Heterogeneous catalysis

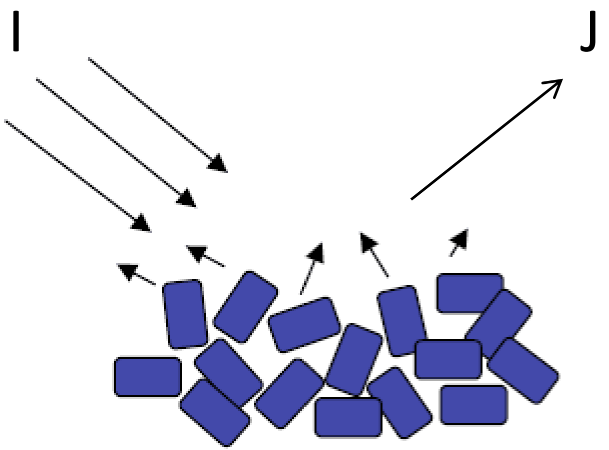
Lecture 5

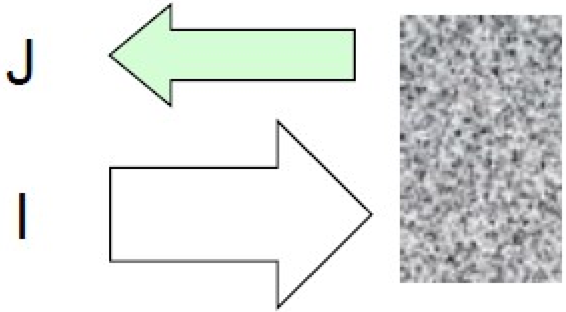
Catalysts characterization

Catalyst characterization

- Outline
  - DRUV
  - **XPS**
  - XANES & EXAFS
  - **Chemisorption**
  - **ToF-SIMS**

Diffuse reflectance UV-Vis spectroscopy (DRUV)



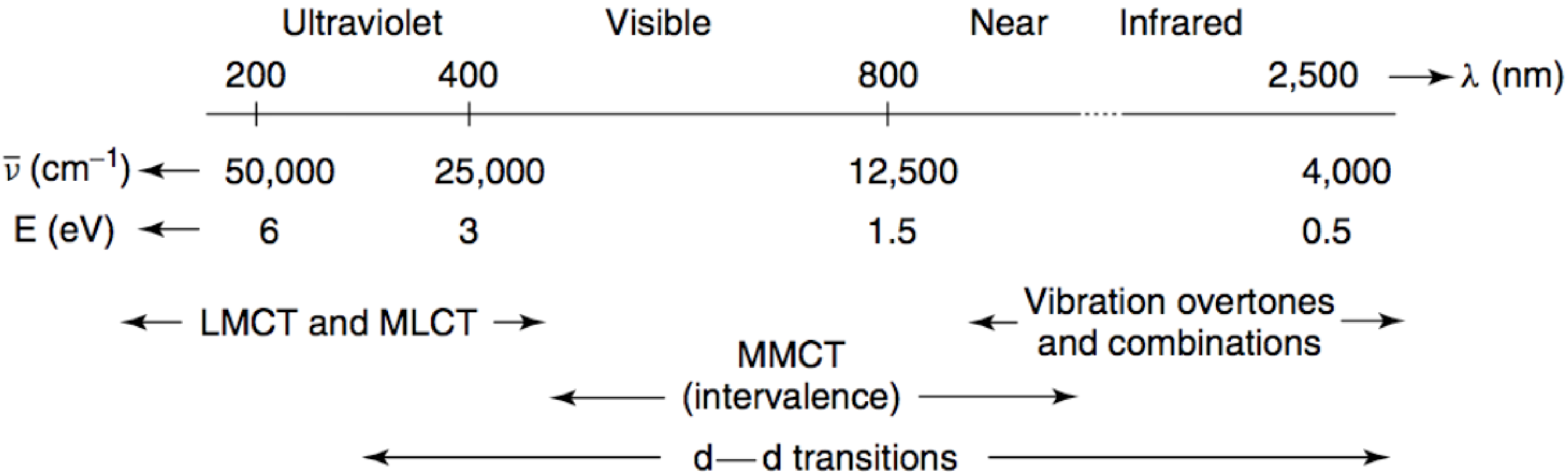


$$R = \frac{J}{I}$$

R...reflectance

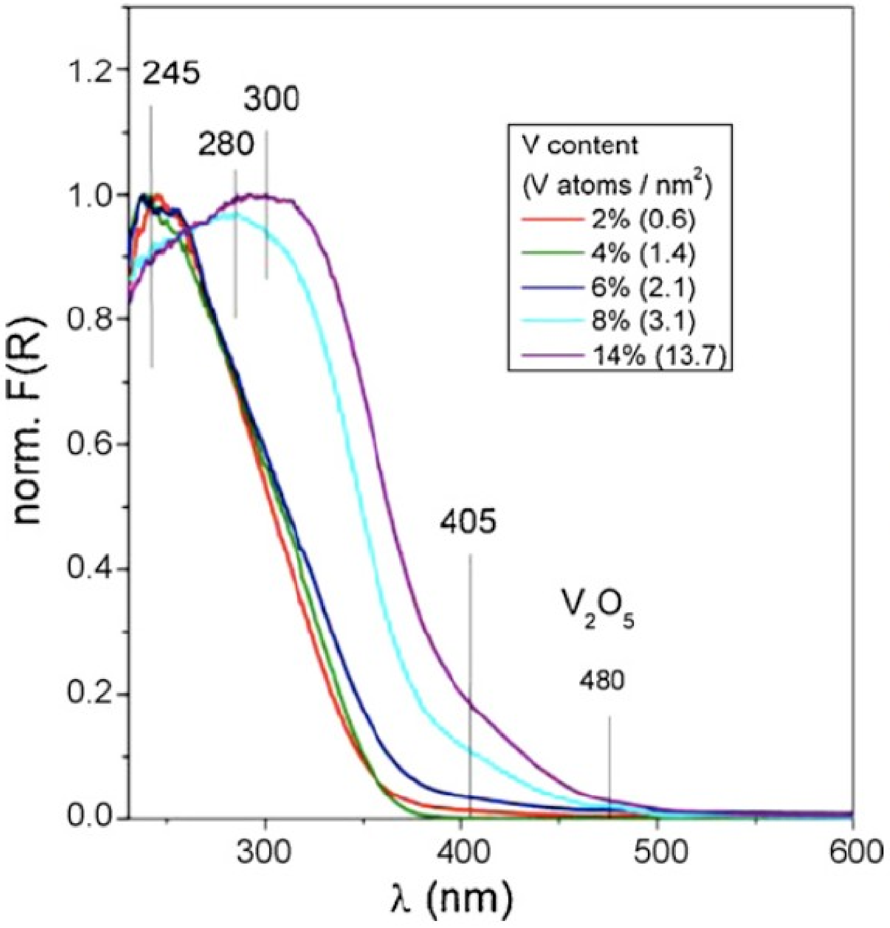
- Is there any link between reflectance and absorbance?
- Yes, there is!
- **Kubelka-Munk model** allows to obtain **quantitatively** the **absorption spectrum** of a solid from diffuse reflectance measurement (theory behind in textbooks)

Diffuse reflectance UV-Vis spectroscopy (DRUV)



- LMCT = ligand-to-metal charge transfer
- MLCT = metal-to-ligand charge transfer
- MMCT = metal-to-metal charge transfer

Diffuse reflectance UV-Vis spectroscopy (DRUV)



Isolated and polymerized V_xO_y ?

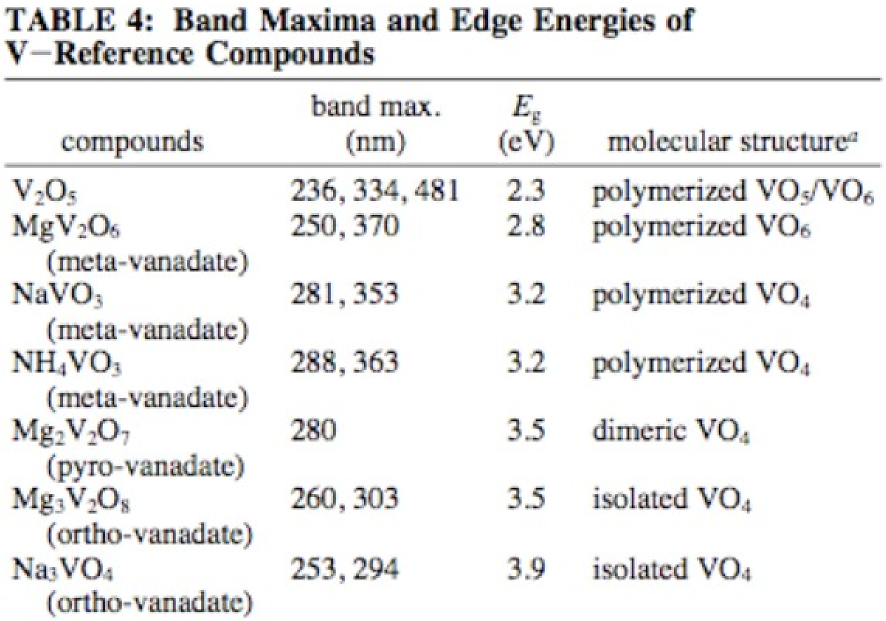
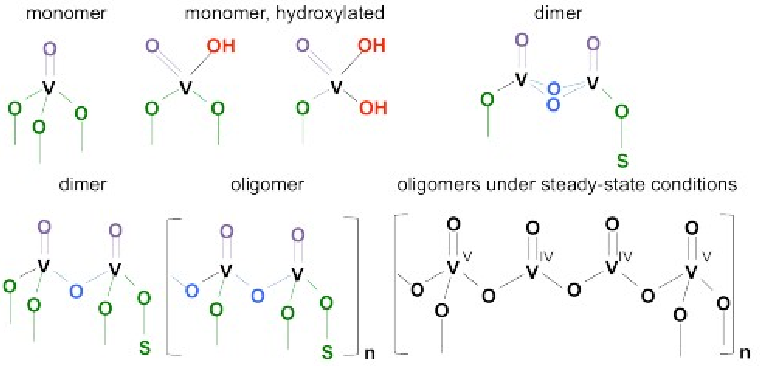


TABLE 4: Band Maxima and Edge Energies of V−Reference Compounds

compounds	band max. (nm)	E_g (eV)	molecular structure[a]
V_2O_5	236, 334, 481	2.3	polymerized VO_5/VO_6
MgV_2O_6 (meta-vanadate)	250, 370	2.8	polymerized VO_6
$NaVO_3$ (meta-vanadate)	281, 353	3.2	polymerized VO_4
NH_4VO_3 (meta-vanadate)	288, 363	3.2	polymerized VO_4
$Mg_2V_2O_7$ (pyro-vanadate)	280	3.5	dimeric VO_4
$Mg_3V_2O_8$ (ortho-vanadate)	260, 303	3.5	isolated VO_4
Na_3VO_4 (ortho-vanadate)	253, 294	3.9	isolated VO_4

Gao et al., J. Phys. Chem. B 102 (1998) 10842.



Ionization Spectroscopies

Photoelectron spectroscopy:

UV: valence shell ionizations

X-ray: core electron ionizations

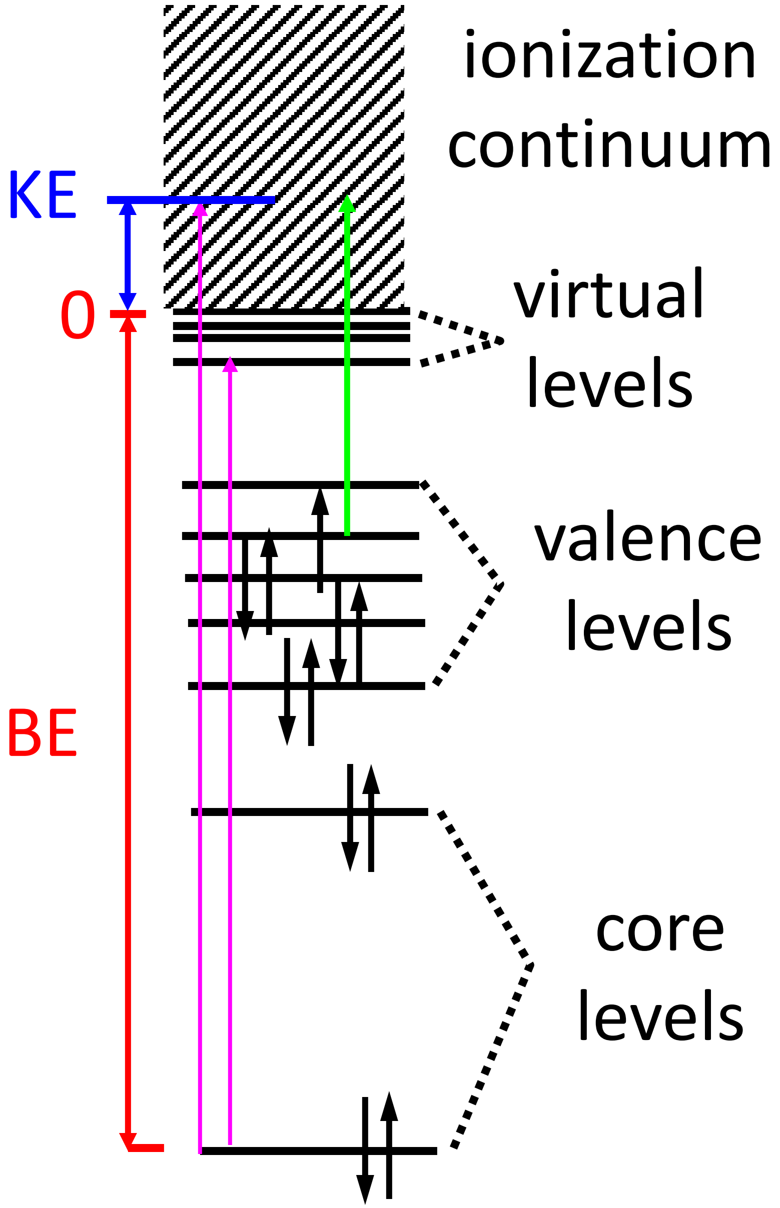
(XPS, XANES, EXAFS):

$E_{\text{photon}} = h\nu =$

BE + kinetic energy (KE)

Photoelectron Spectroscopy analyzes the energies of the ionized electrons **(XPS)**.

X-ray Absorption Spectroscopy analyzes the absorption curve of the X-ray spectrum associated with ionization of a core electron **(XANES and EXAFS)**



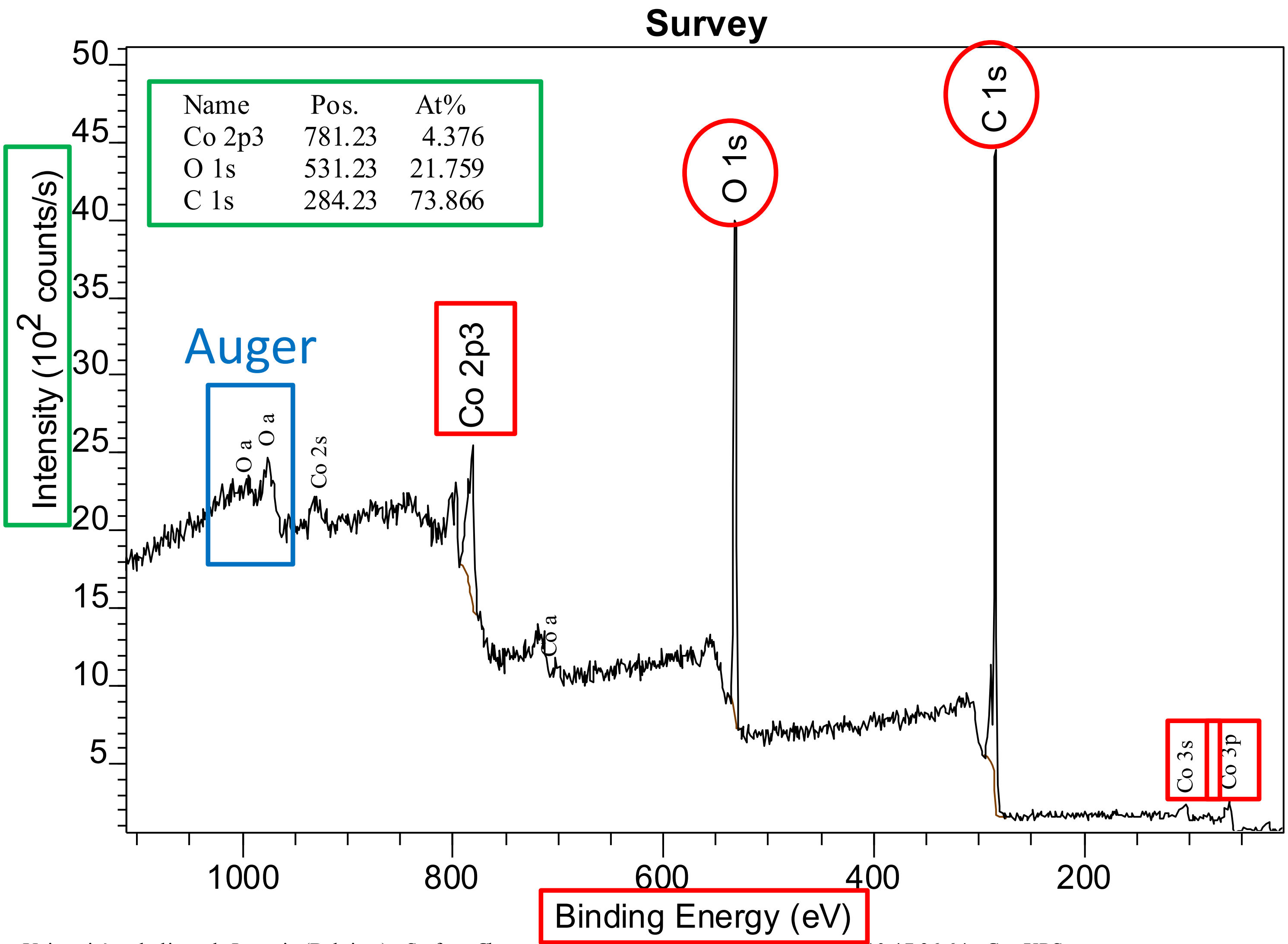
X-ray photoelectron spectroscopy (XPS)

We measure the number and the energy of photoelectrons emitted from the surface layer

$$E_{photon} = h\nu = BE + \text{kinetic energy } (KE)$$

- Number of photoelectrons gives access to quantity
- Energy of photoelectrons gives access to quality
- Depth? 5–20 nm.

