united nations educational, scientific and cultural organization

international atomic energy agency

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international centre for theoretical physics

SMR/1270-36

SCHOOL ON SYNCHROTRON RADIATION

6 November - 8 December 2000

Miramare - Trieste, Italy

Supported in part by the Italian Ministry of Foreign Affairs in connection with the SESEME project

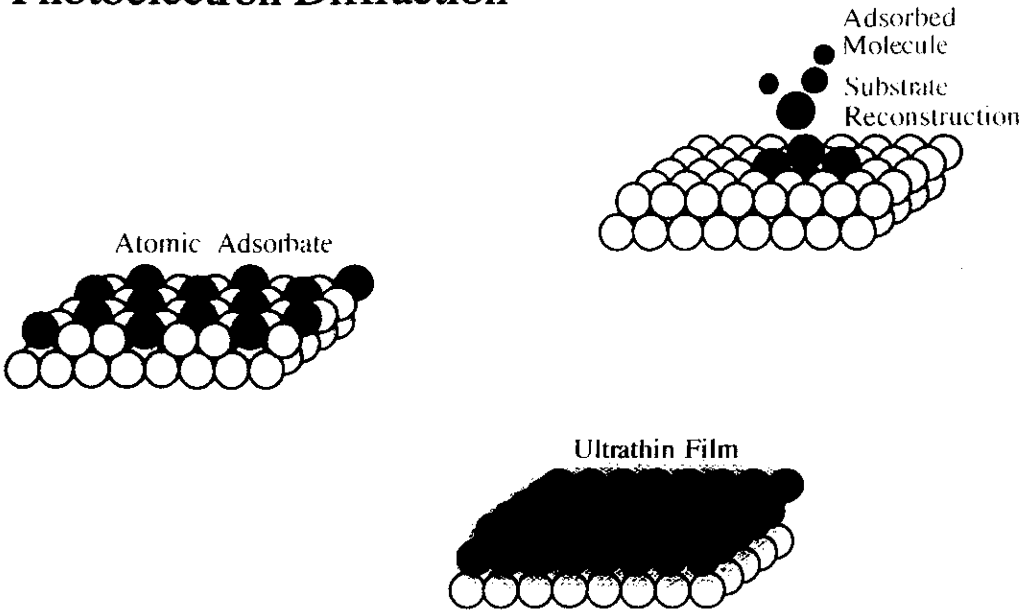
Co-sponsors: Sincrotrone Trieste, Società Italiana di Luce di Sincrotrone (SILS) and the Arab Fund for Economic and Social Development

Exploring the Limits of X-Ray Photoelectron Diffraction

Juerg Osterwalder
Universitaet Zuerich-Irchel
Zurich, Switzerland

Surface Structure Problems

... Solved by
X-Ray Photoelectron Diffraction



Fingerprinting:

- Characteristic XPD pattern
- Forward Scattering Maxima
- Backscattering Cones
- 1st-Order Interference Fringes

Holography:

- Atomic-Resolution Image

Chemical Intuition:

- Reasonable Bond Lengths
- Coordination Number

Structural Refinement:

- **Model Calculations (SSC, MSC)**
- **R-Factor Analysis**

Bond Directions

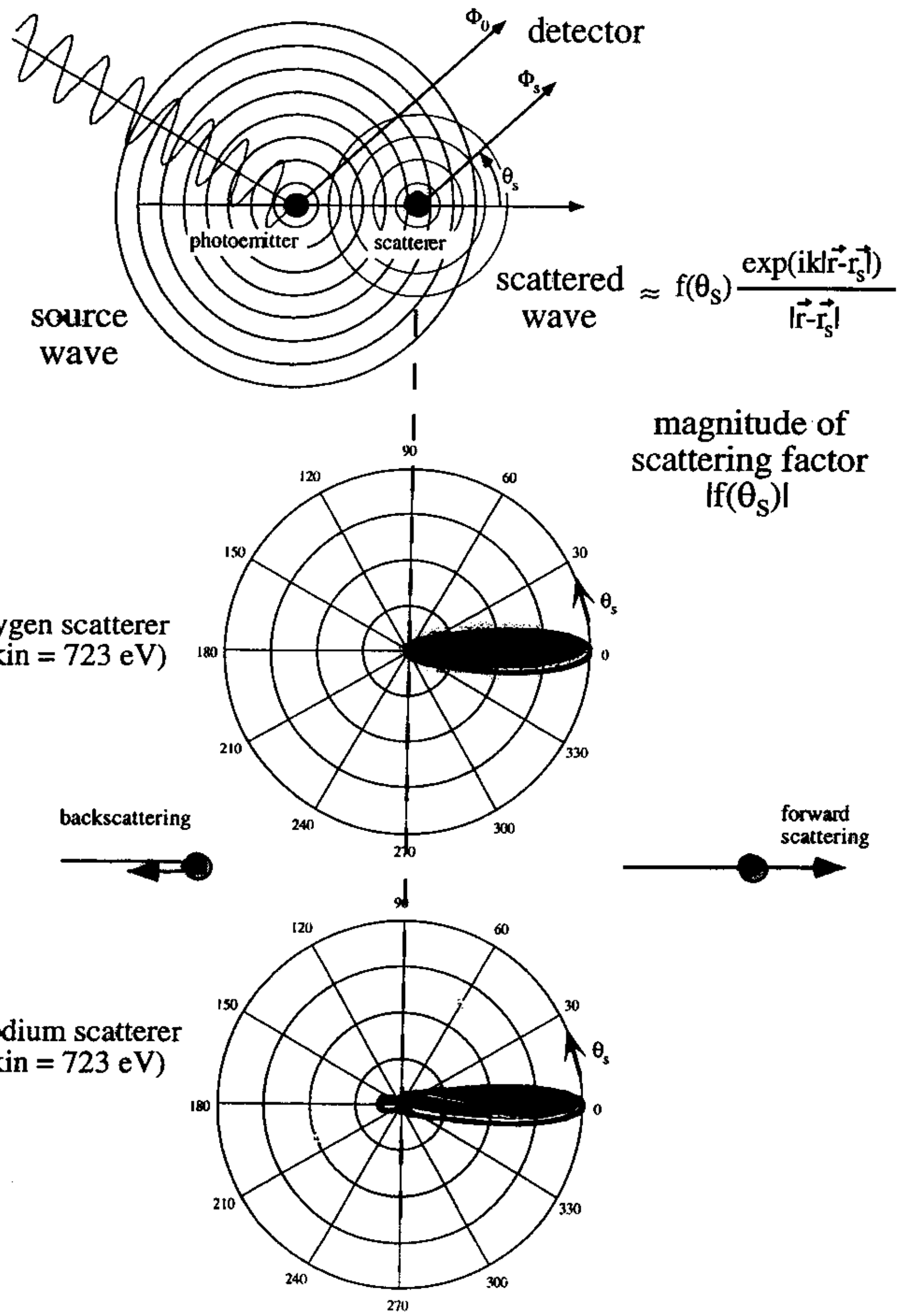
Resolution:

1.0 - 0.5Å

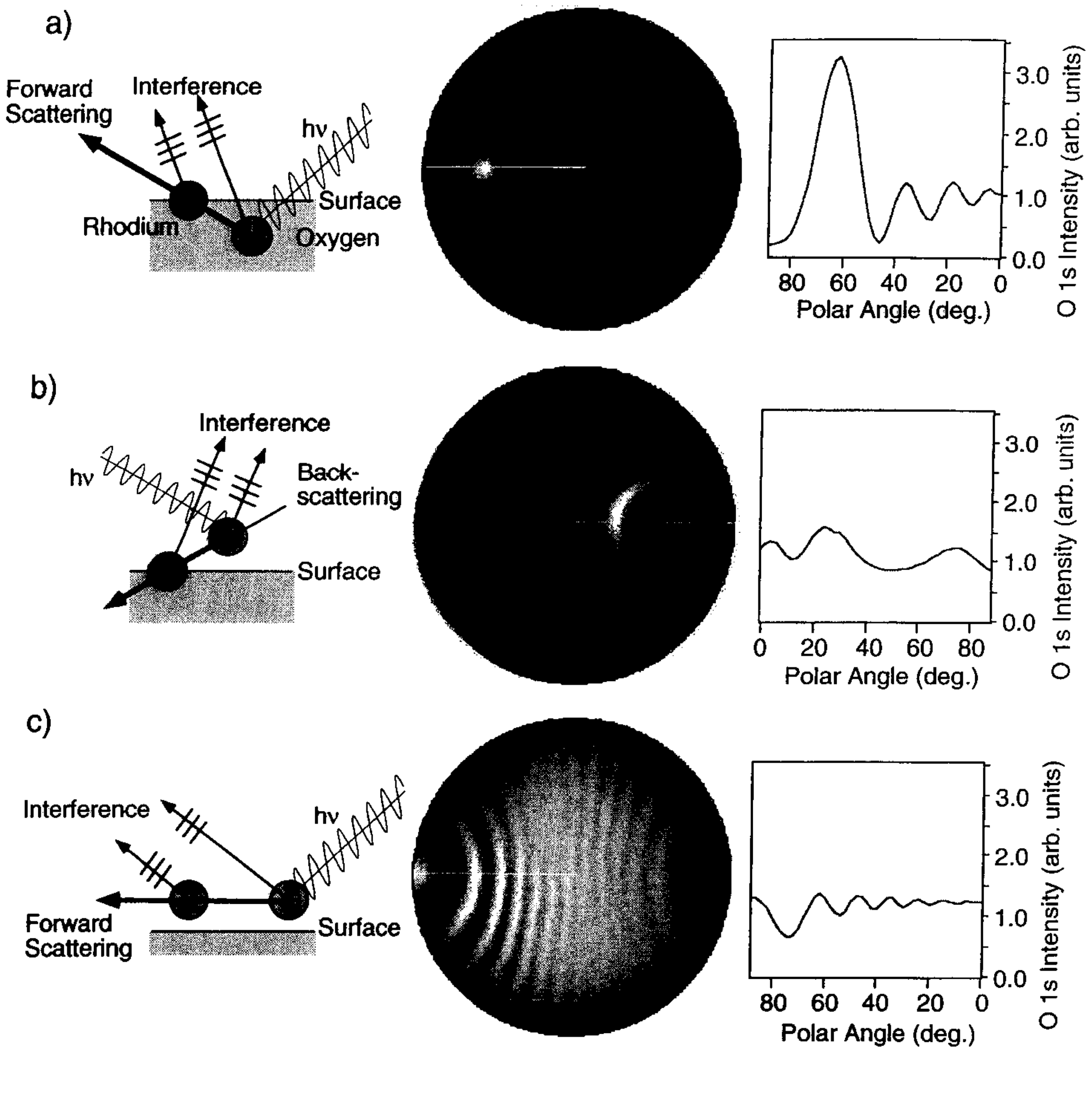
...

0.05Å

Principles of Photoelectron Diffraction

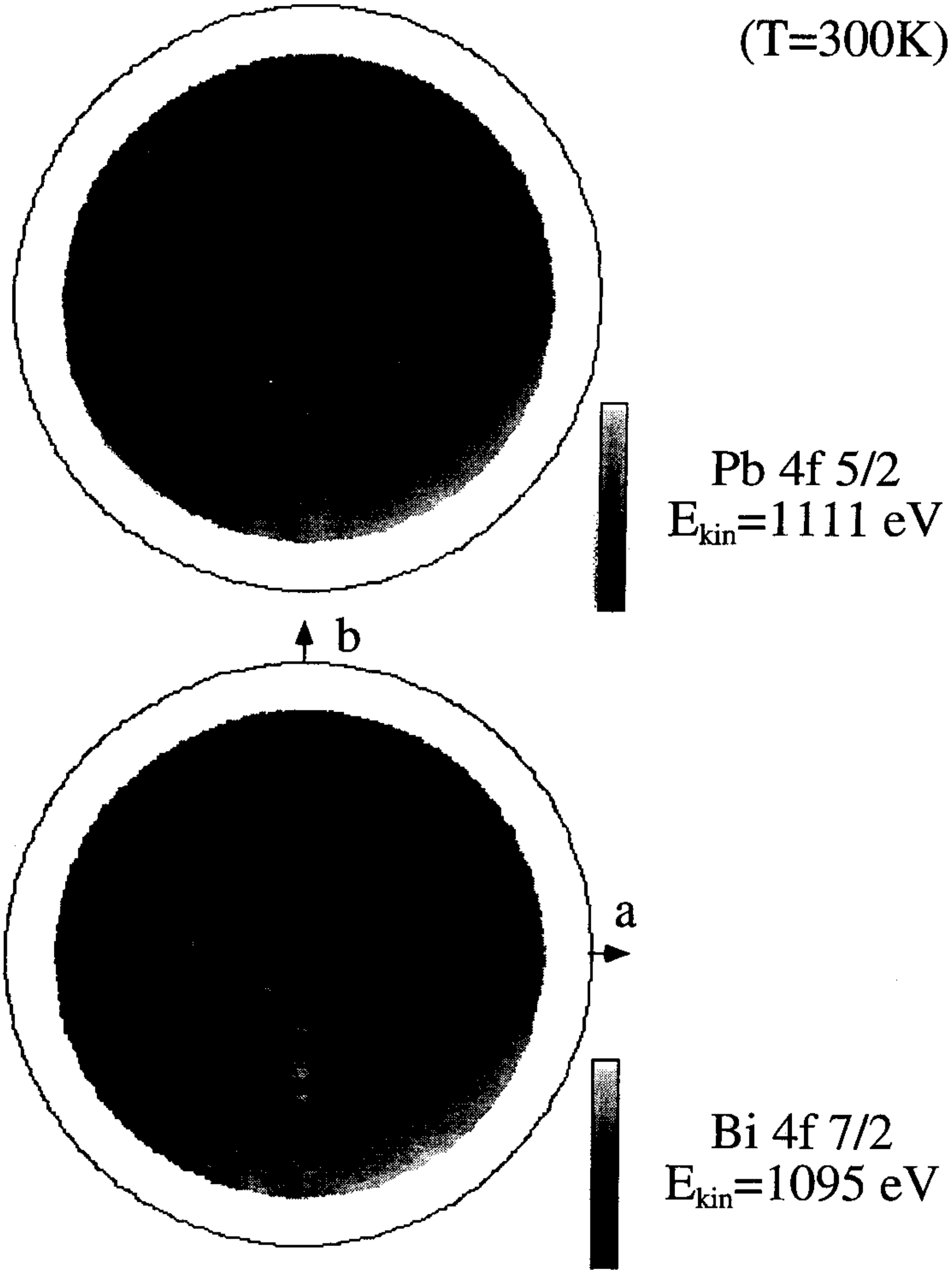


⊕ : dominant scatterers ⇒ axial symmetry

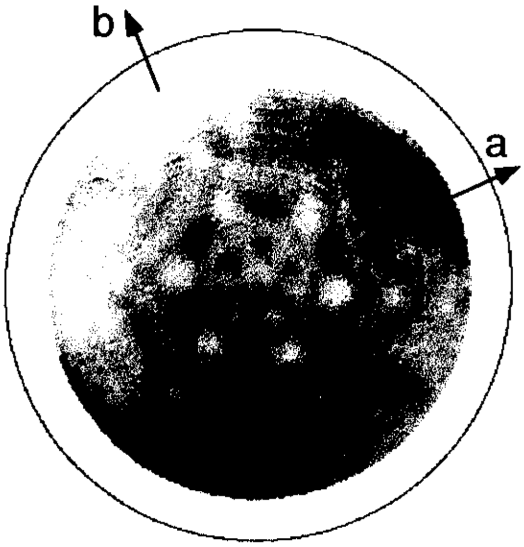


a)
Forward Scattering
Interference
hν
Surface
Rhodium
Oxygen
3.0
2.0
1.0
0.0
80 60 40 20 0
Polar Angle (deg.)
O 1s Intensity (arb. units)
b)
Interference
hν
Back-scattering
Surface
3.0
2.0
1.0
0.0
0 20 40 60 80
Polar Angle (deg.)
O 1s Intensity (arb. units)
c)
Interference
hν
Forward Scattering
Surface
3.0
2.0
1.0
0.0
80 60 40 20 0
Polar Angle (deg.)
O 1s Intensity (arb. units)

