LECTURE SERIES
HETEROGENEOUS CATALYSIS

Modern Methods in Heterogeneous Catalysis Research

MAX-PLANCK-GESELLSCHAFT

Photoelectron Spectroscopy

AC
FHI

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Outline

Photoelectron Spectroscopy: General Principle

Surface sensitivity

Instrumentation

Background subtraction

PES peaks, loss features

Binding energy calibration

Chemical state

Peak fitting

Quantitative Analysis

High pressure XPS

examples

Problem: What is the (chemical) composition of a surface

Goal:

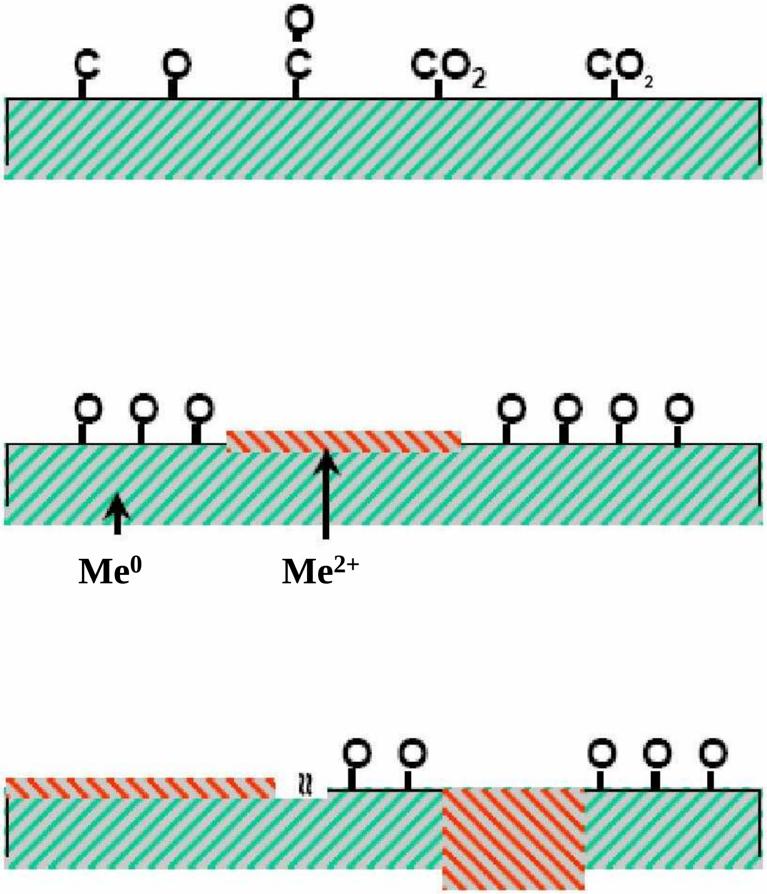
Elemental composition

- Species of atoms on surface
- Concentration of surface atoms
- Vertical distribution
  - → on surface (adsorbate)
  - → near surface

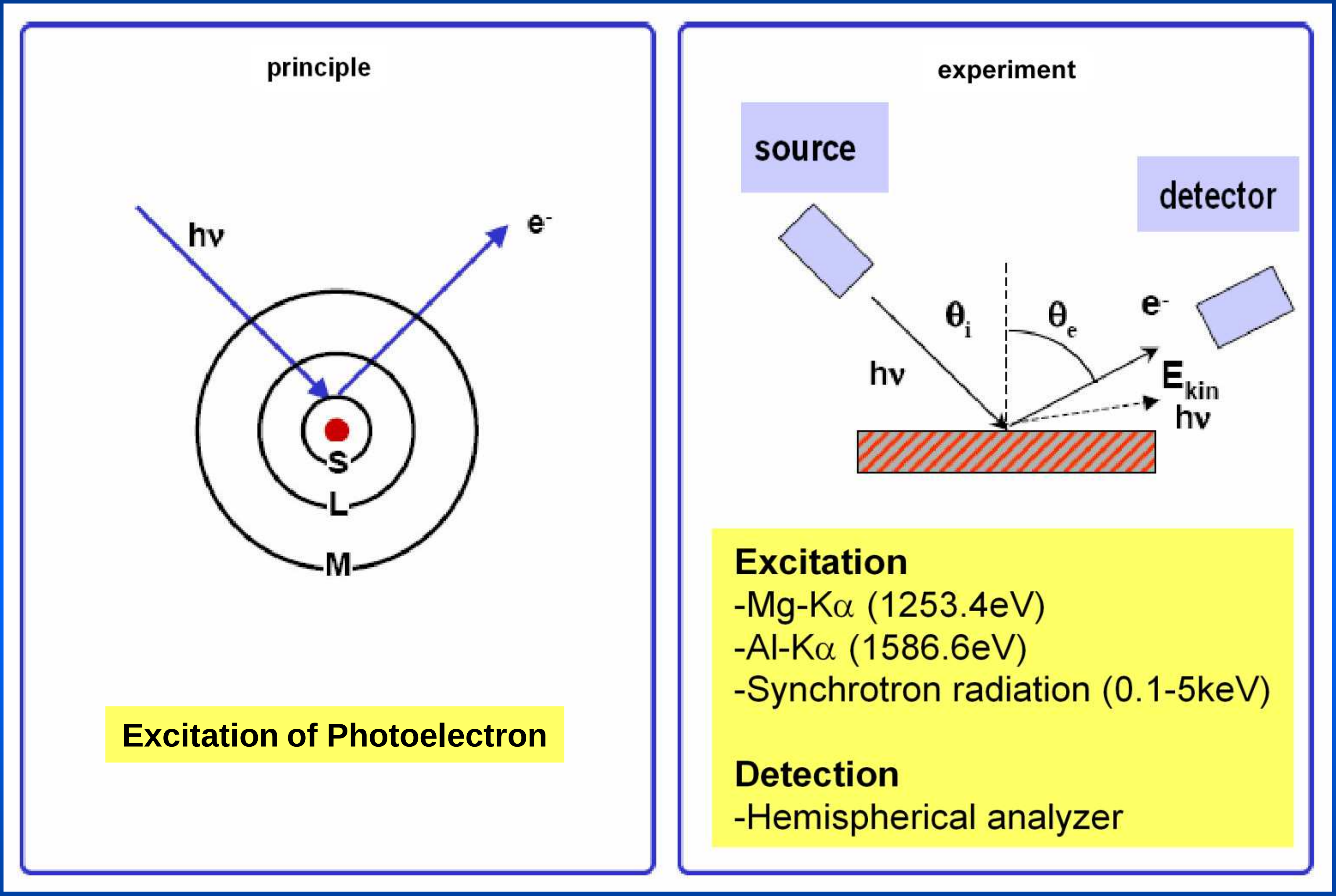
Molecular state of adsorbates

Oxidation state of surface species

- $Me^0 \Leftrightarrow Me^{n+}$



Photoelectron Spectroscopy: General Principle

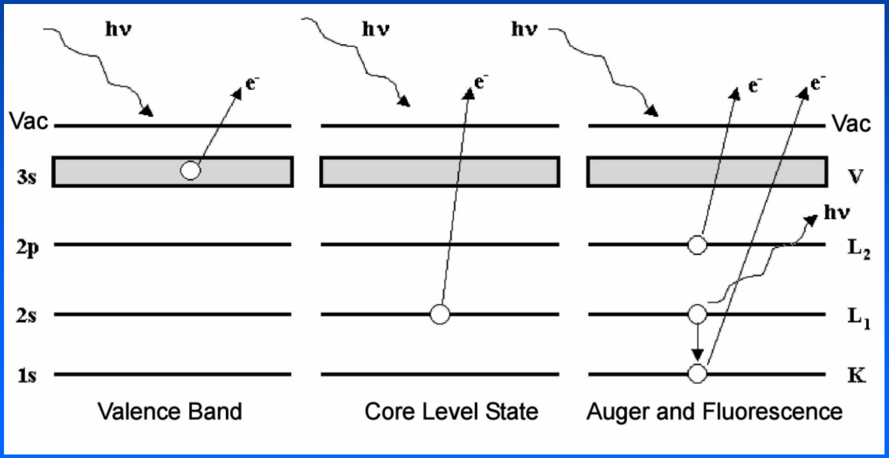


Excitation of Photoelectron

Excitation
-Mg-Kα (1253.4eV)
-Al-Kα (1586.6eV)
-Synchrotron radiation (0.1-5keV)

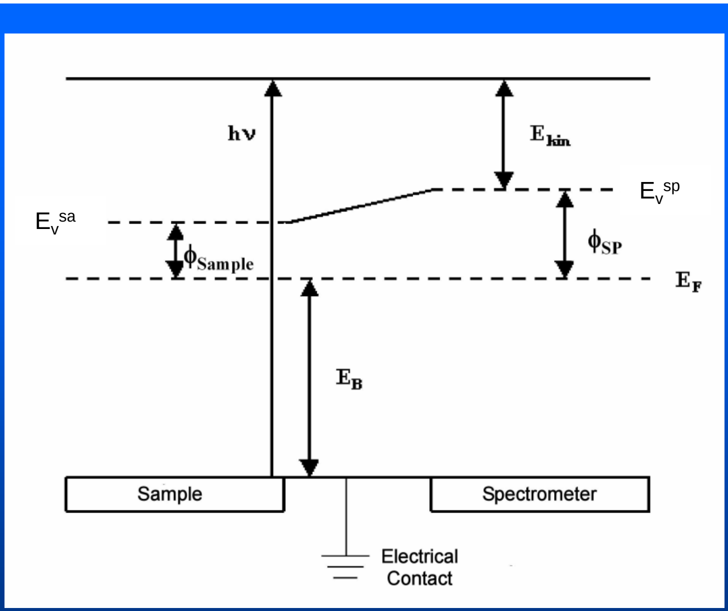
Detection
-Hemispherical analyzer

General Principle



- Detection of photoelectrons from the valence band region and core levels

- Detection of Auger electrons and X-Ray Fluorescence



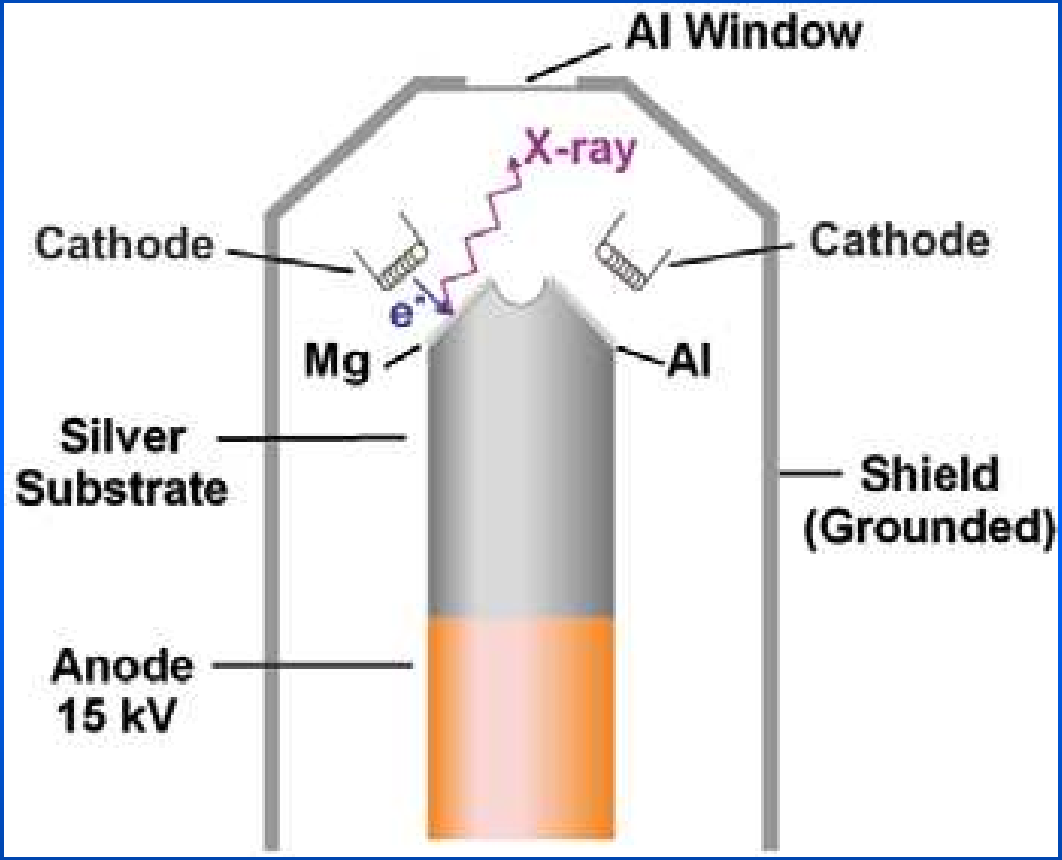
Binding Energy out of:

$$h\nu = E_v^{sp} + E_{kin}$$

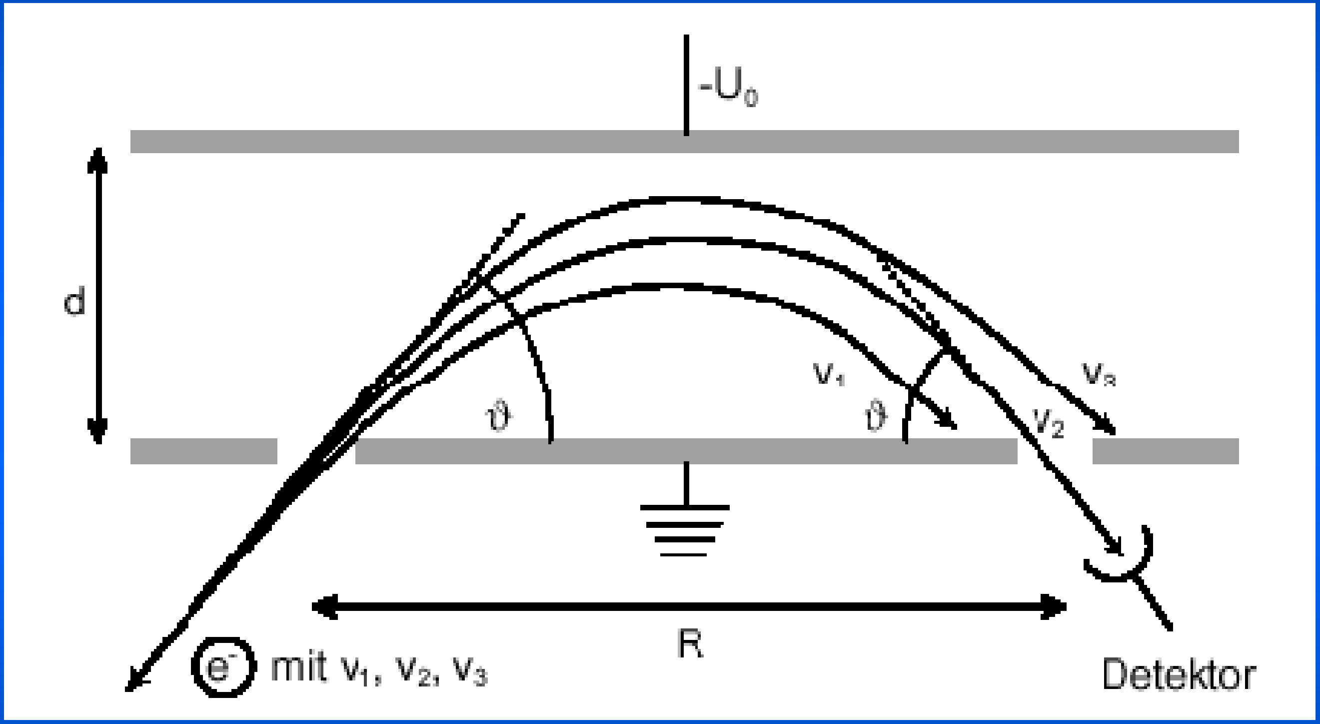
$$h\nu = E_{kin} + E_v^{sa} + \Phi_{sp} - \Phi_{sa}$$

$$h\nu = E_{kin} + E_F + \Phi_{sp}$$

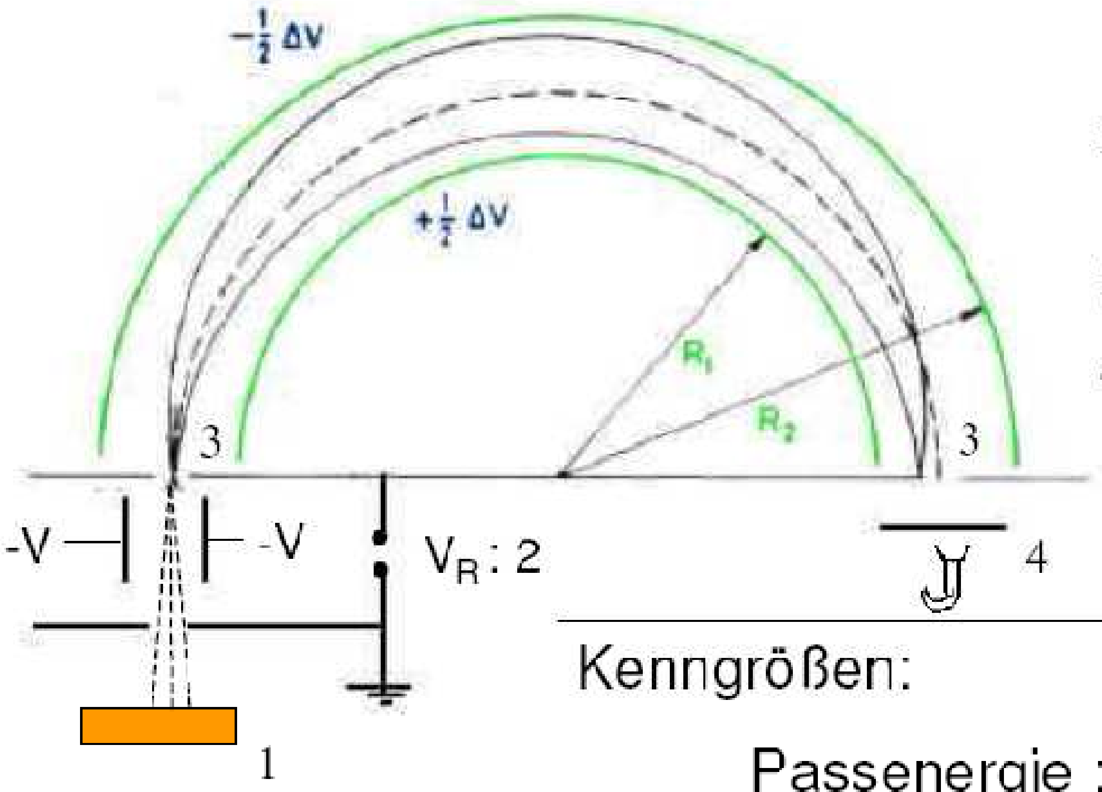
X-ray twin anode



Parallel plate mirror analyser



Halbkugelanalysator



1: Probe
2: Verzögerungspotential
3: Lochblende
4: Detektor : Channeltron

Kenngrößen:

Passenergie : 5 eV

Winkelakzeptanz : 1°

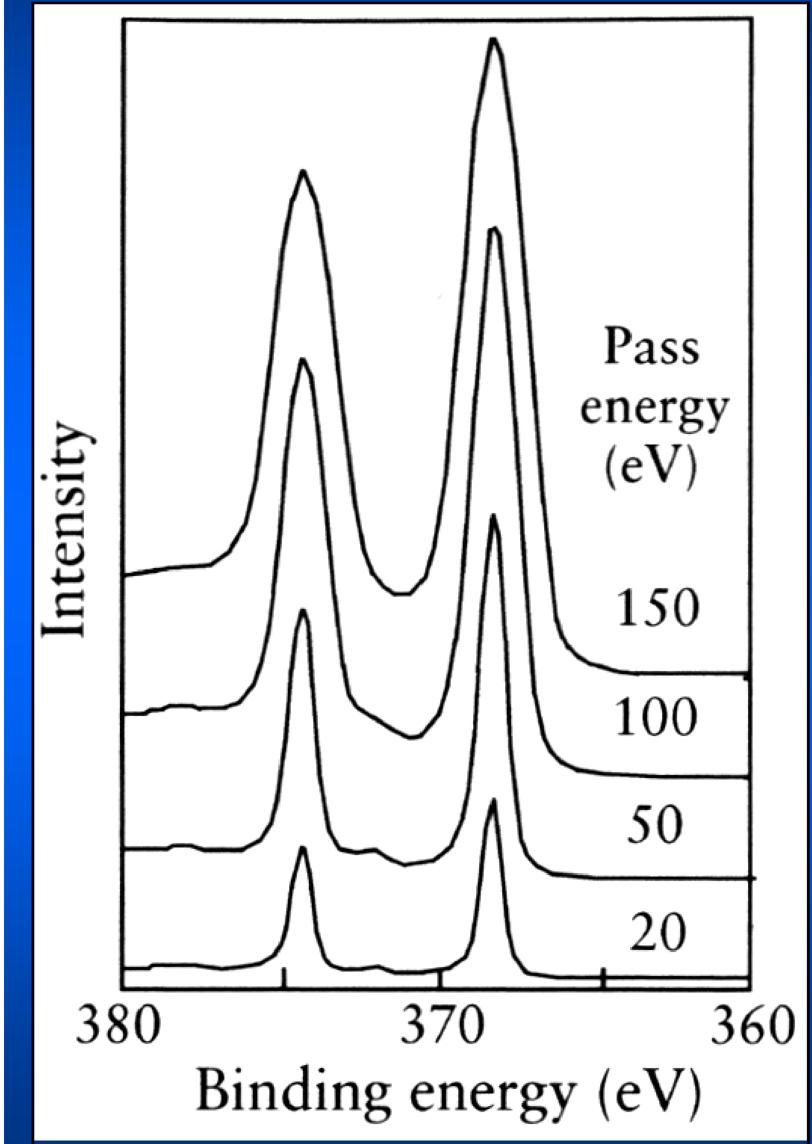
max. Rate : 30.000 /s

Halbkugelanalysator

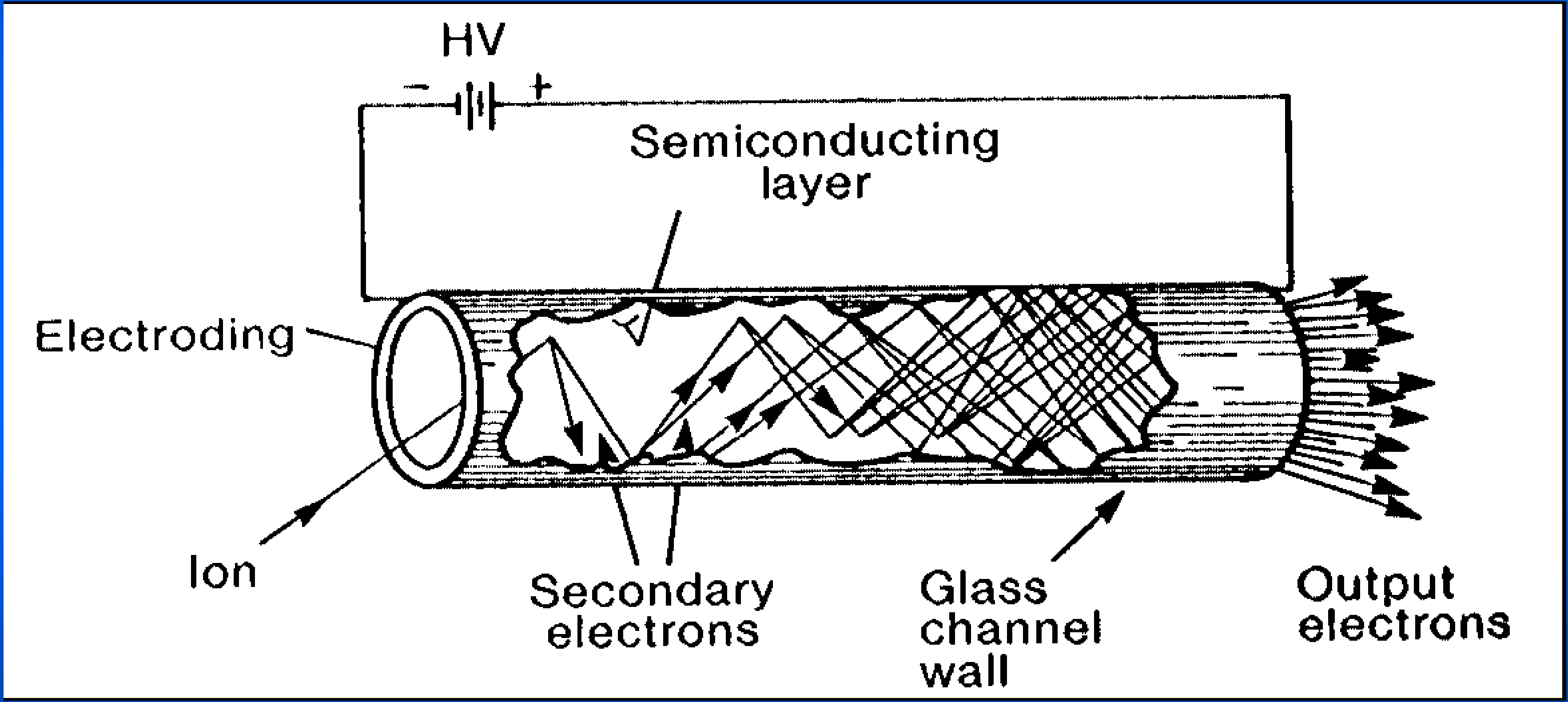
Elektronen werden zunächst um bestimmten Energiebetrag **abgebremst**

Nur Elektronen mit bestimmter **"Passenergie"** können Detektor erreichen

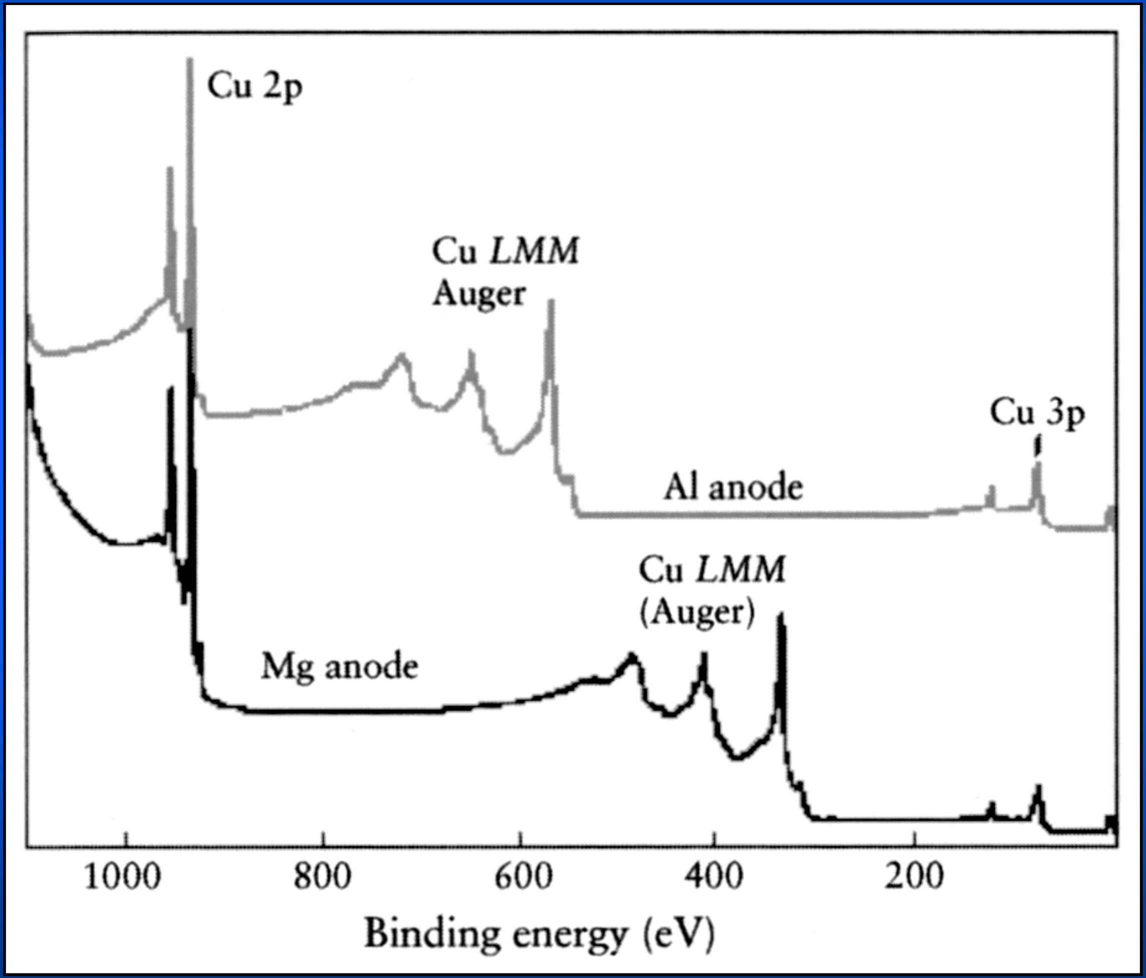
Je kleiner die "Passenergie" desto genauer die Messung



Detector: Channeltron



XP spectra: two different anode materials

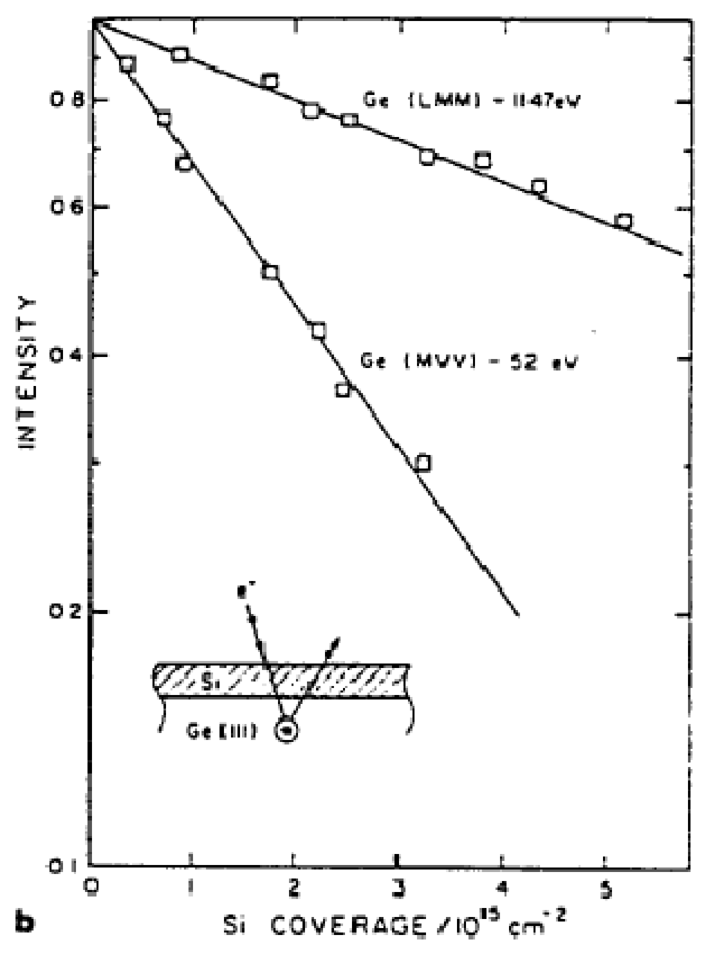


Where do the electrons come from?

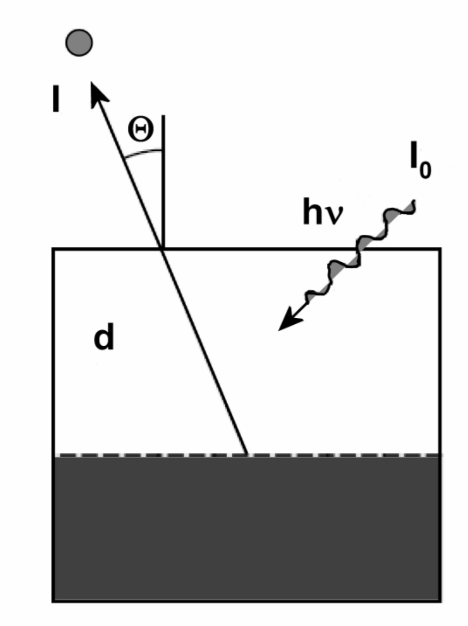
Distance electron can travel in solids depends on:

- Material
- Electron kinetic energy

→ Measure attenuation of electrons by covering surface with known thickness of element



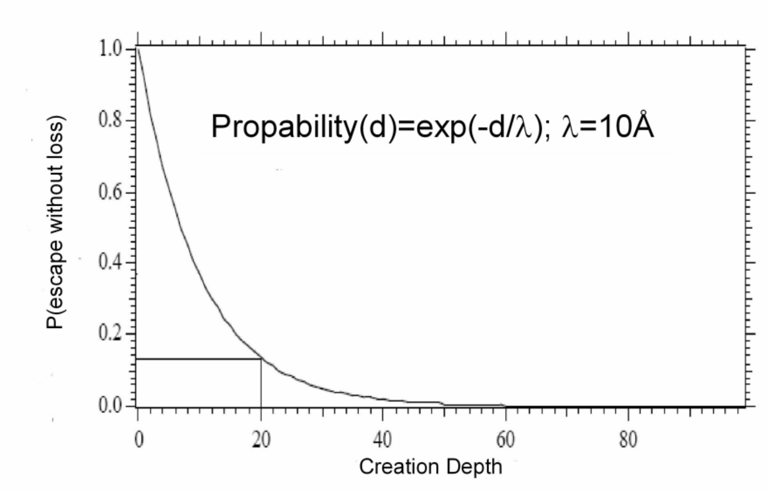
Sampling Depth



Disregarding elastic scattering:

$$I = I_0 \exp\left(\frac{-d}{\lambda \cos\theta}\right)$$

$$\ln\left(\frac{I}{I_0}\right) - \frac{-d}{\lambda \cos\theta}$$



Sampling depth:

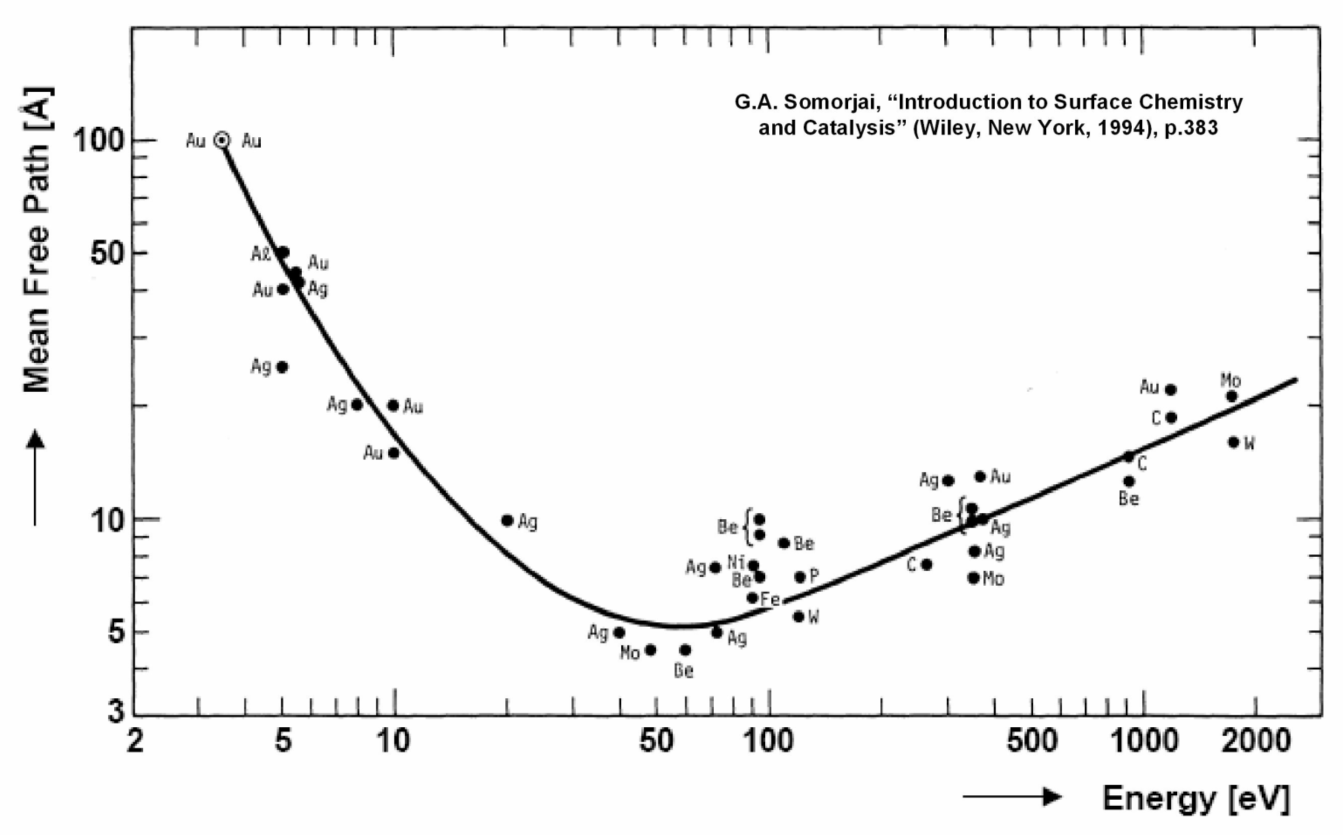
For normal takeoff angle, cosΘ=1:

- When d=λ: $-\ln(I/I_0)=0.367$, i.e. 63.3% from within λ
- When d=2λ: $-\ln(I/I_0)=0.136$, i.e. 86.4% from within 2λ
- When d=3λ: $-\ln(I/I_0)=0.050$, i.e. 95.0% from within 3λ

Mean Free Path of Electrons in Solids

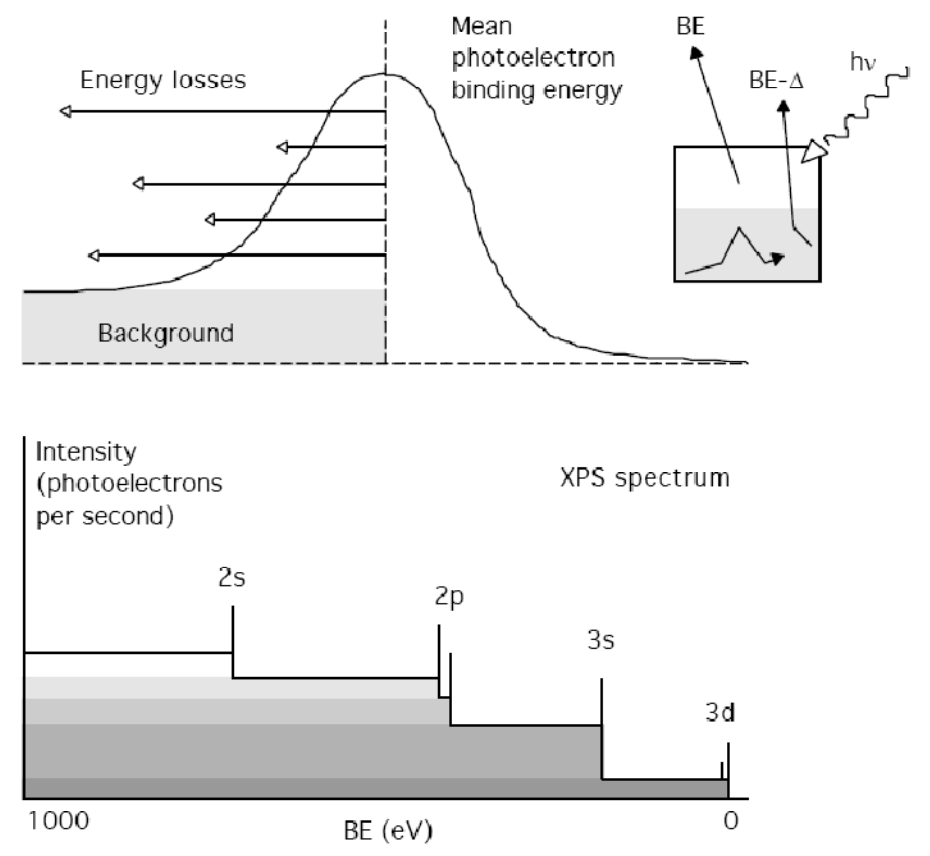
- IMFP is average distance between inelastic collisions
- Minimum λ of 5-10Å for KE ~ 50-100 eV

→ Maximum surface sensitivity



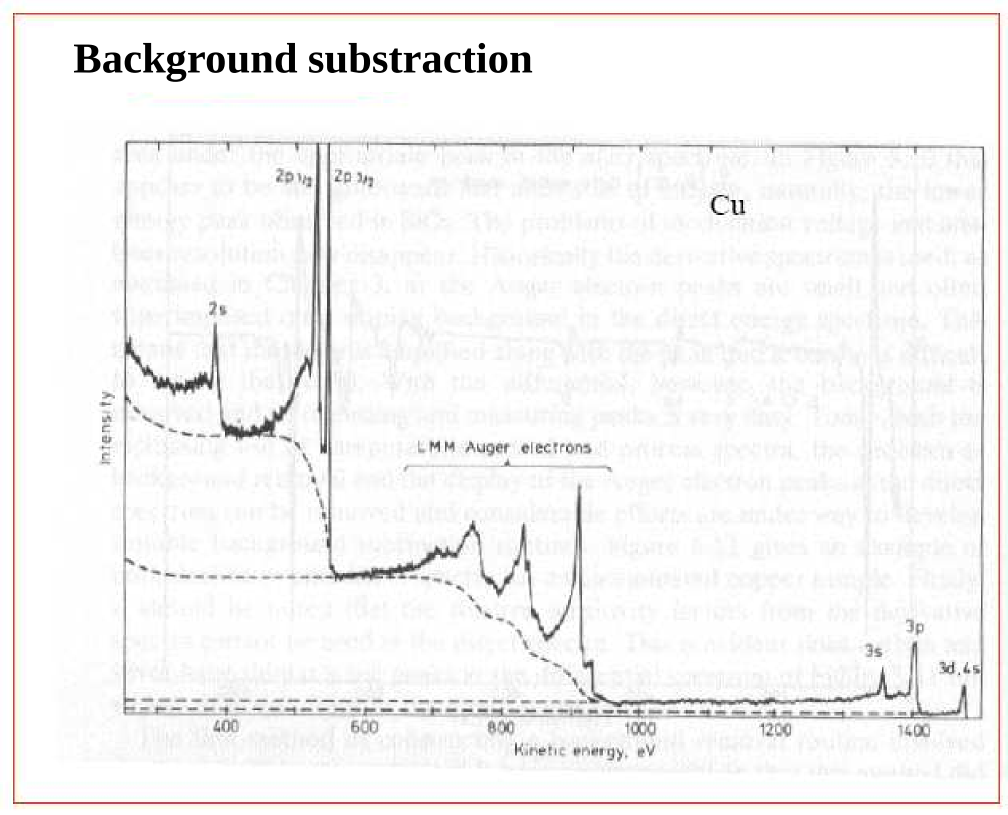
G.A. Somorjai, “Introduction to Surface Chemistry and Catalysis” (Wiley, New York, 1994), p.383

