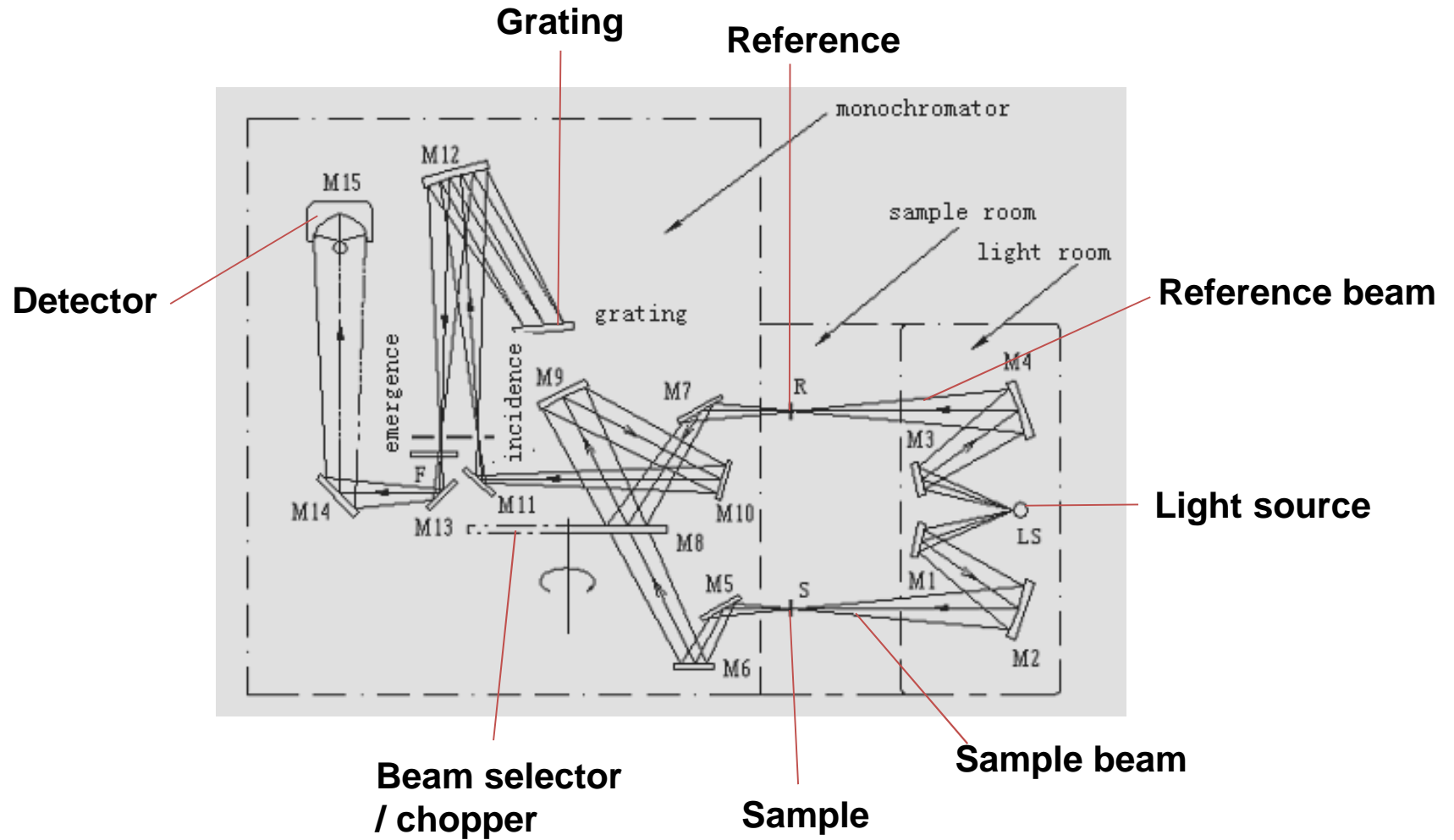


Infrared spectroscopy

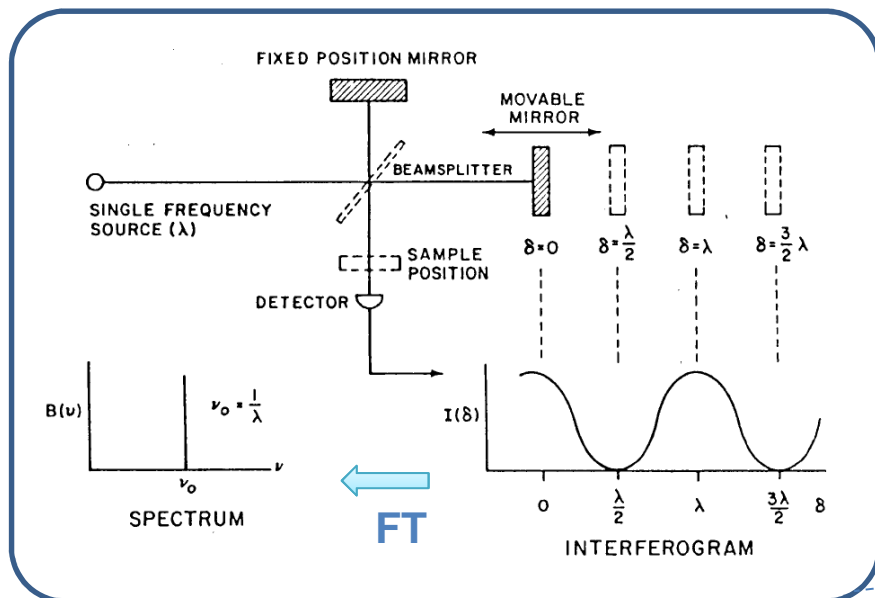
Instrumentation
Techniques
Examples

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

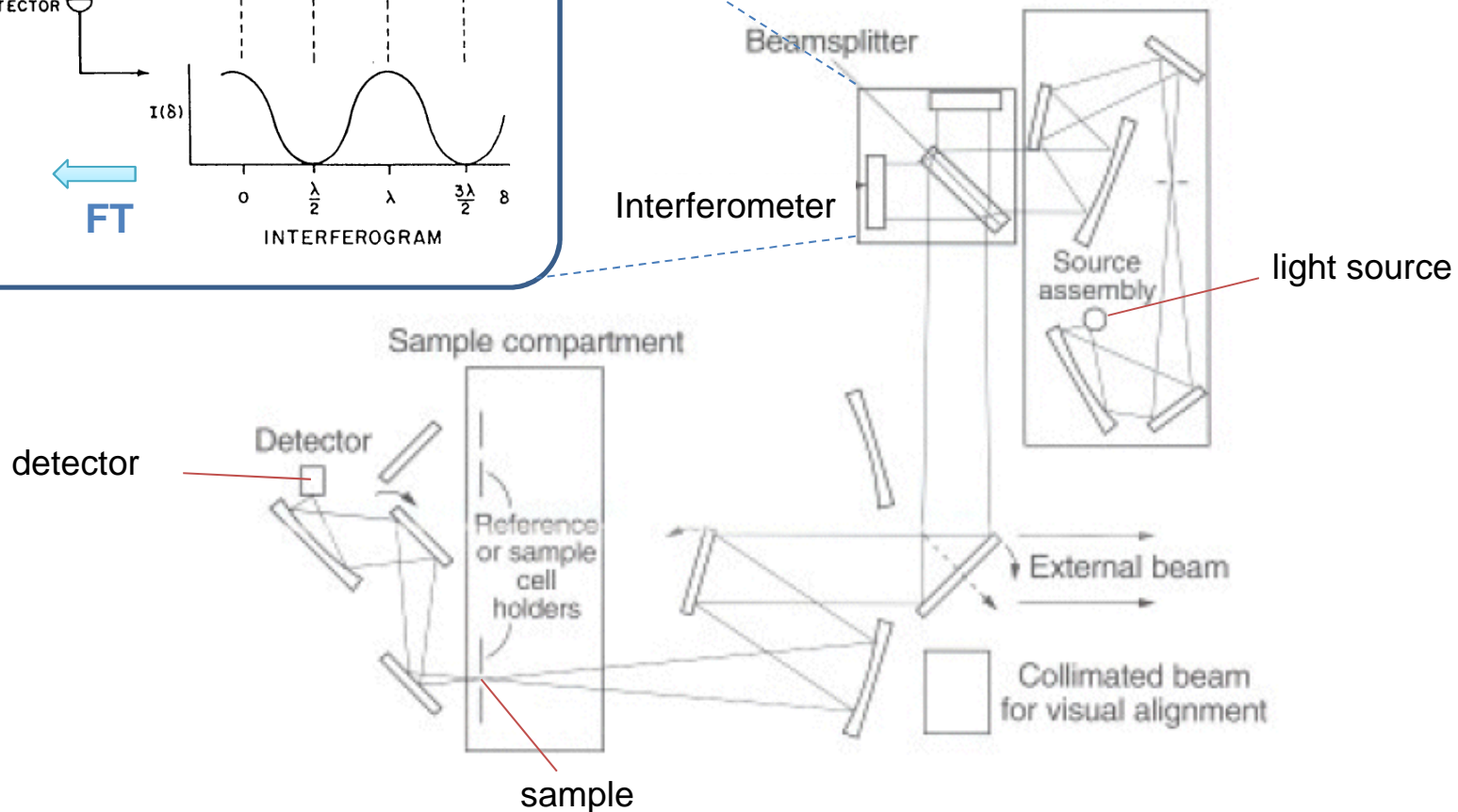
Double beam spectrometer



Fourier transform spectrometer



Currently most of IR spectrometers are FT-IR



Dispersive vs. FT

FT-IR spectrometer has significant advantages over dispersive one

- **Multiplex (Fellgett) advantage**

All source wavelengths are measured simultaneously

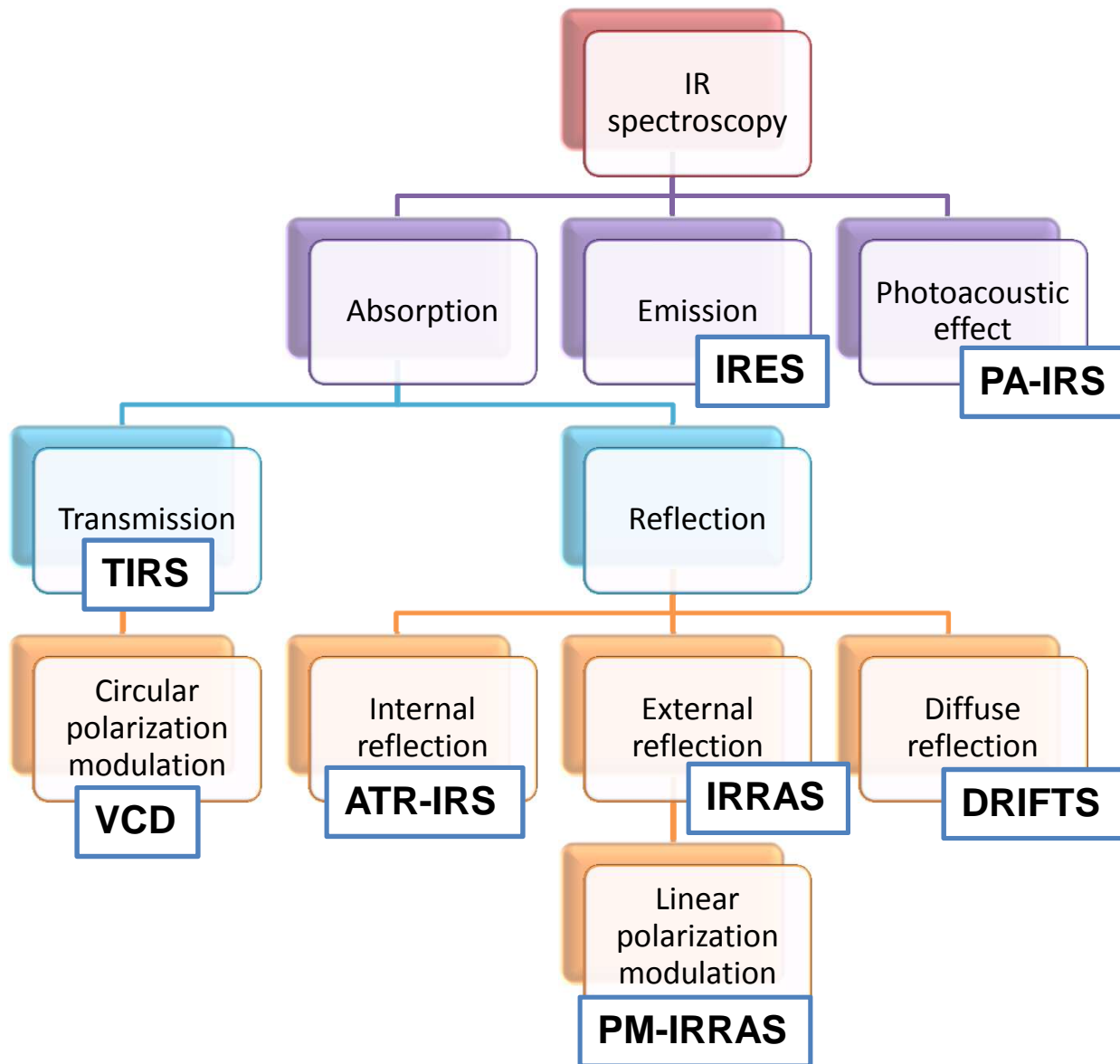
- **Throughput (Jacquinot) advantage**

For the same resolution, the energy throughput in an interferometer can be higher → the same S/N as a dispersive-IR in a much shorter time

- **Precision (Connes) advantage**

The wavenumber scale of an interferometer is derived from a HeNe laser that acts as an internal reference for each scan

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

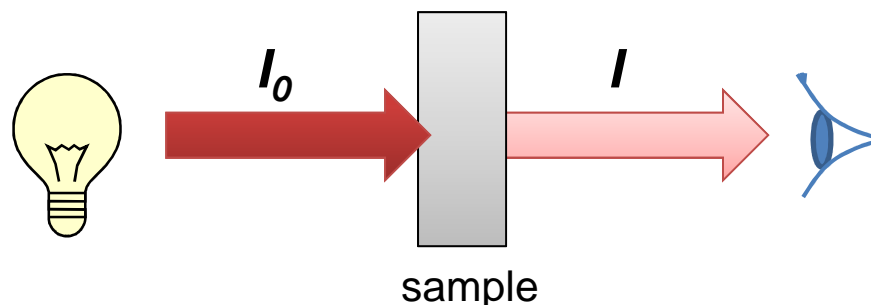
IRRAS: infrared reflection-absorption spectroscopy

PM-IRRAS: polarization-modulation IRRAS

DRIFTS: diffuse reflectance infrared Fourier transform spectroscopy

Transmission IR spectroscopy (TIRS)

■ 'Straight' IR light absorption



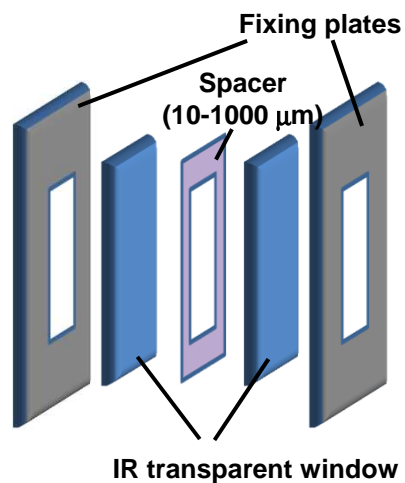
- Popular for detections of gas and liquid samples
- Solids have to be diluted or shaped in a very thin film
- Quantification is more straightforward than other IR techniques

In heterogeneous catalysis

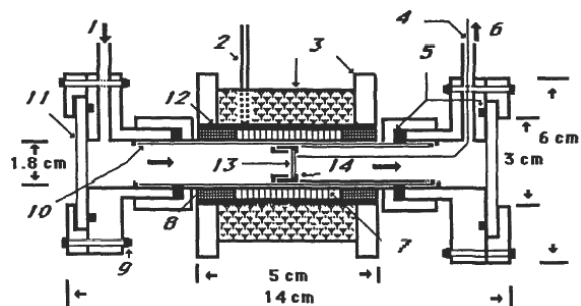
- Popular for *in situ* investigations
- Typically a very thin self-supporting catalyst disk is used
- Powder sample dispersed on transparent grid (W)
- Mass transfer can be an issue

Transmission IR spectroscopy (TIRS)

■ Liquid samples

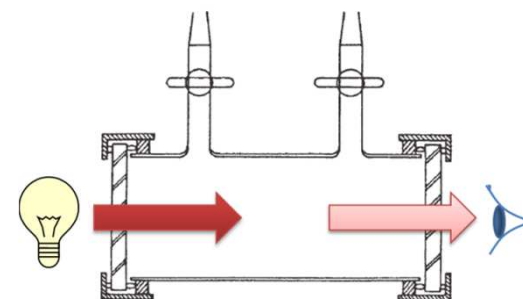


■ Gas-solid Catalysis !



heating up to 800°C
Larkins et al., *Appl. Spec.*, 42 (1988) 906

■ Gas samples



Specac



Temperature-controlled cell
[ca. 200 – 500 K]



Transmission IR spectroscopy (TIRS)

■ *In situ* cells for heterogeneous catalysis studies

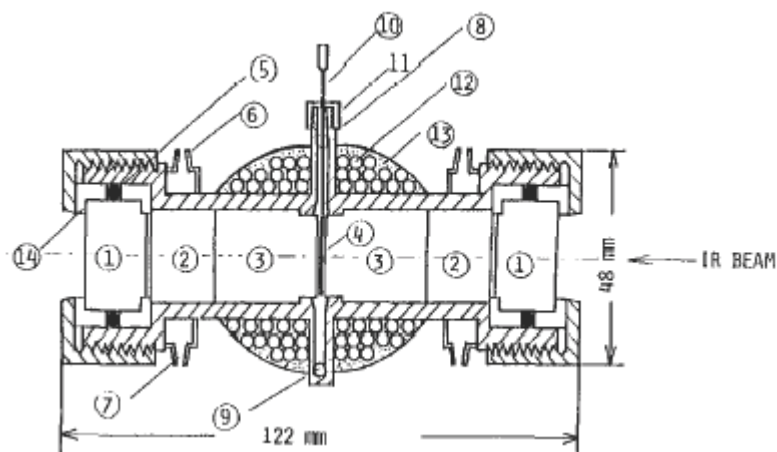
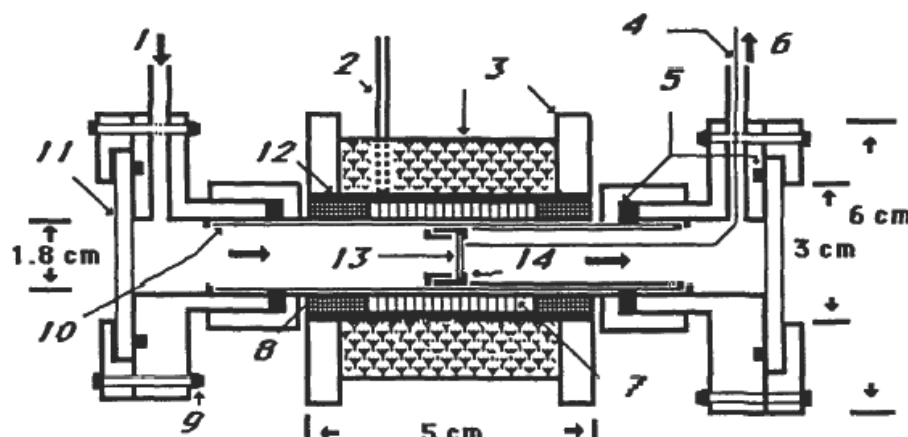


FIG. 1. *In situ* high-pressure and temperature IR cell. 1: CaF_2 window; 2: KBr rod (1); 3: KBr rod (2); 4: catalyst disk; 5: Viton O-ring; 6: cooling water inlet; 7: cooling water outlet; 8: gas inlet; 9: gas outlet; 10: thermocouple; 11: swagelok fitting; 12: heater; 13: asbestos molding; 14: Teflon® window holder.

