Homework 4

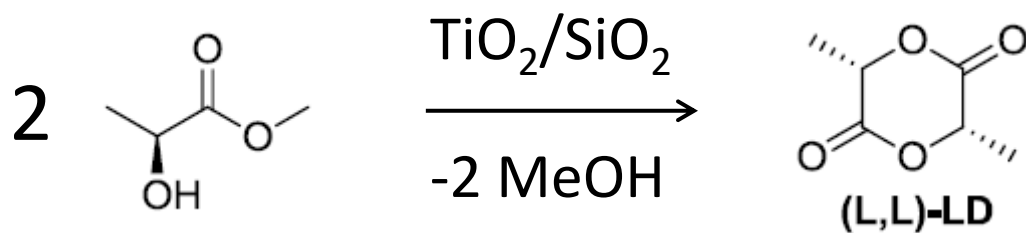2 ... $\xrightarrow[\text{-2 MeOH}]{\text{TiO}_2/\text{SiO}_2}$ ... (L,L)-LD

- Gas phase transesterification
- Continuous flow fixed bed reactor

Temperature [°C]	Conversion sample 1 (4.2 wt% Ti) [%]	Conversion sample 2 (0.9 wt% Ti) [%]
220	39	8.6
230	48	9.6
240	59	13
250	82	17
260	93	21

Selectivity = 90 % in all cases; WHSV = 15.5 h^{-1}

- Create Arrhenius plots for both catalysts (plot ln k [$mol_{LD}\ g_{cat}^{-1}\ h^{-1}$] vs. 1000/T [$K^{-1}$]
- Estimate apparent E_a and A from Arrhenius equation
- What makes the difference between these two catalysts?

ACS Catal. 2018, 8, 9, 8130–8139

Heterogeneous catalysis (C9981)

Lecture 5
Catalysts characterization

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Catalyst characterization

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

Diffuse reflectance UV-Vis spectroscopy (DRUV)

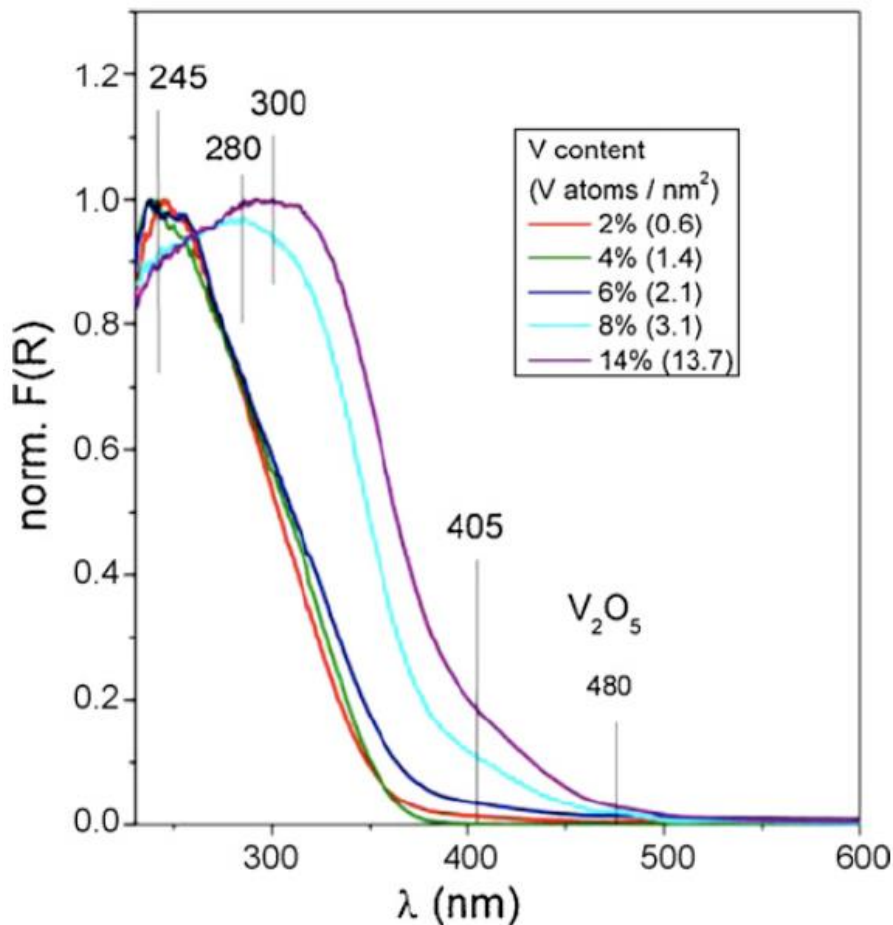$$R = \frac{J}{I}$$
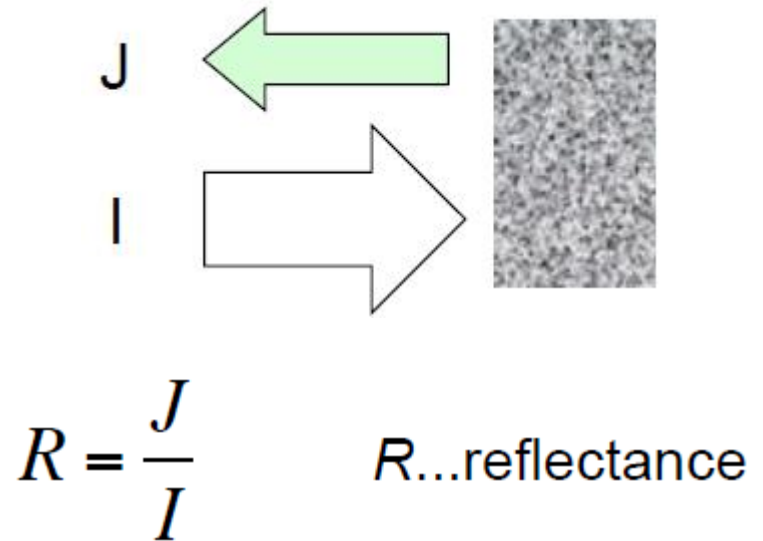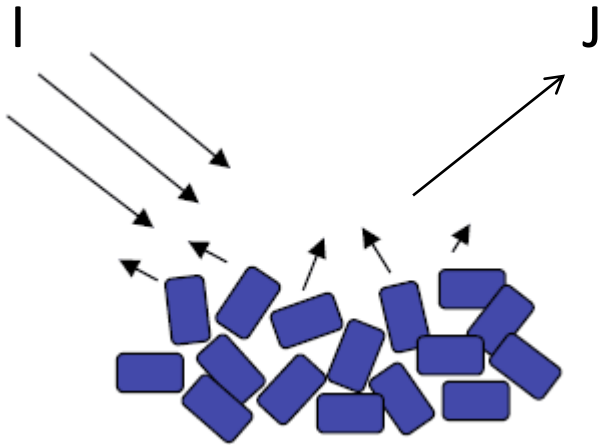
R...reflectance

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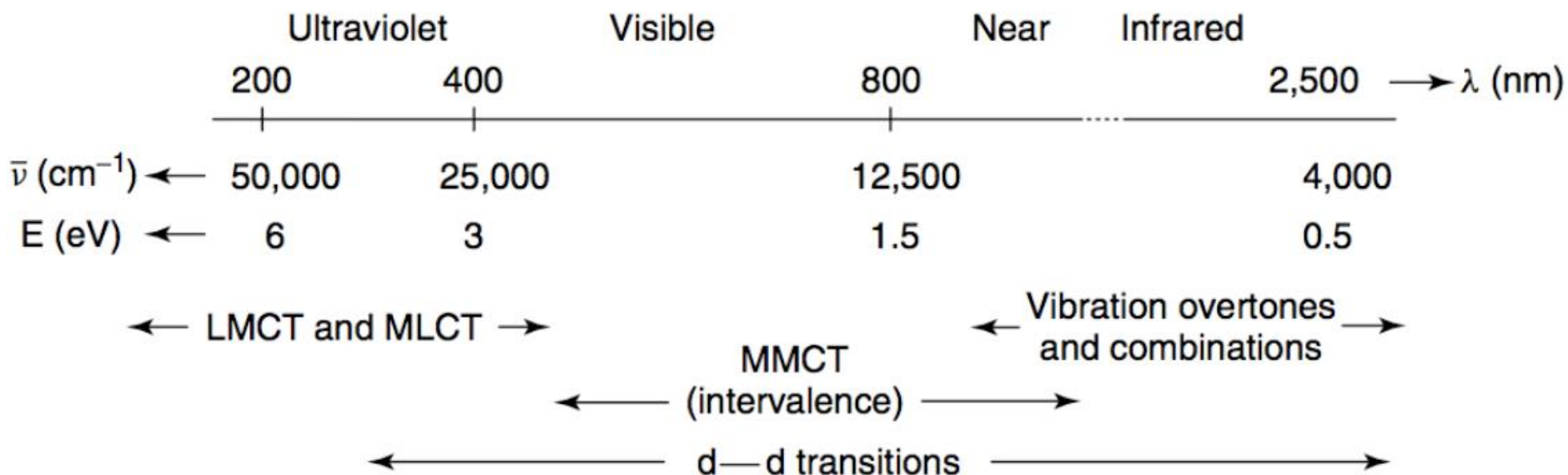
- LMCT = ligand-to-metal charge transfer
- MLCT = metal-to-ligand charge transfer
- MMCT = metal-to-metal charge transfer

Diffuse reflectance UV-Vis spectroscopy (DRUV)

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.
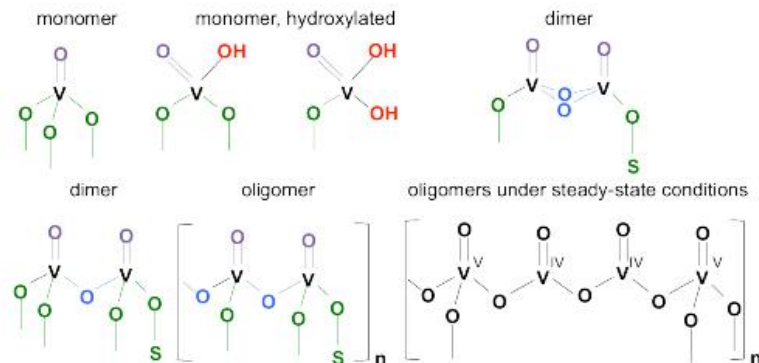
Isolated and polymerized V_xO_y ?

Ionization Spectroscopies

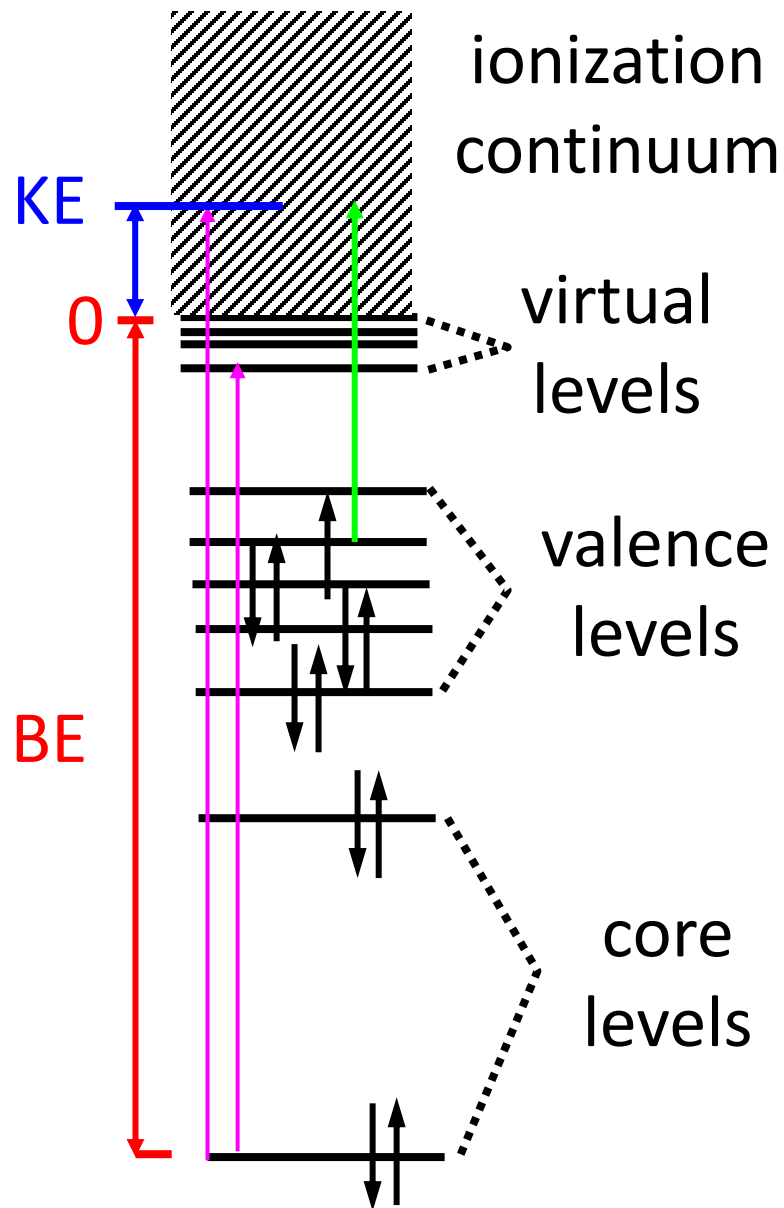Photoelectron spectroscopy:
UV: valence shell ionizations

X-ray: core electron ionizations
(XPS, XANES, EXAFS):

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

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)**

ionization continuum

KE

0

virtual levels

valence levels

BE

core levels

X-ray photoelectron spectroscopy (XPS)

We measure the number and the energy of photoelectrons emitted from the surface layer
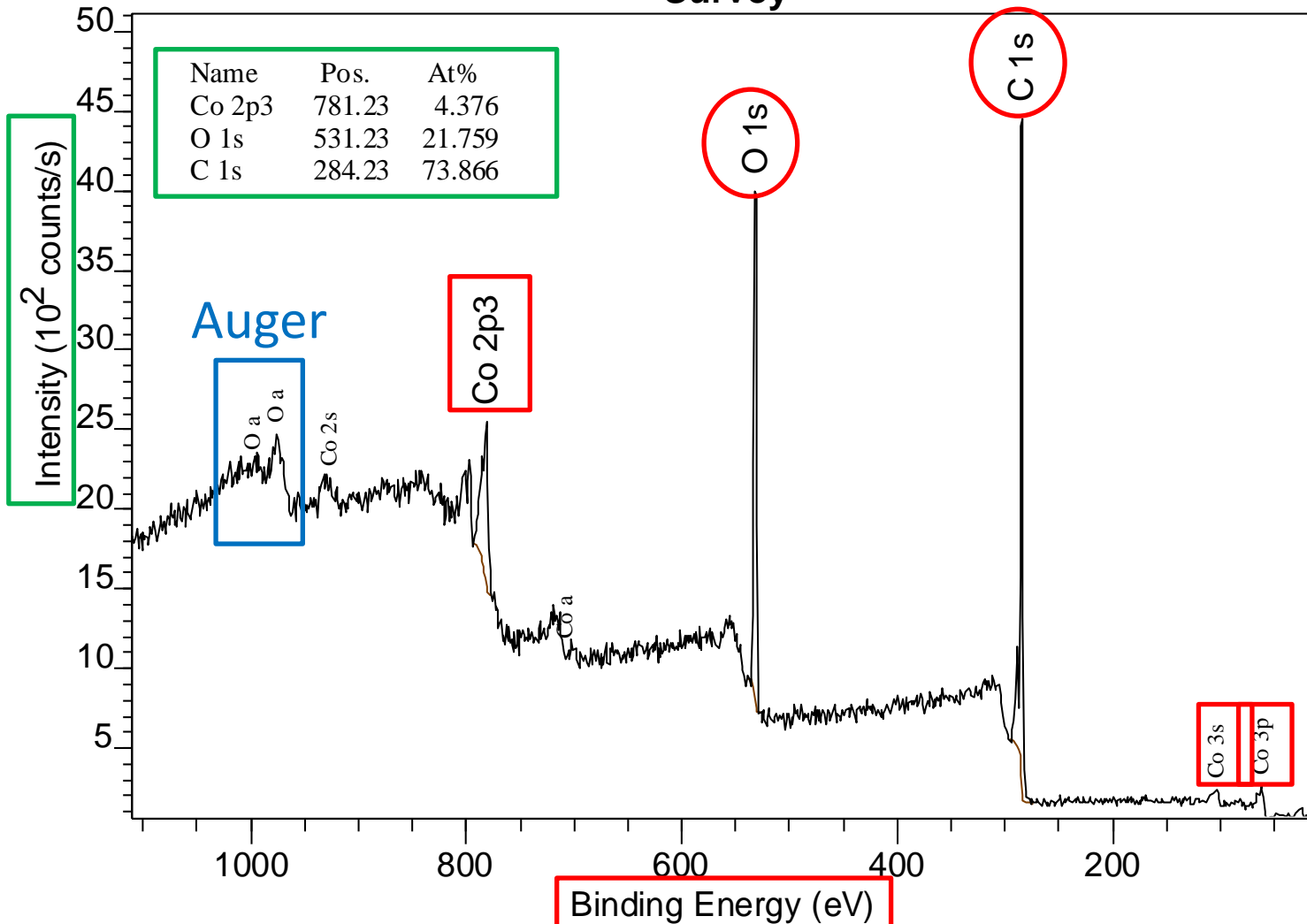
$$E_{photon} = h\nu = \textcolor{red}{BE} + \text{kinetic energy } (\textcolor{blue}{KE})$$

