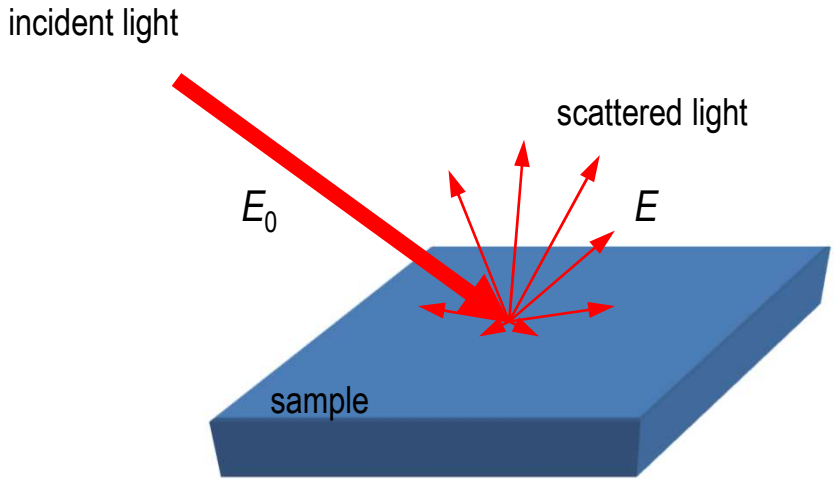






Matam et al., *J. Catal.* **261** (2009) 116

Raman spectroscopy



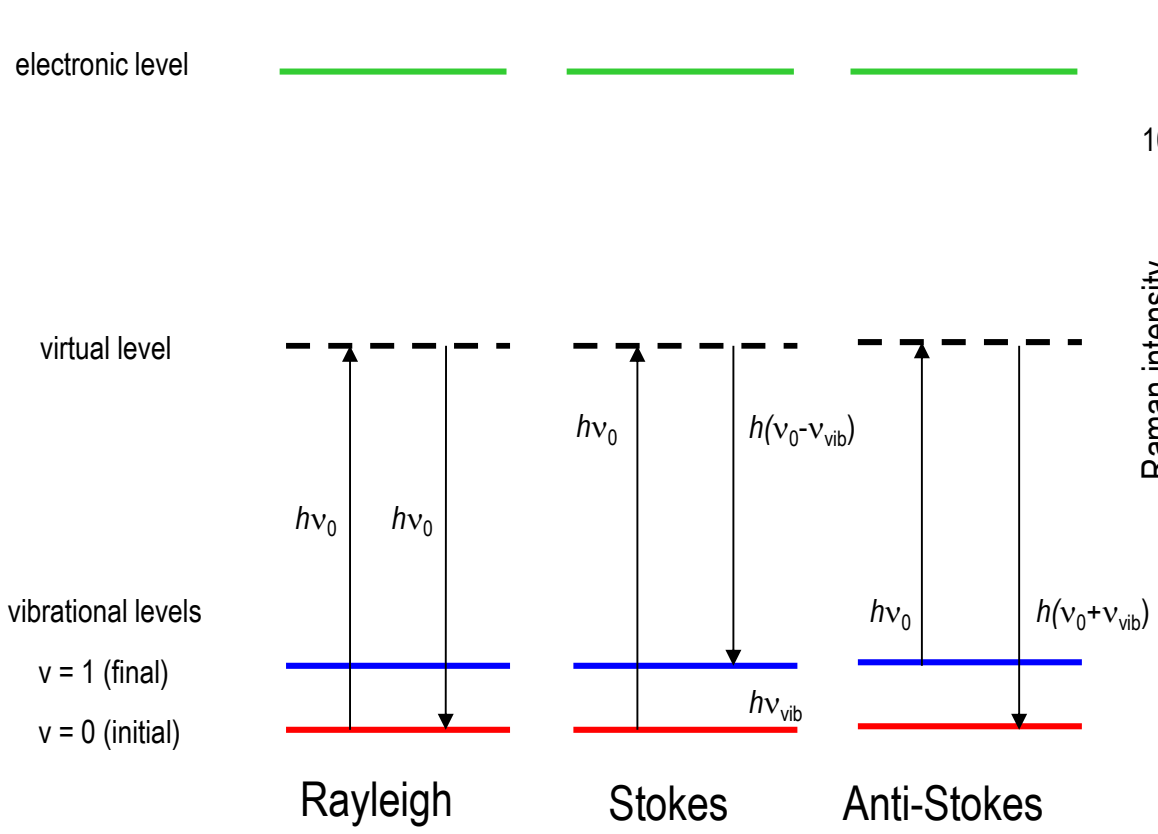
$$E_{vib} = E_0 - E$$

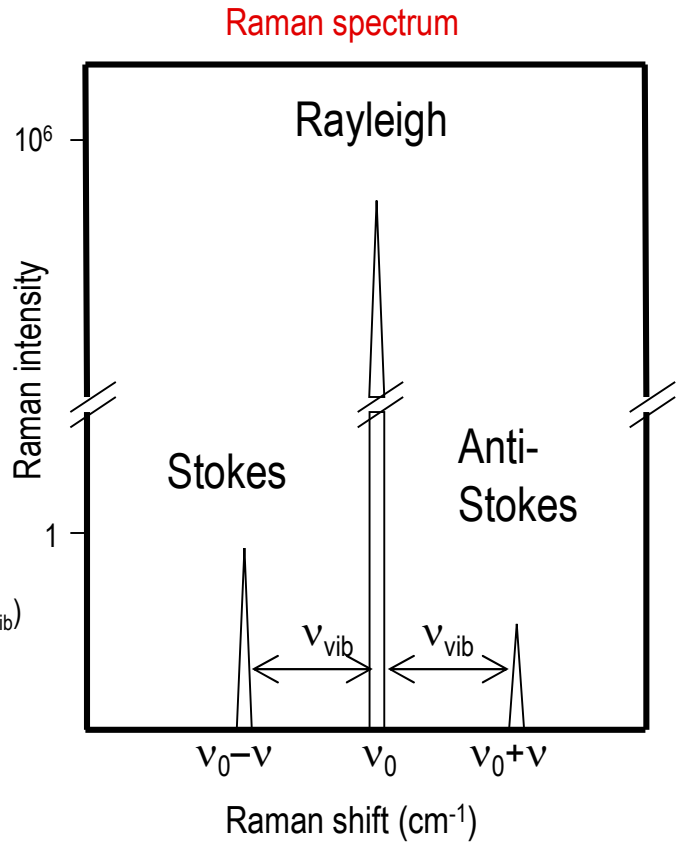
Raman shift

elastic scattering = Rayleigh scattering

inelastic scattering = Raman scattering (ca. 1 over 10^7 photons)

Quantum mechanics approach





Raman effect

- Change of **polarizability**, α
- Intensity of Raman signals depends on:

  - 4th power of ν (4th power law)
  - 2nd power of α
    - properties of molecules
    - strength of bonds

$$E_{sc} = \frac{\alpha^2 (1+\cos^2\theta)}{\lambda^4} E_0$$

  - E_0 = incident beam irradiance
  - α = polarizability of the particle (ease of distortion of the electron cloud)
  - λ = wavelength of the incident radiation
  - θ = angle between incident and scattered ray

covalent bond STRONG bands

ionic bond WEAK bands

- **More scattering at low wavelength** (4th power law), high energy
- Same information contained in Stokes and Anti-Stokes signals
- Same distance from Rayleigh line whatever ν_0

