Modern Methods in Heterogeneous Catalysis Research

Vibrational spectroscopy in catalysis

Basic principles

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LECTURE SERIES
HETEROGENEOUS CATALYSIS

Vibrational spectroscopy in catalysis

Most widely applied technique in catalysis

Accessible information

- phase composition
- surface functional groups
- adsorption sites
- surface deposites
- intermediates

Outline

1. Basic principles
2. Sample geometry – techniques in FTIR
3. Applications
   1. Lattice vibrations and surface functional groups
   2. Adsorption sites – adsorption of probe molecules
   3. In-situ spectroscopy – gas phase/liquid phase

Outline

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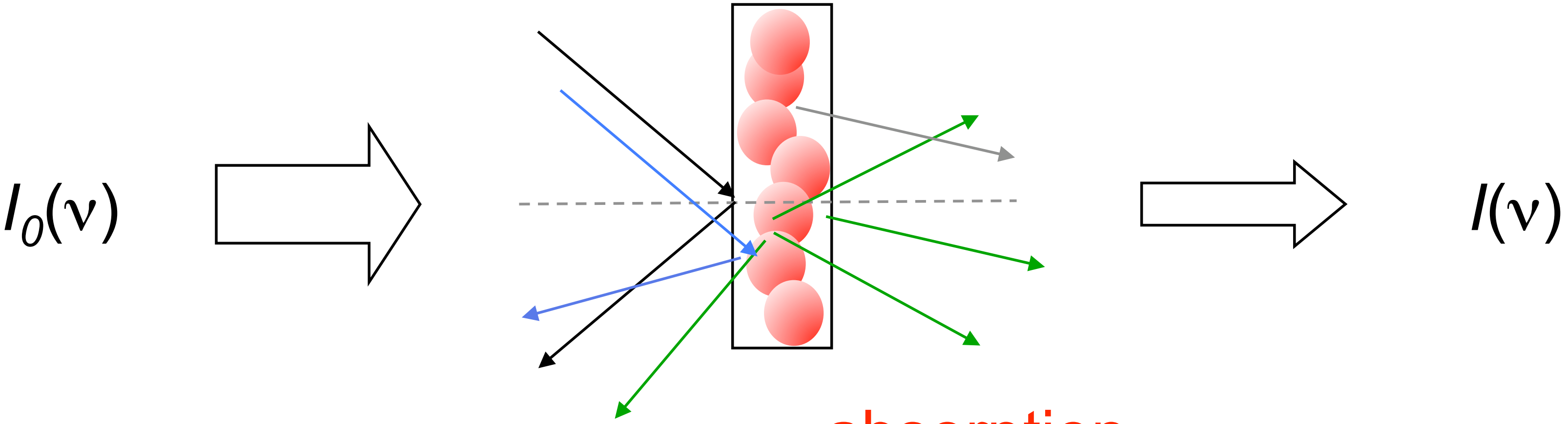
Interaction of light with solid matter

light source

powdered sample

detector



$I_0(\nu)$

$I(\nu)$

specular reflection

multiple reflection/ refraction at the particles of the solid

absorption

scattering

- elastic (Rayleigh, Mie) ν
- inelastic (Raman) $\nu \pm \nu_i$

emission ν_e

$$\boxed{I_0 = I_r + I_s + I_a + I}$$

Excitation of vibrations

Absorption of photons	Scattering		
- Infrared spectroscopy - Photoacoustic spectroscopy - Sum Frequency Generation	***photons***	***electrons***	***neutrons***
	Raman	Electron energy loss spectroscopy	Inelastic neutron scattering

Infrared spectroscopy	
Transmission	
Emission	T=473K, *in-situ* at high temperatures, measurements in regions of support absorption
Reflection	Mirror reflection Reflection-Absorption (RAIRS)
	Attenuated total reflection (ATR)
	Diffuse reflection (DRIFTS)

Origin of molecular spectra

Total energy of a molecule or ion

$$E_{\text{total}} = E_{\text{el}} + E_{\text{vib}} + E_{\text{rot}} \; (+ \, E_{\text{trans}} \text{ thermodynamics, kinetic theory of gases})$$

Discrete changes in state: Bohr‘s frequency condition for transfer of energy from an electromagnetic field to a molecule must be satisfied

$$\Delta E = h\nu \,, \; \nu = \frac{c}{\lambda}$$

$h = 6.62606896(33) \bullet 10^{-34}$ Js $= 4.13566733(10) \bullet 10^{-15}$ eVs

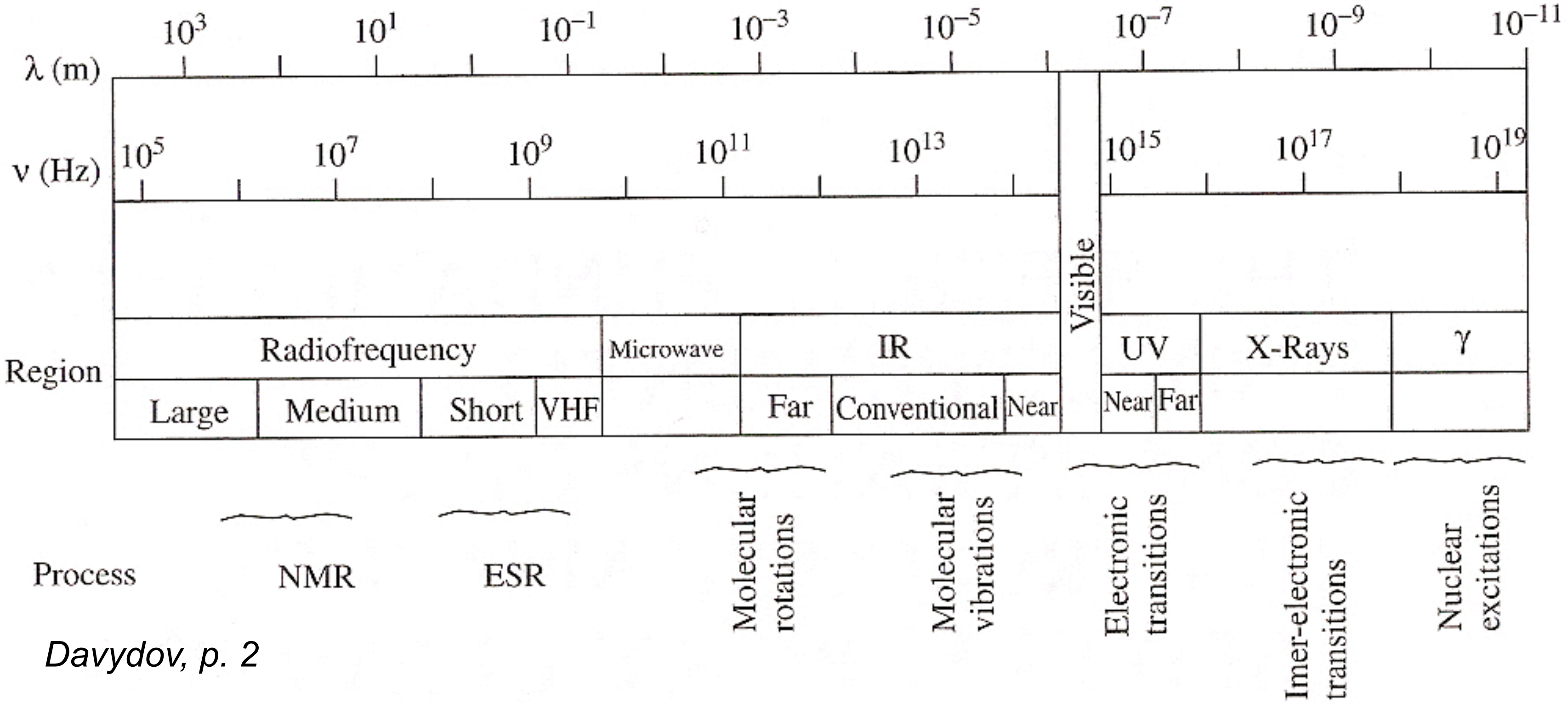
$c = 29\,979\,245\,800$ cm$\bullet$s^{-1}

Wavenumber (number of waves per cm ~ frequency shift)

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{\nu}{c} \qquad \Delta E = hc\tilde{\nu} \qquad 1 \text{ cm}^{-1} = 1.24 \times 10^{-4} \text{ eV}$$

Absorption of energy $\Delta E = E_2 - E_1$ $\tilde{\nu} = \dfrac{\Delta E}{hc}$

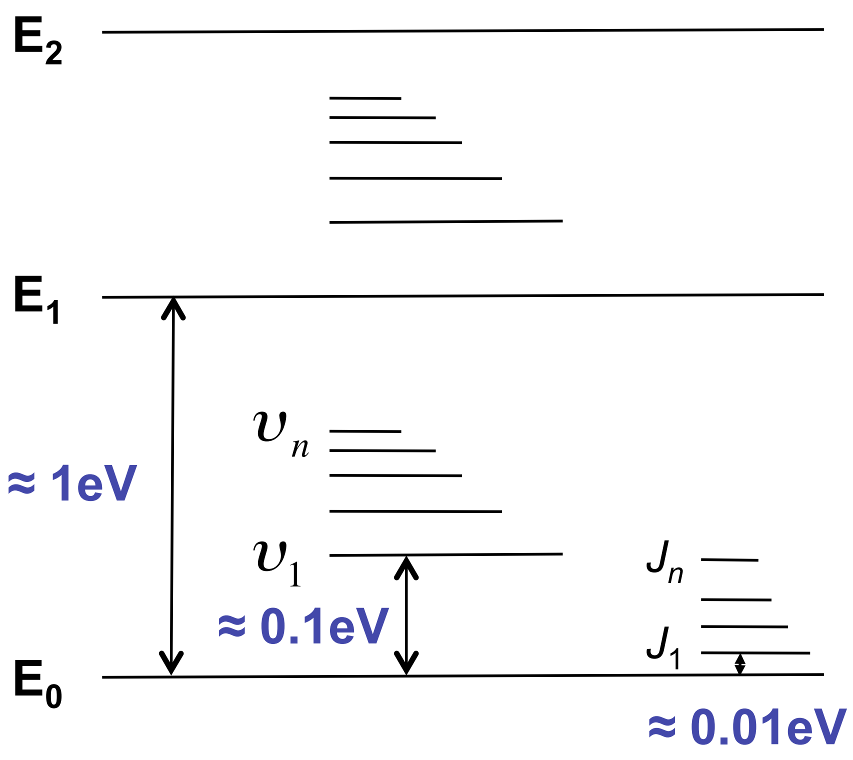
Electromagnetic spectrum



Davydov, p. 2

Infrared region	Wavelength (nm)	Wavenumber (cm^{-1})	Energy (meV)	Vibrations
far	$1x10^{6}$ - $5x10^{4}$	10-200	1.2-25	lattice
mid	$5x10^{4}$ - 2500	200-4000	25-496	molecular
near	2500 - 1000	4000-10000	496-1240	overtones

Energy levels of a diatomic molecule



Energy level diagram

Maxwell-Boltzmann distribution

$$R = \frac{P(\upsilon = 1)}{P(\upsilon = 0)} = e^{-\Delta E_\upsilon / kT}$$

$$\Delta E \geq kT$$

k = 1,3806504(24) · 10^{-23} J/K
= 8,617343(15) · 10^{-5} eV/K

kT = 208 cm^{-1} at 293 K

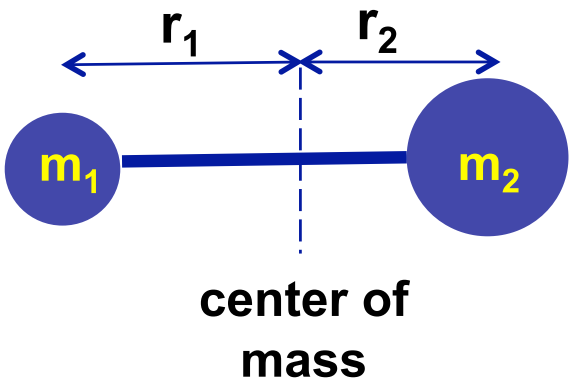
Normally, only the transitions from $\upsilon = 0$ to $\upsilon = 1$ are observed

H_2(4160 cm^{-1}): R = 2.16 10^{-9}

If ΔE_υ becomes small, the population at $\upsilon = 1$ increases:

J_2(213 cm^{-1}): R = 0.27

Vibration of a diatomic molecule – harmonic oscillator



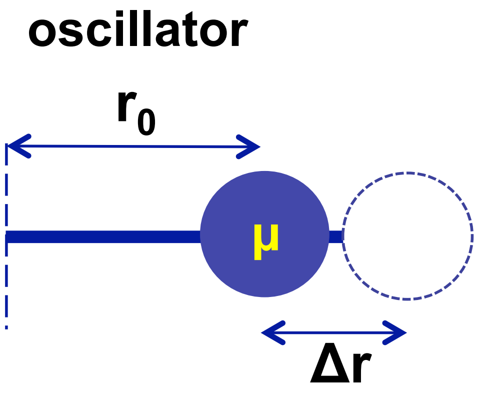
Classical mechanics

$$F = -K\Delta r = \mu a = \mu \frac{d^2 r}{dt^2}$$

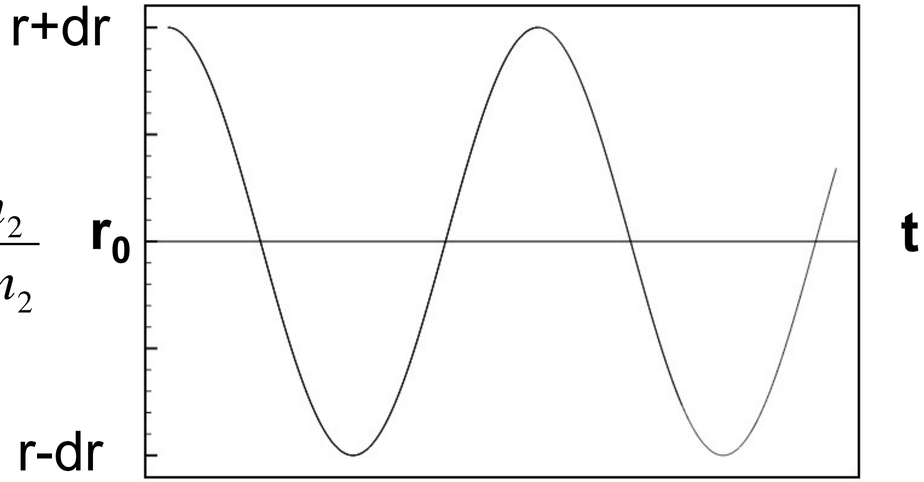
Solution of differential equation:

$$r(t) = r_0 \cos(2\pi \nu t)$$

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



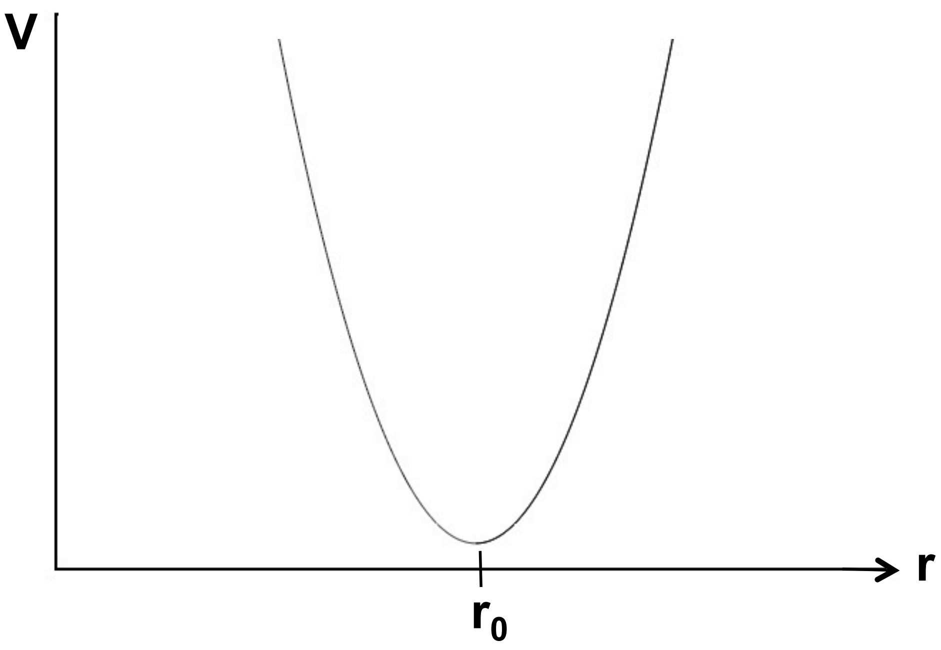
$$\mu = \frac{m_1 \cdot m_2}{m_1 + m_2}$$



μ ... reduced mass

K ... Force constant for the vibration

Vibration of a diatomic molecule – harmonic oscillator

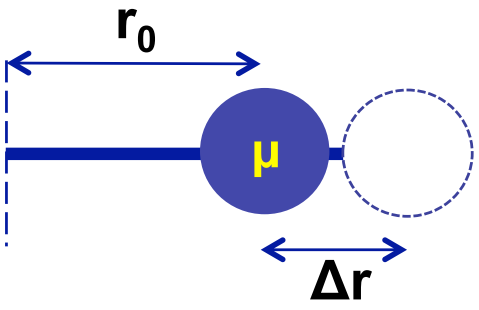


Classical mechanics

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

$$V(r) = \int_0^x F(r)dr = \frac{1}{2}Kr^2$$

$$V = 2\pi^2\mu\nu^2r^2$$



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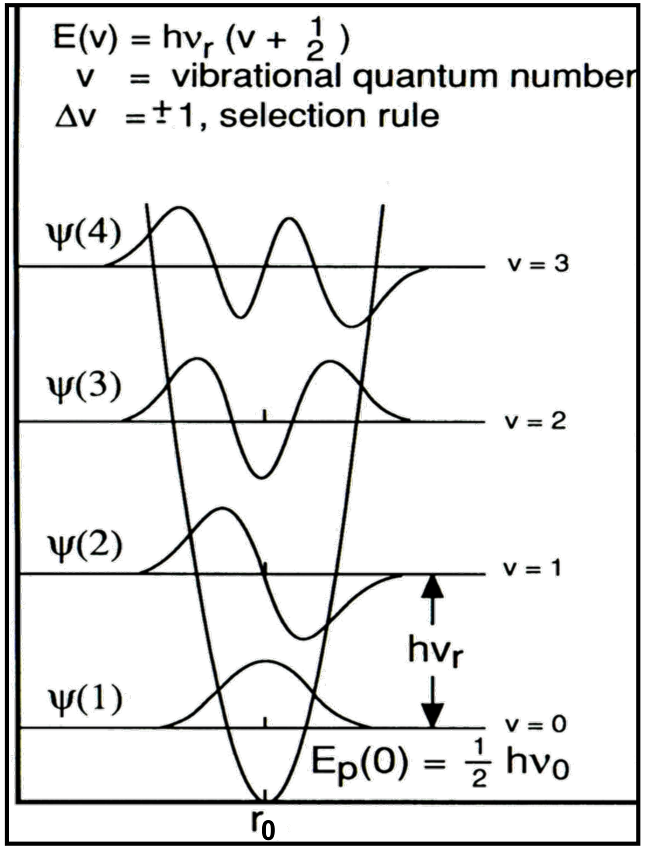
Vibration of a diatomic molecule – harmonic oscillator



Potential energy curve of a harmonic oscillator

Selection rule: $\Delta\upsilon \pm 1$

Quantum mechanics

$$H\Psi = E\Psi$$

$$H = T + V$$

$$V(r) = \int_0^x F(r)dr = \frac{1}{2}Kr^2$$

$$T = \frac{1}{2}mv^2 = \frac{1}{2\mu}p^2$$

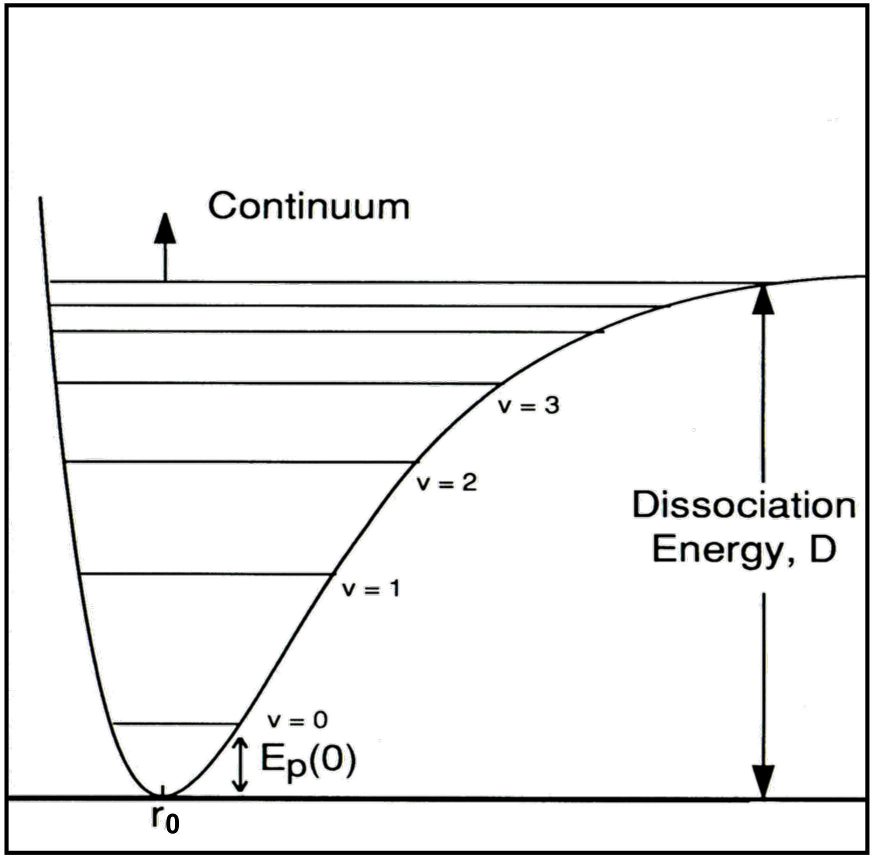
$$\frac{d^2\Psi}{dq^2} + \frac{8\pi^2\mu}{h^2}\left(E - \frac{1}{2}Kq^2\right)\Psi = 0$$

$$E_\upsilon = h\nu\left(\upsilon + \frac{1}{2}\right) = hc\tilde{\nu}\left(\upsilon + \frac{1}{2}\right)$$

υ = 0, 1, 2, ...

