Infrared spectroscopy

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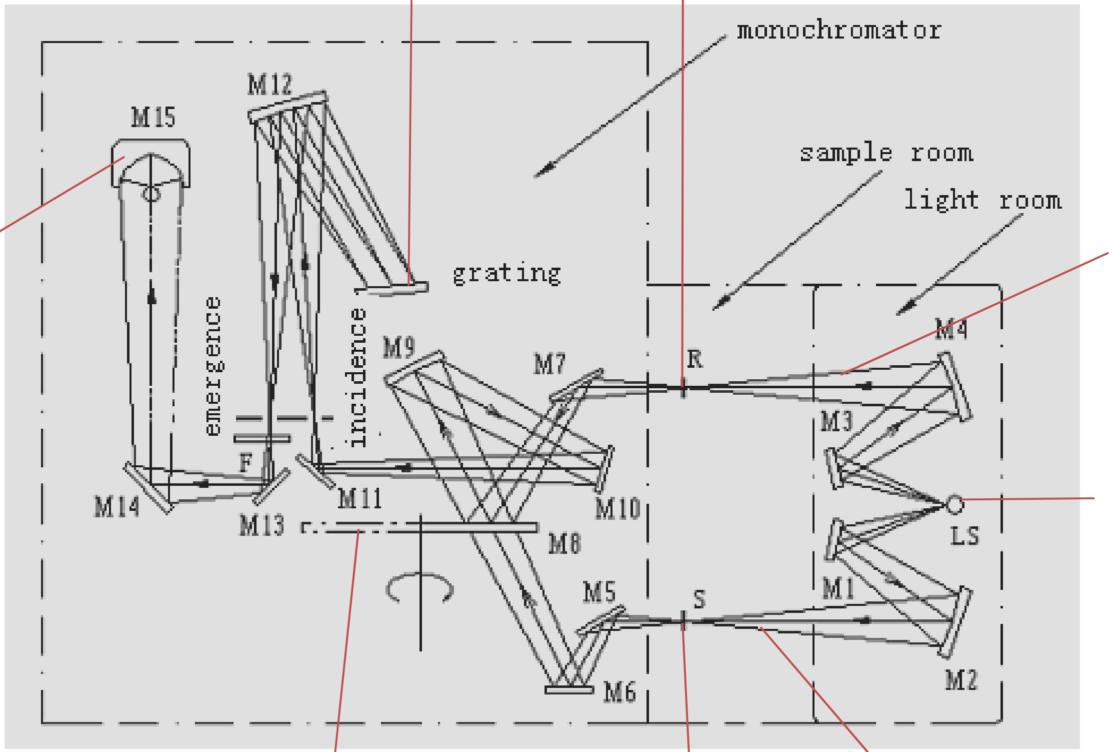
Double beam spectrometer



Grating

Reference

Detector

Reference beam

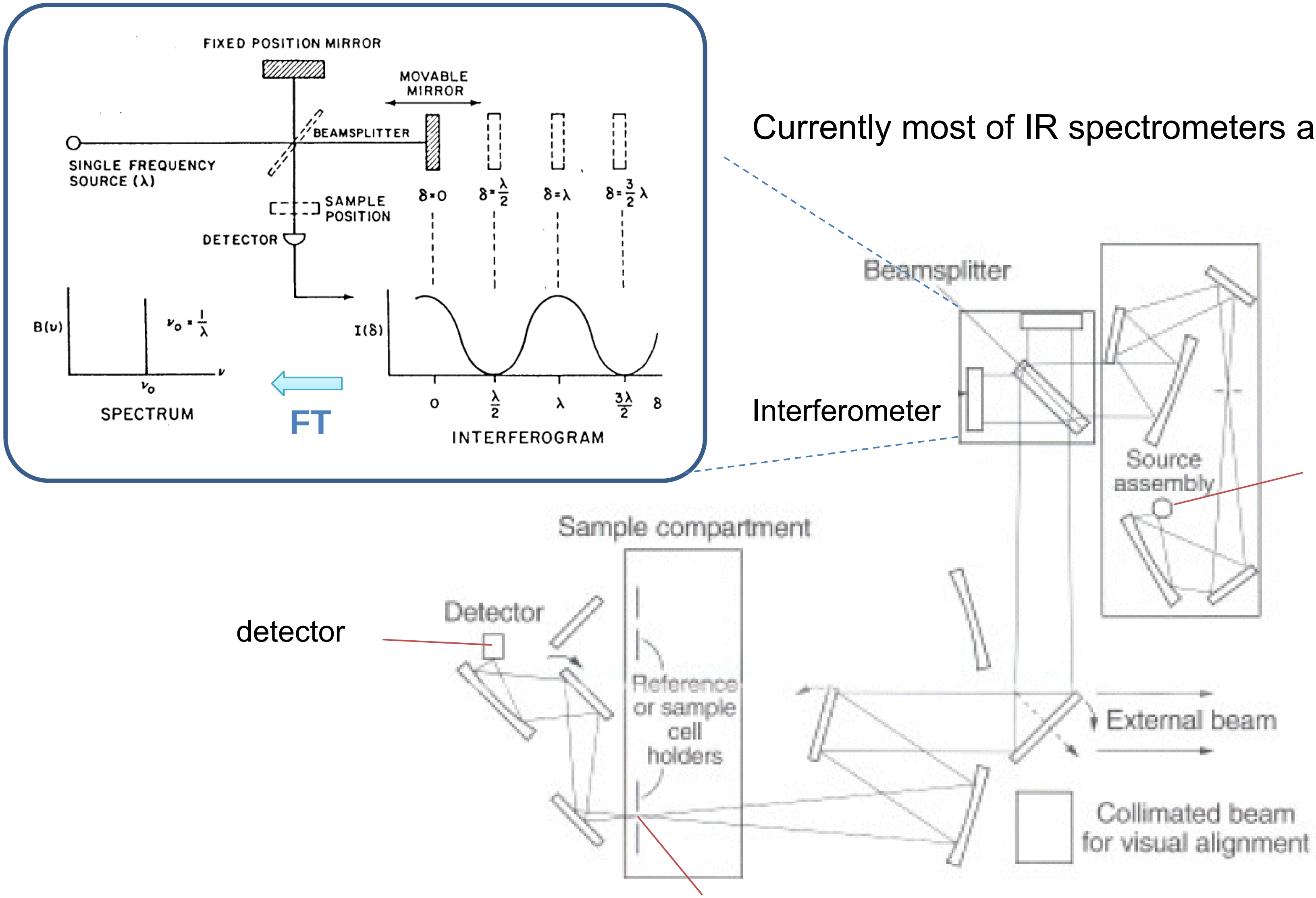
Light source

Beam selector / chopper

Sample

Sample beam

Fourier transform spectrometer



Currently most of IR spectrometers are FT-IR

Interferometer

light source

detector

sample

Dispersive vs. FT

FT-IR spectrometer has significant advantages over dispersive one

- **Multiplex (Fellgett) advantage**

  All source wavelengths are measured simultaneously

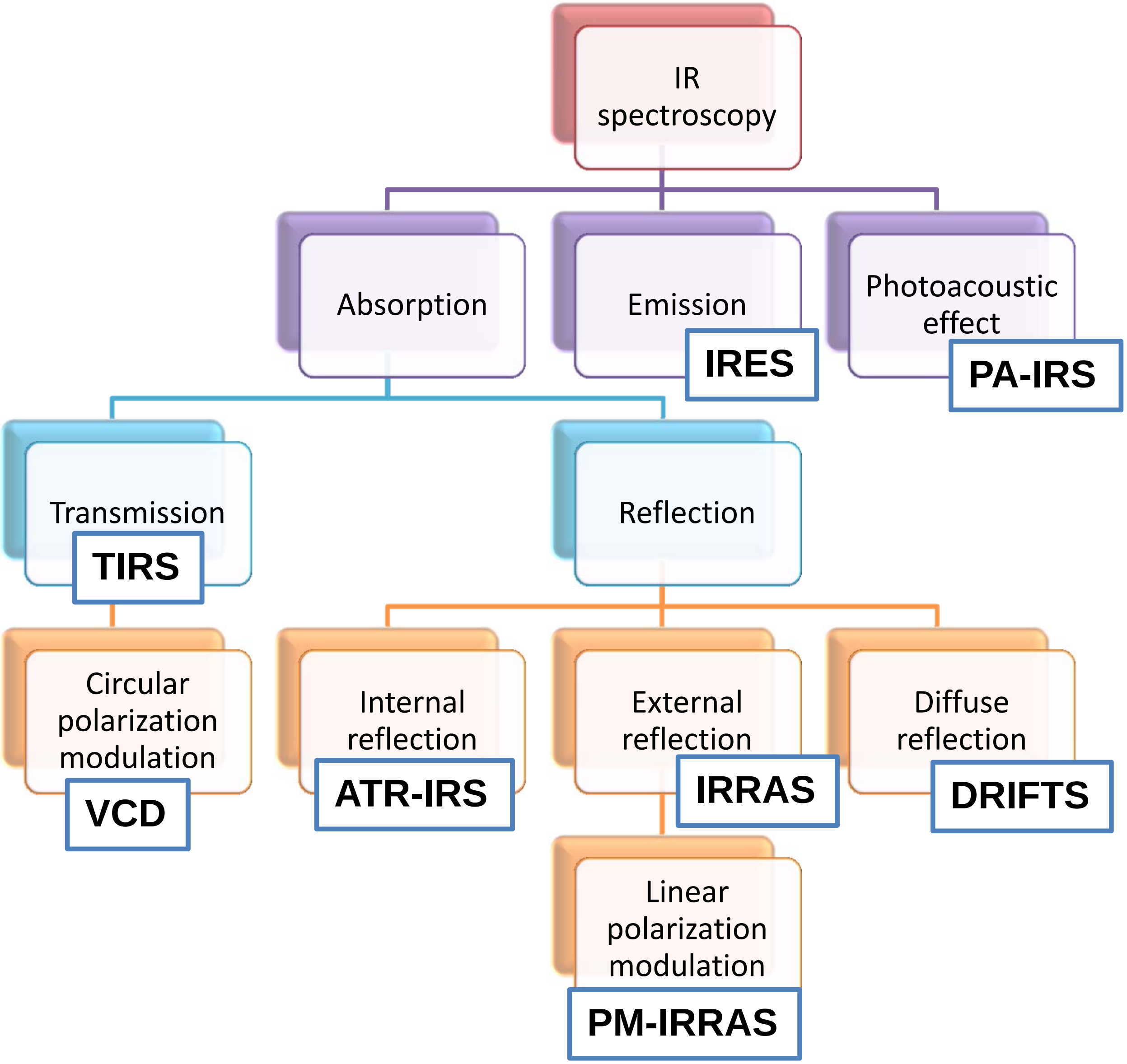
- **Throughput (Jacquinot) advantage**

  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

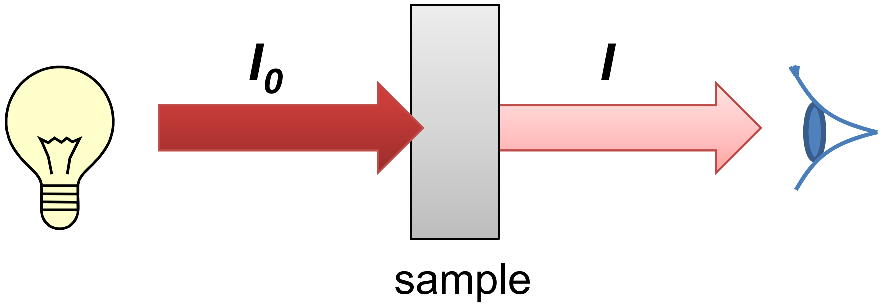
IRRAS: infrared reflection-absorption spectroscopy

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)

- **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

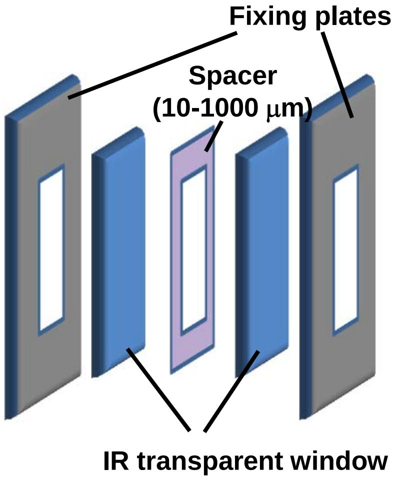
- **Mull method**
  - Most common one is Nujol (liquid paraffin)
  - Samples are ground and suspended in one or two drops of a mulling agent
  - Followed by further grinding until a smooth paste is obtained

- **Film method**
  - By solvent casting or melt casting

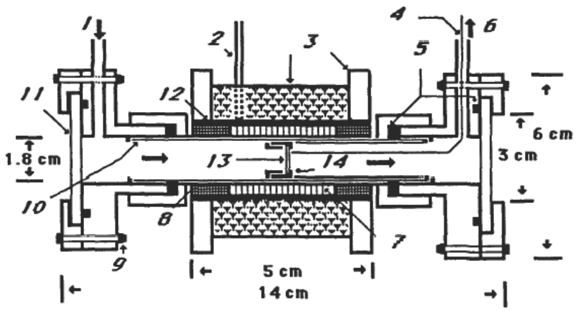
- **NOT** FOR IN SITU/OPERANDO EXPERIMENTS

Transmission IR spectroscopy (TIRS)

■ Liquid samples

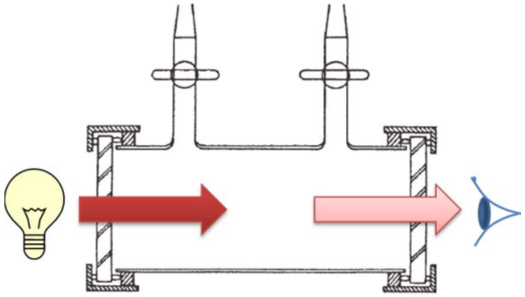


■ Gas-solid Catalysis !



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

■ Gas samples

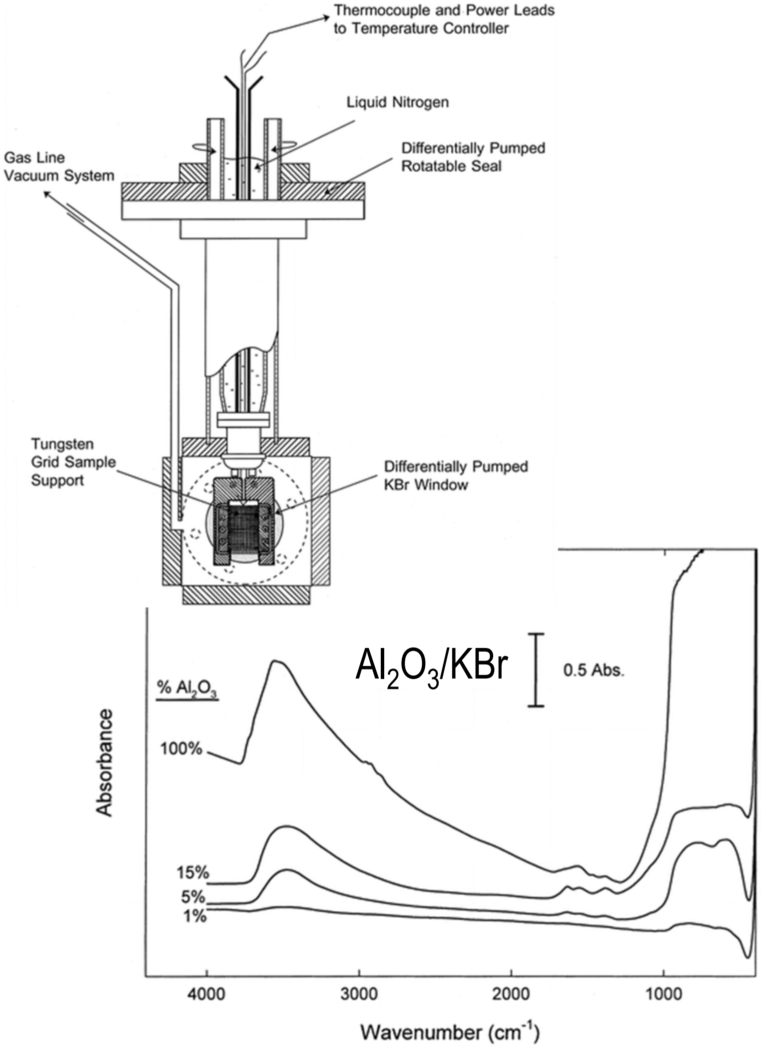


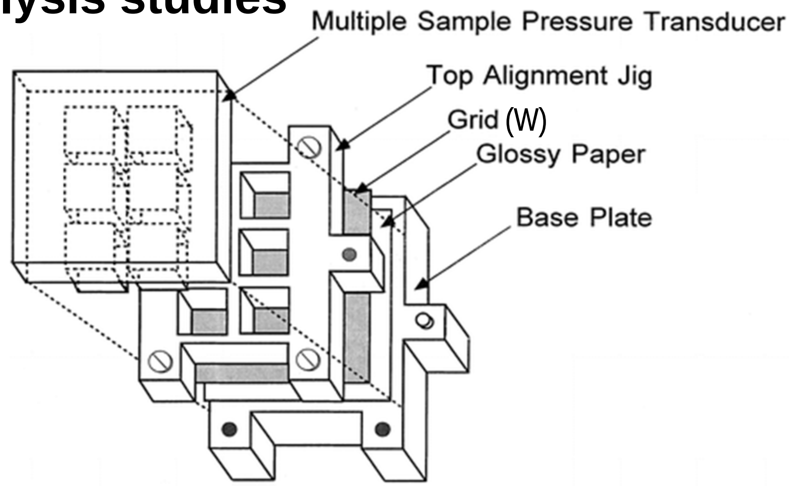
Specac

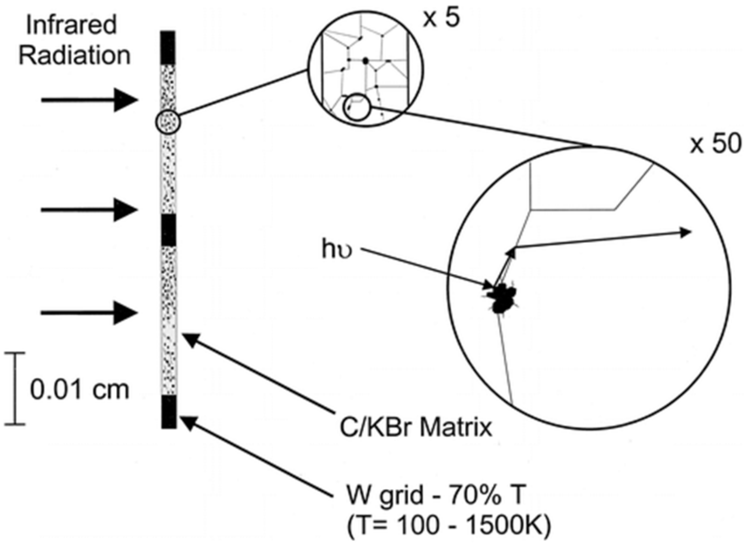
Temperature-
controlled cell
[ca. 200 – 500 K]

Transmission IR spectroscopy (TIRS)