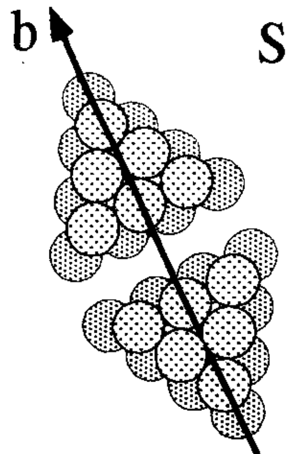
(Pb)Bi-2212(001)
Photoelectron Diffraction



Au/Bi-2212: Structure determination by "fingerprinting"

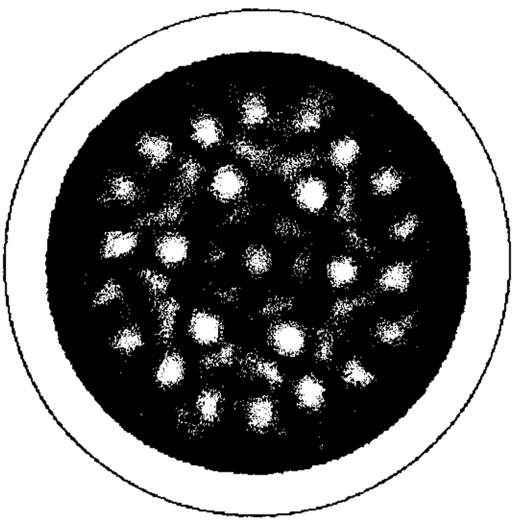


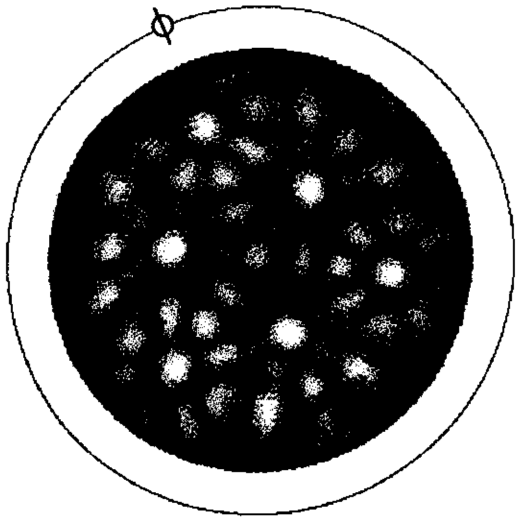
84Å Au/Bi-2212
Au 4f (E_{kin}=1178eV)



Structural model

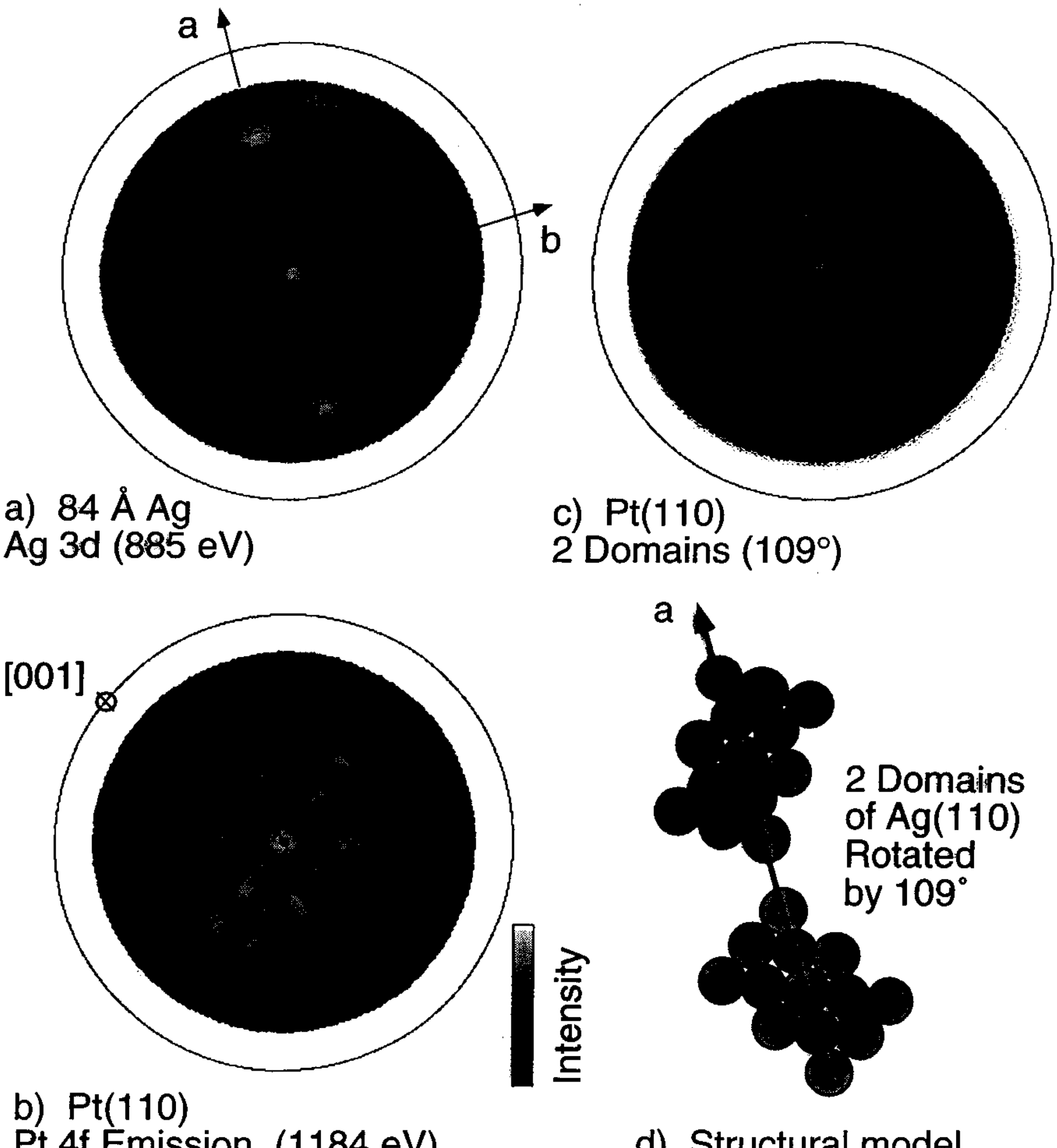
2 Au(111) domains rotated by 180°





2 Domains (180°) ⟵ Au 4d Emission (1405 eV) from 18 ML Au / Cu(111)

Ag / $Bi_2Sr_2CaCu_2O_{8+x}$ (c axis)



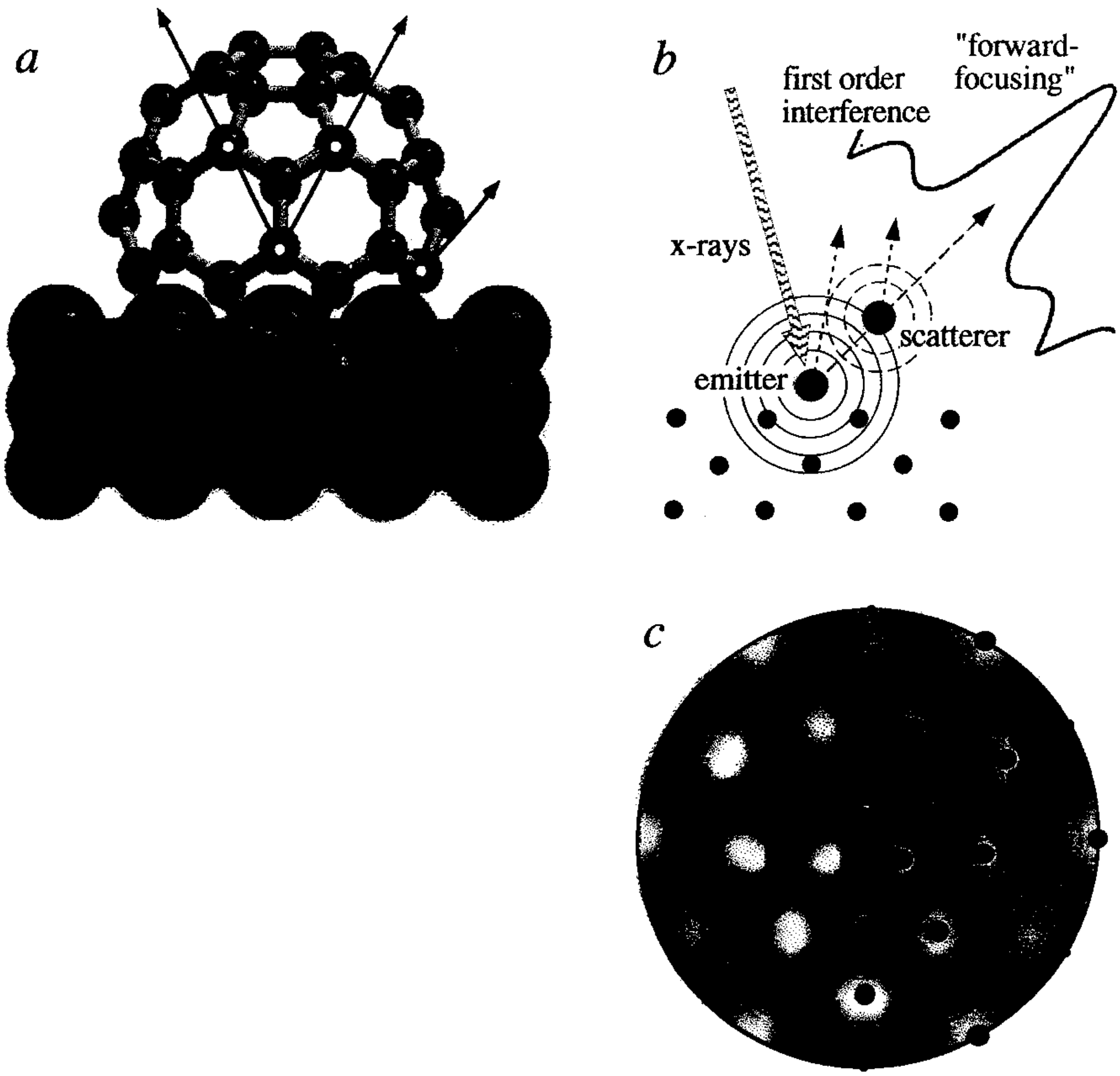
a) 84 Å Ag
Ag 3d (885 eV)

c) Pt(110)
2 Domains (109°)

b) Pt(110)
Pt 4f Emission (1184 eV)

d) Structural model

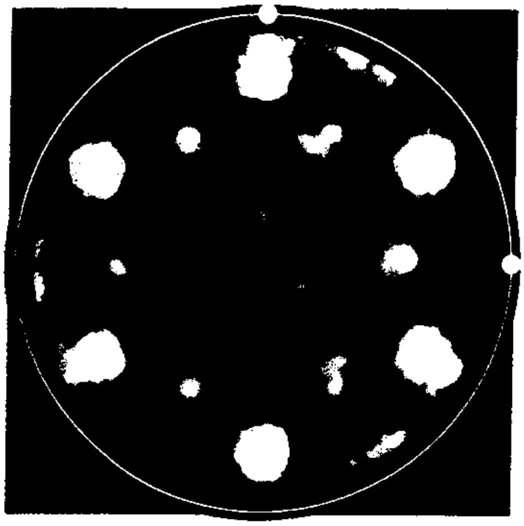
Orientation of Adsorbed C_{60} Molecules



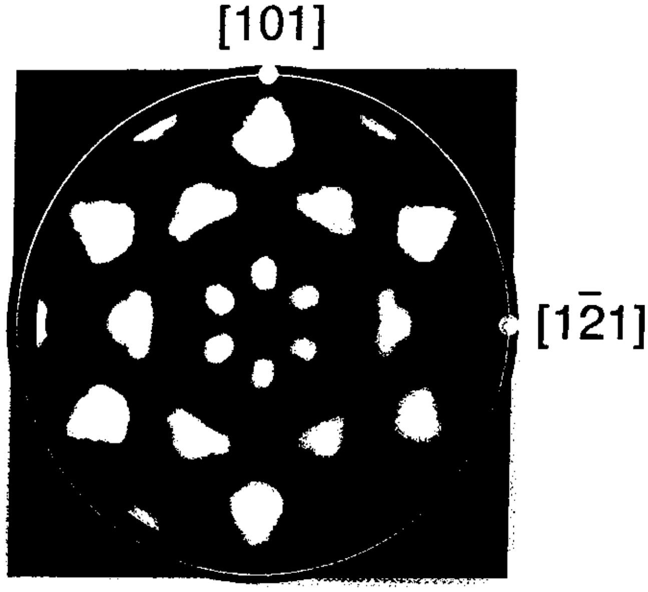
R. Fasel et al.
Institut de Physique
Université de Fribourg

PRL 76, 4733 (1996)

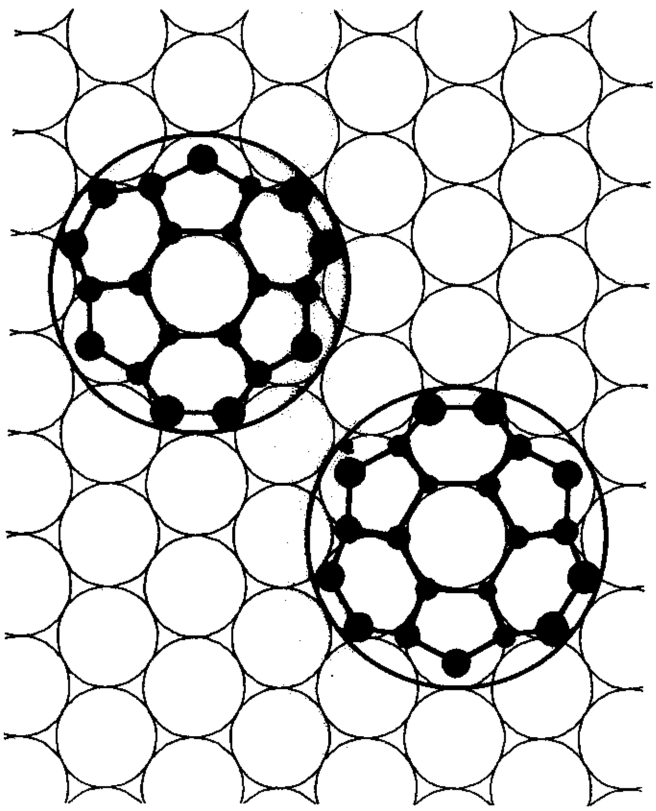
1 ML C_{60} on Cu(111)



XPD Expt. (C 1s, 970eV)



SSC Theory



Molecular Orientation
(Two Domains)