Arakawa et al. *Appl. Spec.*, 40, 884 (1986)

heating up to 500°C
pressure up to 10 MPa



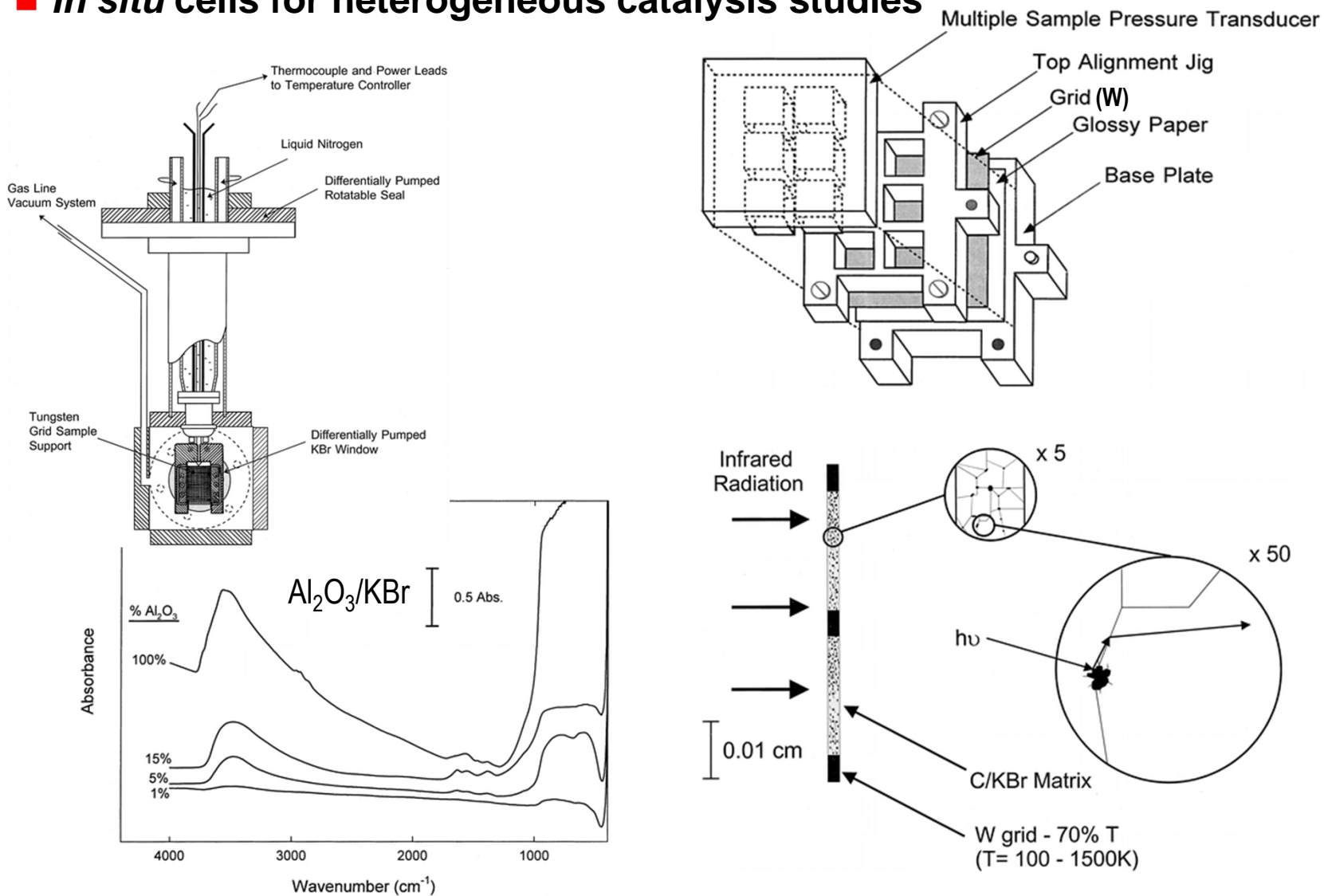
Larkins et al.
Appl. Spec., 42, 906 (1988)

heating up to 800°C

FIG. 1. The high-temperature IR cell: 1, gas inlet; 2, electrical connection; 3, insulating material; 4, Viton O-ring; 5, thermocouple; 6, gas outlet; 7, heating element; 8, ceramic; 9, nut and bolt; 10, Vycor tubing; 11, CaF_2 window; 12, Al_2O_3 tubing; 13, sample; 14, stainless steel sample holder.

Transmission IR spectroscopy (TIRS)

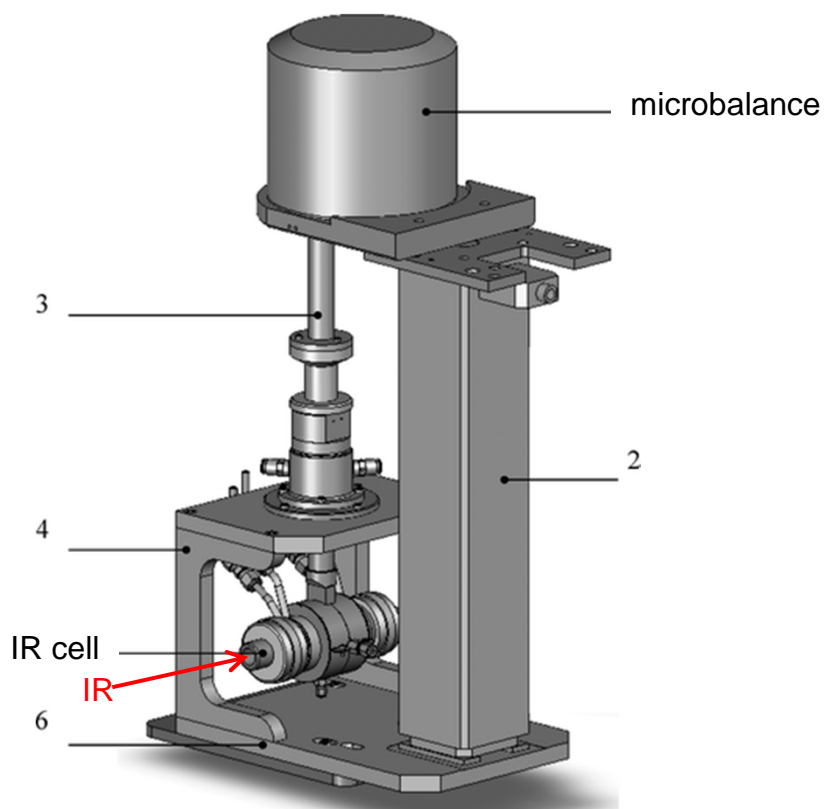
■ *In situ* cells for heterogeneous catalysis studies



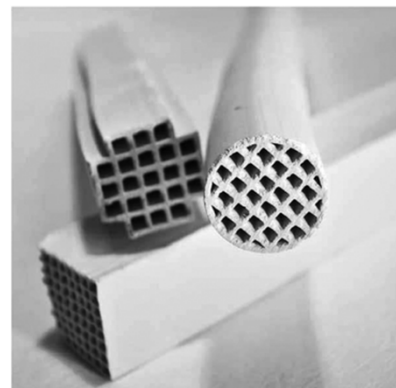
Transmission IR spectroscopy (TIRS)

■ *In situ* cells

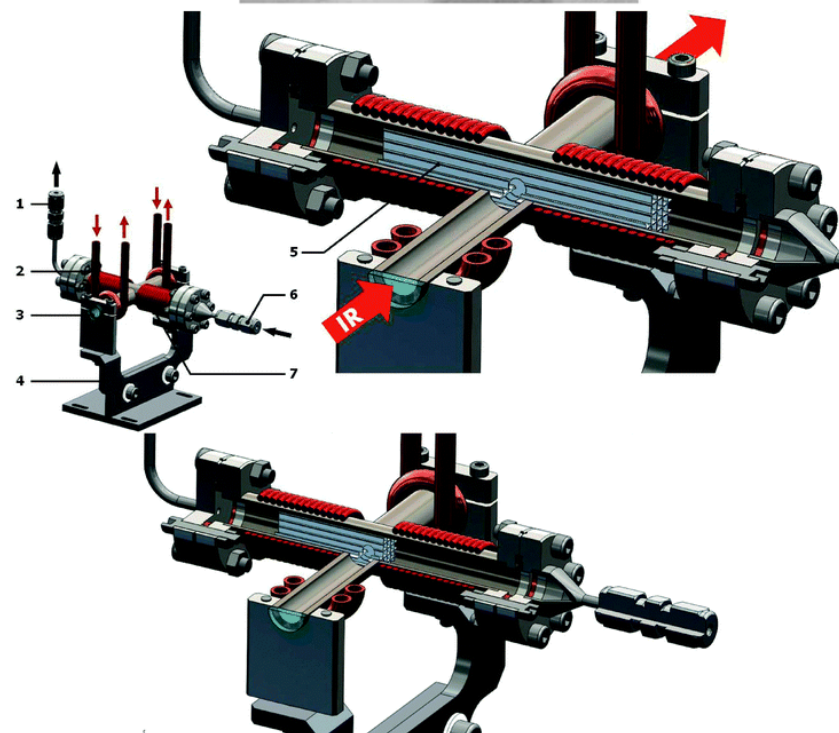
combined TG-FTIR



Bazin et al., *Dalton Trans.* 39 (2010) 8432



FTIR of
monoliths



Rasmussen et al., *PCCP* 14 (2012) 2171

Transmission IR spectroscopy (TIRS)

■ Solid samples

Large solid particles generally absorb too much IR light, therefore particles should be small and also special preparations are often necessary.

Most popular sample preparation methods (for mid-IR):

■ Alkali halide disk method

- Typically solid samples are diluted in KBr and ground
- Then pressurized to form a disk

■ Mull method

- Most common one is Nujol (liquid paraffin)
- Samples are ground and suspended in one or two drops of a mulling agent
- Followed by further grinding until a smooth paste is obtained

■ Film method

- By solvent casting or melt casting

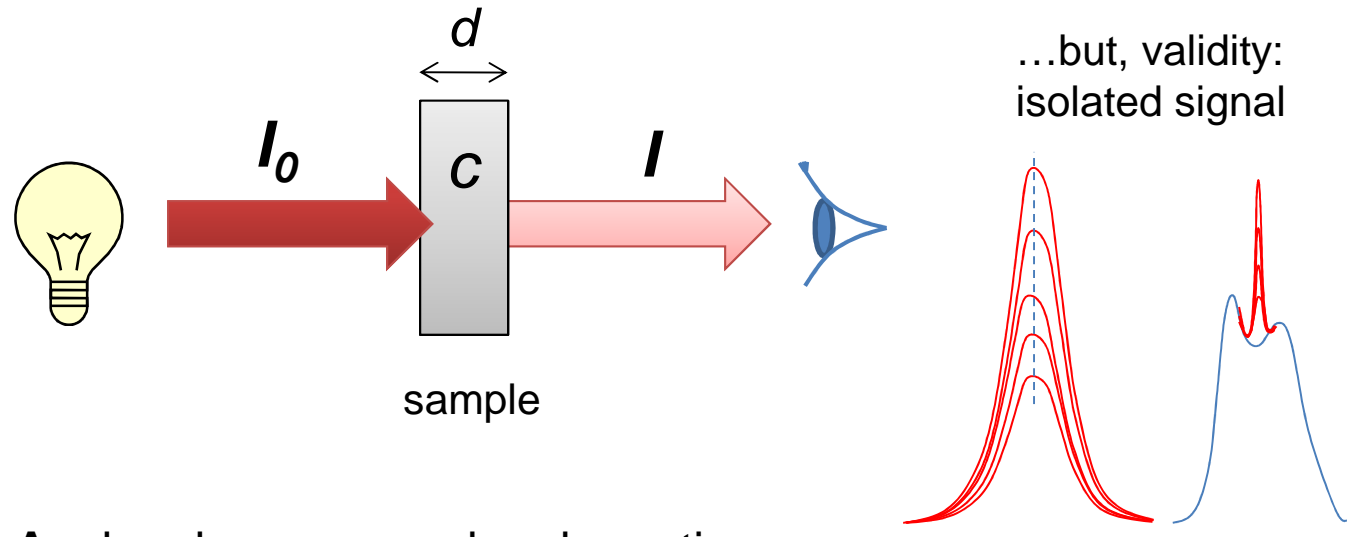
Transmission IR spectroscopy (TIRS)

- Quantification: most straightforward than other techniques

Lambert-Beer law

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

$$A = -\log(T) = -\log\left(\frac{I}{I_0}\right) = \epsilon cd$$



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

Transmission IR spectroscopy (TIRS)

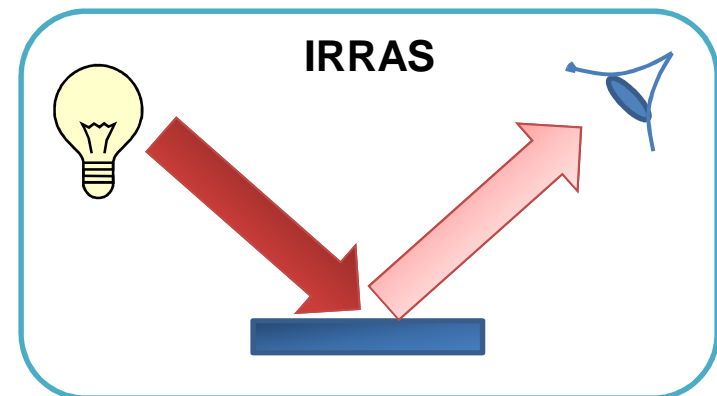
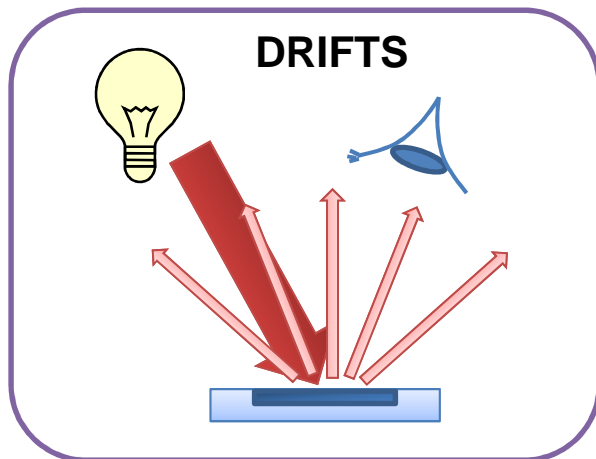
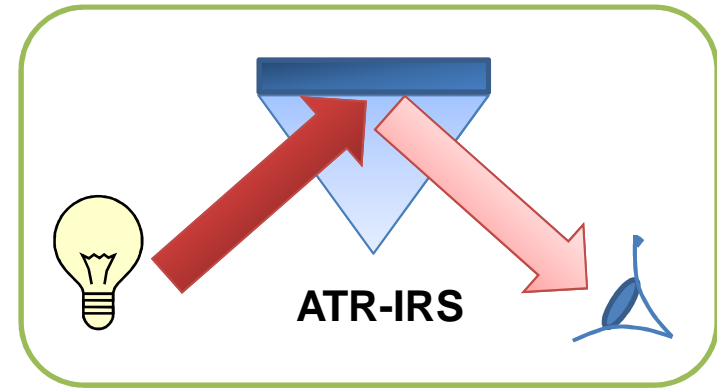
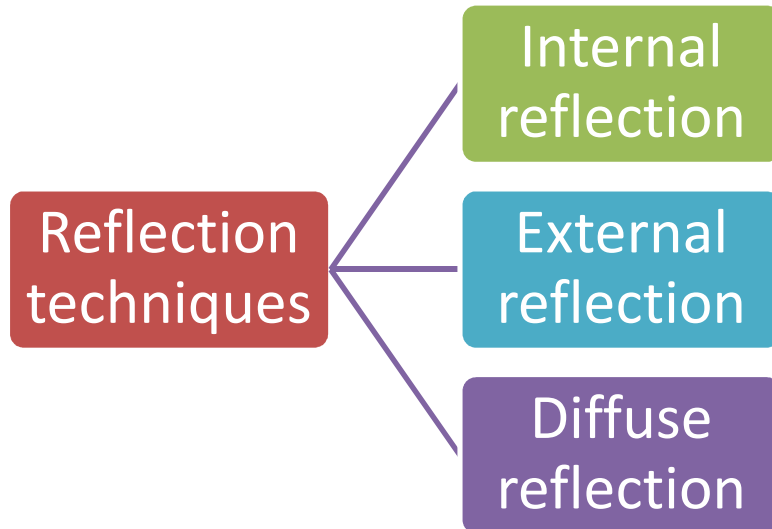
■ Common window materials

Material	Useful range / cm^{-1}	Refractive index	Properties
NaCl	40'000-600	1.52	Soluble in water; slightly soluble in alcohol; low cost
KBr	43'500-400	1.54	Soluble in water; slightly soluble in alcohol; hygroscopic
CaF ₂	77'000-900	1.40	Insoluble in water; chemically resistant; mechanically strong
BaF ₂	66'666-800	1.45	Low water solubility; soluble in acids and NH ₄ Cl
CsI	42'000-200	1.74	Soluble in water and alcohol; hygroscopic
ZnSe	20'000-500	2.43	Soluble in strong acid

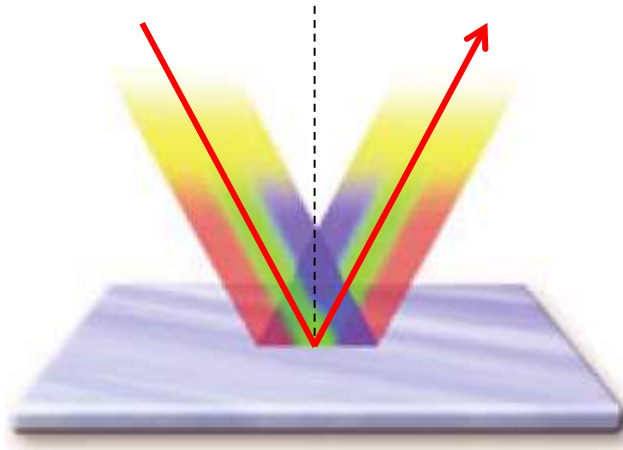
Reflection based techniques

■ Aim for heterogeneous catalysis studies

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

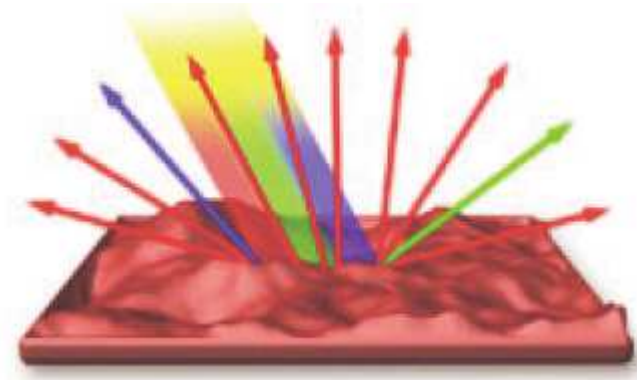


Specular vs. diffuse reflection



**Specular reflection
(smooth surface)**

Surface smoothness like mirror = reflection and incident angles are equal

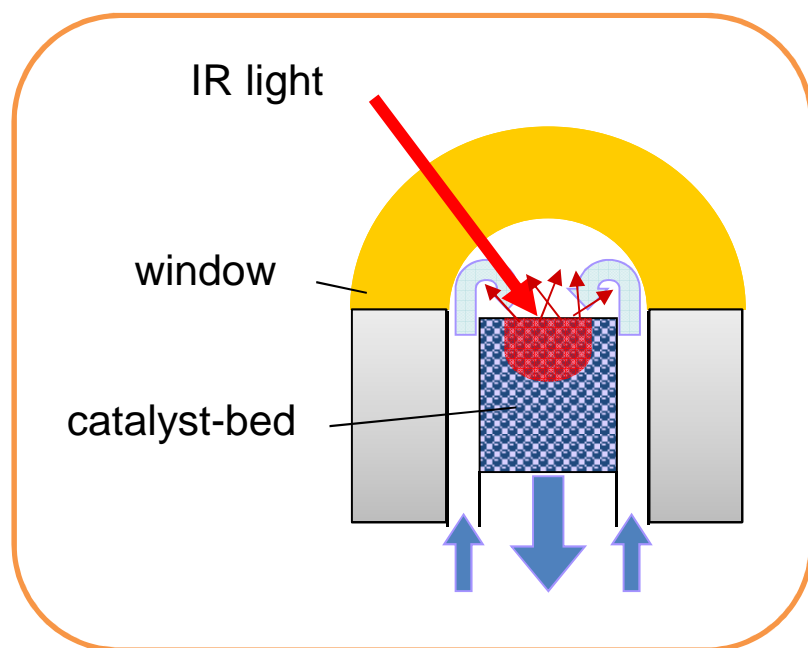


**Diffuse reflection
(rough surface)**

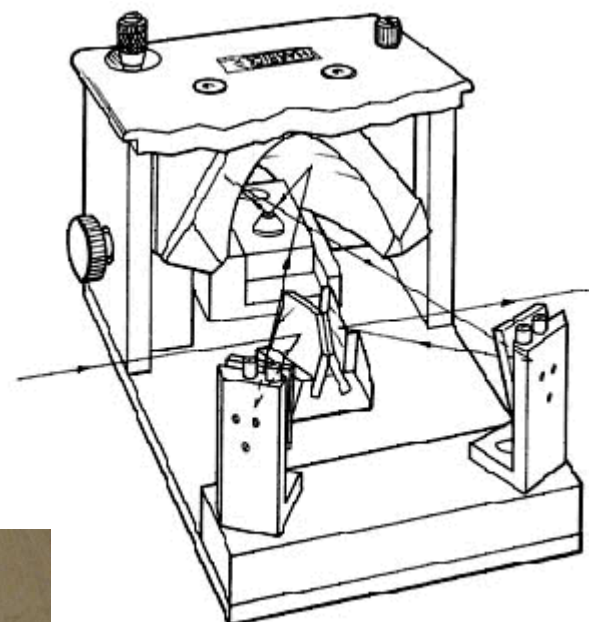
Incident light is reflected to a number of directions due to surface roughness

Diffuse reflectance (DRIFTS)

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



IR light diffuses into the catalyst bed



The praying mantis
(very popular, highly efficient light collection)



In situ DRIFTS cell

Diffuse reflectance (DRIFTS)

qualitative analysis

Very sensitive to surface species due to the diffuse reflective nature of the method; the detected light can be multiply reflected at powder surfaces

quantitative analysis

It can be very complicated; the spectra are largely influenced by a number of experimental parameters such as shape and size of particles, refractive index of particles, absorption characteristics of particles, and porosity of the powder bed

A popular quantitative analysis method is using Kubelka-Munk (K-M) function to transform reflectance to a kind of absorbance (K-M) unit

