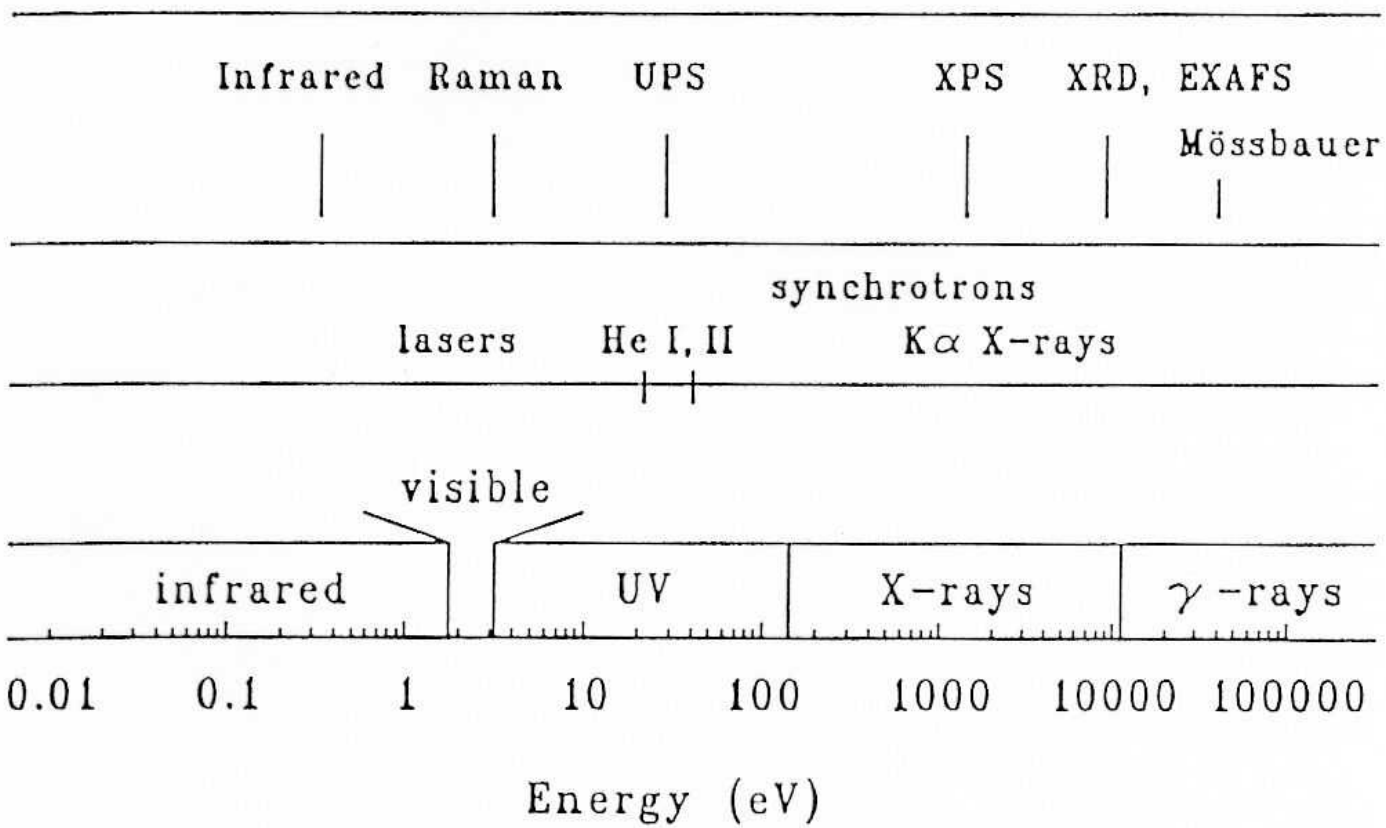
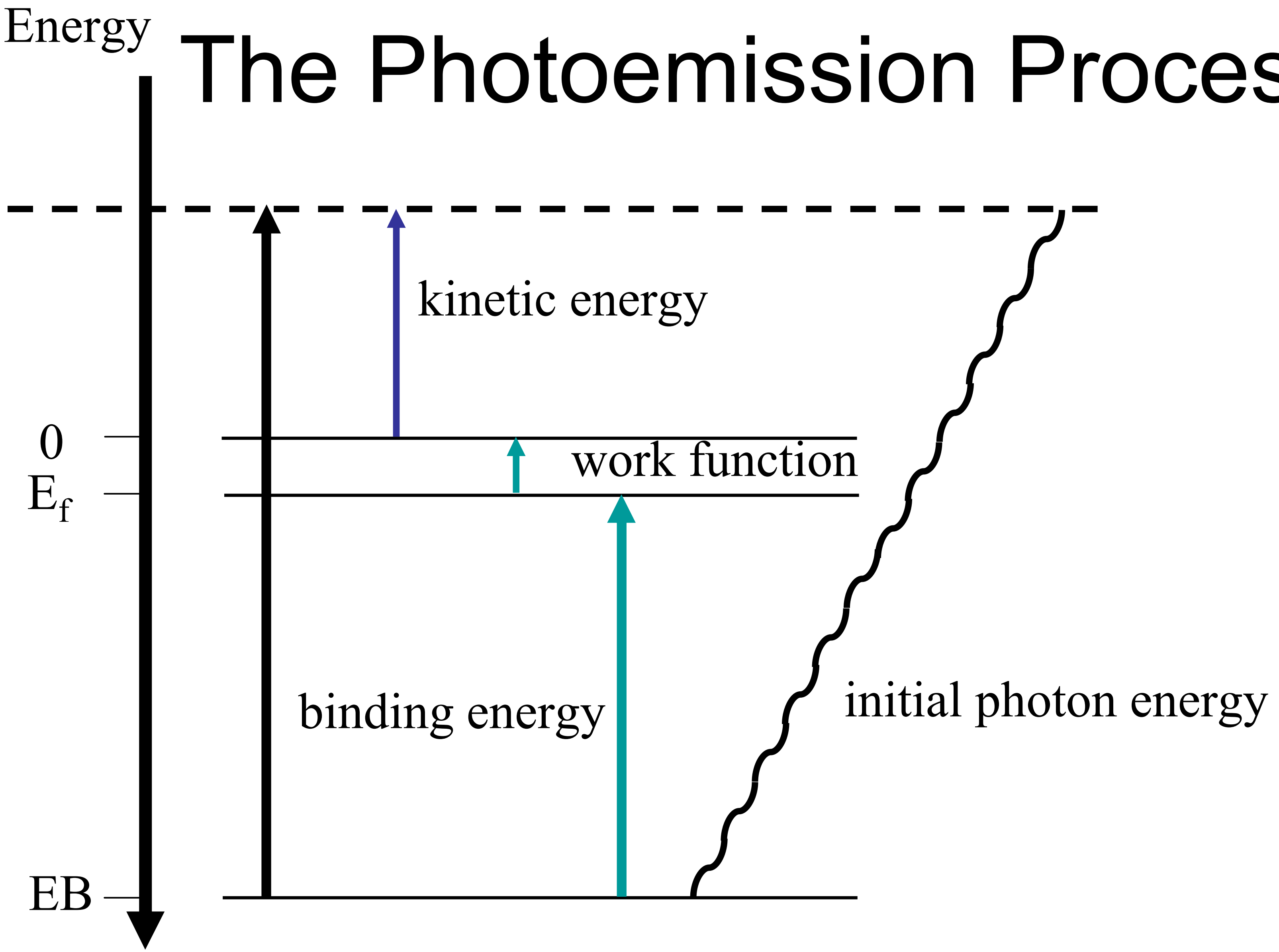
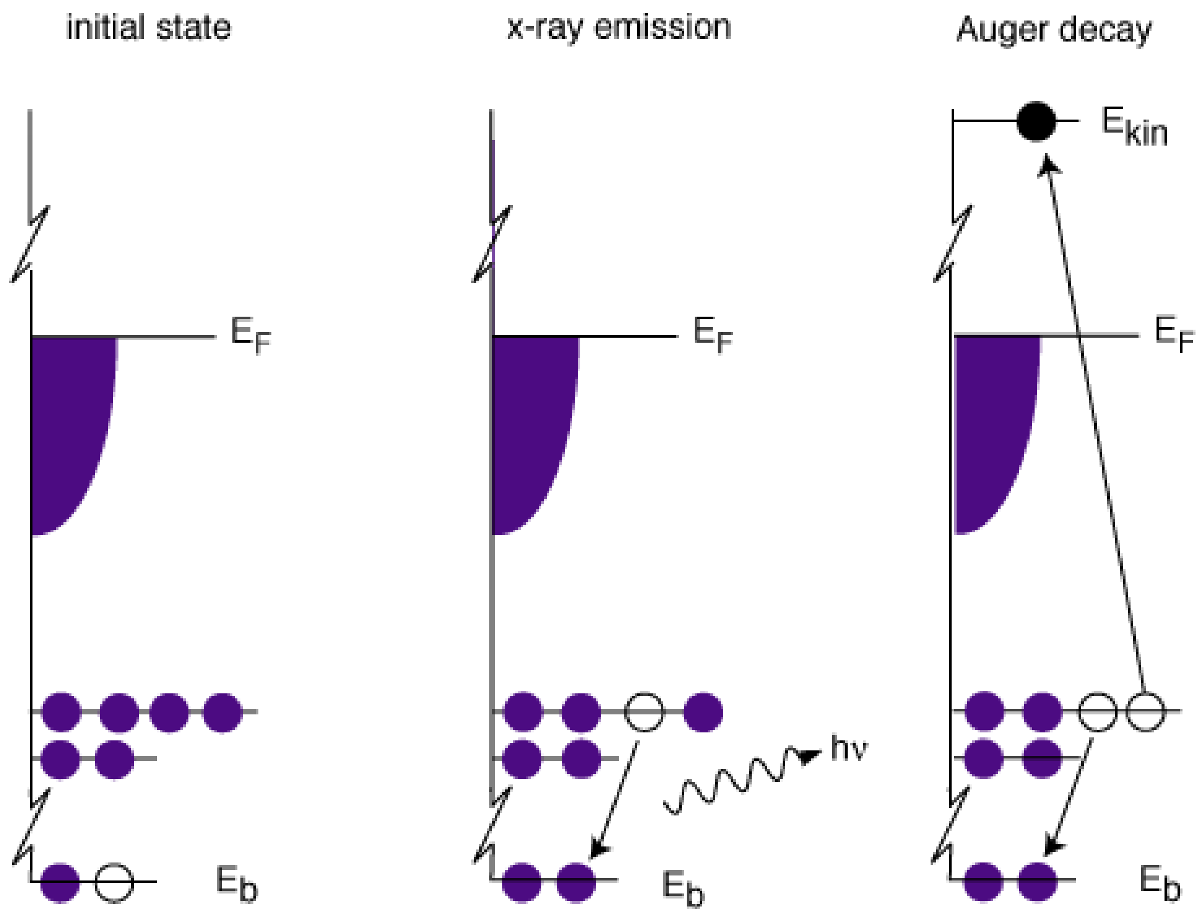
Energy Ranges



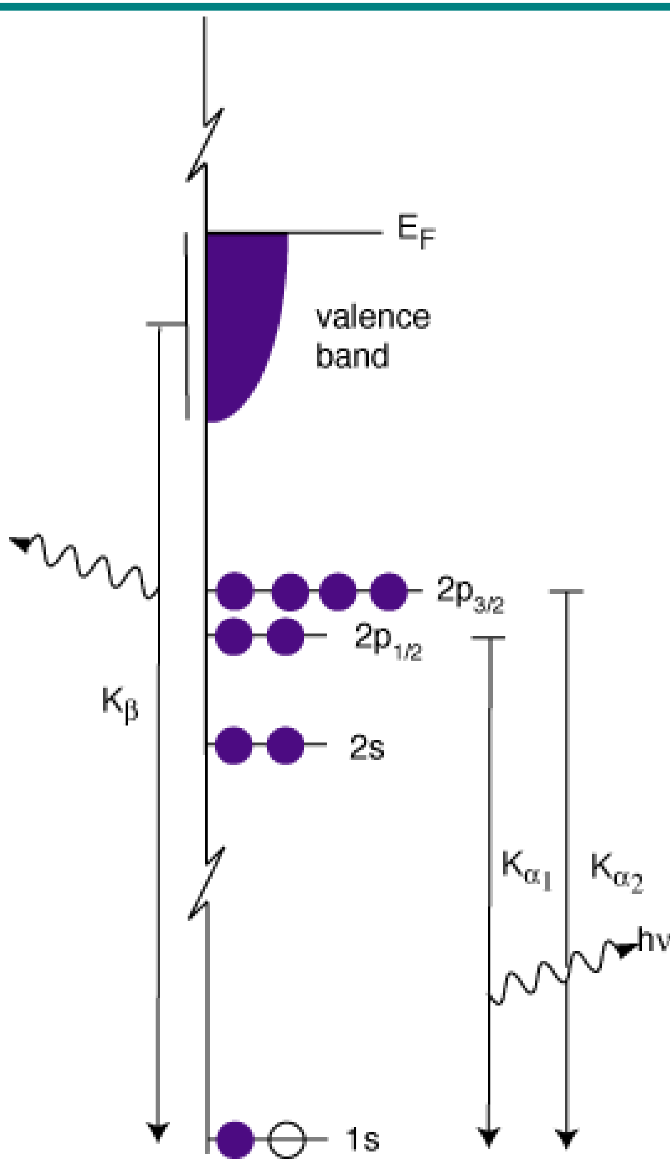
The Photoemission Process



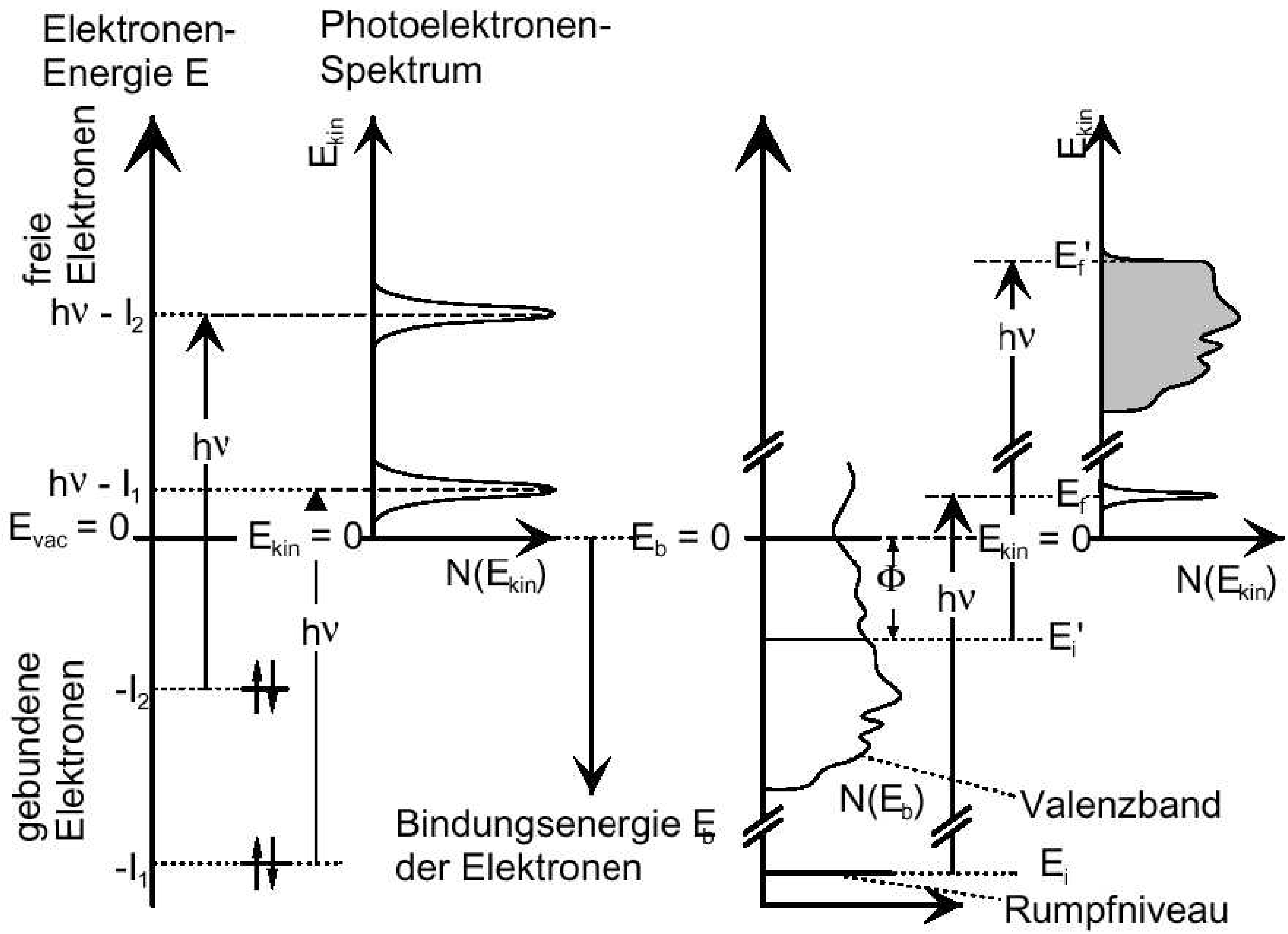
Decay of a core-hole by x-ray emission or the Auger process