Raman *vs.* Infrared

Selection rules

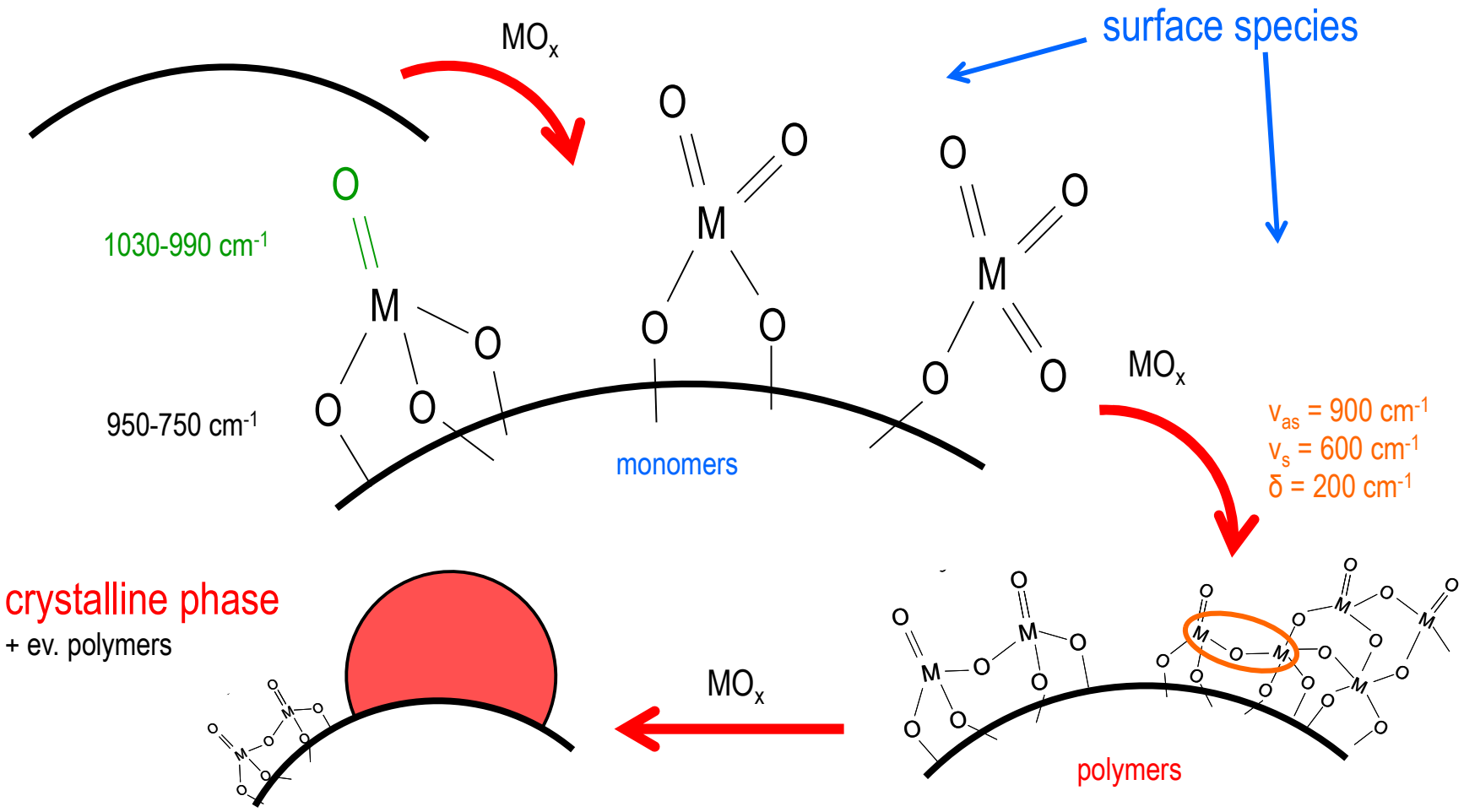
$$\left(\frac{\partial \mu}{\partial Q}\right)^2 \neq 0$$

- high absorption for polar bonds (C=O, H_2O, NH, etc.)
- only asymmetric vibrations IR active

$$\left(\frac{\partial \alpha}{\partial Q}\right)^2 \neq 0$$

- high absorption for easily polarizable bonds
  - large electron clouds
  - not polar
- H_2O is a very weak Raman scatterer
- C=C double bonds strong Raman scatterers
- symmetric and asymmetric vibrations can be Raman active