Origin of background



Background of scattered electrons due to limited IMFP
→ Higher for low KE

Background Correction

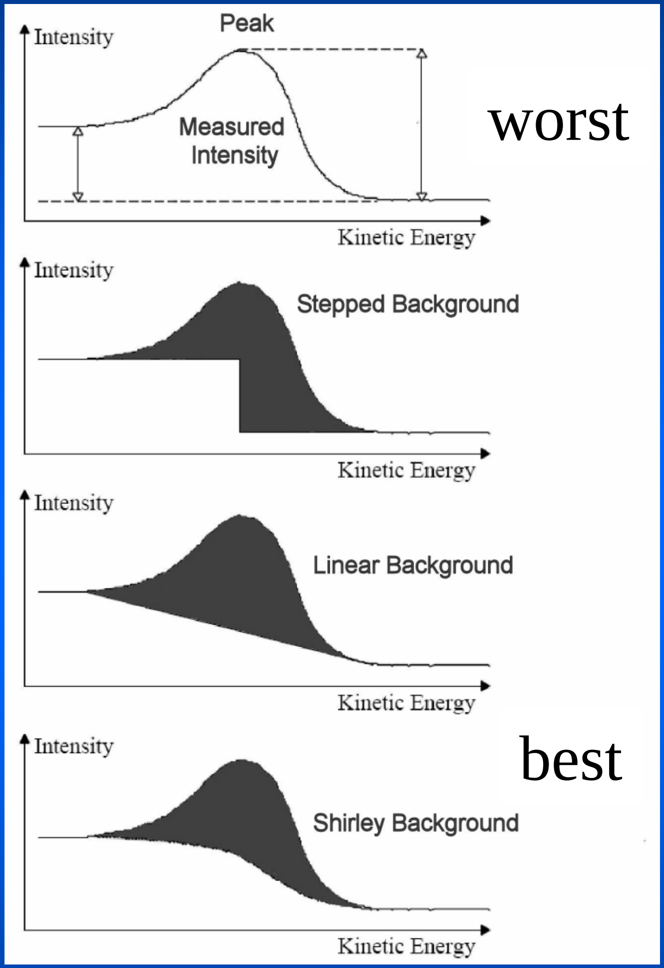


Background substraction

→ **Choose suitable energy range for substraction**

→ **Baseline on high KE side**

Background Correction



Several ways to substract background:

- Stepwise
- Linear
- Method of Tougaard

→Most common:

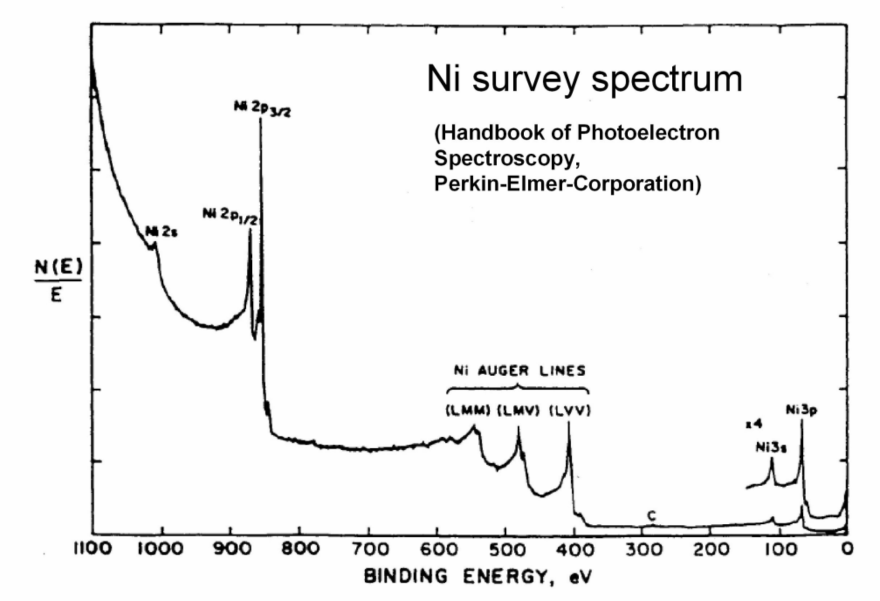
Method of Shirley et al.:

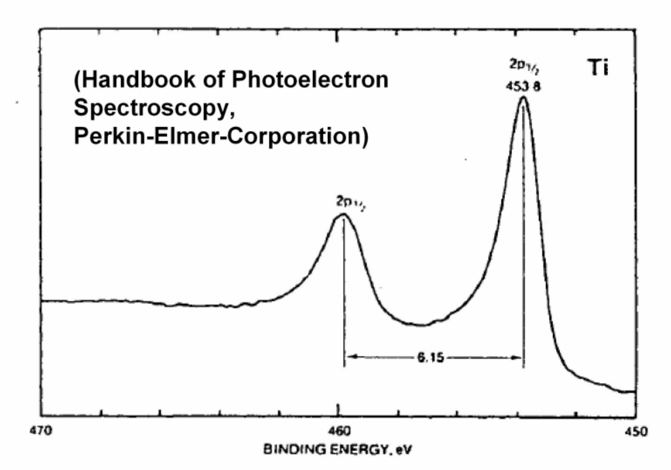
$$b_i = k \sum_{j=i+1}^{N} p_j$$

Always use same background substraction method for all peaks!

D.A. Shirley, Phys. Rev. B, 5, S. 4709, 1972.

Spectral features: PE Peaks





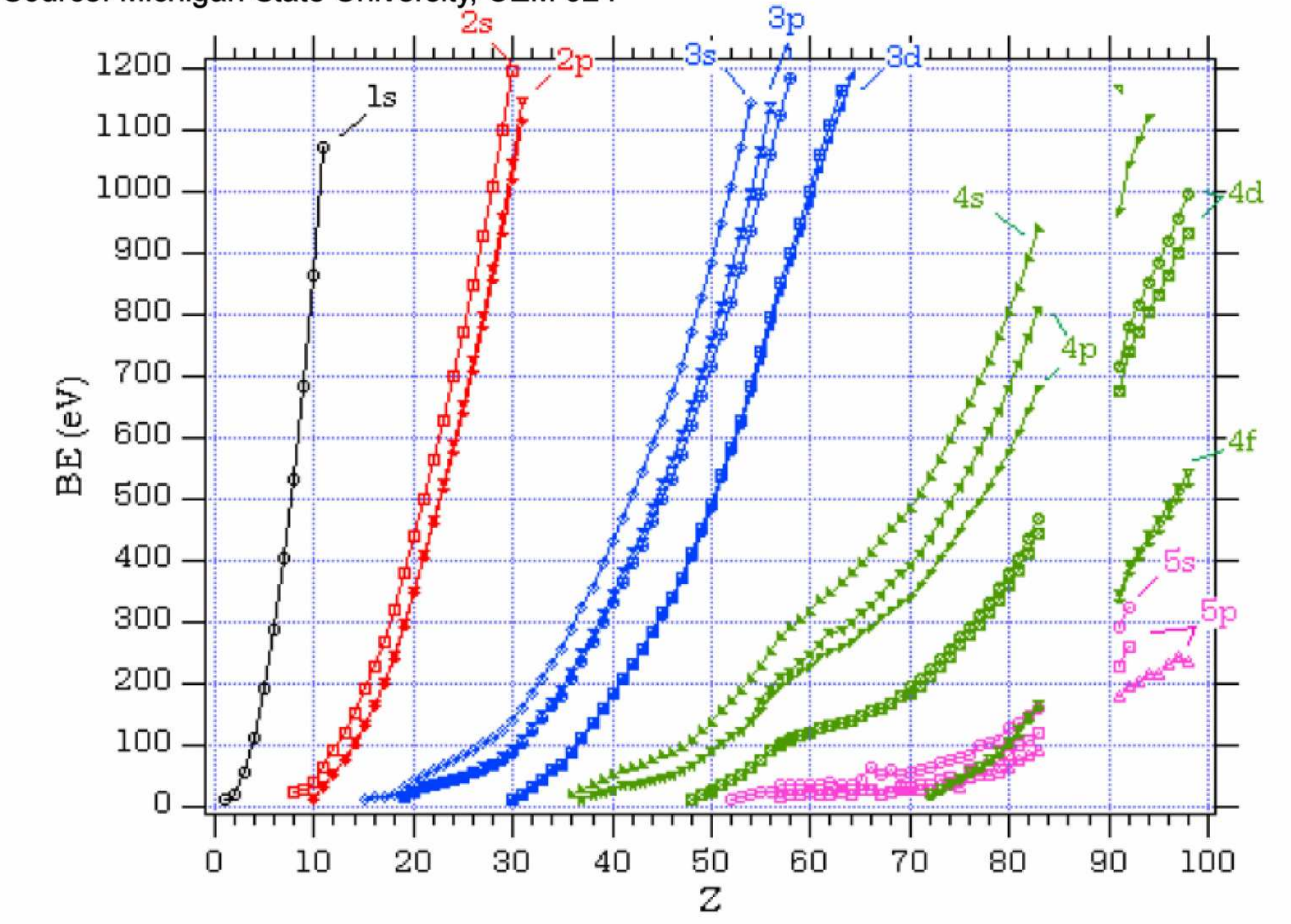
Orbital peaks used to identify different elements in sample

Observation:

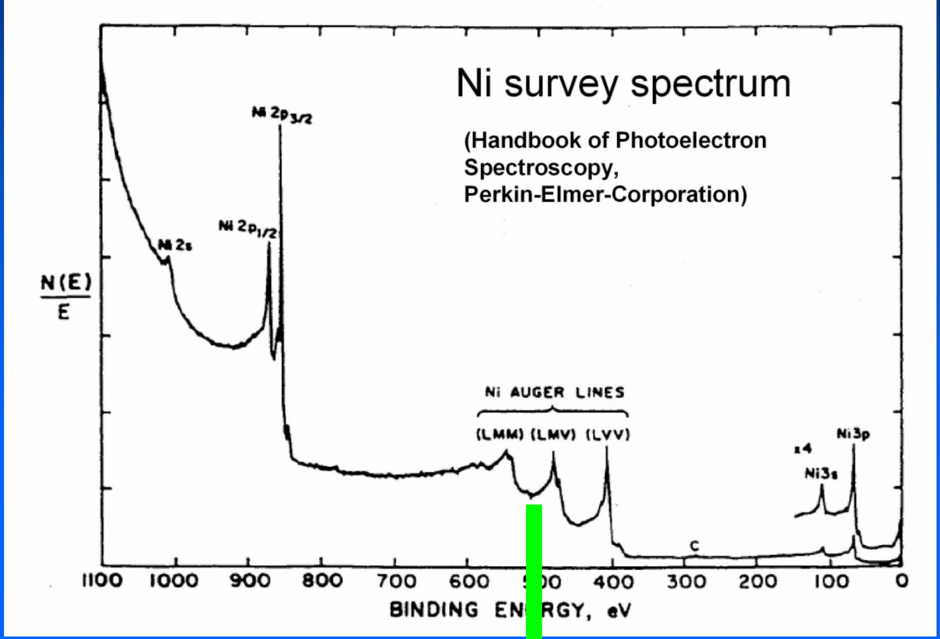
- s orbitals are not spin-orbit splitted → singlet in XPS
- p, d, f.. Orbitals are spin-orbit splitted → doublets in XPS

Spectral features: PE Peaks

Source: Michigan State University, CEM 924



Spectral features: Auger Peaks



(Handbook of Photoelectron Spectroscopy, Perkin-Elmer-Corporation)

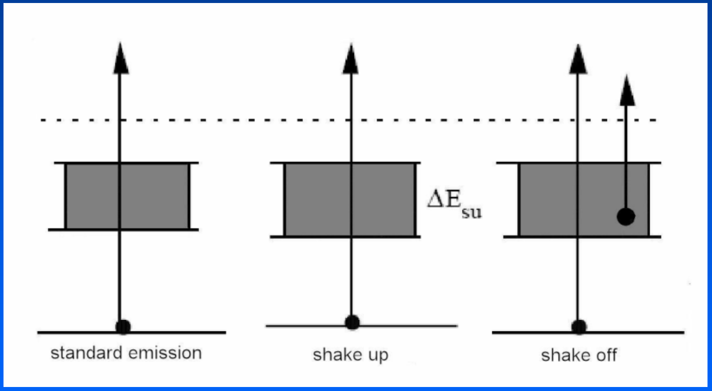
Auger peaks:

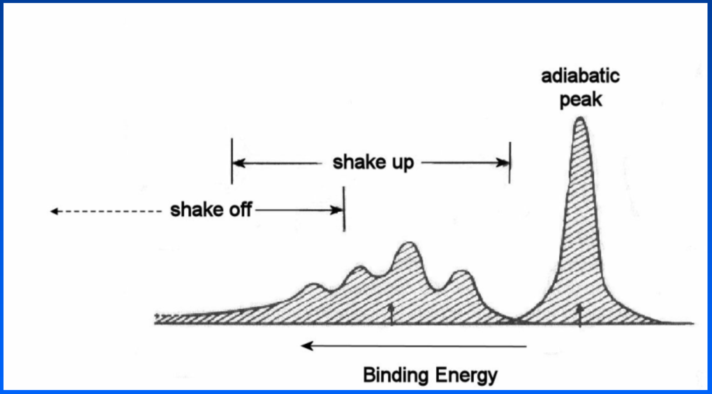
Result from excess energy of atom during relaxation (after core hole creation)

- always accompany XPS
- broader and more complex structure than PES peaks

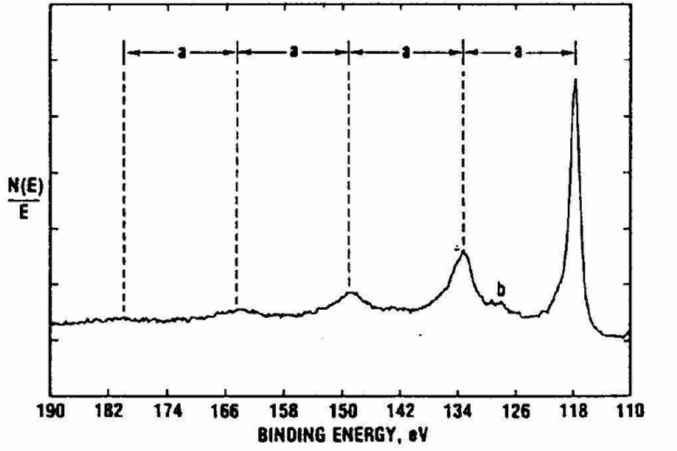
KE energy independent of incident hν

Spectral features: Loss Peaks





Handbook of Photoelectron Spectroscopy, Perkin-Elmer-Corporation



Energy loss (plasmon) lines associated with the 2s line of aluminum

After Emission of PE the remaining electrons rearrange (**<u>Secondary peaks</u>**):

- Relaxation by excitation of valence electron to higher state (***shake up***)

  → loss of kinetic energy of PE leads to new peaks shifted in BE with respect to main peak

- Relaxation by ionisation of valence electron (***shake off***)

  → broad shoulder to main peak

- ***Plasmon*** losses

Spectral features: Loss Peaks

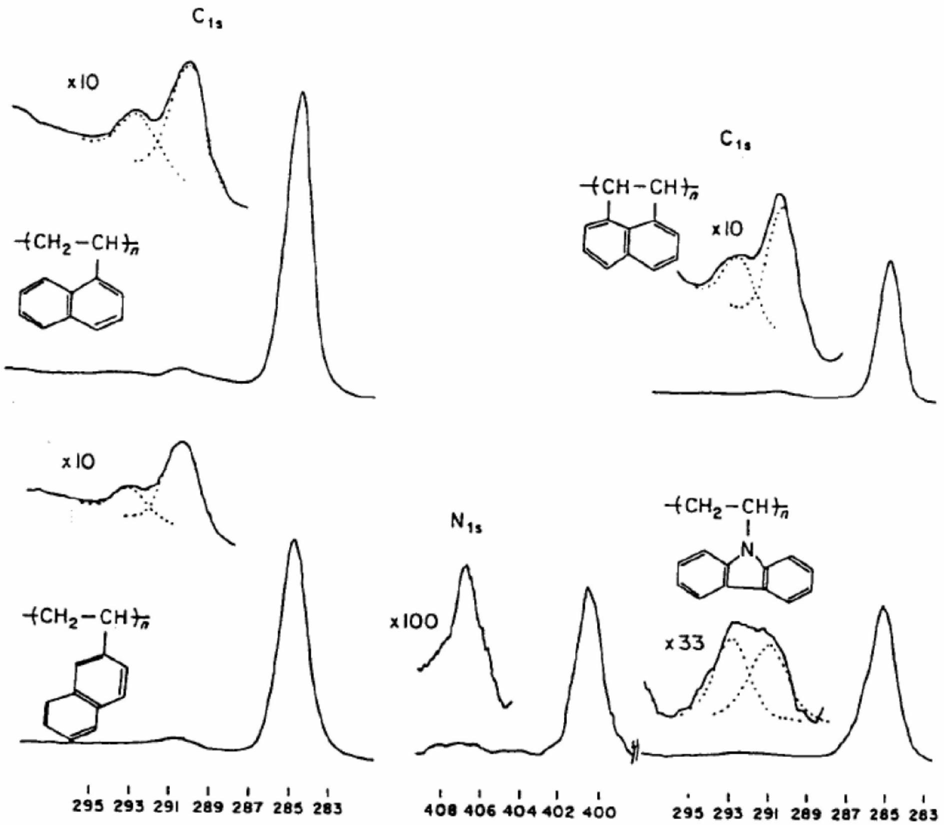


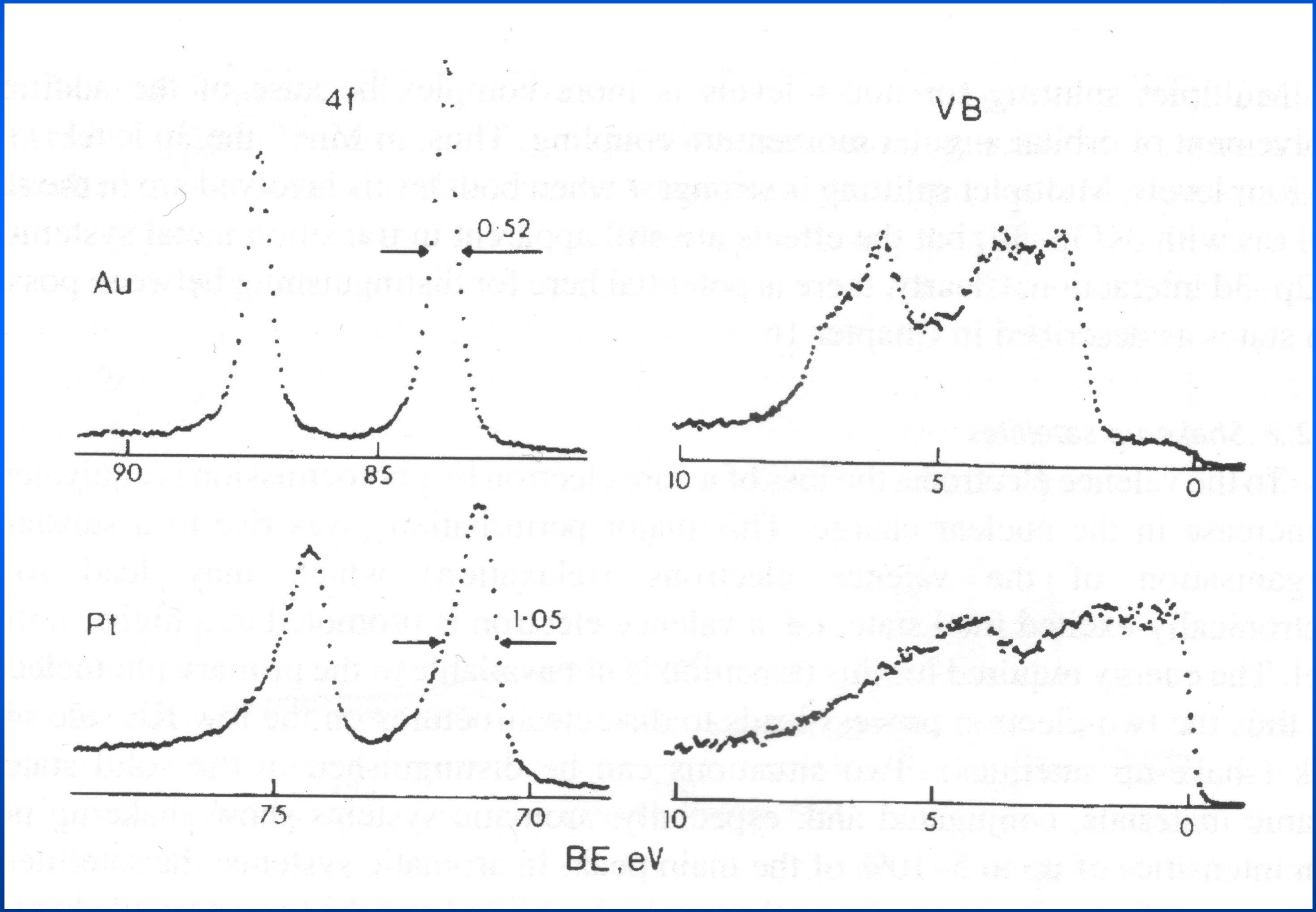
Figure 9.5 Core level spectra of poly-1- and 2-vinylnaphthalene, polyacenaphthalene and polyvinylcarbazole.

