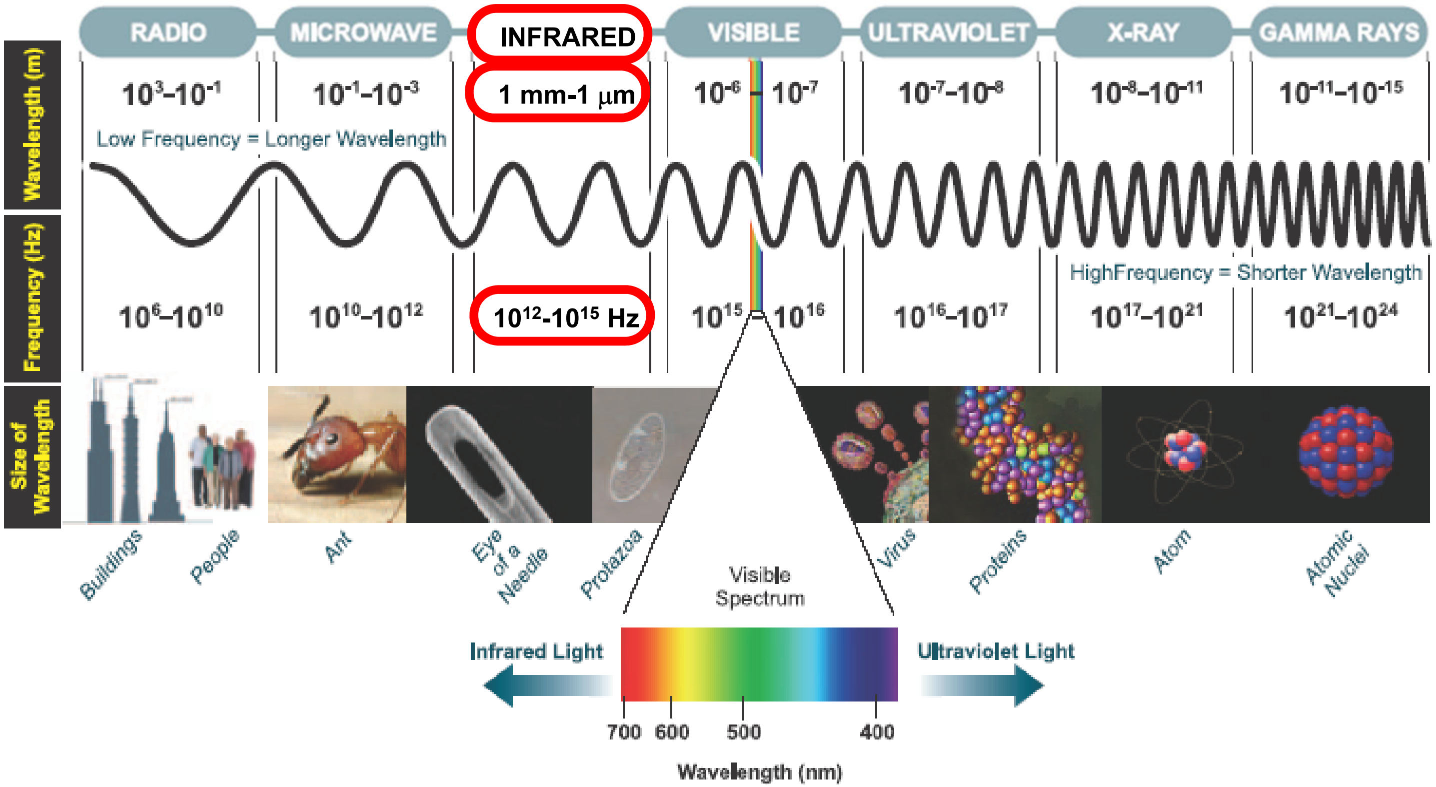
Davide Ferri :: Paul Scherrer Institut

Infrared spectroscopy

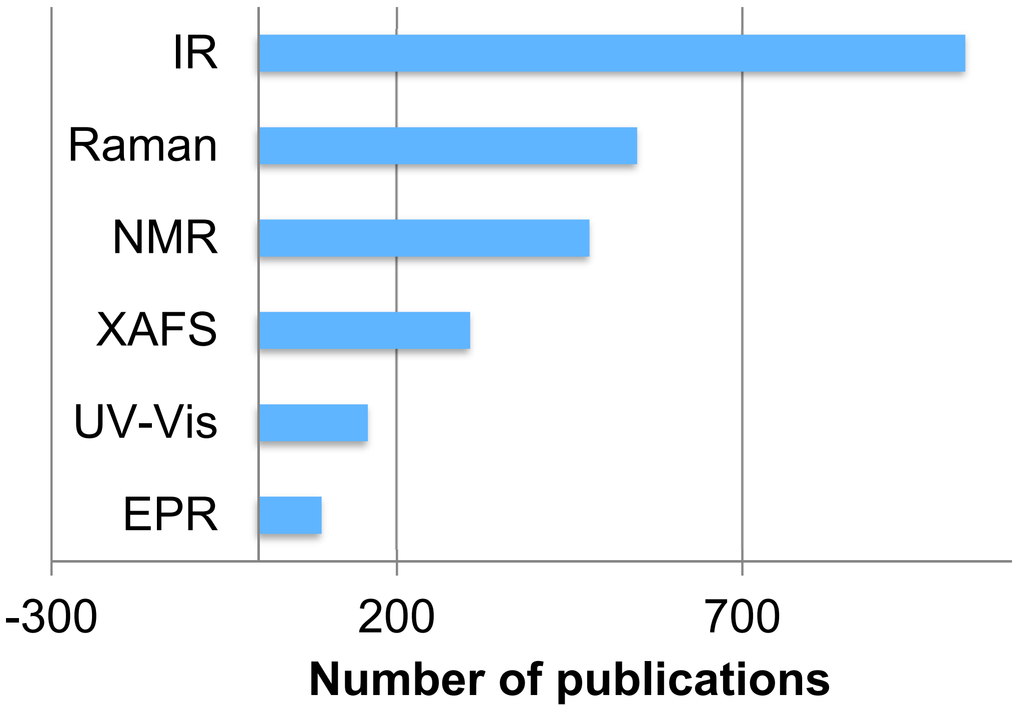
Molecular aspects of catalysts and surfaces :: ETHZ

The electromagnetic spectrum



source: Andor.com

Importance of IR spectroscopy in catalysis

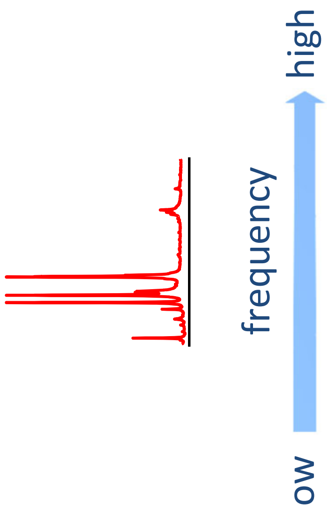


- pros
- economic
- non-invasive
- versatile (e.g. solid, liquid, gas, interfaces)
- very sensitive (concentration)
- fast acquisition (down to ns!)
- cons
- no atomic resolution

Number of publications containing *in situ*, *catalysis*, and respective method

Source: ISI Web of Knowledge (Sept. 2008)

Infrared spectroscopy



visible	wavelength λ [mm]	wavenumber ν [cm^{-1}]	energy 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
microwave				

Why IR spectroscopy

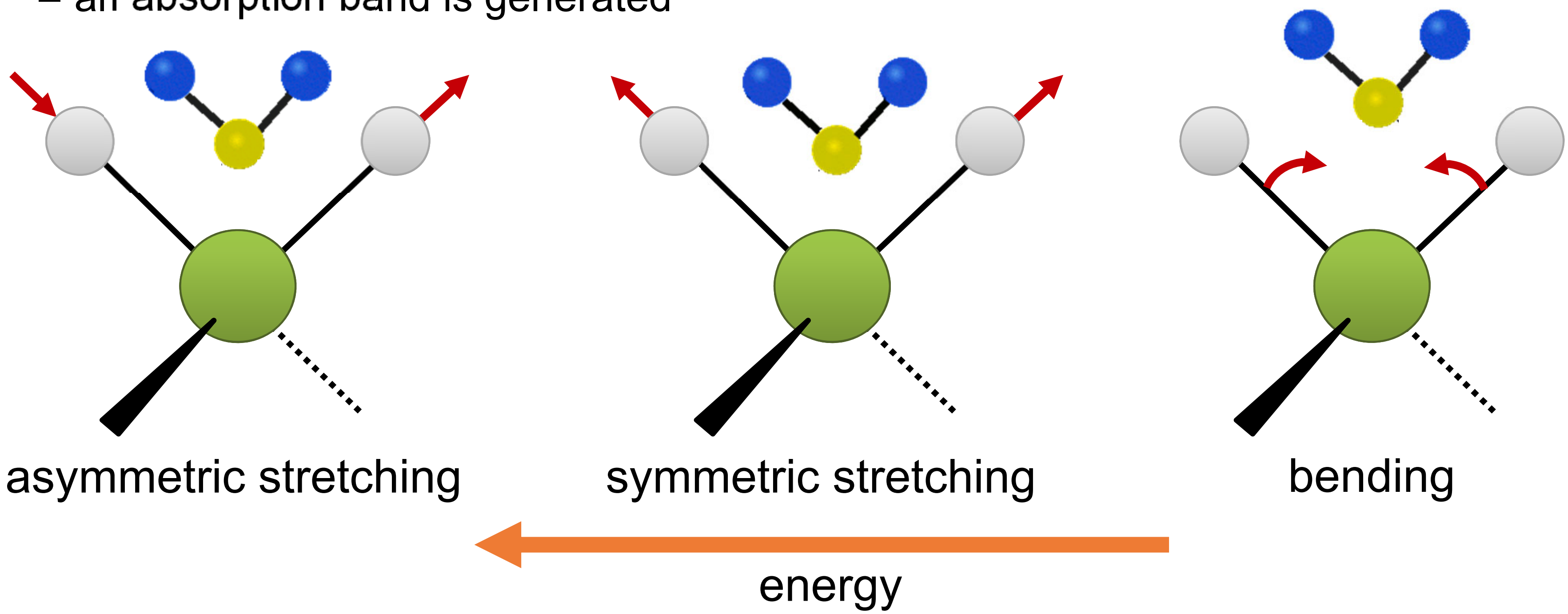
- ‘quality control’: identification of compounds according to their fingerprint spectrum
  - also inorganic materials, e.g. metal oxides
  - ex situ, but also after degassing in cell (vacuum)

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

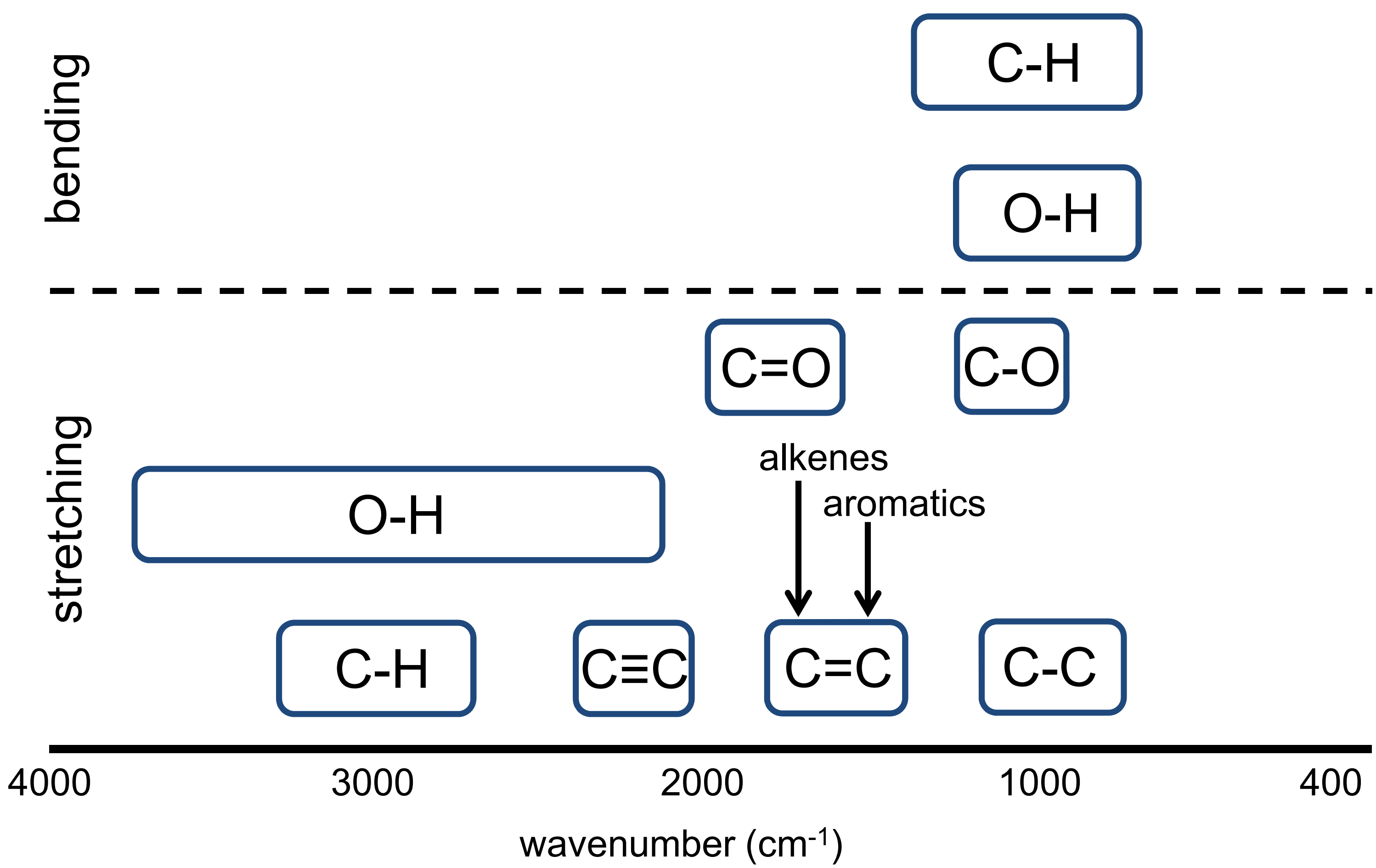
- Identification of surface sites under reaction conditions
  - in situ/operando experiments to obtain molecular reaction mechanism, exposure to reaction conditions

Vibrational spectroscopy

- Interaction with matter
  - energy causes vibration of molecular bonds
  - energy is absorbed in correspondence of vibrational modes
  - an absorption band is generated



Vibrations


bending
C-H
O-H
stretching
C=O
C-O
alkenes
aromatics
O-H
C-H
C≡C
C=C
C-C
4000
3000
2000
1000
400
wavenumber (cm-1)

Vibrations

- Why do vibrations appear in the IR spectrum?

selection rule

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

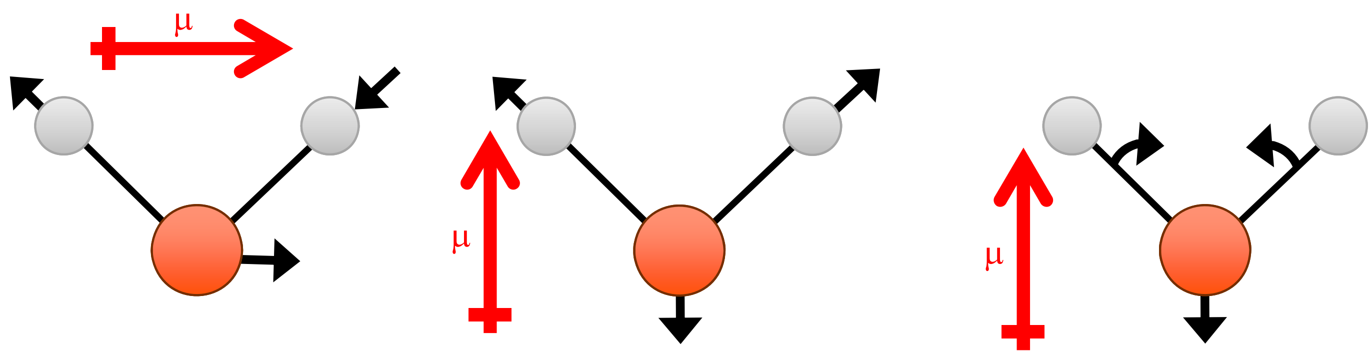
Ar

O_2 HCl

molecular dipole moment μ must change due to vibration or rotation along its coordinate (so called, normal mode or normal coordinate, $\boldsymbol{Q}$)

H_2O

N=3, non-linear, 3 fundamental modes



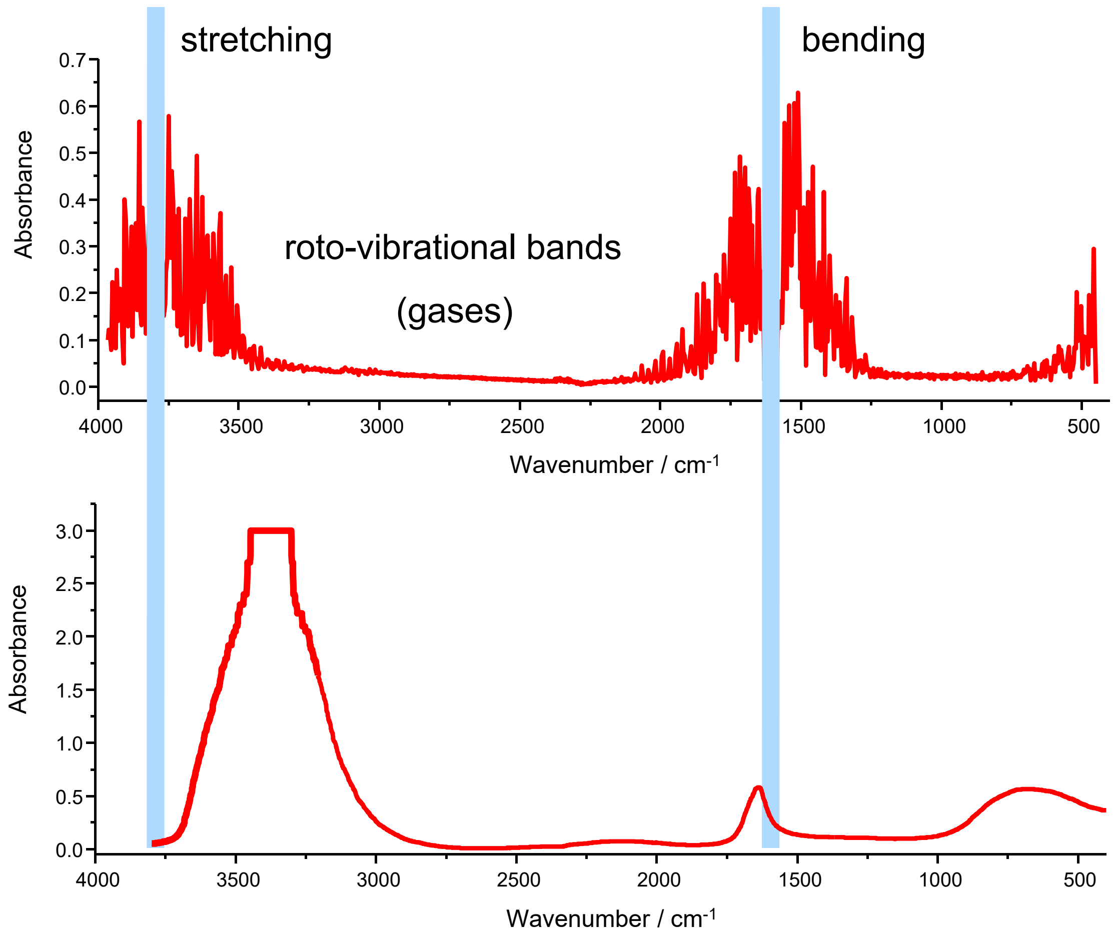
3756 cm^{-1}
asymmetric stretching

3657 cm^{-1}
symmetric stretching

1595 cm^{-1}
scissoring (bending)

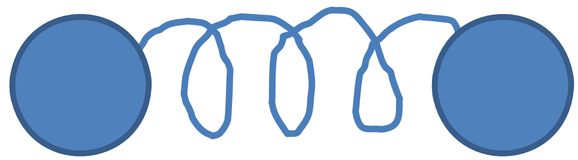
All modes IR active

Gas and liquid phase H_2O



Vibrations

- Harmonic oscillator
  - The stretching frequency of a bond can be approximated by Hooke's law. Two atoms and the connecting bond are treated as a harmonic oscillator composed of two masses (atoms) joined by a spring.



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

k: force constant

$$\mu = \frac{m_1 \times m_2}{m_1 + m_2}$$

m: reduced mass

Vibrations

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

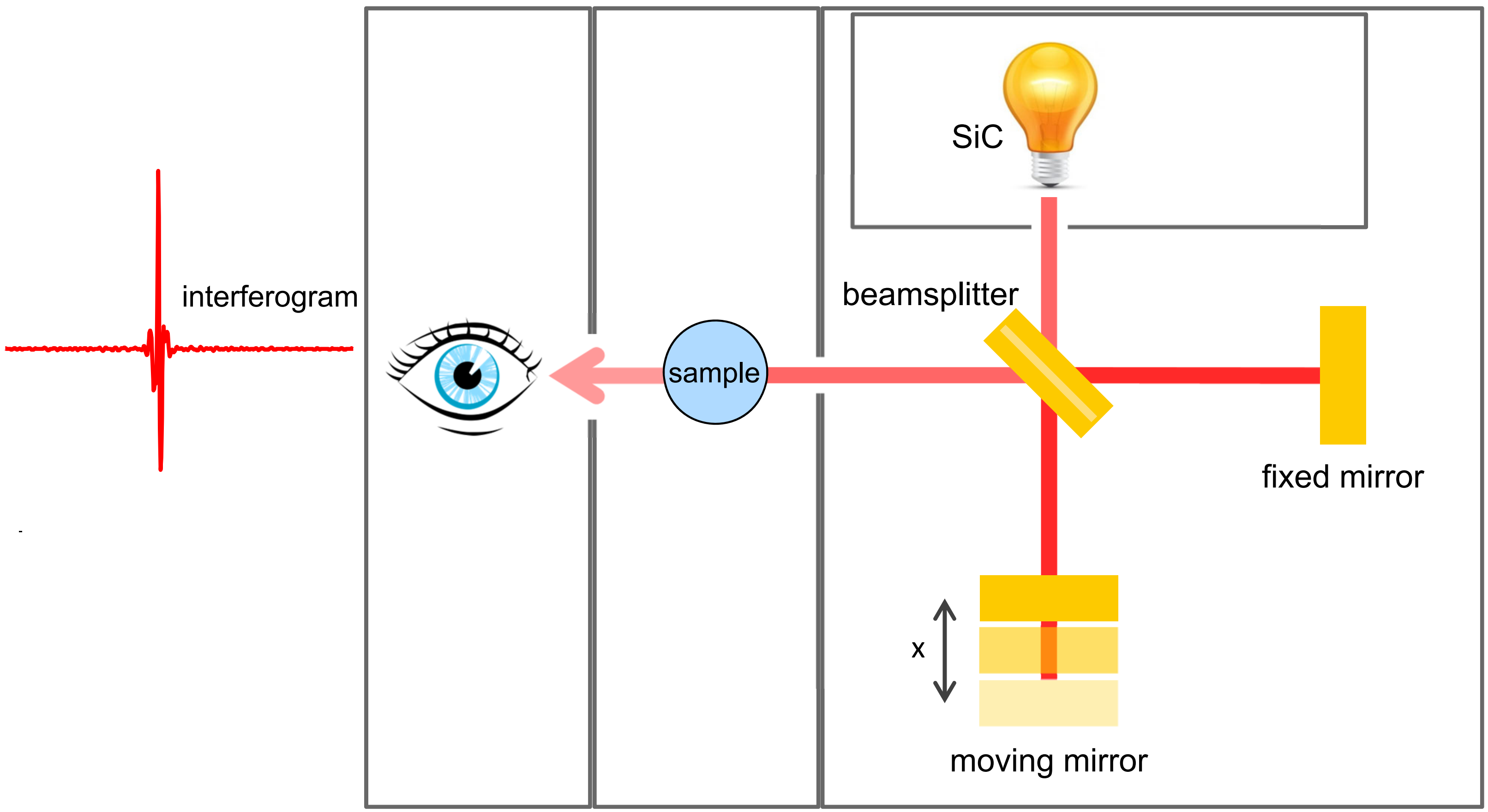
C-C	C=C	C≡C
1200 cm^{-1}	1650 cm^{-1}	2200 cm^{-1}

→ larger k

C-H	C-D	C-C	C-O	C-Cl
3000 cm^{-1}	2100 cm^{-1}	1200 cm^{-1}	1100 cm^{-1}	800 cm^{-1}

→ larger μ

The spectrometer



Dispersive vs. FT

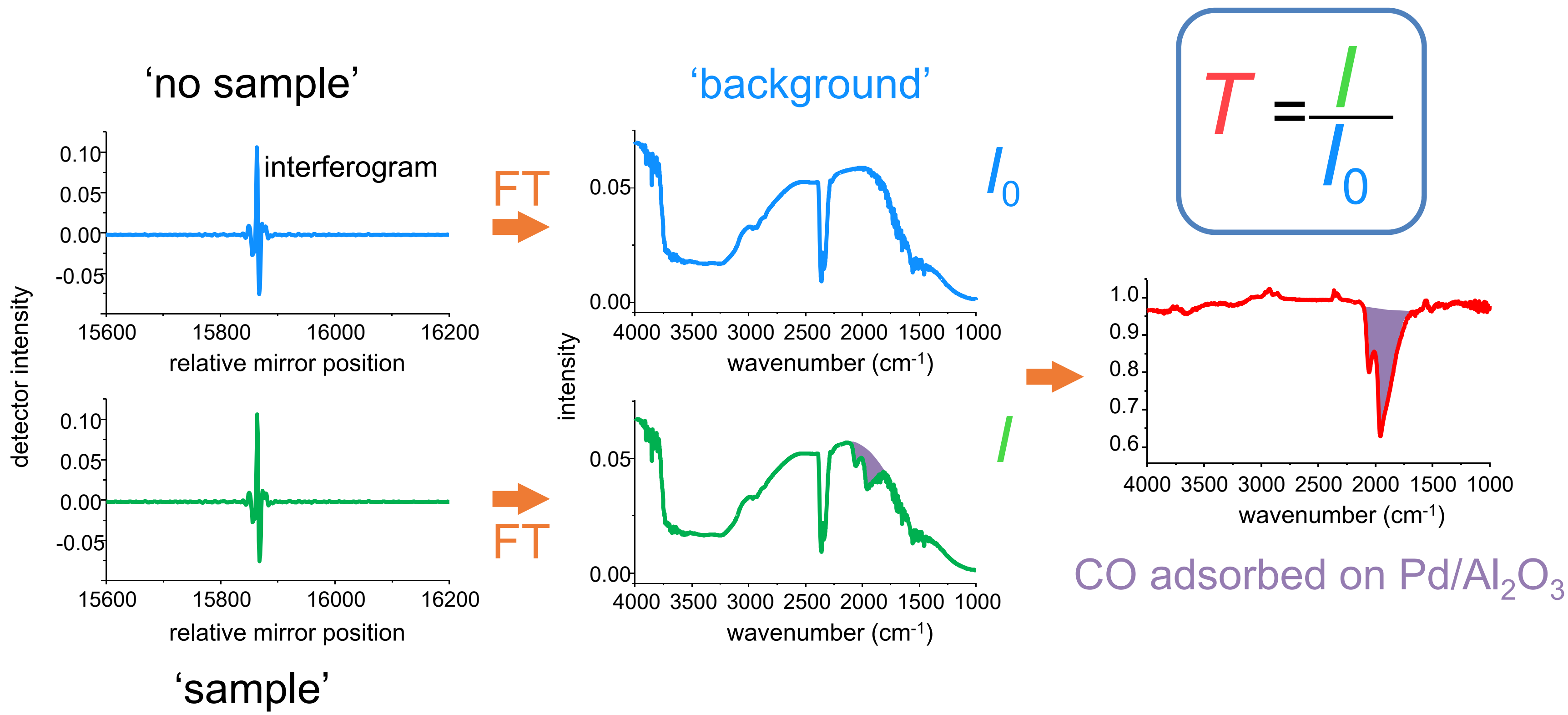
FT-IR spectrometer has significant advantages over dispersive one