Supported metal oxides

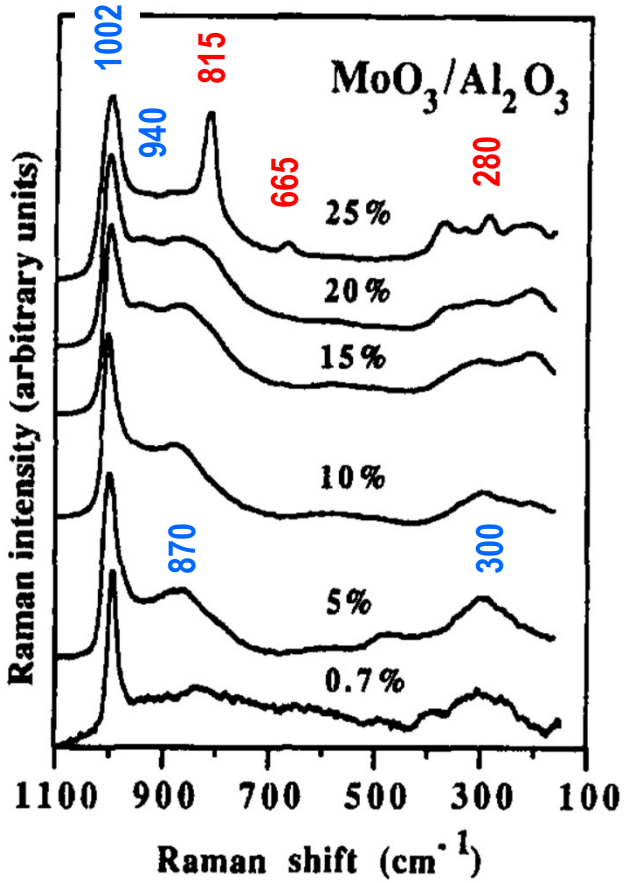


Supported metal oxides

- Monomeric and polymeric species

Advantage over IR

Very weak signals from support oxides as SiO_2 and Al_2O_3 at 800–1100 cm^{-1}

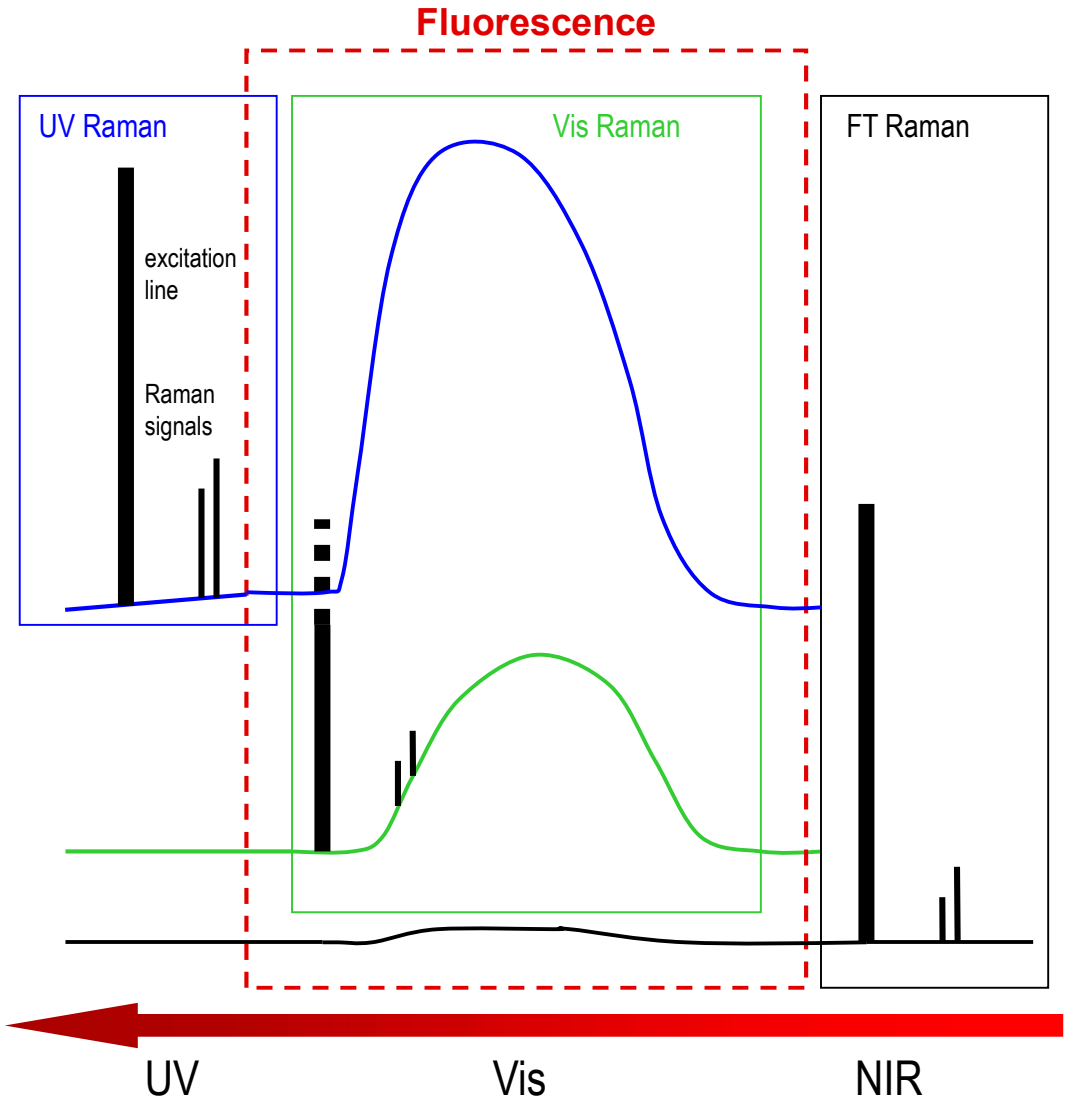


surface MoO_3