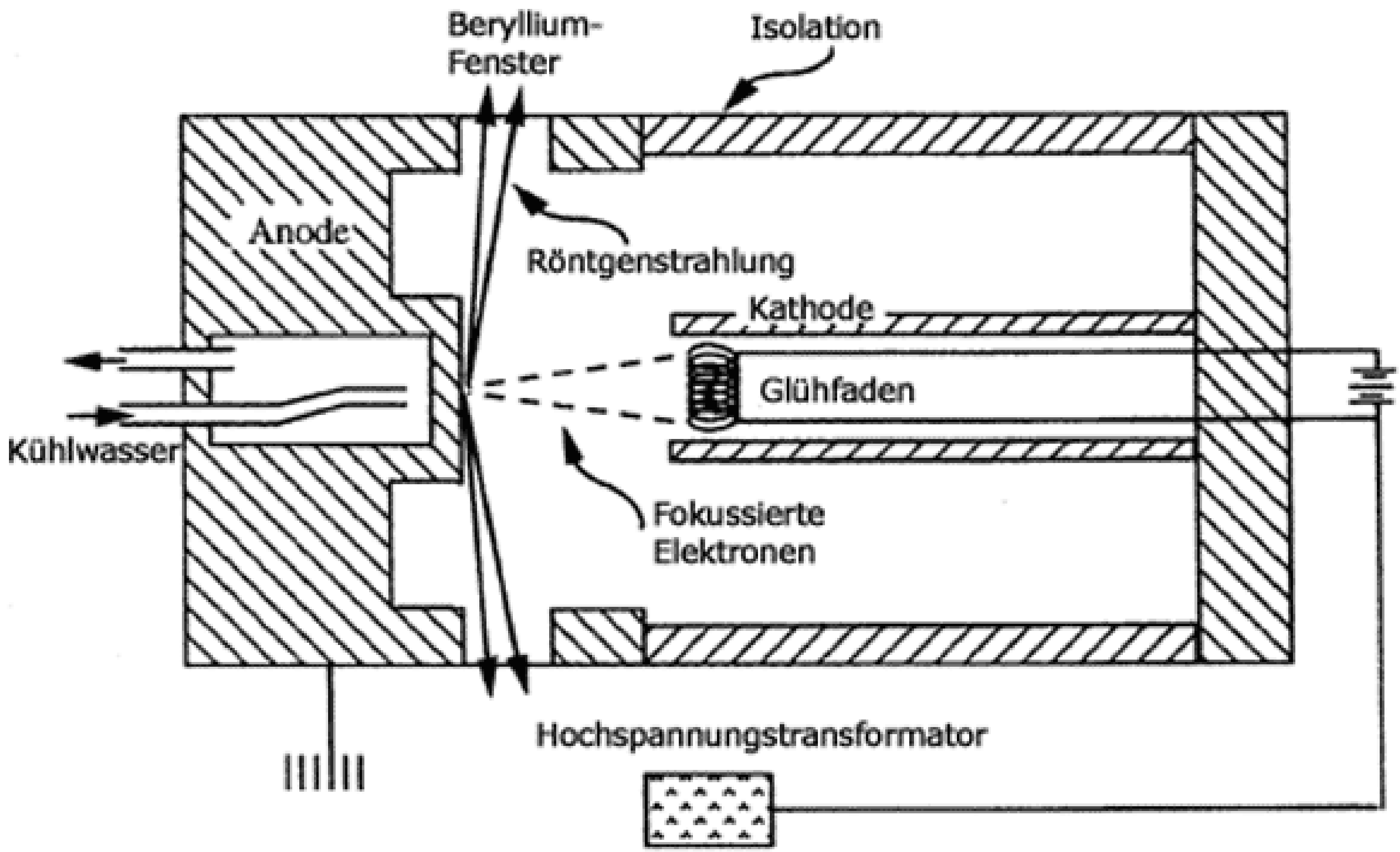
Nomenclature of the x-ray decays



Idealised photoemission of an atom and a solid state

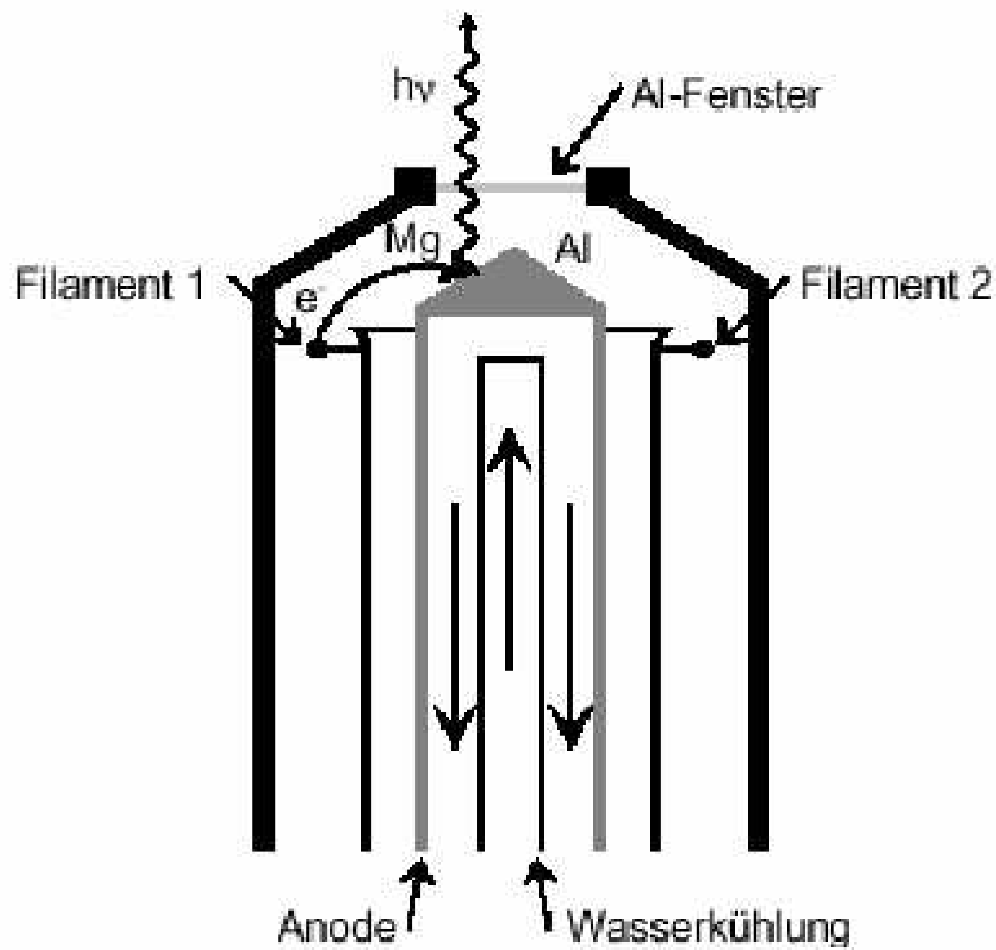


X-ray tube



Beryllium-
Fenster
Isolation
Anode
Röntgenstrahlung
Kathode
Glühfaden
Kühlwasser
Fokussierte
Elektronen
Hochspannungstransformator

X-ray twin anode



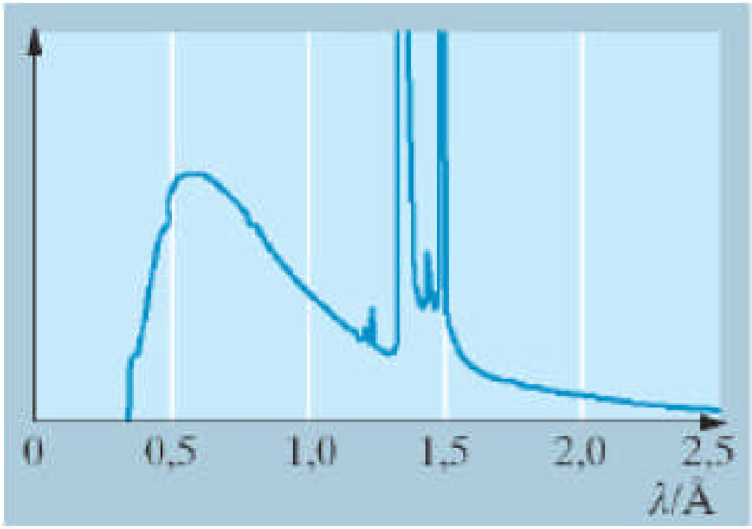
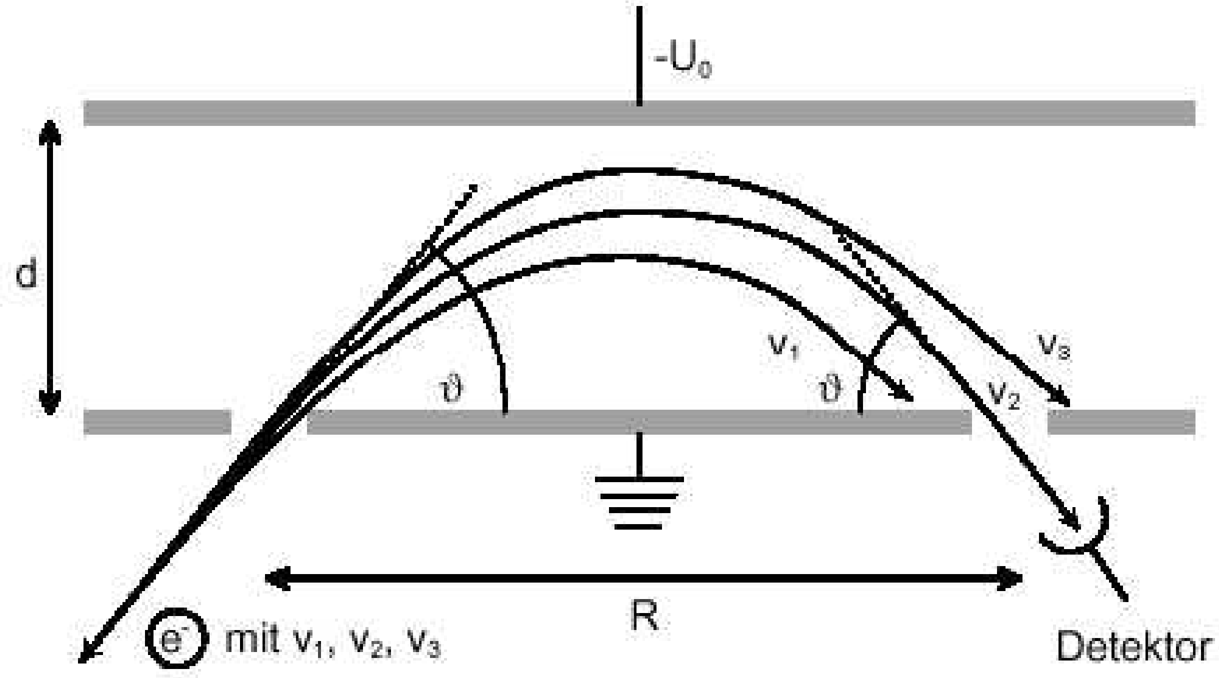
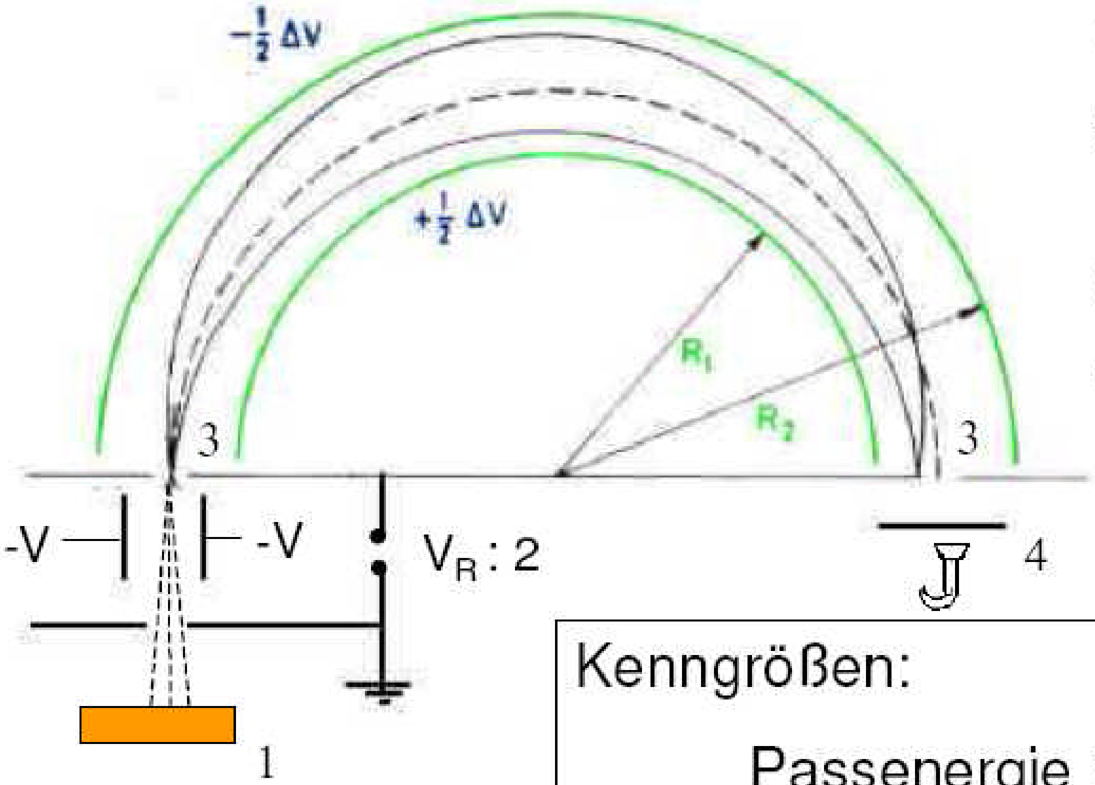


Abb. 8.1 Röntgen-Spektrum einer Kupfer-Anode mit Bremskontinuum und überlagerten Linien K_α und K_β des Kupfers. Röhrenspannung 38 kV. Aus Meschede: Gerthsen Physik, 22. Aufl., Abb. 15.21

Parallel plate mirror analyser



Halbkugelanalysator



1: Probe

2: Verzögerungs-potential

3: Lochblende

4: Detektor : Channeltron

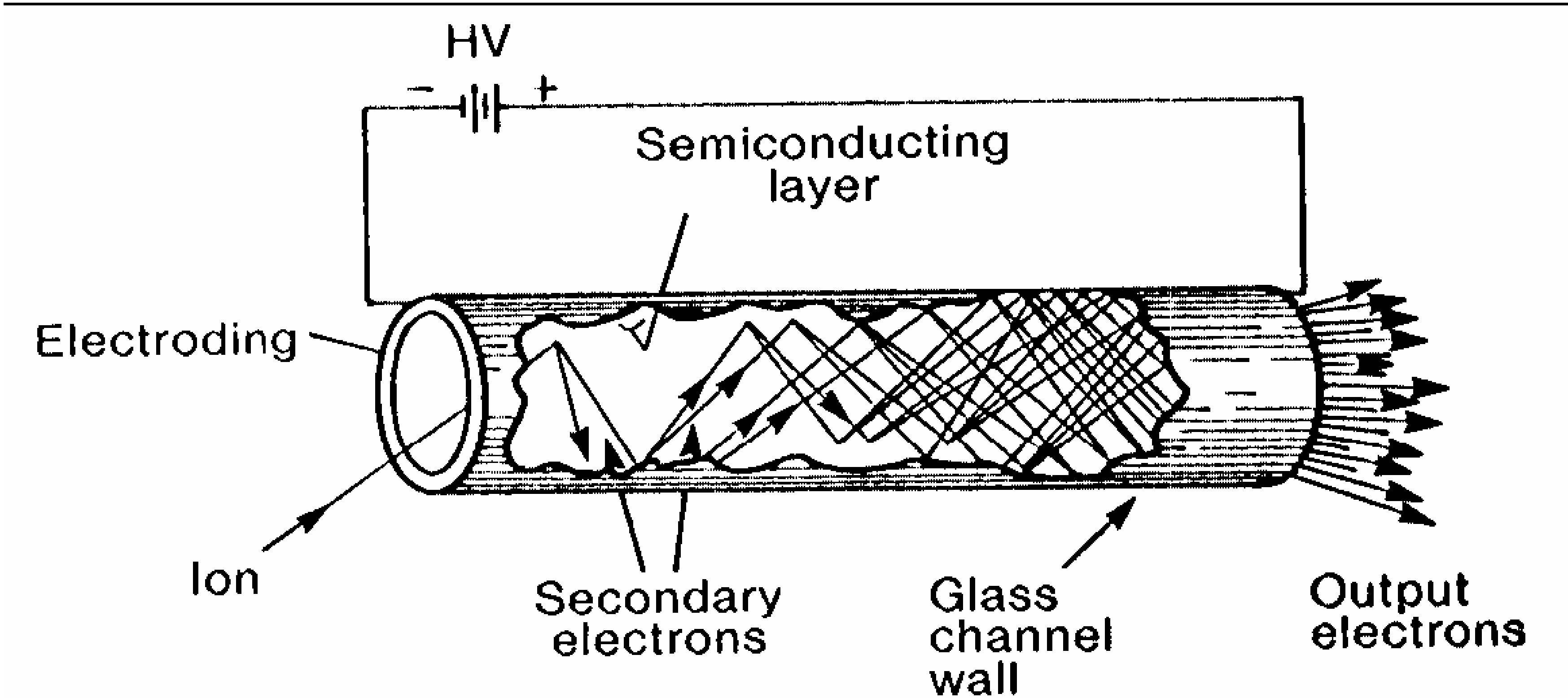
Kenngrößen:

Passenergie : 5 eV

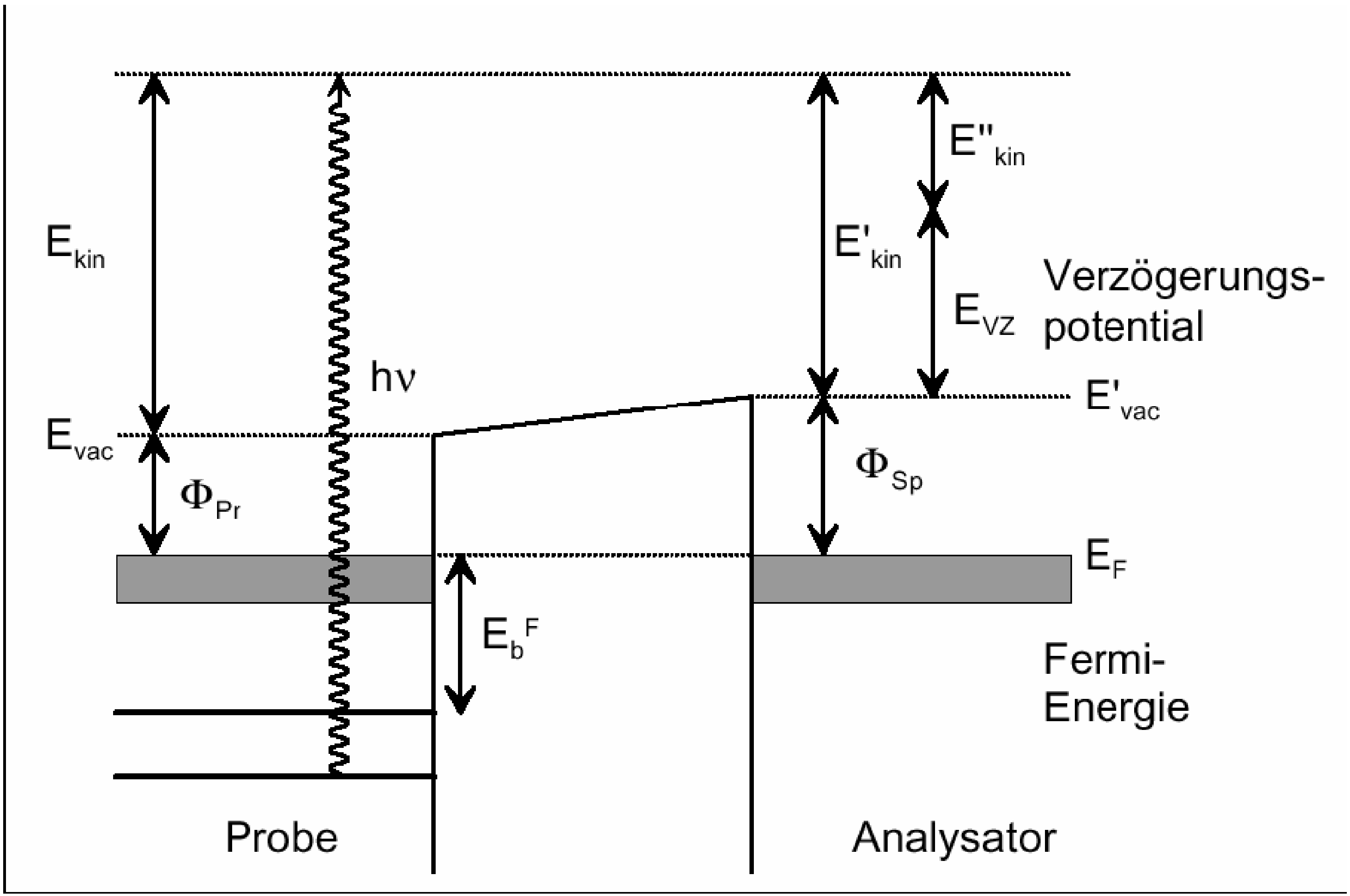
Winkelakzeptanz : 1°

max. Rate : 30.000 /s

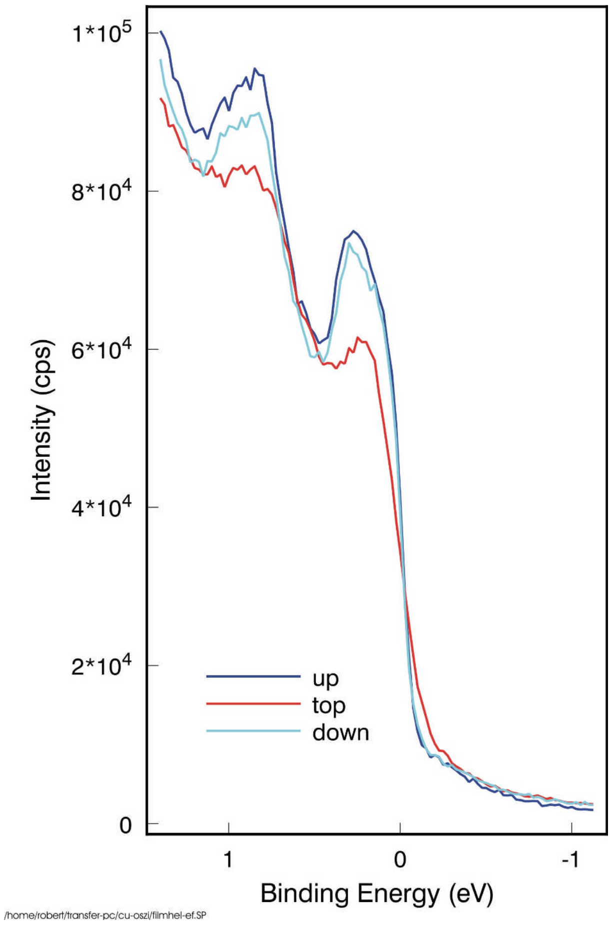
Detector: Channeltron



Energy Calibration



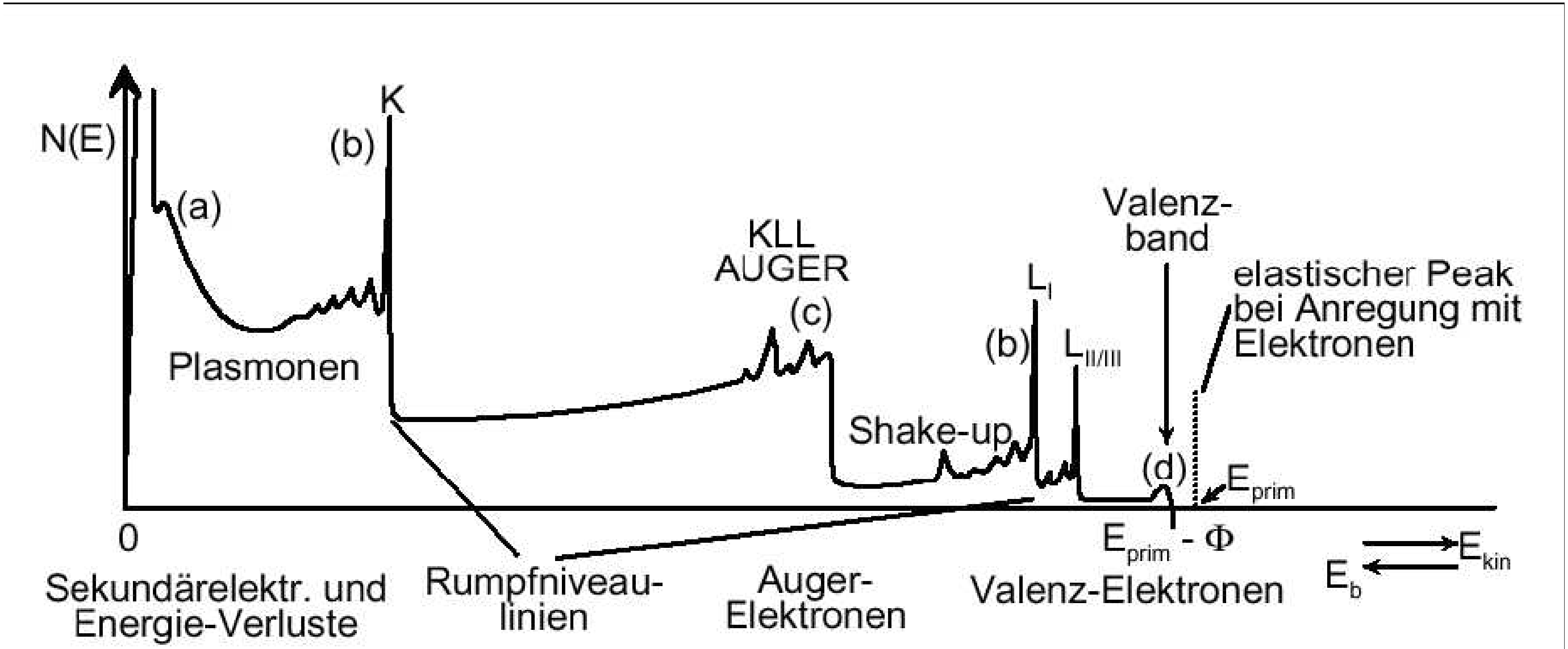
Fermi Edge



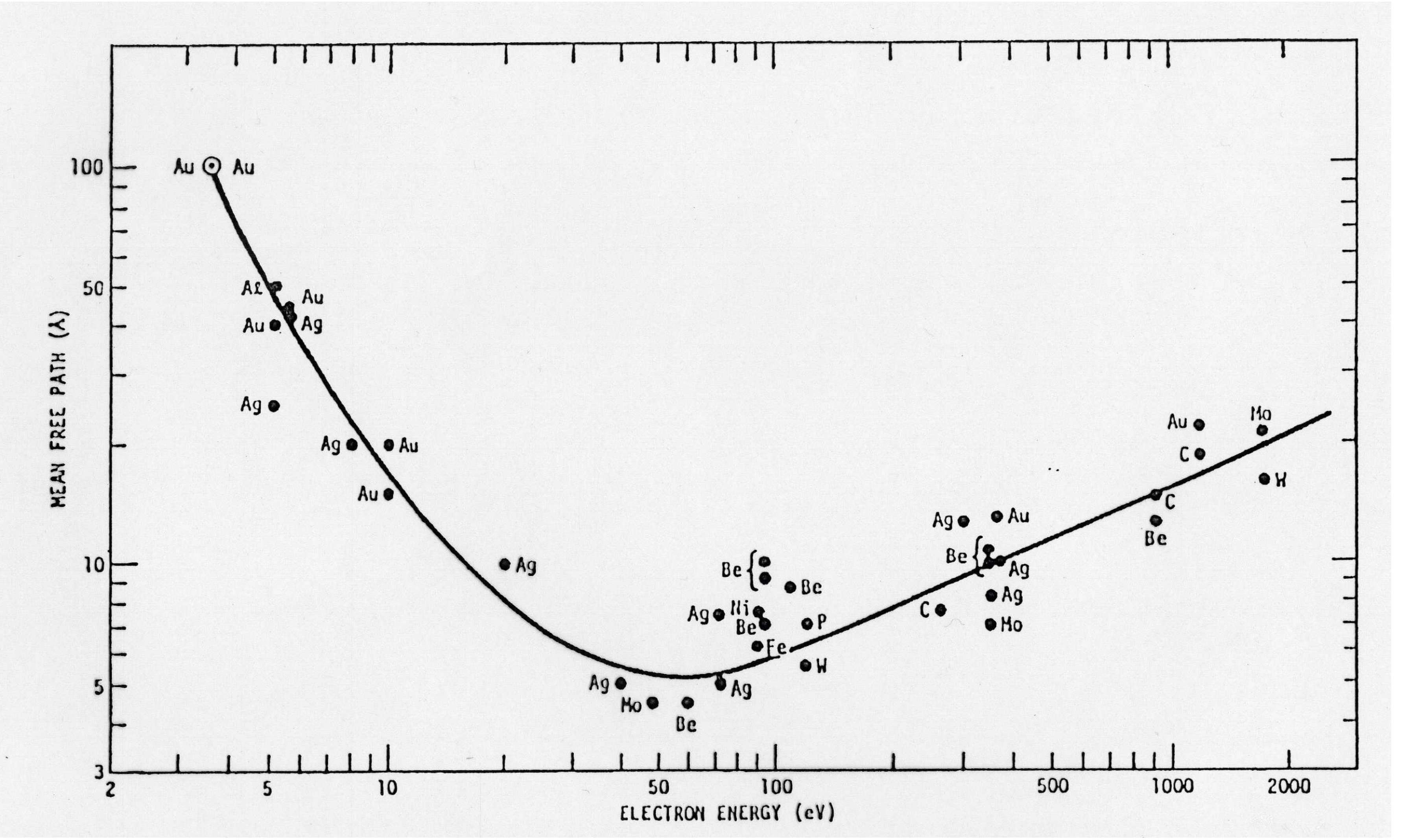
Thermal broadening of the Fermi energy due to the Boltzmann „tail“:

UPS of Cu at 450 K blue and 623 K red.