(Clark et al., Copyright Elsevier Science Publishers)

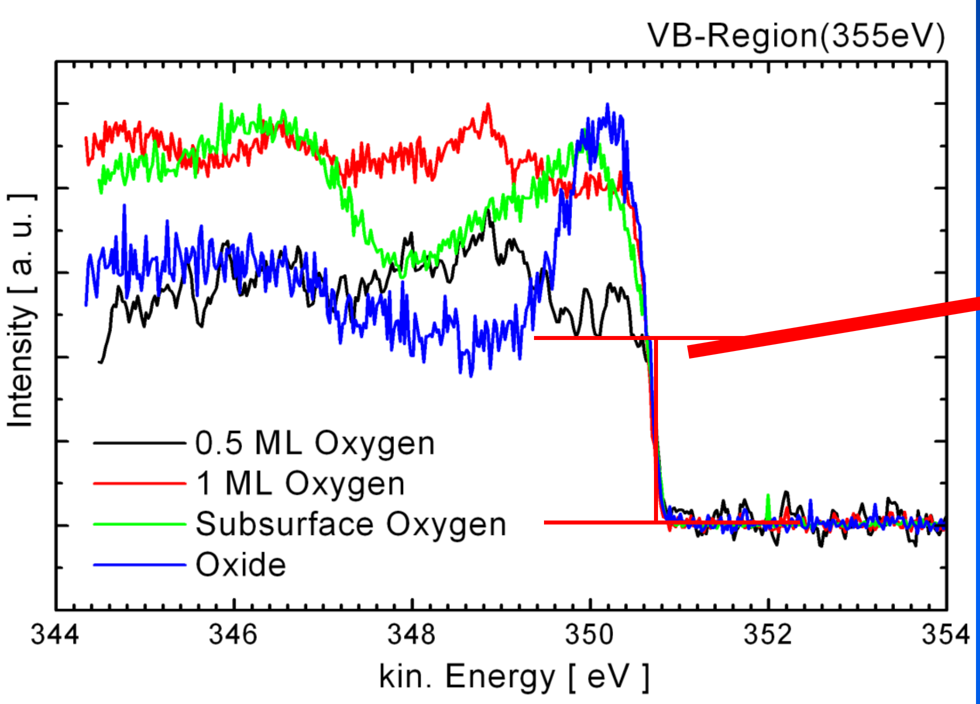
Loss peaks can be used to identify chemical composition

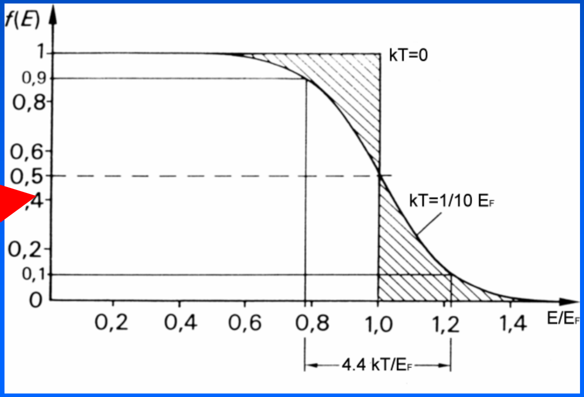
Problem:
References needed (theoretical or experimental)

Relationship between the degree of core level asymmetry and the density of states at the Fermi level (BE=0)



Analyzing the data: Calibration of Binding Energies

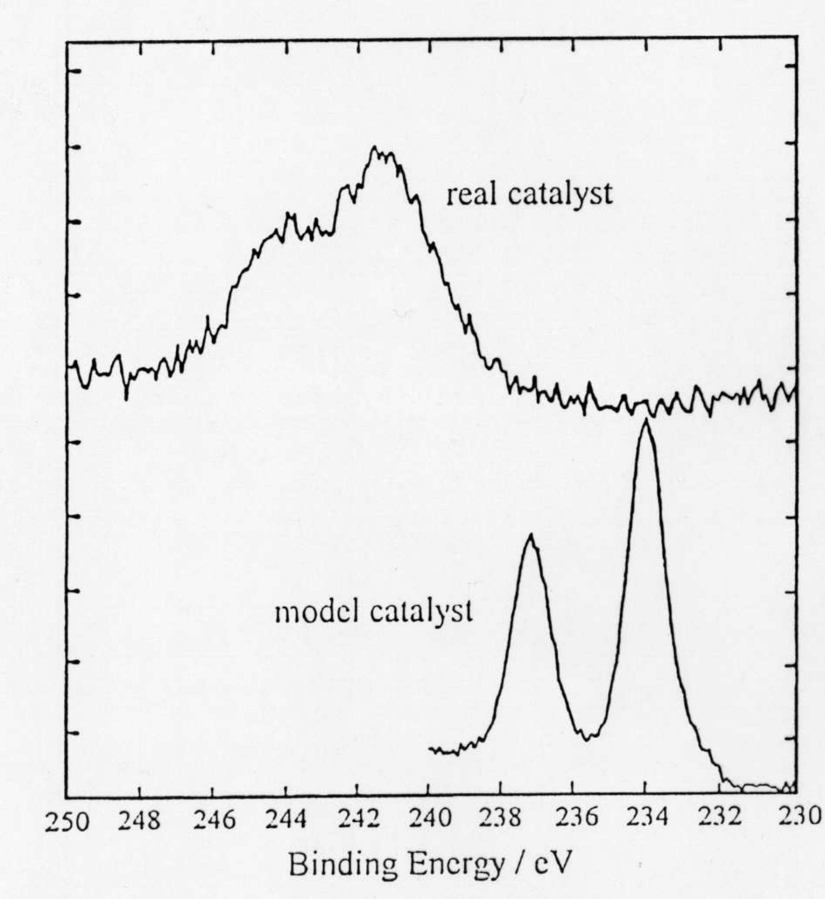




Identification of FE:

Easy for high density of states near E_F, but may be ambigeous for samples with low DOS near E_F, band gap or charged samples

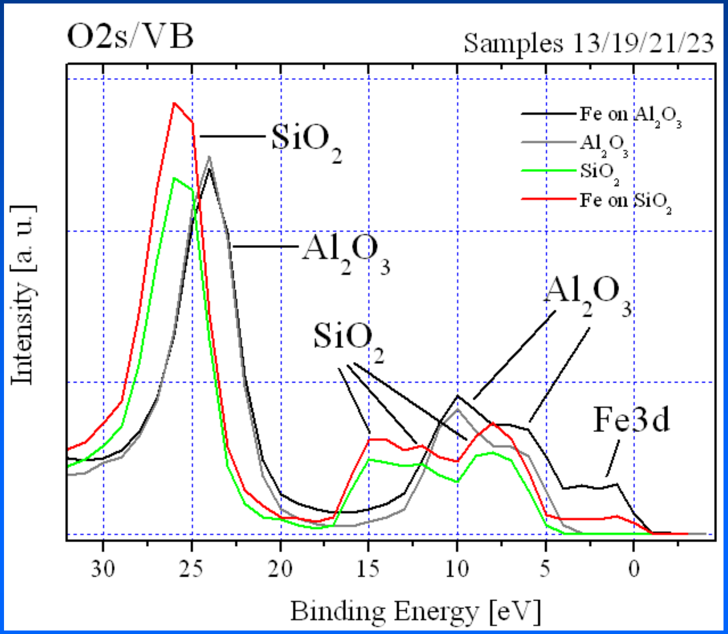
Line profile modification by charging

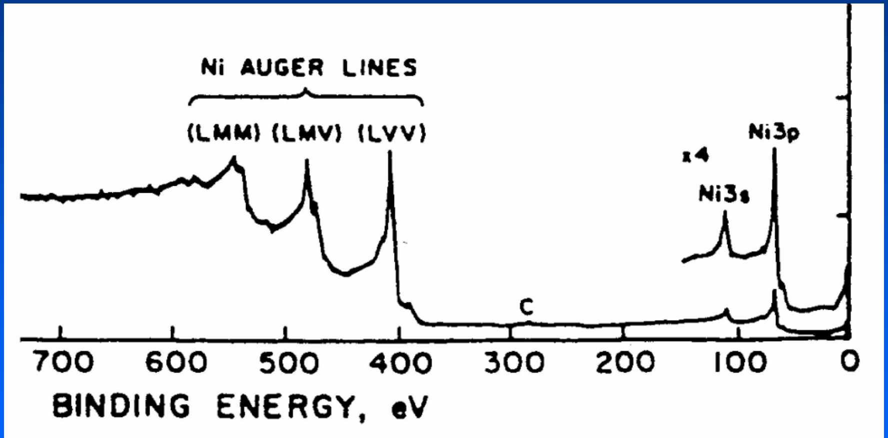


Mo oxide on silica

real catalyst is powder sample after impregnation and calcination.

Analyzing the data: Calibration of Binding Energies





(Handbook of Photoelectron Spectroscopy, Perkin-Elmer-Corporation)

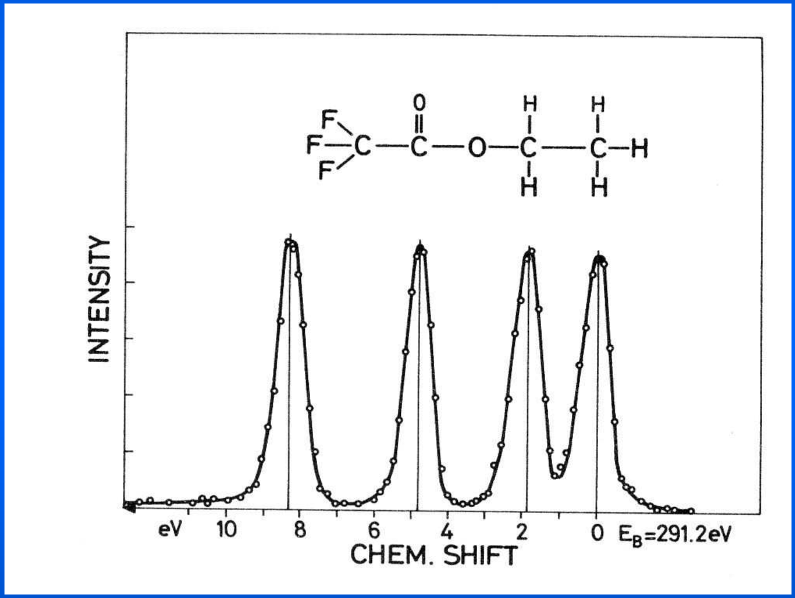
Identification of FE:

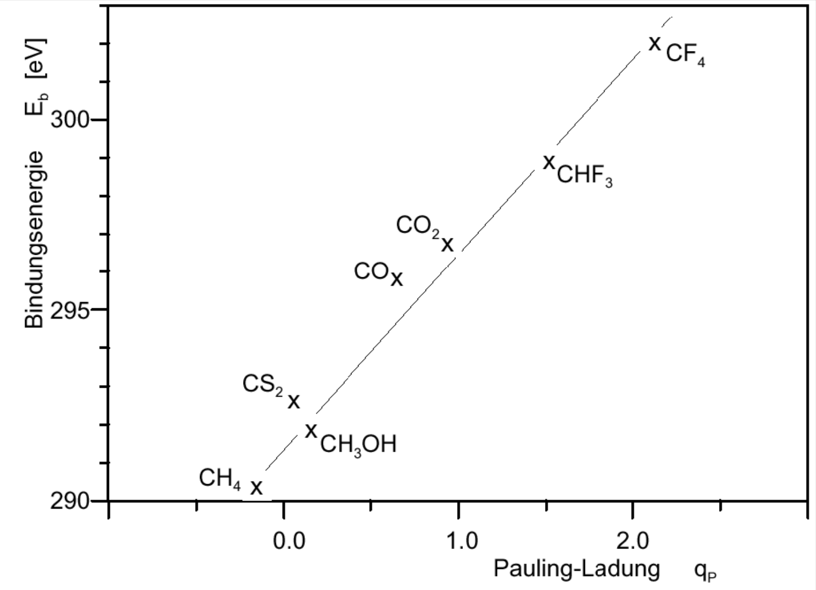
In case of low DOS near E_F, band gap or charged samples (spectrum will move in this case!)

→ Look for reference peaks with known BE (be sure about that!!!)
→ Works for any PE or Auger peak, e.g. peaks originating from substrate

Chemical Shift

BE of core electrons depends on the electron density of the atom (screening of the core electrons), affected by the electronegativity of neighboring atoms



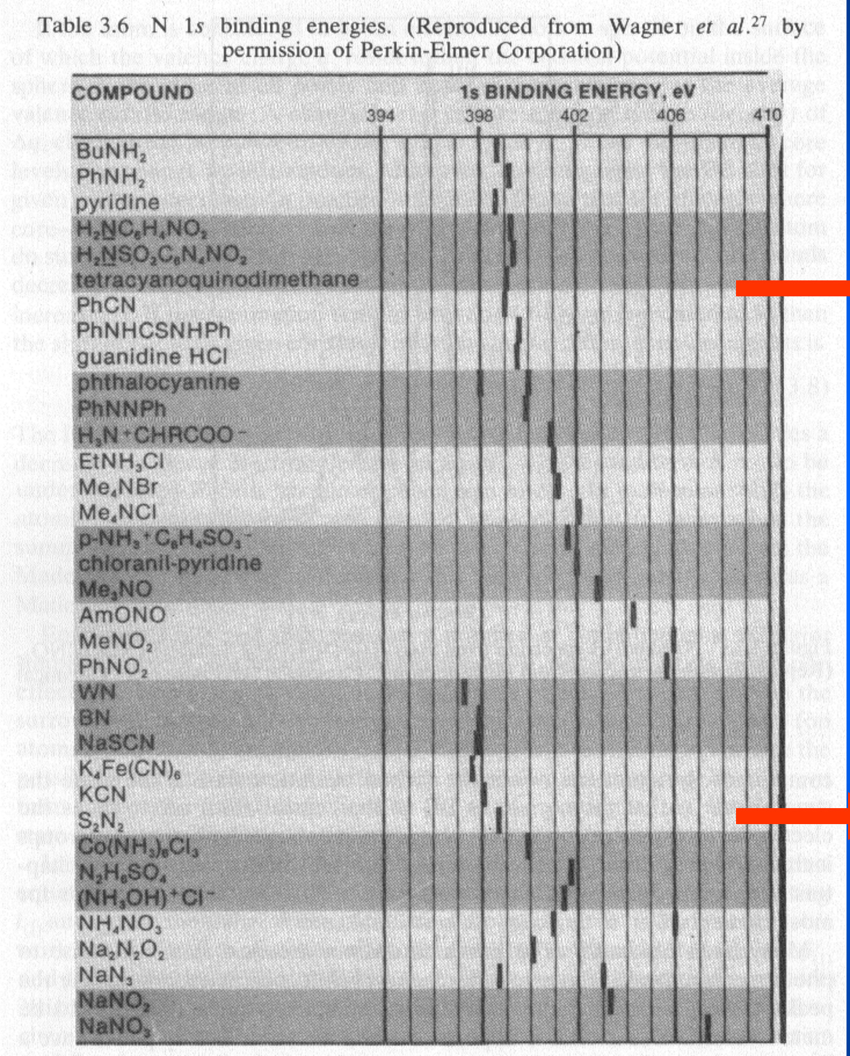


For unknown BE:

- Calculation of Pauling´s Charge (easy, but not always true)
- More elaborate calculations (theorists, also not always true)

Analyzing the data: Chemical States

Table 3.6 N 1*s* binding energies. (Reproduced from Wagner *et al.*[27] by permission of Perkin-Elmer Corporation)

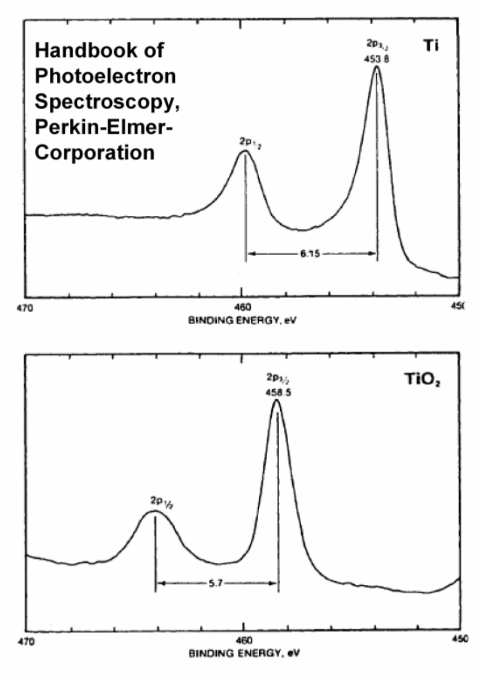


References:

- Use of data bases (NIST, Handbook of Photoelectron Spectroscopy etc.*)
- Clean materials (pure metals, well defined substrates, „untreated“ samples etc.)
- Literature about similar topics

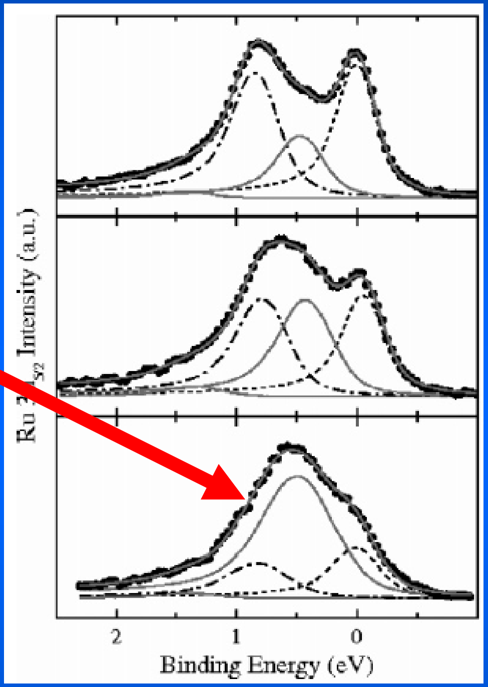
*****„Handbook of Photoelectron Spectroscopy“, Perkin-Elmer, 1992
G. Ertl, J. Küppers;
´´Low Energy Electrons and Surface Chemistry´´; VCH Verlag, 1985
S. Hüfner; ´´Photoelectronspectroscopy´´; Springer, 1995.
D. Briggs, M.P. Seah;
´´Practical Surface Analysis´´, Vol. 1; Wiley + Sons, 1990.

Analyzing the data: Peak Fitting


Handbook of Photoelectron Spectroscopy, Perkin-Elmer-Corporation

Several influences on peak shape:

- Broadening mainly due to excitating light (natural), structural and thermal effects
- Asymmetry due to final state effects
- Species with similar BE



These effects have to be considered when fitting by reasonable chemical/physical model of the sample!!!