- **Multiplex (Fellgett) advantage**
  All source wavelengths are measured simultaneously

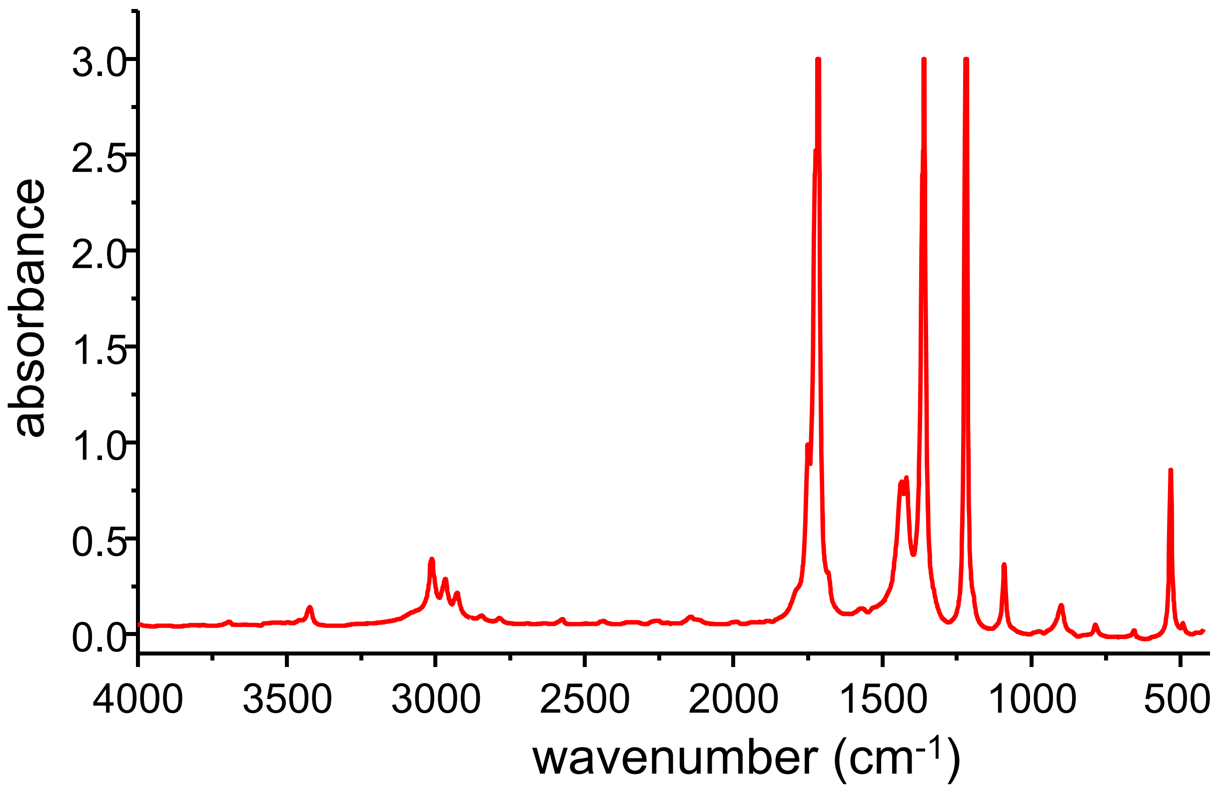
- **Throughput (Jacquinot) advantage**
  For the same resolution, the energy throughput in an interferometer can be higher
  → the same S/N as a dispersive-IR in a much shorter time

- **Precision (Connes) advantage**
  The wavenumber scale of an interferometer is derived from a HeNe laser that acts as an internal reference for each scan

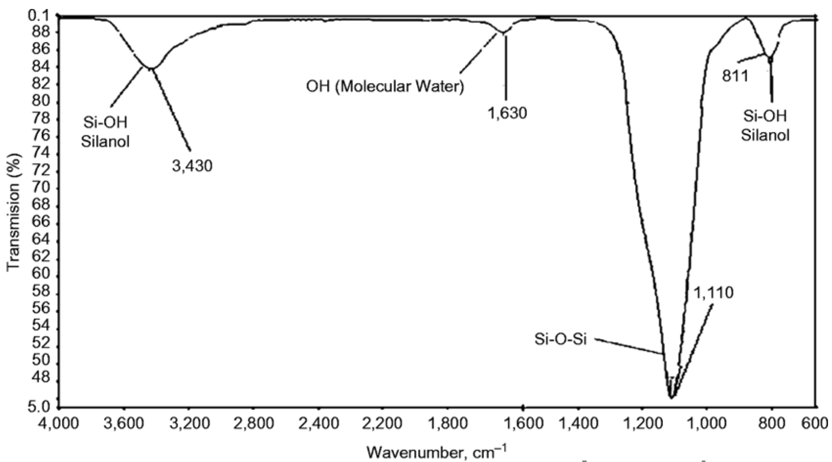
The IR spectrum

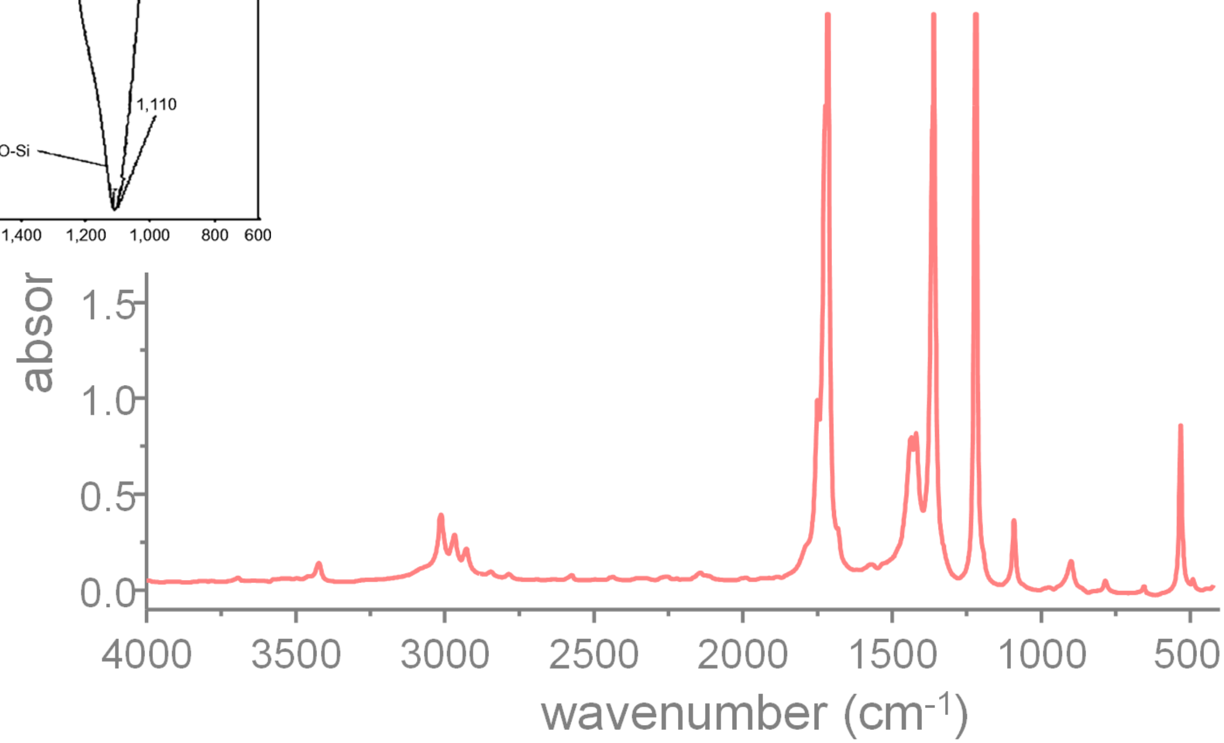


The IR spectrum

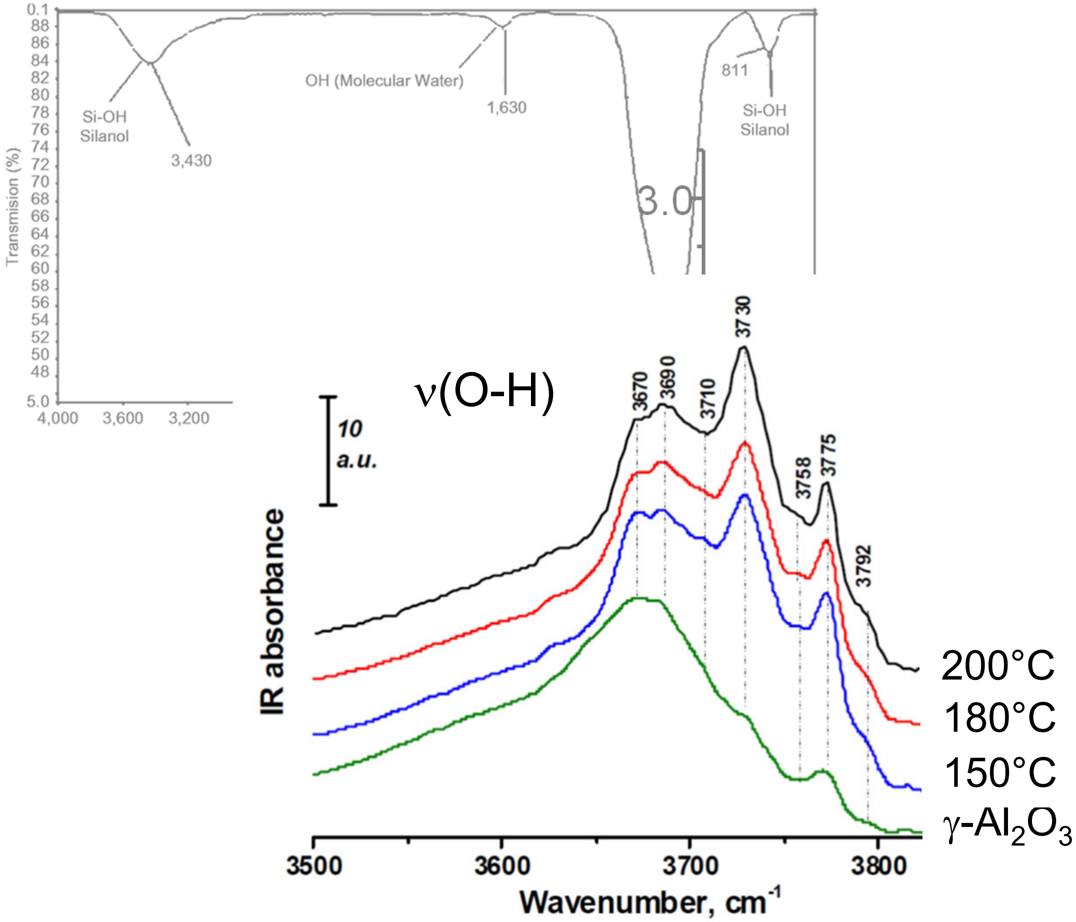


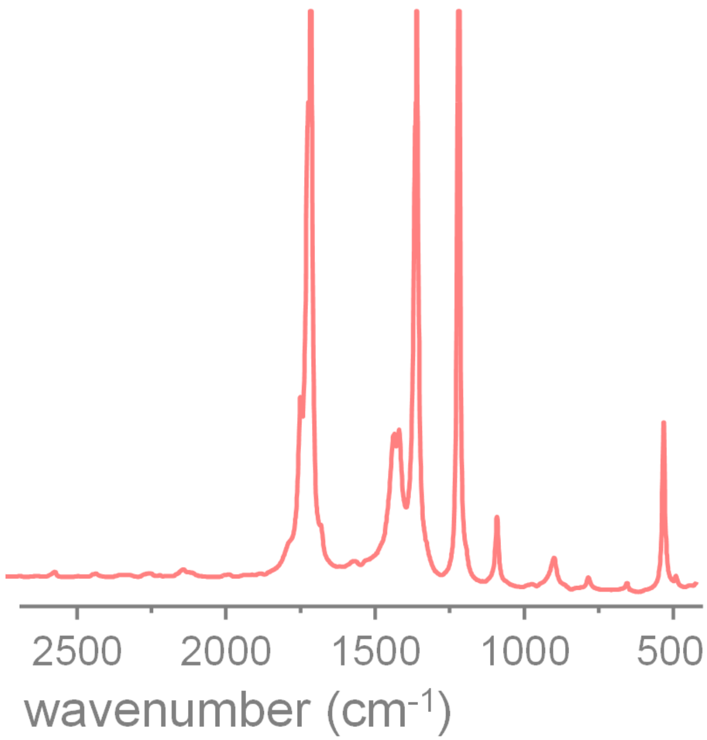
The IR spectrum



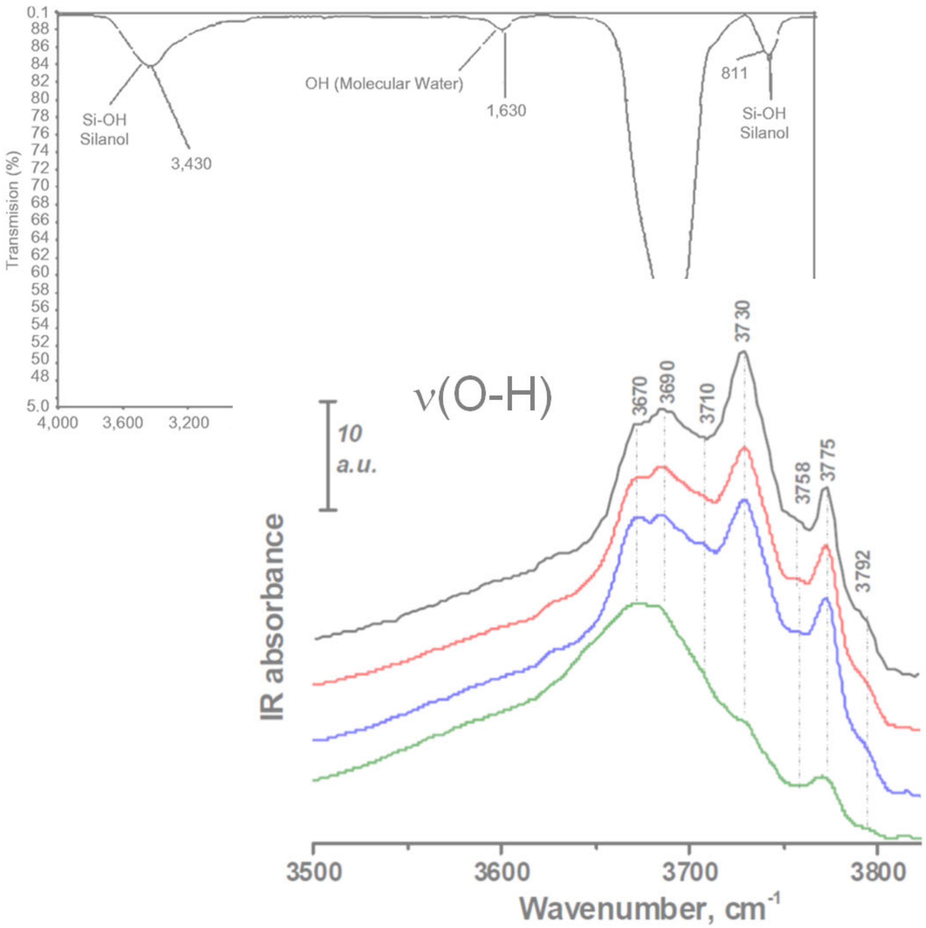


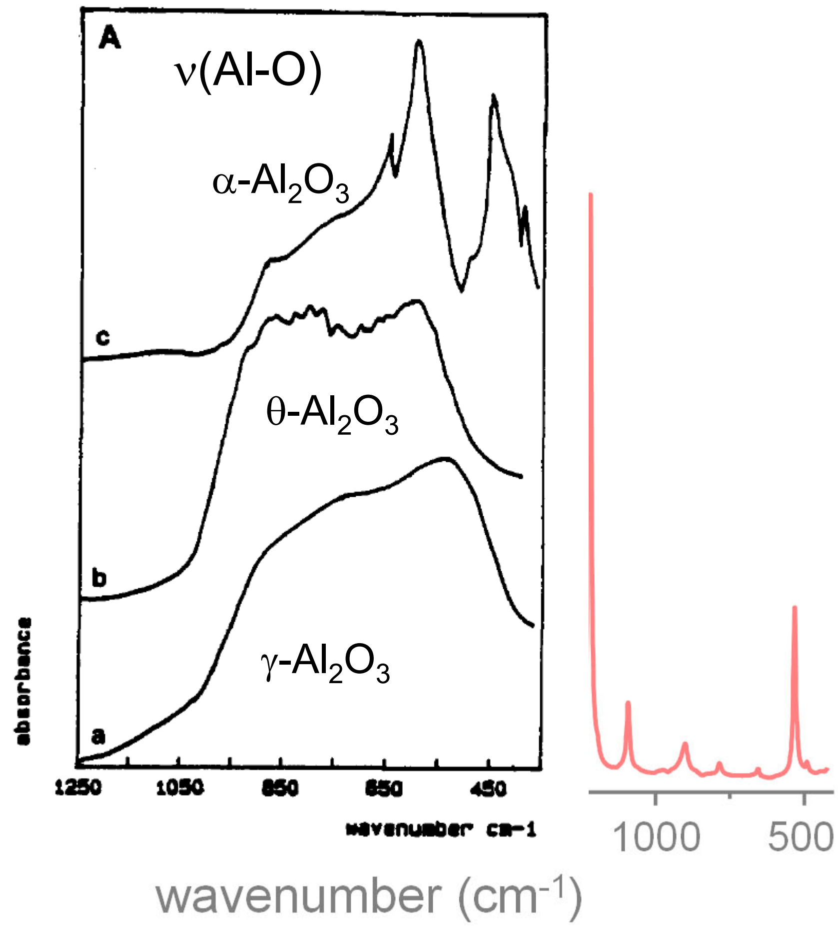
The IR spectrum





The IR spectrum

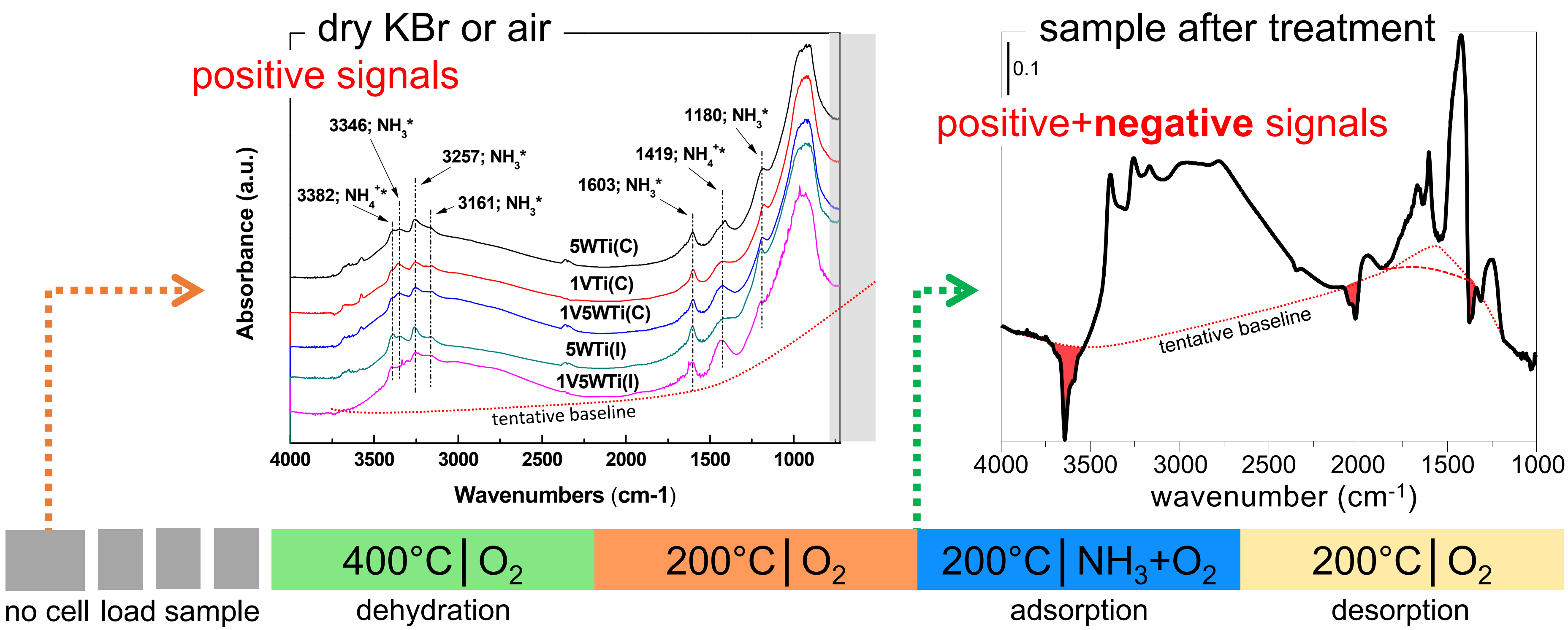




Morterra, Catal. Today 27 (1996) 497

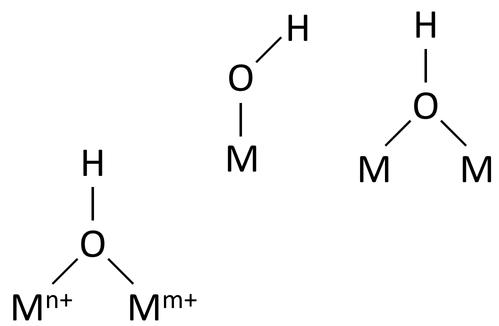
The background

- DRIFT spectra of V-W-TiO_2 catalysts after adsorption of NH_3
  - aspect of spectra changes with background



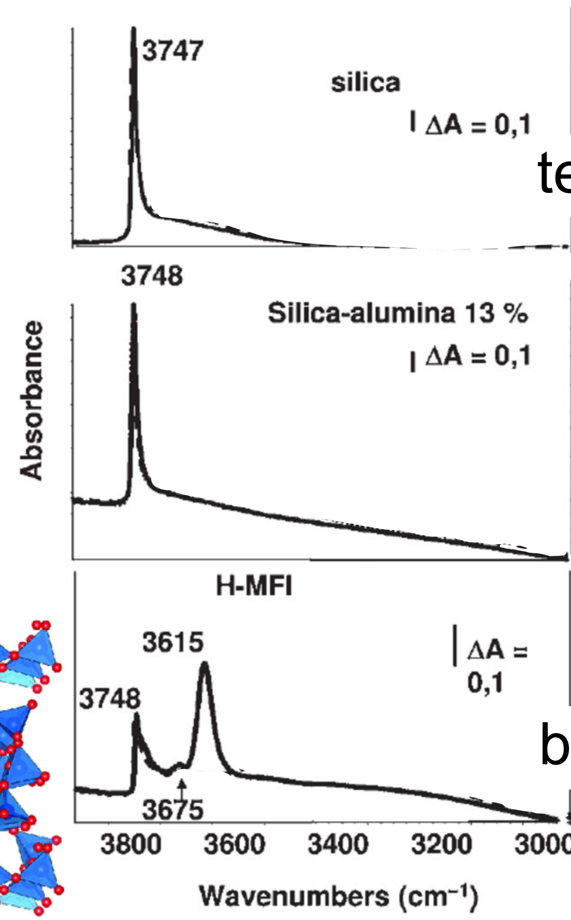
Information on materials

- 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…



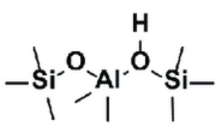
Information on materials

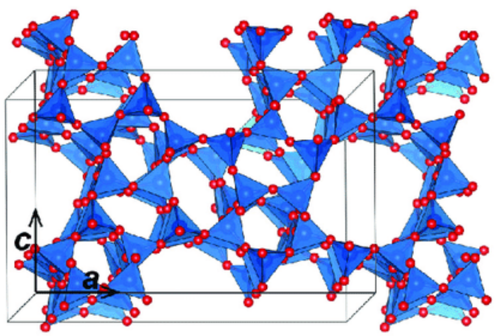
- Perturbation of hydroxyls
  - adsorption of probe molecule



terminal

bridged





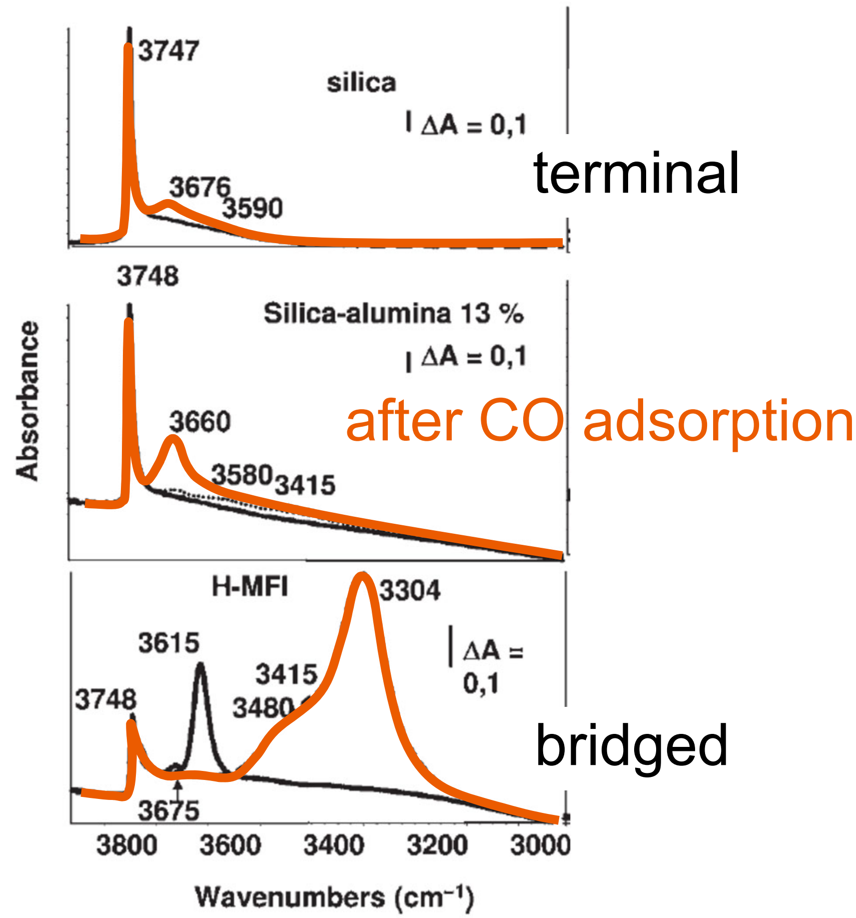
Busca, in Metal Oxide Catalysis, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim (2009) 95 | Uslamin, Zeolite-based catalysis for sustainable aromatics production, Technische Universiteit Eindhoven (2019)

