PIER
Graduate
Week 2017

Interdisciplinary lecture
and workshop week for PhD
students

9 – 12
OCT 2017

CFEL
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Ambient Pressure X- Ray Photoelectron Spectroscopy of catalytically active interphases

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Outline

Photoelectron Spectroscopy: General Principle

Instrumentation

Surface sensitivity

Background subtraction

Binding energy calibration

PES peaks, loss features

Peak fitting

Chemical state

Ambient pressure XPS

Example

XPS at the liquid-solid interface

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

Goal:

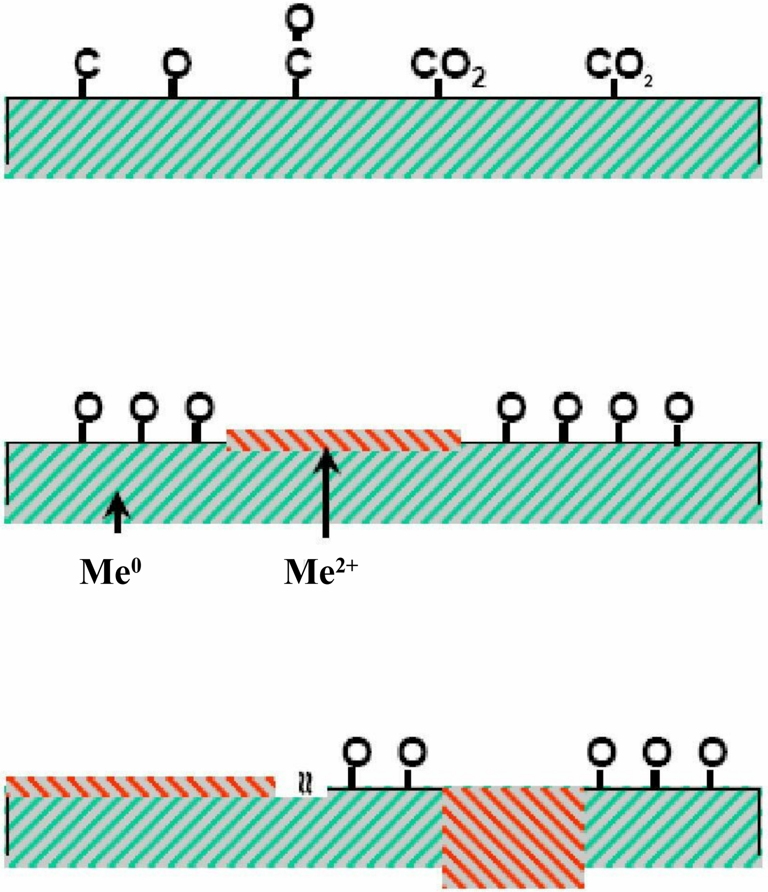
Elemental composition

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

Molecular state of adsorbates

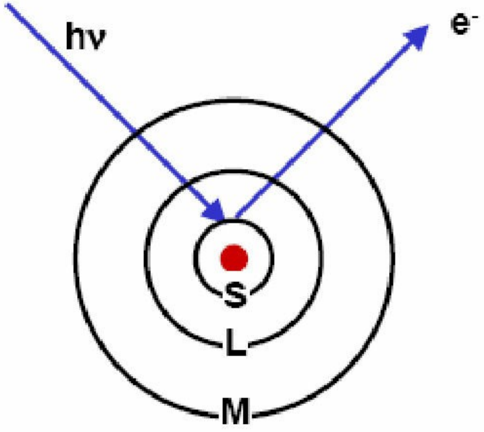
Oxidation state of surface species

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



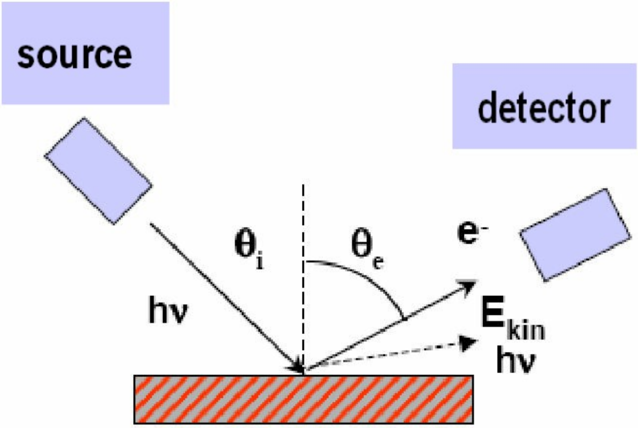
Photoelectron Spectroscopy: General Principle

principle



Excitation of Photoelectron

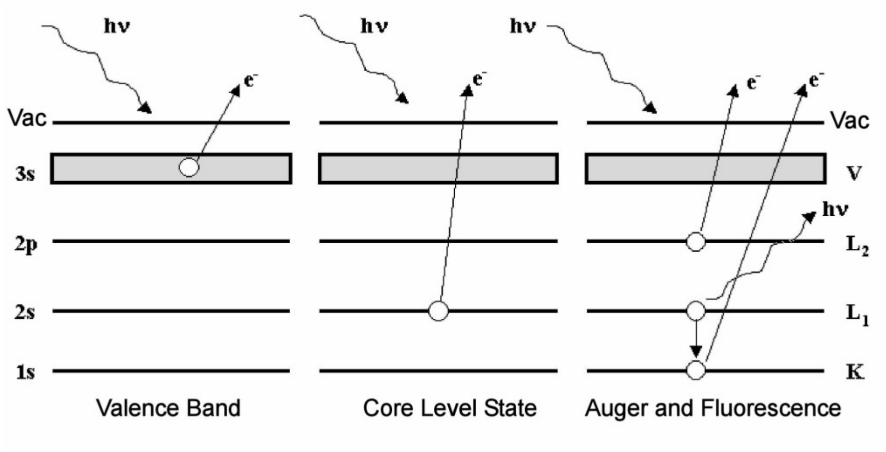
experiment



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

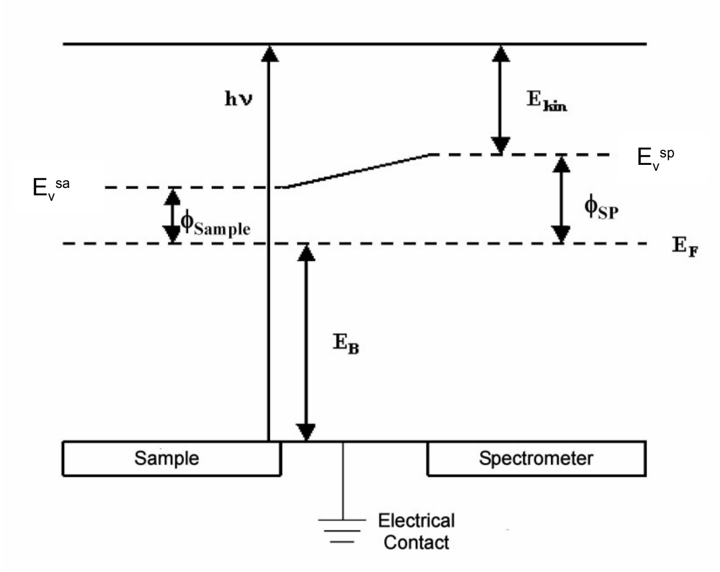
Detection
-Hemispherical analyzer

General Principle



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

- Detection of Auger electrons and X-Ray Fluorescence



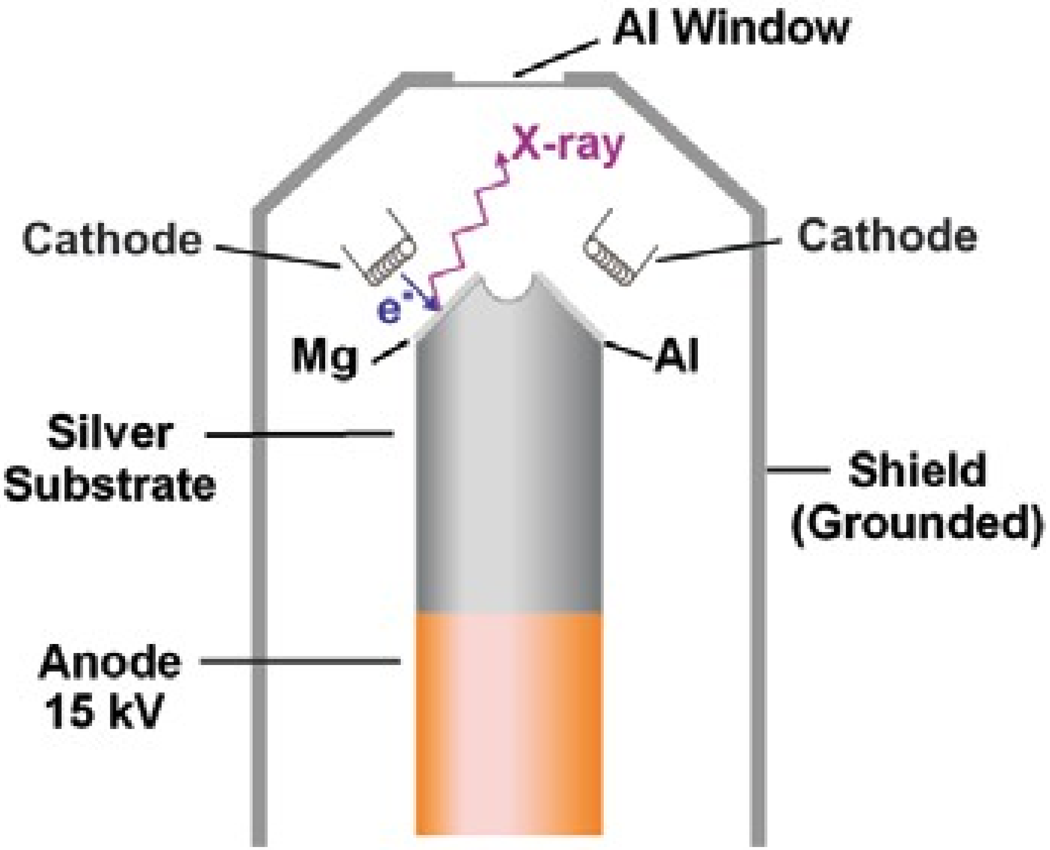
Binding Energy out of:

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

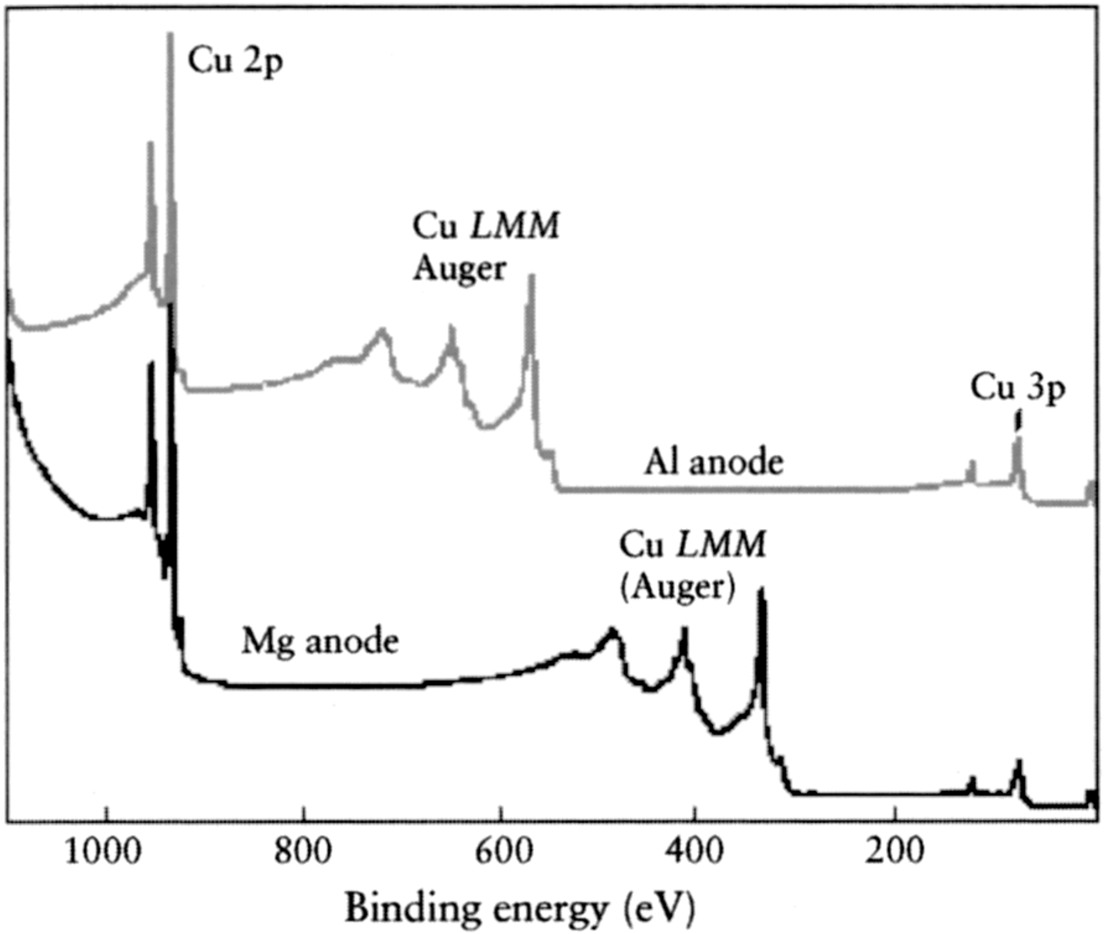
$$h\nu = E_{kin} + E_v^{sa} + \Phi_{sp} - \Phi_{sa}$$

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

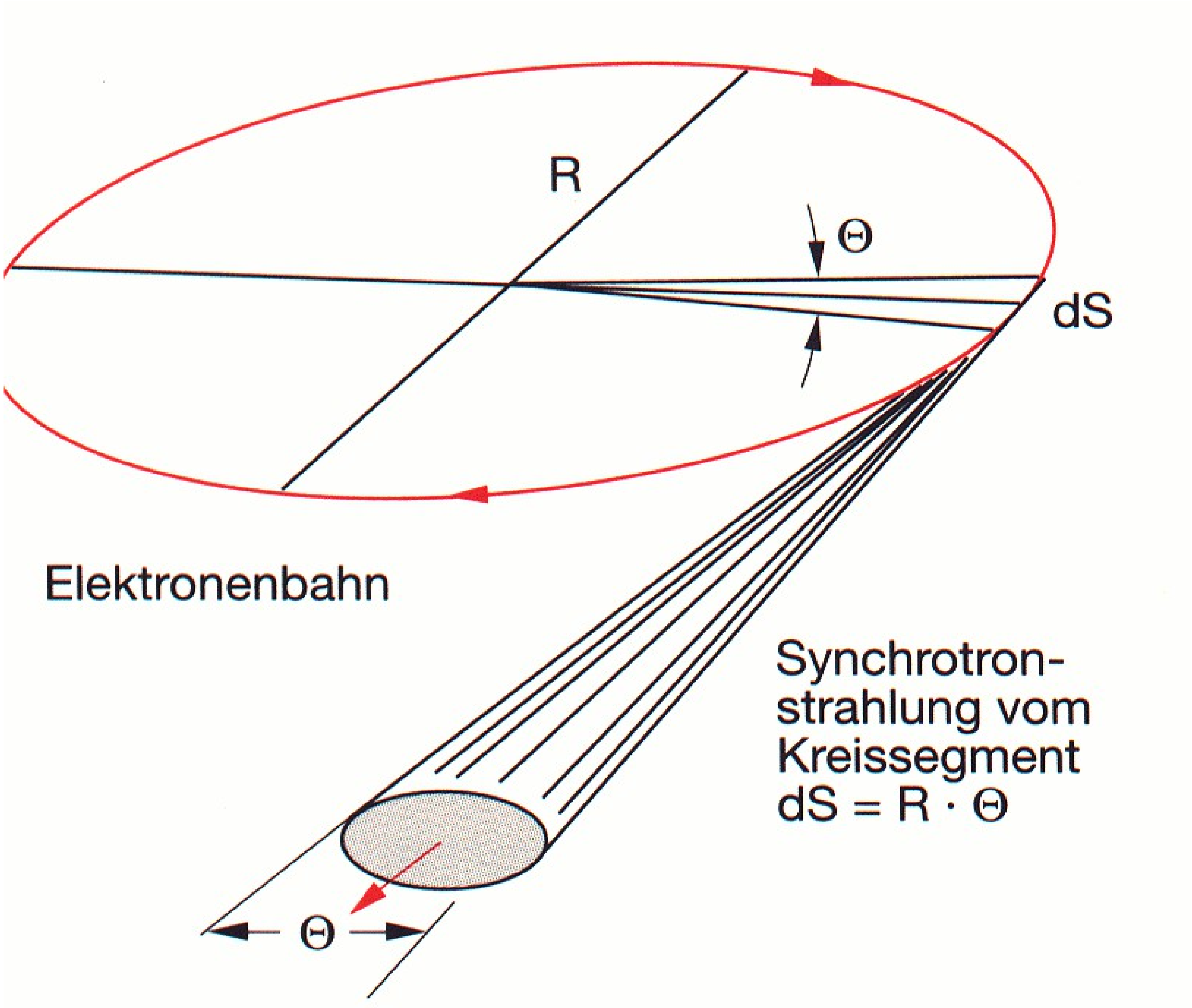
X-ray twin anode



XP spectra: two different anode materials

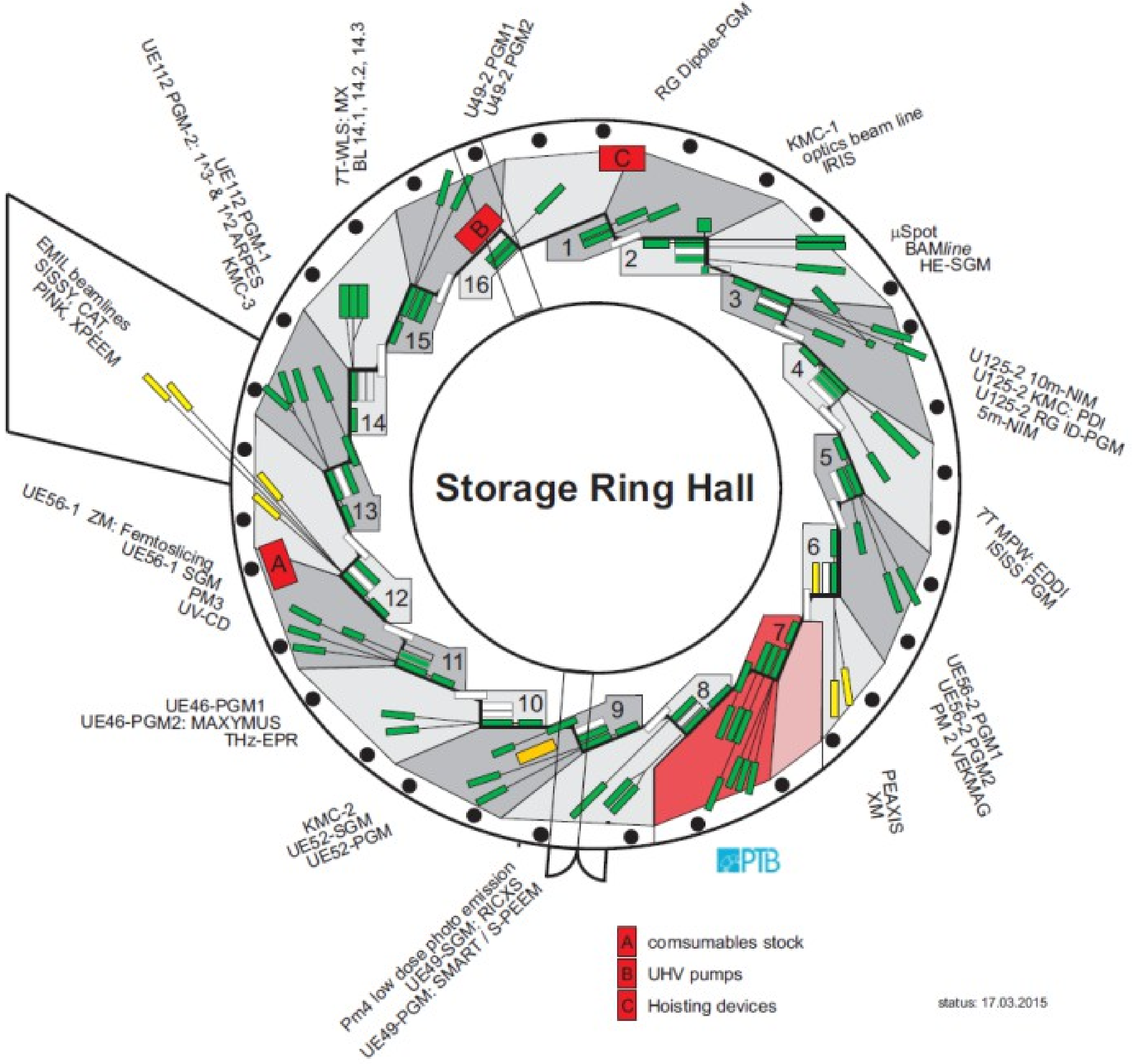


Synchrotron Radiation



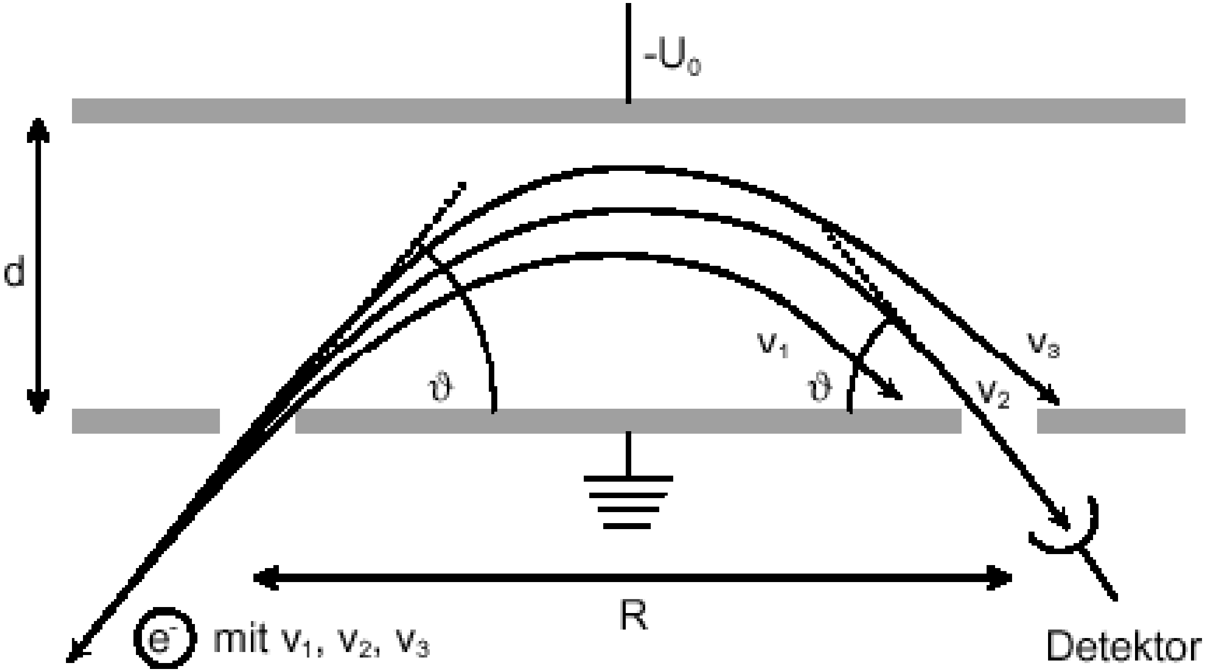
Synchrotronstrahlung vom Kreissegment $dS = R \cdot \Theta$