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

X-ray photoelectron spectroscopy (XPS)
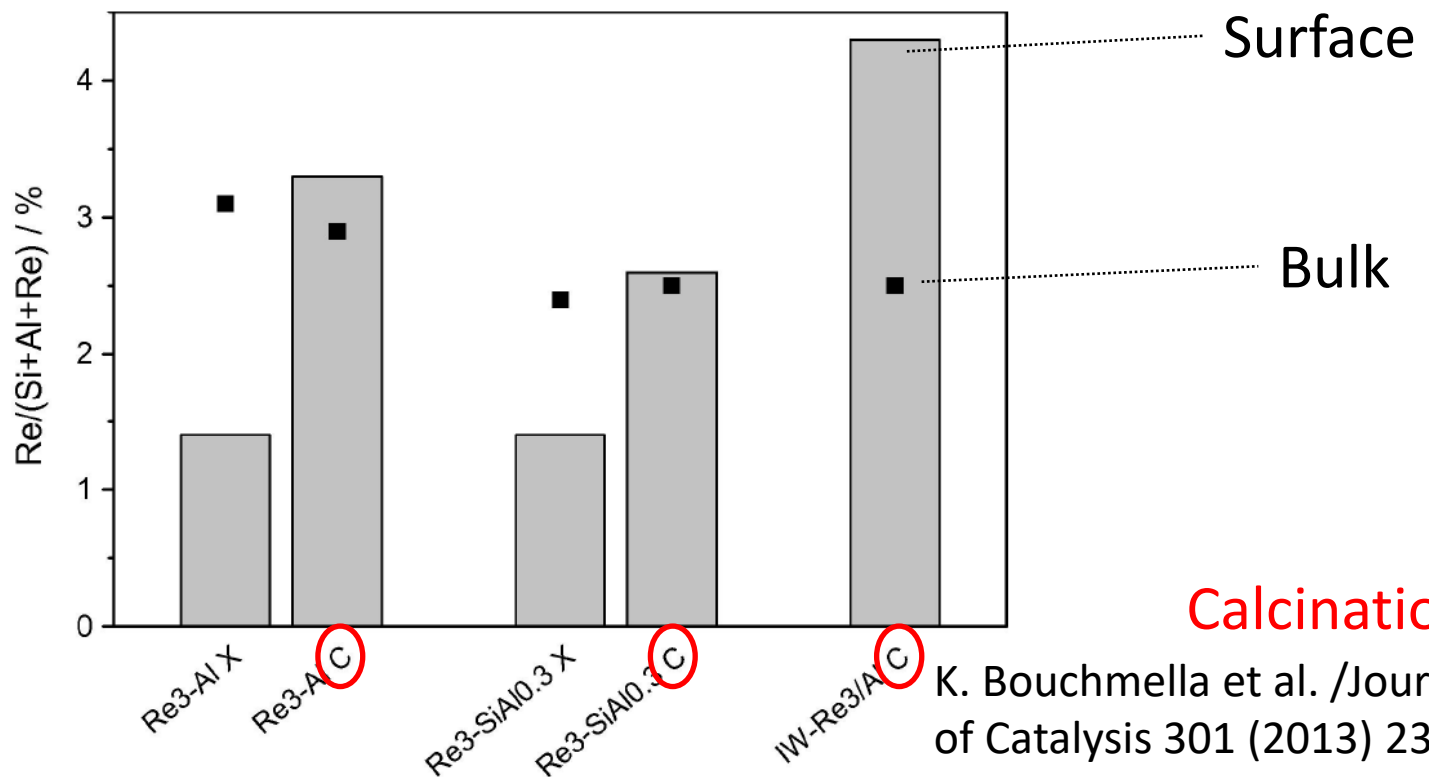
Survey

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

Intensity (10^2 counts/s)

Auger

Co 2p3

O 1s

C 1s

O a O a Co 2s Co a Co 3s Co 3p

Binding Energy (eV)

X-ray photoelectron spectroscopy (XPS)

- Surface vs. bulk composition

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.

K. Bouchmella et al. /Journal of Catalysis 301 (2013) 233–241
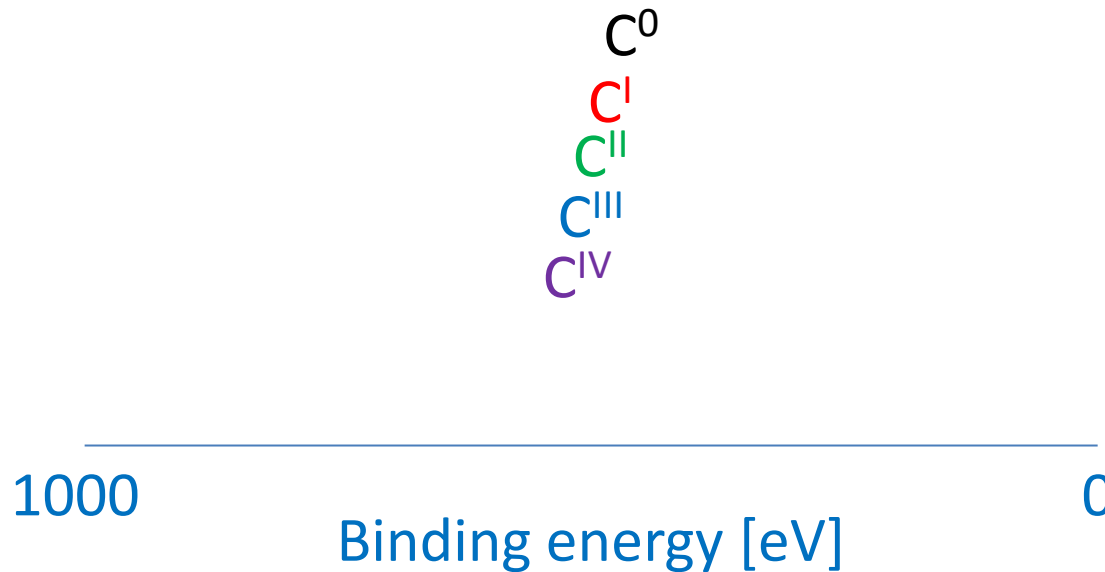
X-ray photoelectron spectroscopy (XPS)

- Oxidation state

C^0
C^I
C^{II} ?
C^{III}
C^{IV}

1000 ———————————————— 0

Binding energy [eV]
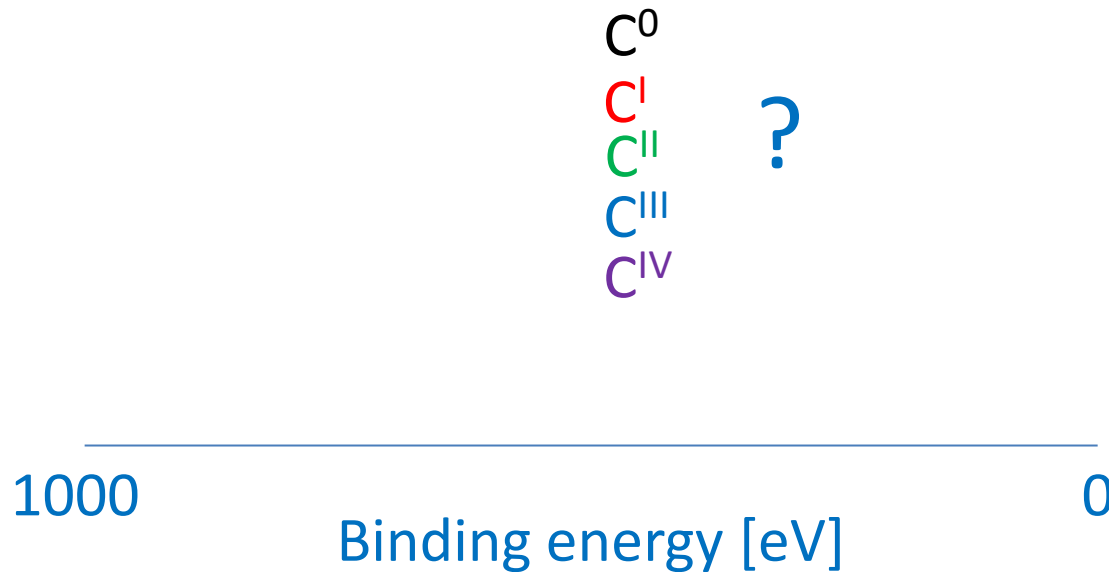
- Who will hold its electrons more powerfully? C^0 or C^{IV}?

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)
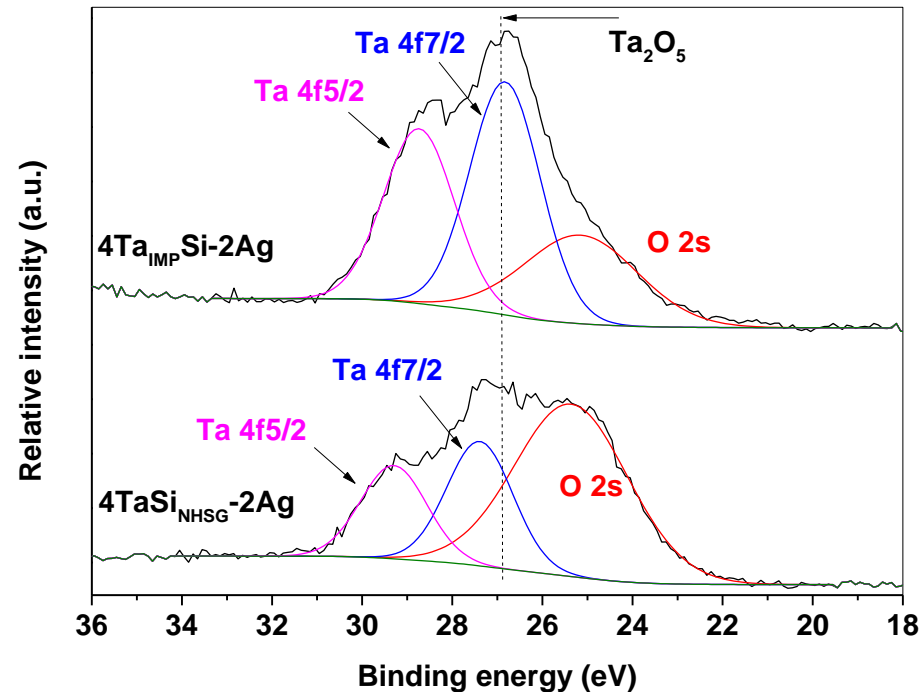
- Oxidation state
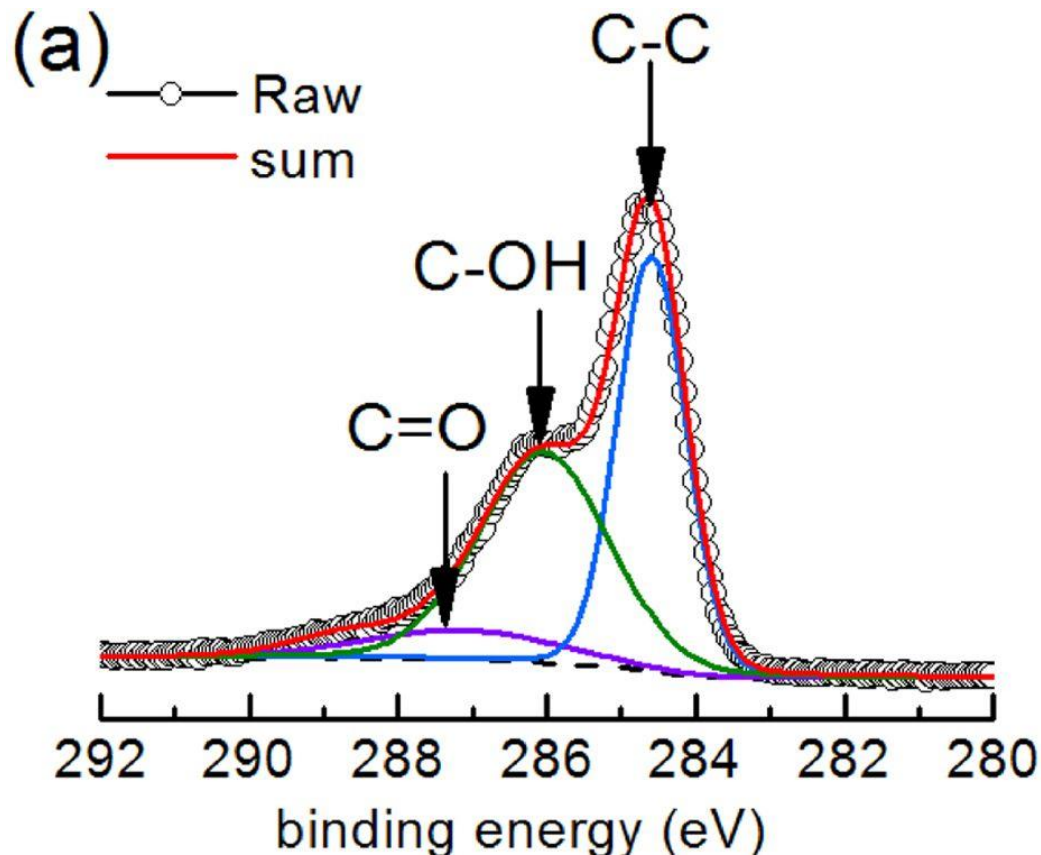
X-ray photoelectron spectroscopy (XPS)

- Similar consideration:

SiO_4 vs. $CSiO_3$

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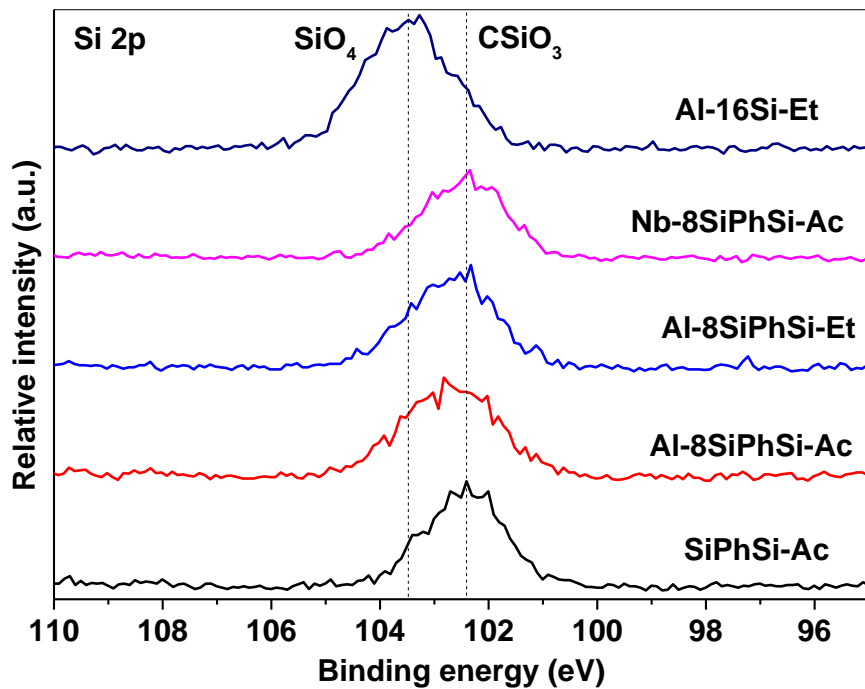
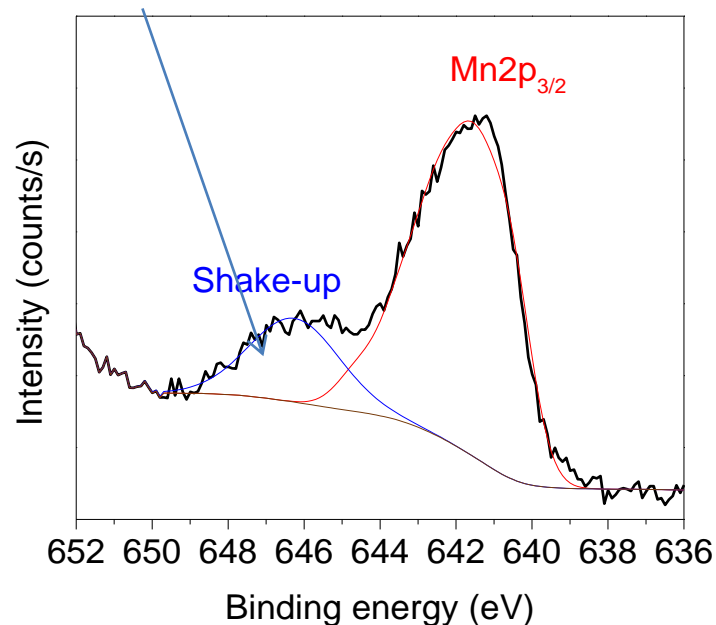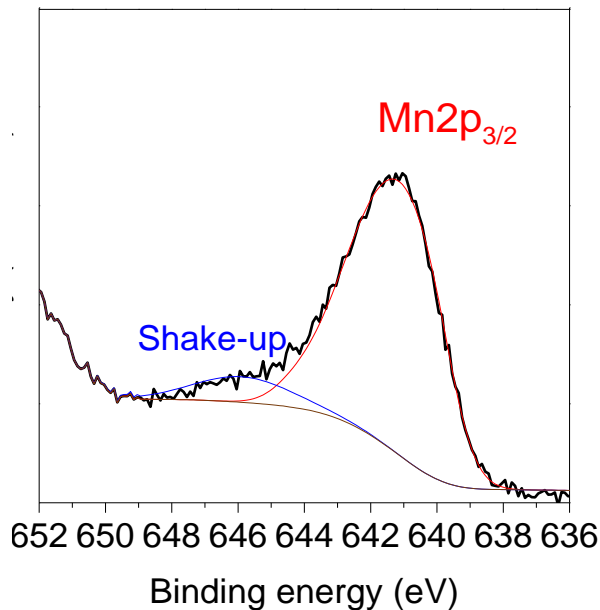

Electronegativity (O) =
Electronegativity (C) =

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
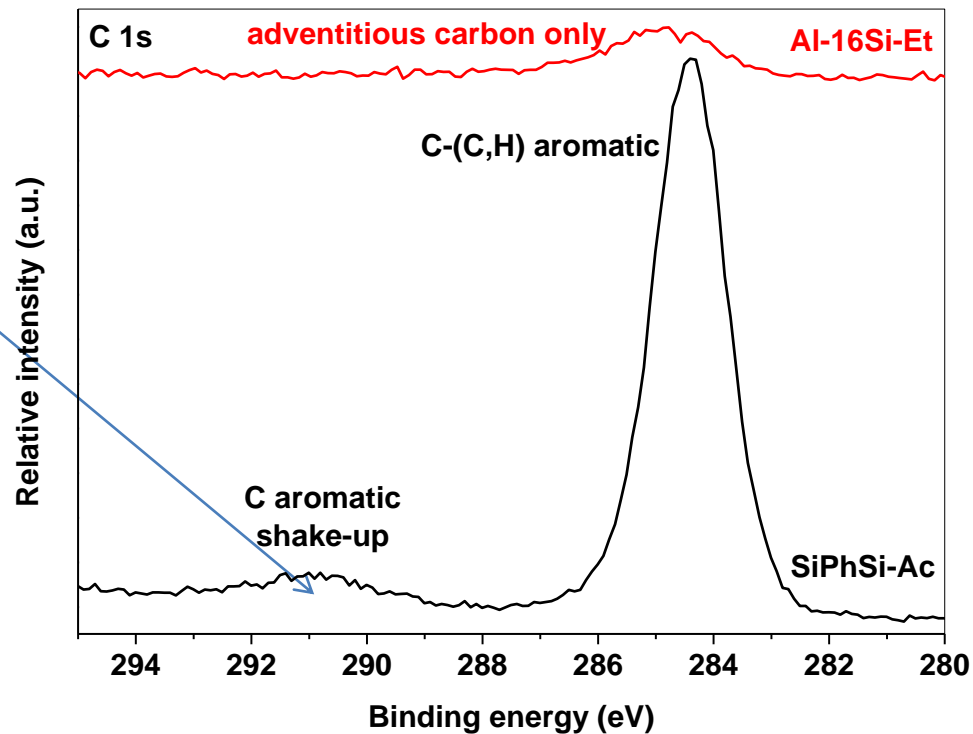
  – Oxidation states

  – 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

Ionization Spectroscopies

Photoelectron spectroscopy:
UV: valence shell ionizations

X-ray: core electron ionizations
(XPS, XANES, EXAFS):
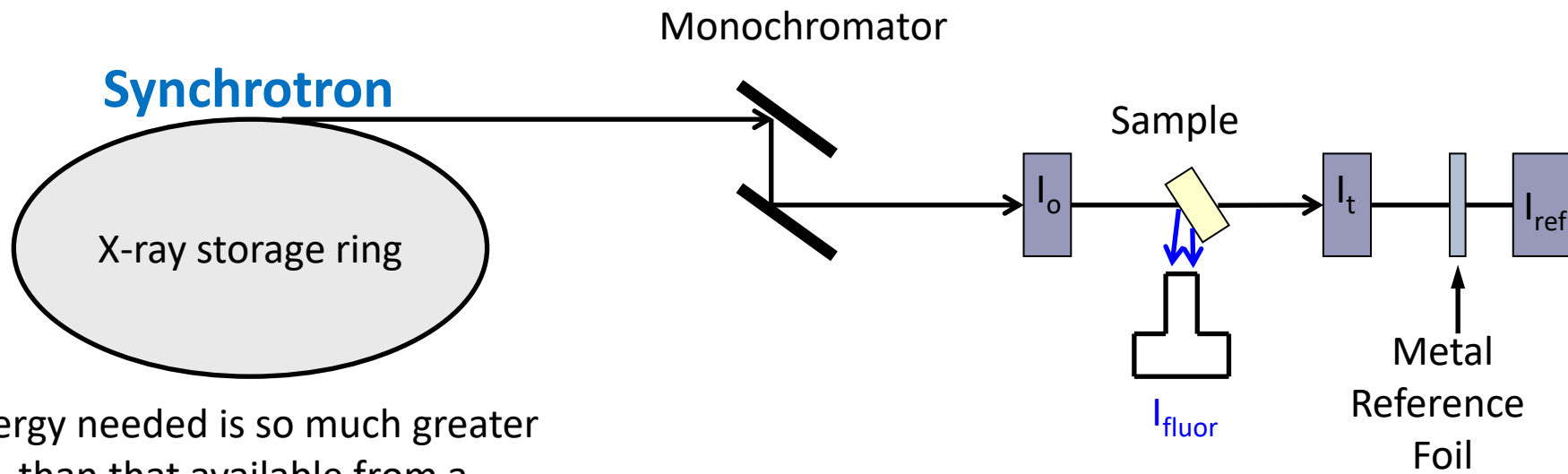
$$E_{photon} = h\nu = BE + kinetic\ energy\ (KE)$$

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)**

ionization continuum

KE

0

virtual levels

valence levels

BE

core levels
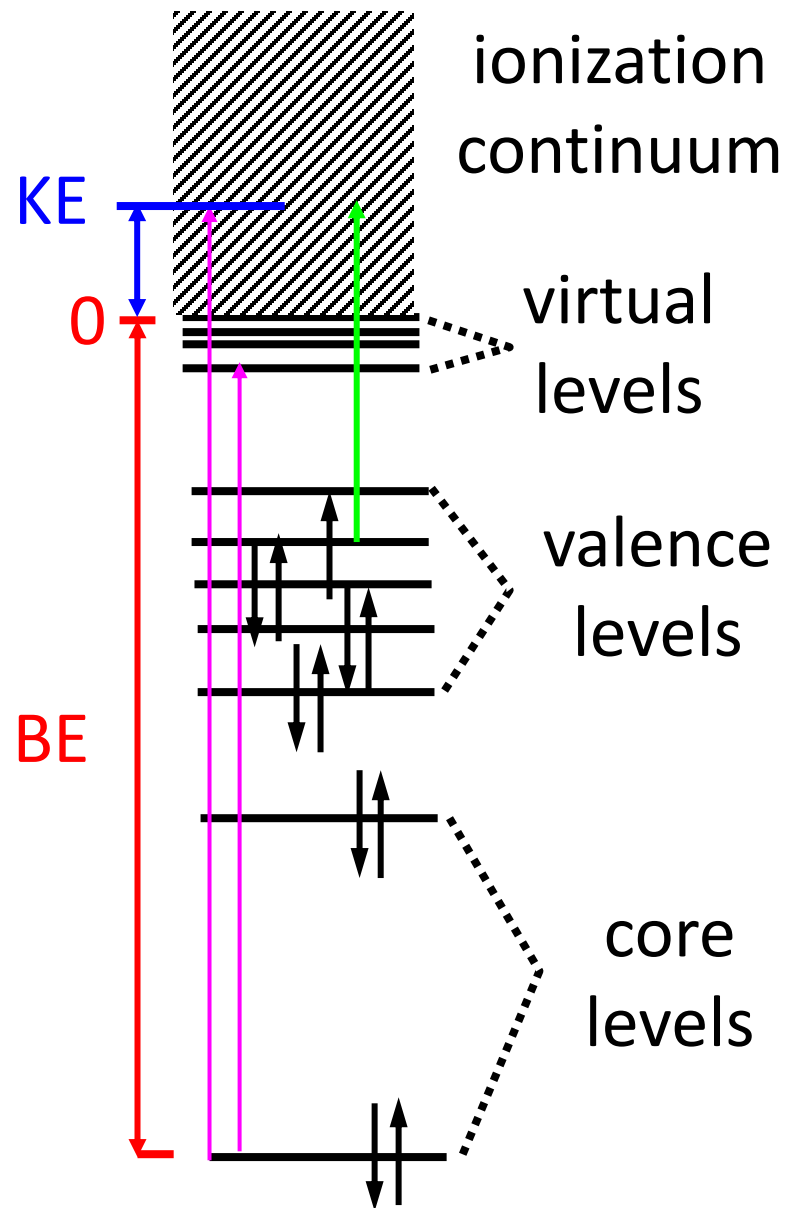
XANES and EXAFS

In XANES and EXAFS we measure number and energy of transmitted photons, which caused ionization of a core electron (i.e. absorbance vs. energy)

Monochromator

Synchrotron

Sample

X-ray storage ring

I_o

I_t

I_{ref}

I_{fluor}

Metal Reference Foil

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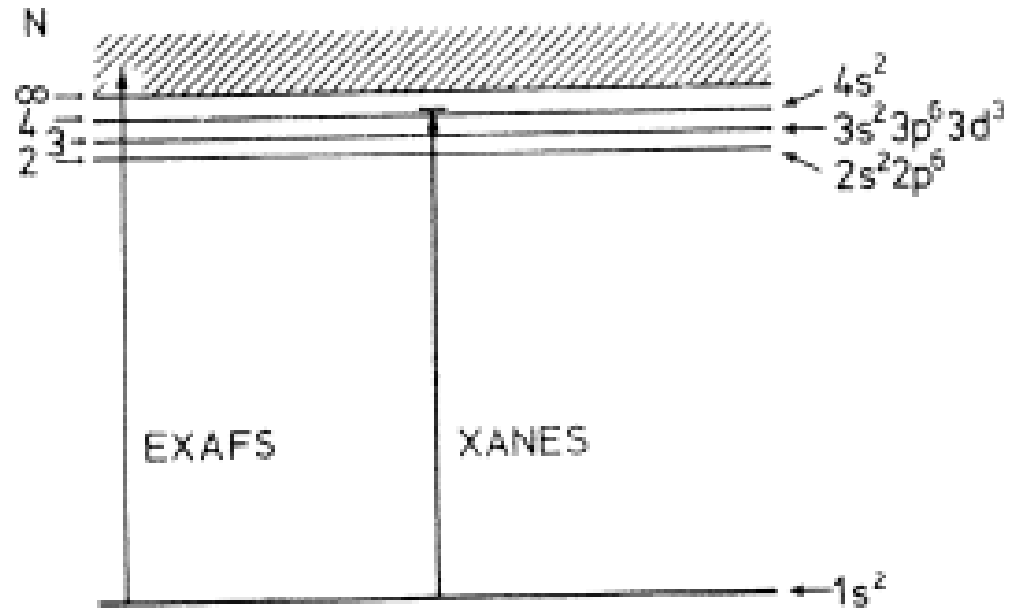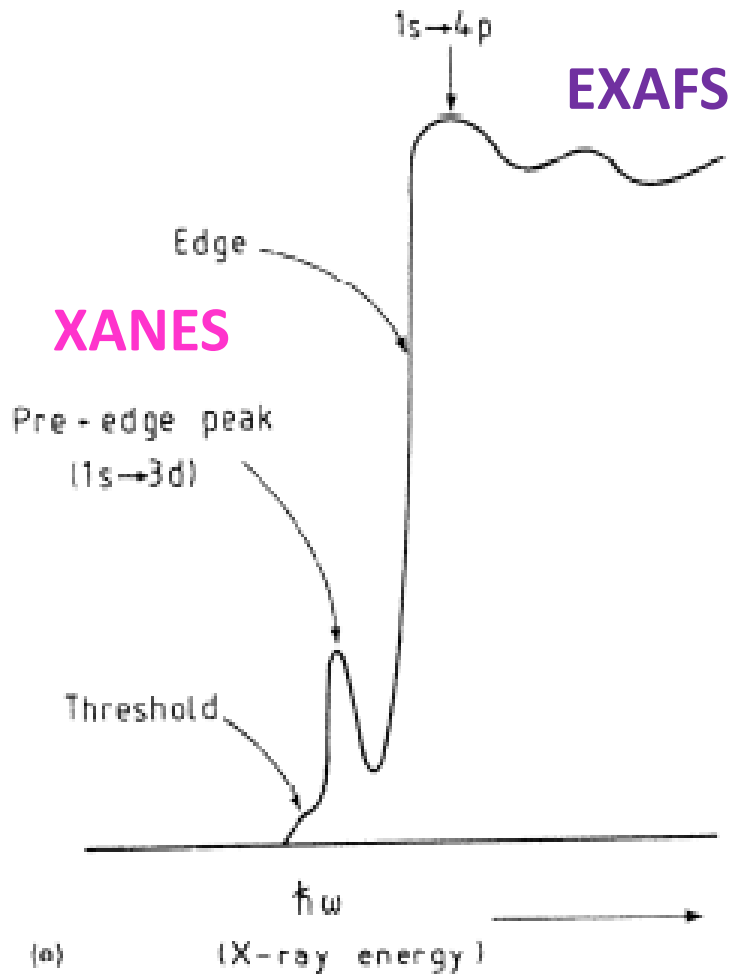
XANES and EXAFS