Information on materials

- Perturbation of hydroxyls
  - adsorption of probe molecule

↓

  - H-bonded hydroxyls



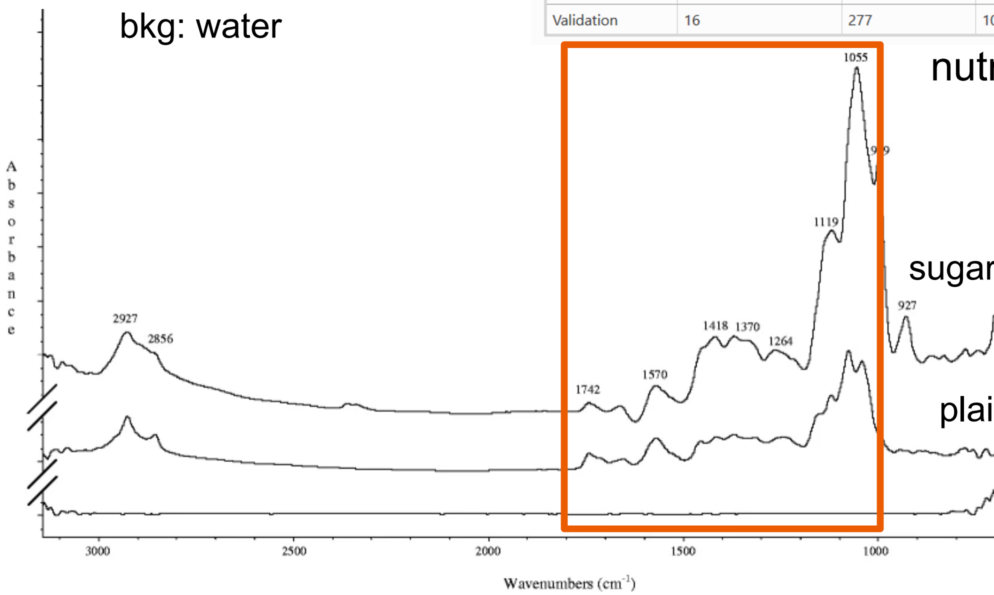
Busca, in Metal Oxide Catalysis, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim (2009) 95

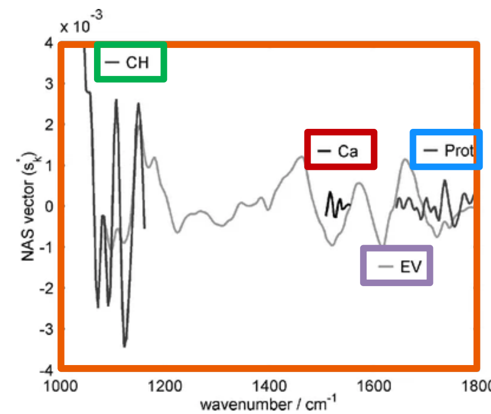
Information on materials

- Also other disciplines…

Single model	Number of samples	Energetical value (kJ/100 g)		Proteins (g/100 g)		Fat (g/100 g)		Carbohydrates (g/100 g)		Calcium (mg/100 g)	
		Mean	± s	Mean	± s	Mean	± s	Mean	± s	Mean	± s
Calibration	19	334	154	4.1	0.7	2.7	3.0	9.4	4.2	135	22
Validation	29	268	106	3.8	0.5	1.6	1.4	8.4	4.4	125	6
Extended model	Number of samples	Energetical value (kJ/100 g)		Proteins (g/100 g)		Fat (g/100 g)		Carbohydrates (g/100 g)		Calcium (mg/100 g)	
		Mean	± s	Mean	± s	Mean	± s	Mean	± s	Mean	± s
Calibration	32	295	137	3.9	0.7	2.1	2.3	8.8	4.4	129	16
Validation	16	277	100	3.9	0.4	1.7	1.4	8.6	4.4	127	12

nutritional parameters of yogurt samples

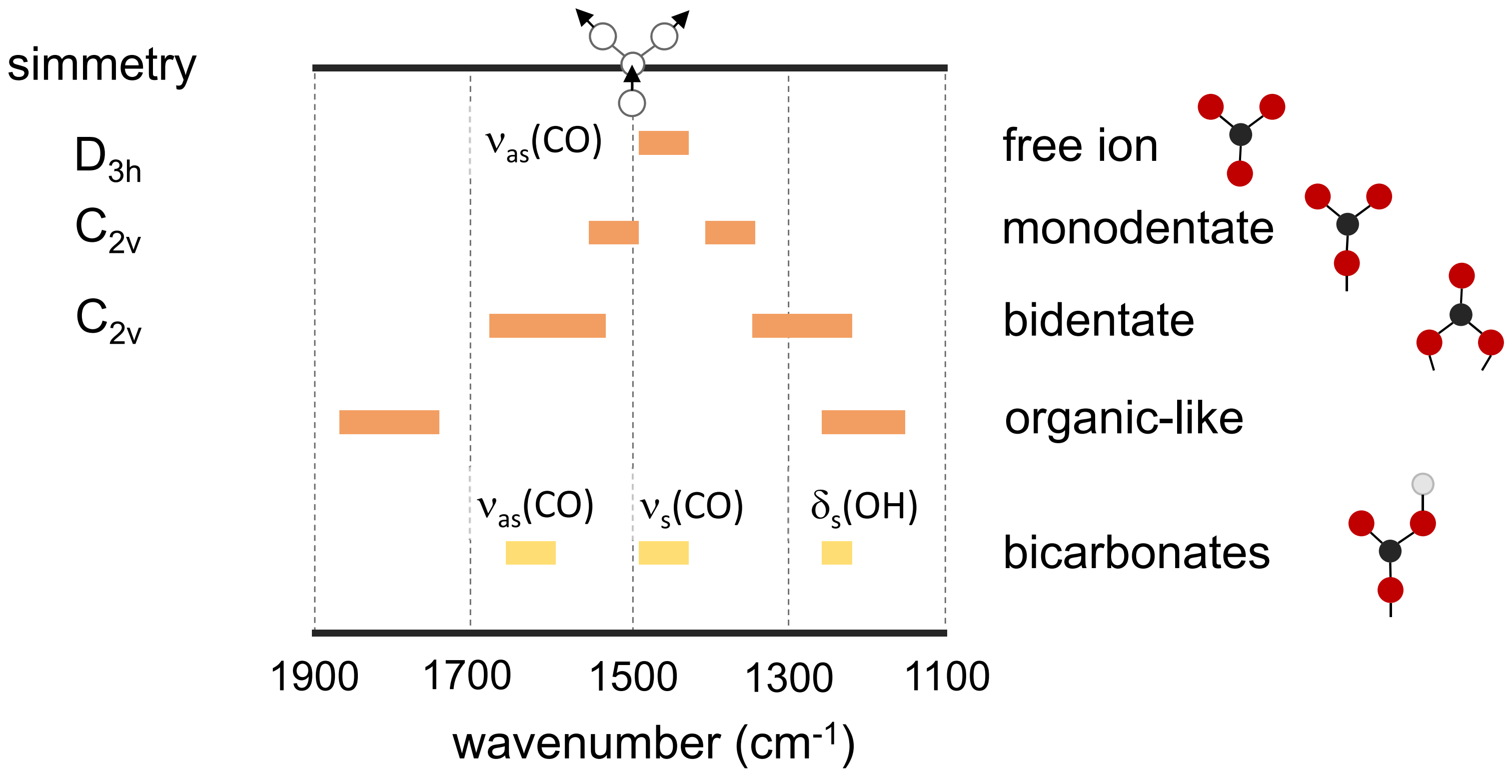




Moros et al., Anal. Bioanal. Chem. 385 (2006) 708

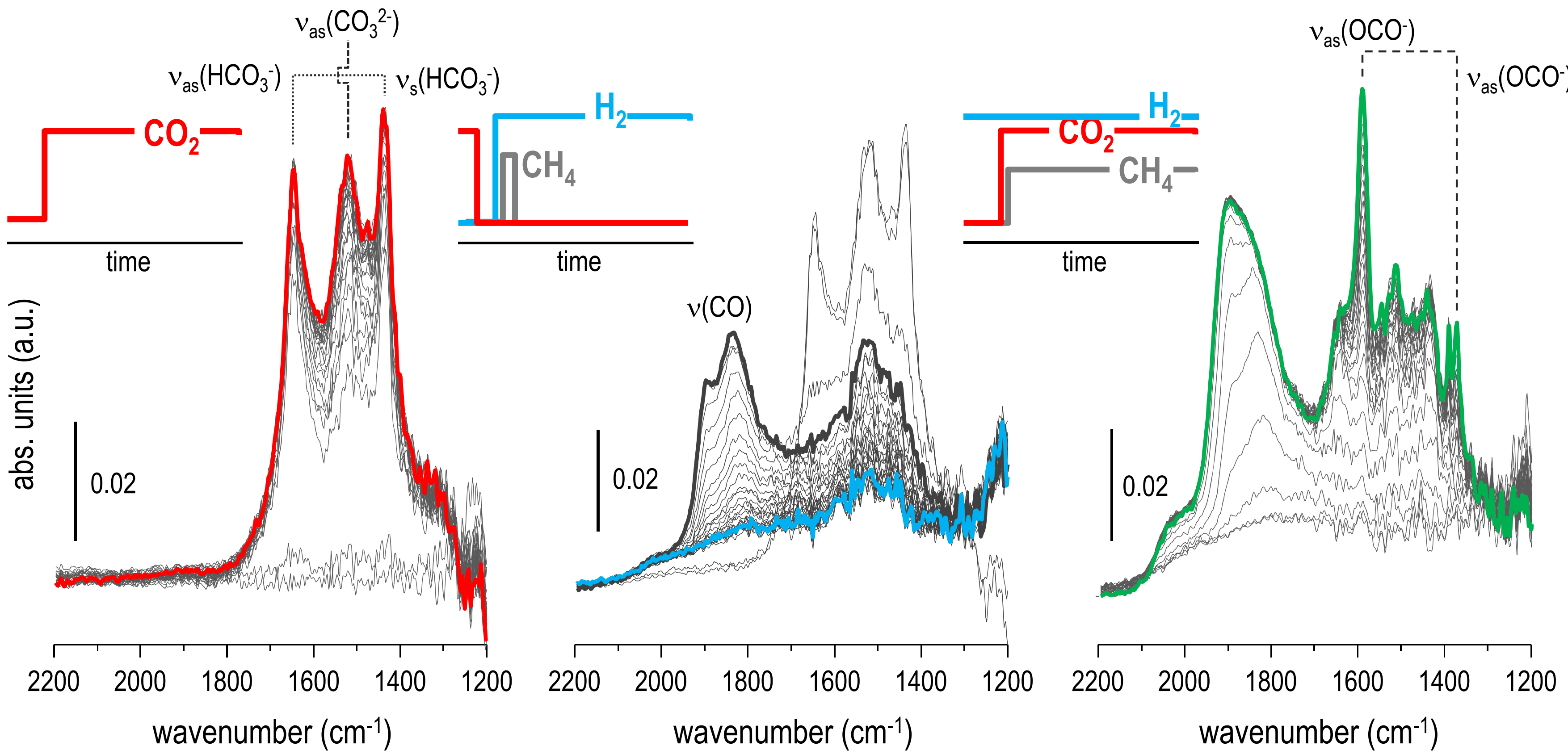
Adsorbates by FTIR

- The carbonate ion

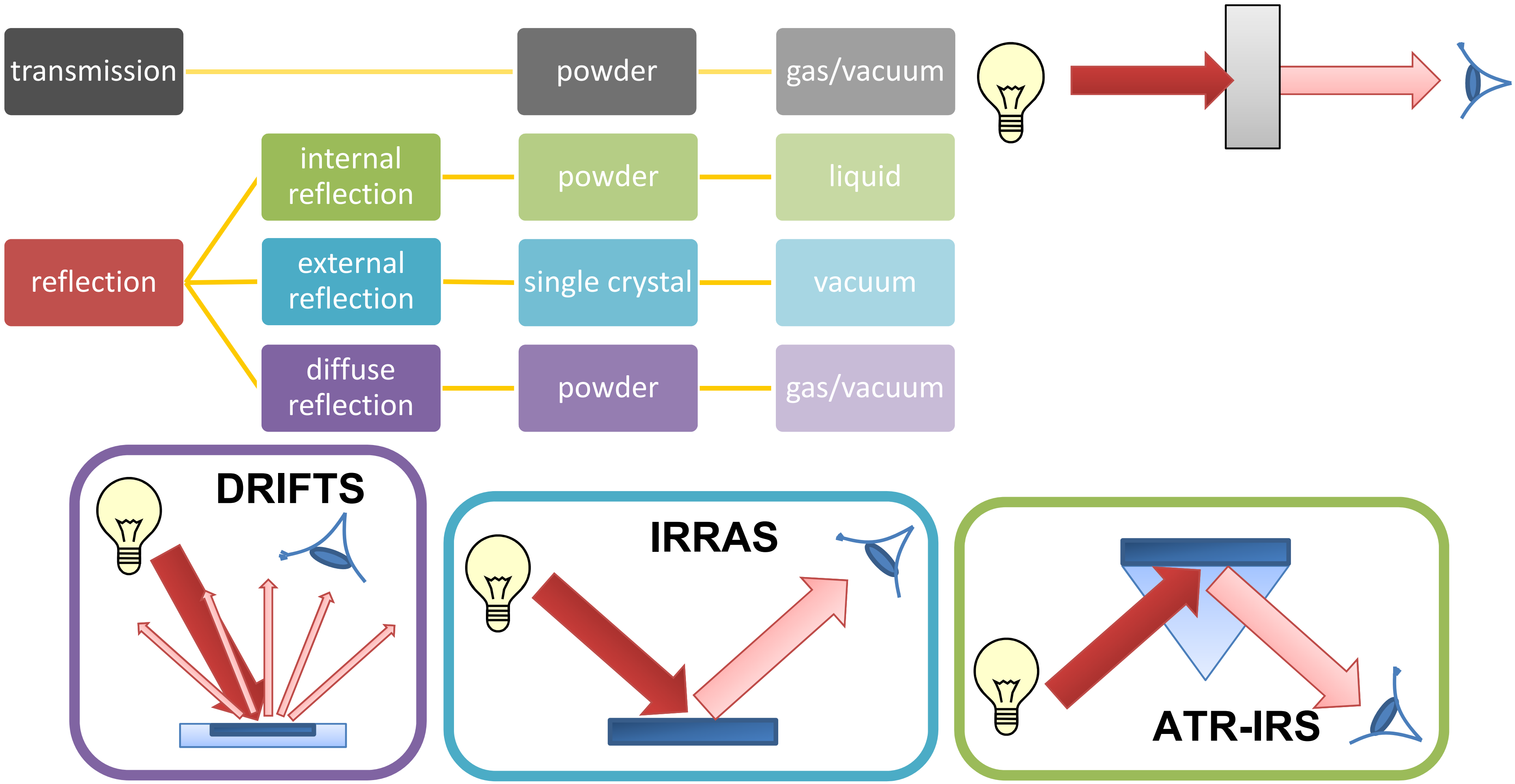


Morterra, Catal. Today 27 (1996) 497

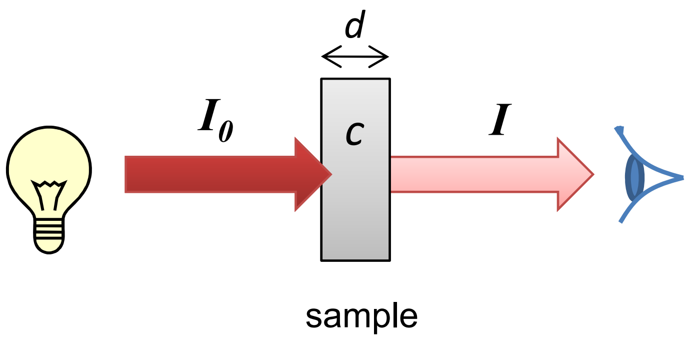
Adsorbates by FTIR



Techniques, sample form, environment



Transmission



- 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

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

Lambert-Beer law

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

Transmission

- **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

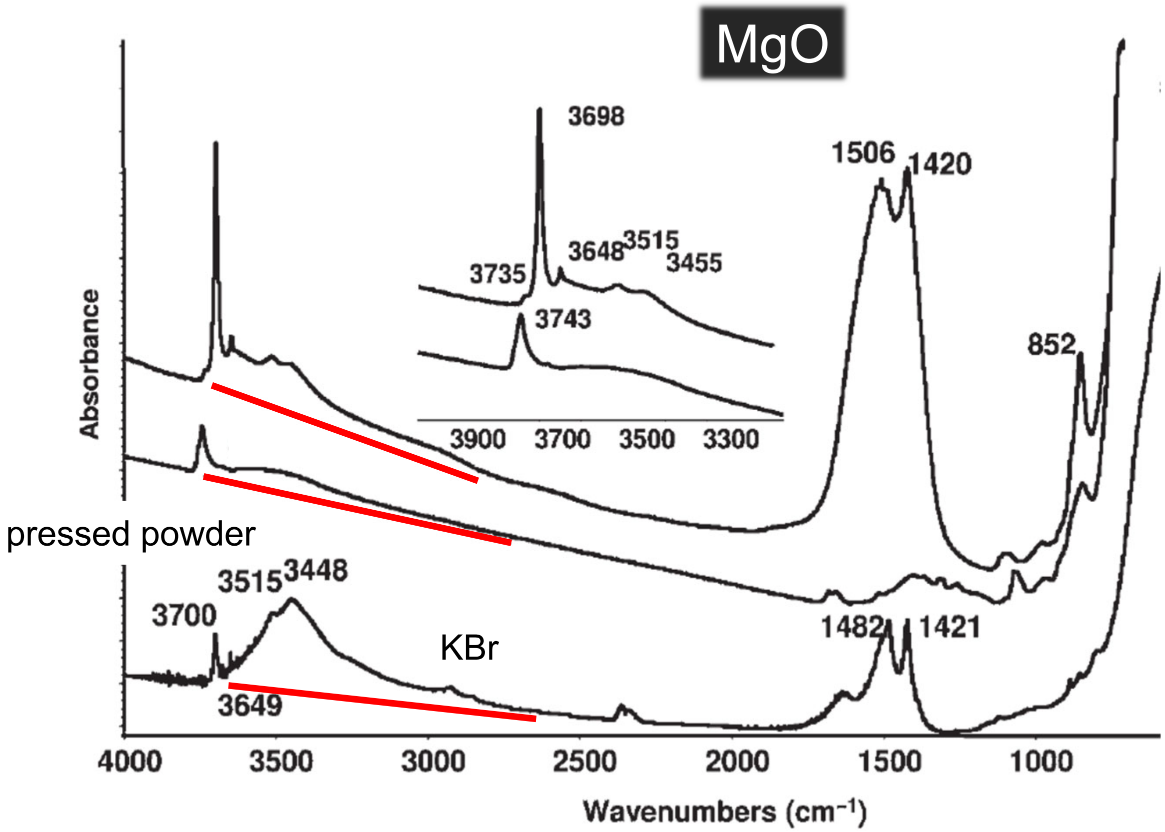
NOT FOR IN SITU/OPERANDO EXPERIMENTS

- **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

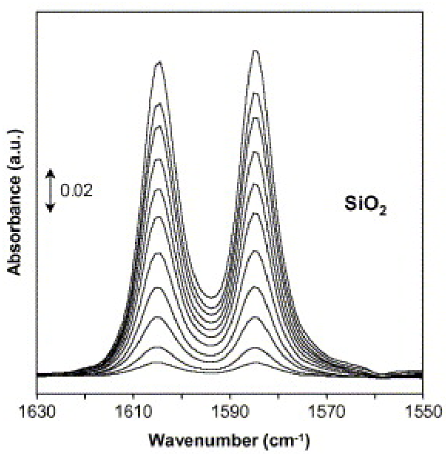
- Sample preparation
  - self supporting wafers (few mg)
- Controlled exp. conditions
  - vacuum and controlled dosages
- Baseline
  - slope increases at high frequency (beam scattering increases with increasing frequency)
  - slope depends on particle size (very steep for powders with large particles, ca. 1 μm)
  - T @ 4000 cm^{-1} is ca. 0 for large particle size oxides

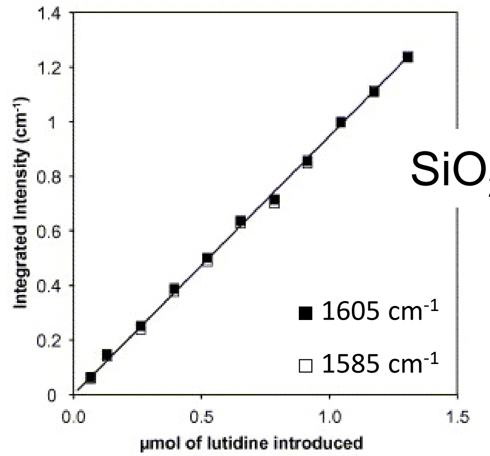


Busca, in Metal Oxide Catalysis, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim (2009) 95

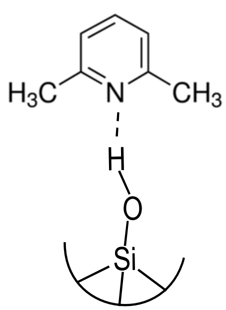
Transmission

- Quantification | Molar absorption coefficient ε





SiO_2



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

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

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

ε, integrated molar absorption coefficient

ℓ, disc thickness (optical path)

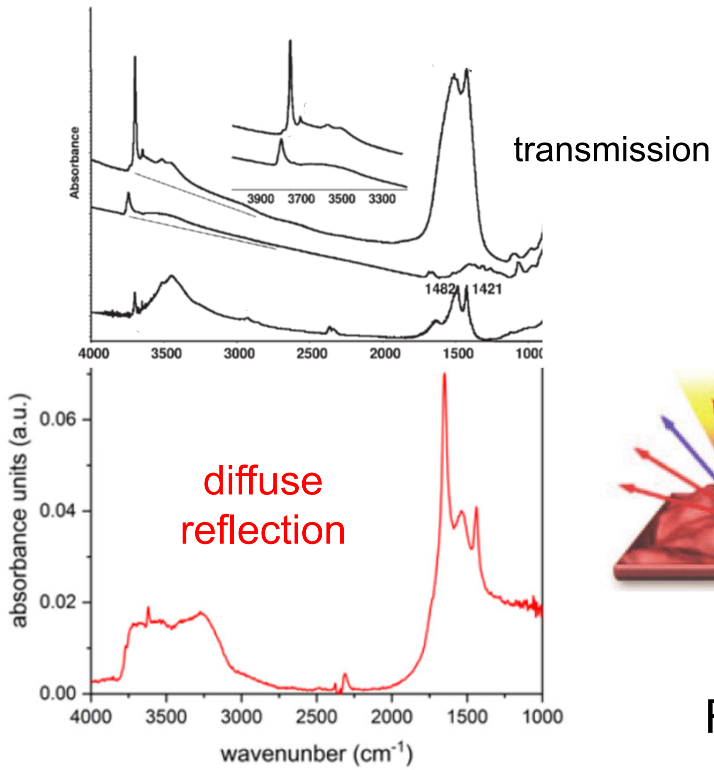
n, amount of adsorbed molecule

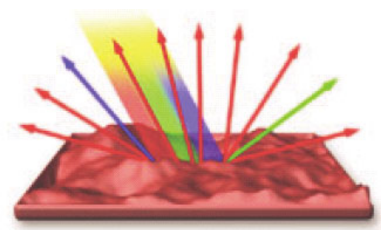
S, disc area

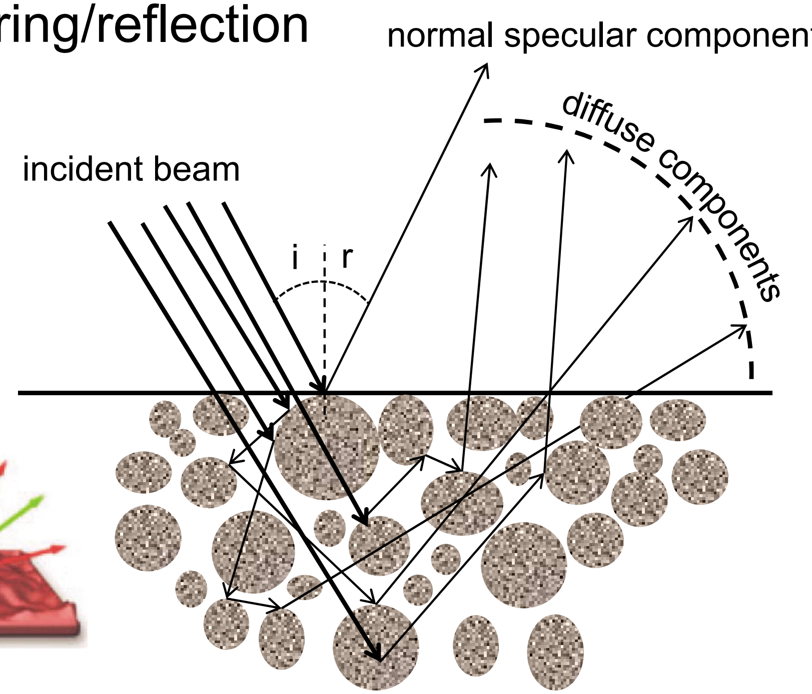
Onfroy et al., Micropor. Mesopor. Mater. 82 (2005) 99

Diffuse reflection

- Combination of transmission and scattering/reflection







Reflectance increases by increasing scattering
→ spectrum baseline is flat or even decreasing

Chalmers and Dent, Industrial analysis with vibrational spectroscopy, 1997, 153

Diffuse reflection

- Qualitative analysis
  - very sensitive to surface species due to its diffuse reflective nature
  - the detected light is reflected multiple times at powder surfaces
- Quantitative analysis
  - can be very complicated
  - the spectra are largely influenced by various experimental parameters, e.g. particles shape and size, refractive index of particles, absorption characteristics of particles, and porosity of the powder bed
  - a popular method is to use the Kubelka-Munk (K-M) function to transform reflectance to a sort of absorbance (K-M) unit
  - solid (approximated) theory
  - applicability and accuracy for highly absorbing and non-absorbing samples is questionable

Kubelka-Munk function

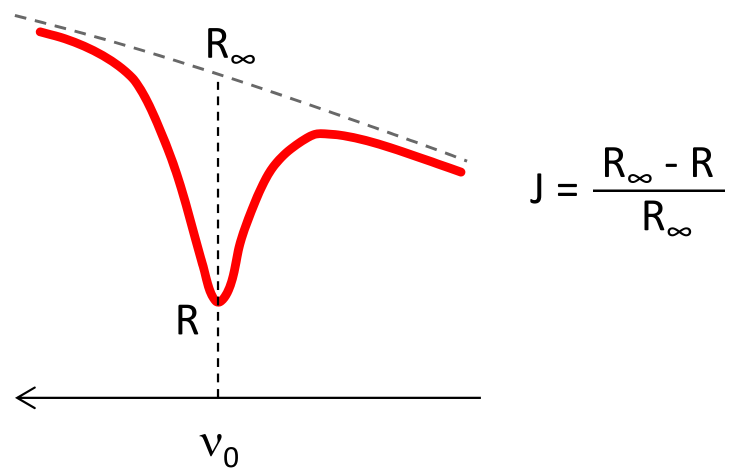
- Infinitely thick medium

$K/S = (1-R_\infty)^2/2R_\infty$

K, absorption coeff.
S, scattering coeff.