X-ray photoelectron spectroscopy (XPS)

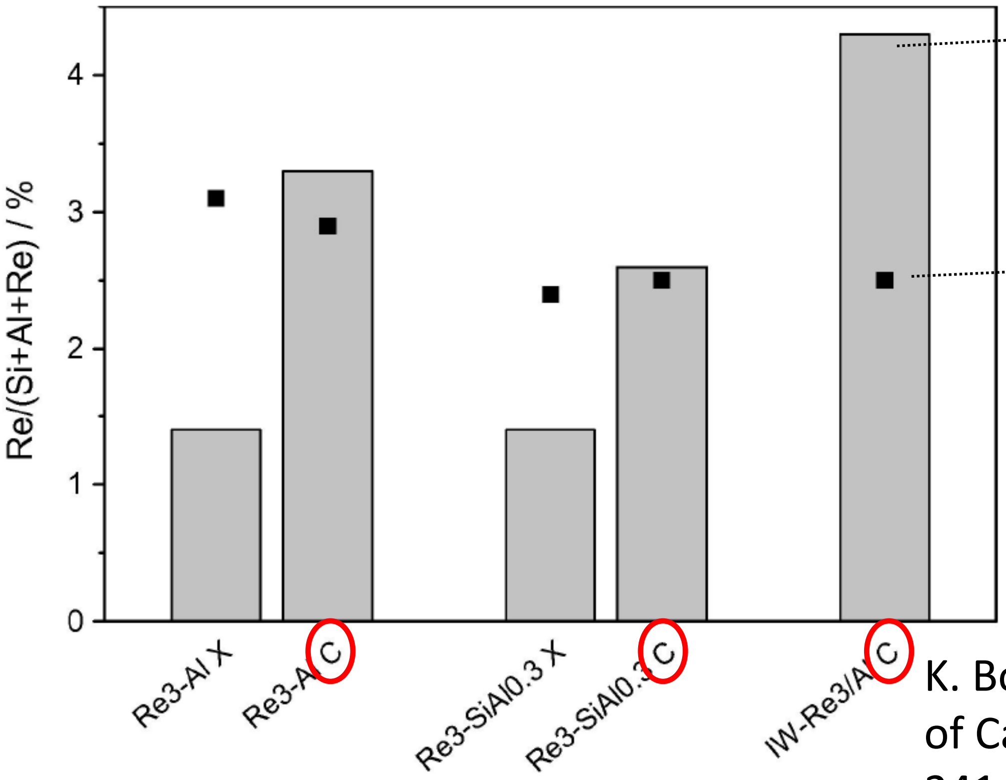


Name	Pos.	At%
Co 2p3	781.23	4.376
O 1s	531.23	21.759
C 1s	284.23	73.866

Université catholique de Louvain (Belgium) - Surface Characterisation platform (SUCH) Tel +32 (0)10 47 36 64 - CasaXPS

X-ray photoelectron spectroscopy (XPS)

- Surface vs. bulk composition



Surface

Bulk

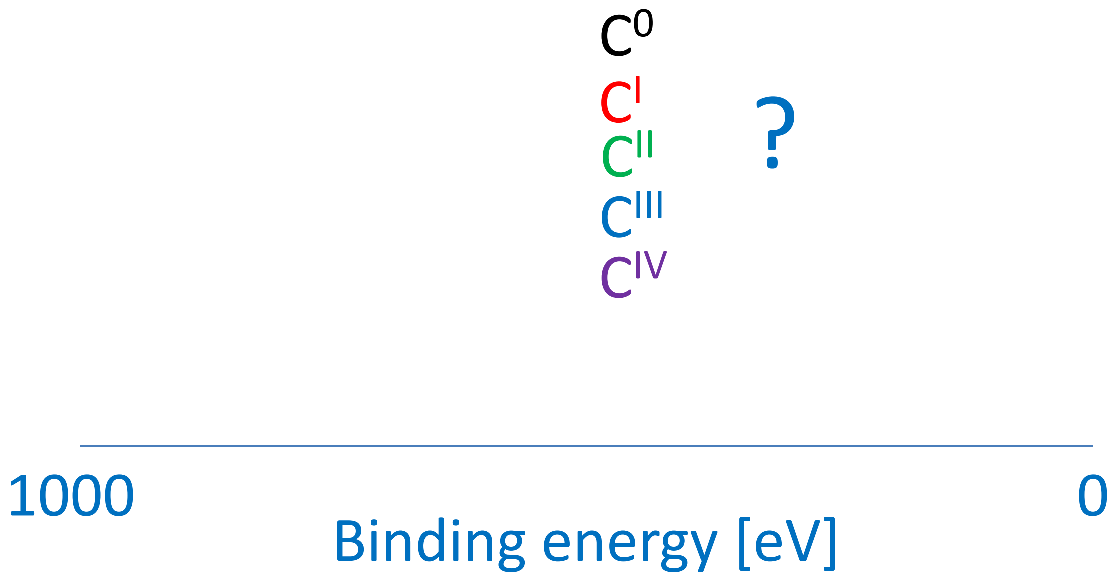
Calcination

K. Bouchmella et al. /Journal of Catalysis 301 (2013) 233–241

Figure 6. Surface Re/(Si + Al + Re) atomic ratios (XPS, gray bars) and bulk Re/(Si + Al + Re) atomic ratios (EDX, black squares) for xerogels and calcined catalysts. Reproduced with permission from [177]. Copyright Elsevier, 2013.

X-ray photoelectron spectroscopy (XPS)

- Oxidation state



C^{0}

C^{I}

C^{II}

C^{III}

C^{IV}

?

1000

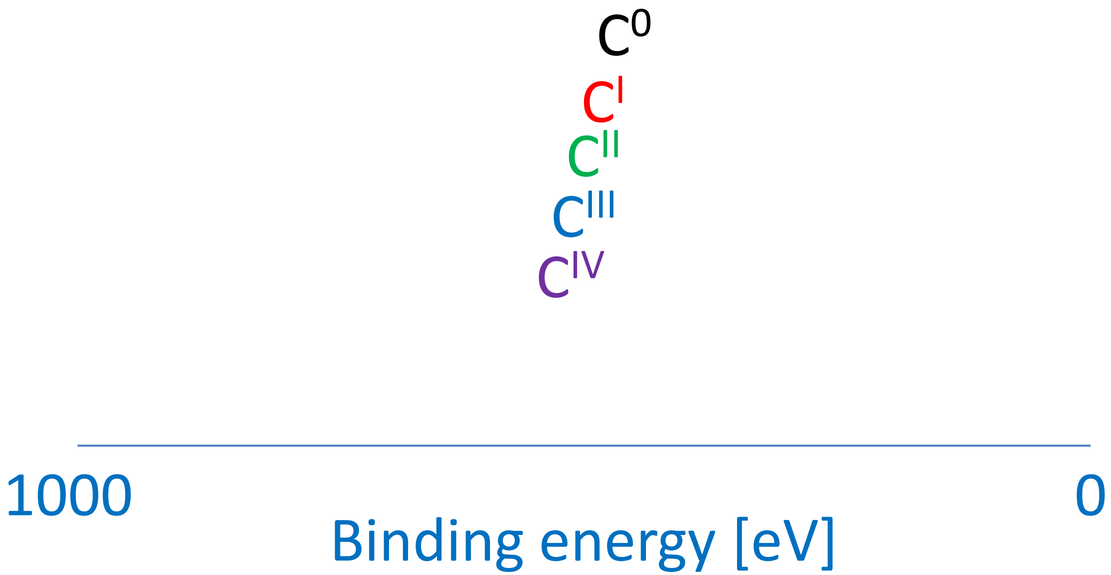
0

Binding energy [eV]

- Who will hold its electrons more powerfully? C^{0} or C^{IV}?

X-ray photoelectron spectroscopy (XPS)

- Oxidation state



C^0

C^I

C^{II}

C^{III}

C^{IV}

1000

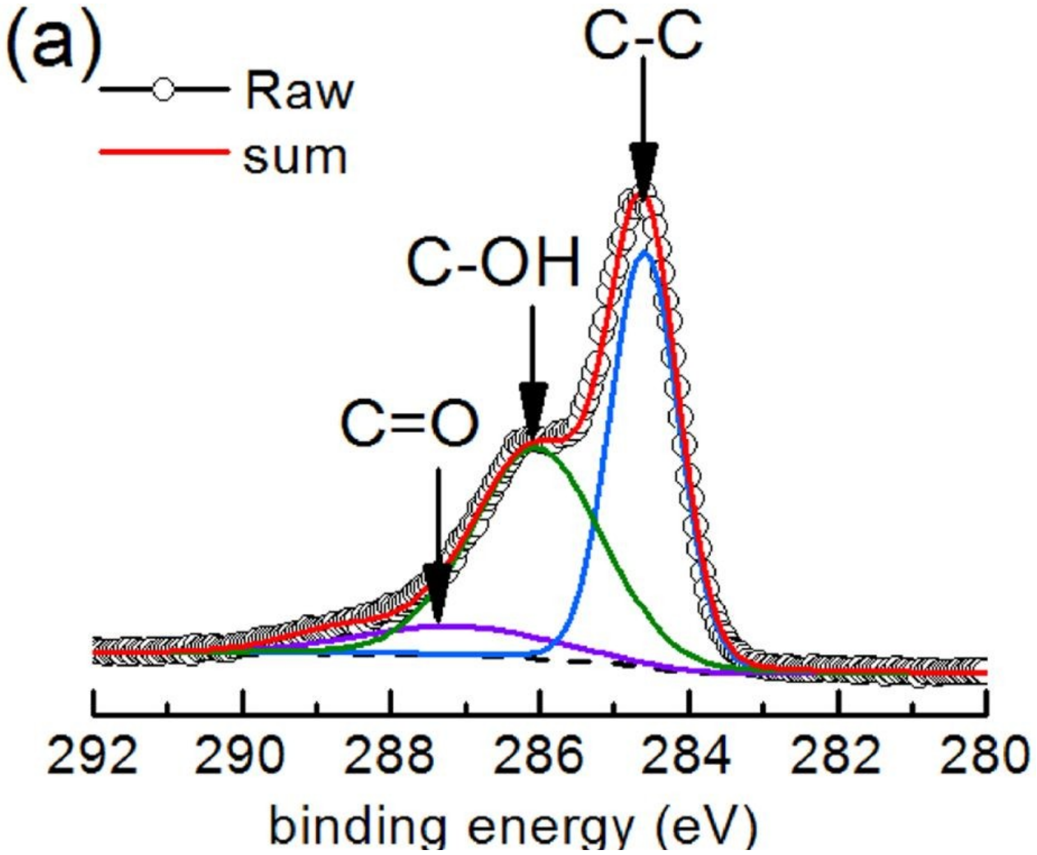
0

Binding energy [eV]

- Why do we talk about carbon?
- **Surface of each sample** contains some carbon impurities = **Adventitious carbon** = **calibration of BE**

X-ray photoelectron spectroscopy (XPS)

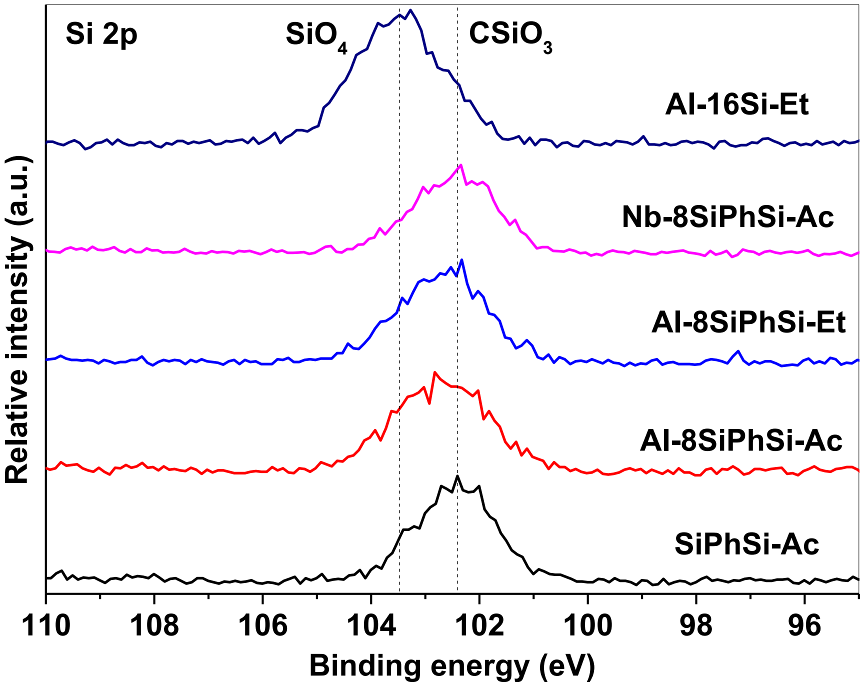
- Oxidation state



X-ray photoelectron spectroscopy (XPS)

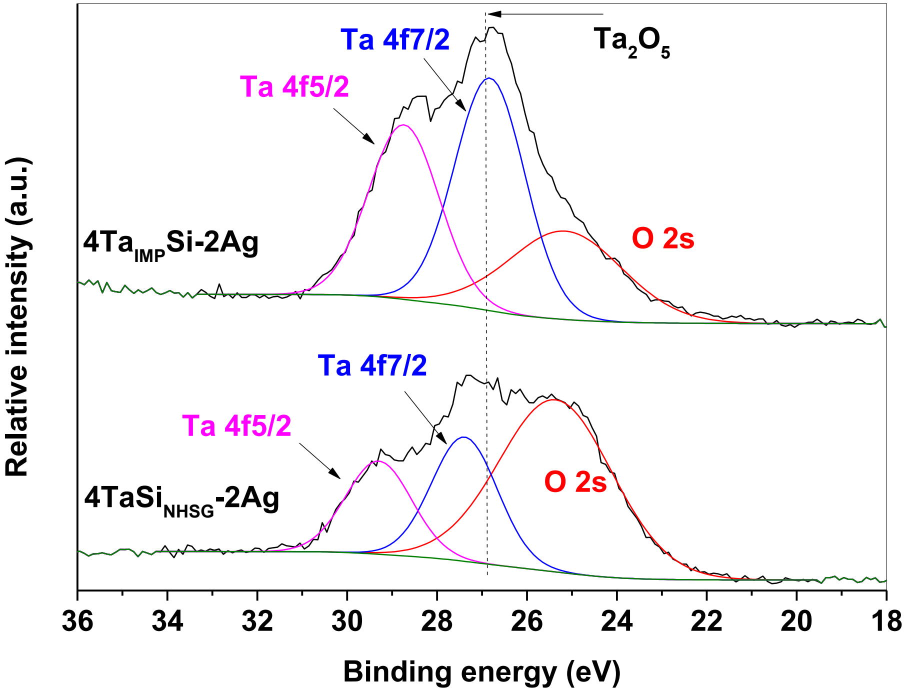
- Similar consideration:

SiO_4 vs. $CSiO_3$



Electronegativity (O) =
Electronegativity (C) =

$Ta(OSi)_x(OTa)_{6-x}$ vs. $Ta(OTa)_6$

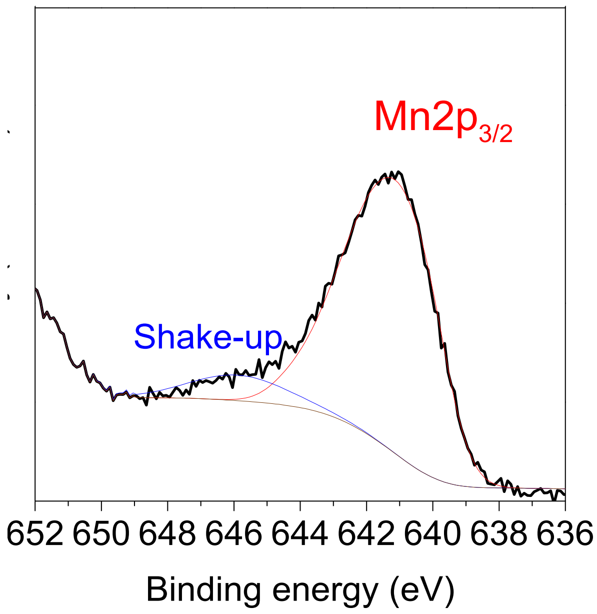


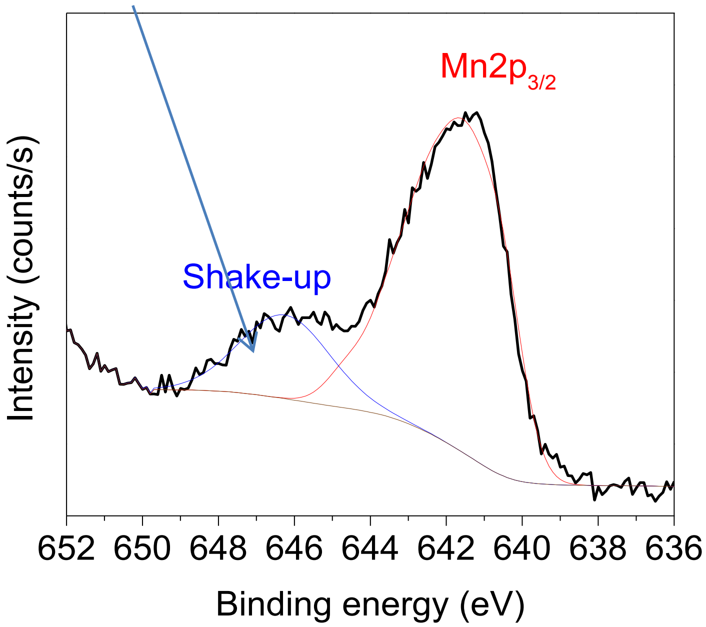
Electronegativity (Si) =
Electronegativity (Ta) =

X-ray photoelectron spectroscopy (XPS)

- Spin-orbital interaction and other electron interactions lead to additional features in XP spectra characteristic for
  - Oxidation states
  - Groups
  - …

Characteristic for Mn^{2+}

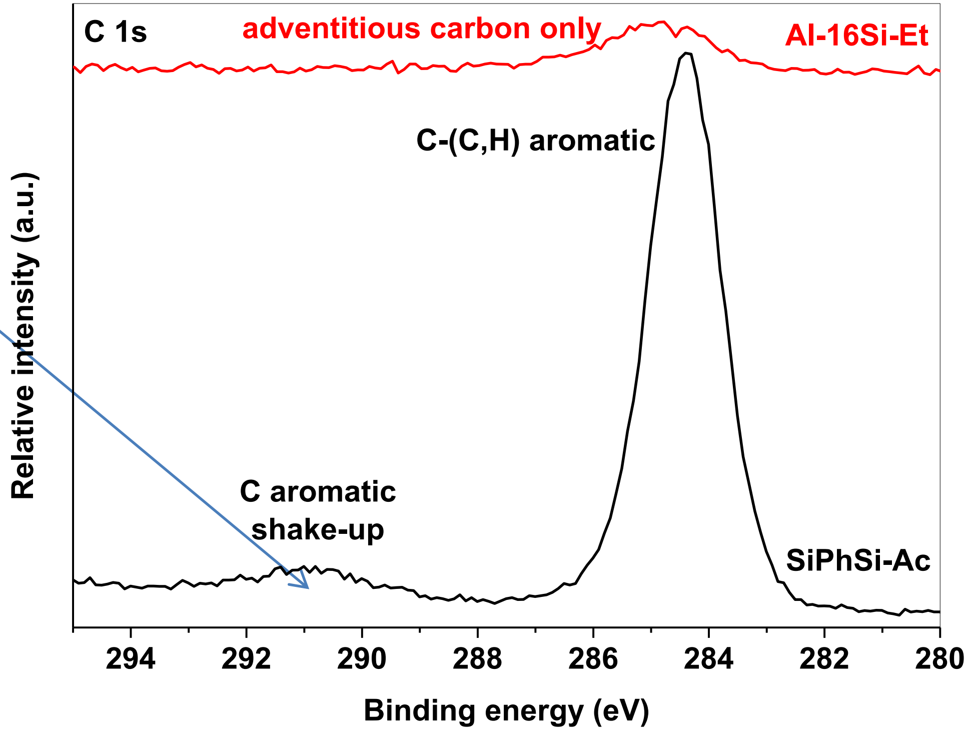




X-ray photoelectron spectroscopy (XPS)

- Spin-orbital interaction and other electron interactions lead to additional features in XP spectra characteristic for
  - Oxidation states
  - Groups
  - …

Characteristic for aromatic carbon



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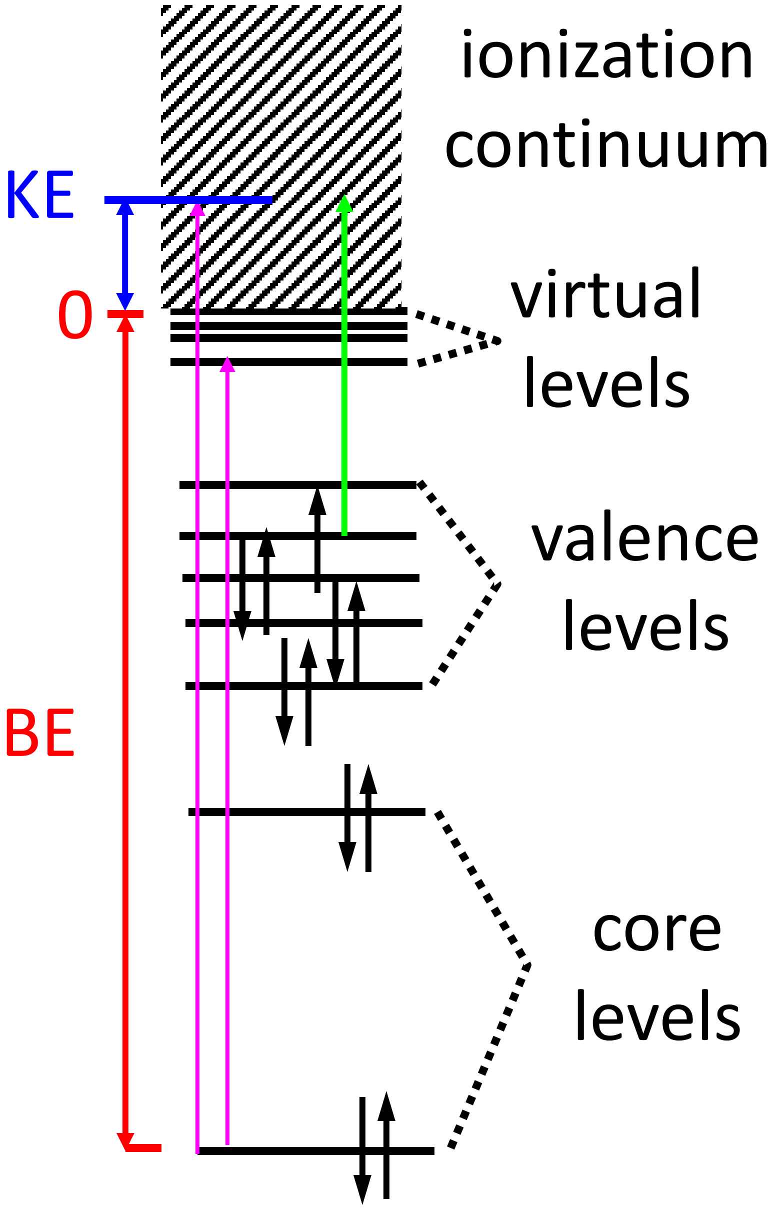
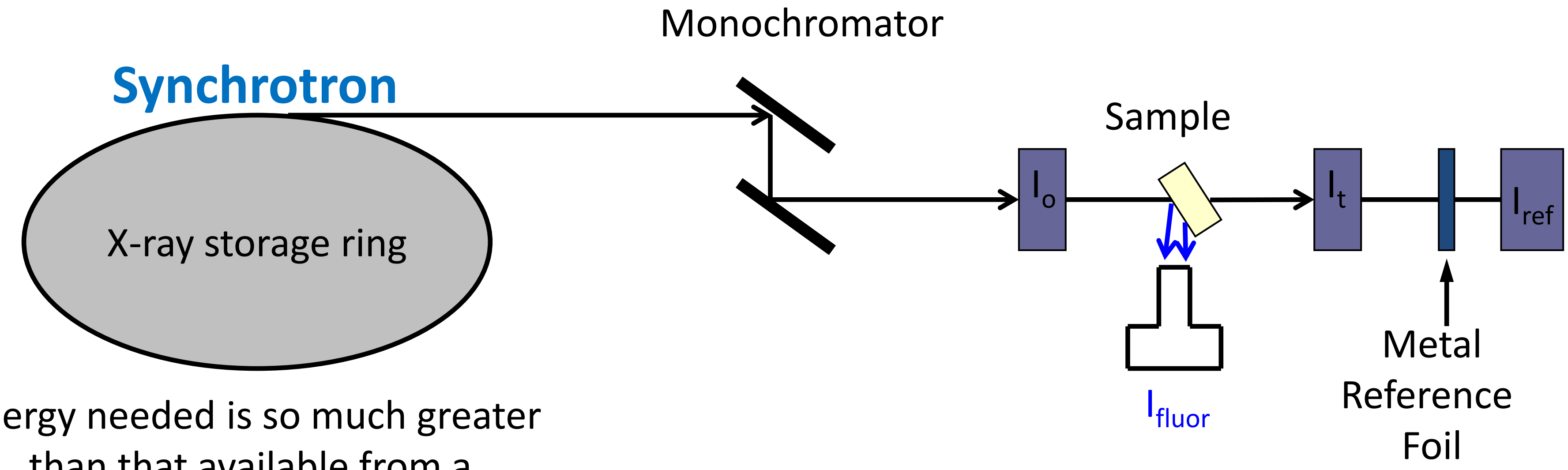


XANES and EXAFS

In XANES and EXAFS we measure number and energy of transmitted photons, which caused ionization of a core electron

(i.e. absorbance vs. energy)



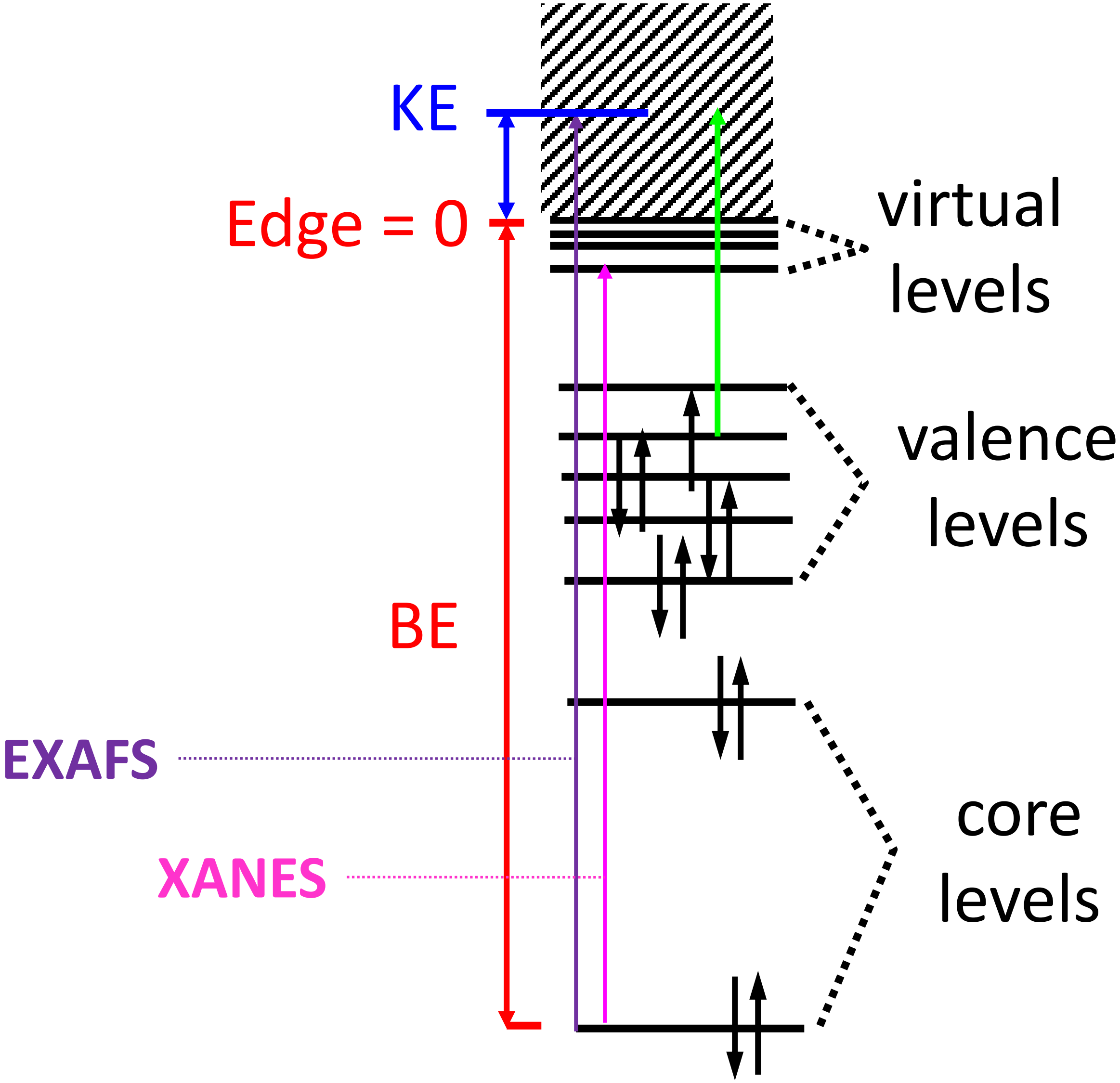
Energy needed is so much greater
than that available from a
typical X-ray tube found in most labs

XANES and EXAFS

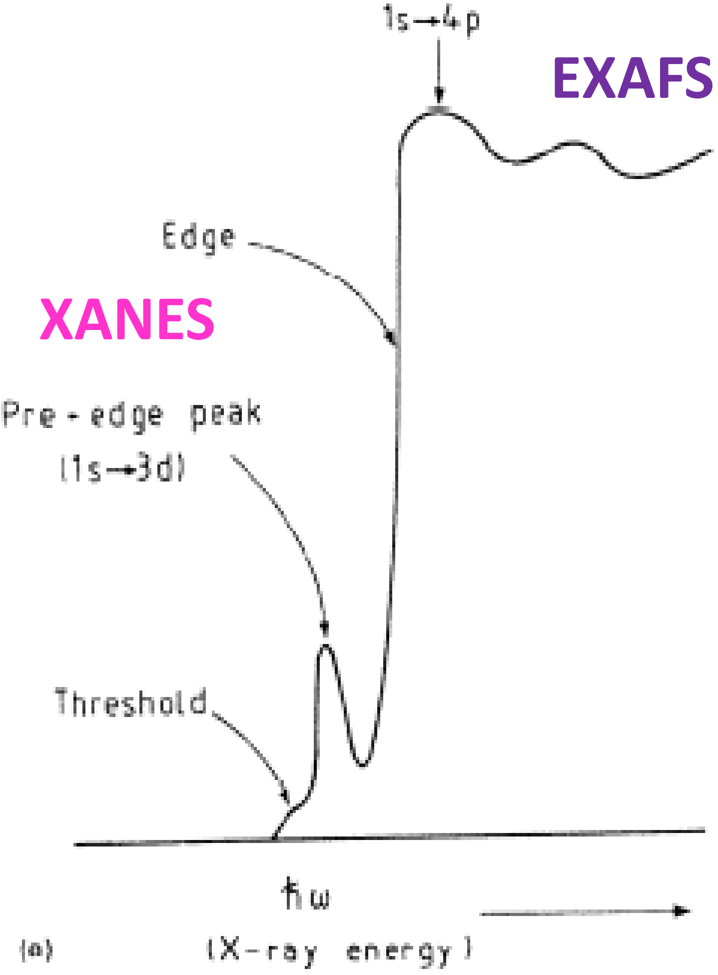
- XAS: X-ray **absorption** spectroscopy; alternatively
  XAFS: X-ray **absorption** fine structure
  - XANES: X-ray **absorption** near edge structure (pre-edge); alternatively NEXAFS (near edge x-ray absorption fine structure)
  - EXAFS: Extended x-ray **absorption** fine structure (= behind edge)

What is an edge?