- ***In situ* cells for heterogeneous catalysis studies**





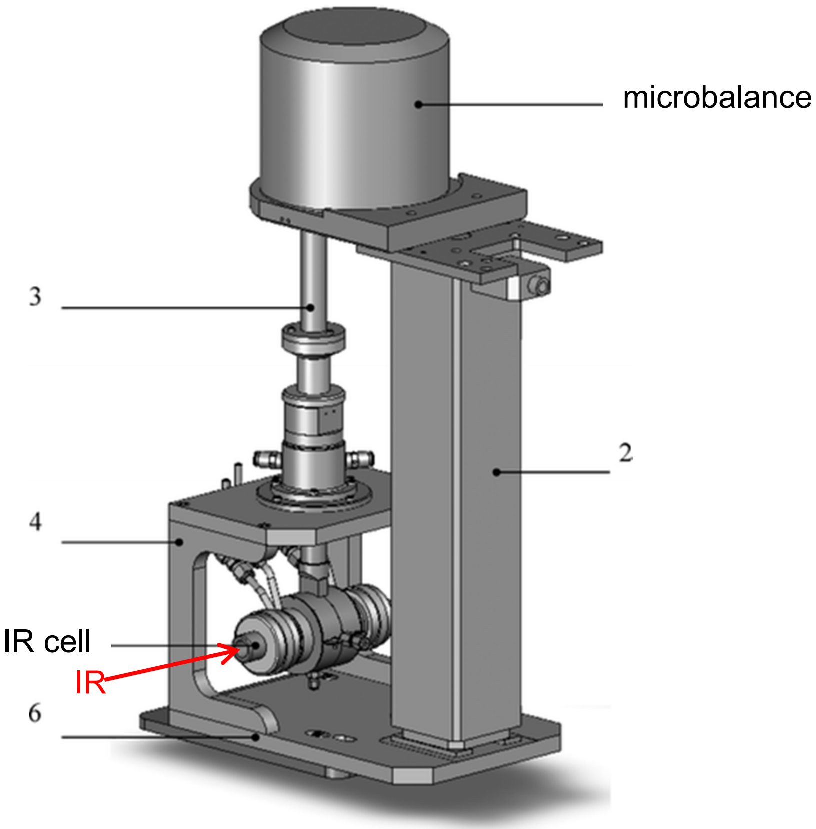


Mawhinney et al., *Langmuir* 15 (1999) 4617; Basu et al., Rev. Sci. Instrum. 59 (1988) 1321

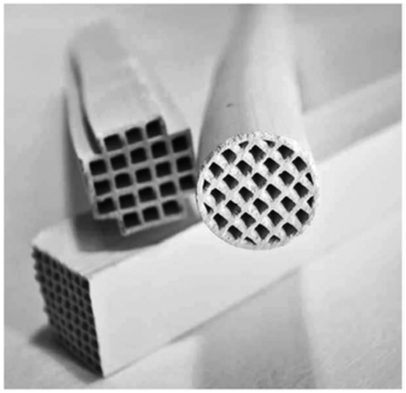
Transmission IR spectroscopy (TIRS)

- ***In situ* cells**

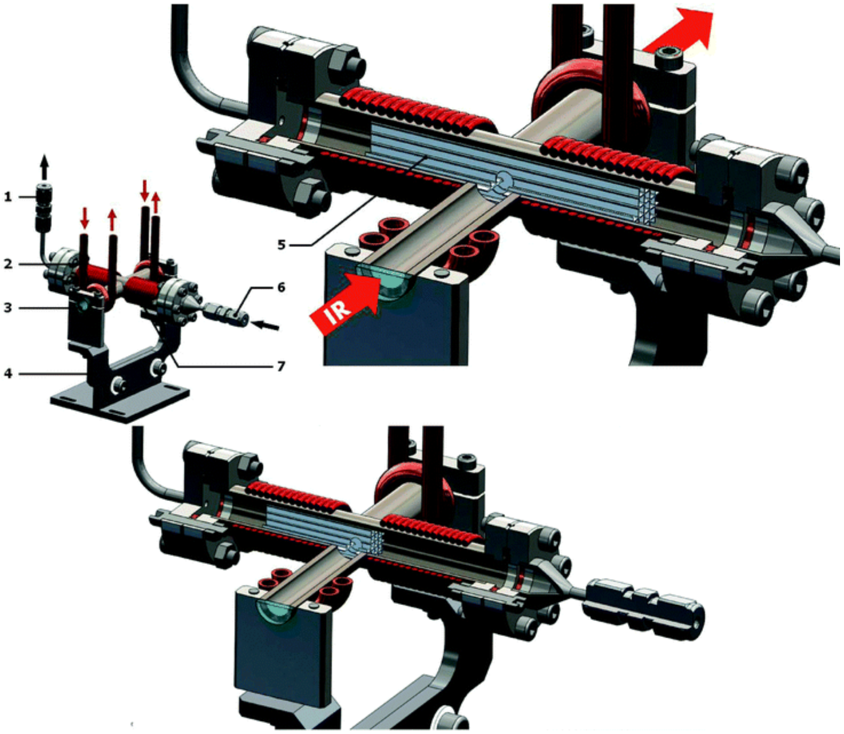
combined TG-FTIR



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



FTIR of monoliths



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

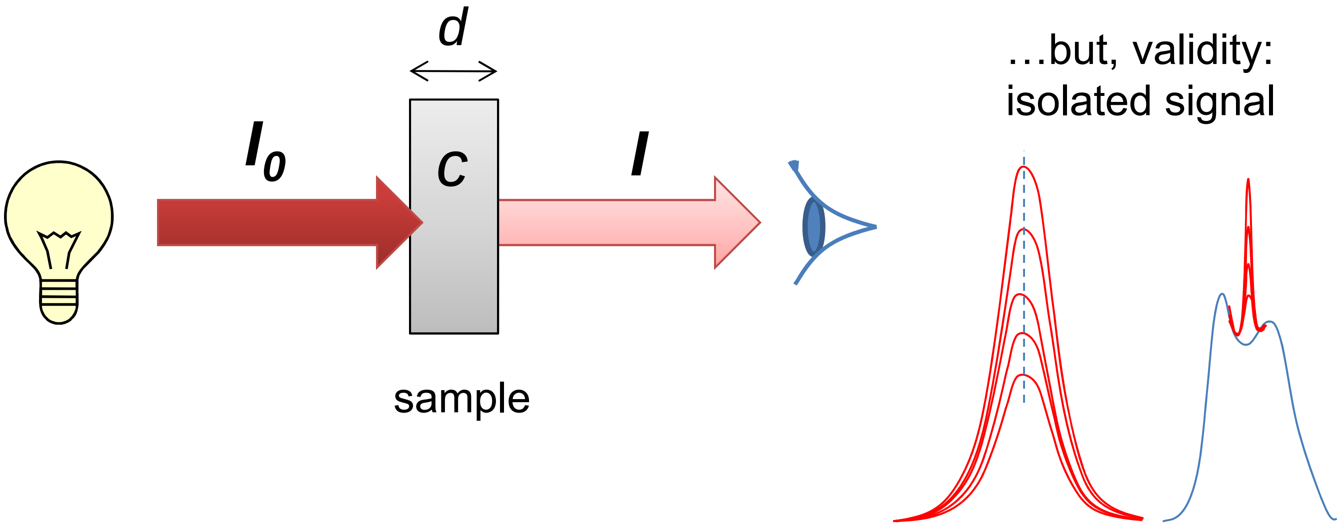
Transmission IR spectroscopy (TIRS)

- **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, **ε**: molar absorption (extinction) coefficient, **c**: concentration, **d**: path length

Transmission IR spectroscopy (TIRS)

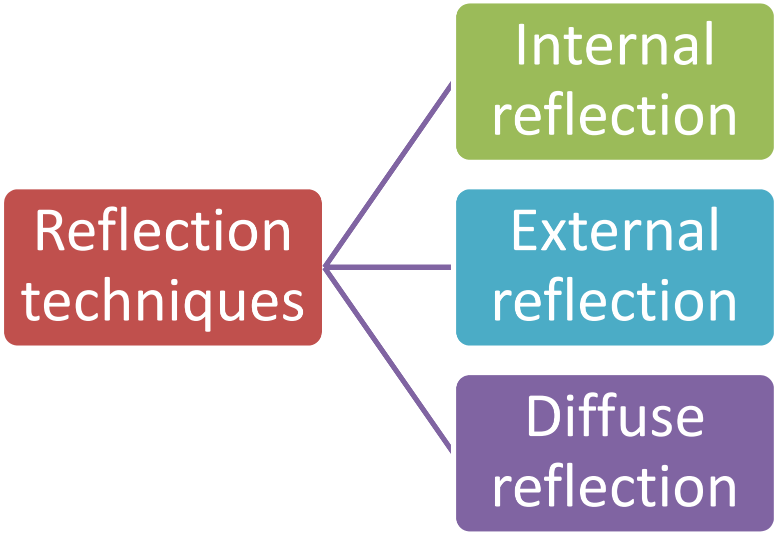
- **Common window materials**

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_4Cl
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

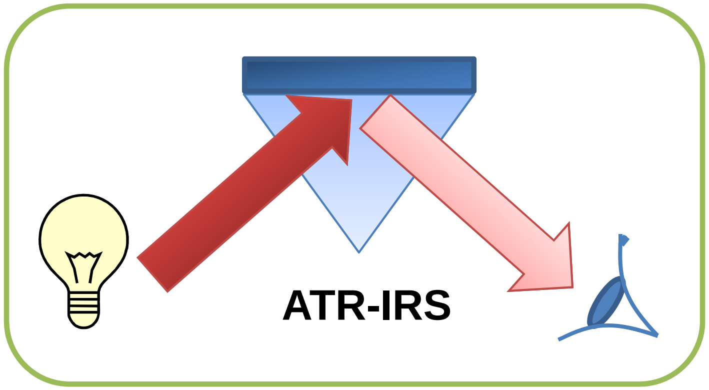
■ Aim for heterogeneous catalysis studies

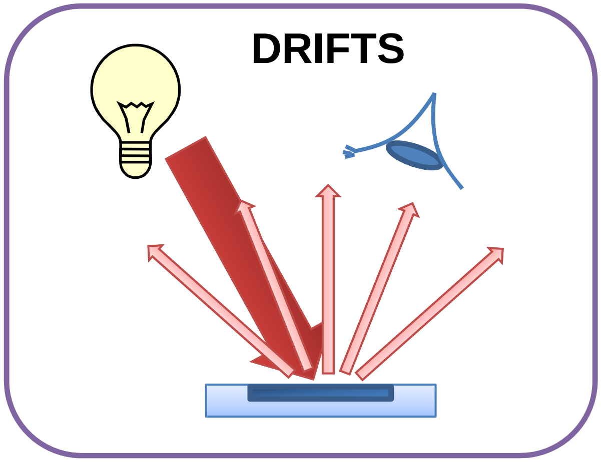
study events occurring at interfaces and maximize signals related to catalysts and active species on surfaces, especially during reactions

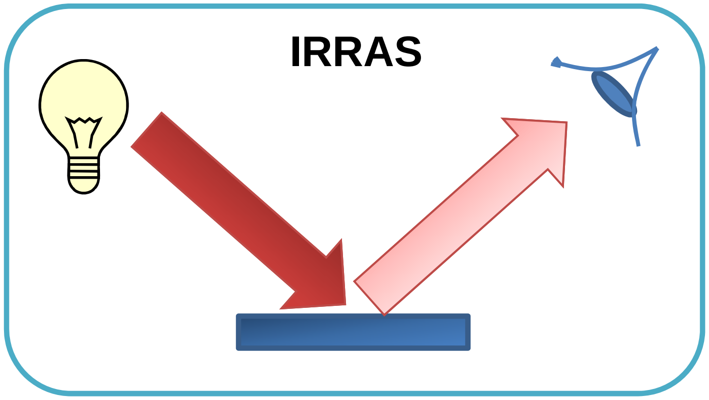


Reflection techniques

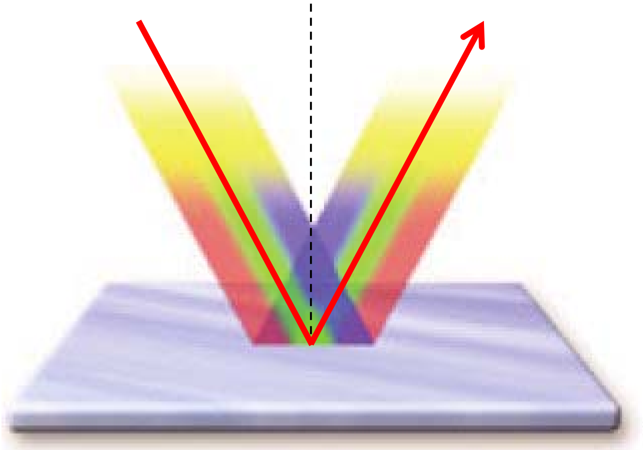
- Internal reflection
- External reflection
- Diffuse reflection





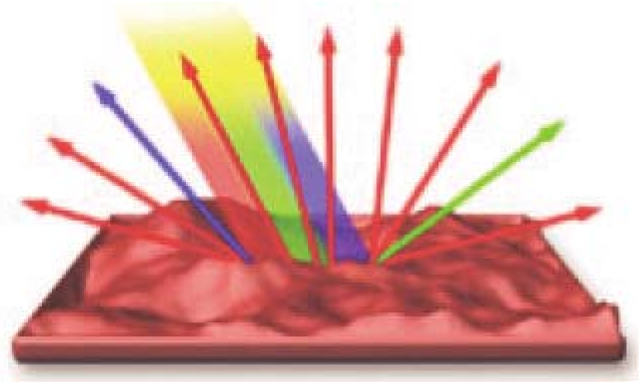


Specular vs. diffuse reflection



Specular reflection
(smooth surface)

Surface smoothness like mirror = reflection and incident angles are equal

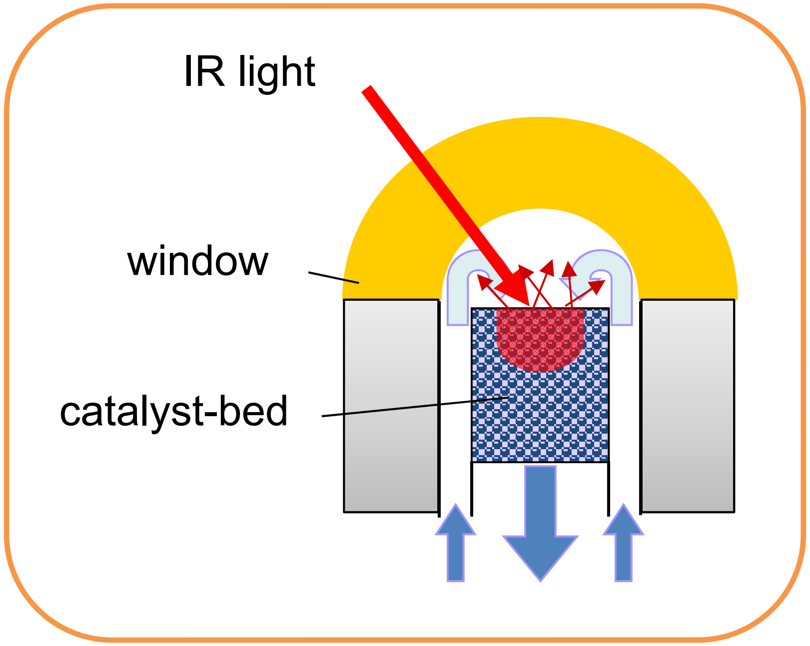


Diffuse reflection
(rough surface)

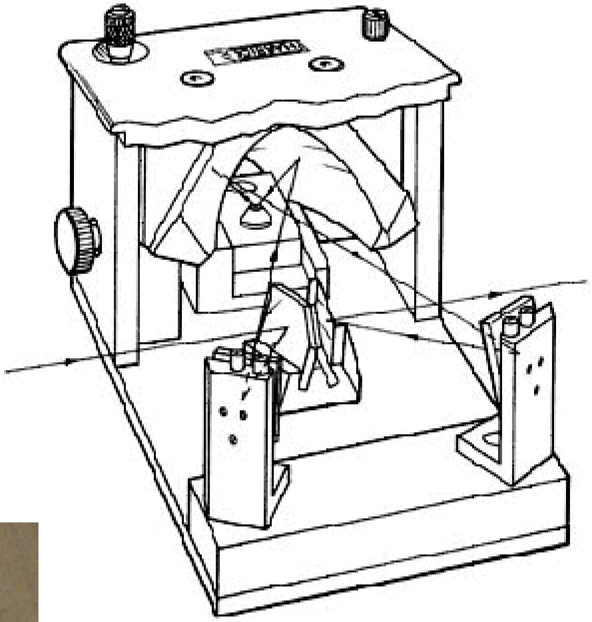
Incident light is reflected to a number of directions due to surface roughness

Diffuse reflectance (DRIFTS)

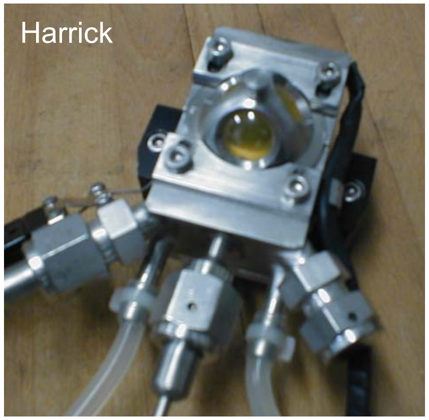
Very popular for *in situ* measurements of physicochemical processes at **gas-solid interfaces** using realistic **powder catalysts**



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

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

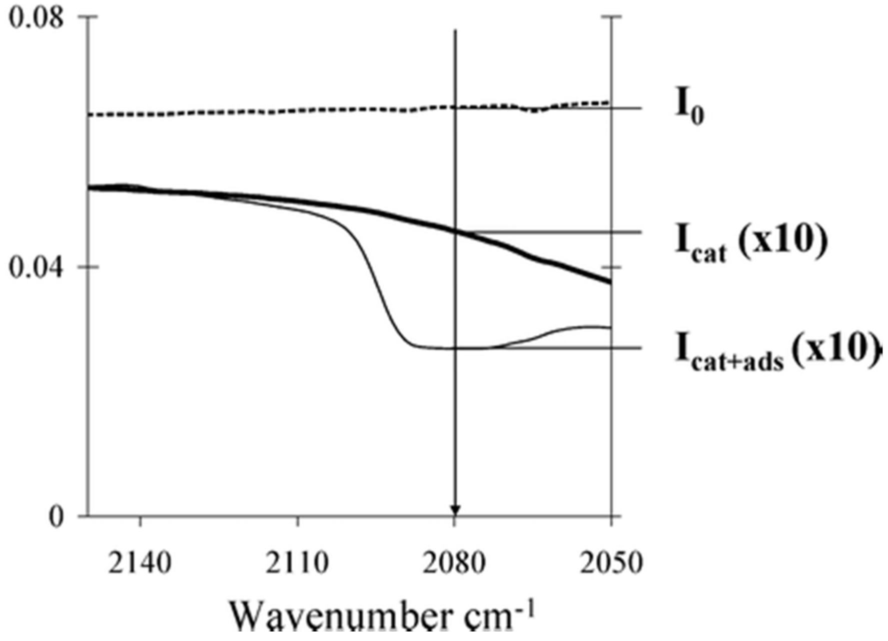
k: molar absorption coefficient, *k*=2.303αc, α: absorptivity, *c*: concentration, σ: diffusion (scattering) coefficient

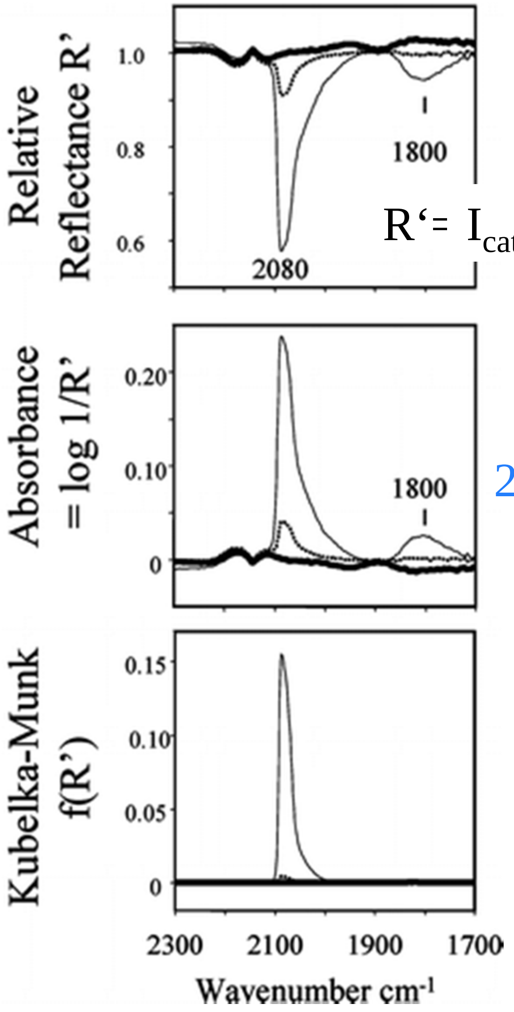
There is a solid (approximated) theory behind and the K-M function is widely used; however its applicability and accuracy for highly absorbing and non-absorbing samples is questionable