- 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
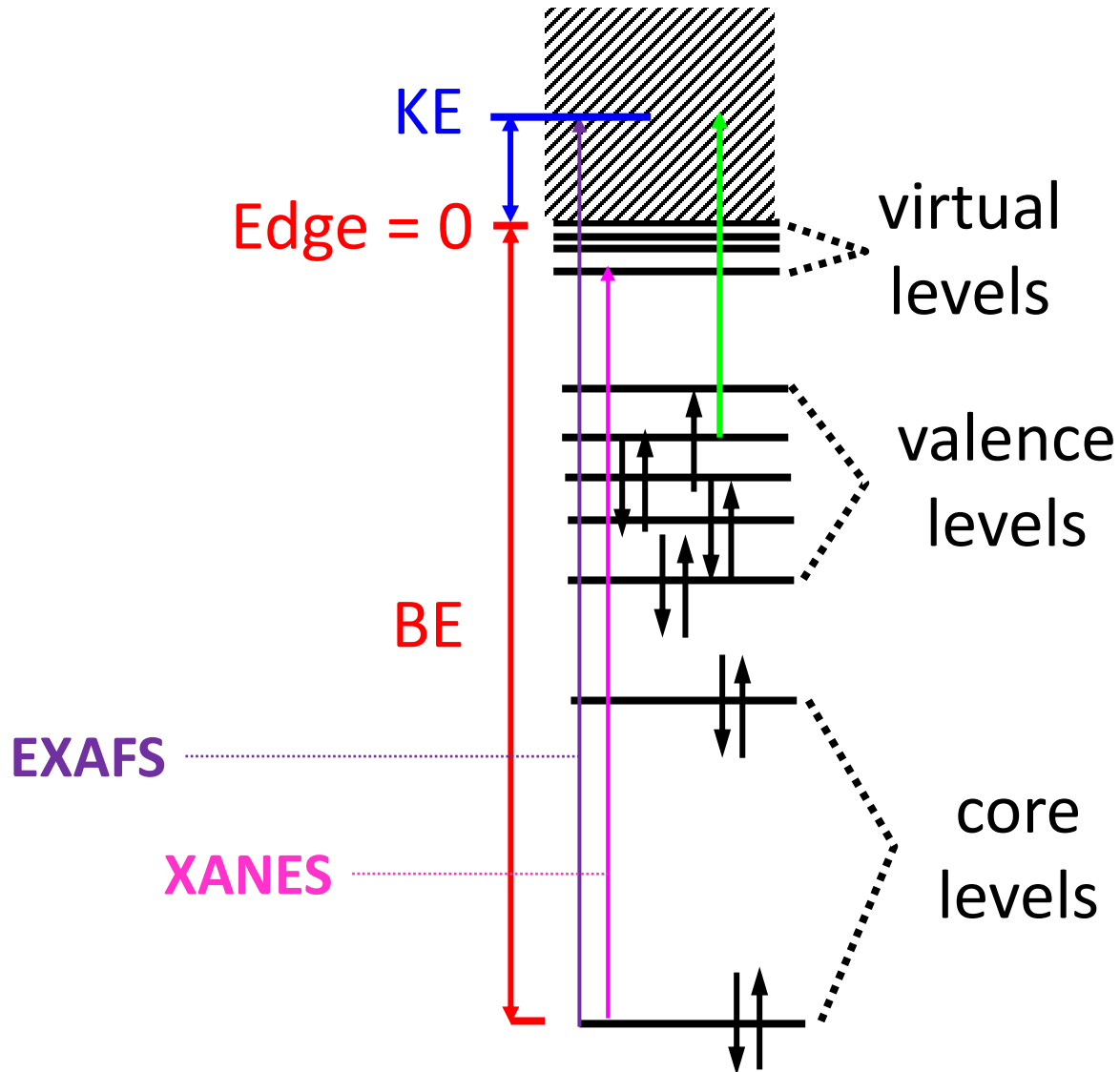
XANES and EXAFS

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.
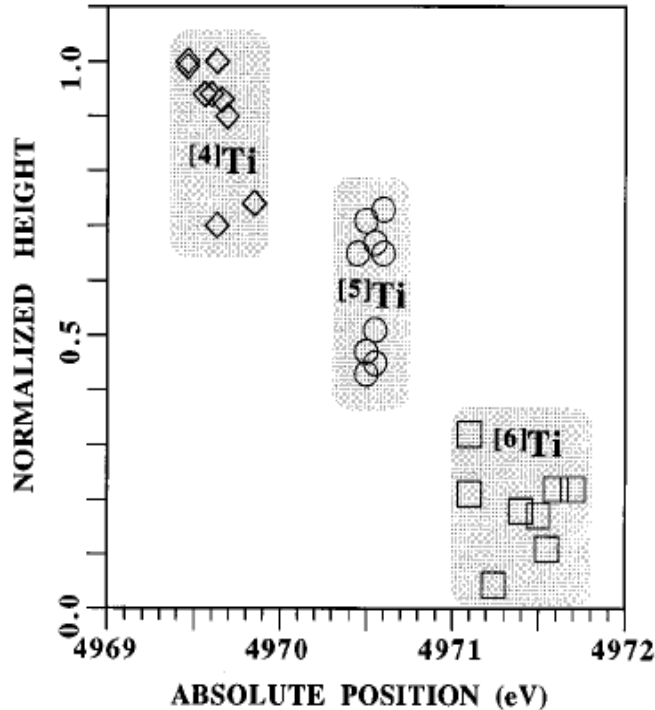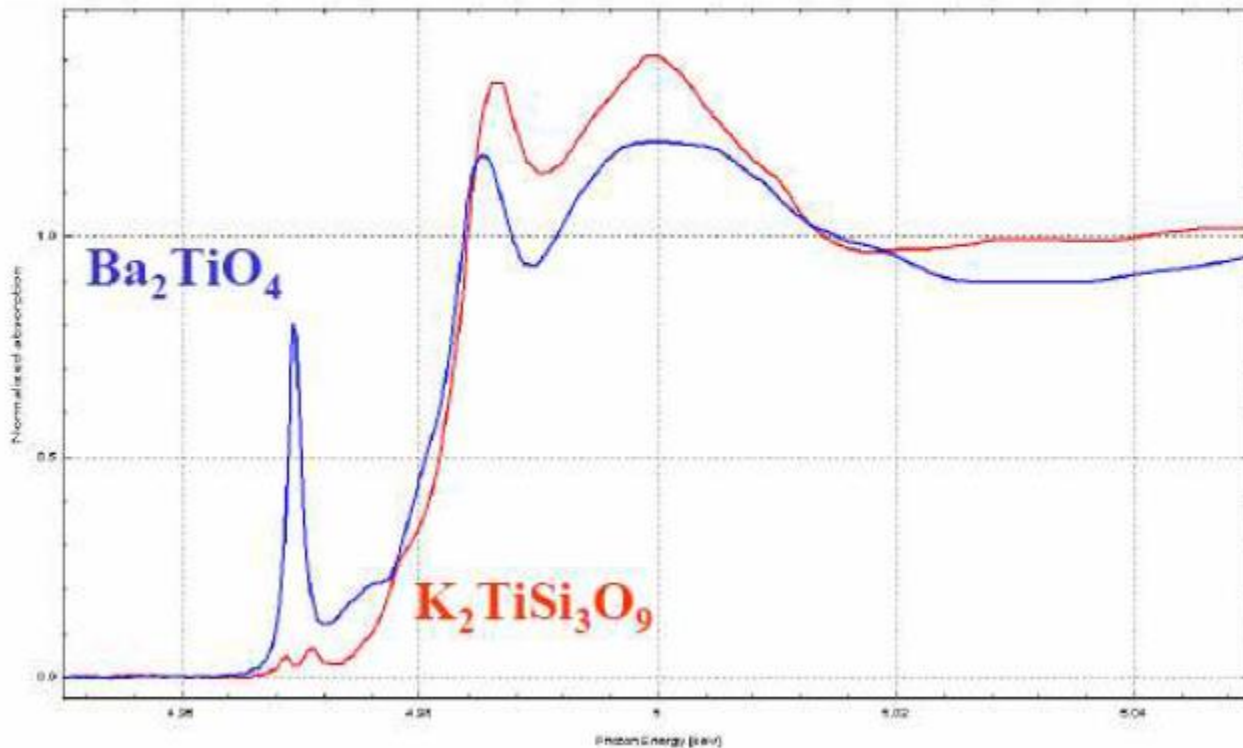
XANES

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

EXACT

Relative absorbance [a.u.]

XANES

EXAFS

E_o →

- What type of information is hidden there???

Absorbance

Energy
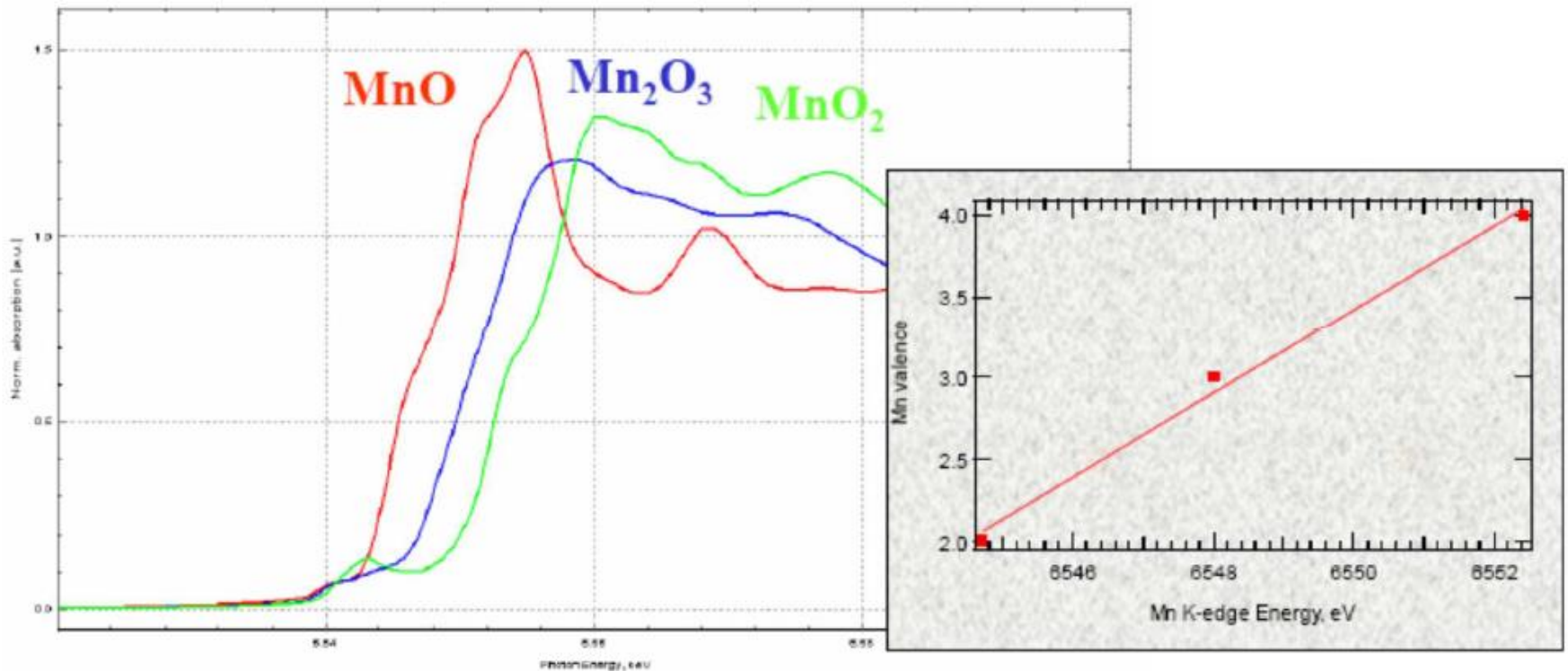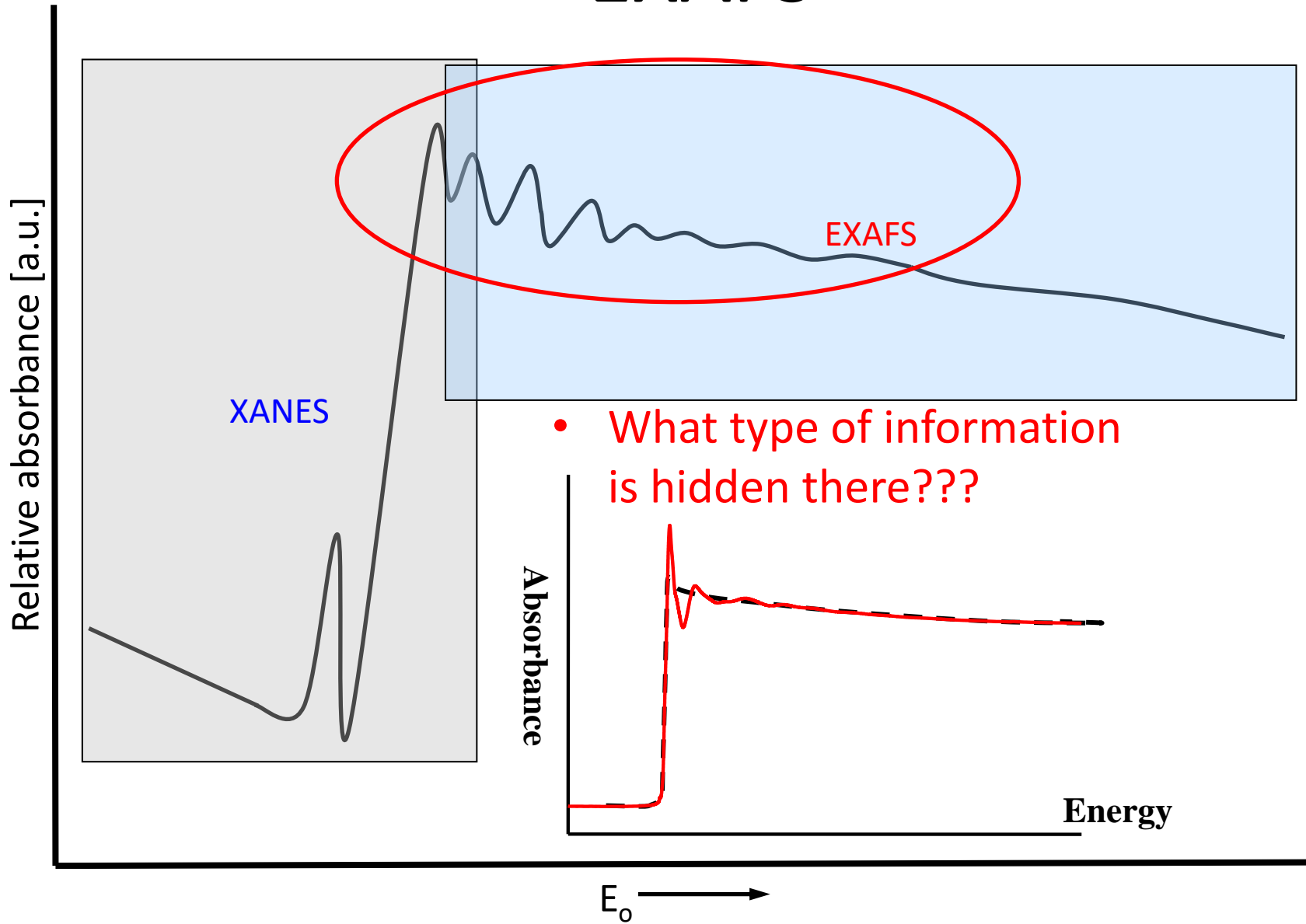
EXAFS

- The scattering phenomena

Scattering from Ti

Back-scattering from "neighbors"