Kubelka-Munk function

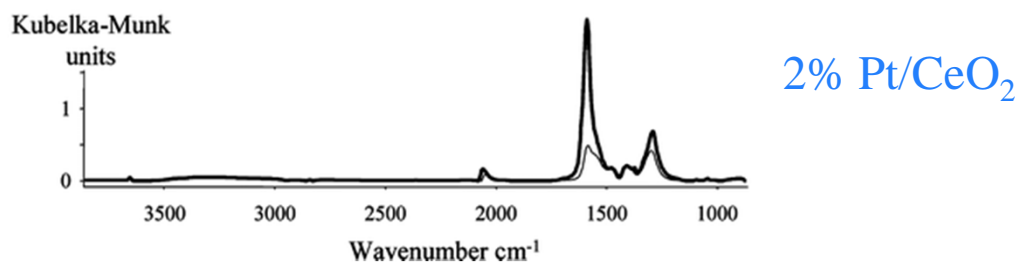
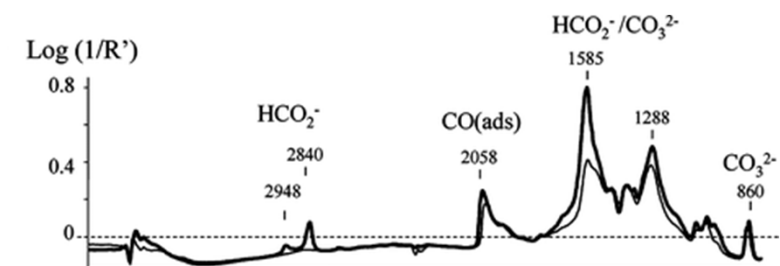
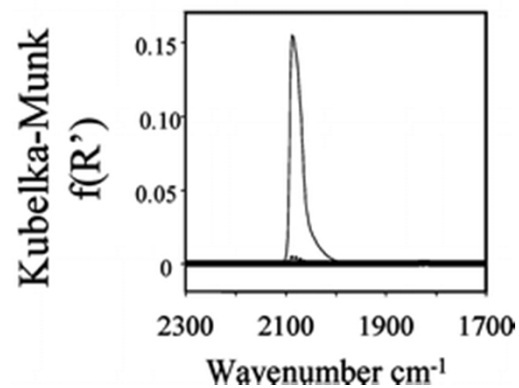
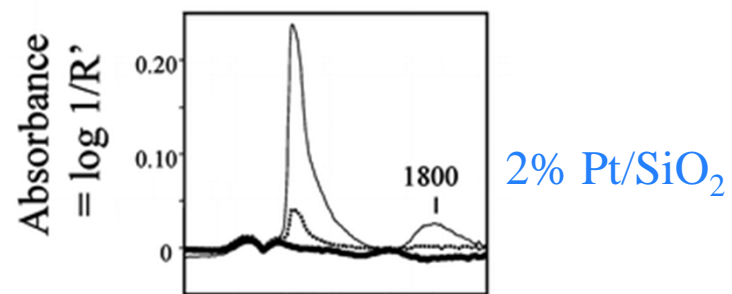
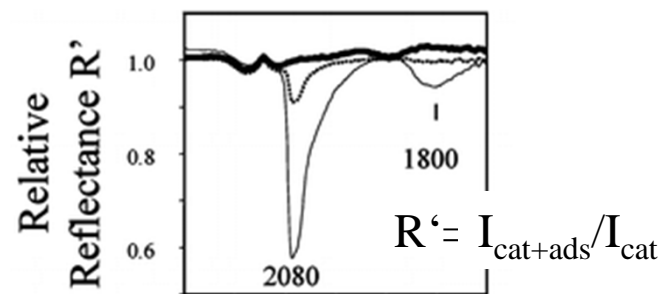
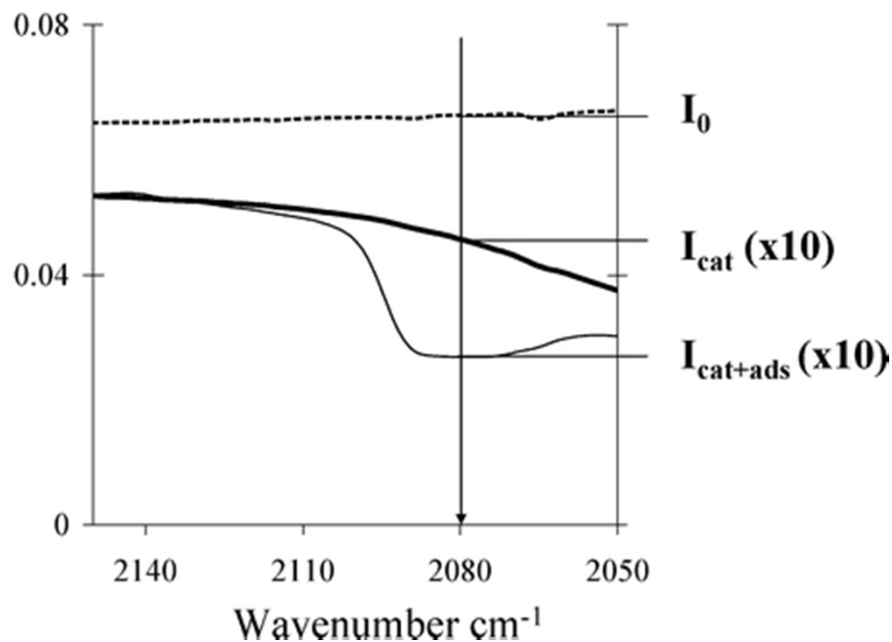
$$f(R) = \frac{(1-R)^2}{2R} = \frac{k}{s}$$

k : molar absorption coefficient,
 $k=2.303\alpha c$, α : absorptivity,
 c : concentration, s : diffusion
(scattering) coefficient

There is a solid (approximated) theory behind and the K-M function is widely used; however its applicability and accuracy for highly absorbing and non-absorbing samples is questionable

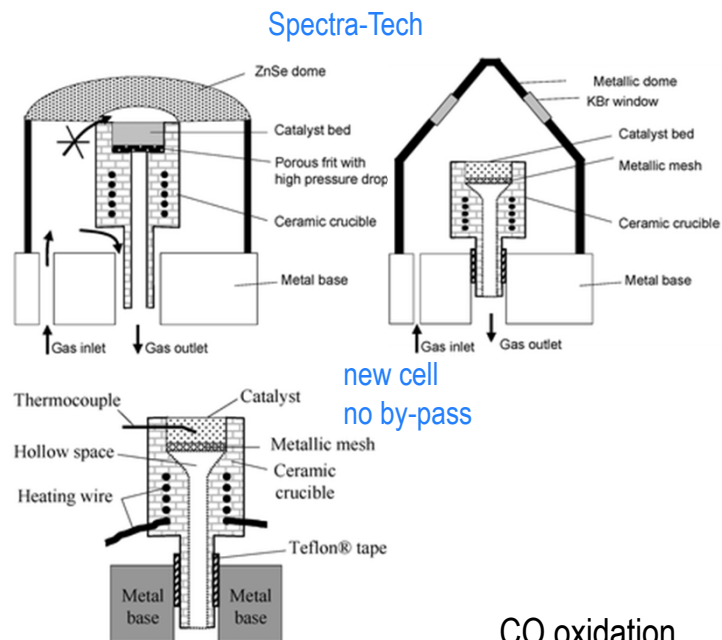
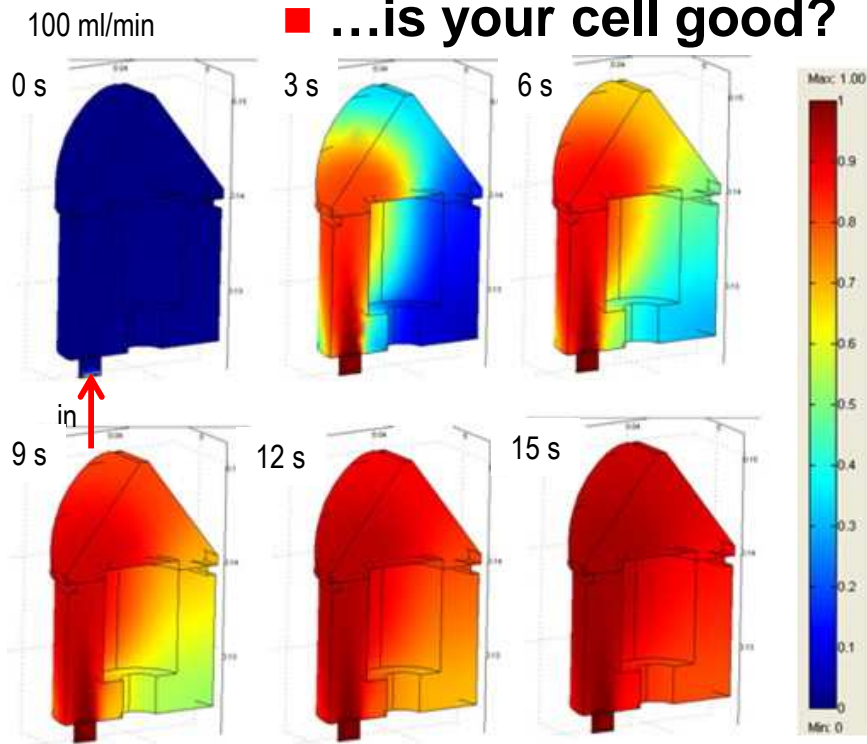
recent discussion on this topic: Sirita et al., *Anal. Chem.* 79 (2007) 3912

Diffuse reflectance (DRIFTS)

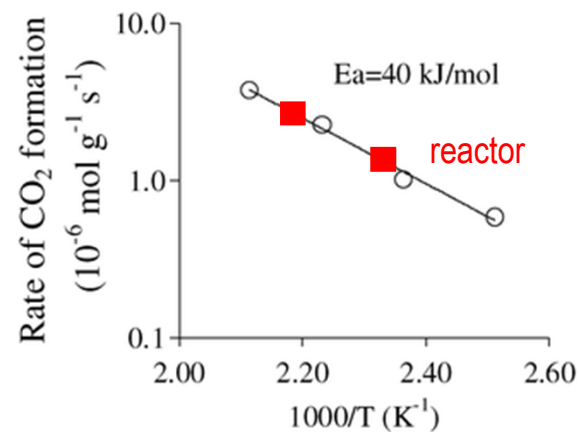
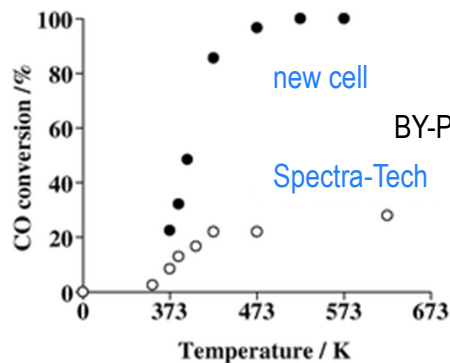
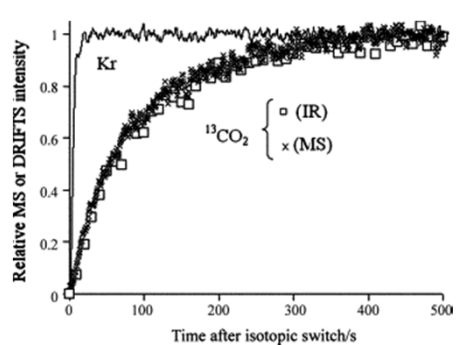


Diffuse reflectance (DRIFTS)

■ ...is your cell good?



CO oxidation
DRIFT cell vs. microreactor



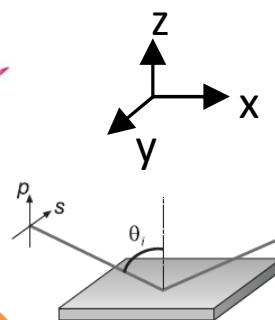
Meunier et al., *Appl. Catal. A* 340 (2008) 196

Meunier et al., *J. Catal.* 247 (2007) 277

Reflection-absorption (IRRAS)

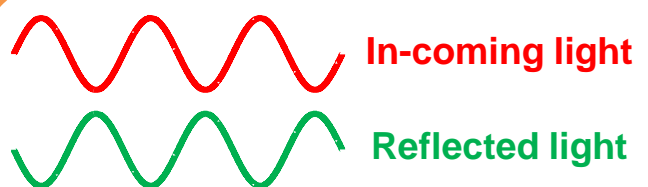
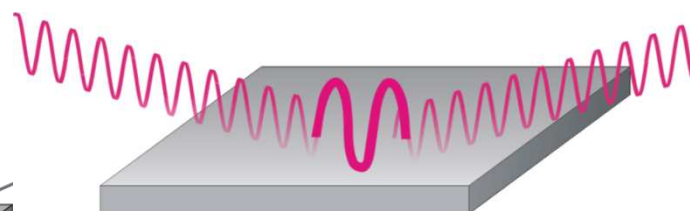
- Also RAIRS; specular/external reflection method

Perpendicular (s-) polarization (y-axis)



Parallel (p-) polarization (x, z-axis)

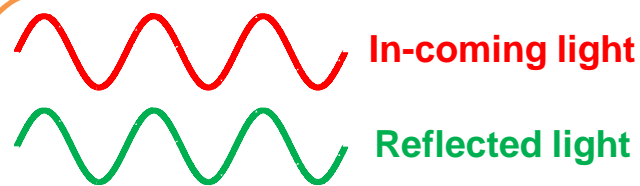
Parallel: parallel to the plane of incident light



Net electric field
near surface

Destructive interference

This s-polarization does not contain information about surface species



Net electric field
near surface

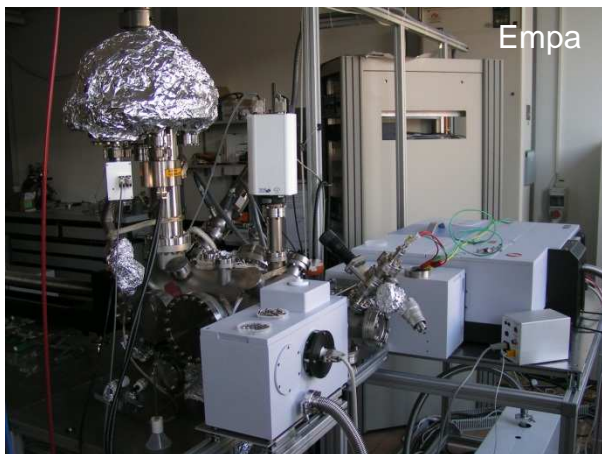
Constructive interference

This p-polarization is used for IRRAS

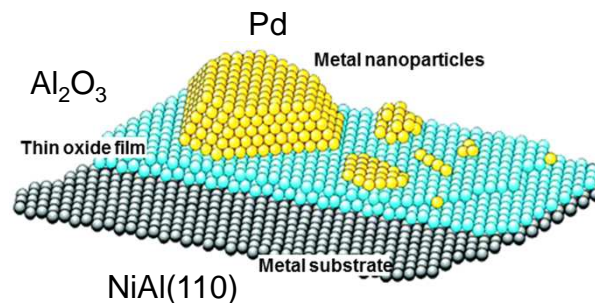
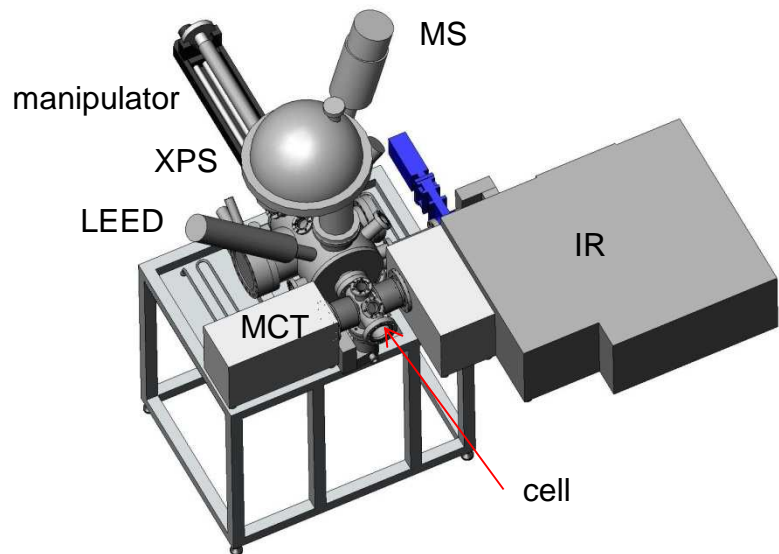
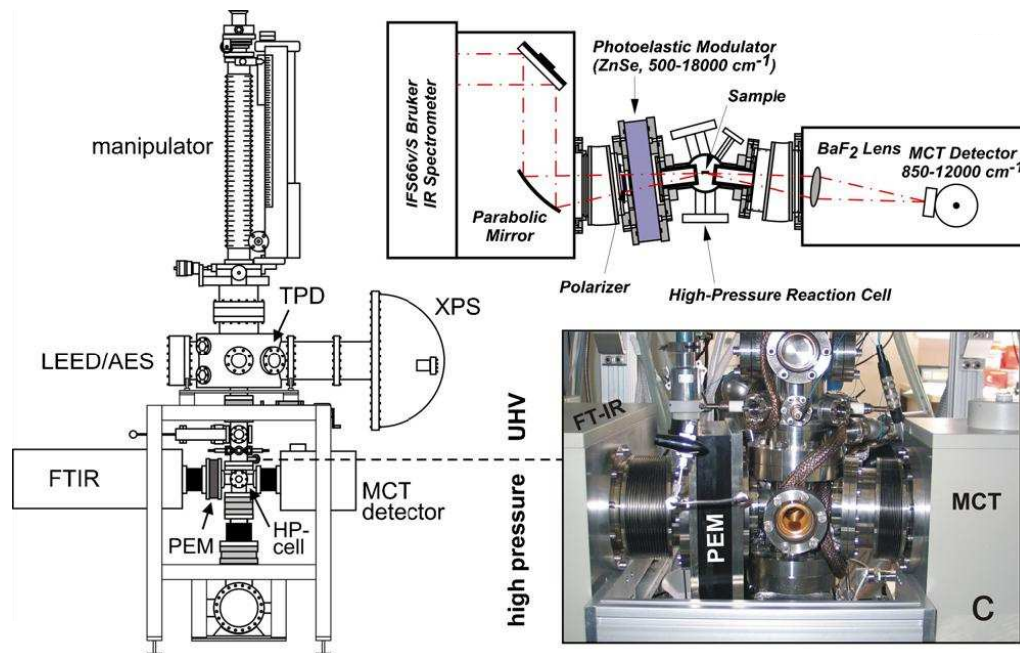
Reflection-absorption (IRRAS)

■ Model system investigation

- single crystals
- well-defined nano-particles



Rupperechter, Catal. Today 126 (2007) 3

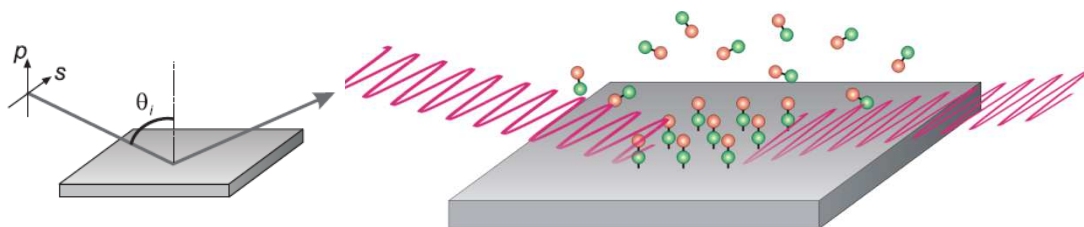


Phase-modulation IRRAS (PM-IRRAS)

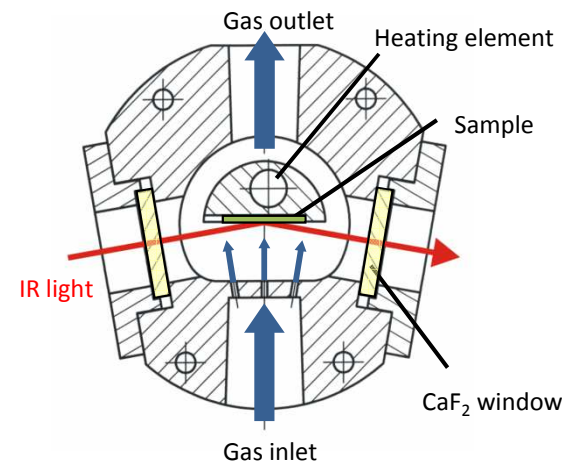
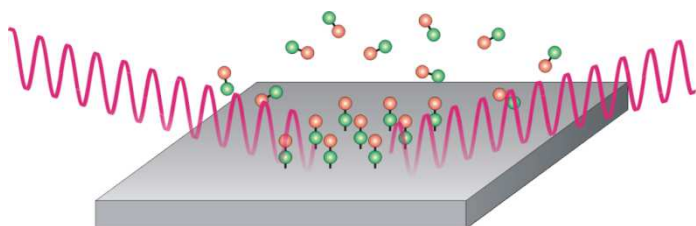
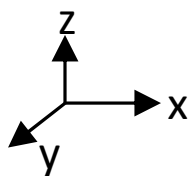
■ Generation of 2 polarizations (photoelastic modulator)

- excellent gas-phase compensation
- non-UHV experiments possible
- highly sensitive, time-resolved studies possible

Perpendicular (s-) polarization (y-axis)



Parallel (p-) polarization (x, z-axis)



Urakawa et al., *J. Chem. Phys.* 124 (2006) 054717

$$R_p - R_s = \Delta R$$

Parallel polarization Perpendicular polarization Difference

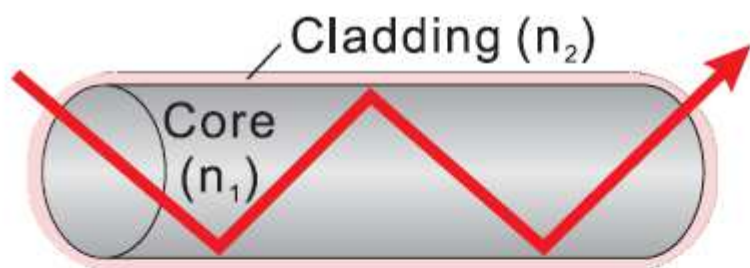
surface + gas gas surface

The surface spectra are often shown in $\Delta R/R$
($R=R_s+R_p$)