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

Vibration of a diatomic molecule



Actual potential of a diatomic molecule

Selection rule: $\Delta \upsilon \pm 1,2,3,\ldots$

Overtone: multiples of the fundamental

Combination band: sum or difference of two or more fundamentals

Anharmonicity

$$E_\upsilon = h\omega_e\left(\upsilon + \frac{1}{2}\right) - hcx_e\omega_e\left(\upsilon + \frac{1}{2}\right)^2 + \cdots$$

$\omega_e \cdots$ wavenumber corrected for anharmonicity

$x_e \cdots$ magnitude of anharmonicity

$$E_\upsilon - E_0 = h\nu = hc\tilde{\nu}$$

$$\tilde{\nu} = \frac{E_\upsilon - E_0}{hc} = \upsilon\omega_e - x_e\omega_e(\upsilon^2 + \upsilon) + \cdots$$

Fundamental:	$\tilde{\nu}_1 = \omega_e - 2x_e\omega_e$
First overtone:	$\tilde{\nu}_2 = 2\omega_e - 6x_e\omega_e$
Second overtone:	$\tilde{\nu}_3 = 3\omega_e - 12x_e\omega_e$

Vibration of a diatomic molecule

Relationships between vibrational frequency, reduced mass, and force constant

		Observed stretching frequency and overtones of CO
Fundamental:	$\tilde{\nu}_1 = \omega_e - 2x_e\omega_e$	2143.31 cm^{-1}
First overtone:	$\tilde{\nu}_2 = 2\omega_e - 6x_e\omega_e$	4259.70 cm^{-1}
Second overtone:	$\tilde{\nu}_3 = 3\omega_e - 12x_e\omega_e$	6349.17 cm^{-1}

$$\omega_e = 2170.23\, cm^{-1} \qquad x_e\omega_e = 13.46\, cm^{-1}$$

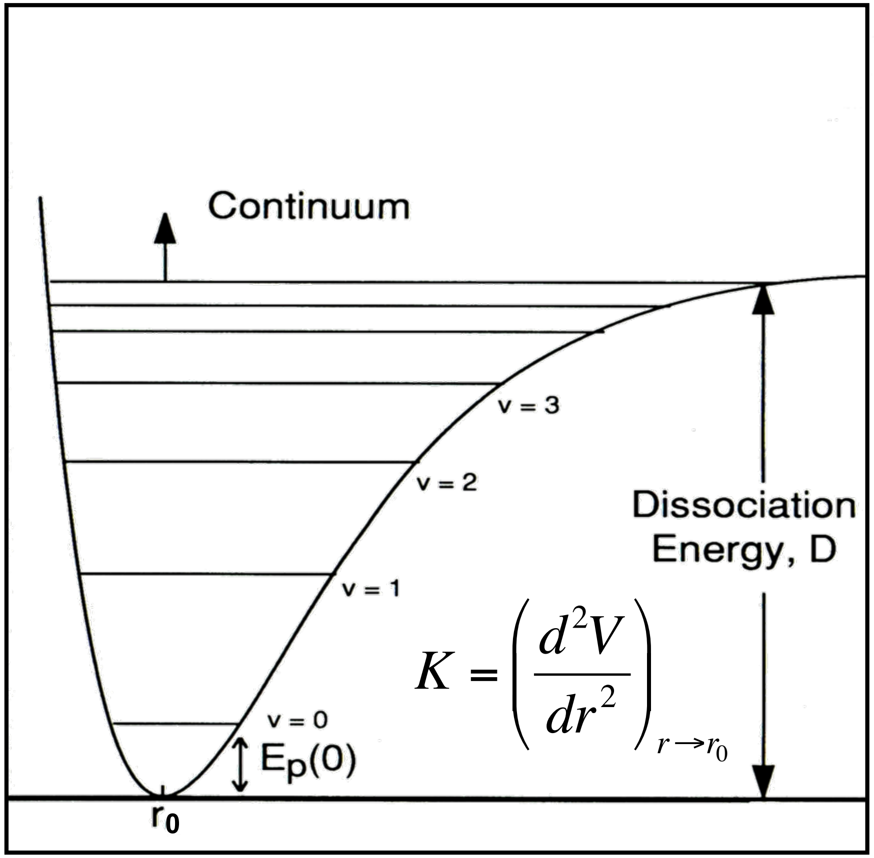
$$\omega_e = \frac{1}{2\pi c}\sqrt{\frac{K}{\mu}} \qquad K = 4\pi^2 c^2 \omega_e{}^2 \mu$$

$$K = \frac{4\cdot(3.14)^2(3\cdot 10^{10})^2}{6.025\cdot 10^{23}}\omega_e{}^2\mu = (5.8883\cdot 10^{-2})\omega_e{}^2\frac{12\cdot 16}{12+16} = (5.8883\cdot 10^{-2})(2170)^2 6.8584$$

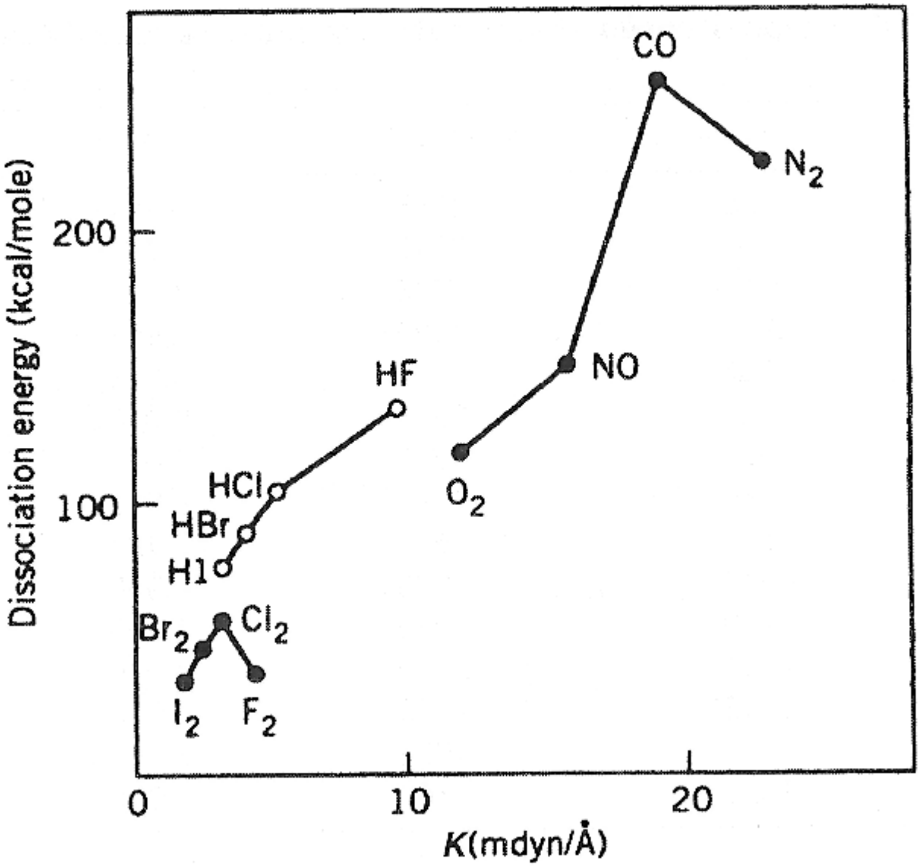
$$K = 1900\; N/m$$

Vibration of a diatomic molecule

Relationships between vibrational frequency, reduced mass, and force constant



$$K = \left(\frac{d^2V}{dr^2} \right)_{r \to r_0}$$



Nakamoto, p. 14

Theoretical calculation of force constants:

Calculation of the total electronic energy of a molecule as a function of the displacement near the equilibrium position and calculation of its second derivative

Difficult to derive a general theoretical relationship between K and D

Empirical relationships

Relationships between vibrational frequency, Mo-O bond distance and order

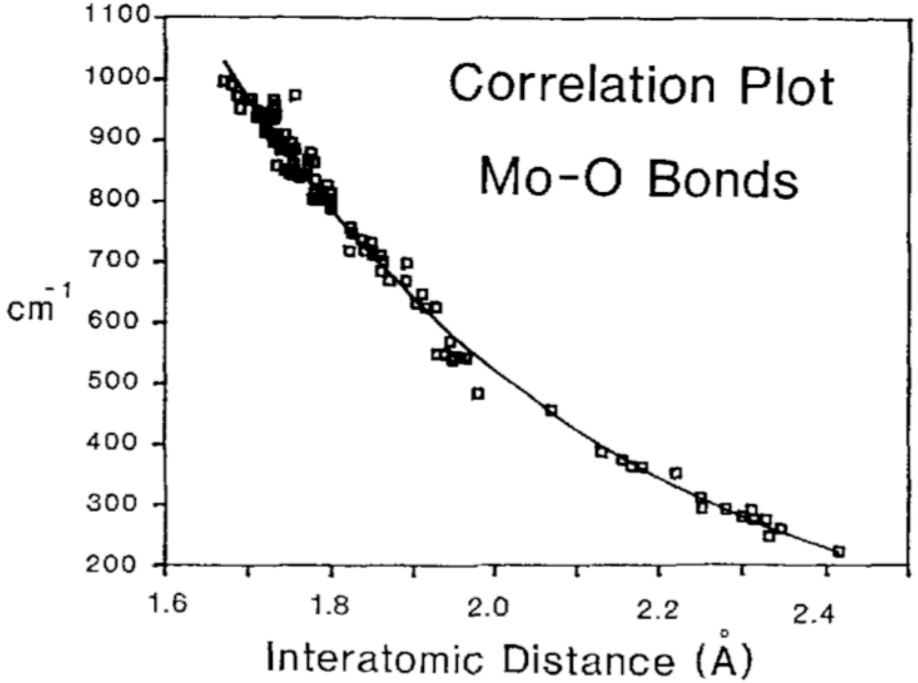


Figure 1. Mo–O correlation plot relating bond distance (Å) to stretching frequency (cm^{-1}). The 108 data points are fit to the exponential function ν (cm^{-1}) = 32 895 exp ($-2.073R$), where R is the bond distance in ångströms.

F.D. Hardcastle, I.E. Wachs, J. Raman Spectrosc. 21 (1990) 683.

Empirical relationships

Relationships between vibrational frequency, V-O bond distance and order

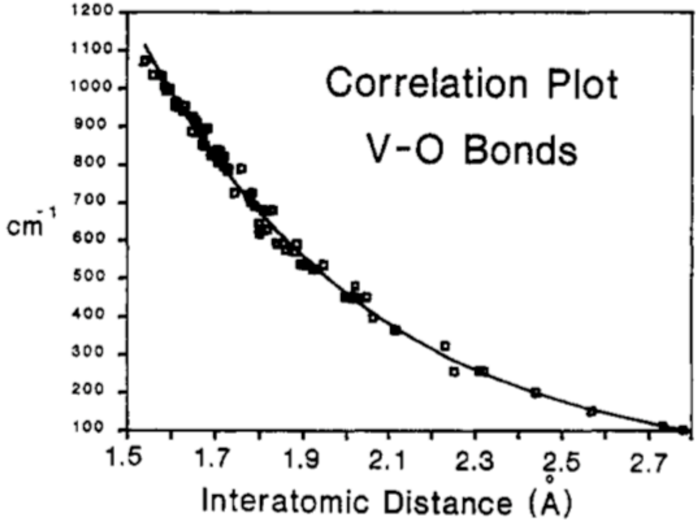


Figure 1. Correlation plot relating V–O bond lengths (Å) to V–O stretching frequencies. The data points are fit to the exponential function $\nu = 21349 \exp(-1.9176R)$, where R is the V–O bond length in angstroms; ν is in cm^{-1}.

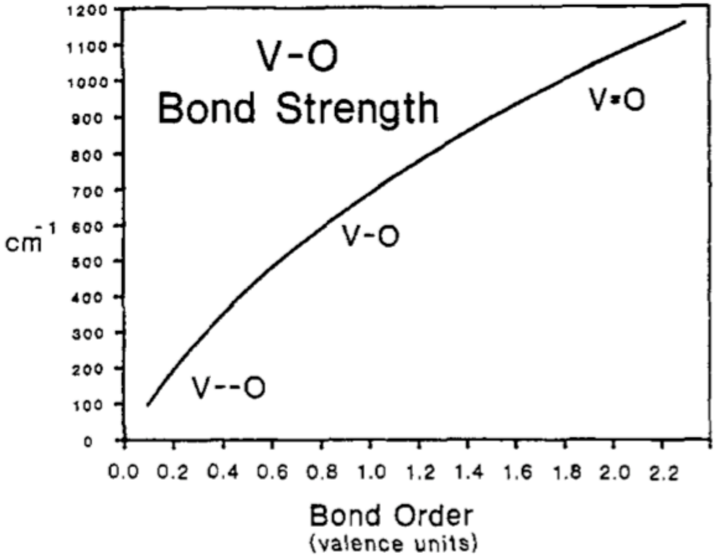


Figure 2. Correlation plot relating vanadium–oxygen bond strength (in valence units) to vanadium–oxygen stretching frequencies, according to eq 4.

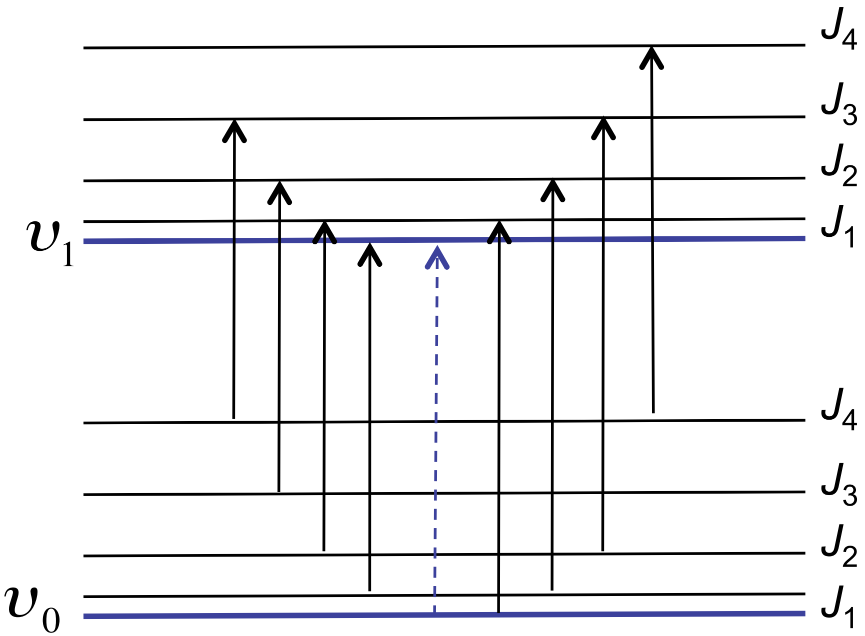
$$s(V\text{-}0) = [0.2912\ \ln (21349/v)]^{-5.1}$$

F.D. Hardcastle, I.E. Wachs, J. Phys. Chem. 95 (19901) 5031.

Rotational fine structure of diatomic molecules

Vibrational transitions are accompanied by rotational transitions

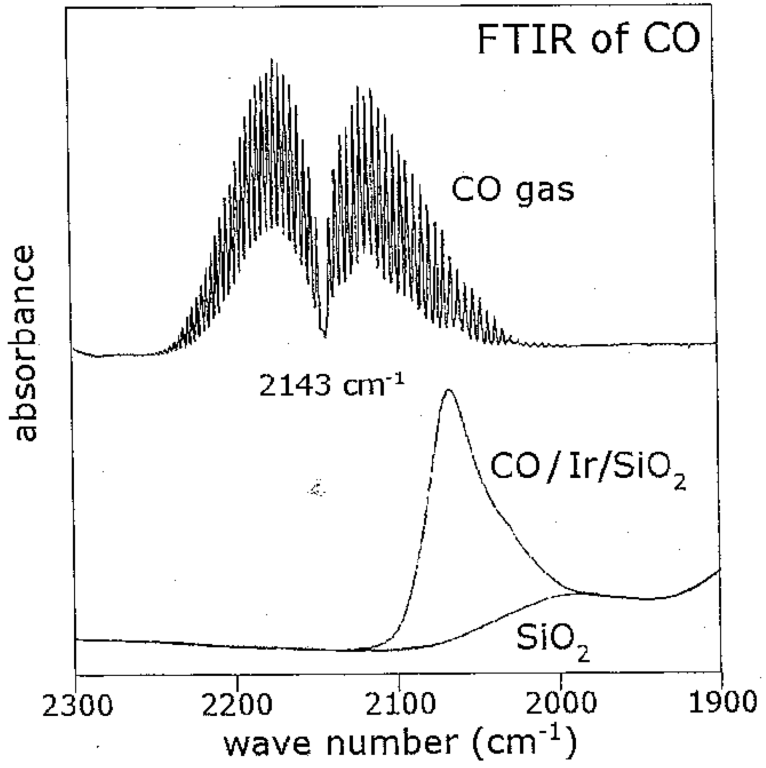
Rotational fine structure is not observed in solid or liquid phase or in solutions due to molecular interactions



ΔJ=-1 (P branch) ΔJ=+1 (R branch)

Selection rules: ΔJ=±1

$$\Delta\upsilon \pm 0,1,2,3,\ldots$$

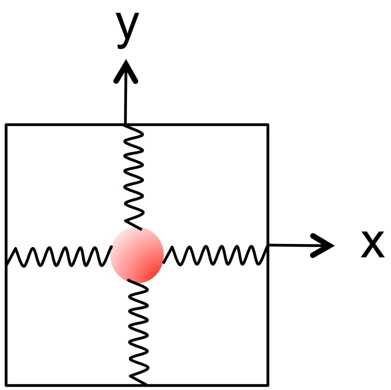


Niemantsverdriet, p. 207

Normal vibrations of polyatomic molecules

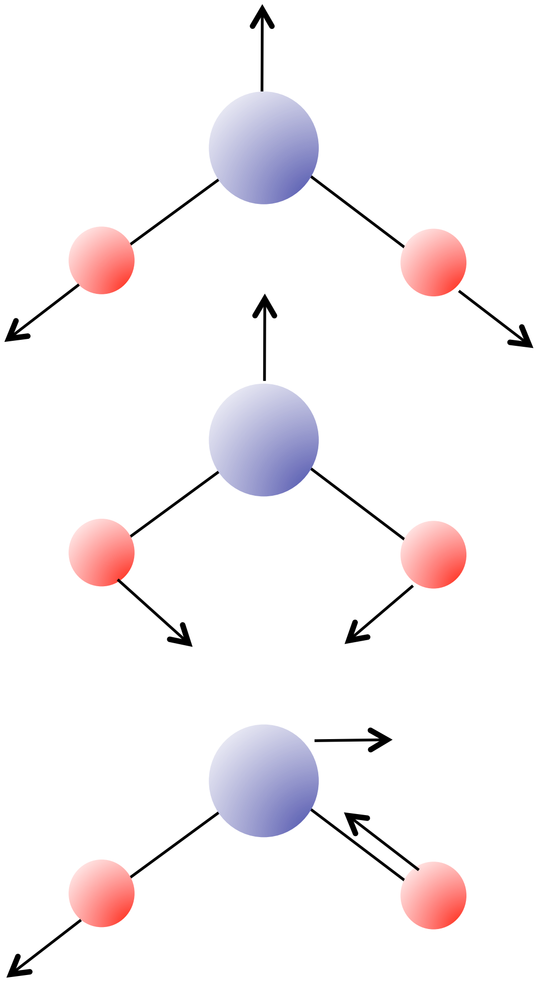
In polyatomic molecules, all nuclei perform their own anharmonic oscillations

N	number of atoms in a molecule
3N	number of coordinates to describe the molecule = degrees of freedom of movement of the molecule
3	degrees of freedom for translation in *x, y, z*
3N-3	degrees of freedom for rotation and vibration
3N-5	**degrees of freedom for vibration of a linear molecule**
3N-6	**degrees of freedom for vibration of a nonlinear molecule**



Any of the complicated vibrations of a molecule may be represented by a superposition of 3N-5 (linear molecules) or 3N-6 (nonlinear molecules) ***normal vibrations***