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

courtesy Dr. Urakawa

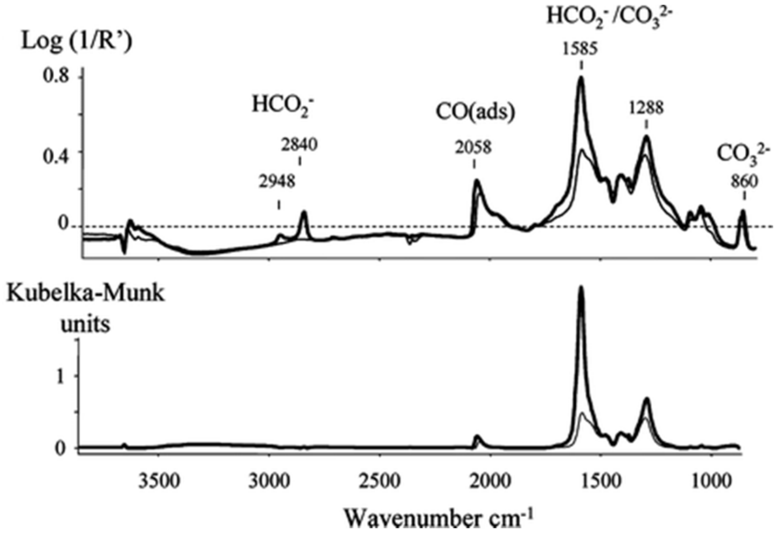
Diffuse reflectance (DRIFTS)





R' = $I_{cat+ads}/I_{cat}$

2% Pt/SiO$_2$

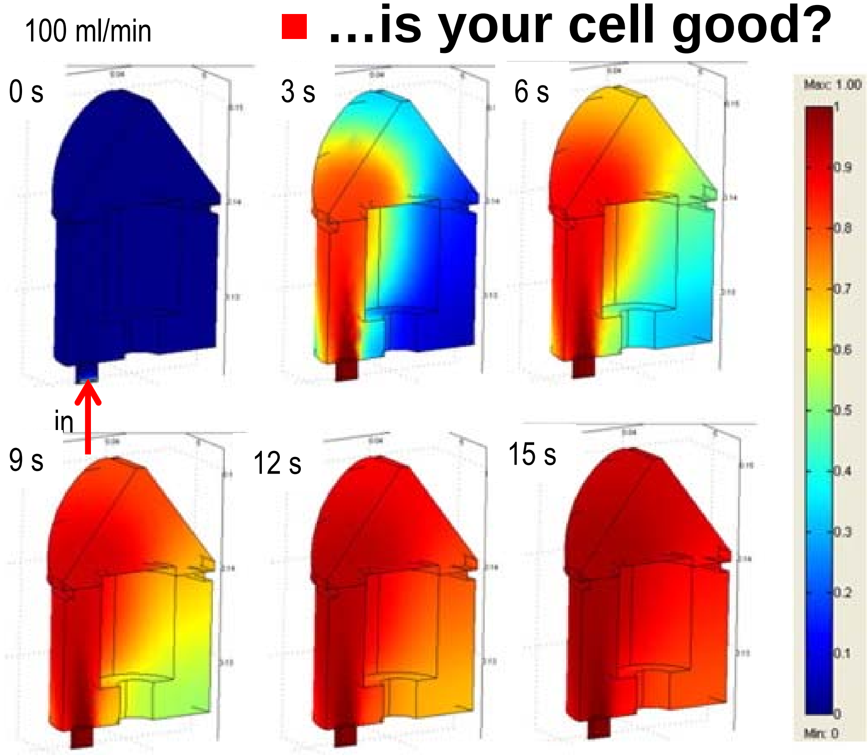


2% Pt/CeO$_2$

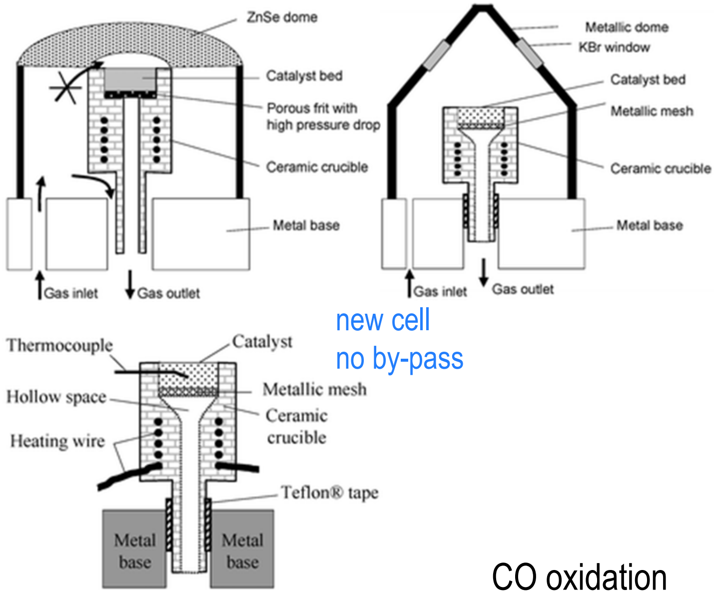
Sirita et al., *Anal. Chem.* 79 (2007) 3912

Diffuse reflectance (DRIFTS)

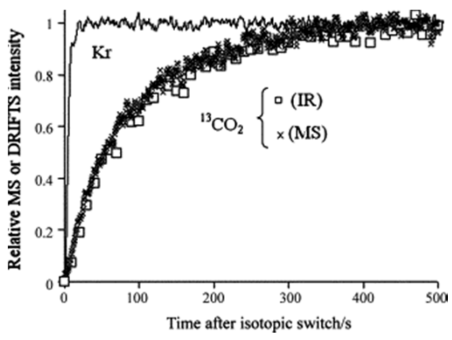
- …is your cell good?

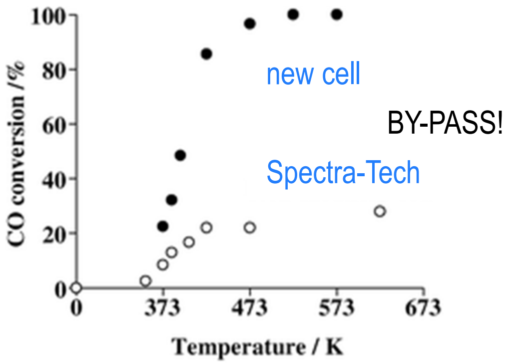


Spectra-Tech



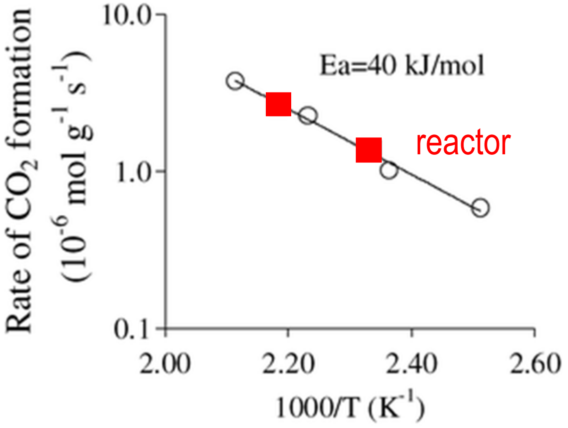
new cell
no by-pass





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

CO oxidation
DRIFT cell vs. microreactor

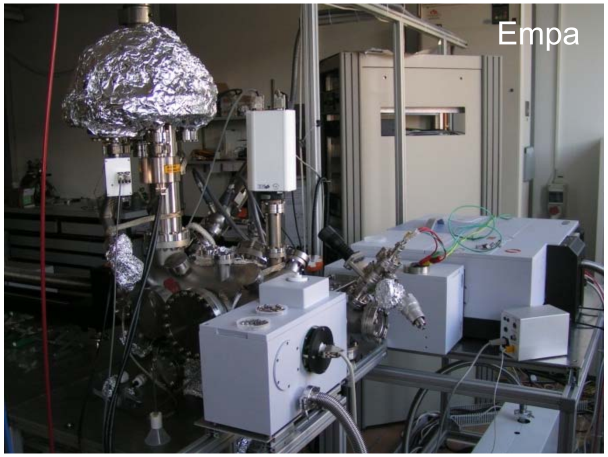


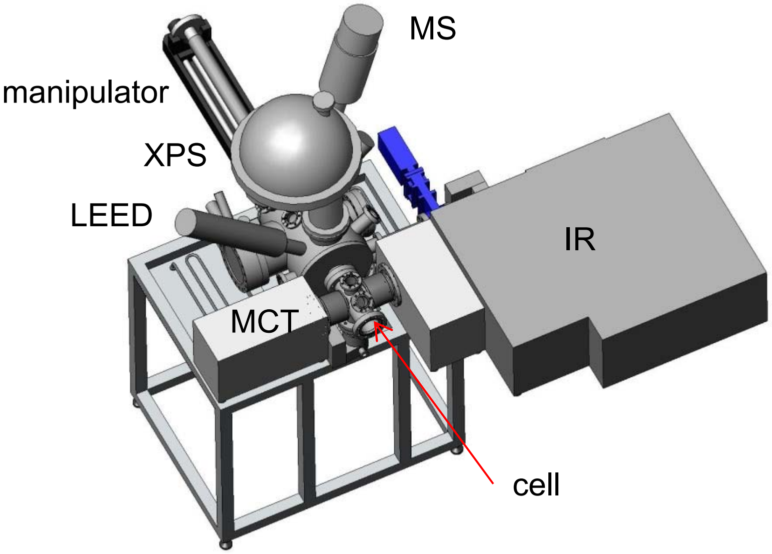
Meunier et al., *J. Catal.* 247 (2007) 277

Meunier, *Chem. Soc. Rev.* 39 (2010) 4602

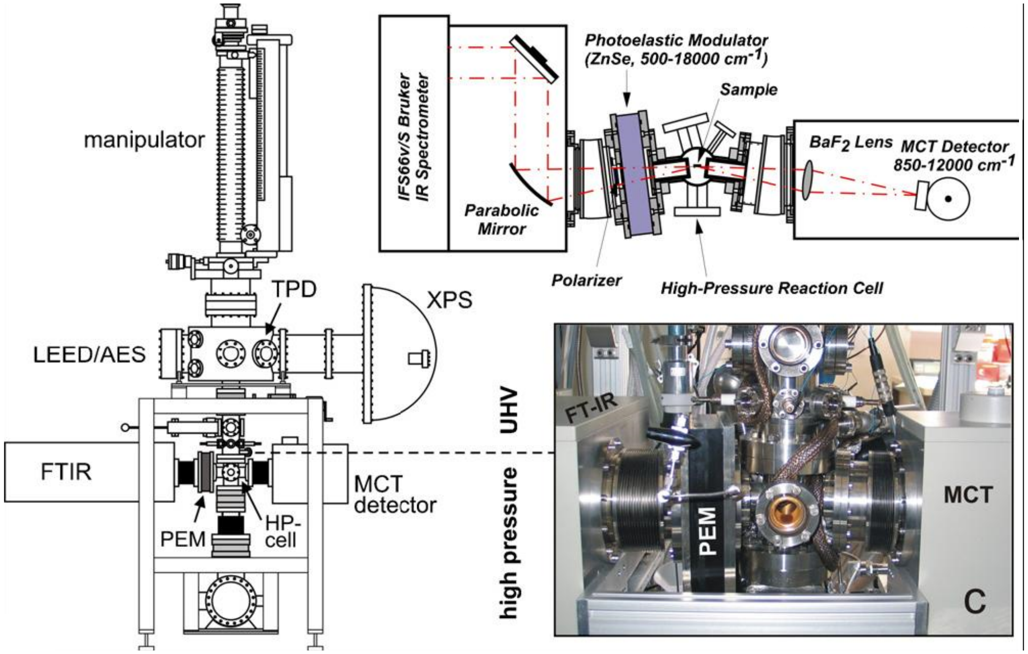
Reflection-absorption (IRRAS)

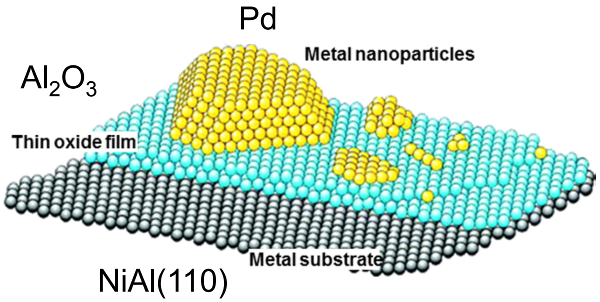
- **Model system investigation**
  - single crystals
  - well-defined nano-particles





Rupprechter, Catal. Today 126 (2007) 3





The surface selection rule

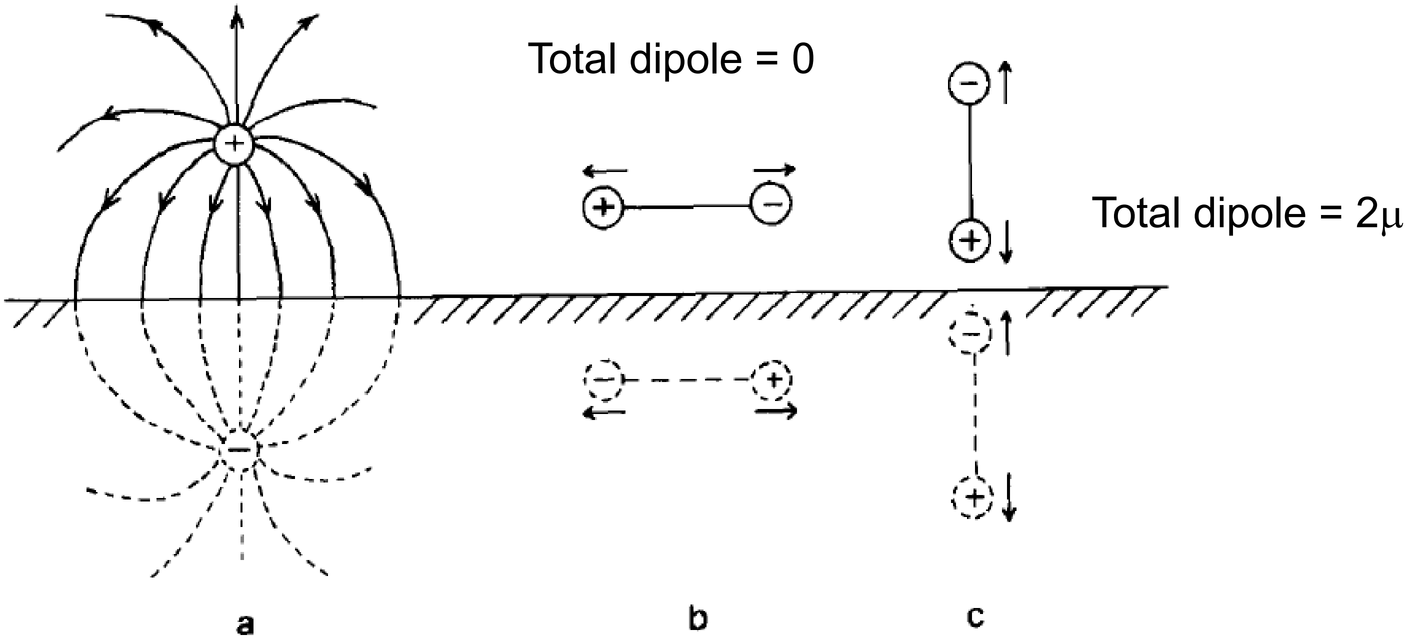
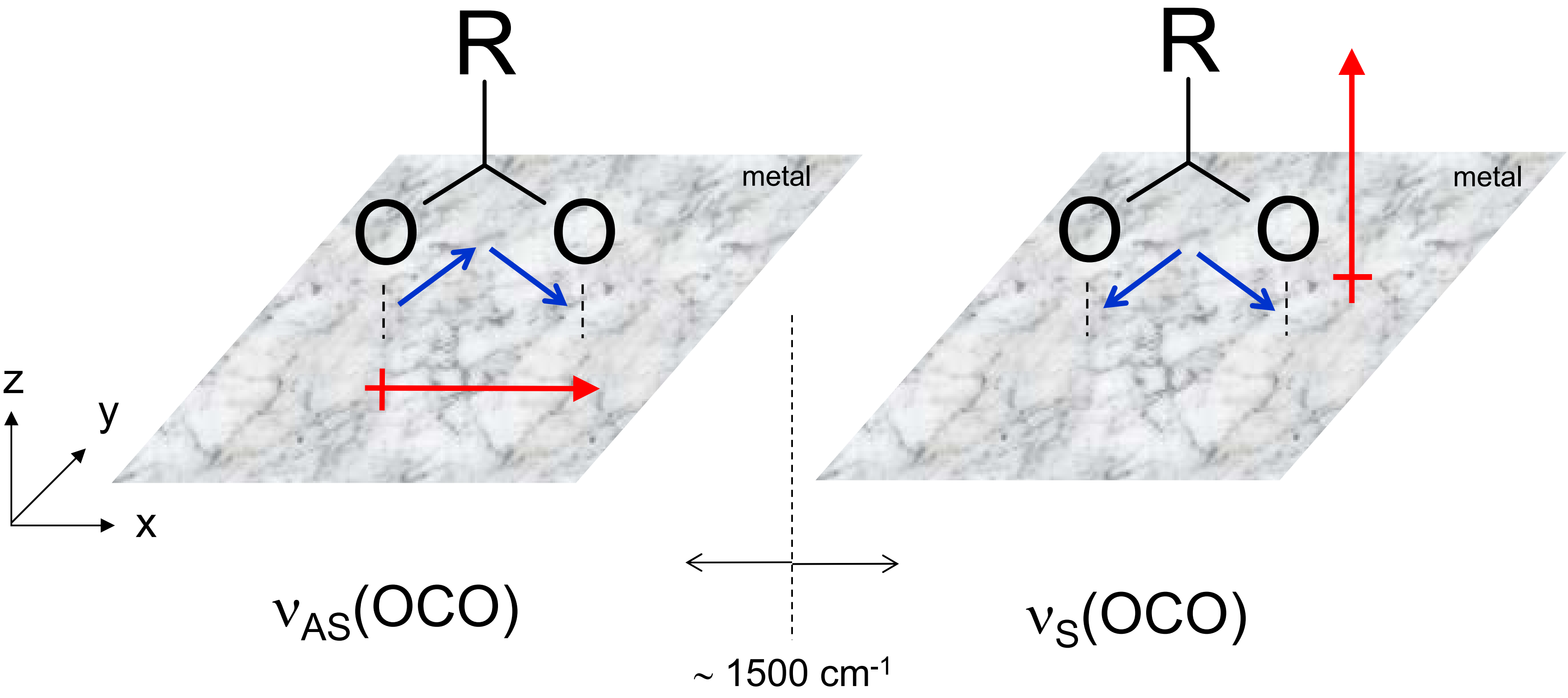