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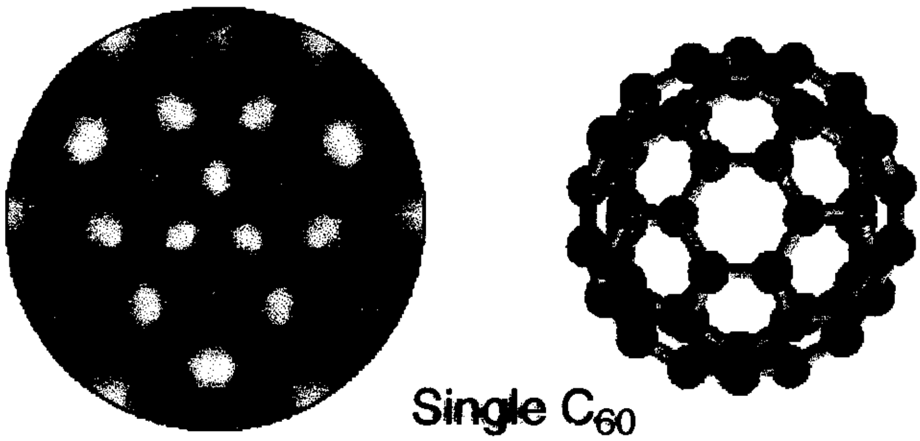
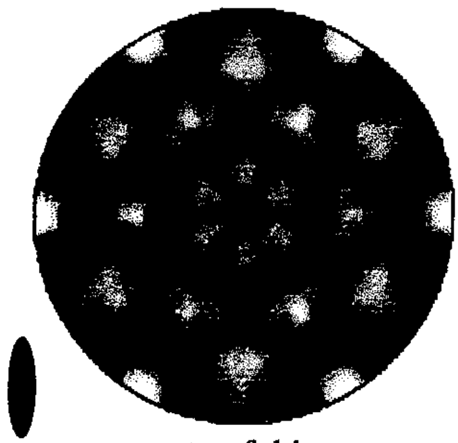
Fribourg

C_{60} Adsorbed on Metal Surfaces of Given Rotational Symmetries

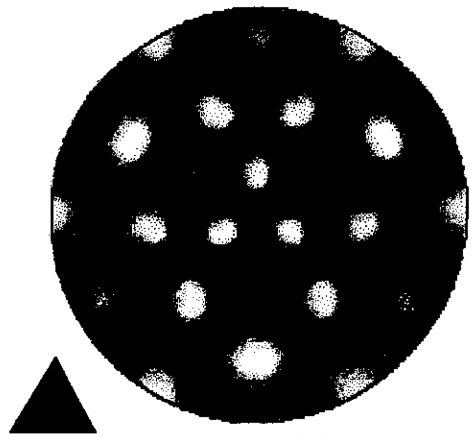


Single C_{60}
Bonded through 6-Ring

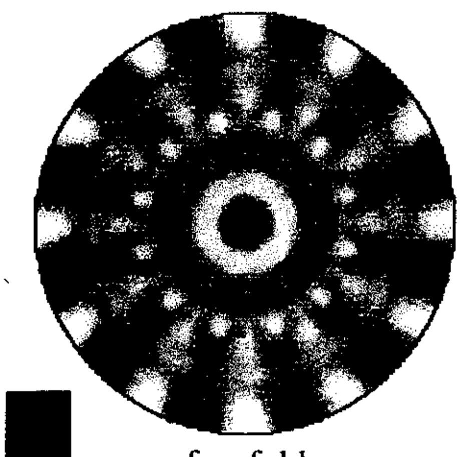
On Substrates:



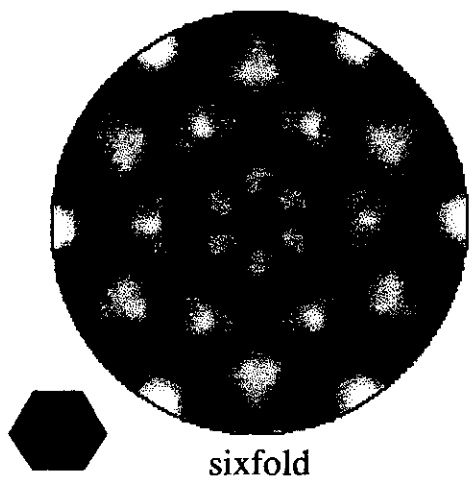
twofold



threefold

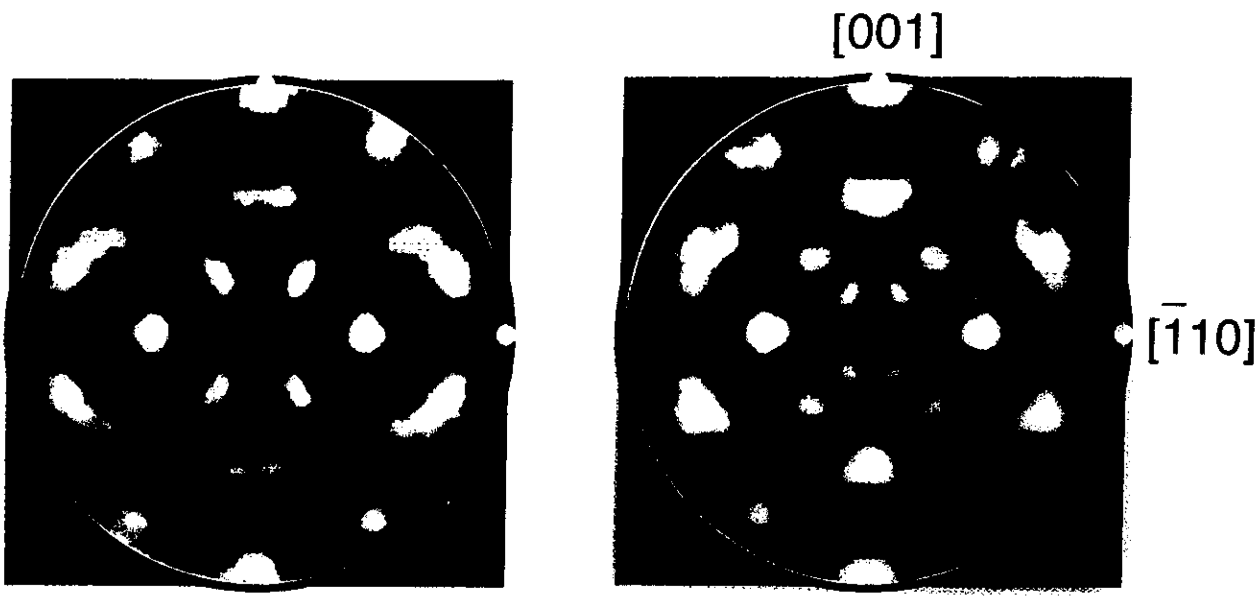


fourfold



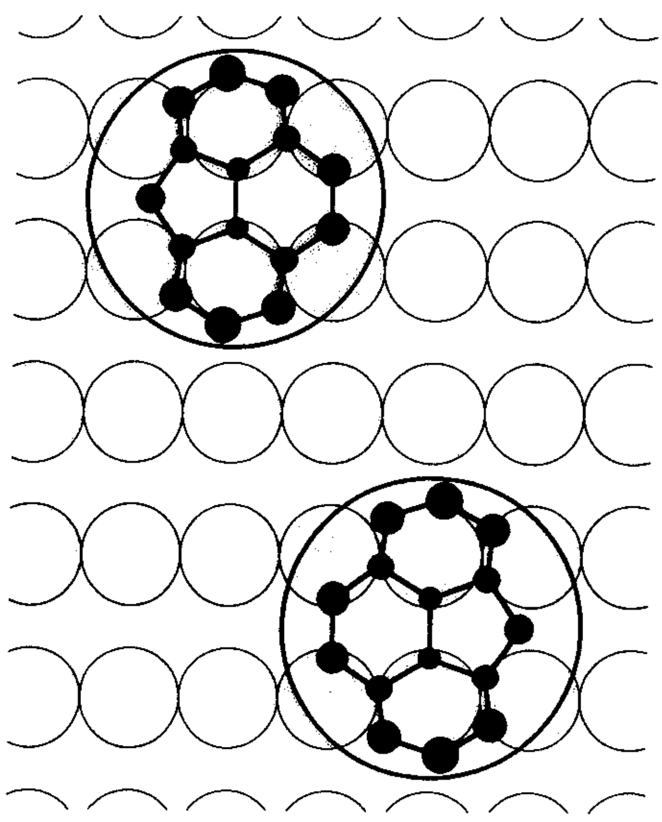
sixfold

1 ML C_{60} on Cu(110)



XPD Expt. (C 1s, 970eV)

SSC Theory



Molecular Orientation
(Two Domains)

R. Fasel et al.
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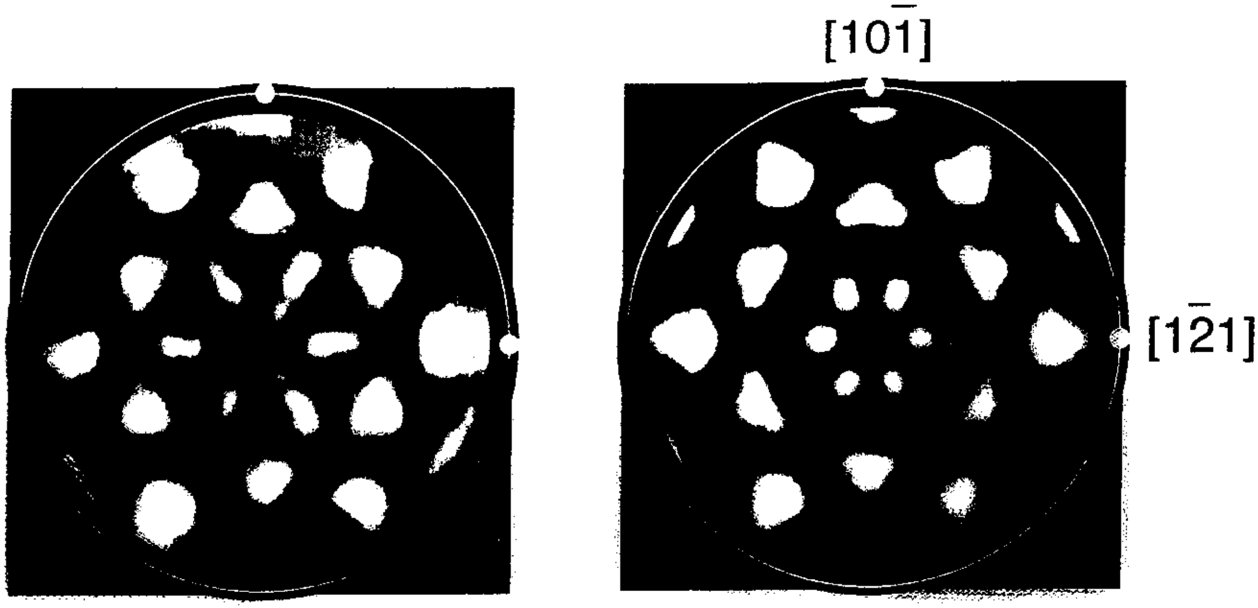
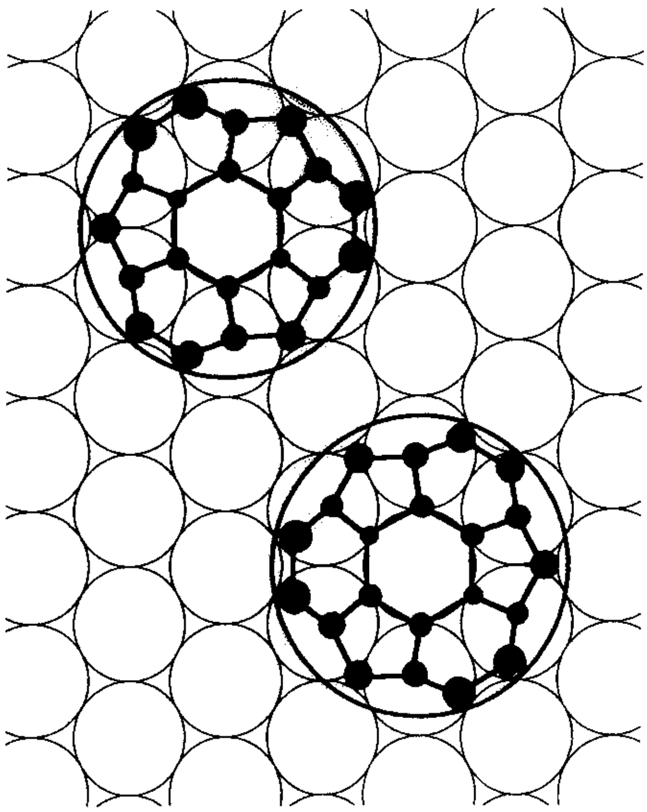
Fribourg

1 ML C_{60} on Al(111)



XPD Expt. (C 1s, 970eV) SSC Theory



Molecular Orientation
(Two Domains)

R. Fasel et al.
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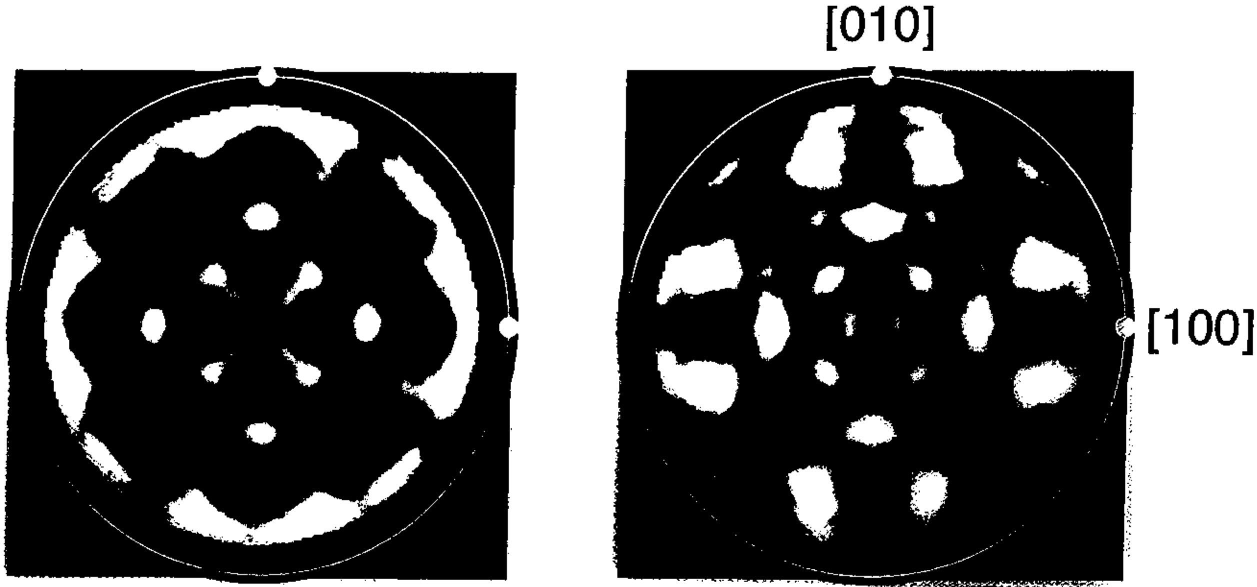
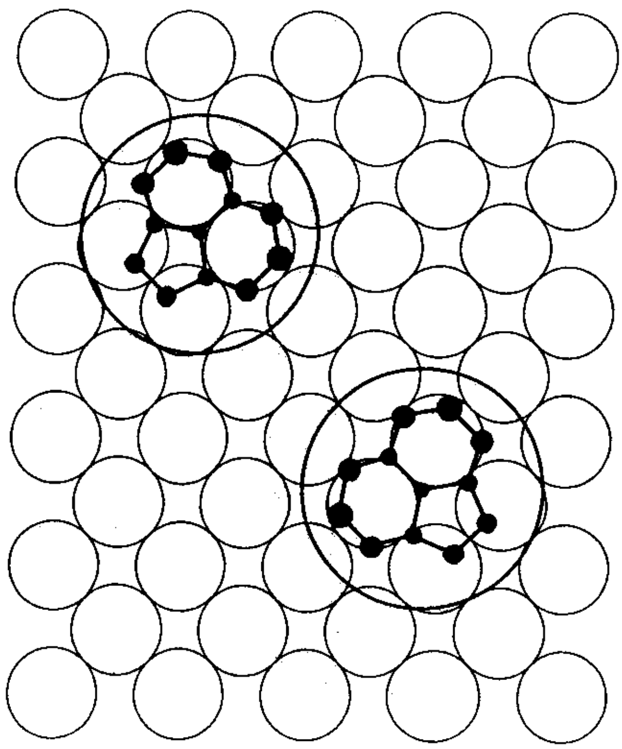
Fribourg