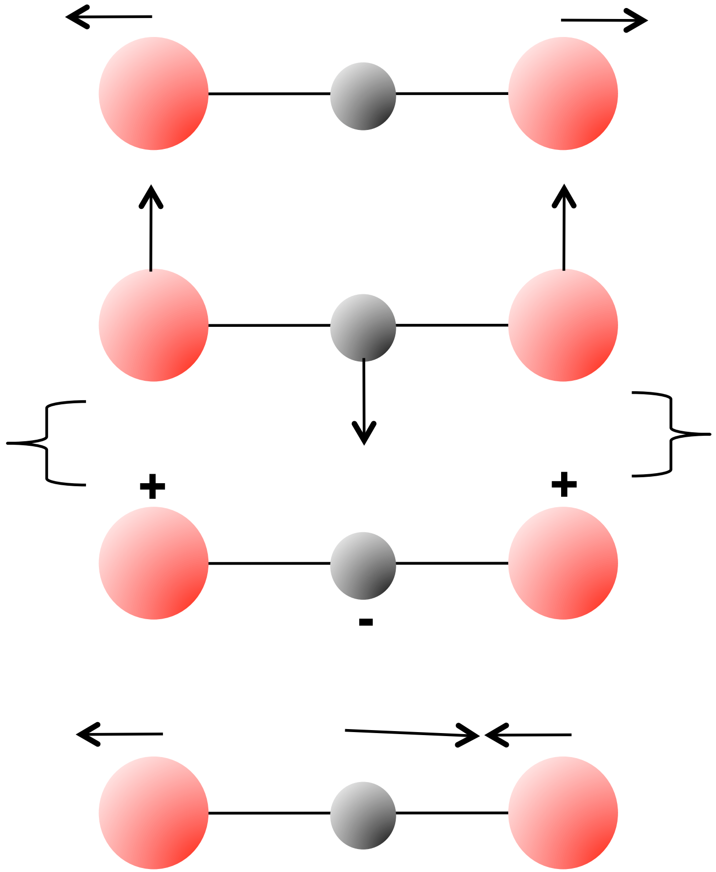
Normal vibrations of polyatomic molecules



C_{2v}	H_2O	cm^{-1}
$v_1(A_1)$		3657
$v_2(A_1)$		1595
$v_3(B_2)$		3756

Normal vibrations of polyatomic molecules

$D_{\infty h}$ O=C=O cm^{-1}



$v_1(\Sigma_g^+)$ 1340

$v_2(\Pi_u)$ 667

$v_3(\Sigma_u^+)$ 2350

Symmetry and selection rules

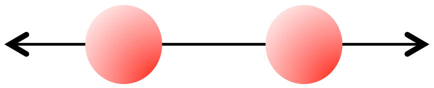
The vibration is IR active if the dipole moment is changed during the vibration

$$[\mu]_{\upsilon'\upsilon''} = \int \Psi^*_{\upsilon'}(Q_a)\mu\Psi_{\upsilon''}(Q_a)dQ_a \neq 0$$

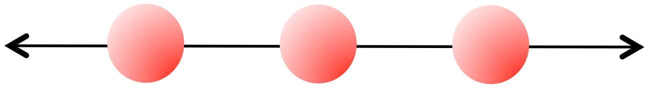
The selection rule is determined by the symmetry of the molecule

The intensity of the infrared band is proportional to the change in the dipole moment

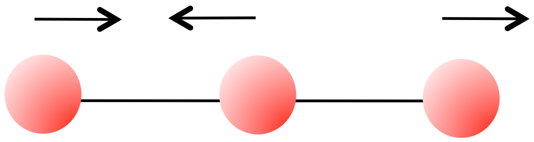
Fundamental modes of vibration – linear molecules



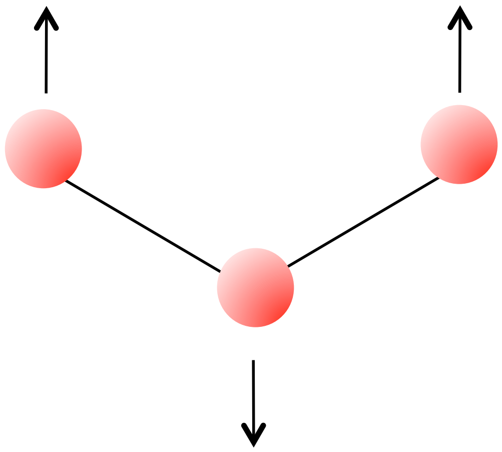
stretching



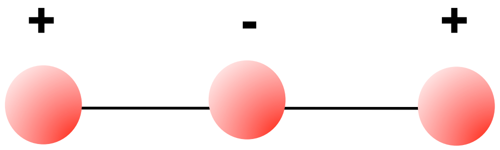
symmetric stretching



asymmetric stretching

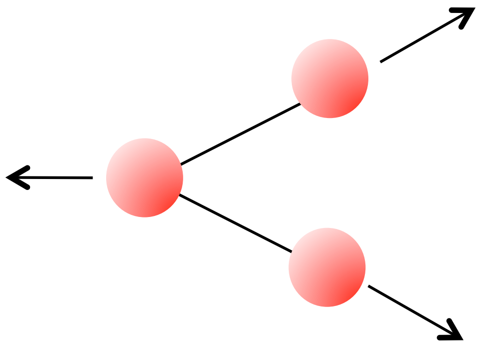


bending

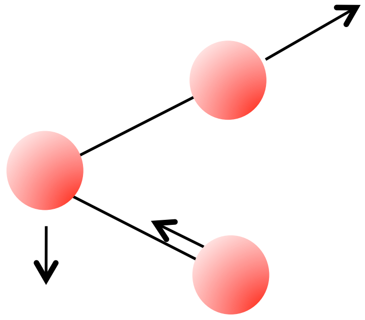


bending

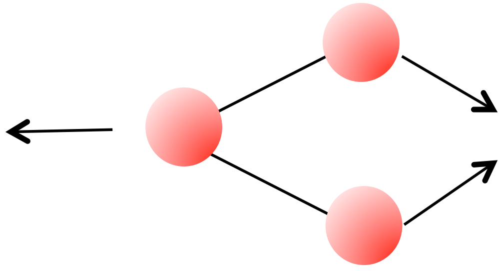
Fundamental modes of vibration - nonlinear molecules



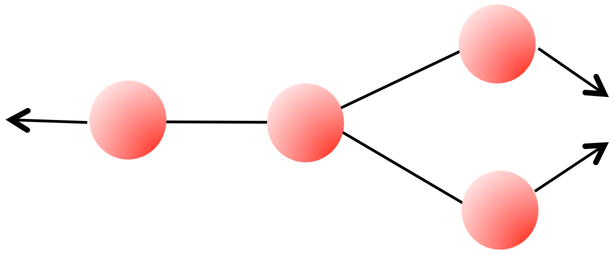
symmetric stretching (v_s)



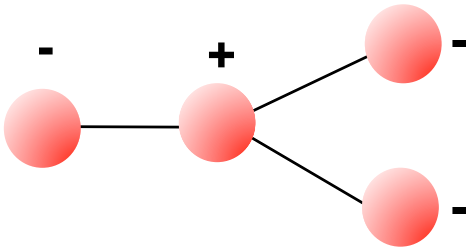
asymmetric stretching (v_{as})



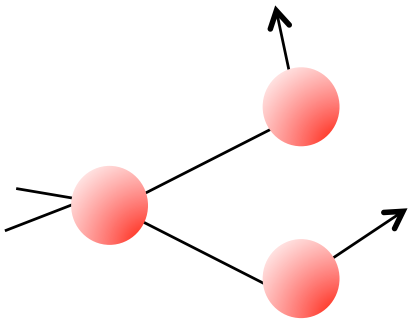
bending (δ)



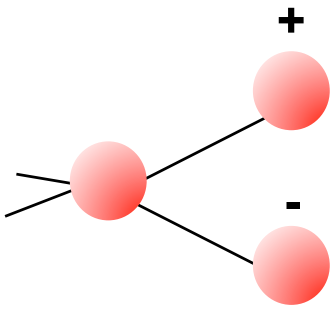
bending in plane (α, β)



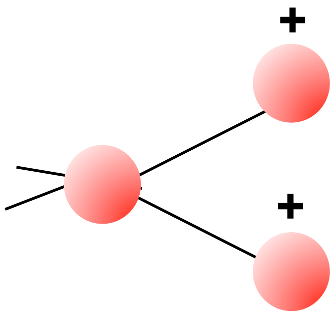
bending out of plane (γ)



rocking (*r*)



twisting (*τ*)



wagging (*ω*)

Assignment of vibrations

Group frequency concepts state:

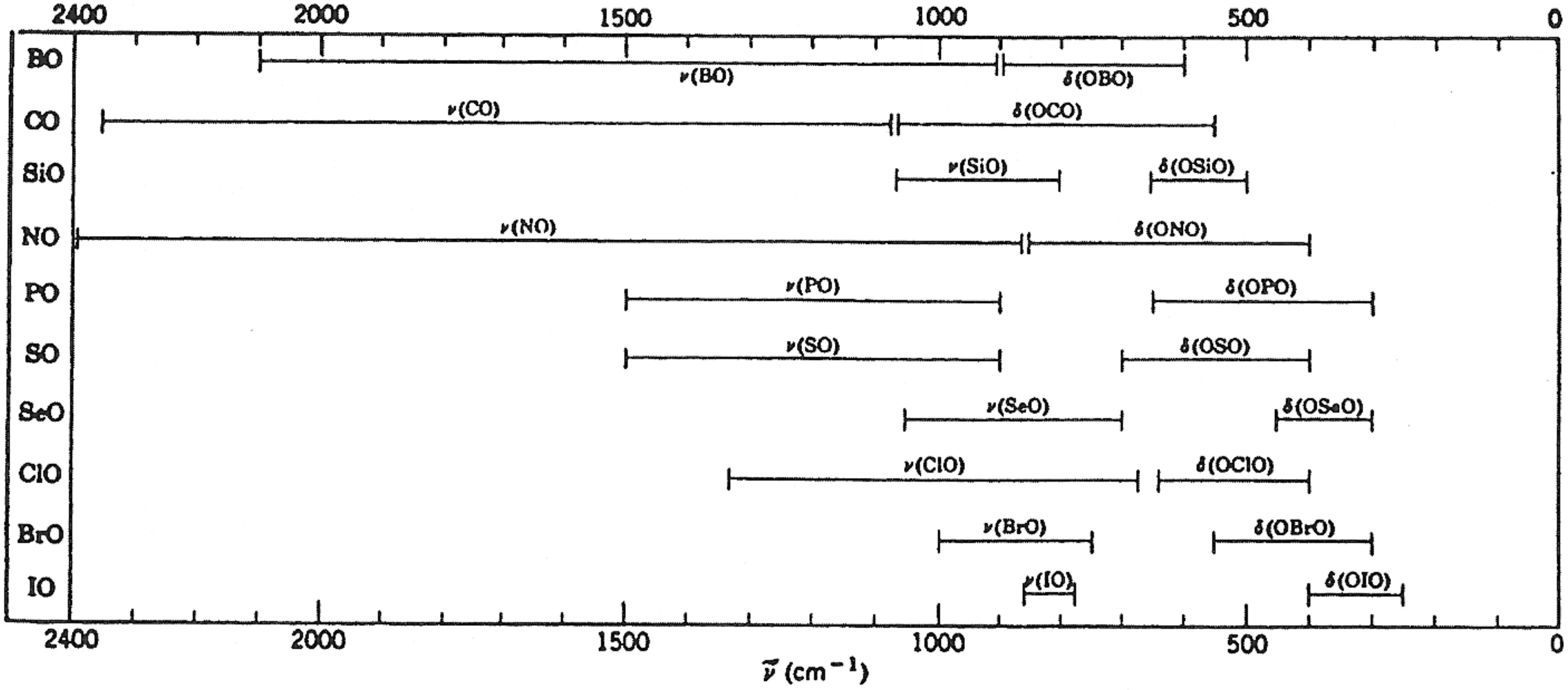
Groups of atoms (including heavy atoms or multiple bonds) absorb over a narrow range of frequencies regardless of the rest of the molecule

Functional groups in molecules may be treated as independent oscillators

4000 – 2500 cm^{-1}	H-X (X = O, N, C, S)
2500 – 2000 cm^{-1}	triple bond region (e.g. CO)
2000 – 1500 cm^{-1}	double bond region (e.g. carbonyl)
1500 – 500 cm^{-1}	fingerprint region C-X (X = N, O, S, halides)
200 – 450 cm^{-1}	M-X (X = C, O, N, S)

Assignment of vibrations

Group frequency charts:



(*b*) Oxygen stretching and bending frequencies

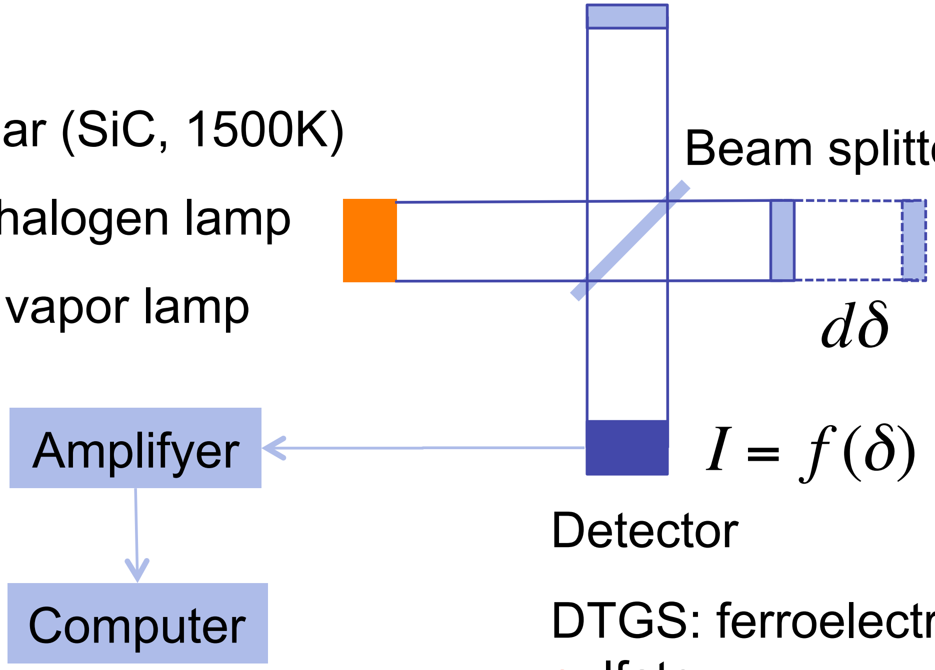
Nakamoto, p. 389

Outline

1. Basic principles
2. Sample geometry – techniques in FTIR
3. Applications
   I. Lattice vibrations and surface functional groups
   II. Adsorption sites – adsorption of probe molecules
   III. In-situ spectroscopy – gas phase/liquid phase

FTIR spectrometer

Michelson Interferometer



M1

Source

IR: Globar (SiC, 1500K)

NIR: W halogen lamp

FIR: Hg vapor lamp

Beam splitter

M2

$d\delta$ optical path difference

Amplifyer

Computer

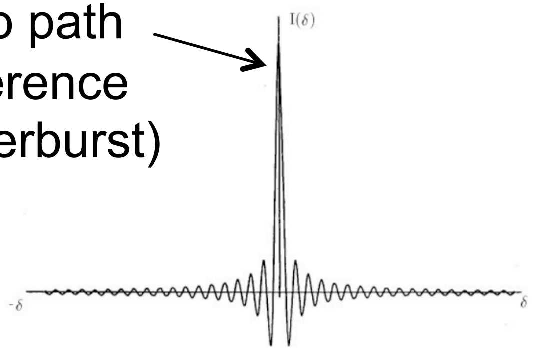
$I = f(\delta)$

Detector

DTGS: ferroelectric effect of deuterated triglycerine sulfate

MCT: photoelectric effect of $Hg_{0.8}Cd_{0.2}Te$

zero path difference (centerburst)



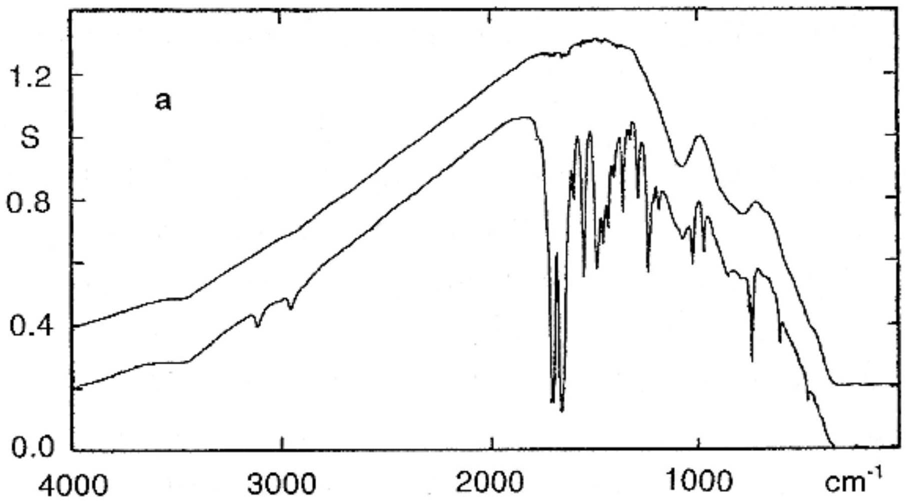
Interferogram:

$$I(\delta) = \int_{-\infty}^{\infty} B(\tilde{\nu}) \exp(-2\pi i \tilde{\nu} \delta) d\tilde{\nu}$$

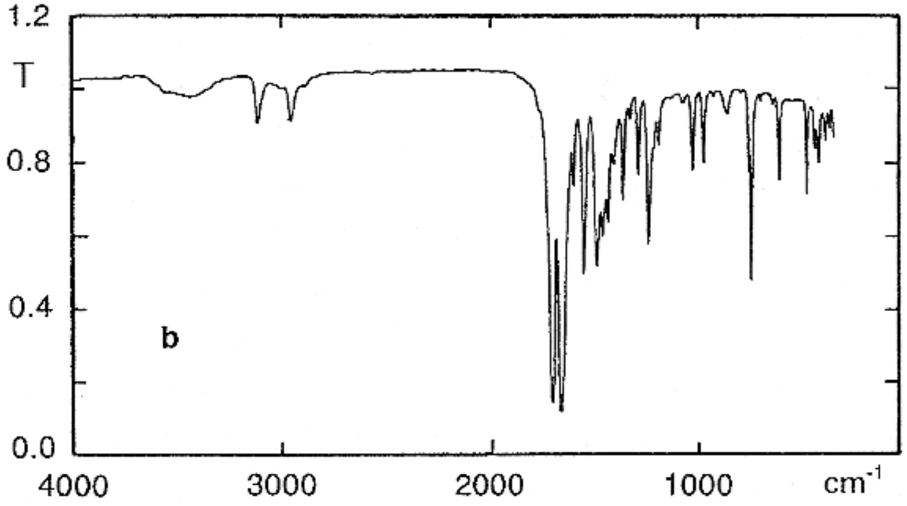
FTIR spectrometer

$B(\tilde{\nu})$

single channel spectra



ratio



Günzler, p. 65

FTIR spectrometer

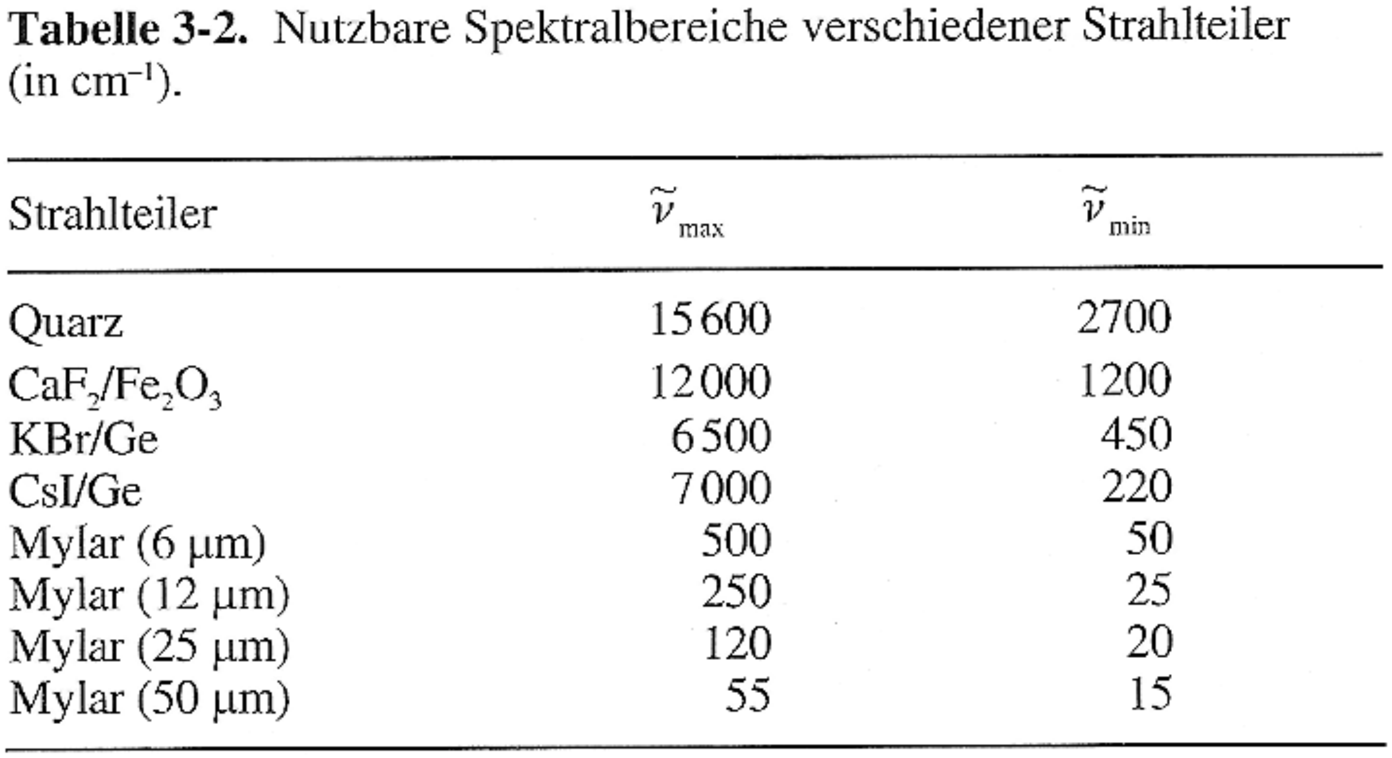


Tabelle 3-2. Nutzbare Spektralbereiche verschiedener Strahlteiler (in cm^{-1}).