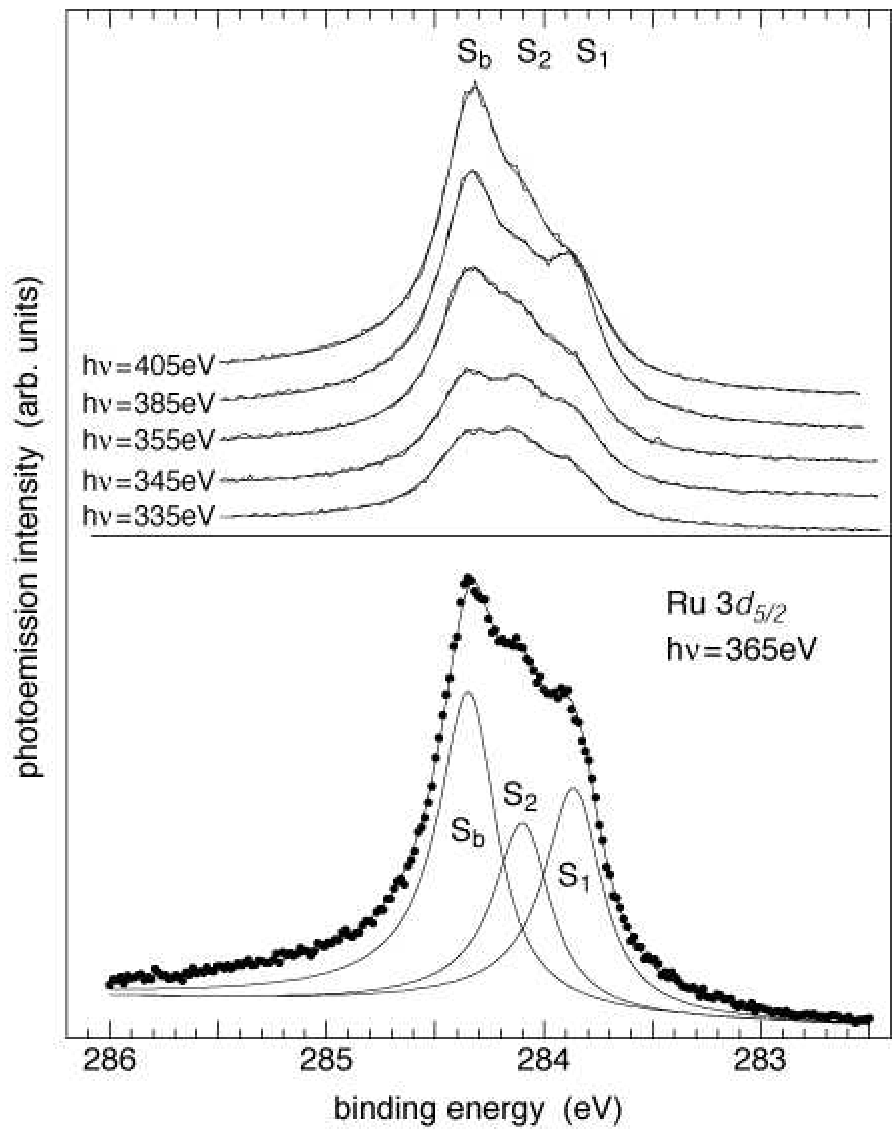
Typical XP spectrum



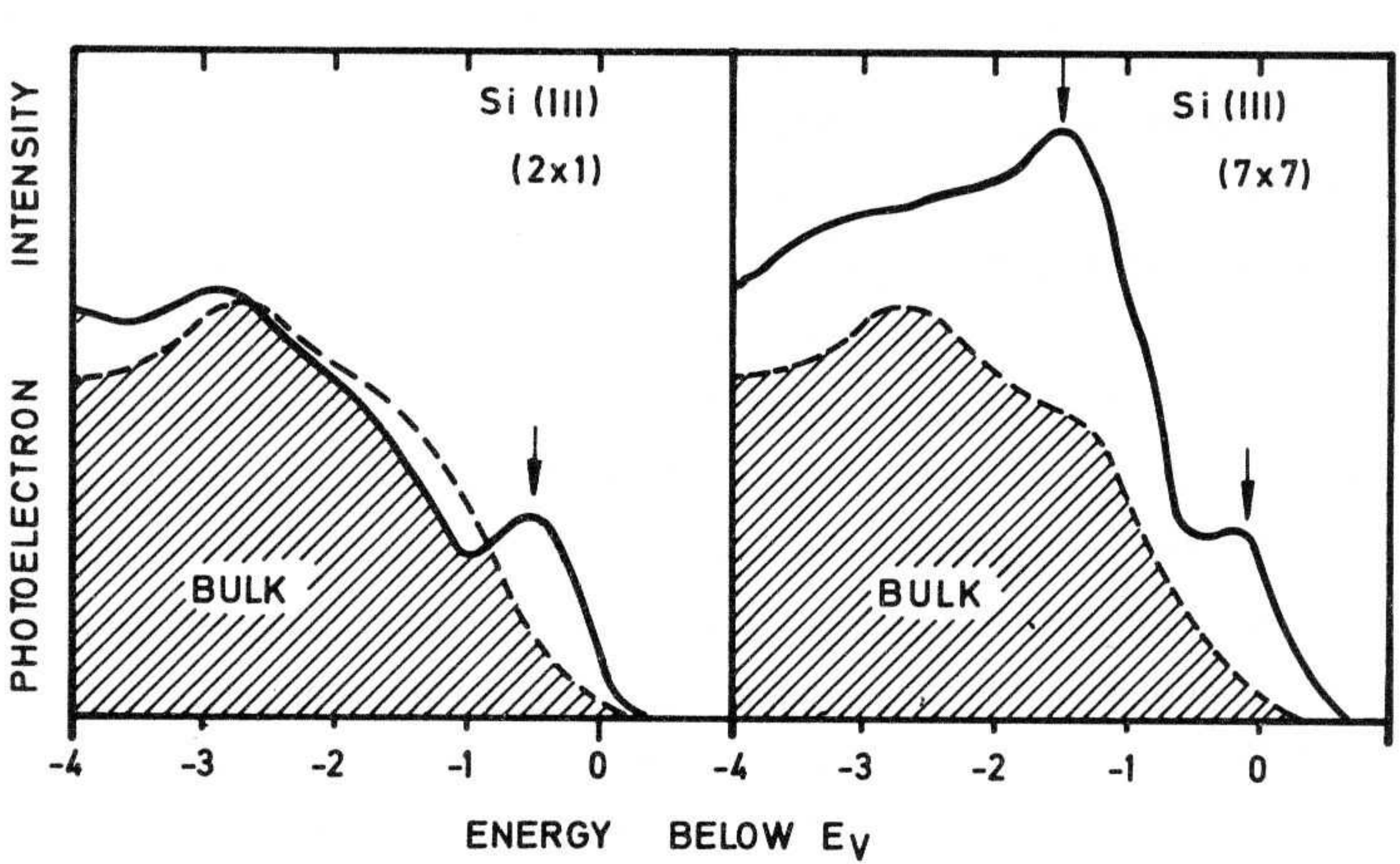
Mean free path



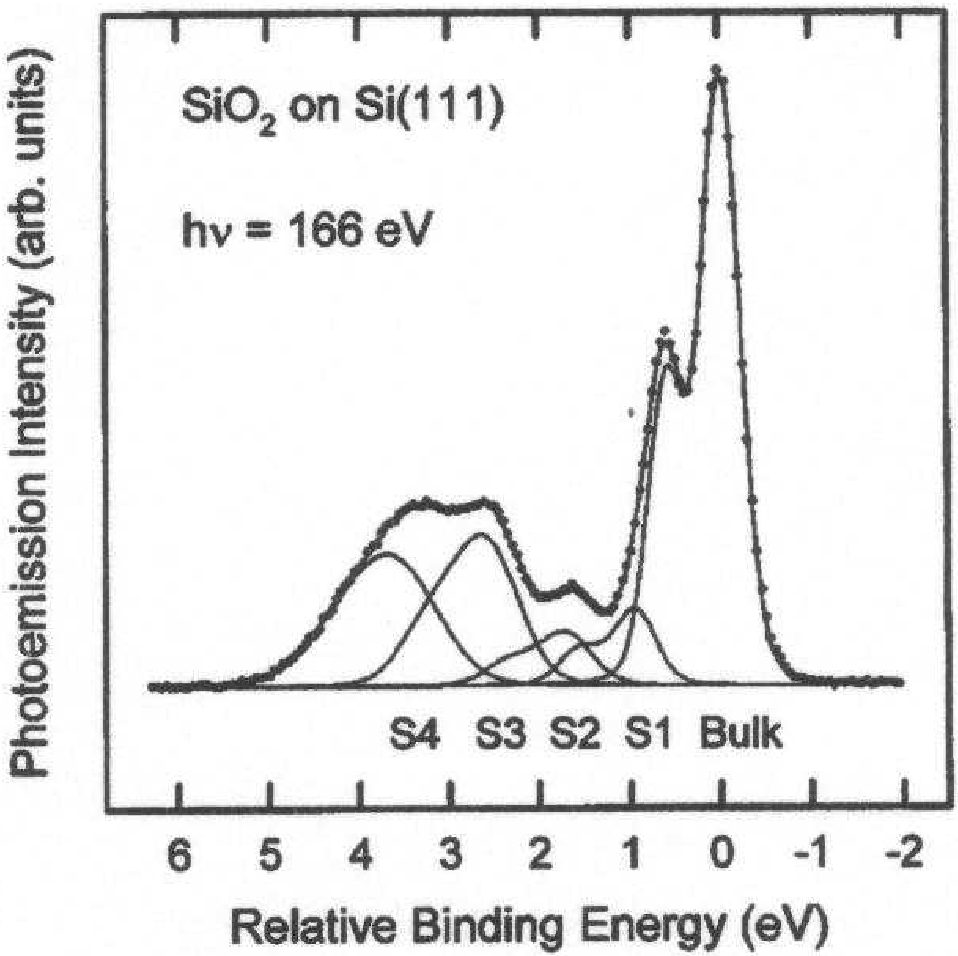
Ru 3d $_{5/2}$ core level spectra



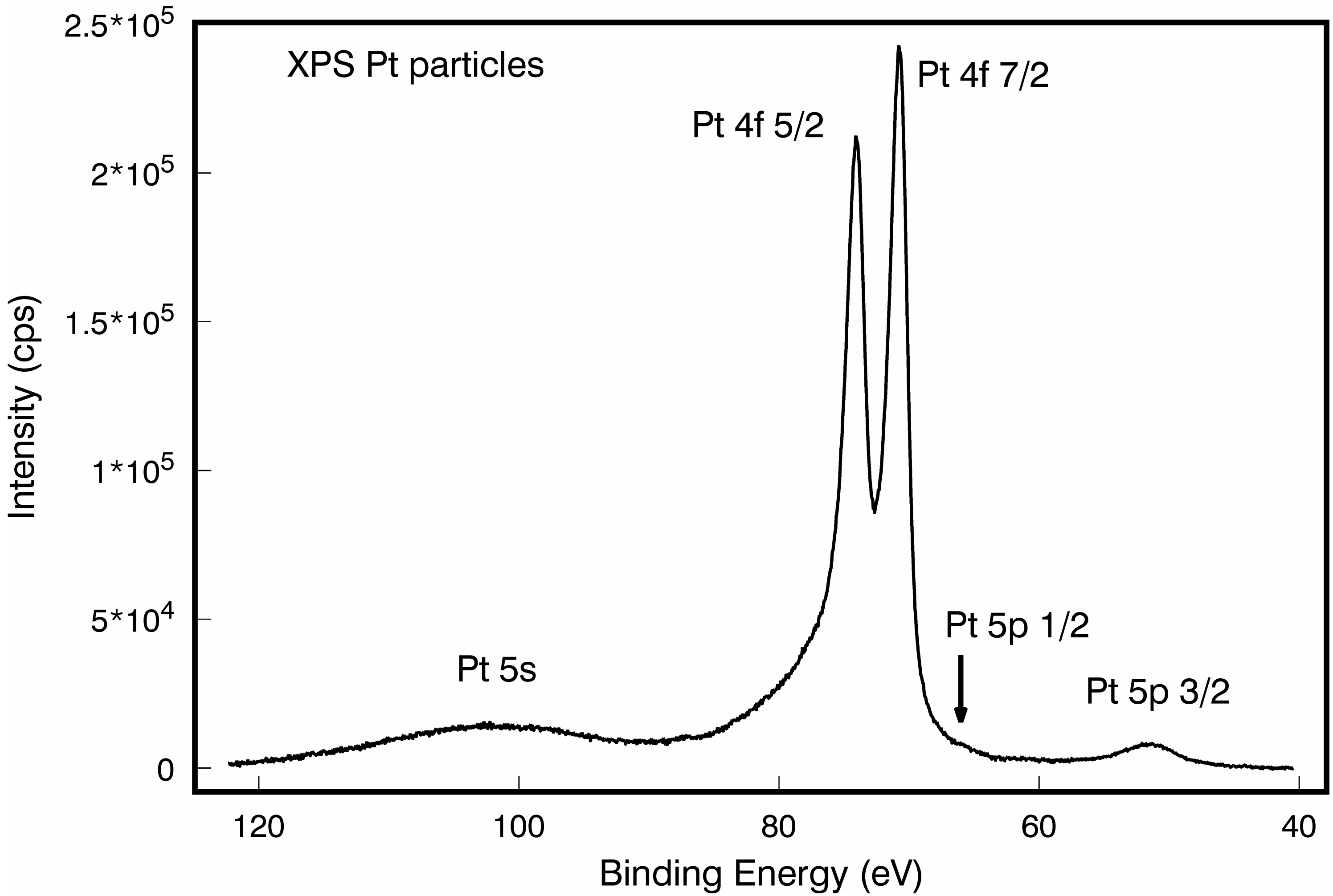
Surface Sensitivity (reconstruction of Si(111) surface)



High resolution Si2p photoelectron spectrum of SiO_2/Si(111)

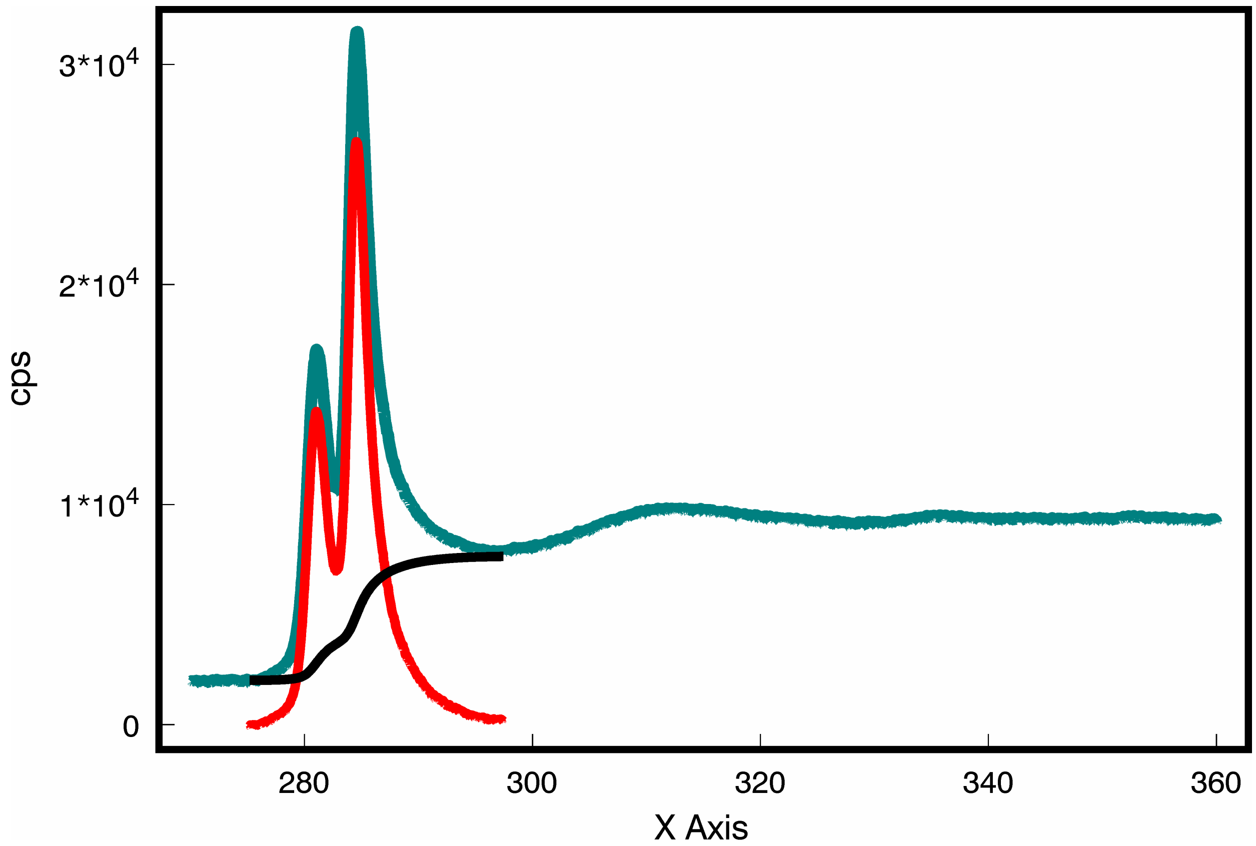


Pt 4f spectrum

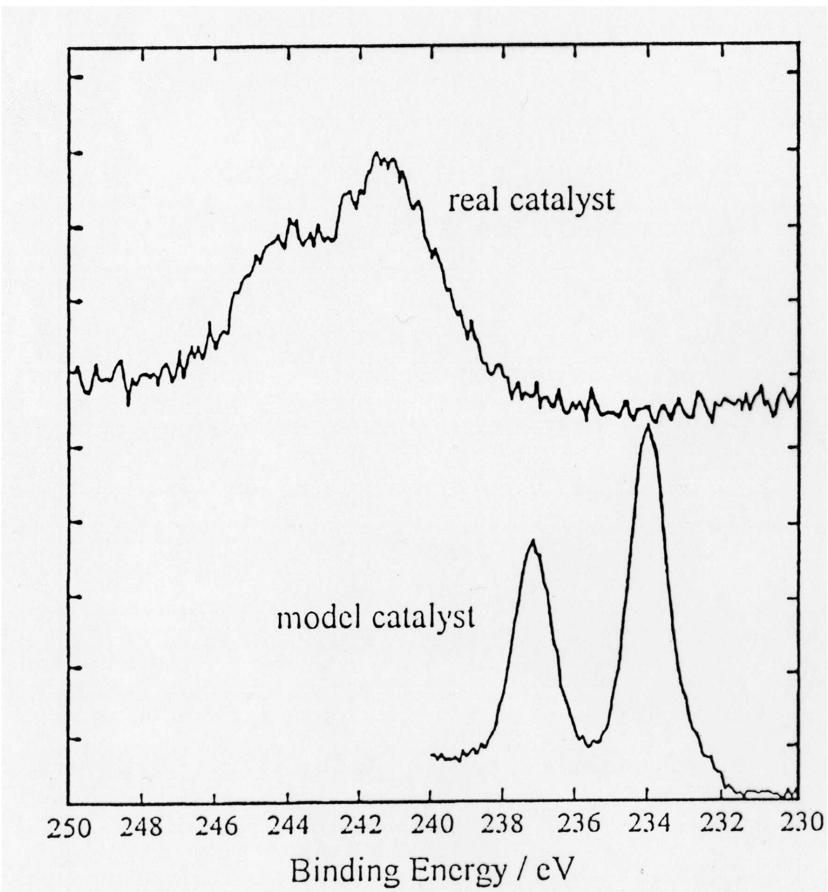


Background Subtraction

Ru metal on nanotube carbon



Line profile modification by charging



Mo oxide on silica

real catalyst is powder sample after impregnation and calcination.

Which parameters do influence the binding energy?

$$E_{kin} = h\nu - E_b - \Phi$$

$$E_b^{eff} = E_b + \Delta E_{chem} + \Delta E_{Mad} + \Delta E_r^{int} + \Delta E_r^{ext}$$