EXAFS

Step 1: The data

EXAFS

Arbitrary Units

E_o →
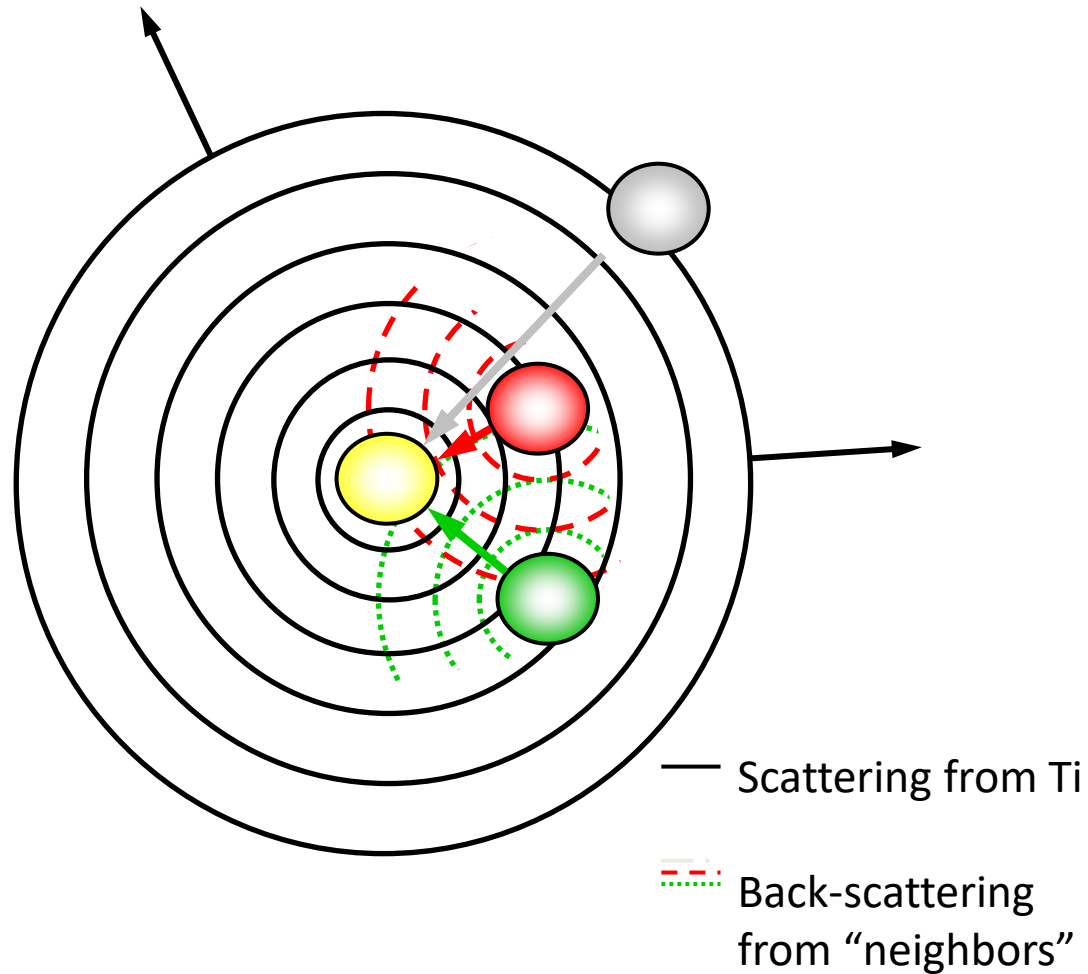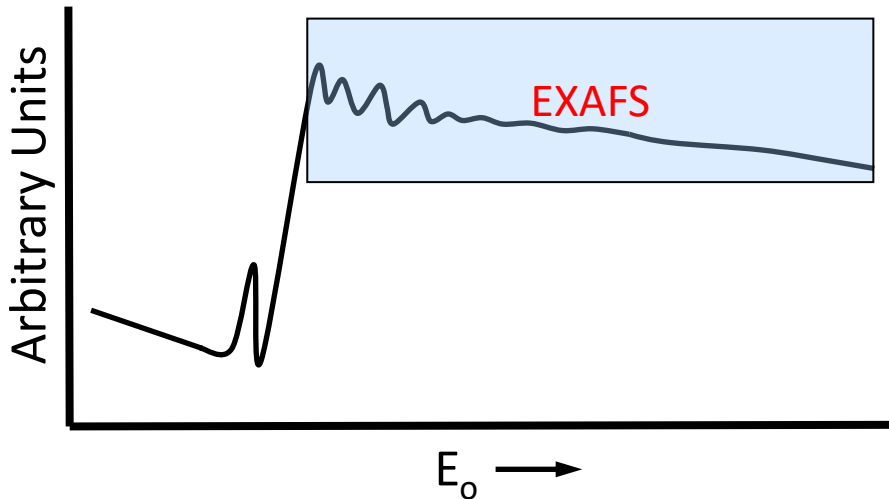
Math →

Step 2: Extract $\chi(k)$

$k^3 \chi(k)$ ($\AA^{-3}$)

k ($\AA^{-1}$)

— $\chi(k)$
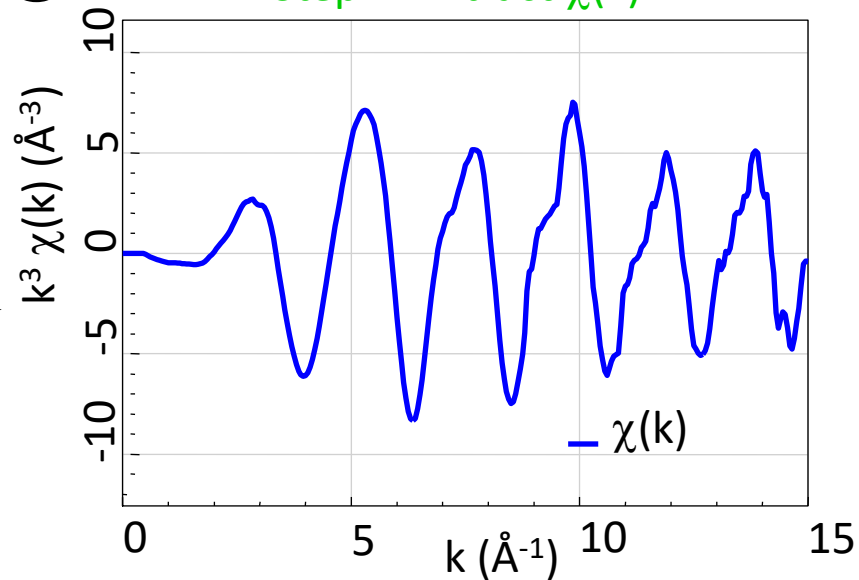
Fourier Transform ↓

Step 3: The FT
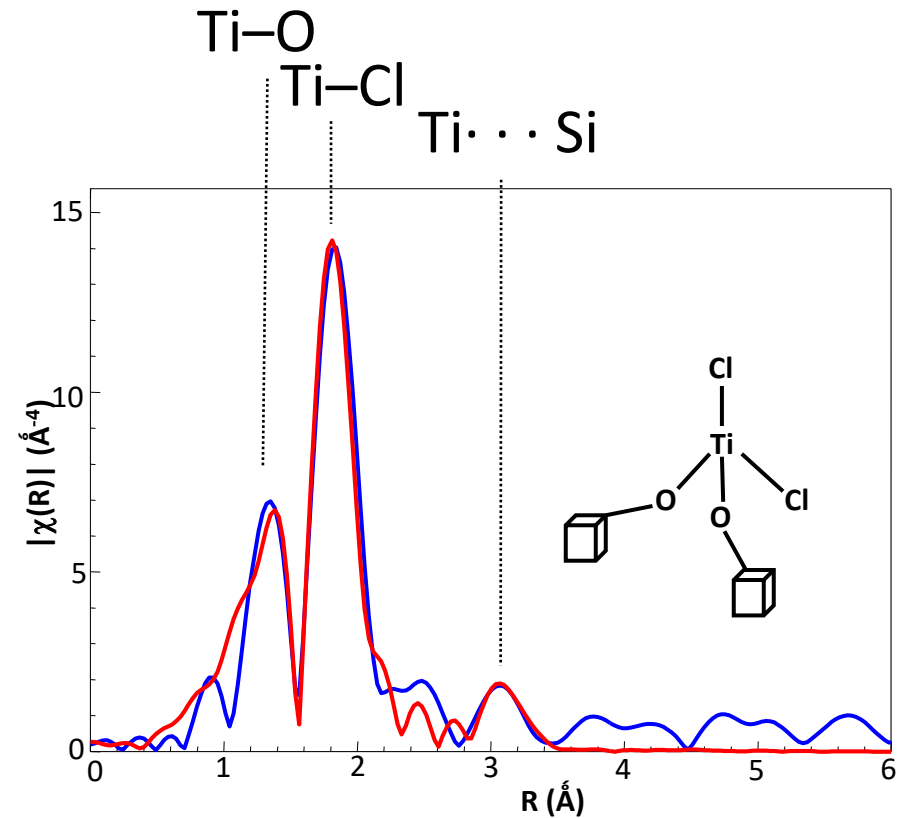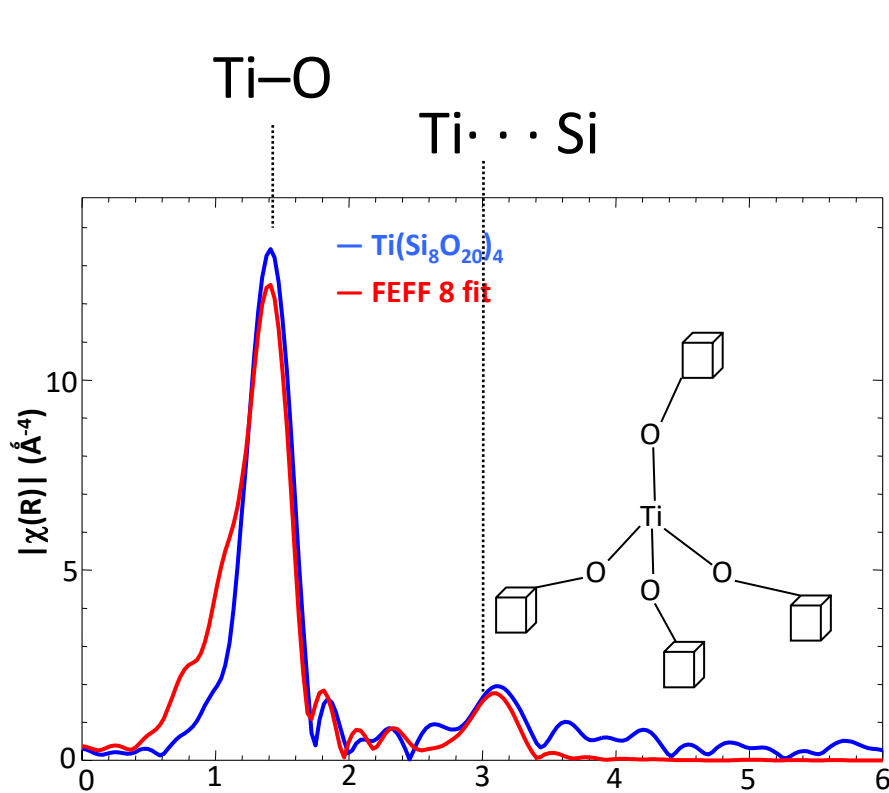

— RM5_K2

$|\chi(R)|$ ($\AA^{-3}$)

R ($\AA$)
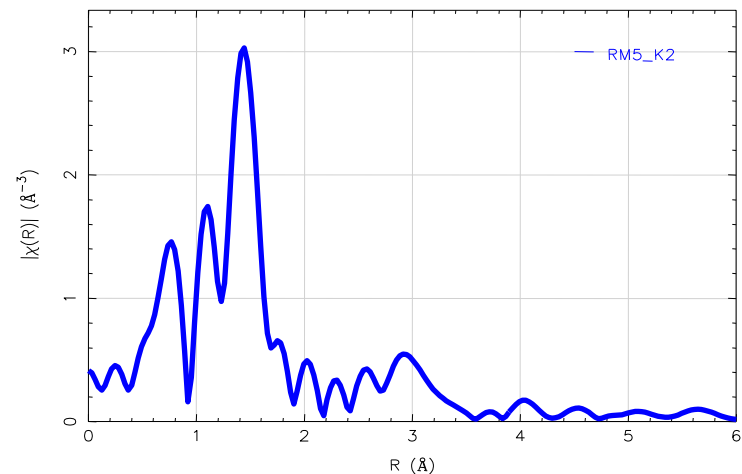
Step 4:

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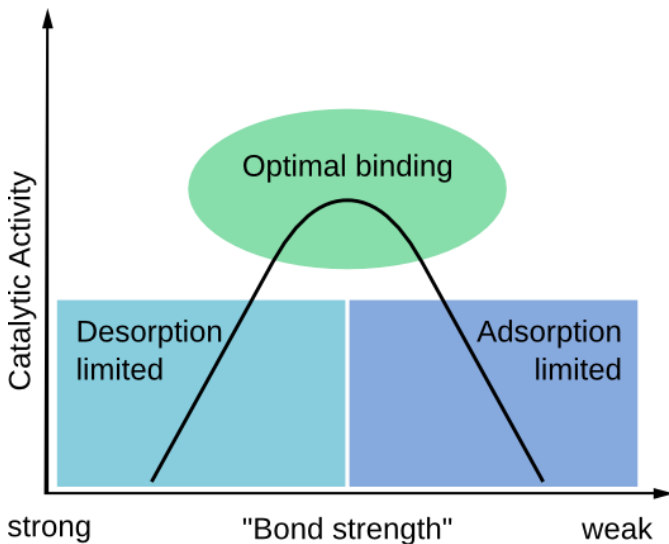that fits that data
d(M-X), CN(X),
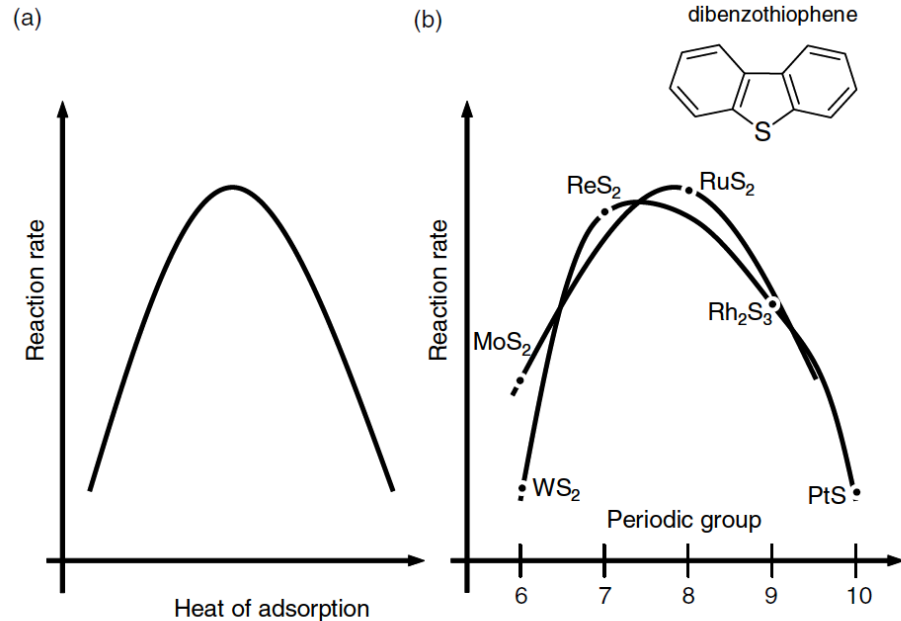AtNum(X)