Strahlteiler	$\tilde{\nu}_{\text{max}}$	$\tilde{\nu}_{\text{min}}$
Quarz	15600	2700
CaF_2/Fe_2O_3	12000	1200
KBr/Ge	6500	450
CsI/Ge	7000	220
Mylar (6 µm)	500	50
Mylar (12 µm)	250	25
Mylar (25 µm)	120	20
Mylar (50 µm)	55	15

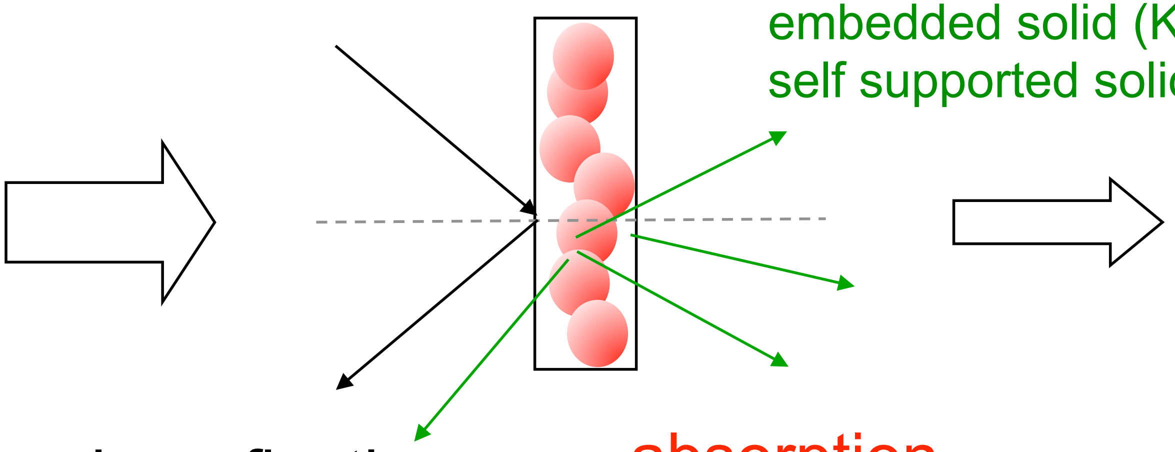
Mylar ... Polyethylentherephthalat

Günzler, p. 63

How to measure FTIR spectra of solid catalysts?

Sample preparation	geometry	remarks
KBr technique	transmission	Quantitative measurements difficult Chemical interaction with KBr may happen Differences in refractive index Particle size effect of embedded material, differences in refractive index (Christiansen effect) No pretreatment, no adsorption
Suspension in paraffin oil (Nujol®)	transmission	
Self supported wafer	transmission	Pretreatment and adsorption possible
powder	DR	Used in *in-situ* FTIR spectroscopy
Powder or suspension	ATR	Used to study solid-liquid interface

Transmission spectra



light source

sample

solution
embedded solid (KBr, Nujol®)
self supported solid

detector

$I_0(\nu)$

$I(\nu)$

specular reflection

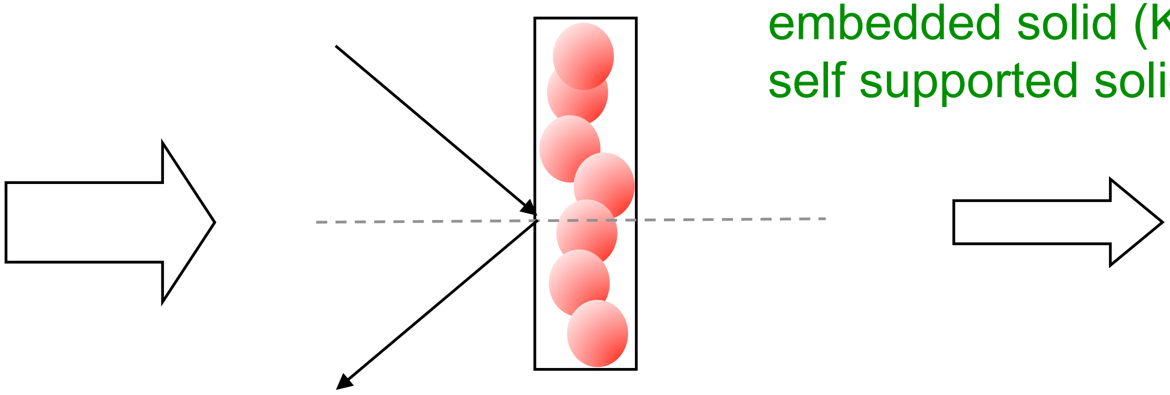
absorption

scattering

- elastic (Rayleigh, Mie) ν

$$\boxed{I_0 = I_r + I_s + I_a + I}$$

How to deal with phase boundary reflection?



light source

sample

solution
embedded solid (KBr, Nujol®)
self supported solid

detector

$I_0(\nu)$

$I(\nu)$

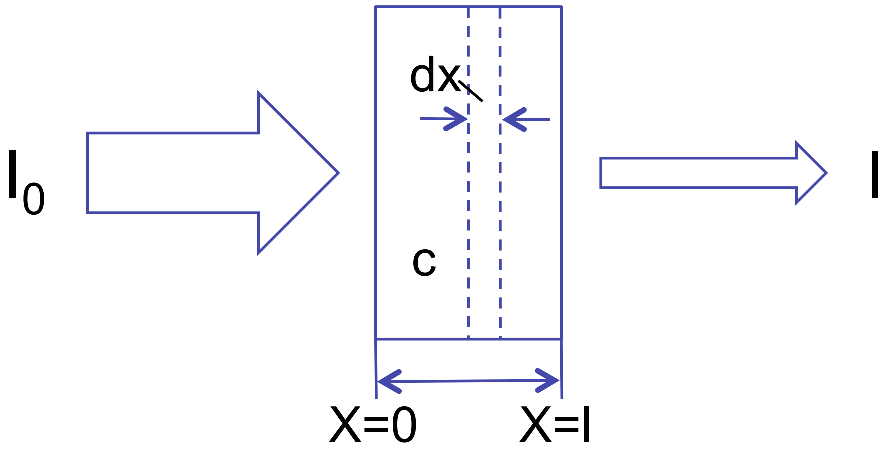
reflection $\boldsymbol{I_r}$

absorption

$$\boxed{I_0 = \boldsymbol{I_r} + I_s + I_a + \boldsymbol{I}}$$

- fraction of reflected light $\boldsymbol{I_r}$ can be eliminated through reference measurement with same materials (cuvette + (solvent))

Transmitted light and absorption properties



τ: transmittance

α: absorptance

$$\boxed{\tau_\lambda = \frac{I}{I_0} \qquad \alpha_\lambda = \frac{I_0 - I}{I_0} \qquad \tau_\lambda = 1 - \alpha_\lambda}$$

$$dI = -I\, k\, dx = -I\, \kappa\, c\, dx$$

decrease of I in an infinitesimally thin layer

c: molar concentration of absorbing species [mol/m^{-3}]
κ: the molar napierian extinction coefficient [m^2/mol]

$$\int_{I_0}^{I} \frac{dI}{I} = -\int_{x=0}^{x=l} \kappa\, c\, dx$$

separation of variables and
integration over sample thickness l

$$\ln \frac{I}{I_0} = -\kappa\, c\, l$$

Transmitted light and absorption properties

$$\tau = \frac{I}{I_0} = e^{-\kappa c l} = 1 - \alpha$$

Lambert-Beer Law

$$A_e = B = \kappa\, c\, l = -\ln(\tau)$$

$$\log e = 0.434$$

napierian absorbance
Napier-Absorbanz

$$A_{10} = \varepsilon\, c\, l = -\log(\tau)$$

$$\varepsilon = 0.434\kappa$$

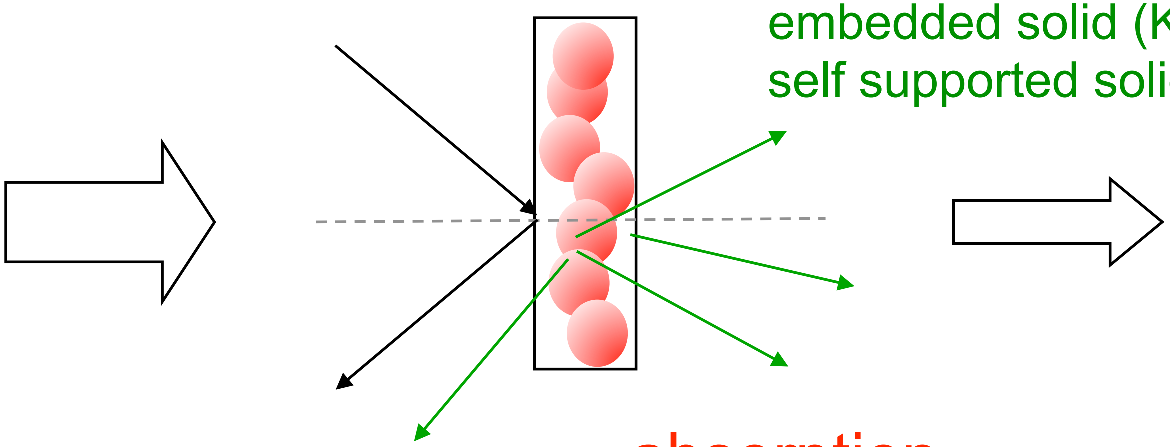
(decadic) absorbance
dekadische Absorbanz

standard spectroscopy software uses A_{10}!

extinction	E (means absorbed + scattered light)
absorbance	A (A_{10} or A_e)
optical density	O.D.

all these quantities are DIMENSIONLESS !!!!

Transmission spectra- loss due to scattering



light source

sample

solution
embedded solid (KBr, Nujol®)
self supported solid

detector

$I_0(\nu)$

$I(\nu)$

specular reflection

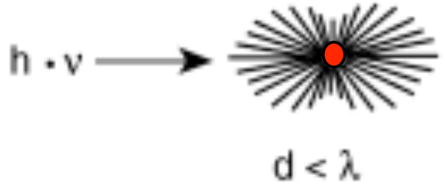
absorption

scattering

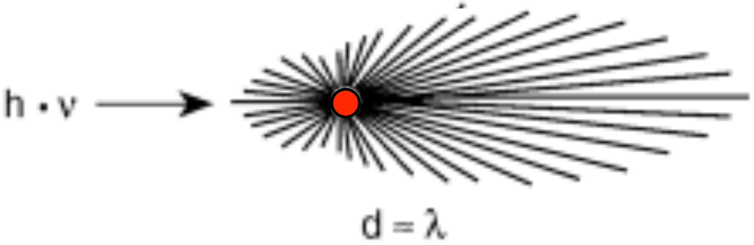
- elastic (Rayleigh, Mie) ν

$$\boxed{I_0 = I_r + I_s + I_a + I}$$

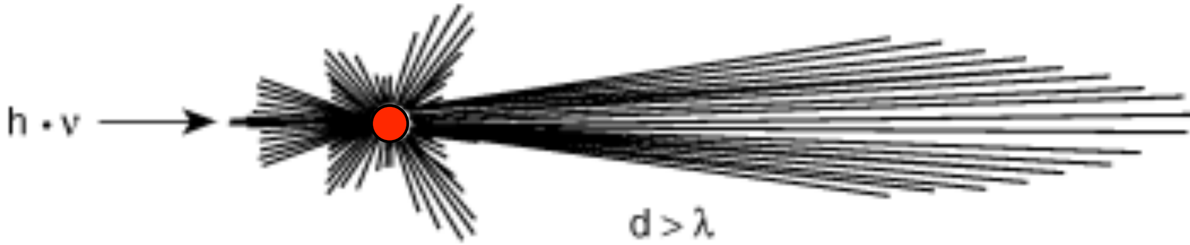
Rayleigh and Mie scattering



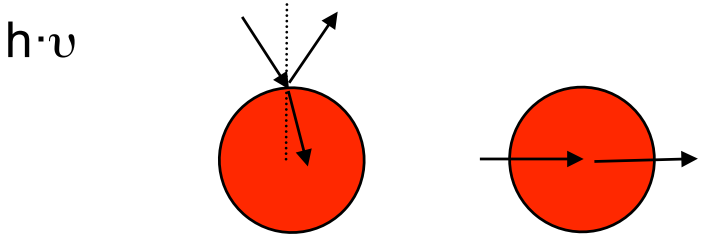
d < λ: Rayleigh-Scattering
isotropic distribution



d = λ: Mie-Scattering
in forward and backward directions



d > λ: Mie-Scattering
predominantly in forward direction



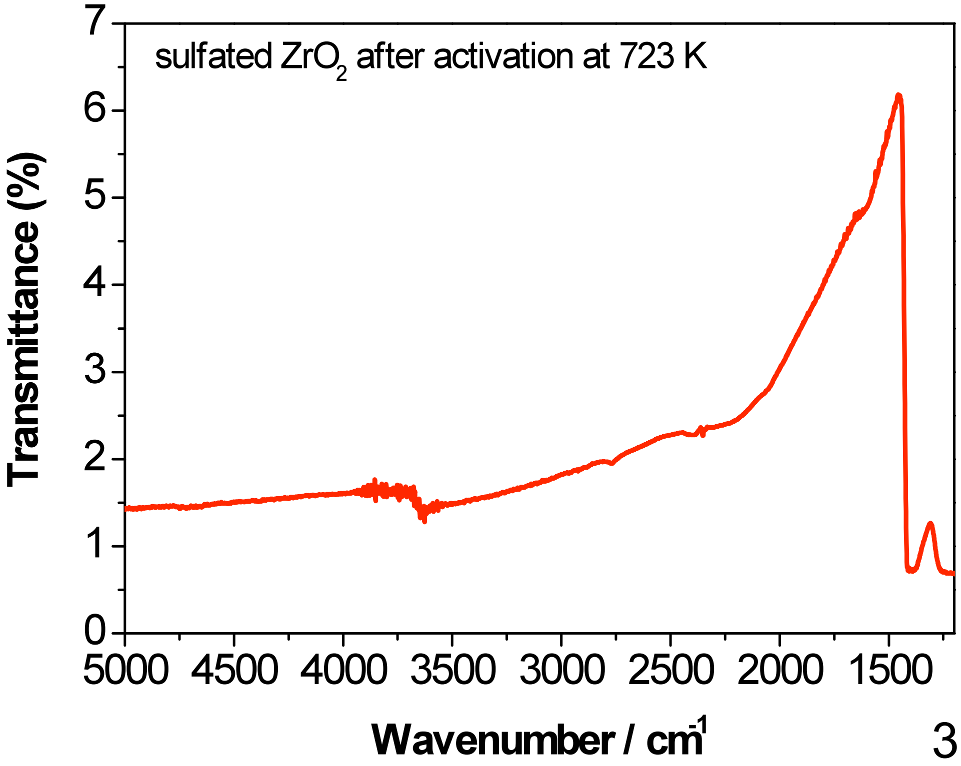
d >> λ: Mie-Theory approaches laws of geometric optics

Quelle: RÖMPP on line

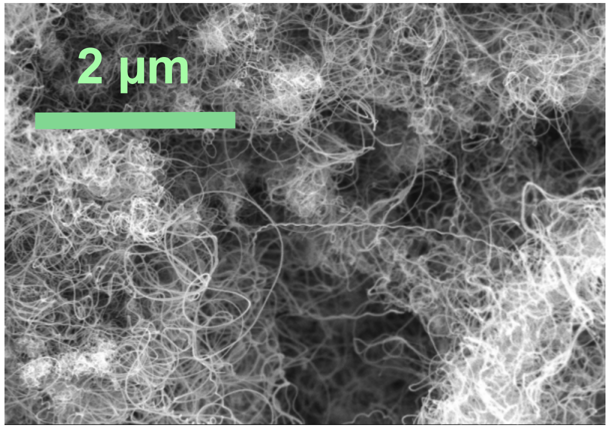
Loss due to scattering

Infrared region	Wavelength (nm)	Wavenumber (cm^{-1})	Energy (meV)	Vibrations
far	$1x10^6$ - $5x10^4$	10-200	1.2-25	lattice
mid	$5x10^4$ - 2500	200-4000	25-496	molecular
near	2500 - 1000	4000-10000	496-1240	overtones

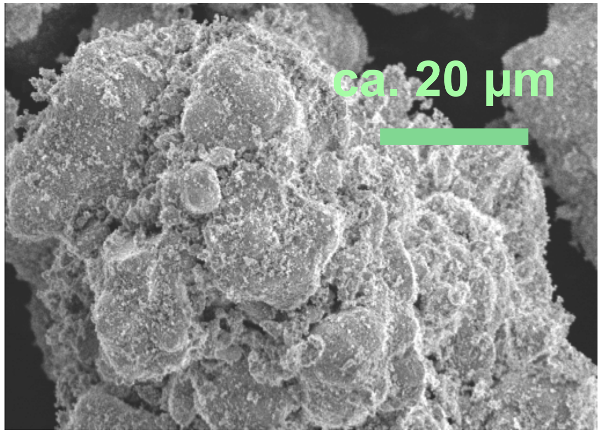
- Scattering is negligible in molecular disperse media (solutions)
- Scattering is considerable for colloids and solids when the wavelength is in the order of magnitude of the particle size



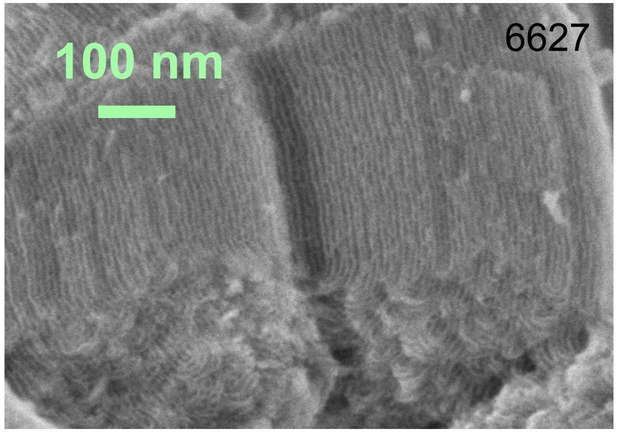
Typical catalyst particles



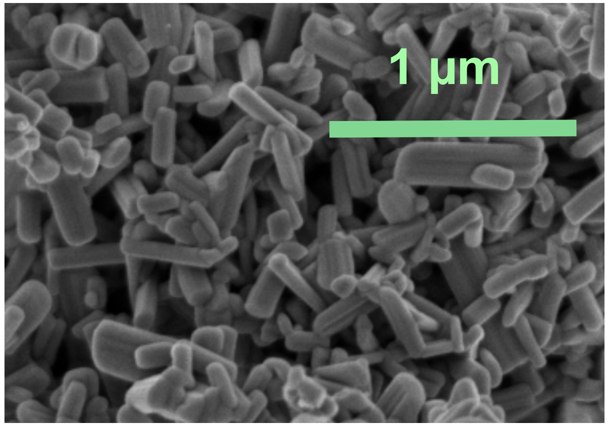
MWCNT



ZrO_2



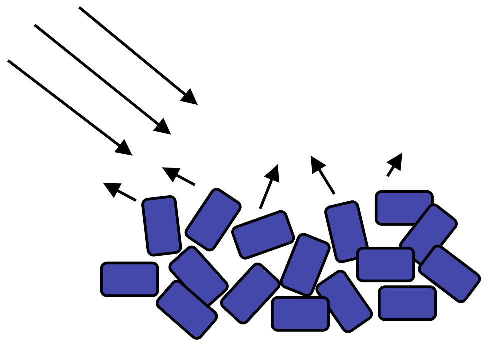
SiO_2



MoVTeNbO

- Need theory that treats light transfer in an absorbing and scattering medium
- Want to extract absorption properties!

Diffuse reflection (DR)

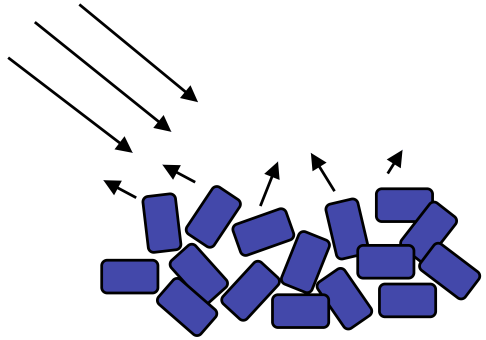


Intensity of diffusely reflected light independent of angle of incidence

Result of multiple reflection, refraction, and diffraction (scattering) inside the sample

Randomly oriented crystals in a powder:
light diffusely reflected

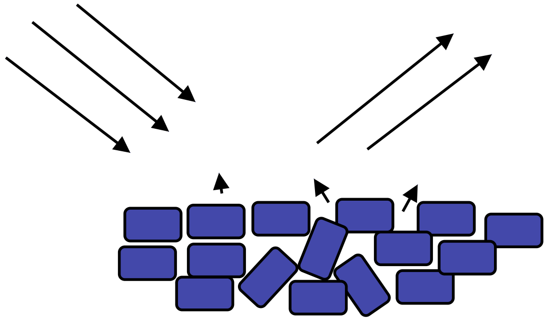
Diffuse reflection (DR)



Intensity of diffusely reflected light independent of angle of incidence

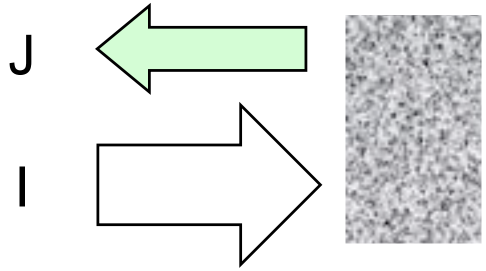
Result of multiple reflection, refraction, and diffraction (scattering) inside the sample

Randomly oriented crystals in a powder:
light diffusely reflected



Flattening of the surface or pressing of a pellet can cause orientation of the crystals, which are "elementary mirrors"
Causes "glossy peaks" if angle of observation corresponds to angle of incidence
Solution: roughen surface with (sand)paper or press between rough paper, or use different observation angle!

