united nations
educational, scientific
and cultural
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international atomic
energy agency

the
abdus salam
international centre for theoretical physics

SMR/1270-37

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

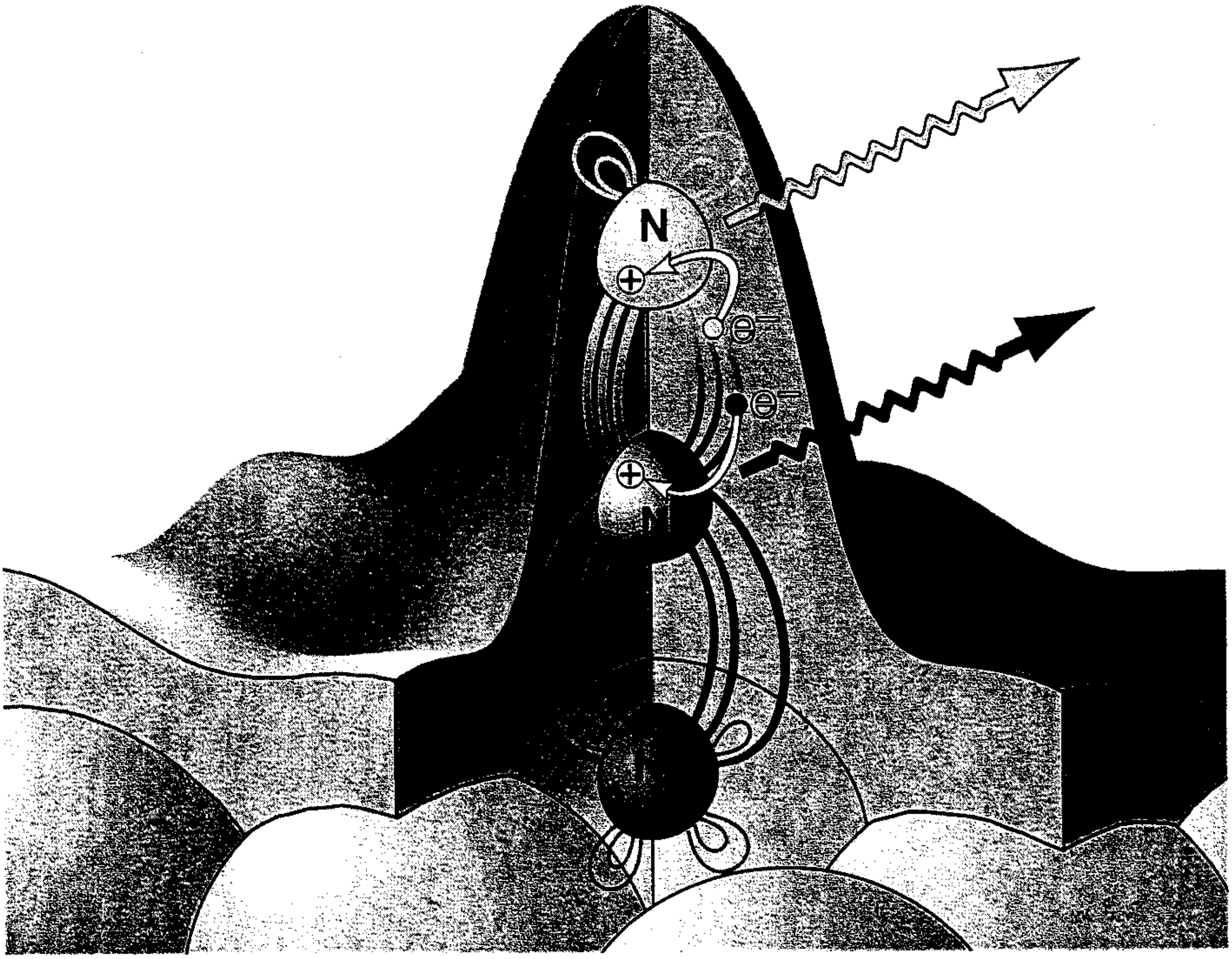
Co-sponsors: Sincrotrone Trieste, Società Italiana di Luce di Sincrotrone (SILS) and the Arab Fund for Economic and Social Development

X-ray emission and absorption spectroscopy

A. Nilsson
University of Uppsala
Sweden

An Atom Specific Probing of the Surface Chemical Bond

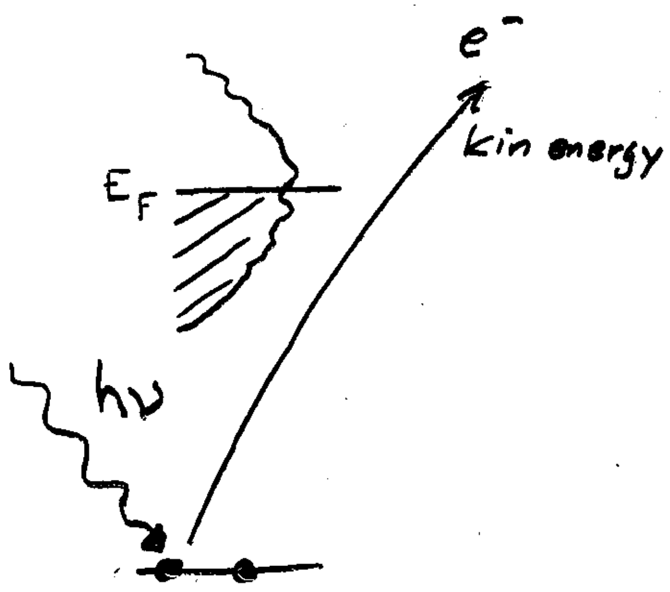
Anders Nilsson
Department of Physics
Uppsala University
Stanford University



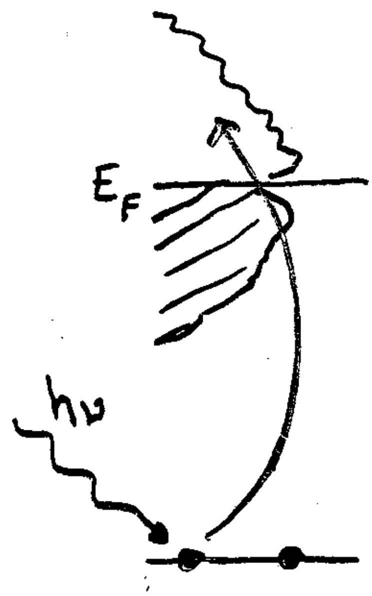
Atom and orbital symmetry specific electron structure

X-ray Emission Spectroscopy (XES)
Resonant Inelastic X-ray Scattering (RIXS)

a) creation of core holes

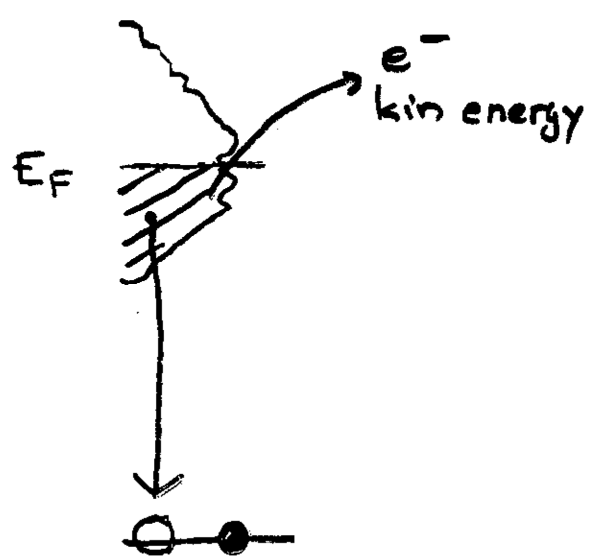


Jonization
(XPS or ESCA)

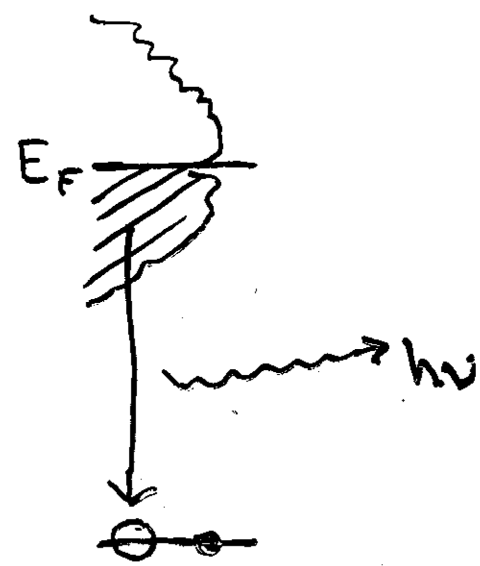


Excitation
(XAS or NEXAFS)

b) core hole decay



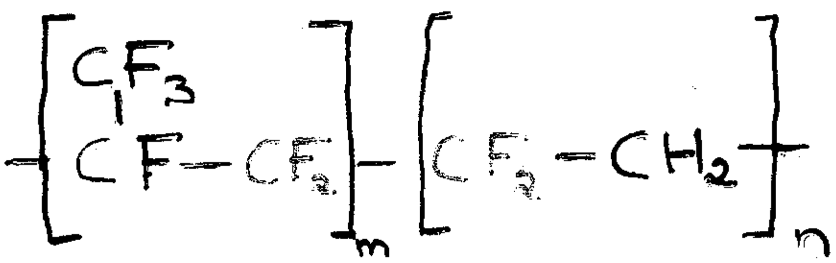
Autoionization
or
Auger decay

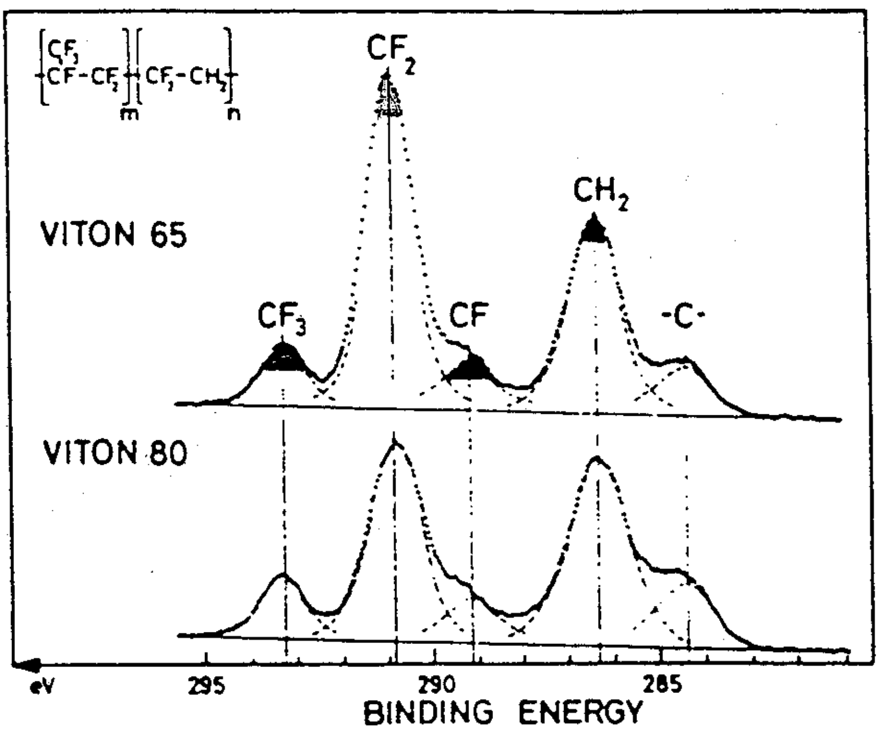


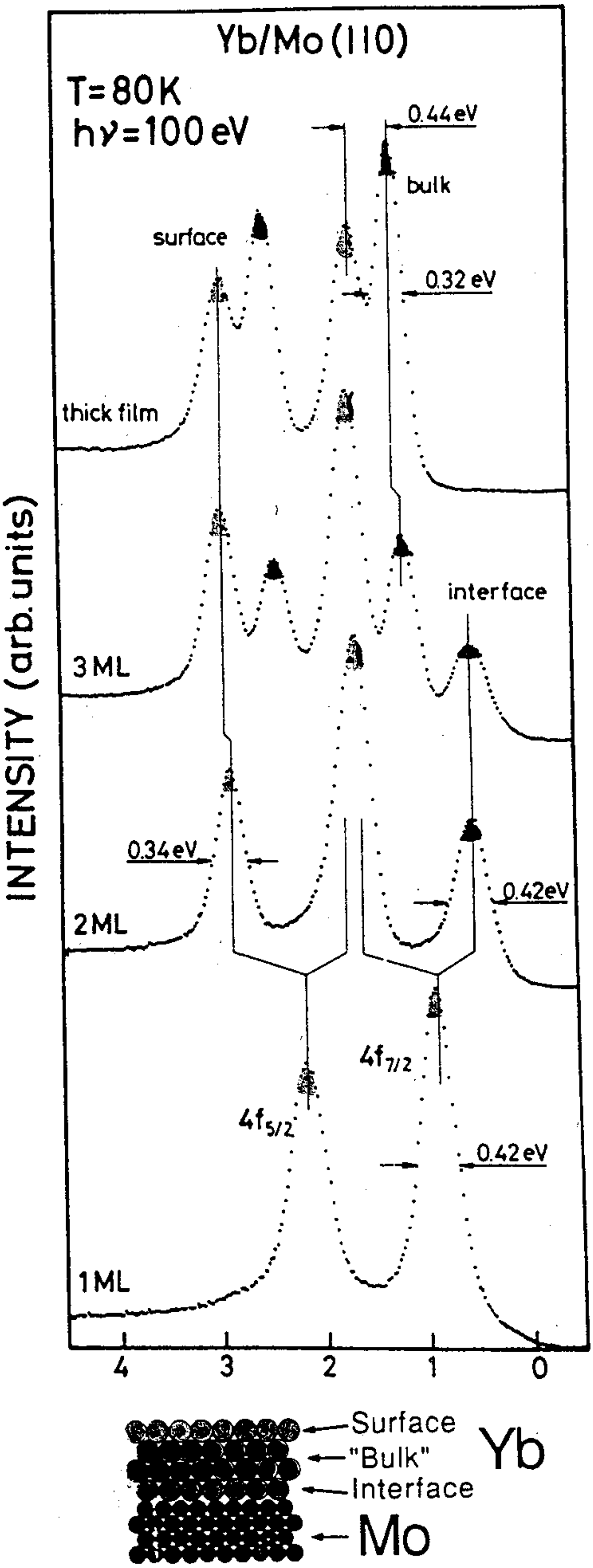
X-ray emission

Chemical shifts in XPS

Viton Polymers







Mårtensson et. al
Phys. Rev. Lett.
<u>60</u>, 1731 (1988)