Synchrotron Radiation Facility- BESSY II

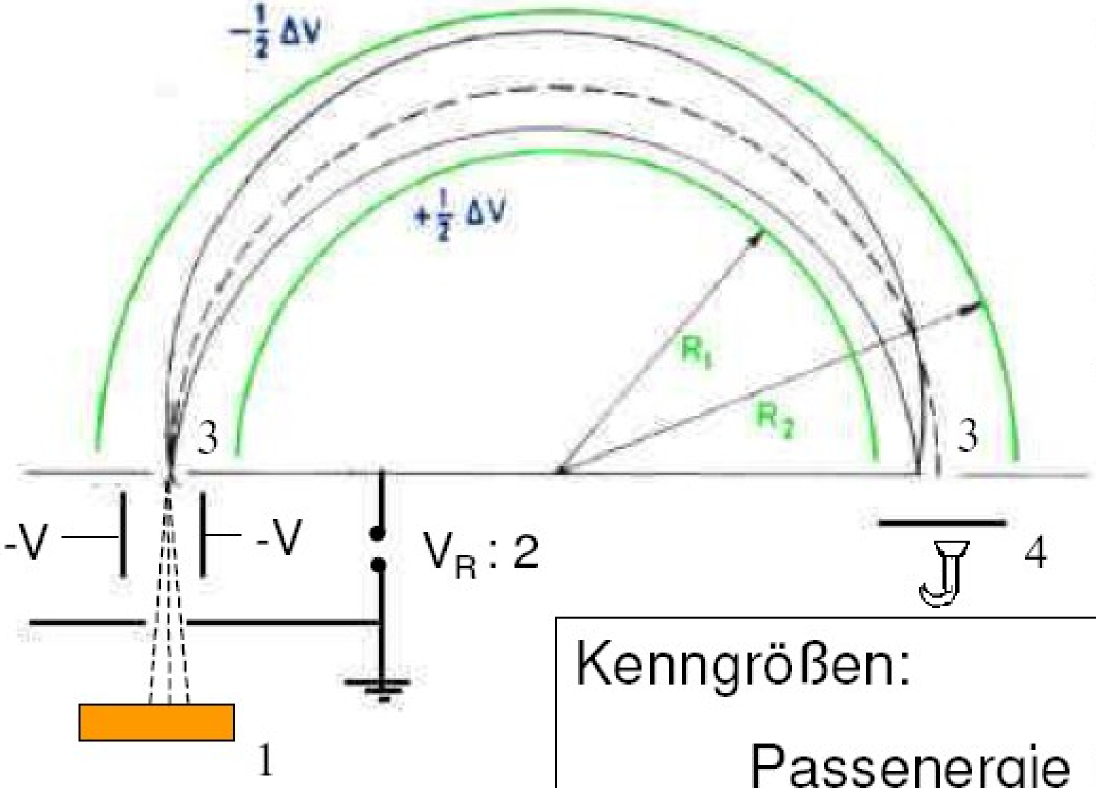


status: 17.03.2015

Parallel plate mirror analyser



Halbkugelanalysator



1: Probe

2: Verzögerungspotential

3: Lochblende

4: Detektor : Channeltron

Kenngrößen:

Passenergie : 5 eV

Winkelakzeptanz : 1 °

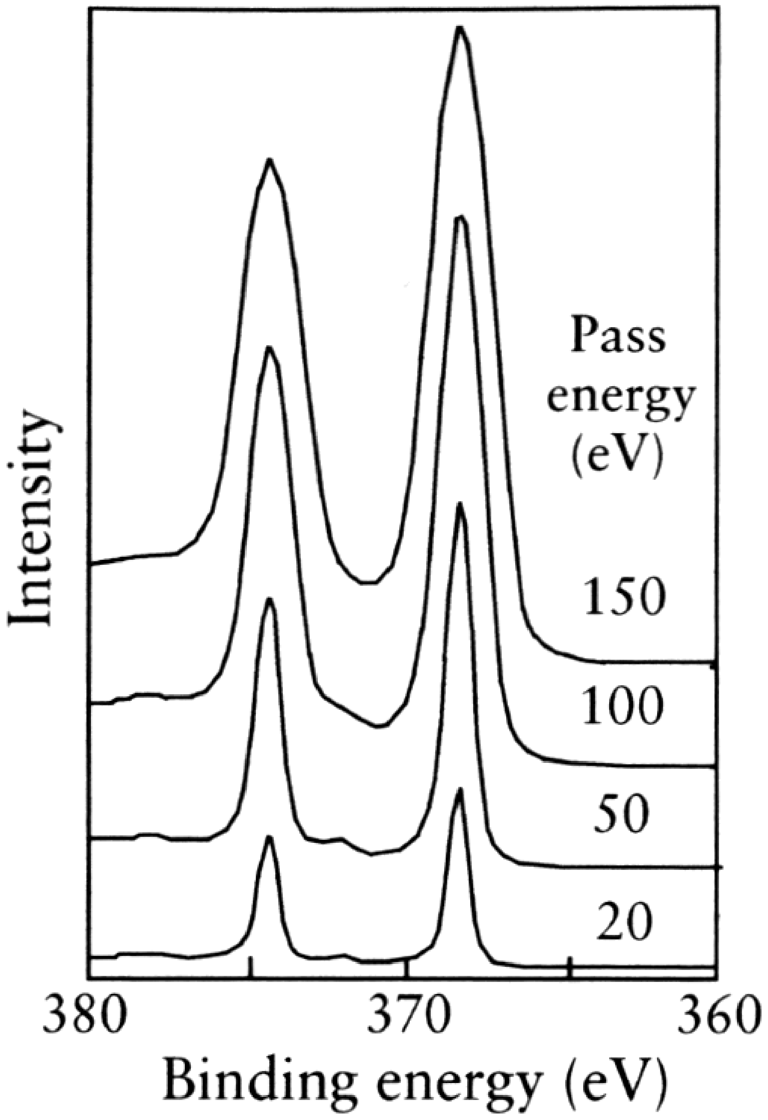
max. Rate : 30.000 /s

Halbkugelanalysator

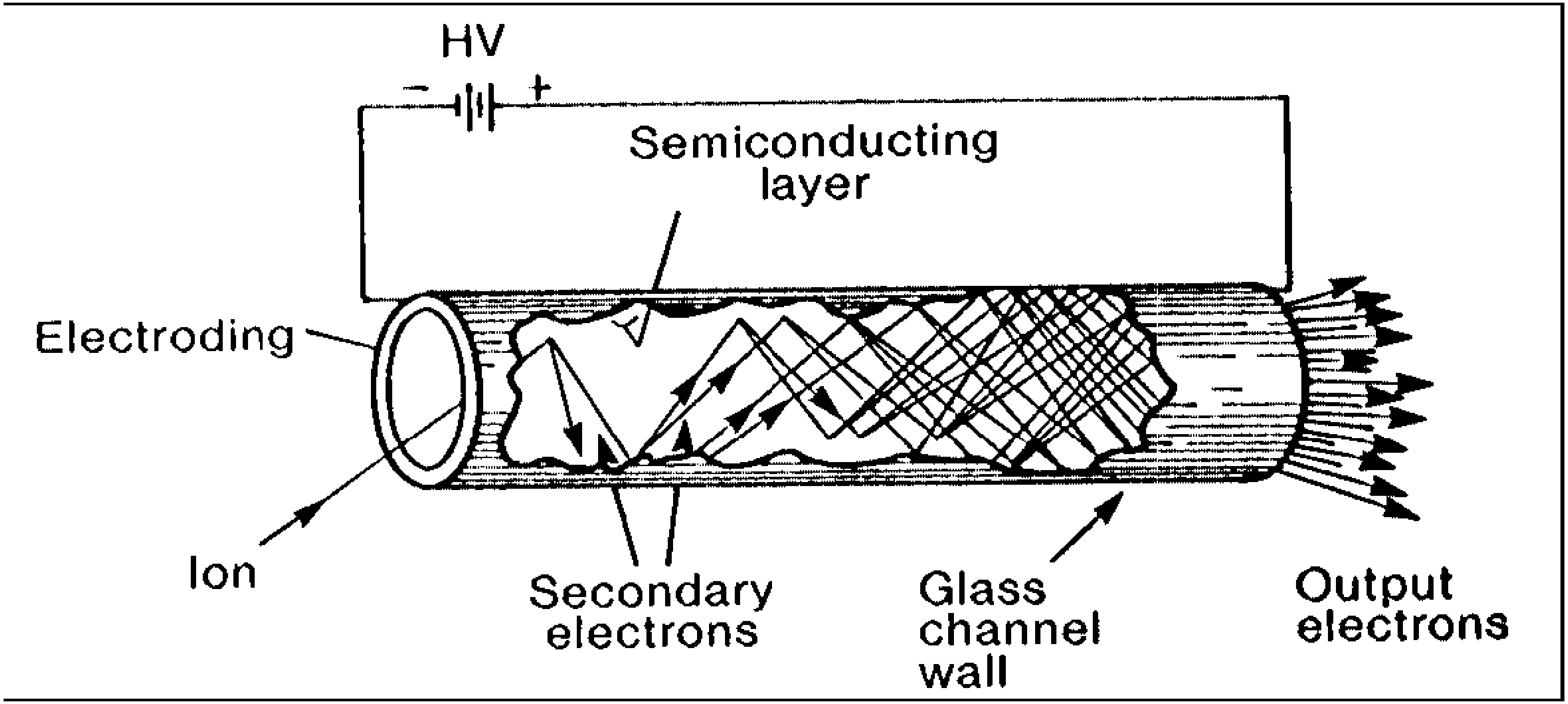
Elektronen werden zunächst auf einen bestimmten Energiebetrag **abgebremst**

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

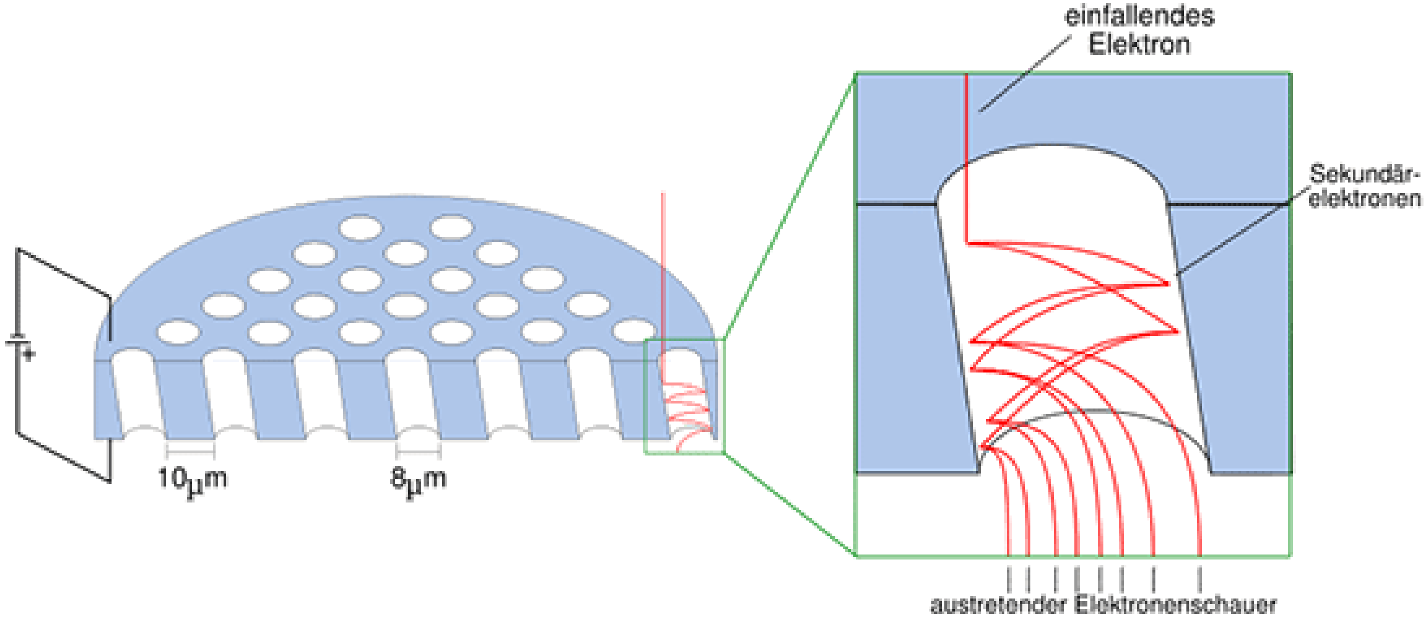
Je kleiner die "Passenergie" desto besser die Energieauflösung



Detector: Channeltron



Detector: Microchannel Plate

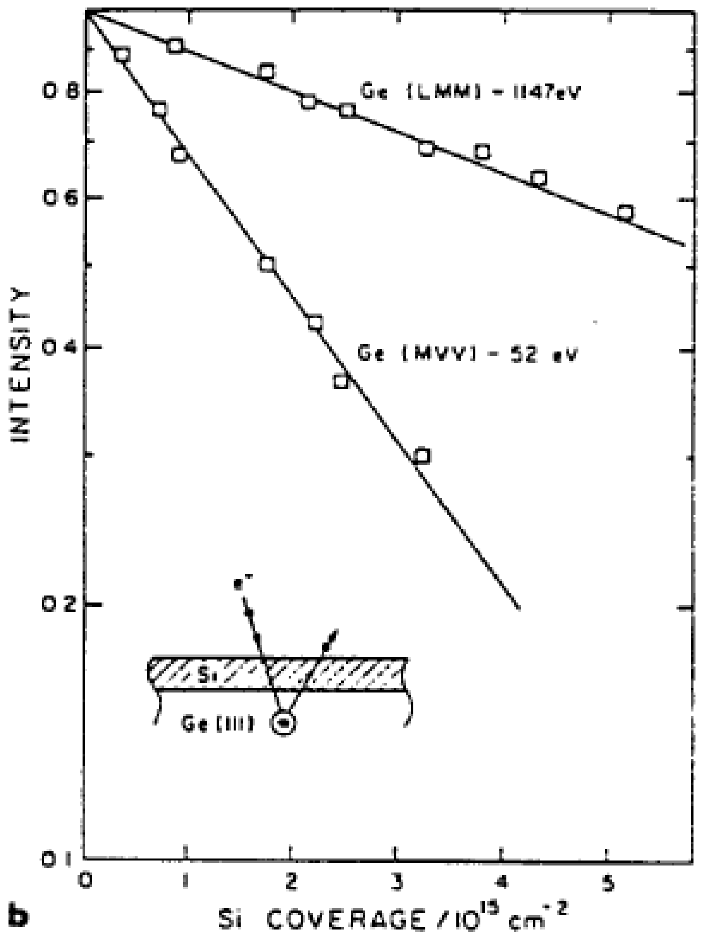


Where do the electrons come from?

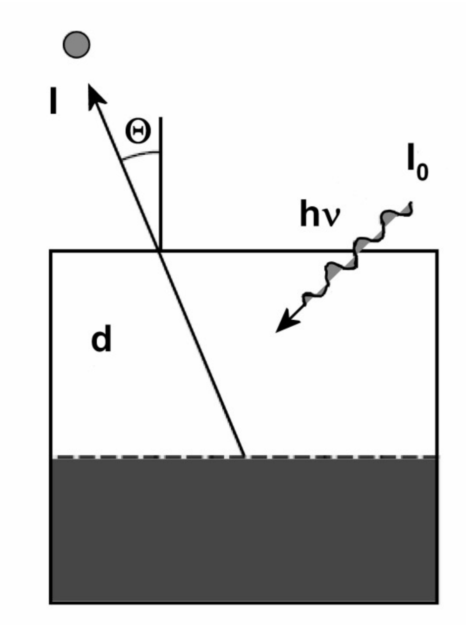
Distance electron can travel in solids depends on:

- Material
- Electron kinetic energy

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



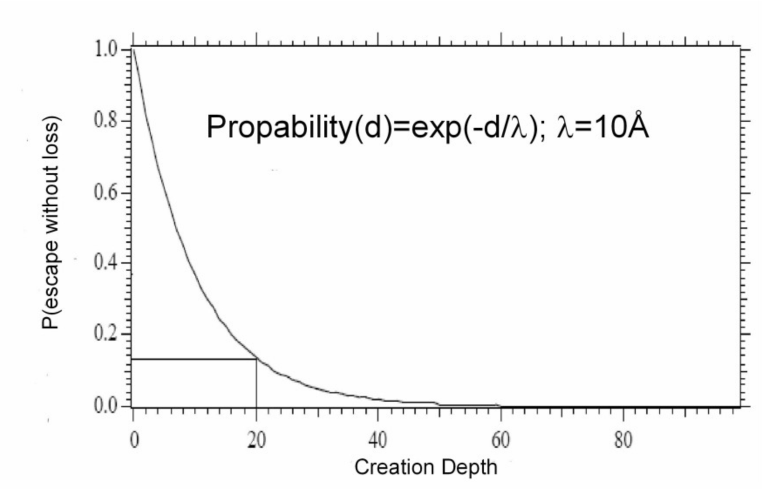
Sampling Depth



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:

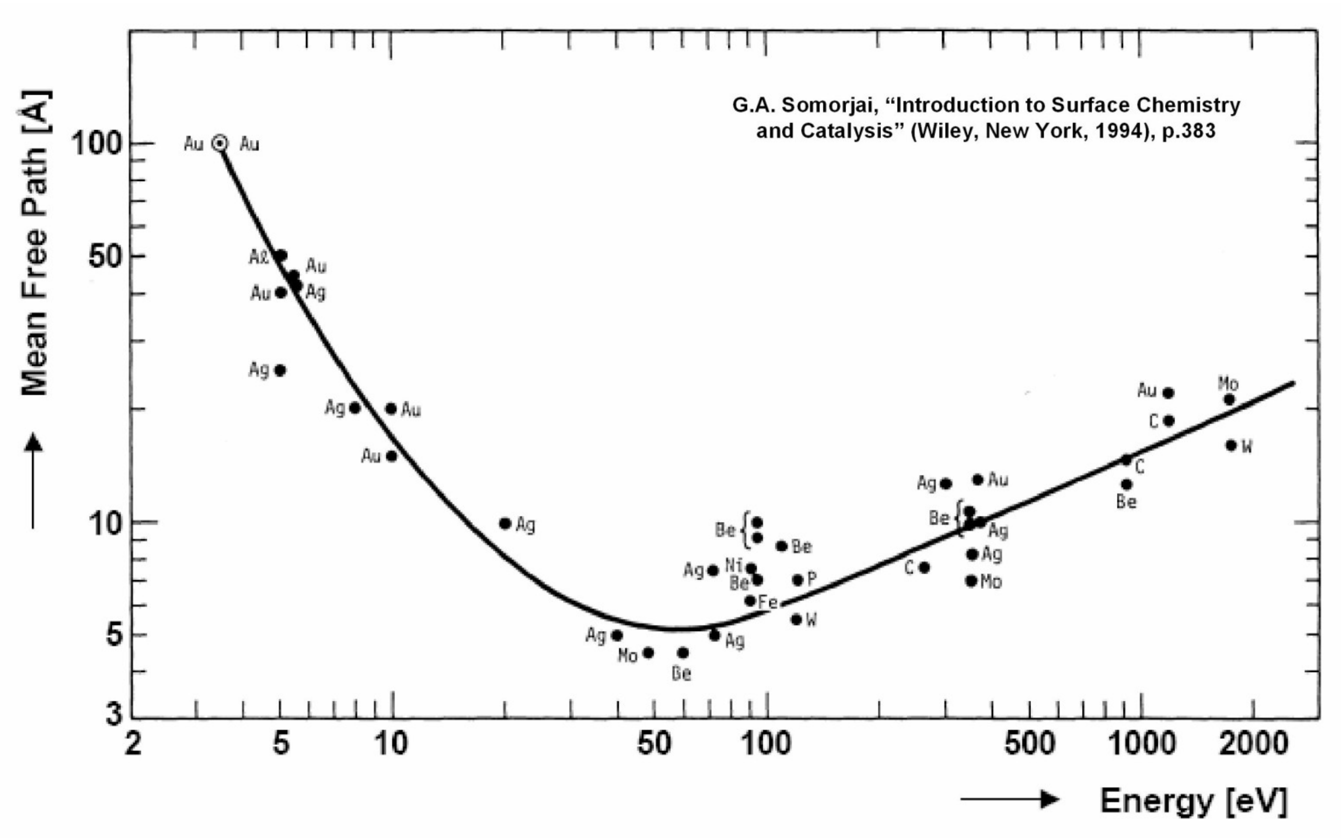
For normal takeoff angle, cosΘ=1:

- 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

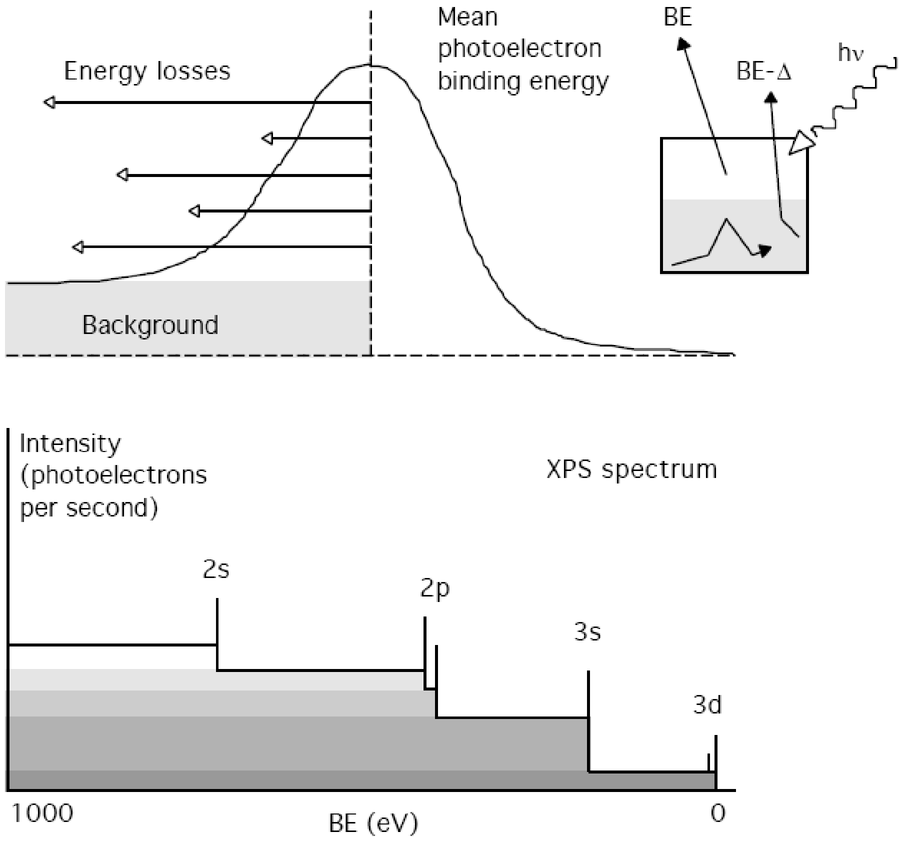
Mean Free Path of Electrons in Solids

- 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

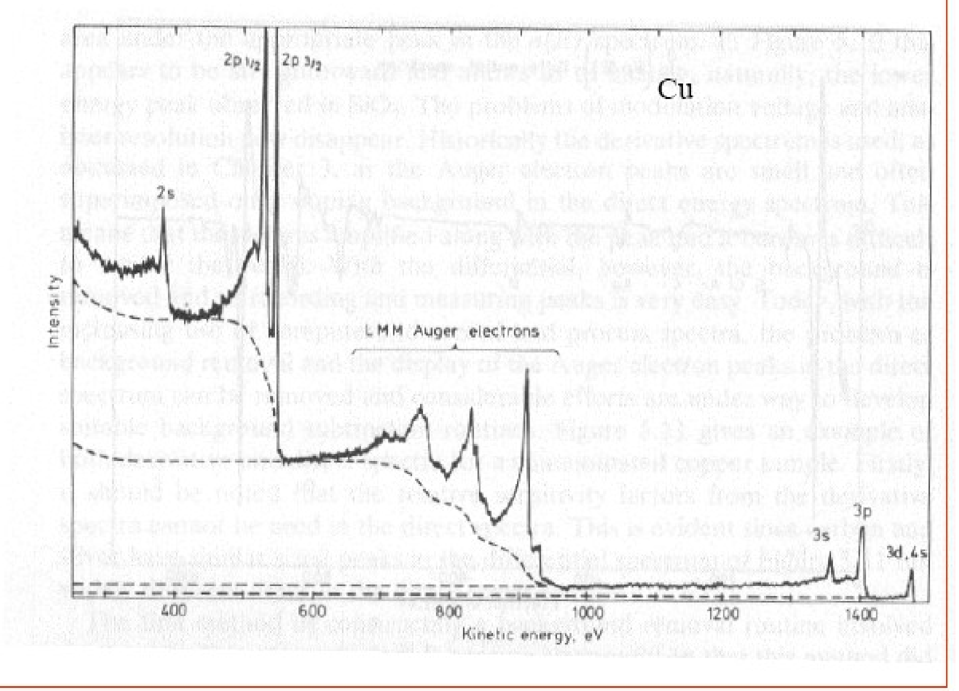
Origin of background



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

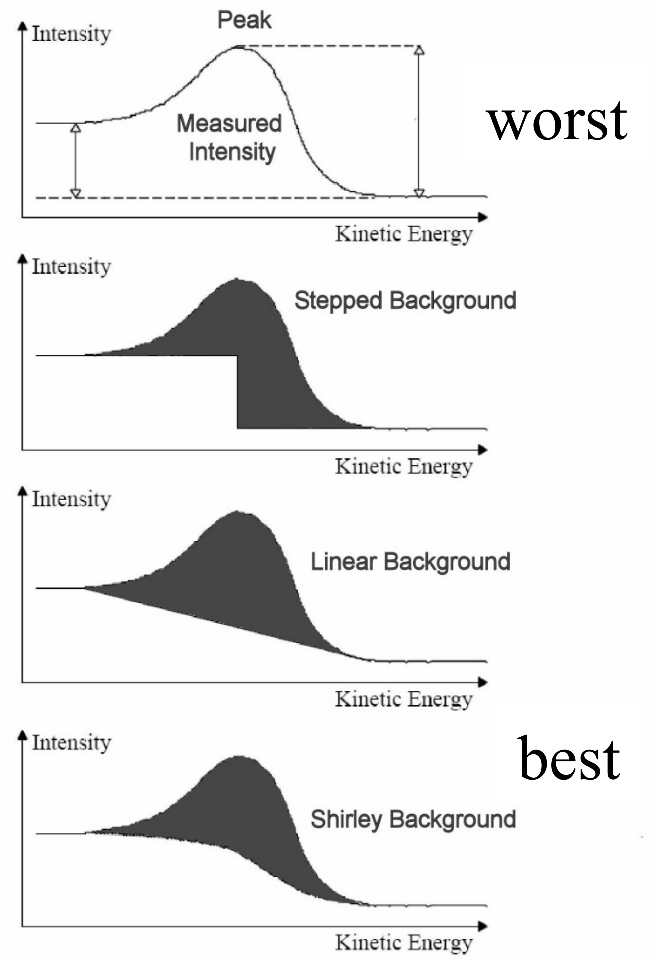
Background Correction

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:

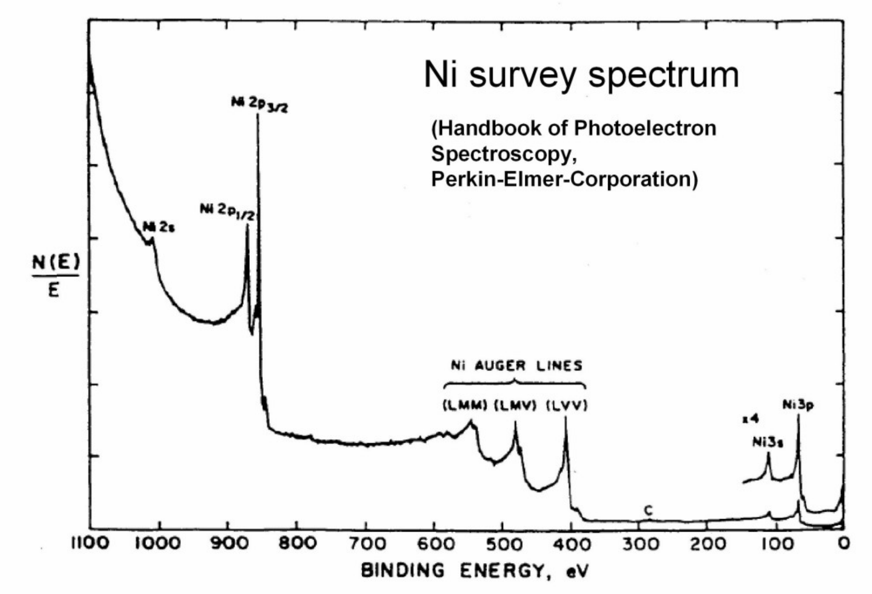
Method of Shirley et al.:

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

Always use same background substraction method for all peaks!

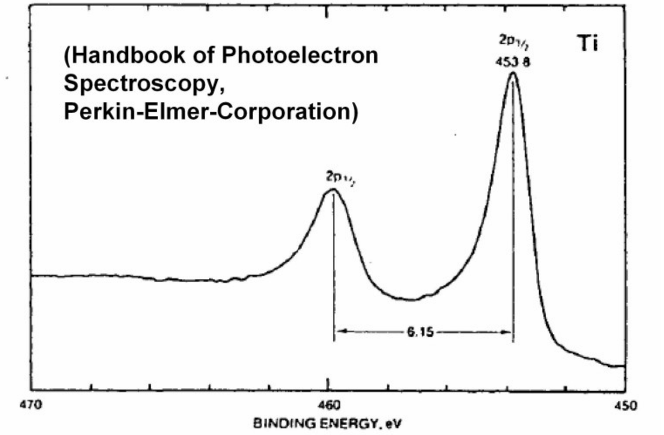
D.A. Shirley, Phys. Rev. B, 5, S. 4709, 1972.

Spectral features: PE Peaks



Ni survey spectrum

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



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

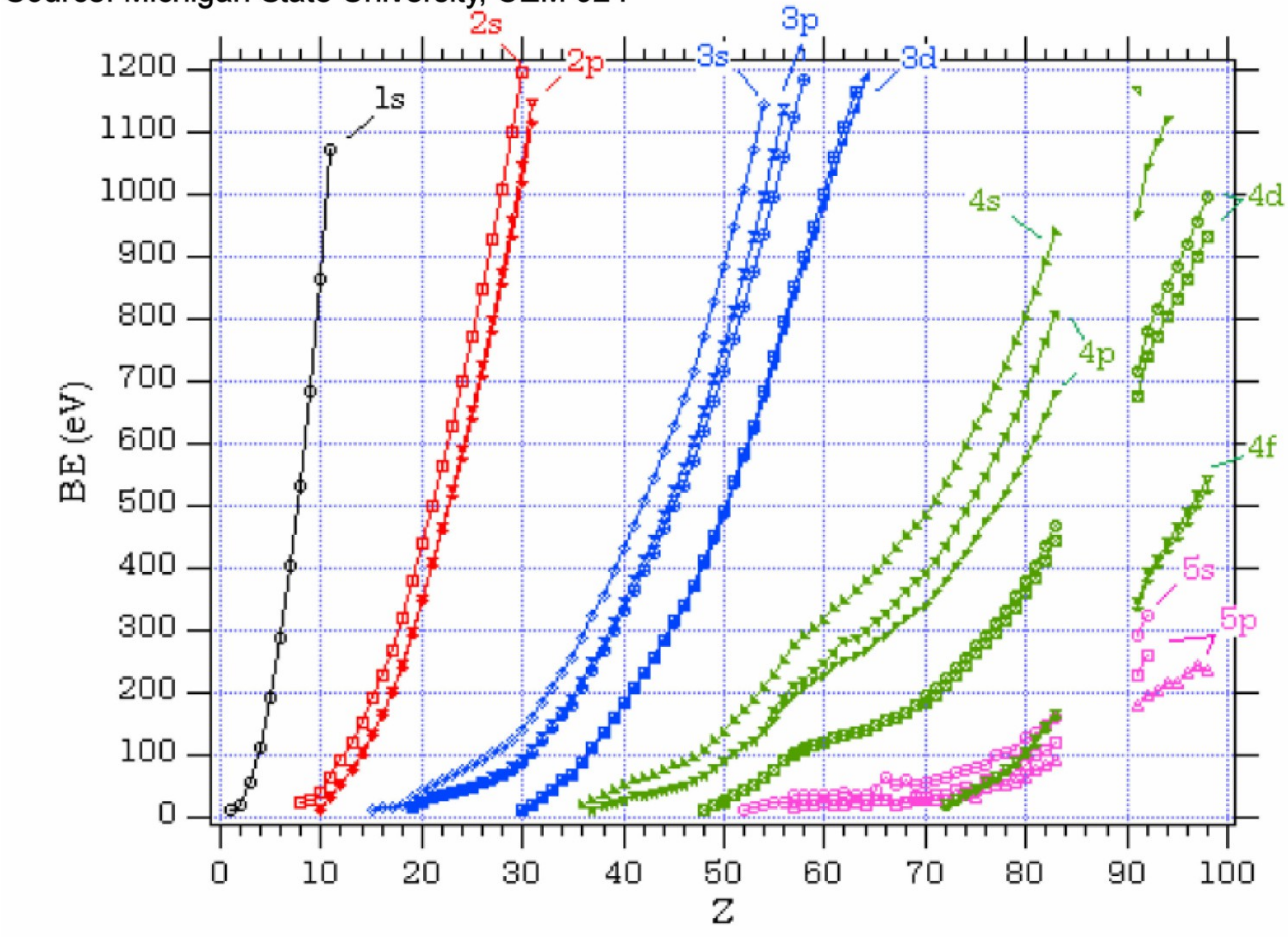
Orbital peaks used to identify different elements in sample

Observation:

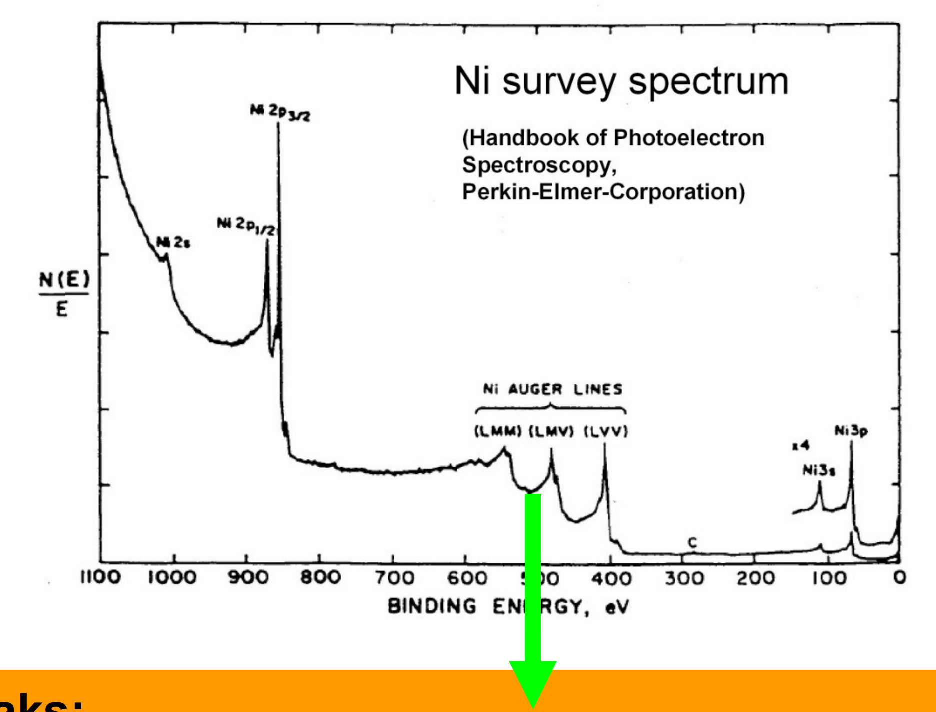
- s orbitals are not spin-orbit splitted → singlet in XPS
- p, d, f.. Orbitals are spin-orbit splitted → doublets in XPS

Spectral features: PE Peaks

Source: Michigan State University, CEM 924



Spectral features: Auger Peaks



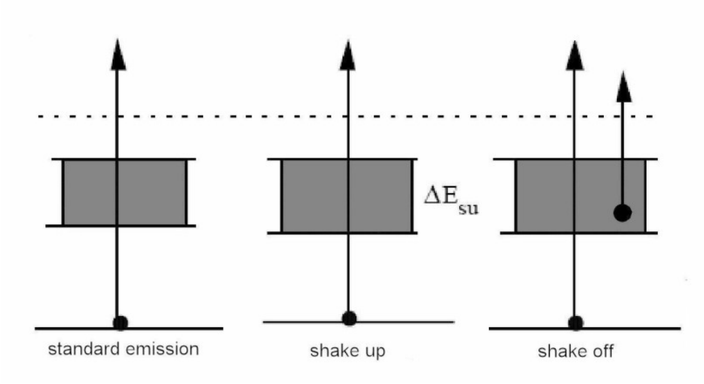
Auger peaks:

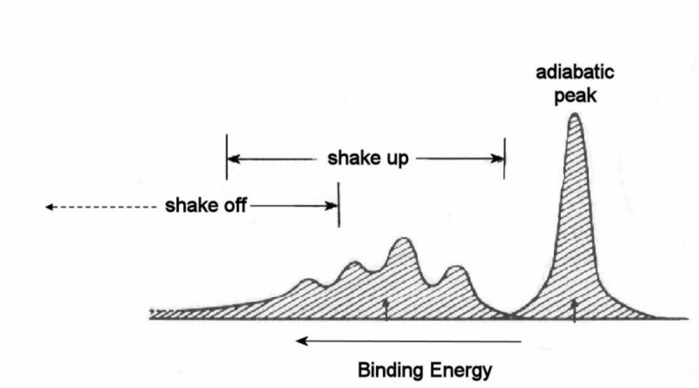
Result from excess energy of atom during relaxation (after core hole creation)

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

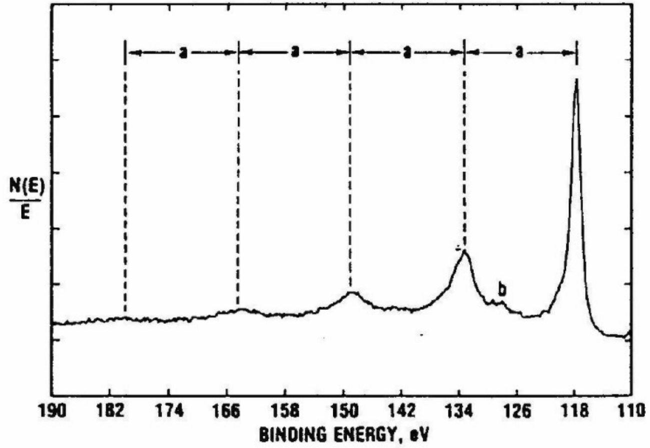
KE energy independent of incident hν

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 (**Secondary peaks**):