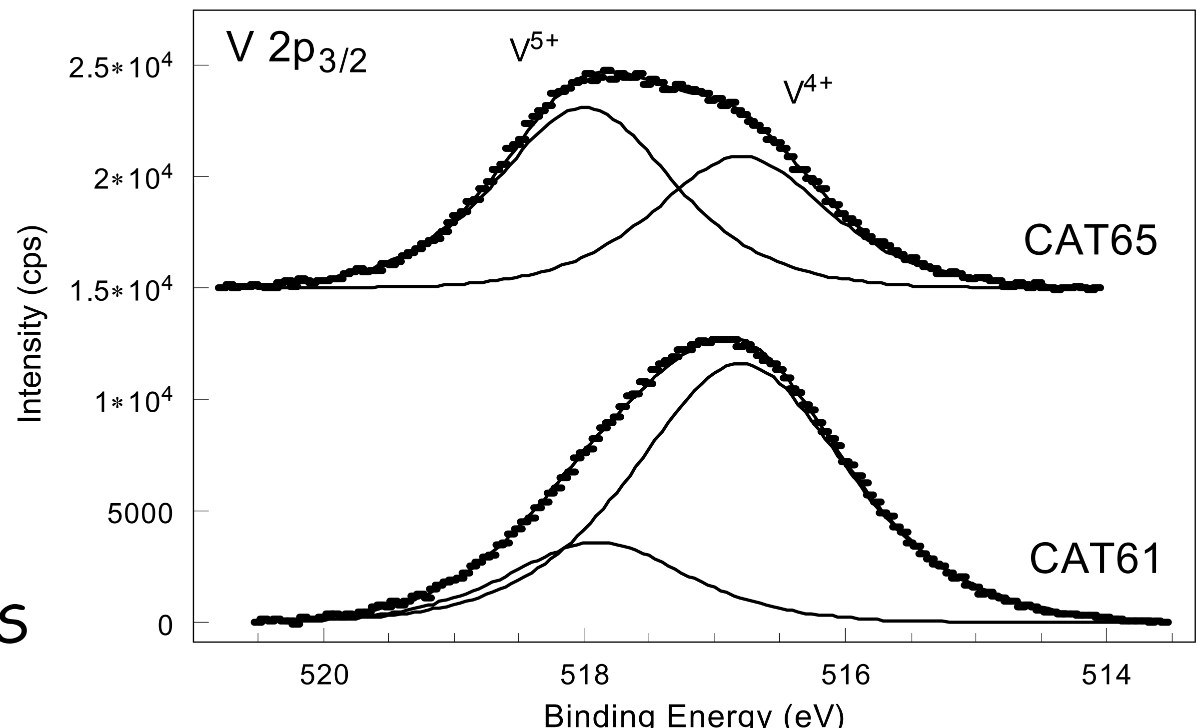
ΔE_{chem} : chemical shift

ΔE_{Mad} : Madelung Term

ΔE_r^{int} : intraatomic relaxation

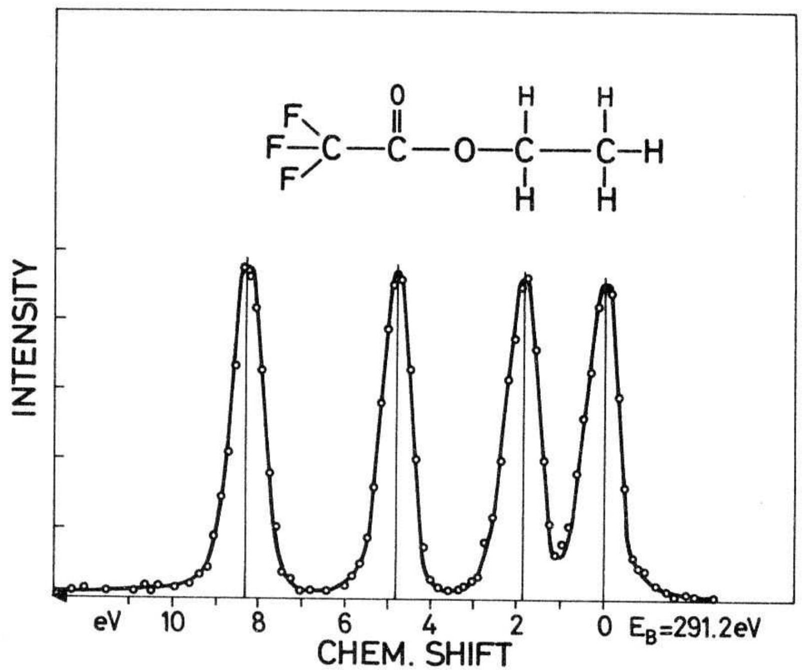
ΔE_r^{ext} : interatomic relaxation

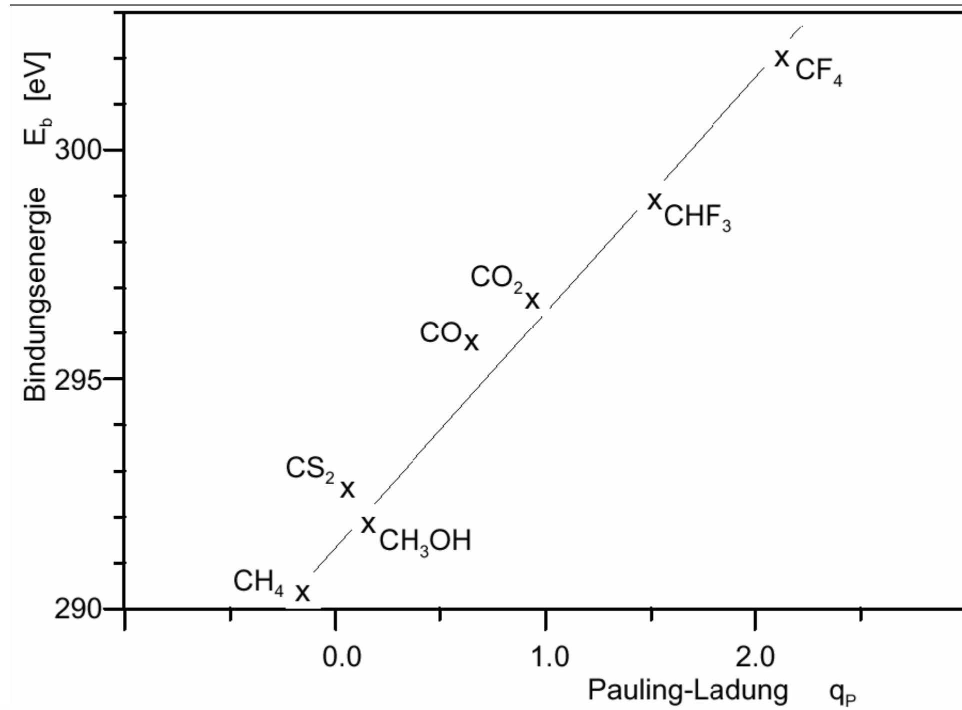
Oxidation state by XPS



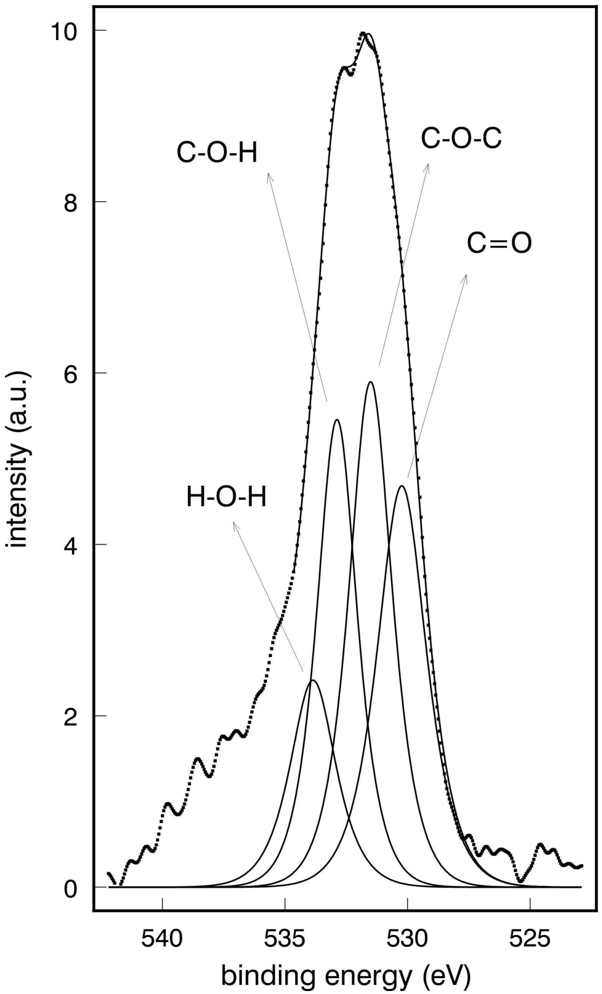
conventional XPS after catalytic operation in attached prep chamber: data at 300 K

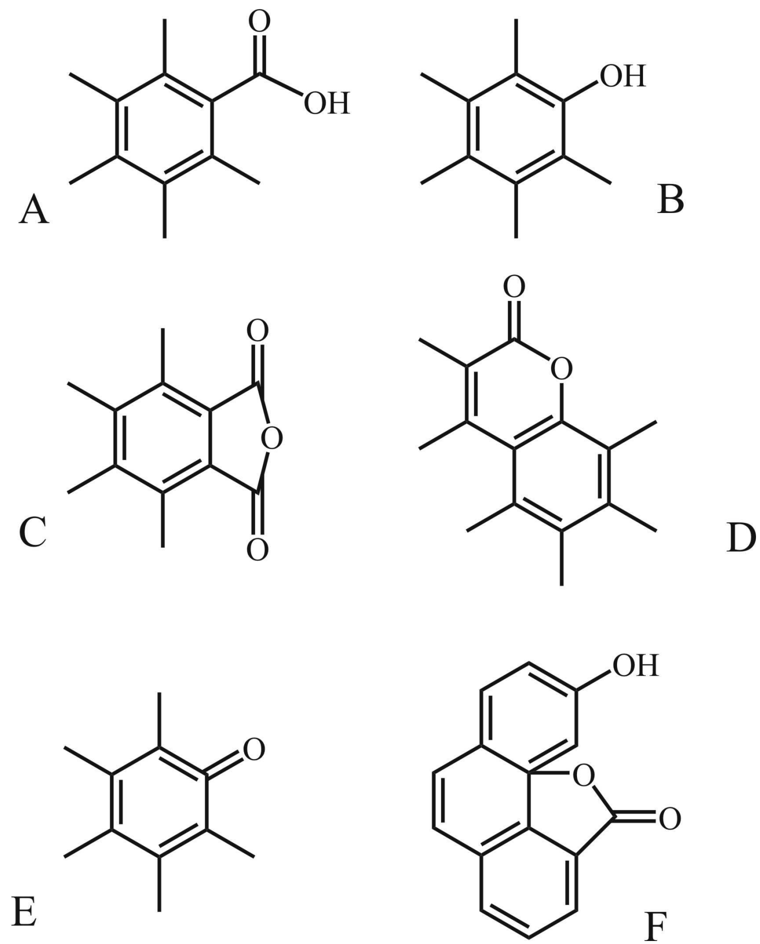
Chemical Shift



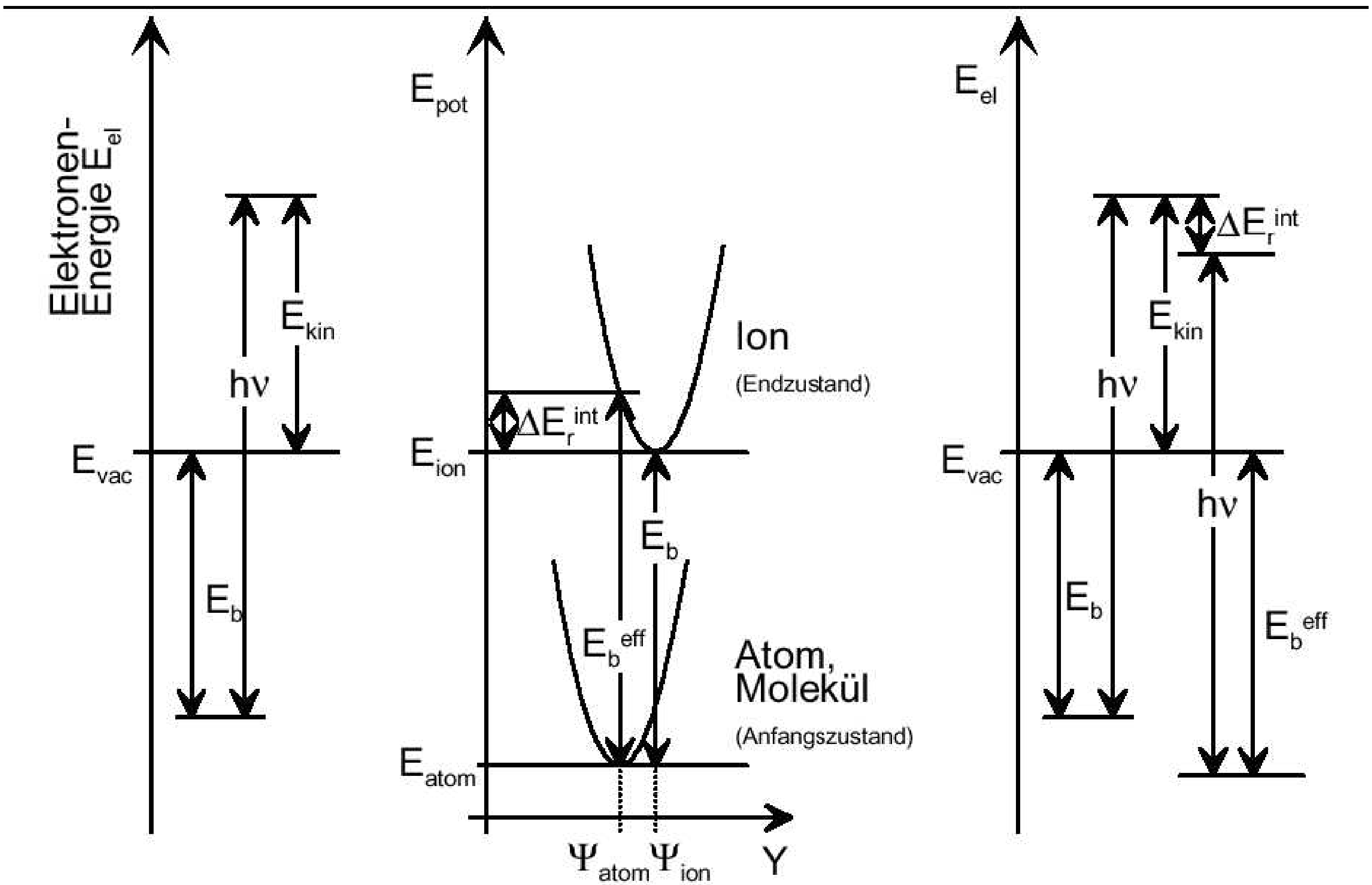


A simple line: oxygen 1s





Relaxation Effects



Homogeneous sample lateral and in depth

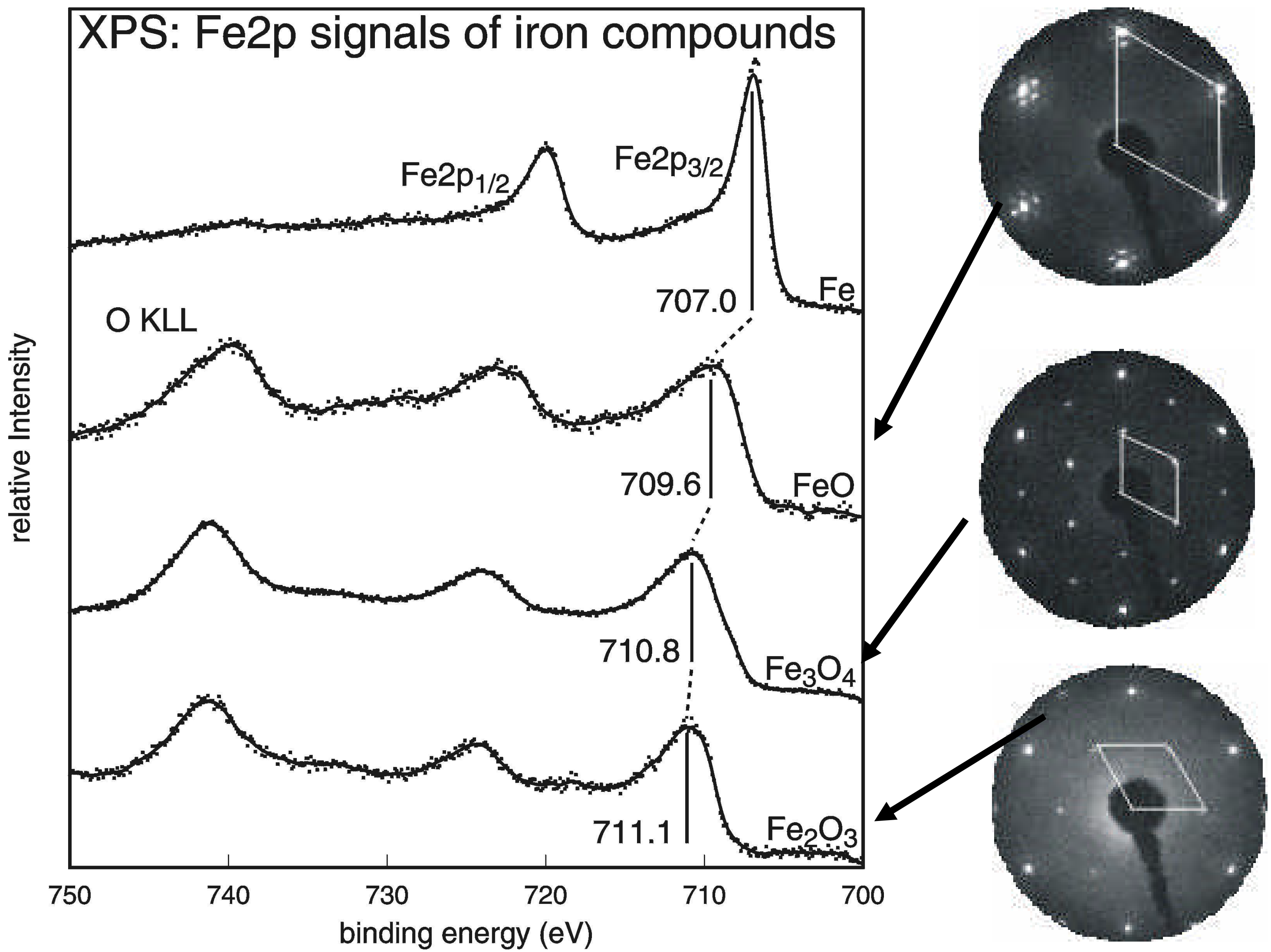
I = f(instrument) (transmission function of the analyser)

+ f(electron-photon interaction) (cross sections or reference samples)

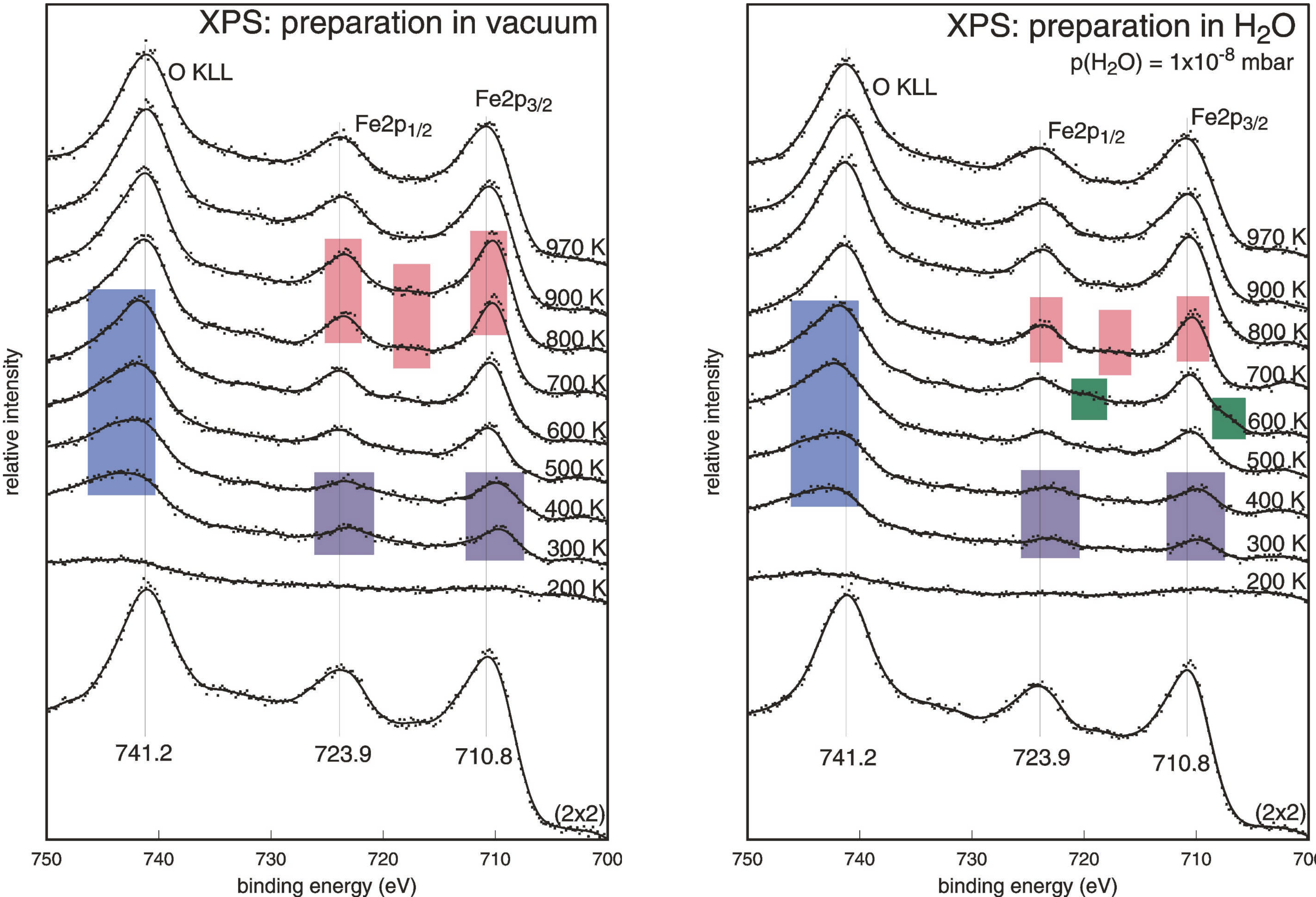
+ f(electron-electron interaction) (mean free path)

+ f(atomic abundance)