XANES and EXAFS



XANES and EXAFS



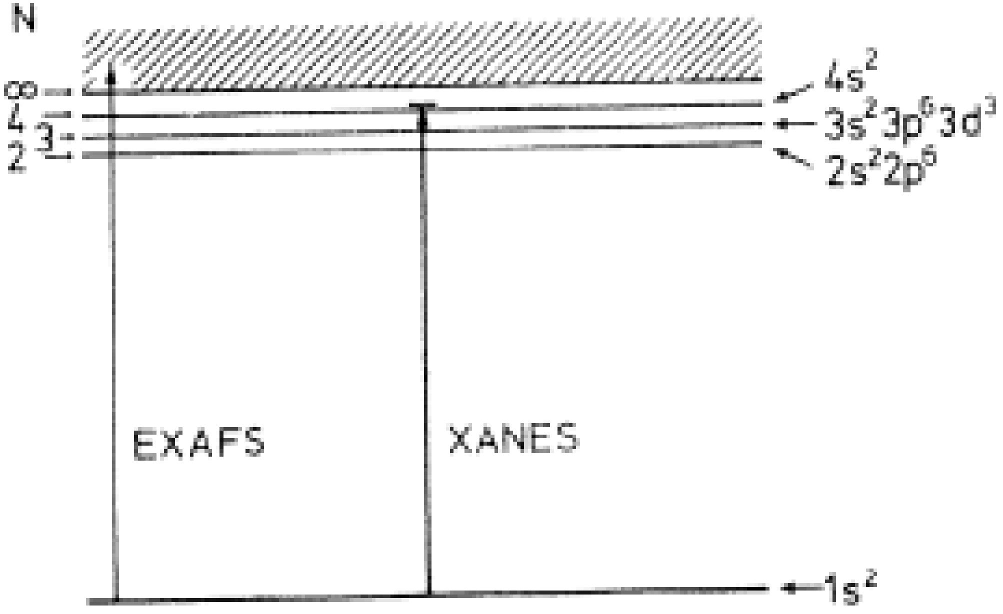


Figure 3.36 (a) Representation of the X-ray K-edge absorption spectra (XANES) obtained from solids containing vanadium. (b) Schematic energy level diagram for vanadium. The transitions are from the K-shell to empty valence states. XANES involves transitions to valence states and can thus be used to probe chemical bonding.

XANES

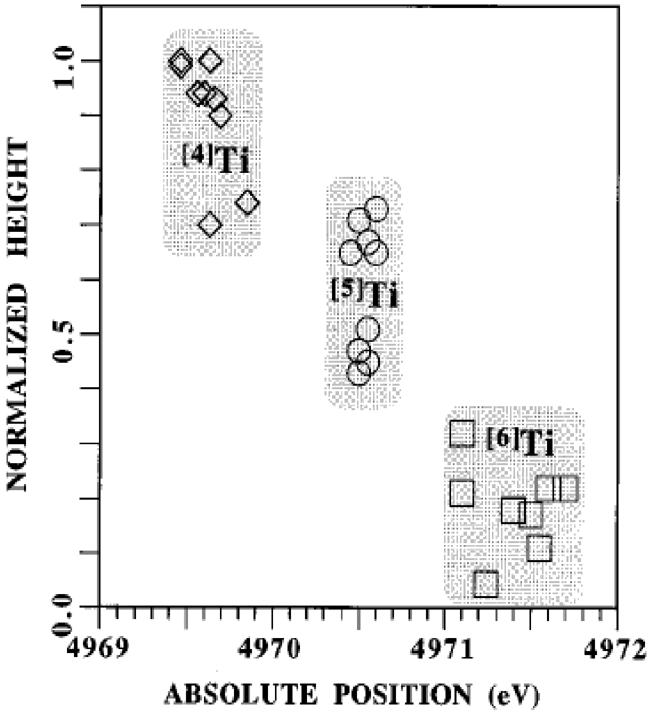
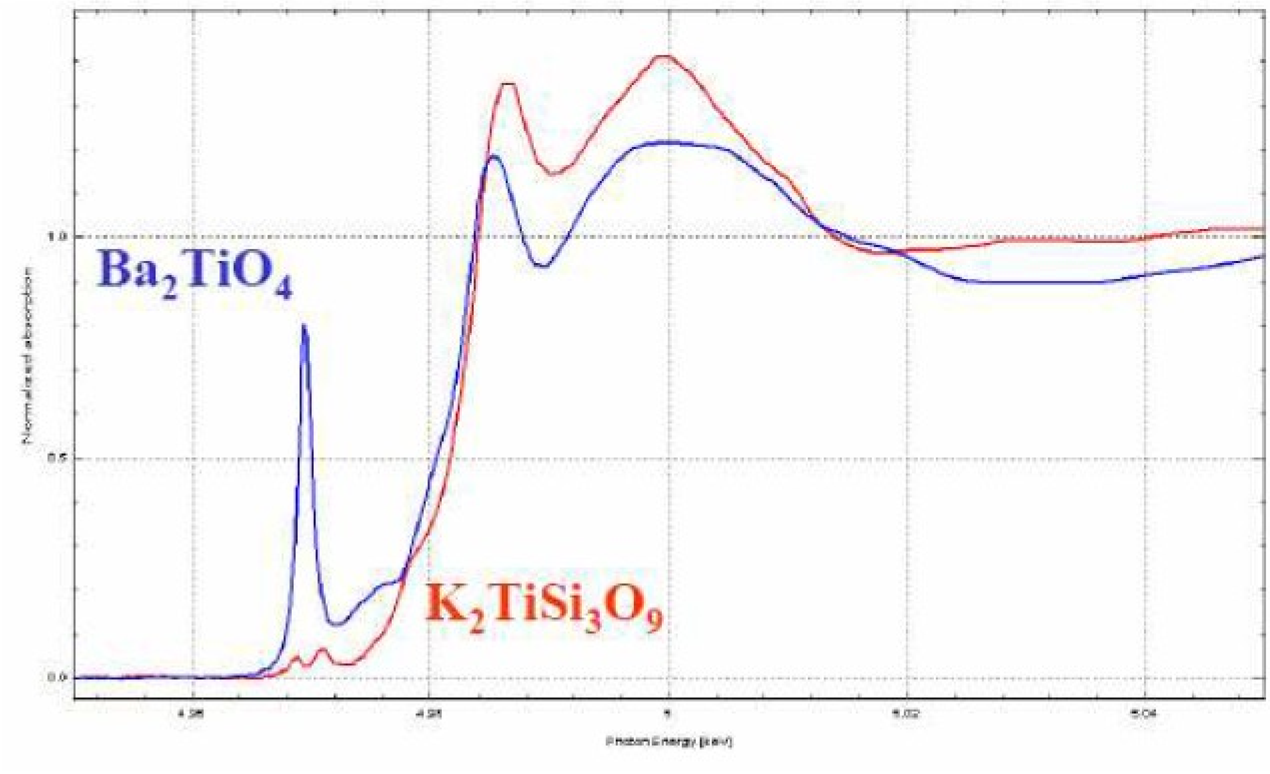


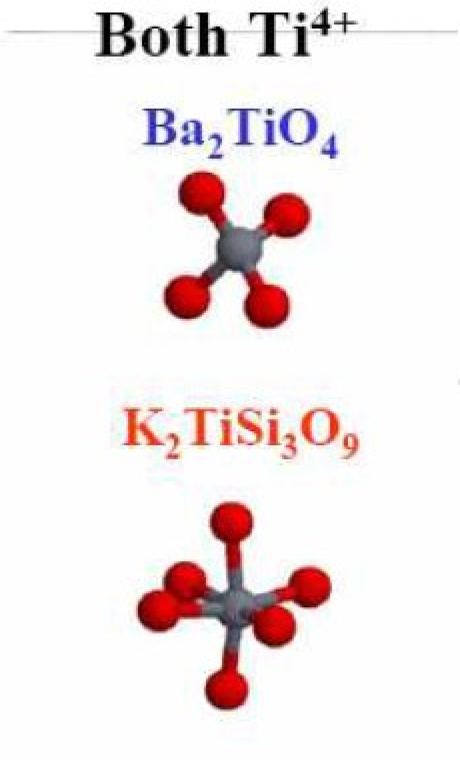
FIG. 2. Normalized pre-edge height vs energy position for Ti *K*-pre-edge features in model compounds listed on Table I showing three domains for fourfold, fivefold, and sixfold coordinated Ti.

- Qualitative information on coordination environment (dipole selection rules apply)
  - Is there a pre-edge feature?
    - Yes – no inversion center
    - No – there is an inversion center
- Quantitative info also possible
- Figure from Farges, et. al. *Physical Review B: Condens. Matter* **1997**, 56(4), 1809-1819.