1 ML C_{60} on Al(001)



XPD Expt. (C 1s, 970eV) SSC Theory



Molecular Orientation
(Four Domains)

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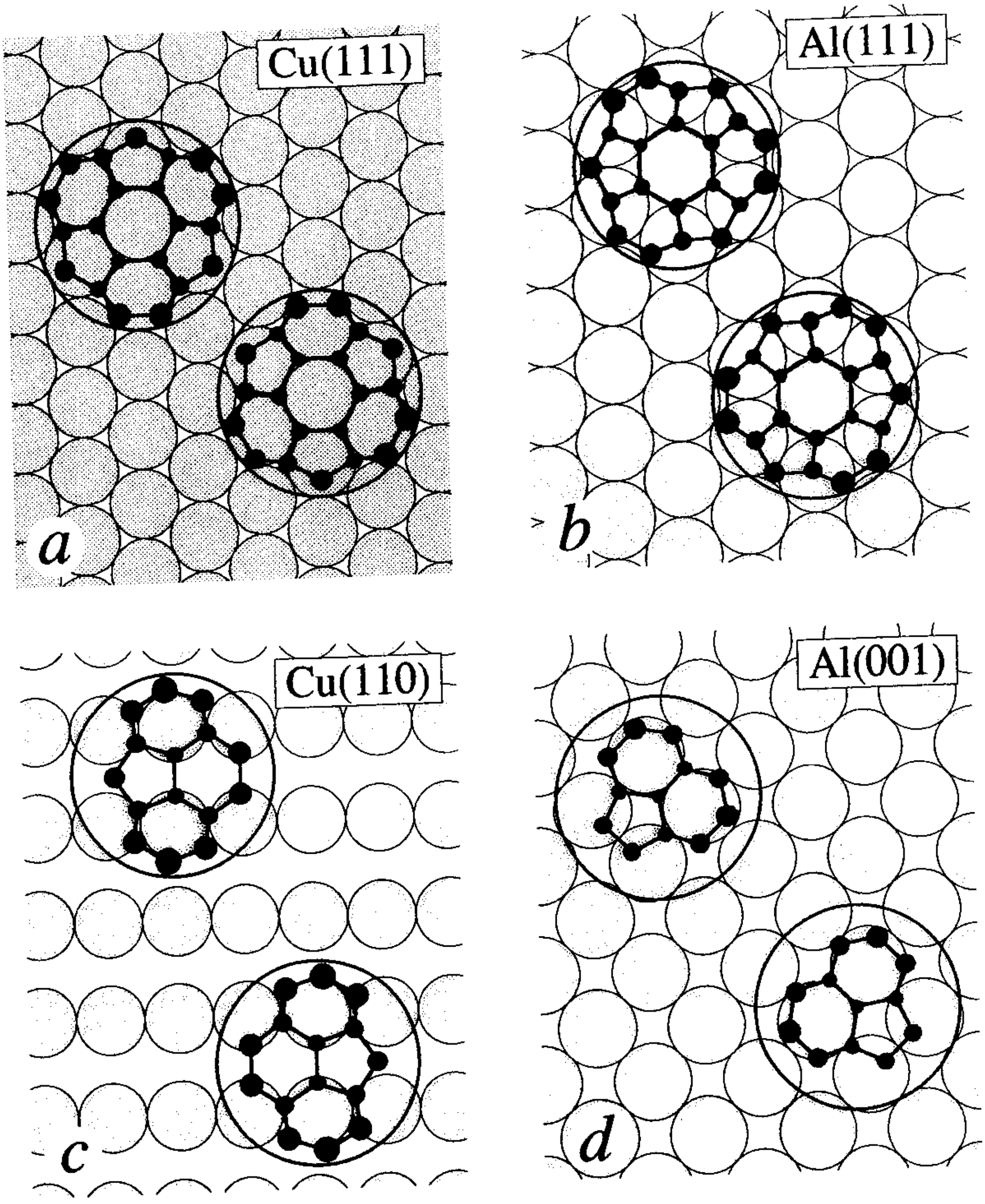

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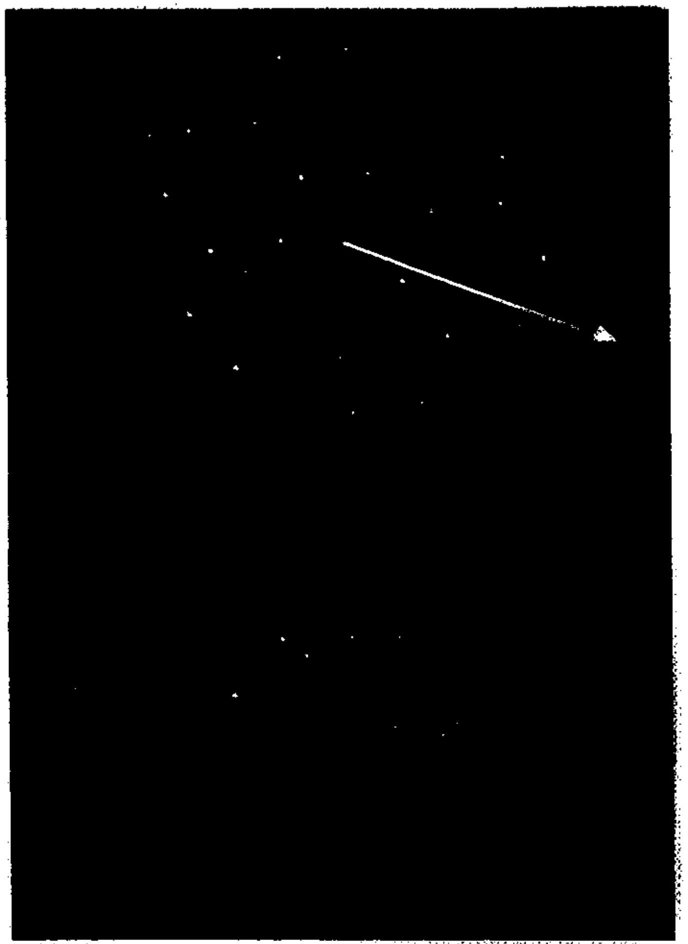
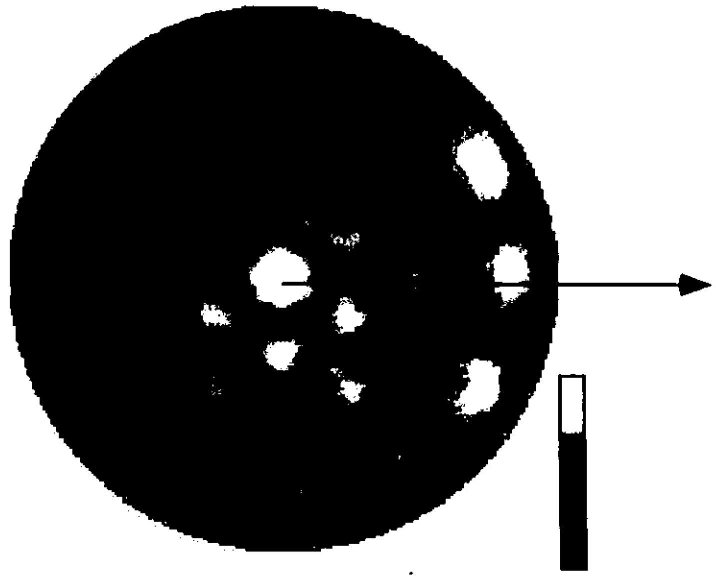
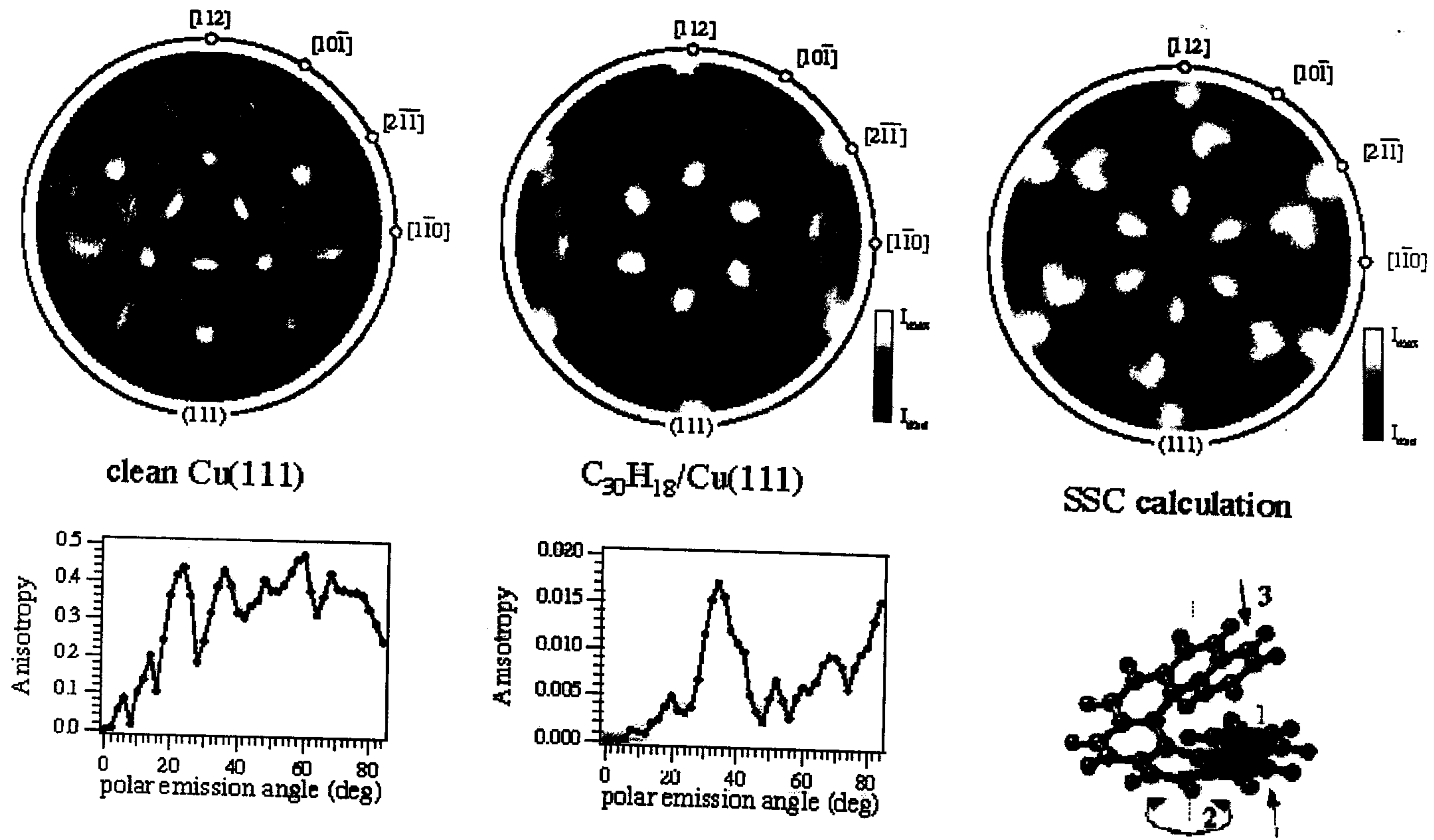
Université de Fribourg

$C_{30}H_{18}$ [7]-Helicene(M) Benzophenanthrophenanthrene



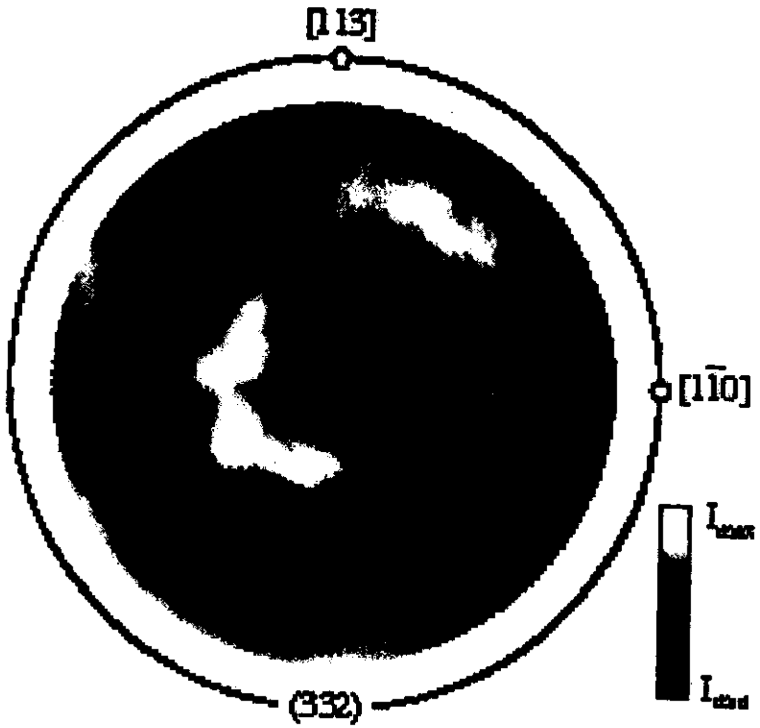


SSC Calculation
C 1s Emission
(964 eV)

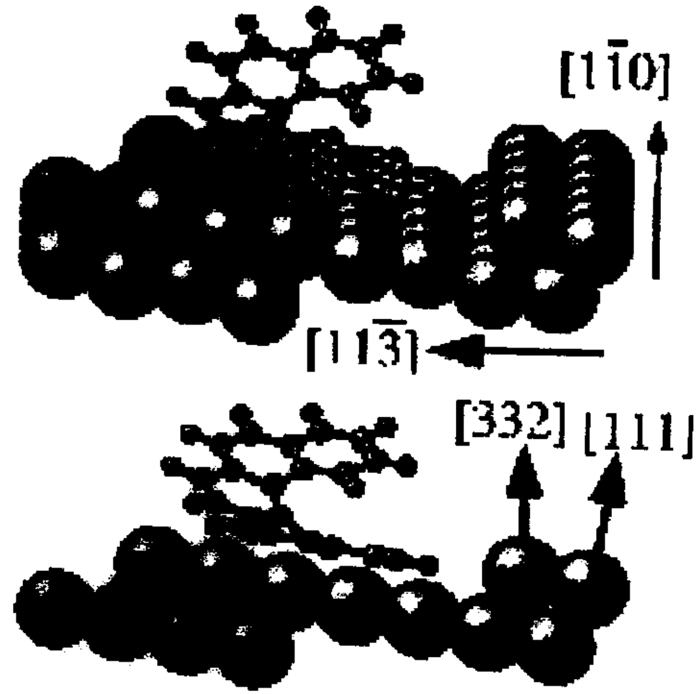


[112]
[10$\bar{1}$]
[2$\bar{1}\bar{1}$]
[1$\bar{1}$0]
(111)
clean Cu(111)
$C_{30}H_{18}$/Cu(111)
SSC calculation
I_{max}
I_{min}
Anisotropy
polar emission angle (deg)
3
1
2