crystalline MoO_3

MoO_3/Al_2O_3
dehydrated at 500^0C

Wachs, *Catal. Today* 27 (1996) 437

Fluorescence and Raman signals



10^7 stronger than Raman scattering

Emission of visible light during a time posterior to the sample irradiation

E_{sc} proportional to ν^4

Fluorescence proportional to ν

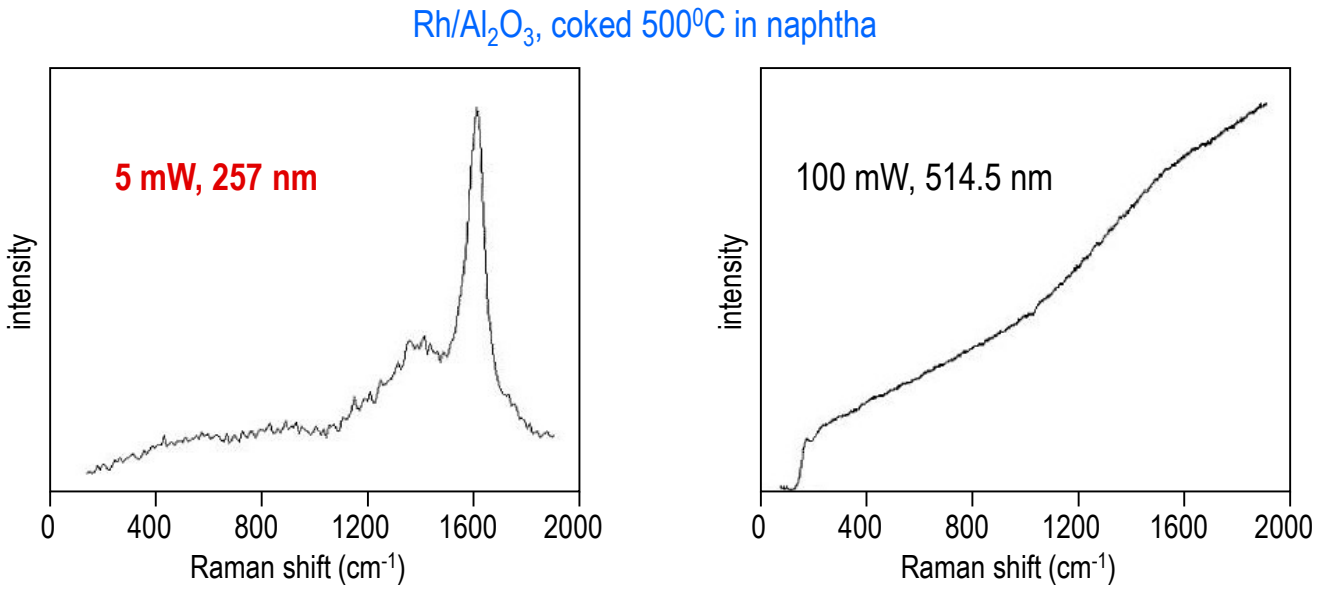
Solution

- IR excitation
- UV excitation
- Pulsed Lasers

Fluorescence and Raman signals

- UV-Raman
  - No fluorescence

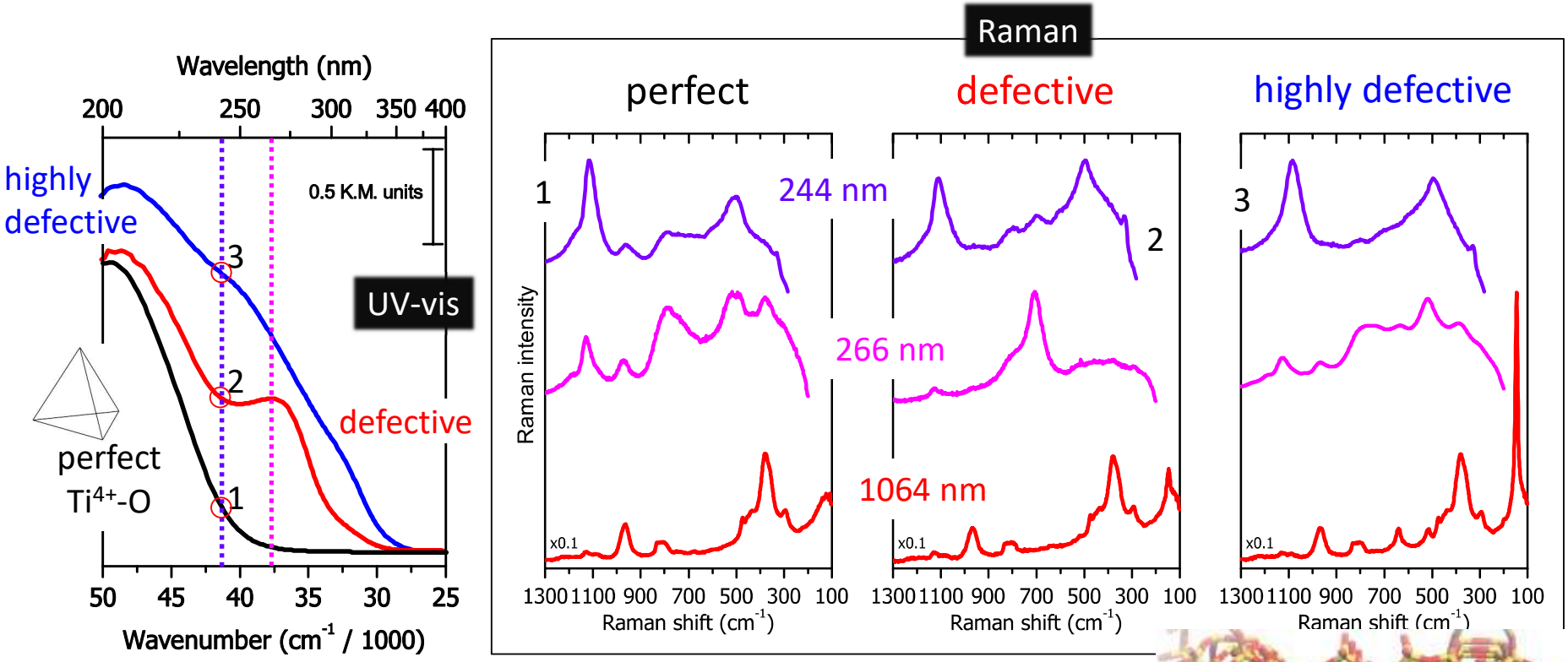
  (only few molecules fluoresce below 260 nm)