Analyzing the data: Peak Fitting

Most fitting programs provide useful tools:

Levenberg-Marquardt algorithm to minimize the χ^2

$$\chi^2(p) = \frac{1}{N-P}\sum_i \left[\frac{M(i)-S(i;p)}{\sqrt{M(i)}}\right]^2$$

M: measured spectrum
N: energy values
S: synthesized spectrum
P: parameter values

Asymmetric Peak shapes modeled by Doniach-Sunjic functions (convoluted with Gaussian profiles)

$$DS(E) = \beta \cdot \frac{\cos\left\{\pi\frac{\alpha}{2} + (1-\alpha)\arctan\left[\frac{E-E_0}{\beta}\right]\right\}}{[(E-E_0)^2+\beta^2]^{\frac{1-\alpha}{2}}}$$

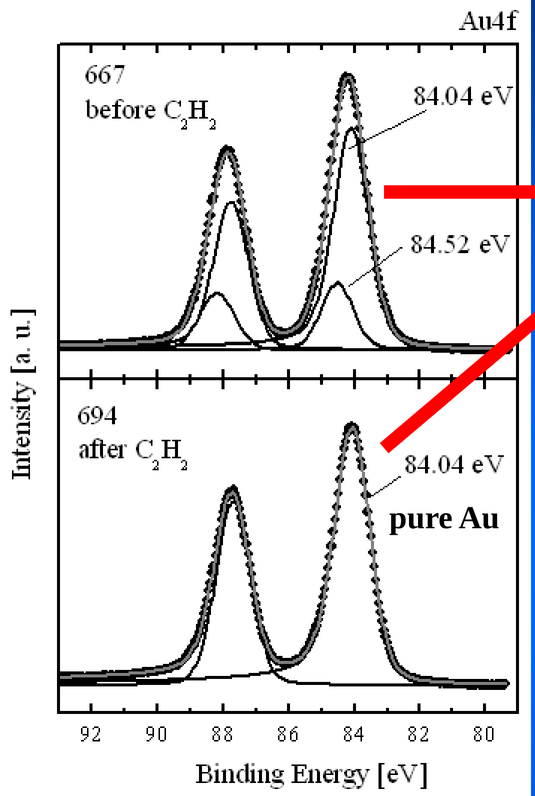
β: peak parameter
M: mixing ratio
α: asymmetry parameter
h: peak height
α → 0: Lorentzian profile

Convolution of Lorentz (or D.S.) Gaussian profiles suited best!!

$$f(E) = f(L*G) = \int_{-\infty}^{\infty} L(E')G(E-E')\,dE'$$

→ Voigt function

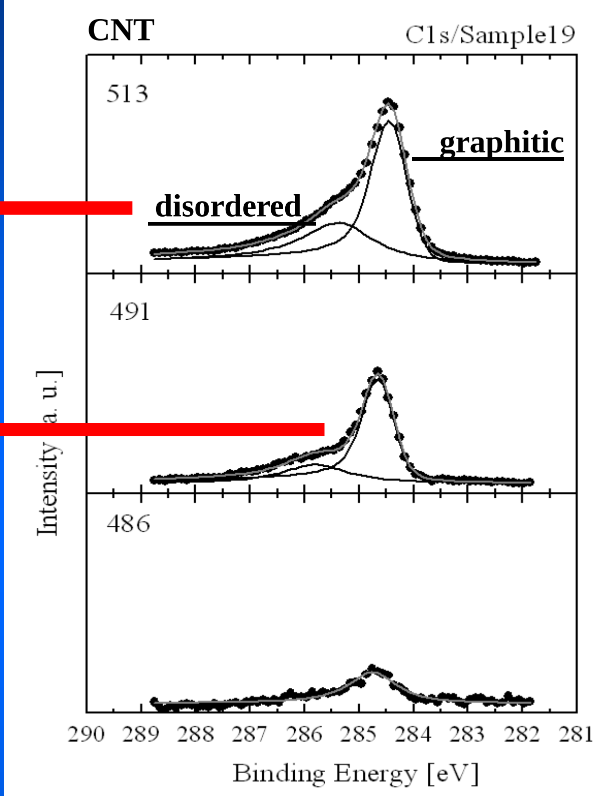
Analyzing the data: Peak Fitting



Strategy:

- Use of references for asymmetry and broadening
- Reasoning of most likely chemical composition

Peak broadening and asymmetry *should* be the same for same component in different spectra



But: both may differ for different components
→ discrepancy for different peaks should always be based on physical reasons

Quantitative Analysis

Goal:

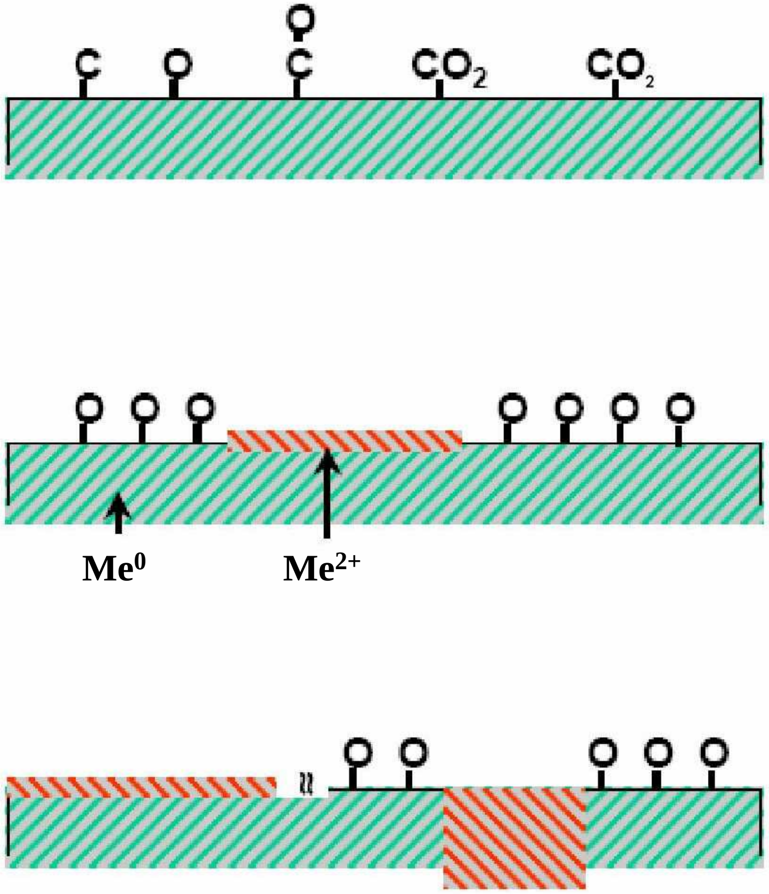
Elemental composition

- Species of atoms on surface
- Concentration of surface atoms
- Vertical distribution
  - → on surface (adsorbate)
  - → near surface

Molecular state of adsorbates

Oxidation state of surface species

- $Me^0 \Leftrightarrow Me^{n+}$



Quantitative Analysis: First Steps

In general:

$$I_X = B \times \sigma \times \lambda_{tot} \times T \times n_X$$

B: *all instrumental contributions*
σ: ionisation cross section for given photon energy
λ_{tot}: total escape depth
T: transmission through surface
n_X: atomic density of analyzed species in sample

$$\sigma = \sigma_{tot} \times f(X,\alpha)$$

with $f(X,\alpha) = 1+(\beta(X)/4)\ (1-3\cos^2\alpha)^*$

σ_{tot}: total ionisation cross section
f: form function accounting for asymmetry of peak
β: asymmetry parameter
α: angle between photon beam and emitted electron
(different for standard x-ray source and synchrotron)

*Yeh and Lindau, Atomic data nucl. data tables32(1985)1

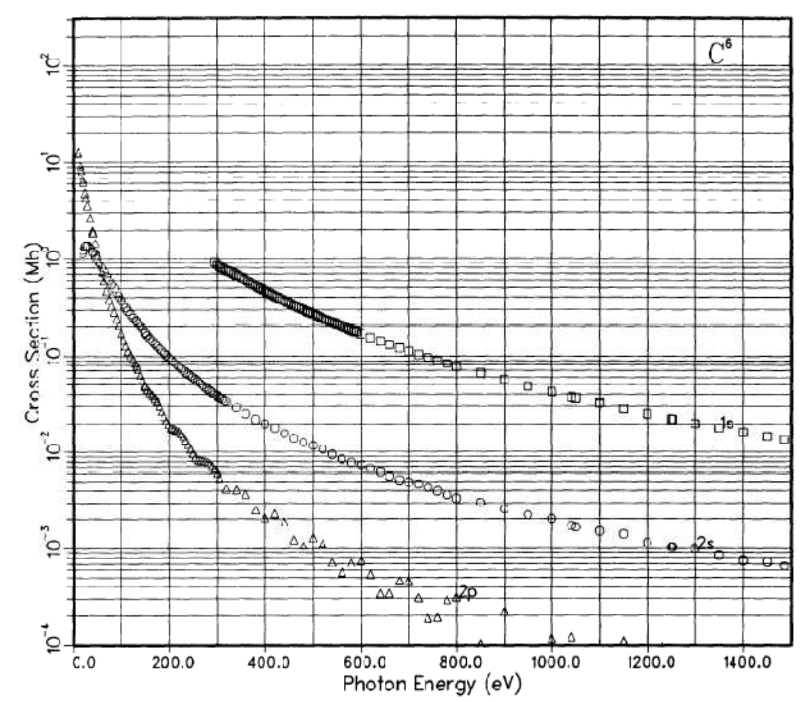
$$\lambda_{tot} = E(X) \times 1/a[\ln(E(X)-b)^*$$

E: KE of electron
a, b: parameters dependent on dielectric function and concentration of host

*Penn, J.of Electr.Spectr. And Rel. Phen. 9(1976)29

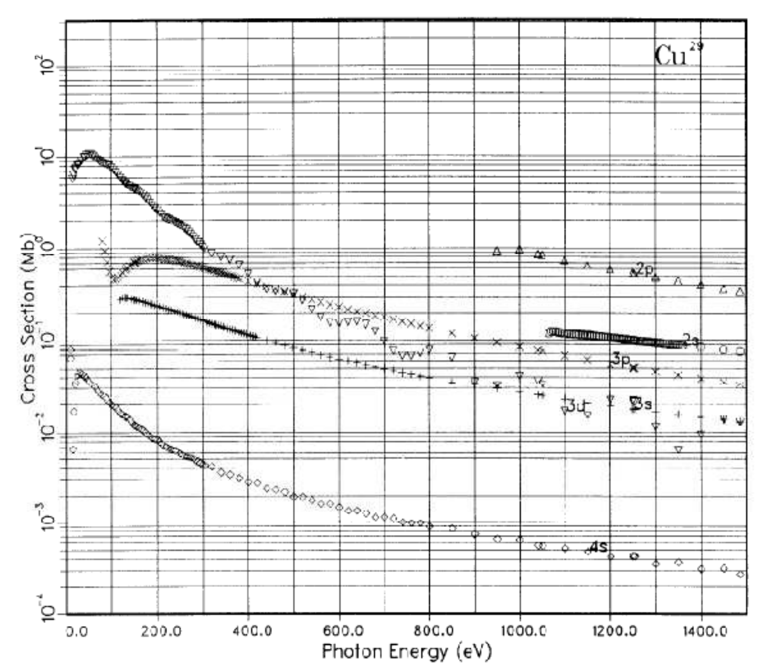
Cross section changes with energy of incident beam!!!

Quantitative Analysis: Cross Section



C binding energies(eV) are:

1s(2) 290.860 2s(2) 17.5409 2p(2) 8.98202



Cu binding energies(eV) are:

1s(2) 8838.79 2s(2) 1063.32 2p(6) 939.062
3s(2) 117.495 3p(6) 77.6900 4s(1) 6.92903
3d(10) 10.1316

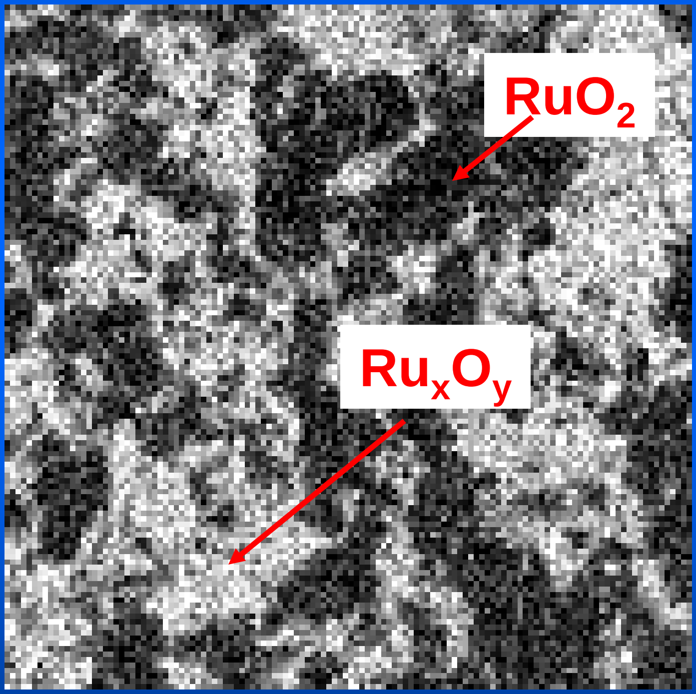
Calculated changes of Cross section beam energy

(Yeh, Lindau; Atomic data and nuclear data tables 32 (1985) 1)

Quantitative Analysis

In most cases the sample surface is quite heterogeneous

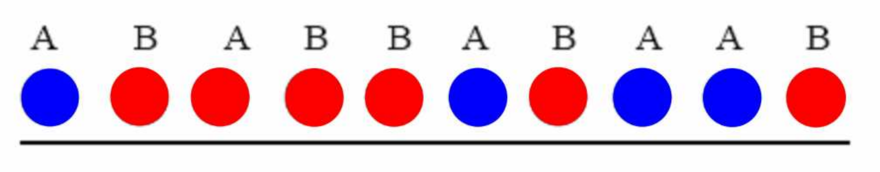
→ Need of *models* to extract an accurate approximation of composition out of spectral intensities



Ru 3d5/2-map of the chemical states on Ru(0001) after pre-treatment with O
performed with Scanning Photoelectron Microscopy (ELETTRA):

Quantitative Analysis: Useful Examples

A. Heterogeneous mixture (e.g. alloy):



with the formulas above follows

$$\frac{I_A}{I_B}\cdot\frac{I_B^0}{I_A^0}=\frac{N_A}{N_B}\cdot\frac{N_B^0}{N_A^0}\cdot\frac{\lambda_{AB}(E_A)}{\lambda_{AB}(E_B)}\cdot\frac{\lambda_B(E_B)}{\lambda_A(E_A)}$$

and

$$\lambda_A = 0.41\cdot a_A^{1.5}\cdot E_A^{0.5}$$

$$\frac{N_A}{N_B}\cdot\frac{N_B^0}{N_A^0}=\frac{X_A}{X_B}\cdot\left(\frac{a_A}{a_B}\right)^3$$

a_A: „radius of A“

→ Mol fraction

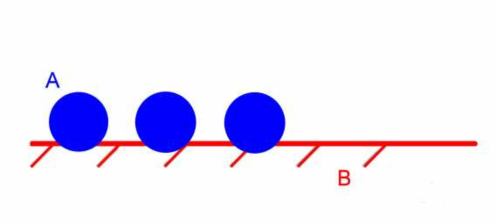
follows

$$\frac{X_A}{X_B}=\left(\frac{a_B}{a_A}\right)^{1,5}\cdot\frac{I_A/I_A{}^0}{I_B/I_B{}^0}$$

$I_{A,B}{}^0$: reference of clean material

Quantitative Analysis: Useful Examples

B. Partial Coverage (e.g. adsorbat):



Contribution of B:

$$I_B = I_B \ \textbf{(direct)} \ + I_B \ \textbf{(attenuated by A)}$$
$$= (1-\Theta_A) I_B{}^0 + I_B{}^0 \Theta_A \exp\left(-\frac{a_A}{\lambda_A \cos\Theta}\right)$$

Θ: angle between surface normal and emitted electron

For signals of A and B follows

$$I_B = I_B{}^0 \left[1 - \Theta_A + \Theta_A \cdot \exp\left(-\frac{a_A}{\lambda_A \cos\Theta}\right)\right]$$

$$I_A = I_A{}^0 \cdot \Theta_A$$

Θ_A: coverage of A on B

Which gives

$$\frac{I_A}{I_B} = \frac{I_A{}^0}{I_B{}^0} \cdot \frac{\Theta_A}{1 - \Theta_A\left[1 - \exp\left(-\frac{a_A}{\lambda_A} \cos\Theta\right)\right]}$$

$I_{A,B}{}^0$: reference of clean material

Quantitative Analysis: Useful Examples

C. Thin layer of A on B (e.g. oxide):

Contribution of B:

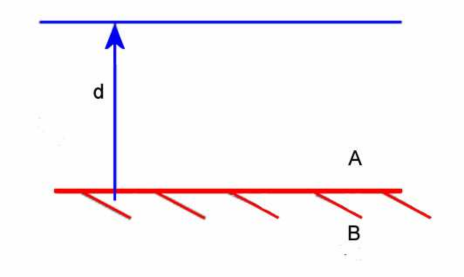
$$I_B = I_B{}^0 \exp\left(-\frac{d_A}{\lambda_A(E_B)}\cdot\cos\Theta\right)$$

Contribution of A:

$$I_A = I_A{}^0 \exp\left[1-\exp\left(-\frac{d_A}{\lambda_A(E_A)}\cos\Theta\right)\right]$$

Which gives

$$\frac{I_A}{I_B} = \frac{I_A{}^0}{I_B{}^0}\cdot\frac{1-\exp\left(-\frac{d_A}{\lambda_A(E_A)}\cos\Theta\right)}{\exp\left(-\frac{d_A}{\lambda_A(E_B)}\cos\Theta\right)}$$



➔ Special case:

$\lambda_A(E_A) \sim \lambda_A(E_B)$ **i.e.** $E_A \sim E_B$

follows

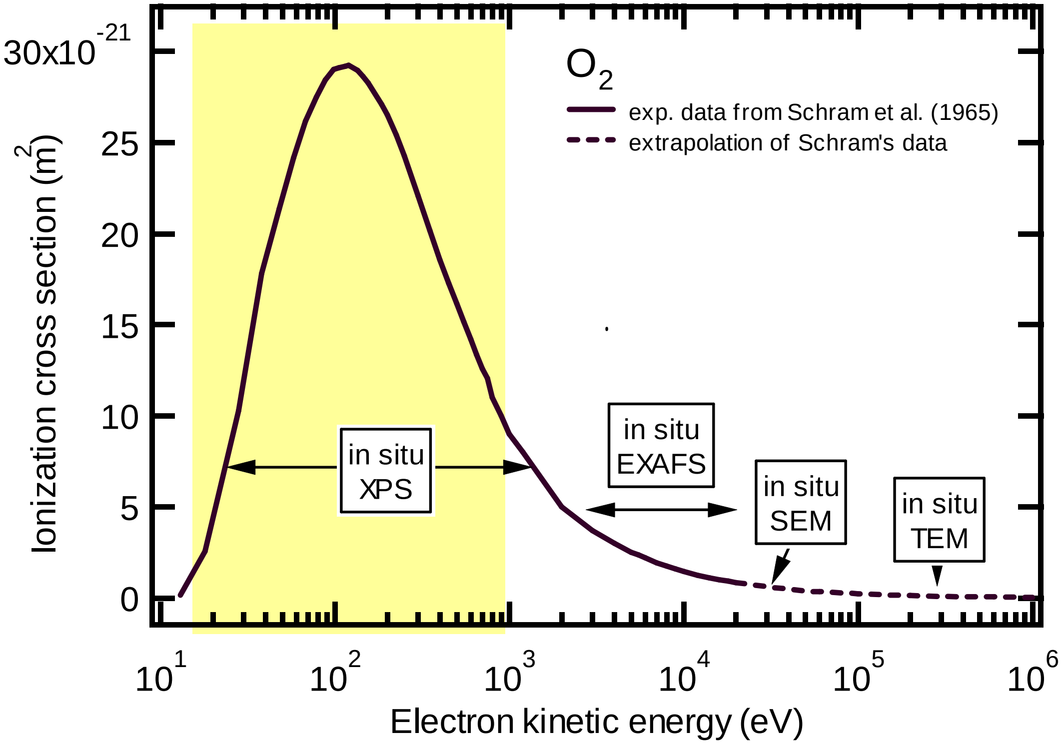
$$d_A \approx \frac{\lambda_A}{\cos\Theta}\cdot\ln\left[1+\frac{I_A}{I_B}\cdot\frac{I_B{}^0}{I_A{}^0}\right]$$

General problem here:
proper background substraction

In situ XPS: obstacles

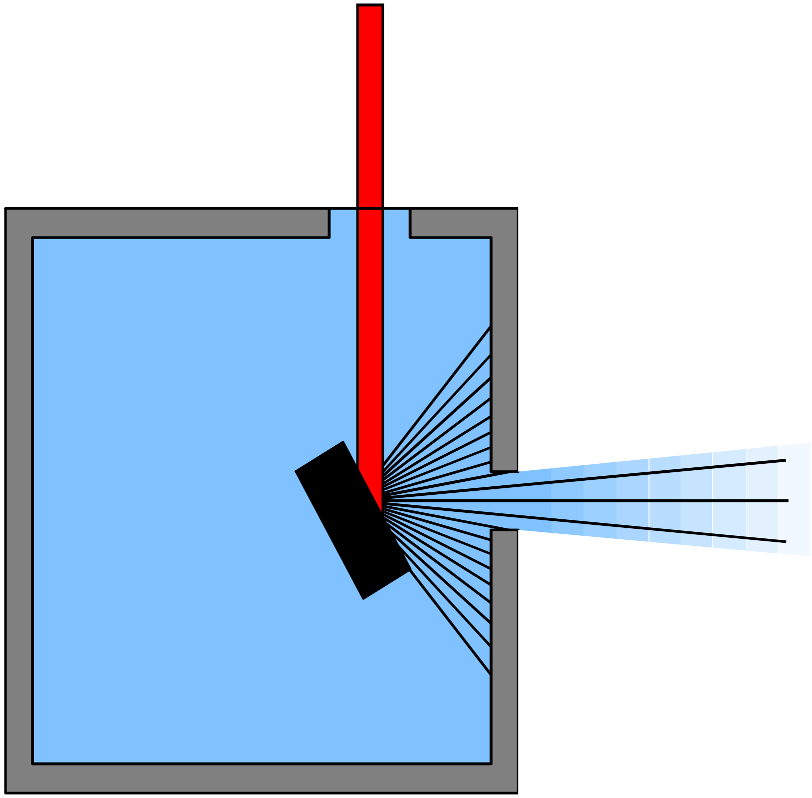
Fundamental limit:

elastic and inelastic scattering of electrons in the gas phase



Technical issues:
- Differential pumping to keep analyzer in high vacuum
- Sample preparation and control in a flow reactor