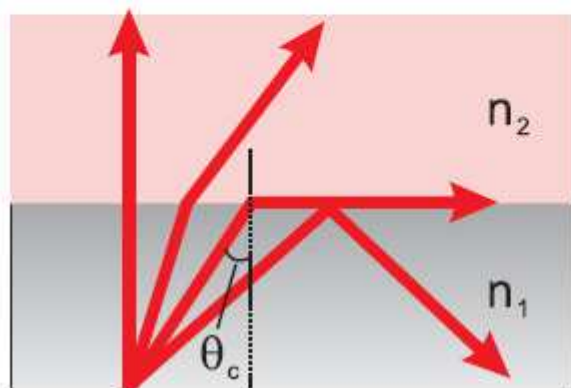
Internal reflection (ATR-IRS)

■ Attenuated total reflection infrared spectroscopy

- The most rapidly developing IR method over the last years in bioscience, organic-, inorganic chemistry, and catalysis



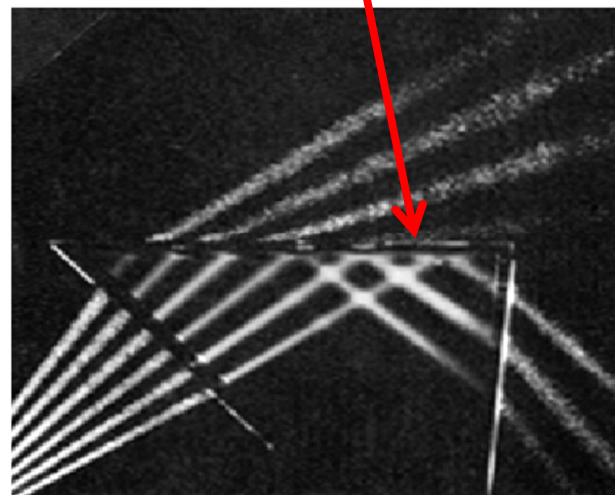
$$n_1 > n_2$$



$$\sin\theta_c = n_2/n_1$$

Above critical angle θ_c
ATR phenomenon
occurs

Total internal reflection
(attenuated total reflection)



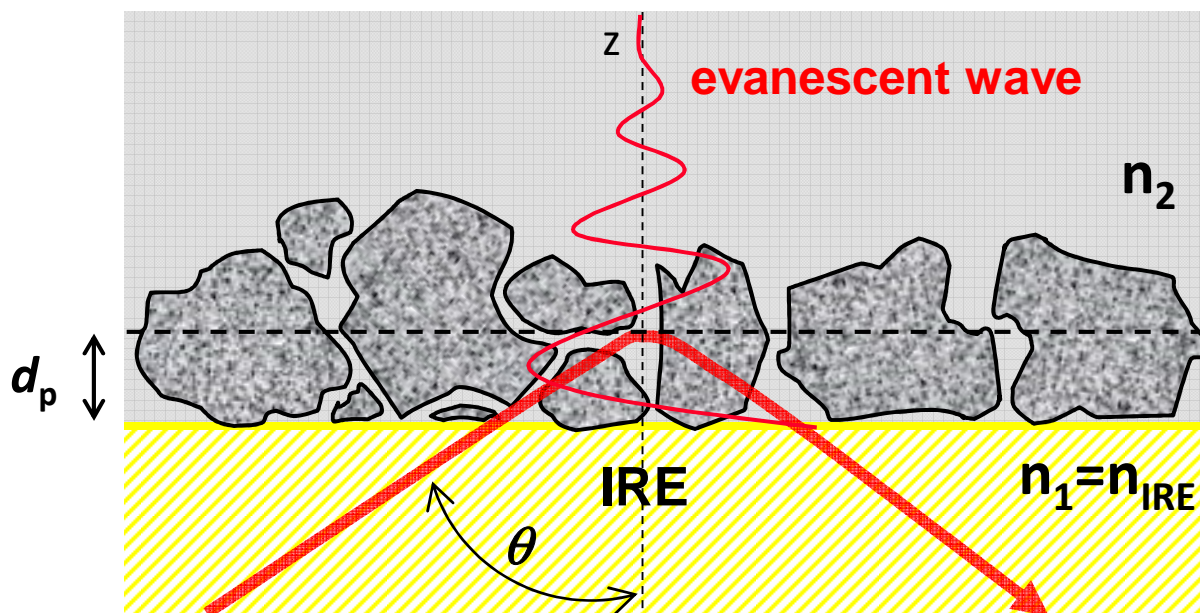
Q

Calculate the critical angle at ZnSe/air interface $n(\text{ZnSe}) = 2.4$, $n(\text{air}) = 1.0$

Internal reflection (ATR-IRS)

■ 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

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

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

Q

Assuming that n_1 and n_2 are constant, how much difference do you expect in the penetration depth at 400 and 4000 cm^{-1} ?

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

Internal reflection (ATR-IRS)

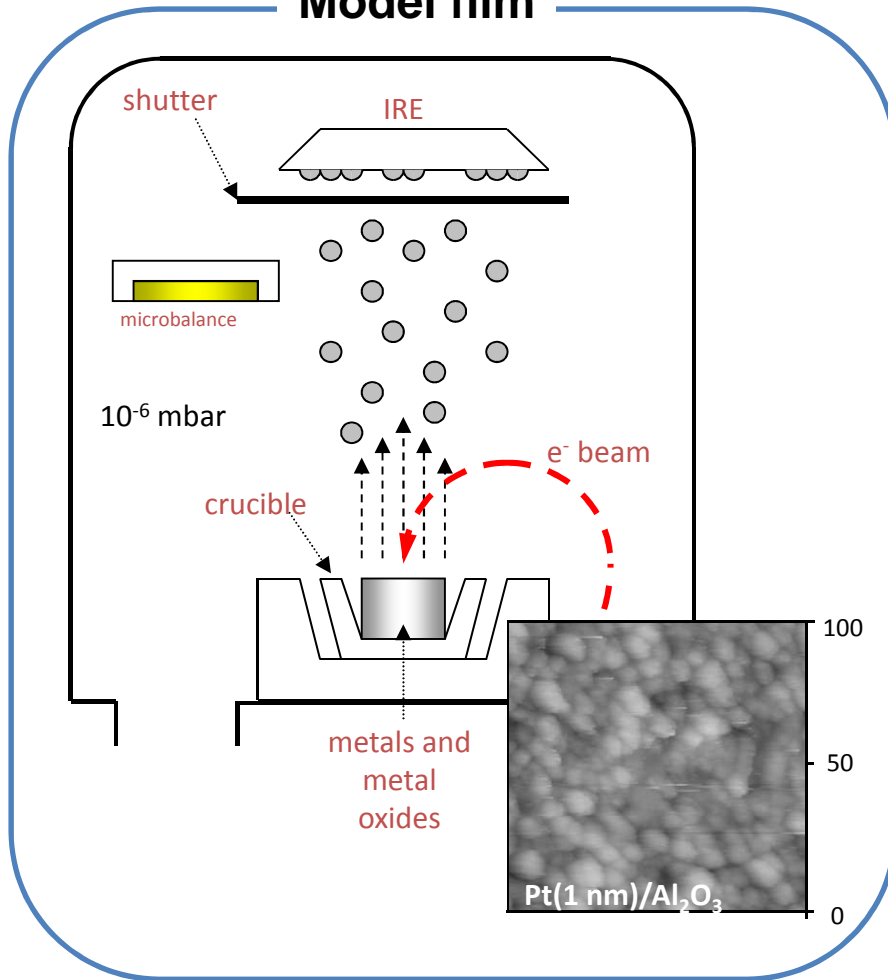
■ Common window materials

Material	Useful range / cm^{-1}	Refractive index	Properties
ZnSe	20 000-700	2.43	Soluble in strong acid; usable up to ca. 573 K
Ge	5000-900	4.02	Good chemical resistance; hard and brittle; becomes opaque at 400 K
Si	9400-1500; 350-FIR	3.42	Excellent chemical resistance; hard; usable up to ca. 573 K
KRS-5 (Thallium bromiodide)	14 000-330	2.45	Toxic; slightly soluble in water and soluble in base; usable up to ca. 473 K

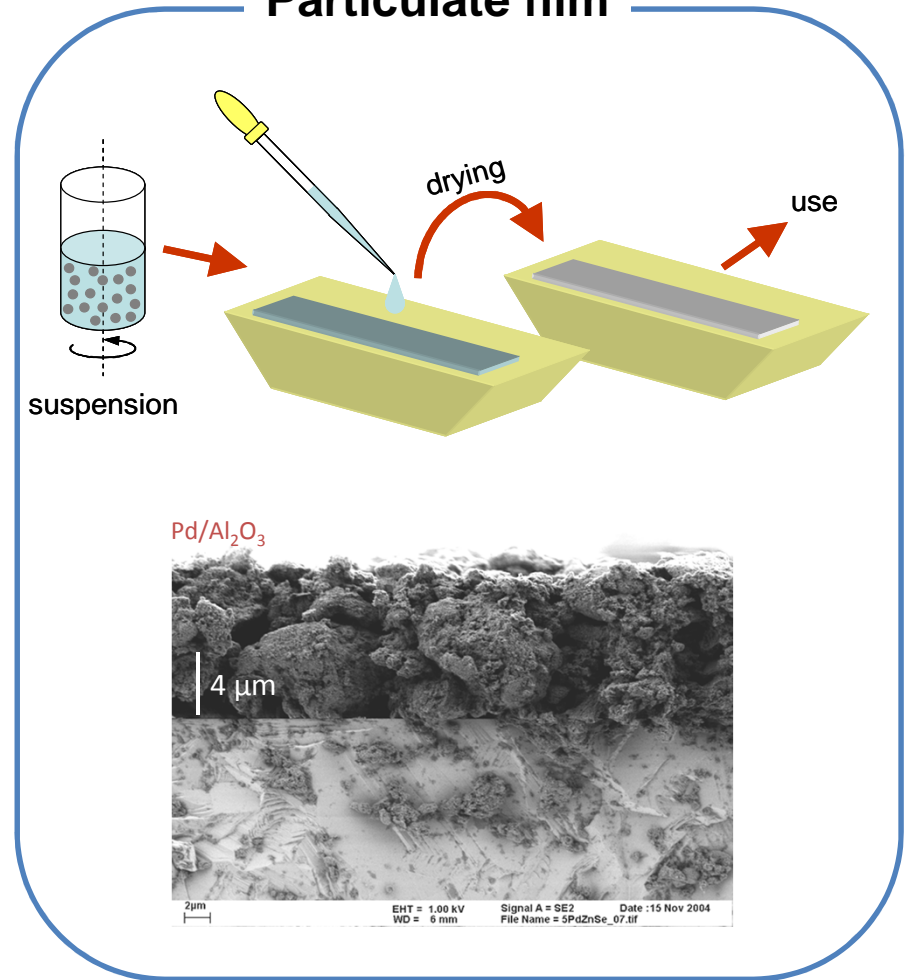
Internal reflection (ATR-IRS)

- Stable films needed for in situ investigations

Model film



Particulate film



Internal reflection (ATR-IRS)

■ Quantification

- Similar to Lambert-Beer law but replacing d by wavelength dependent thickness, i.e. effective thickness d_e (Harrick)

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

$$d_e = \frac{n_{21} E_0^2 d_p}{2 \cos \theta}$$

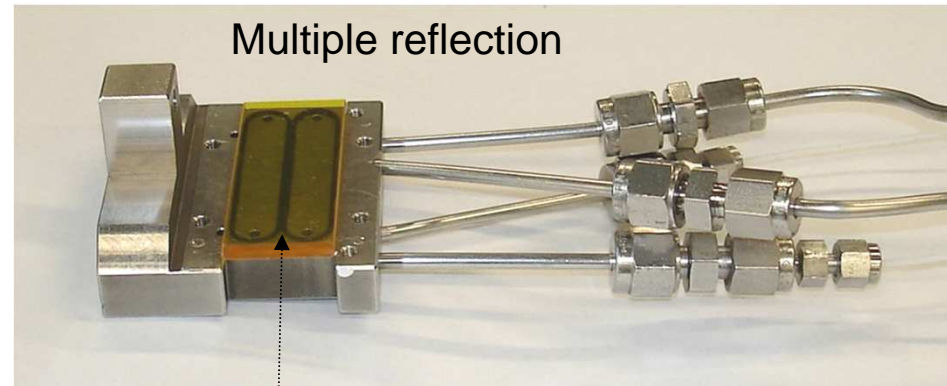
Reflectivity, polarization, and phase changes at the interfaces can be accurately calculated using **Fresnel equations**, which forms a basis for quantitative and orientation analysis

Internal reflection (ATR-IRS)

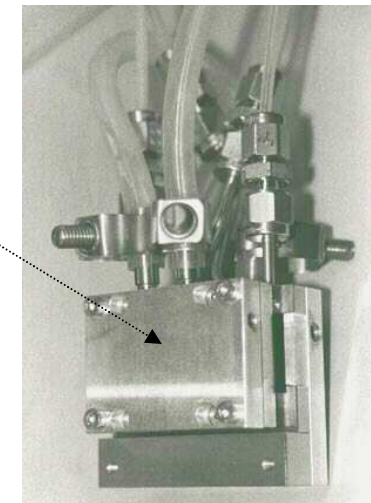
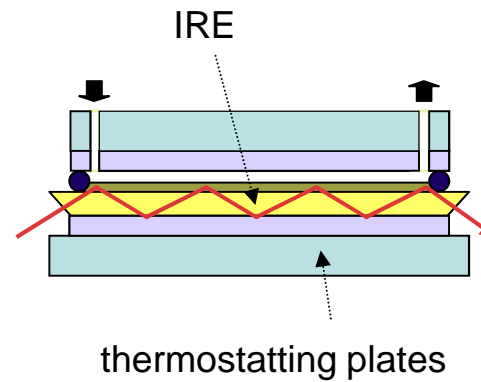
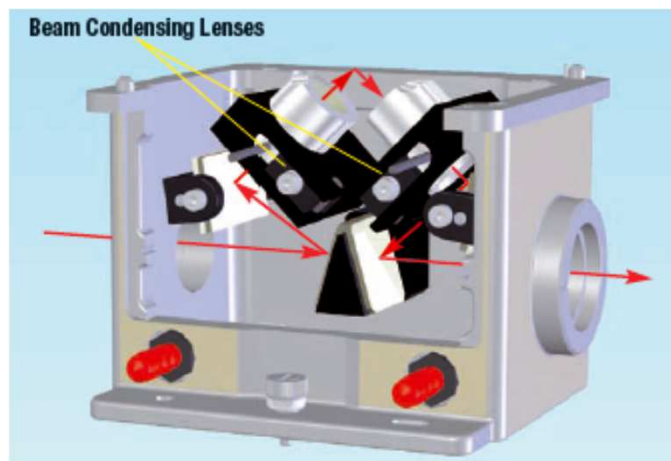
■ Cells



Single reflection

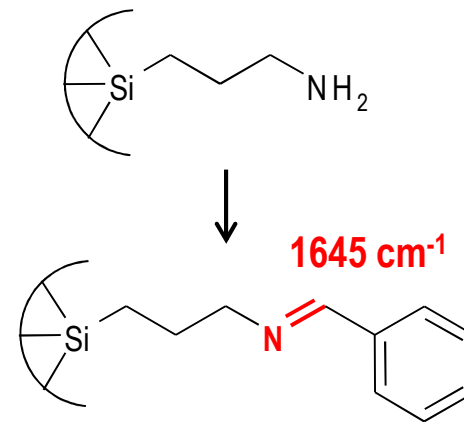
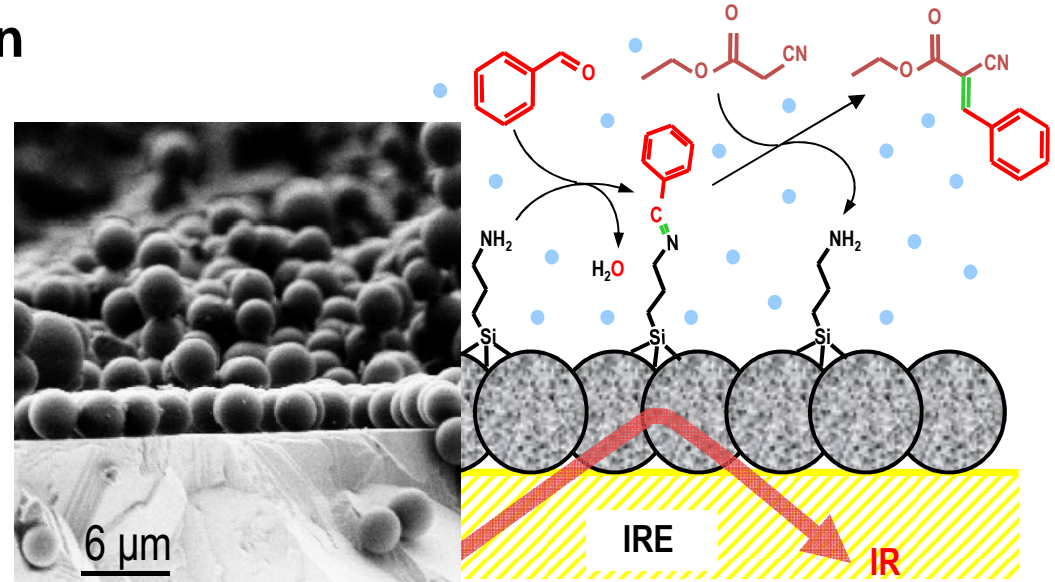
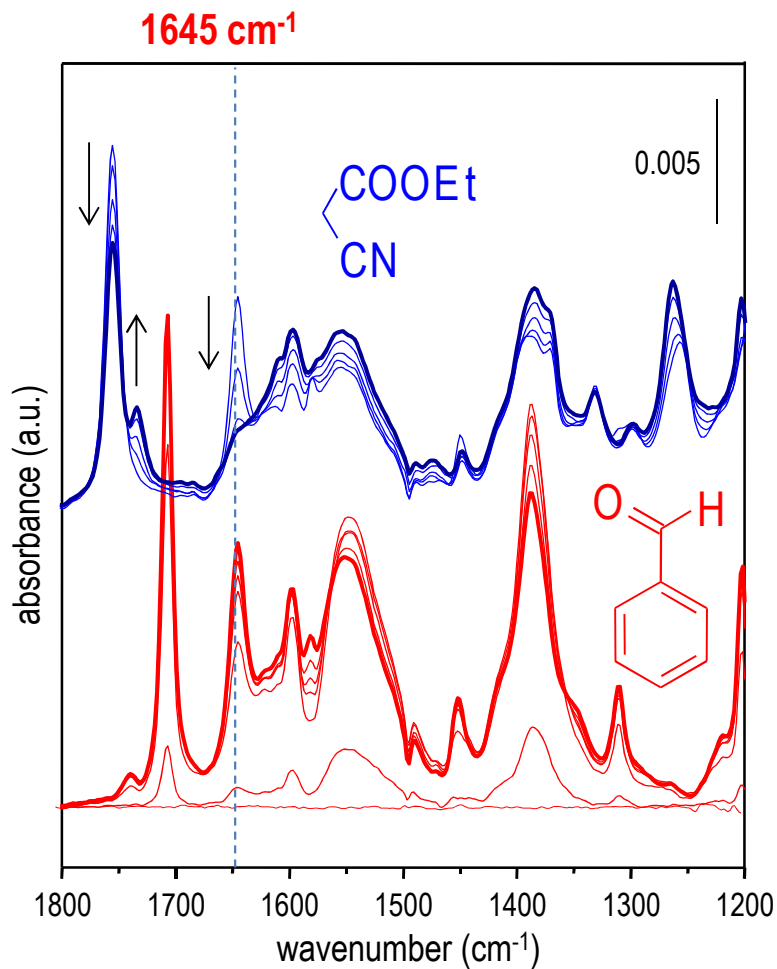