Stair et al., *J. Vacuum Technol. A* **15** (1997) 1679

Resonance Raman spectroscopy

- **Multiwavelength approach to achieve different resonances | TS-1**

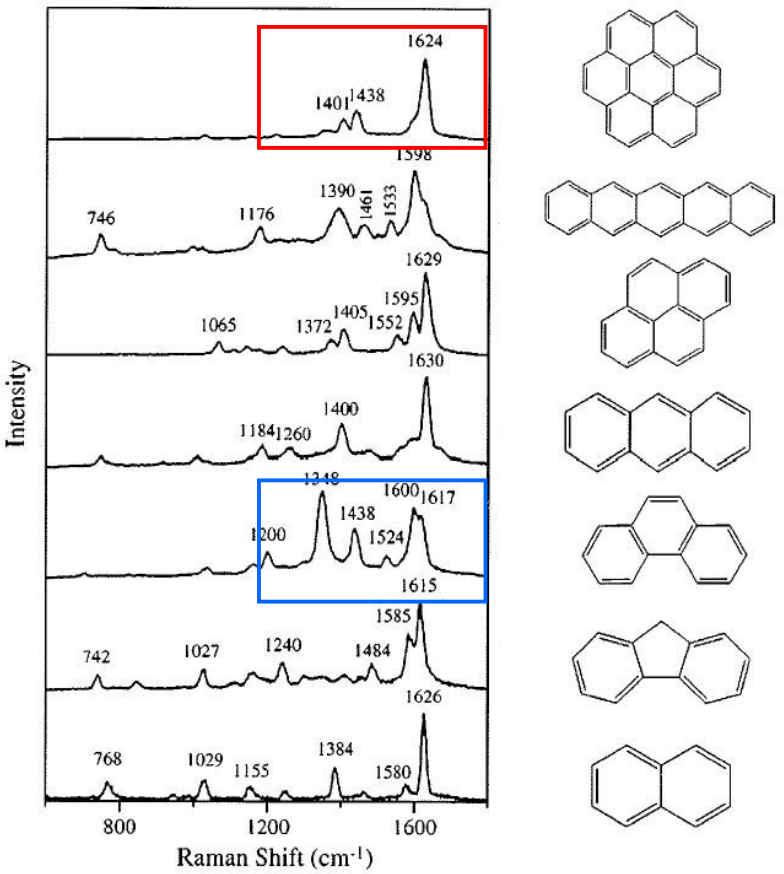


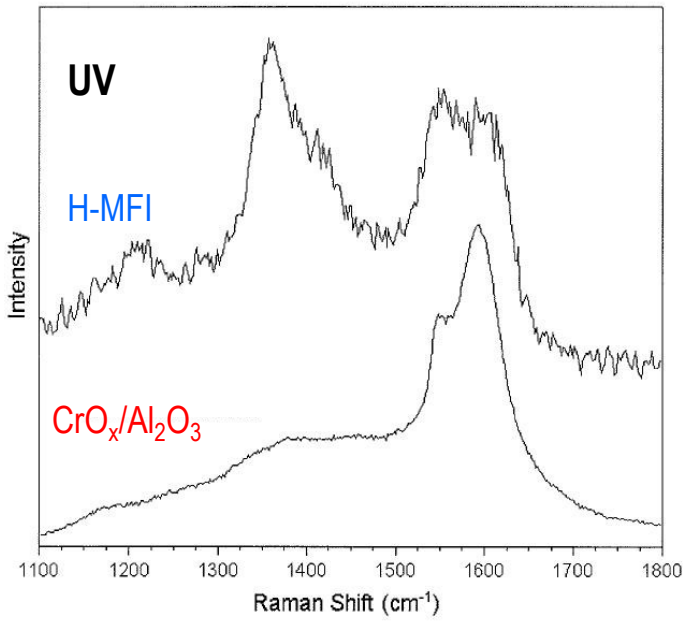
- 244 nm ⟶ perfect sites
- 266 nm ⟶ defect sites, perfect sites + ligands
- 1064 nm (out of resonance) ⟶ SiO_2 framework, bulk TiO_2

courtesy of M. Signorile, UniTO