Fig. 1. (a) The lines of force and the electrical "image" resulting from a positive charge over the surface of a conductor (the metal surface is the upper line above the hatched area). (b) The changes during the vibration of a dipole parallel to the surface of the metal; the "image" dipole change is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

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

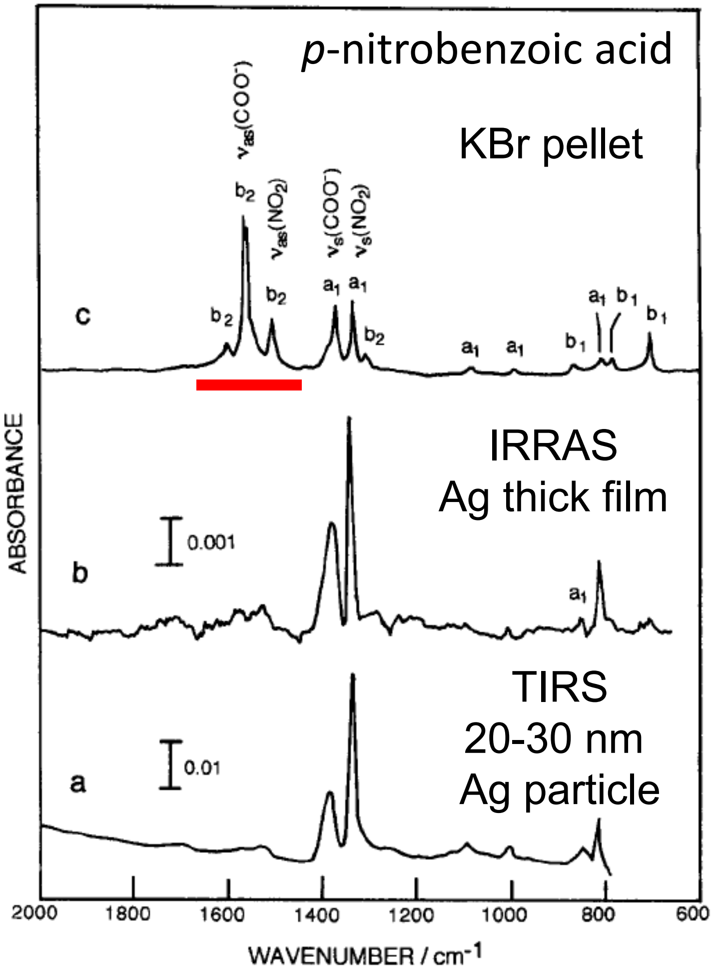
The surface selection rule

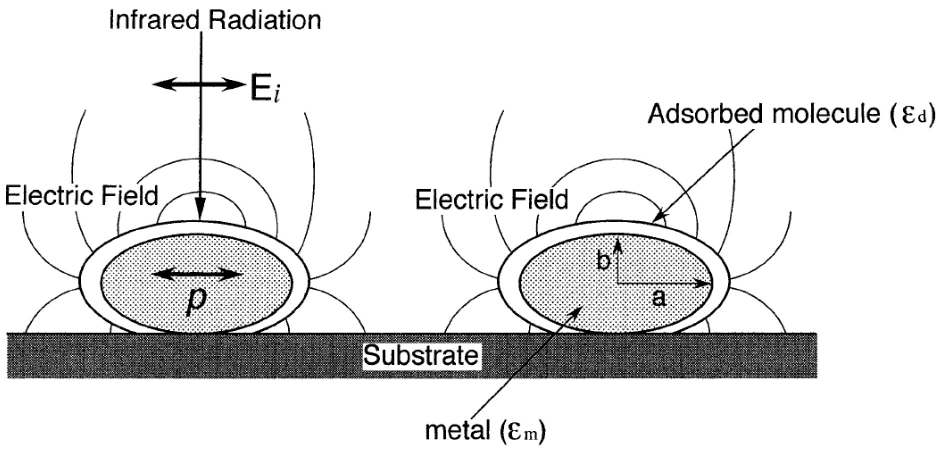
- **Carboxylate groups**



The surface selection rule

- **Also valid for small (nm) metal particles?**





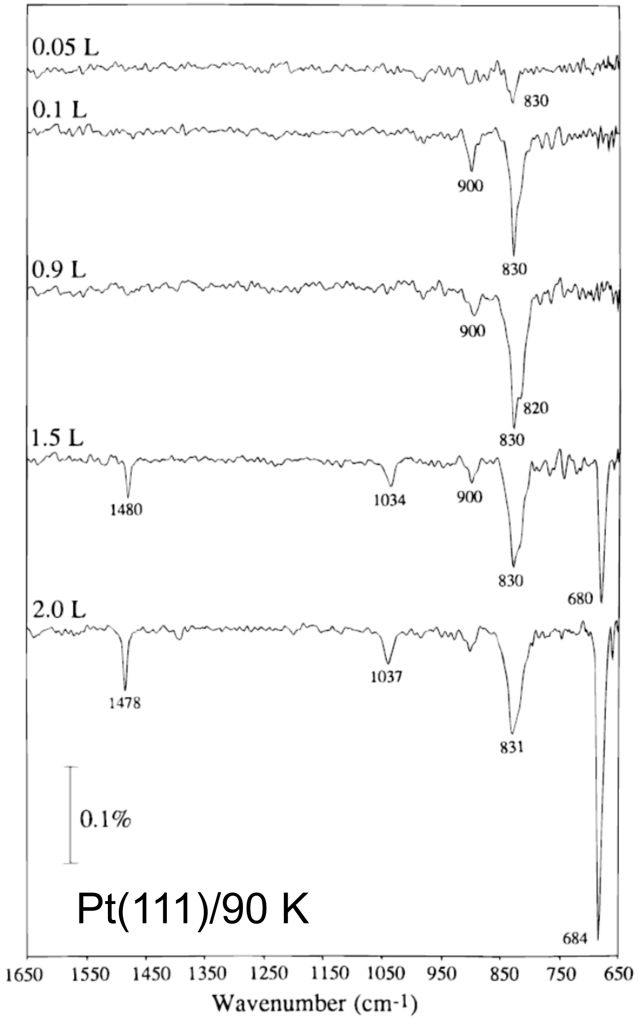
Osawa et al. Appl. Spectroscopy 47 (1993) 1497

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

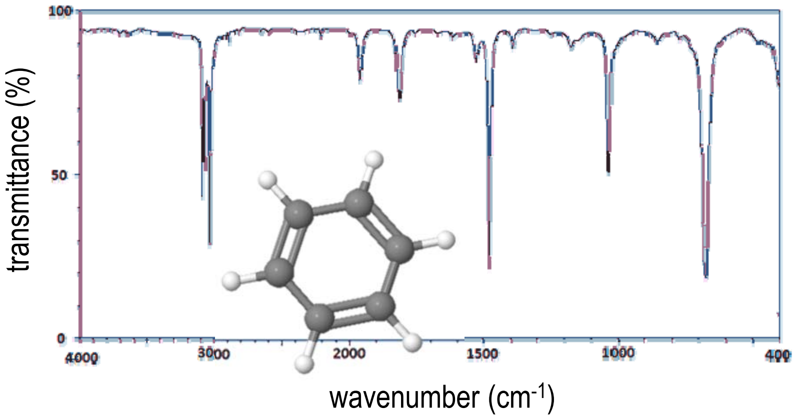
Greenler et al. Surf. Sci. 118 (1982) 415

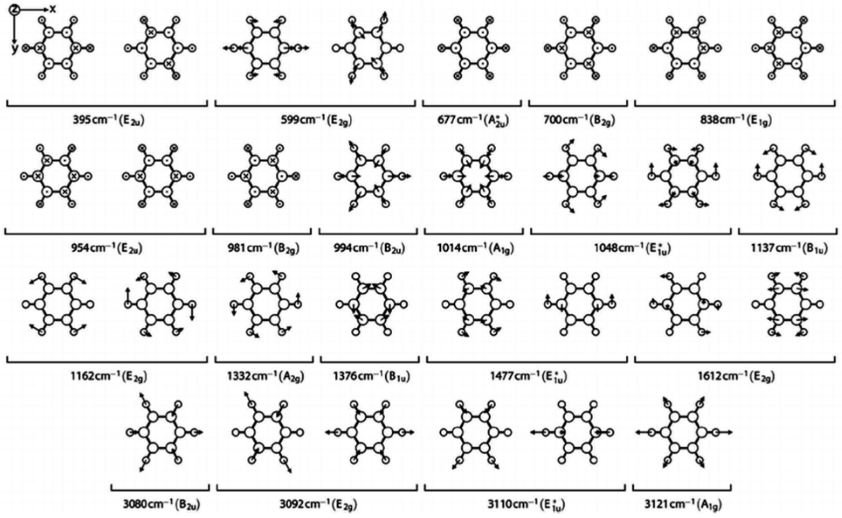
Reflection-absorption (IRRAS)

- **Also RAIRS; specular/external reflection method**



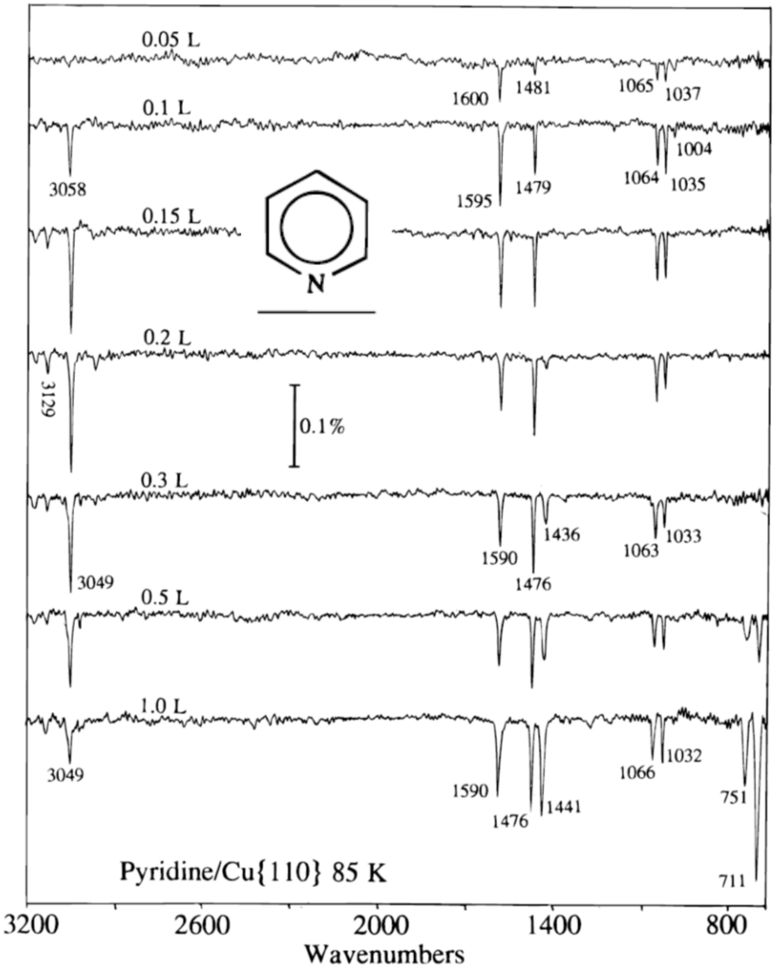
L (Langmuir)= exposure of 10^{-6} Torr gas for 1 s

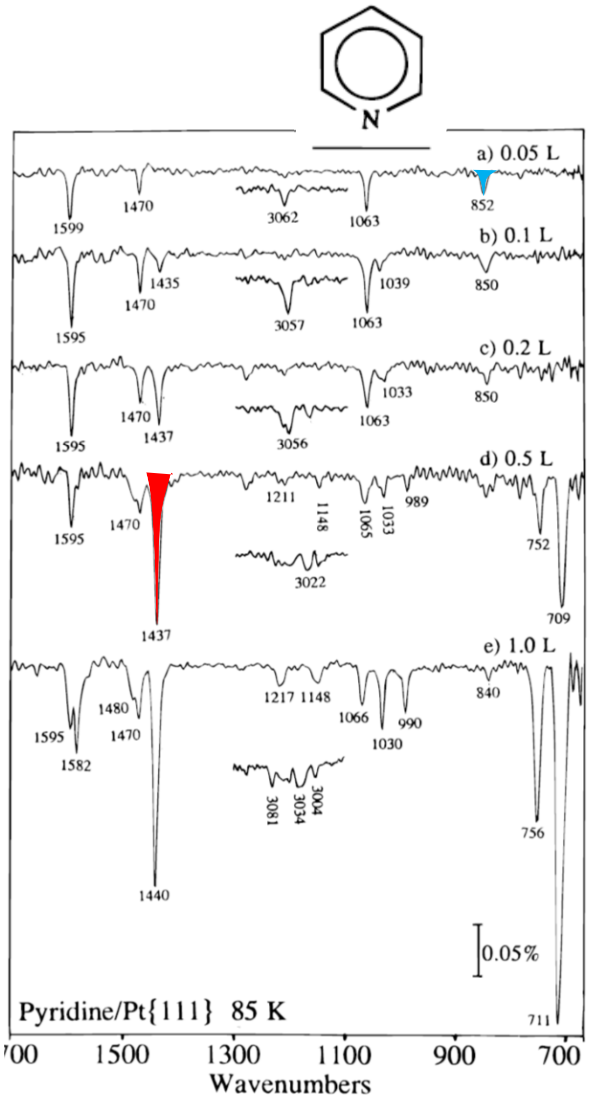


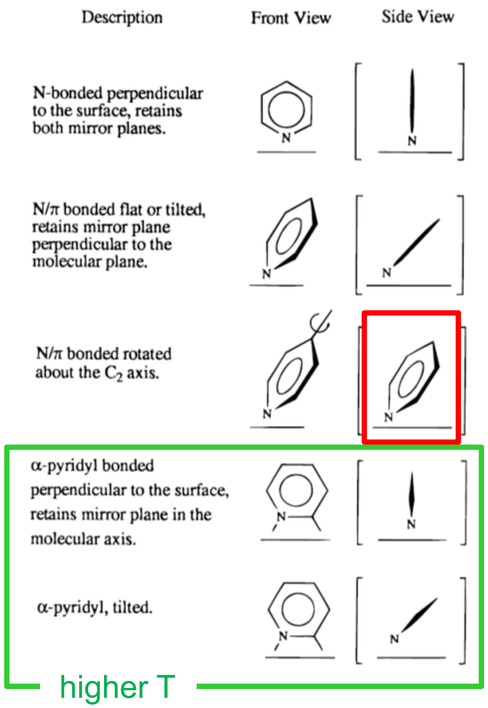


Haq et al., *J. Phys. Chem.* 100 (1996) 16957; Preuss et al., Phys. Rev. B 73 (2006) 155413

Reflection-absorption (IRRAS)







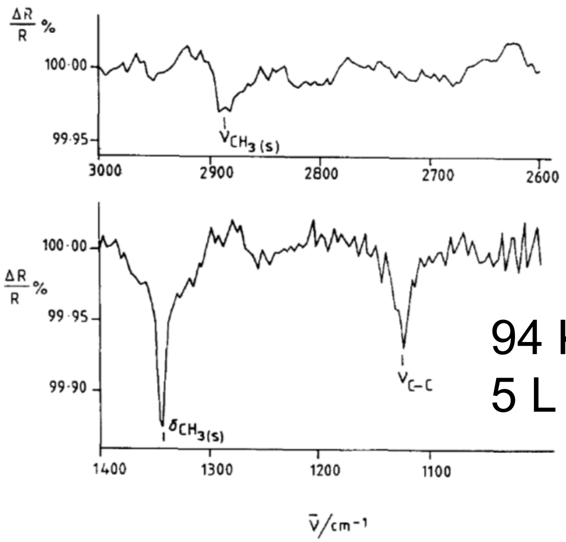
Description	Front View	Side View
N-bonded perpendicular to the surface, retains both mirror planes.	N	N
N/π bonded flat or tilted, retains mirror plane perpendicular to the molecular plane.	N	N
N/π bonded rotated about the C_2 axis.	N	N
α-pyridyl bonded perpendicular to the surface, retains mirror plane in the molecular axis.	N	N
α-pyridyl, tilted.	N	N

higher T

Haq et al., *J. Phys. Chem.* 100 (1996) 16957

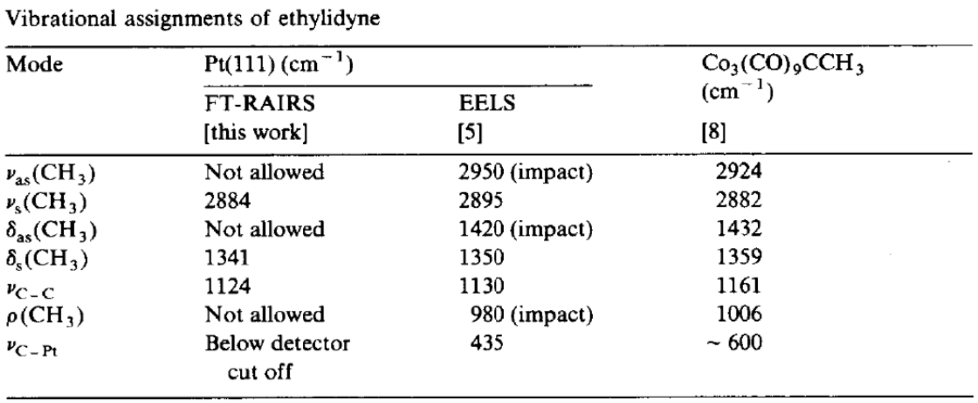
Reflection-absorption (IRRAS)

- **Adsorption of ethylene**



94 K

5 L C_2H_4



Vibrational assignments of ethylidyne

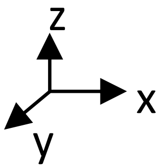
Mode	Pt(111) (cm^{-1}) FT-RAIRS [this work]	 EELS [5]	$Co_3(CO)_9CCH_3$ (cm^{-1}) [8]
$\nu_{as}(CH_3)$	Not allowed	2950 (impact)	2924
$\nu_s(CH_3)$	2884	2895	2882
$\delta_{as}(CH_3)$	Not allowed	1420 (impact)	1432
$\delta_s(CH_3)$	1341	1350	1359
ν_{C-C}	1124	1130	1161
$\rho(CH_3)$	Not allowed	980 (impact)	1006
ν_{C-Pt}	Below detector cut off	435	~ 600

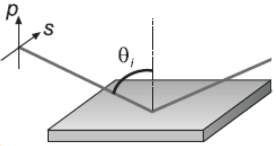
Chesters et al., *Surf. Sci.* 187 (1987) L639

Reflection-absorption (IRRAS)

- Also RAIRS; specular/external reflection method

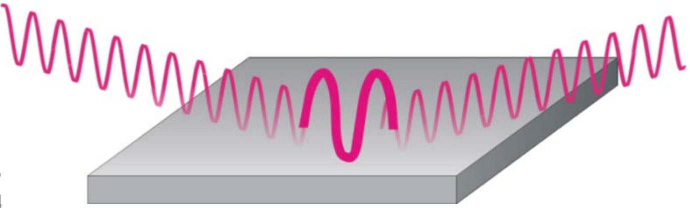
Perpendicular (s-) polarization (y-axis)

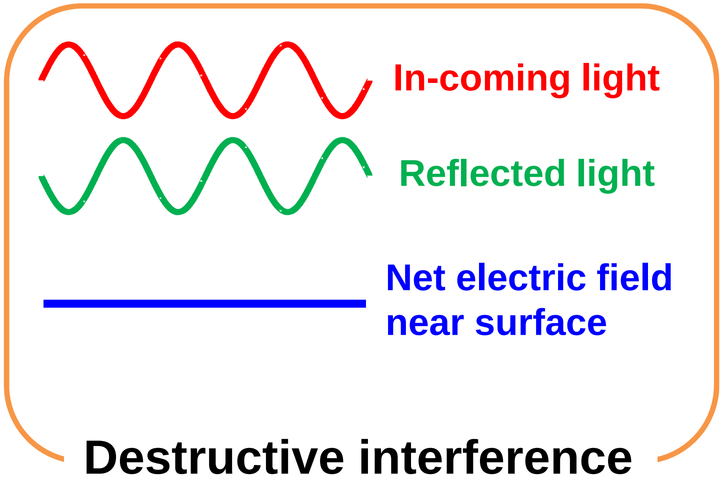




Parallel (*p*-) polarization (x, z-axis)