Quantification of DRIFT spectra: Kubelka-Munk function



$$R = \frac{J}{I}$$

R...reflectance

2 constants are needed to describe the reflectance:
absorption coefficient K, function of the frequency
scattering coefficient S

for K→0 (no absorption) $R_\infty \rightarrow 1$, i.e. all light reflected
for S→0 (no scattering) $R_\infty \rightarrow 0$, i.e. all light transmitted or absorbed

The Kubelka-Munk function transforms the measured spectrum R(v) into the absorption spectrum K(v)

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S}$$

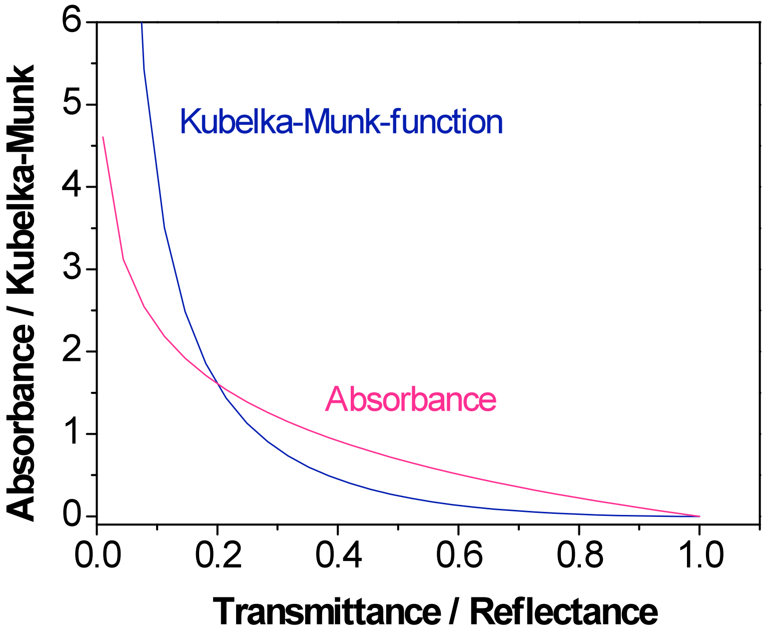
Kubelka-Munk function
remission function

Transmission vs. reflection spectroscopy

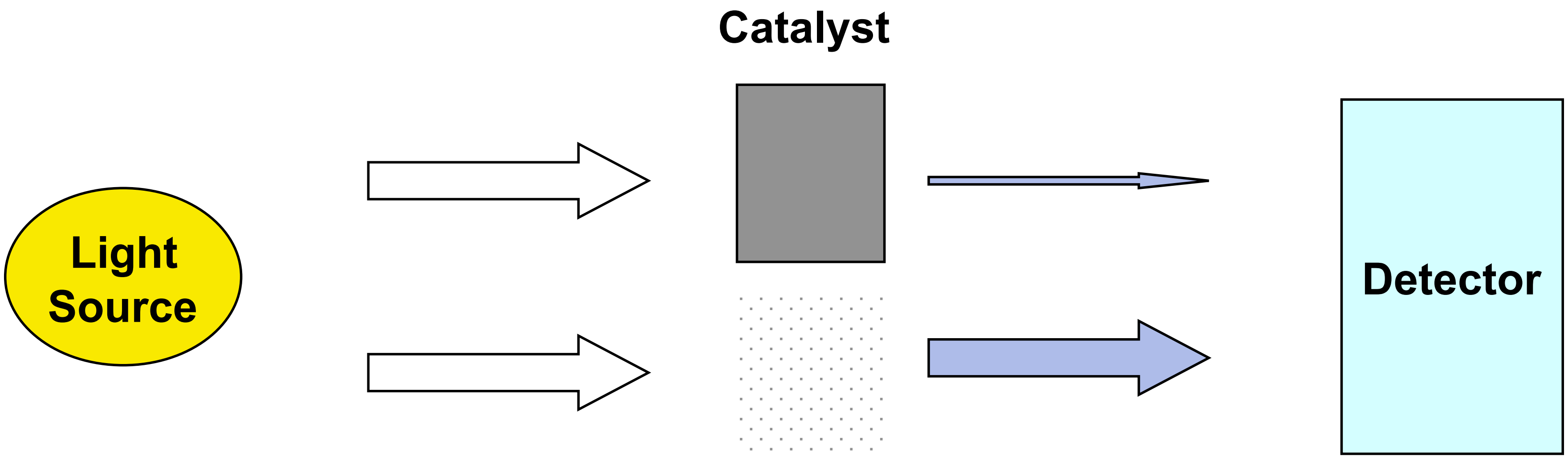
- For quantification and to be able to calculate difference spectra: calculate absorbance / Kubelka-Munk function

$$A = -\ln T$$

$$F(R) = \frac{(1-R)^2}{2R}$$



Spectroscopy in transmission



Catalyst

Light Source

Detector

reference „nothing“
= void, empty cell,
cuvette with solvent

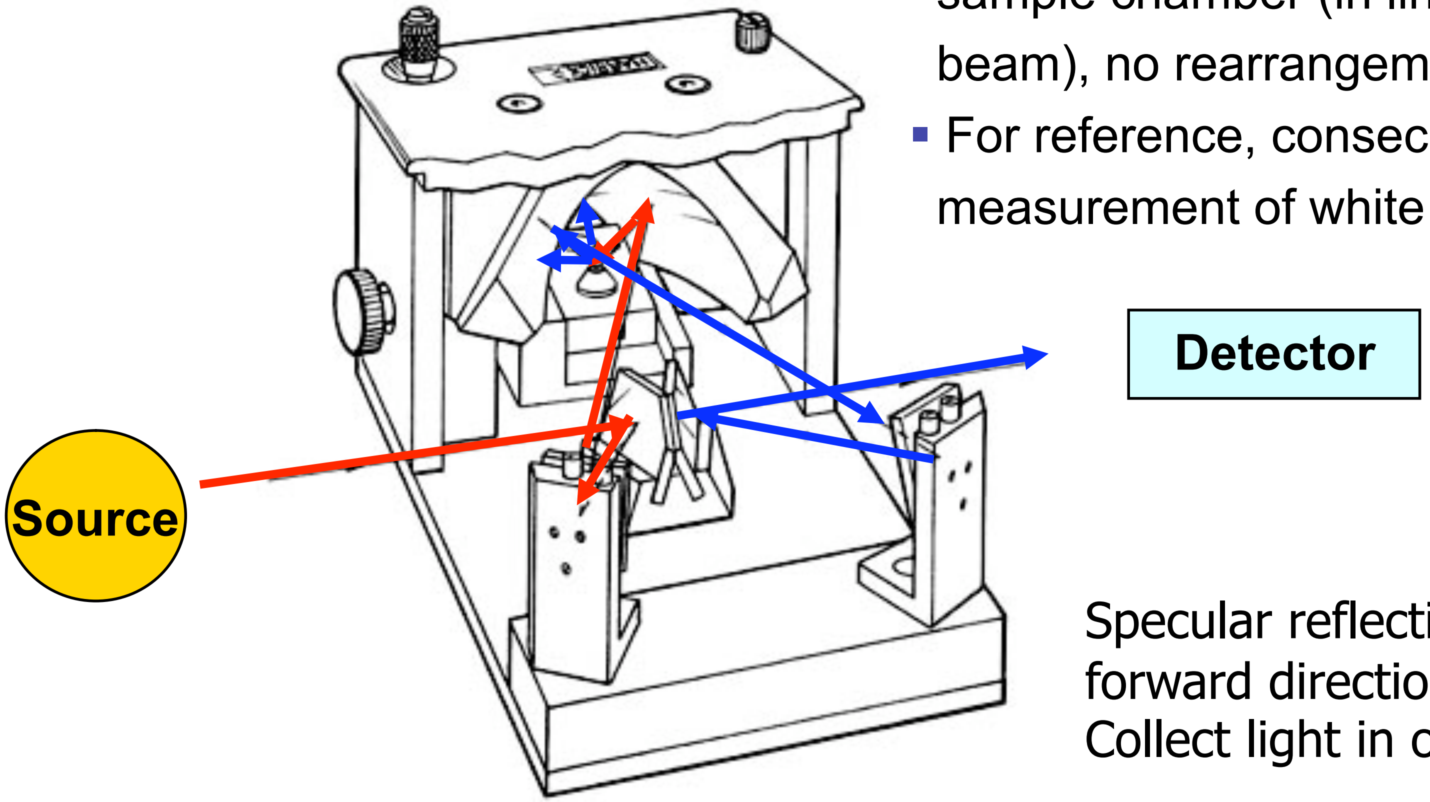
spectrum: transmission of
catalyst vs. transmission of
reference

Double beam spectrometer: direct comparison sample - reference

Single beam spectrometer: consecutive measurement

Mirror optical accessory for reflection spectroscopy

- can be placed into the normal sample chamber (in line with beam), no rearrangement necessary
- For reference, consecutive measurement of white standard

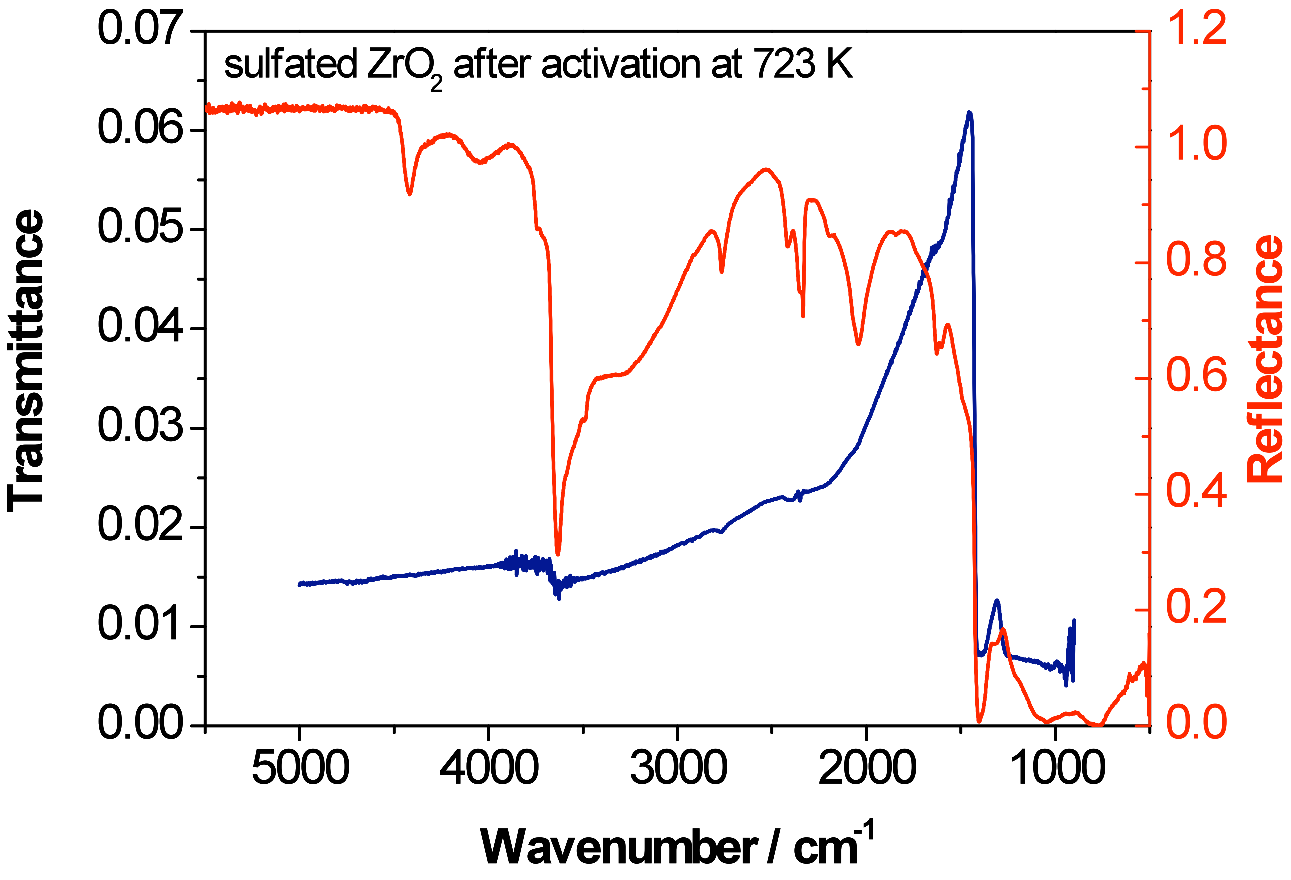


Specular reflection is strongest in forward direction
Collect light in off-axis configuration

- First ellipsoidal mirror focuses beam on sample
- Second ellipsoidal mirror collects reflected light
- 20% of the diffusely reflected light is collected

Transmission vs. reflection spectroscopy

Transmission: self-supporting wafer
Reflectance: powder bed

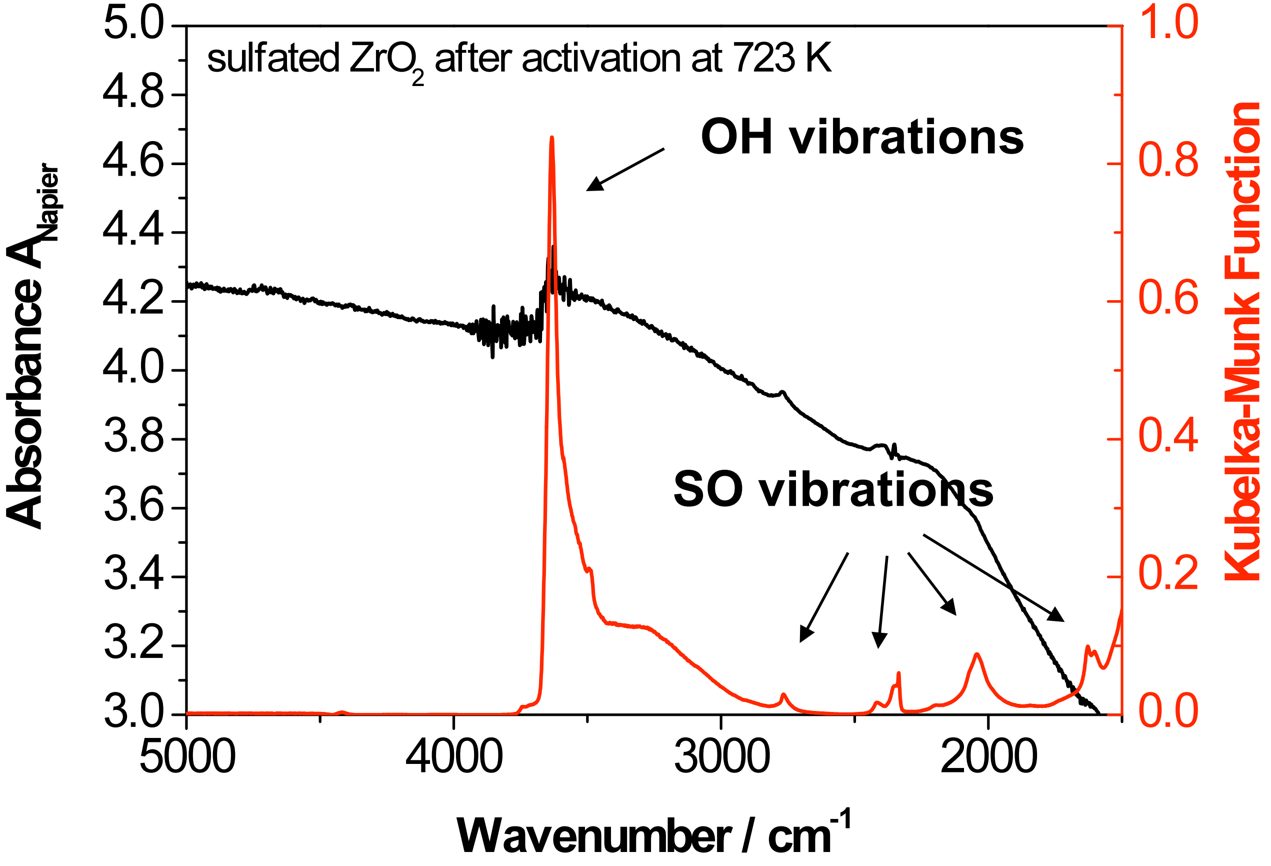


Spectra can have very different appearance

Transmittance decreases, reflectance increases with increasing wavenumber

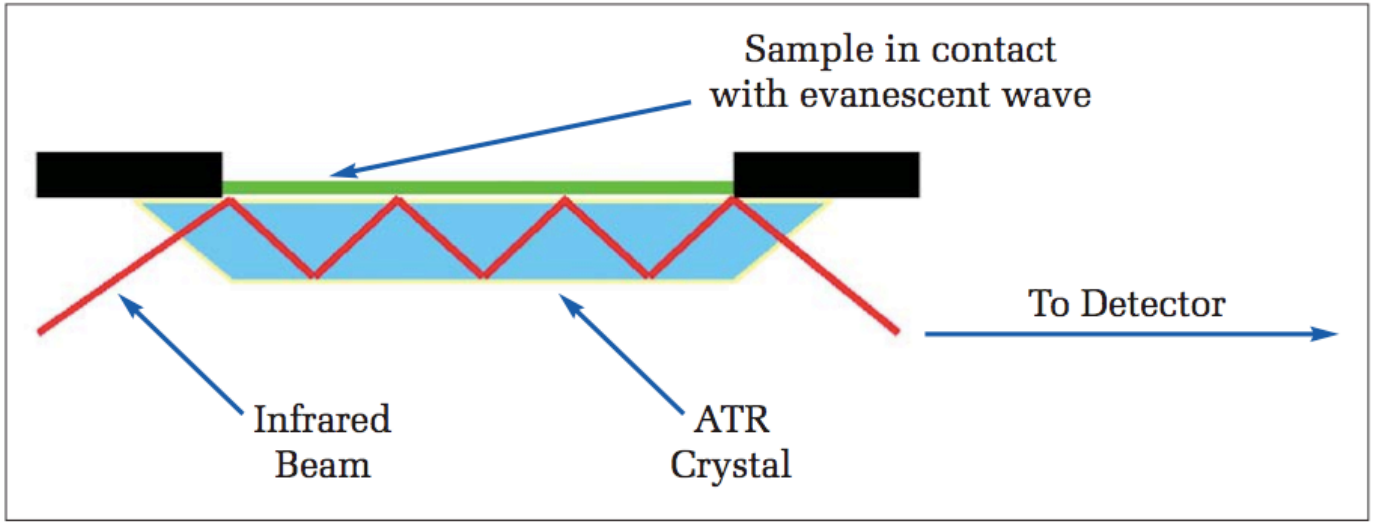
Transmission vs. reflection spectroscopy

Transmission: self-supporting wafer
Reflectance: powder bed



Vibrations of surface species may be more evident in DR spectra

Attenuated Total Reflection (ATR)



www.perkinelmer.de

$$\theta_c = \sin^{-1}\frac{n_2}{n_1}$$

The refractive index of the crystal n_1 must be significantly greater than that of the sample n_2

Crystal materials: ZnSe, Si, Ge, C (diamond)

Attenuated Total Reflection (ATR)

Depth of penetration (I=1/e)

$$d_p = \frac{\lambda_1}{2\pi(\sin^2\theta - n_{21}{}^2)^{1/2}}$$

$$\lambda_1 = \lambda / n_1$$

$$n_{21} = n_2 / n_1$$

Figure 7. Applying pressure to a solid sample on the Universal diamond ATR top-plate.

www.perkinelmer.de

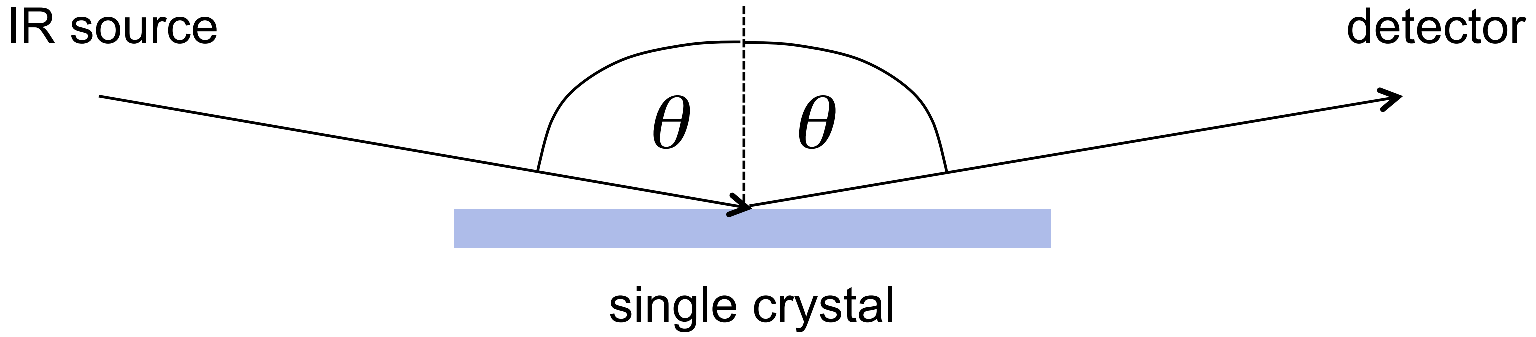
Germanium has by far the highest refractive index of all the ATR materials available which means that the effective depth of penetration is approximately 1 micron

This is an advantage when analyzing highly absorbing materials (carbon)

Reflection Absorption Infrared Spectroscopy (RAIRS, IRAS)

- grazing-incidence reflection of the IR light
- studies of single crystals in presence of gas phase
- low sensitivity owing to the small number of adsorbing molecules
- selection rule: vibrational modes which give rise to an oscillating dipole perpendicular (normal) to the surface are IR active

Review: Sheppard & Erkelens, Appl. Spec. 38 (1984) 471.