XANES

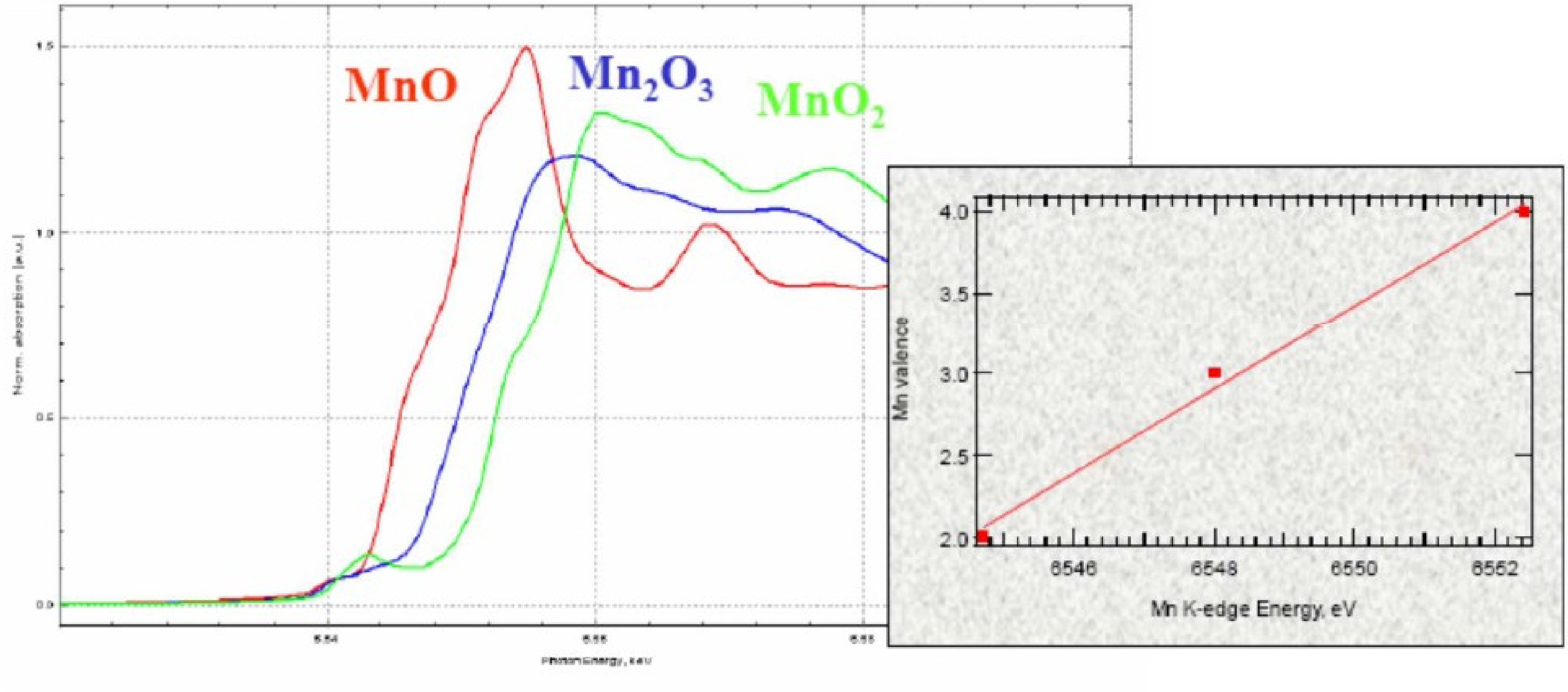
- Coordination environment



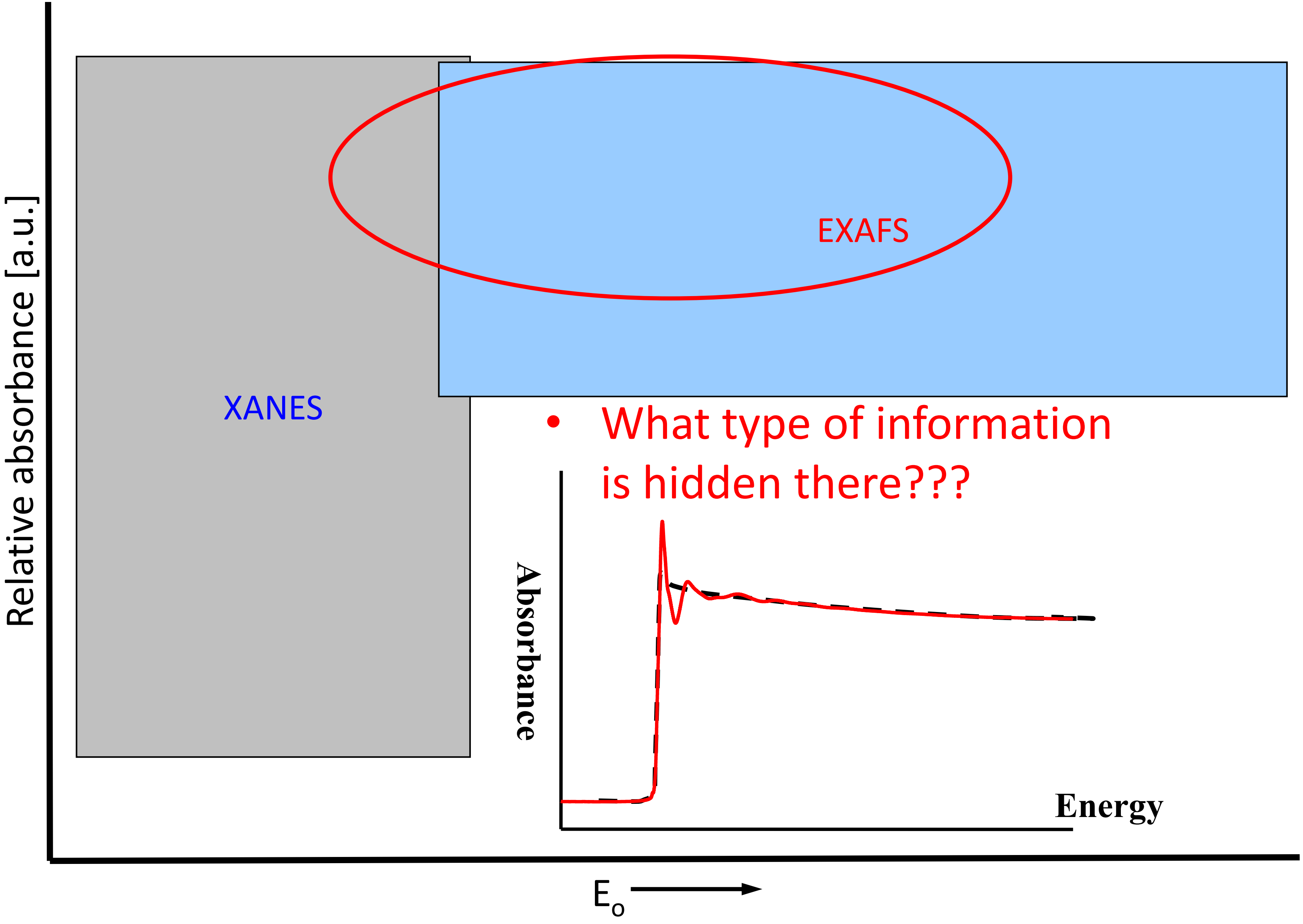


XANES

- Position of the edge…binding energy…oxidation state



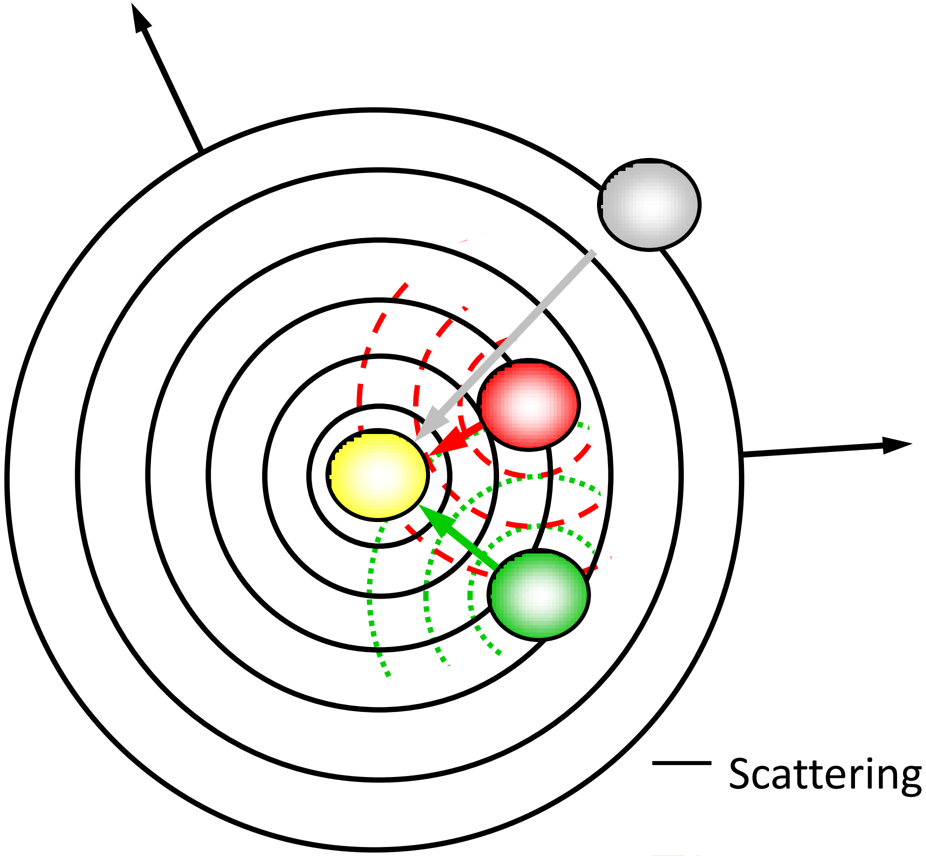
EXAFS



- What type of information is hidden there???

EXAFS

- The scattering phenomena

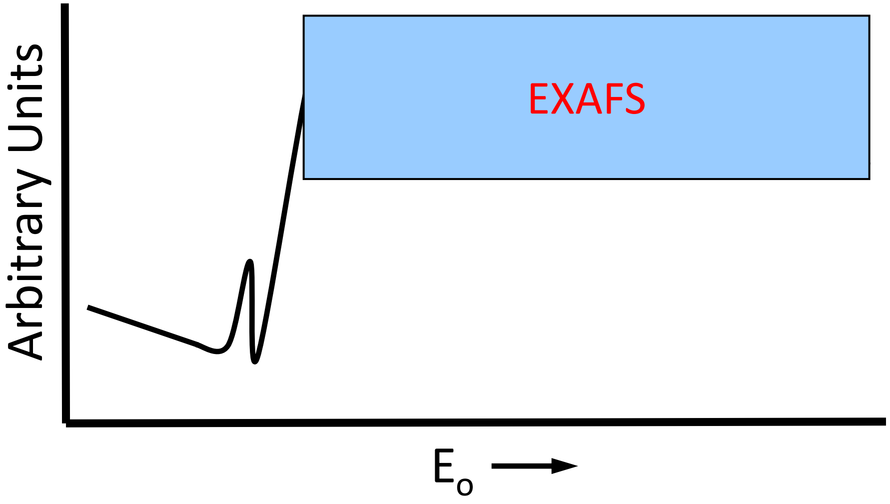


— Scattering from Ti

Back-scattering from “neighbors”

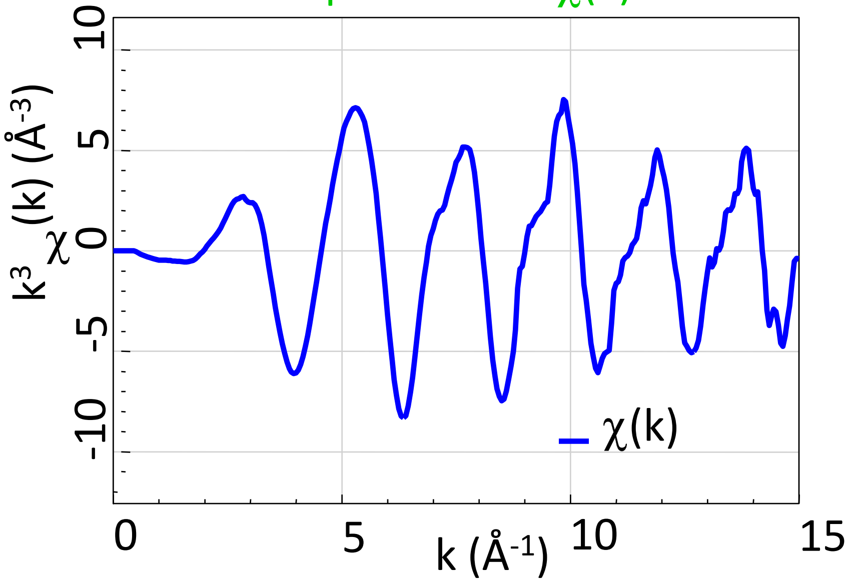
EXAFS

Step 1: The data



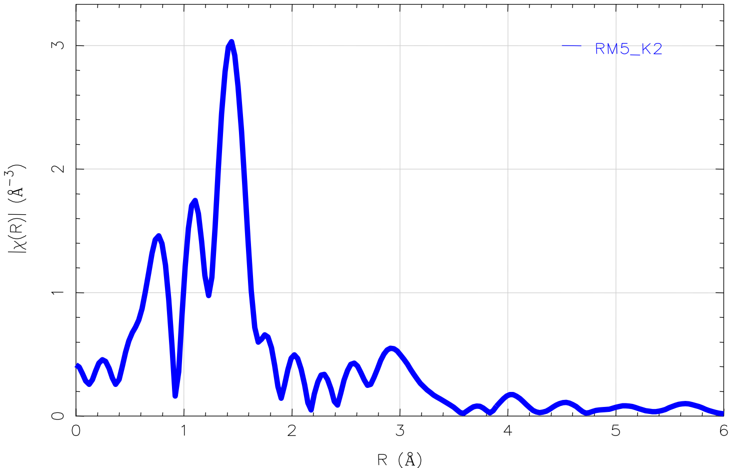
Math

Step 2: Extract $\chi(k)$



Fourier Transform

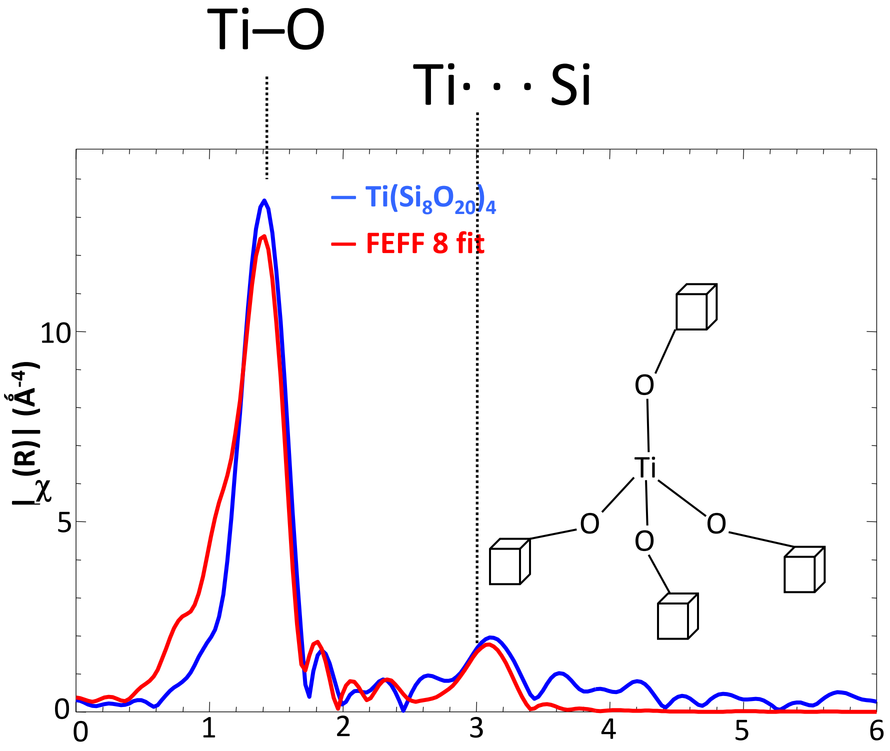
Step 3: The FT

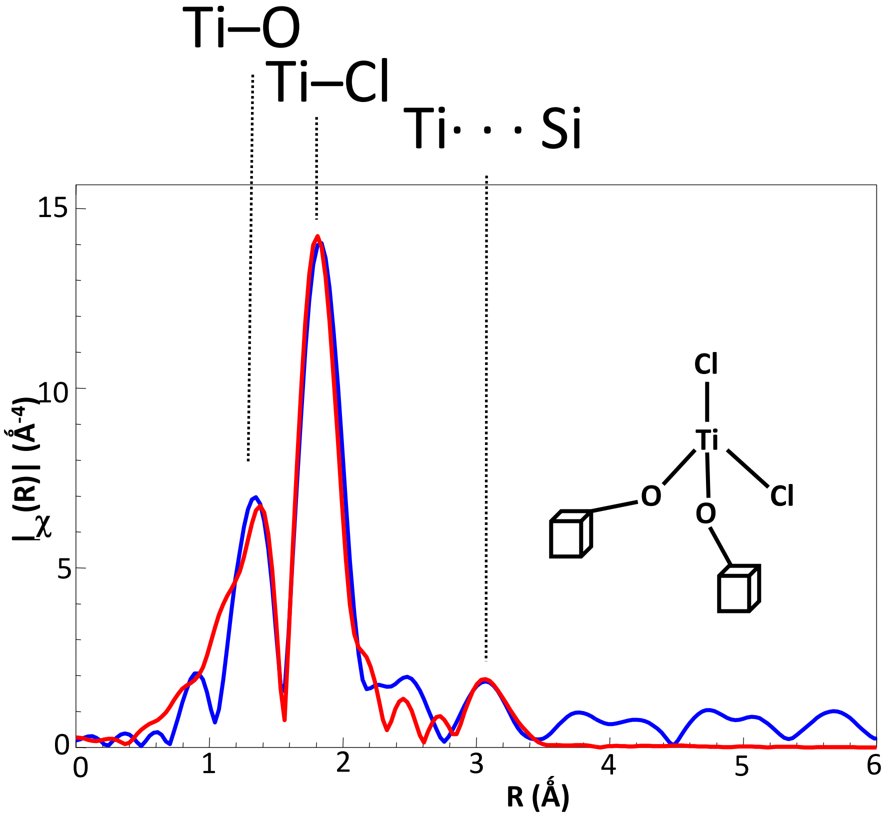


Step 4:

Develop structural model that fits that data d(M-X), CN(X), AtNum(X)

EXAFS

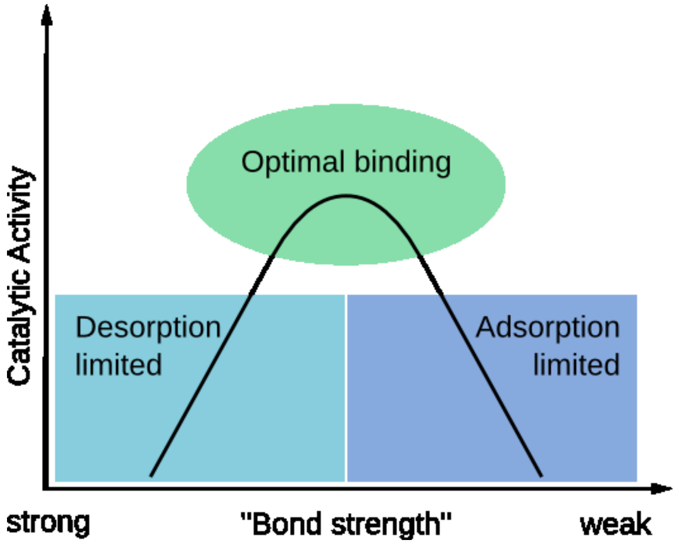




- Structure elucidation of an amorphous material!
- If more Ti sites, than average; analysis more difficult!

Chemisorption

- Interactions of A,B, and P with catalyst not too weak, not too strong
  (= physi/chemisorption on catalyst surface)



Sabatier's principle;

Volcano plot@Lecture 1

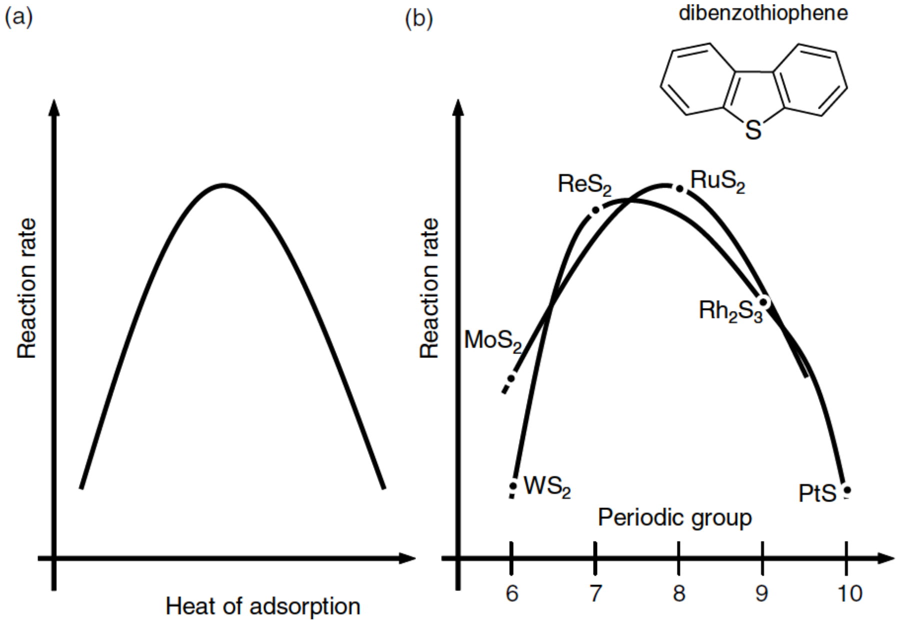


Figure 2.15 Examples of volcano plots, describing the reaction rate as a function of the heat of adsorption (*left*), and the activity of the second-row and third-row transition metal sulfides in the hydrodesulfurization of dibenzothiophene (*right*).