Multiple reflection



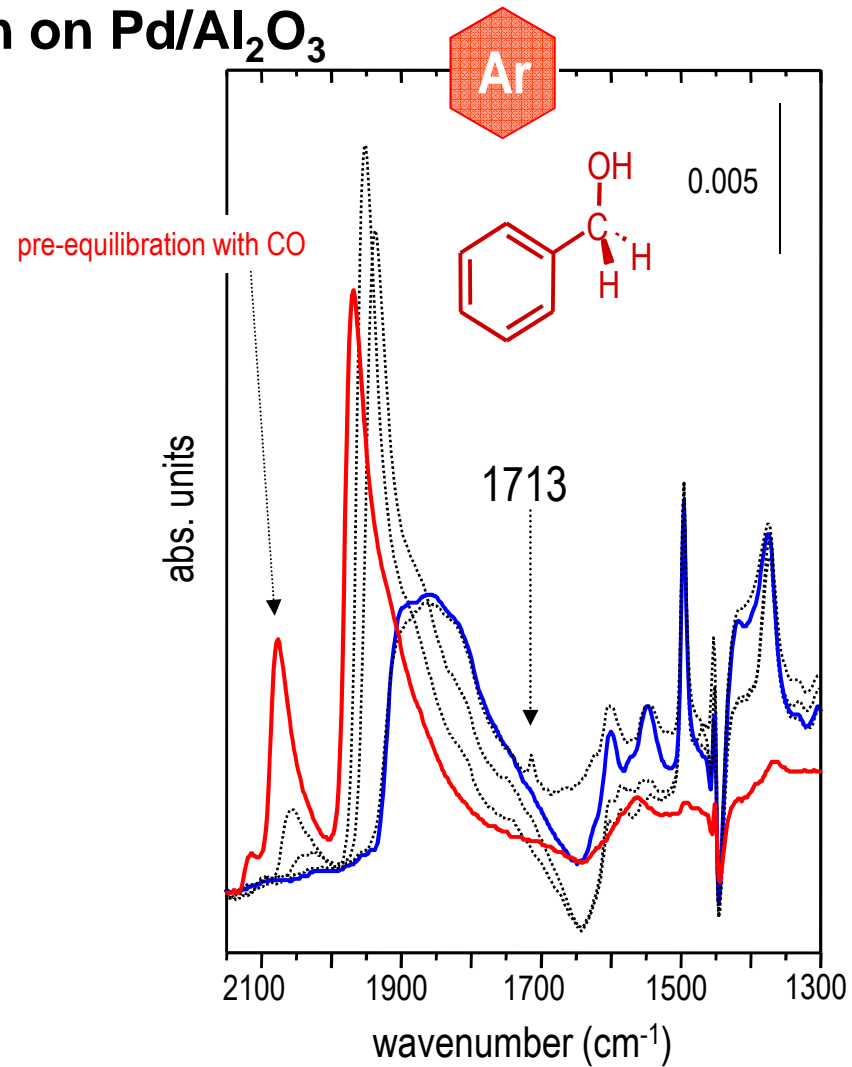
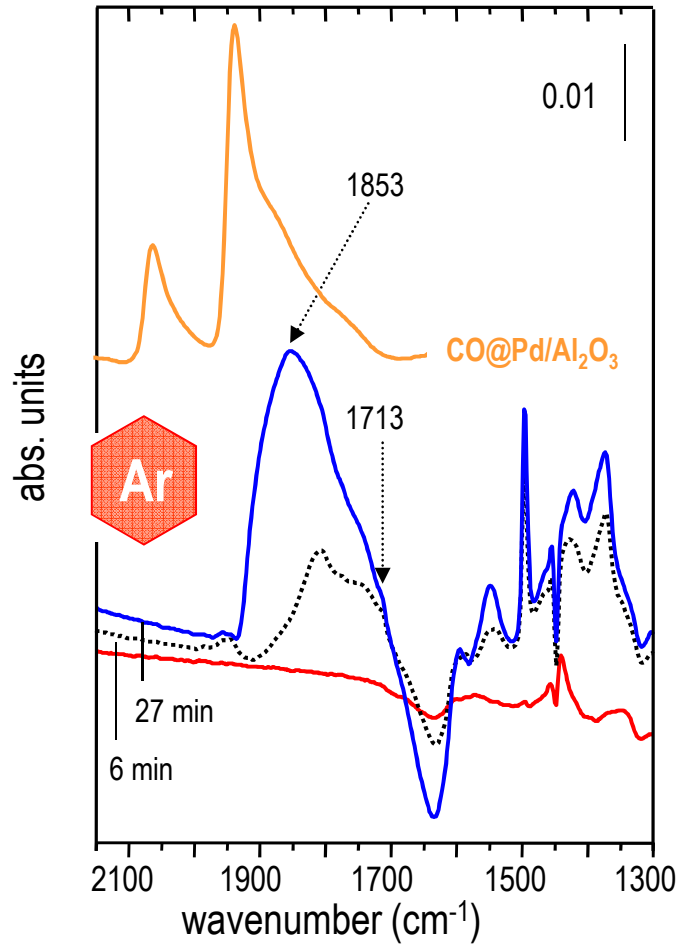
Internal reflection (ATR-IRS)

■ Knoevenagel condensation



Internal reflection (ATR-IRS)

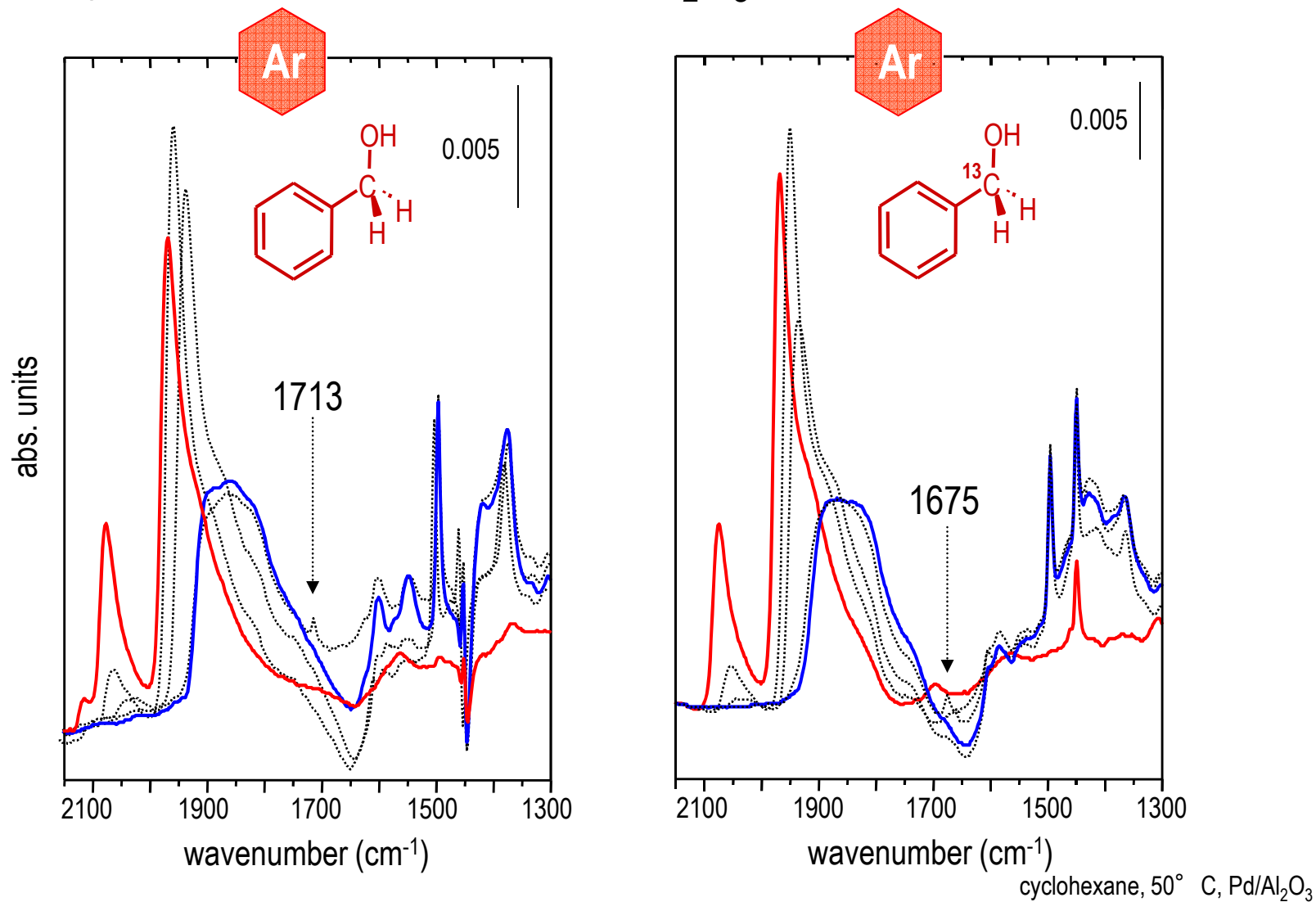
■ Benzyl alcohol oxidation on Pd/Al₂O₃



cyclohexane, 50° C, Pd/Al₂O₃

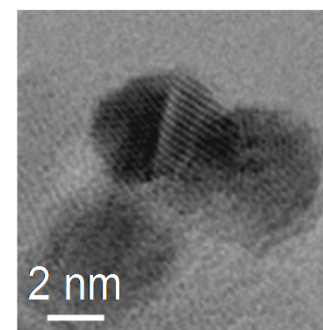
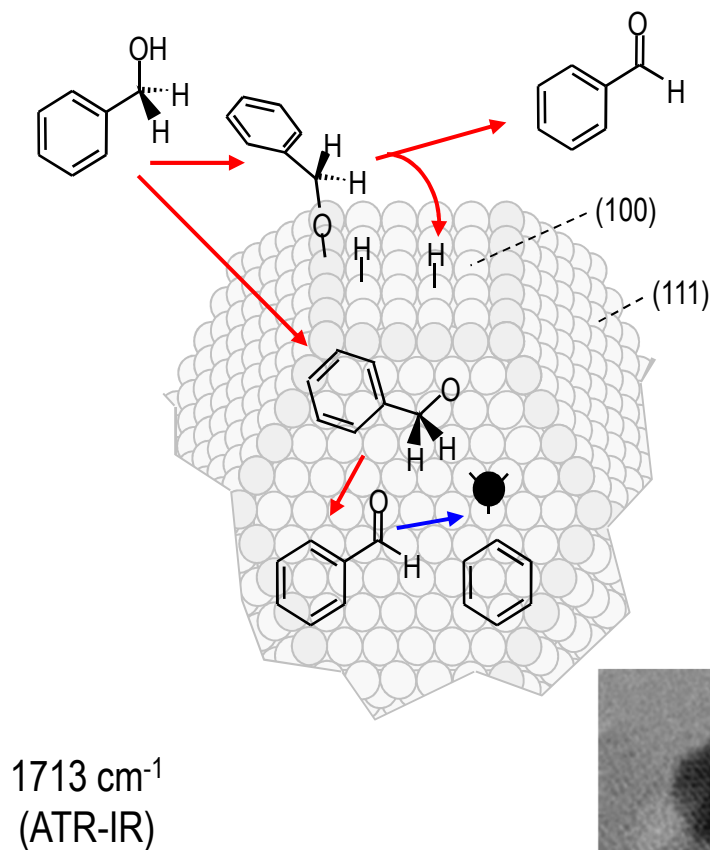
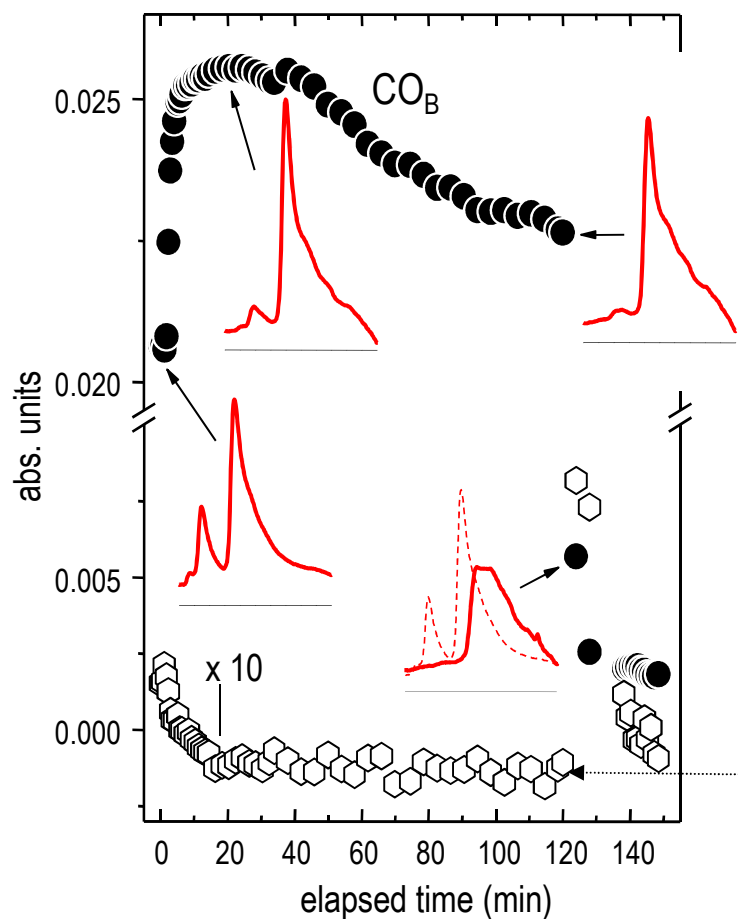
Internal reflection (ATR-IRS)

- Benzyl alcohol oxidation on Pd/Al₂O₃



Internal reflection (ATR-IRS)

Active sites



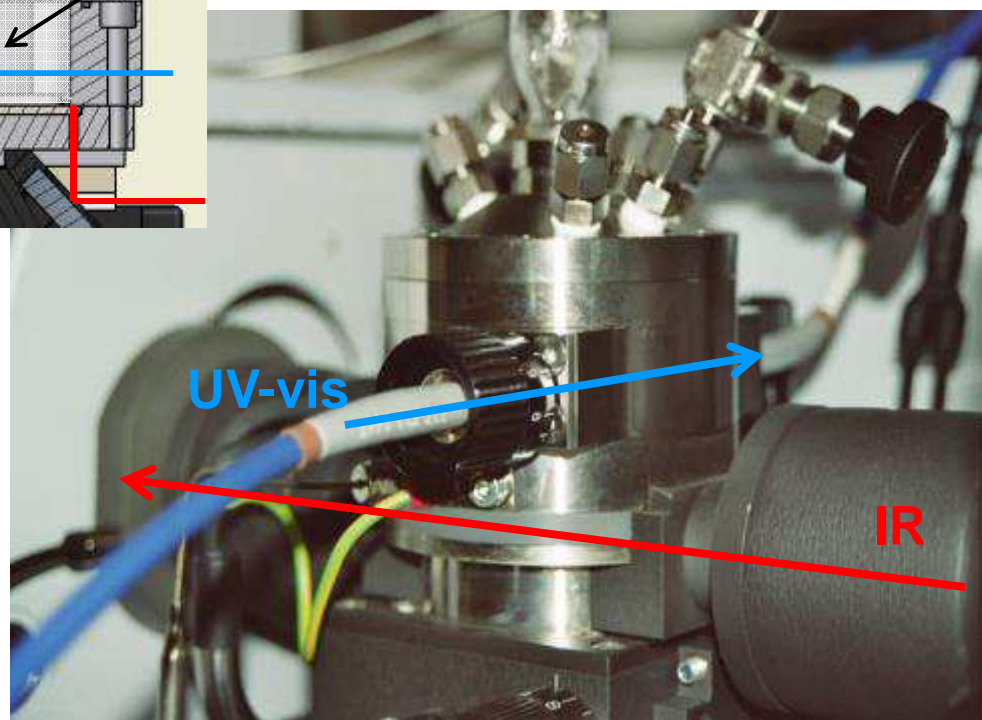
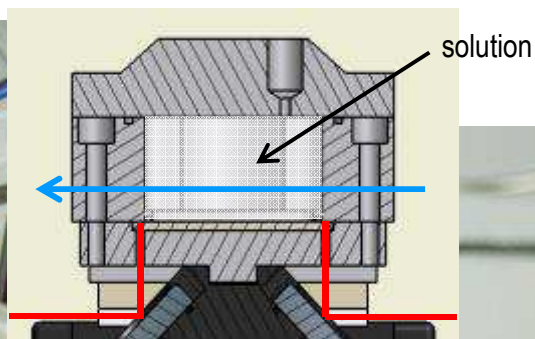
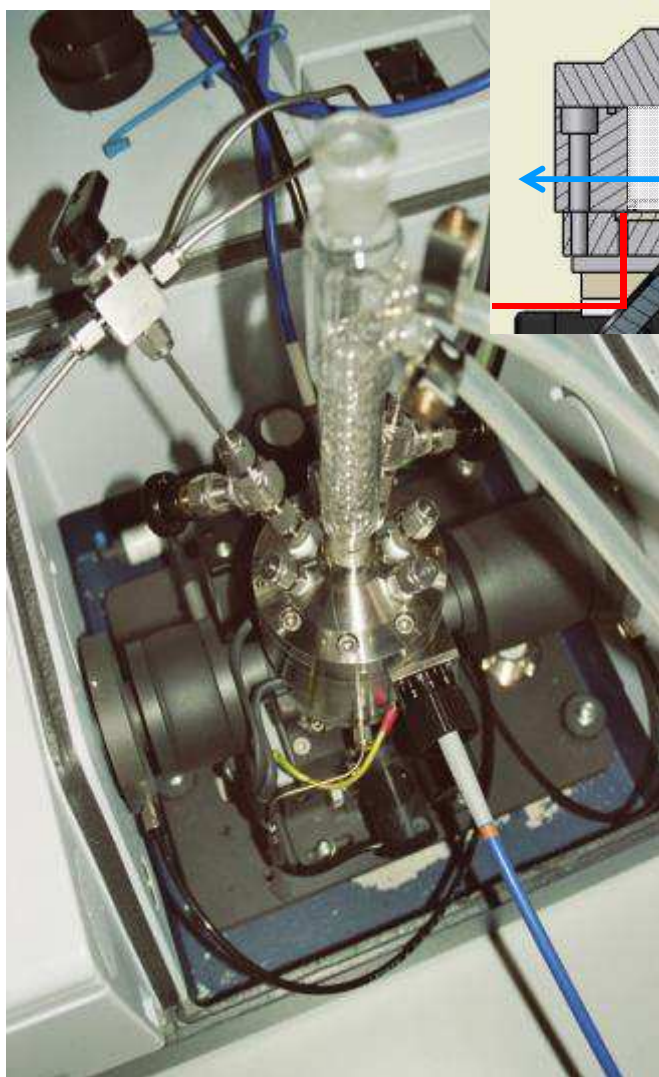
cyclohexane, 50° C, Pd/Al₂O₃



- (111): decarbonylation site
- (100) + edges: alcohol dehydrogenation

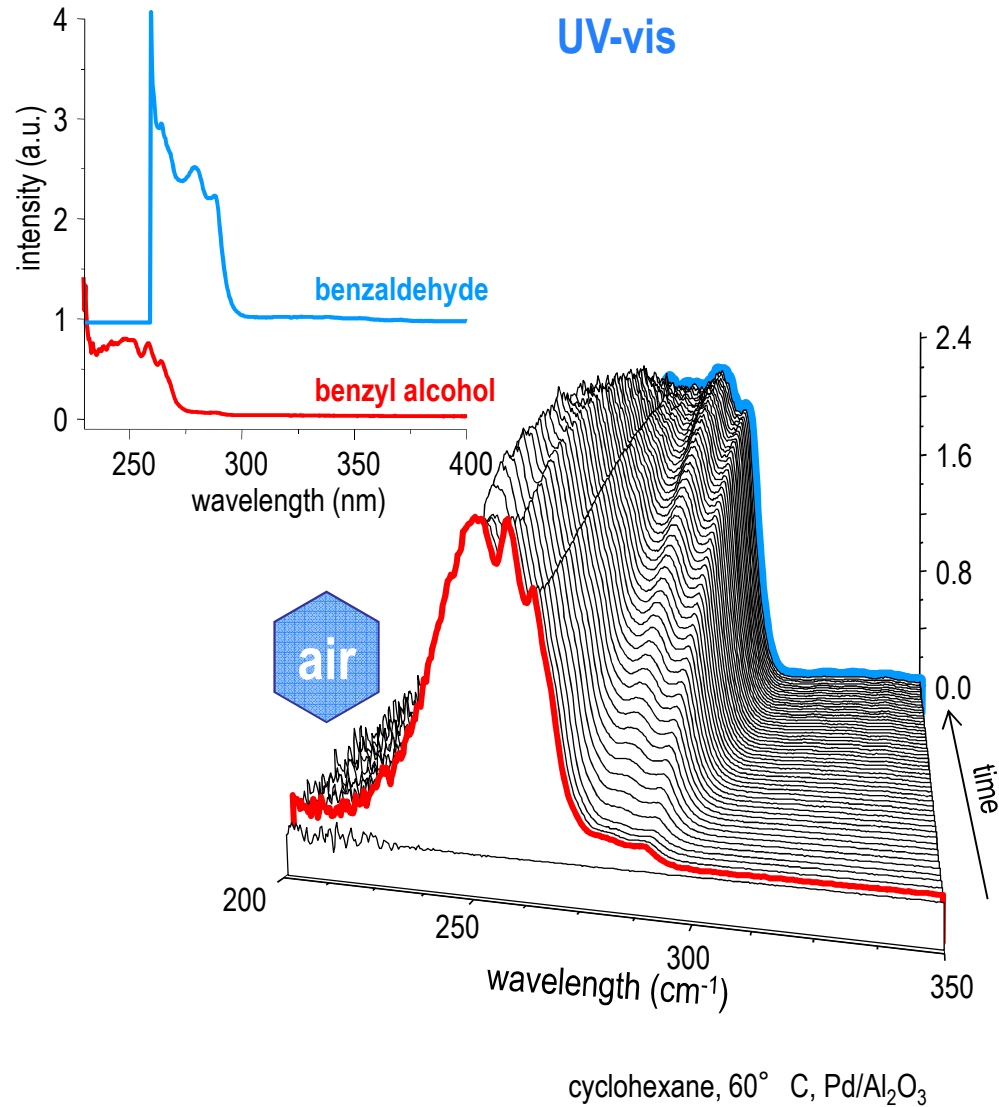
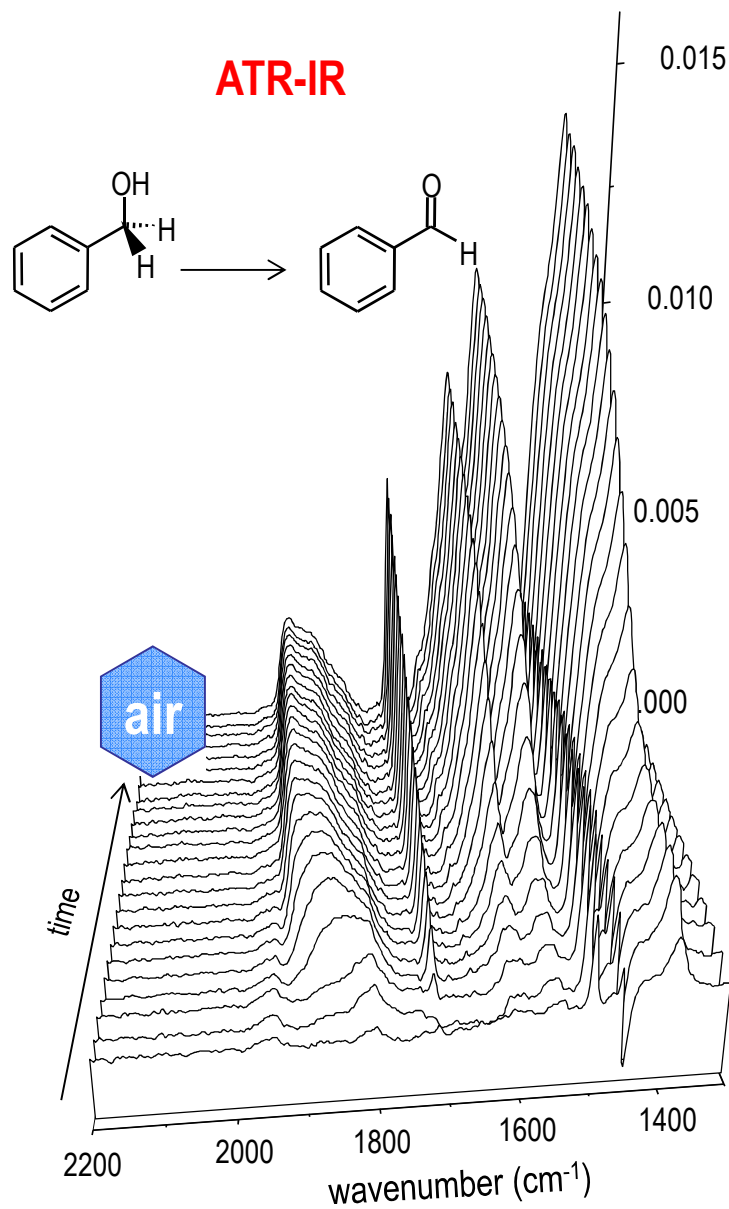
Internal reflection (ATR-IRS)