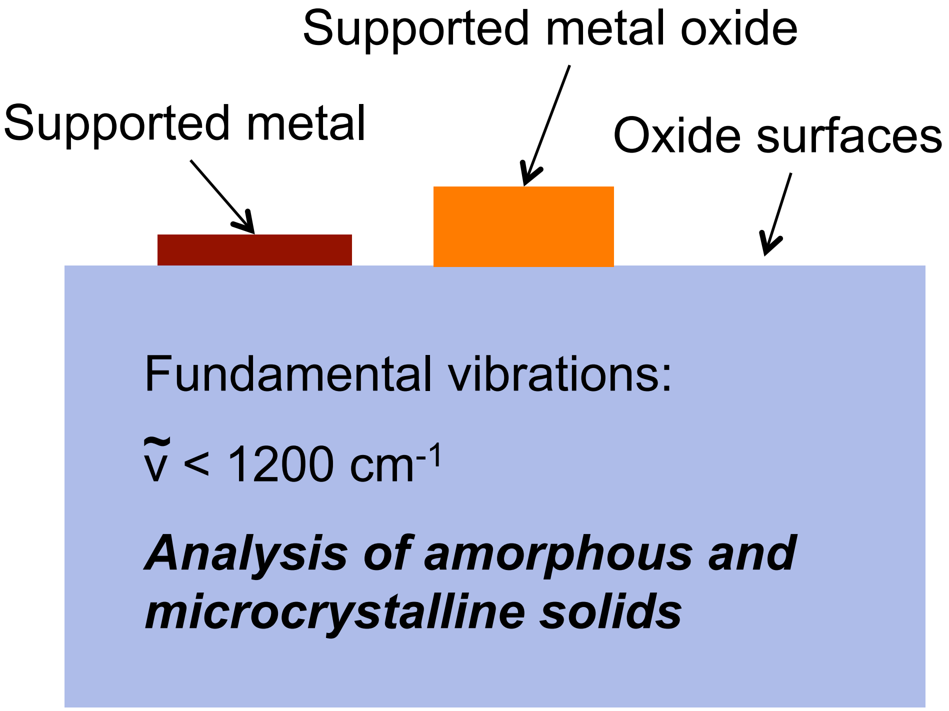


Outline

1. Basic principles
2. Sample geometry – techniques in FTIR
3. Applications
    - I. Lattice vibrations and surface functional groups
    - II. Adsorption sites – adsorption of probe molecules
    - III. In-situ spectroscopy – gas phase/liquid phase

FTIRS: Study of bulk structure and surface sites

Analysis of surface sites



Supported metal oxide

Supported metal

Oxide surfaces

Fundamental vibrations:

$\tilde{\nu} < 1200\ \mathrm{cm}^{-1}$

Analysis of amorphous and microcrystalline solids

Surface center (active site):

Microscopic group of atoms, which determines the specific chemical activity of the surface

- surface sites of supported metal particles
- electron donating oxygen atoms
- coordinatively unsaturated metal cations
- hydroxyl-hydrate cover

Vibration of metal-oxygen bonds on oxide surfaces

Davydov, p. 32

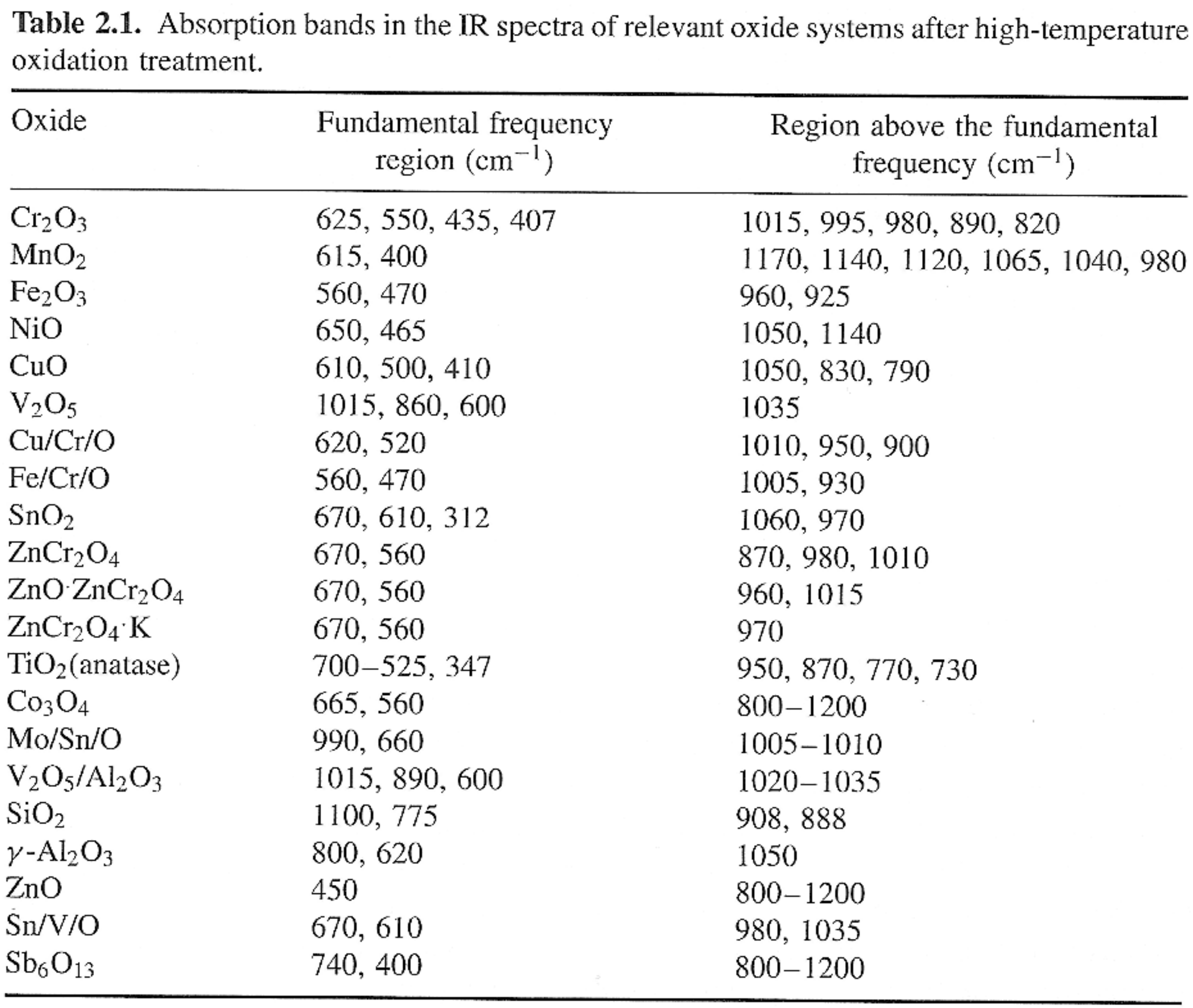


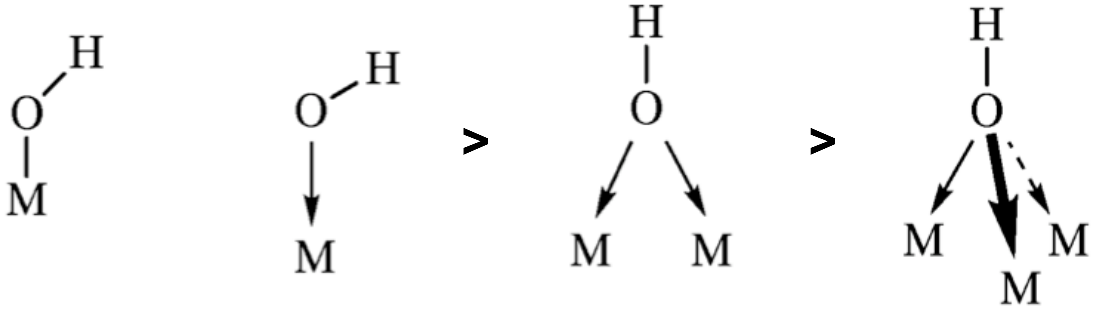
Table 2.1. Absorption bands in the IR spectra of relevant oxide systems after high-temperature oxidation treatment.

Oxide	Fundamental frequency region (cm^{-1})	Region above the fundamental frequency (cm^{-1})
Cr_2O_3	625, 550, 435, 407	1015, 995, 980, 890, 820
MnO_2	615, 400	1170, 1140, 1120, 1065, 1040, 980
Fe_2O_3	560, 470	960, 925
NiO	650, 465	1050, 1140
CuO	610, 500, 410	1050, 830, 790
V_2O_5	1015, 860, 600	1035
Cu/Cr/O	620, 520	1010, 950, 900
Fe/Cr/O	560, 470	1005, 930
SnO_2	670, 610, 312	1060, 970
$ZnCr_2O_4$	670, 560	870, 980, 1010
$ZnO \cdot ZnCr_2O_4$	670, 560	960, 1015
$ZnCr_2O_4 \cdot K$	670, 560	970
TiO_2(anatase)	700–525, 347	950, 870, 770, 730
Co_3O_4	665, 560	800–1200
Mo/Sn/O	990, 660	1005–1010
V_2O_5/Al_2O_3	1015, 890, 600	1020–1035
SiO_2	1100, 775	908, 888
γ-Al_2O_3	800, 620	1050
ZnO	450	800–1200
Sn/V/O	670, 610	980, 1035
Sb_6O_{13}	740, 400	800–1200

- surface M-O bonds of greater strength
- combination vibrations of fundamental absorption frequencies in this region!

Surface hydroxyl groups

$\tilde{\nu}_{O\text{-}H} = 3800\text{-}3000\ cm^{-1}$



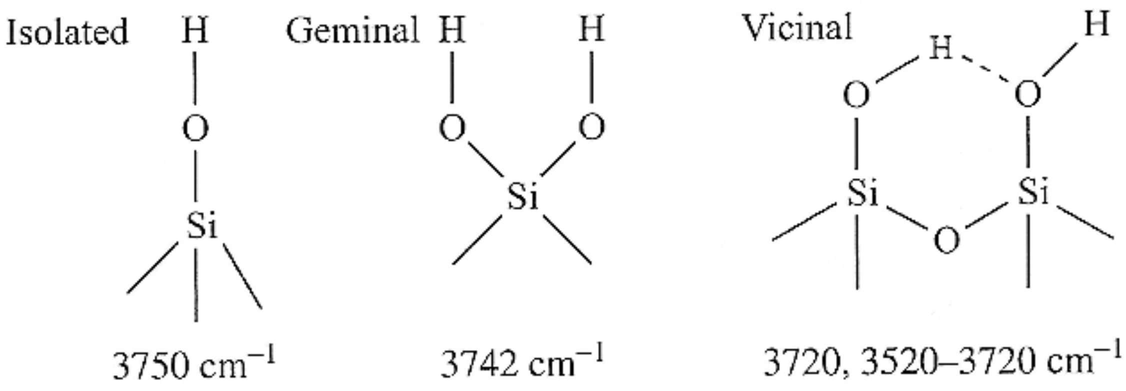
The position and shape of the OH bands of surface hydroxyl groups is informative of their coordination

- Covalent oxide components usually give rise to very typical strong sharp peaks; in covalent oxide coordination of oxygen is mostly two and this also occurs at the surface where the OHs are, consequently, terminal
- On ionic oxides the coordination of oxygen is higher than two, so that bridging and triply bridging hydroxy groups are formed at the surface
- Relation between OH stretching frequency and structure and acidity is not straightforward:

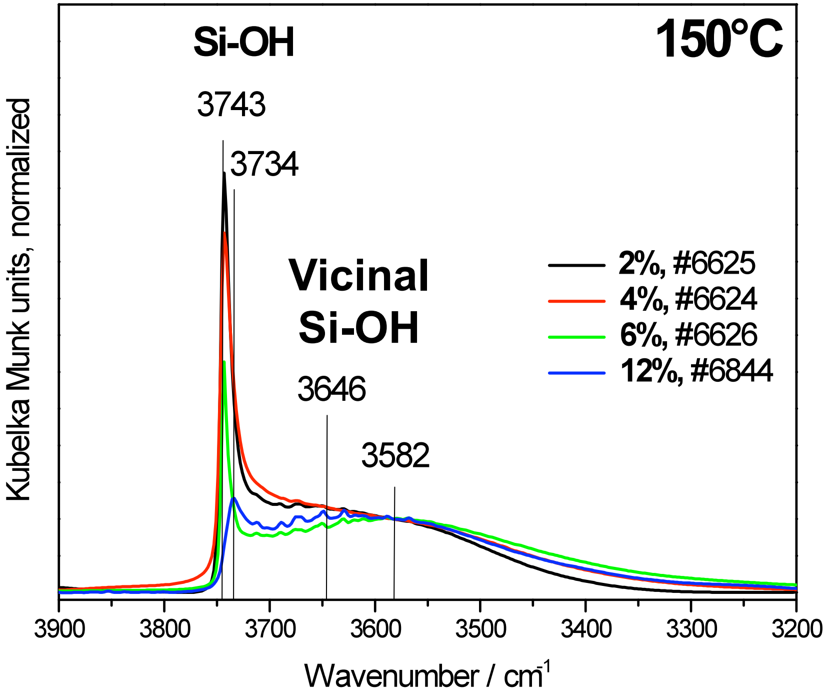
OH band of MgO, amorphous silica and silica-alumina at 3745 ±3 cm^{-1}.

G. Busca, PCCP 1 (1999) 723.

Silanol groups on amorphous silica (SBA-15)

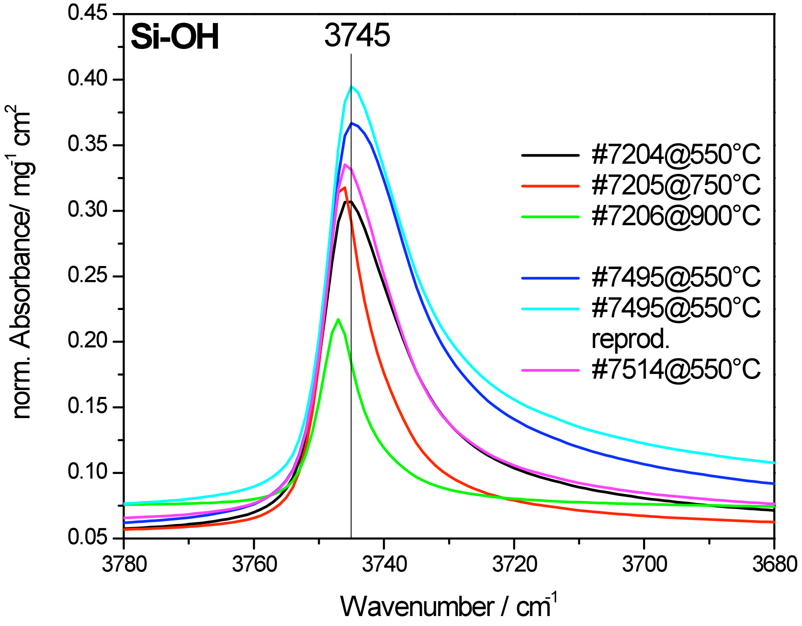


Davydov S. 60



x%V/SBA-15

Quantification of silanol groups in SBA-15



$$A_{10} = \varepsilon \, c \, l \quad = \varepsilon \, c \, \frac{m}{A}$$

$$\varepsilon = 1.91 \pm 0.17 \cdot 10^5 \ cm^2 mol^{-1}$$

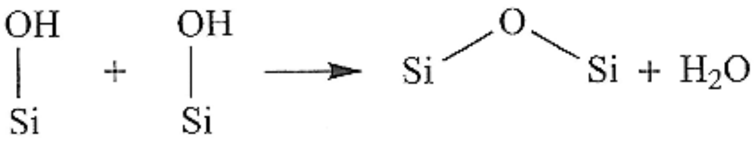
K. Heger, G. Marx, Mikrochim. Acta 133, (2000) 187.

A... area of the wafer

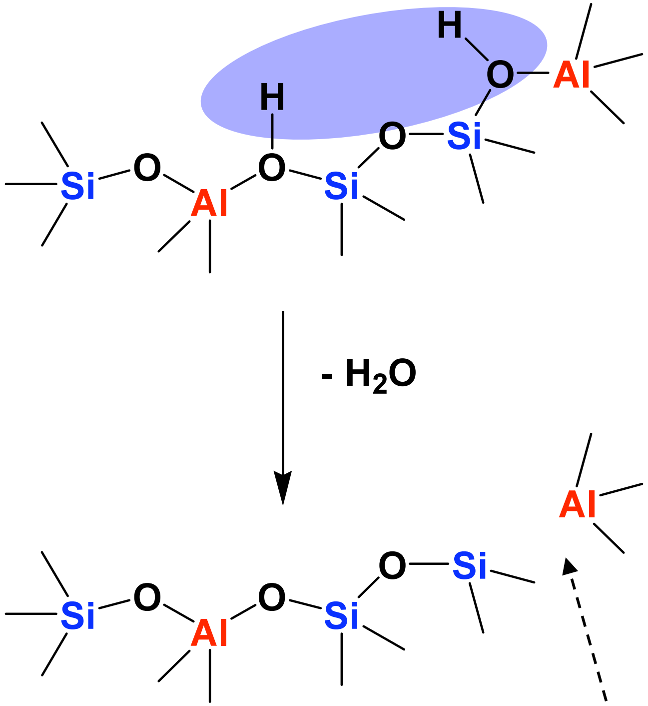
m...mass of wafer

Spectra normalized by the area weight of the wafer

SN	**area weight** mg cm^{-2}	**area of Si-OH** A. cm^{-1}	**OH conc.** mol kg^{-1} [mmol g^{-1}]	**BET** m^2 g^{-1}	**OH density** µmol m^{-2}
7204@550°C	6.57	31.7397	**25.29**	712	**35.5**
7206@900°C	9.52	15.1948	**8.36**	317	**26.4**

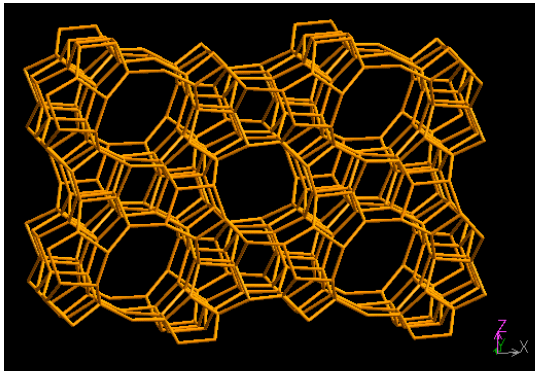


Brønsted acid sites in crystalline alumosilicates



Brønsted acid site

in H-exchanged zeolites



MFI viewed along [010]