- 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

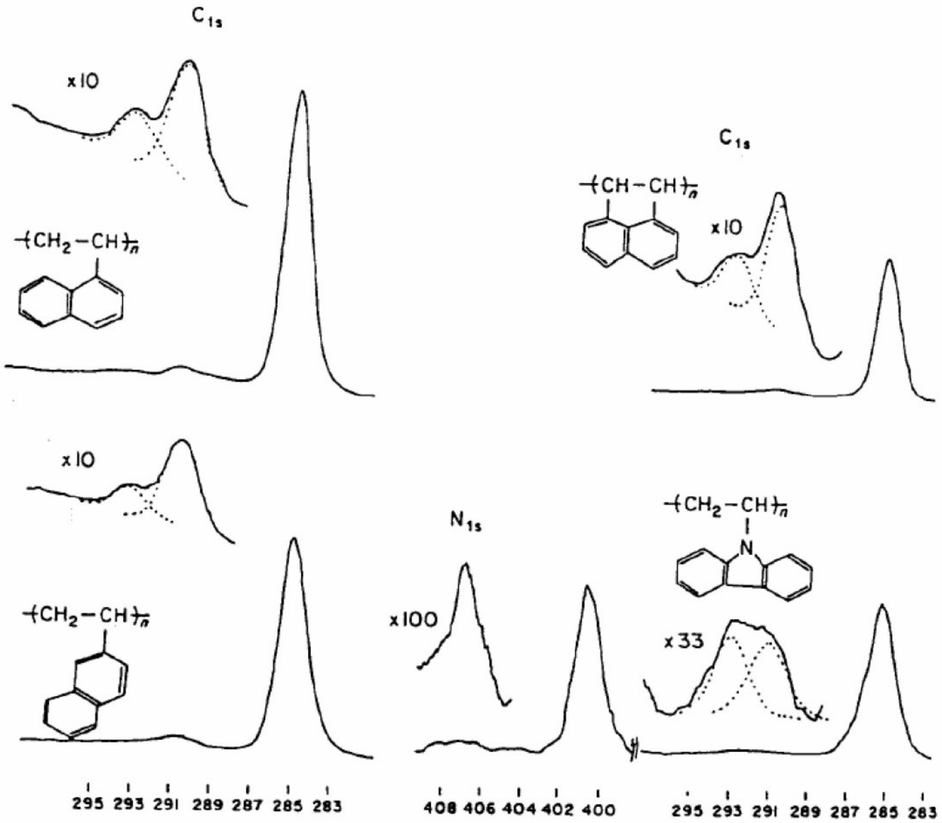
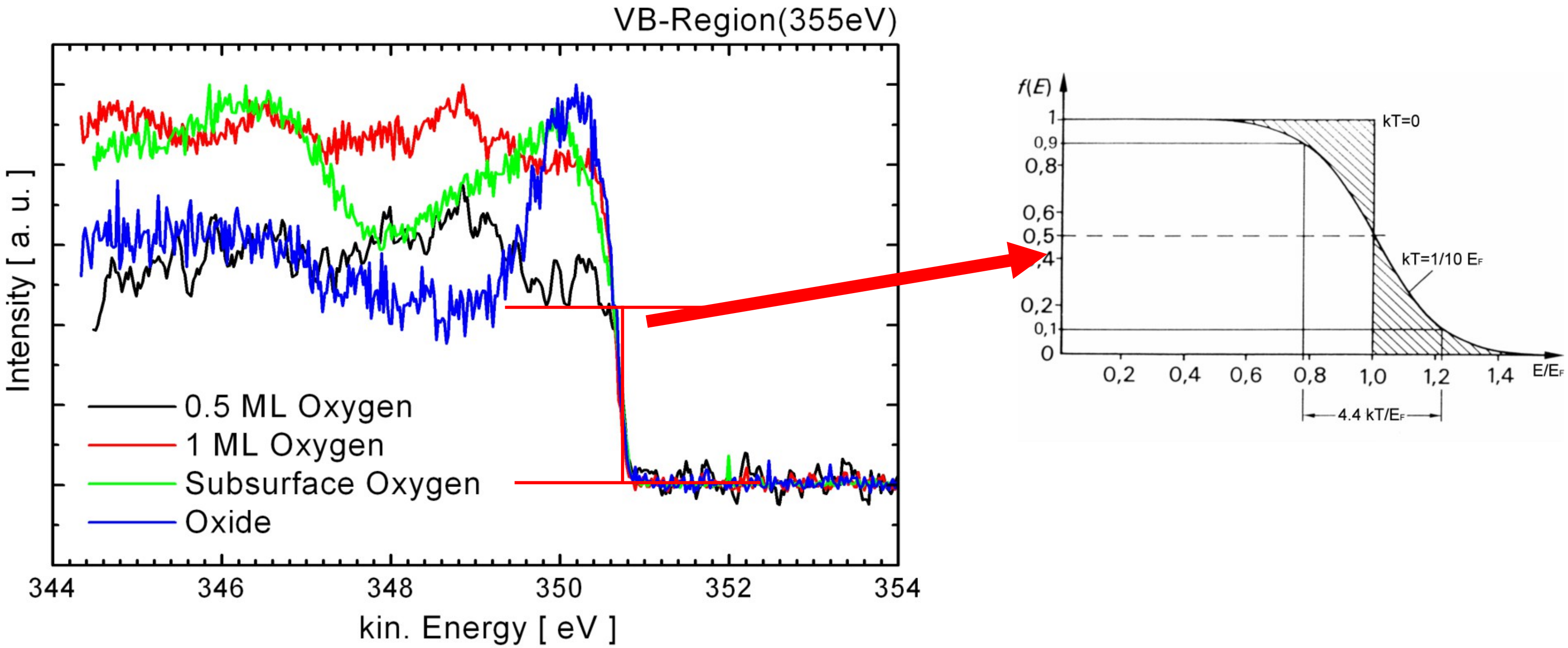


Figure 9.5 Core level spectra of poly-1- and 2-vinylnaphthalene, polyacenaphthalene and polyvinylcarbazole.
(Clark et al., Copyright Elsevier Science Publishers)

Loss peaks can be used to identify chemical composition

Problem:
References needed (theoretical or experimental)

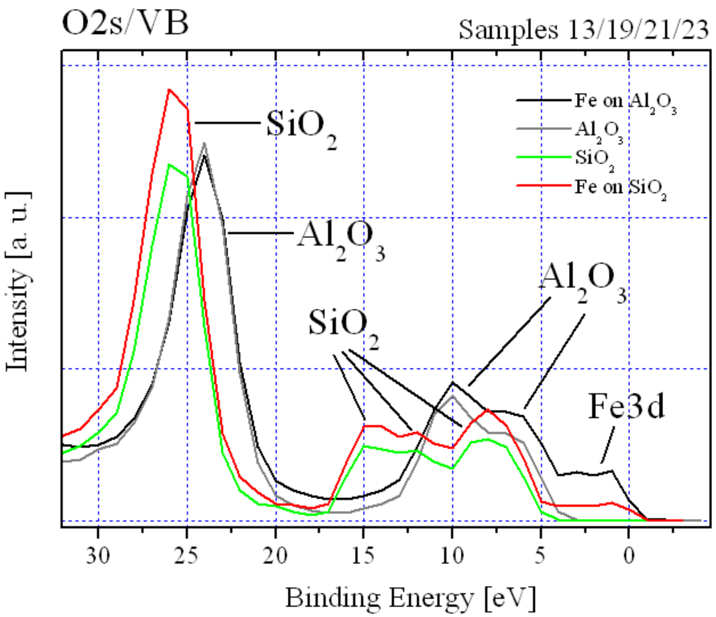
Analyzing the data: Calibration of Binding Energies

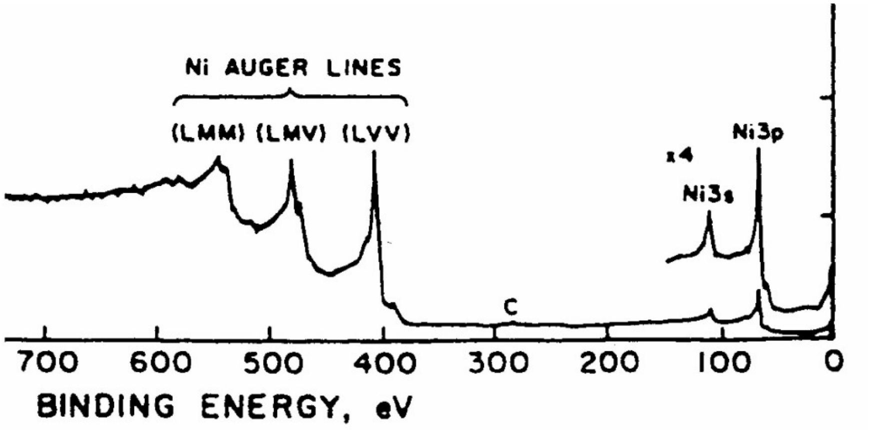


Identification of FE:

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

Analyzing the data: Calibration of Binding Energies





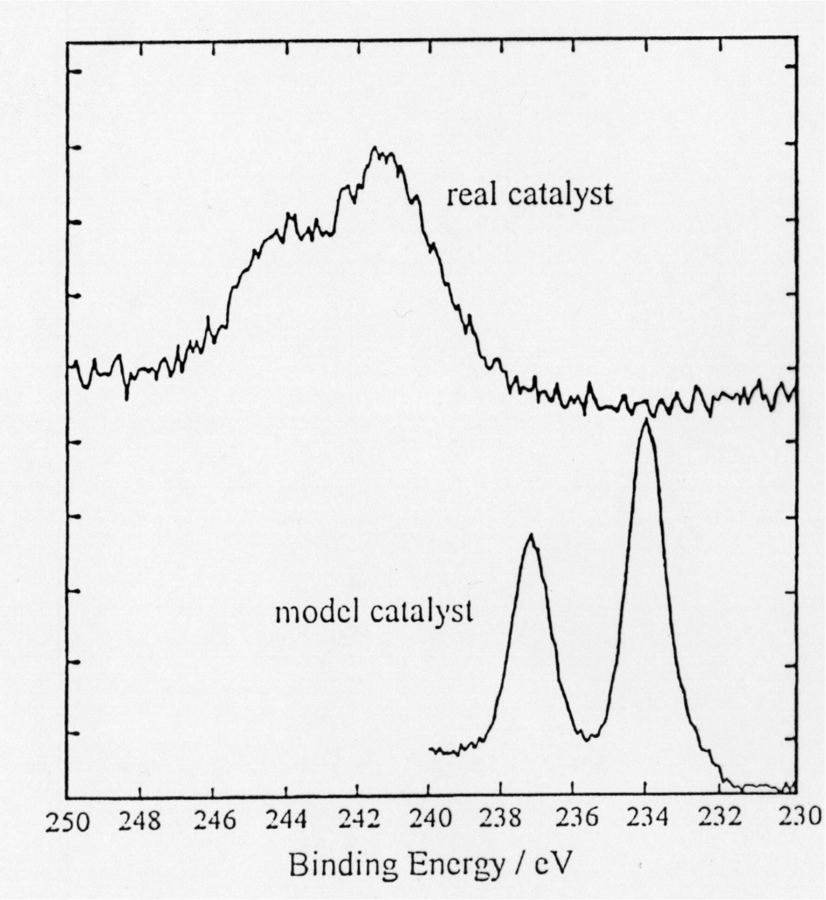
(Handbook of Photoelectron Spectroscopy, Perkin-Elmer-Corporation)

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 <u>known</u> BE (be sure about that!!!)
→ Works for any PE or Auger peak, e.g. peaks originating from substrate

Line profile modification by charging

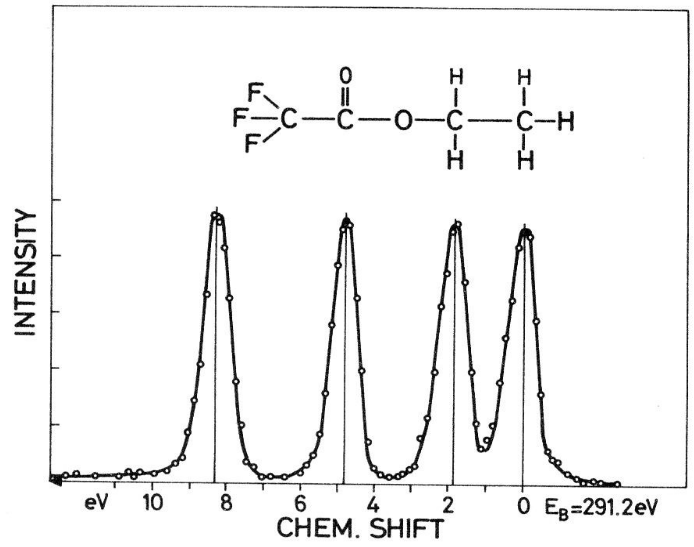


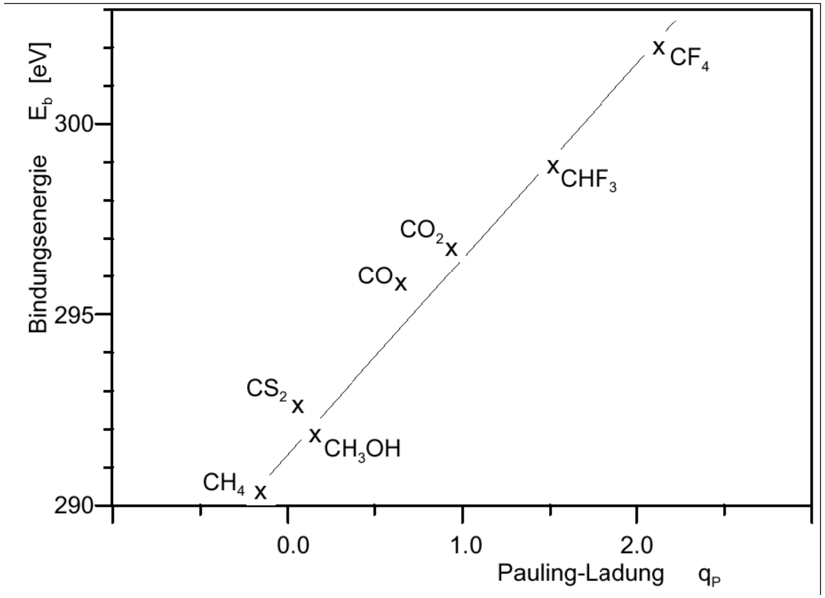
Mo oxide on silica

real catalyst is powder sample after impregnation and calcination.

Chemical Shift

BE of core electrons depends on the electron density at the atom, 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

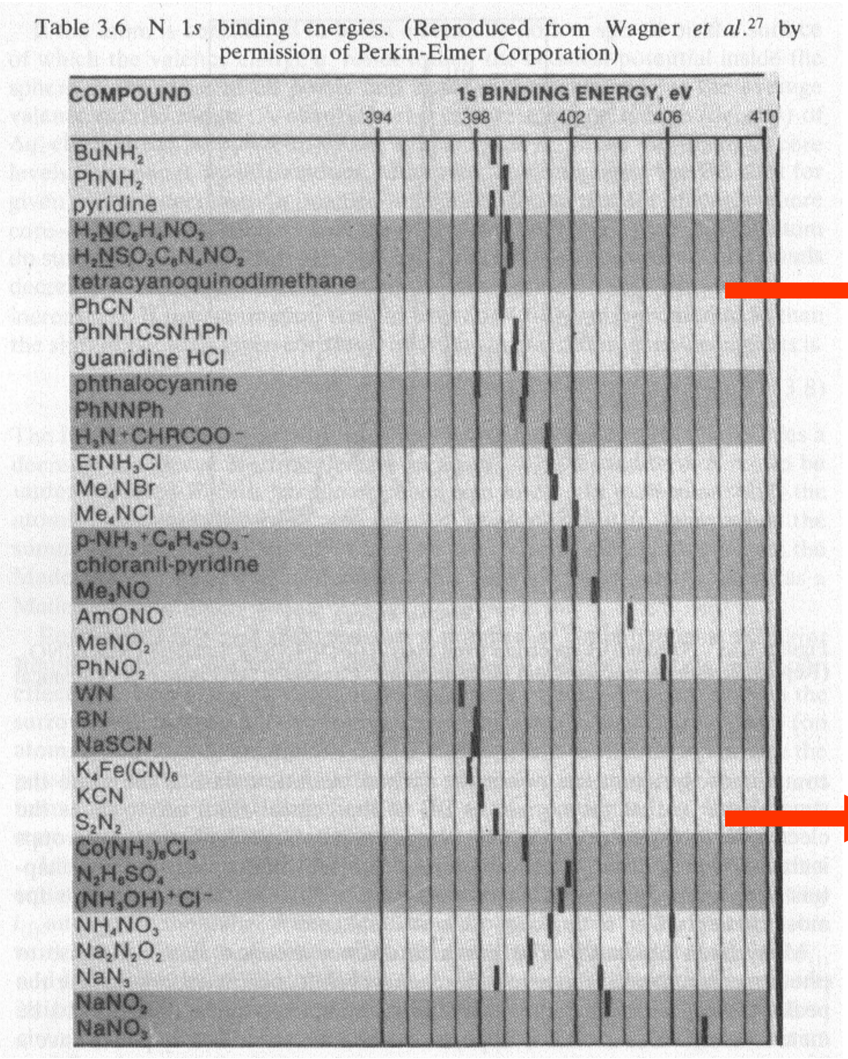


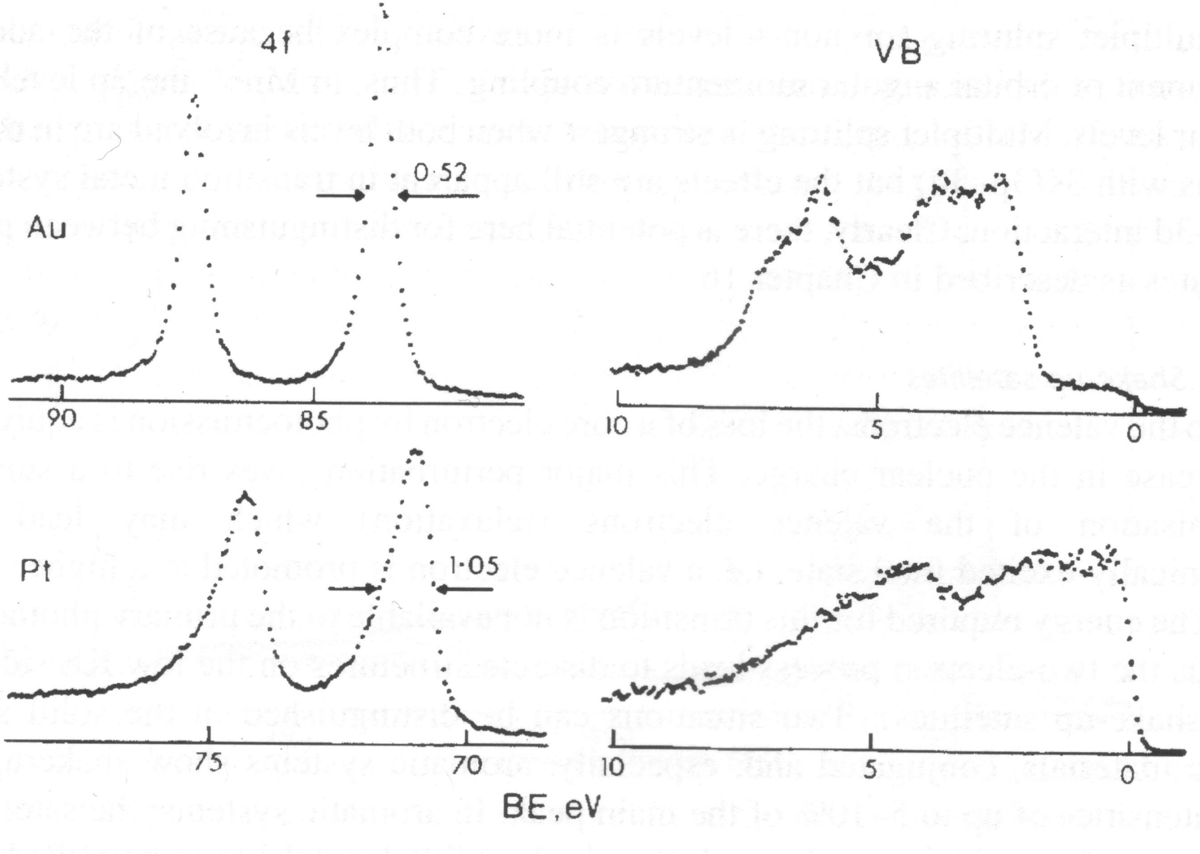
Table 3.6 N 1*s* binding energies. (Reproduced from Wagner *et al.*[27] by permission of Perkin-Elmer Corporation)

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.

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



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)

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

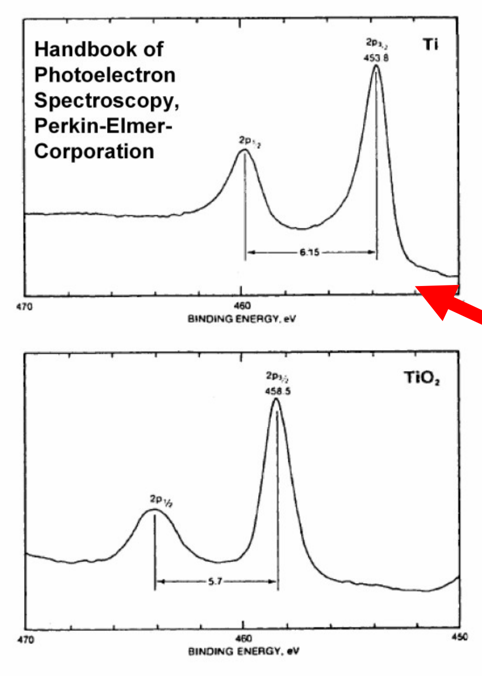
β: peak parameter
M: mixing ratio
α: asymmetry parameter
h: peak height
α → 0: Lorentzian profile

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

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

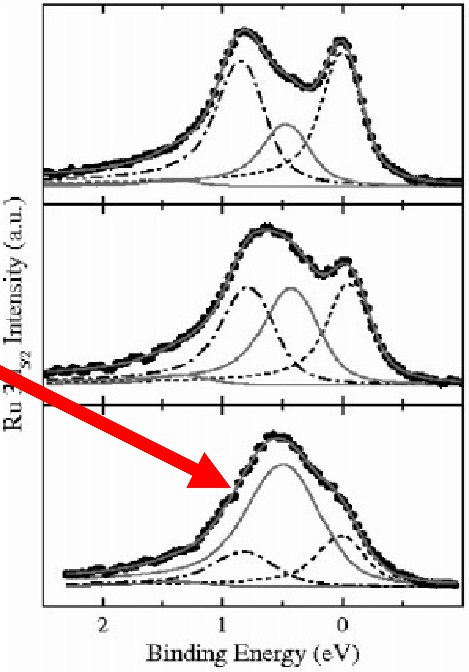
→ Voigt function

Analyzing the data: Peak Fitting


Handbook of Photoelectron Spectroscopy, Perkin-Elmer-Corporation

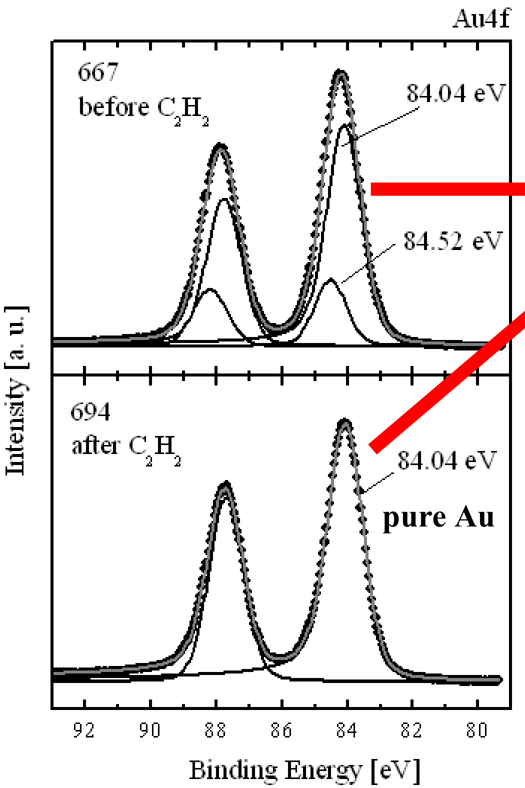
Several influences on peak shape:

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



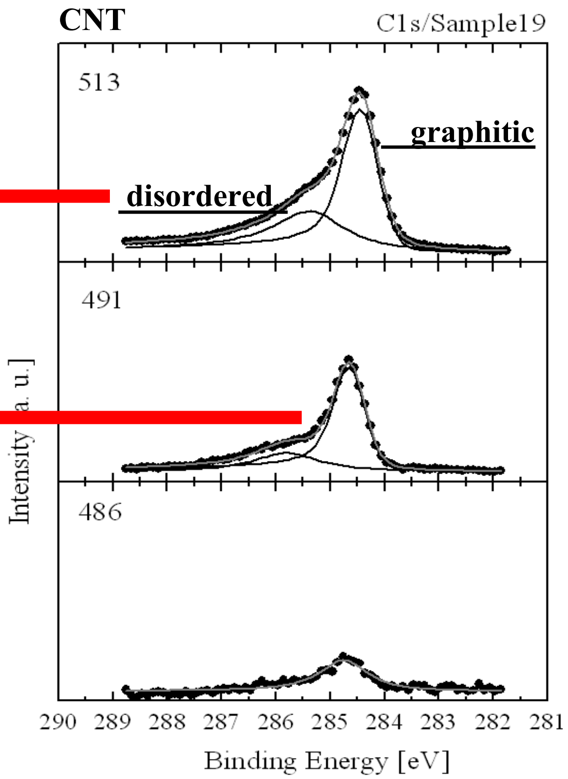
These effects have to be considered when fitting by reasonable chemical/physical model of the sample!!!