■ Batch reactor cell

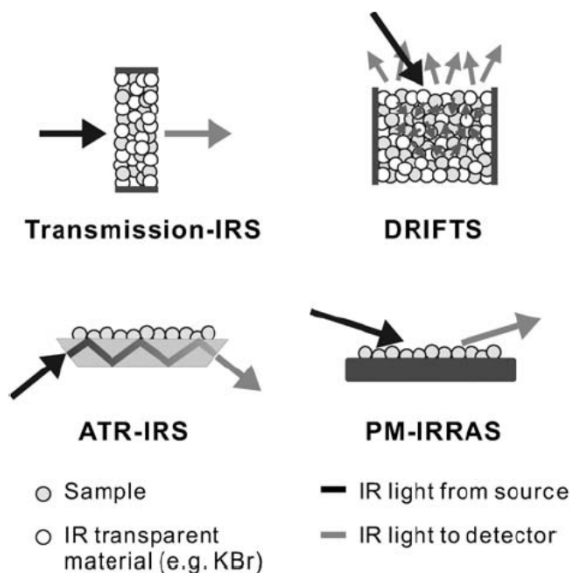


- **IR**: surface species, material, solution
- **UV-vis**: solution

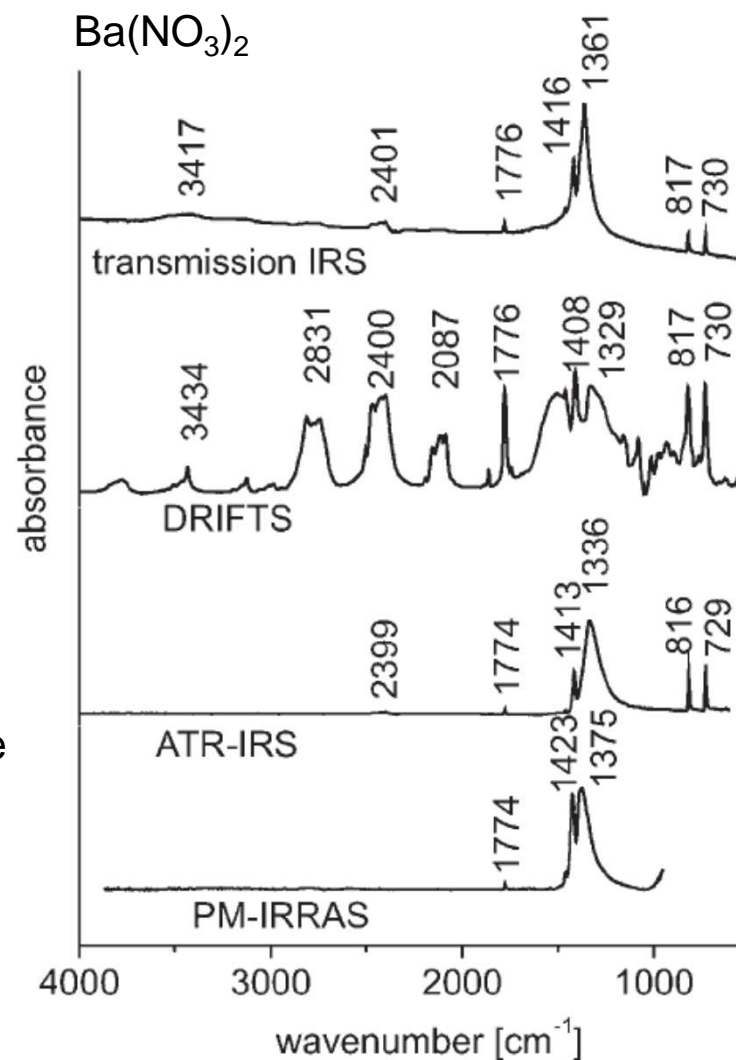
Internal reflection (ATR-IRS)



Comparison of techniques



- Comparison between techniques with different sensitivity (bulk/surface) should be careful
- Band assignment depends on surface sensitivity of the technique
- PM-IRRAS suitable for investigation of powder samples...



Adsorbed molecules

■ 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)

The surface selection rule

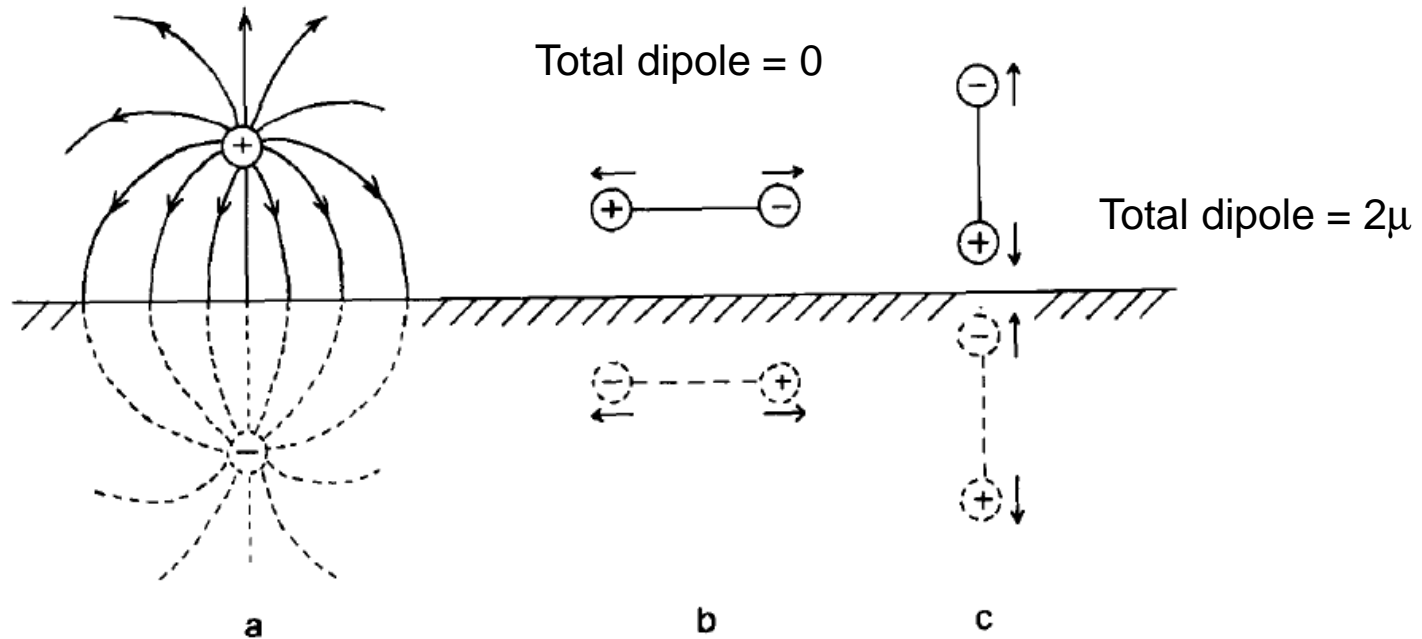
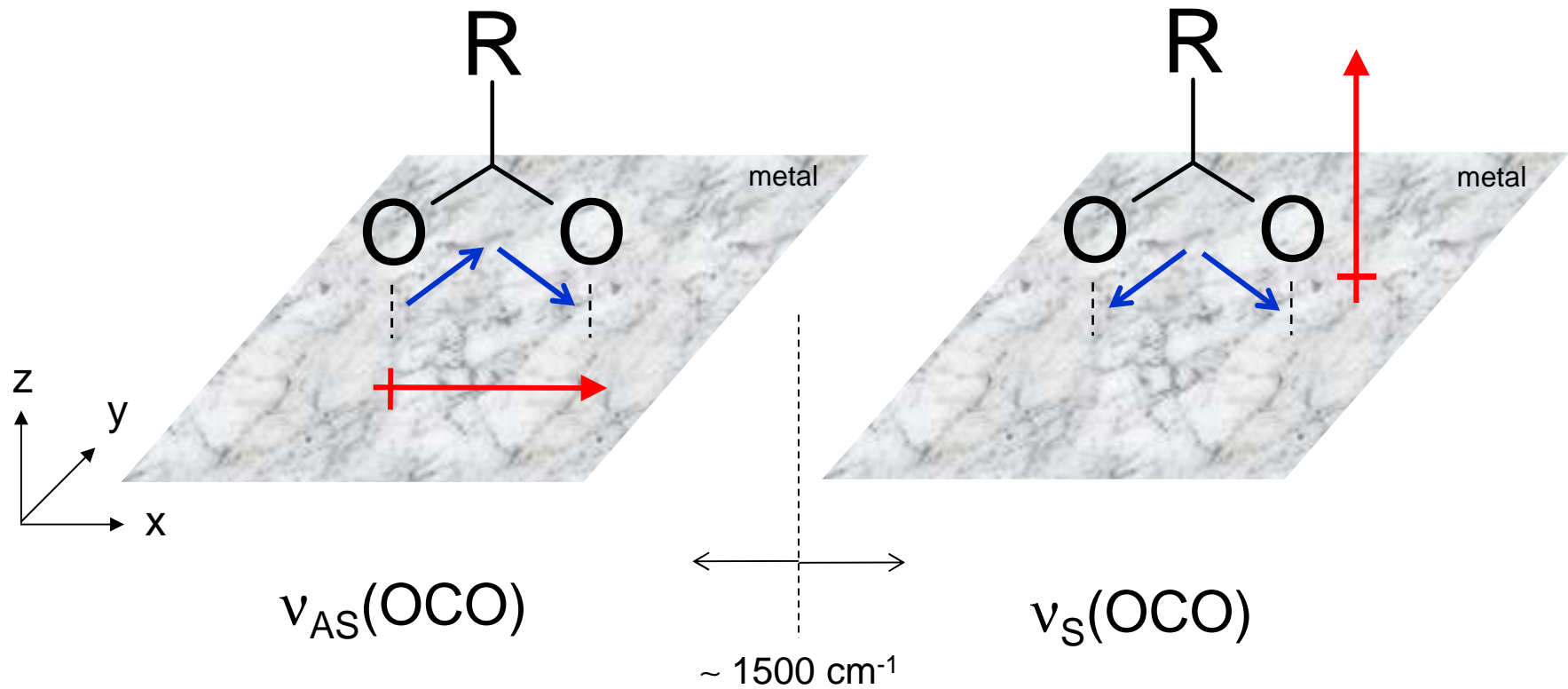


Fig. 1. (a) The lines of force and the electrical "image" resulting from a positive charge over the surface of a conductor (the metal surface is the upper line above the hatched area). (b) The changes during the vibration of a dipole parallel to the surface of the metal; the "image" dipole change is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

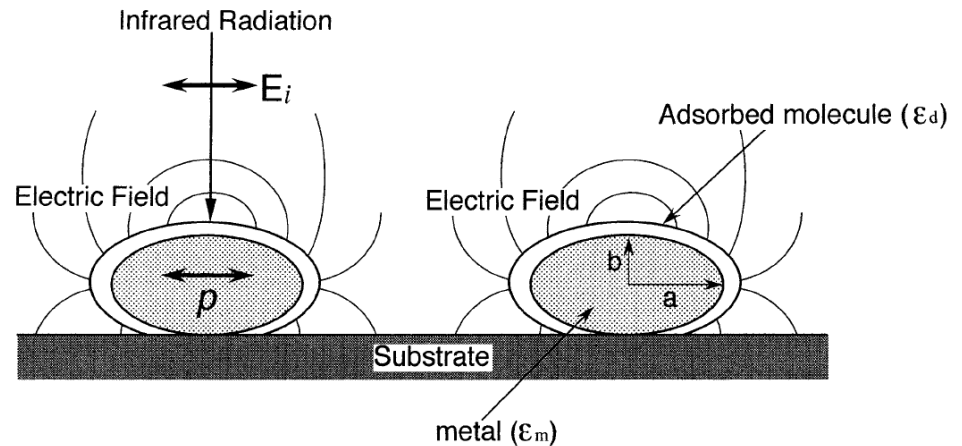
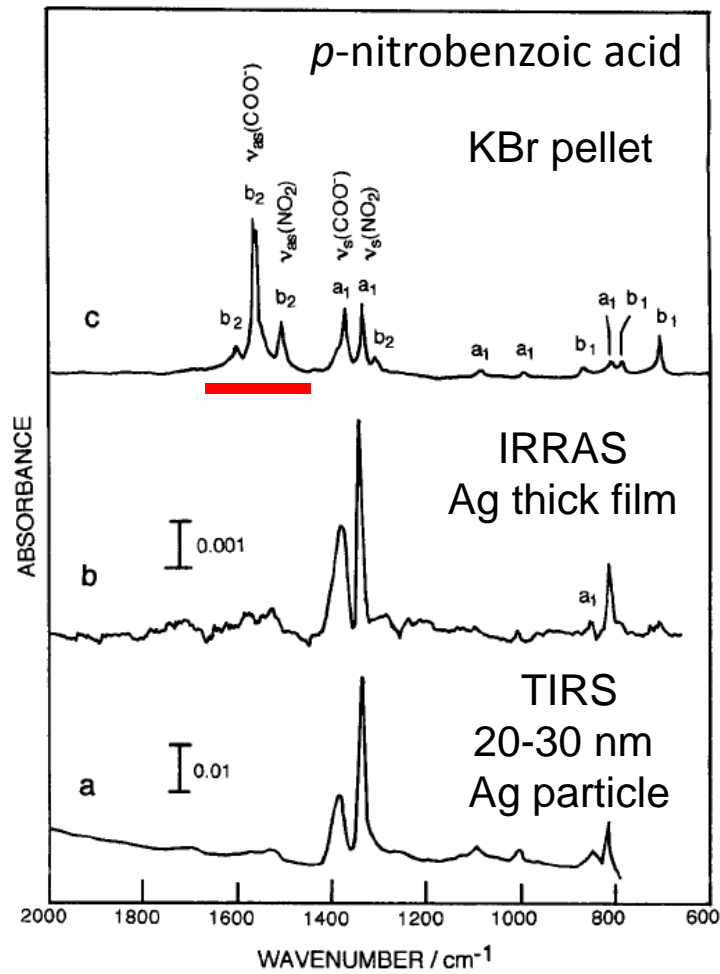
The surface selection rule

■ Carboxylate groups



The surface selection rule

- Also valid for small (nm) metal particles?



Osawa et al. Appl. Spectroscopy 47 (1993) 1497

Please note that the selection rule can break down for particles smaller than ca. 2 nm

Greenler et al. Surf. Sci. 118 (1982) 415

IR spectroscopy for catalysis

■ Ex situ experiments

- structure determination (M-O bonds, OH groups), nature of adsorbates

■ In situ experiments

- structure determination (M-O bonds, OH groups), nature of adsorbates
- determination of adsorption sites (probe molecules)
- determination of acidity and basicity (probe molecules)

- typically, vacuum experiments and low T (LN₂)
- other atmospheres and T possible

■ Operando experiments

Combination of

- spectroscopic measurement (not only IR!)
- simultaneous detection of reactants and products (MS, GC, ...)

- Evolution of adsorbates with changes in reaction conditions (e.g. T)
- simulation of reactor studies (pay attention to reactor design issue)
- adsorption-desorption experiments under relevant conditions (not vacuum)

Probe molecules

- **Quality and quantity of acid sites**

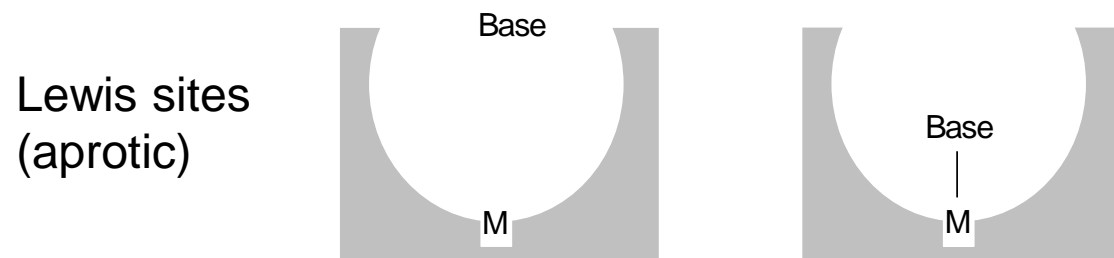
- **Criteria**

- 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
- ...

- Example
 - 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



amines

NH_3

pyridine

CH_3CN

CO

alkanes

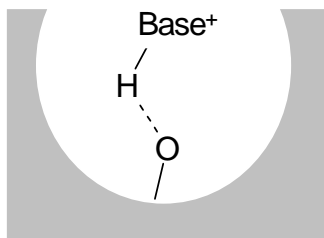
N_2

H_2



Probe molecules

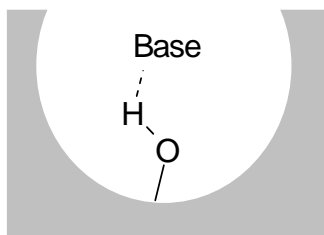
■ Acid sites: Pyridine



Brønsted (B)

1535–1550 cm^{-1}

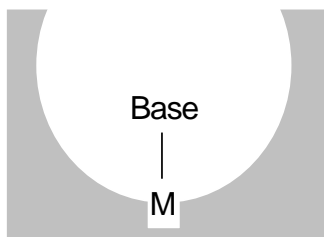
1640 cm^{-1}



Hydrogen bonded

1440–1447 cm^{-1}

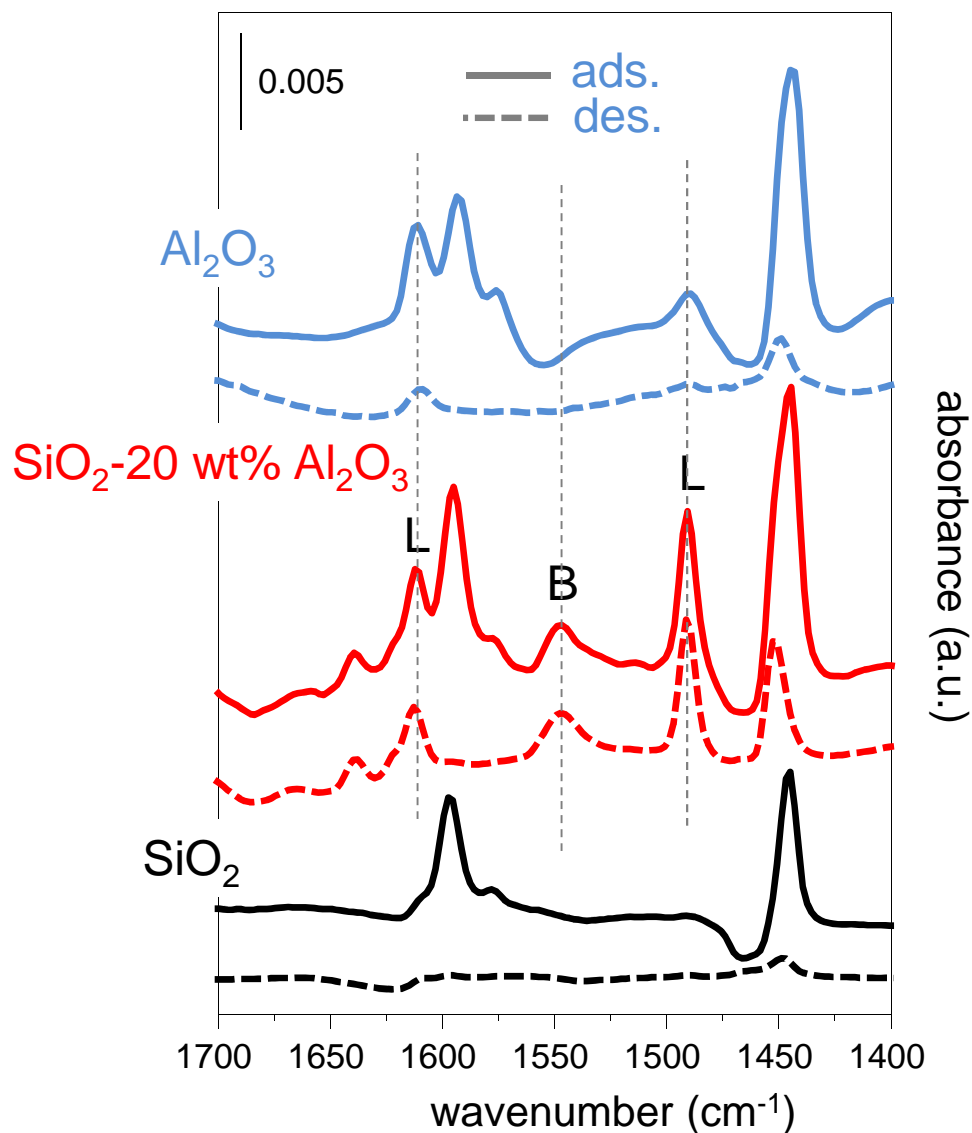
1580–1600 cm^{-1}



Lewis (L)