←

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
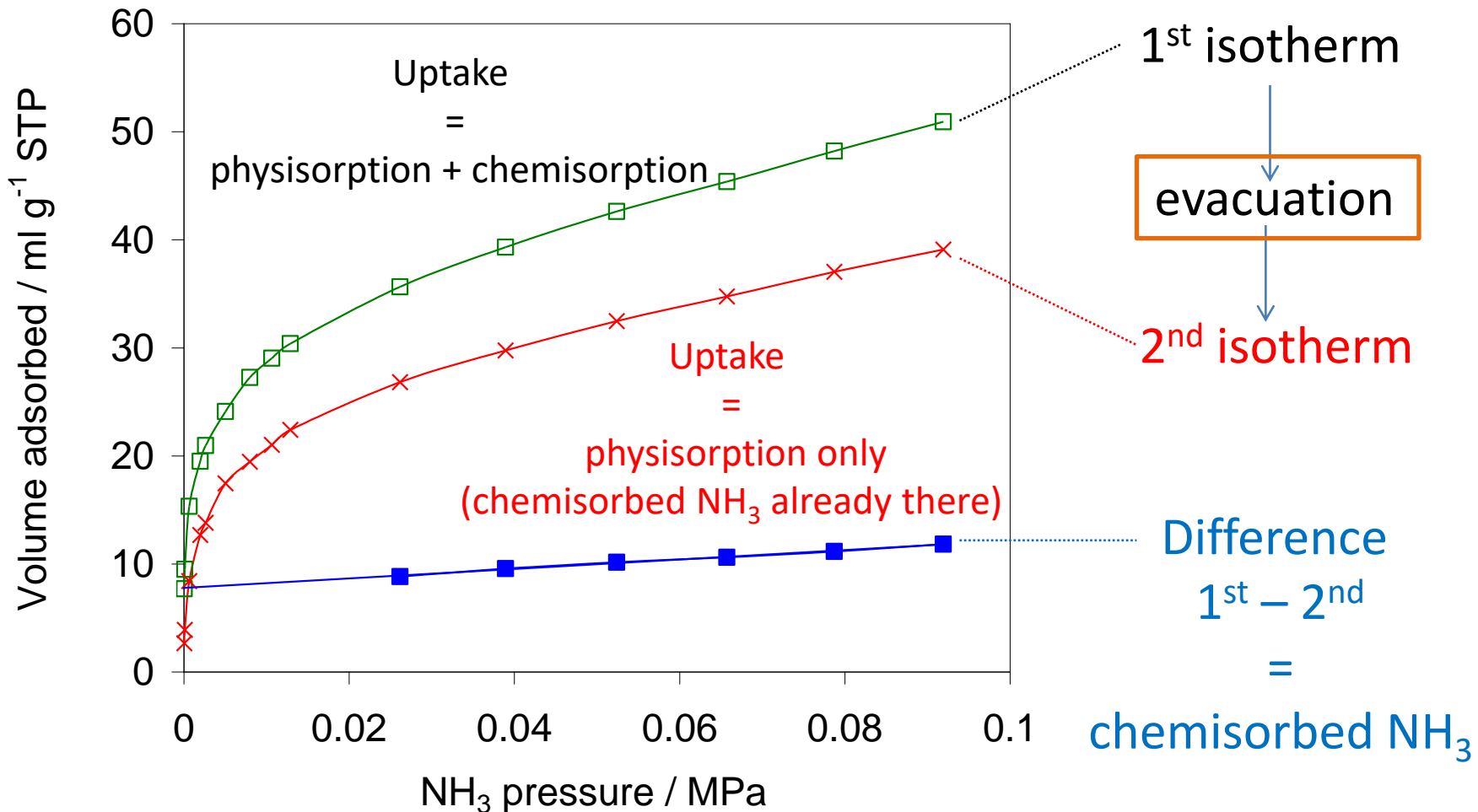 - Chemisorption of IR (NMR) active molecules and their analysis by IR (NMR)

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)
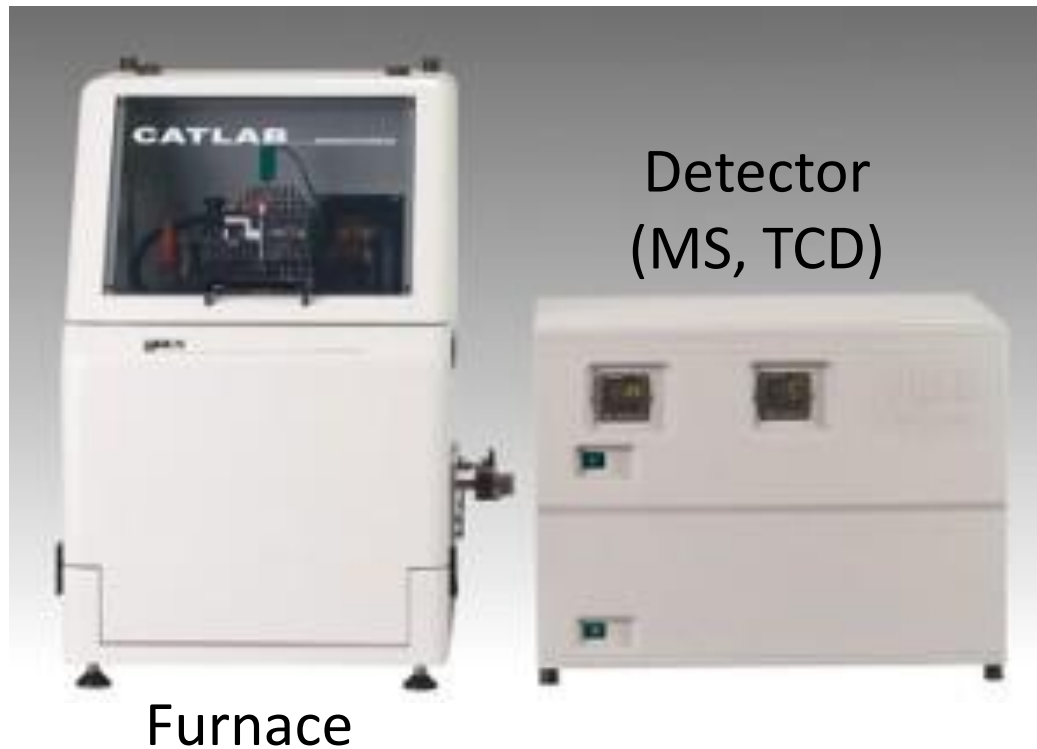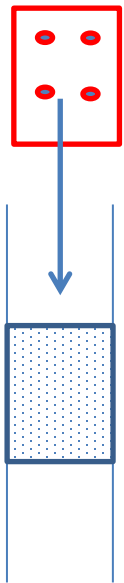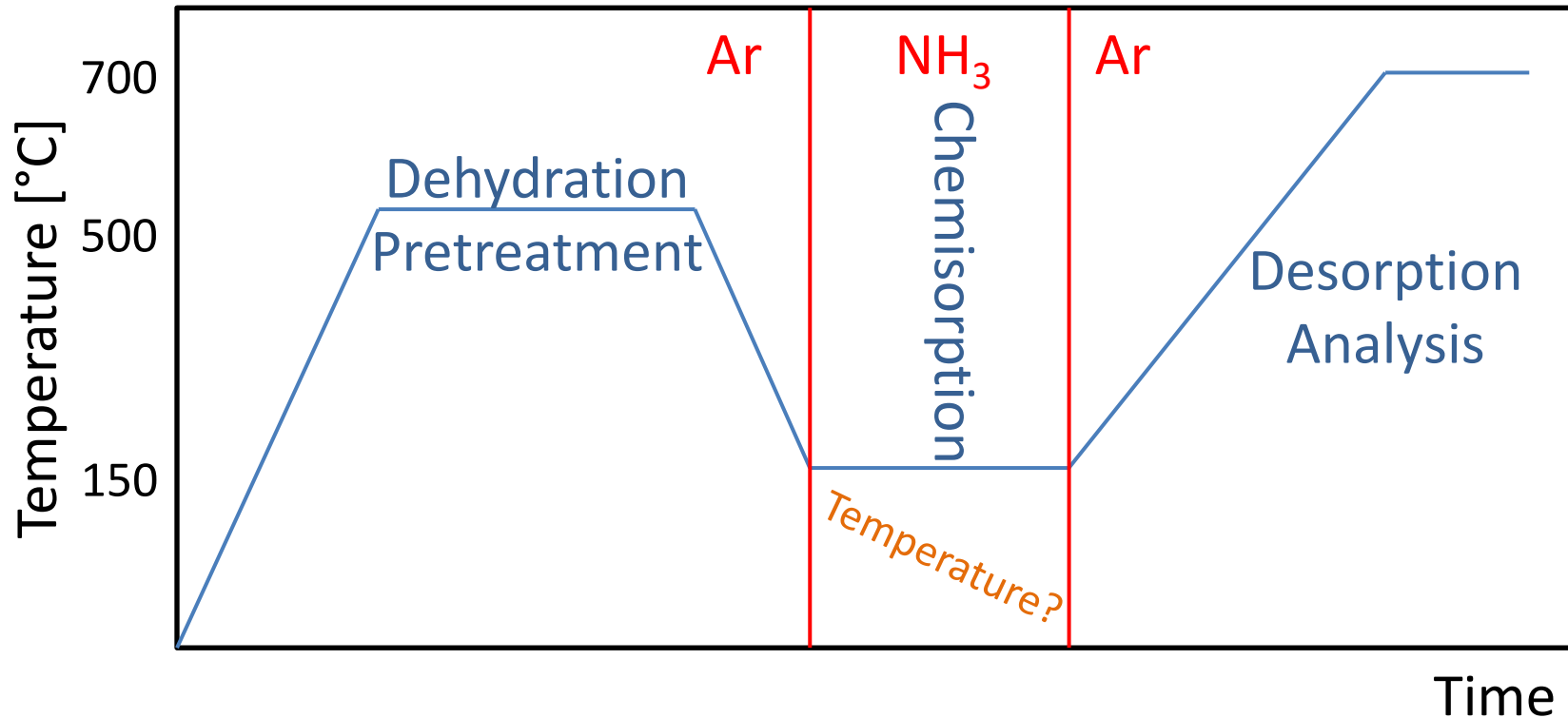
Chemisorption

Temperature?

- Volumetric

1st isotherm

evacuation

2nd isotherm

Difference
1st − 2nd
=
chemisorbed NH$_3$

Chemisorption

- Thermally programmed desorption/oxidation/reduction

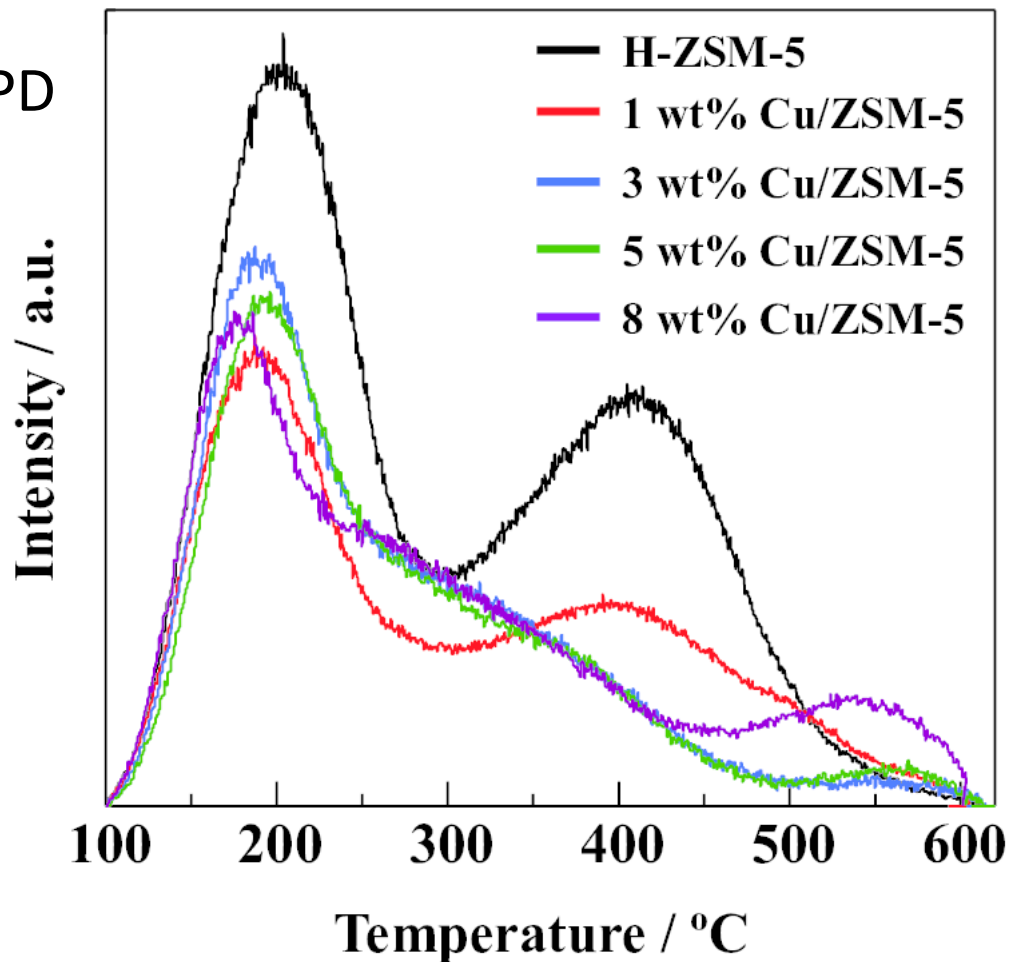Detector (MS, TCD)

Furnace

Chemisorption

- Thermally programmed desorption/oxidation/reduction

Chemisorption

- Thermally programmed …

NH$_3$ TPD

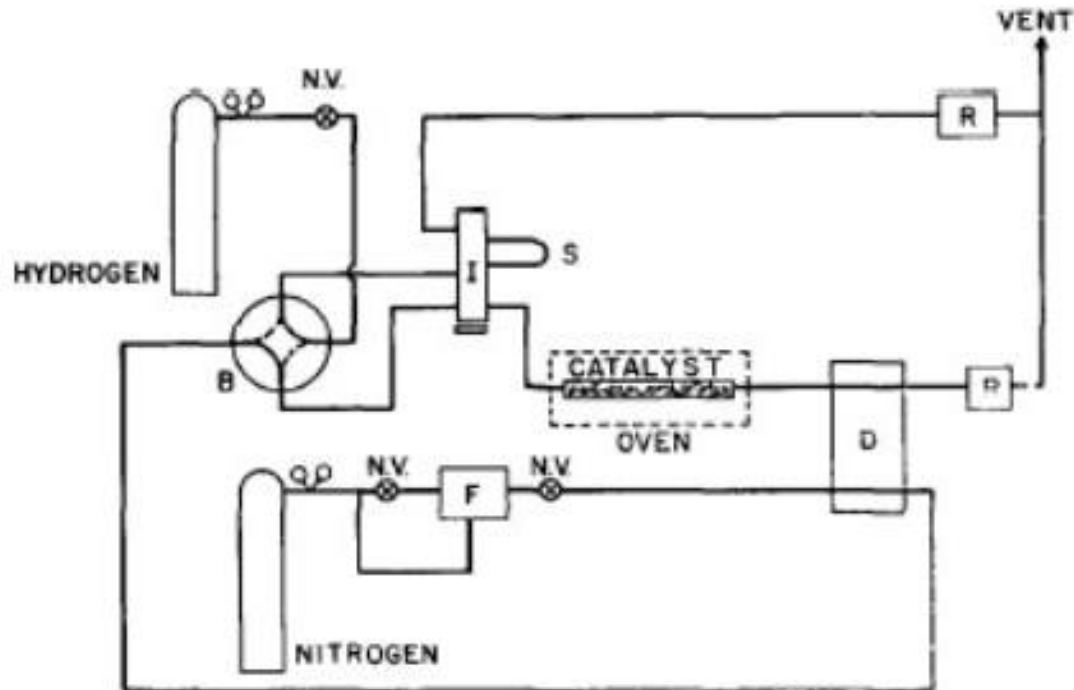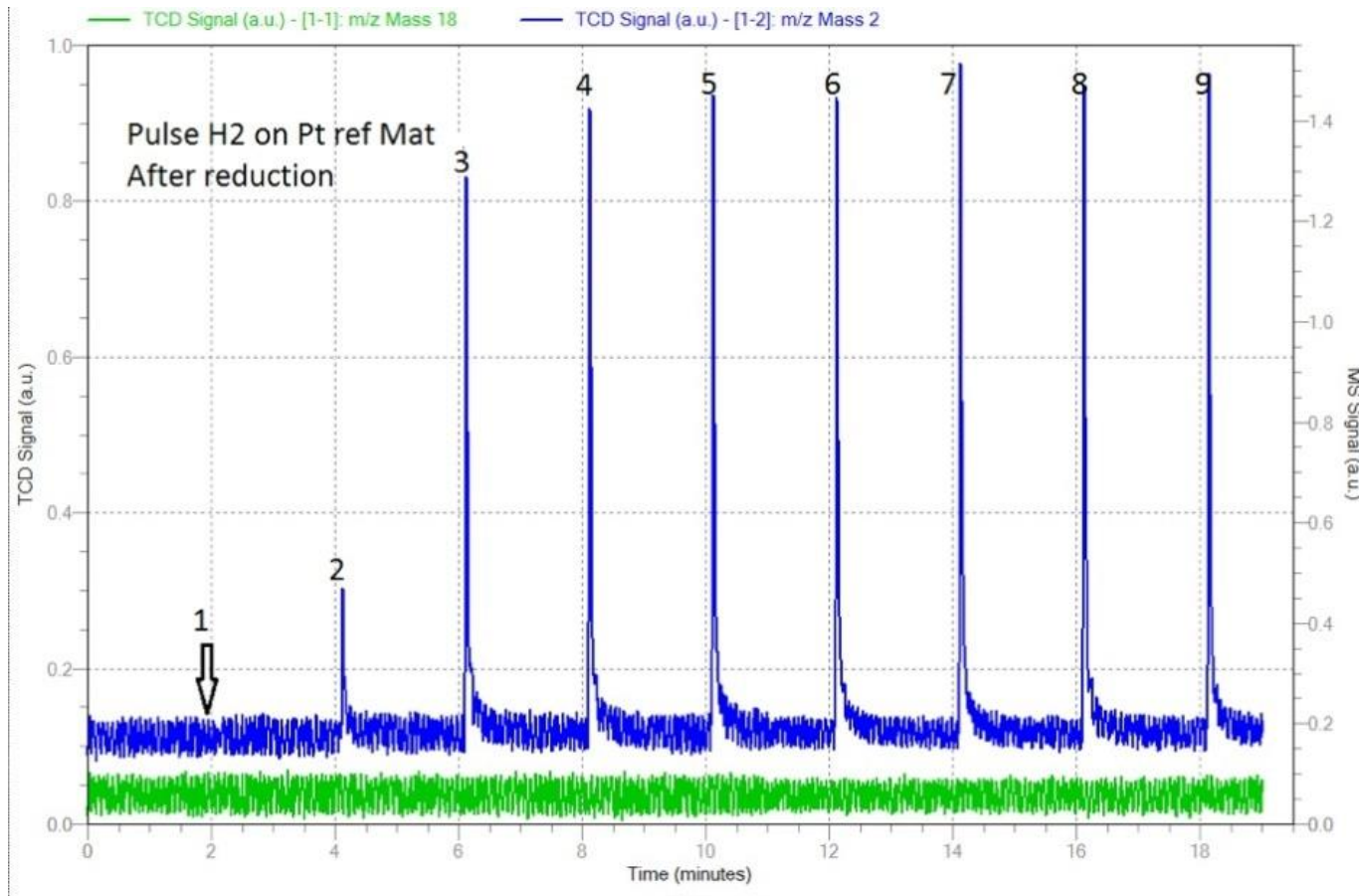# Chemisorption