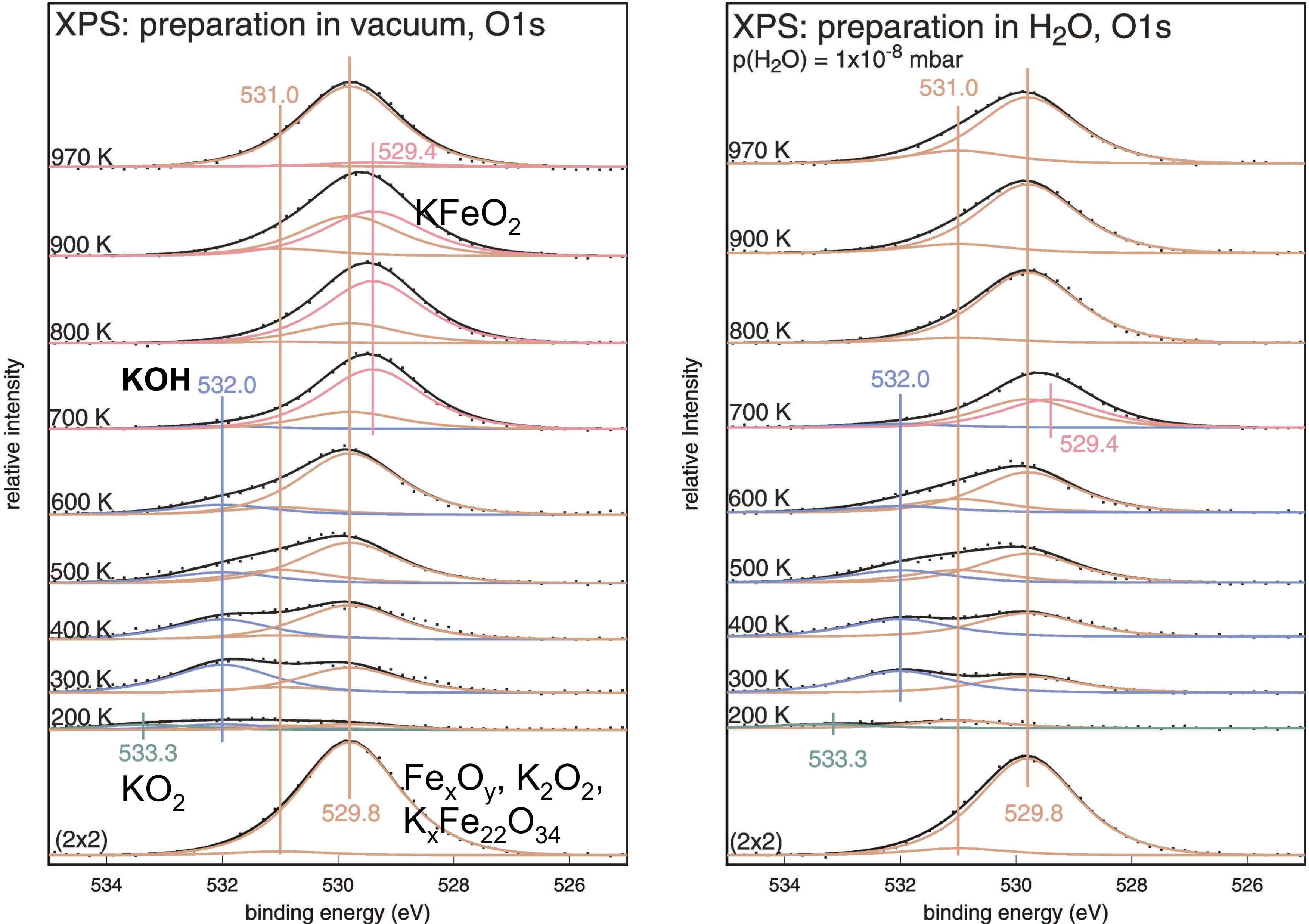
XPS - Referenzspektren der Oxide



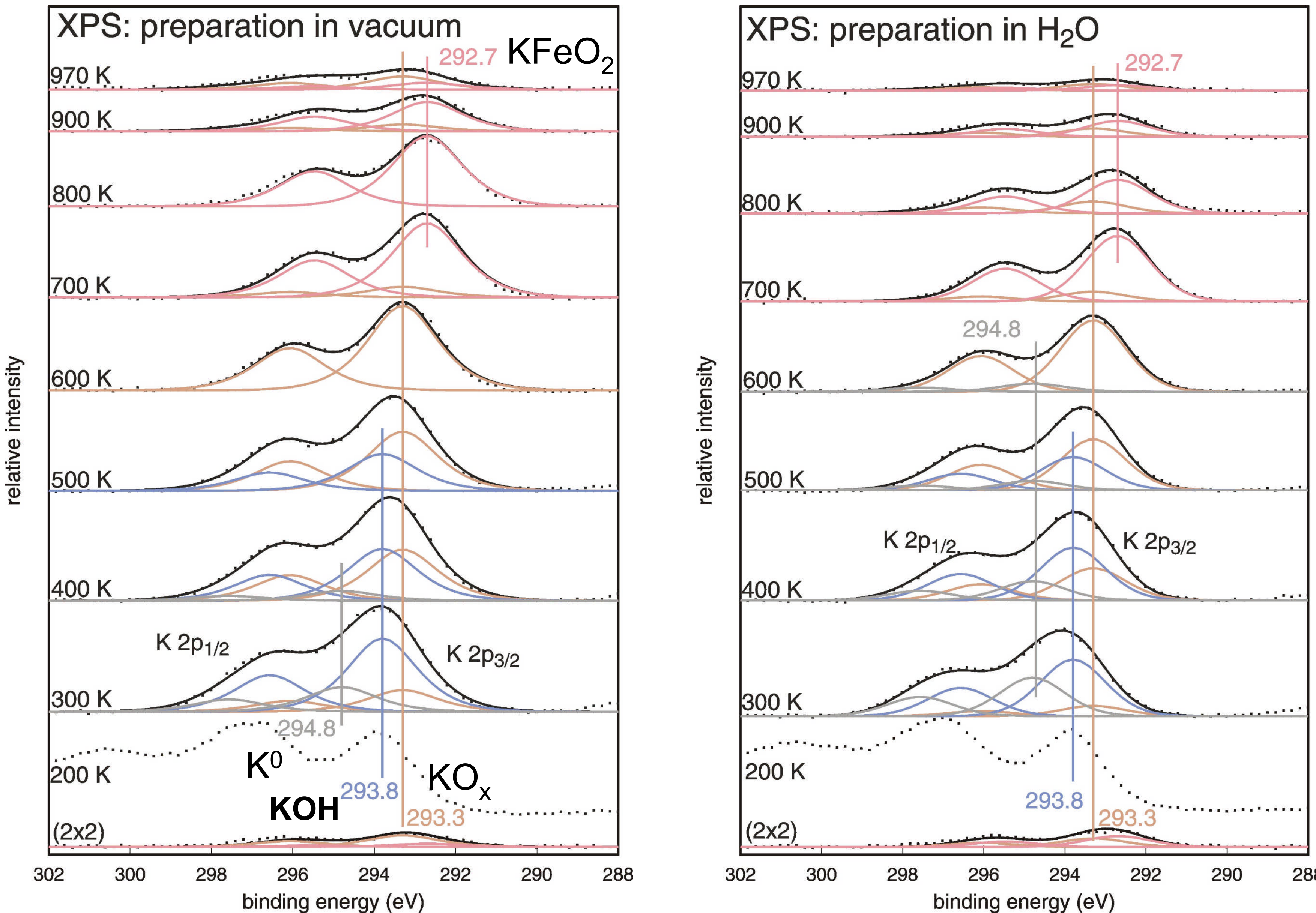
Präparationszyklus - Fe 2p Spektren



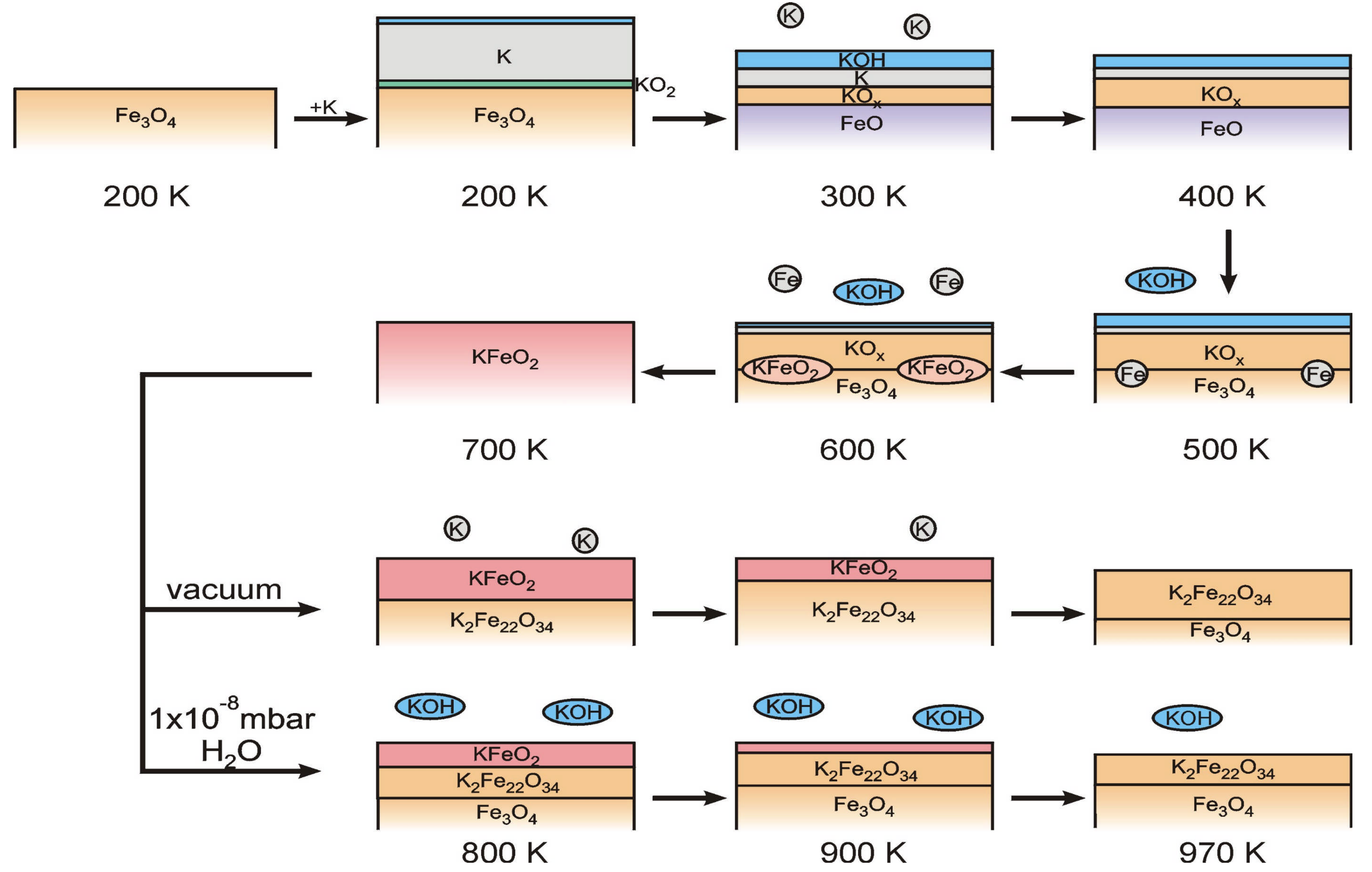
Präparationszyklus - O 1s Spektren



Präparationszyklus - K 2p Spektren



Wachstum

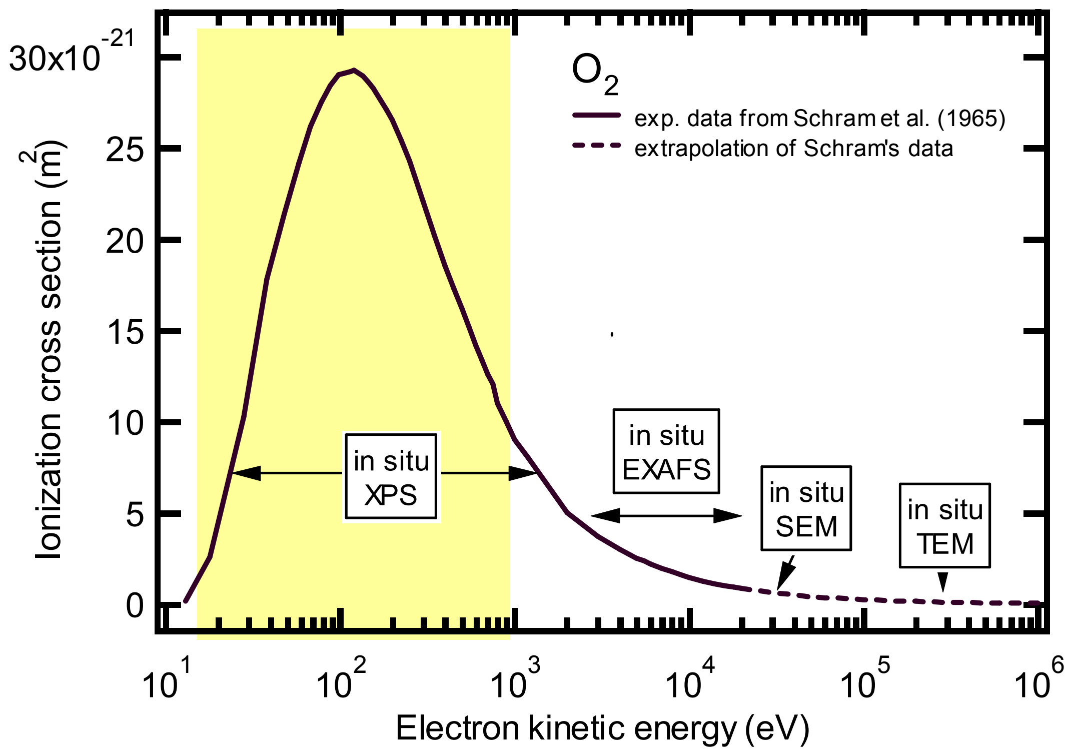


Fe_3O_4
+K
K
KO_2
Fe_3O_4
KOH
K
KO_x
FeO
KO_x
FeO
200 K
200 K
300 K
400 K
KOH
Fe
KOH
Fe
$KFeO_2$
KO_x
$KFeO_2$
$KFeO_2$
Fe_3O_4
KO_x
Fe
Fe
Fe_3O_4
700 K
600 K
500 K
vacuum
$KFeO_2$
$K_2Fe_{22}O_{34}$
$KFeO_2$
$K_2Fe_{22}O_{34}$
$K_2Fe_{22}O_{34}$
Fe_3O_4
1x10^{-8}mbar
H_2O
KOH
$KFeO_2$
$K_2Fe_{22}O_{34}$
Fe_3O_4
$K_2Fe_{22}O_{34}$
Fe_3O_4
$K_2Fe_{22}O_{34}$
Fe_3O_4
800 K
900 K
970 K

In situ XPS: obstacles

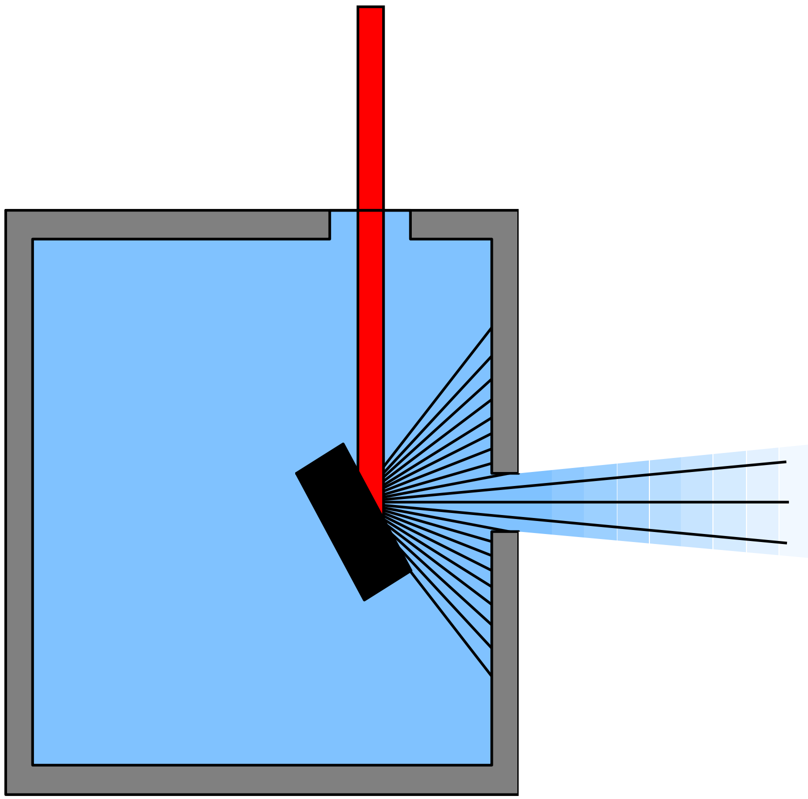
Fundamental limit:

elastic and inelastic scattering of electrons in the gas phase



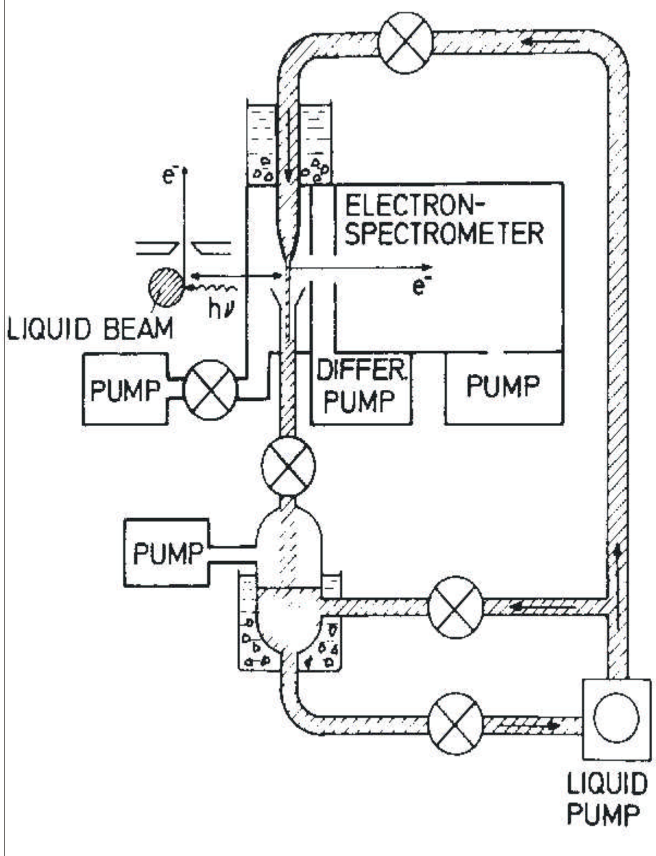
Technical issues: - Differential pumping to keep analyzer in high vacuum
- Sample preparation and control in a flow reactor

In situ XPS: basic concept



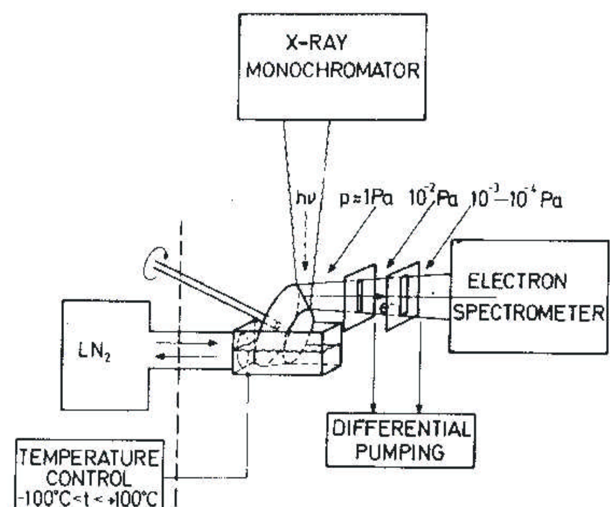
- Photons enter through a window
- Electrons and a gas jet escape through an aperture to vacuum