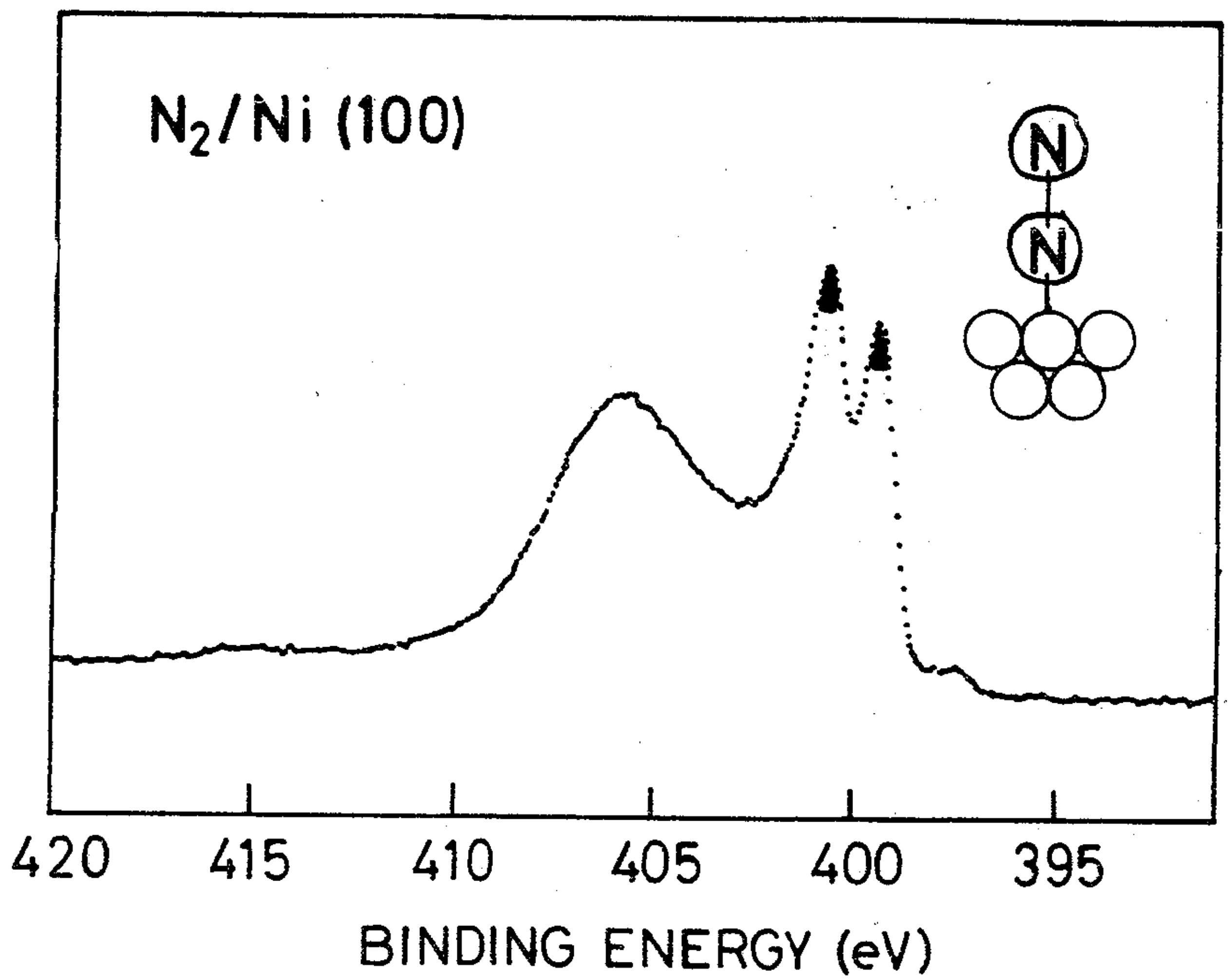
70%
GA

Chemical shifts

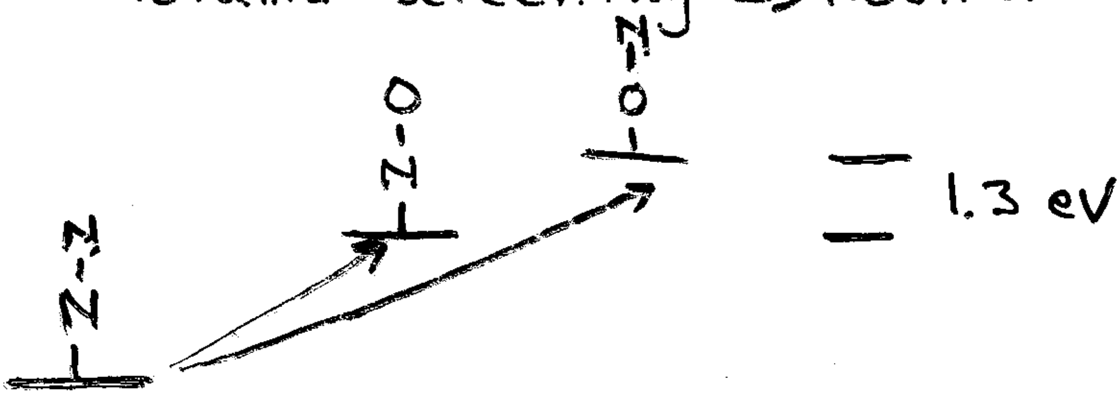
Different atoms within an molecule

standing up configuration

Nilsson et.al. Phys Rev Lett 67, 1015 (1991)

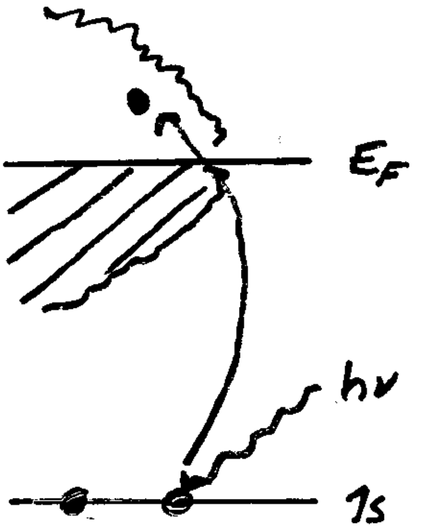


metallic screening ⇒ neutral final state



X-ray Absorption Spectroscopy XAS

XAS or NEXAFS



Probing unoccupied states

Dipole selection rule

$\langle \psi_i | \vec{r} | \psi_f \rangle$

one center approximation $\Rightarrow$

atomic orbitals selection rule

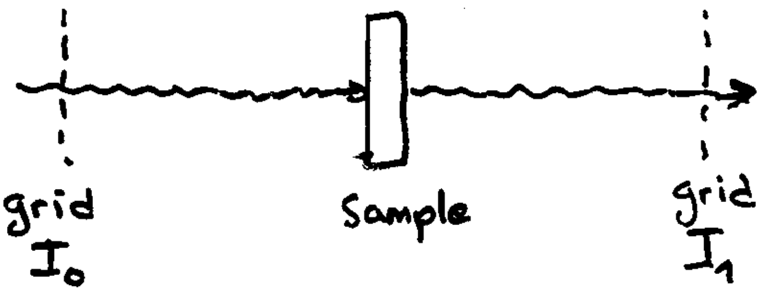
1s $\rightarrow$ 2p

2p $\rightarrow$ 3d, 4s

etc.

X-ray Absorption measurements:

- transmission

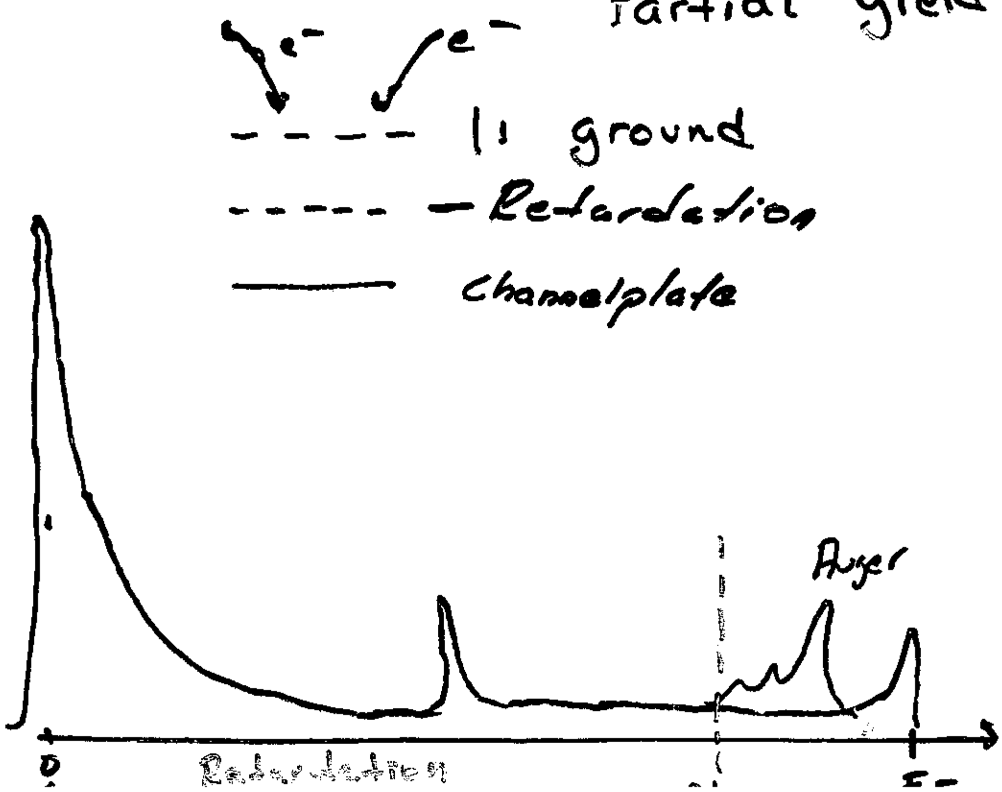


- number of core holes created

electron yield ⇒ Auger Processes

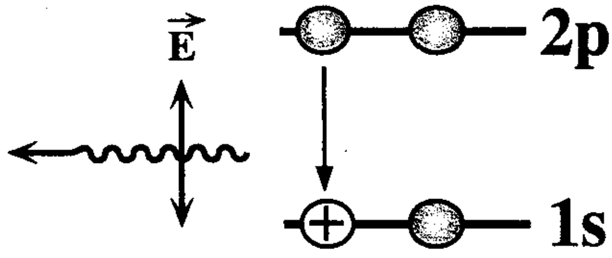
fluorescence yield ⇒ x-ray emission

Partial yield detector

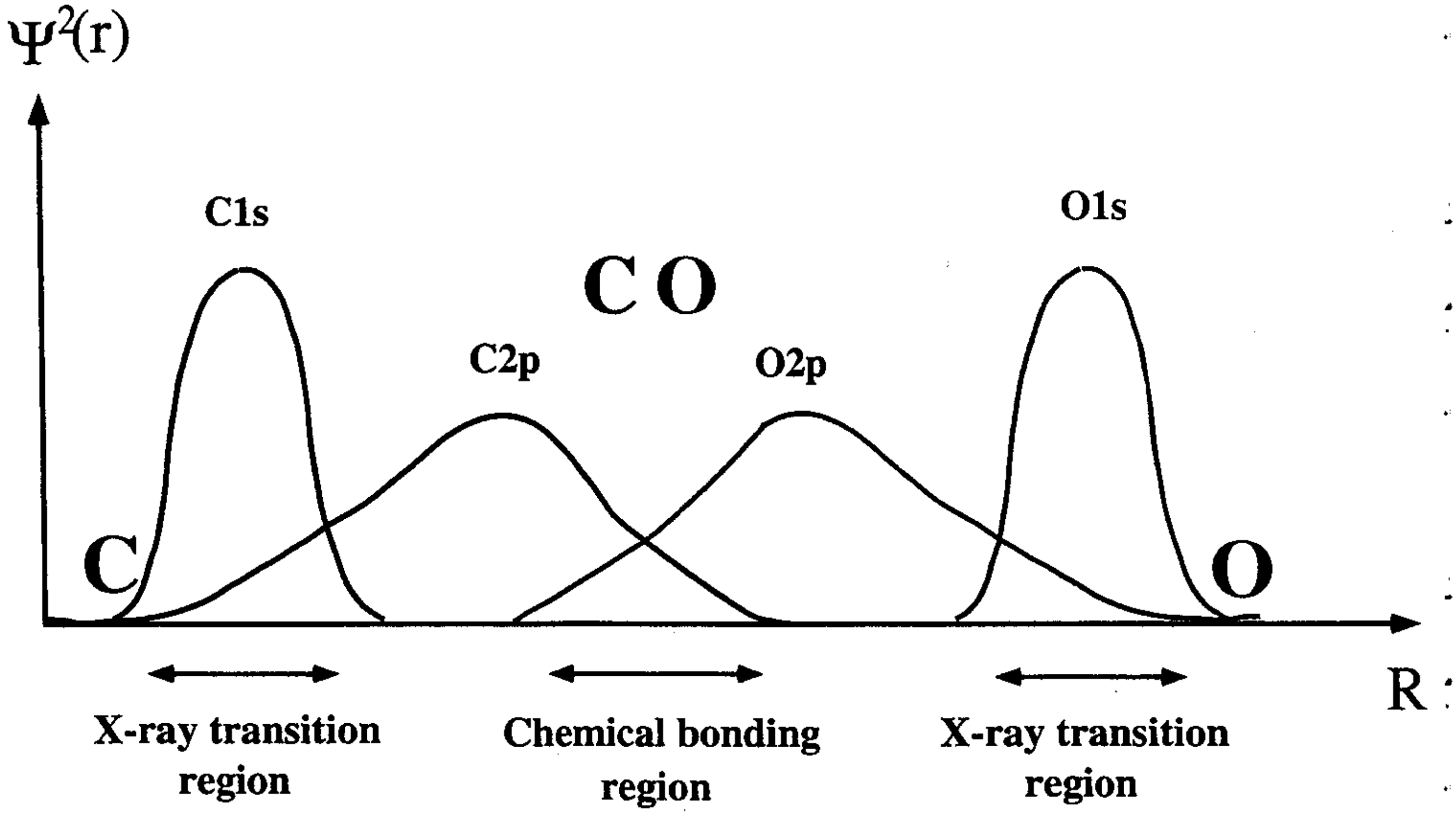


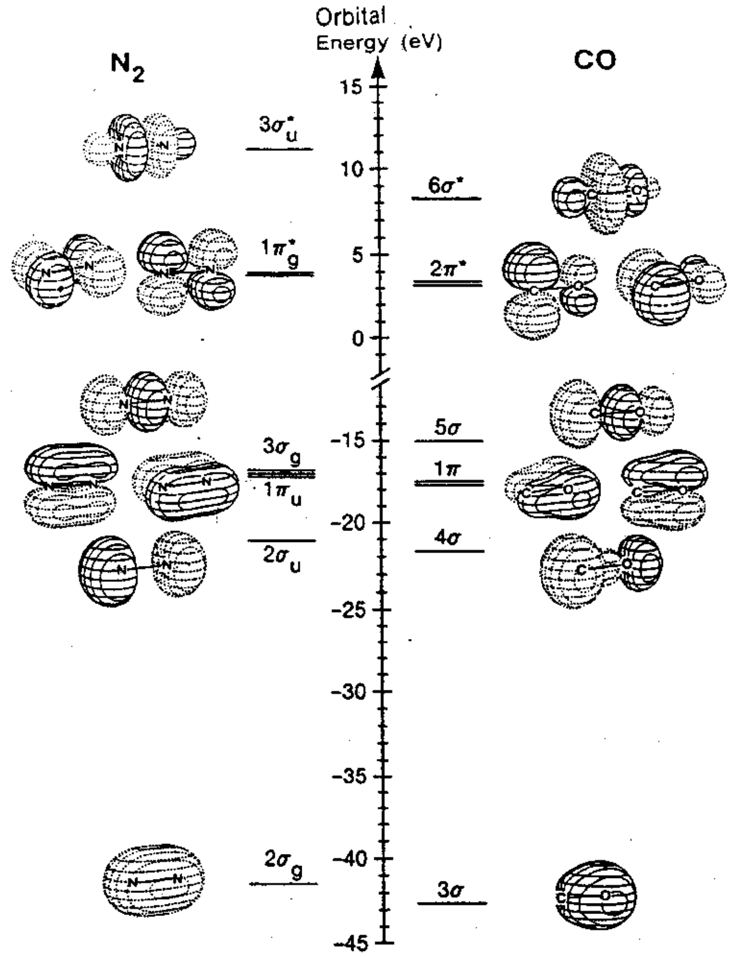
X-ray Emission Spectroscopy (XES)

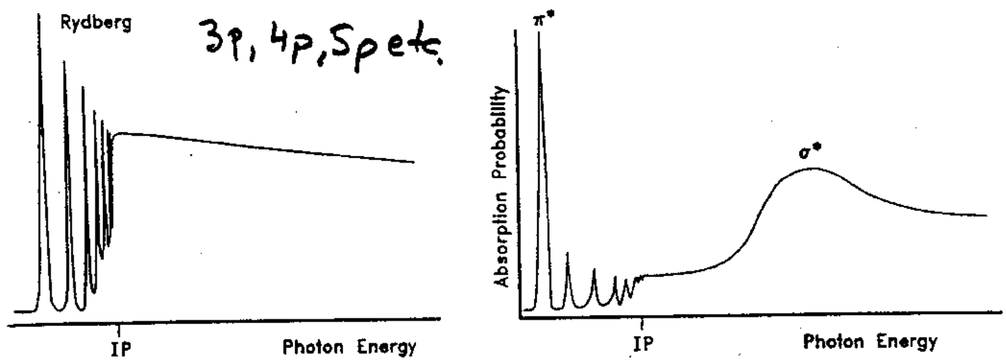
Dipole selection rule

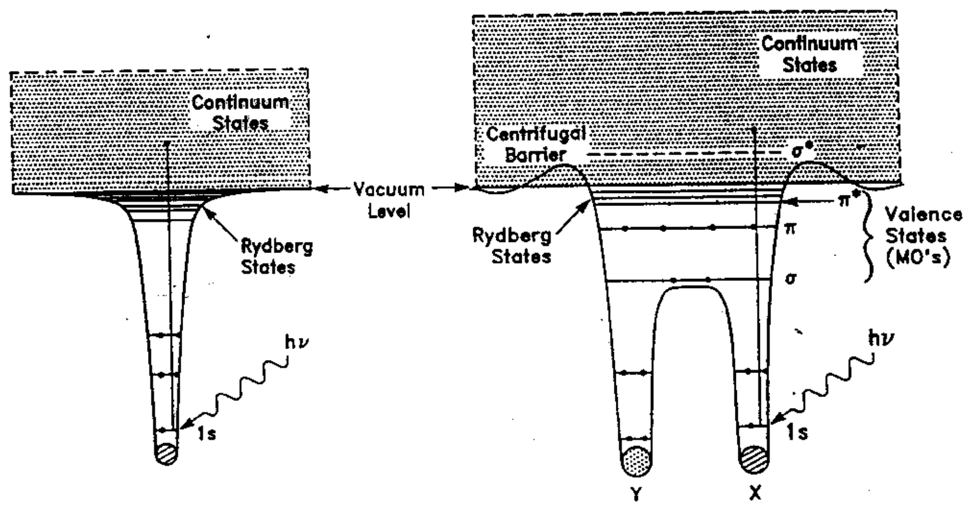


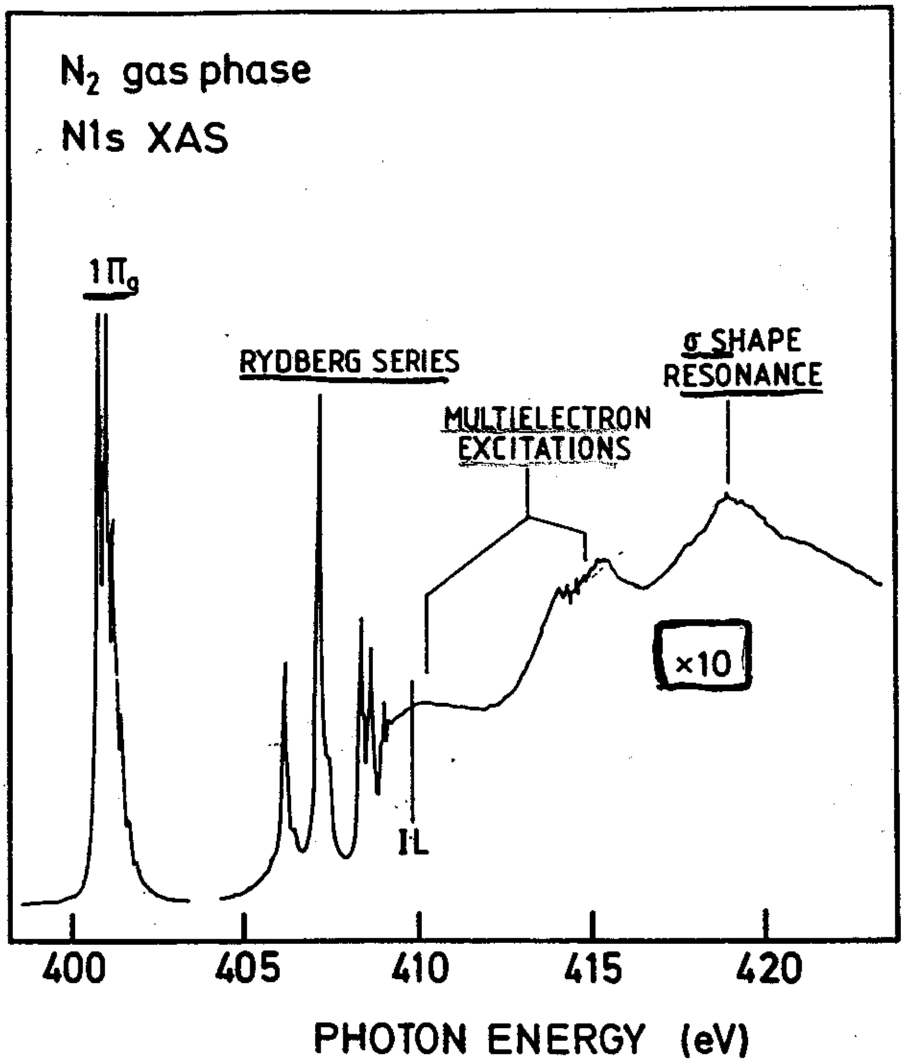
One center approximation




Orbital Energy (eV)
N_2
CO
15
10
5
0
-15
-20
-25
-30
-35
-40
-45
$3\sigma_u^*$
$1\pi_g^*$
$3\sigma_g$
$1\pi_u$
$2\sigma_u$
$2\sigma_g$
$6\sigma^*$
$2\pi^*$
5σ
1π
4σ
3σ


Rydberg
3p, 4p, 5p etc.
IP
Photon Energy
π^*
σ^*
Absorption Probability
IP
Photon Energy


Continuum States
Rydberg States
$h\nu$
1s
Vacuum Level
Continuum States
Centrifugal Barrier
σ^*
π^*
π
σ
Valence States (MO's)
Rydberg States
$h\nu$
1s
Y
X



Ma et al Phys. Rev. A 44, 1848 (1991)

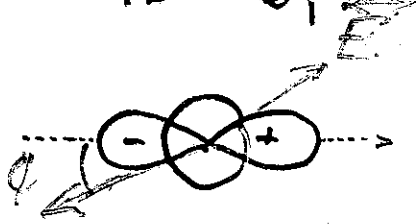
Moleculor orbitals

Rydberg states: extended atomic like states

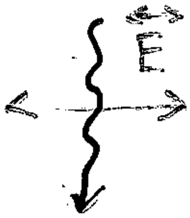
Multielectron excitations:

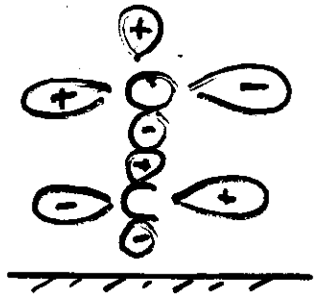
shake-up processes

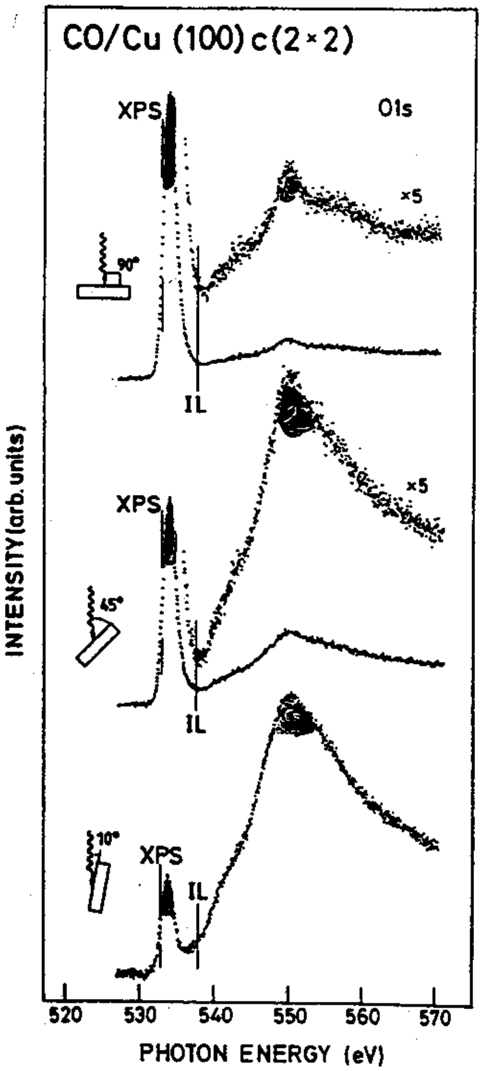
$1s \rightarrow 2p$

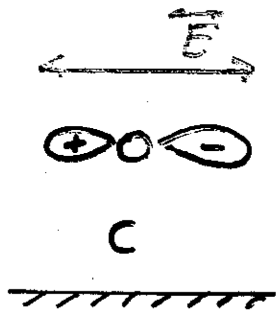


$$I \propto \cos^2\theta$$

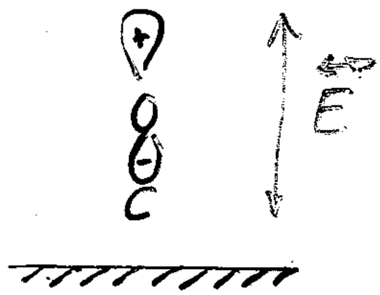






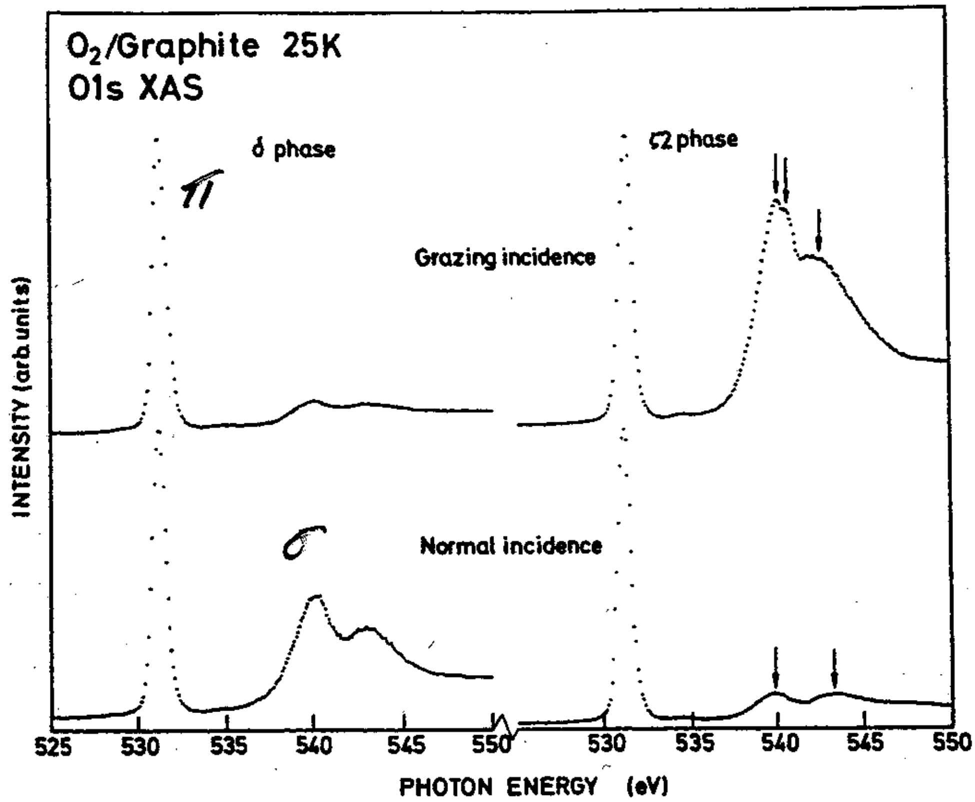


π-states



σ-states

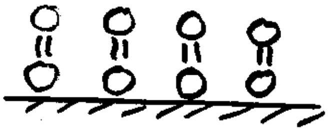
Bjøreholm et.al. Phys. Rev. B47, 2308 (1993)



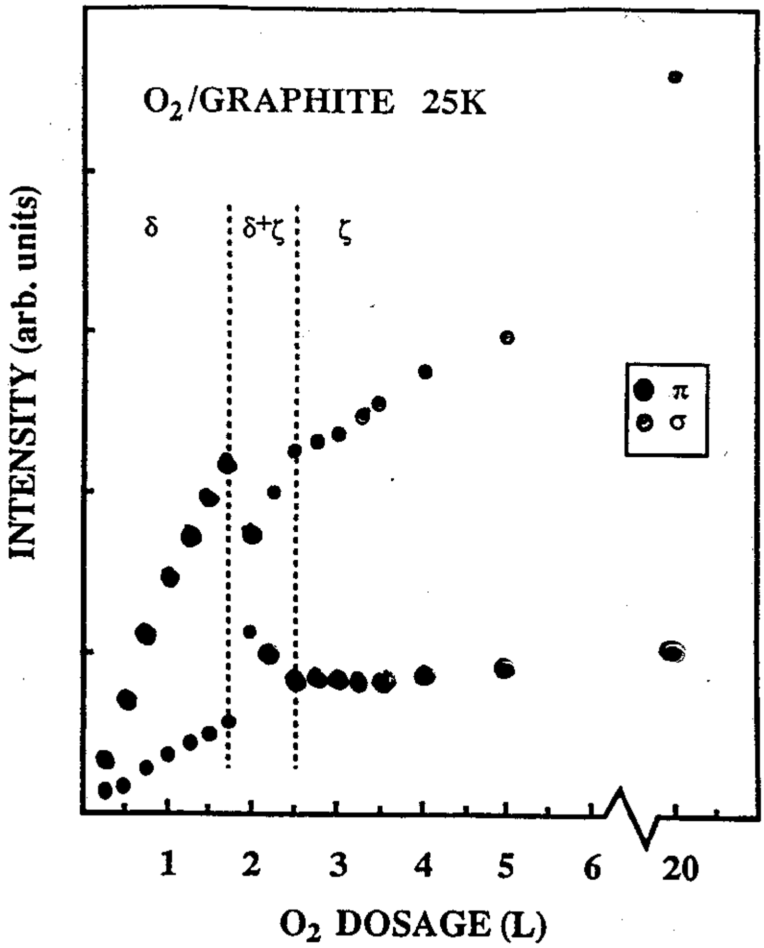
Guest et al. Surf. Sci. 269/270, 432 (1992)