Analyzing the data: Peak Fitting



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:

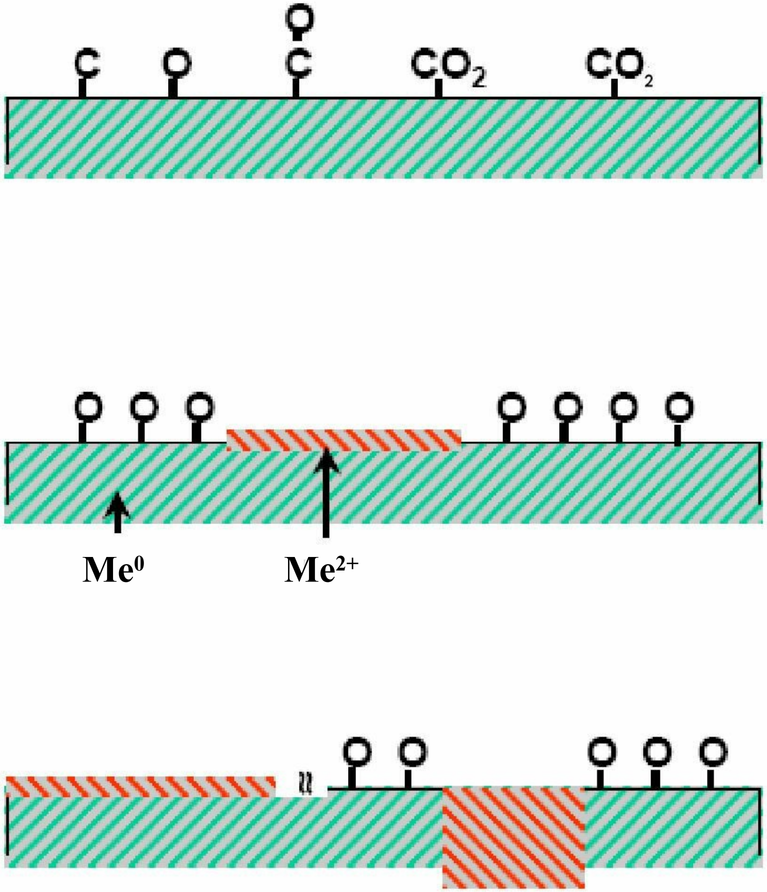
Elemental composition

- 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

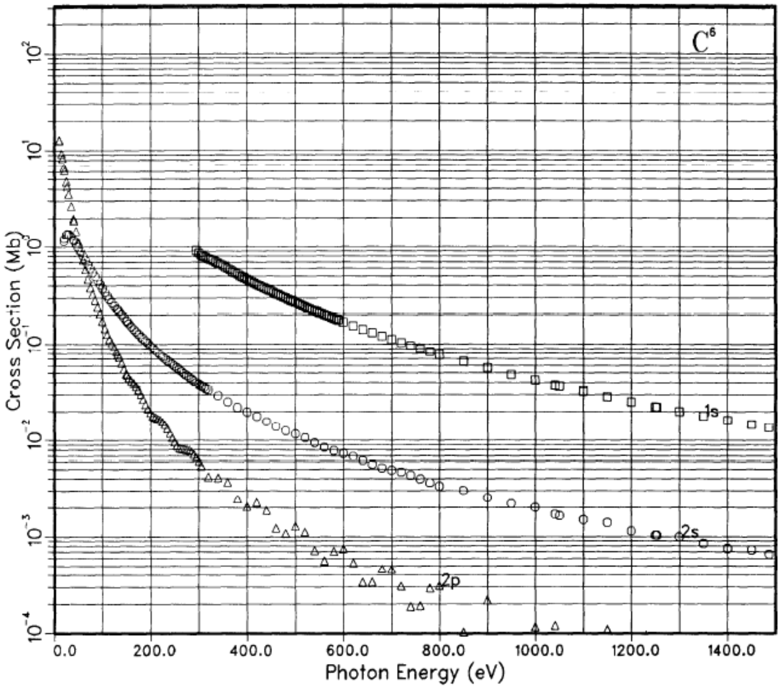
$$\lambda_{tot} = E(X) \times 1/a[\ln(E(X)-b)^*$$

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

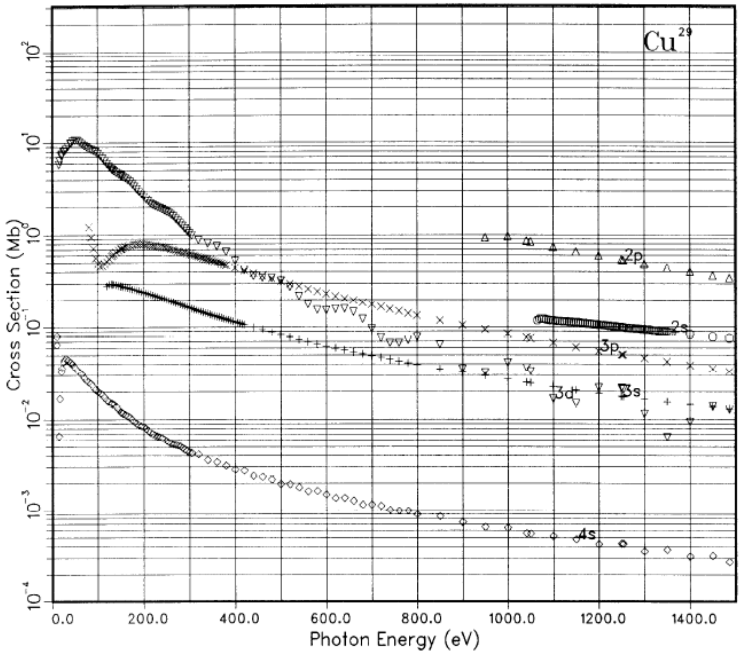
Cross section changes with energy of incident beam!!!

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

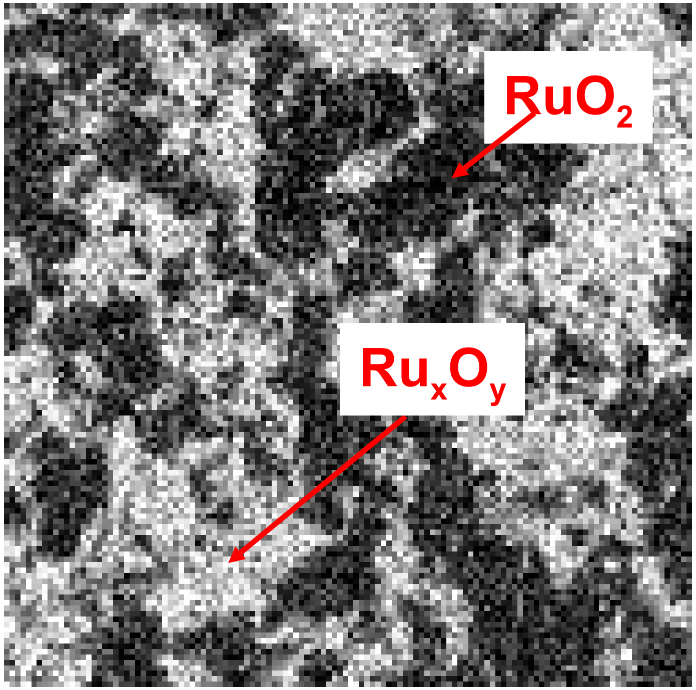
Calculated changes of Cross section beam energy

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

Quantitative Analysis

In most cases the sample surface is quite heterogeneous

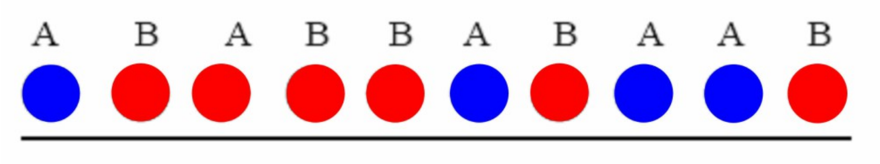
→ Need of *models* to extract an accurate approximation of composition out of spectral intensities



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

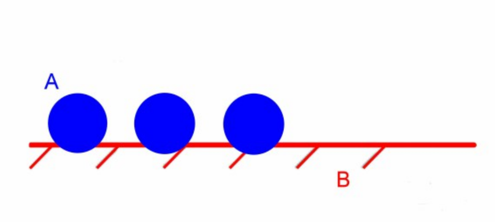
follows

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

$I_{A,B}{}^0$: 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

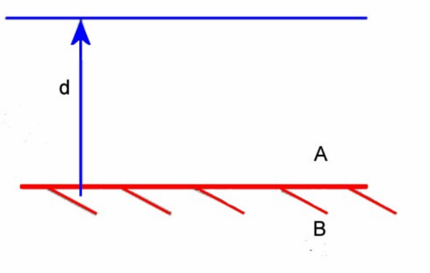
Which gives

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

$I_{A,B}{}^0$: 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

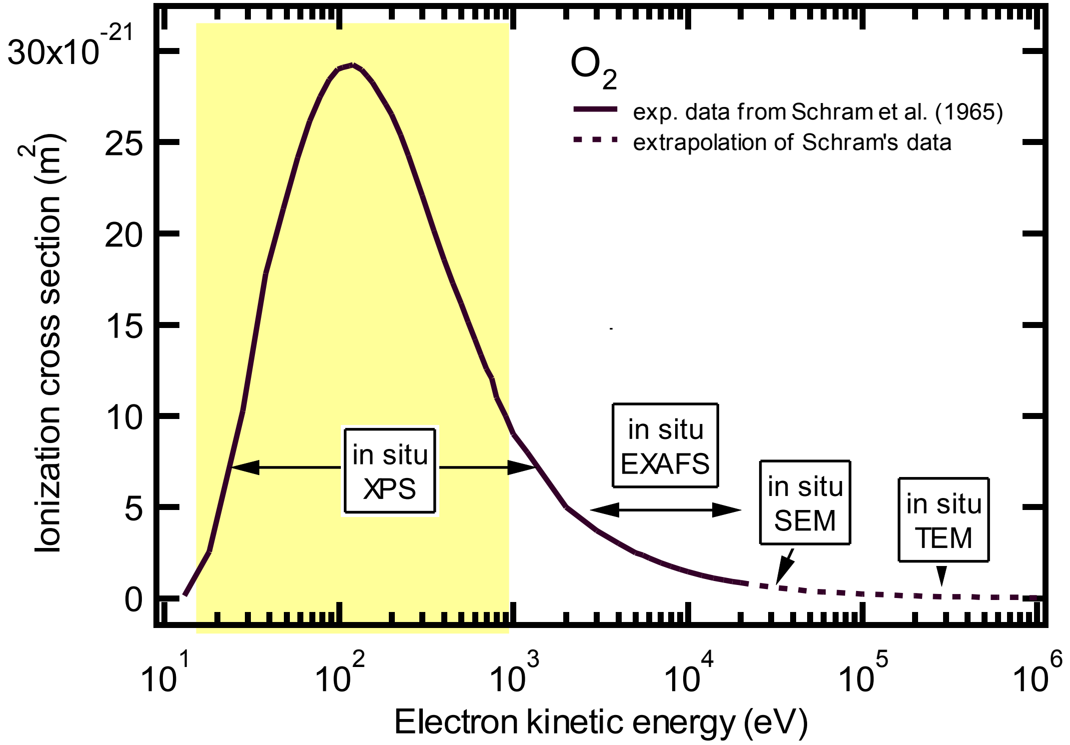
$$d_A \approx \frac{\lambda_A}{\cos\Theta} \cdot \ln\left[1 + \frac{I_A}{I_B} \cdot \frac{I_B{}^0}{I_A{}^0}\right]$$

General problem here:
proper background substraction

In situ XPS: obstacles

Fundamental limit:

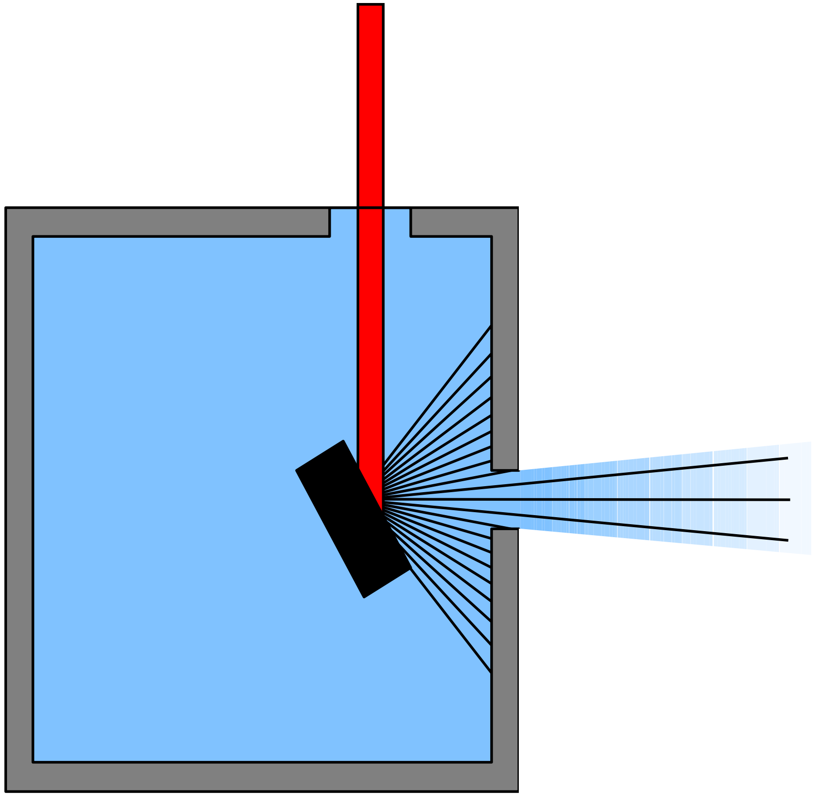
elastic and inelastic scattering of electrons in the gas phase



Technical issues: - Differential pumping to keep analyzer in high vacuum

- Sample preparation and control in a flow reactor

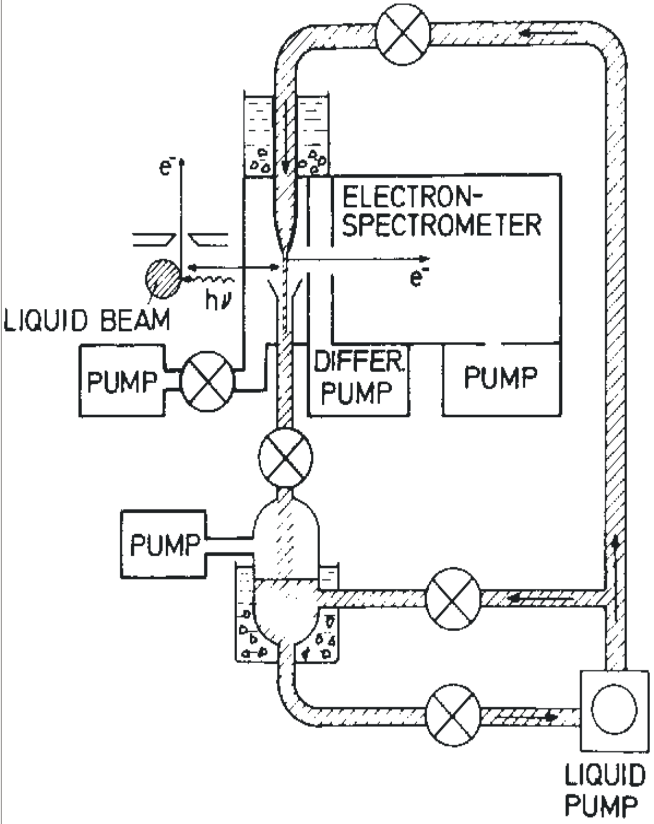
In situ XPS: basic concept



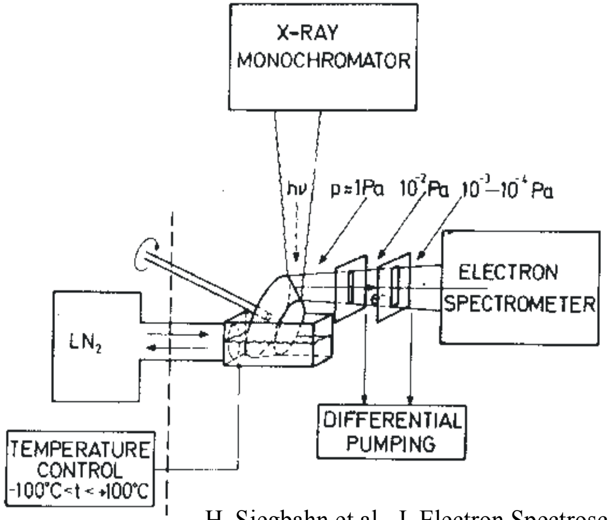
- Photons enter through a window
- Electrons and a gas jet escape through an aperture to vacuum

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)