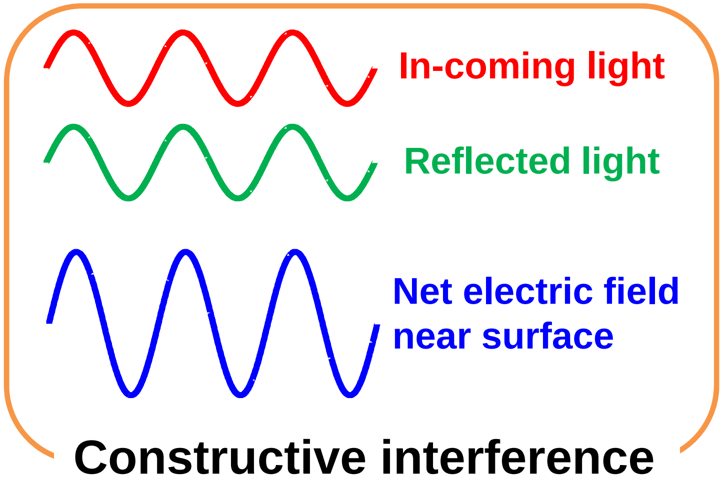
Parallel: parallel to the plane of incident light





Destructive interference

This *s*-polarization does not contain information about surface species



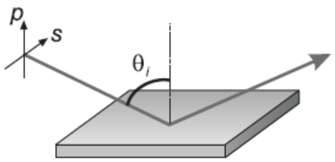
Constructive interference

This *p*-polarization is used for IRRAS

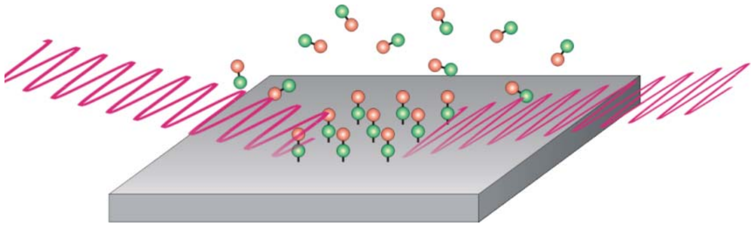
Greenler, *J. Chem. Phys.* 44 (1966) 310

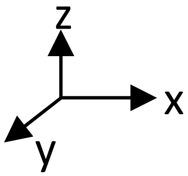
Phase-modulation IRRAS (PM-IRRAS)

- **Generation of 2 polarizations (photoelastic modulator)**
  - excellent gas-phase compensation
  - non-UHV experiments possible
  - highly sensitive, time-resolved studies possible

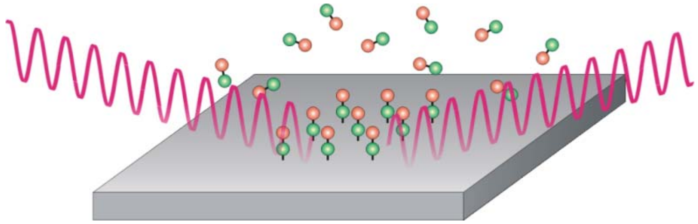


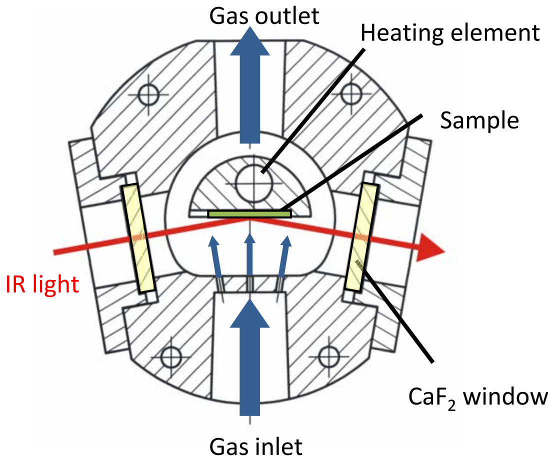
Perpendicular (*s*-) polarization (y-axis)





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





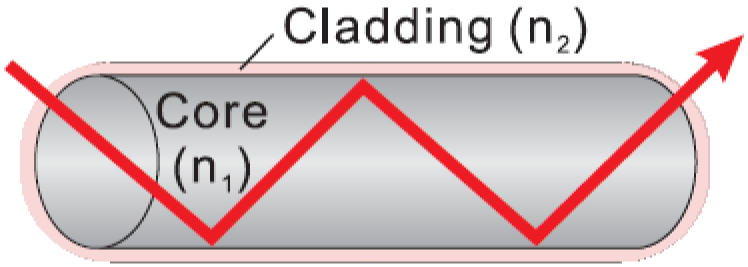
Urakawa et al., *J. Chem. Phys.* 124 (2006) 054717

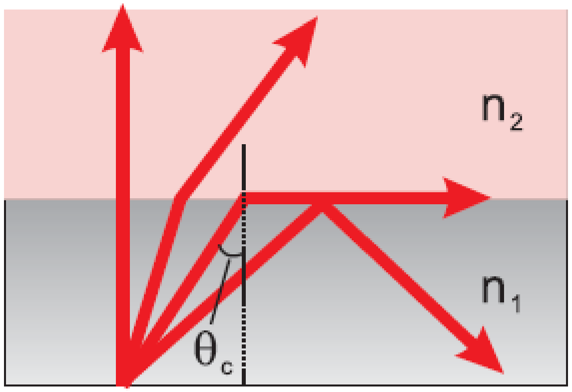
R_p	-	R_s	=	ΔR
Parallel polarization		**Perpendicular polarization**		**Difference**
surface + gas		**gas**		**surface**

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



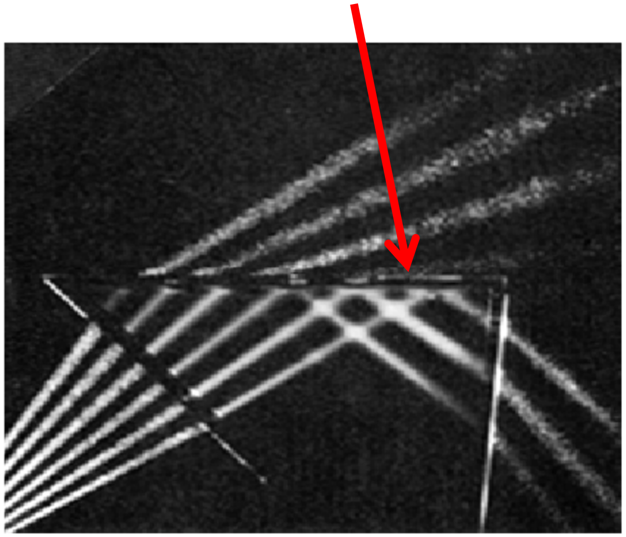


Above critical angle θ_c ATR phenomenon occurs

$n_1 > n_2$

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

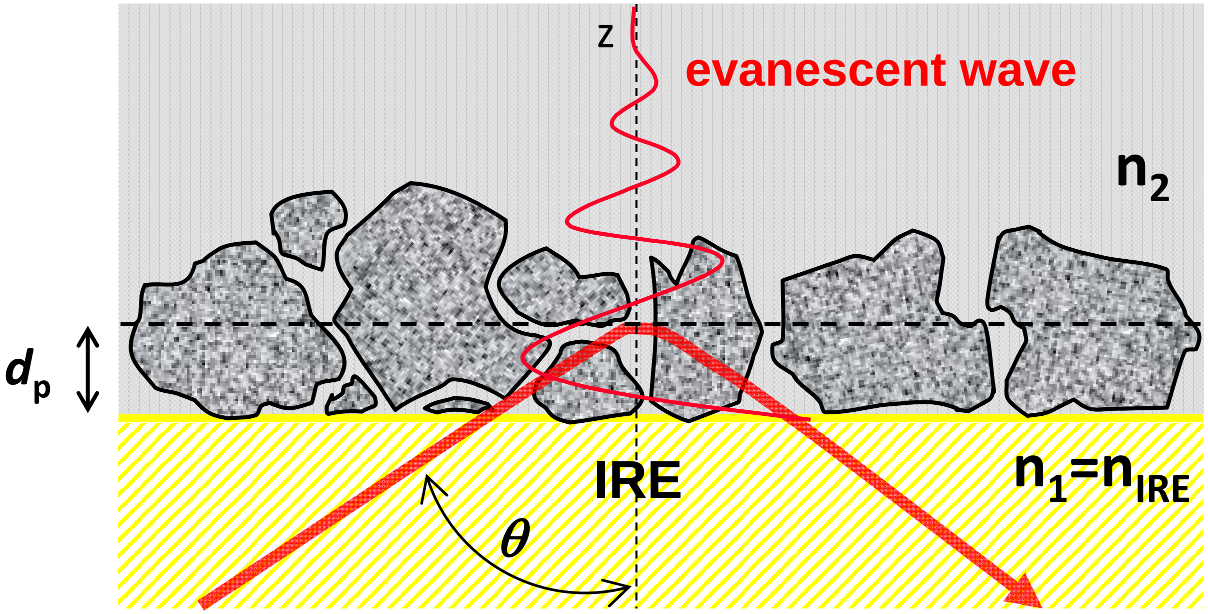
Total internal reflection (attenuated total reflection)



Q Calculate the critical angle at ZnSe/air interface n(ZnSe) = 2.4, n(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

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

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

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}?

- (catalytic) **solid-liquid interfaces**

Internal reflection (ATR-IRS)

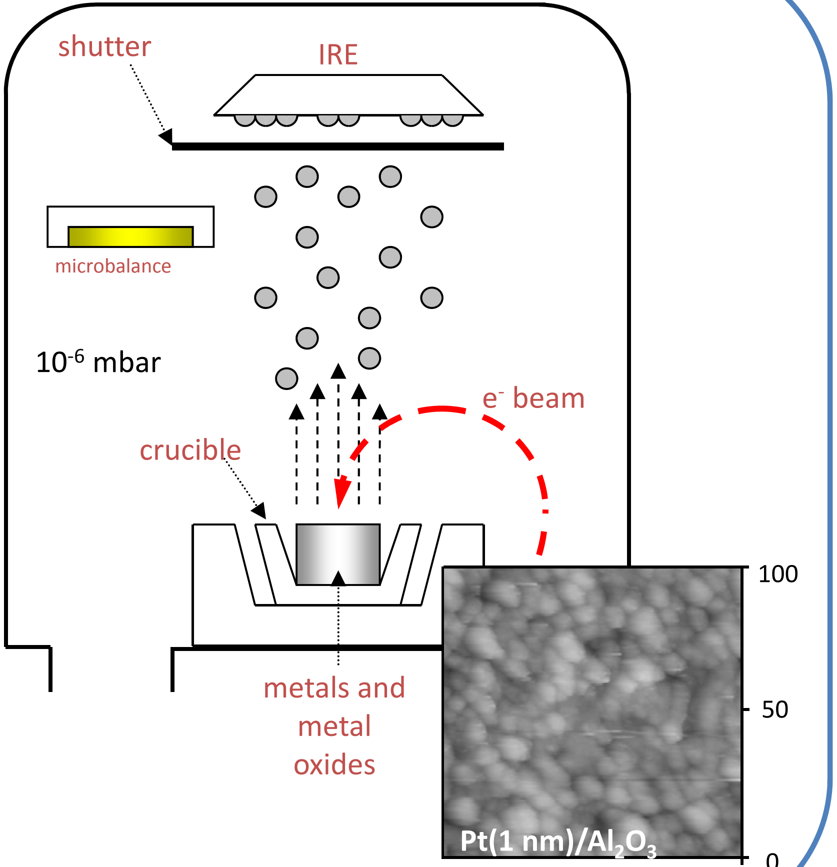
- **Common window materials**

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 bromoiodide)	14 000-330	2.45	Toxic; slightly soluble in water and soluble in base; usable up to ca. 473 K

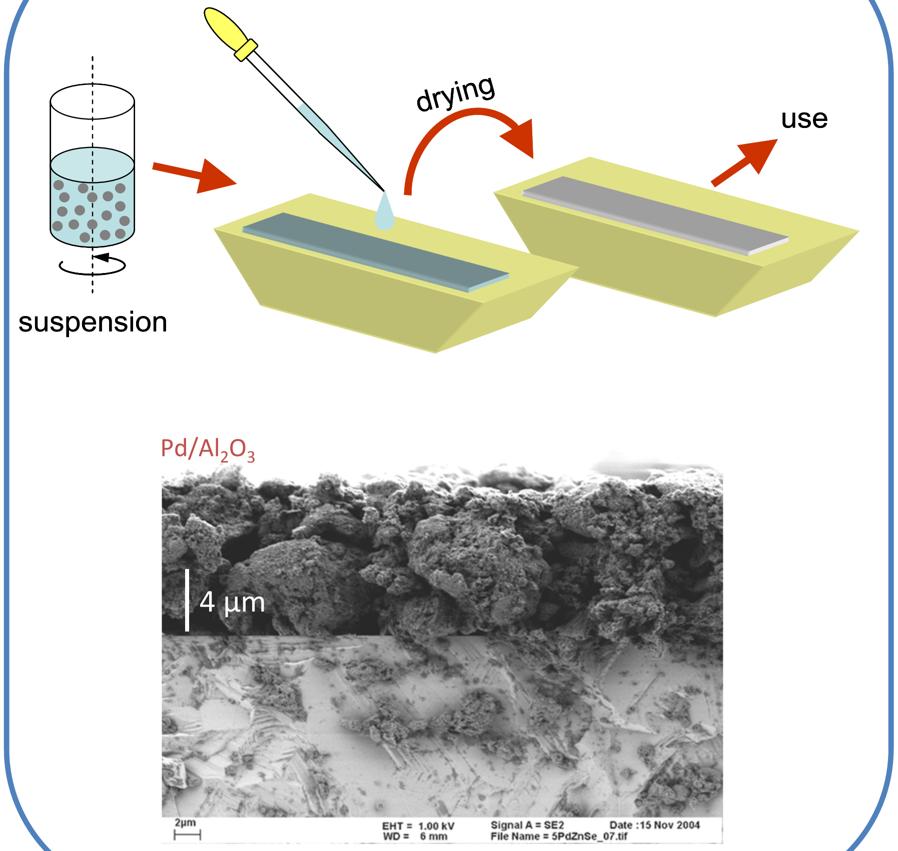
Internal reflection (ATR-IRS)

- **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)

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

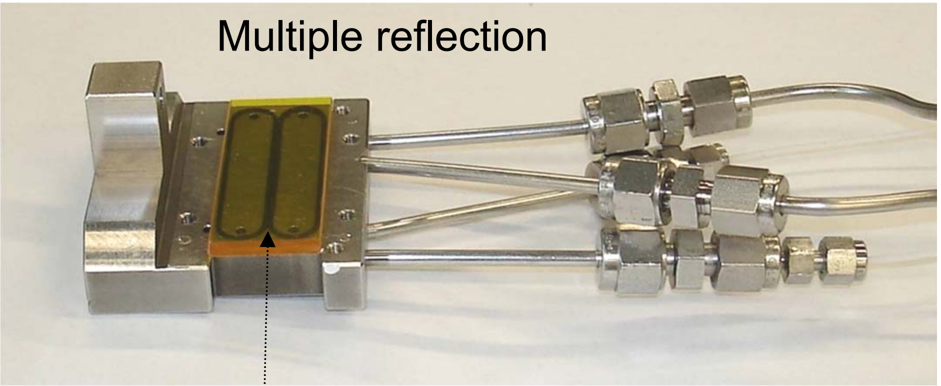
$$d_e = \frac{n_{21} E_0^2 d_p}{2\cos\theta}$$

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)