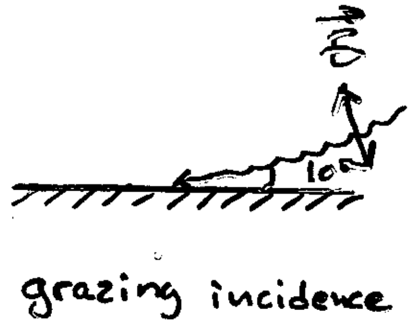
O_2 physisorbed on graphite

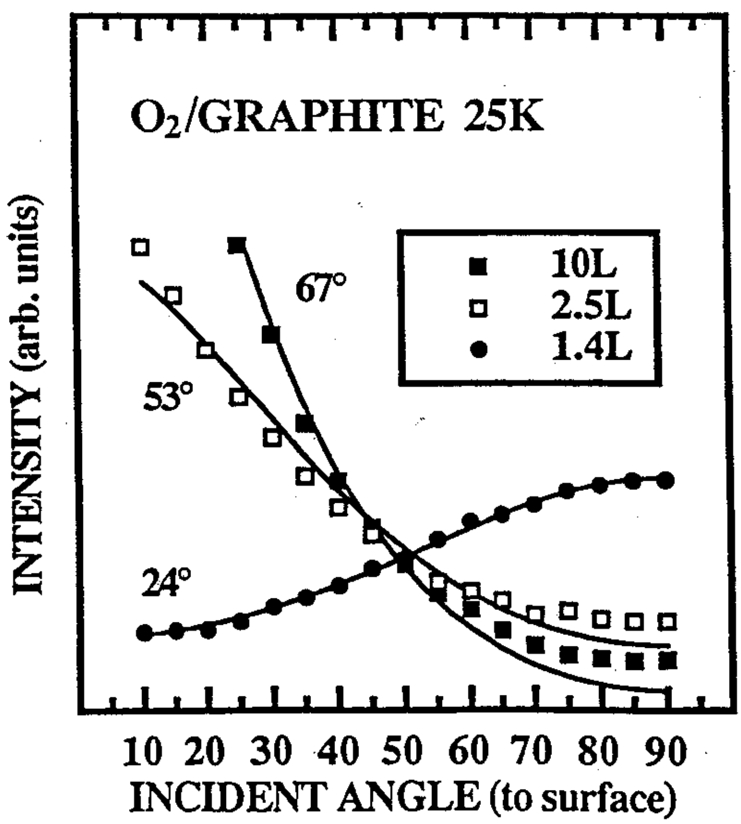
δ-phase



ε2-phase

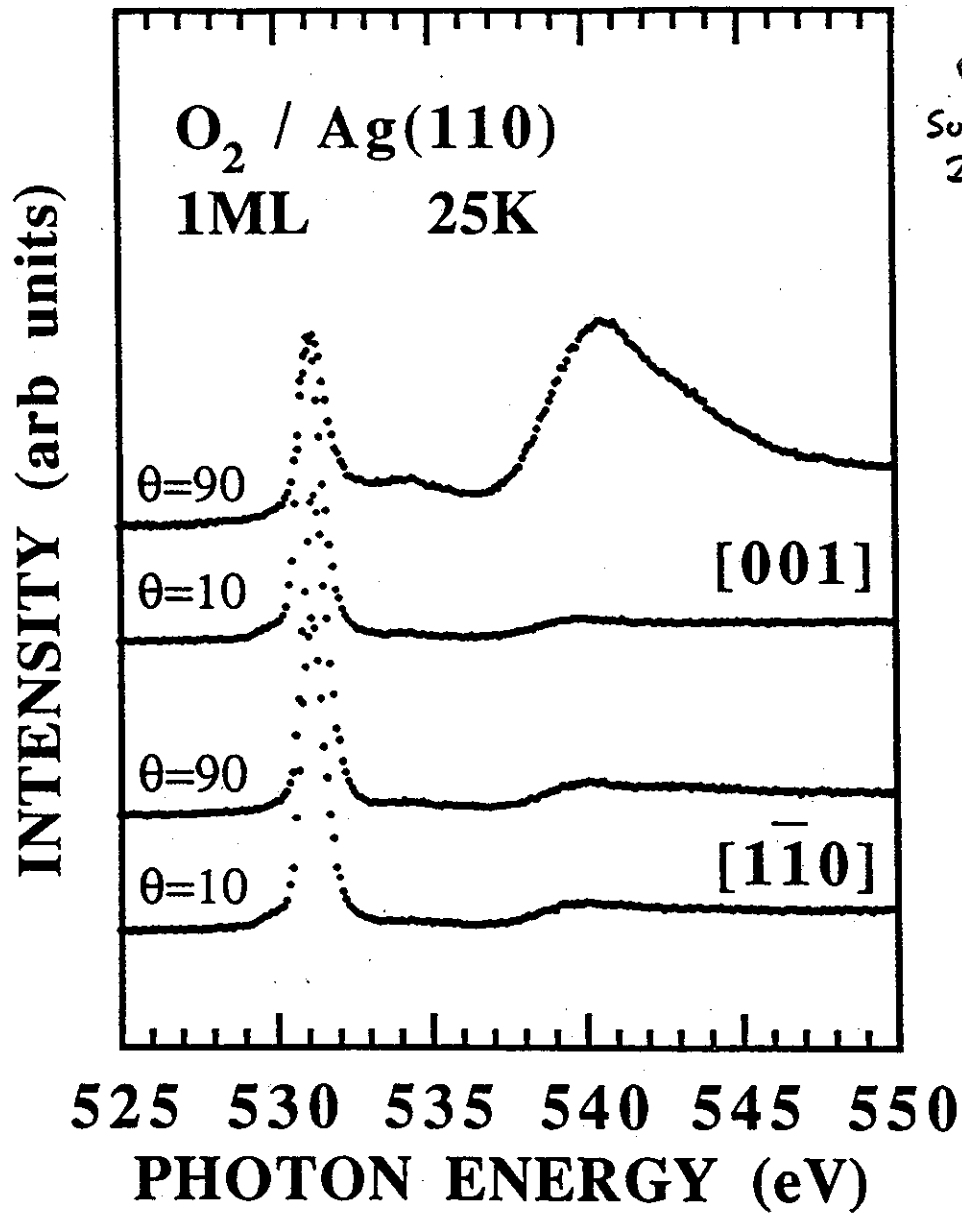


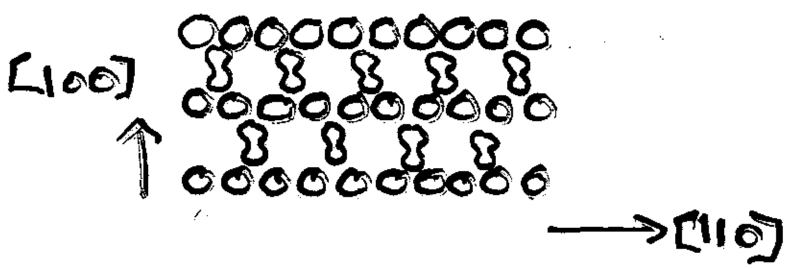


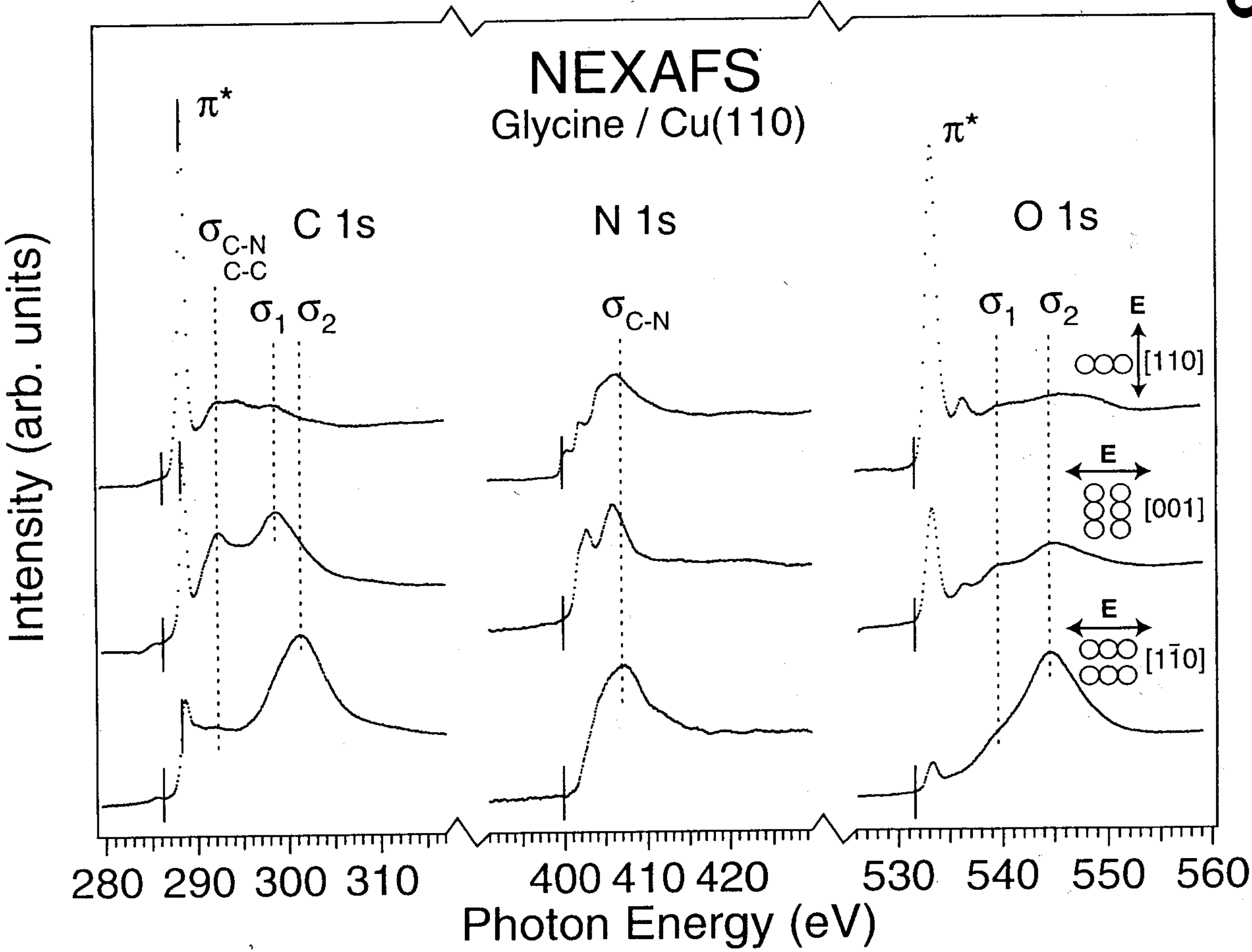


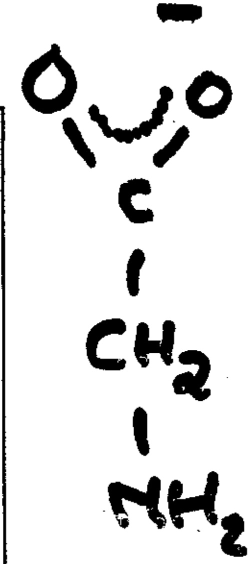
Guest et.al Surf. Sci. 269/270, 432 (1992)

Guest et.al
Surf. Sci 278, 239 (1992)





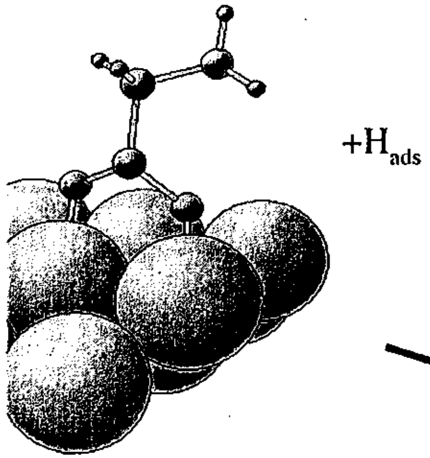

NEXAFS
Glycine / Cu(110)
C 1s
N 1s
O 1s
π^*
σ_{C-N} C-C
σ_1 σ_2
σ_{C-N}
σ_1 σ_2
E
[110]
[001]
[1$\bar{1}$0]
Intensity (arb. units)
280 290 300 310
400 410 420
530 540 550 560
Photon Energy (eV)



Glycine chemistry on Cu(110)

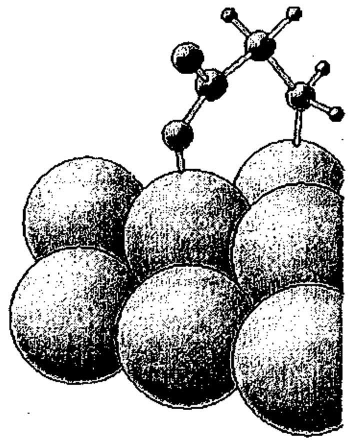
$NH_2CH_2COOH(g)$
+
Cu(110)