Chemisorption

- Different sites = different probes
  - Acid sites
    - NH_3, alkylamines, pyridine, 2,6-dimethylpyridine, CO
  - Basic sites
    - CO_2
  - Redox
    - H_2, O_2, N_2O
  - Reactants can be used as probes
    - e.g. ethanol dehydration = I can study chemisorption of ethanol

Chemisorption

- Different ways how to do it
  - Volumetric
  - Thermally programmed desorption/oxidation/reduction
  - Pulse titration
  - Chemisorption of IR (NMR) active molecules and their analysis by IR (NMR)

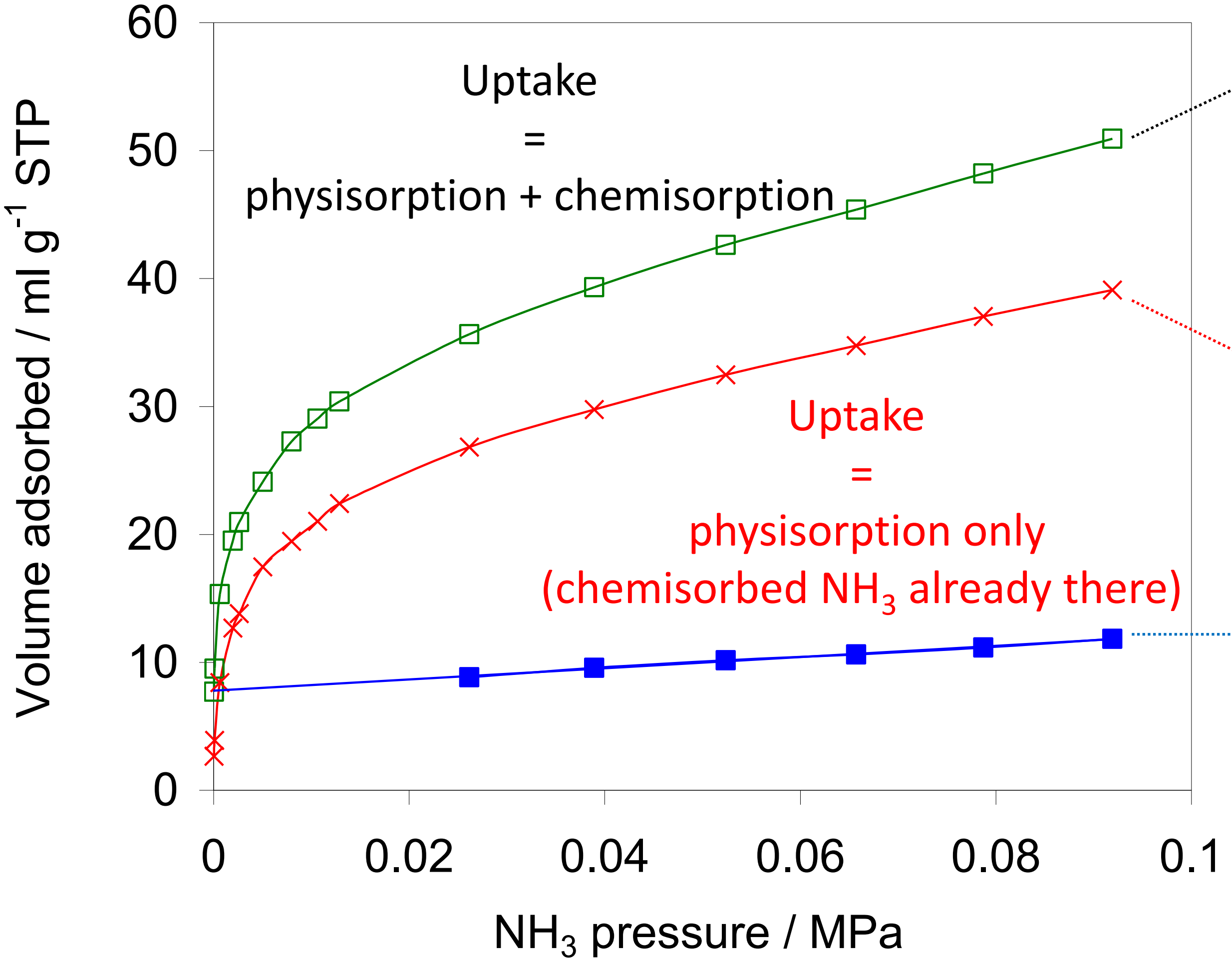
Chemisorption

- Volumetric
  - Similar to N_2 physisorption (glass tube of known volume, addition of known volume of gas, pressure measurement)
  - NH_3 adsorption isotherms measured twice, sample evacuated between the two measurements
    (physisorption vs. chemisorption)
  - High temperatures in contrary to N_2 physisorption (e.g. 50 °C)

Chemisorption

Temperature?

- Volumetric



Uptake
=
physisorption + chemisorption

Uptake
=
physisorption only
(chemisorbed NH_3 already there)

1st isotherm

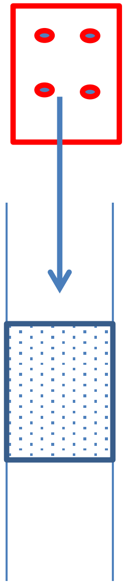
evacuation

2nd isotherm

Difference
1st – 2nd
=
chemisorbed NH_3

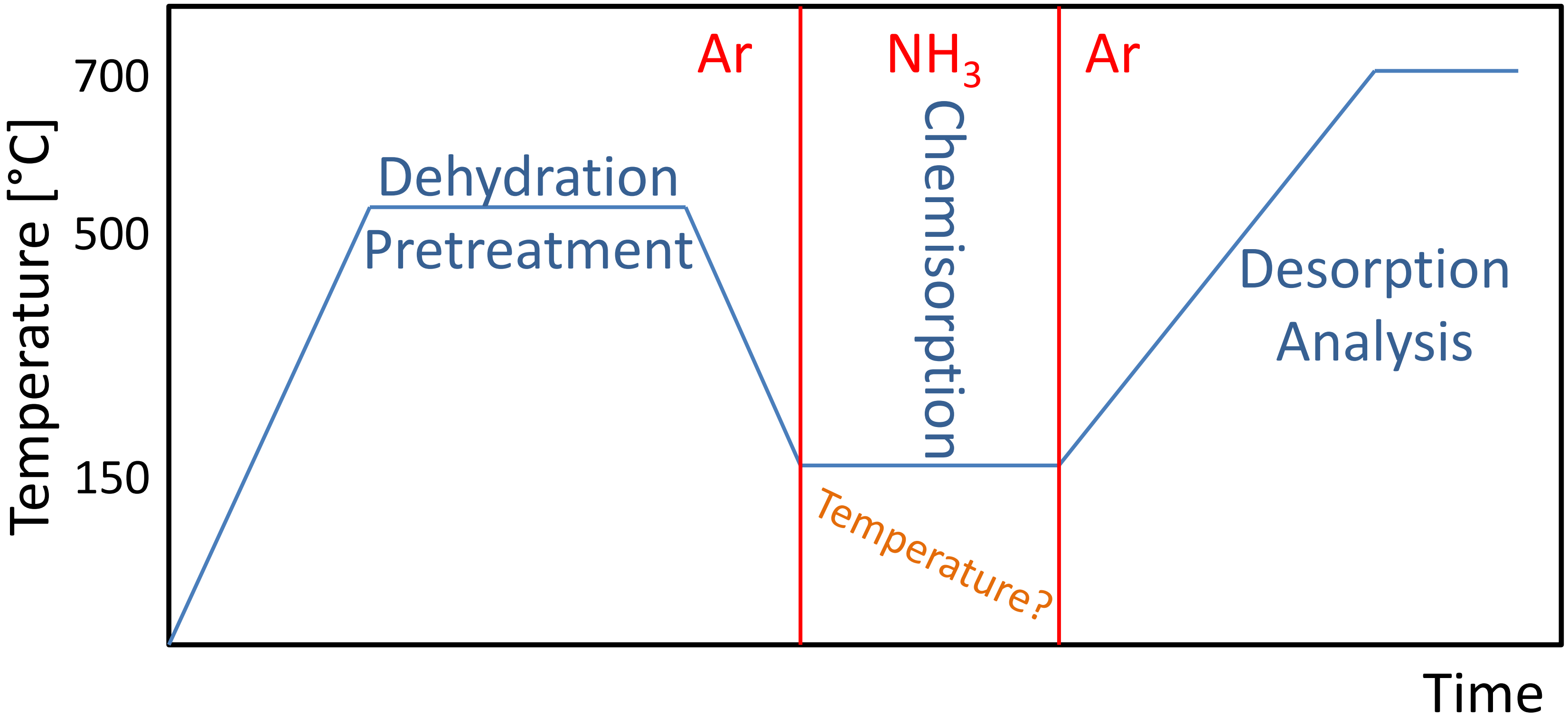
Chemisorption

- Thermally programmed desorption/oxidation/reduction



Chemisorption

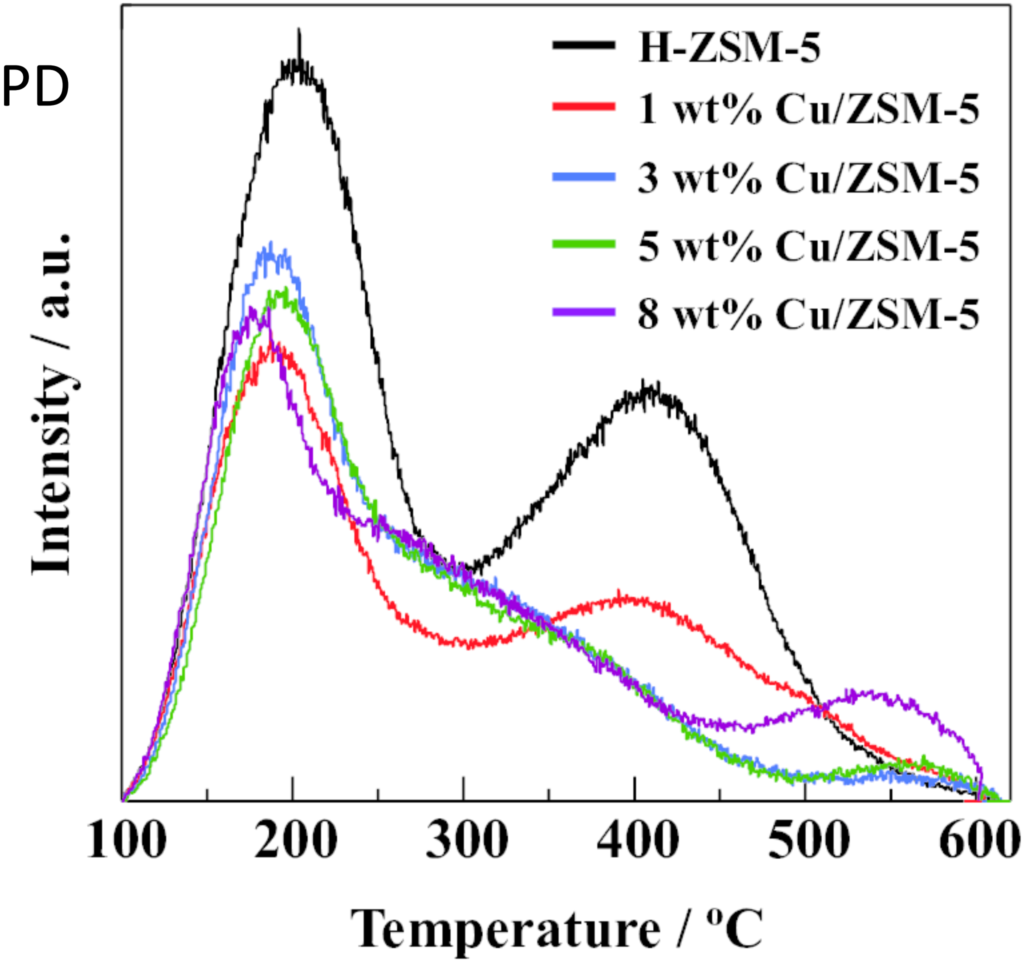
- Thermally programmed desorption/oxidation/reduction



Chemisorption

- Thermally programmed …

NH_3 TPD



Chemisorption

- Pulse titration

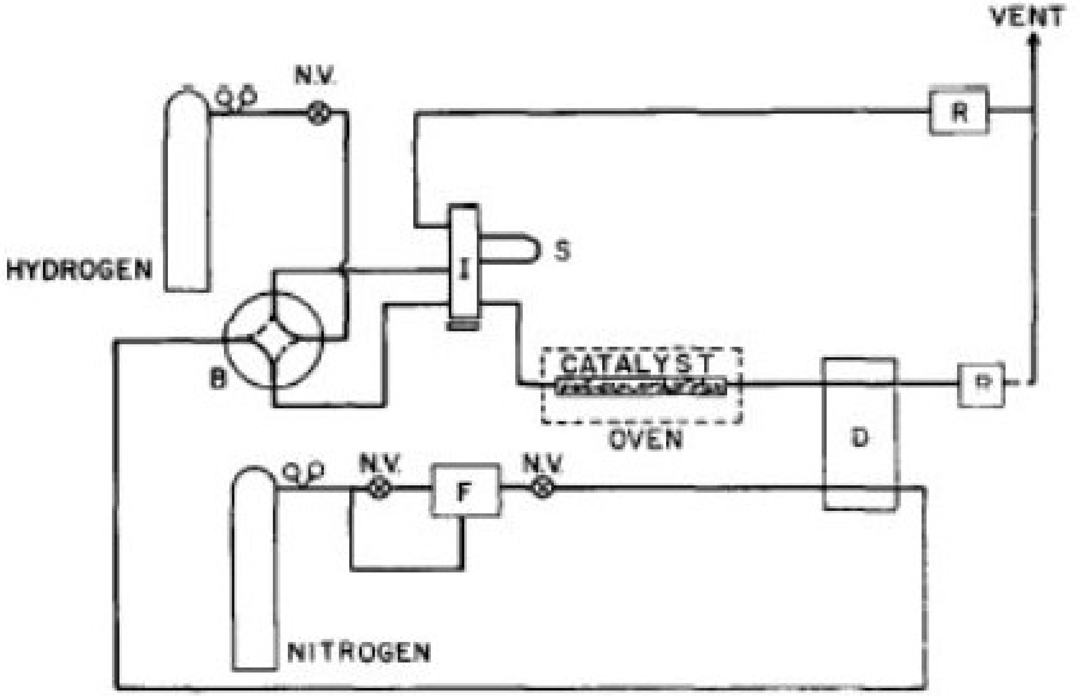
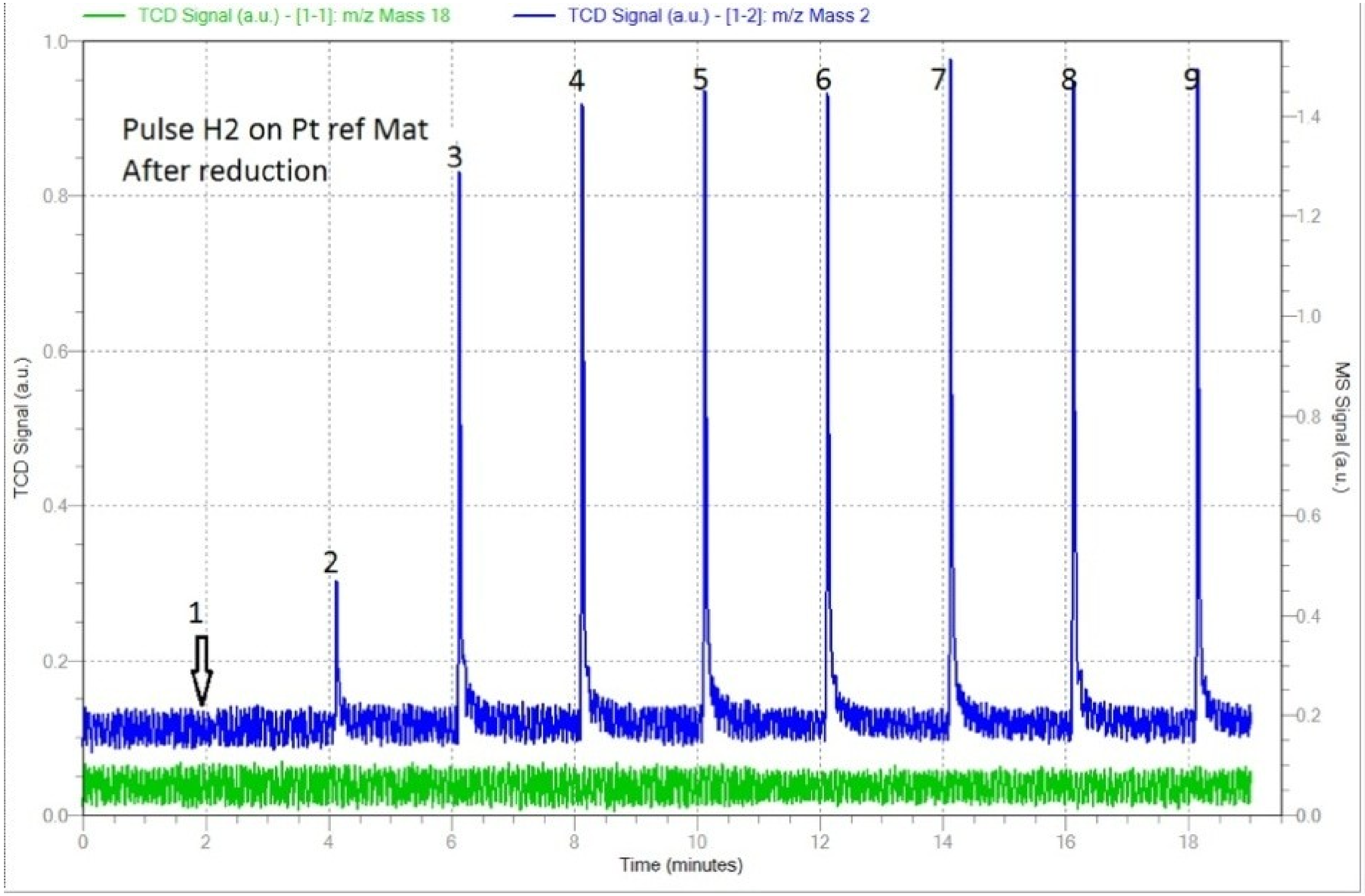


FIG. 1. Schematic of the flow system. F = "Moore" flow controller, N.V. = needle valve, D = thermal conductivity detector, B = glc backflush valve, I = 6-port "Varian" sample-injector, S = sample loop, R = rotameter. The setup for hydrogen adsorption is shown. Prereduction was carried out with the valve B in its alternate position. Oxygen chemisorption was studied by replacing the hydrogen source with oxygen.