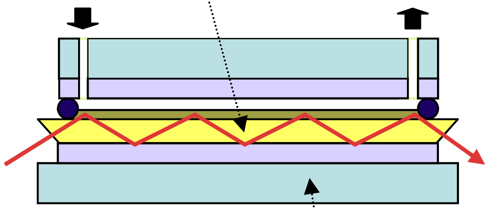
- **Cells**

Single reflection

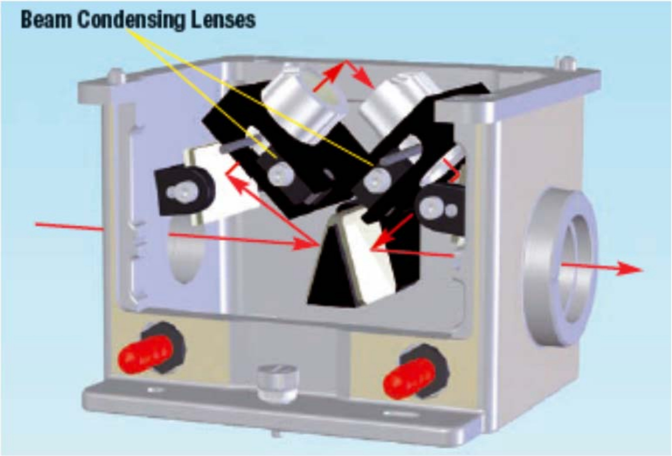


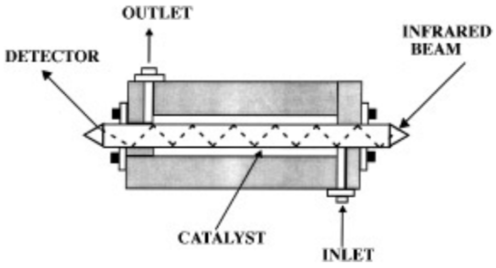
Multiple reflection

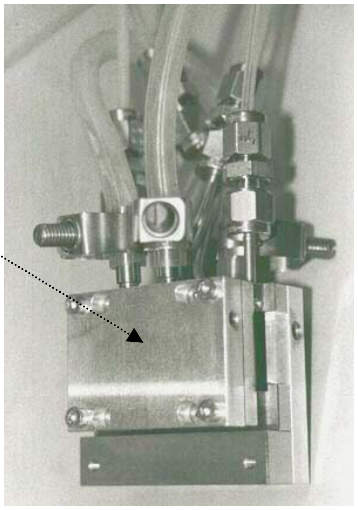
IRE



thermostatting plates

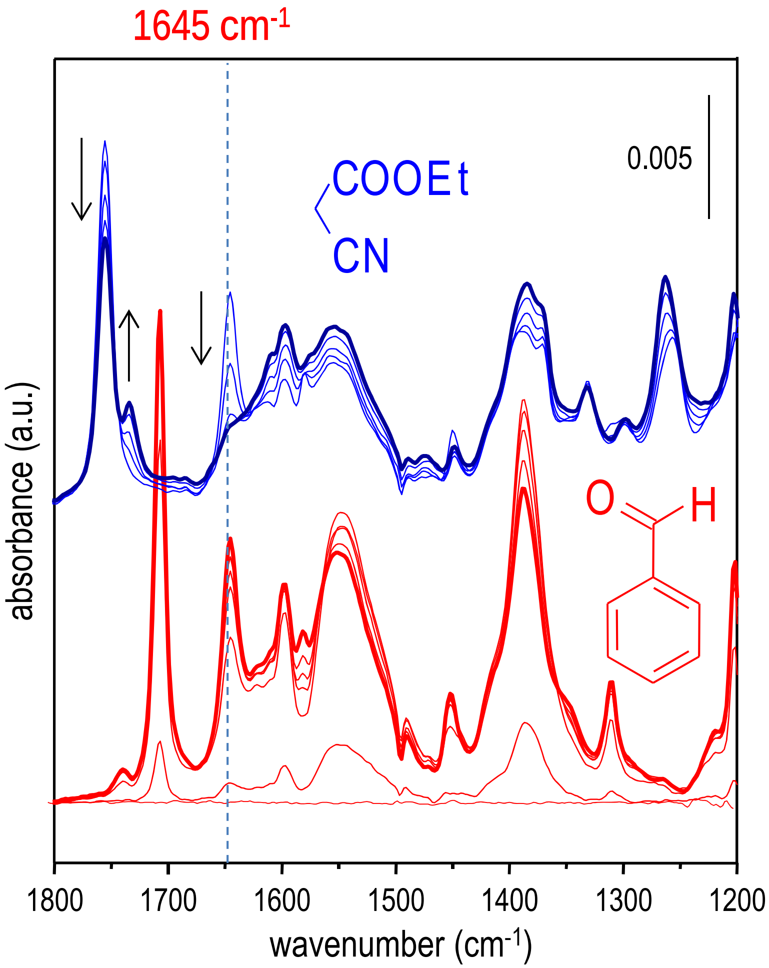


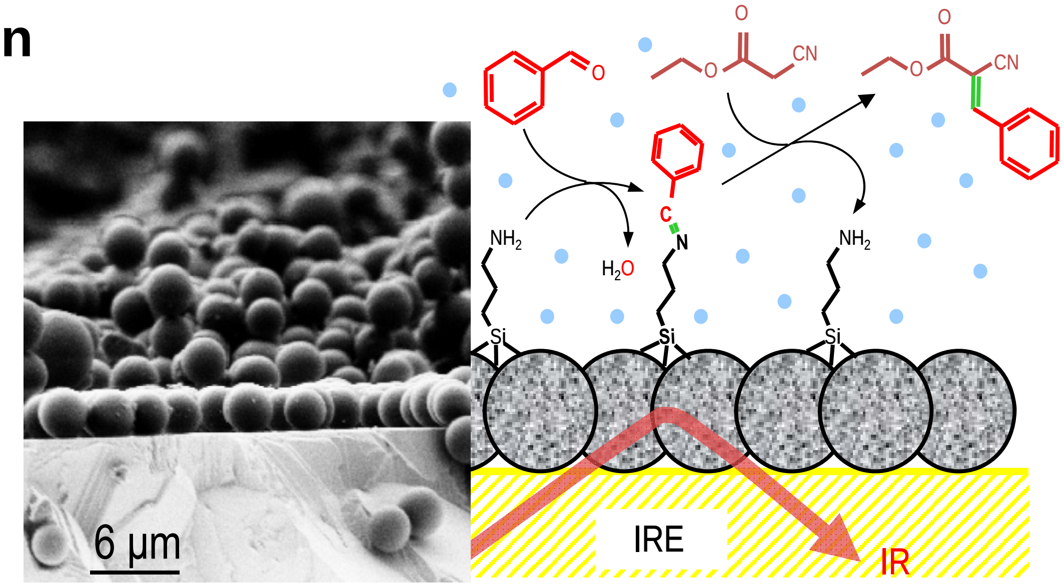


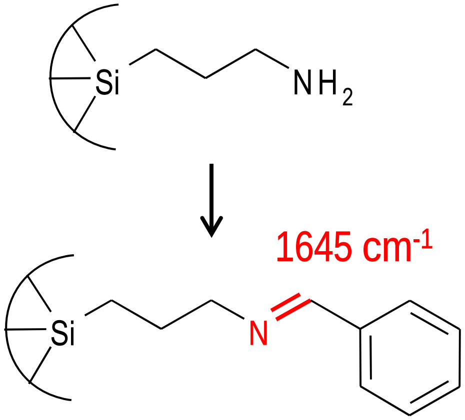


Internal reflection (ATR-IRS)

- **Knoevenagel condensation**

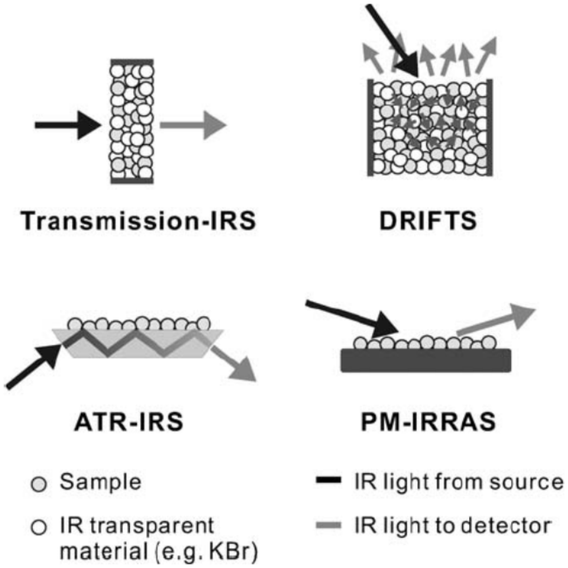


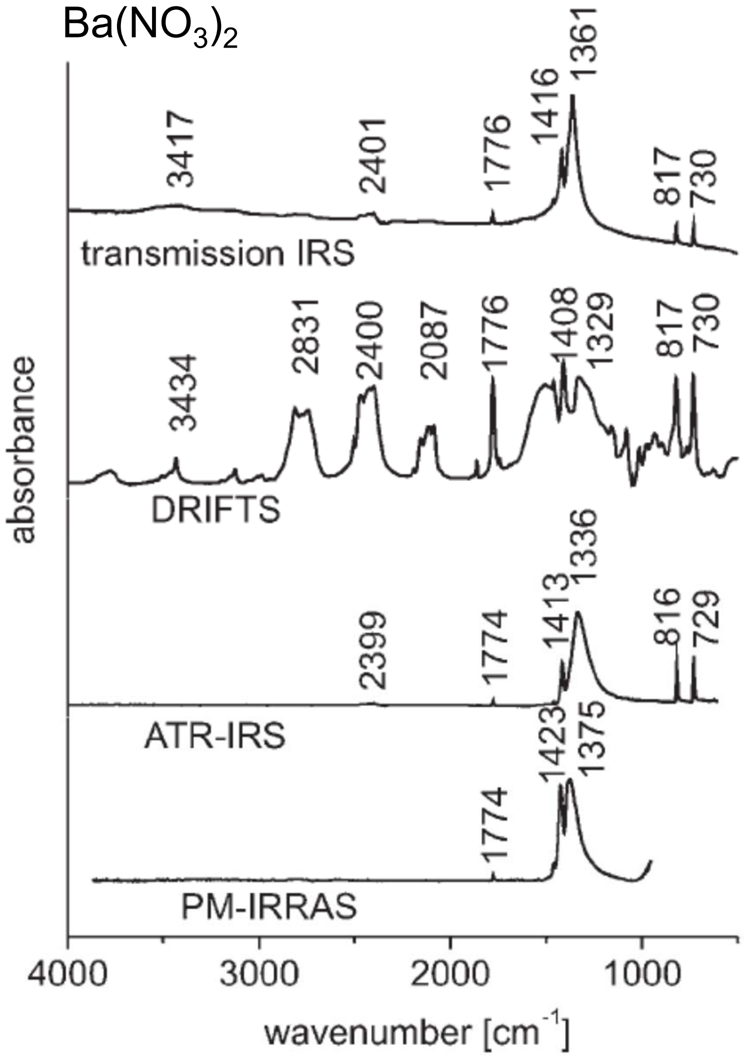




Wirz et al., *Langmuir* 22 (2008) 3698

Comparison of techniques





- Comparison between techniques with different sensitivity (bulk/surface) should be careful
- Band appearance depends on surface sensitivity of the technique

Urakawa et al., *PCCP* 10 (2008) 6190

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)

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 (LN_2)
  - 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**

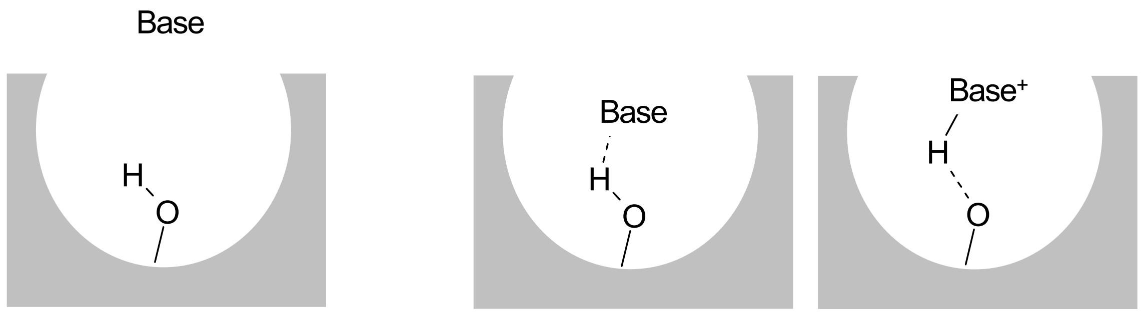
- unequivocal analysis of intermolecular interaction
- selective interaction with acidic or basic sites
- sufficient accuracy in frequency shift determination
- high (and available) extinction coefficients of adsorbed probe
- appropriate acid (base) strength to induce interaction - Hard–Soft classification 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)

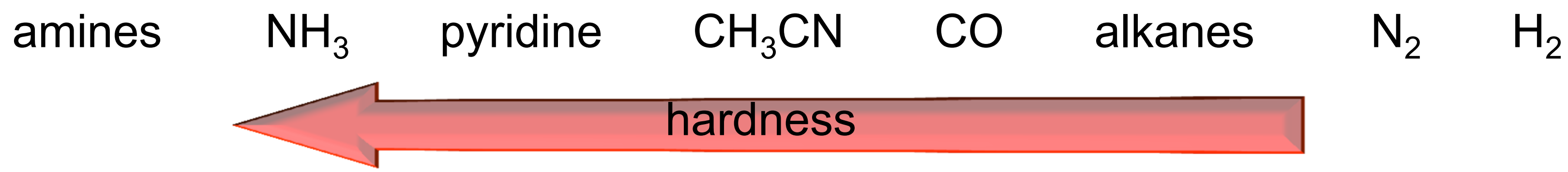
Probe molecules

- **Acid sites**

Brønsted sites
(protic)



Lewis sites
(aprotic)

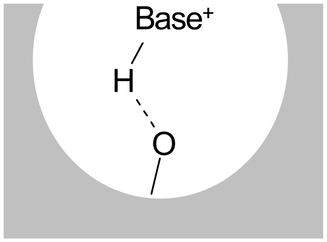


amines NH$_3$ pyridine CH$_3$CN CO alkanes N$_2$ H$_2$

hardness

Probe molecules

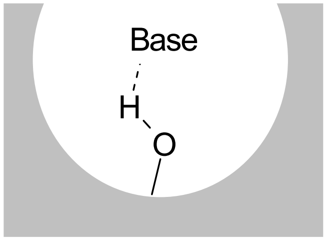
■ Acid sites: Pyridine



Brønsted (**B**)

1535–1550 cm^{-1}

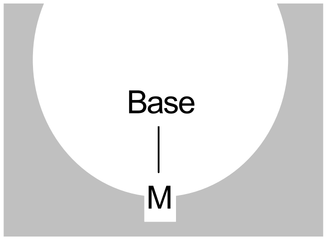
1640 cm^{-1}



Hydrogen bonded

1440–1447 cm^{-1}

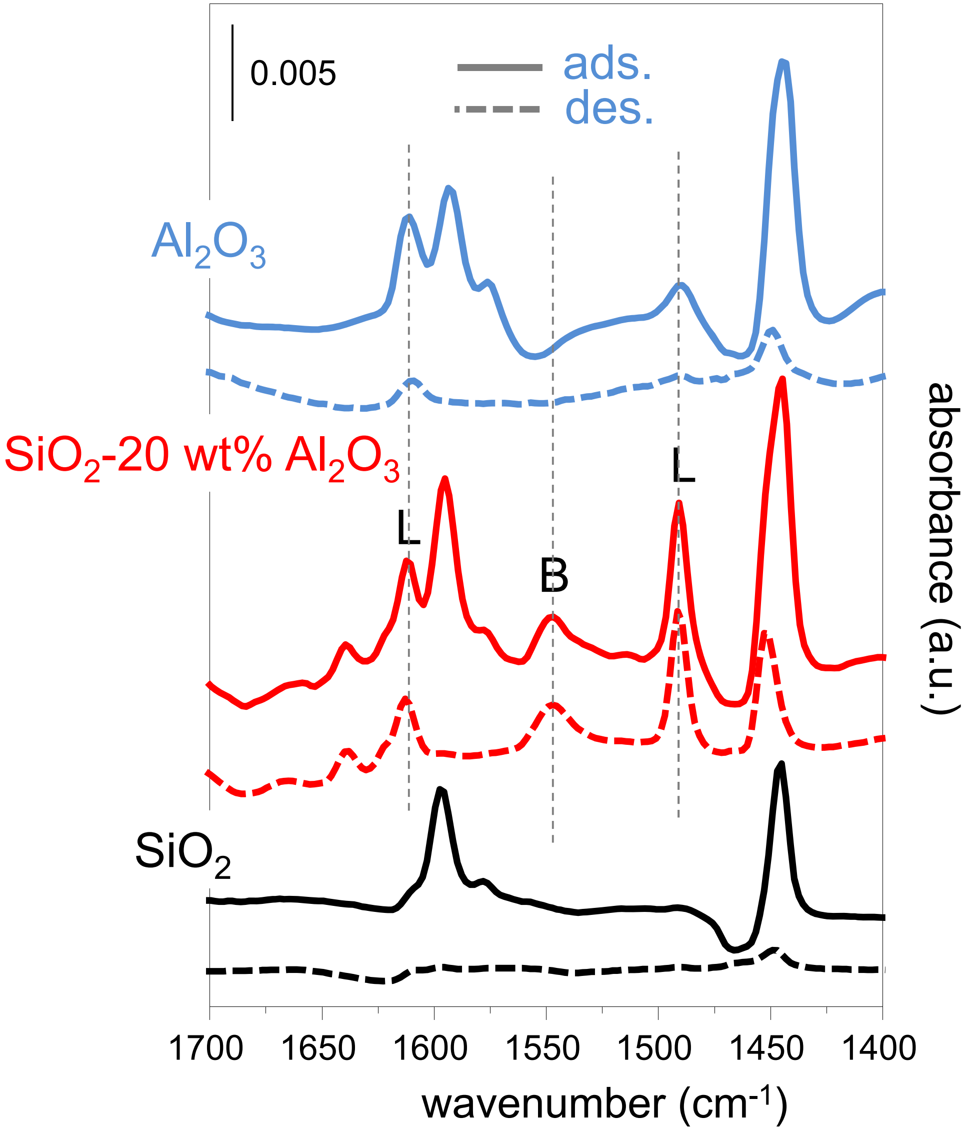
1580–1600 cm^{-1}



Lewis (**L**)

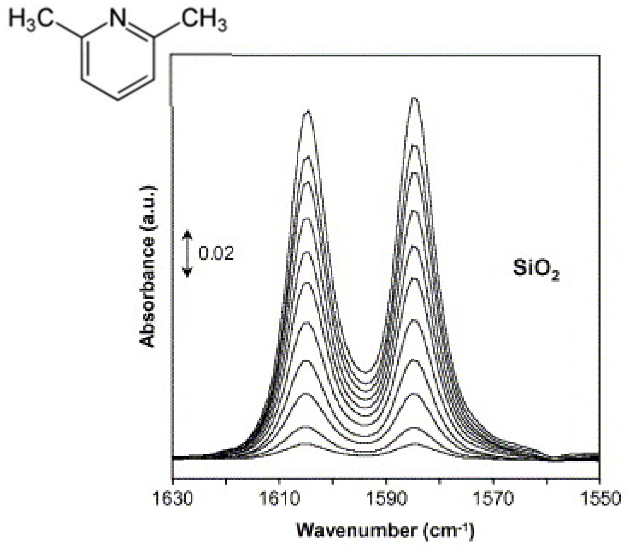
1447–1464 cm^{-1}

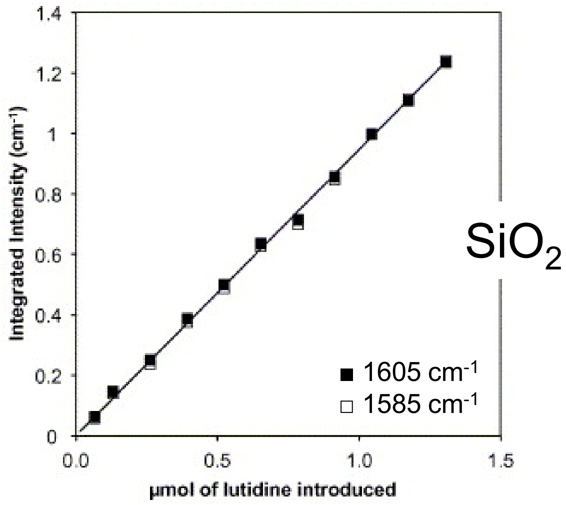
1600–1635 cm^{-1}

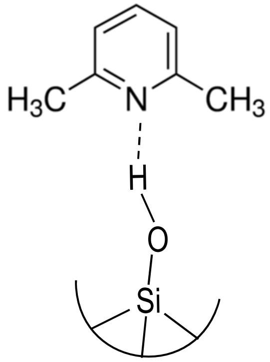


SiO_2-Al_2O_3 > Al_2O_3 >> SiO_2; next issue: coordination environment of acid site

Molar absorption coefficient of adsorbates







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

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

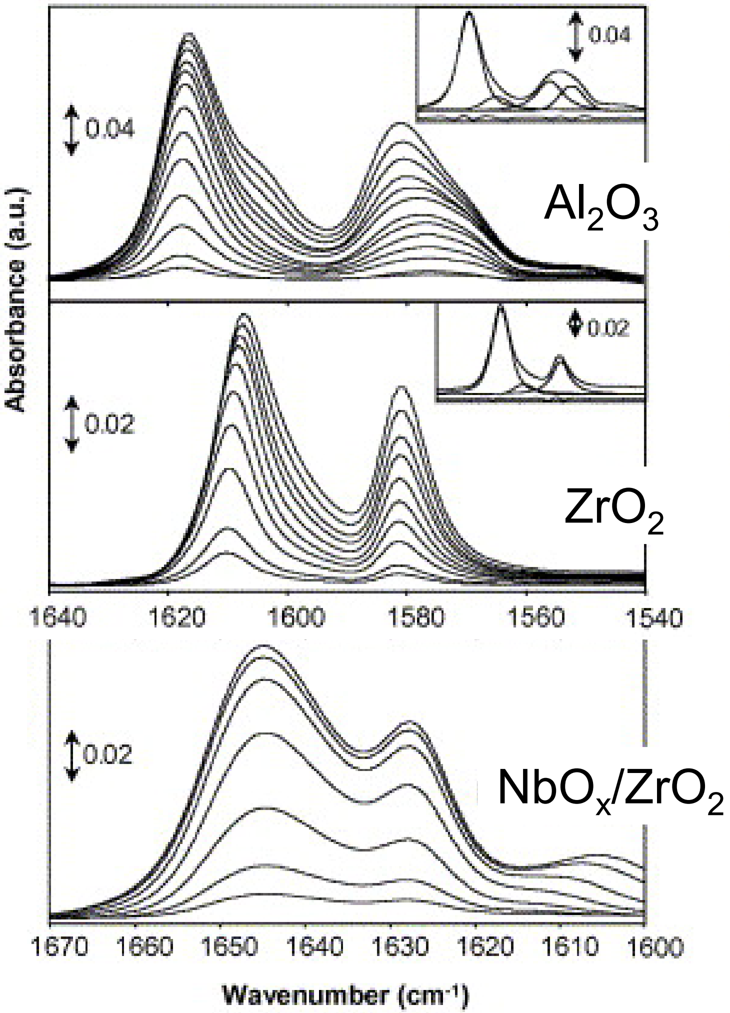
$$\varepsilon = \frac{SA}{n}$$

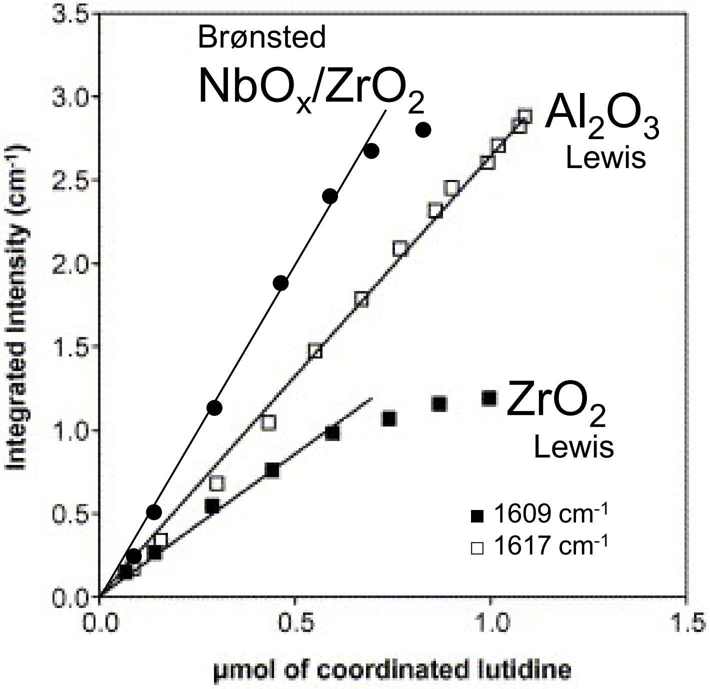
ε, integrated molar absorption coefficient
ℓ, disc thickness (optical path)
n, amount of adsorbed molecule
S, disc area