Applications

- (Polyaromatic) Coke formation and characterization





Coke classification
1D topology, chain-like
2D topology, sheet-like

Coke from:
H-MFI: methanol-to-hydrocarbons (MTH)
CrO_x/Al_2O_3: C_3H_8 dehydrogenation (ODH)

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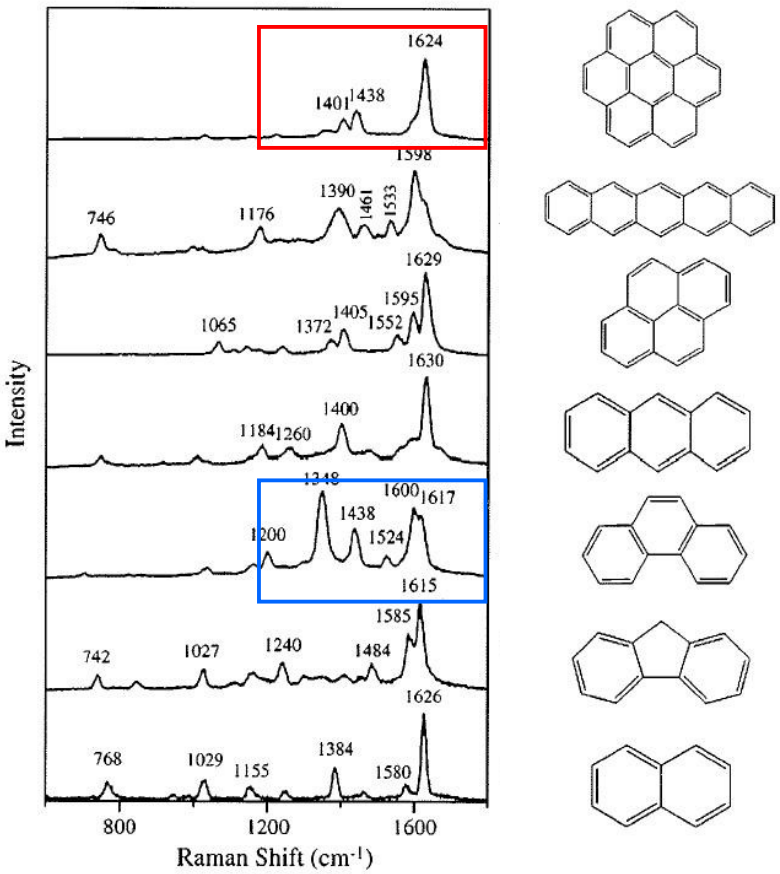
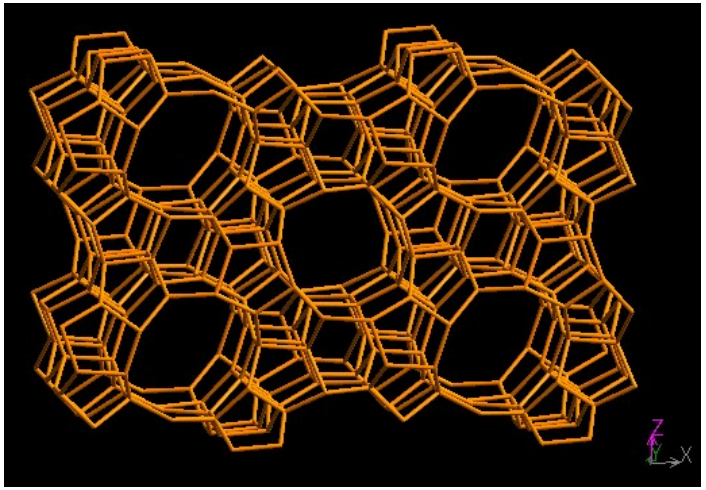
Applications