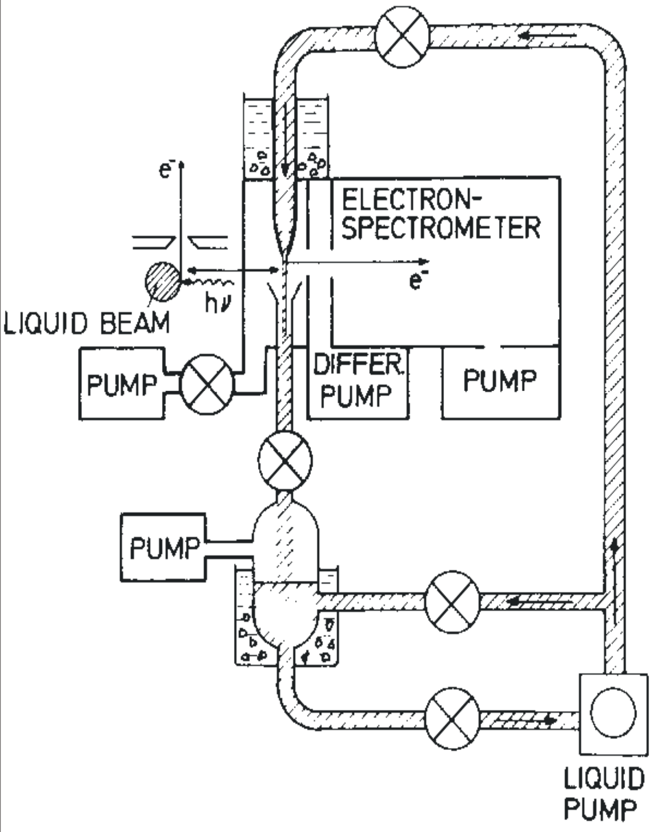
In situ XPS: basic concept



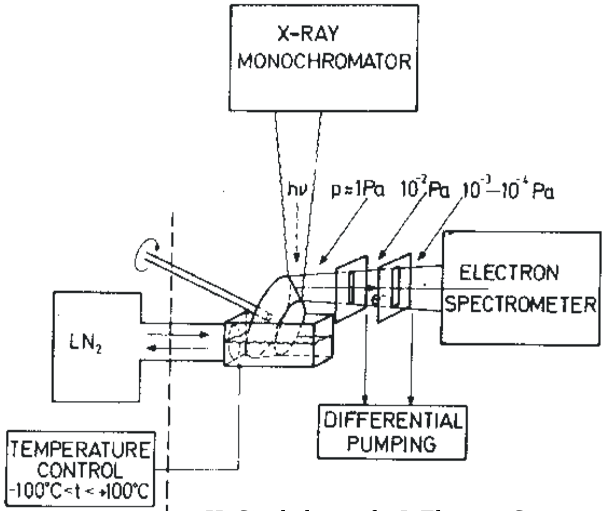
- Photons enter through a window
- Electrons and a gas jet escape through an aperture to vacuum

In situ XPS instruments: previous designs

- H. Siegbahn et al. (1973-)
- M.W. Roberts et al. (1979)
- M. Faubel et al. (1987)
- M. Grunze et al. (1988)
- P. Oelhafen (1995)

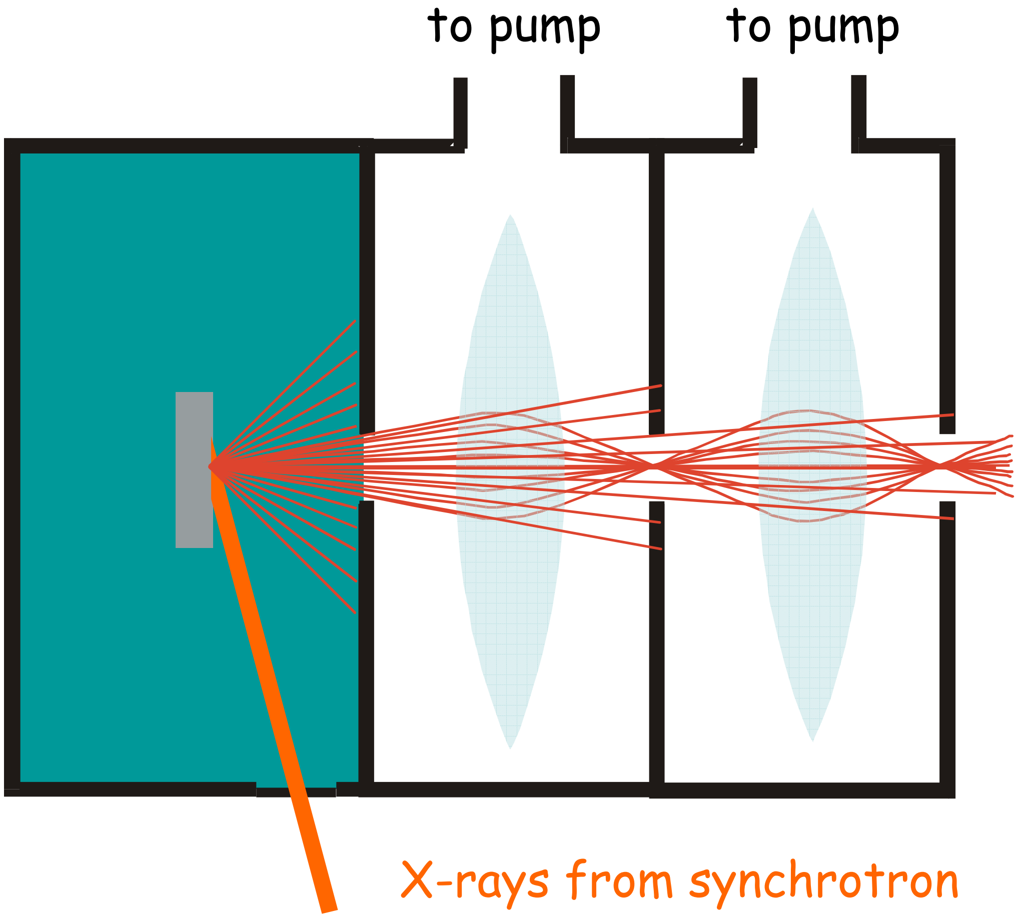


H. Siegbahn et al., J. Electron Spectrosc. Relat. Phenom. **2**, 319 (1973)



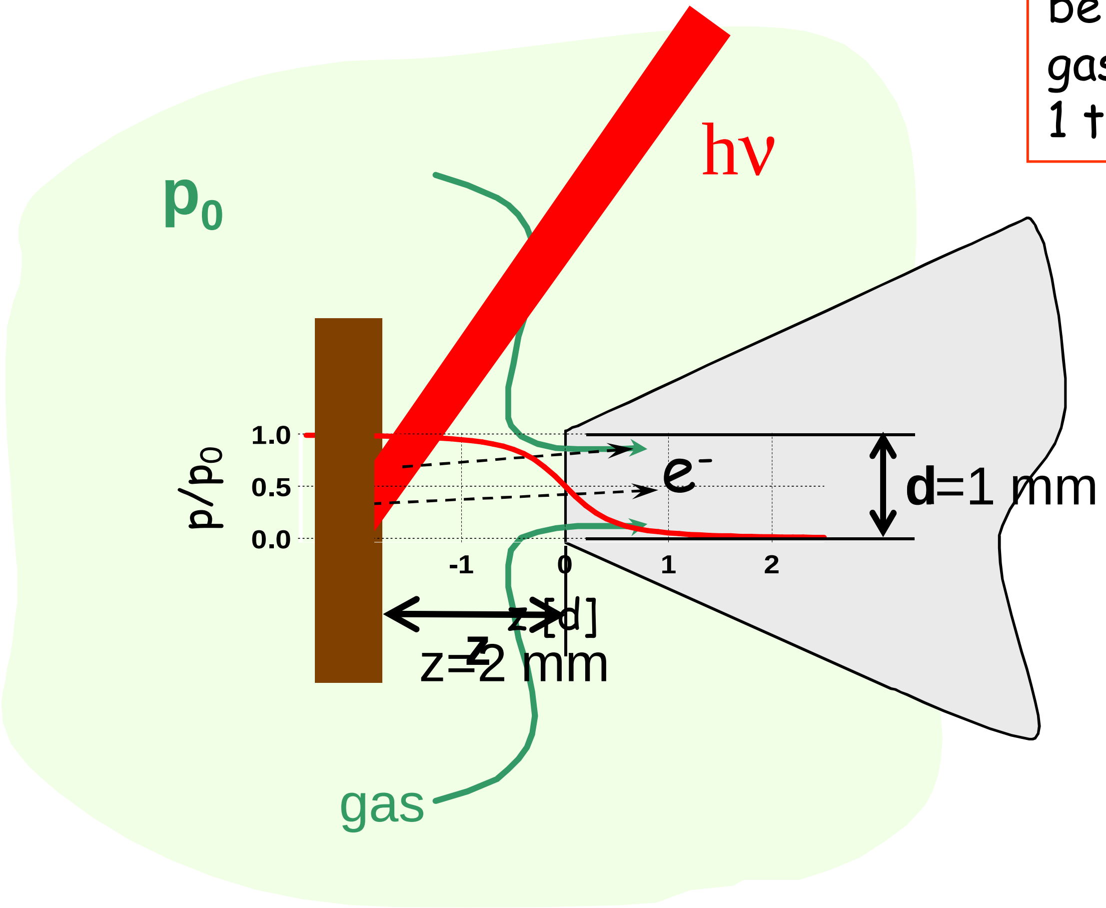
H. Siegbahn et al., J. Electron Spectrosc. Relat. Phenom. **24**, 205 (1981)

In situ XPS using differentially pumped electrostatic lenses



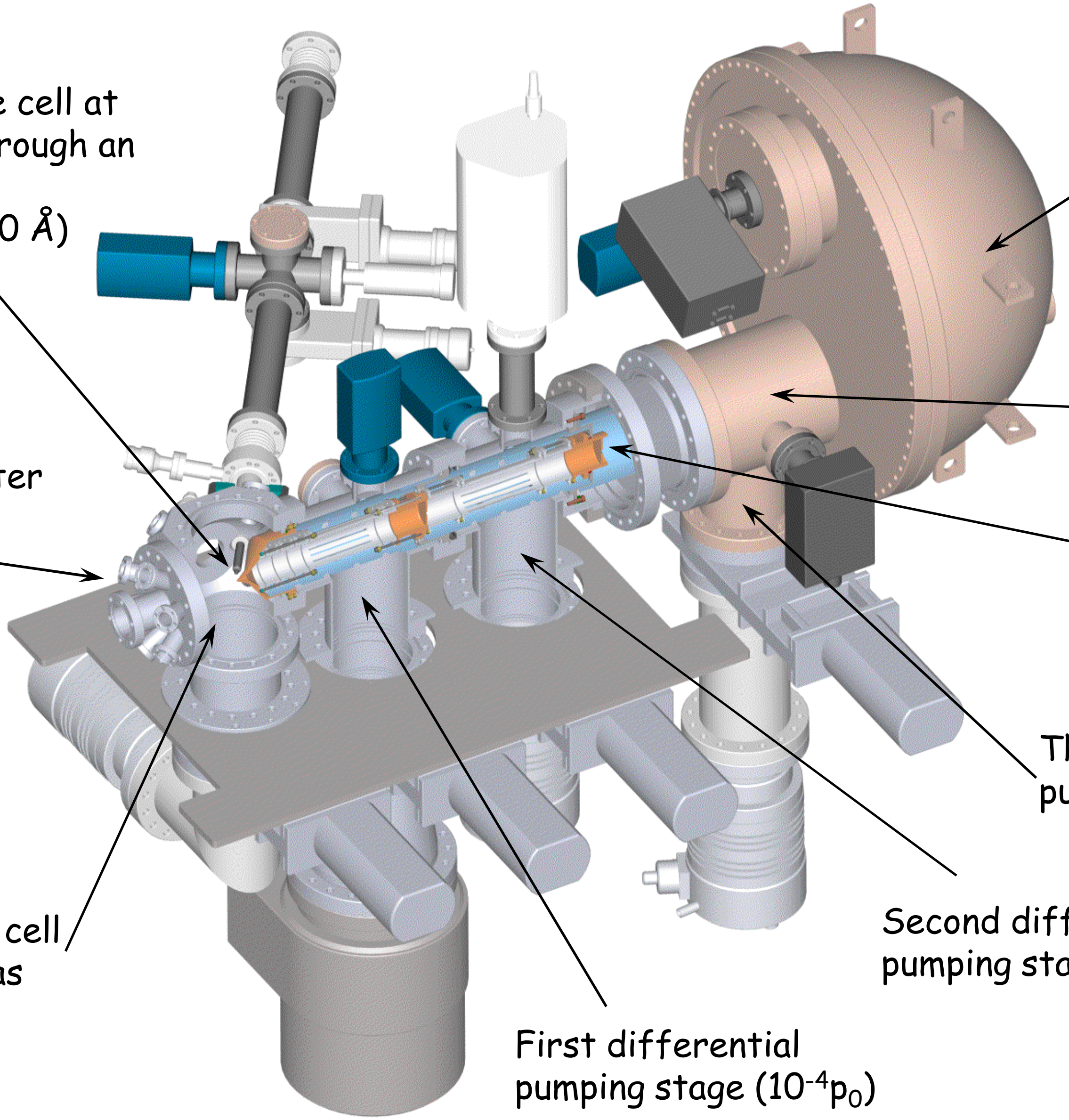
D.F. Ogletree, H. Bluhm, G. Lebedev, C.S. Fadley, Z. Hussain, M. Salmeron, Rev. Sci. Instrum. 73 (2002) 3872.

Close-up of sample-first aperture region



Gas phase composition can be measured by XPS.
gas phase signal:
1 torr·mm ~ a few monolayers

In situ XPS system



X-rays enter the cell at 55° incidence through an SiN_x window (thickness ~ 1000 Å)

mass spectrometer and additional pumping

Experimental cell supplied by gas lines (p_0)

First differential pumping stage ($10^{-4}p_0$)

Second differential pumping stage ($10^{-6}p_0$)

Third differential pumping stage ($10^{-8}p_0$)

Focal point of analyzer input lens

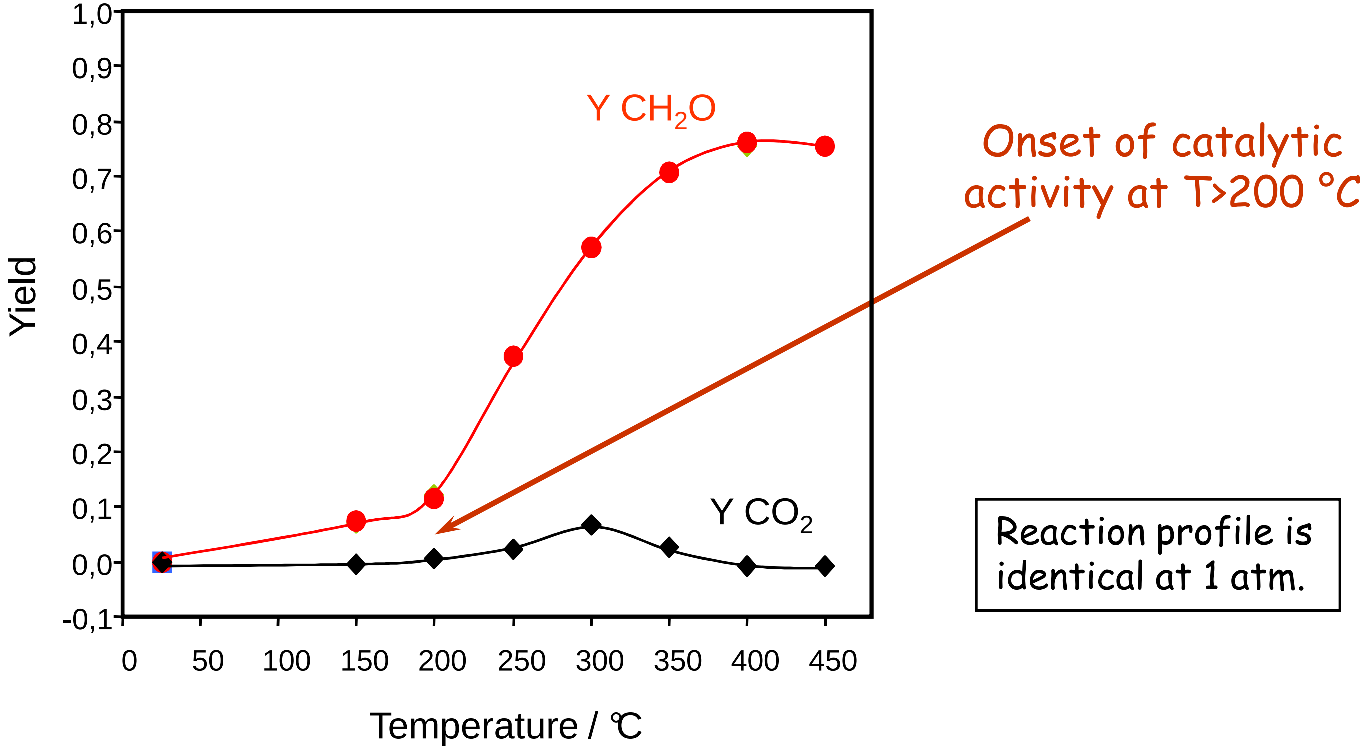
Analyzer input lens

Hemisphercal electron analyzer ($10^{-9}p_0$)

Application of in situ XPS to catalysis: methanol oxidation on Cu

Partial oxidation: $CH_3OH + \frac{1}{2}O_2 \xrightarrow{Cu} CH_2O + H_2O$

Total oxidation: $CH_3OH + \frac{3}{2}O_2 \xrightarrow{Cu} CO_2 + 2H_2O$



Onset of catalytic activity at T>200 °C

Reaction profile is identical at 1 atm.

What is the state of the surface under reaction conditions?

Partial oxidation of methanol

UHV XPS

I.E. Wachs & R.J. Madix, Surf. Sci. 76, 531 (1978); A. F. Carley et al., Catal. Lett. 37, 79 (1996).

$$O^-(a) + 2CH_3OH(g) \longrightarrow 2CH_3O^-(a) + H_2O(g)$$

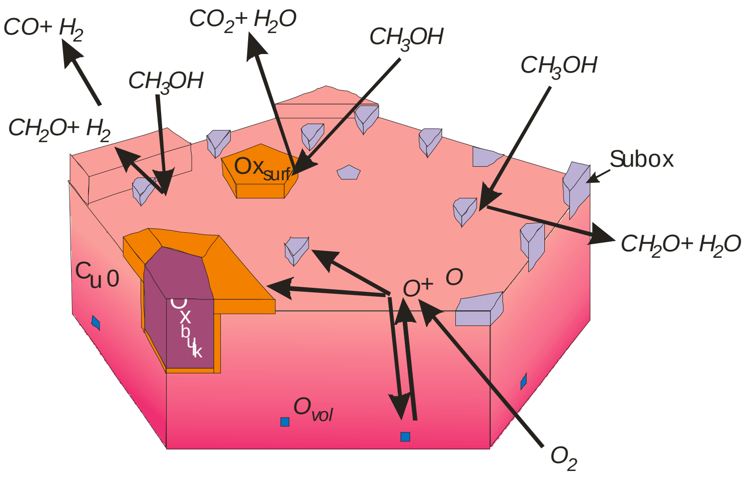
$$CH_3O^-(a) \longrightarrow CH_2O(g) + H^+(a)$$

In situ NEXAFS

A. Knop-Gericke et al., Topics Catal. 15, 27 (2001).

$CH_3OH + O_2 \sim$ 0.5 mbar

<u>suboxide phase</u>:
- only present in situ



Questions for in situ XPS: - Quantitative analysis of surface species
- Carbon species on the surface
- Depth-dependent analysis

Experimental conditions

sample: polycrystalline Cu foil

Variations of mixing ratios: $CH_3OH : O_2$ = 1:2, 3:1, 6:1; T = 400 °C; p = 0.6 mbar