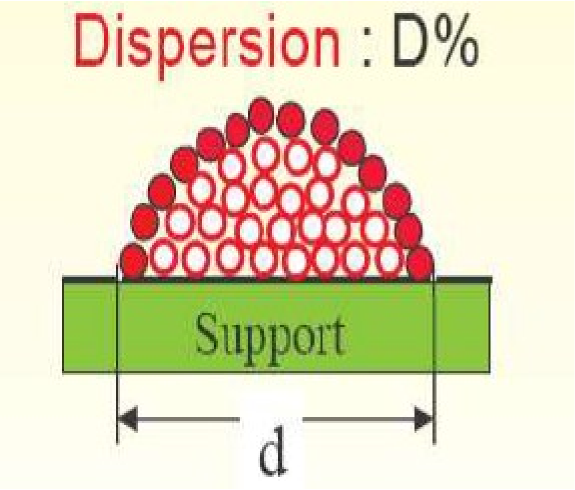
Chemisorption

- Pulse titration



Chemisorption

- Pulse titration
  - Correct choice of gas (H_2, CO, O_2, N_2O)
  - Correct choice of temperature
    - = Monolayer
    - = Dispersion, particle size, „active metal surface area“



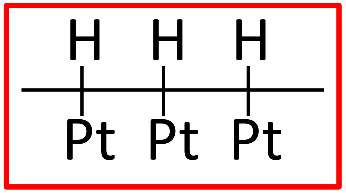
Number of surface atoms

$$D = 100\frac{N_S}{N_T}$$

Total number of atoms

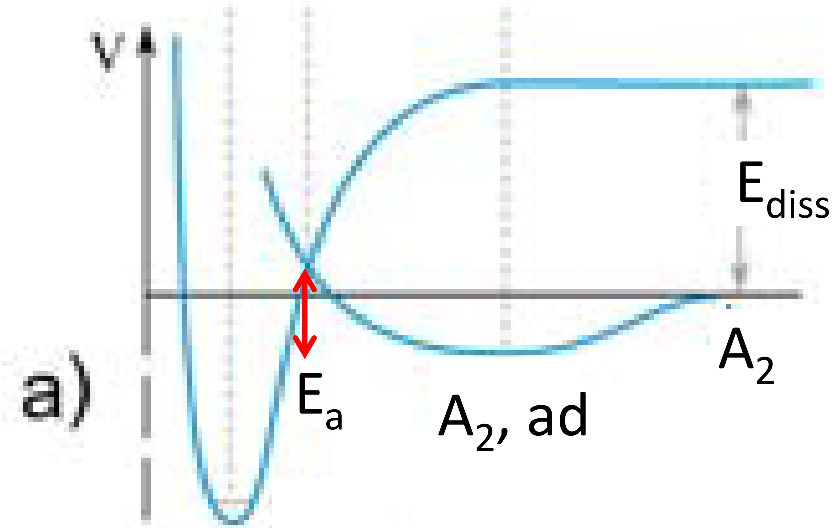
Chemisorption

- Pulse titration
  - Very good correlation can be observed between active surface area by H_2 chemisorption and activity in hydrogenation of … for classical hydrogenation catalyts (Pt, Pd)
  - H_2 chemisorption is **dissociative**!
  - H–H bond breaks at the time of chemisorption, this is the key to high reactivity (adsorbed **molecular** hydrogen)
  - This is Langmuir‘s chemistry



Chemisorption

- X_2 dissociative chemisorption (detour)



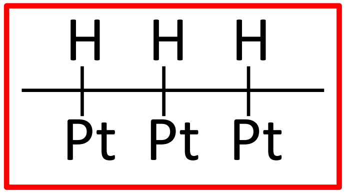
E_{diss}, noncatalyzed

E_a

A_2

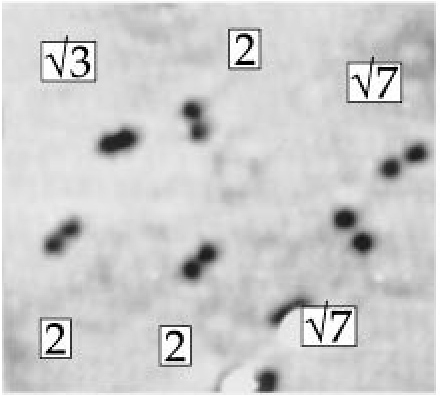
A_2, ad

2A, ad



H H H

Pt Pt Pt



„Hot“ O atoms

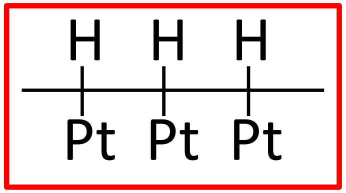
Lifetime 10^{-13} s

O_2 adsorption on Pt(111) surface @165 K

O–O in O_2 = 1.2Å, here much longer

Chemisorption

- Pulse titration
  - Very good correlation can be observed between active surface area by H_2 chemisorption and activity in hydrogenation of … for classical hydrogenation catalyts (Pt, Pd)
  - BUT

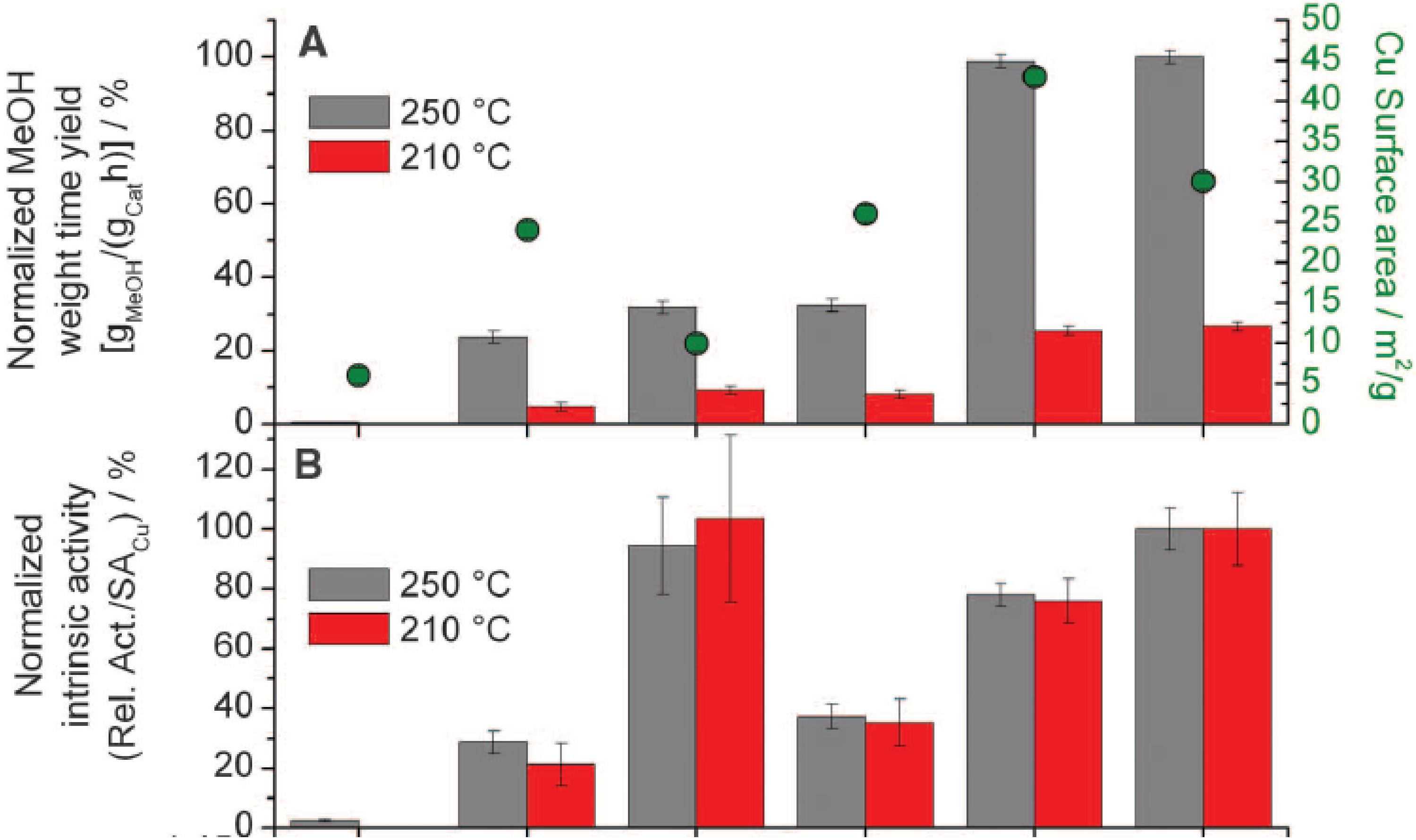


- Example: methanol synthesis over Cu NPs
  - $CO_2 + 2\ H_2 \rightarrow CH_3OH$

Science 18 May 2012:
Vol. 336, Issue 6083, pp. 893-897

Chemisorption

- Example: methanol synthesis over Cu NPs



Chemisorption

- Example: methanol synthesis over Cu NPs

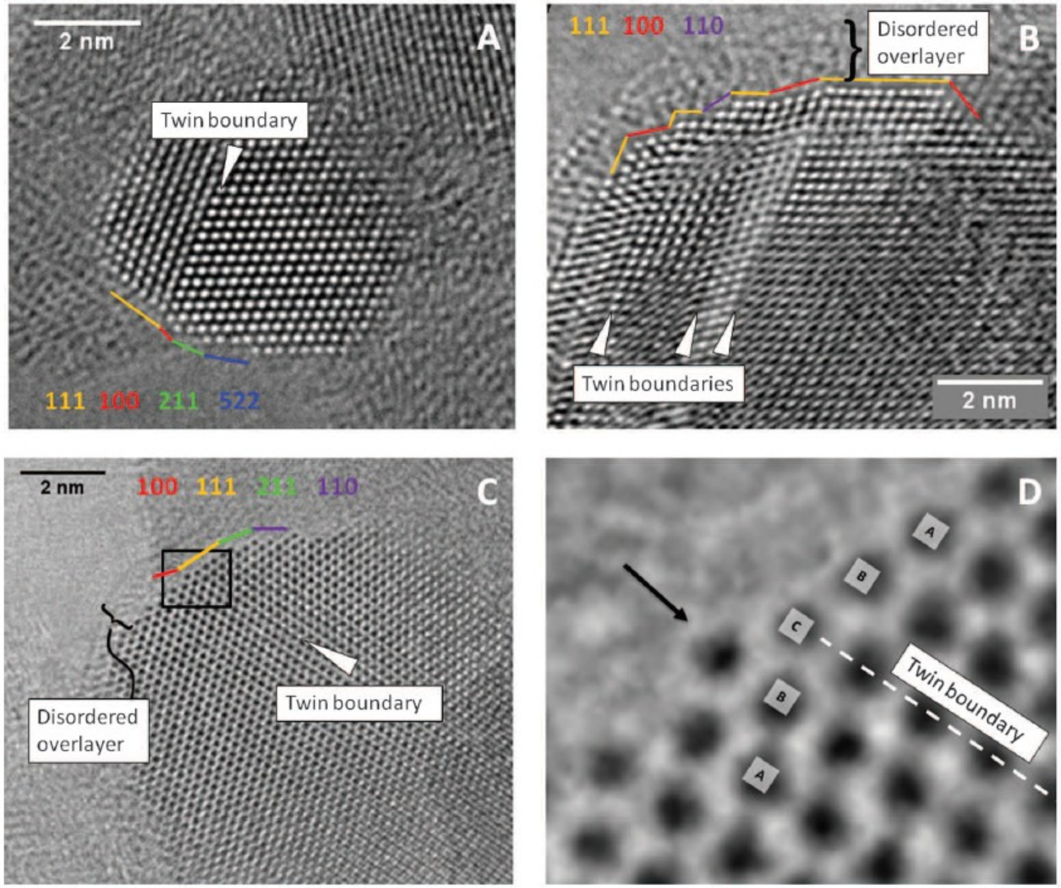
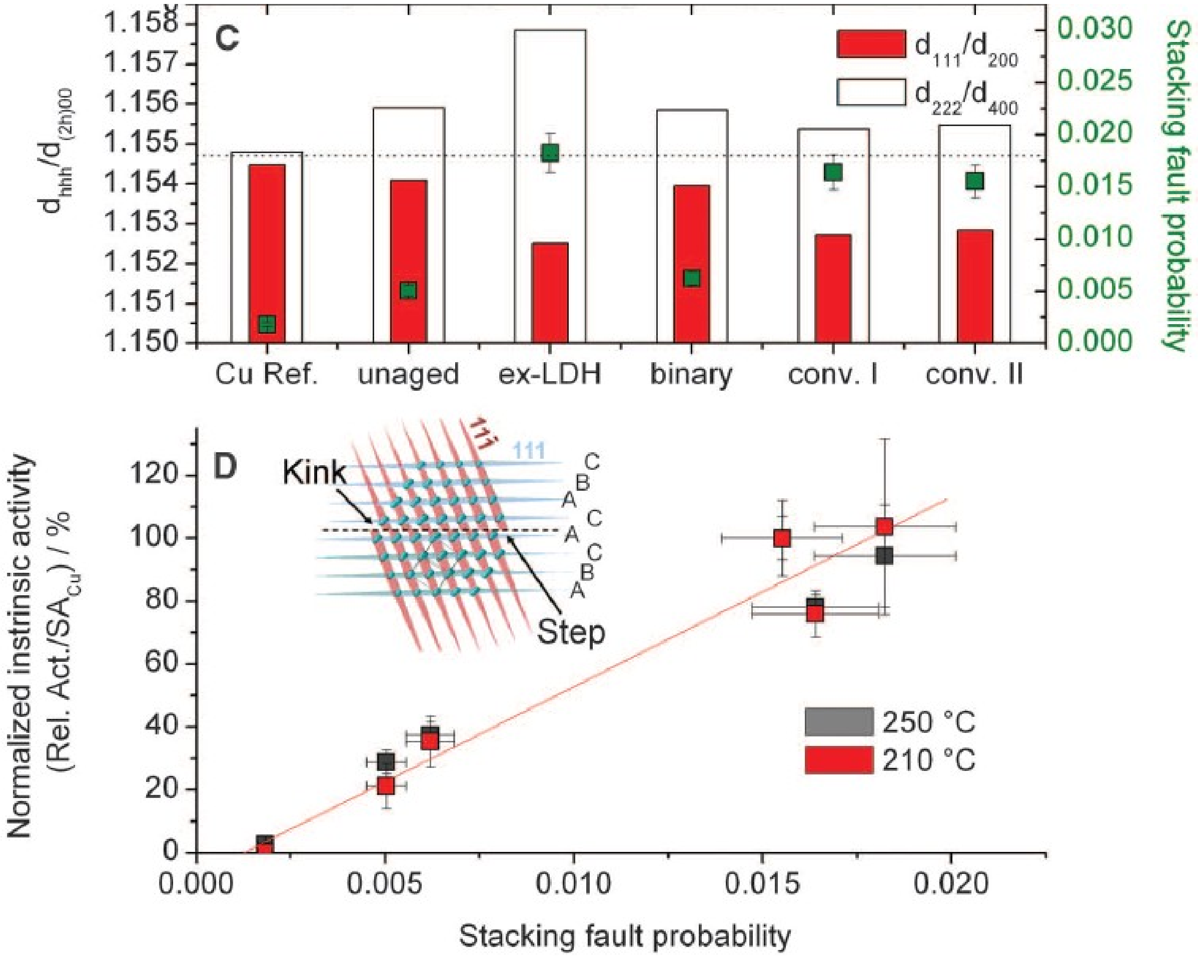


Fig. 3. (**A** to **D**) Aberration-corrected HRTEM images of Cu particles in the conventionally prepared, most-active Cu/ZnO/Al$_2$O$_3$ catalyst. (D) is a close-up of the marked area in (C).

Chemisorption

- Example: methanol synthesis over Cu NPs



Chemisorption

- Pulse titration
  - **Homework**
  - Silver (2.2 wt% on silica)
  - Surface reaction:
    $2Ag_{surf} + O_2 \rightarrow 2\ AgO_{surf}$
    @T = 170 C (no bulk oxidation!)
  - m_{sample} = 0.5021 g
    V_{pulse} = 0.00925 cm^3 O_2@RT@1atm
    Max TCD signal = 0.022
  - D = ?