1.2 eV



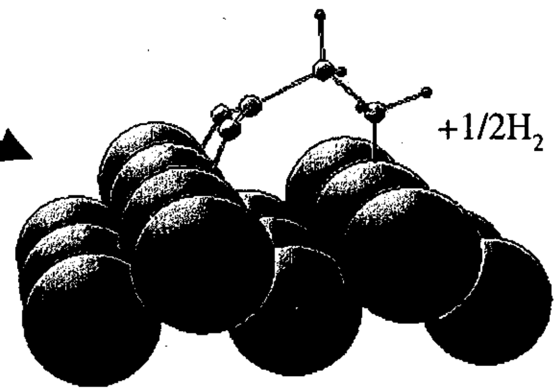
$+H_{ads}$

0.11 eV

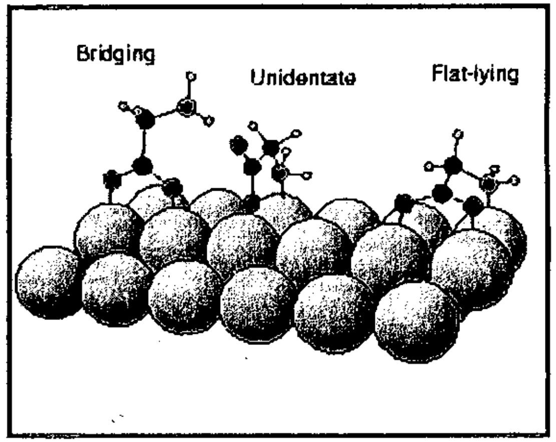


$+H_{ads}$

1.03 eV



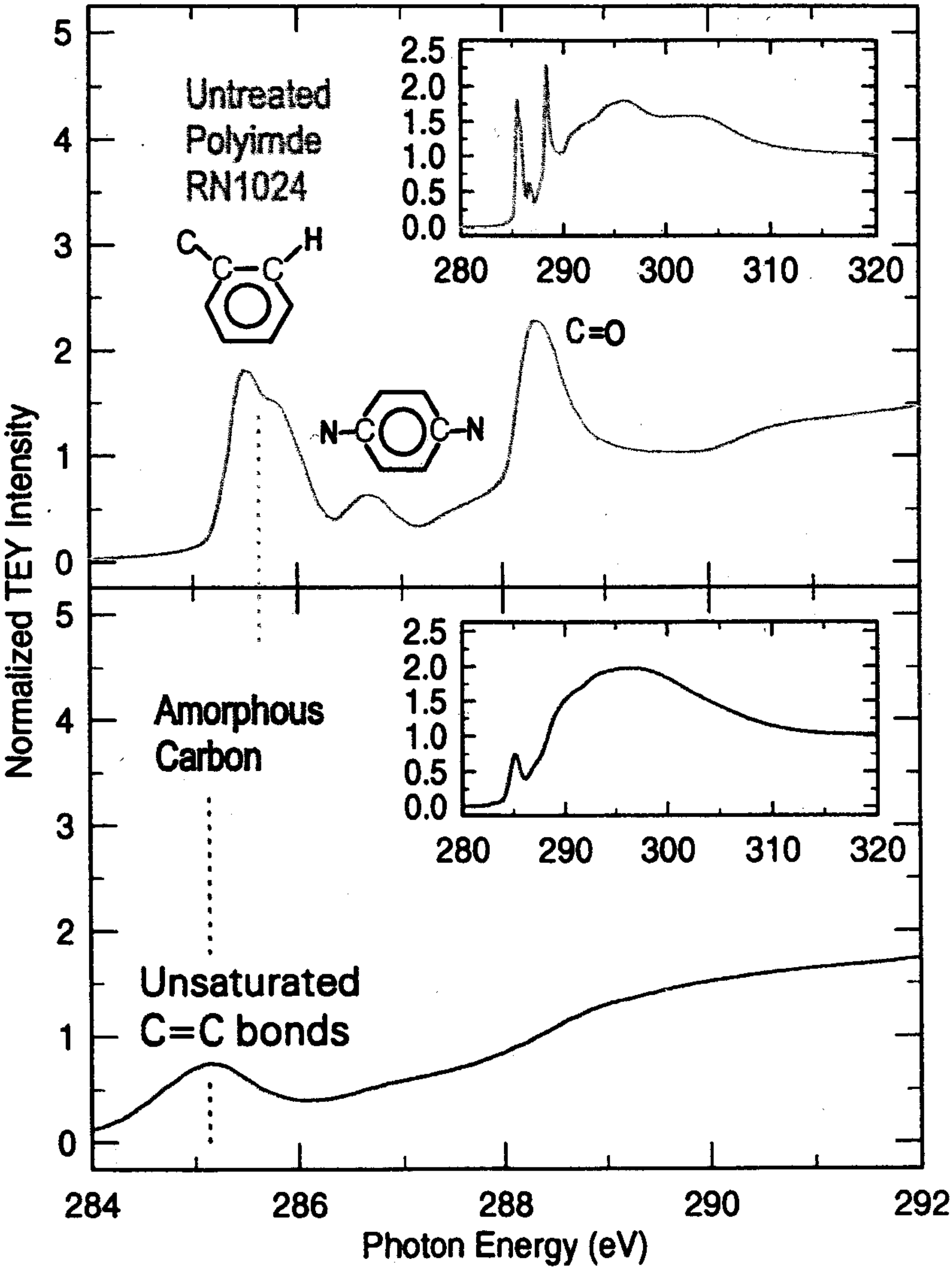
$+1/2H_2$



Sequence determined using IRAS by Barlow *et al*

Energies from DFT cluster model calculations

NEXAFS of Polyimide and Amorphous Carbon

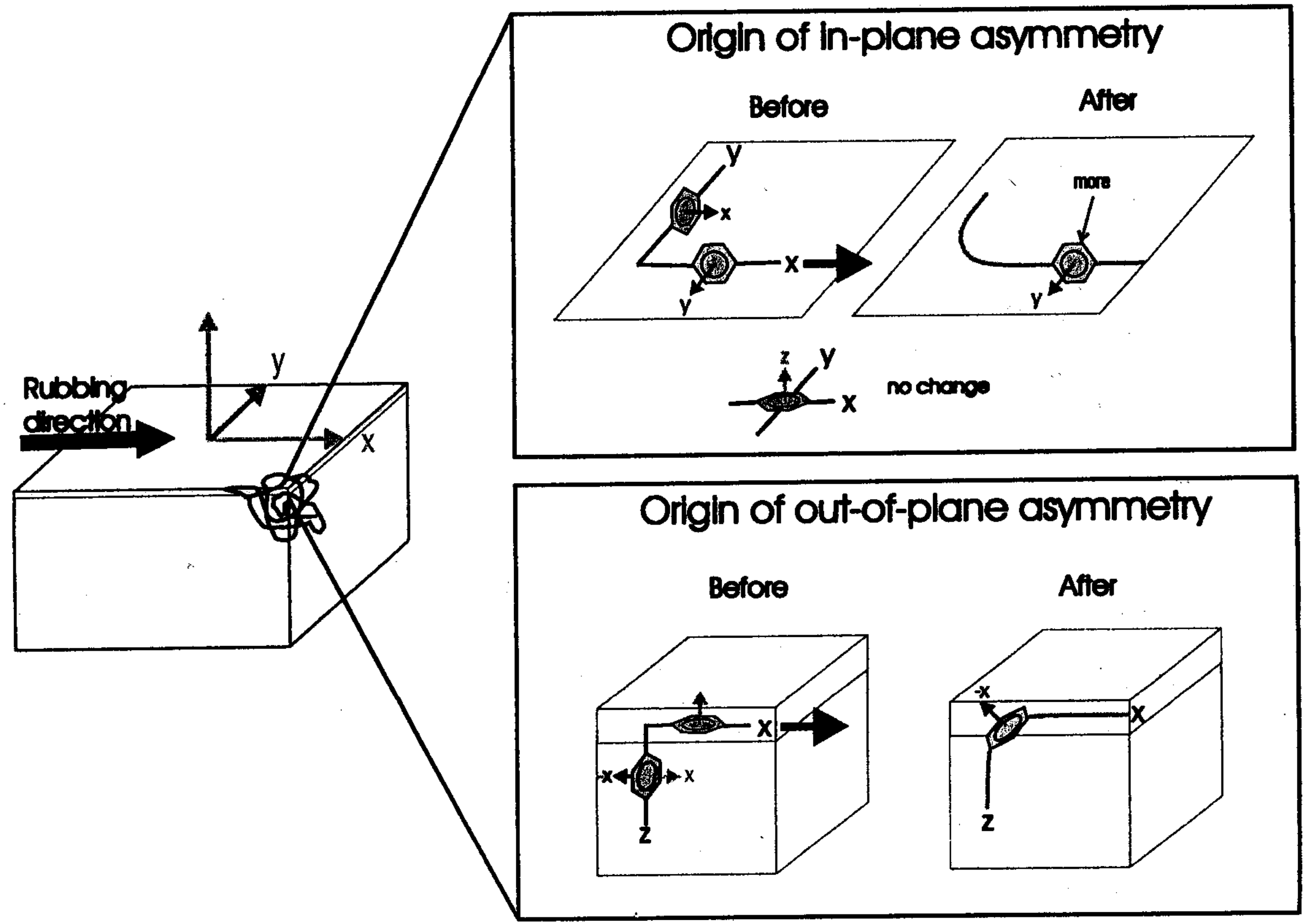


ibnexafs.cdr

IBM Almaden

7

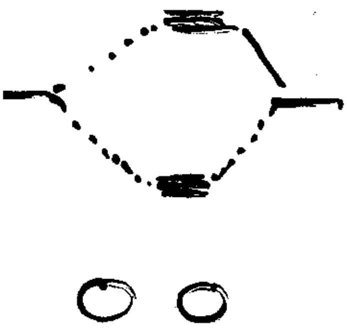
[illegible] fibers orient polymer chains at surface by pulling

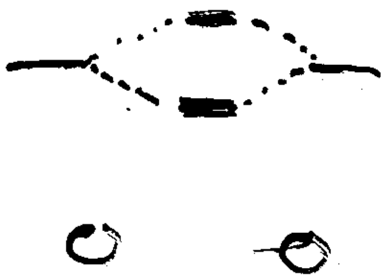


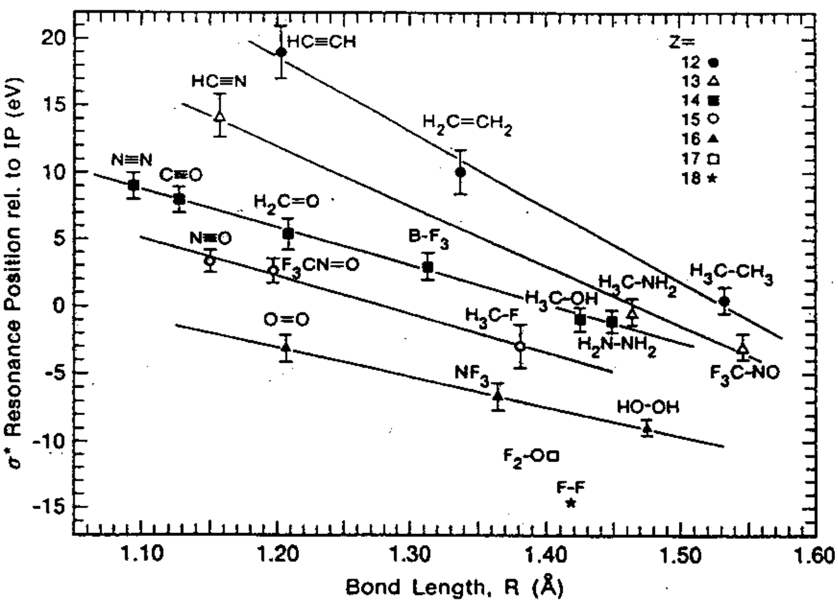
σ - resonance ⇔ bond length

multiple scattering in molecular potential

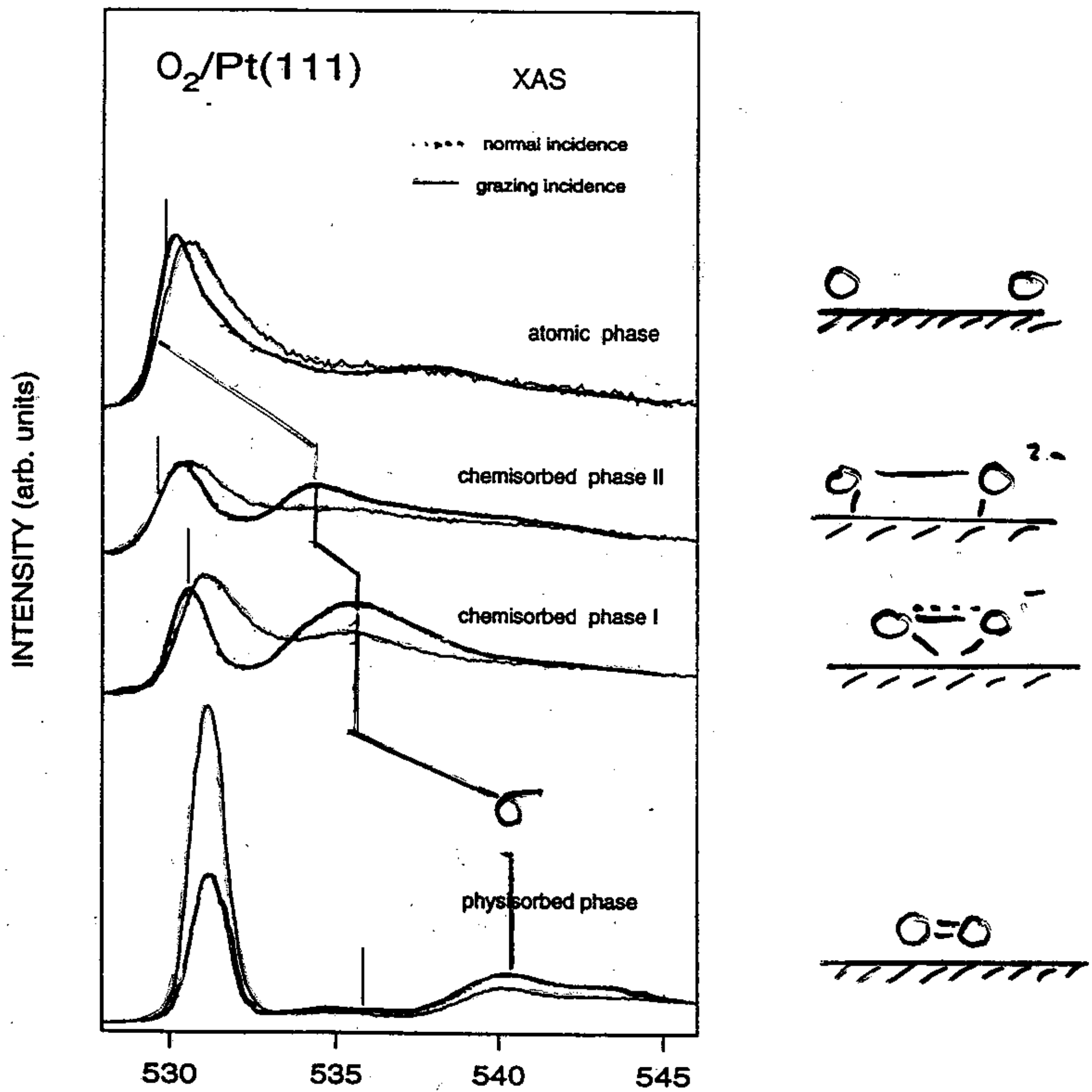
bonding ⇔ antibonding



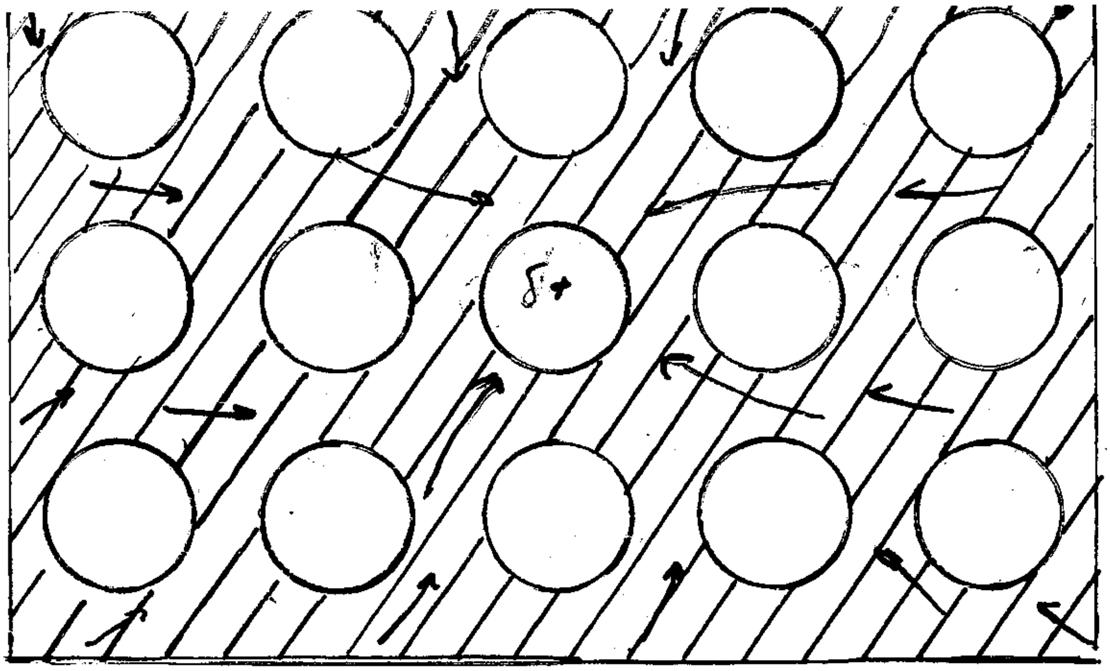


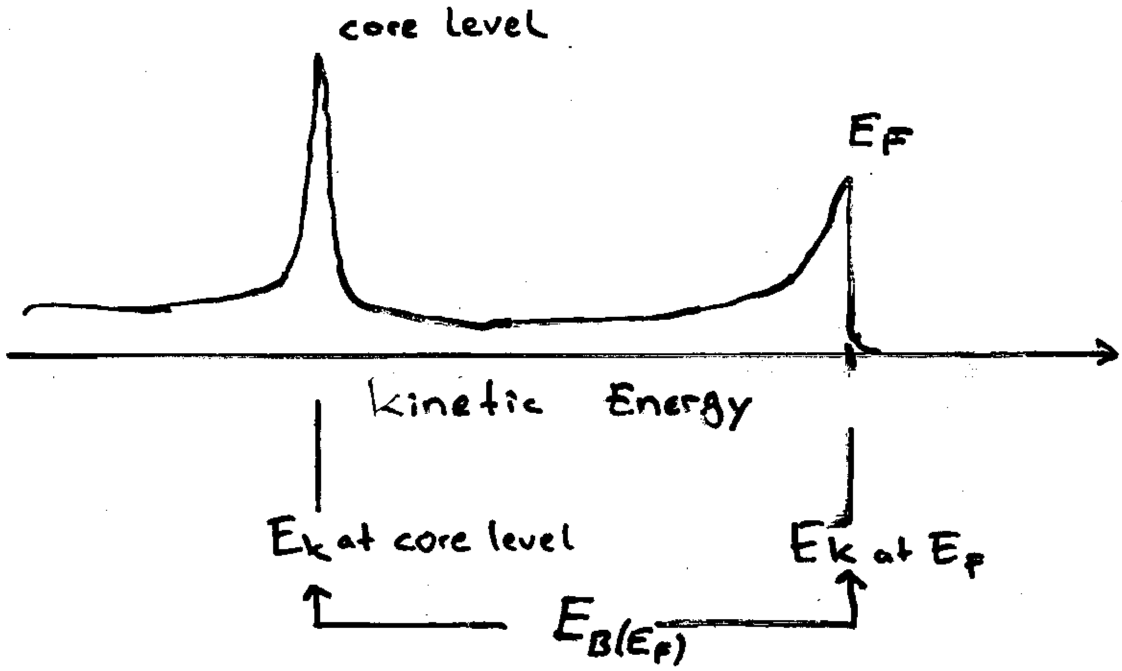


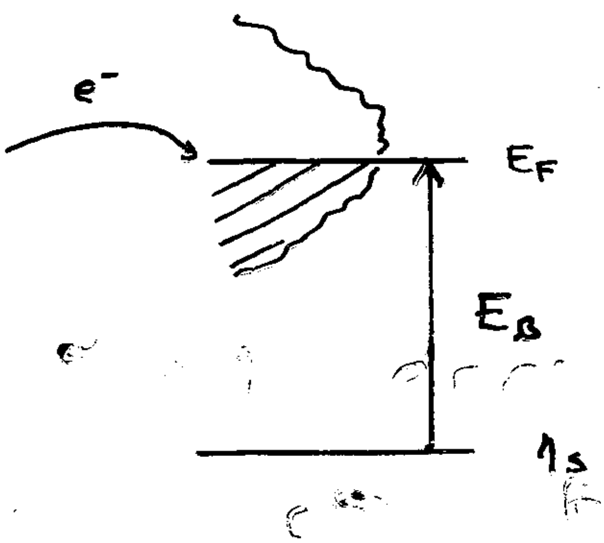
Stöhr, "NEXAFS spectroscopy"