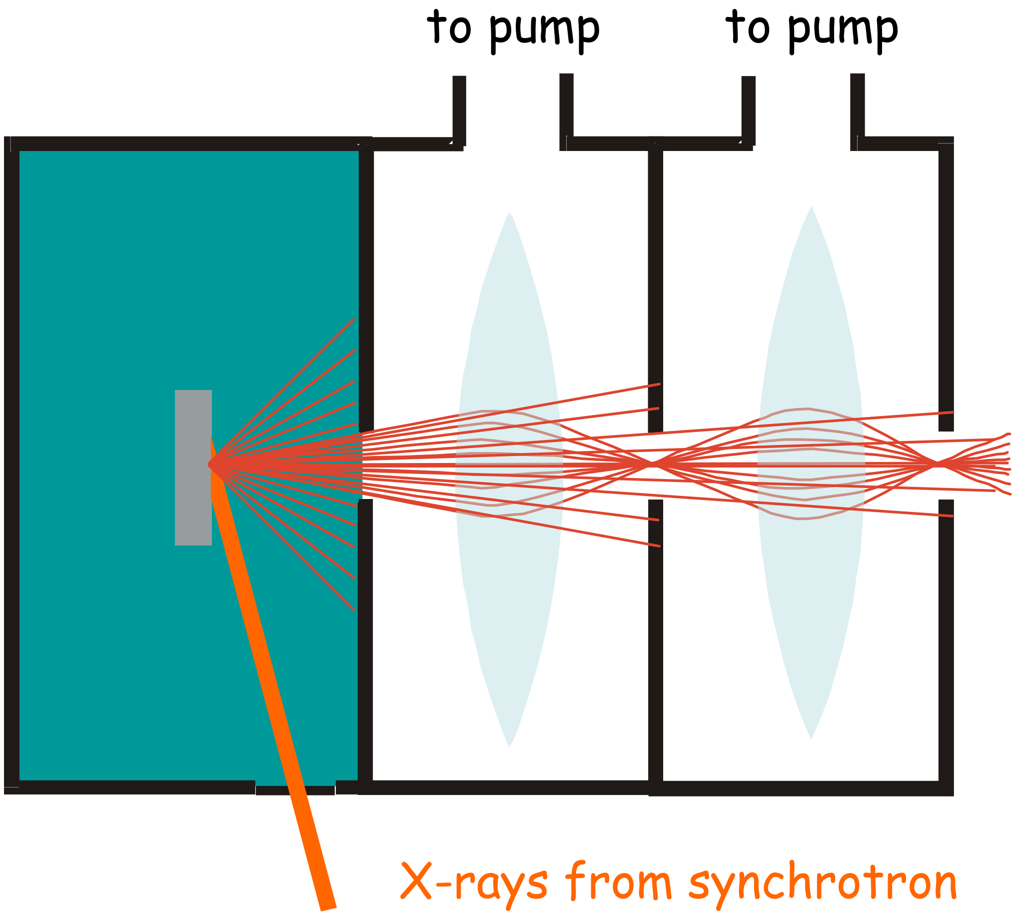


H. Siegbahn et al., J. Electron Spectrosc. Relat. Phenom. **2**, 319 (1973)



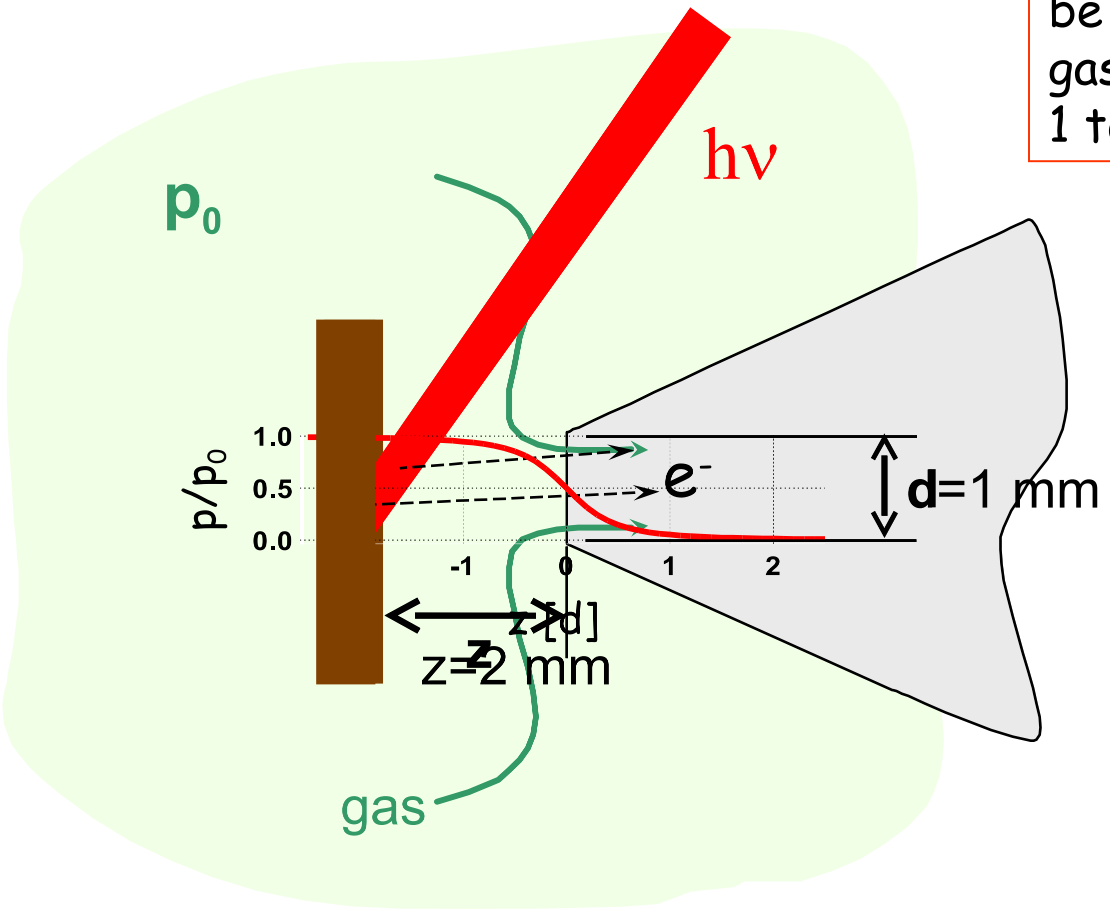
H. Siegbahn et al., J. Electron Spectrosc. Relat. Phenom. **24**, 205 (1981)

In situ XPS using differentially pumped electrostatic lenses



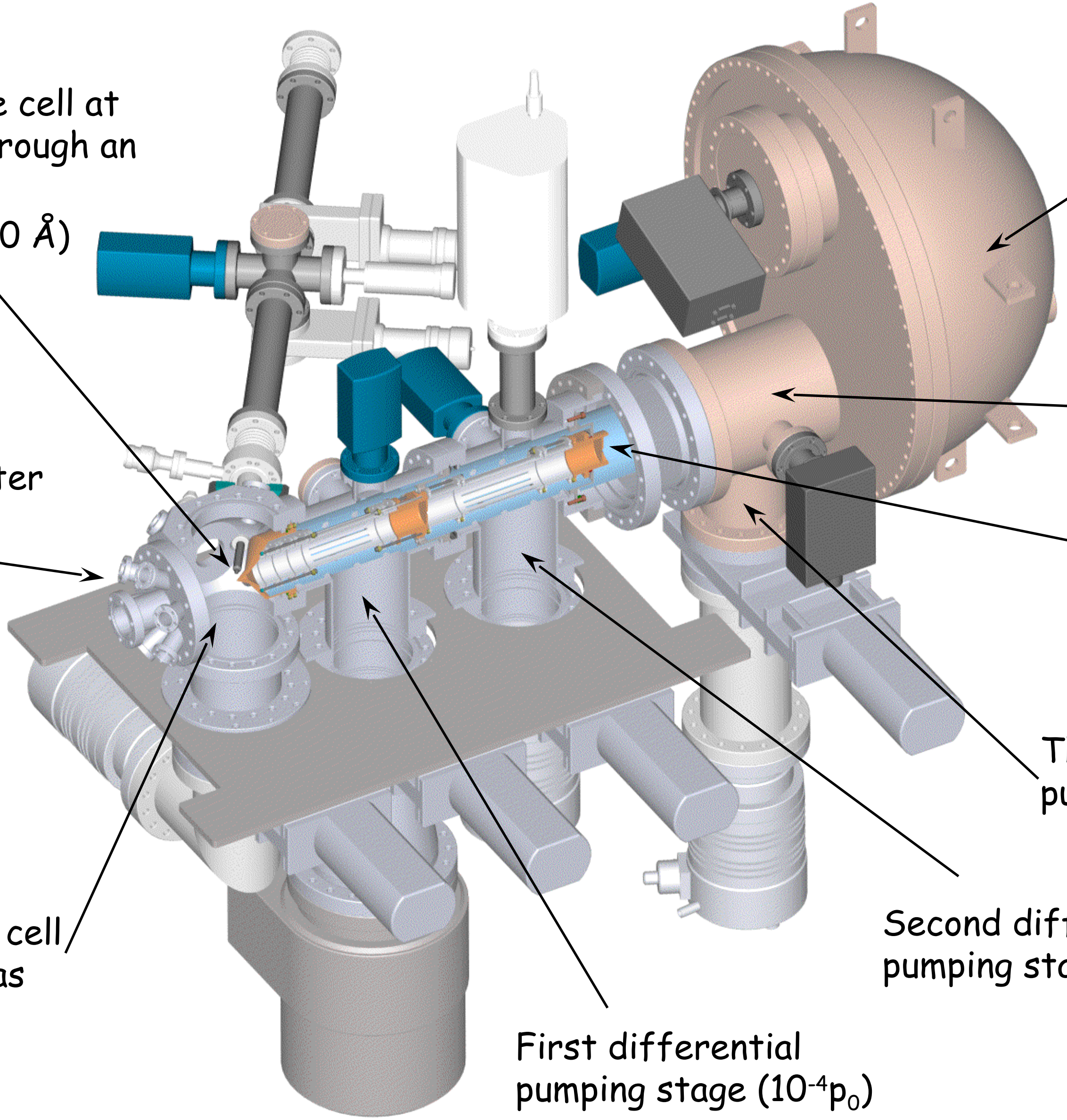
D.F. Ogletree, H. Bluhm, G. Lebedev, C.S. Fadley, Z. Hussain, M. Salmeron, Rev. Sci. Instrum. 73 (2002) 3872.

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)

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

Analyzer input lens

mass spectrometer and additional pumping

Focal point of analyzer input lens

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

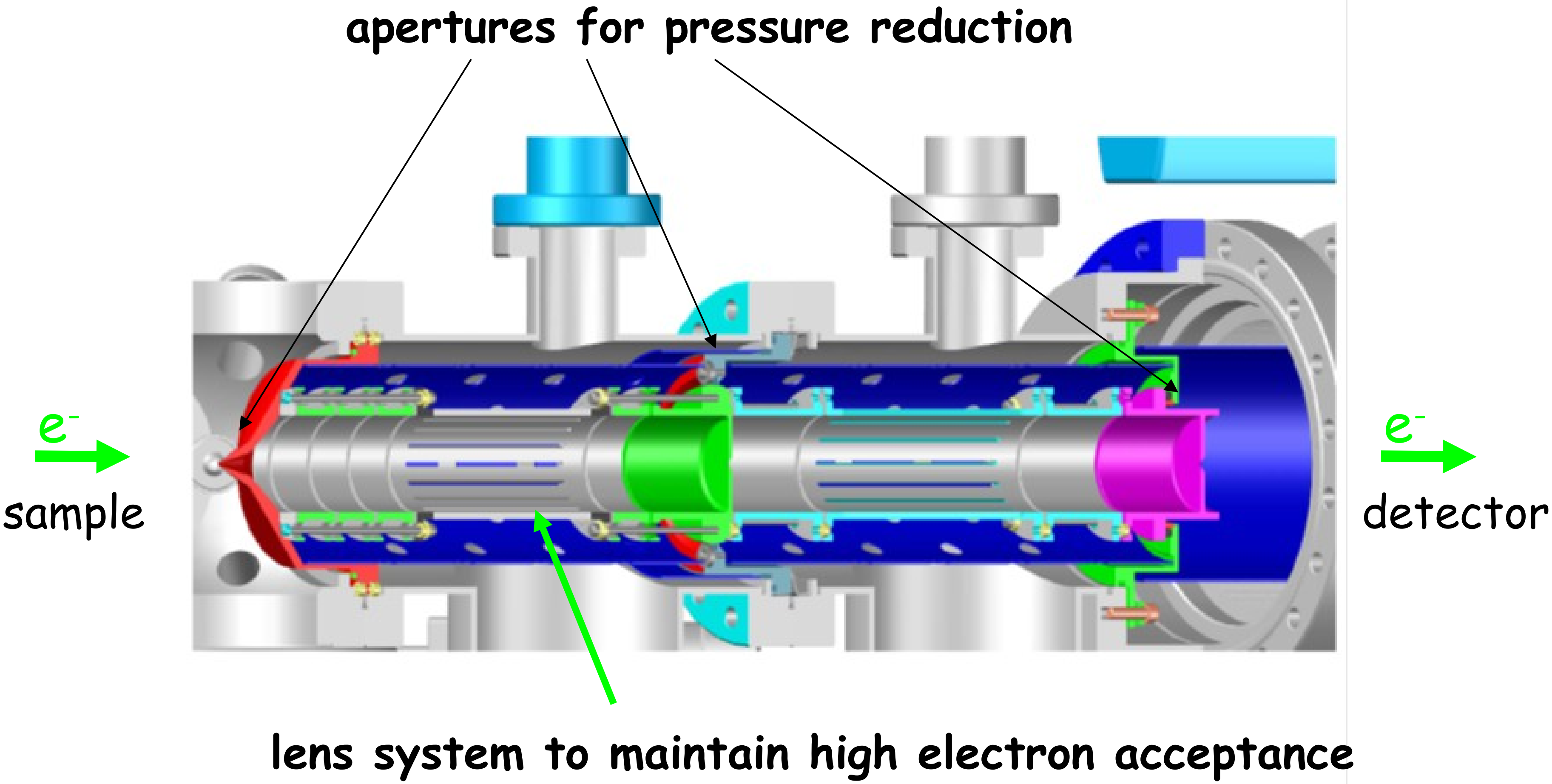
Second differential pumping stage ($10^{-6}p_0$)

Experimental cell supplied by gas lines (p_0)

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

NAP-XPS: General Design

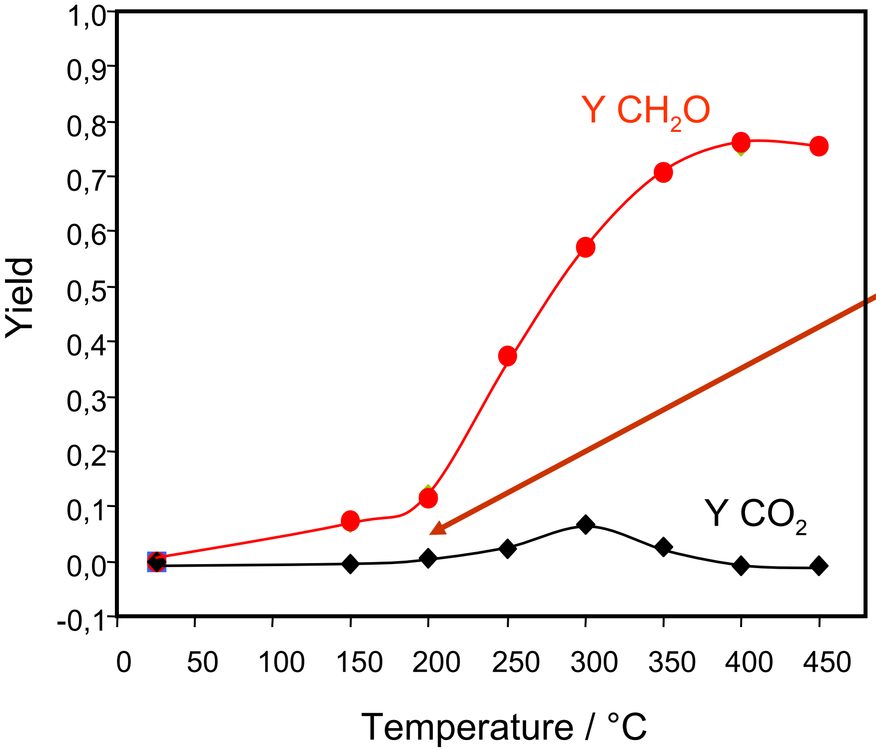
Differential pumping via apertures combined with electrostatic lens system



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).

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

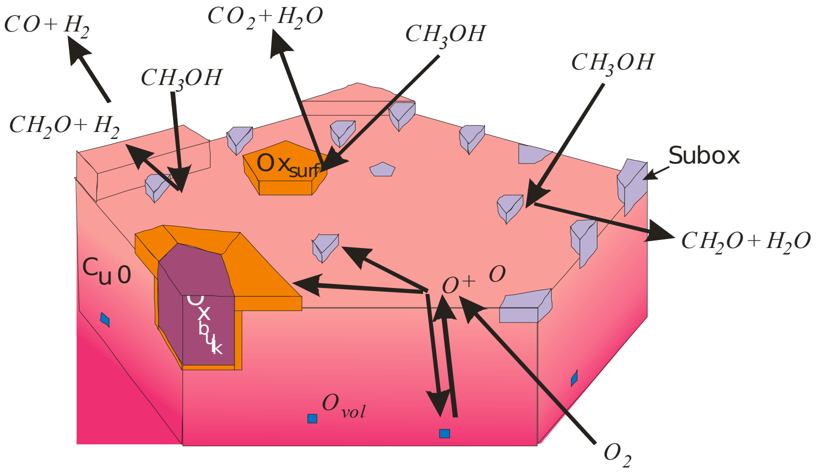
$$CH_3O^-(a) \longrightarrow CH_2O(g) + H^+(a)$$