- Adsorbate on infinitely thick medium

$(K+\varepsilon C)/S = (1-R)^2/2R$



$F(R) = J(1/R-R_\infty) = 2\varepsilon C/S$

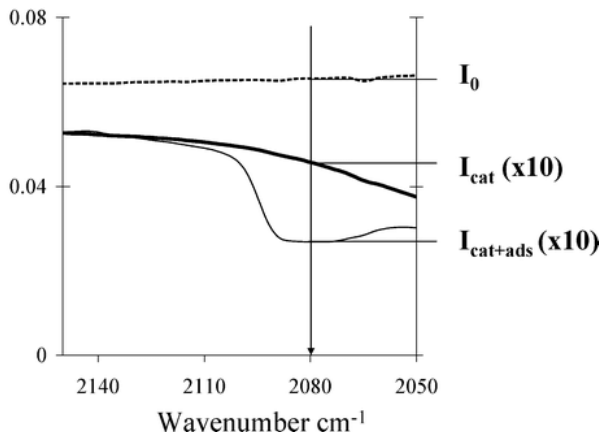
Kubelka-Munk function

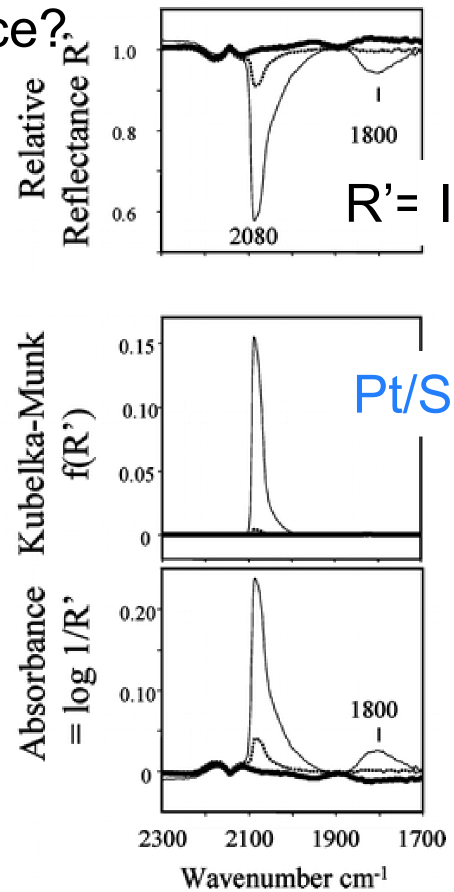
optical length (*d* in L-B Law) much larger than in transmission → more sensitivity

Matyshak et al., Catal. Today 25 (1995) 1

Diffuse reflection

- Reflectance or Absorbance?

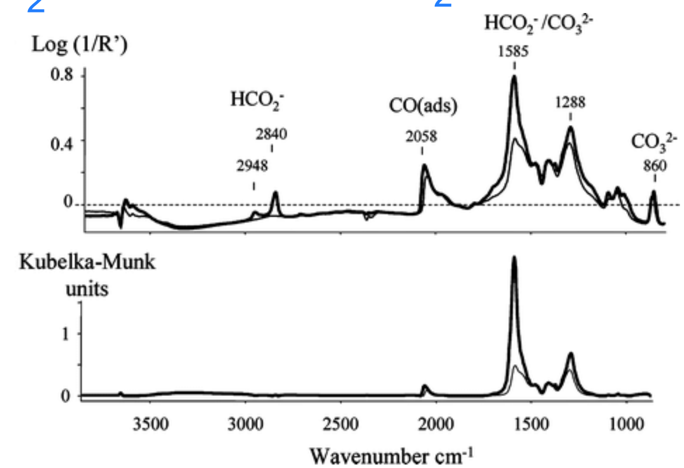




$R' = I_{cat+ads}/I_{cat}$

Pt/SiO_2

Pt/CeO_2



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

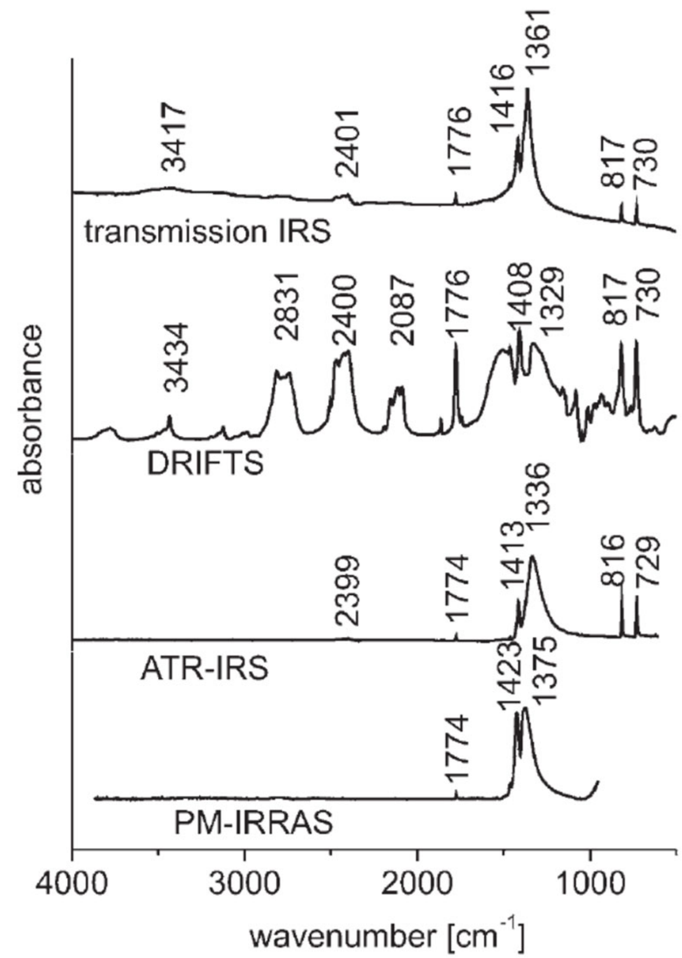
Diffuse reflection vs Transmission

- Advantages of diffuse reflection
  - easier sampling
  - applicability to powders that scatter too much in transmission, assuming the surface area is sufficiently high to detect surface
  - vibrations with a sufficiently high signal-to-noise ratio
  - slightly lower sensitivity to bulk conduction phenomena, because of a higher surface-to-bulk sensitivity ratio
  - ideally suited for in situ/operando studies

- Disadvantages of diffuse reflection
  - less obvious optical setup
  - work in flow rather than in vacuum
  - more difficult sample activation (i.e. water removal from highly porous materials)

Diffuse reflection vs Transmission

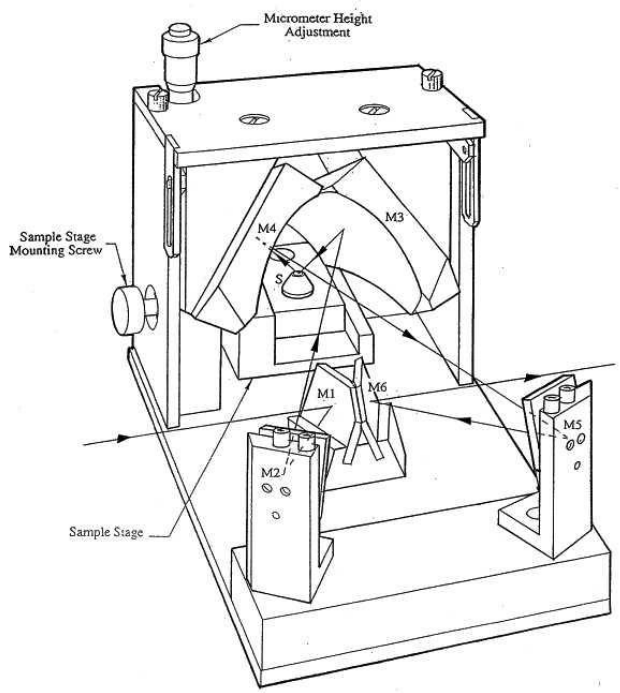
- Comparison between techniques with different sensitivity (bulk/surface) should be careful
- DRIFTS more sensitive than TIRS
- Band assignment depends on surface sensitivity of the technique



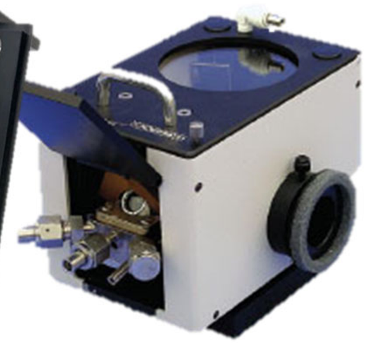
Rödel et al., PCCP 10 (2008) 6190

Diffuse reflection

- Typical mirror unit, sample holder and in situ cell



mirror unit



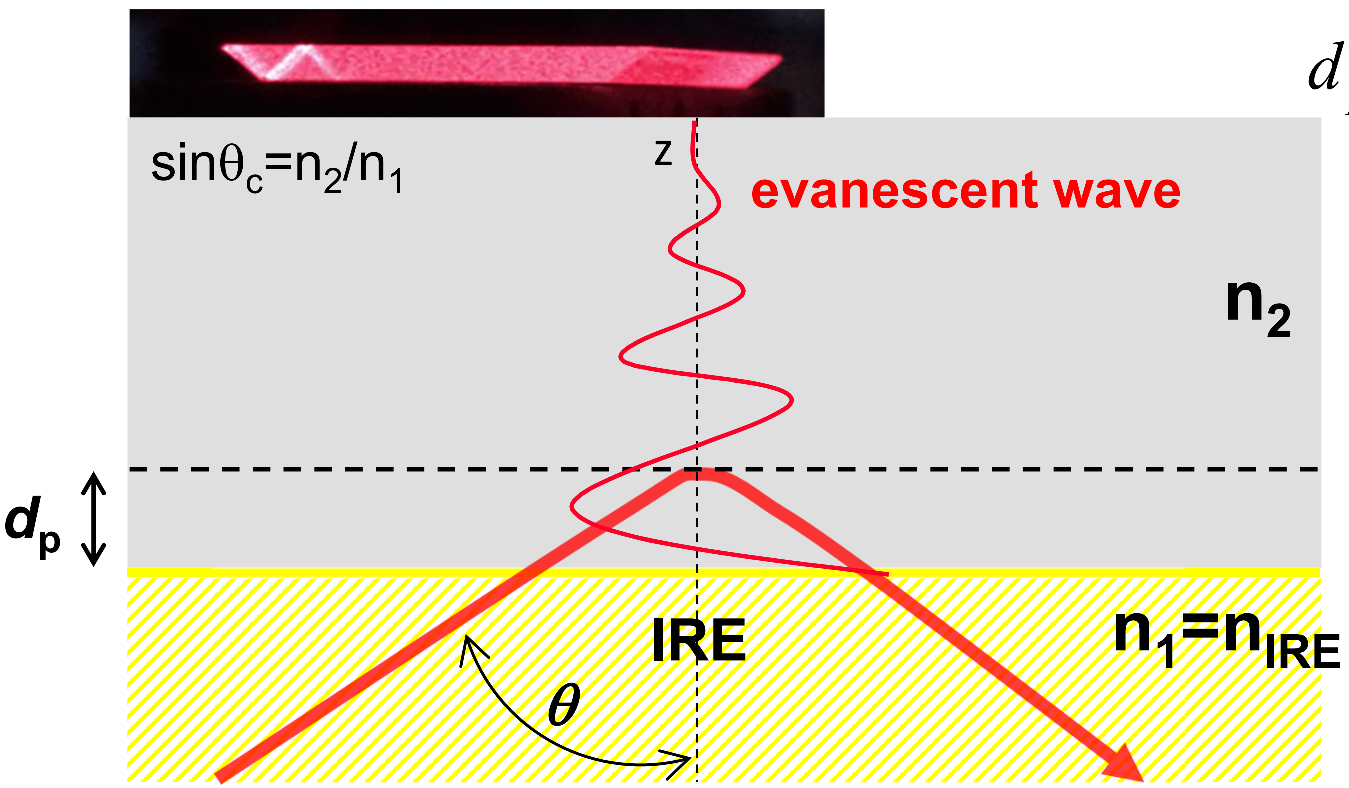
in situ cell

sample holder

HARRICK

Harrick Scientific | Praying Mantis

Attenuated total reflection



IRE, internal reflection element; high refractive index material

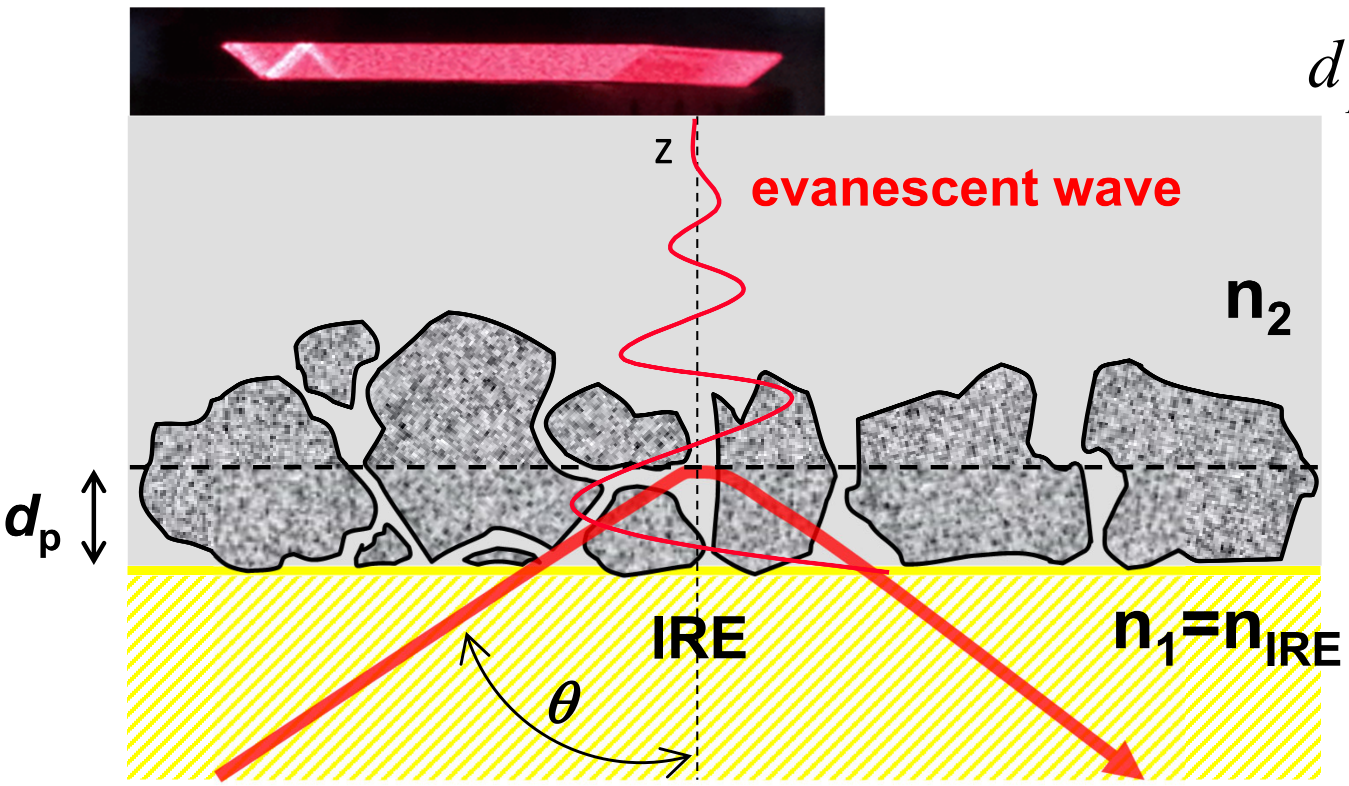
$$d_p = \frac{\lambda_1}{2\pi\sqrt{\sin^2\theta - n_{21}^2}}$$

θ : angle of incidence

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

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

Attenuated total reflection



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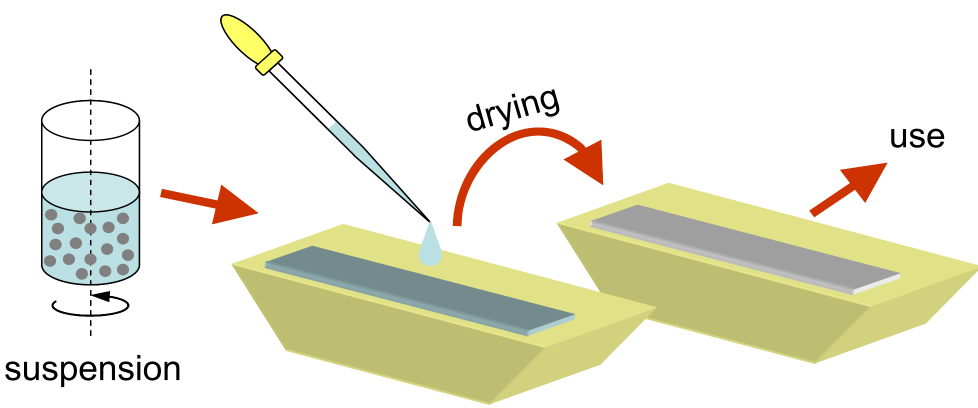
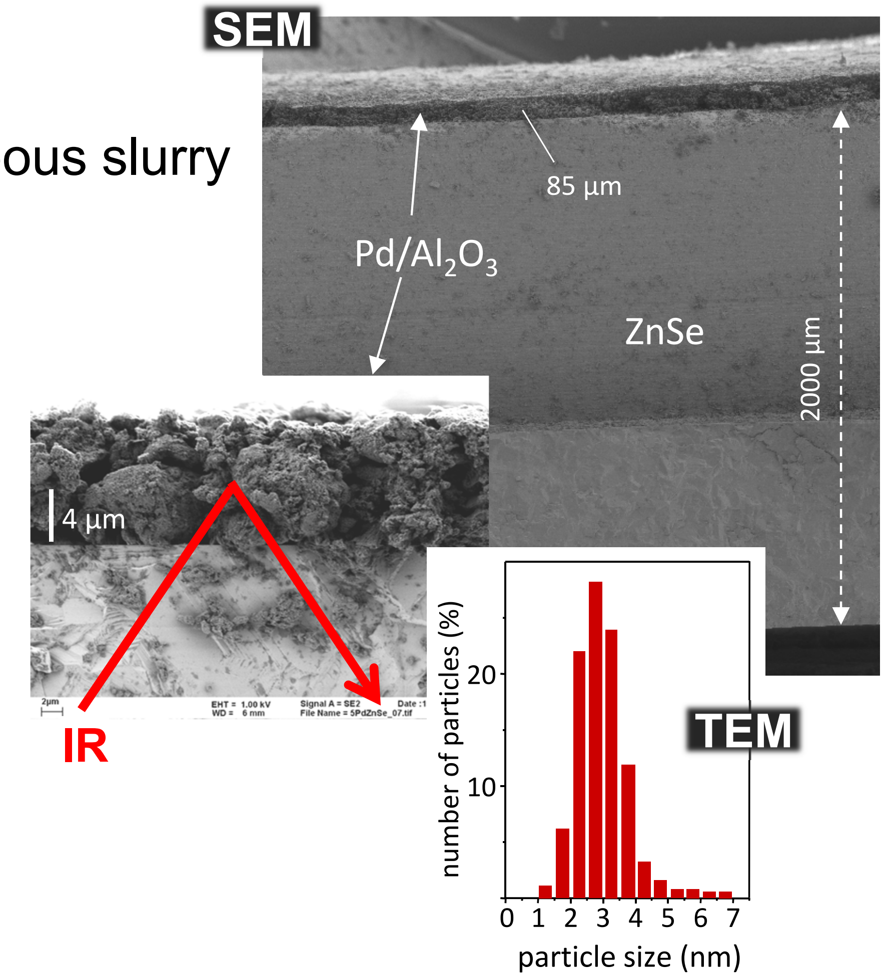
Attenuated total reflection

- Sample preparation
  - sample deposition on IRE from aqueous slurry
  - dry in air

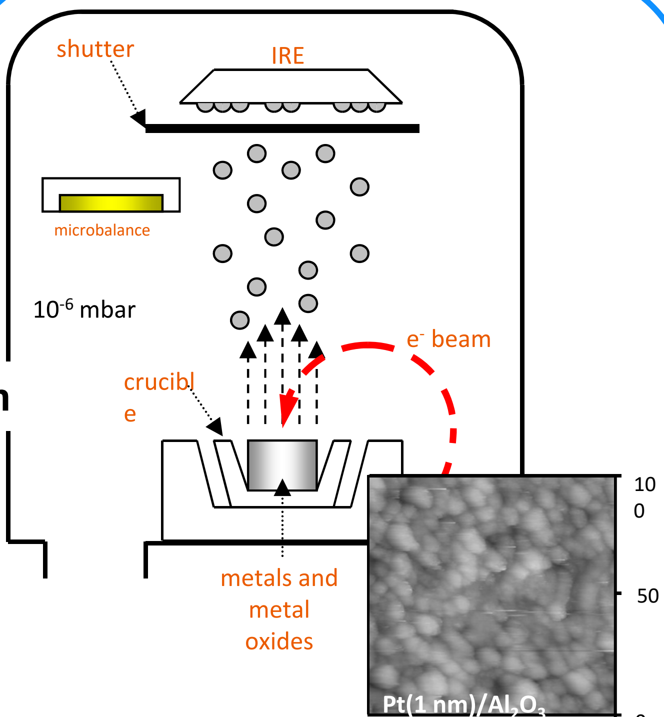




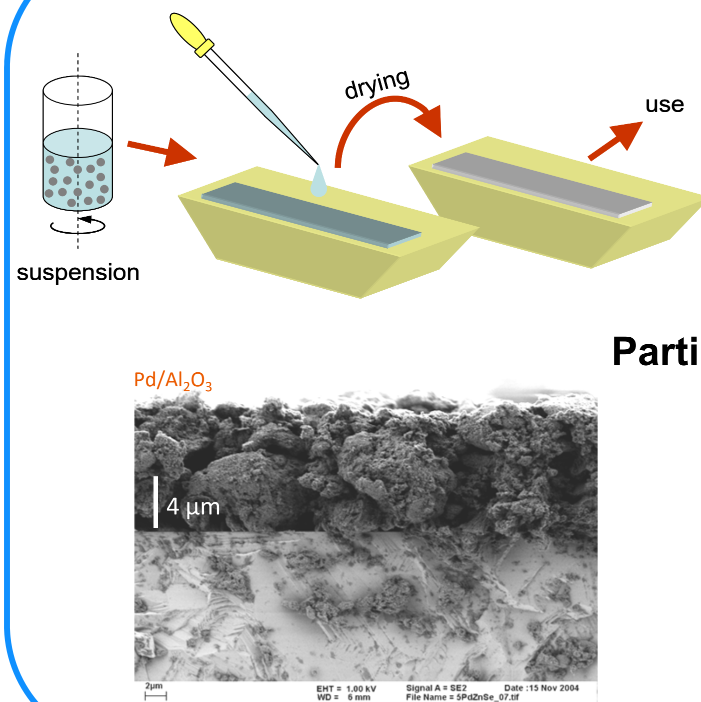
Attenuated total reflection

- Stable films needed for in situ investigations

Model film



Particulate film

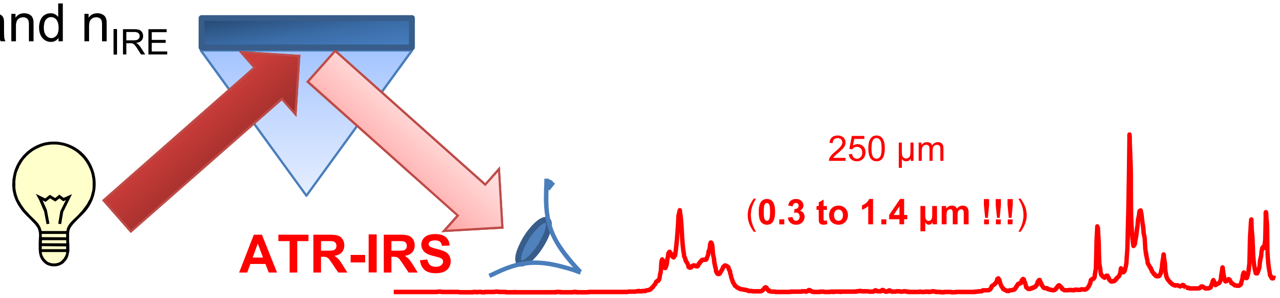


Materials for internal reflection elements

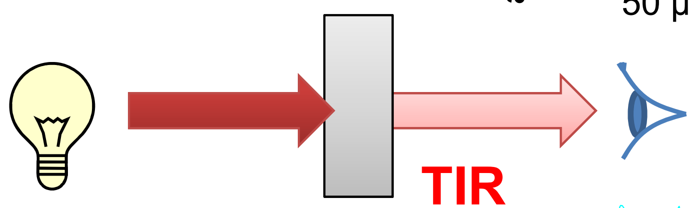
Material	Useful range / cm^{-1}	n	d_p	Properties
ZnSe	20000-700	2.43	long	soluble in strong acid; usable up to ca. 300°C
Ge	5000-900	4.02	short	good chemical resistance; hard and brittle; becomes opaque at 250°C
Si	9400-1500; 350-FIR	3.42	short	excellent chemical resistance; hard; usable up to ca. 300°C
KRS-5 (Thallium bromoiodide)	14000-330	2.45	long	toxic; slightly soluble in water and soluble in base; usable up to ca. 200°C