- (Polyaromatic) Coke formation and characterization





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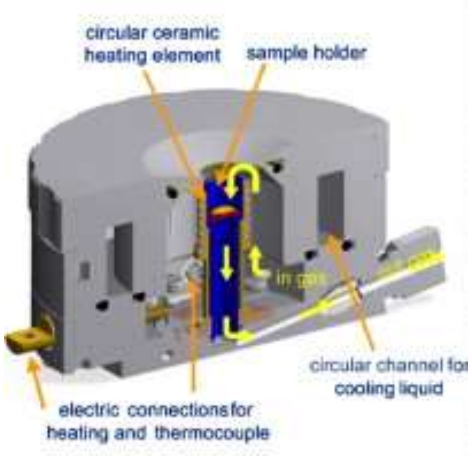
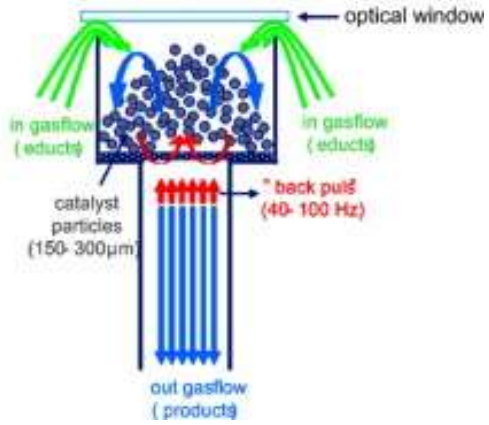
Stair, *Adv. Catal.* 51 (2007) 75

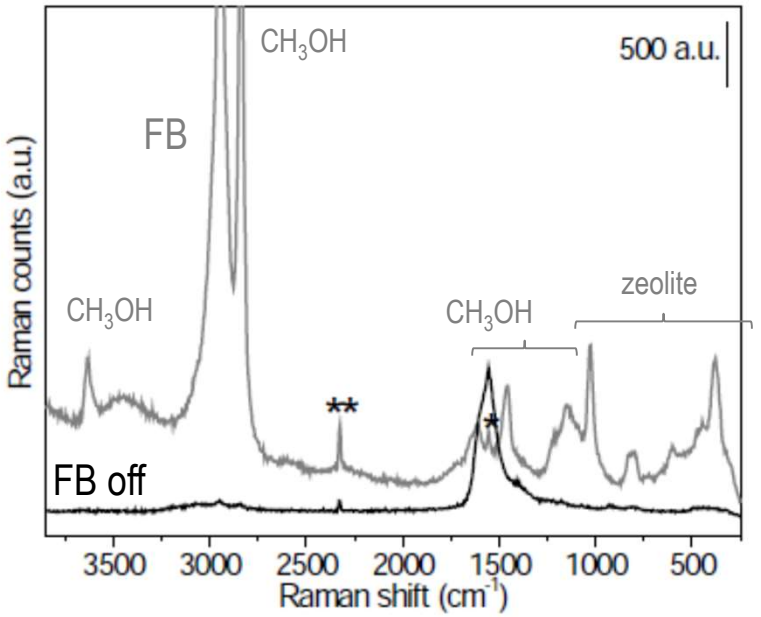
Applications

- Fluidized bed reactor cell





CH_3OH steam reforming (r.t.) on H-ZSM5
λ= 244 nm



Laser induced CH_3OH decomposition

Beato et al., *Catal. Today* 205 (2013) 128