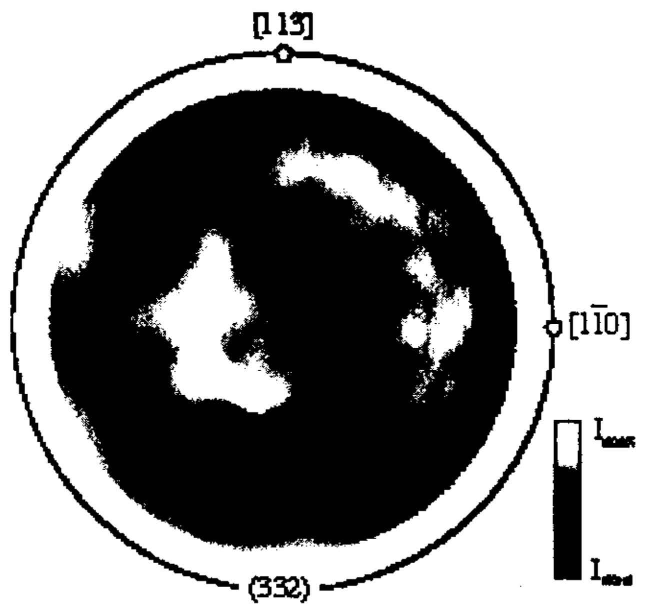
Experiment



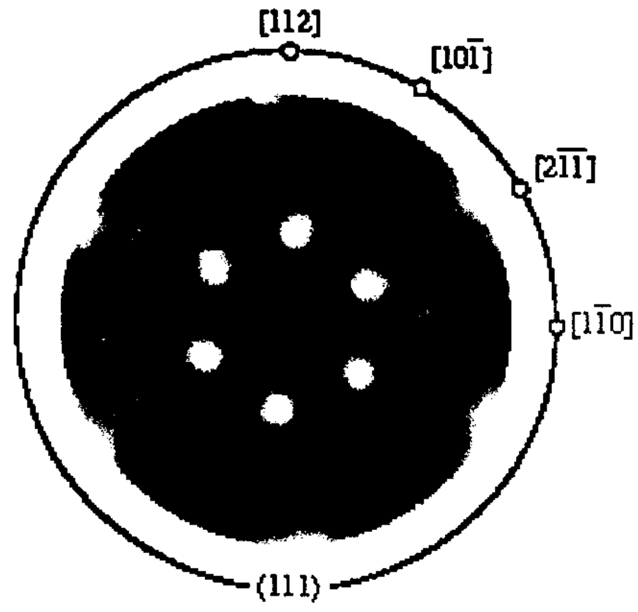
$C_{30}H_{18}$/Cu(332)



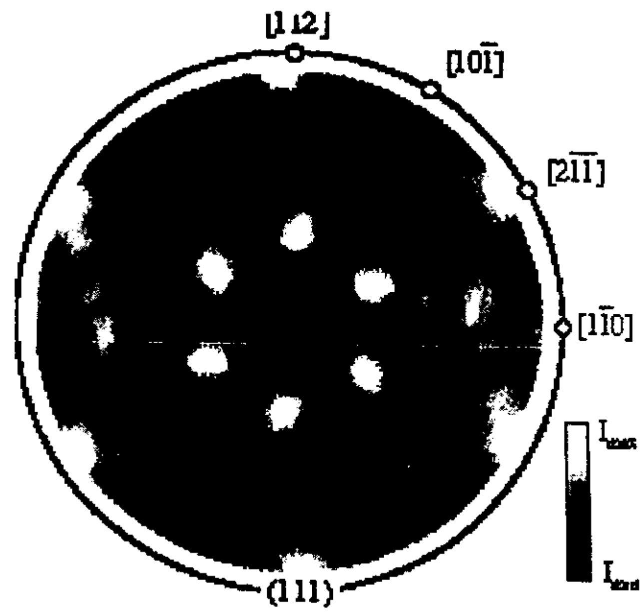
Molecular orientation



$C_{30}H_{18}$/Cu(332)

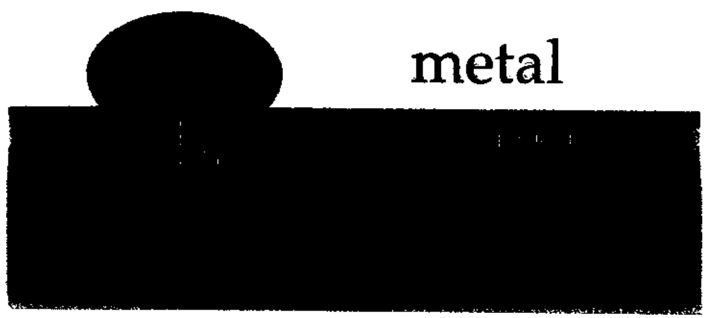


6-fold average around [111]



$C_{30}H_{18}$/Cu(111)

The System:



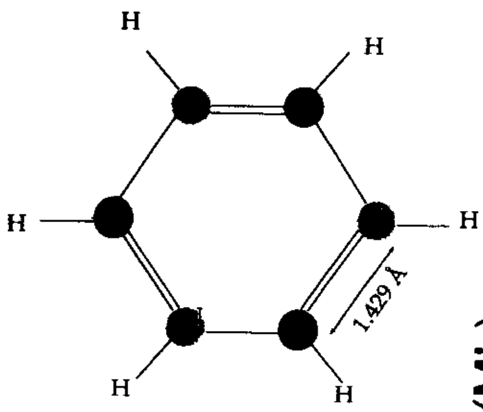
Hexagonal Boron-Nitride Monolayers on Ni(111)

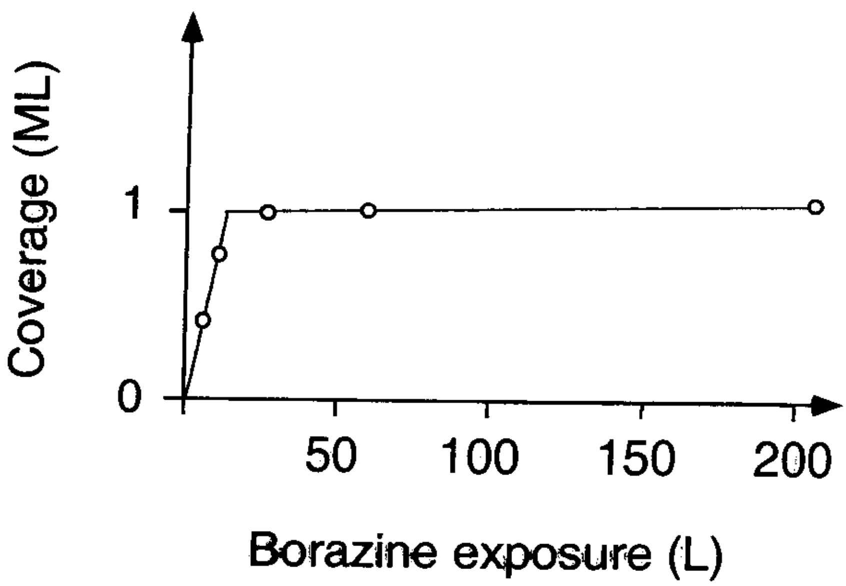
W. Auwärter, T. Greber et al.

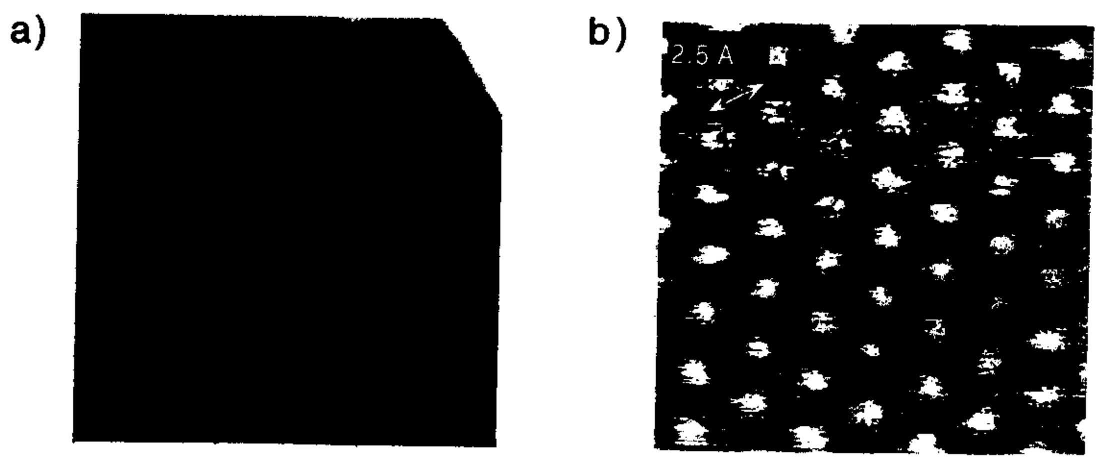
Preparation:

$$(BN)_3H_6 + Ni(111) \xrightarrow{1100\,K} h\text{-}BN \text{ on } Ni(111) + 3H_2$$