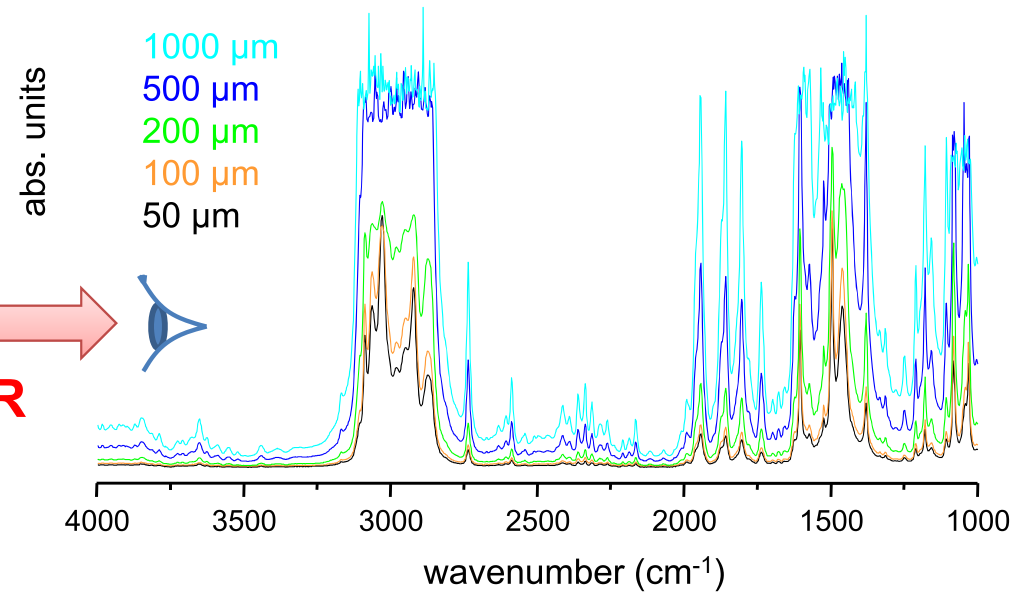
Attenuated total reflection

- The meaning of d_p and n_{IRE}



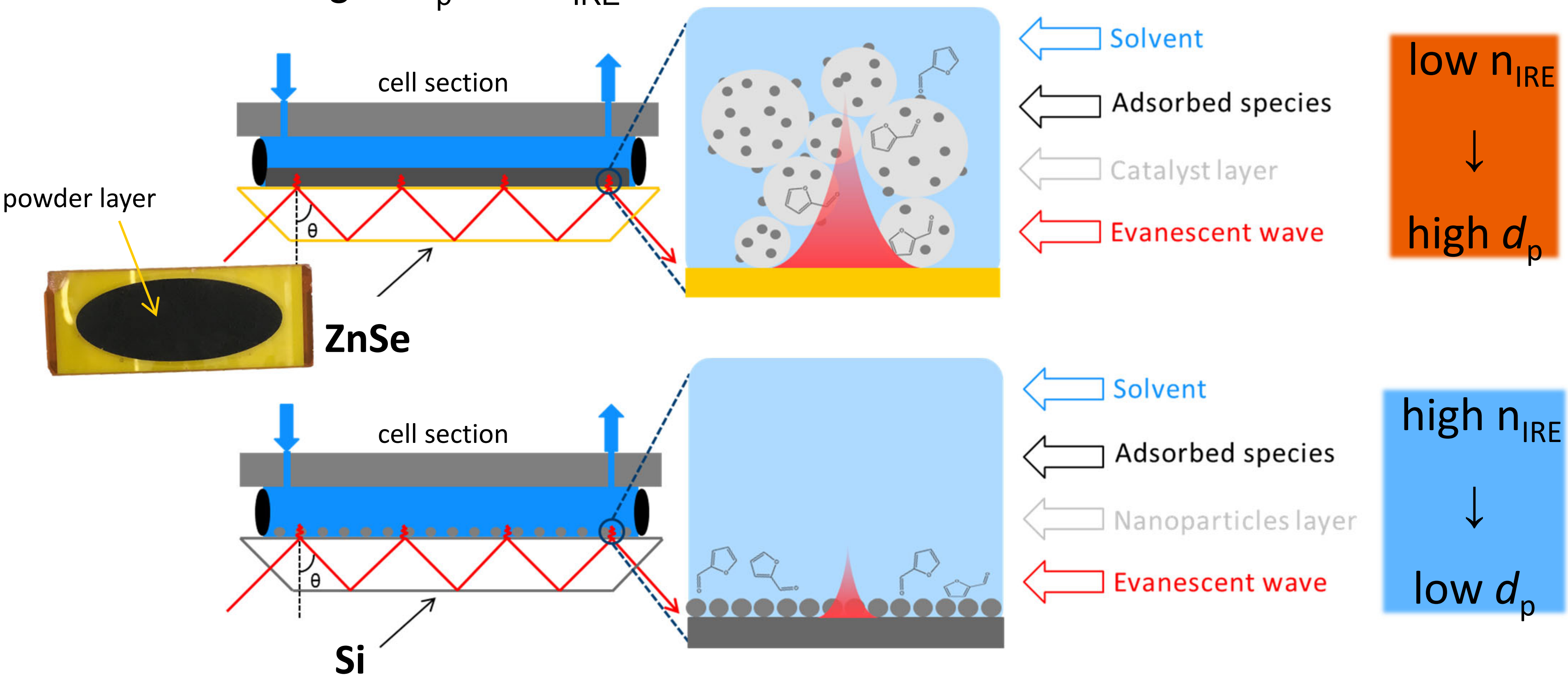
same spectrum as in transmission but with much smaller sample thickness





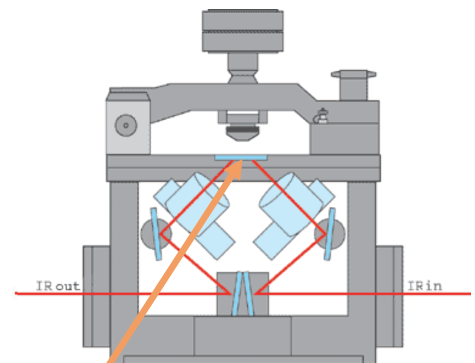
Attenuated total reflection

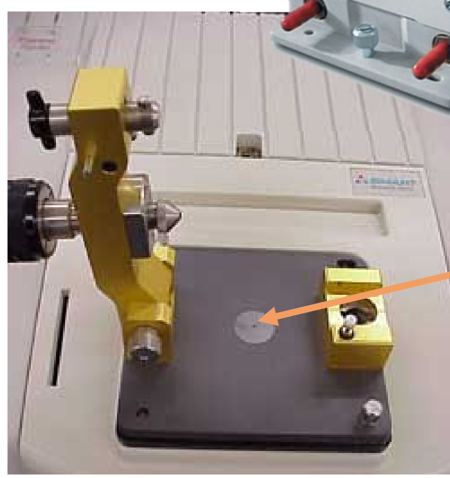
- The meaning of d_p and n_{IRE}



Attenuated total reflection

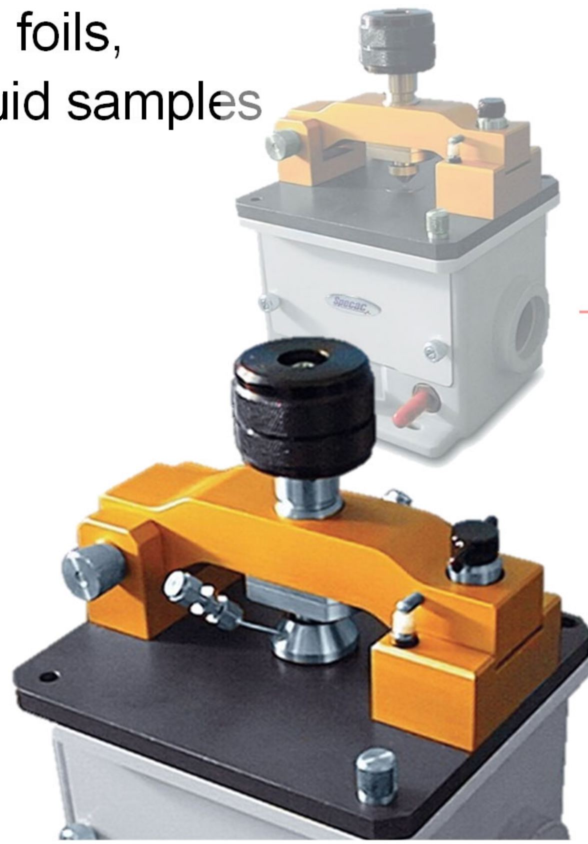
- Solid (powders, crystals, foils, plates, seeds…) and liquid samples
- Ex situ
  - structure assignment
  - identification
  - quality control

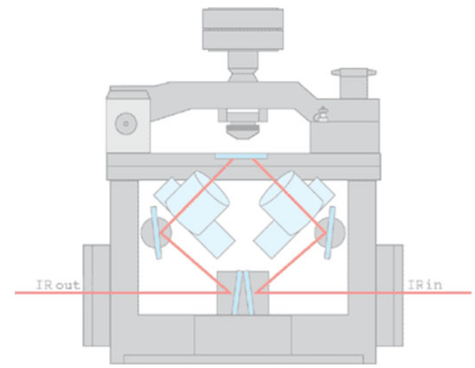




Attenuated total reflection

- Solid (powders, crystals, foils, plates, seeds…) and liquid samples
- Ex situ

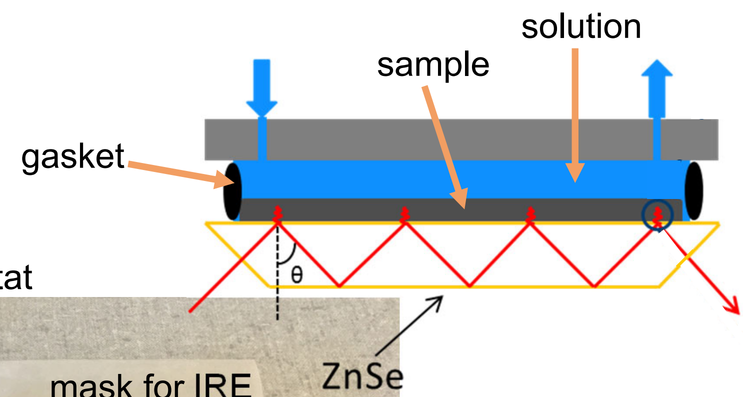


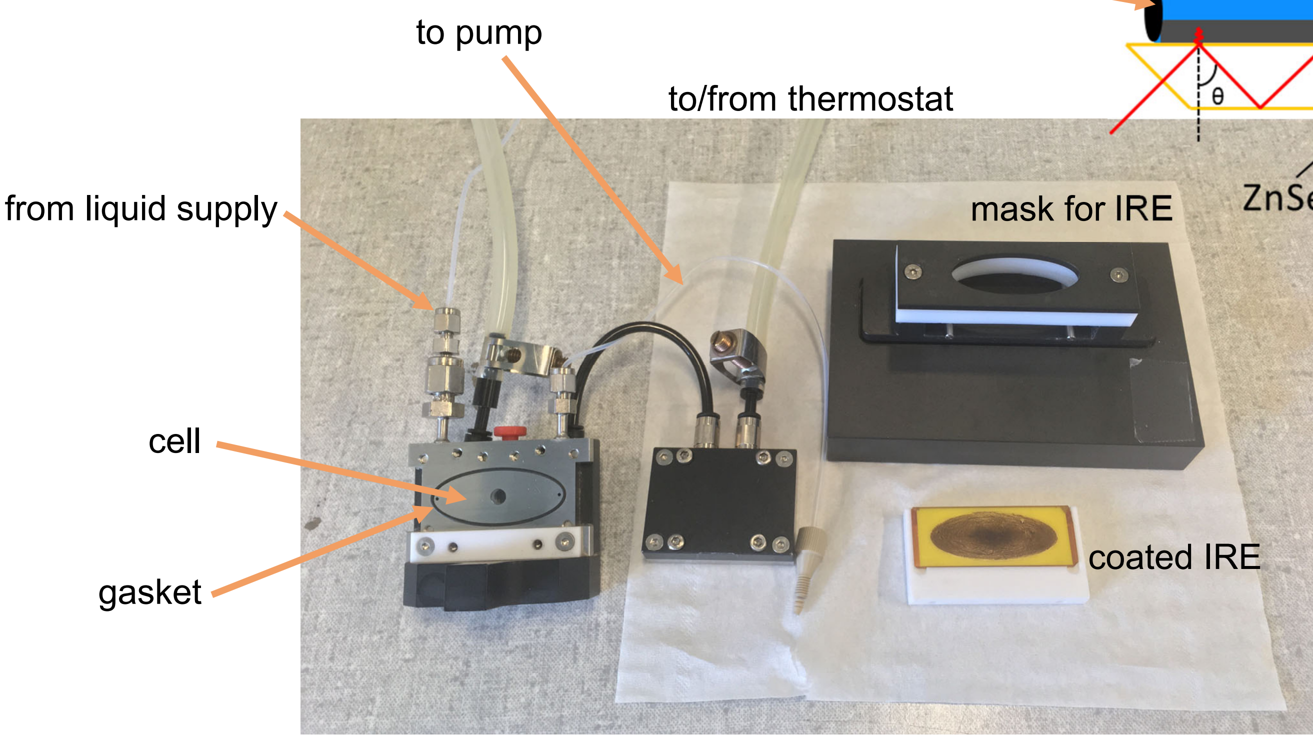


- In situ/operando
  - only liquids
  - suspensions
  - solid in contact with liquid

Attenuated total reflection

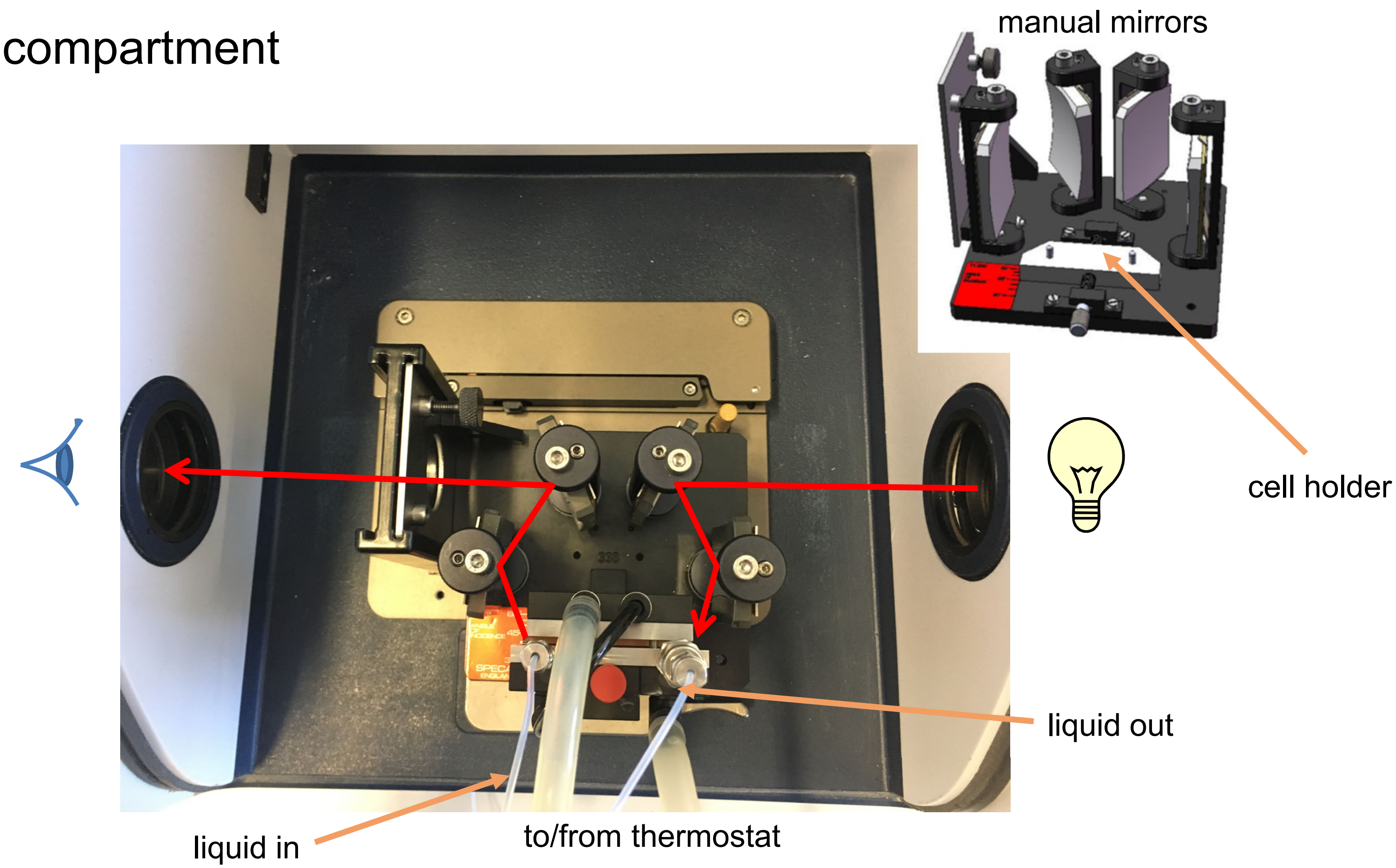
- Cell mounting



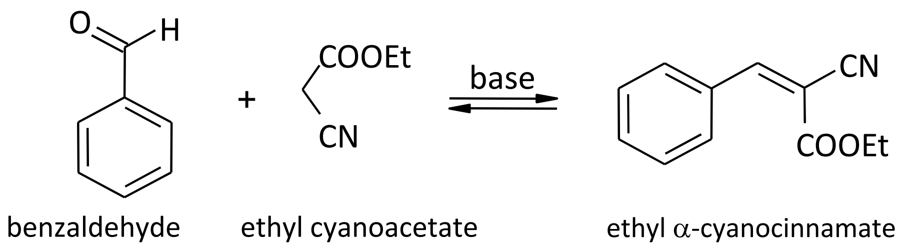


Attenuated total reflection

- Sample compartment

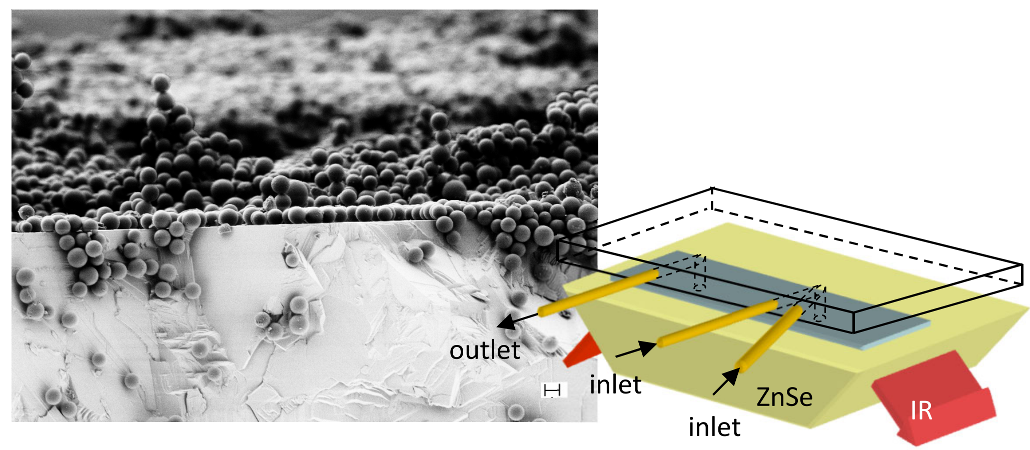


Knoevenagel condensation

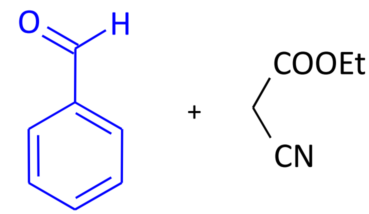


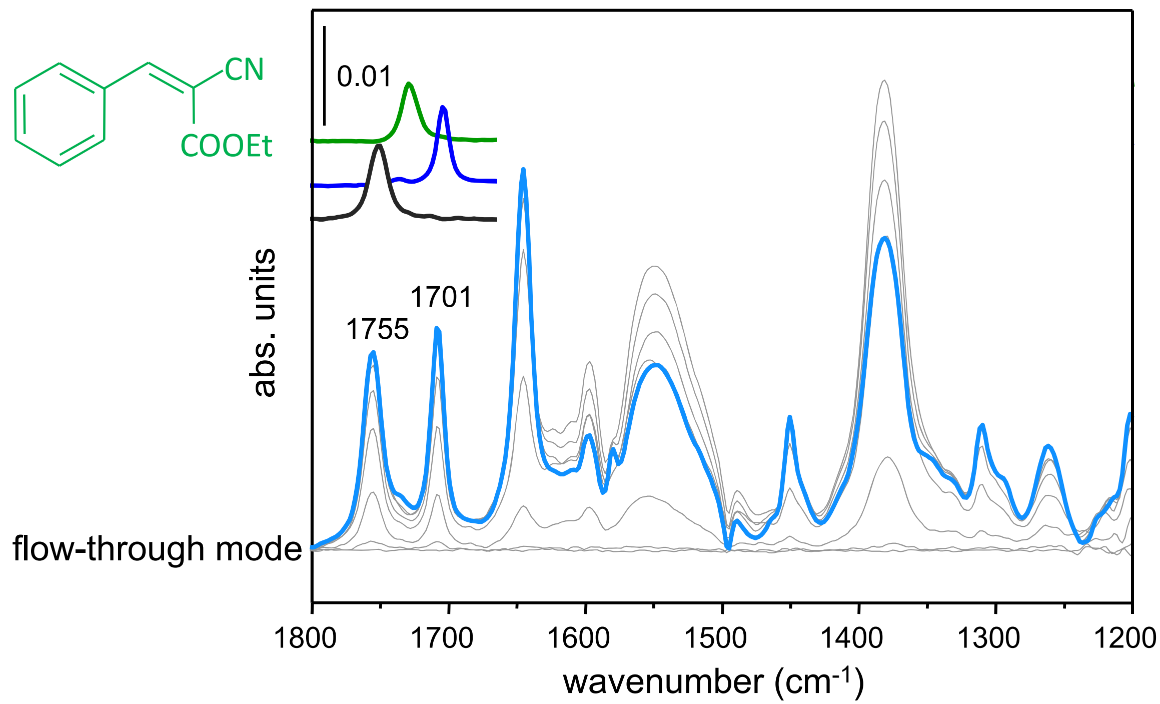
- γ-aminopropyl modified SiO_2 (APS-SiO_2)
  - 1.5 mmol/g NH_2
  - 202 m^2/g
  - deposited on ZnSe from
    - CCl_4 slurry
    - toluene/PE slurry prep. 80ºC
  - dried in *vacuum*