Pulse	**TCD signal**
#1	0
#2	0
#3	0
#4	0
#5	0
…	…
#28	0
#29	0
#30	0.002
#31	0.005
#32	0.011
#33	0.016
#34	0.019
#35	0.021
#36	0.022

Chemisorption

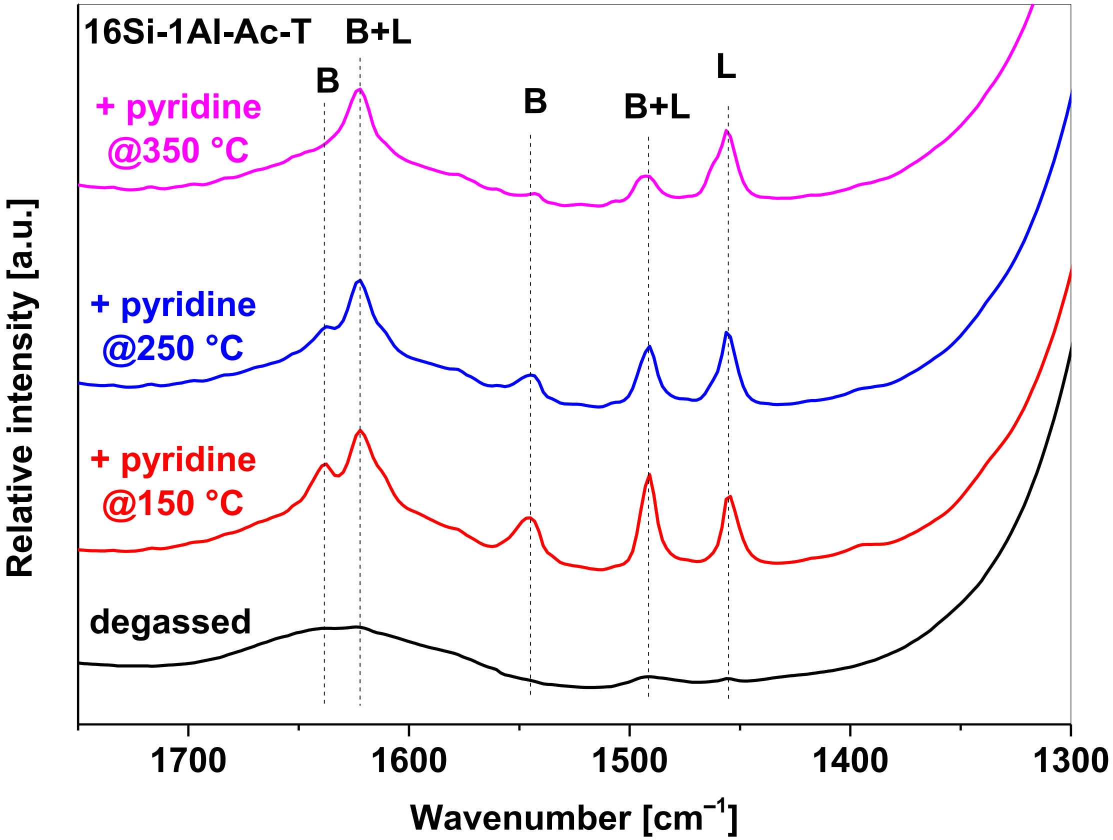
- Adsorption of IR (NMR) active molecules
  - Pyridine and its derivatives
  - CO
  - Trialkylphosphine oxides
  - …

Chemisorption

- Adsorption of IR (NMR) active molecules
  - Number of sites
    - Lambert-Beer law
  - Strength of sites
    - Desorption under vacuum at different temperatures
  - Nature of sites
    - Different vibration modes

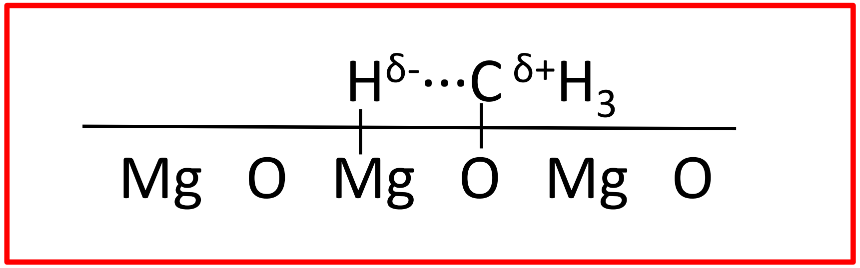
Chemisorption

- Adsorption of IR (NMR) active molecules
- Example: pyridine adsorption on an acid catalyst



Chemisorption

- Adsorption of IR (NMR) active molecules
- Example: CO adsorption on MgO, a catalyst that activates methane for oxidation, ideal products are ethane and ethylene
  - $2\ CH_4 + 0.5\ 0_2 \rightarrow C_2H_6 + H_2O$
  - $2\ CH_4 + 0_2 \rightarrow C_2H_6 + 2\ H_2O$



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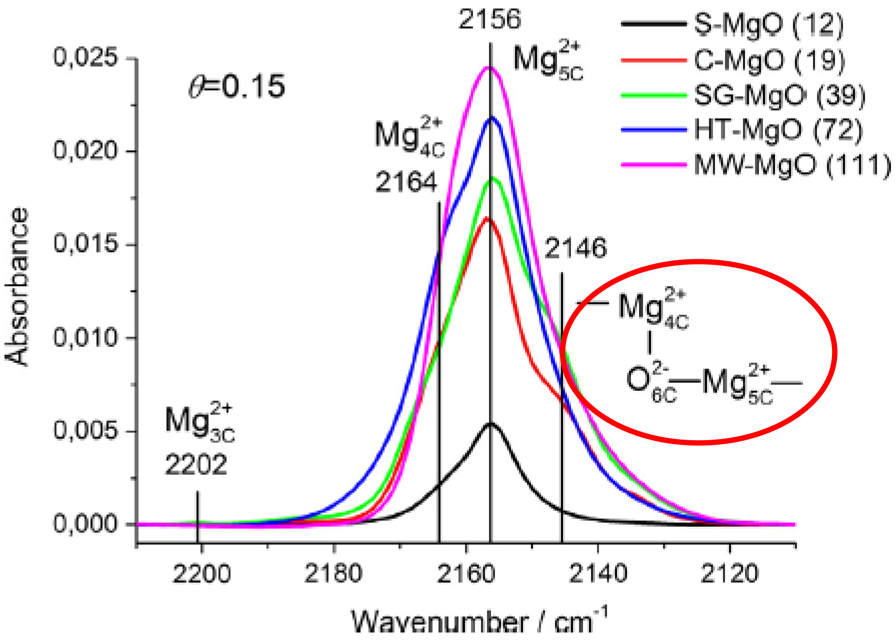
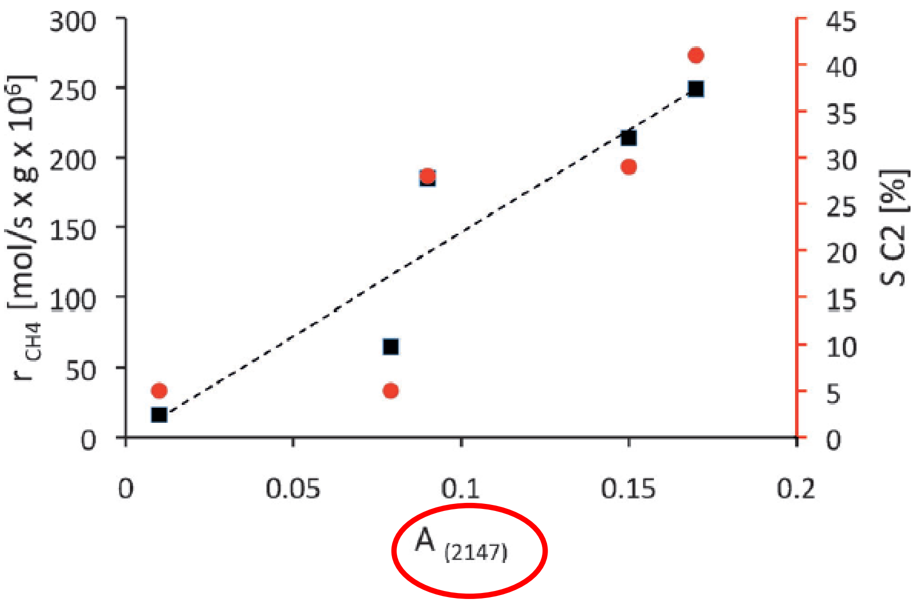
Chemisorption

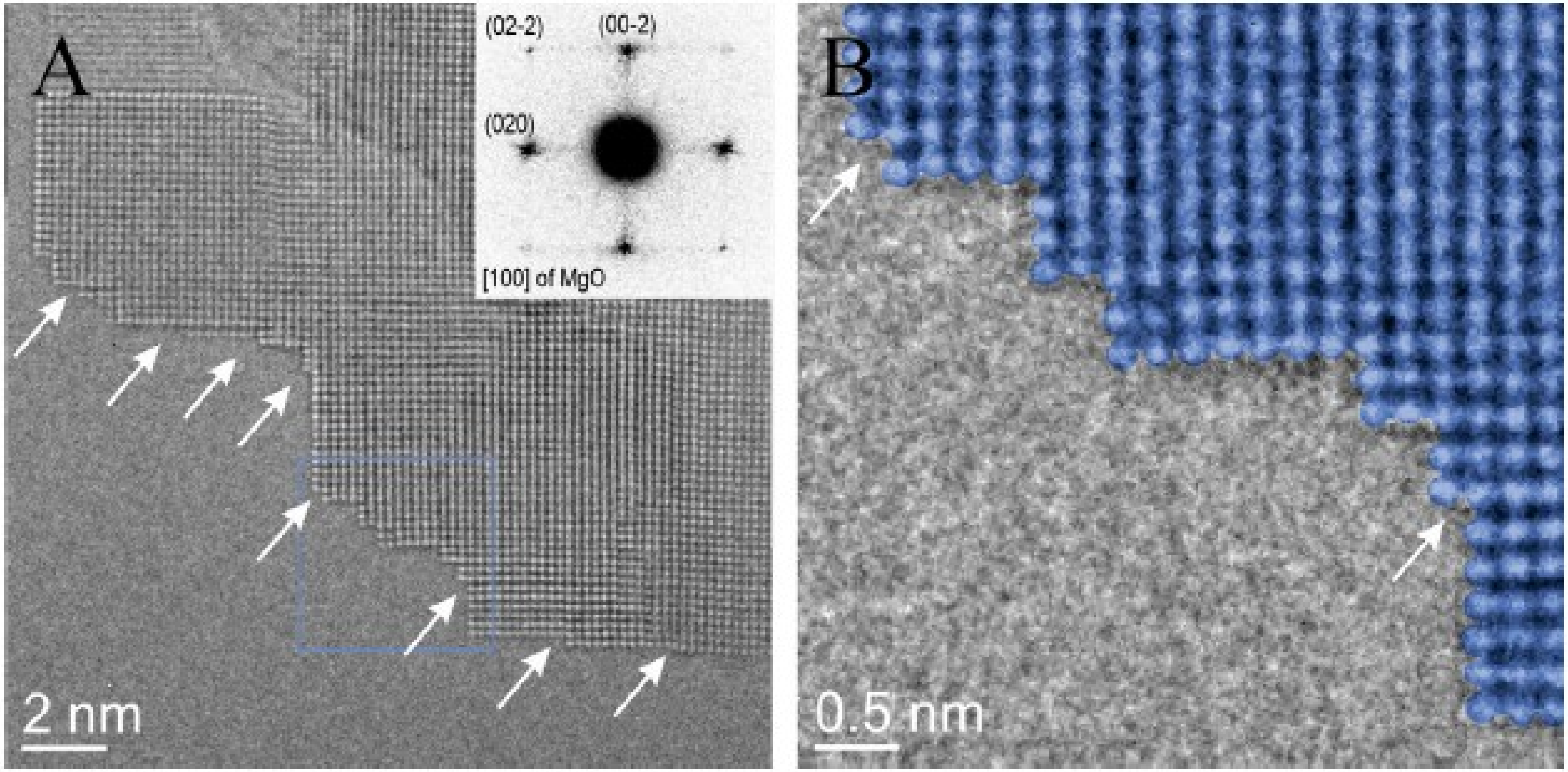
- Example: CO adsorption on MgO





Chemisorption

- Example: CO adsorption on MgO



Chemisorption

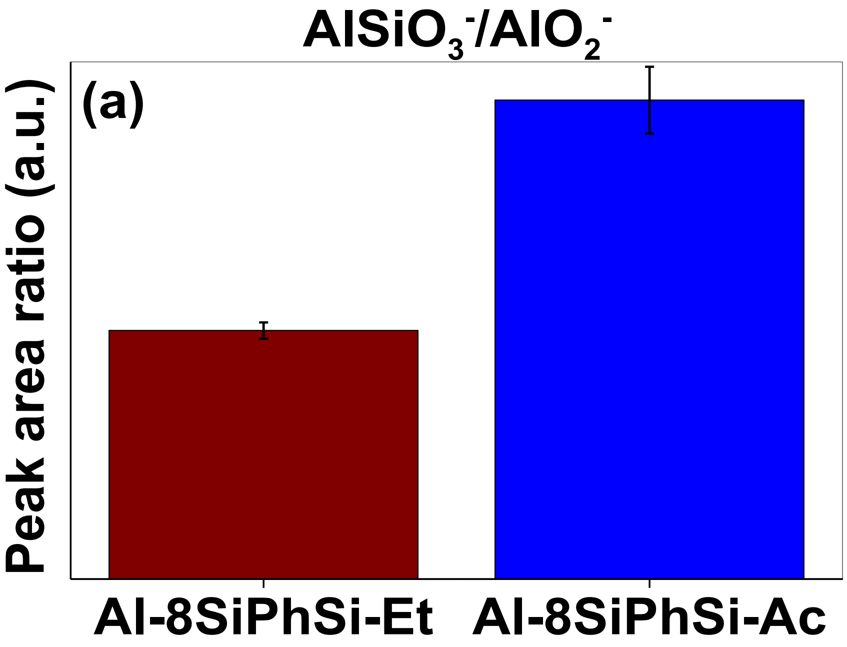
- Example: CO adsorption on MgO
- Single step edge is the active site
  - Good correlation between integral of absorption band at 2147 cm^{-1} and catalytic activity
  - Band at 2147 cm^{-1} represents single step edge
  - Au atoms selectively deposits on single step edges (observed by HR-TEM) = catalyst poisoning, active site „titration“

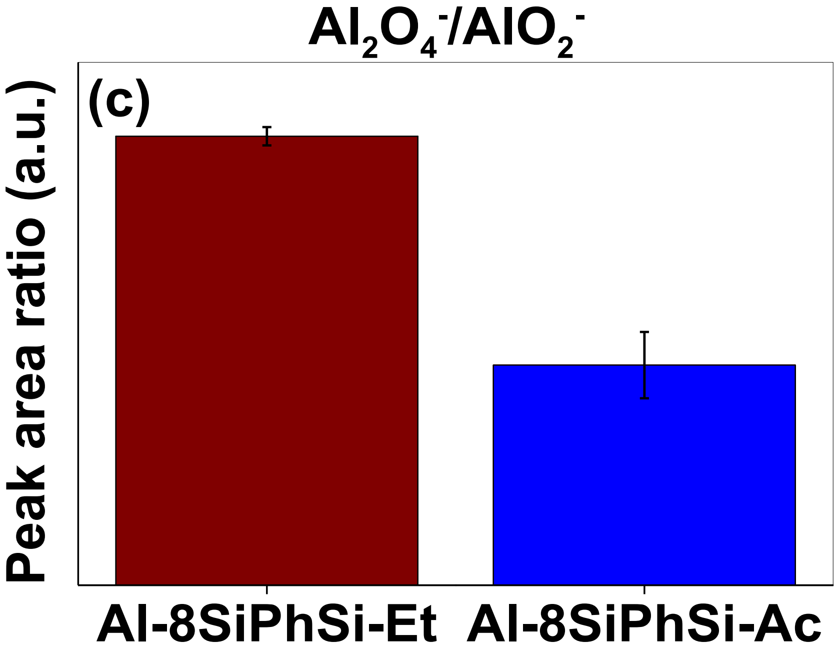
ToF-SIMS

- Time of flight secondary ion mass spectrometry
- Catalyst surface bombarded by „primary“ ions (e.g. Bi_5^+)
- Surface atoms (top ≈1 nm) expelled by this bombardment forming charged clusters = secondary ions created
- Analysis of secondary ions gives us information about catalyst surface

ToF-SIMS

- Surface composition
  - AlO_2^- is a function of Al concentration in top 1 nm
  - $AlSiO_3^-$ is a mixed Al-Si cluster (good Al dispersion)
  - $Al_2O_4^-$ signifies badly dispersed Al species





Catalyst characterization

- Outline
  - DRUV
  - **XPS**
  - XANES & EXAFS
  - **Chemisorption**
  - **ToF-SIMS**