- 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.
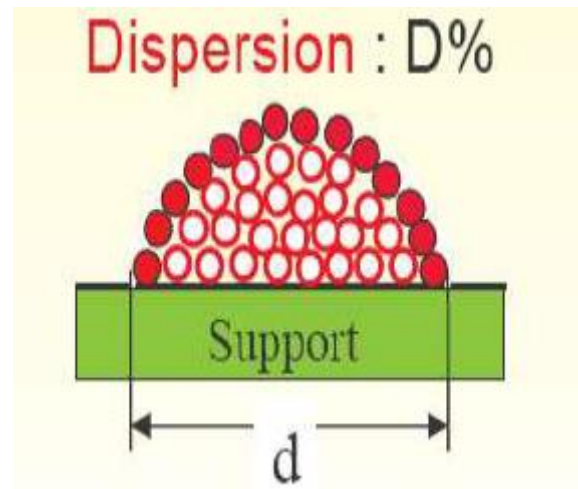
Chemisorption

- 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"

Dispersion : D%

Support

d

Number of surface atoms

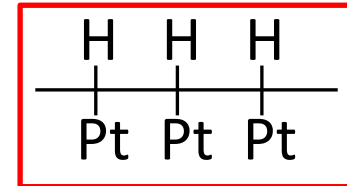$$D = 100 \frac{N_S}{N_T}$$

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)
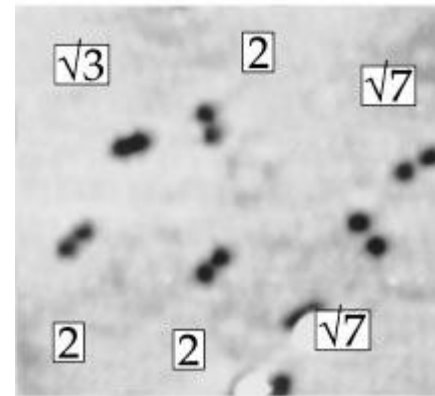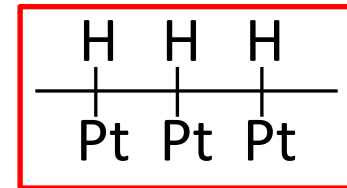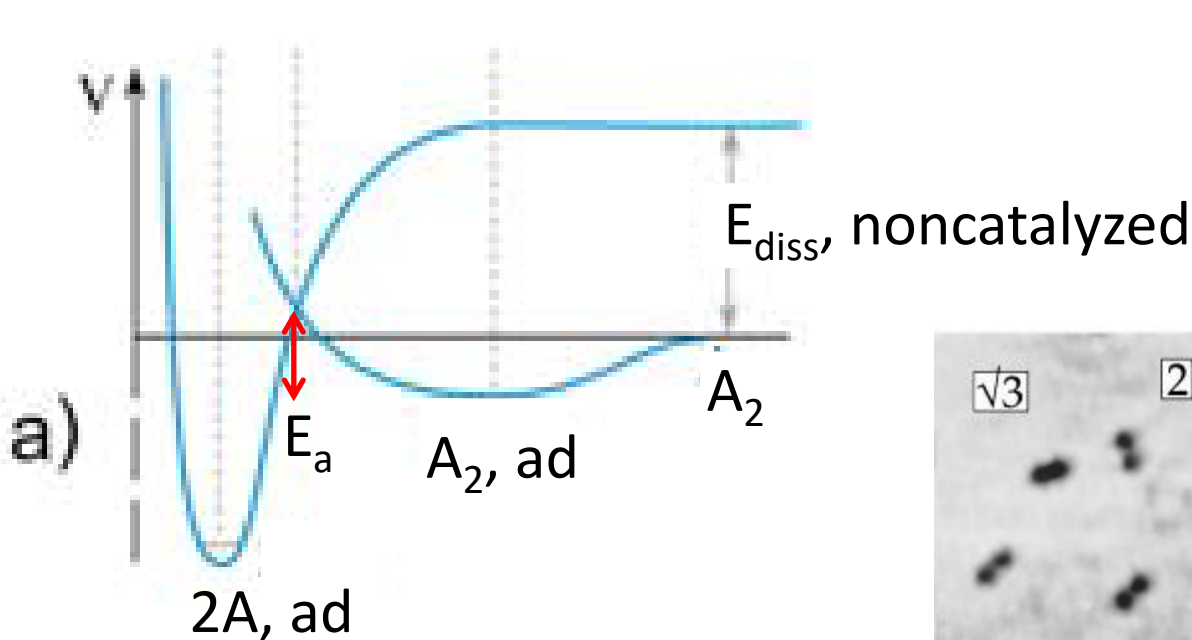 - H_2 chemisorption is **dissociative**!
  - H–H bond breaks at the time of chemisorption, this is the key to high reactivity (adsorbed **molecular** hydrogen)
  - This is Langmuir's chemistry

```
H   H   H
|   |   |
————————————
Pt  Pt  Pt
```

Chemisorption

- X_2 dissociative chemisorption (detour)

E_{diss}, noncatalyzed

E_a

A_2, ad

2A, ad

A_2

H H H
Pt Pt Pt

"Hot" O atoms
Lifetime 10^{-13} s
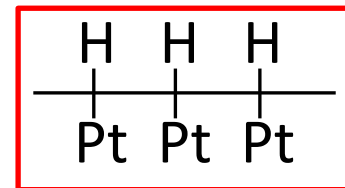
O_2 adsorption on Pt(111) surface @165 K
O–O in O_2 = 1.2Å, here much longer

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)
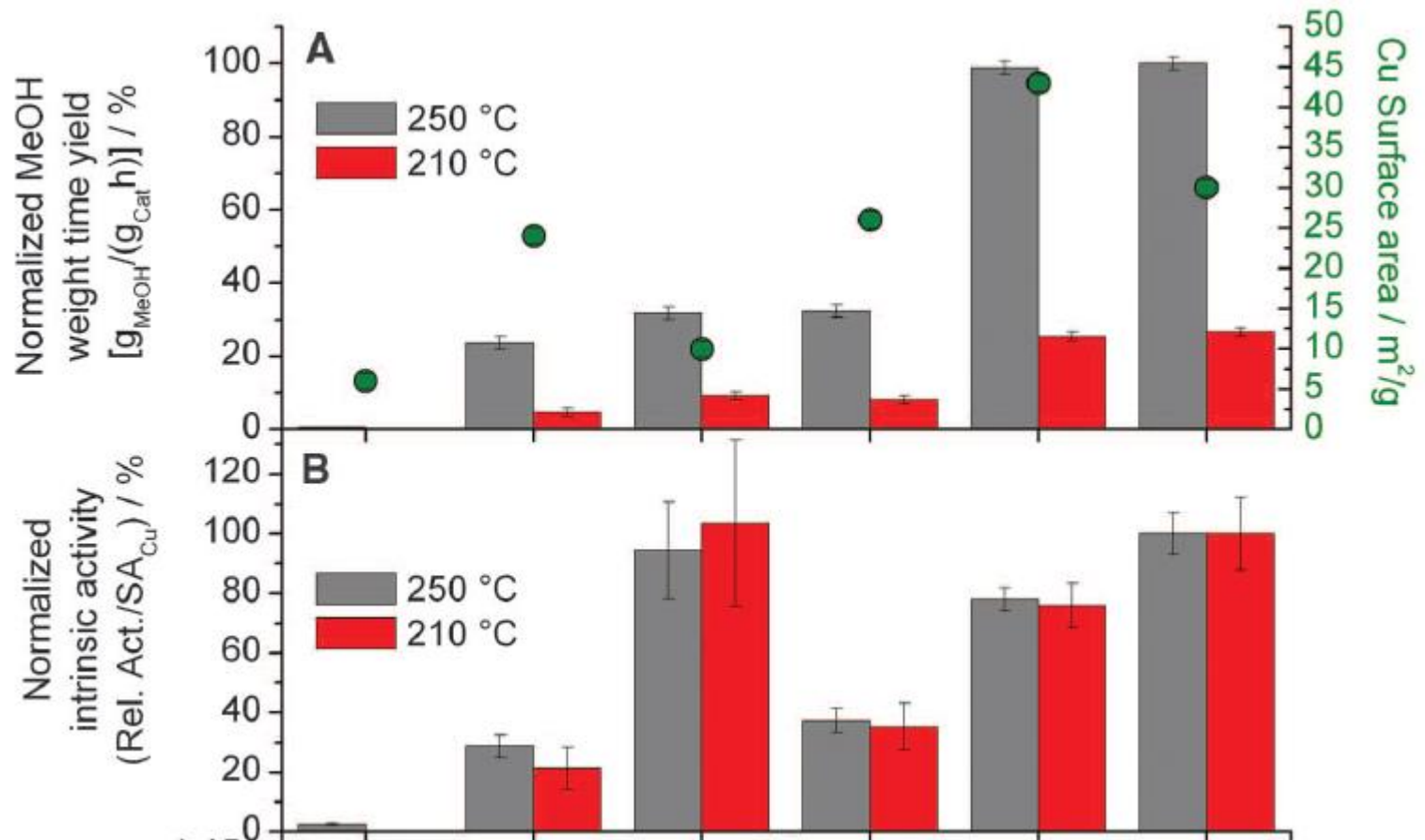
  - BUT

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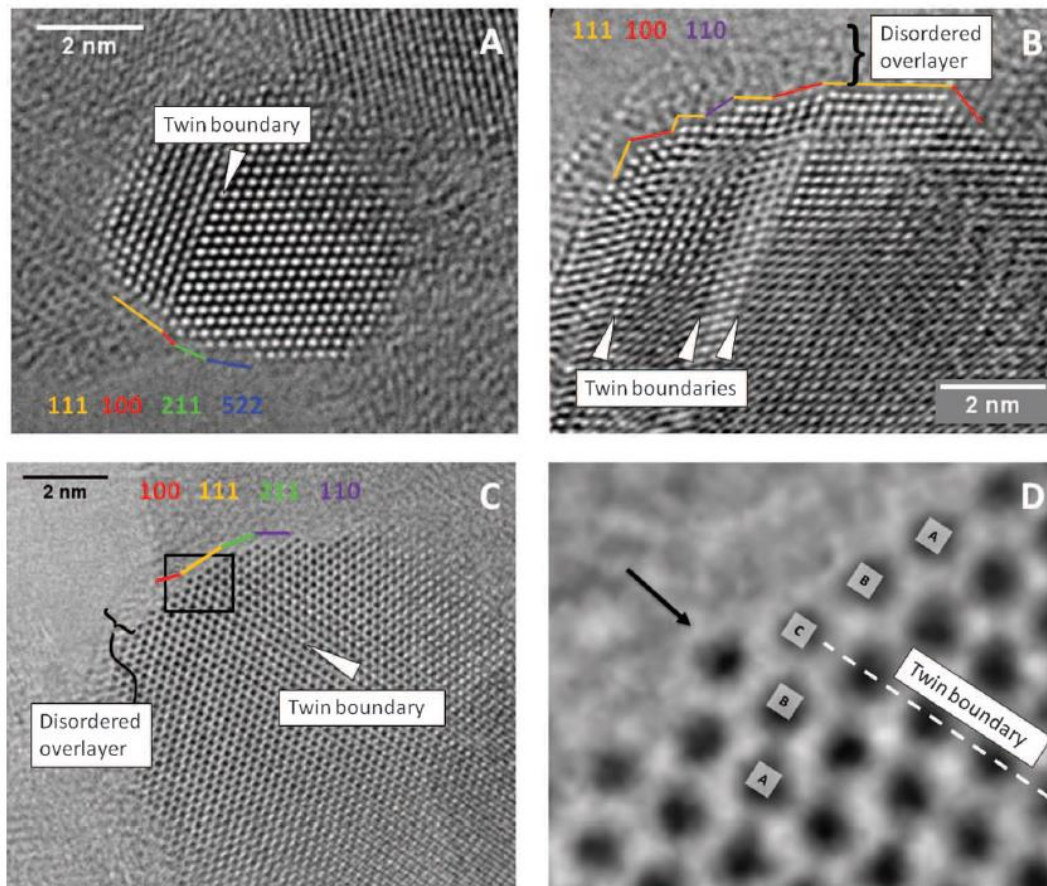 - $CO_2 + 2\ H_2 \rightarrow CH_3OH$

Chemisorption

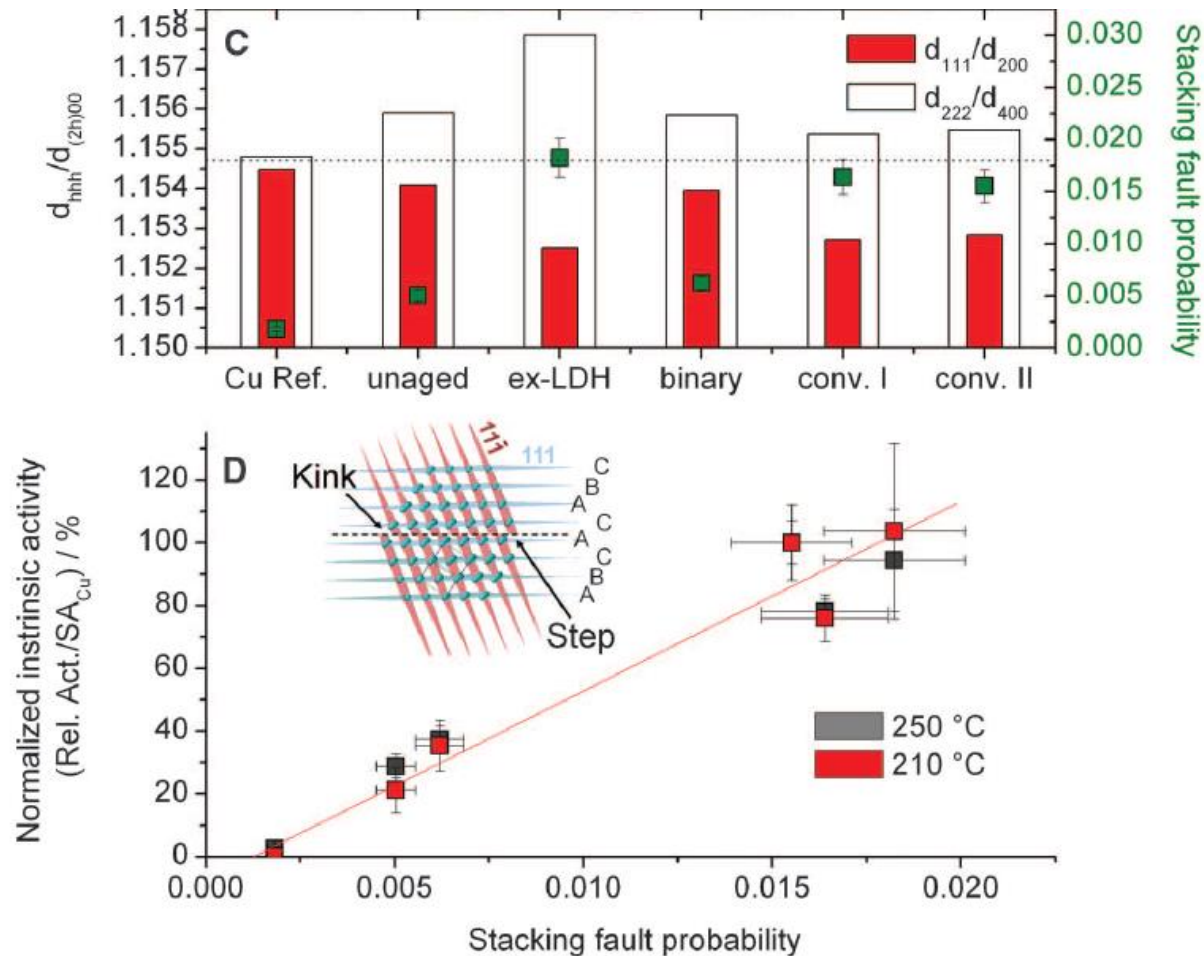- Example: methanol synthesis over Cu NPs