- toluene, 60ºC



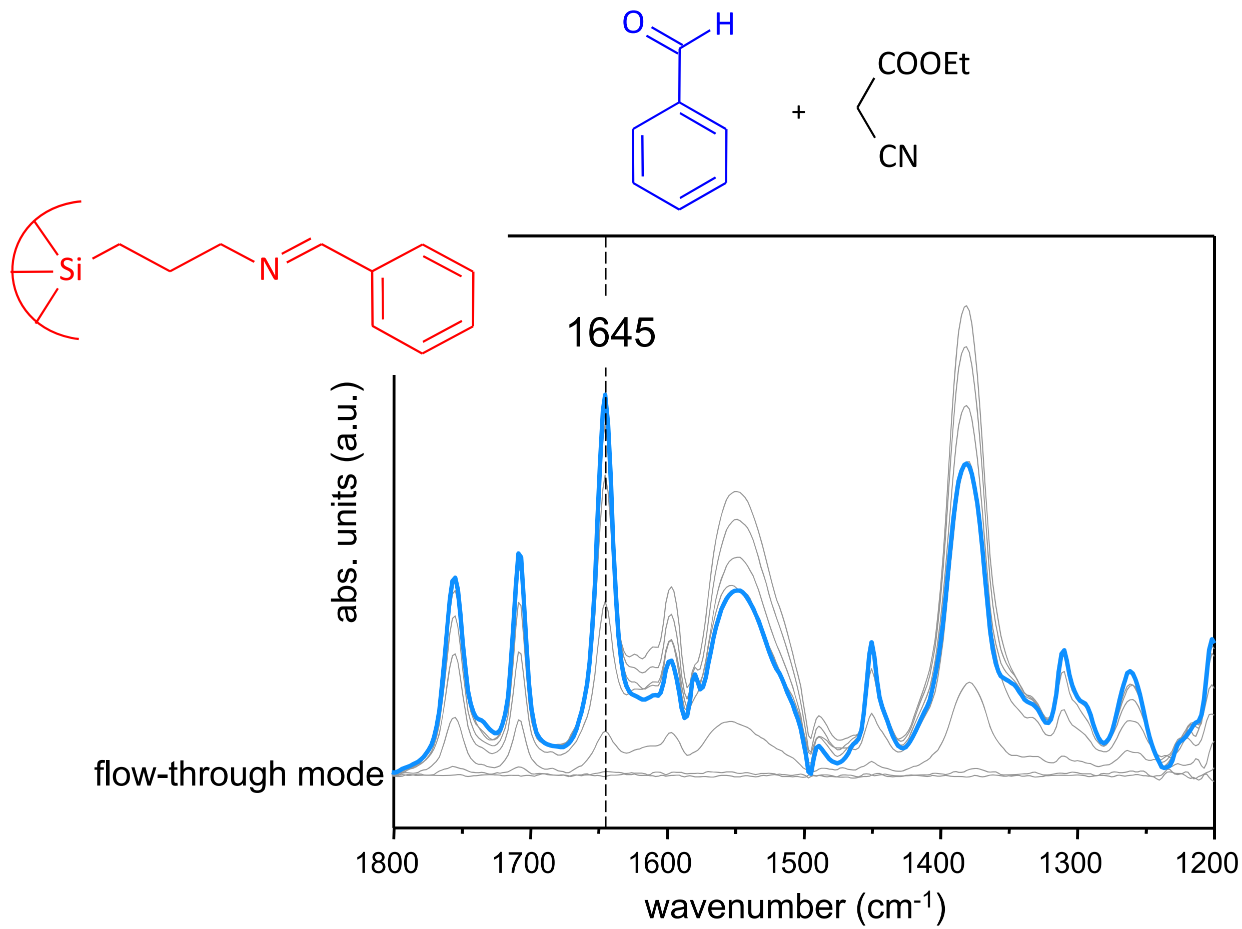
Knoevenagel condensation





toluene, 60°C, 20 mM

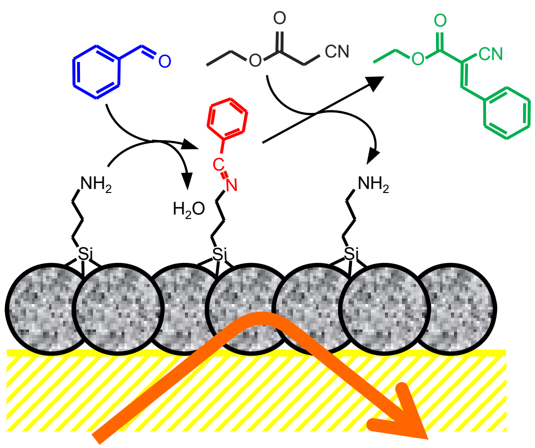
Knoevenagel condensation

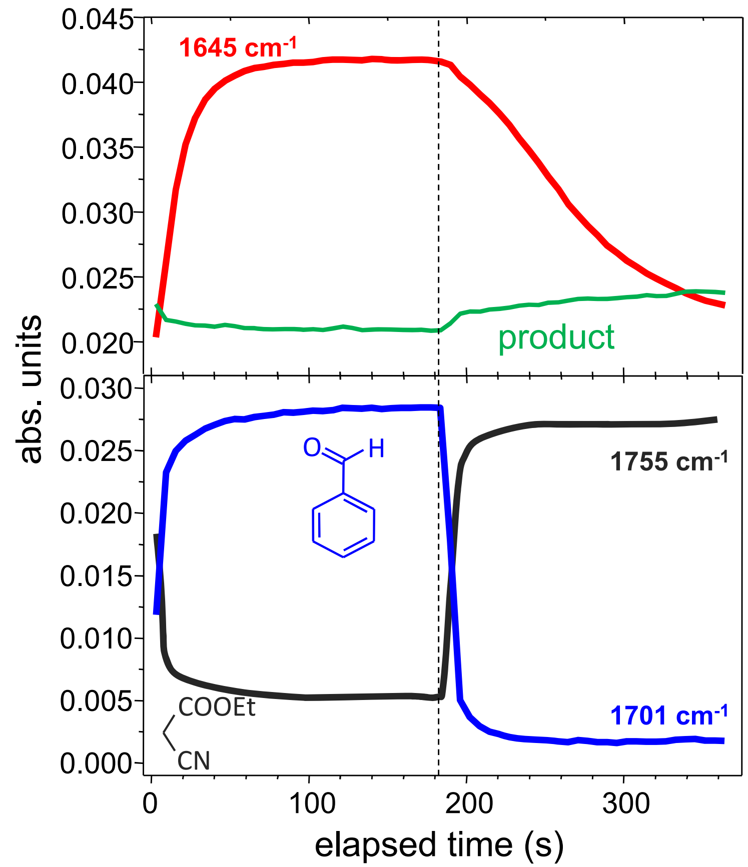


toluene, 60°C, 20 mM

Knoevenagel condensation

- Consecutive dosage of reactants
- Time dependence

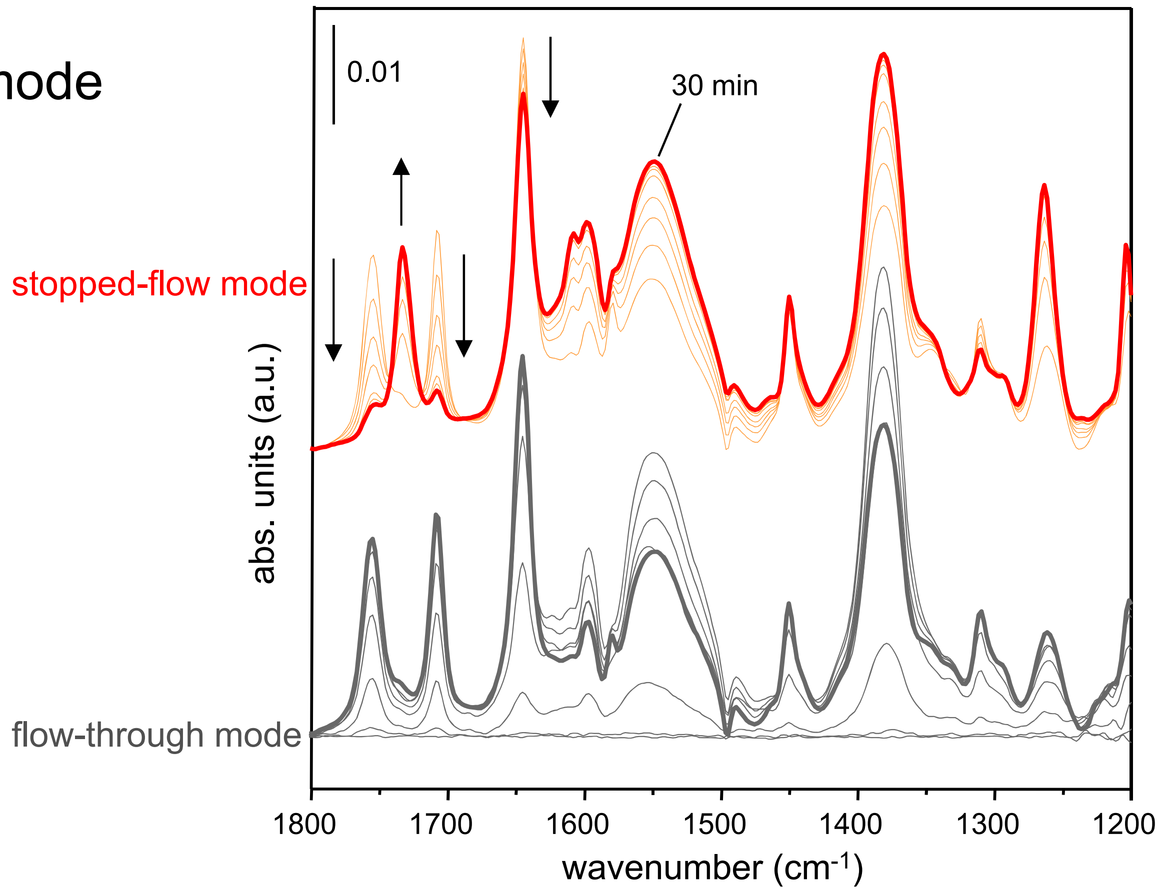




Wirz et al., Langmuir 22 (2006) 3698

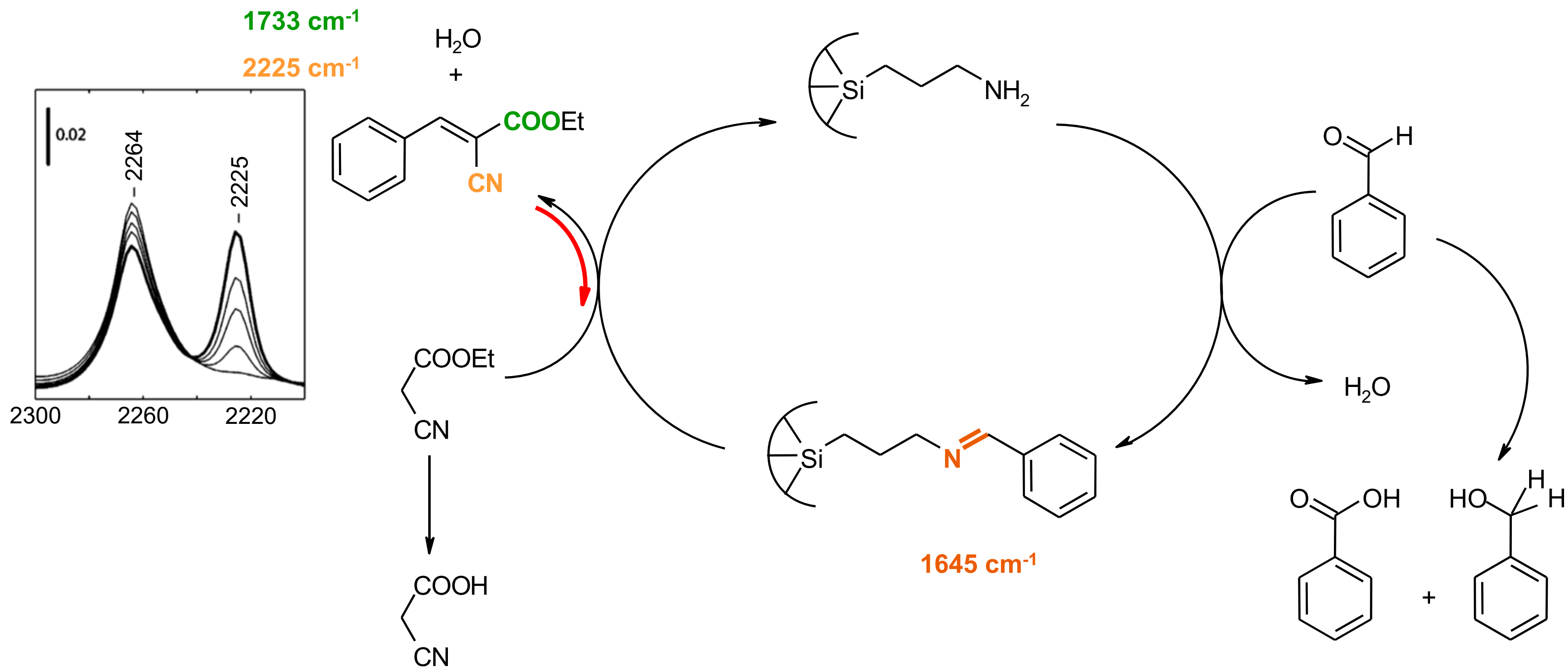
Knoevenagel condensation

- Stopped-flow mode



toluene, 60°C, 20 mM

Knoevenagel condensation



Wirz et al., Langmuir 22 (2006) 3698

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…

Adsorption sites on metals?

Acid sites?

Basic sites?

…

Acid sites

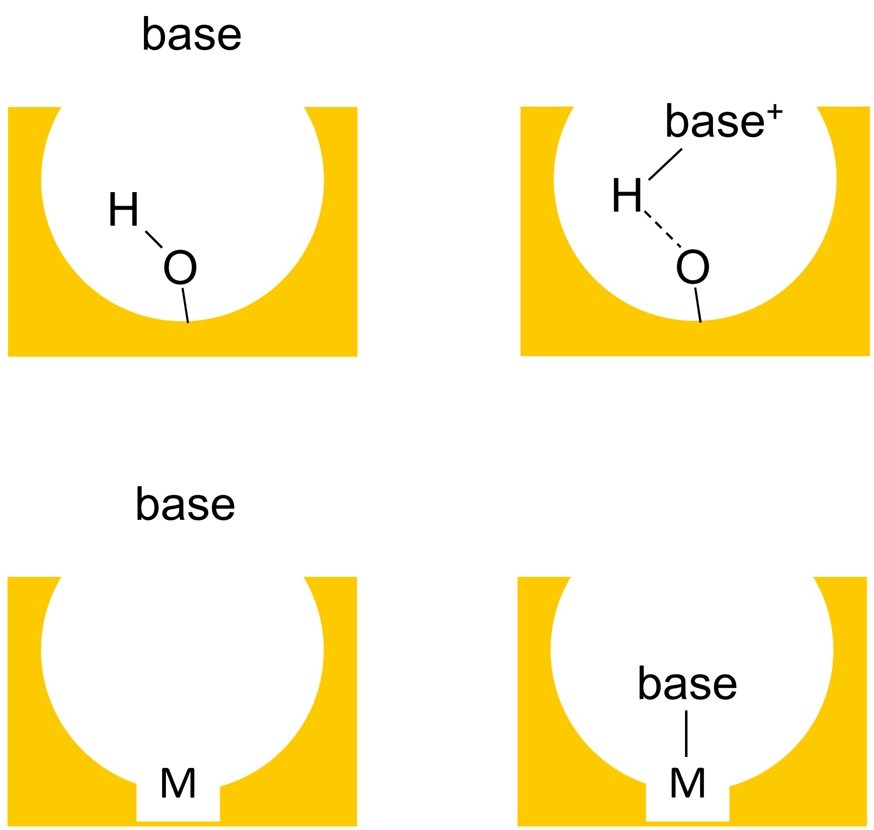
- Quality and quantity of acid sites | Criteria
  - unequivocal analysis of intermolecular interaction
  - selective interaction with acidic or basic sites
  - sufficient accuracy in frequency shift determination
  - high (and available) extinction coefficients of adsorbed probe
  - appropriate acid (base) strength to induce interaction
  - high specificity (allow discrimination between sites with different strength) - Use different molecules !
  - small molecular size - Use different molecules !
    - pyridine (smaller channels) and picoline (larger channels or surface only)
  - low reactivity under exp. conditions

- Examples
  - acidity of zeolites with different channel sizes
  - acid sites located in all channels

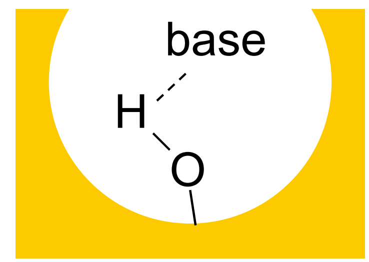
Acid sites

BAS
Brønsted sites
(protic)

LAS
Lewis sites
(aprotic)

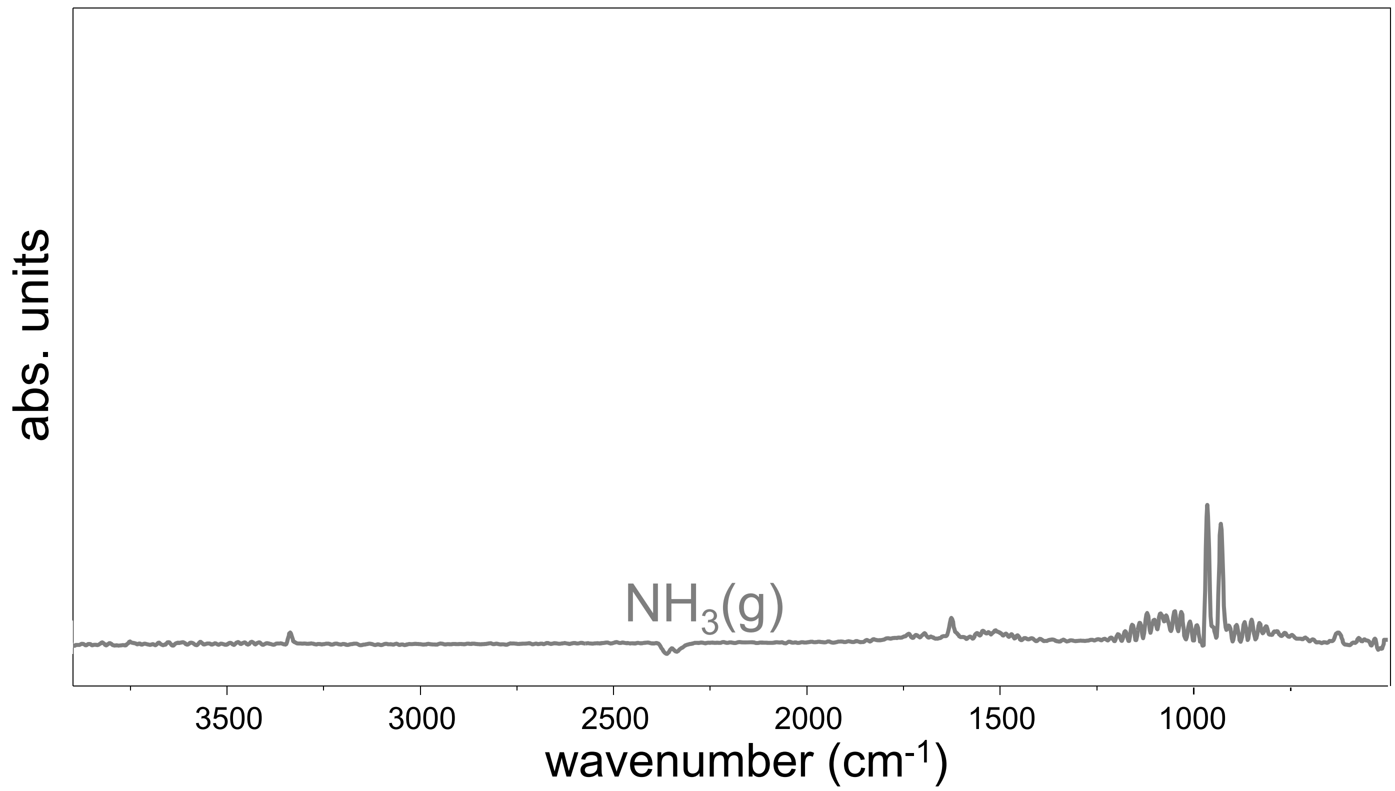


HB
hydrogen bond



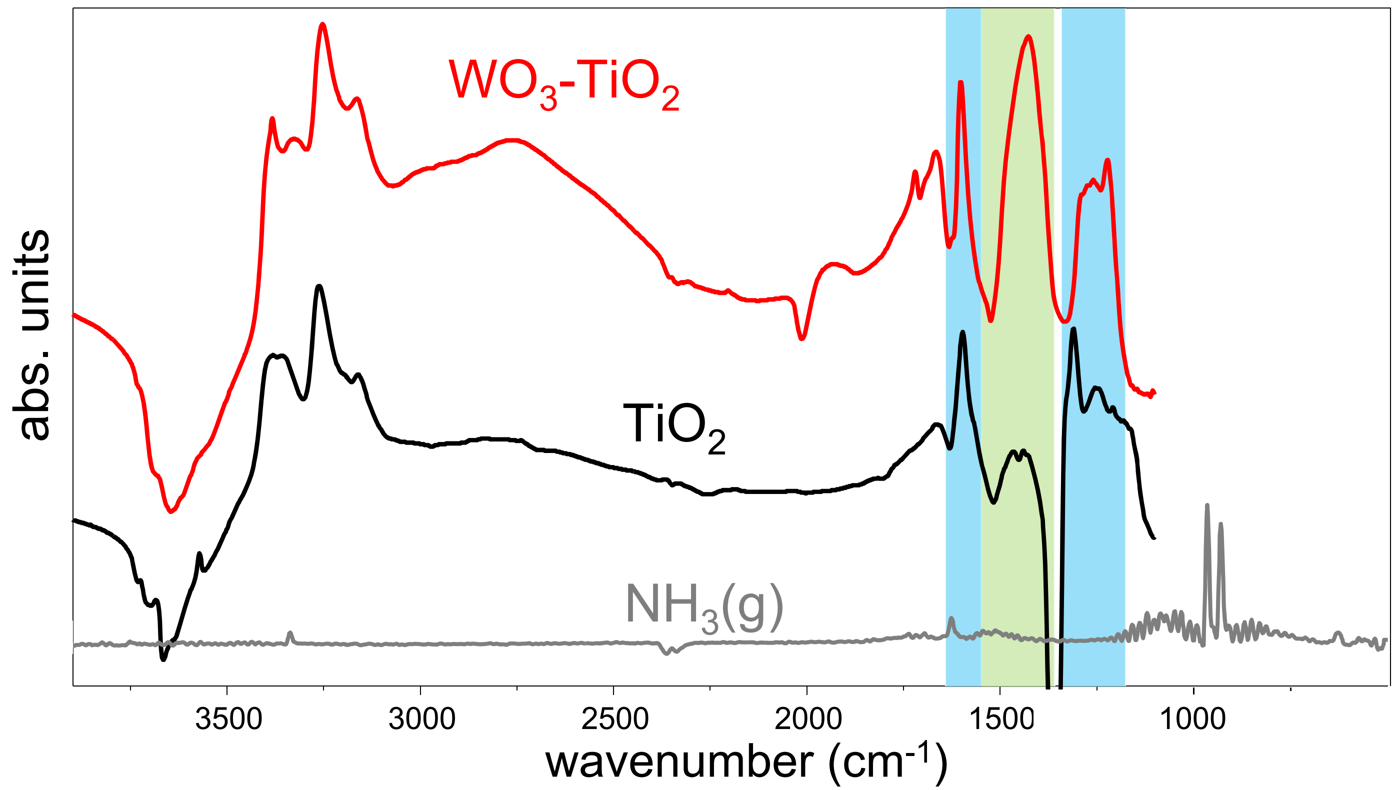
Probe molecules

- Adsorption of NH_3



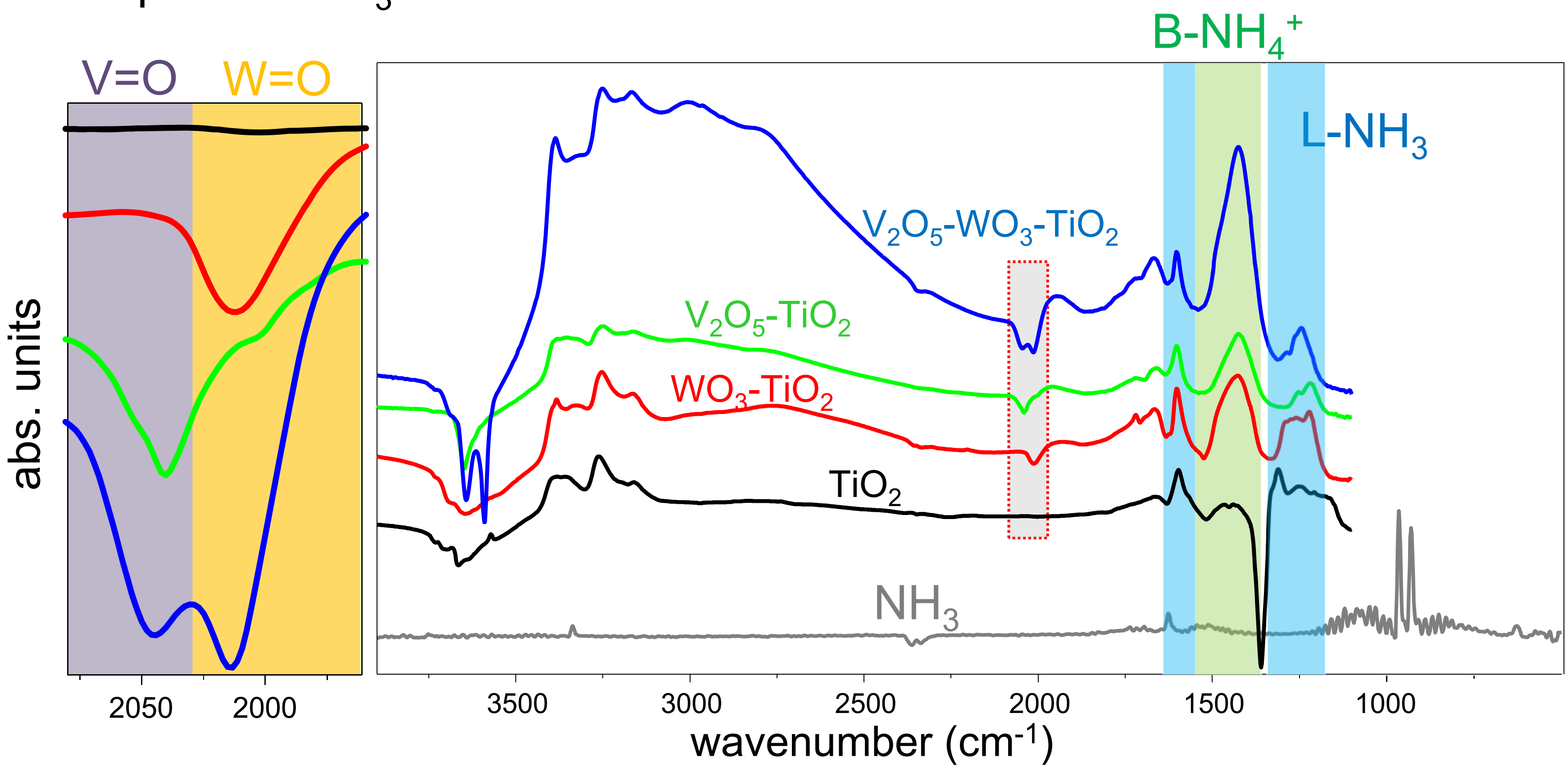
Probe molecules

- Adsorption of NH_3



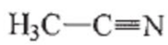
Probe molecules

- Adsorption of NH_3

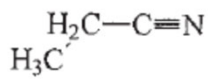


Acid sites

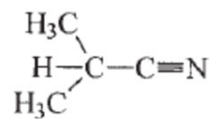
- Probe molecules for the study of localization of active sites in microporous materials



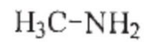
acetonitrile



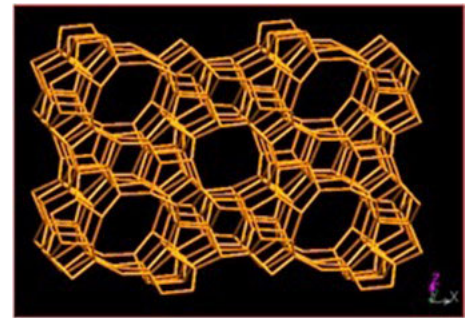
propionitrile

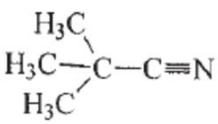


isobutyronitrile

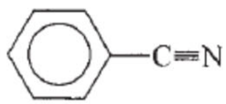


methanolamine

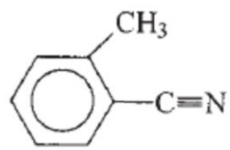




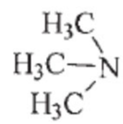
pivalonitrile



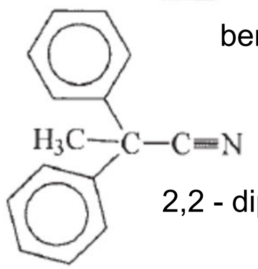
benzonitrile



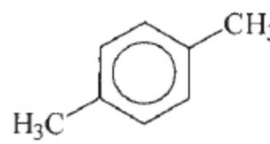
o-toluonitrile



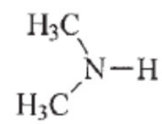
trimethylamine



2,2 - diphenylpropionitrile

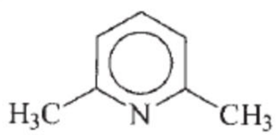


p-xylene

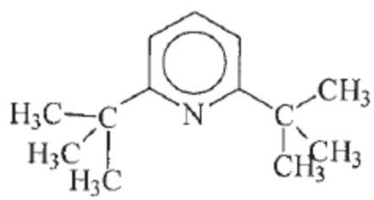


dimethyl amine

pyridine

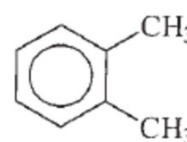


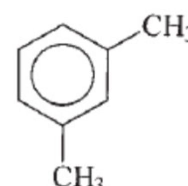
2,6-dimethyloyridine



di-tert-butyl-pyridine

o-xylene



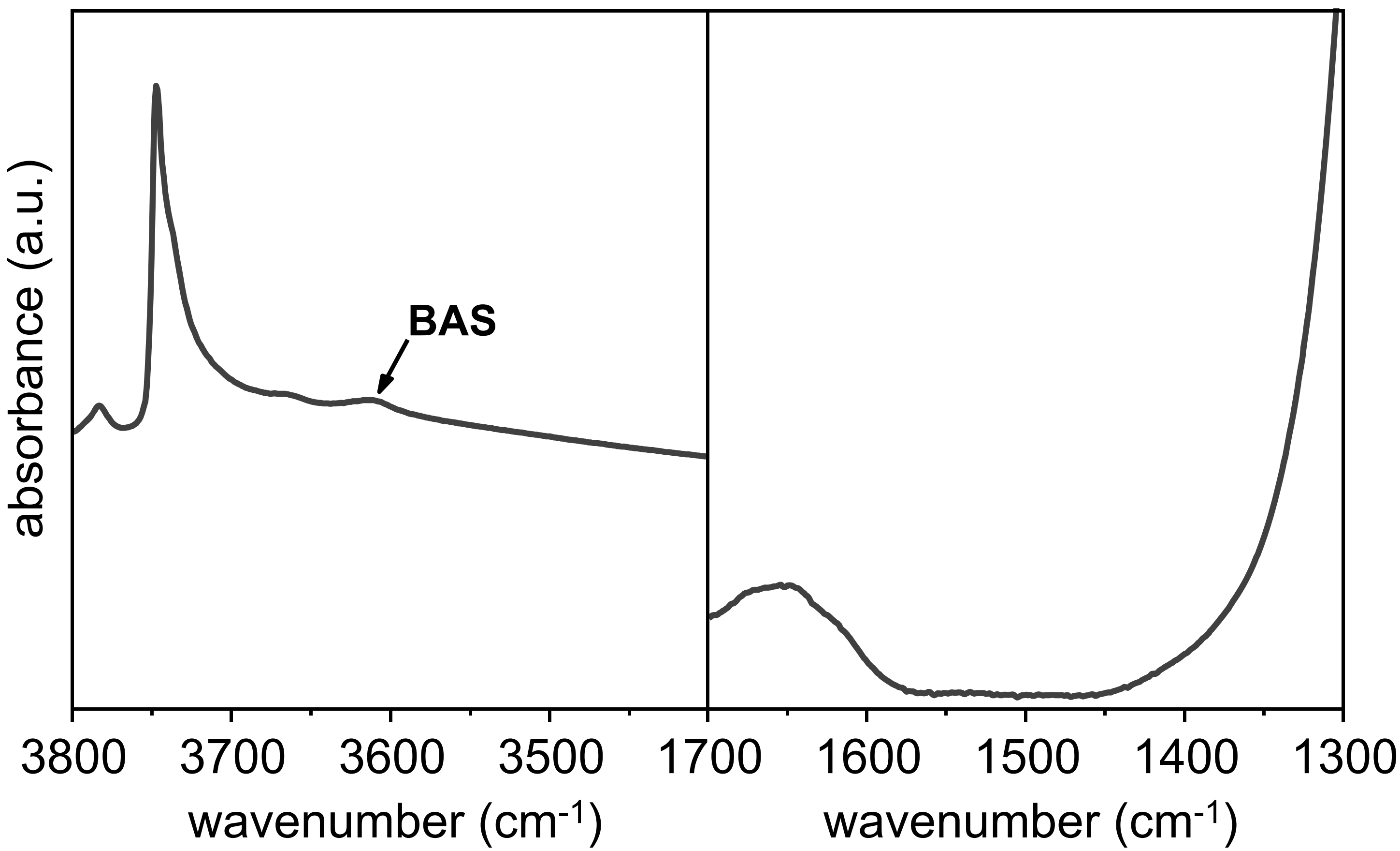


m-xylene

Busca, in Metal Oxide Catalysis, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim (2009) 95 oX