- **Transmission IR**

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

Molar absorption coefficient of adsorbates





	H-bond	coordination	protonation
SiO$_2$	ε_{1585} = 1.9		
	ε_{1605} = 1.9		
Al$_2$O$_3$		ε_{1617} = 5.3	
ZrO$_2$		ε_{1609} = 3.4	
NbO$_x$/ZrO$_2$			$\varepsilon_{1644+1628}$ = 7.3
Average	ε_{1585} = 1.9	ε_{Lewis} = 4.35	$\varepsilon_{Brønsted}$ = 6.8
	ε_{1605} = 1.9		
nd: not determined; ε= cm µmol^{-1}			

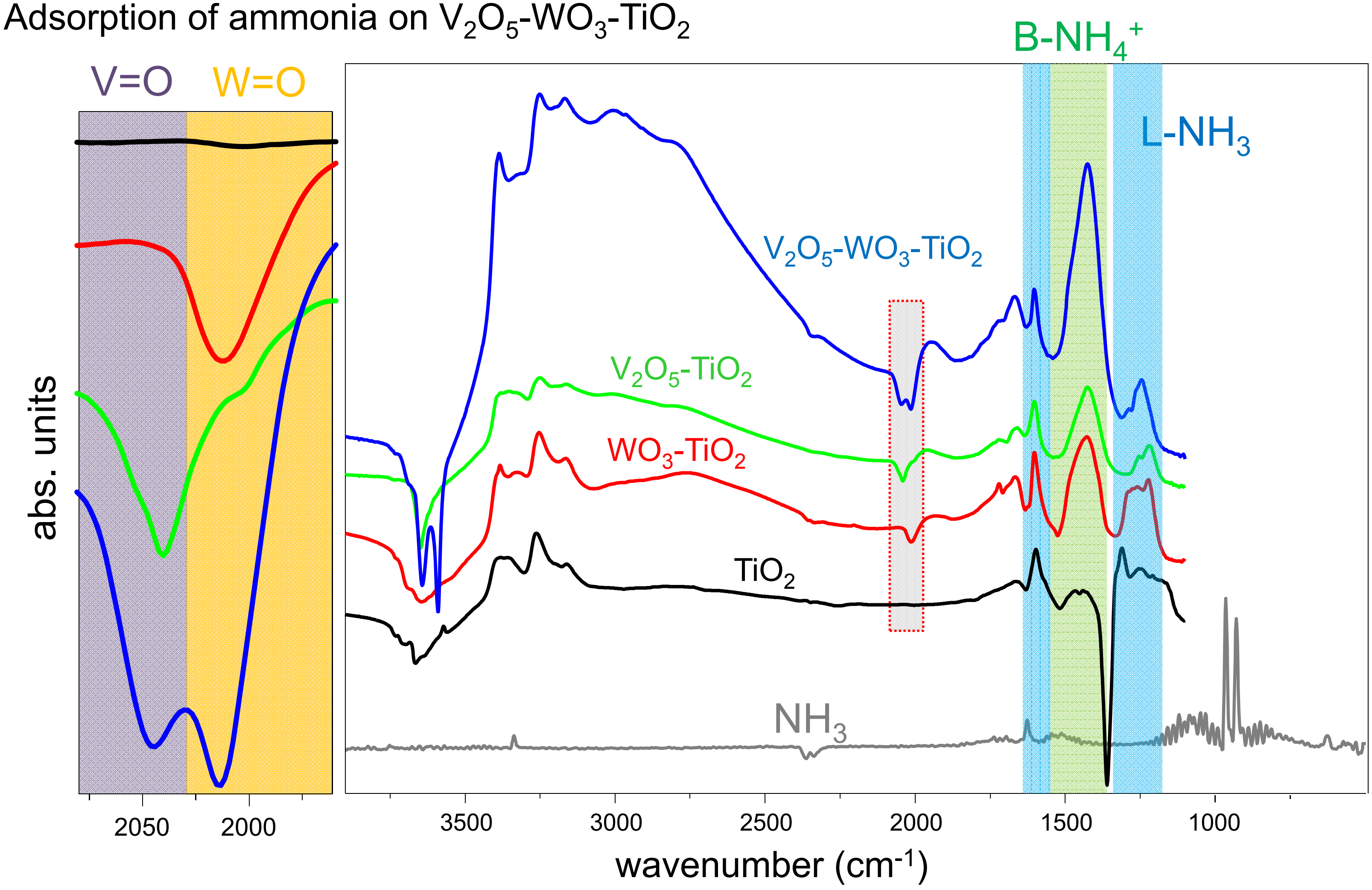
- **Transmission IR**

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

Probe molecules

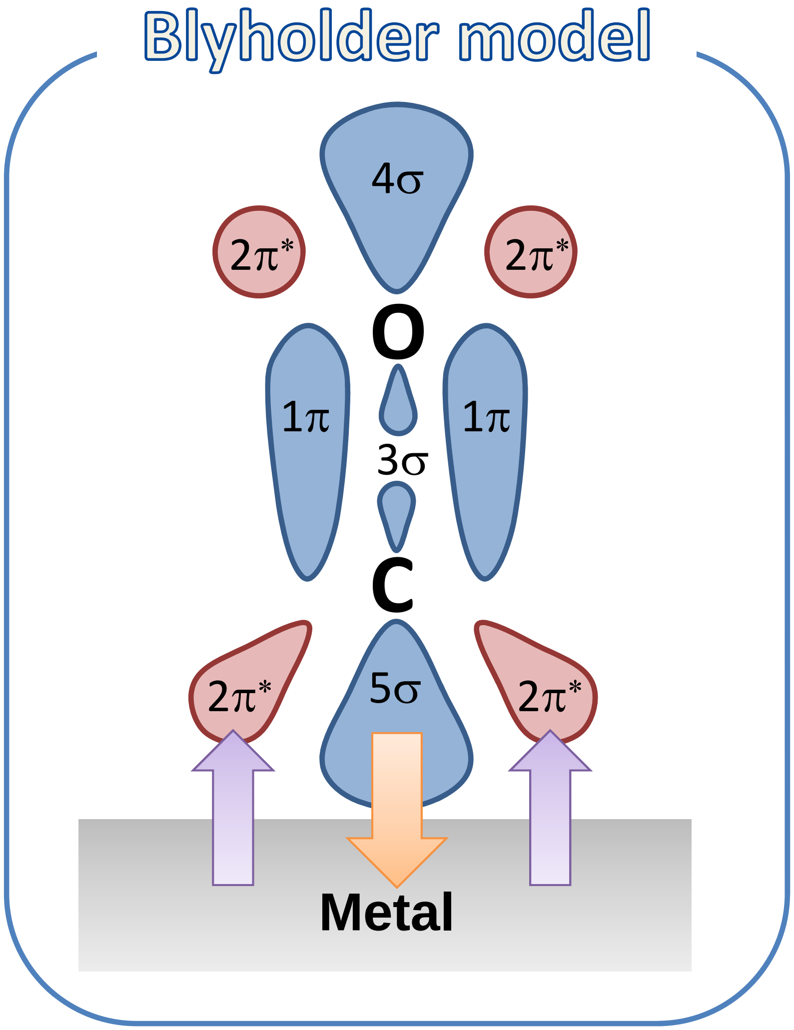
- **Indirect characterization of supported metal oxides**

Adsorption of ammonia on V_2O_5-WO_3-TiO_2



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

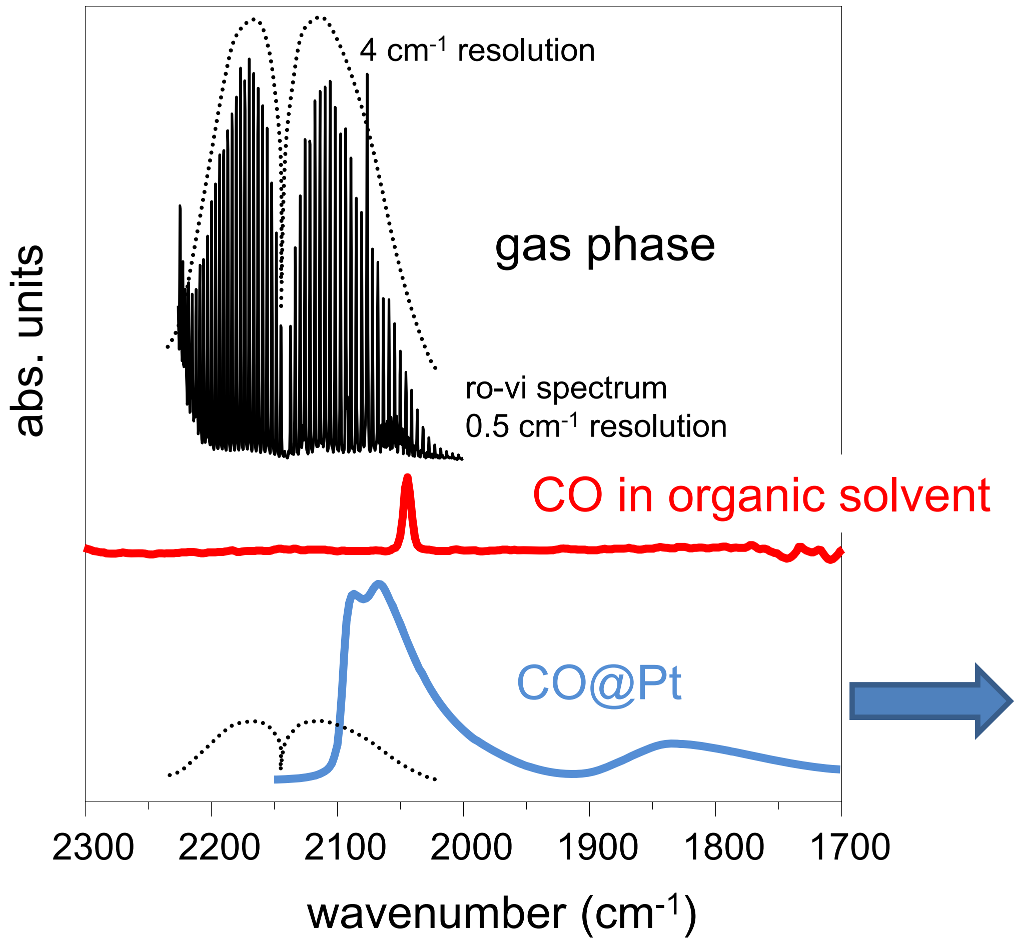
- Low coverage: ν_{CO} depends on the geometry of **adsorption site** (face order: **terrace – corner – edge**) – **BD is strong**
- High coverage: ν_{CO} depends on **dipole-dipole interactions** – **BD is weak**

Probe molecules

- **Carbon monoxide (CO)**

(red-) shift

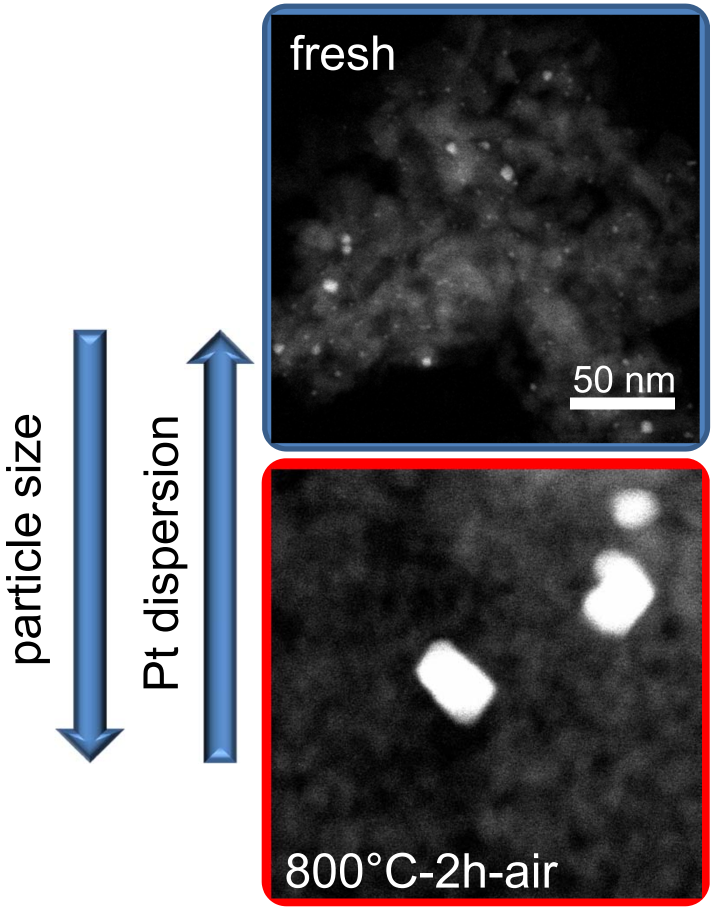
effect of bond order and condensed phase

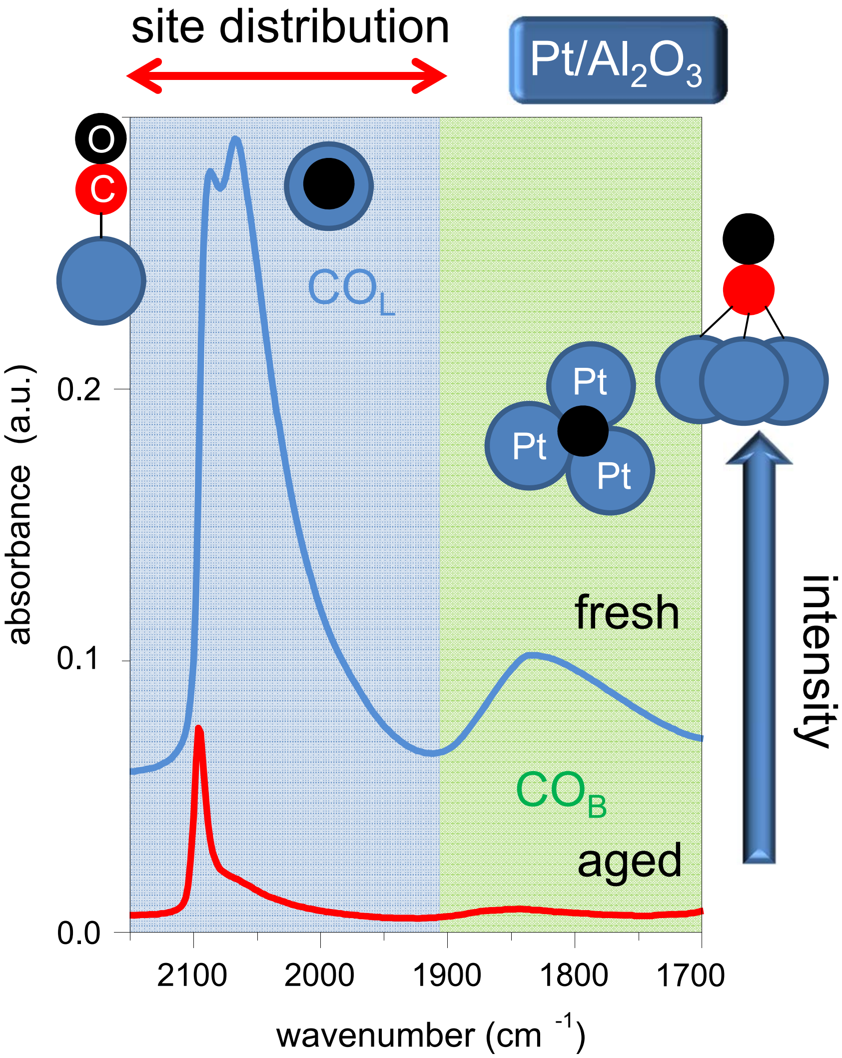


Adsorbate
assignments on powders by comparison with reference UHV studies (single crystals)

Probe molecules

- **Carbon monoxide (CO)**



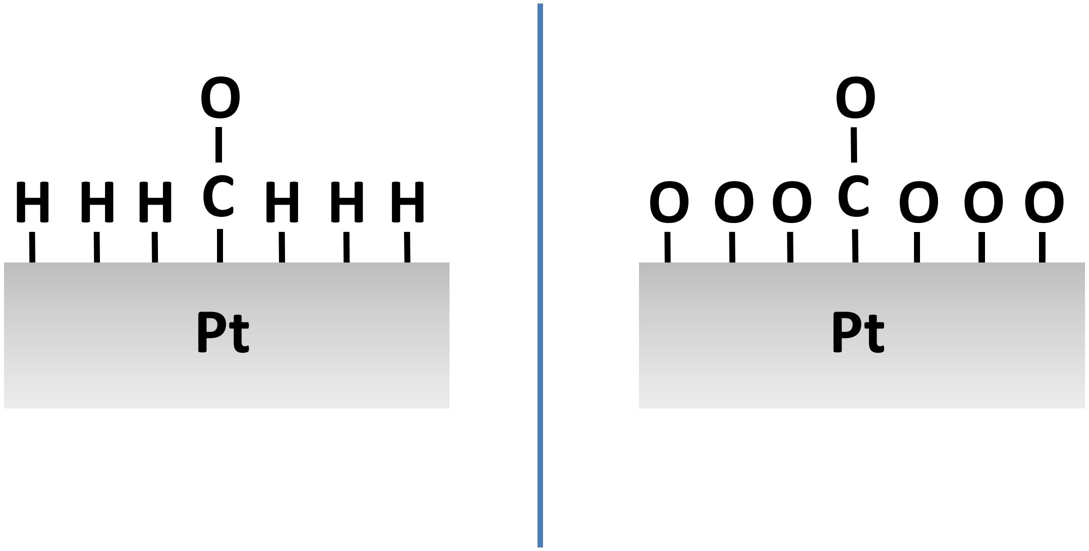


- The larger the particles, the less CO adsorbs (**intensity**)
- The larger the particles, the less defects available (**nr. of signals**)