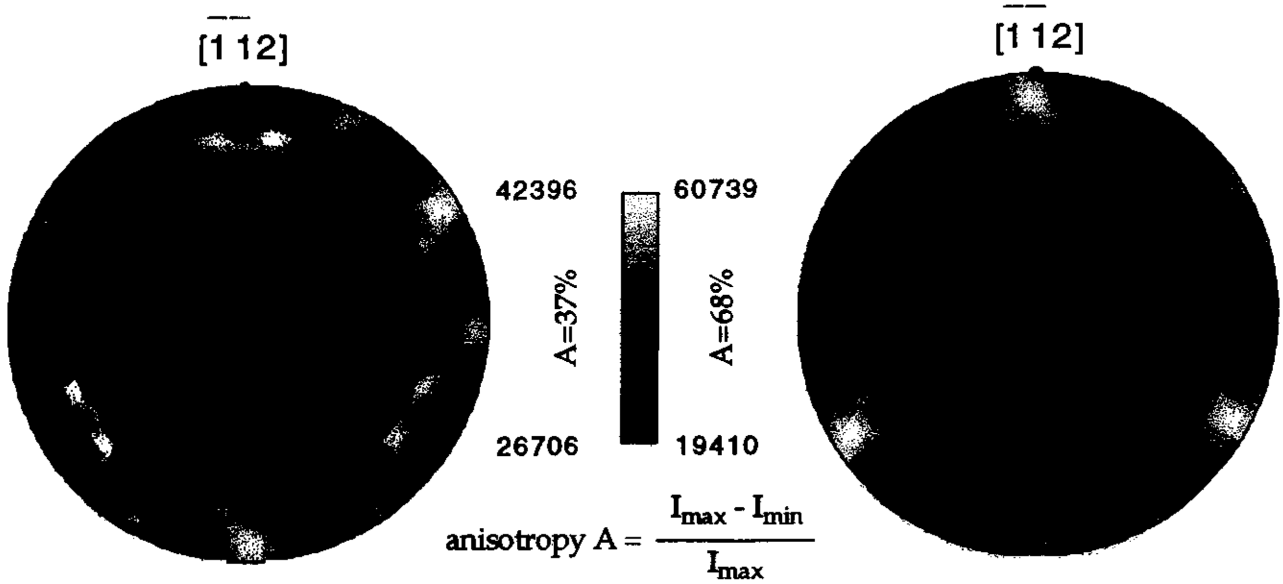
Borazine







XPD Experiment



$$\text{anisotropy } A = \frac{I_{max} - I_{min}}{I_{max}}$$

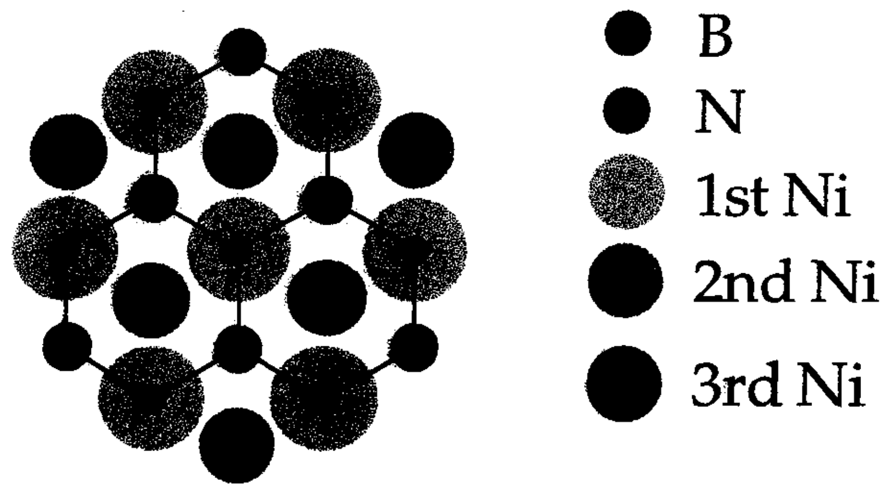
h-BN/Ni(111): N1s 2π scan

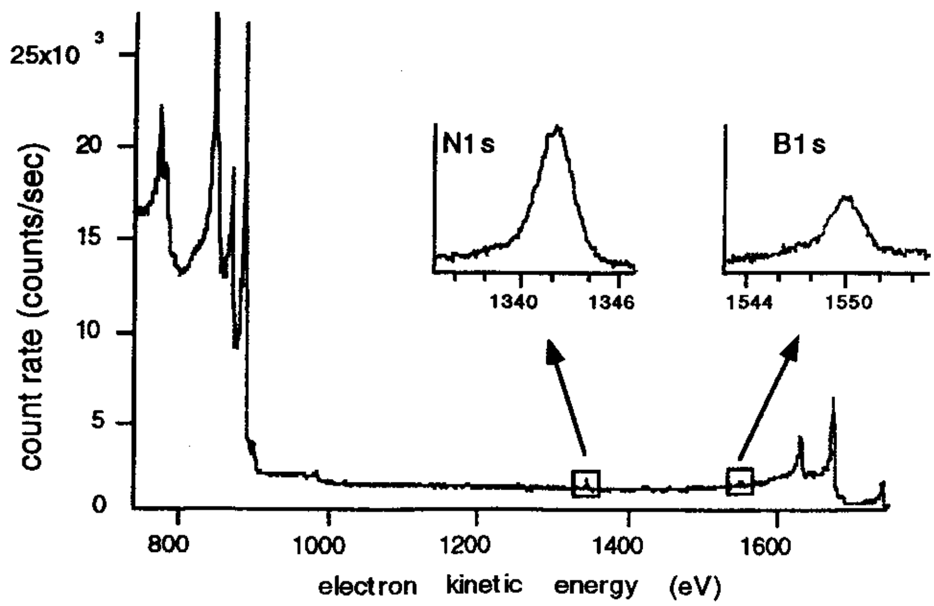
kin. Energy: 1341.9 eV, SiKα, t=23.8h

h-BN/Ni(111): B1s 2π scan

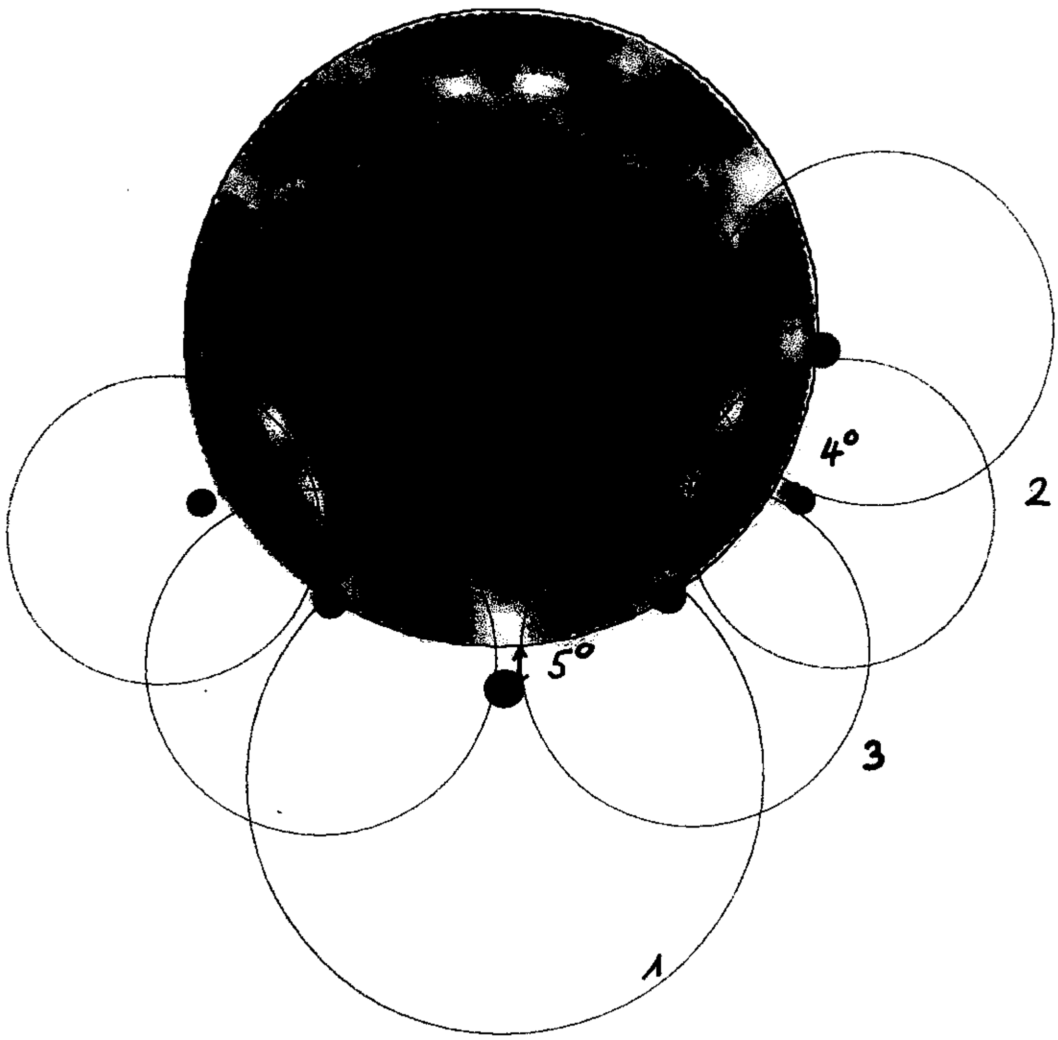
kin. Energy: 1549.8 eV, SiKα, t=37.8h

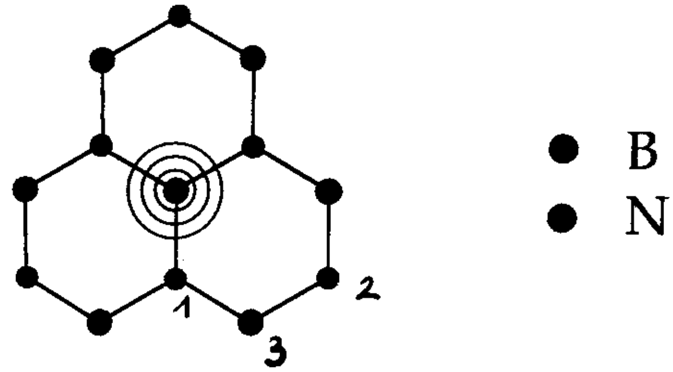
Model by Y. Gamou et al.
Sci. Rep. RITU A44, (1997) 221.





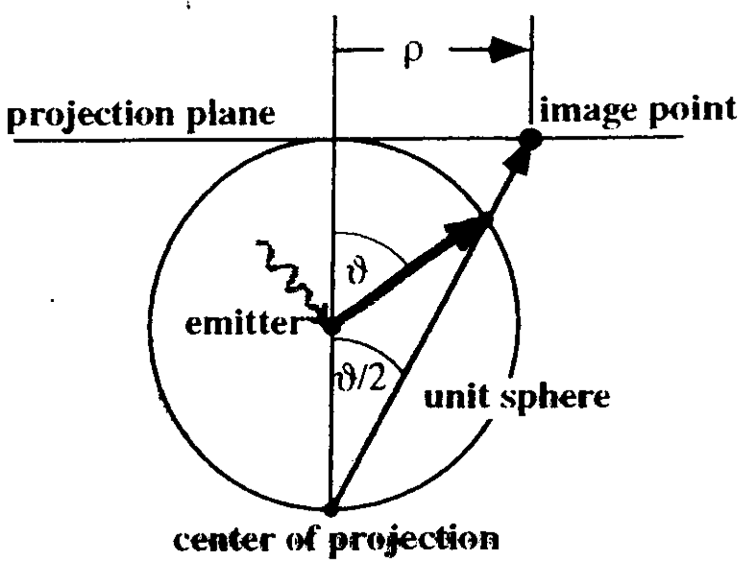
N 1s





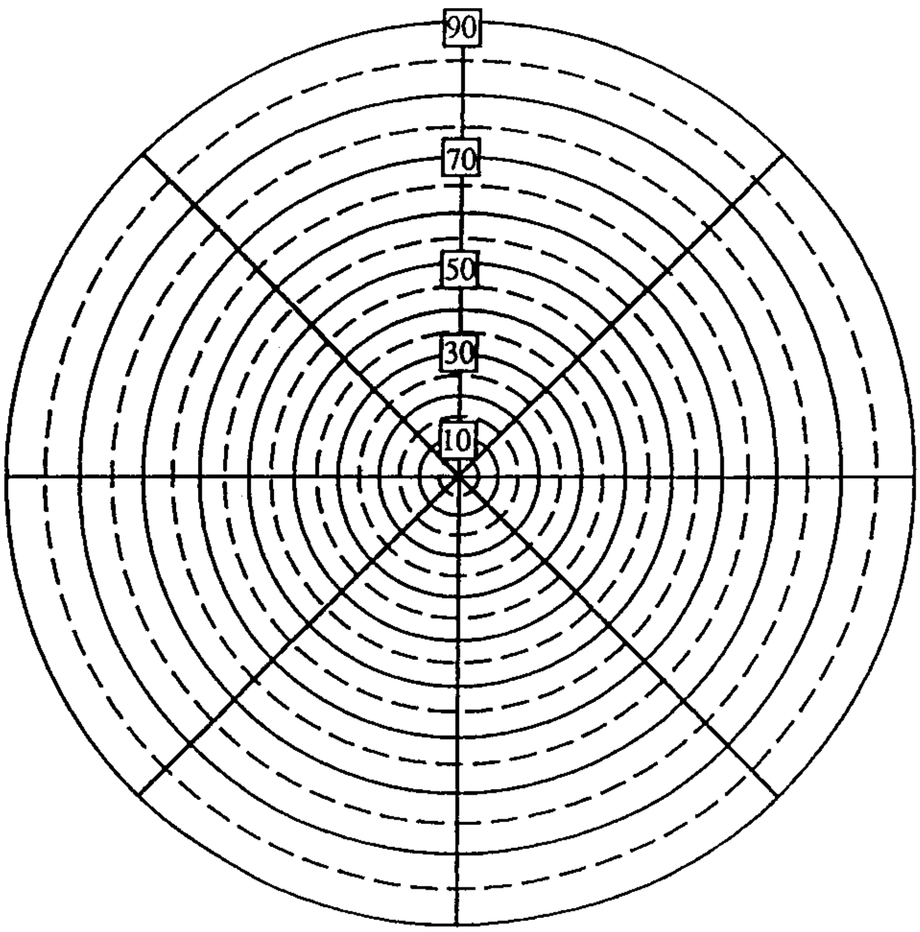
Centers of 1st order fringes → corrugation angle 4°

stereographic projection

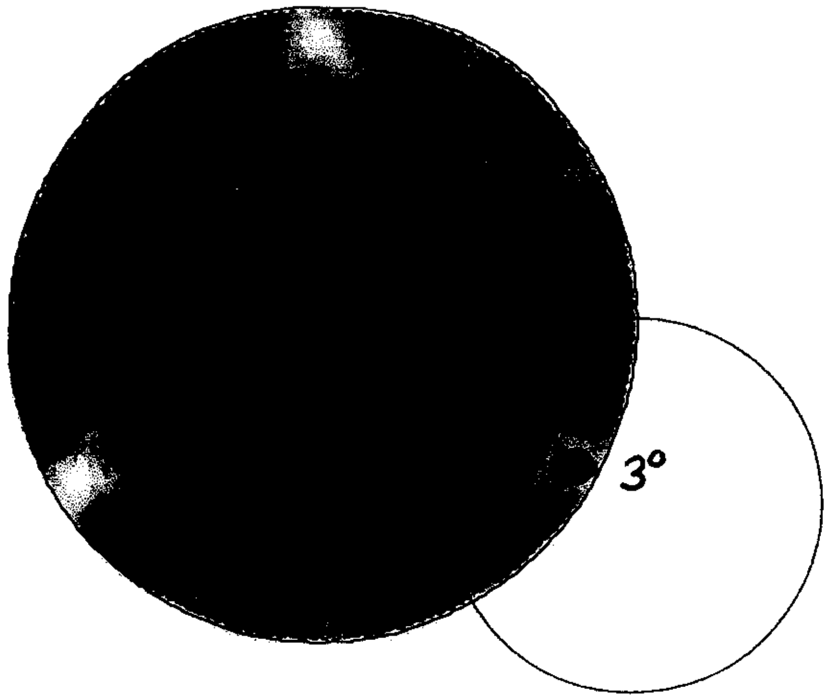


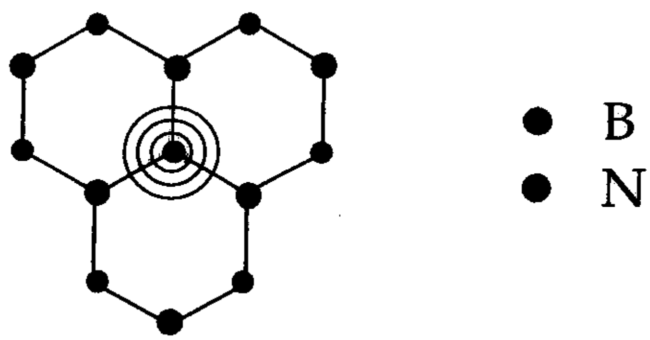
$$\boxed{\rho = 2 \tan(\vartheta/2)}$$

... maps circles into circles !



B 1s

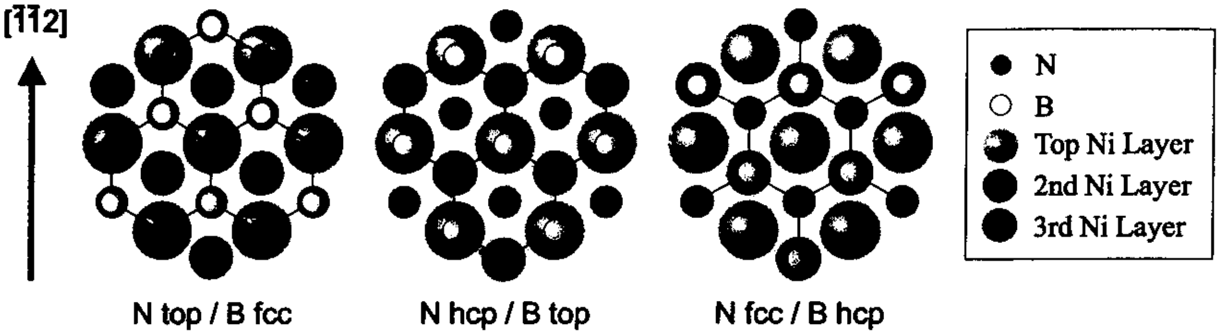




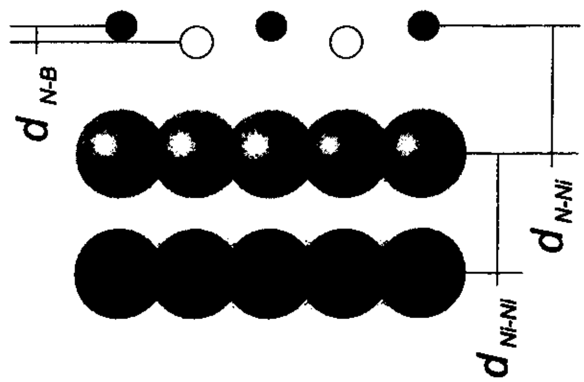
Determination of Film Registry by XPD

M. Muntwiler, W. Auwärter, F. Baumberger, M. Hoesch, Th. Greber, J. Osterwalder, Surf. Sci. 2000.

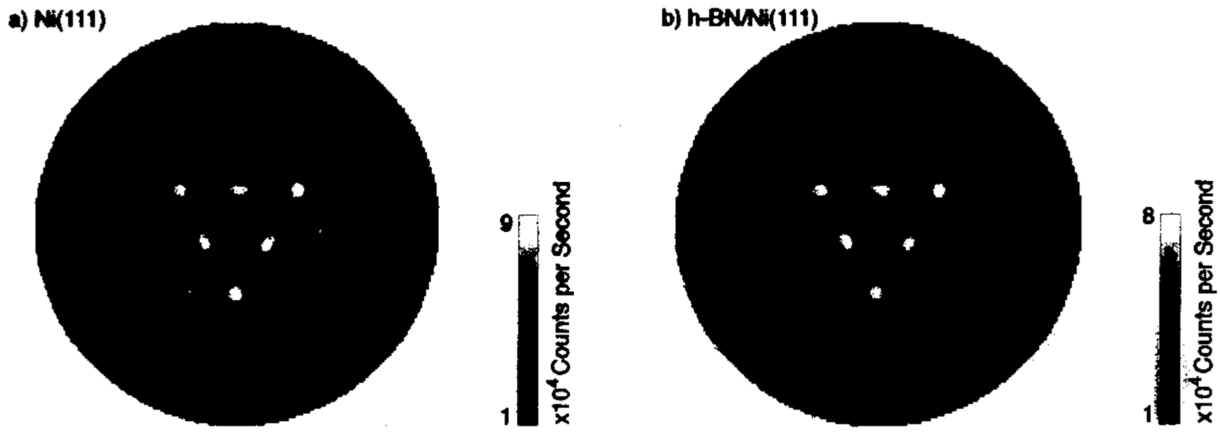
We now know the film structure,
but how is its registry to the substrate?



Can we find out from the substrate (Ni 2p) emission?



Ni 2p (884 eV) XPD:

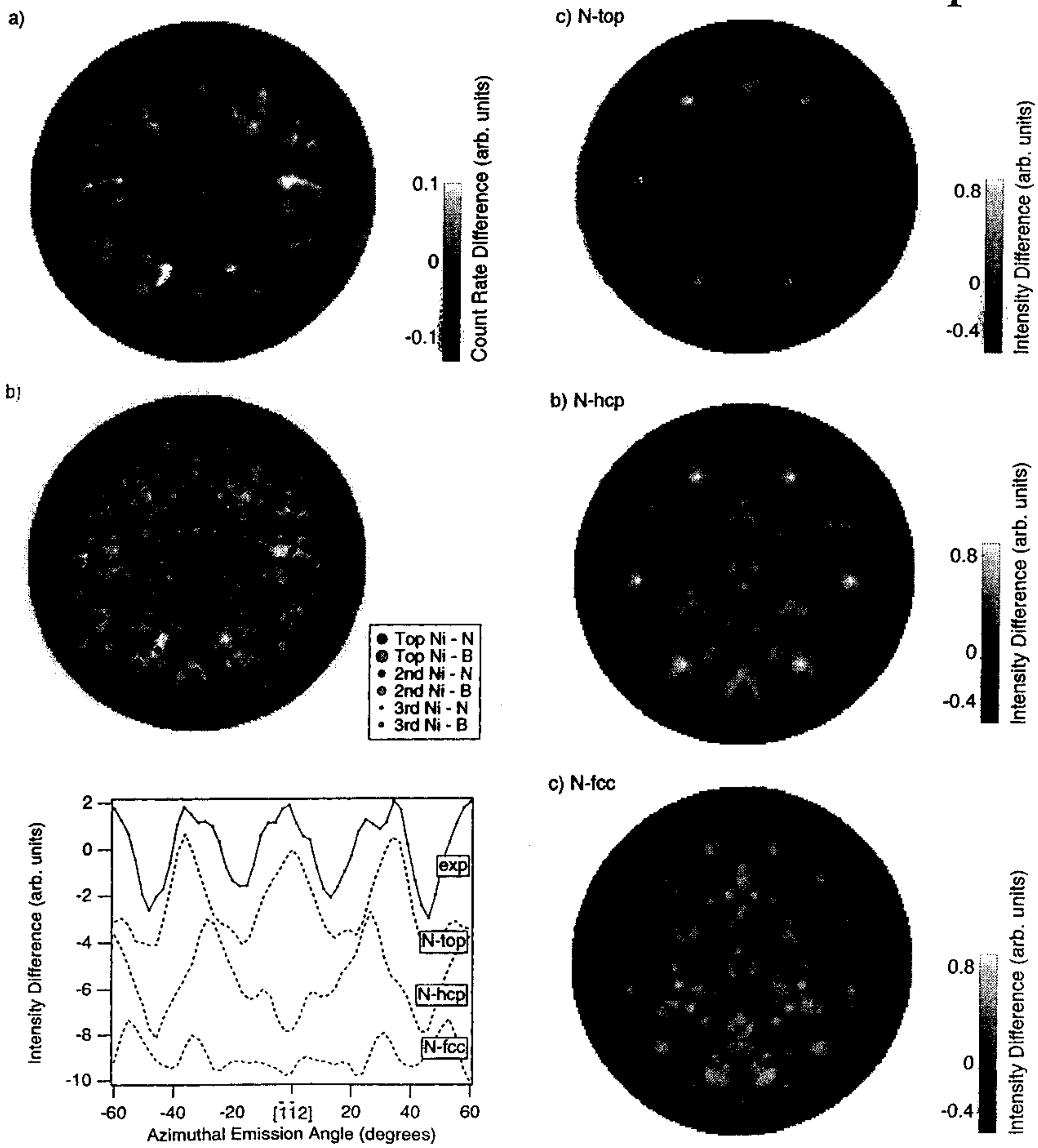


Does not look very promising!