1447–1464 cm^{-1}

1600–1635 cm^{-1}

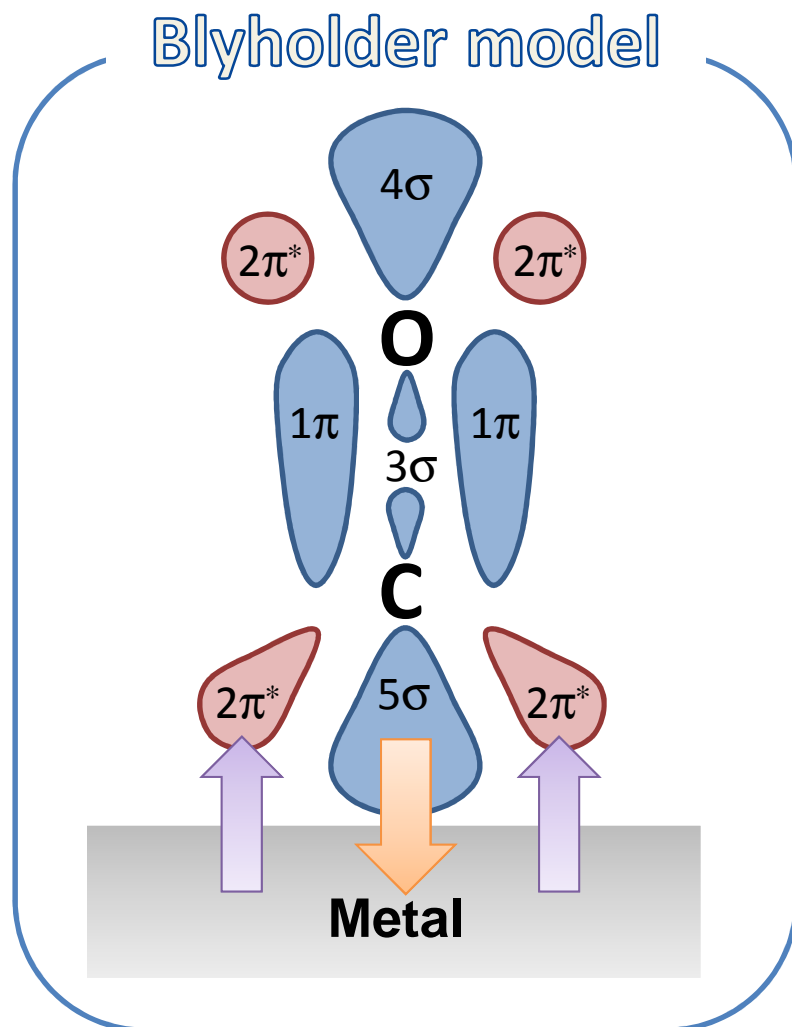


SiO_2 - Al_2O_3 > Al_2O_3 >> SiO_2 ; next issue: coordination environment of acid site

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

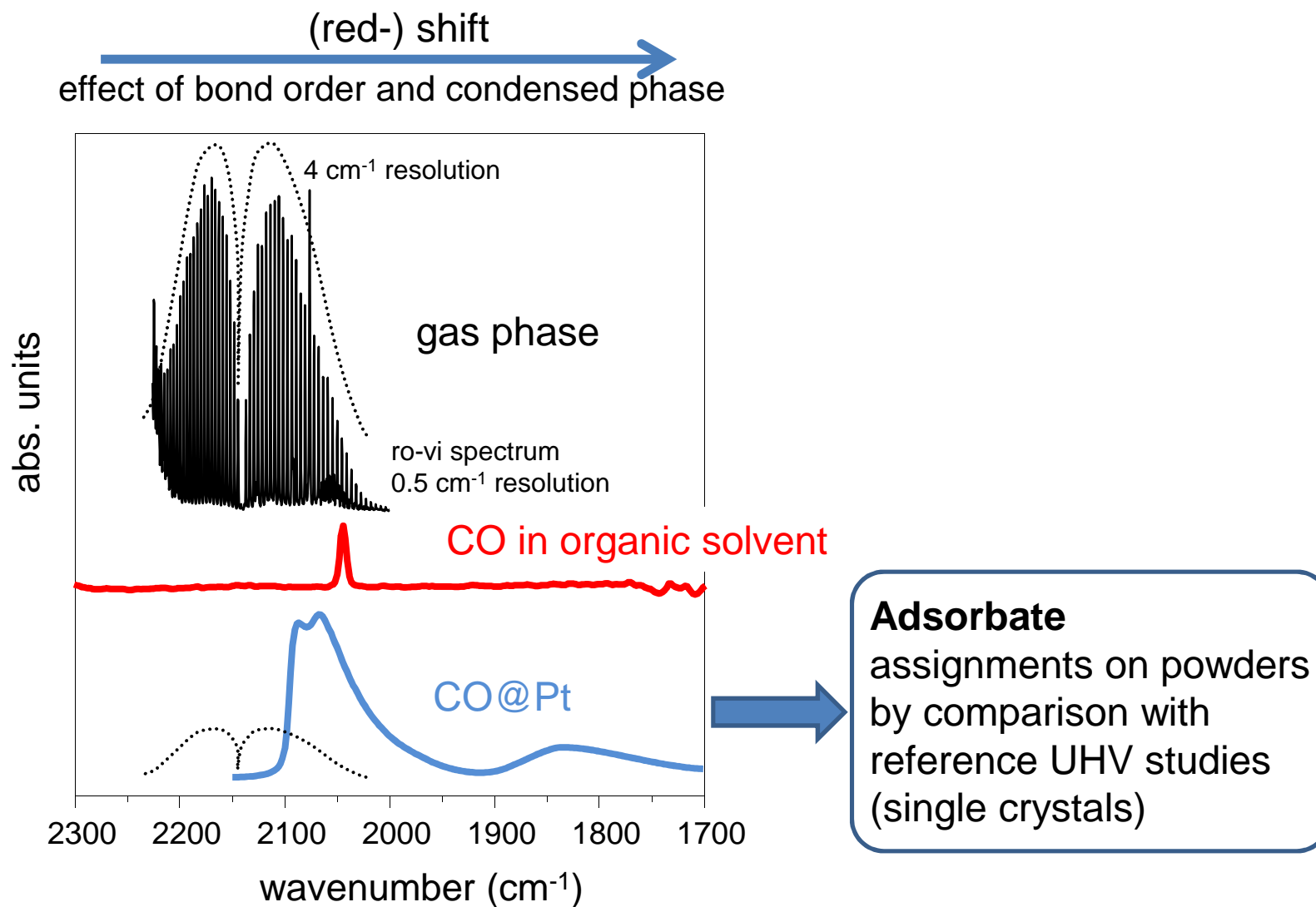
Back-donation (BD)

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

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

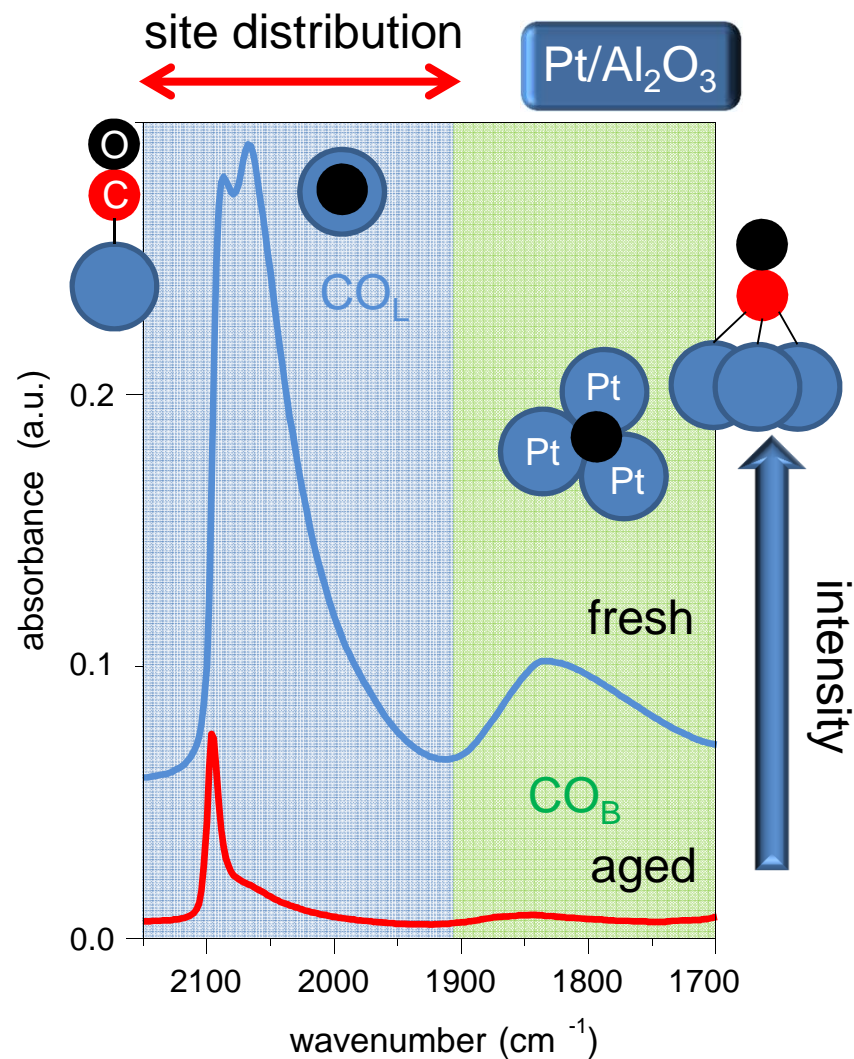
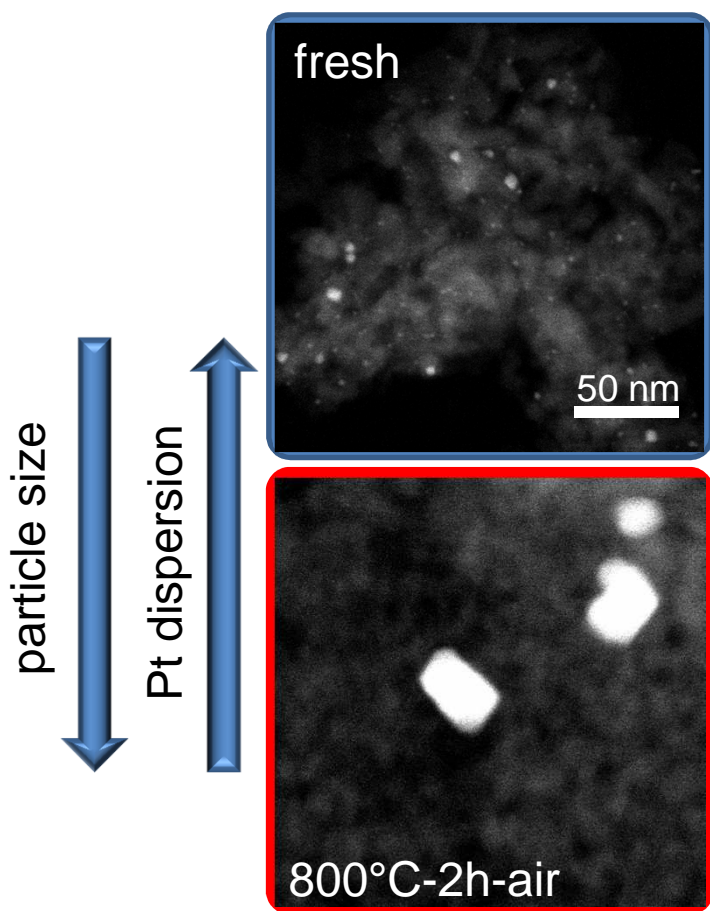
Probe molecules

■ Carbon monoxide (CO)



Probe molecules

■ Carbon monoxide (CO)

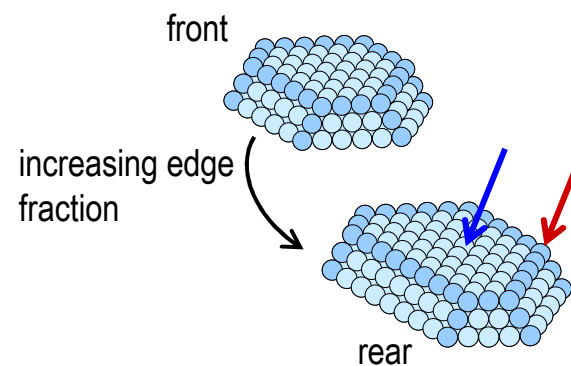
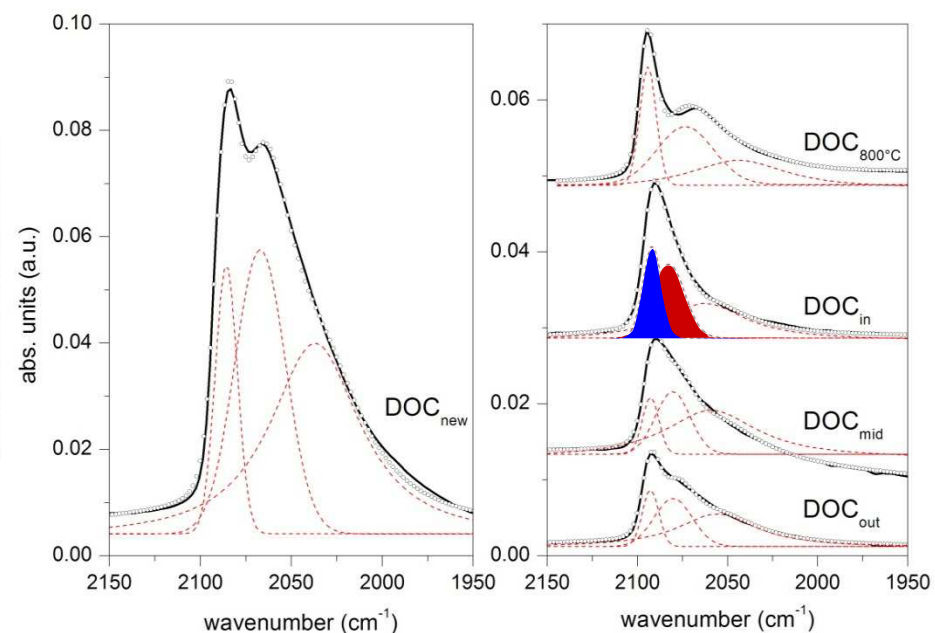
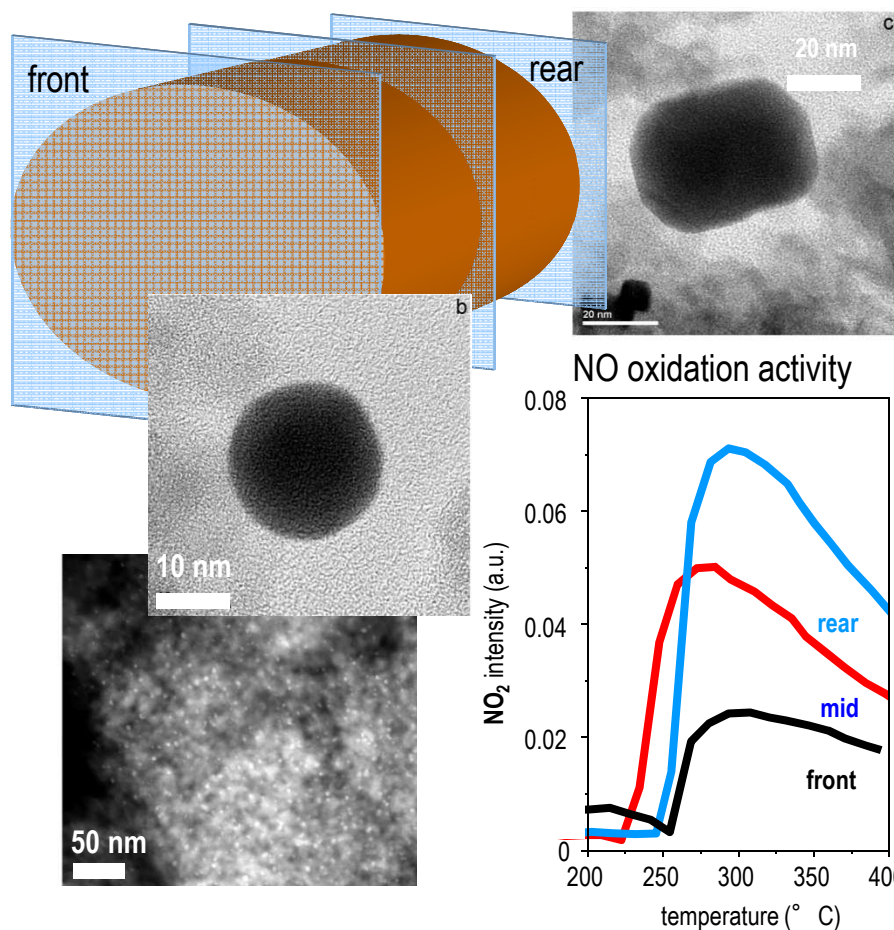


- The larger the particles, the less CO adsorbs (**intensity**)
- The larger the particles, the less defects available (**nr. of signals**)

Probe molecules

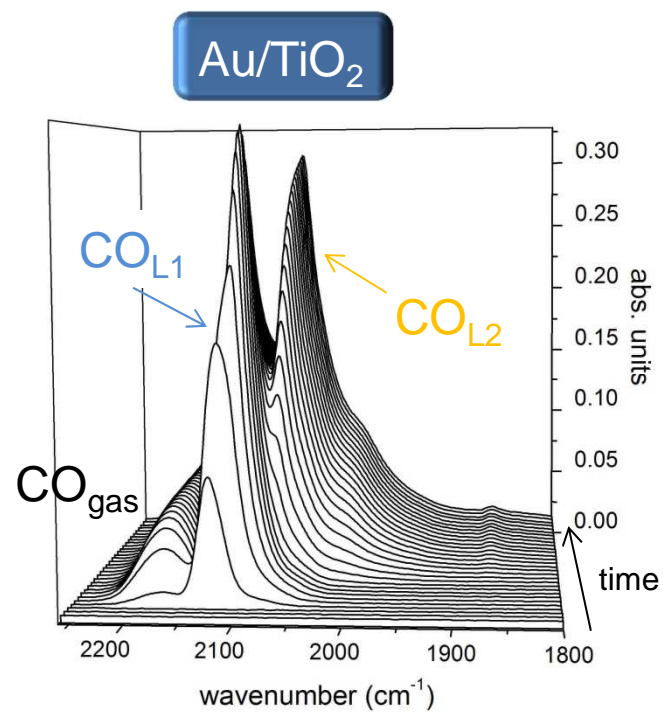
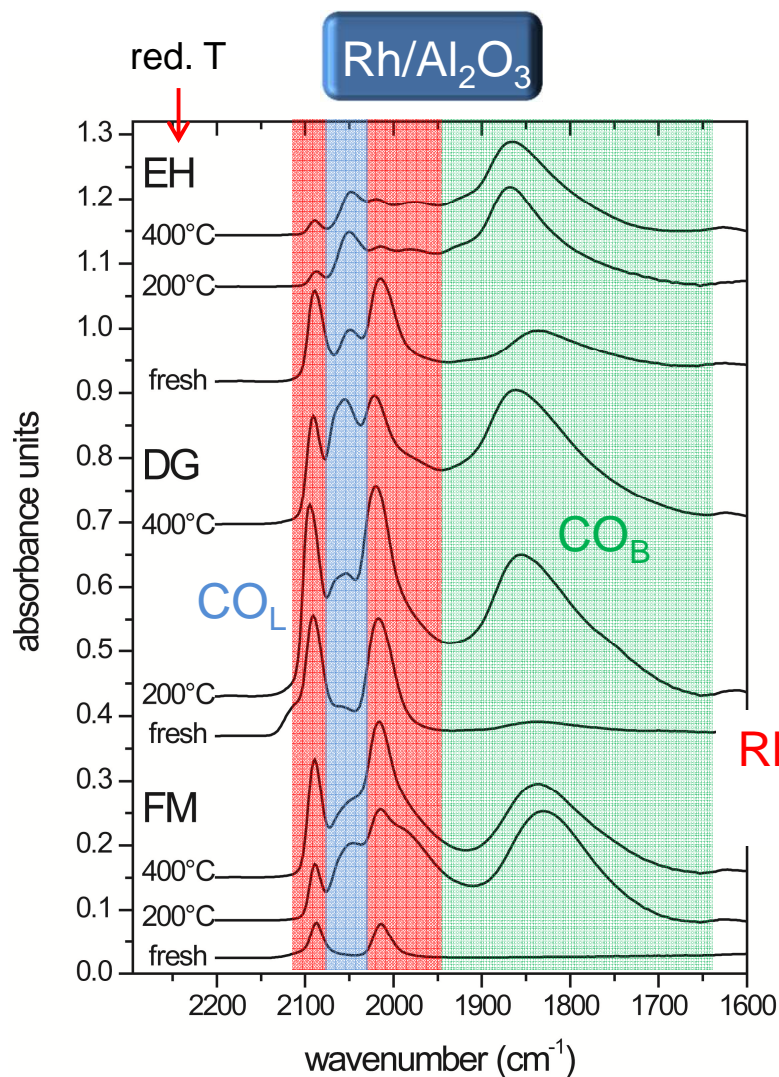
■ Diesel oxidation catalyst (DOC)