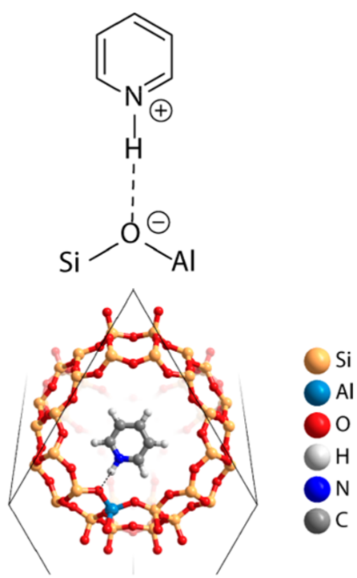
Acid sites

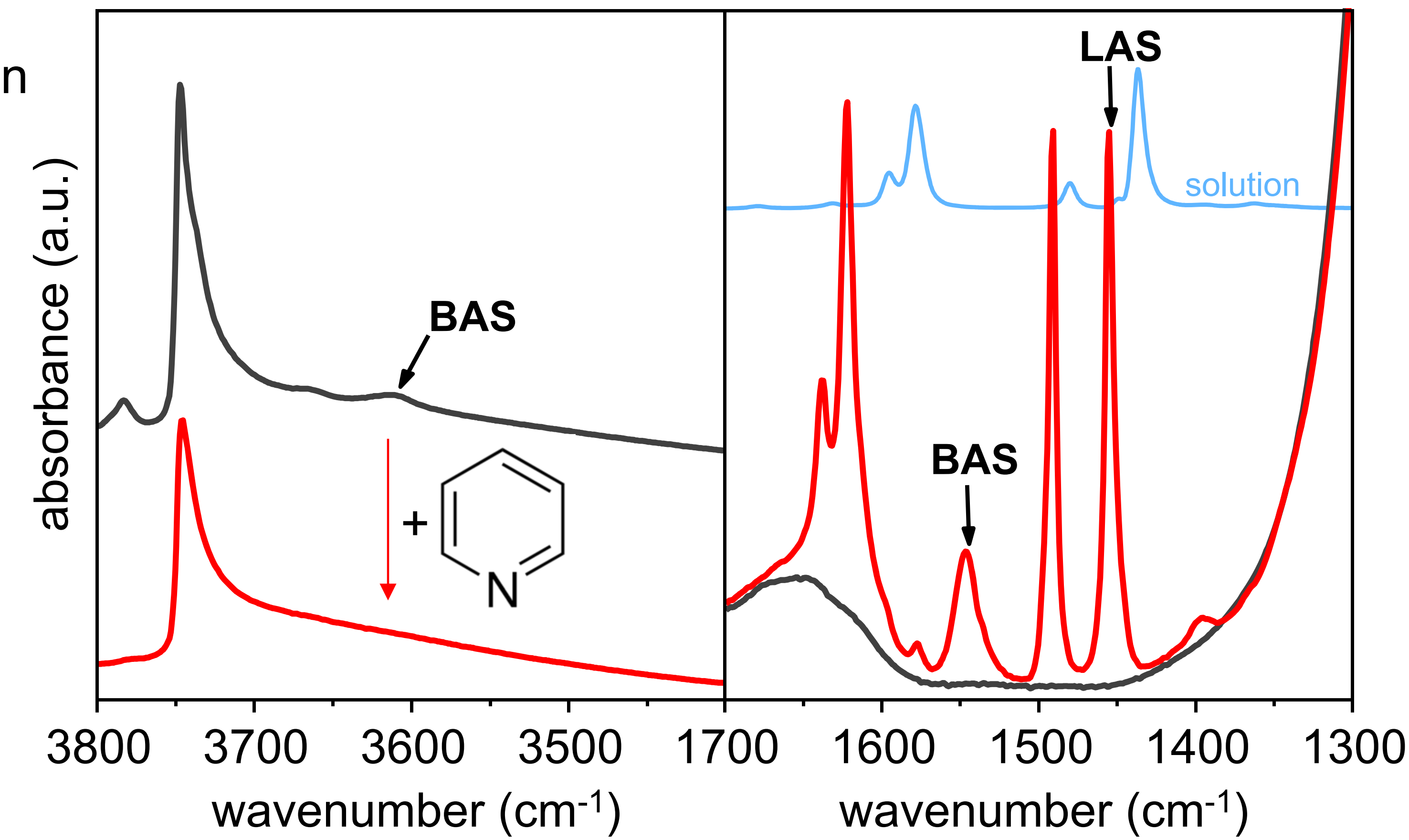
- Pyridine
  - Transmission



Acid sites

- Pyridine
  - Transmission

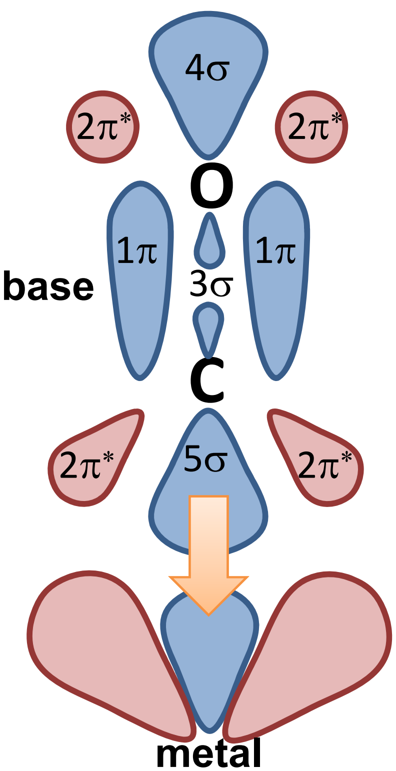




Liu et al., J. Phys. Chem. C 121 (2017) 23520

Probe molecules

- Carbon monoxide

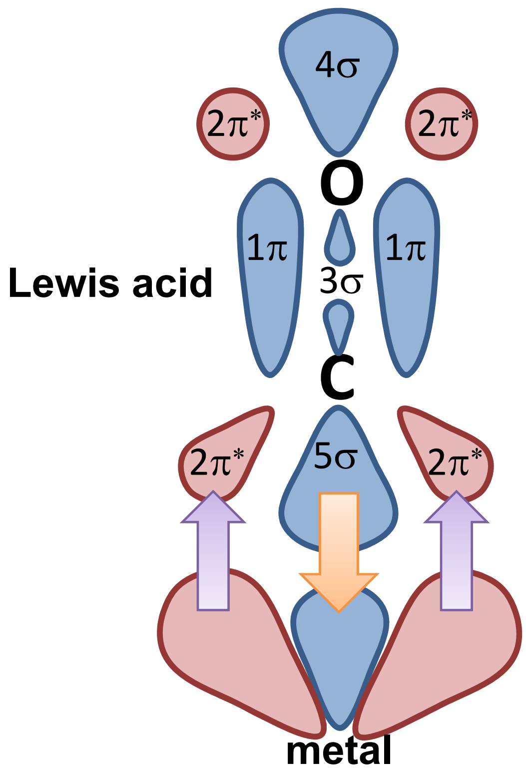


Donation

CO donates electrons from the s orbital to the metal

CO adsorption

Blyholder model



Donation

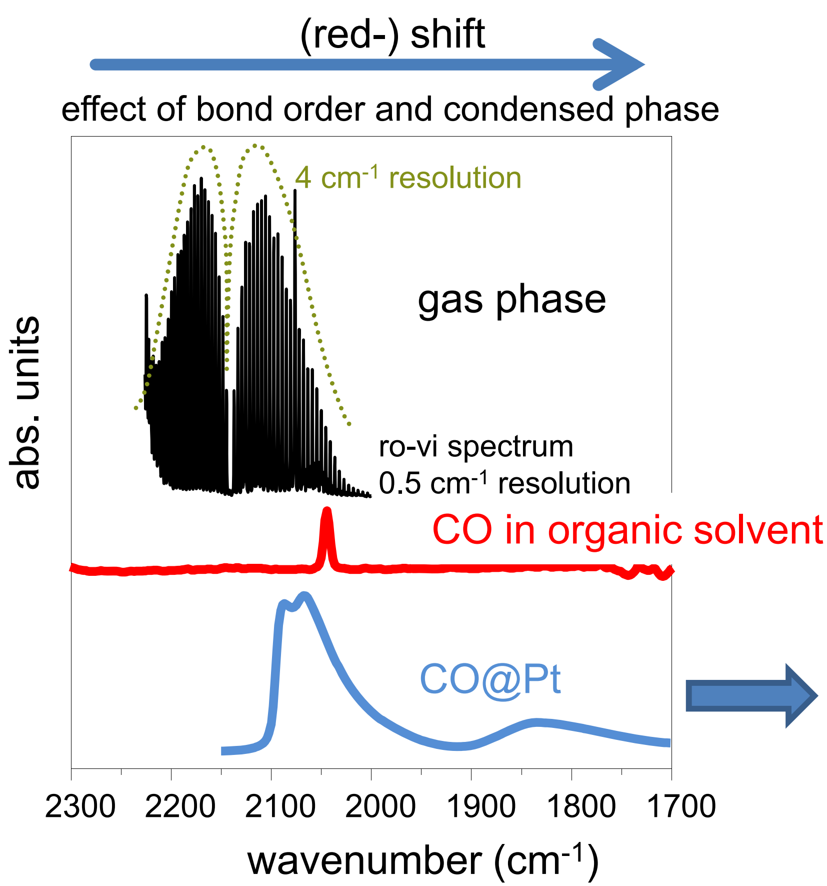
CO donates electrons from the s orbital to the metal

Back-donation (BD)

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

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

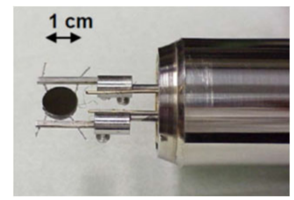
CO adsorption

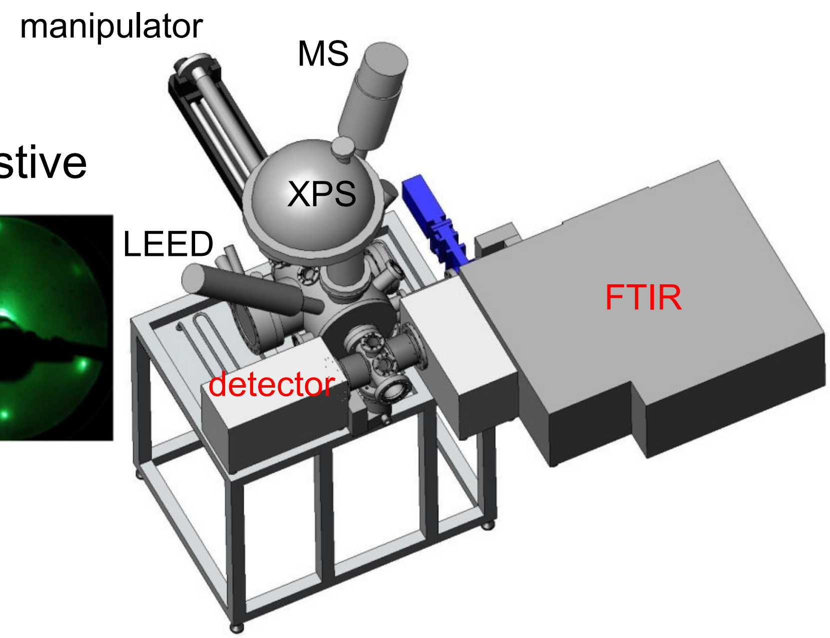


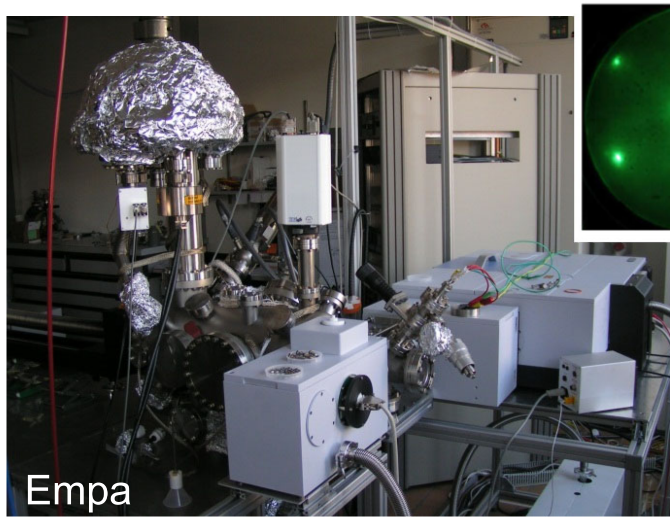
Adsorbate
assignments on powders by comparison with reference exps. in UHV (single crystals)

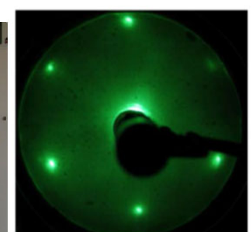
CO adsorption

- Model studies – Surface science
  - stainless steel UHV setup with flanges, pumps, pressure gauges, etc.
  - 10^{-10} to 10^{-11} mbar base pressure
  - tools and components for preparation, characterization, sample manipulation, resistive heating



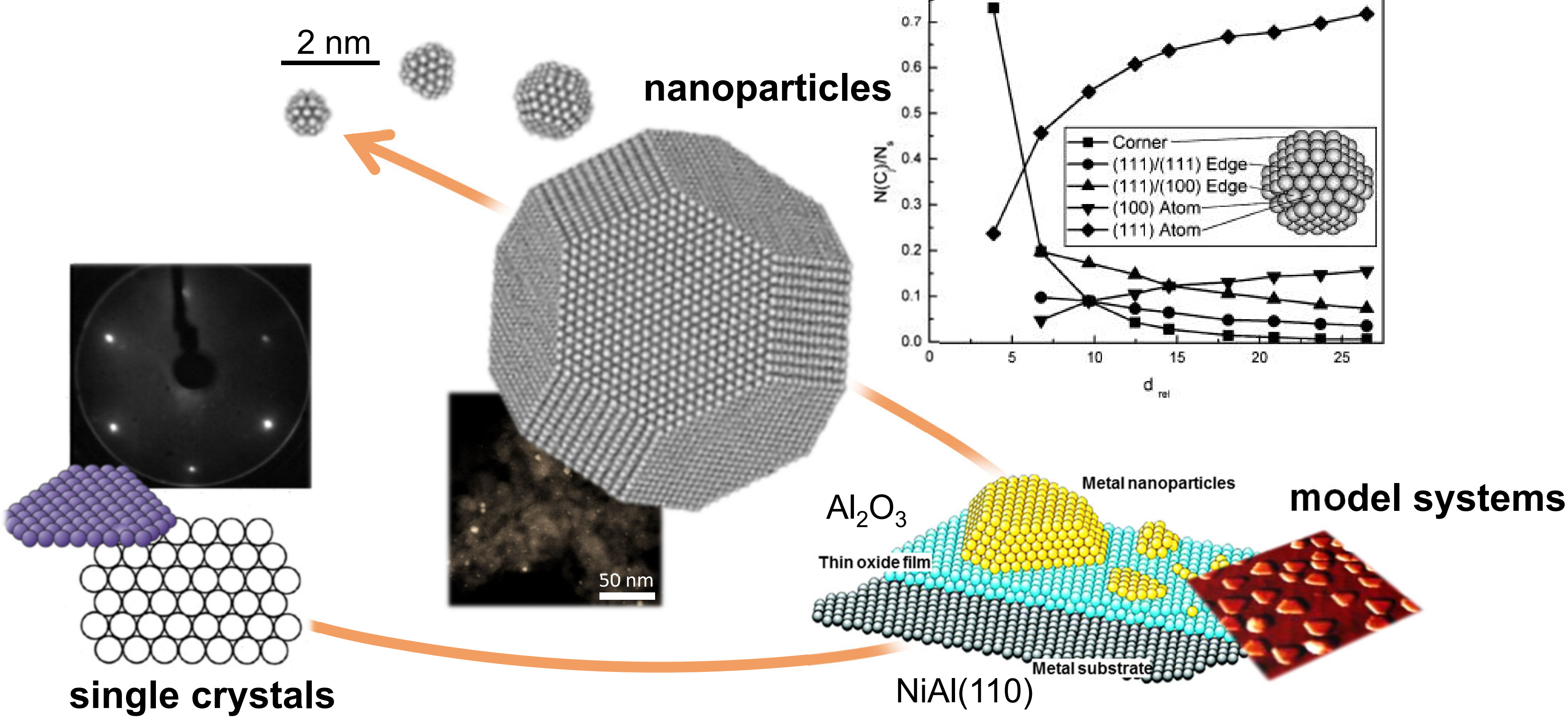






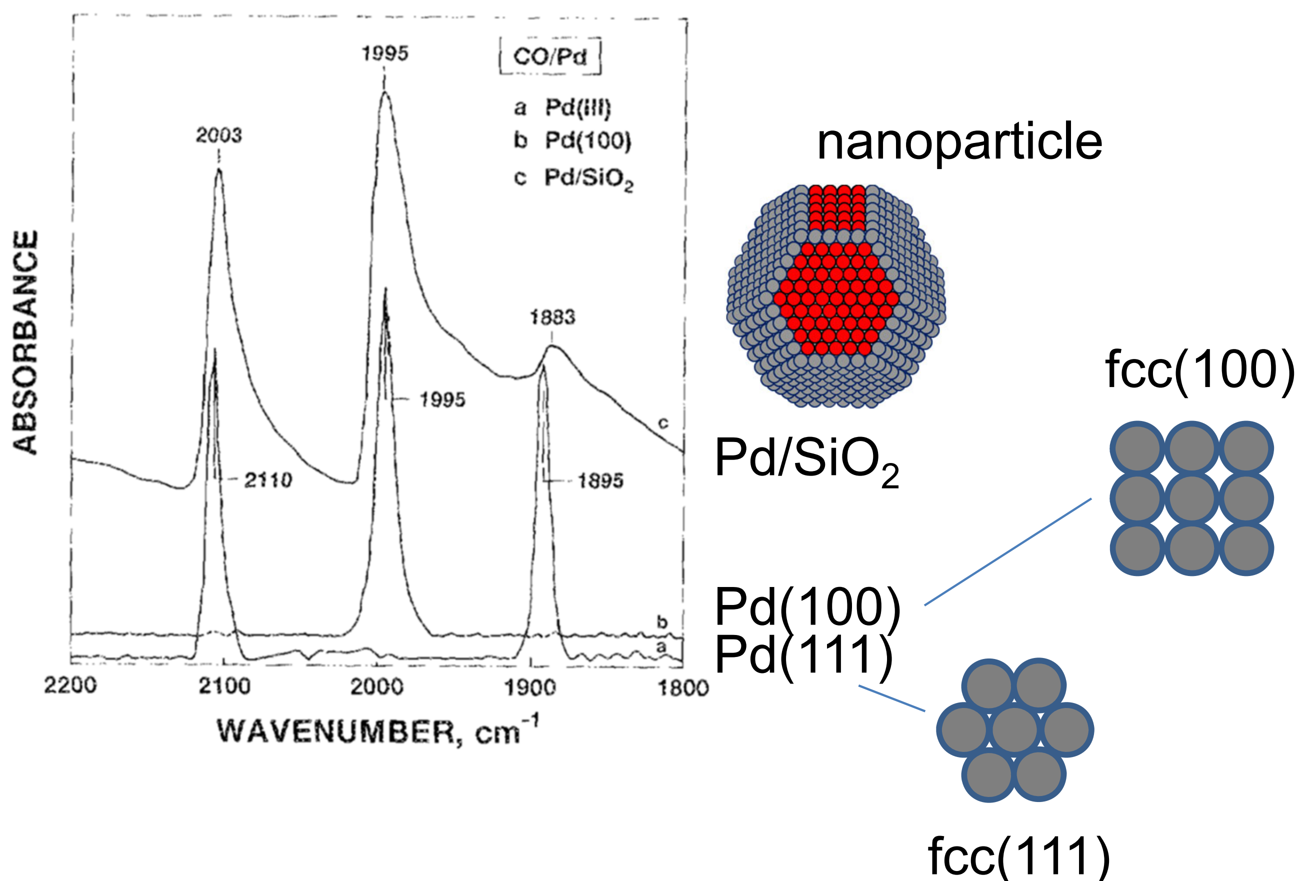
CO adsorption

- Model studies – Surface science



CO adsorption

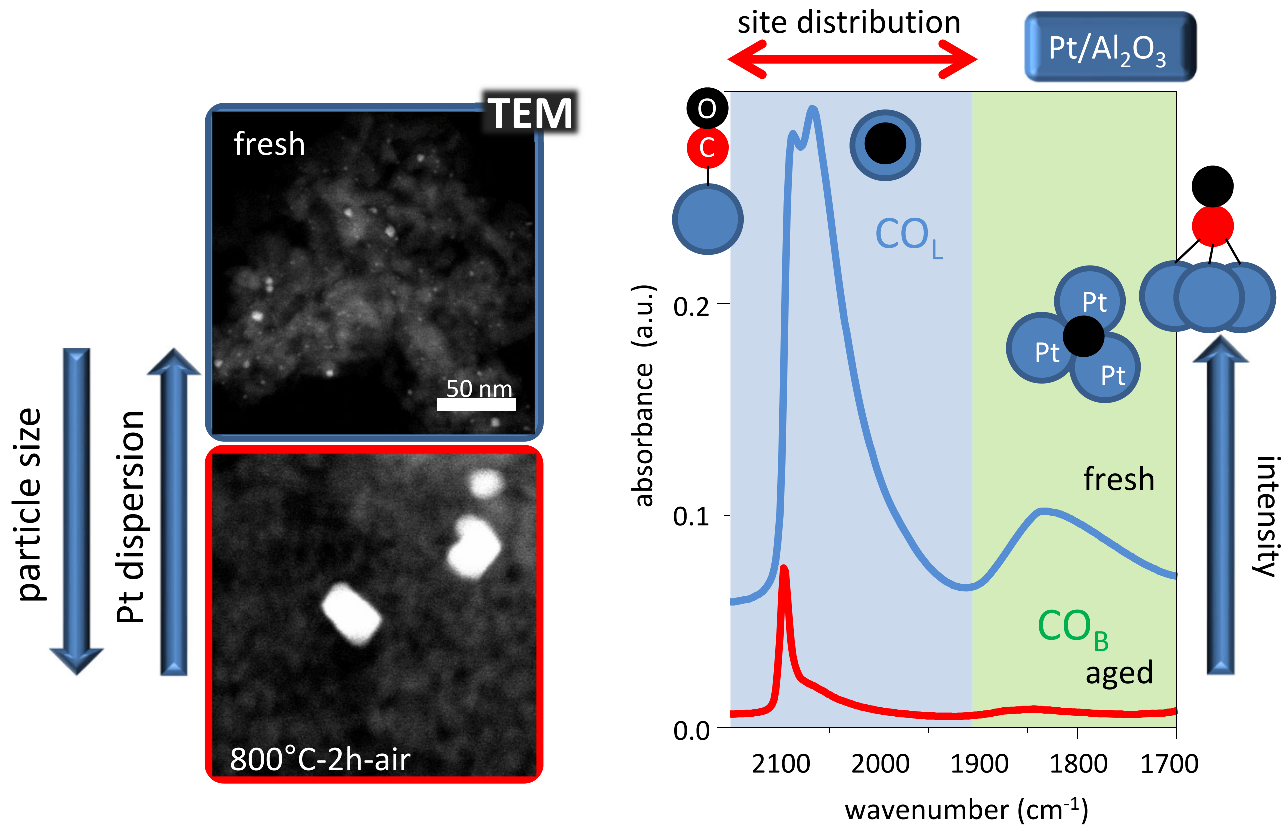
- Powders



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

CO adsorption

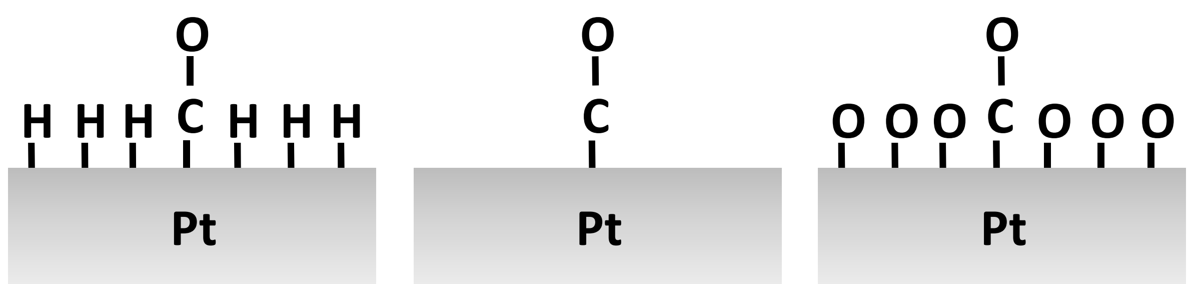
- Powders



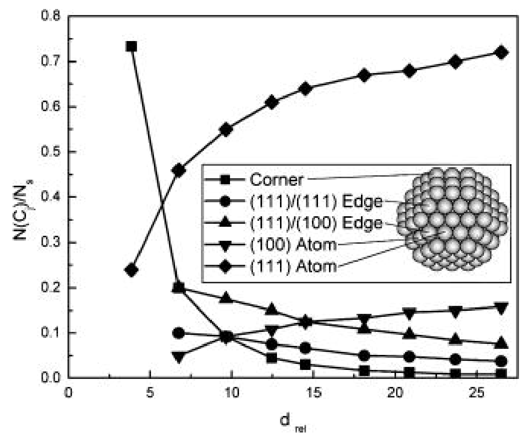
– the larger the particles, the less CO adsorbs (**intensity**)
– the larger the particles, the less the available defects (**nr. of signals**)