But: Work with Difference Spectra !

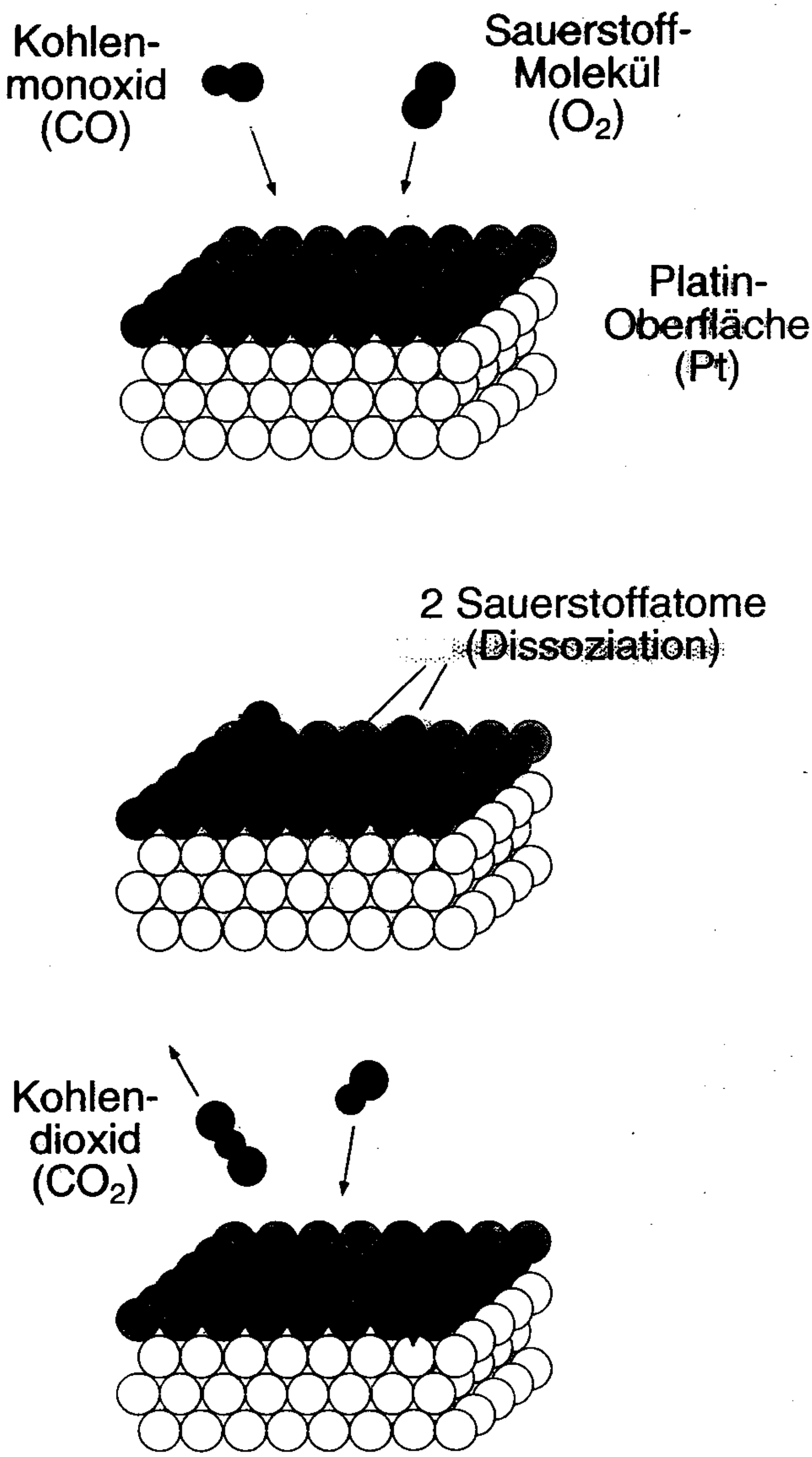
Experiment	Multiple Scattering Calcs. 3 Ni layers (Kaduwela/Fadley Code)
I_{exp} (h-BN/Ni(111)) - I_{exp} (Ni(111))	I_{msc} (h-BN/Ni(111)) - I_{msc} (Ni(111))

=> N top !