Puglia, etal Surf. sci. in press





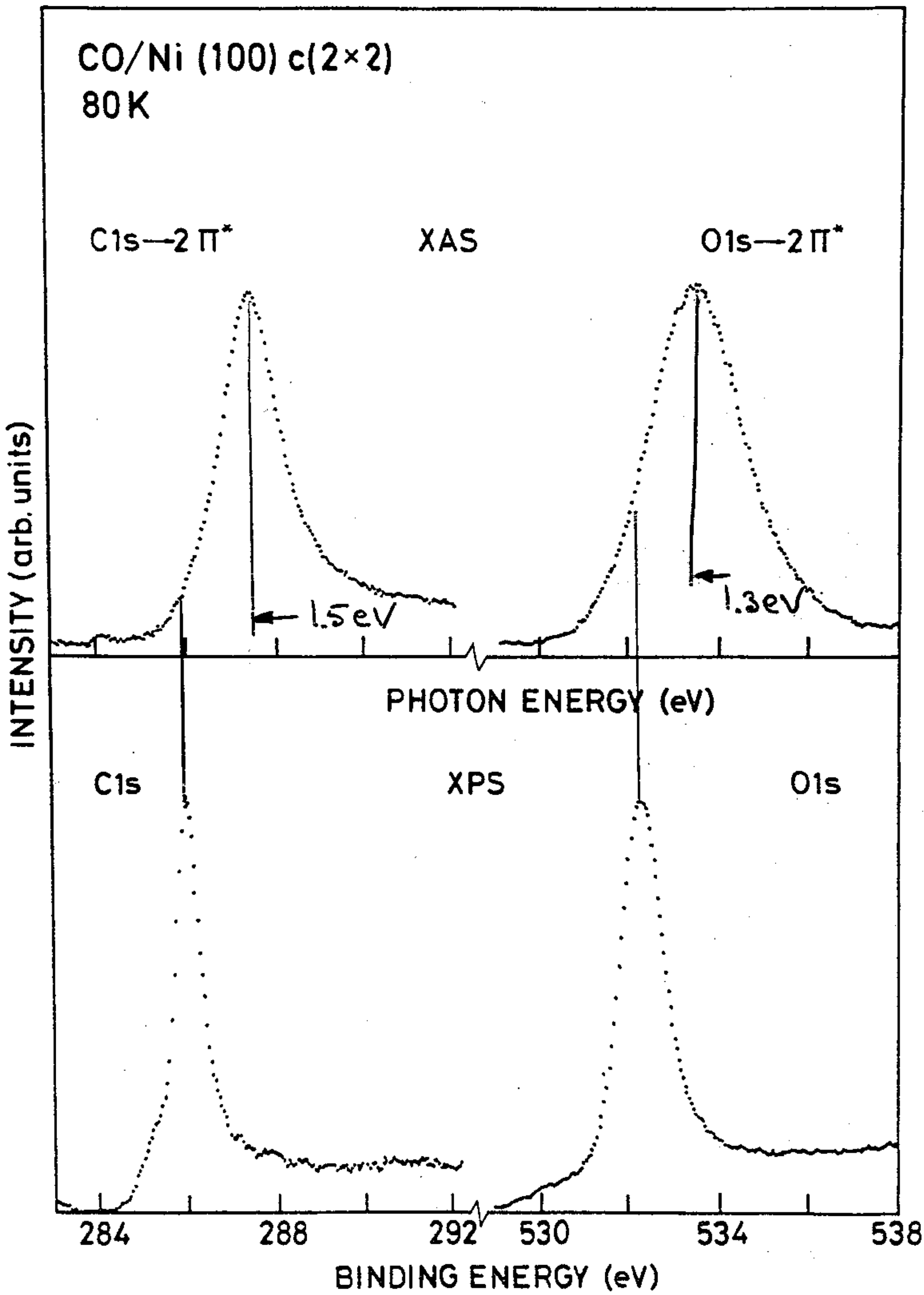


Metallic system

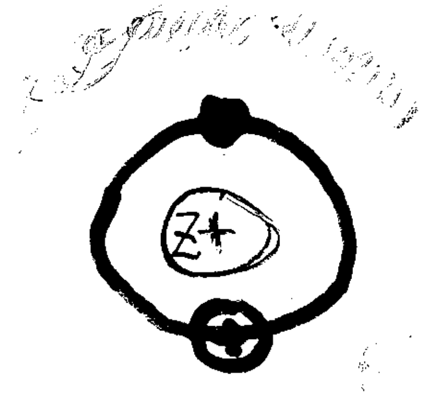
$N \sim N-1$

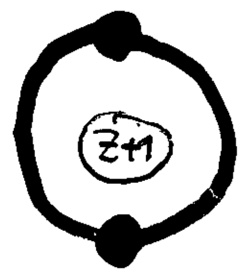
when $N \sim 10^{26}$

Unoccupied states



Core hole state



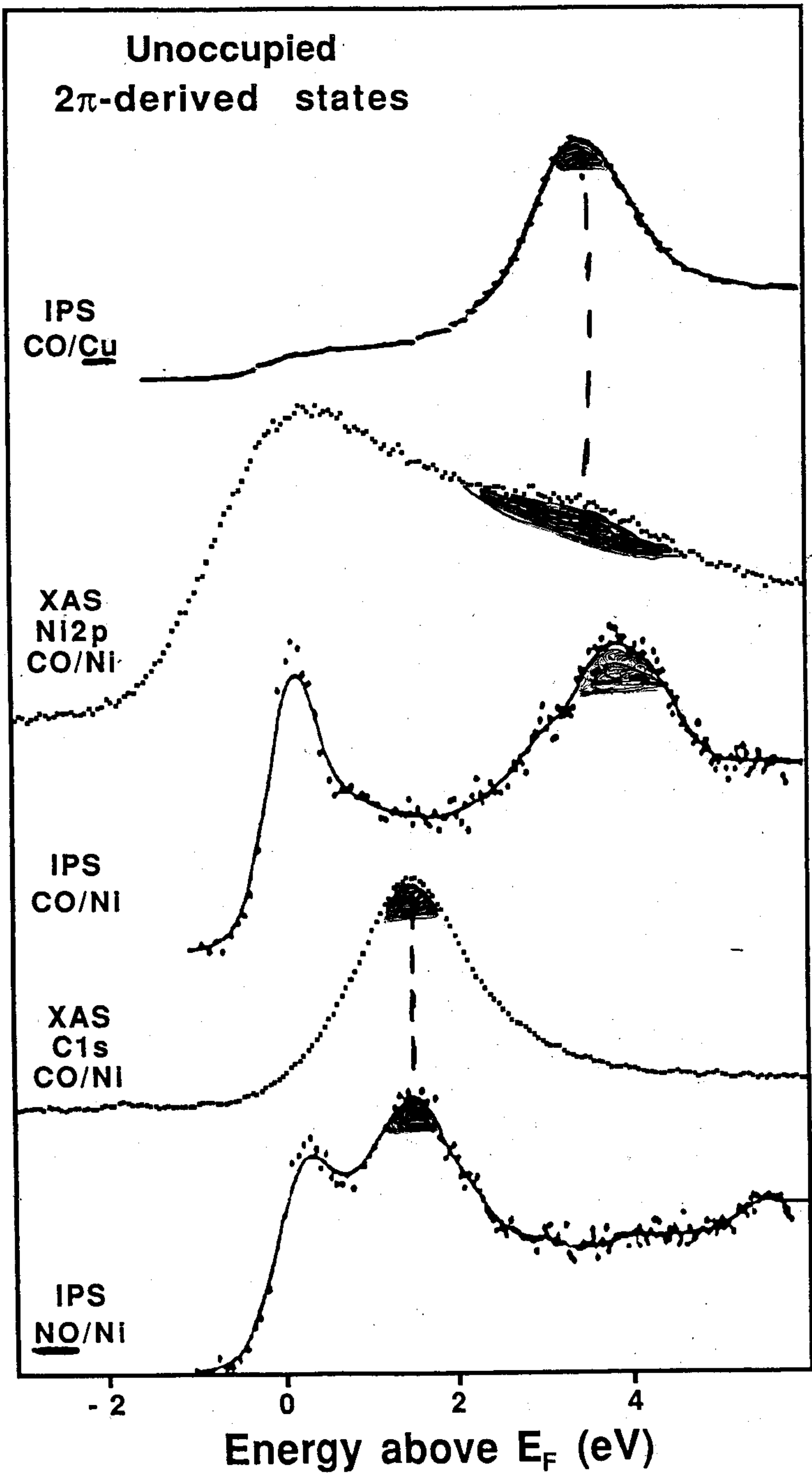


Z+1 approximation

$C^{*}O \Rightarrow NO$

$CO^{*} \Rightarrow CF$

$NN^{*} \Rightarrow NO$

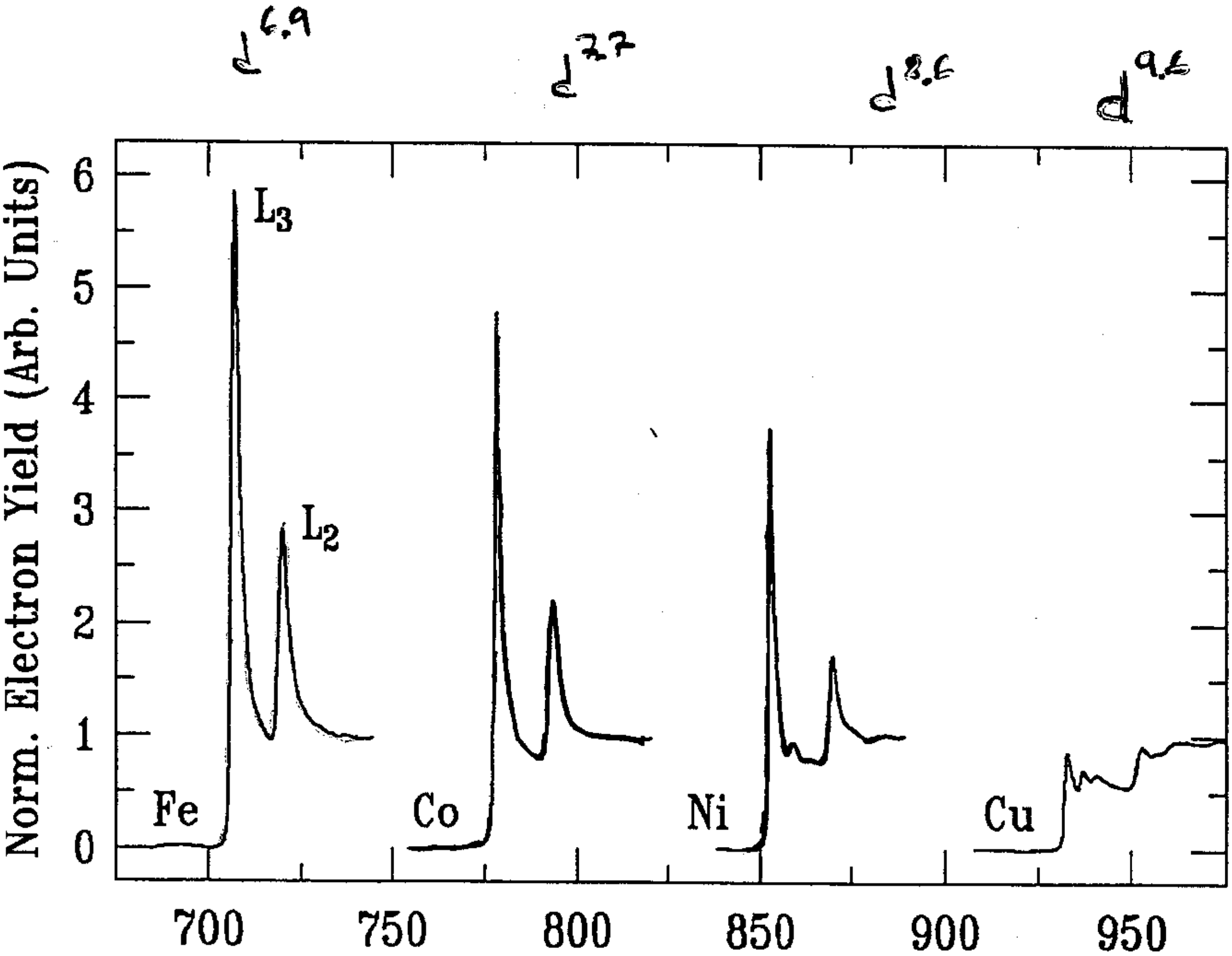