In situ XPS instruments: previous designs



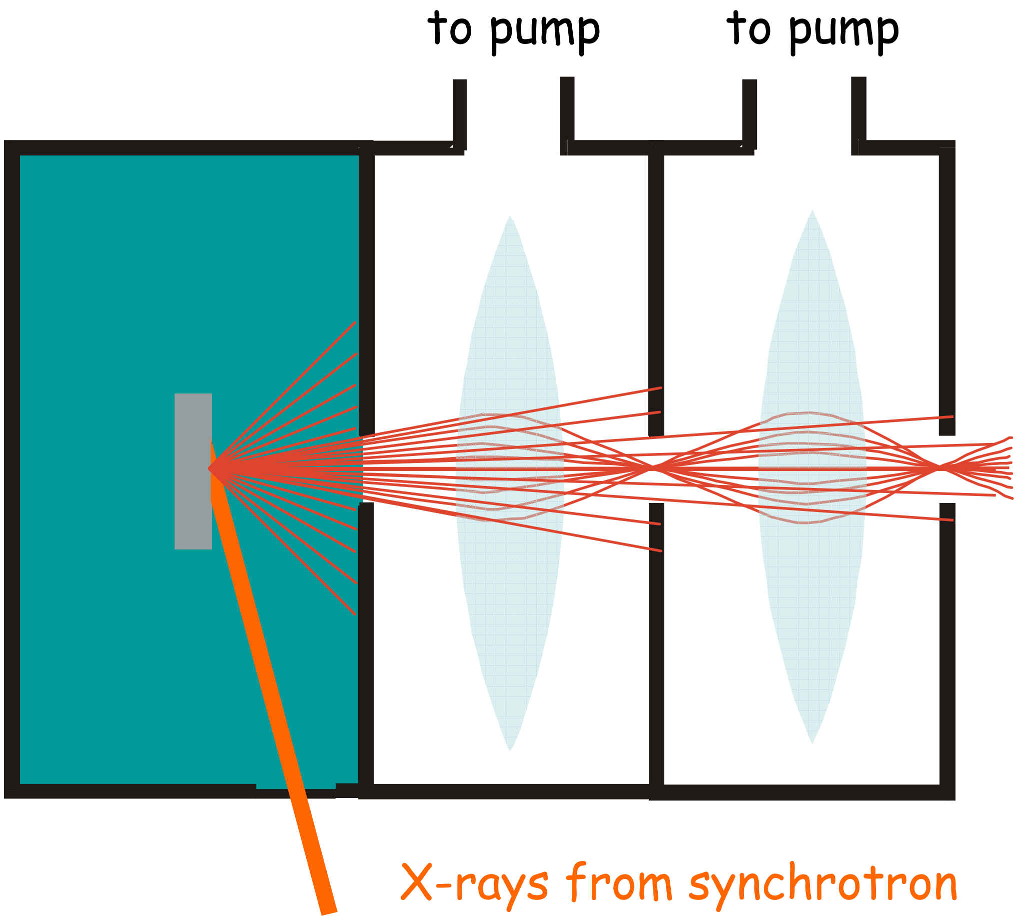
H. Siegbahn et al., J. Electron Spectrosc. Relat. Phenom. **2**, 319 (1973)

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



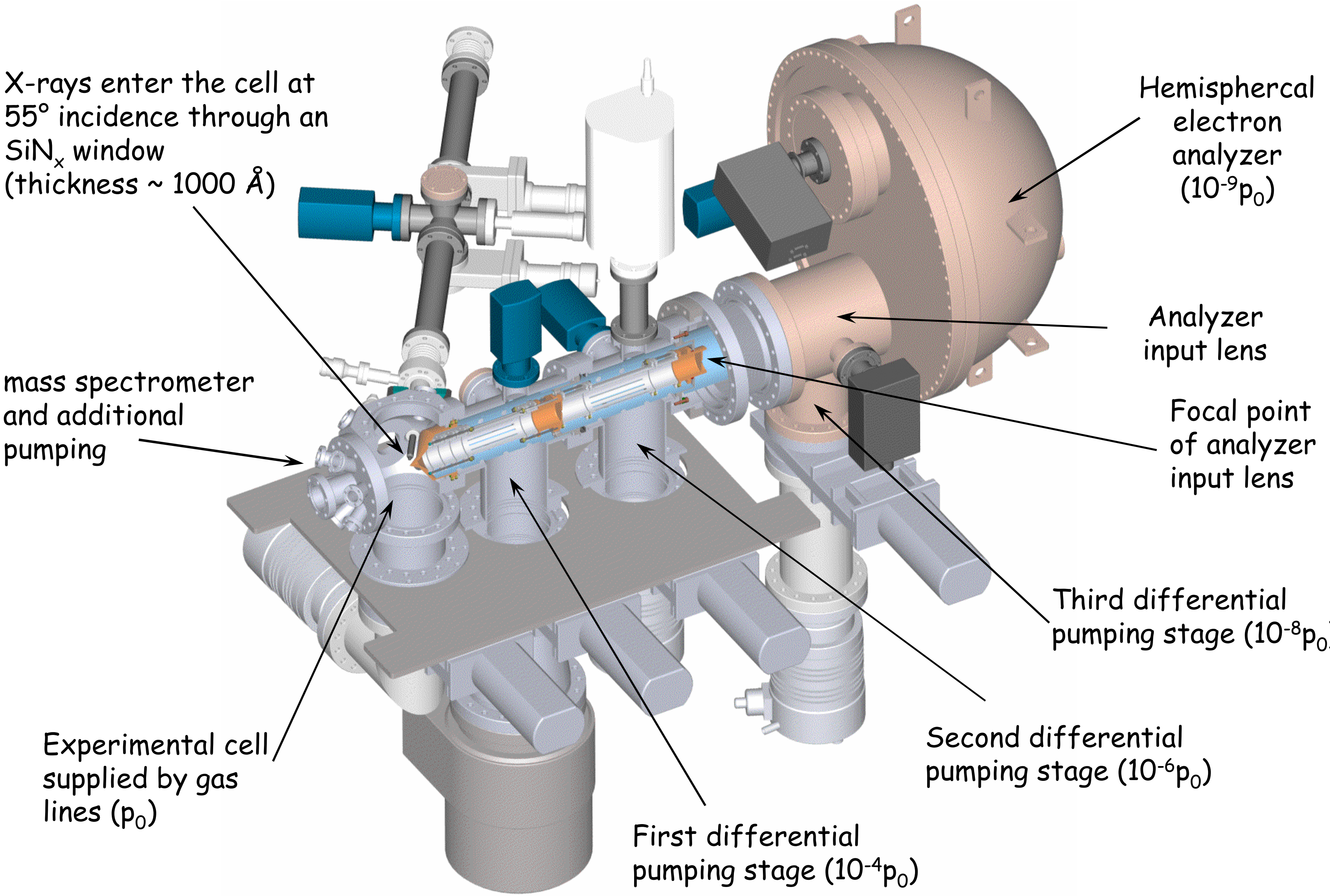
H. Siegbahn et al., J. Electron Spectrosc. Relat. Phenom. **24**, 205 (1981)

In situ XPS using differentially pumped electrostatic lenses



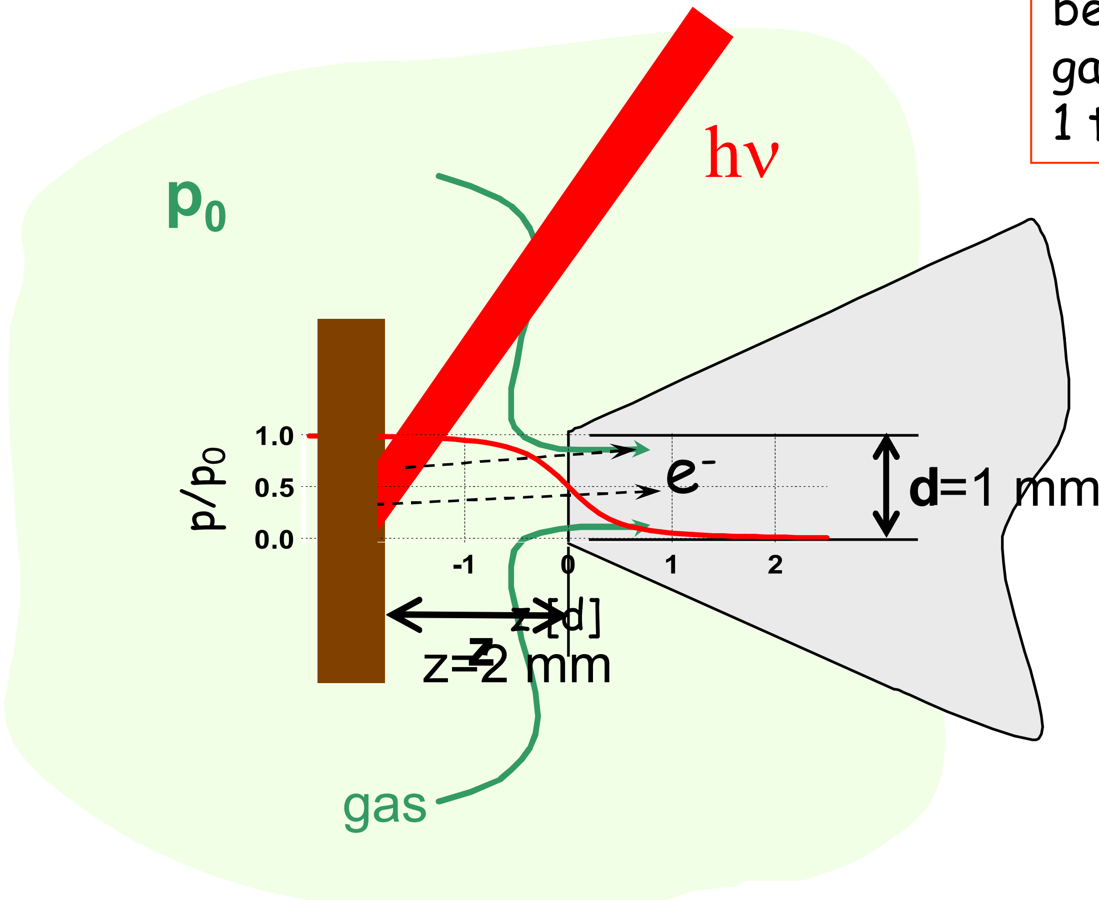
D.F. Ogletree, H. Bluhm, G. Lebedev, C.S. Fadley, Z. Hussain, M. Salmeron, Rev. Sci. Instrum. 73 (2002) 3872.

In situ XPS system



Close-up of sample-first aperture region

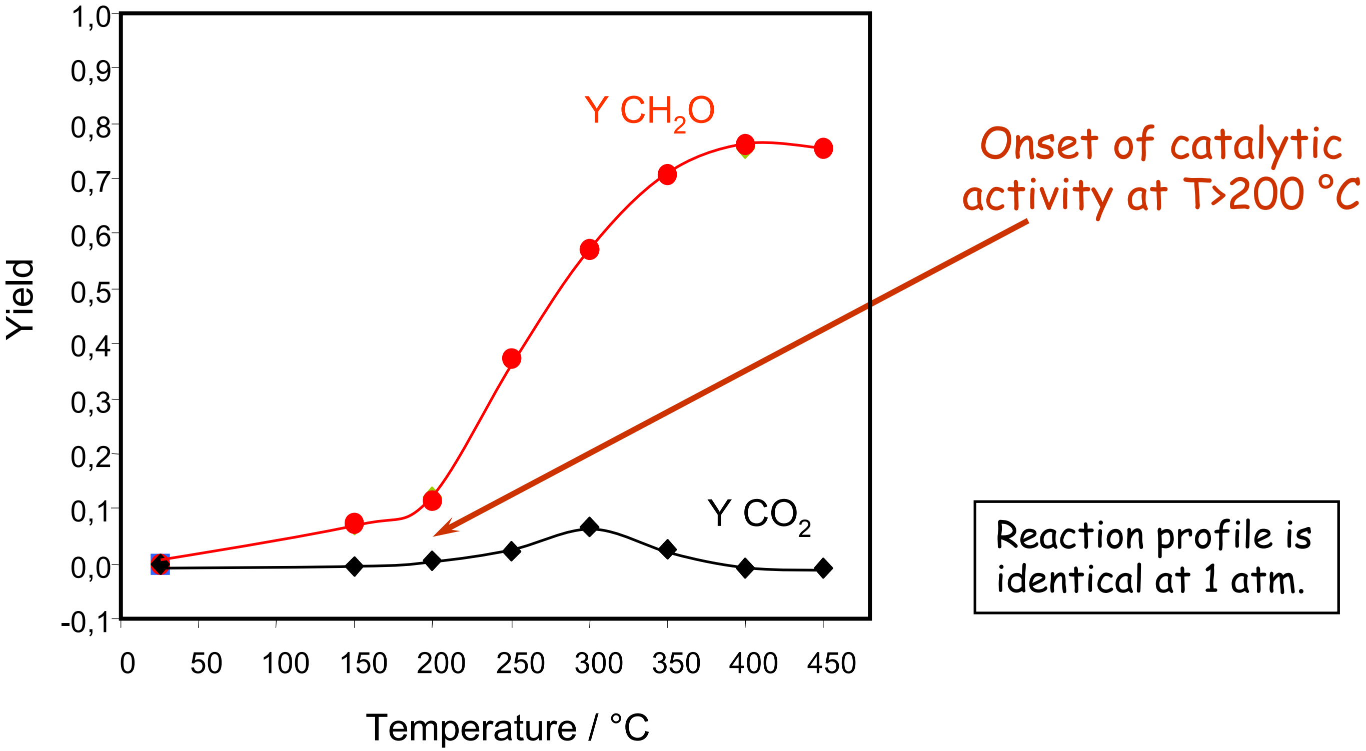
Gas phase composition can be measured by XPS.
gas phase signal:
1 torr·mm ~ a few monolayers



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



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).

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

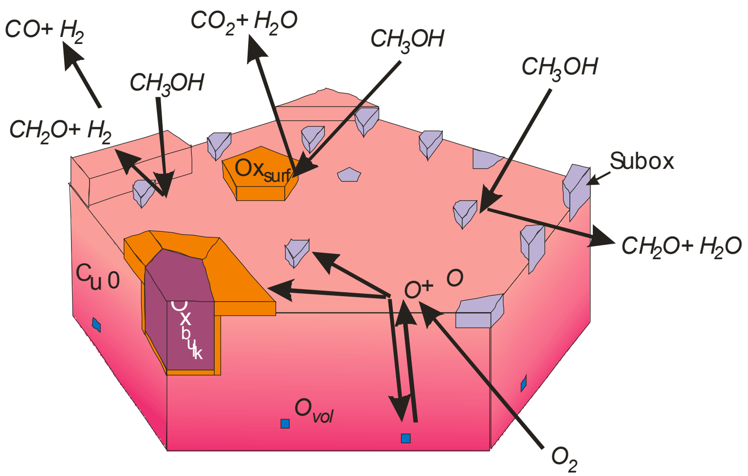
$$CH_3O^{-}(a) \longrightarrow CH_2O(g) + H^{+}(a)$$

In situ NEXAFS

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

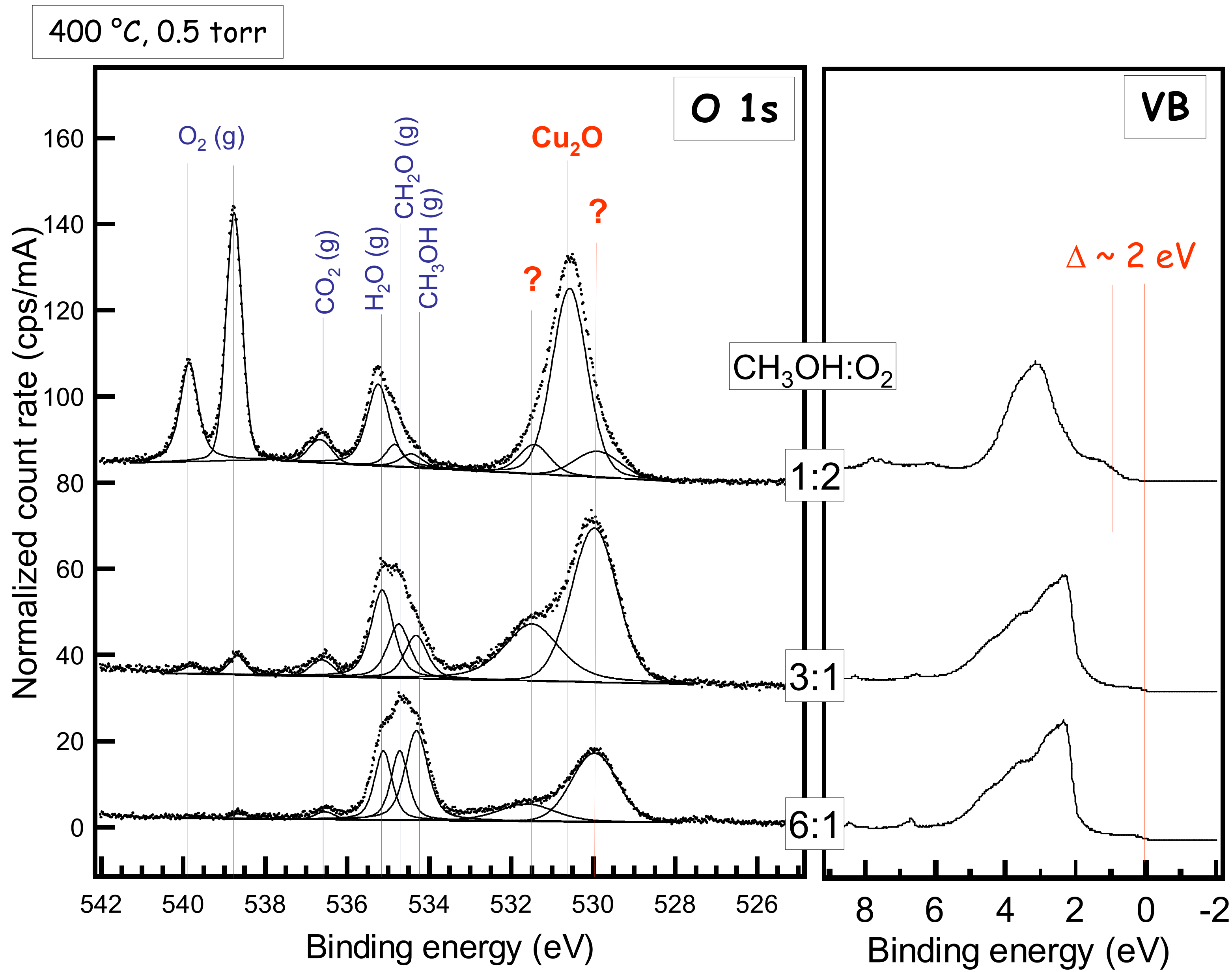
$CH_3OH + O_2$ ~ 0.5 mbar

suboxide phase:
- only present in situ



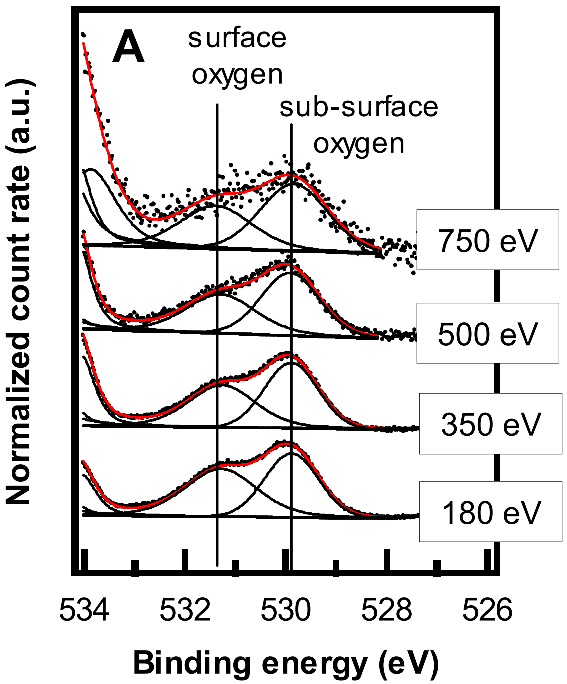
Questions for in situ XPS:
- Quantitative analysis of surface species
- Carbon species on the surface
- Depth-dependent analysis