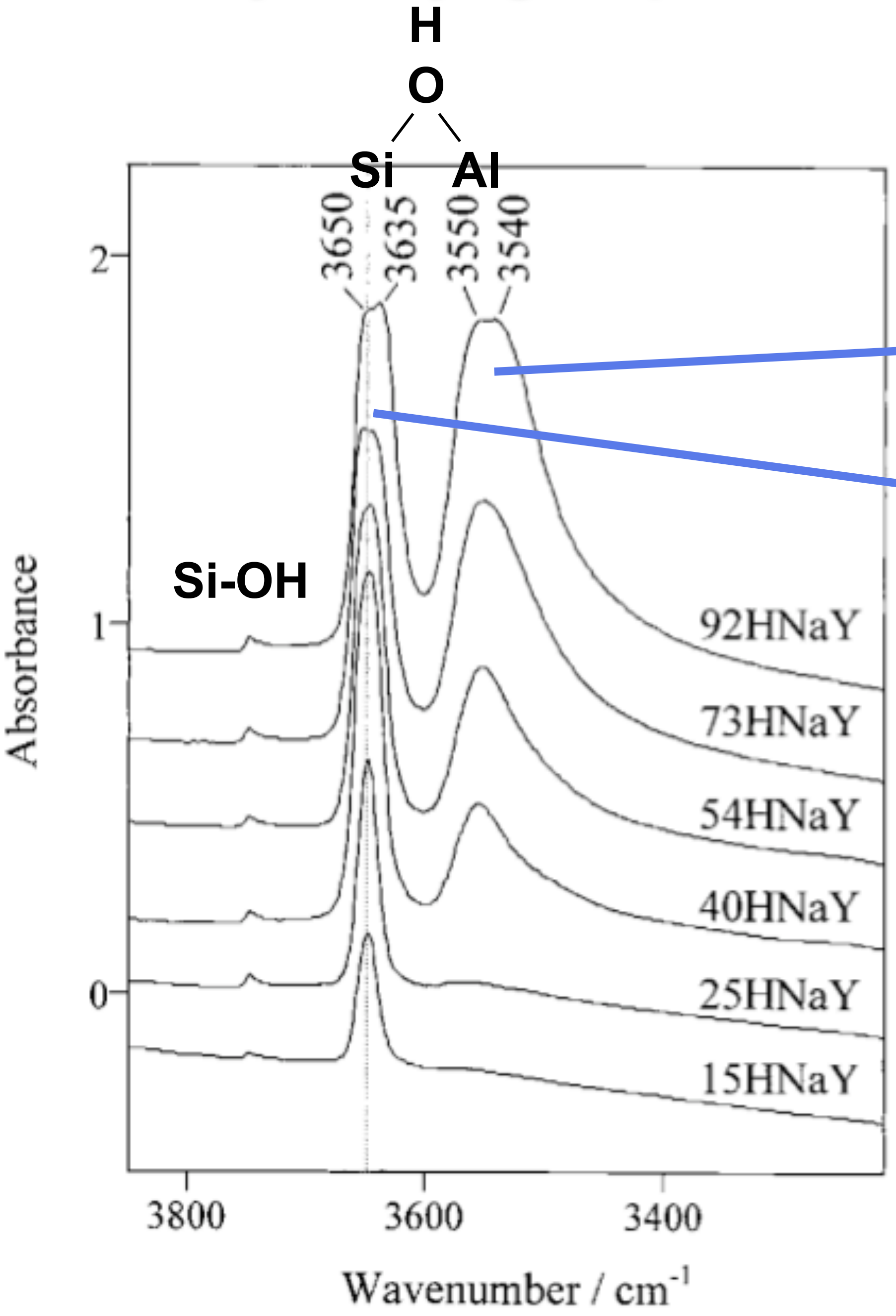
d = 5.3x5.6 Å

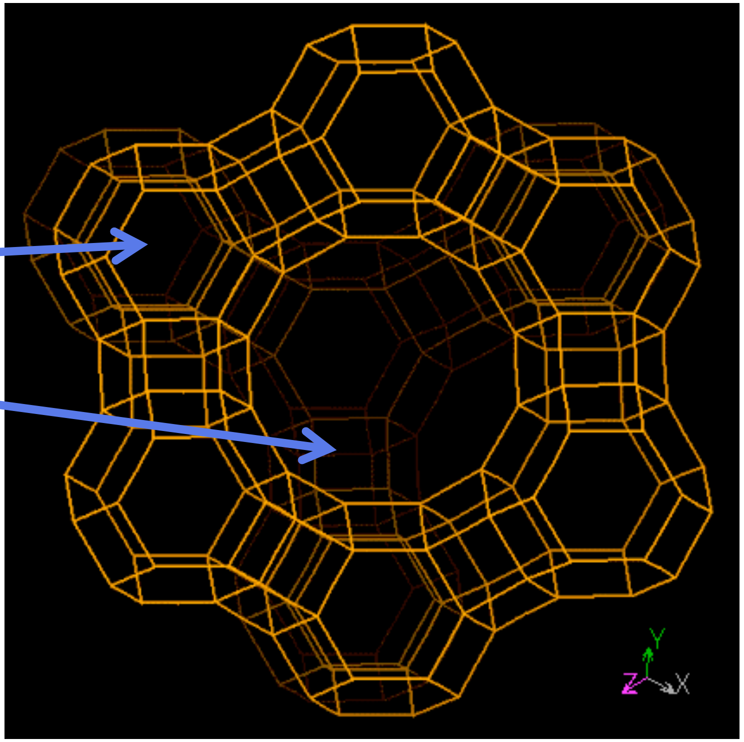
or extraframework Al^{3+}

Lewis acid sites

www.iza-structure.org/databases/

Hydroxyl groups in Y-type zeolites (FAU)

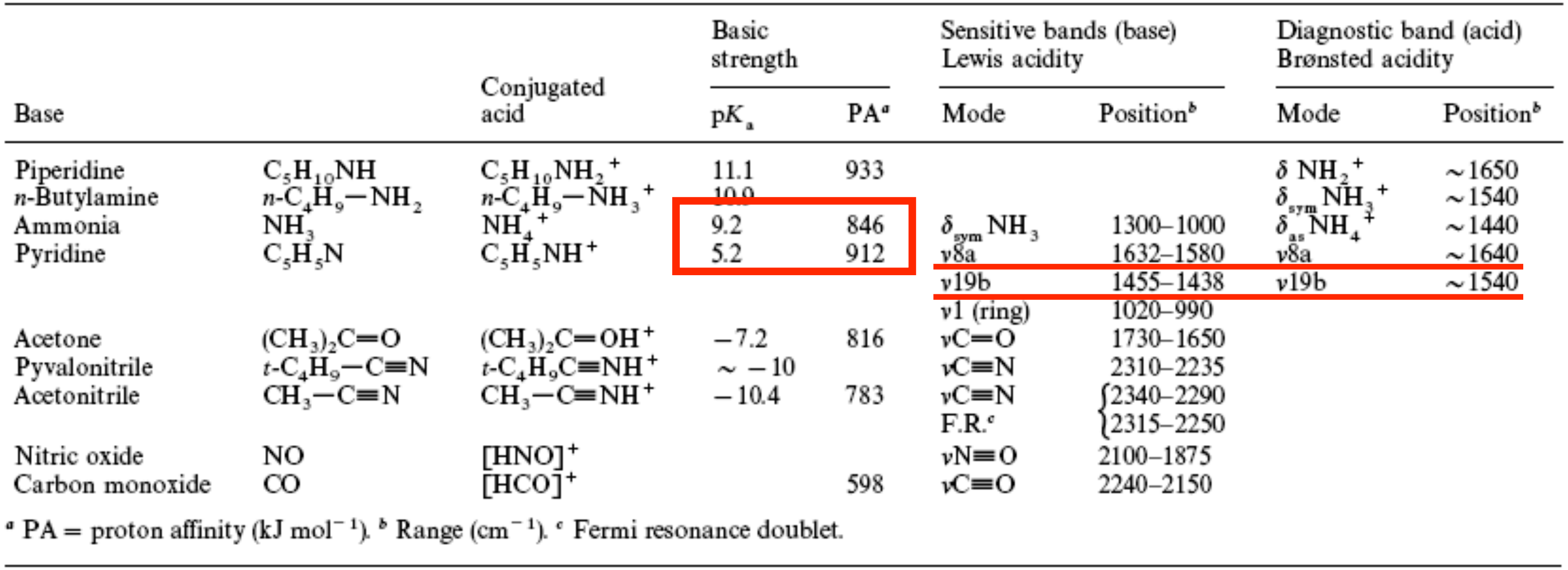




$Na_{53.3}[Al_{53.3}Si_{138.7}O_{384}]$

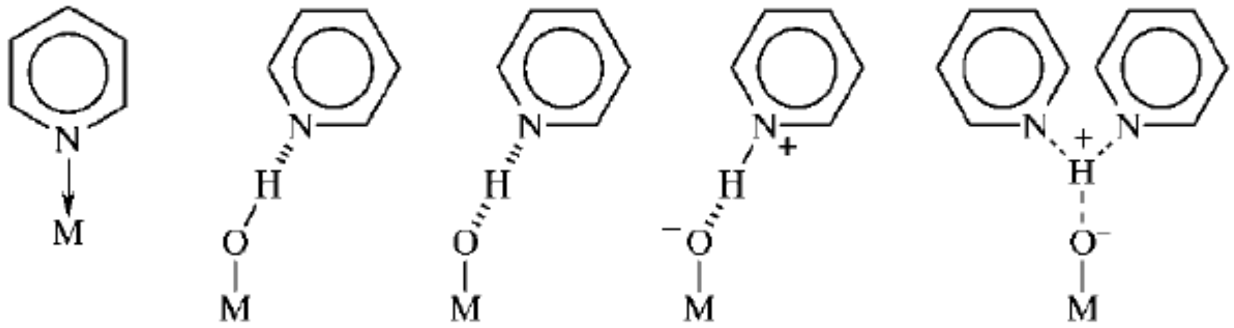
A. Trunschke, B. Hunger, Topics in Catalysis 19 (2002) 215.

FTIRS of adsorbed bases



Base		Conjugated acid	Basic strength		Sensitive bands (base) Lewis acidity		Diagnostic band (acid) Brønsted acidity	
			pK_a	PA[a]	Mode	Position[b]	Mode	Position[b]
Piperidine	$C_5H_{10}NH$	$C_5H_{10}NH_2^+$	11.1	933			δ NH_2^+	~1650
n-Butylamine	$n\text{-}C_4H_9{-}NH_2$	$n\text{-}C_4H_9{-}NH_3^+$	10.9				δ_{sym} NH_3^+	~1540
Ammonia	NH_3	NH_4^+	9.2	846	δ_{sym} NH_3	1300–1000	δ_{as} NH_4^+	~1440
Pyridine	C_5H_5N	$C_5H_5NH^+$	5.2	912	ν8a	1632–1580	ν8a	~1640
					ν19b	1455–1438	ν19b	~1540
					ν1 (ring)	1020–990		
Acetone	$(CH_3)_2C{=}O$	$(CH_3)_2C{=}OH^+$	−7.2	816	νC=O	1730–1650		
Pyvalonitrile	$t\text{-}C_4H_9{-}C{\equiv}N$	$t\text{-}C_4H_9C{\equiv}NH^+$	~ −10		νC≡N	2310–2235		
Acetonitrile	$CH_3{-}C{\equiv}N$	$CH_3{-}C{\equiv}NH^+$	−10.4	783	νC≡N	2340–2290		
					F.R.[c]	2315–2250		
Nitric oxide	NO	$[HNO]^+$			νN≡O	2100–1875		
Carbon monoxide	CO	$[HCO]^+$		598	νC≡O	2240–2150		

[a] PA = proton affinity (kJ mol^{-1}). [b] Range (cm^{-1}). [c] Fermi resonance doublet.



I II III IV V

G. Busca, PCCP 1 (1999) 723.

TPD of ammonia on Y-type zeolites (FAU)

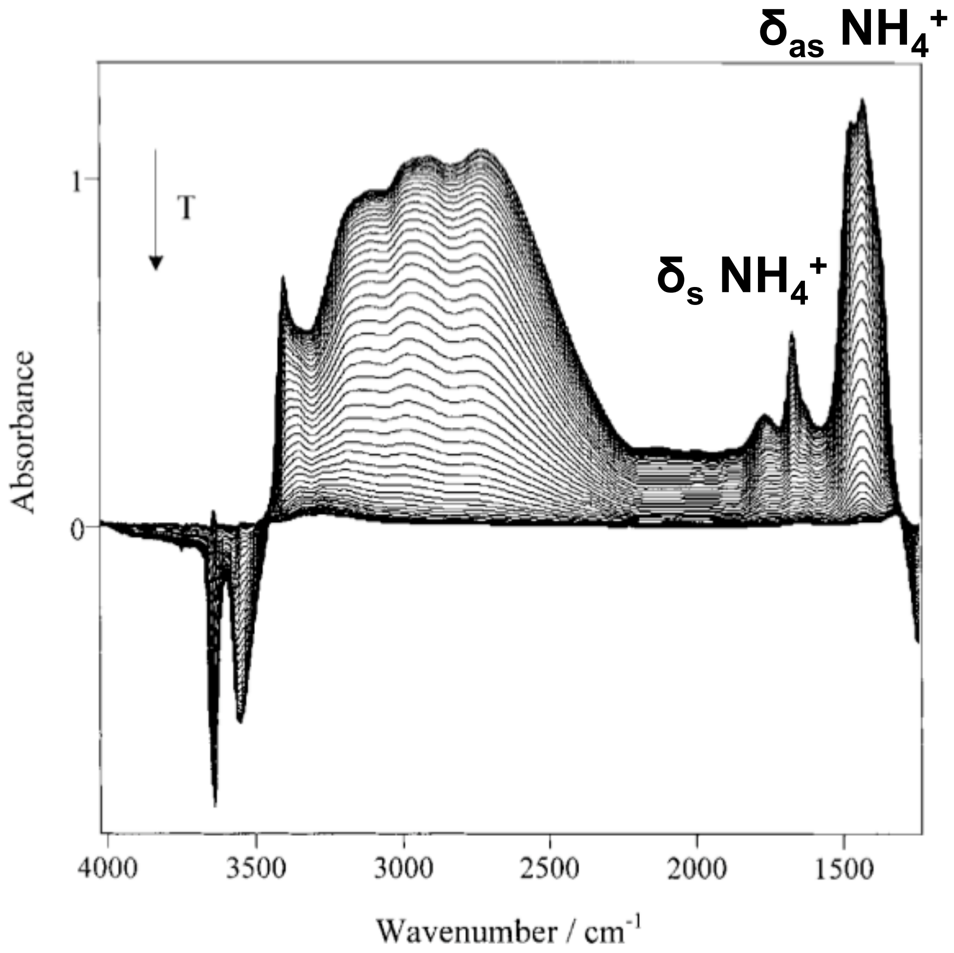


Figure 10. Spectra of 73HNaY during TPD of ammonia ($\Delta T = 5$ K).

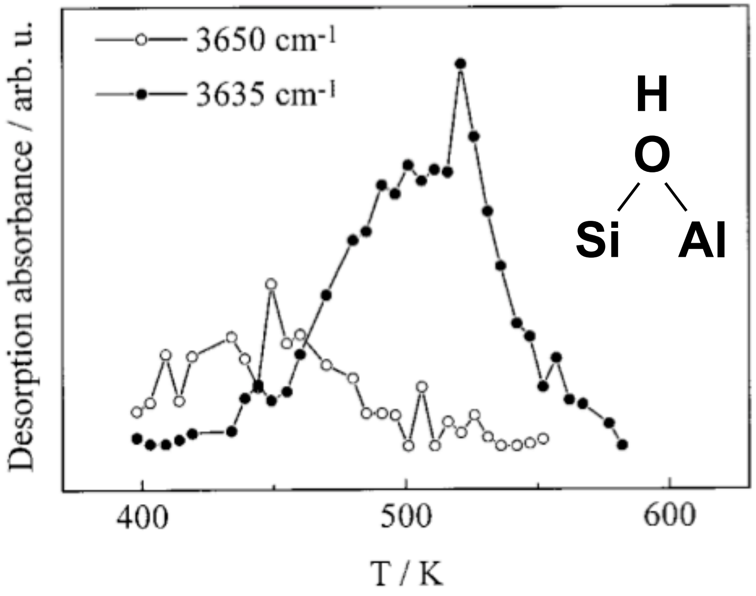
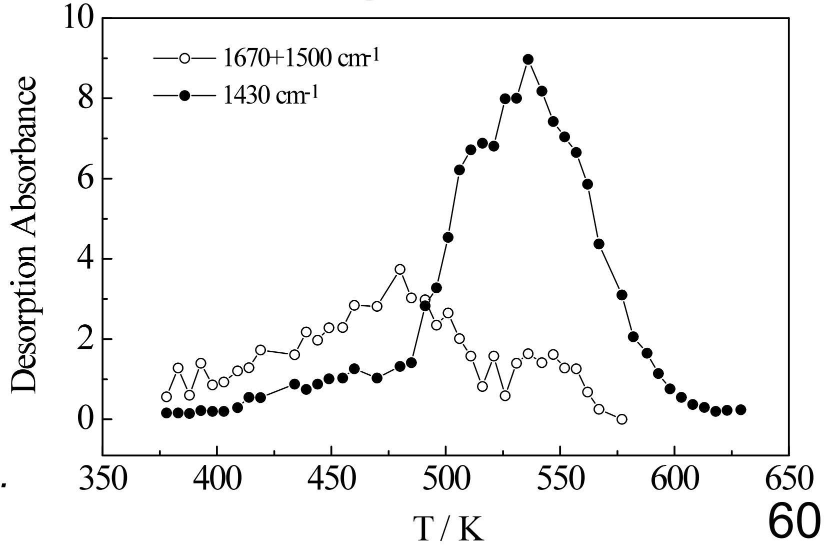


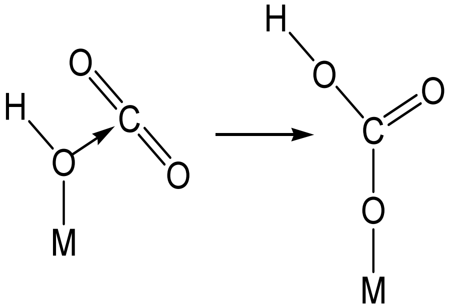
Figure 14. Desorption absorbances of the sub-bands in the region of OH stretching modes on 73HNaY.



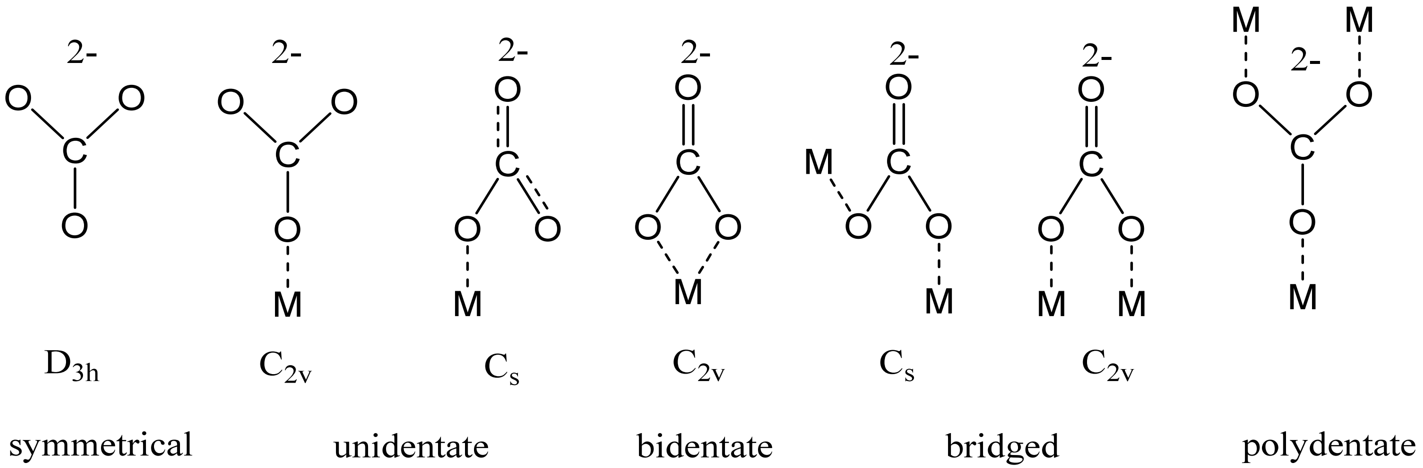
A. Trunschke, B. Hunger, Topics in Catalysis 19 (2002) 215.

CO_2 as probe for basic sites

Formation of bicarbonates by reaction of CO_2 with basic OH groups



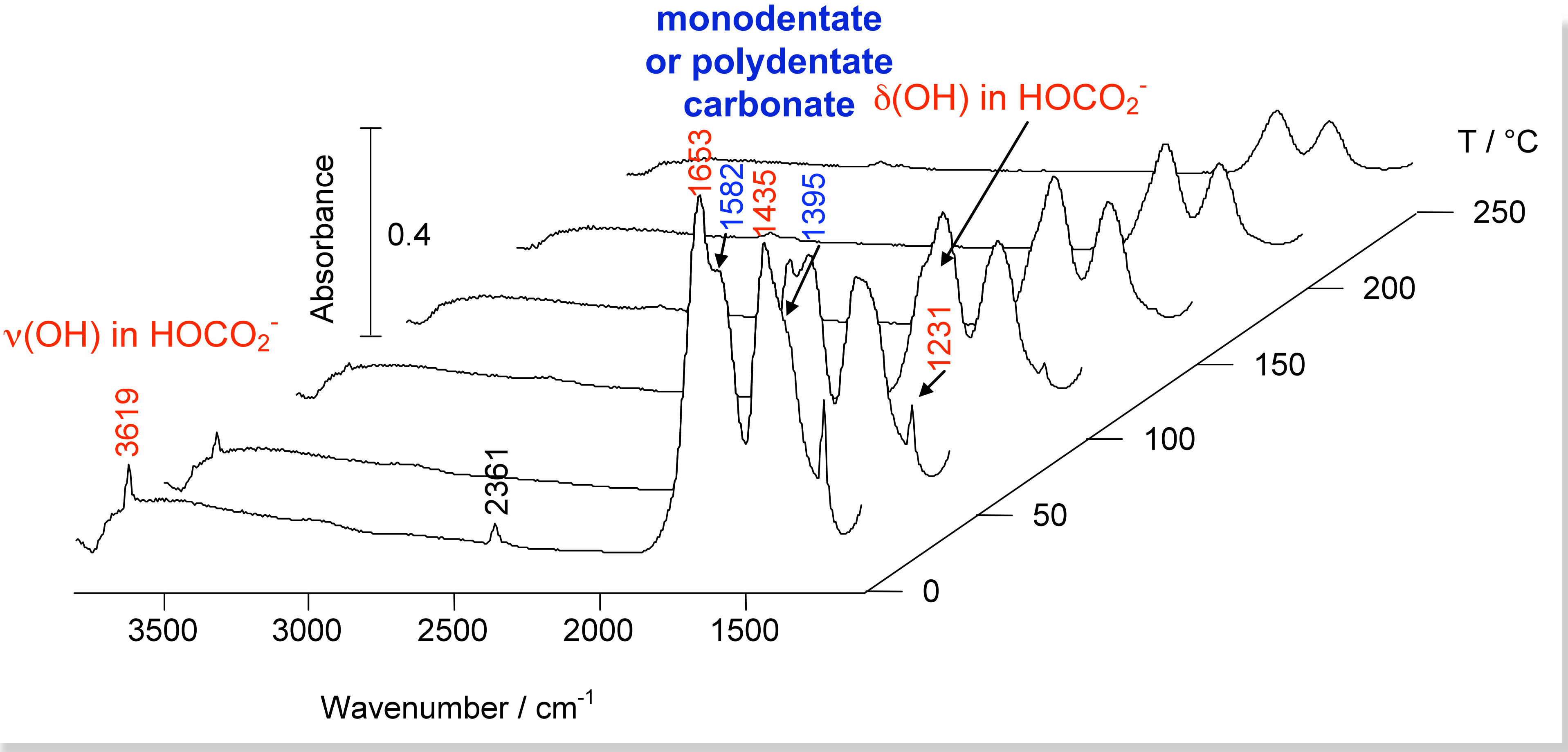
Free carbonate and surface carbonates formed by CO_2 adsorption