Temperature series: gas mixture at room temperature: $CH_3OH : O_2$ = 3:1;
p = 0.6 mbar; temperature: 25 °C → 450 °C

flow rates: 10 ... 20 sccm

XPS measurements

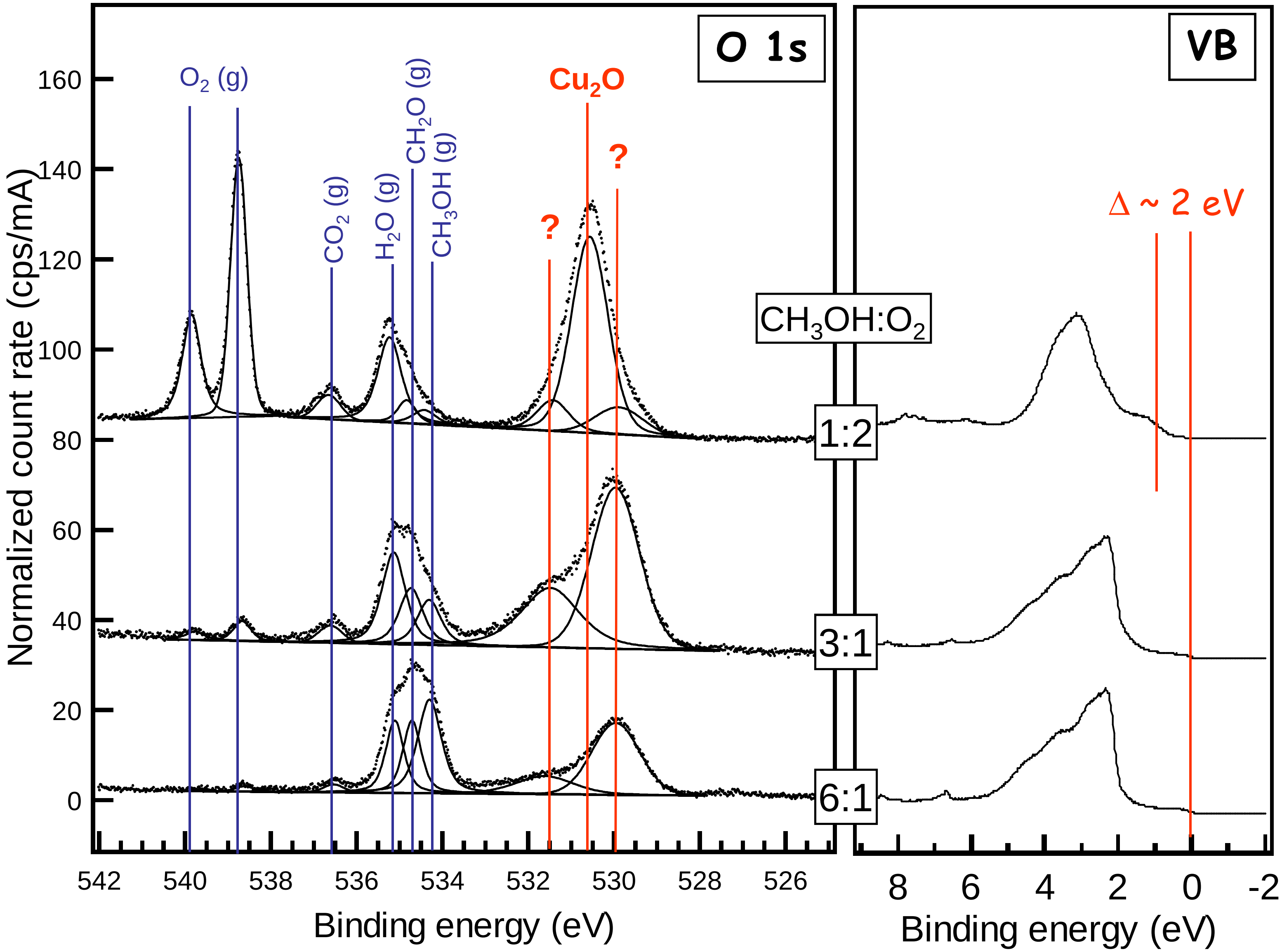
Beam line U49/2-PGM1 at Bessy
Energy range 100...1500 eV
total spectral resolution 0.1 eV @ 500 eV

O 1s, C 1s, Cu 3p, Cu 2p: KE ~ 180 eV
Valence Band: KE ~ 260 eV

Depth profiling with KEs 180 eV, 350 eV,
500 eV, 750 eV

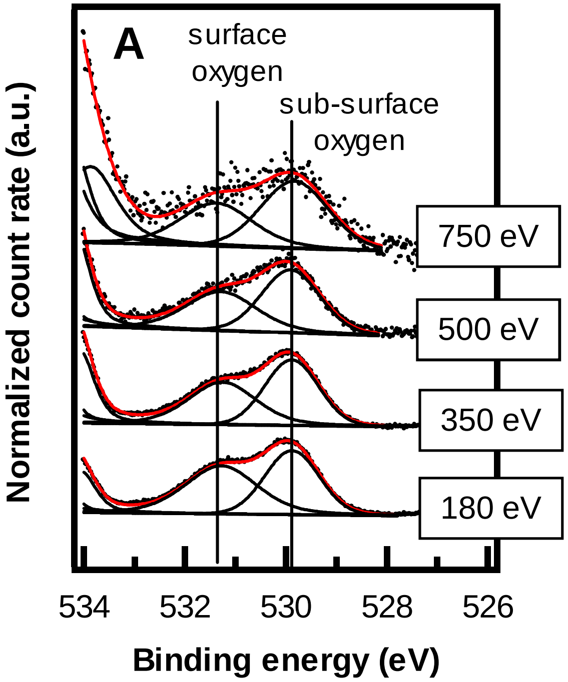
Methanol oxidation on Cu: O1s spectra

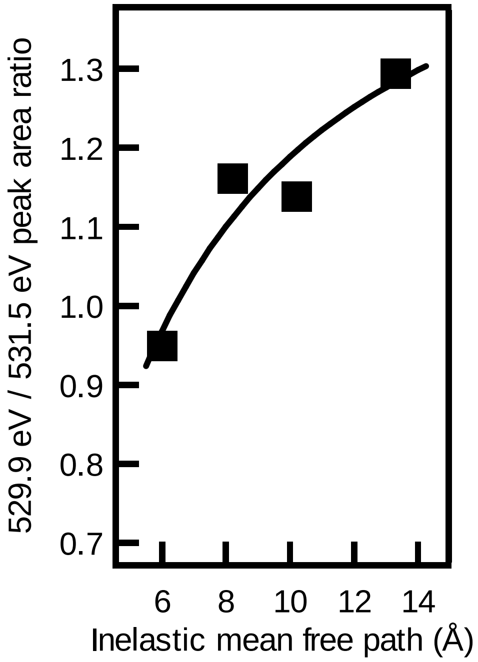
400 °C, 0.5 torr

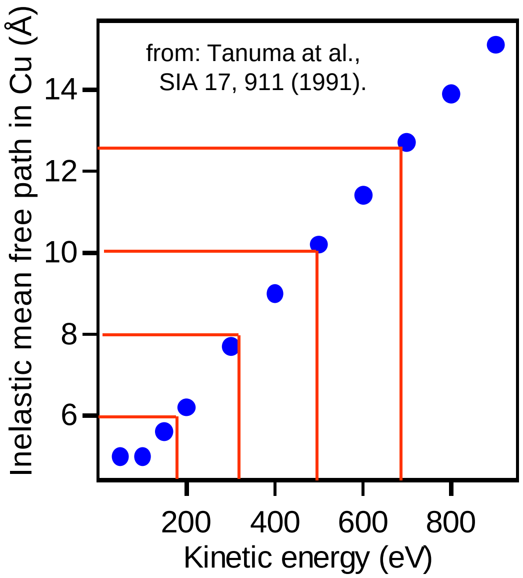


O1s depth profiling

$CH_3OH : O_2 = 3:1$





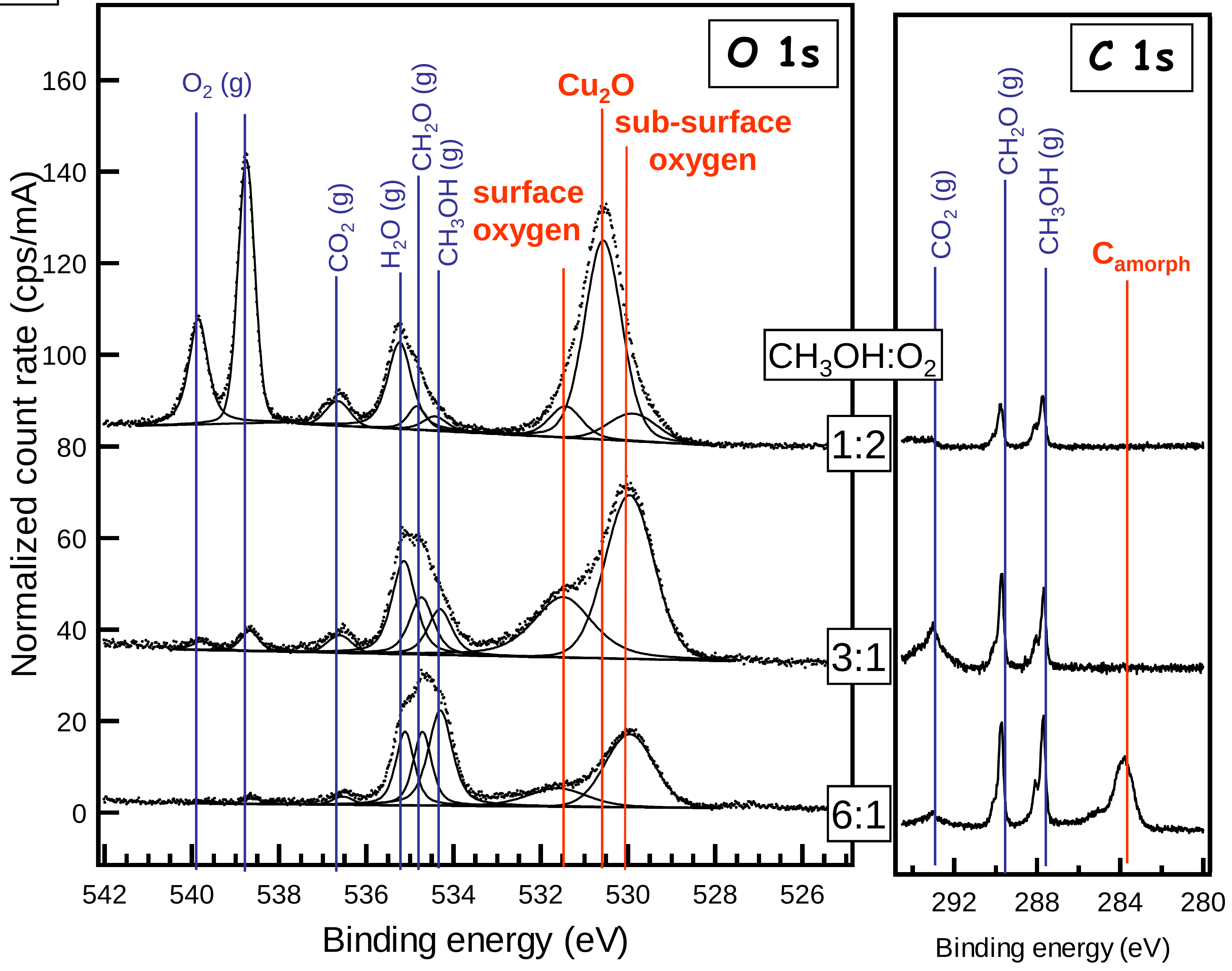

from: Tanuma at al., SIA 17, 911 (1991).

$$I_{529.9}/I_{531.5}=n_{529.9}/n_{531.5}\cdot\exp[-(z_{531.5}-z_{529.9})/\lambda]$$

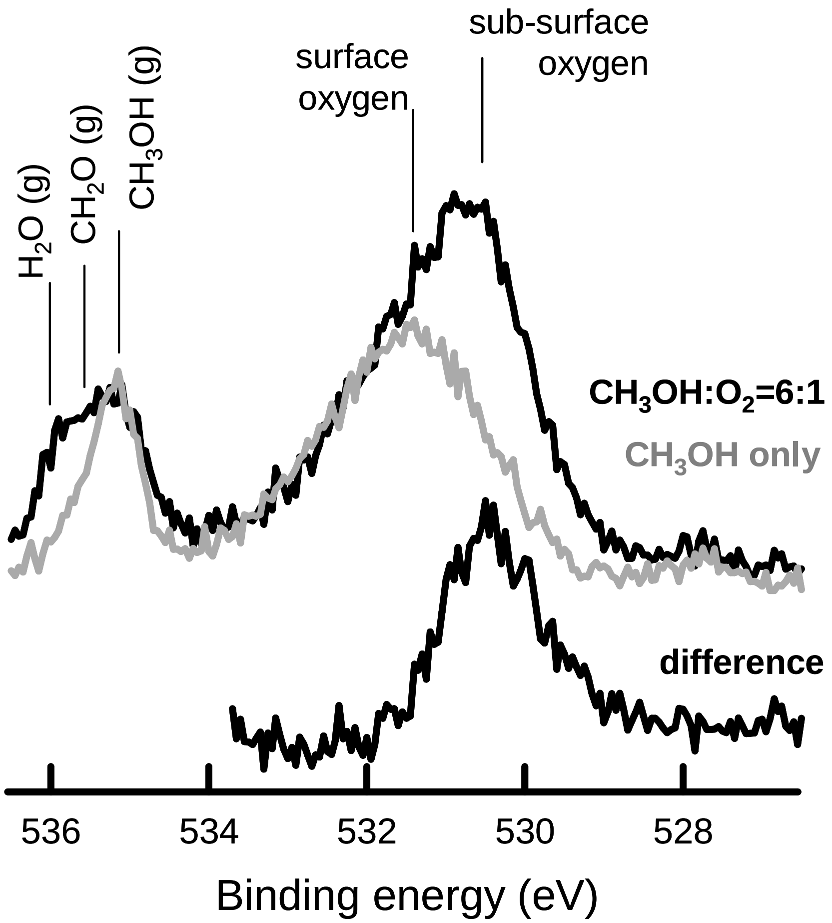
$\Delta z = 3$ Å, $n_{529.9}/n_{531.5} = 1.6$

Methanol oxidation on Cu: C1s spectra

400 °C

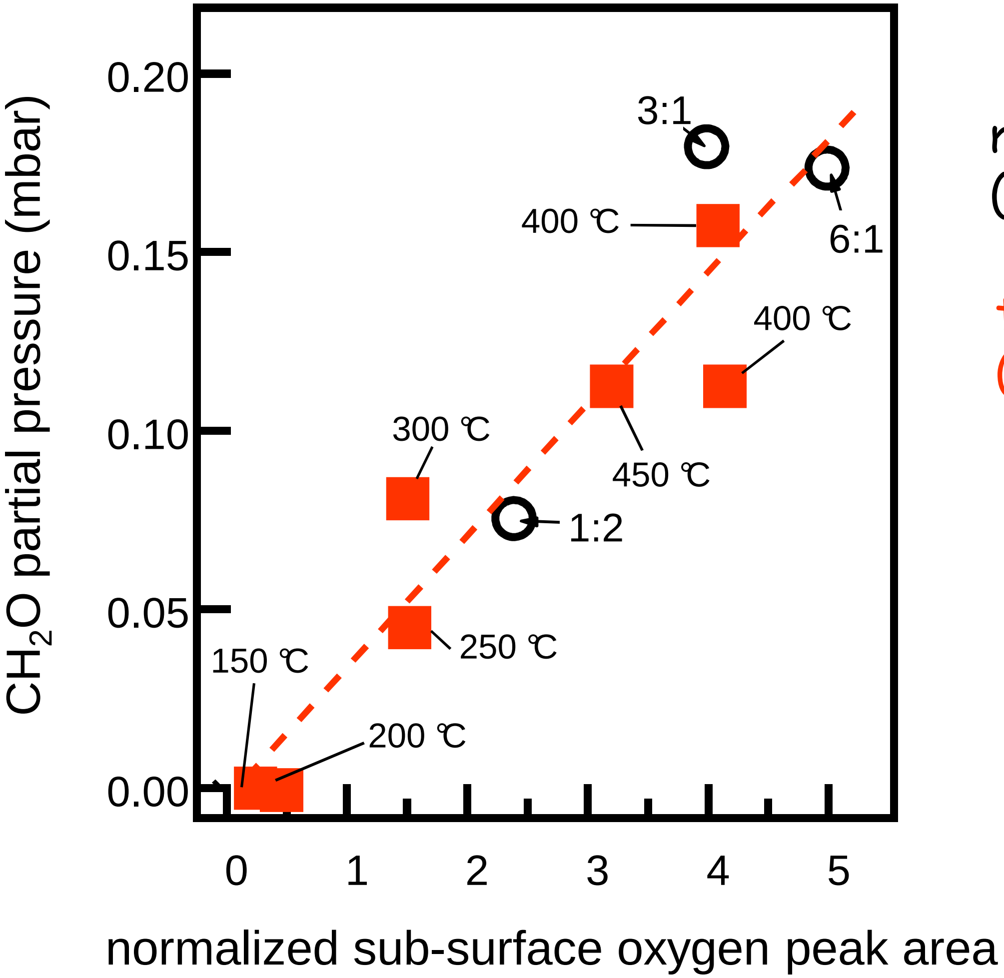


Metastability of the Sub-Surface Oxygen



Correlation of catalytic activity and surface species

CH_2O yield vs sub-surface oxygen peak area



mixing ratio series
(T = 400 °C)

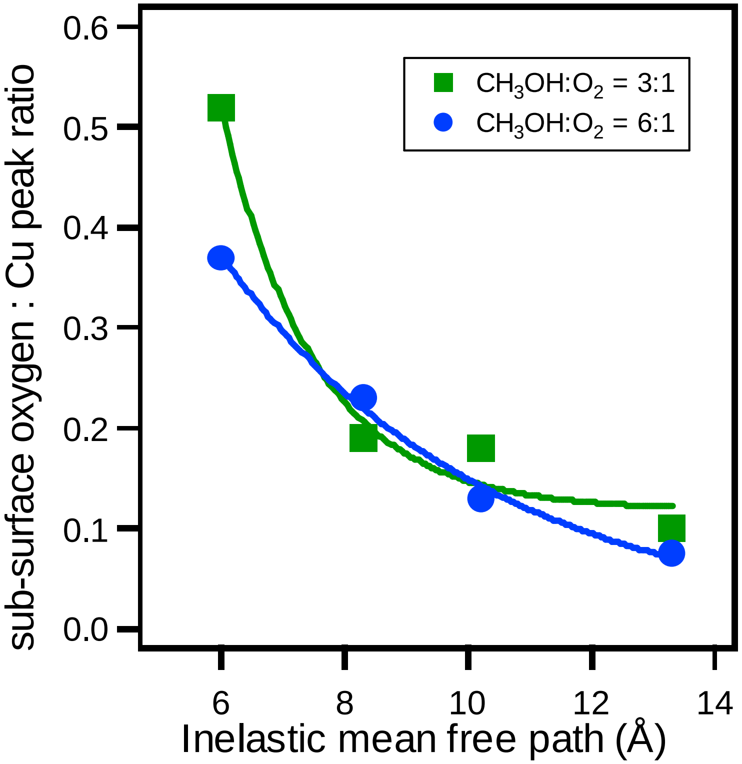
temperature series
($CH_3OH:O_2=3:1$)

Open questions:
What is the nature of the sub-surface oxygen species?
What is its role in the catalytic reaction?

Depth profiling

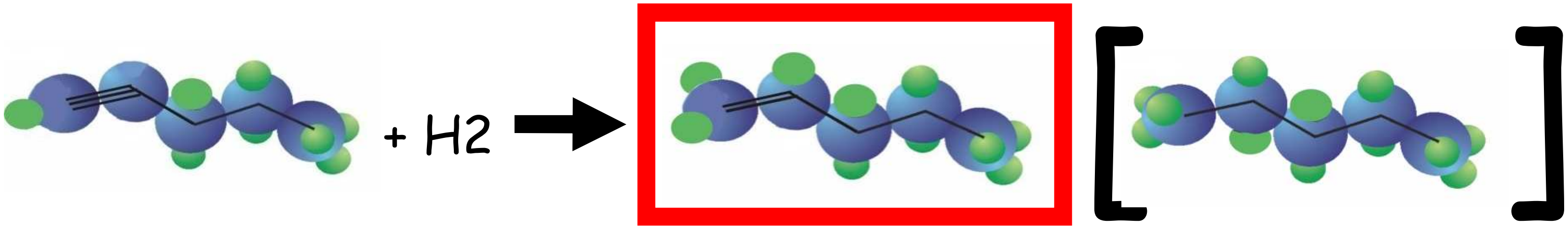
(calculated from Cu 3*p* and sub-surface O 1*s*)

Reducing conditions



Open questions: What is the nature of the sub-surface oxygen species?
What is its role in the catalytic reaction?