Probe molecules

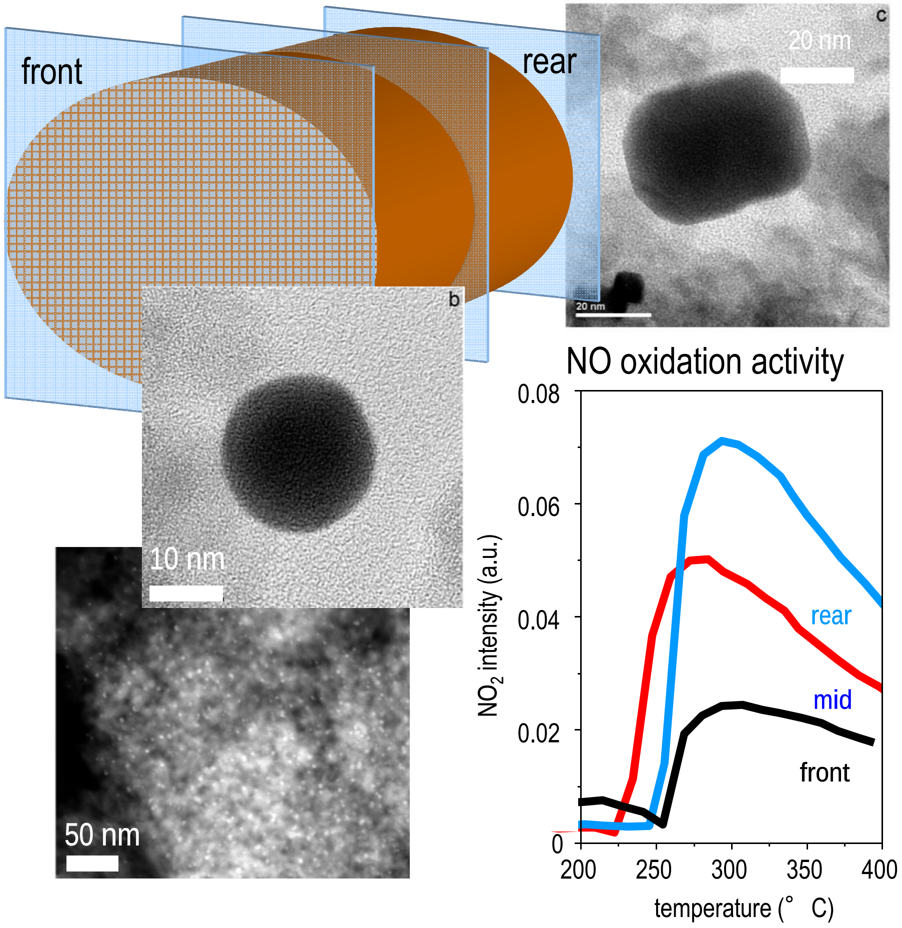
- **Carbon monoxide (CO)**

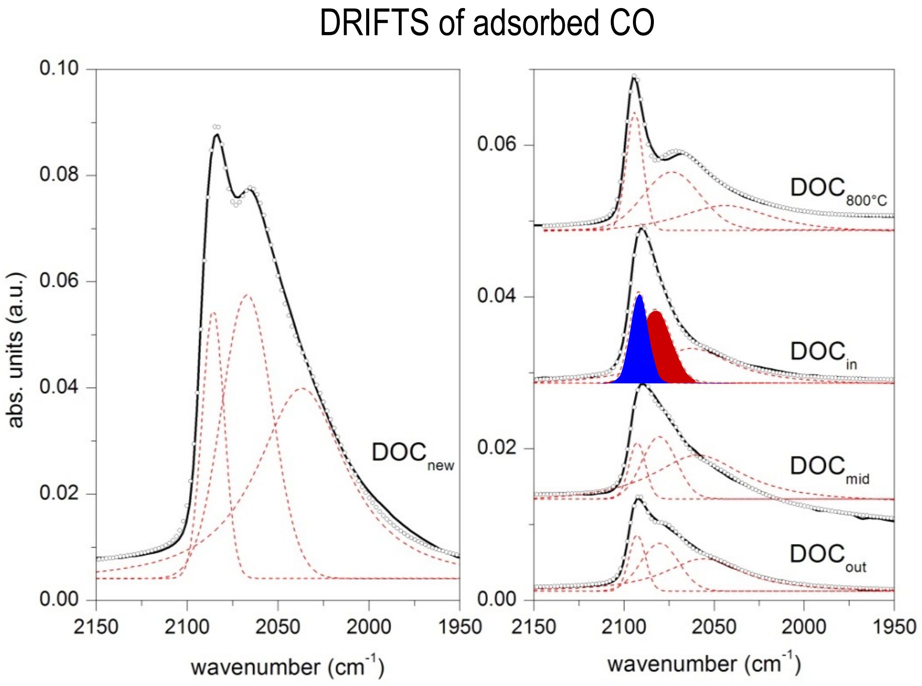
Q How does the CO stretching frequency shift when a Pt surface is covered with hydrogen or oxygen?

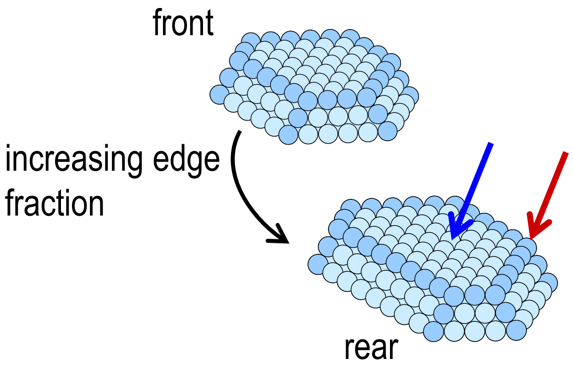


Probe molecules

- **Diesel oxidation catalyst (DOC)**





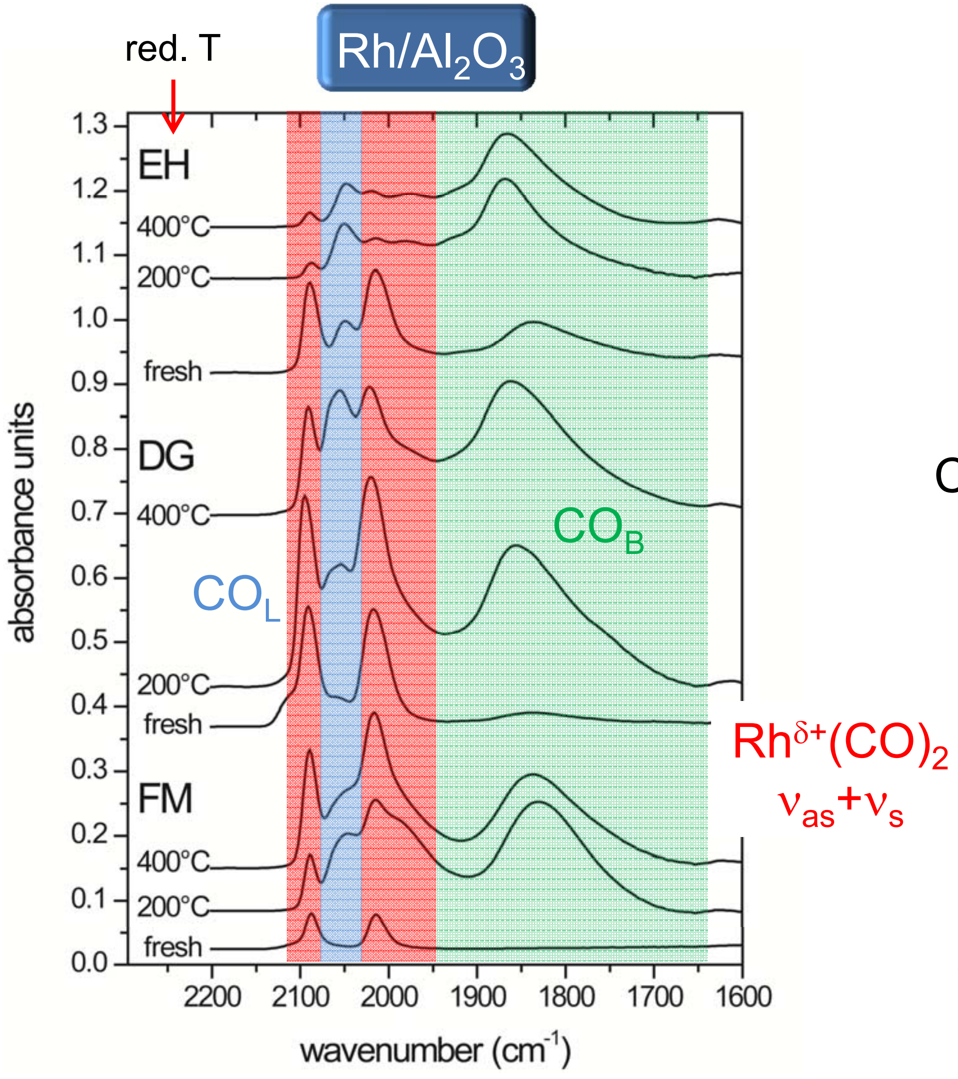


Winkler et al., *Appl. Catal. B* 93 (2009) 177; Matam et al., *Appl. Catal. B* 129 (2013) 214

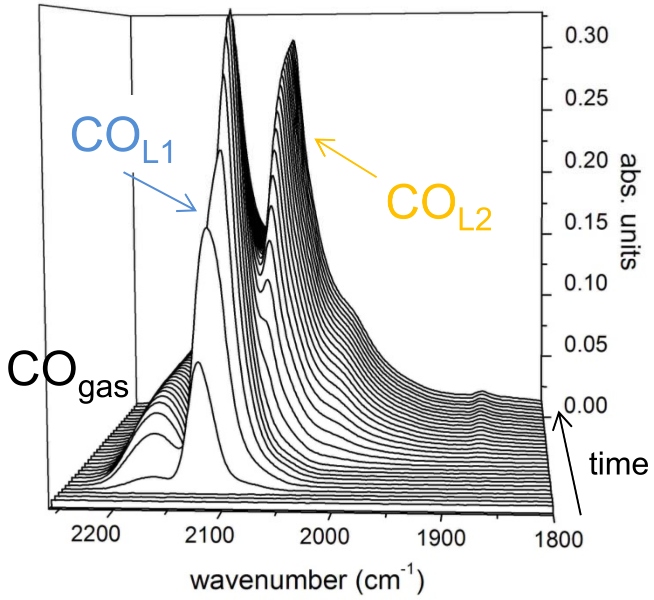
Probe molecules

- **Carbon monoxide (CO)**

Rh/Al$_2$O$_3$



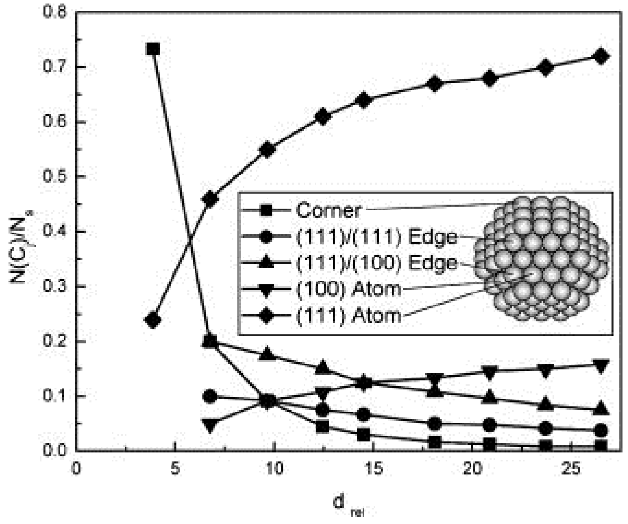
Au/TiO$_2$

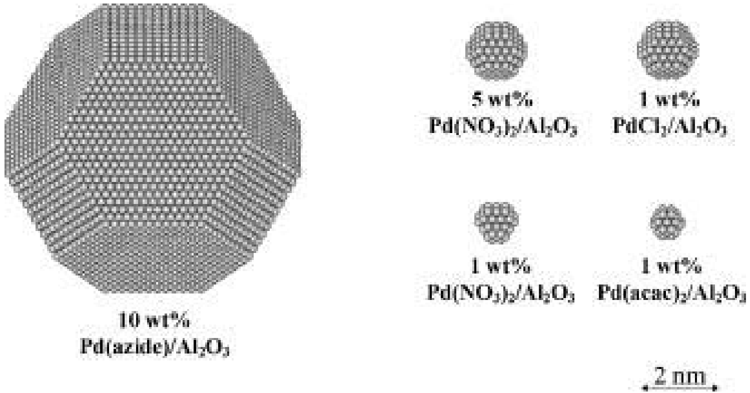


Watch out!
surface reconstruction induced by CO
- CO is corrosive

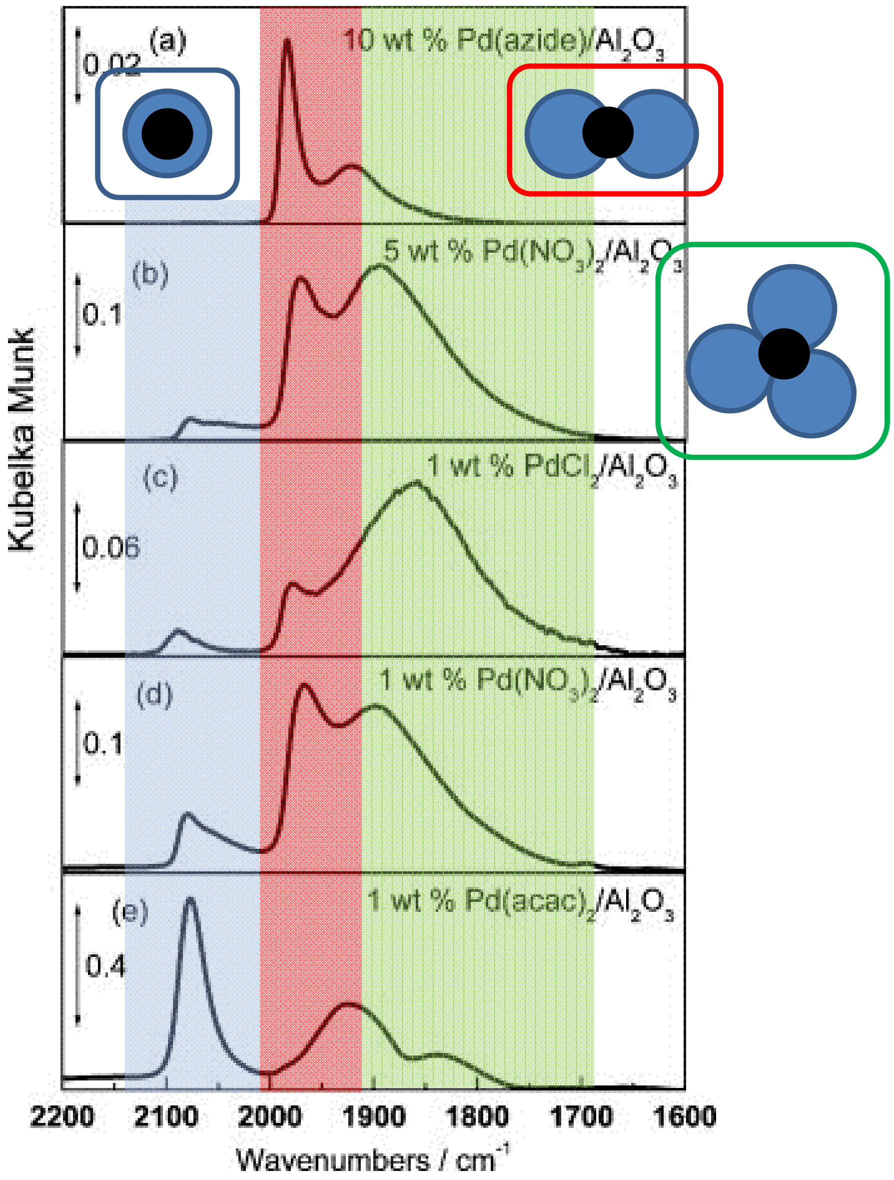
Probe molecules

- **Carbon monoxide (CO)**



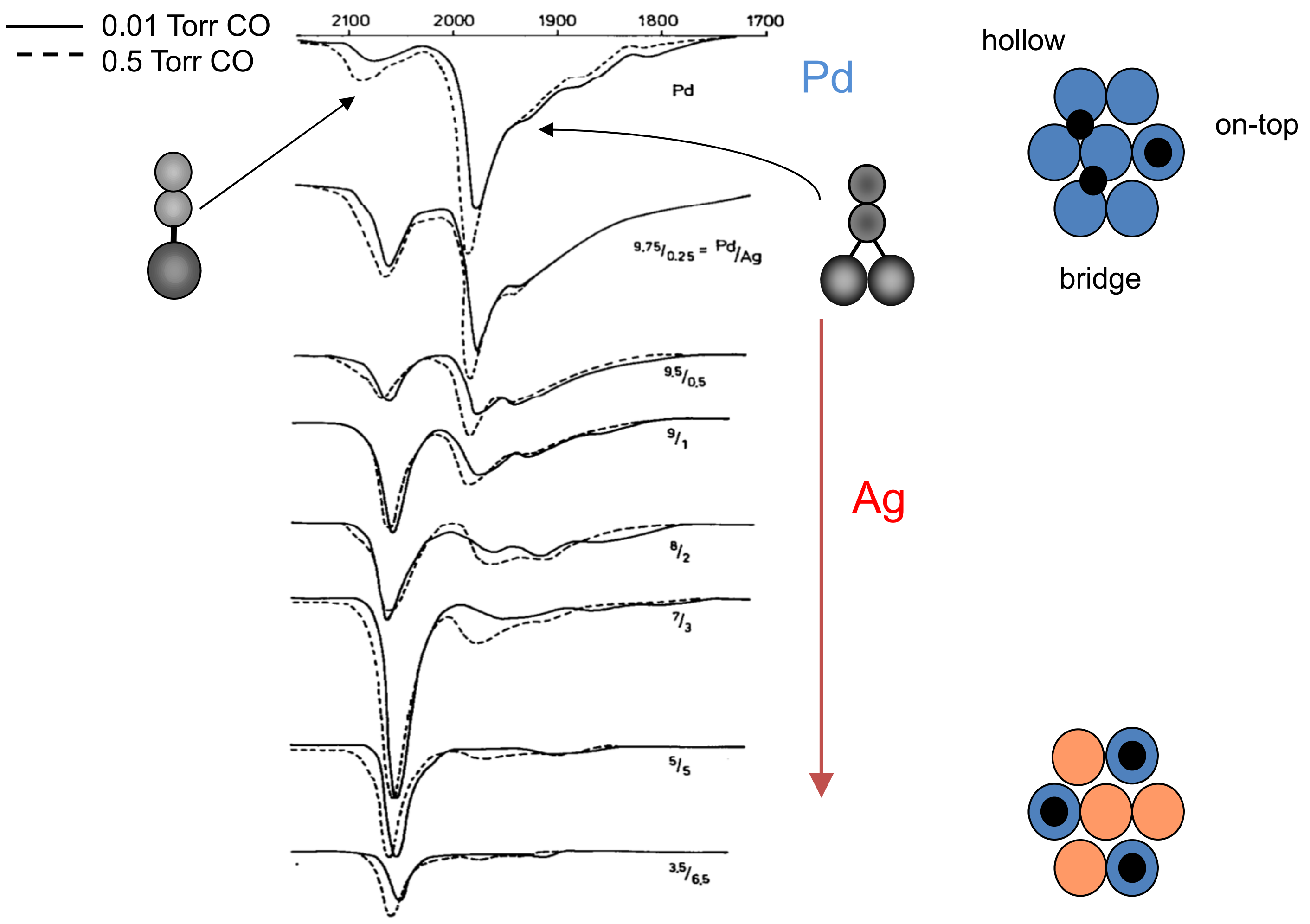


size confirmed by TEM



Lear et al., *J. Chem. Phys.* 123 82005) 174706

Probe molecules



Pd/Ag alloy on SiO_2

Y. Soma-Noto, W.M.H. Sachtler, *J. Catal.* 32 (1974) 315