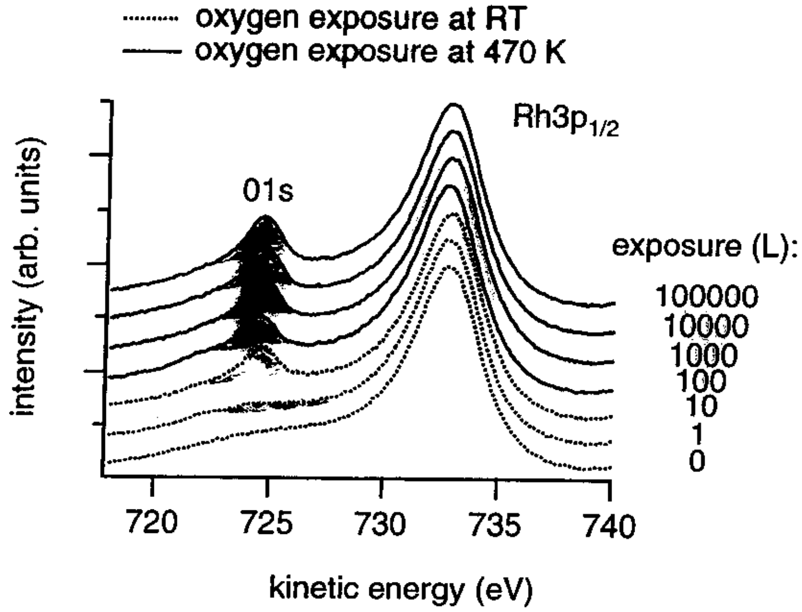


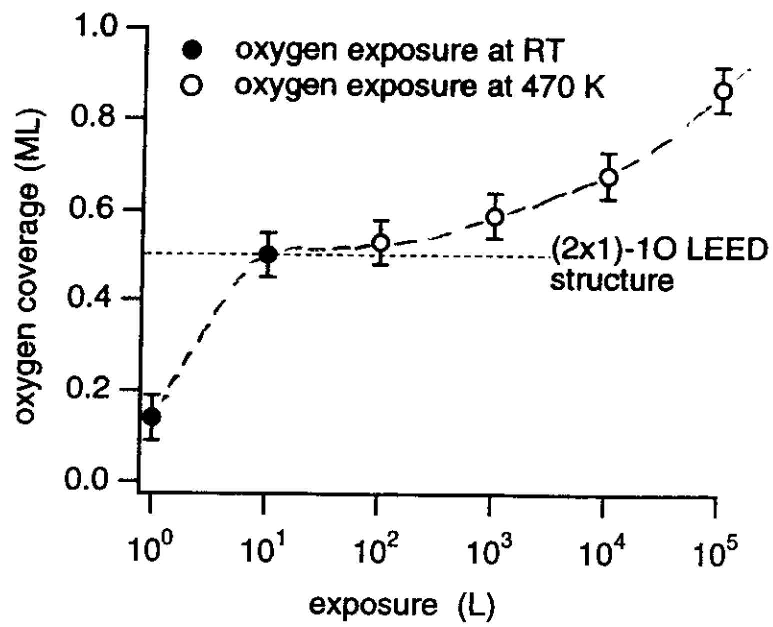
25

Katalytische Verbrennung von Kohlenmonoxid



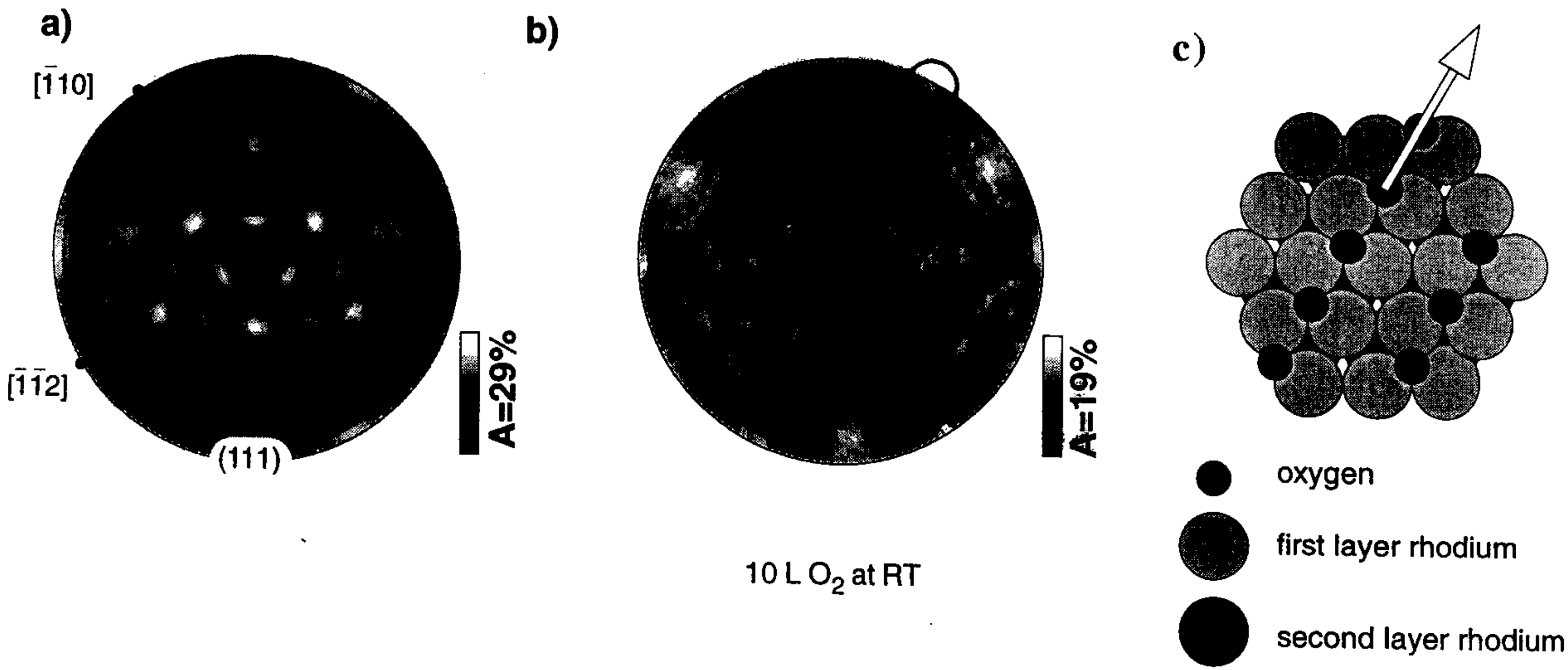
O/Rh(111)
Coverage vs. Oxygen Exposure

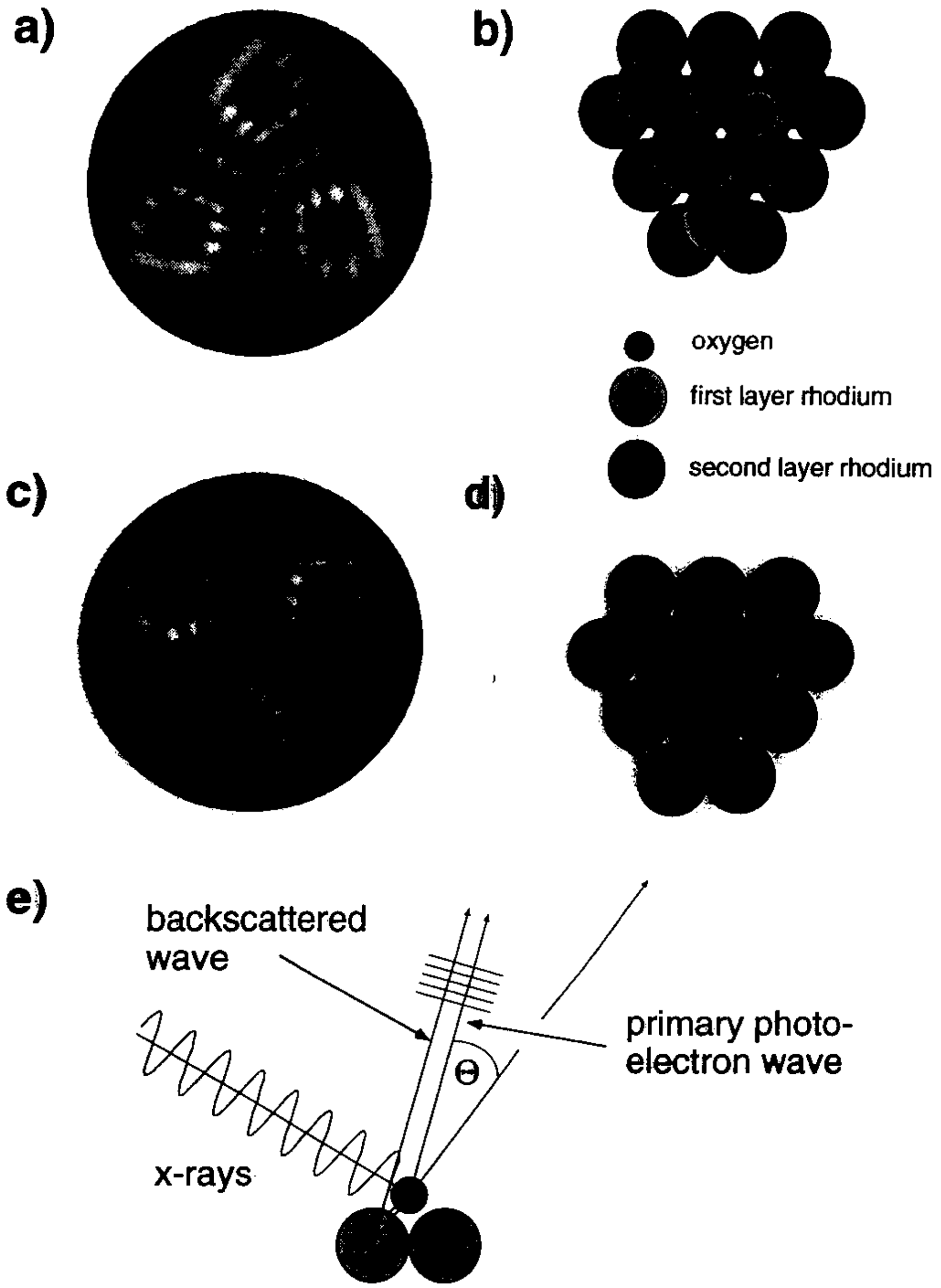




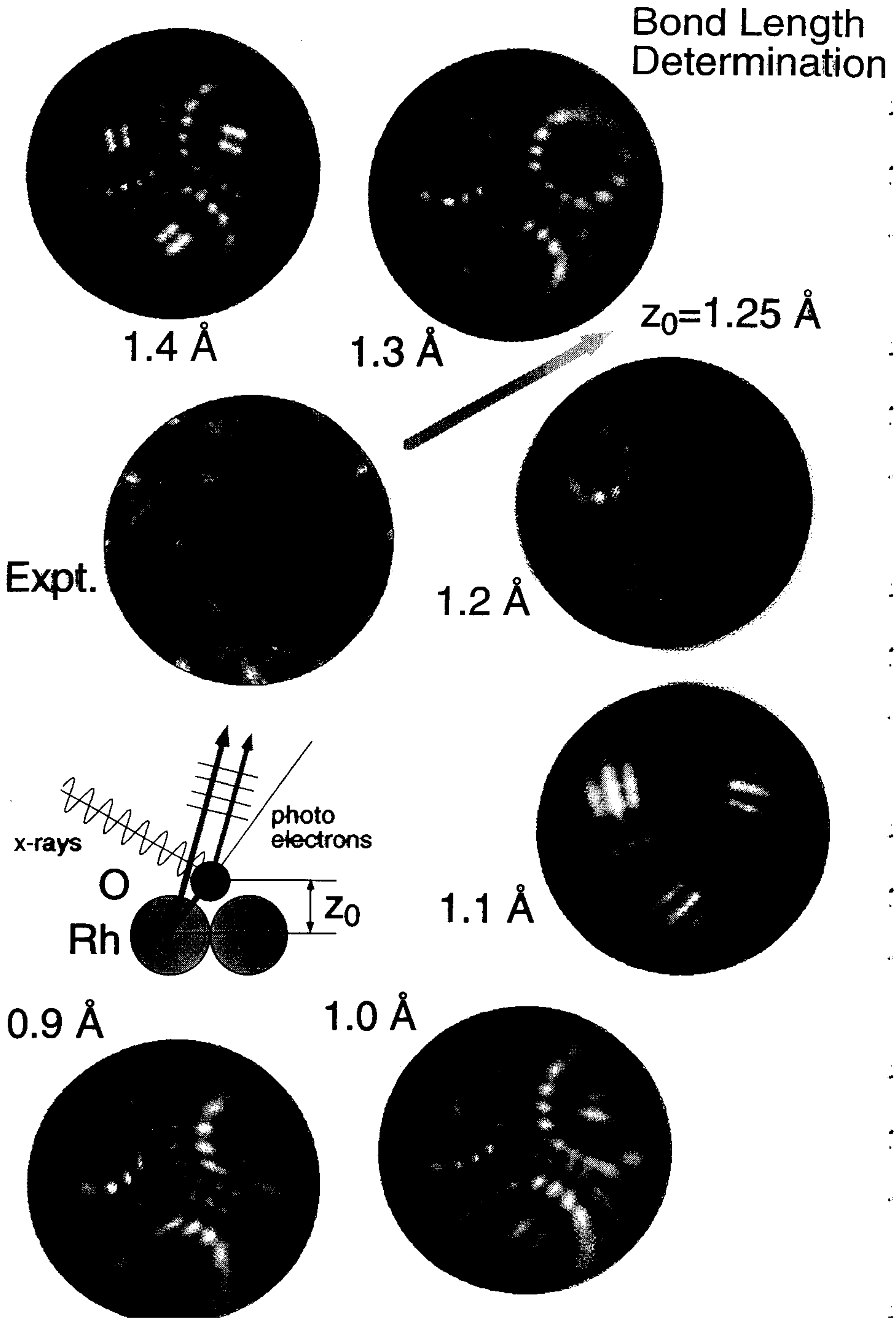
(logarythmic scale !)

O/Rh(111) at RT Saturation: (2x1)-1O Structure



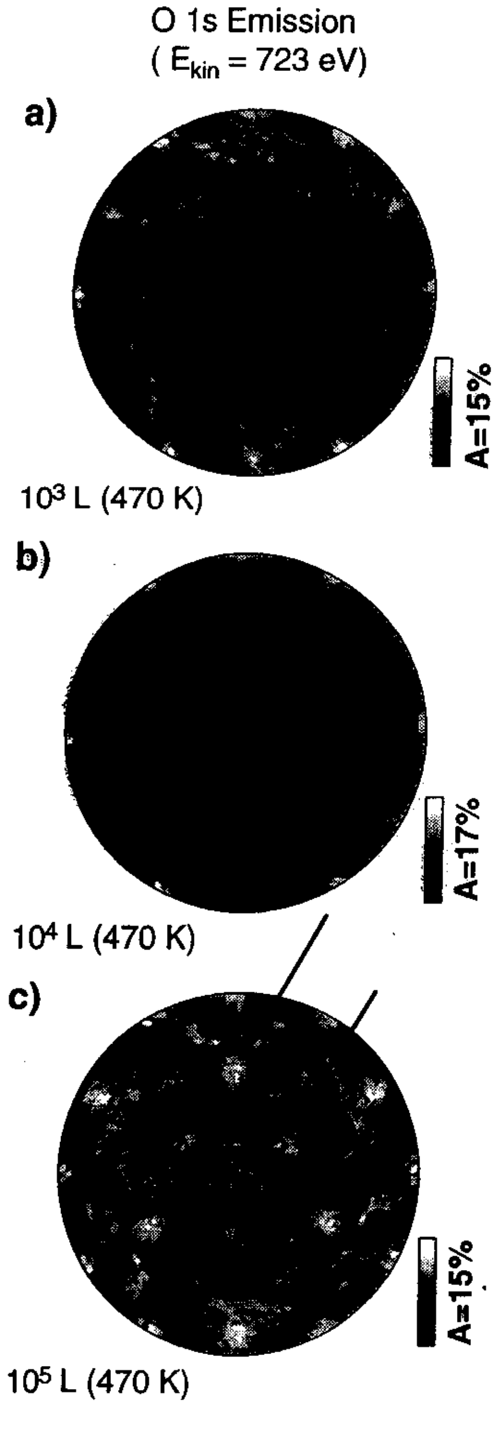


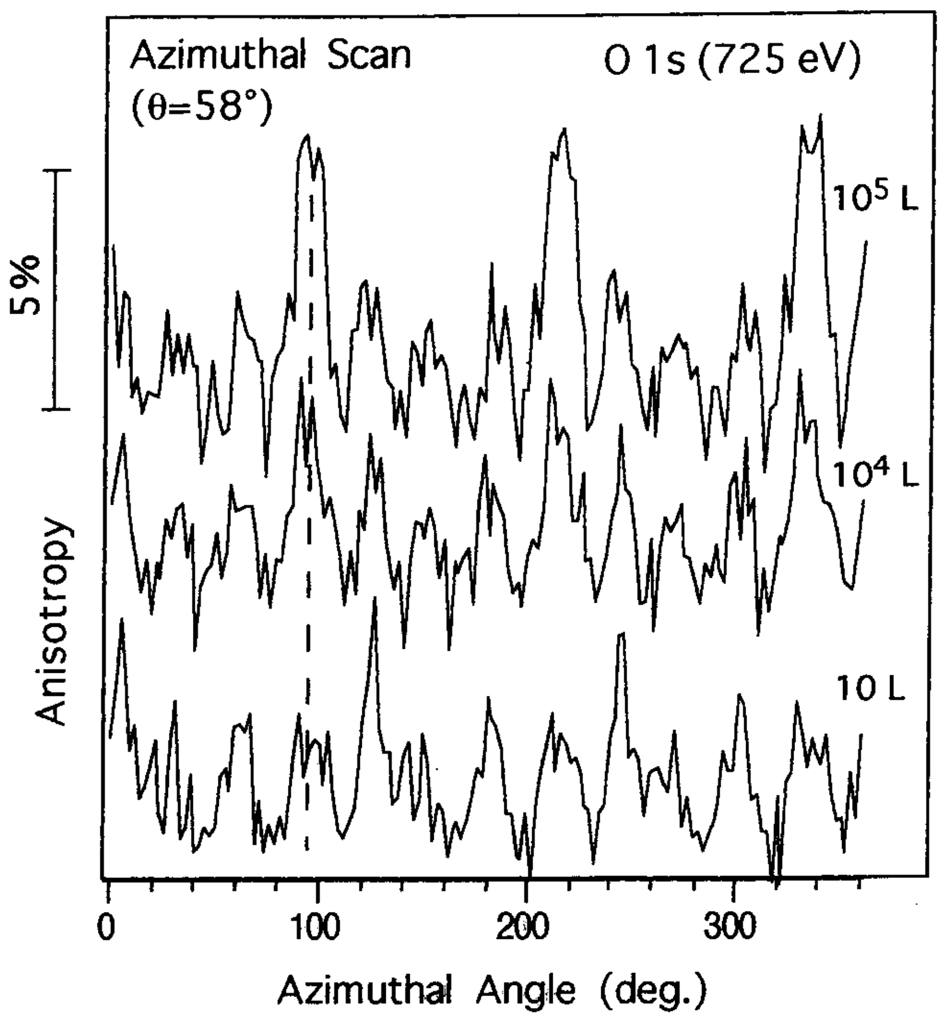
T. Greber et al., PRL $\underline{81}$, 1654 (1998).



Bond Length
Determination
1.4 Å
1.3 Å
z_0=1.25 Å
Expt.
1.2 Å
x-rays
photo
electrons
O
Rh
z_0
1.1 Å
0.9 Å
1.0 Å

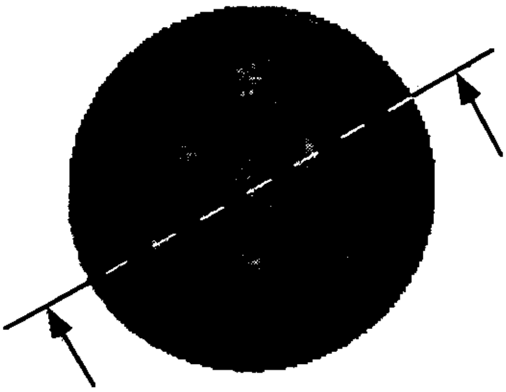
O/Rh(111):
Exposure at 470 K




Azimuthal Scan
(θ=58°)
O 1s (725 eV)
5%
Anisotropy
10^5 L
10^4 L
10 L
0
100
200
300
Azimuthal Angle (deg.)

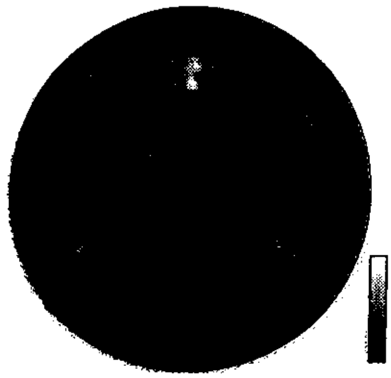
The Subsurface Site

O 1s XPD (723 eV)

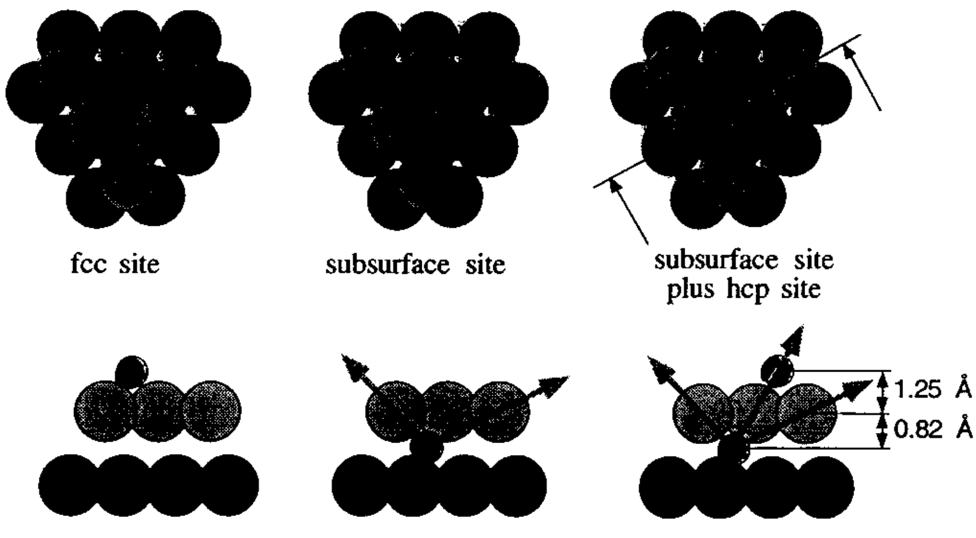


Experiment:

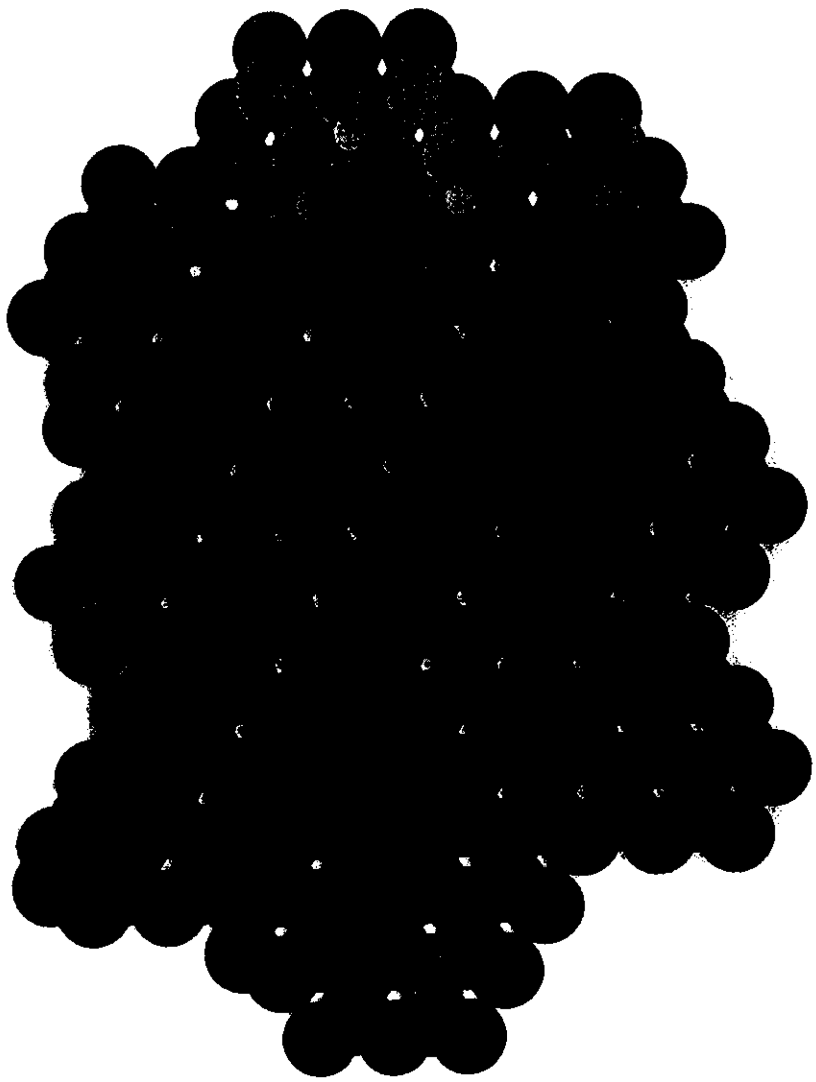
10^5 L Data - 10^3 L Data



Theory (SSC)



The Oxygen - Rh(111) System



fcc (2x1) - O

Rh 1st layer

Rh 2nd layer

RT-saturation

hcp - O

fcc - O

Subsurface oxygen (0.05 ML)

High exposure (470 K)