Introduction



Literature

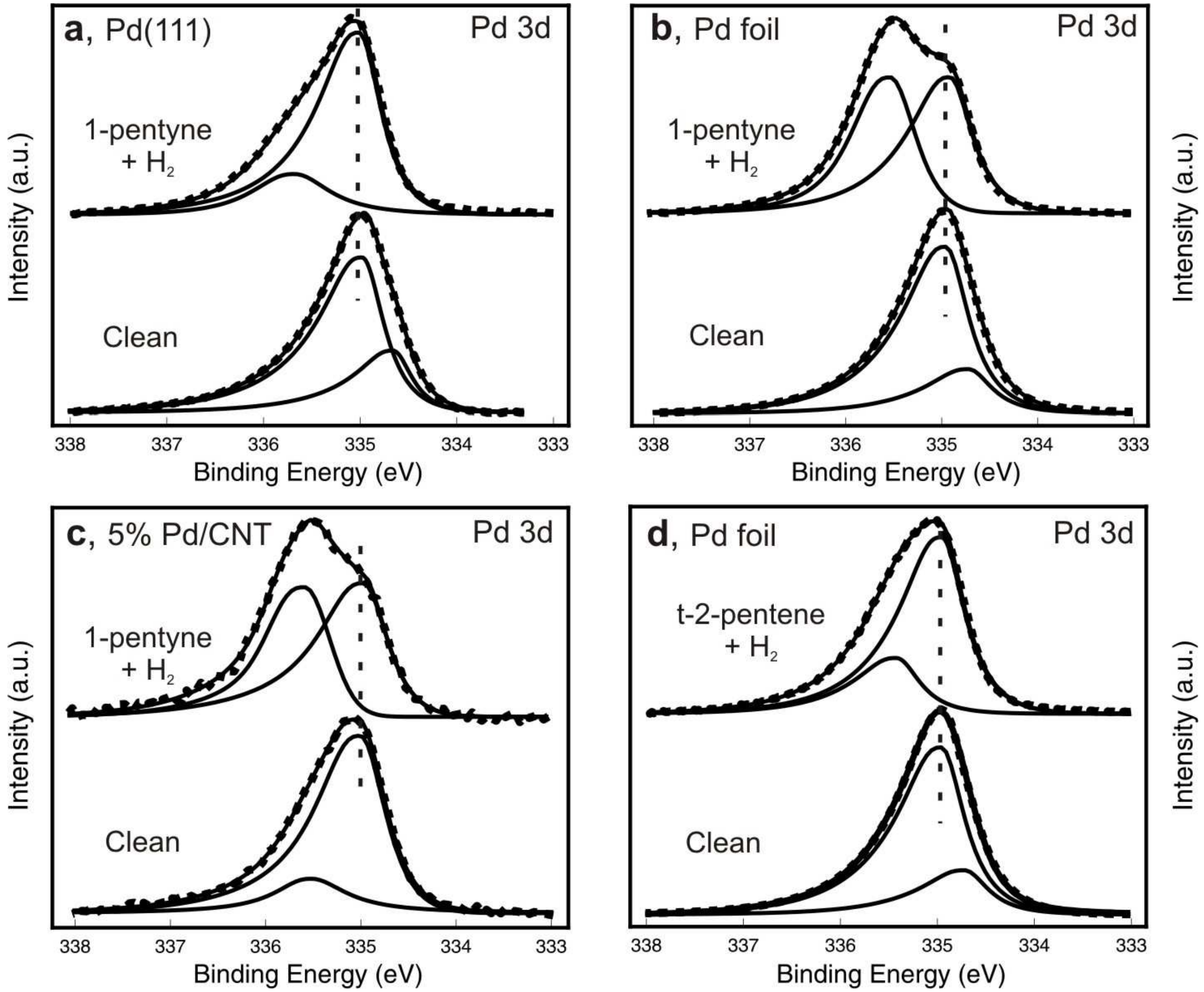
carbon laydown → selective hydrogenation

“similar” catalysts → different activity & selectivity

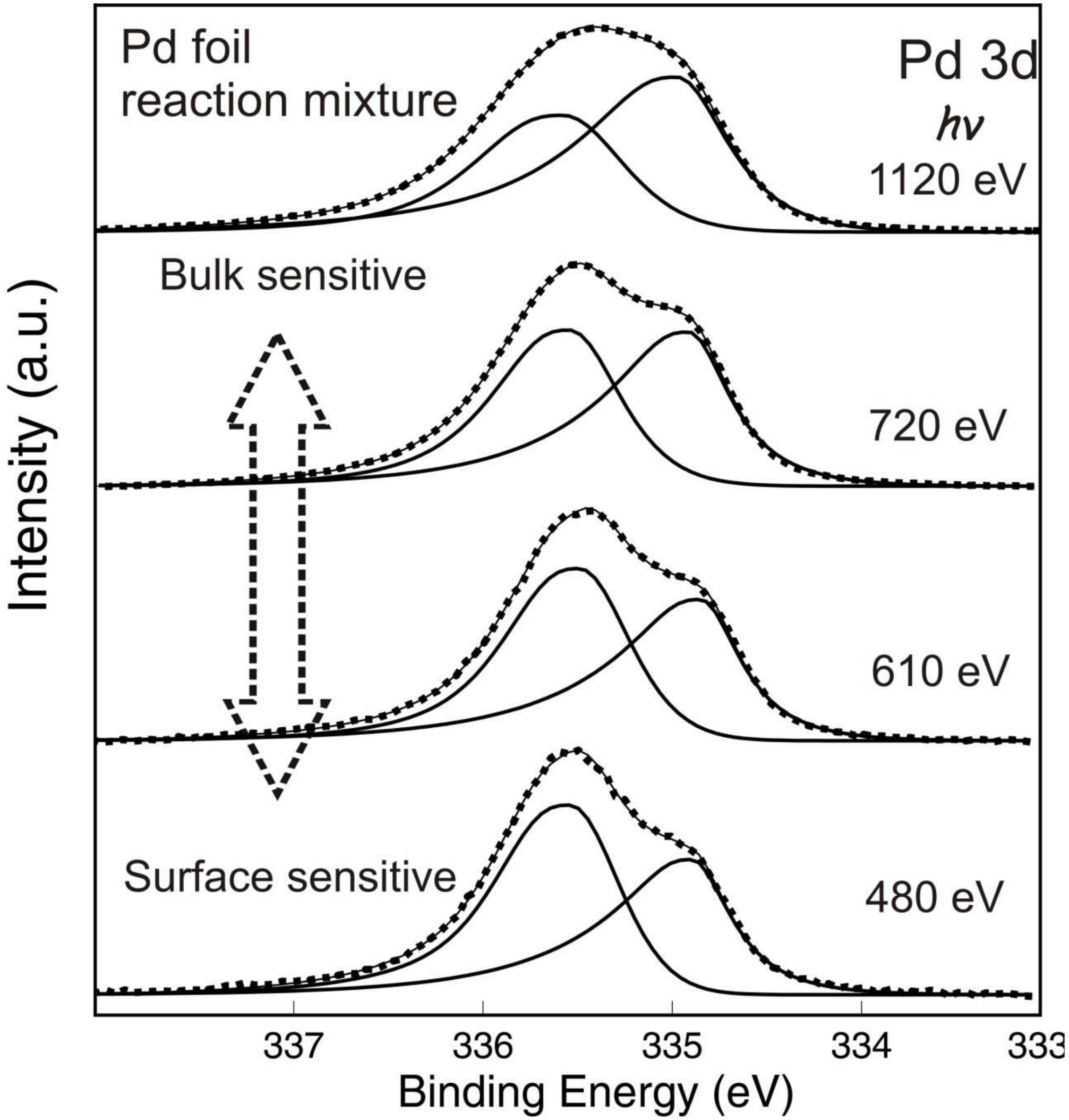
(structure sensitivity?)

Selectivity issue: what defines selectivity?

In-situ XPS: Pd 3d (hν: 720 eV)



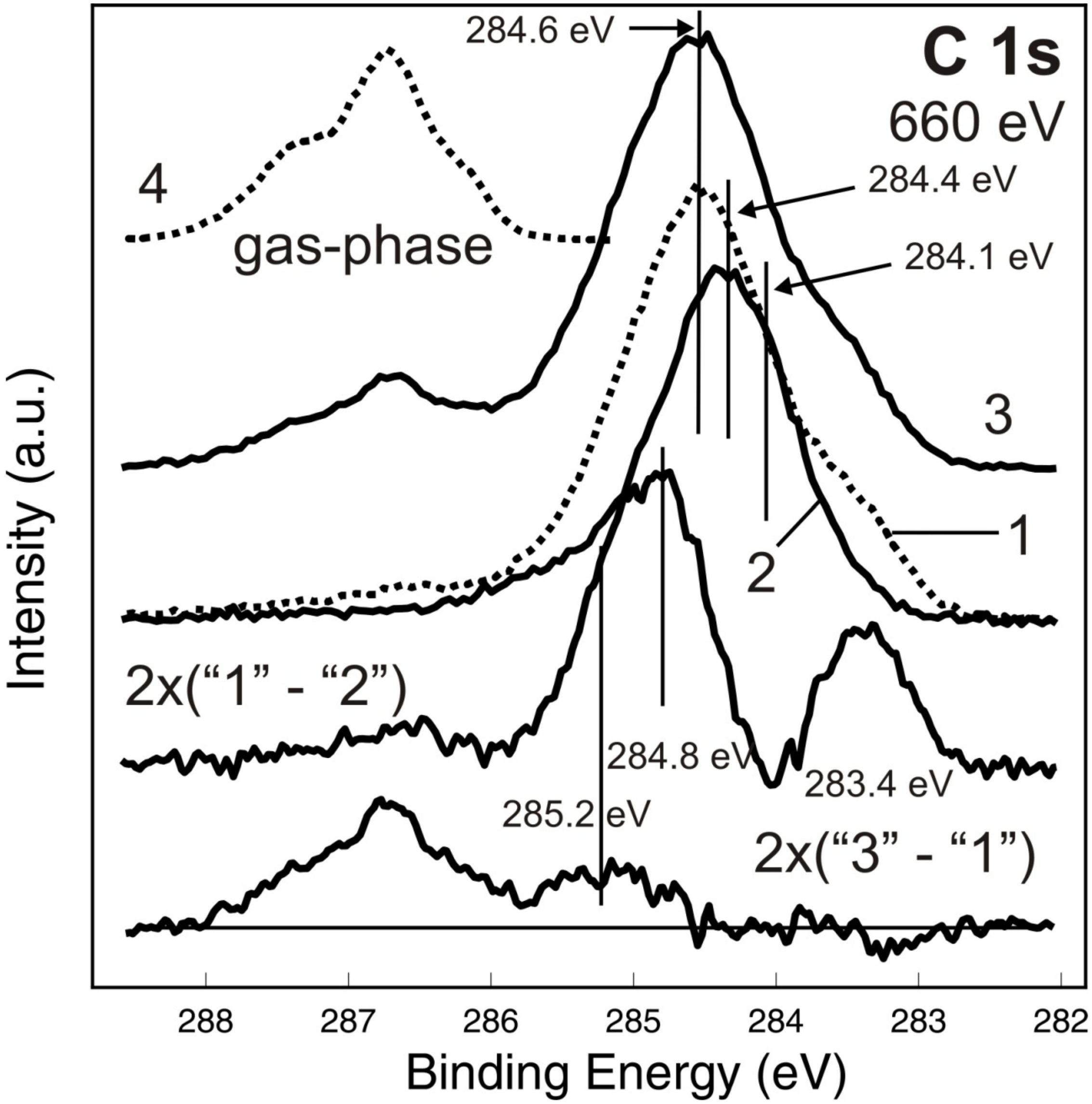
In-situ XPS: Pd 3d depth profiling



Not only adsorbate-induced surface core level shift !

But on-top location!

In-situ XPS: C1s (Switching off experiments)



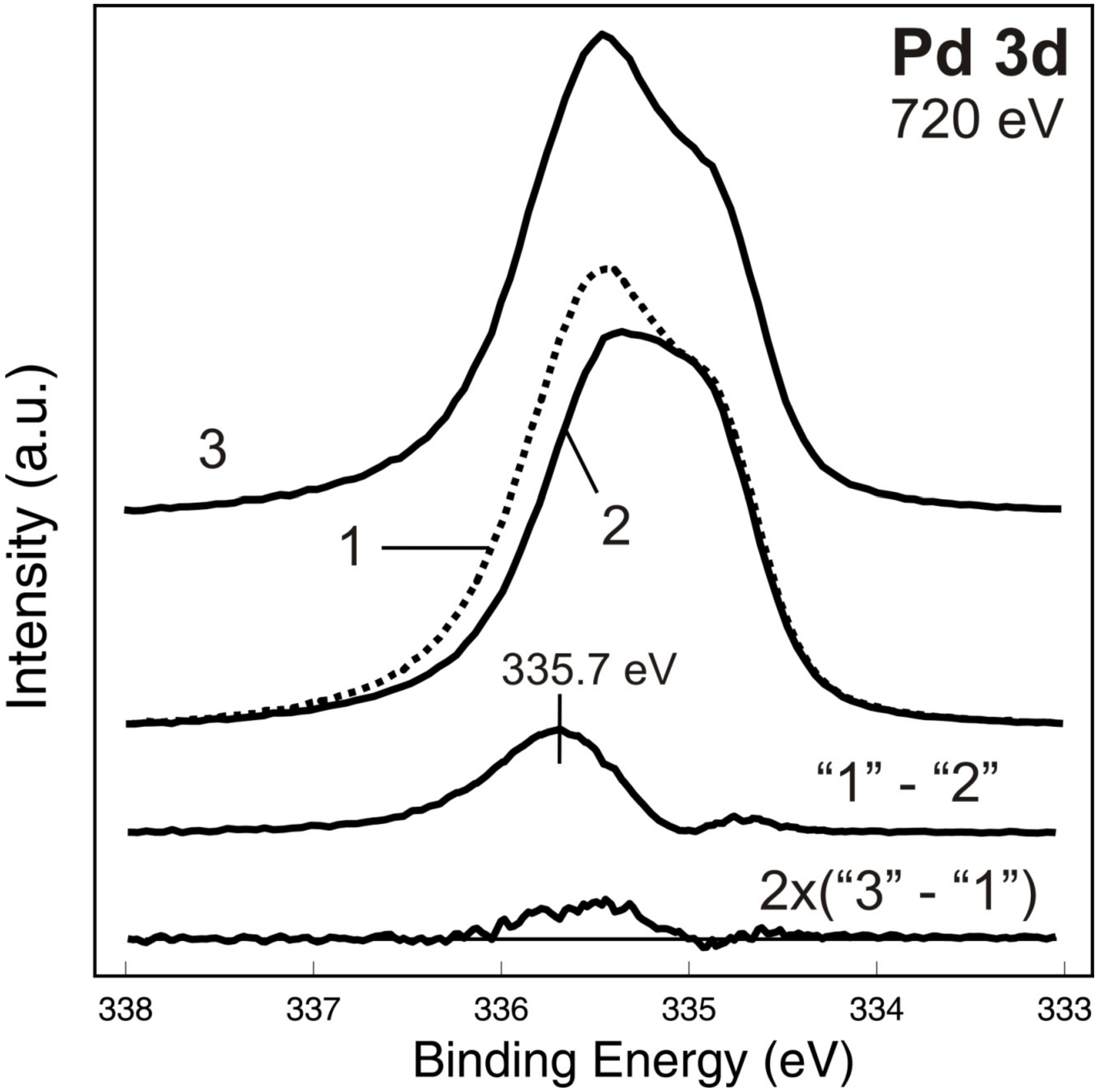
1: reaction mix.

2: C5 off

3: H2 off

4: C5 gas-phase

In-situ XPS: Pd 3d (Switching off experiments)



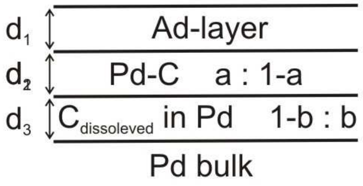
1: reaction mix.

2: C5 off

3: H2 off

In-situ XPS: Pd vs. C depth profiling

Model



d1 Ad-layer

d2 Pd-C a : 1-a

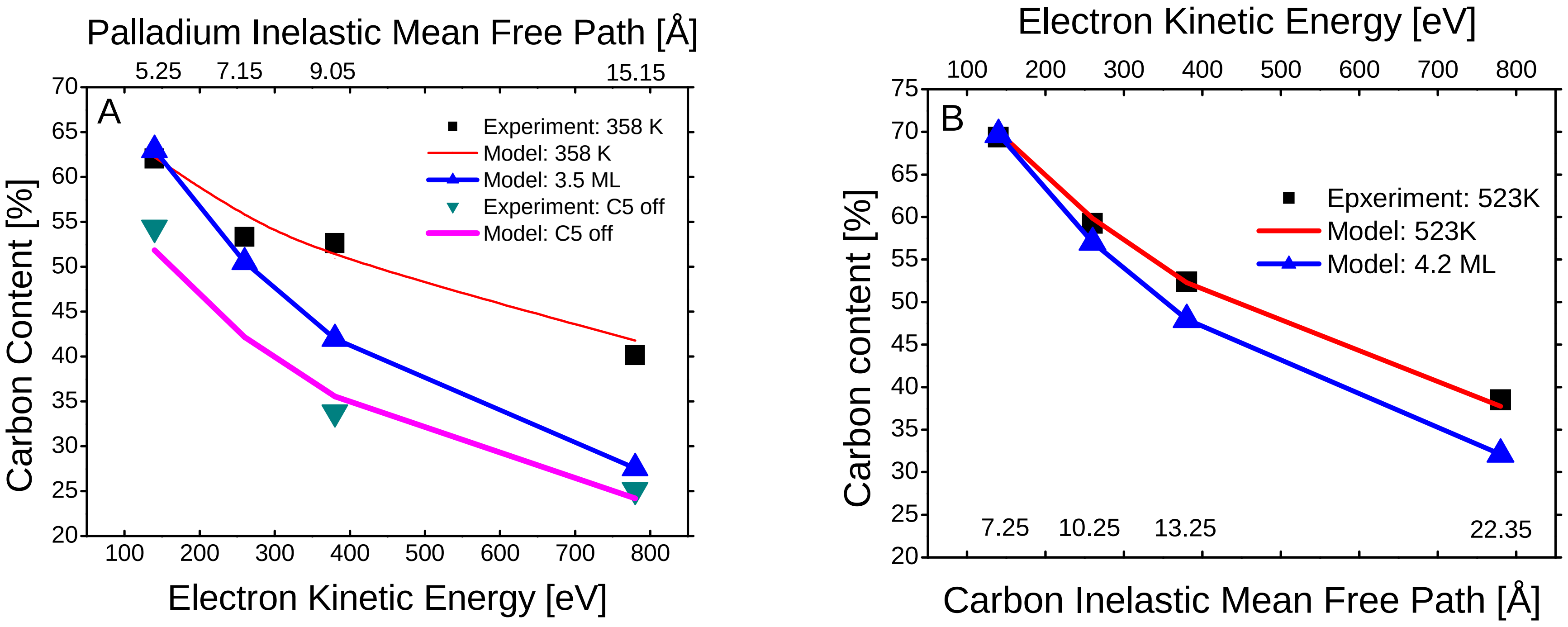
d3 $C_{dissoleved}$ in Pd 1-b : b

Pd bulk

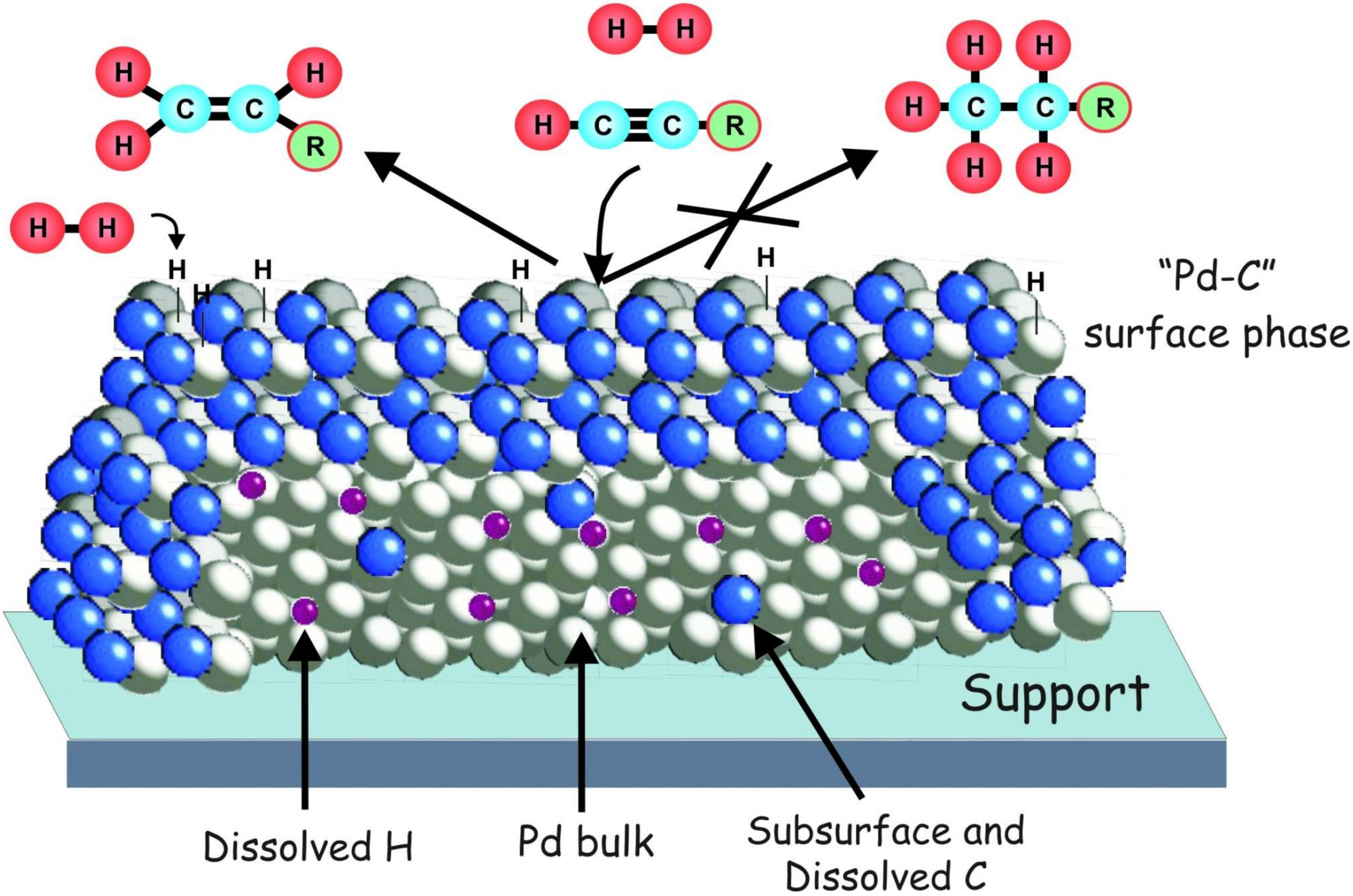
= 0.3 nm

1.4 nm

14 nm



Model


H
H
H
C
C
H
R
H
H
H
C
C
R
H
H
H
H
C
C
R
H
H
H
H
H
H
H
H
H
H
"Pd-C" surface phase
Support
Dissolved H
Pd bulk
Subsurface and Dissolved C

Summary

core states
atom specific
quantitative
complex final state effects
chemical shift concept
theoretically difficult accessible
can be applied in the mbar range
surface sensitive
depth profiling

Literature

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