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
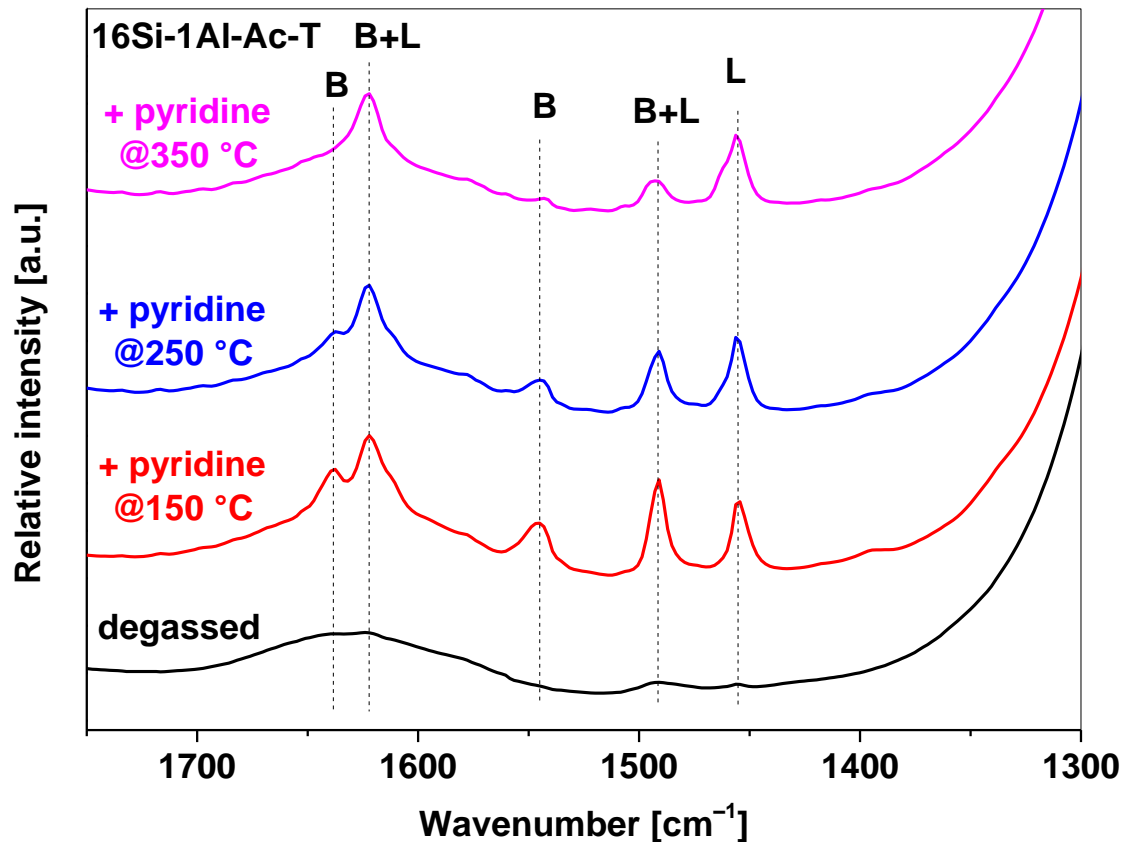
Chemisorption

- 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
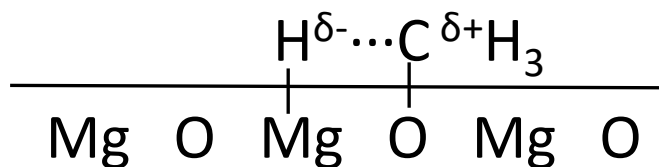   - Different vibration modes

Chemisorption

- Adsorption of IR (NMR) active molecules

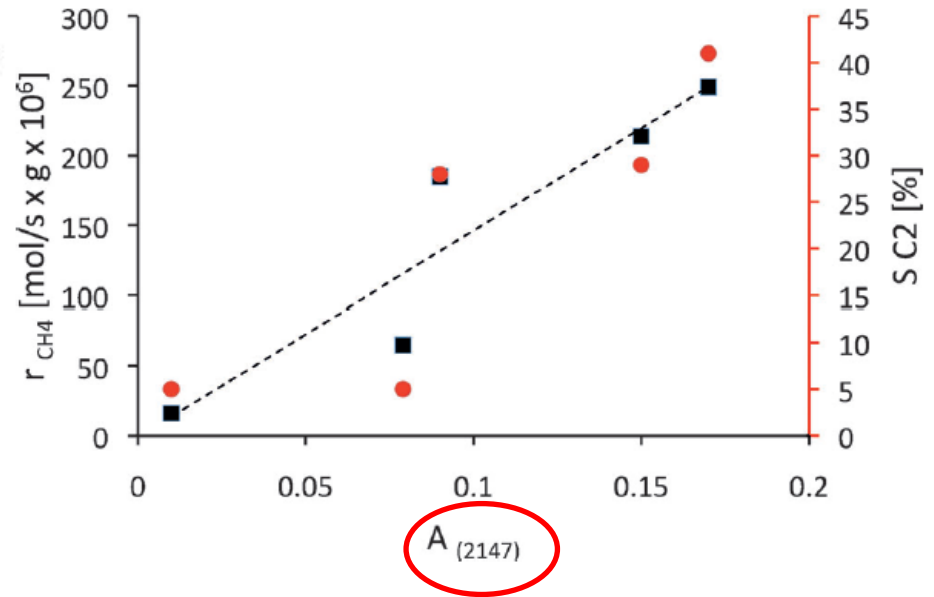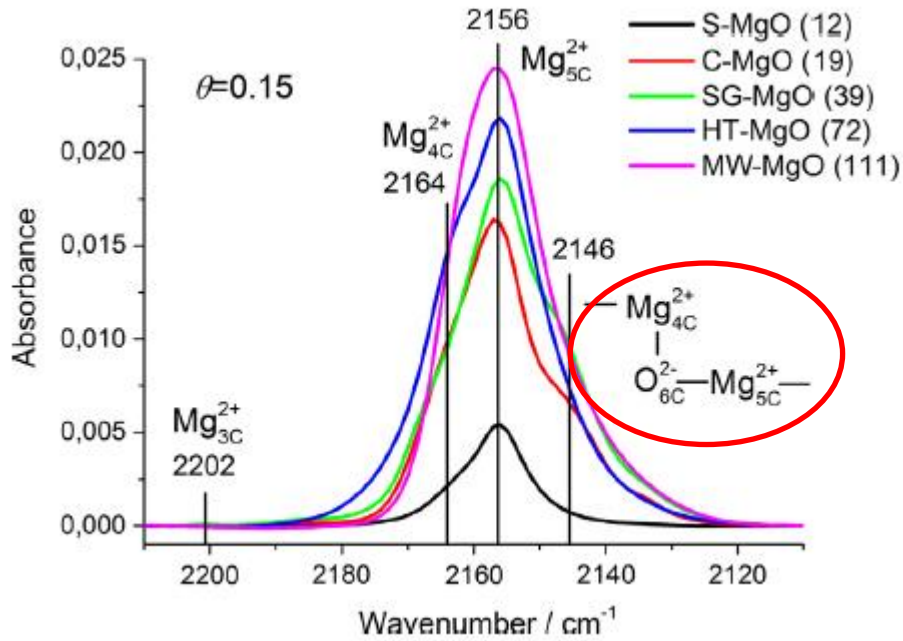- Example: pyridine adsorption on an acid catalyst

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

  - $2\ CH_4 + 0.5\ O_2 \rightarrow C_2H_6 + H_2O$

  - $2\ CH_4 + O_2 \rightarrow C_2H_6 + 2\ H_2O$

$$H^{\delta-}\cdots C^{\delta+}H_3$$
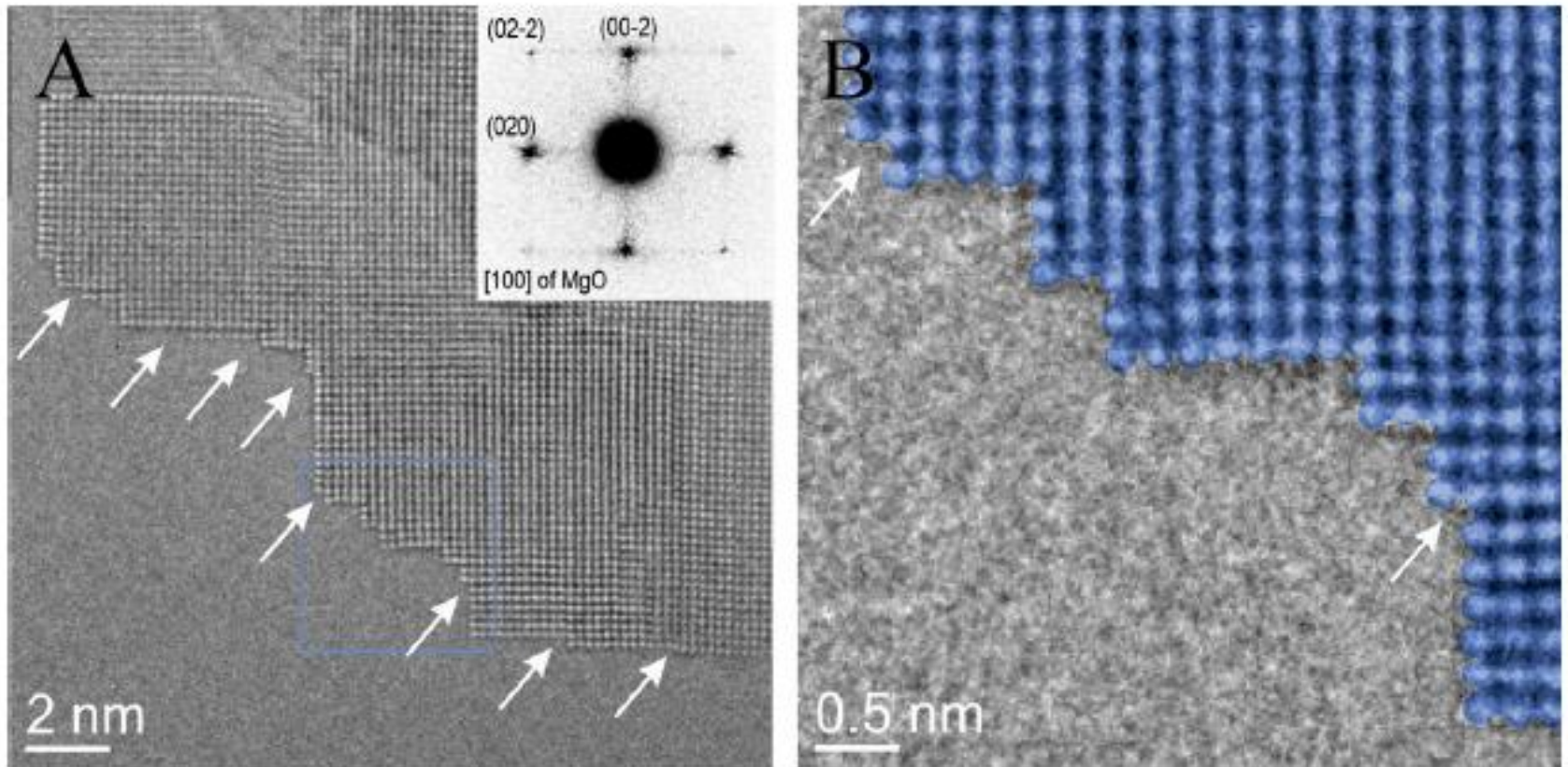
Mg   O   Mg   O   Mg   O

Chemisorption

- Example: CO adsorption on MgO

Chemisorption

- Example: CO adsorption on MgO

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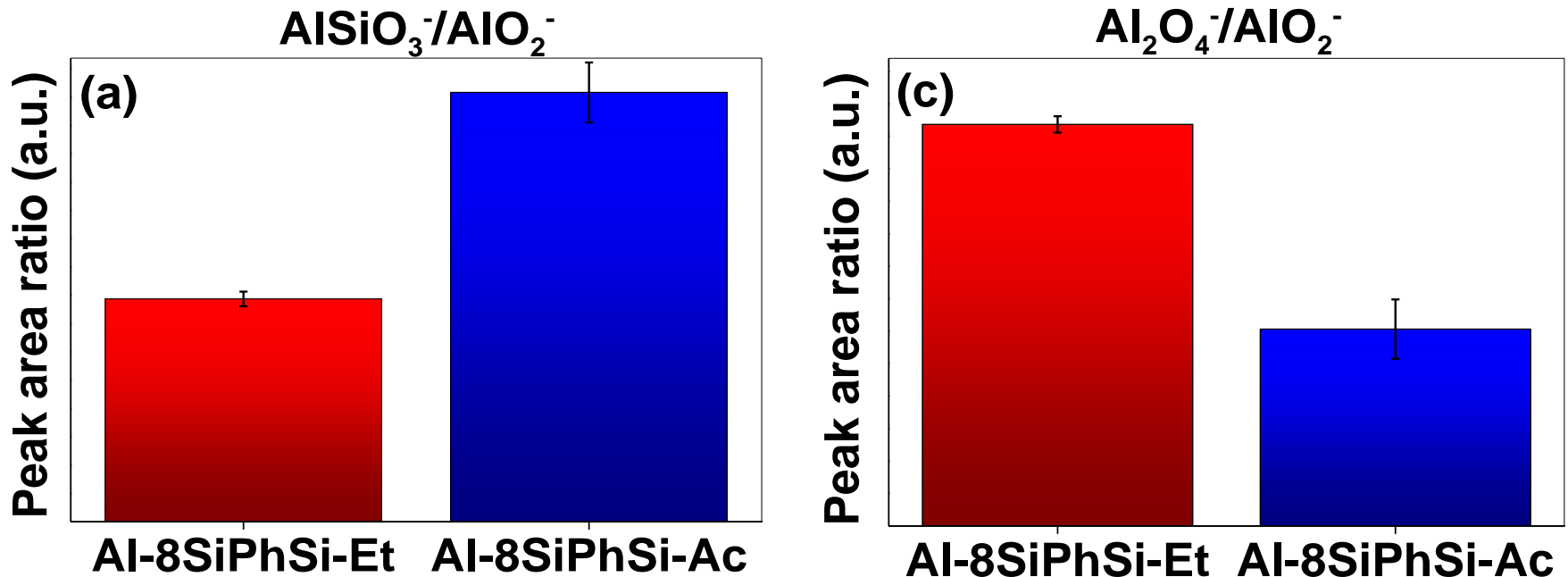
- Example: CO adsorption on MgO
- Single step edge is the active site
  - Good correlation between integral of absorption band at 2147 cm^{-1} and catalytic activity
  - Band at 2147 cm^{-1} represents single step edge
  - Au atoms selectively deposits on single step edges (observed by HR-TEM) = catalyst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