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

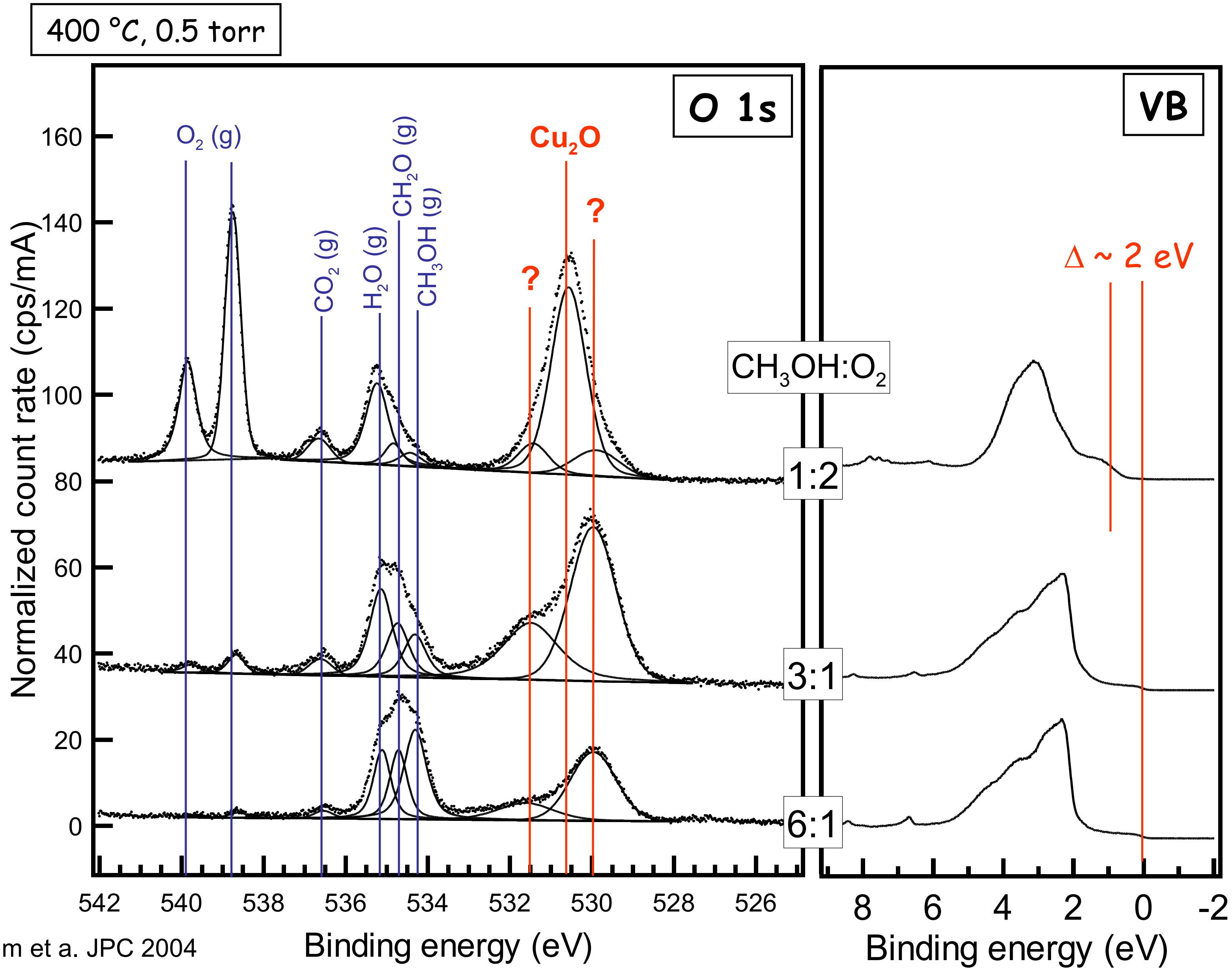
XPS measurements

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

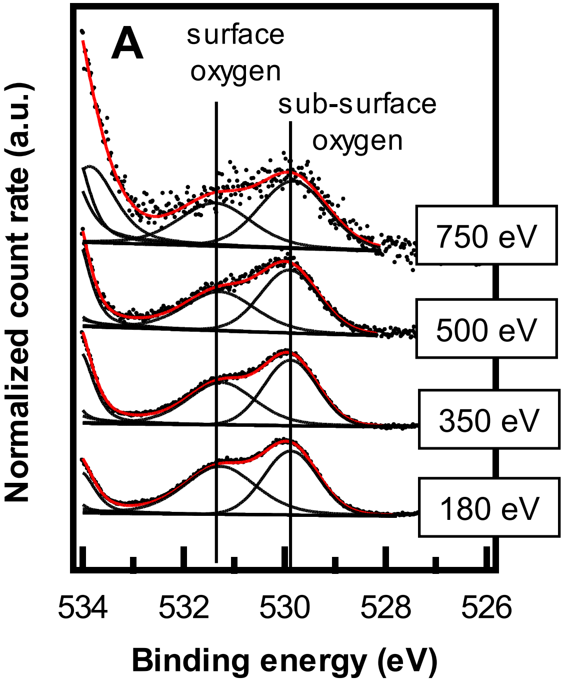
Methanol oxidation on Cu: O1s spectra

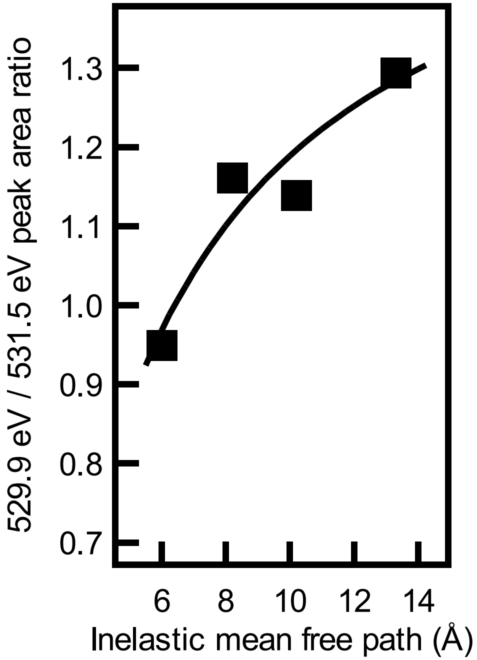


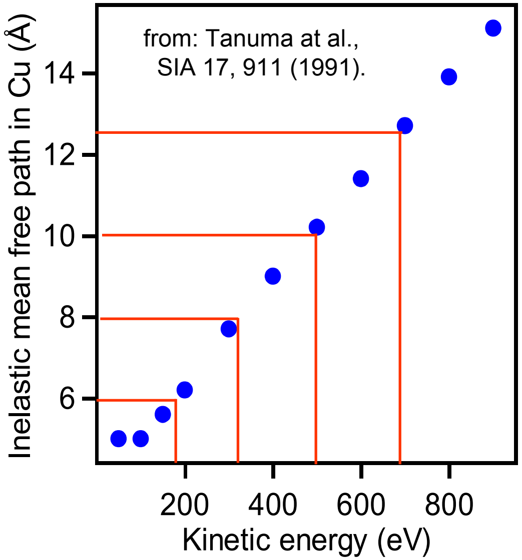
Bluhm et a. JPC 2004

O1s depth profiling

$CH_3OH : O_2 = 3:1$







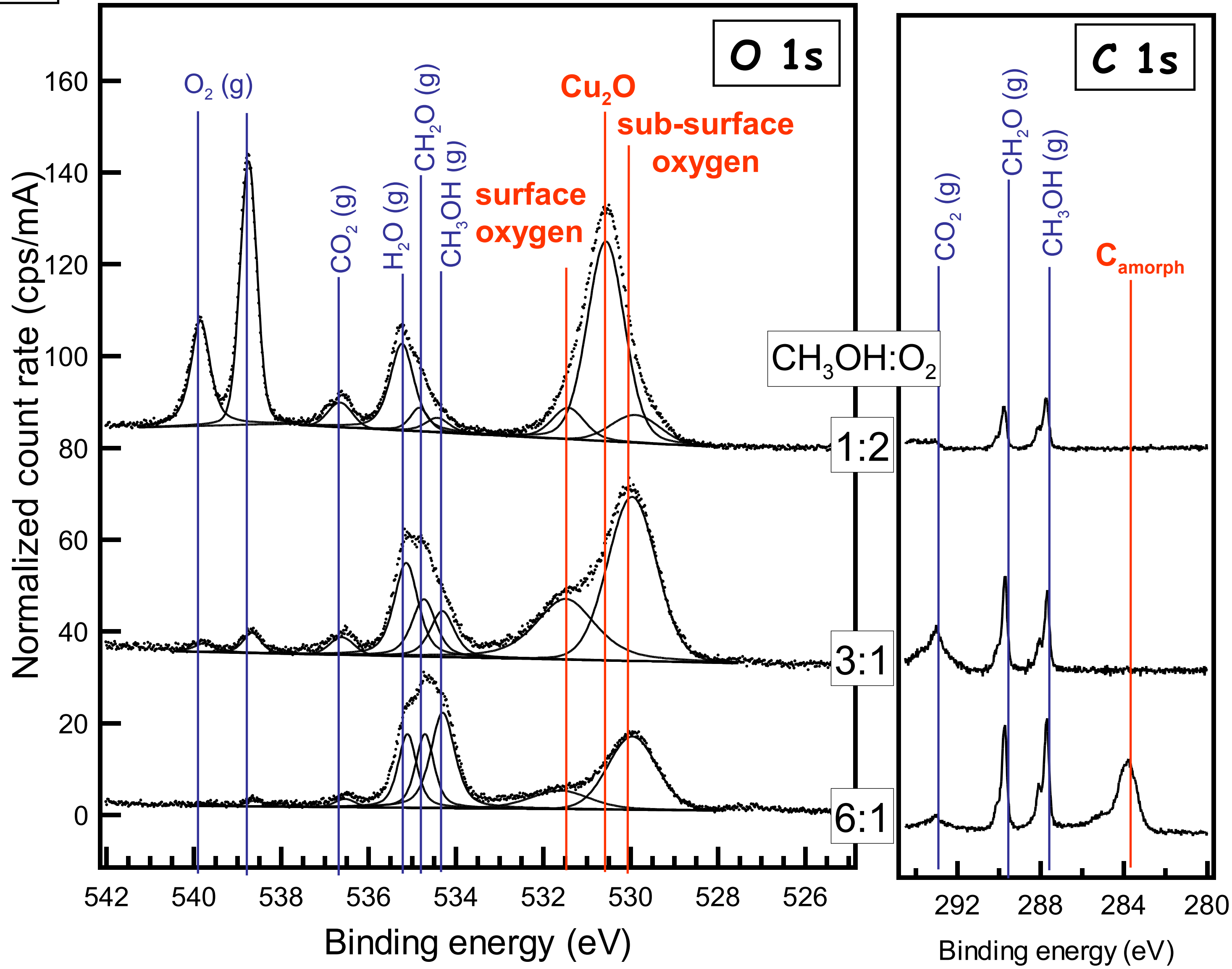
$$I_{529.9}/I_{531.5}=n_{529.9}/n_{531.5}\cdot\exp[-(z_{531.5}-z_{529.9})/\lambda]$$

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

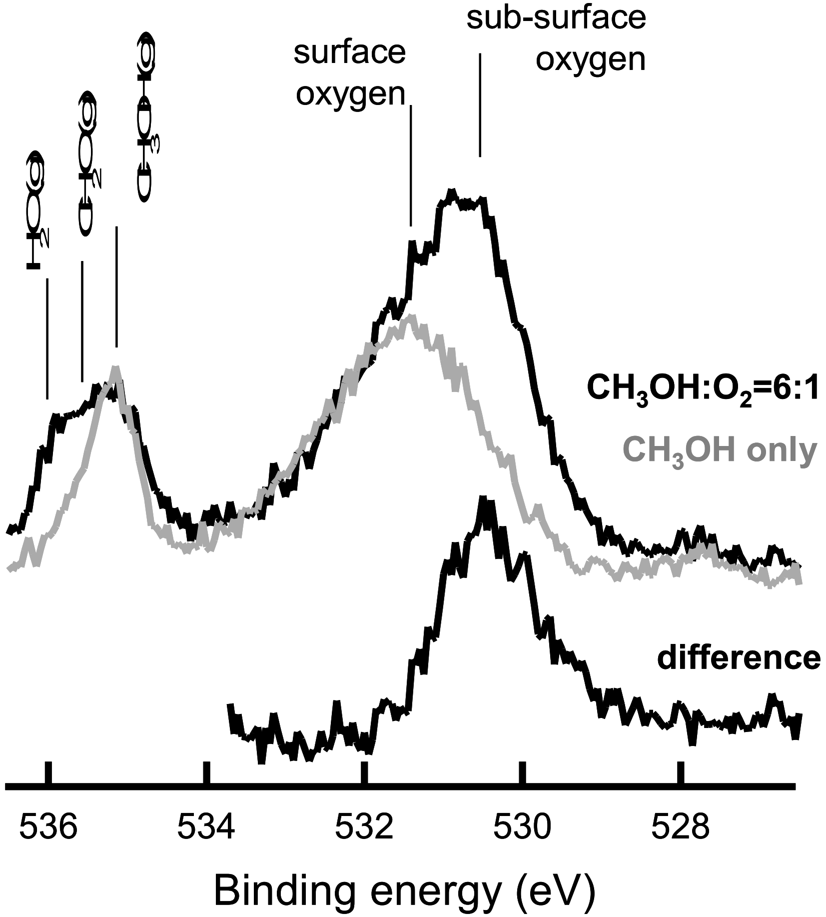
Bluhm et a. JPC 2004

Methanol oxidation on Cu: C1s spectra

400 °C



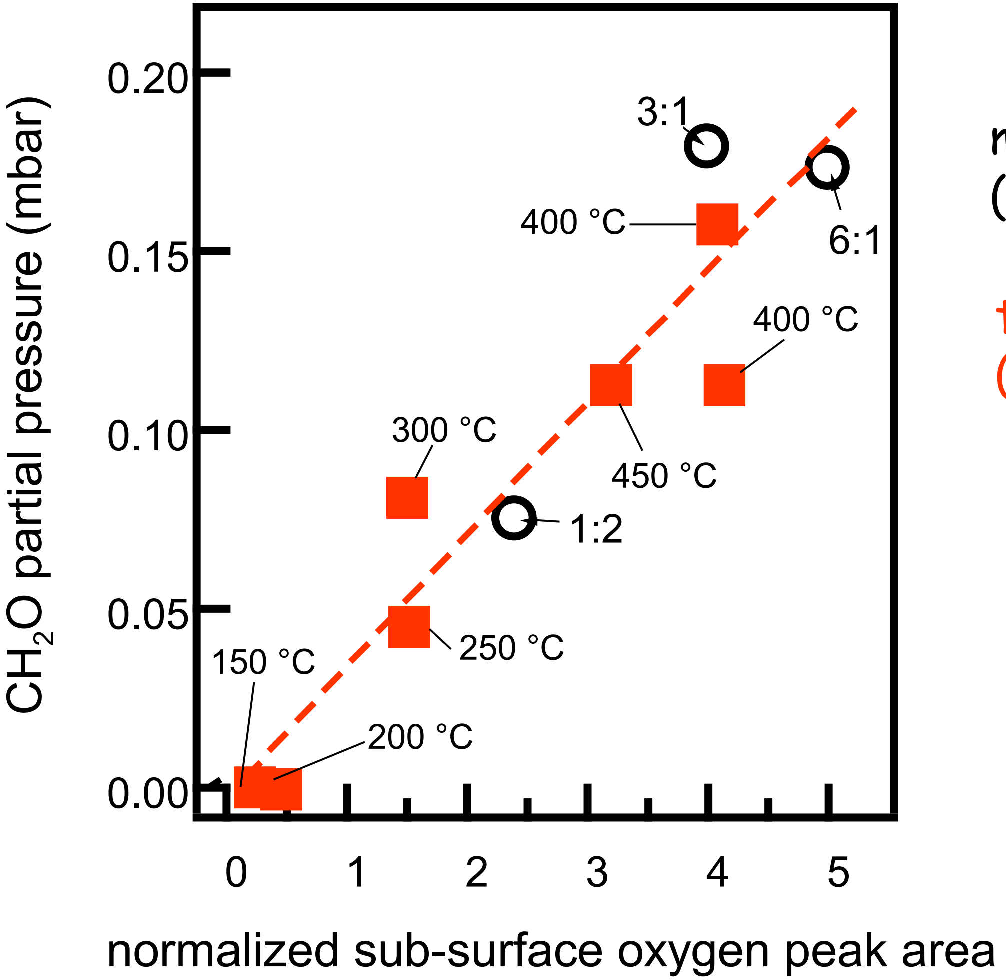
Metastability of the Sub-Surface Oxygen



Knop-Gericke et a. Adv. In Catalysis 2009

Correlation of catalytic activity and surface species

CH_2O yield vs sub-surface oxygen peak area



mixing ratio series
(T = 400 °C)

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

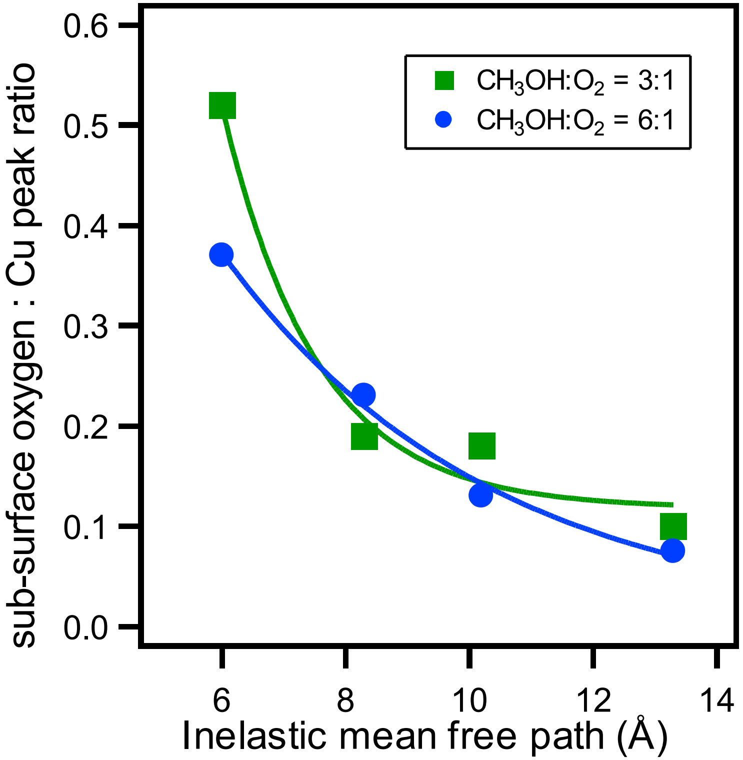
Open questions:
What is the nature of the sub-surface oxygen species?
What is its role in the catalytic reaction?

Bluhm et a. JPC 2004

Depth profiling

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

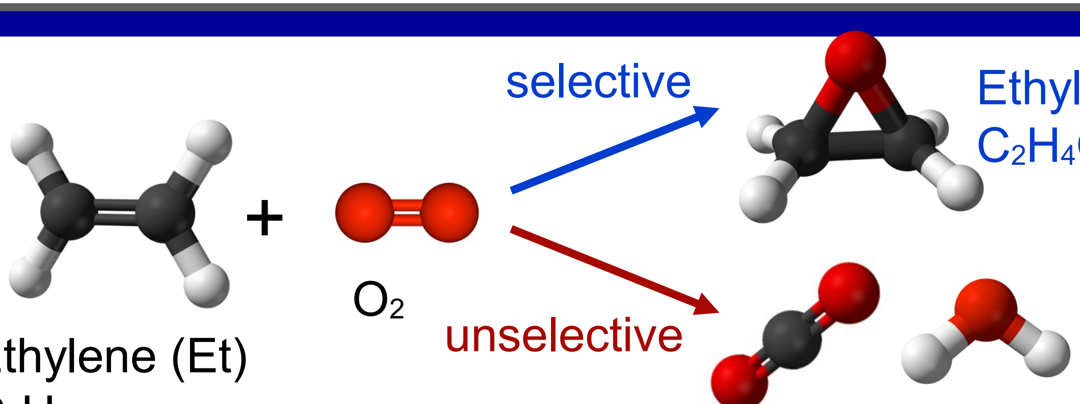
Reducing conditions



Bluhm et a. JPC 2004

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

Ethylene epoxidation



selective

unselective

Ethylene oxide (EO)
C_2H_4O

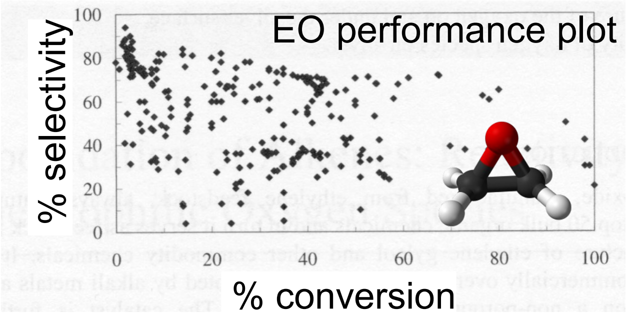
Ethylene (Et)
C_2H_4

O_2

CO_2 H_2O

Large scale industrial process

- 16th most produced chemical
- 25 million ton/year (2012)



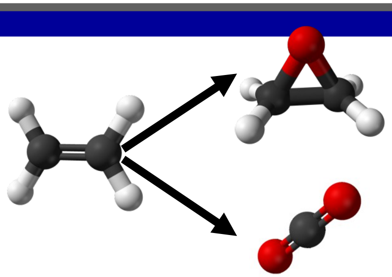
Hodnet, Heterogeneous ictalytic oxidation.(2000)

feedstock chemical

intermediate
for various
consumer products

After 50+ years of research,
Ag is still the ***ONLY catalyst***!

The mechanism of epoxidation on Ag



main goal is to understand fundamental issues

what controls the selectivity?

Different mechanisms proposed in the literature:

1) Different “forms” of oxygen on Ag

- derived from surface science
- ***Oelec*** => attack C=C
- ***Onucl*** => attack C-H
- <u>selectivity = distribution of O species</u>

2) Common intermediate

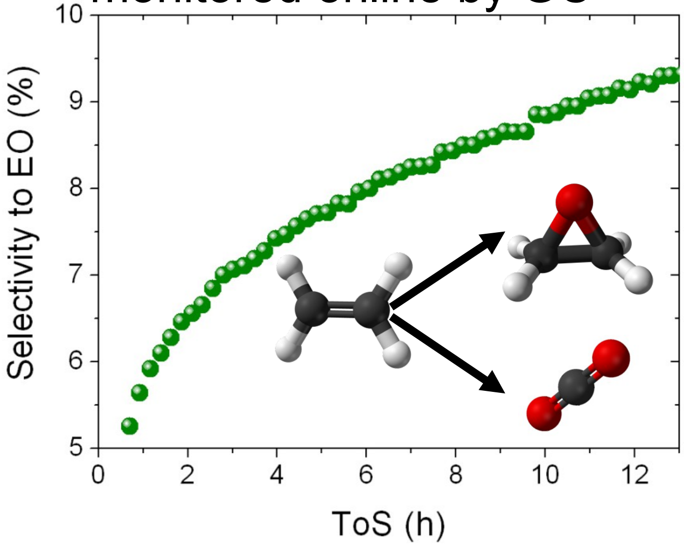
- reinforced by DFT
- OMC intermediate
- limited experimental evidences
- <u>selectivity = energetics of TS</u>

We have to look at surface intermediates!

Ethylene epoxidation on Ag

Catalytic performance

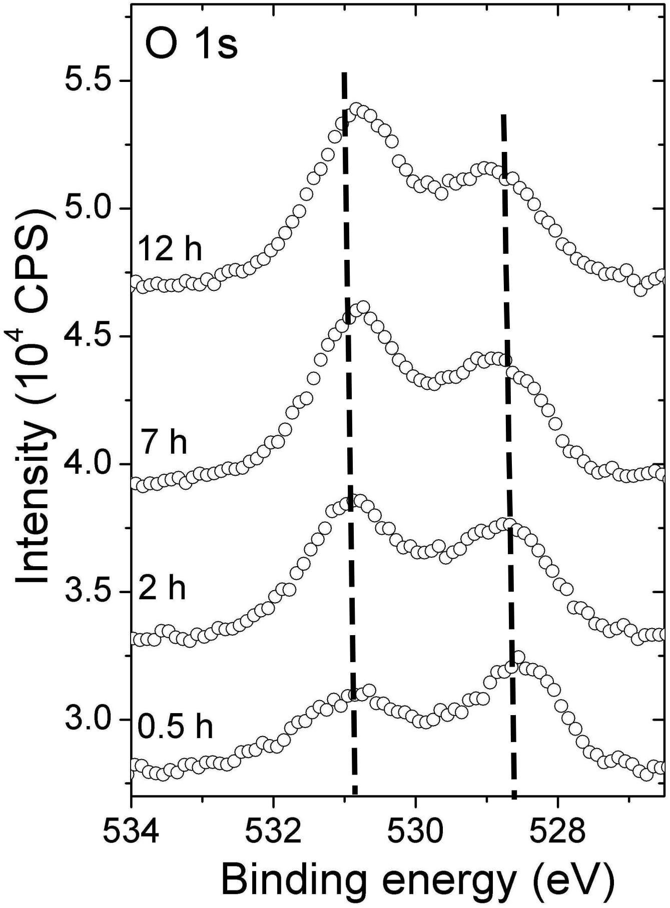
Reaction products monitored online by GC



Ag powder
100-200 nm
$C_2H_4+O_2$ (1:2)
230 ℃

Surface spectroscopy

C1s shows no signal. No measurable C-intermediates



O1s shows **two features** which evolve in

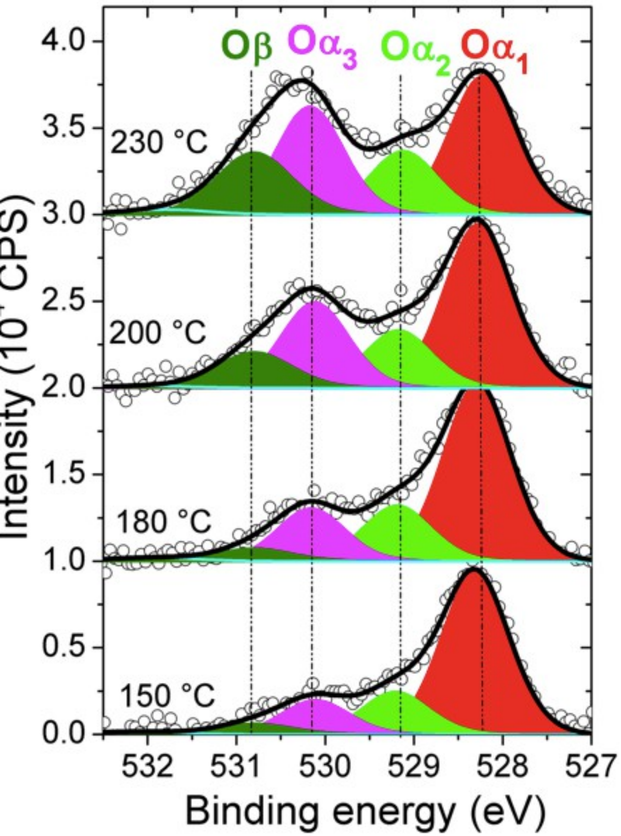
*Different forms of Oxygen, **Oelec** and **On***

How to correlate changes in O1s with selectivity?