Other probes: e.g., SO_2, pyrrole, $CHCl_3$, CH_3CN, $B(OCH_3)_3$

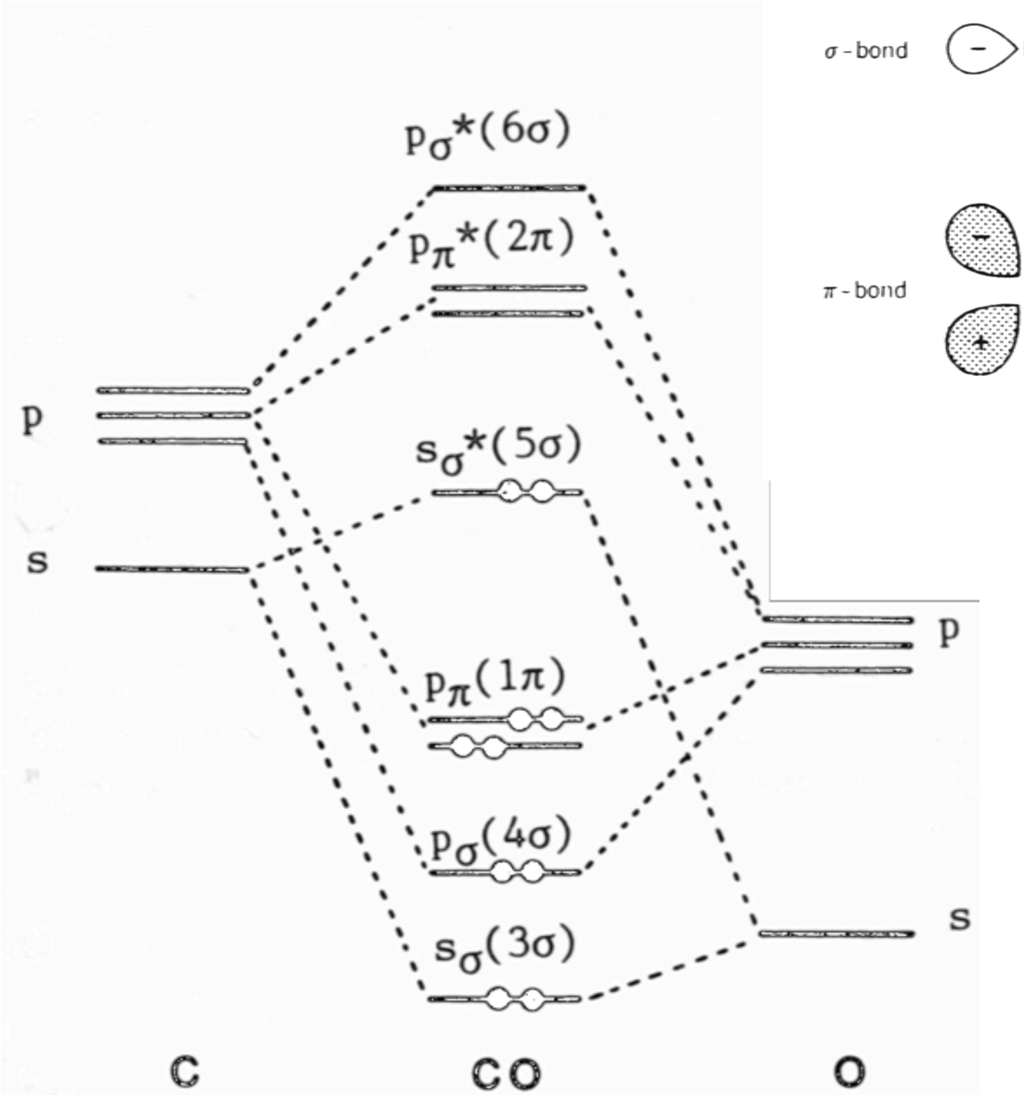
J.C. Lavalley, Catal. Today 27 (1996) 377.

CO_2 TPD



Adsorption and temperature-programmed desorption of CO_2 on MgO-Al_2O_3 (Mg/Al=0.6)

CO as probe molecule



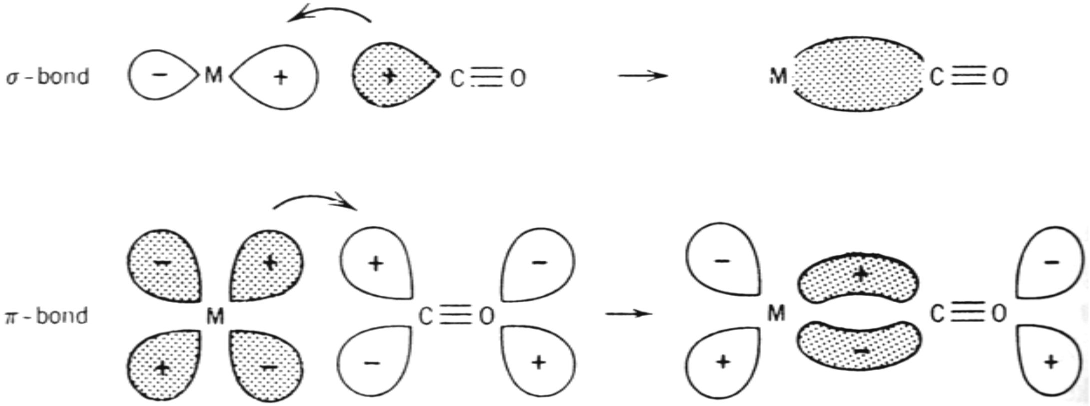


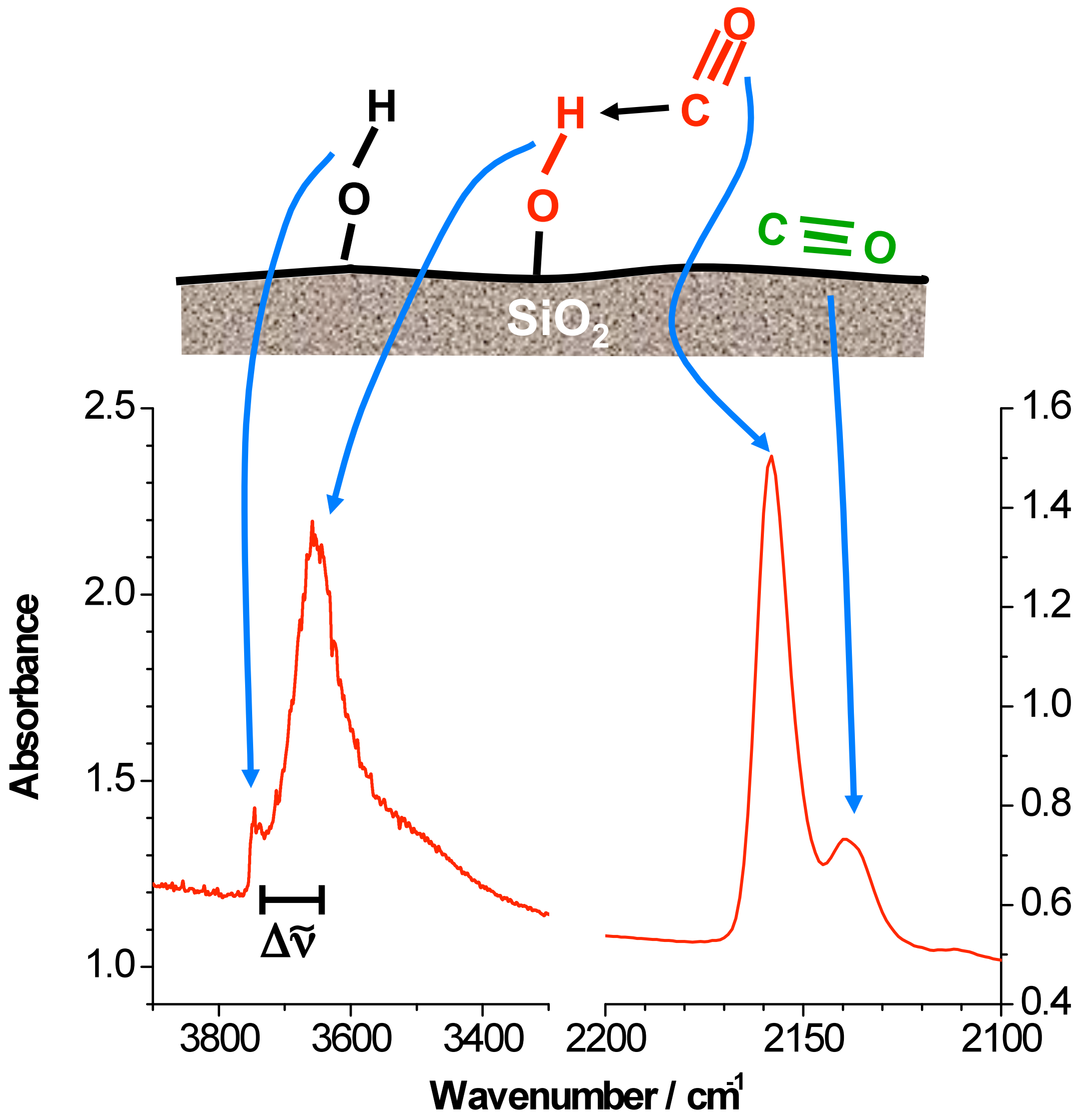
Fig. III-51. The σ- and π-bonding in metal carbonyls.

CO gas phase frequency 2143 cm^{-1}

σ-donor bond: ν↑

π-backbonding: ν↓

CO adsorption on silica



Classical approach: consider positions (shifts) of vibrational bands

Small effect: frequency shifts ≈ 10%

CO adsorption on Lewis acid sites

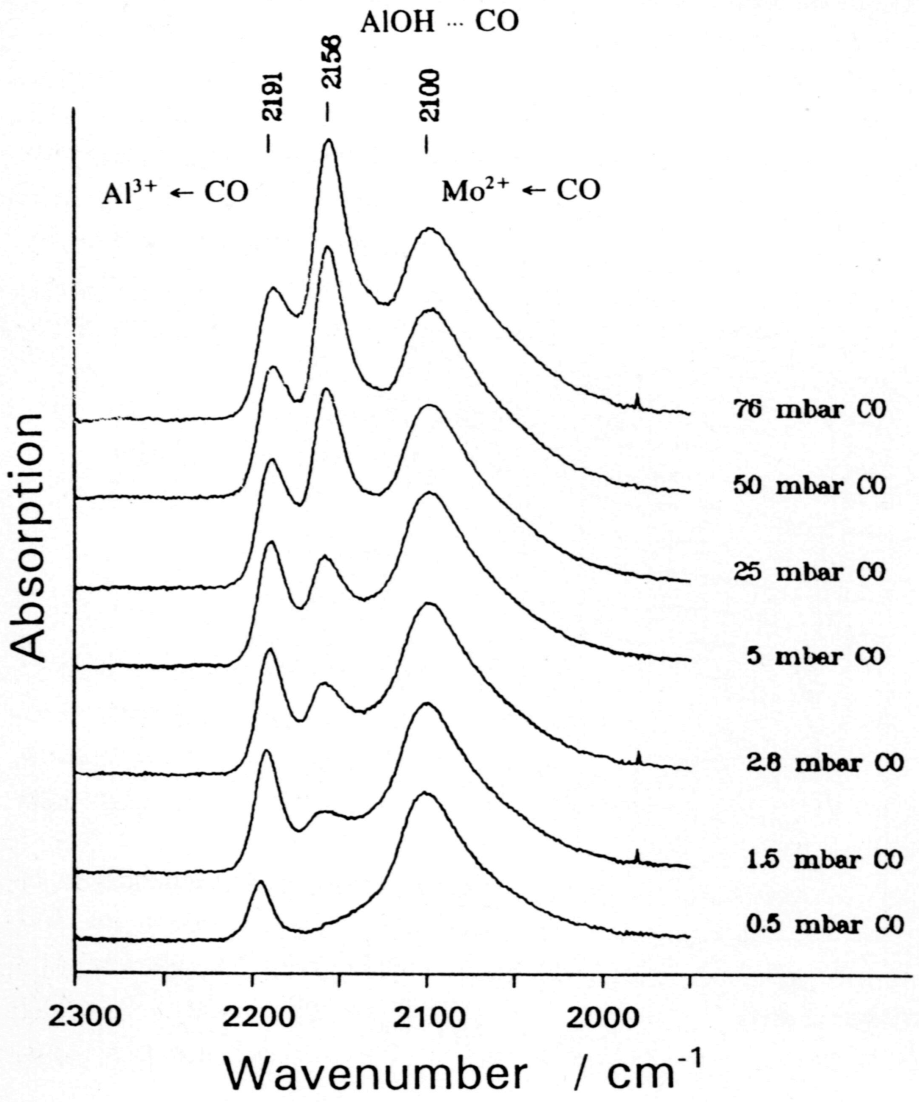


Fig. 3: Pressure dependence of carbonyl infrared spectra of CO adsorbed at 80 K on MoS_2/Al_2O_3.

H. Knözinger, Springer Series in Surface Sciences Vol. 33, Eds. E. Umbach, H.-J. Freund, Adsorption on Ordered Surface of Ionic Solids and Thin Films, Springer, Berlin, 1993, p. 257-267.

Correlation between frequency of adsorbed CO and coordination and charge of the metal cation site

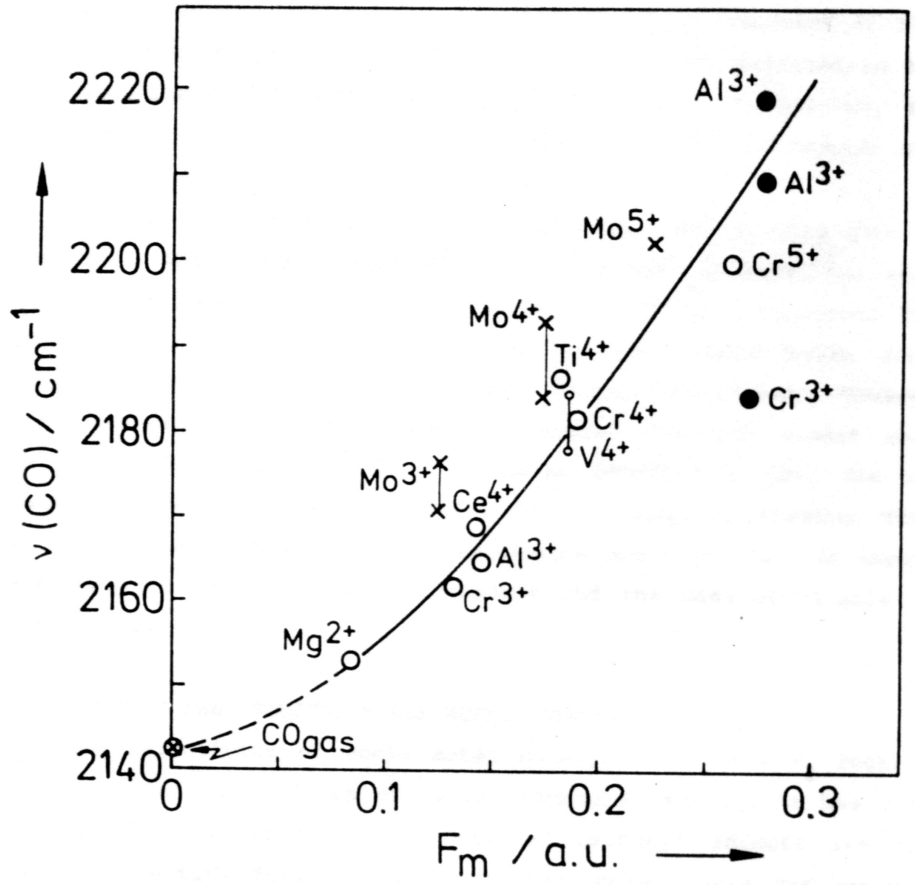


Fig. 5. Correlation of carbonyl stretching frequency of adsorbed CO with modified electric field strength F_m (equ. (v)). ○:5-coordinate ions; ●:3-coordinate ions; x:5-coordinate Mo^{x+}, supported; o:5-coordinate V, supported.

“Modified electric field strength”

$$F_m = Z/N * R_m^{-2}$$

Z: cation charge

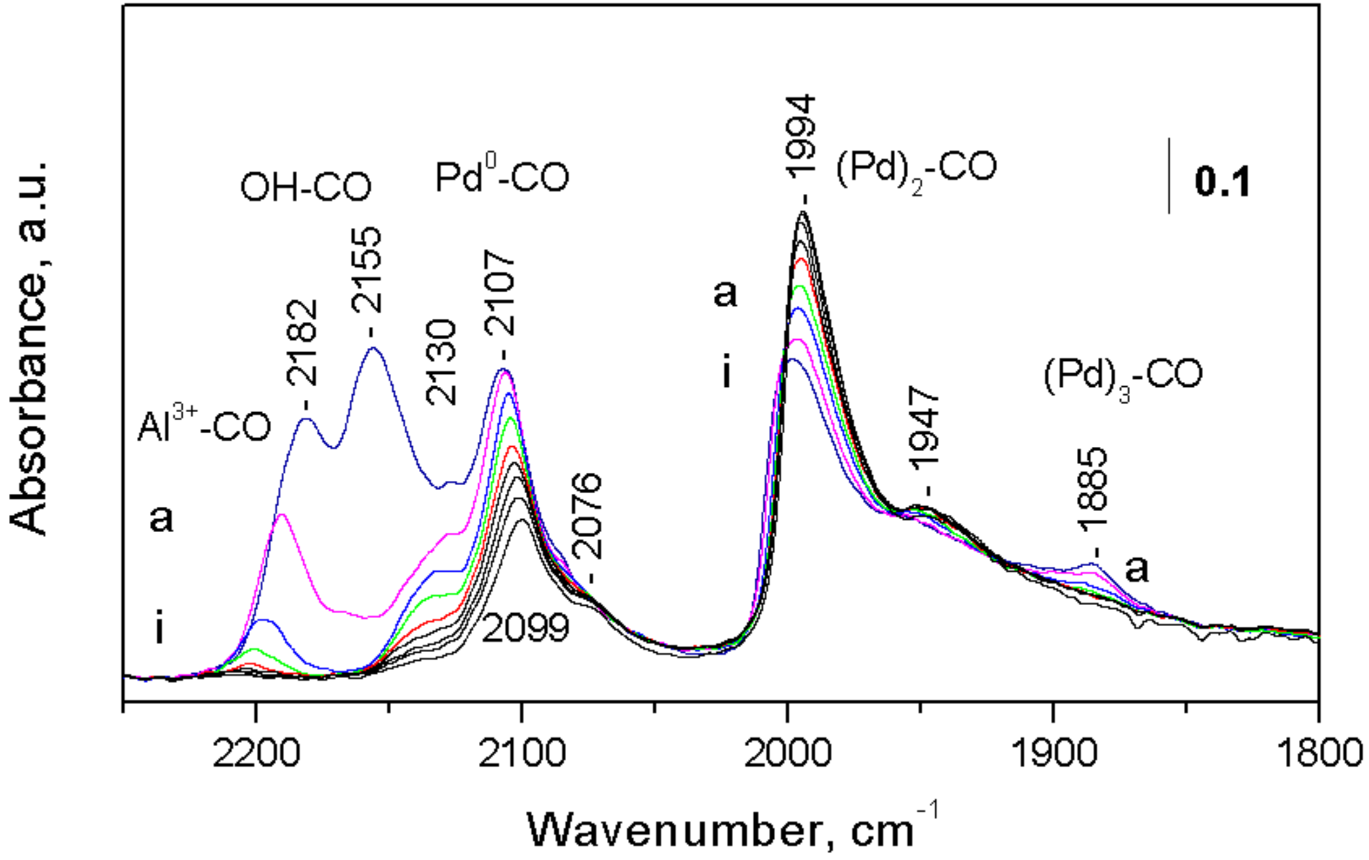
N: coordination number in cus state

R_m: sum of effective ionic radius and van der Waals radius

H. Knözinger, Proc. Int. Symp. Acid-Base Catalysis Sapporo 1988
Eds. K. Tanabe, H. Hattori, T. Yamaguchi, T. Tanaka

CO adsorption sites on metal particles

Activation - evacuation at 400 deg for 1h



Adsorption of CO on Pd/Al_2O_3 at 77 K: adsorption of 1 mbar CO at 77 K (a), evacuation at LT (b-f), evac. at 106 K (g), 110 K (h), 124 K (i)

Further reading

1. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Sixth Edition, Part A, John Wiley & Sons, Hoboken, New Jersey, 2009.
2. K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Sixth Edition, Part B, John Wiley & Sons, Hoboken, New Jersey, 2009.
3. A. Davydov, Molecular Spectroscopy of Oxide Catalyst Surfaces, John Wiley & Sons, Chinchester, England, 2003.
4. H. Günzler, H.-U. Gremlich, IR Spektroskopie, Eine Einführung, Wiley-VCH, Weinheim, 2003.
5. J.W. Niemantsverdriet, Spectroscopy in Catalysis, An Introduction, Wiley-VCH, Weinheim, 2000.
6. G. Kortüm, “Reflectance Spectroscopy” / “Reflexionsspektroskopie” Springer 1969.

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Thank you for your attention