DRIFTS of adsorbed CO



Probe molecules

■ Carbon monoxide (CO)

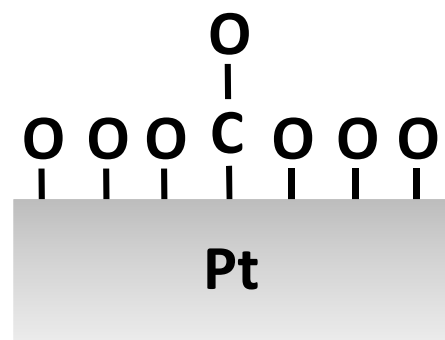
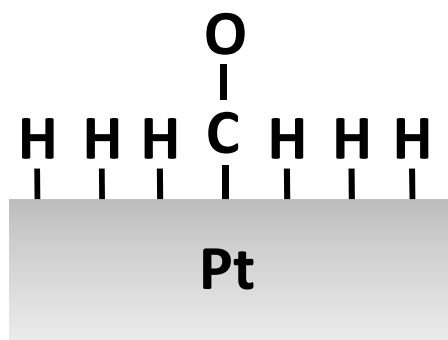


Watch out!
surface reconstruction induced by CO
- CO is corrosive

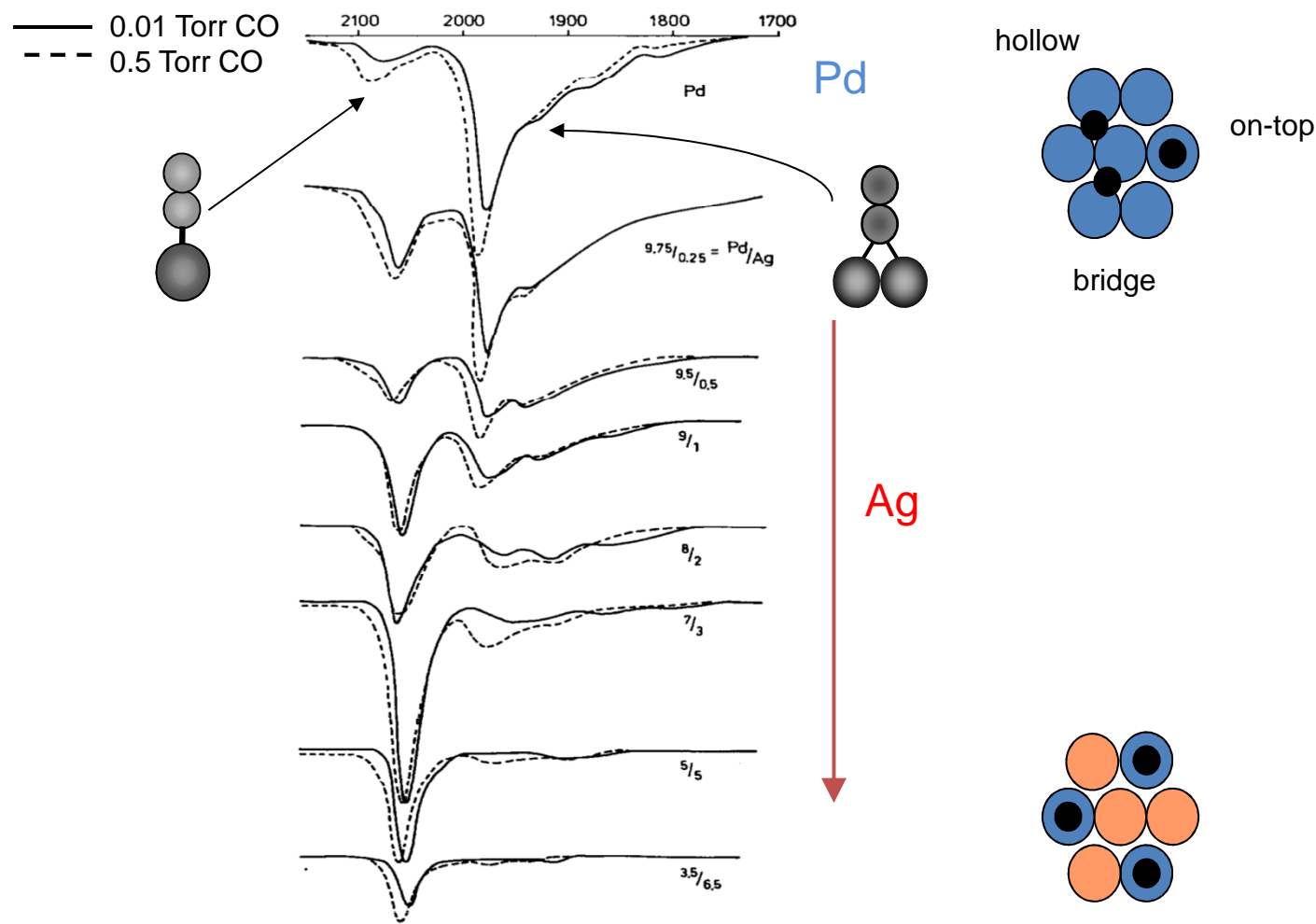
Probe molecules

■ Carbon monoxide (CO)

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



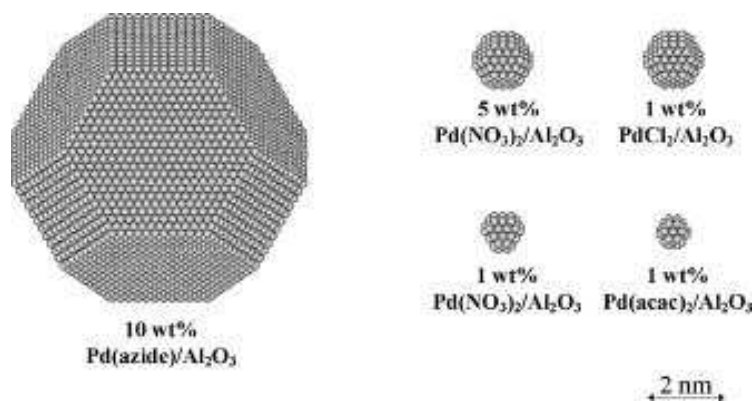
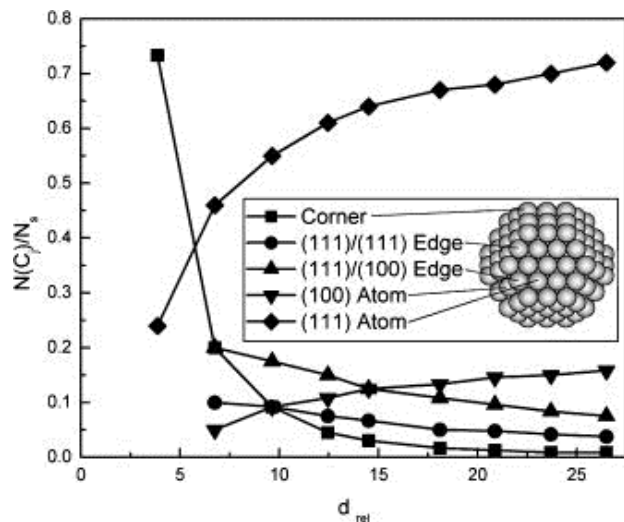
Probe molecules



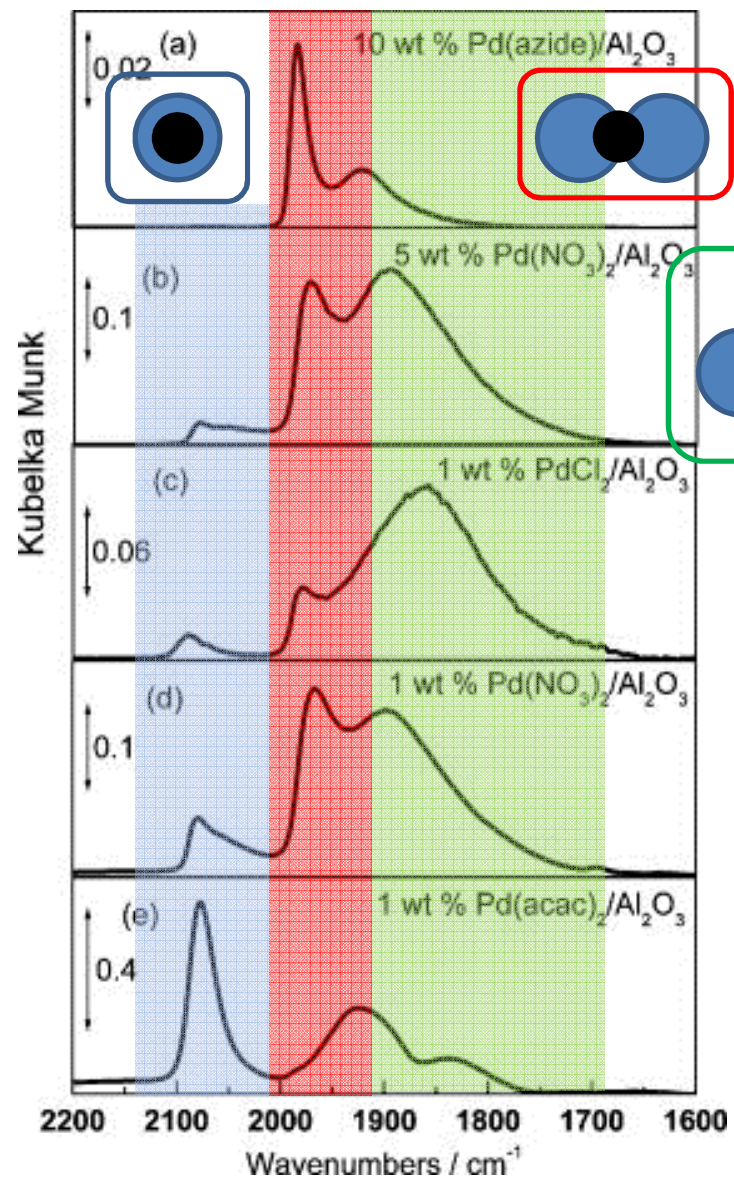
Pd/Ag alloy on SiO₂

Probe molecules

■ Carbon monoxide (CO)

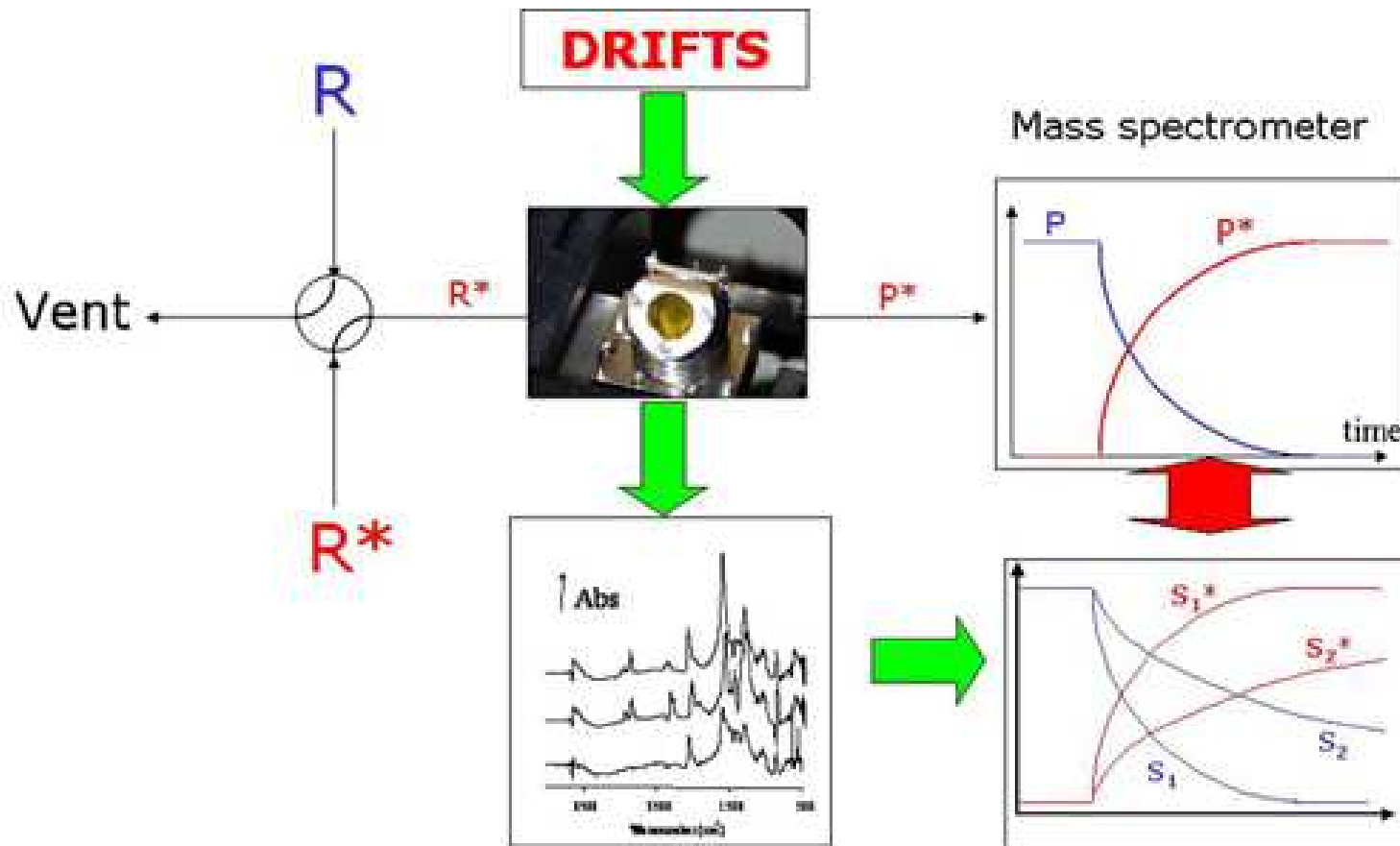


size confirmed by TEM



DRIFTS-SSITKA

- **SSITKA: Steady-State Isotopic Transient Kinetic Analysis**



DRIFTS-SSITKA

- The reaction: $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$

observed species at steady state

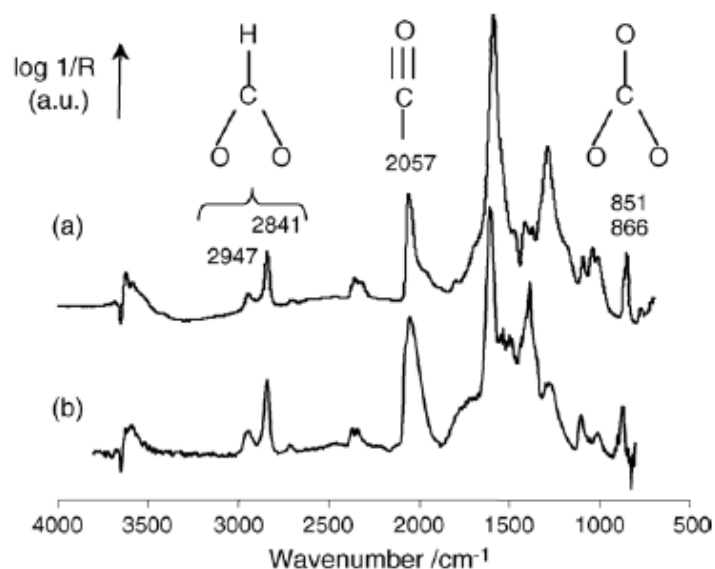
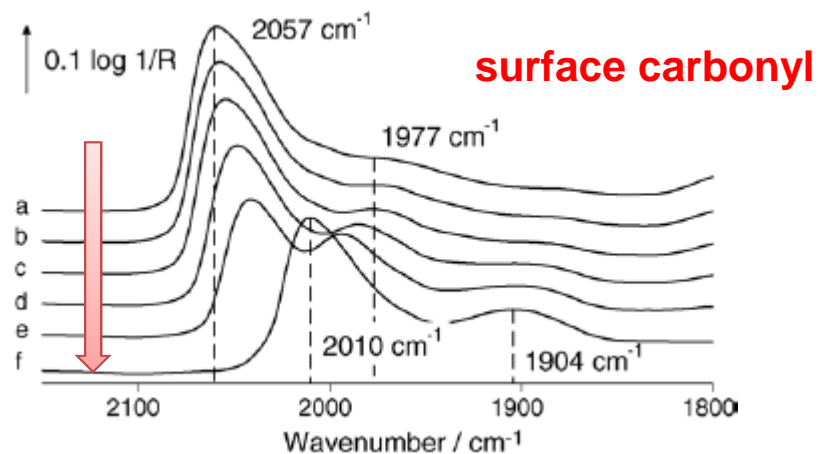
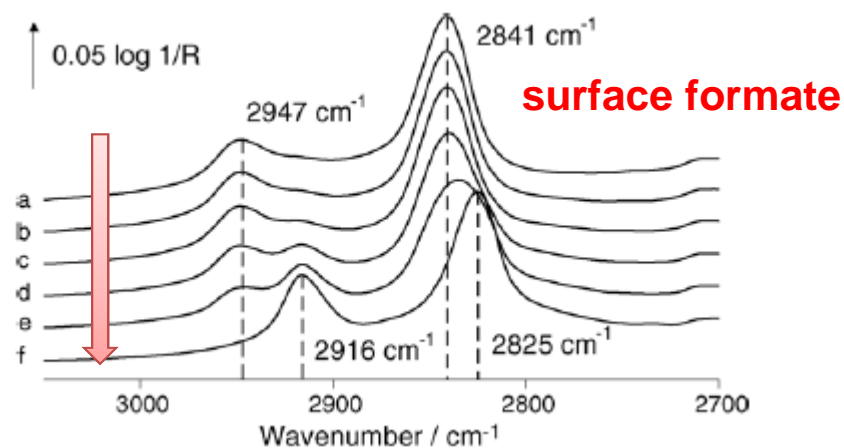
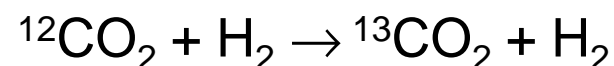


Fig. 1. Typical in situ DRIFT spectra obtained over of a 2% Pt/CeO₂ at steady-state conditions under (a) a RWGS feed: 1% CO₂ + 4% H₂ in Ar at 498 K and (b) a WGS feed: 1% CO + 10% H₂O in Ar at 473 K.

perturbation of steady state



DRIFTS-SSITKA

- Carbonates exchange much faster than formates...

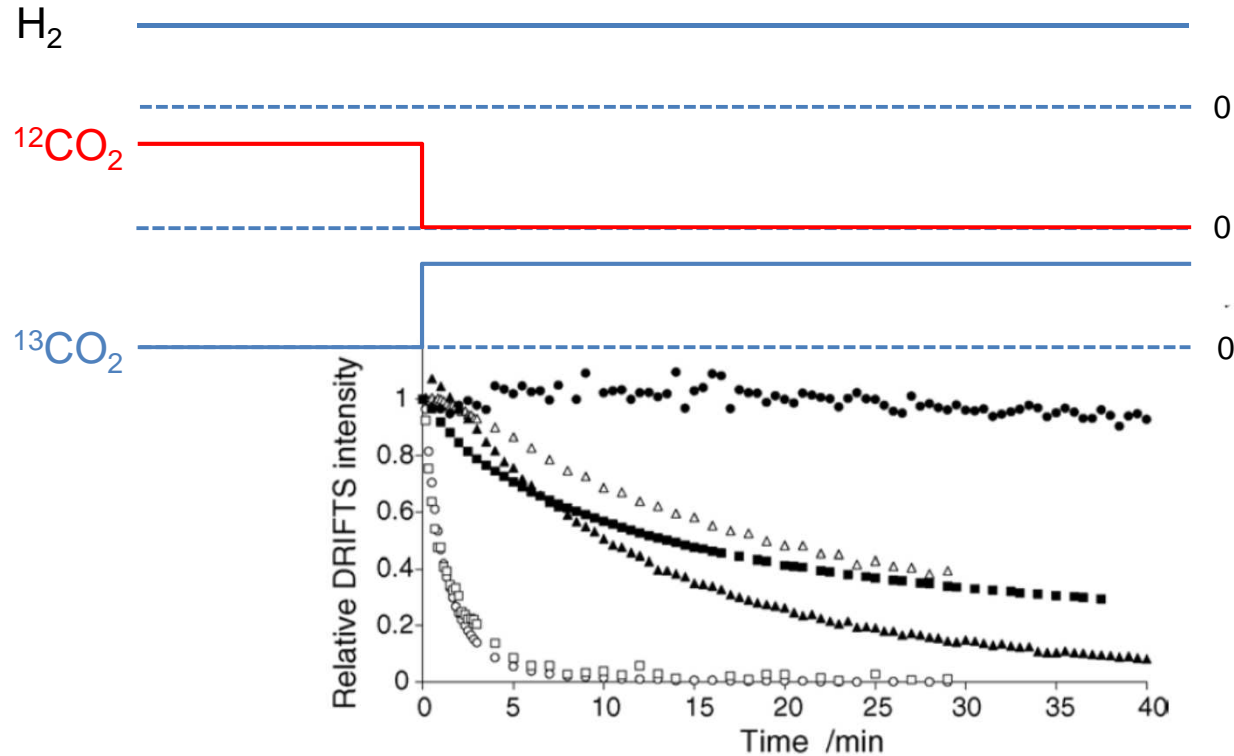


Fig. 13. Relative intensity of the IR bands of the formate (\blacktriangle , \triangle), carbonyl (\blacksquare , \square) and carbonate (\bullet , \circ) species as a function of time on stream in Ar (solid symbols) and under RWGS stream containing $^{13}CO_2$ (open symbols). The sample was at steady-state state in 1% $^{12}CO_2$ + 4% H_2 and $T = 498$ K before switching to either Ar or the $^{13}CO_2$ -containing feed.