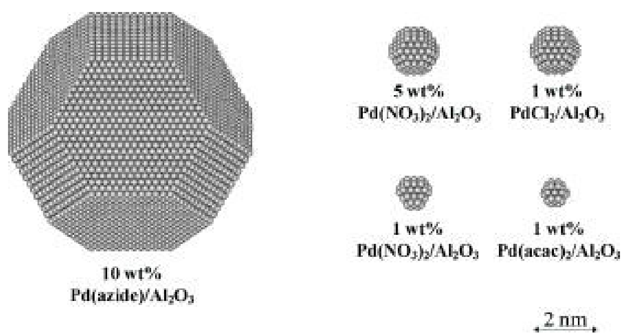
CO adsorption

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

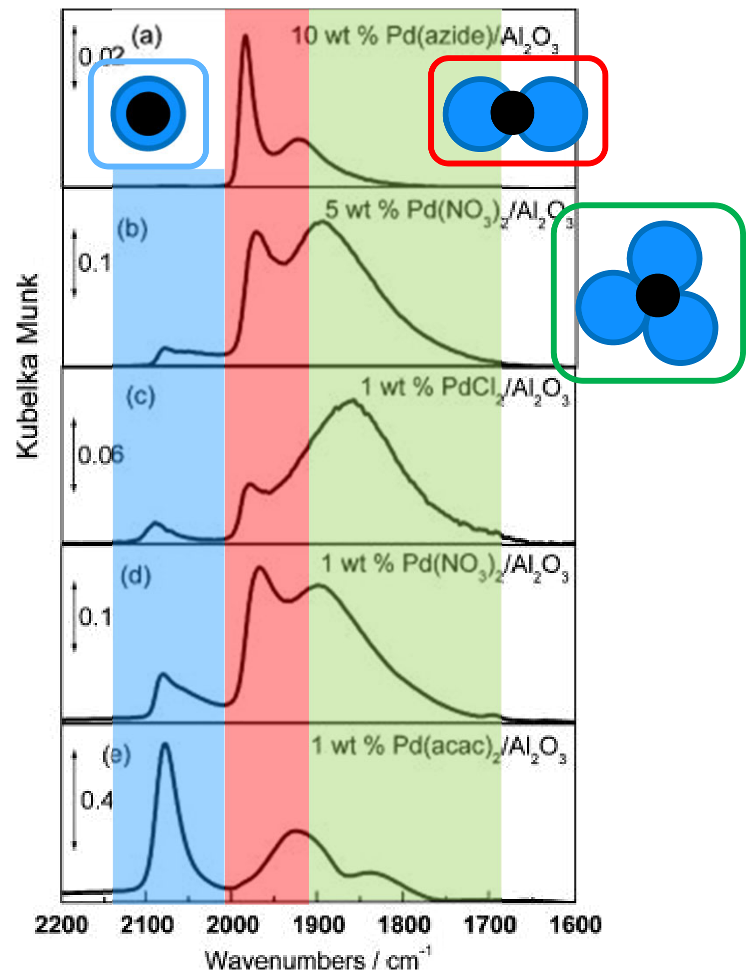


CO adsorption



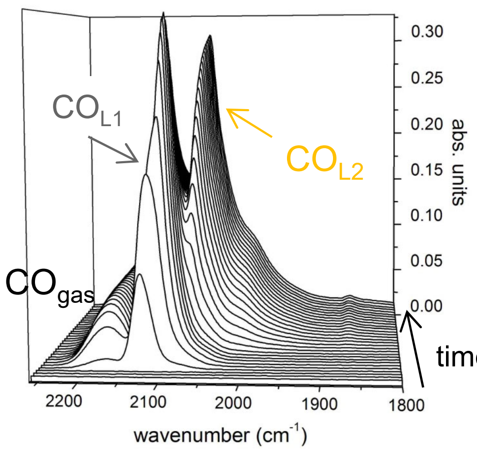


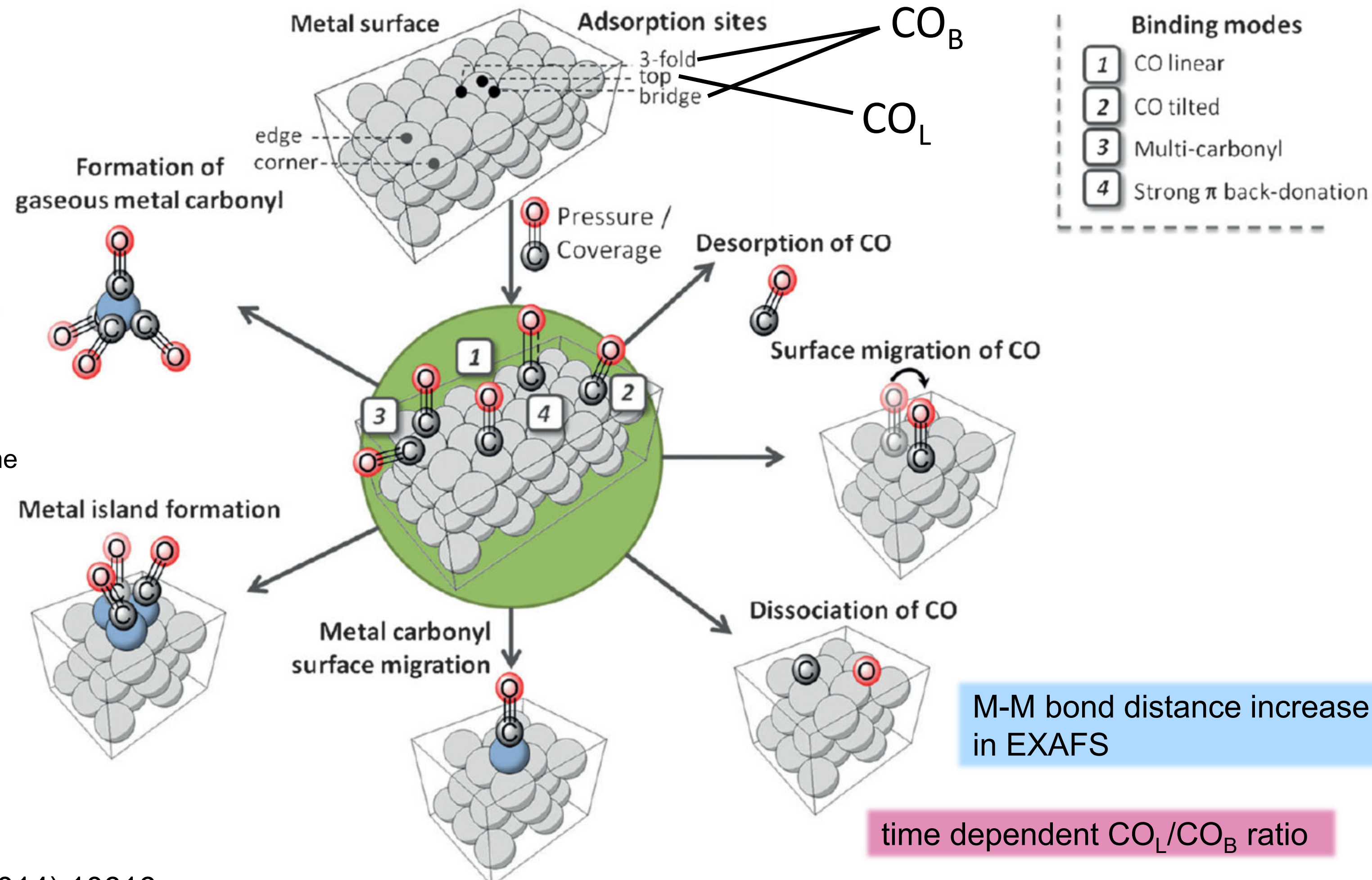
size confirmed by TEM



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

CO adsorption



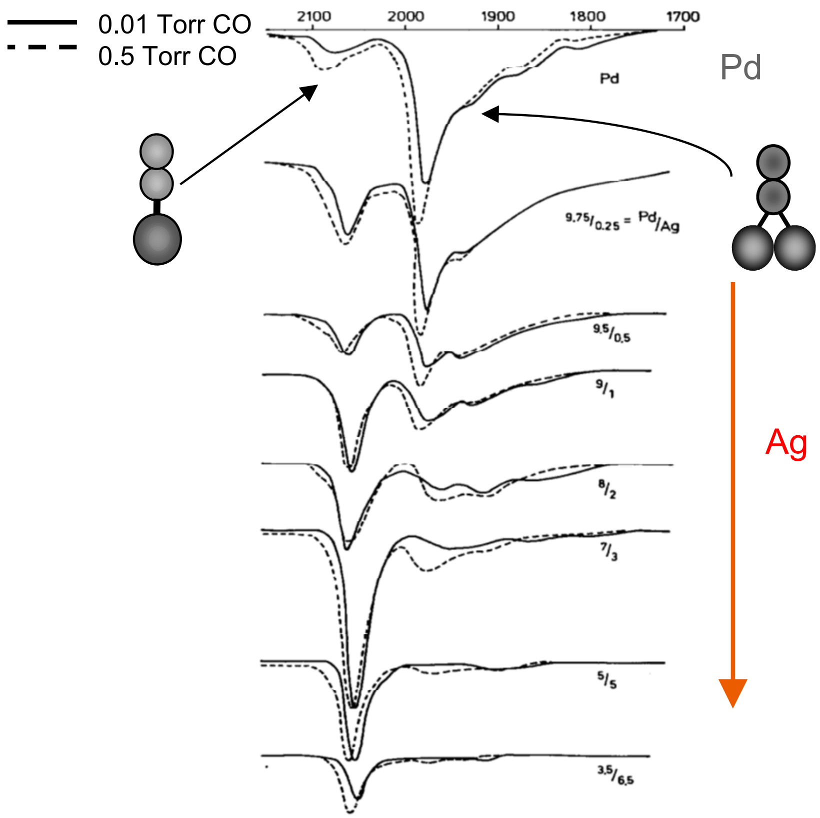


M-M bond distance increase in EXAFS

time dependent CO_L/CO_B ratio

Carenco, Chem. Eur. J. 20 (2014) 10616

CO adsorption



Pd/Ag alloy on SiO_2

Y. Soma-Noto et al., *J. Catal.* 32 (1974) 315

The surface selection rule

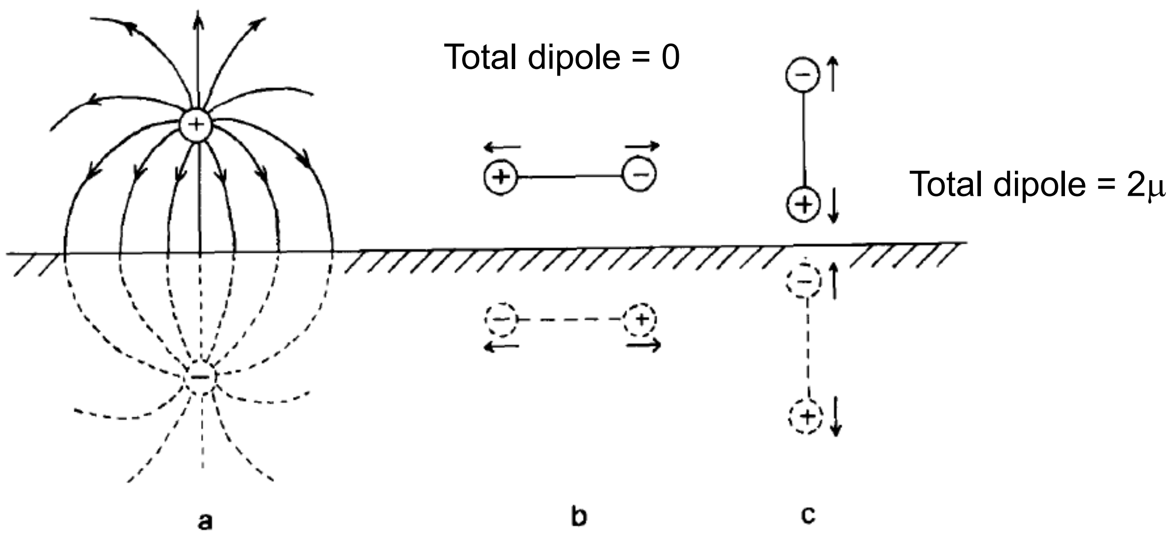
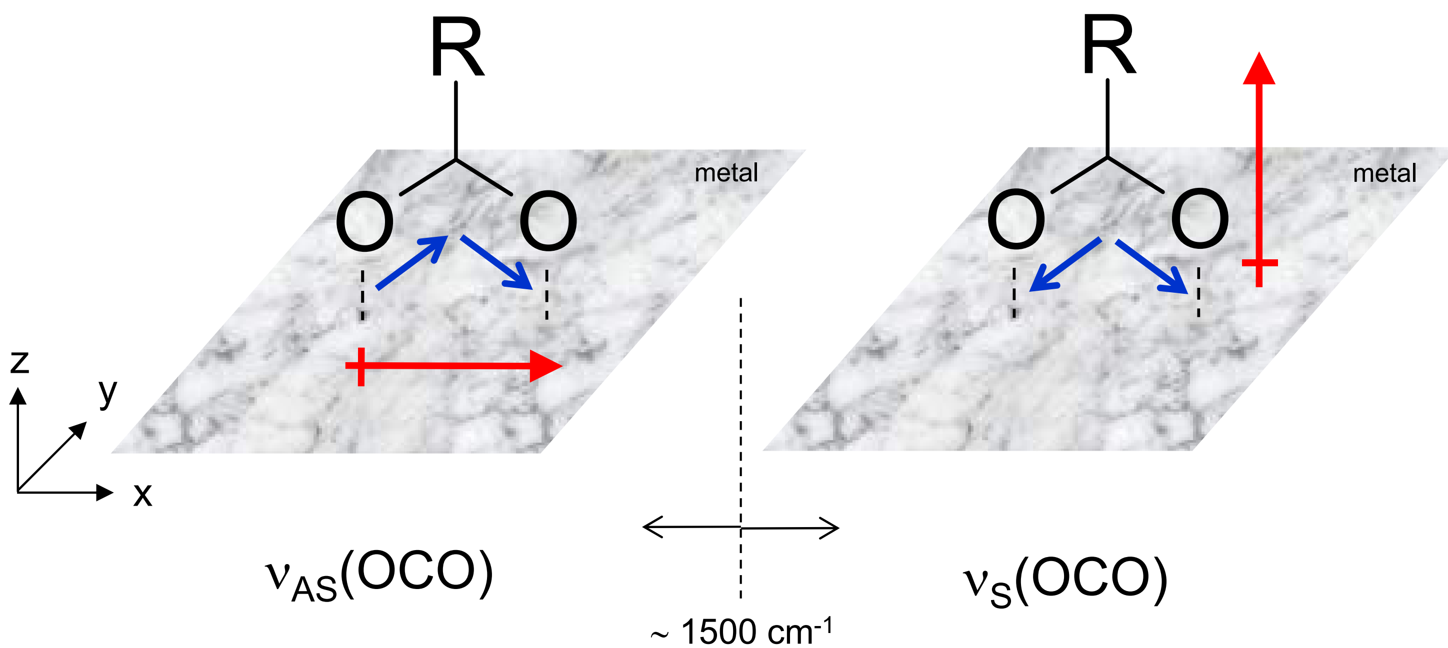


Fig. 1. (a) The lines of force and the electrical "image" resulting from a positive charge over the surface of a conductor (the metal surface is the upper line above the hatched area). (b) The changes during the vibration of a dipole parallel to the surface of the metal; the "image" dipole change is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

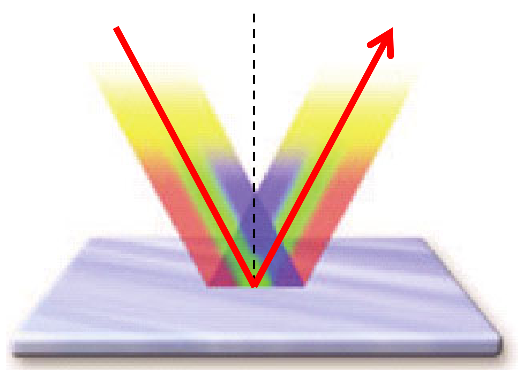


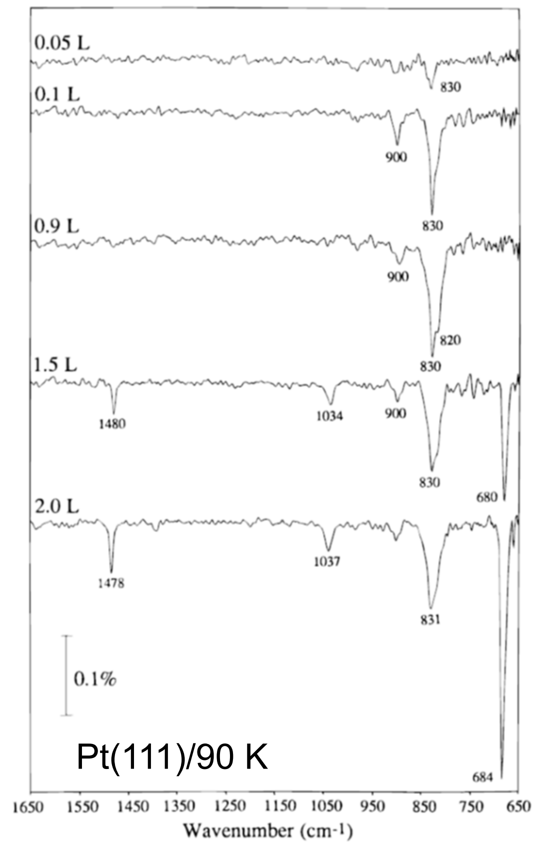
Note that the selection rule can break down for particles smaller than ca. 2 nm

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

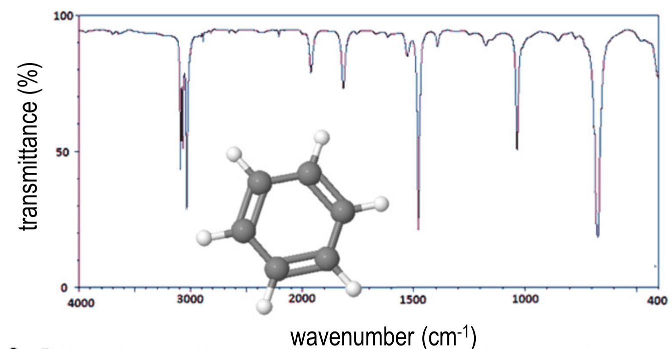
Reflection-absorption (IRRAS)

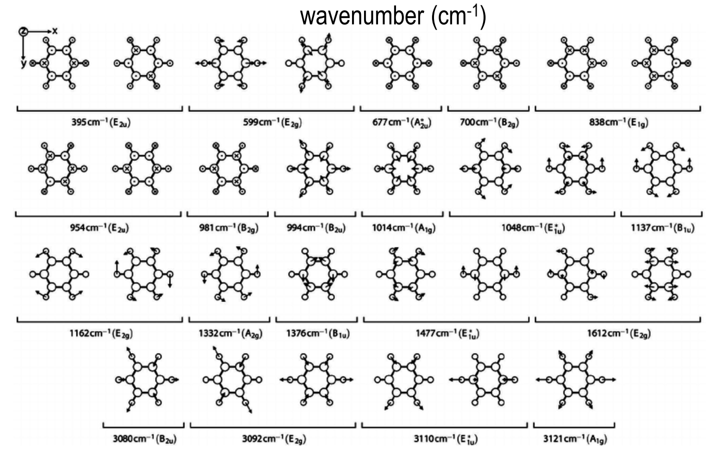
- Also RAIRS; specular/external reflection method





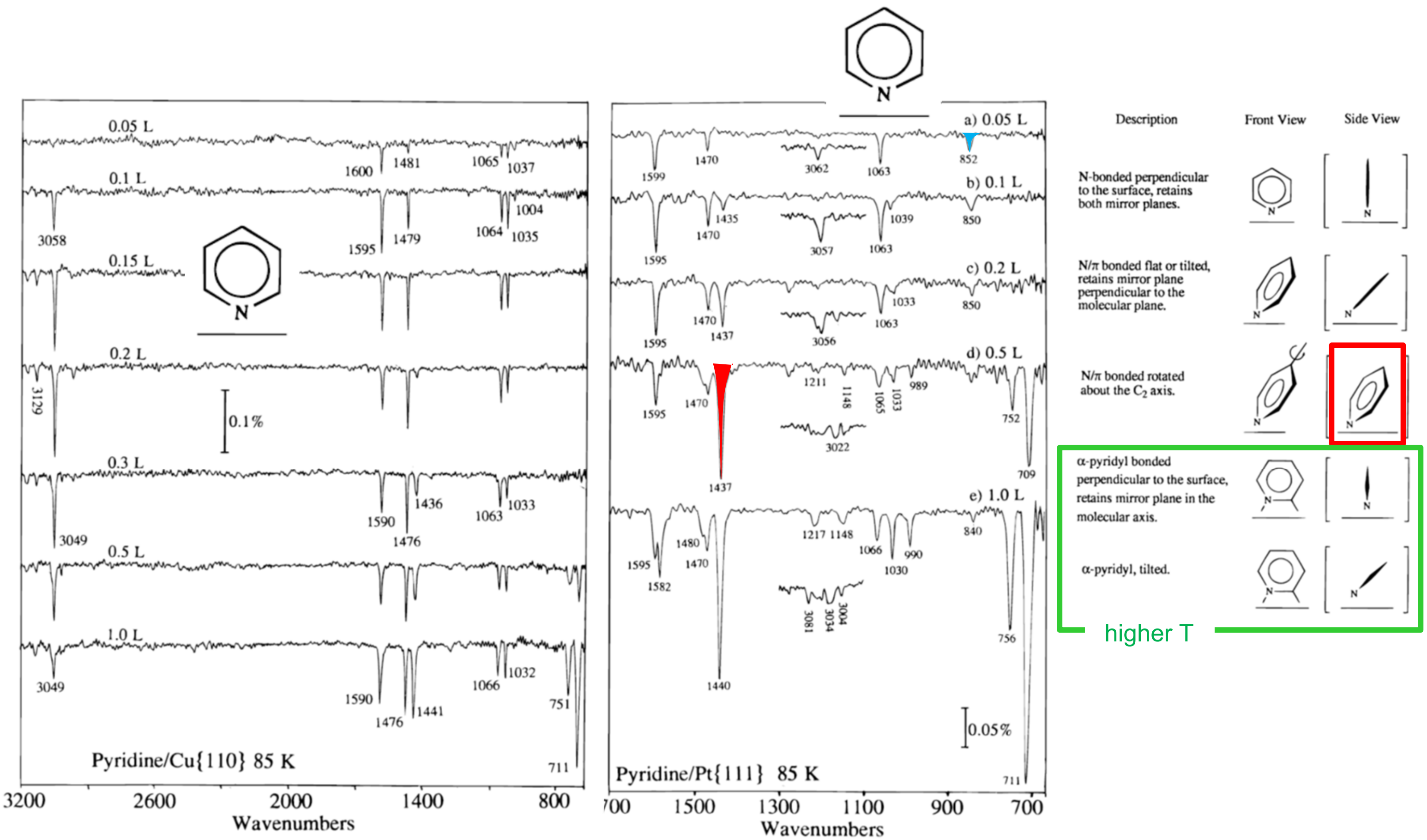
L (Langmuir)= exposure of 10^{-6} Torr gas for 1 s





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

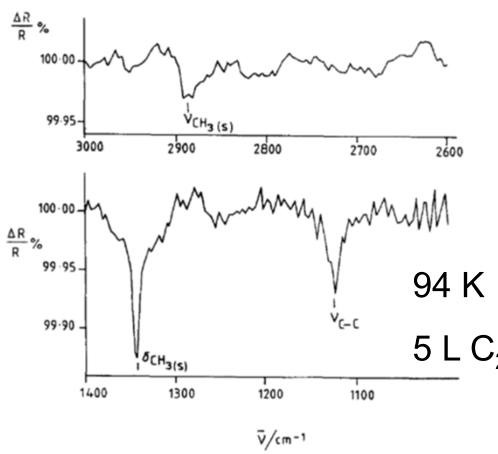
Reflection-absorption (IRRAS)



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

Reflection-absorption (IRRAS)

- Adsorption of ethylene



94 K

5 L C_2H_4

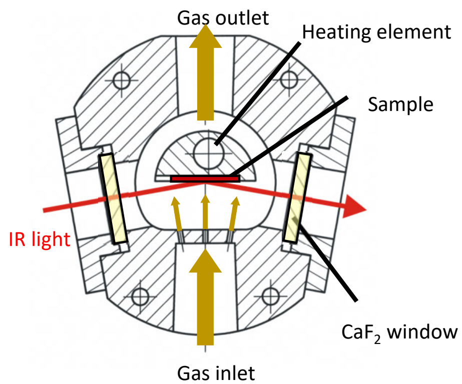
Vibrational assignments of ethylidyne

Mode	Pt(111) (cm^{-1}) FT-RAIRS [this work]	Pt(111) (cm^{-1}) 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

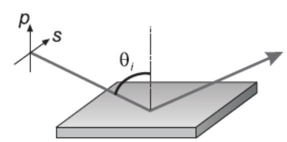
Chesters et al., *Surf. Sci.* 187 (1987) L639

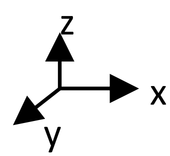
Phase-modulation IRRAS (PM-IRRAS)

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

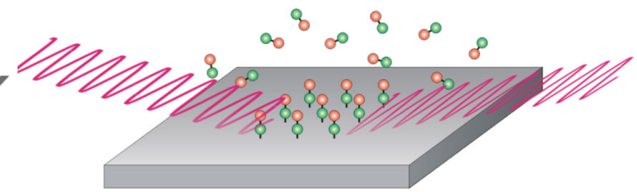


Urakawa et al., *J. Chem. Phys.* 124 (2006) 054717

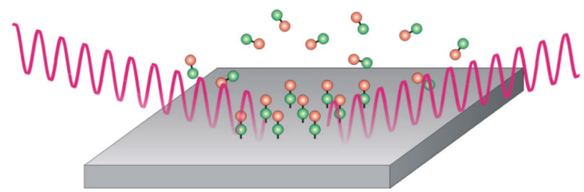




Perpendicular (*s*-) polarization (y-axis)



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



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

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

Open positions

- PhD
  - Control of N_2O emissions from NH_3 fuelled engines using selective catalytic reduction catalysts

- PhD
  - Near IR spectroscopy of urea synthesis under reaction conditions