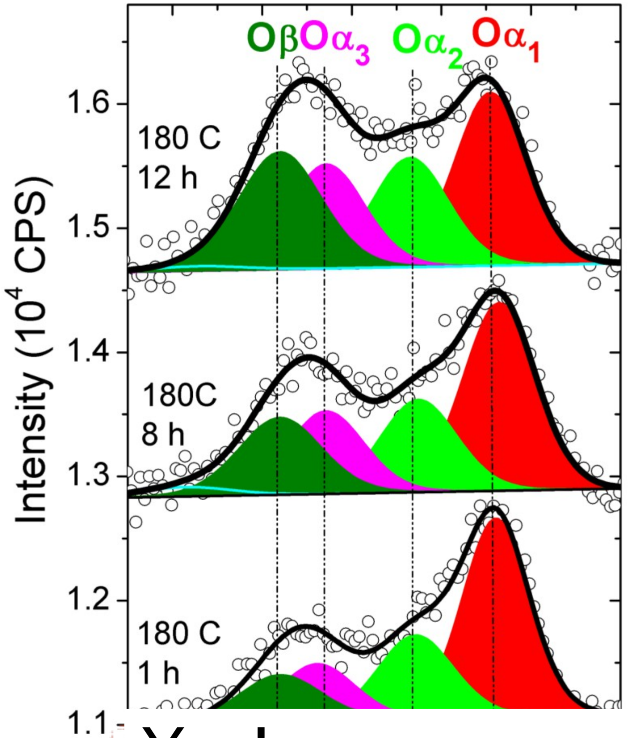
The Ag-O interaction

Are there different forms of O on Ag? O1s XPS spectra

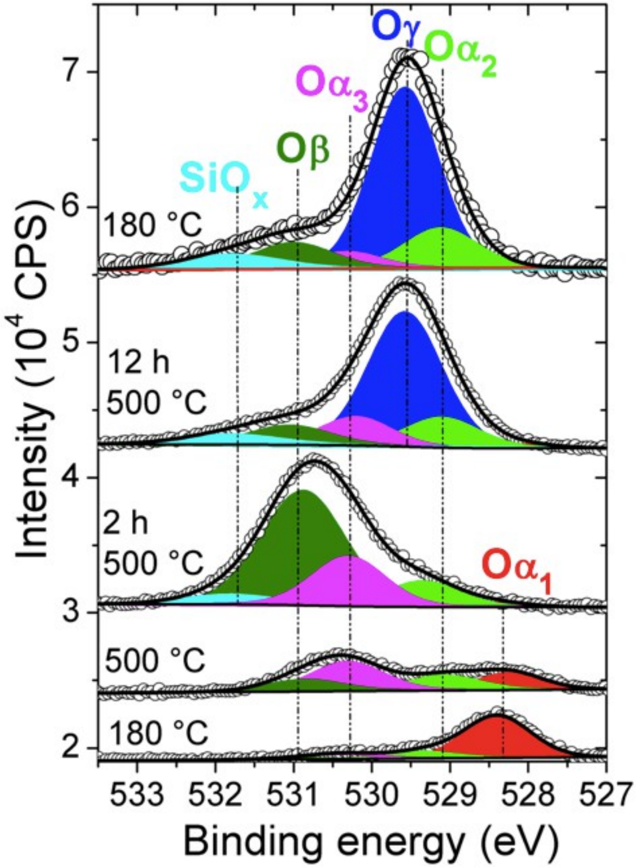
Ag(110) at 0.5 mbar O2



Ag nanopowder at 0.5 mbar O2



Agfoil at 0.5 mbar O2



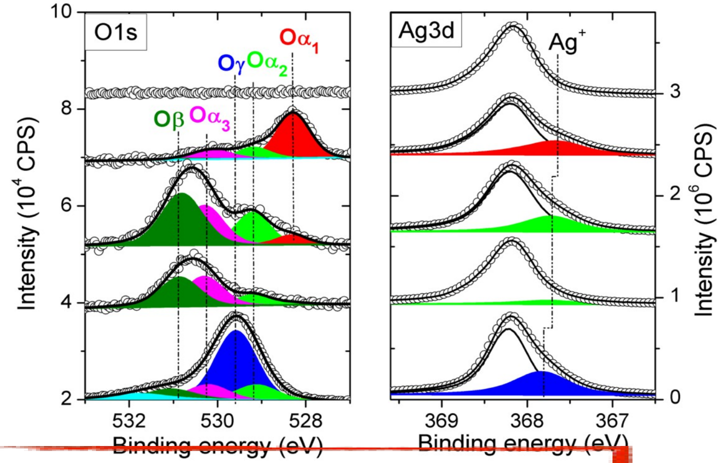
Yes!

And they change with temp/time

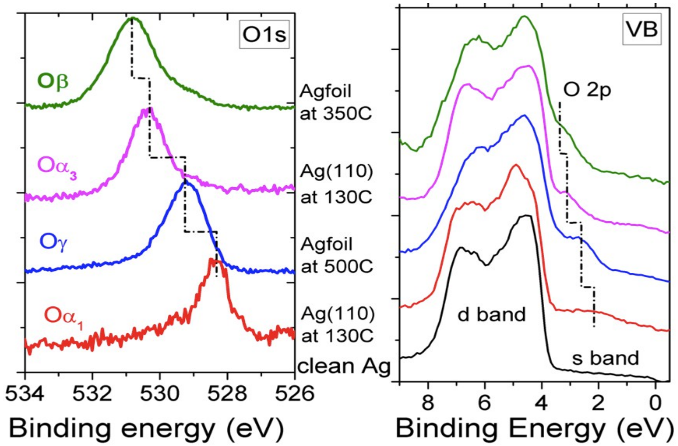
The O species on Ag

How different are they? Properties?

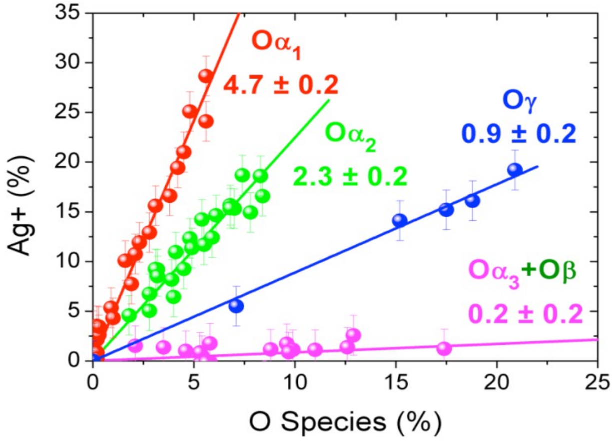
Amount of Ag$^{\delta+}$



Valence band



Ag-O charge transfer



Rocha et al PCCP 14 4554 (2012)

BE calculations

adsorption site	charge transfer	BE (eV)
(111) fcc-hollow	n=2 n=1	528.0 530.3
(110) added row	n =2 n =1	528.5 530.5

intermixing/hybridization
O2p - Ag 5s4d

A. Ishikawa H Nakatsuji J. Comp. Chem. (2013)

O1s assignments

What are these species?

Assignments

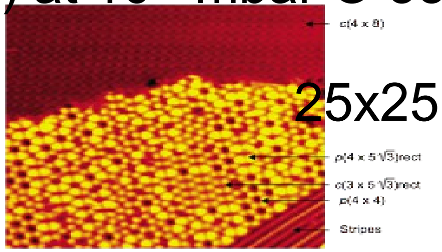
Dynamics/kinetics

spectroscopic features (BE, Ag$^{\delta+}$, XAS,VB)

Desorption/stability

DFT

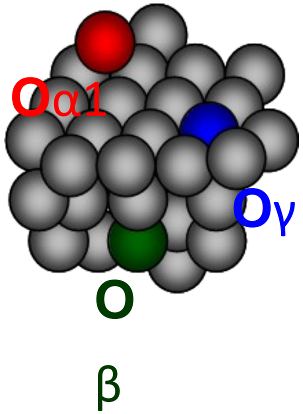
Ag (111) at 10^{-8} mbar O 350K



25x25 nm

J. Schnadt et al PRB 80, 075424 (2009)

Lable	BE (eV)	Ag$^{\delta+}$/O	VB (eV)	location	DFT	reactivity
Oα_1	528.1-528.7	4.7	2.1	surface	reconstructions (surface oxides)	nucleophilic
Oα_2	529.2-529.4	2.3	-			
Oγ	529.5-529.8	0.9	2.6	lattice	substitutional	
Oα_3	530.1-530.4	0.2	3.0	surface	*? (surface O modifed by sub)*	electrophilic
Oβ	530.8-531.1		3.3	sub-surface	octahedral	



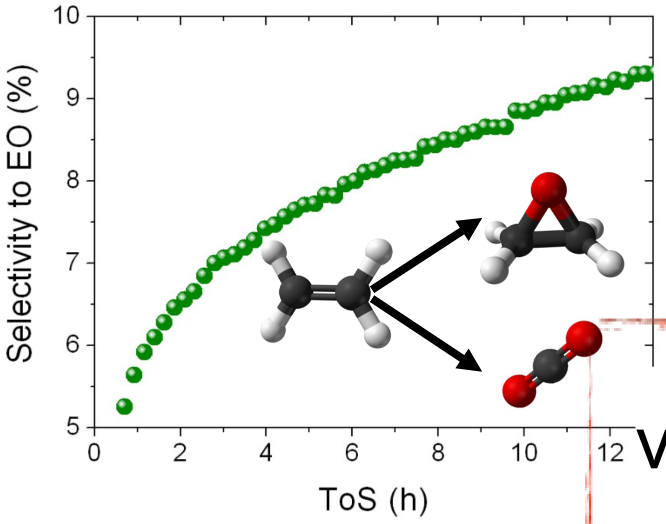
Rocha et al PCCP 14 4554 (2012)

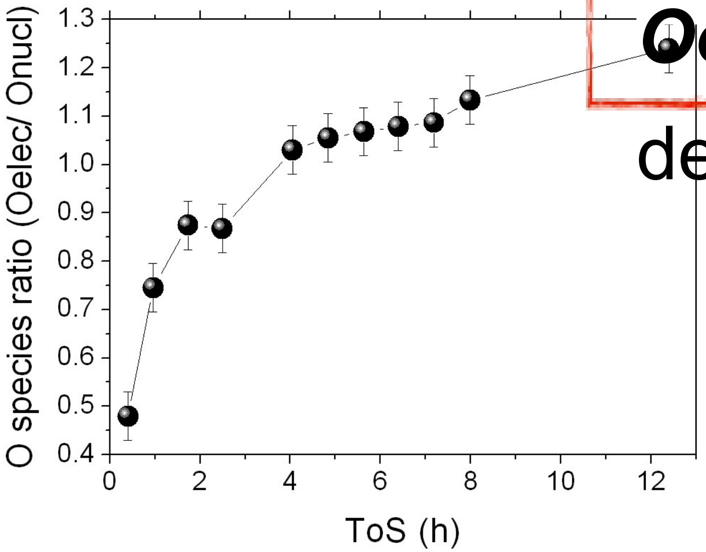
Back to epoxidation

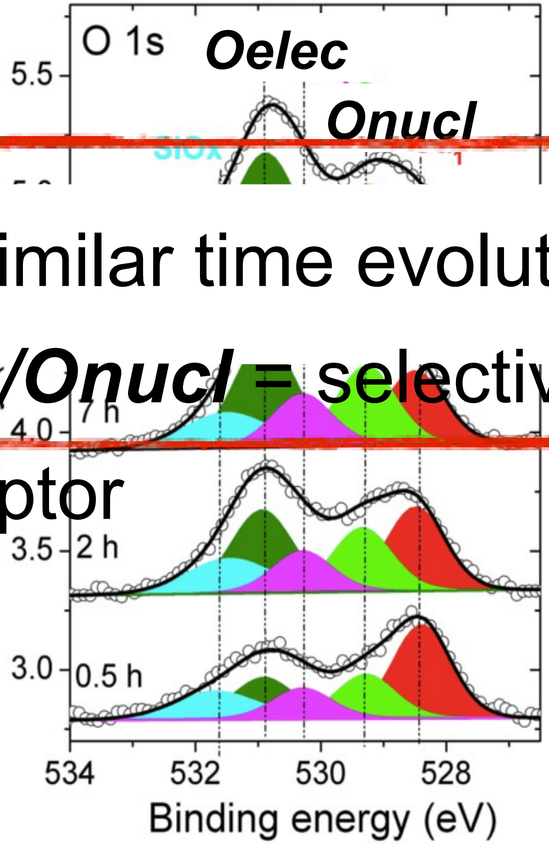
Agpowder 100-200 nm
$C_2H_4+O_2$ (1:2) 230 ℃

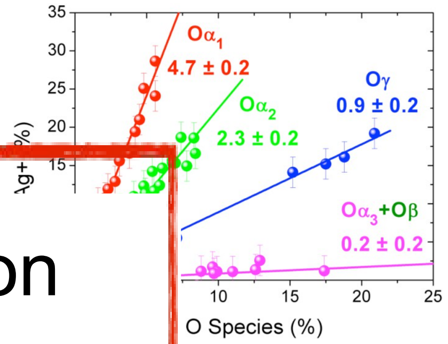
Onucl → attack C-H → CO_2 → “oxide-like” = $O\alpha_1$, $O\alpha_2$

Oelec → attack C=C → EO → “less charged” = $O\alpha_3$ (+$O\beta$)







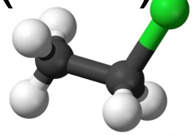


very similar time evolution

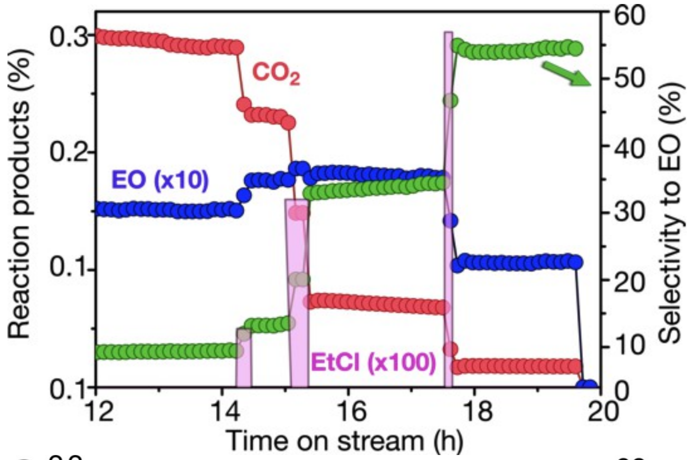
Oelec/Onucl = selectivity descriptor

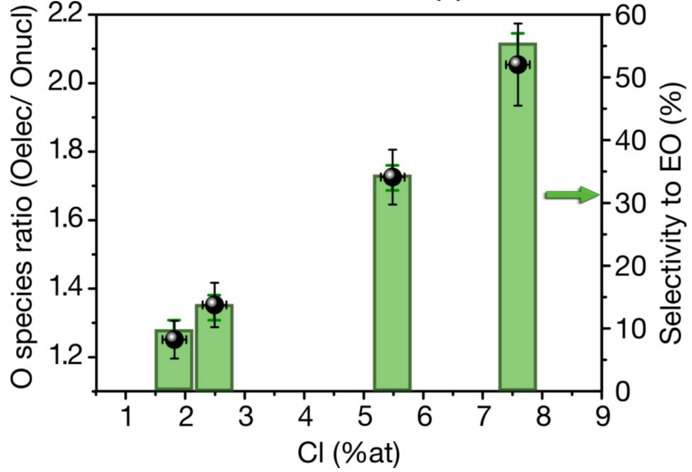
Promotion of Ag catalysts

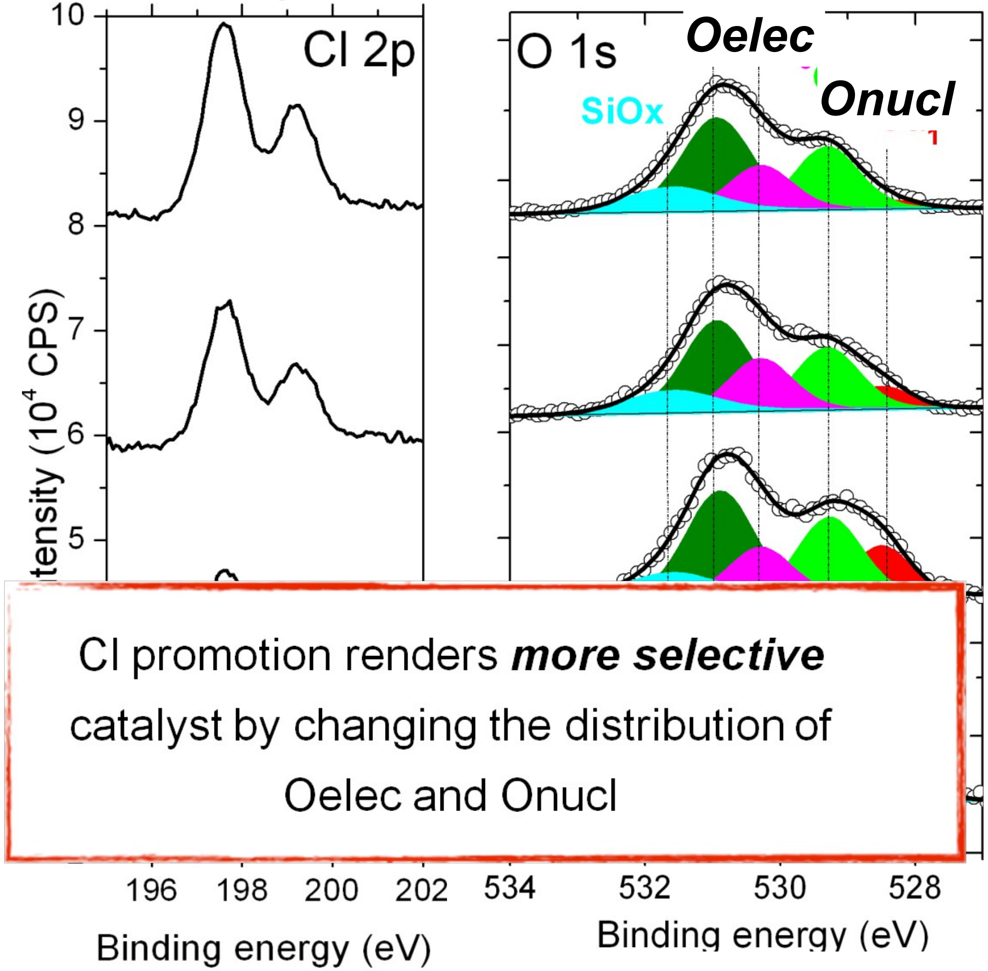
Cl was added as ethyl chloride (EtCl) in the gas feed



few ppm EtCl as pulses



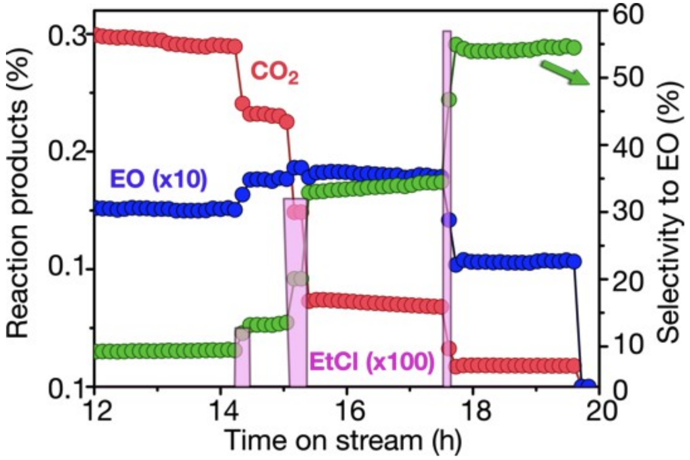


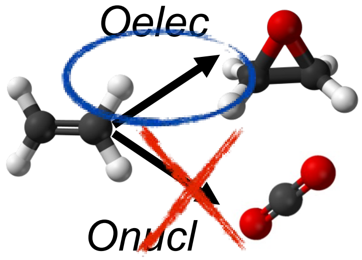


Cl promotion renders ***more selective*** catalyst by changing the distribution of Oelec and Onucl

Rocha et al JACS. (submitted)

Promotion effect of Cl





EtCl pulse	***Onucl (%at)***	***Oelec (%at)***	***Osum (%at)***
0	7.4	9.3	16.7
1st	7.0	9.5	16.5
2nd	6.0	10.6	16.6
3rd	4.9	10.0	14.9

affect unselective path (CO_2)
remove ***Onucl***
(site blocking)

enhance selective path (EO)
more ***Oelec***
(charge withdraw)

At high Cl coverages:
poisoning effect = blocks oxygen activation

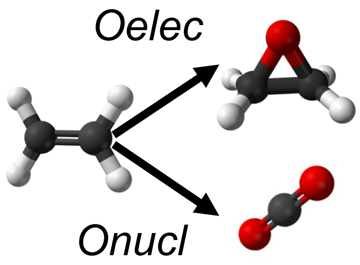
Summary

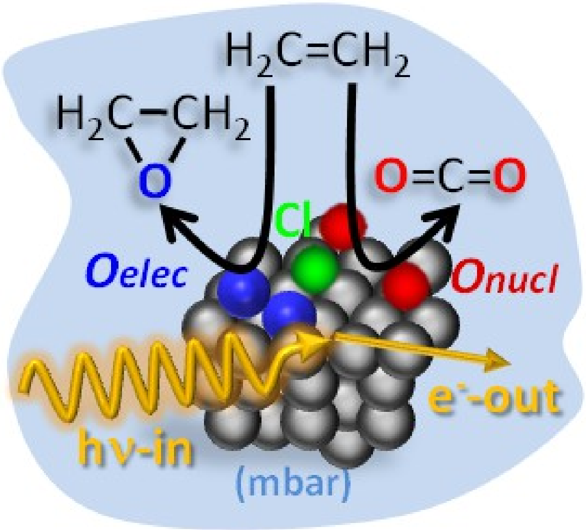
O species with diff. characteristics (BE, $Ag^{\delta+}$, VB)

distinctive Ag-O bonding
intermixing of O2p Ag4d/5s

different roles in oxidation reaction
Oelec vs Onucl

Oelec/Onucl *as a selectivity descriptor*

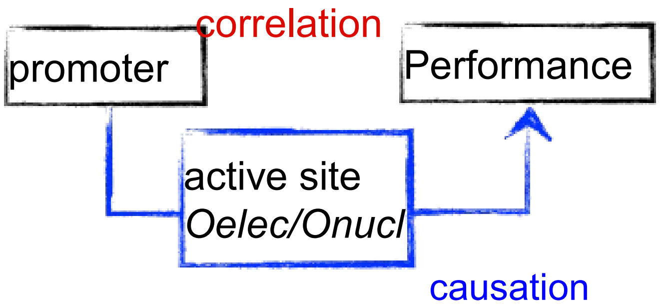




Cl promotion

removes ***Onucl*** (site blocking)

enhances ***Oelec*** (electronic effect)



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

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