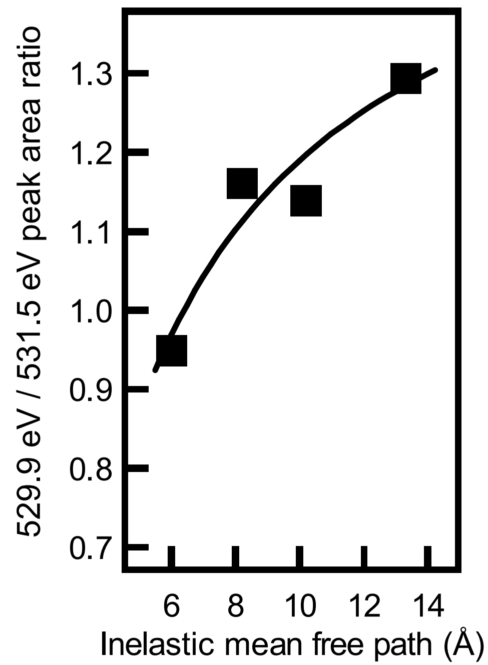
Methanol oxidation on Cu: O1s spectra

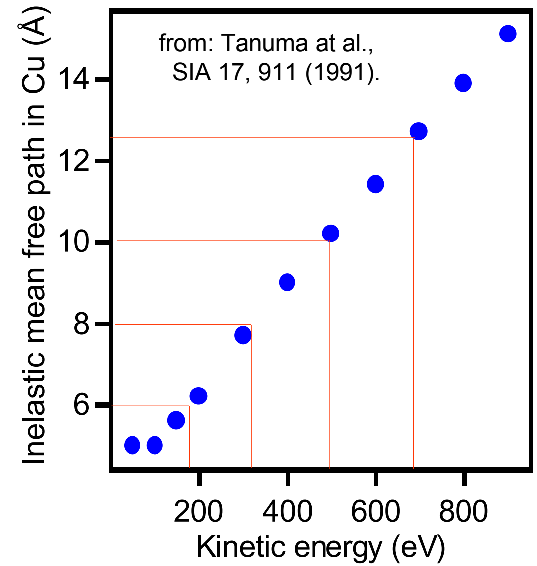


O1s depth profiling

$CH_3OH : O_2 = 3:1$







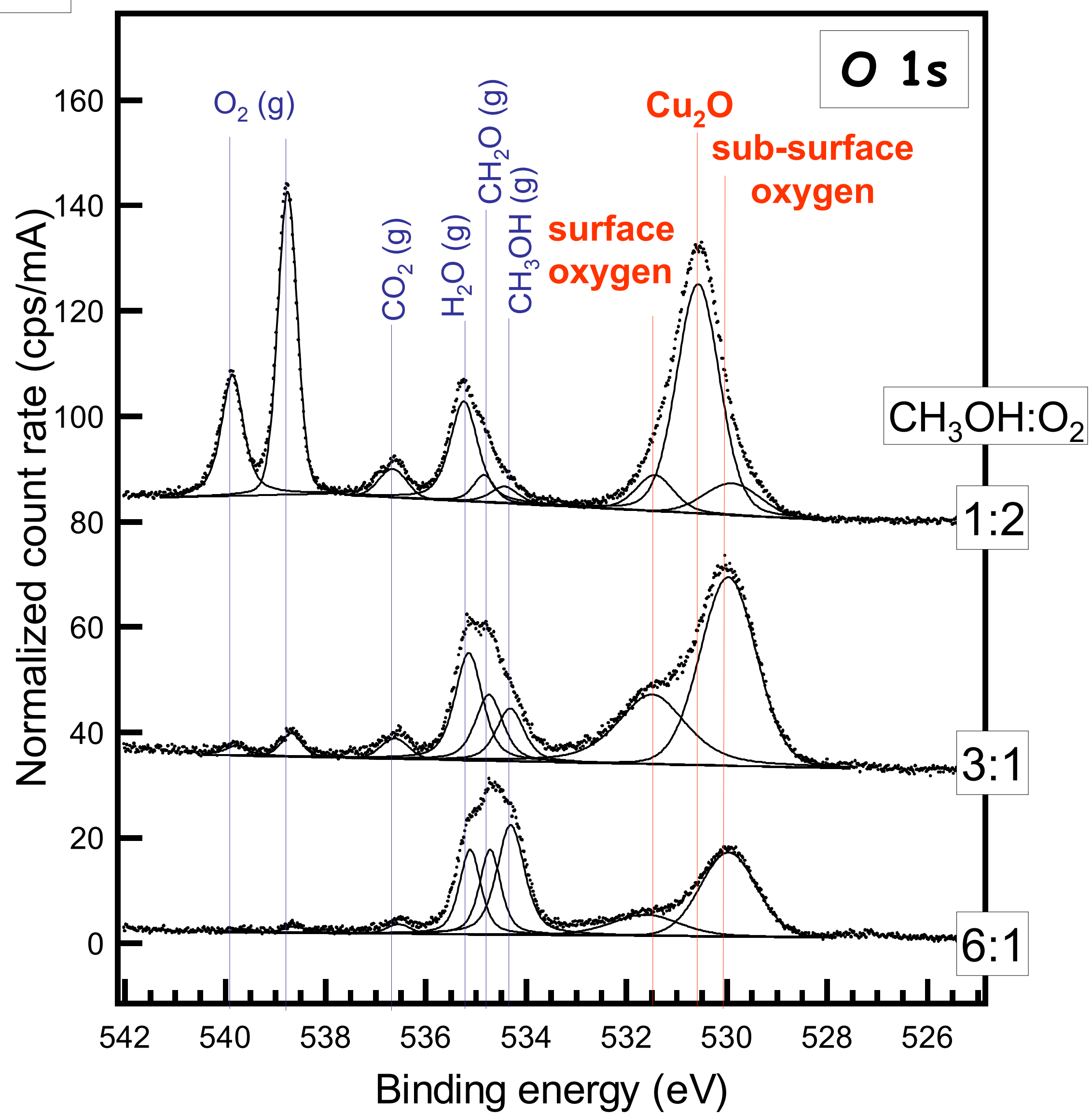
$$I_{529.9}/I_{531.5}=n_{529.9}/n_{531.5}\cdot\exp[-(z_{531.5}-z_{529.9})/\lambda]$$

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

H. Bluhm et al JPCB 108 (2004) 14340

Variation of the gas phase composition

400 °C

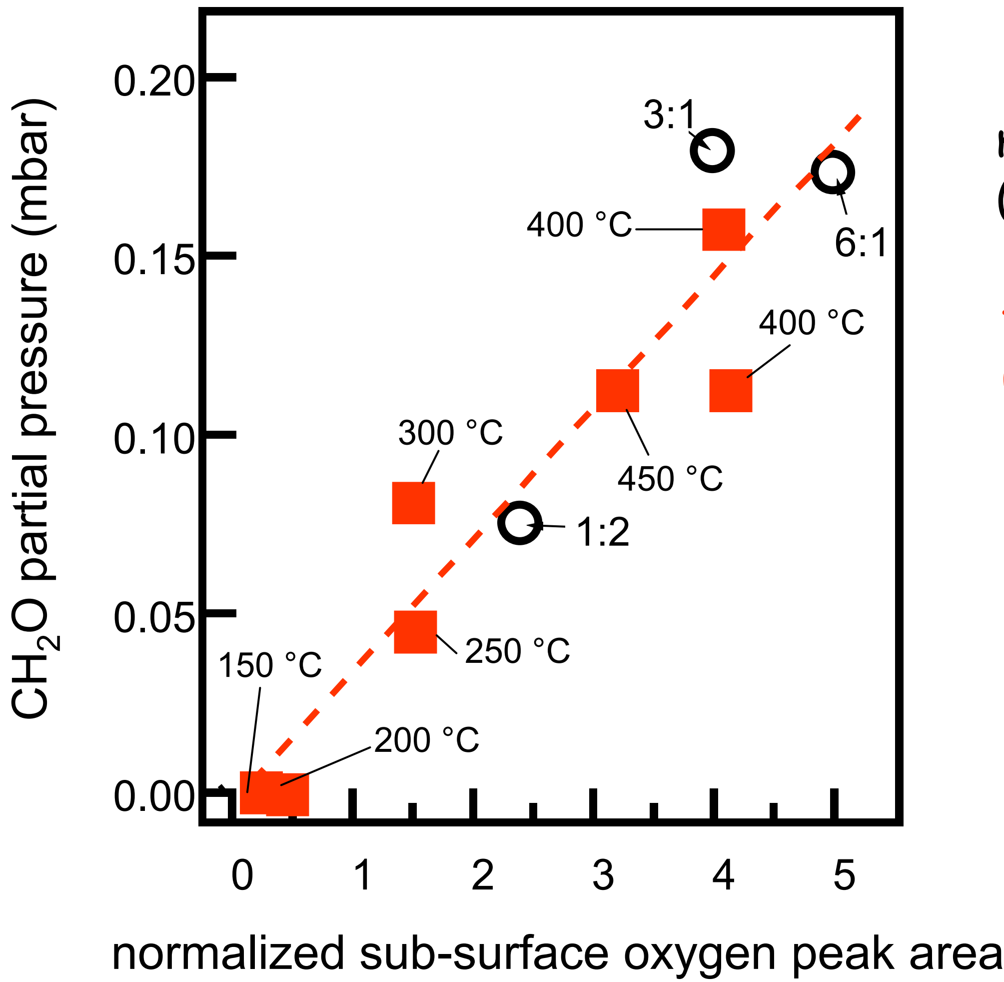


conversion CH_3OH (part. press. CH_3OH)	yield CH_2O (part. press. CH_2O)	yield CO_2 (part. press. CO_2)
0.68 0.053	0.46 0.075	0.22 0.072
0.58 0.167	0.45 0.179	0.13 0.103
0.38 0.307	0.35 0.173	0.03 0.030

partial pressures in mbar

Correlation of catalytic activity and surface species

CH_2O yield vs sub-surface oxygen peak area



mixing ratio series
(T = 400 °C)

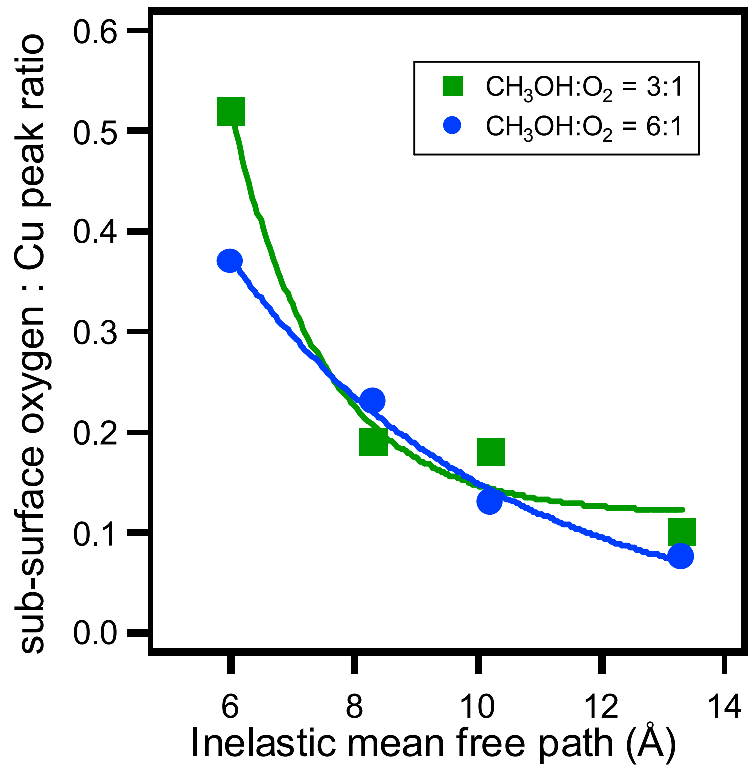
temperature series
($CH_3OH:O_2$=3:1)

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

Depth profiling

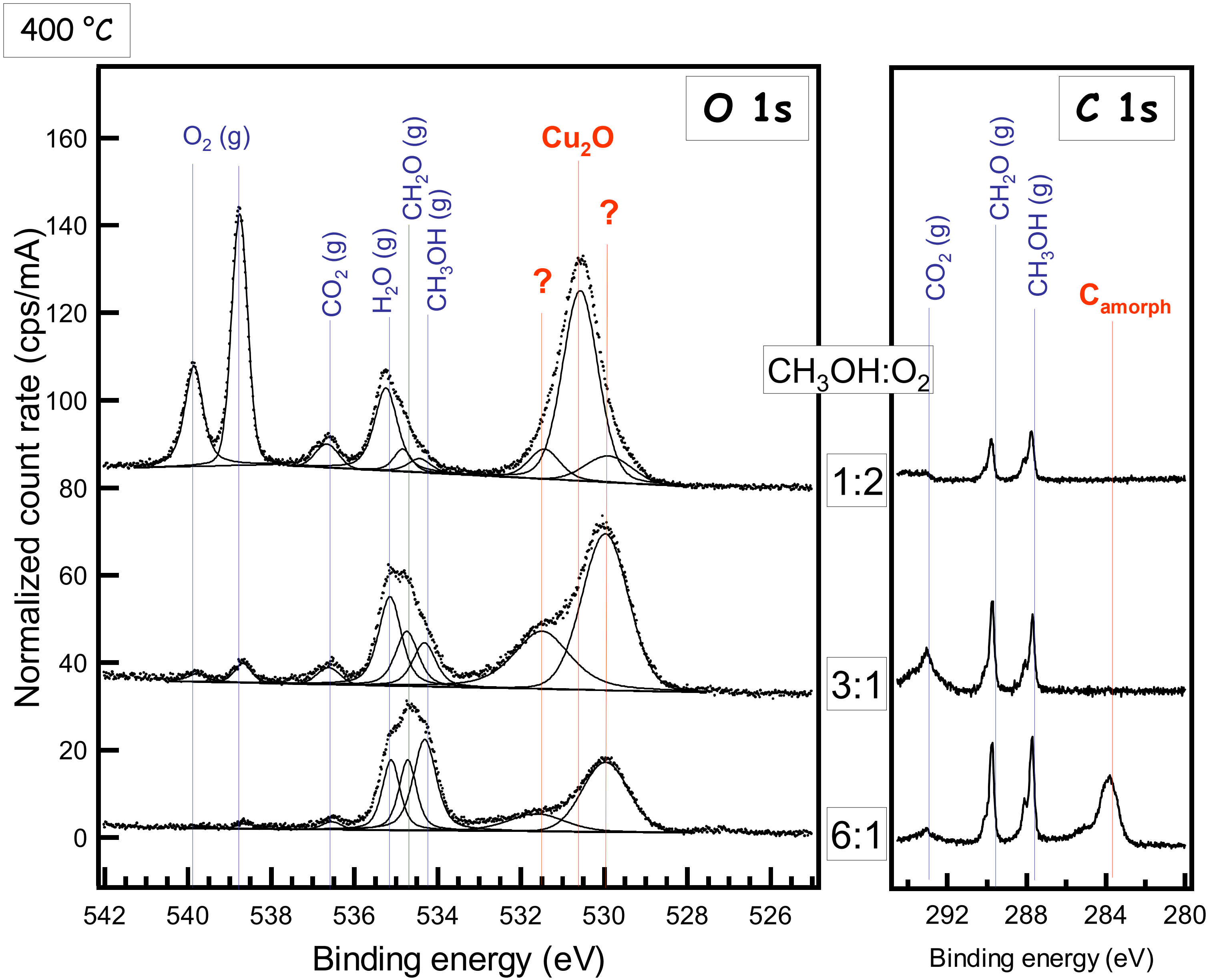
(calculated from Cu 3*p* and sub-surface O 1*s*)

Reducing conditions



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

Methanol oxidation on Cu: C1s spectra



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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3. W. Göpel, Chr. Ziegler : ***Einführung in die Materialwissenschaften***, Teubner Verlagsgesellschaft, Stuttgart-Leipzig, 1996
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5. C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, G. E. Muilenberg: ***Handbook of X-Ray Photoelectron Spectroscopy***, Physical Electronics Division, Perkin-Elmer Corporation, Eden Prairie, Minnesota, 1979
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9. M. Cardona, L. Ley: ***Photoemission of Solids***, Topics in Applied Physics, Band 26 und 27, Springer Berlin, 1978
10. M. Grasserbauer, H. J. Dudek, M. F. Ebel: ***Angewandte Oberflächenanalyse mit SIMS, AES und XPS***, Springer Berlin, 1979