Dose et.al

P. Johnssc. et.al

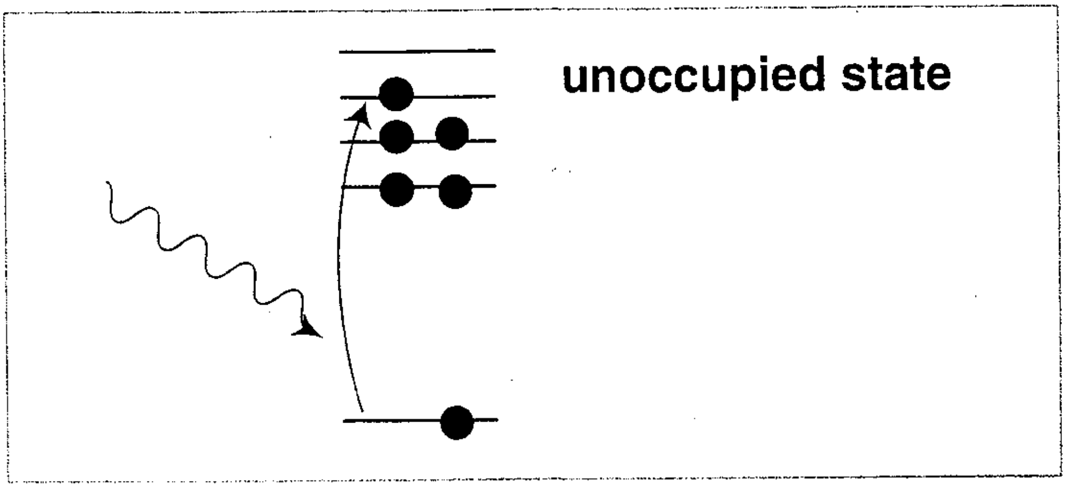
Nilsson et.al. Physica B208&209

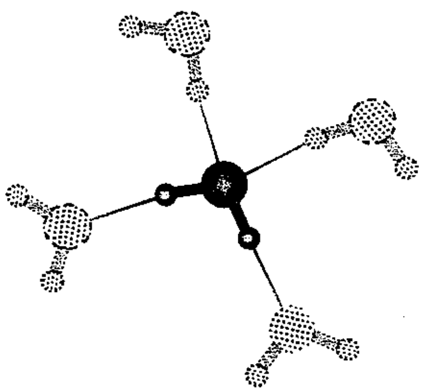
Initial State Rule in XAS



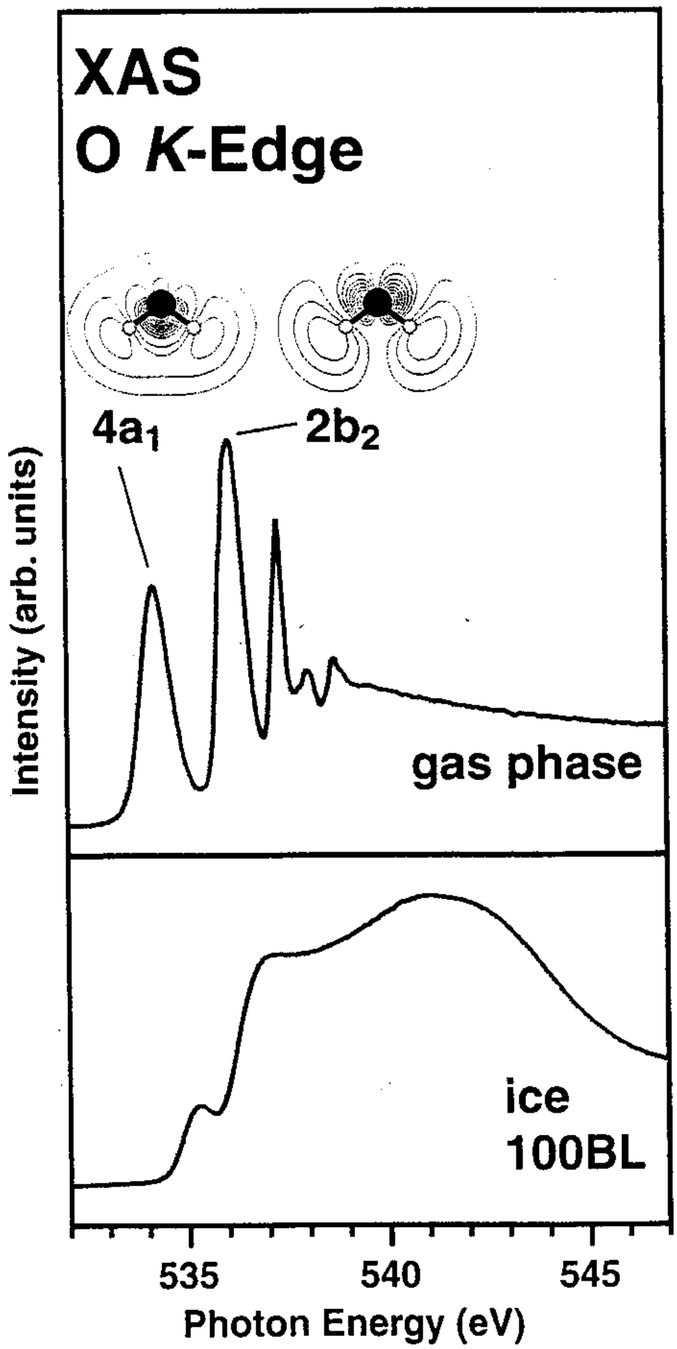
Stohr 3dexp.exg 08/17/94 11:52

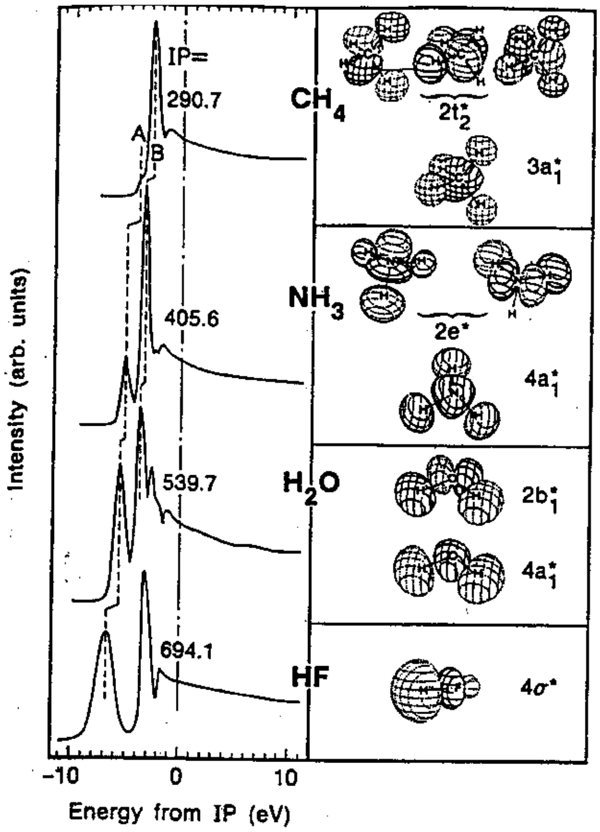
X-ray absorption spectra of water

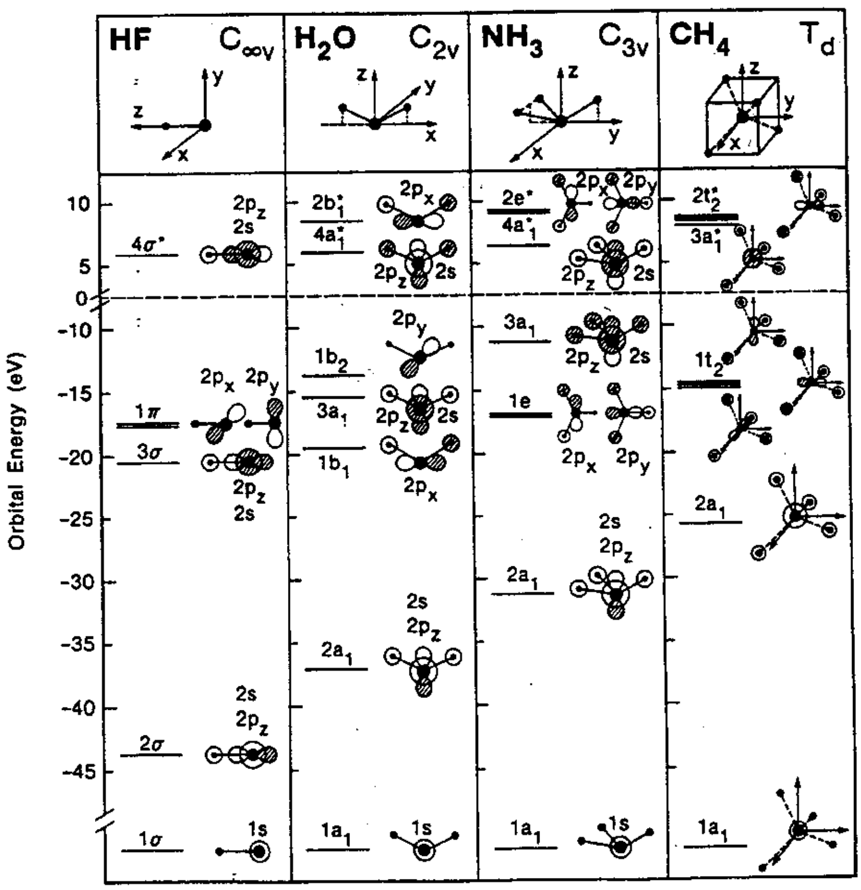




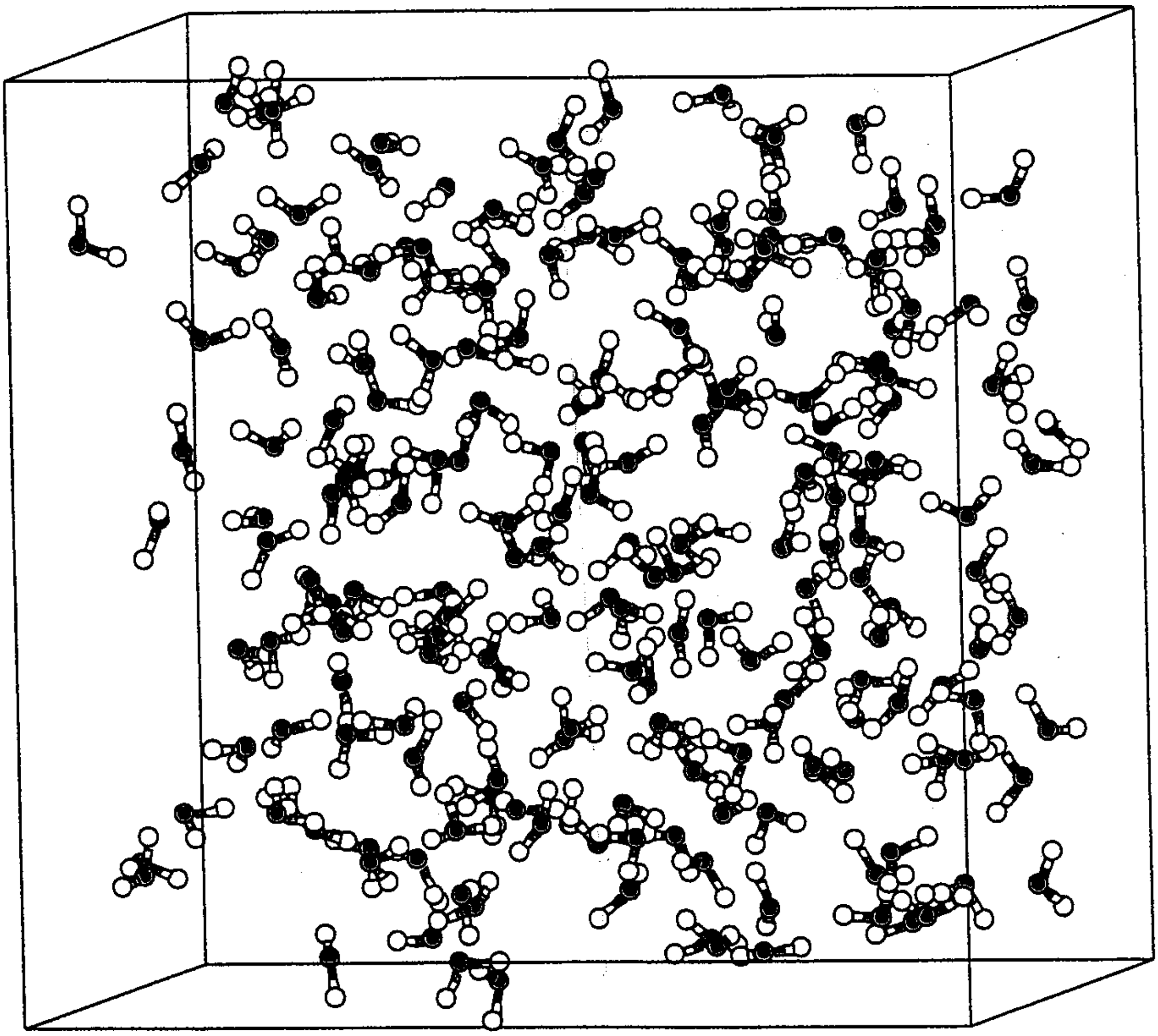
Tetrahedral coord



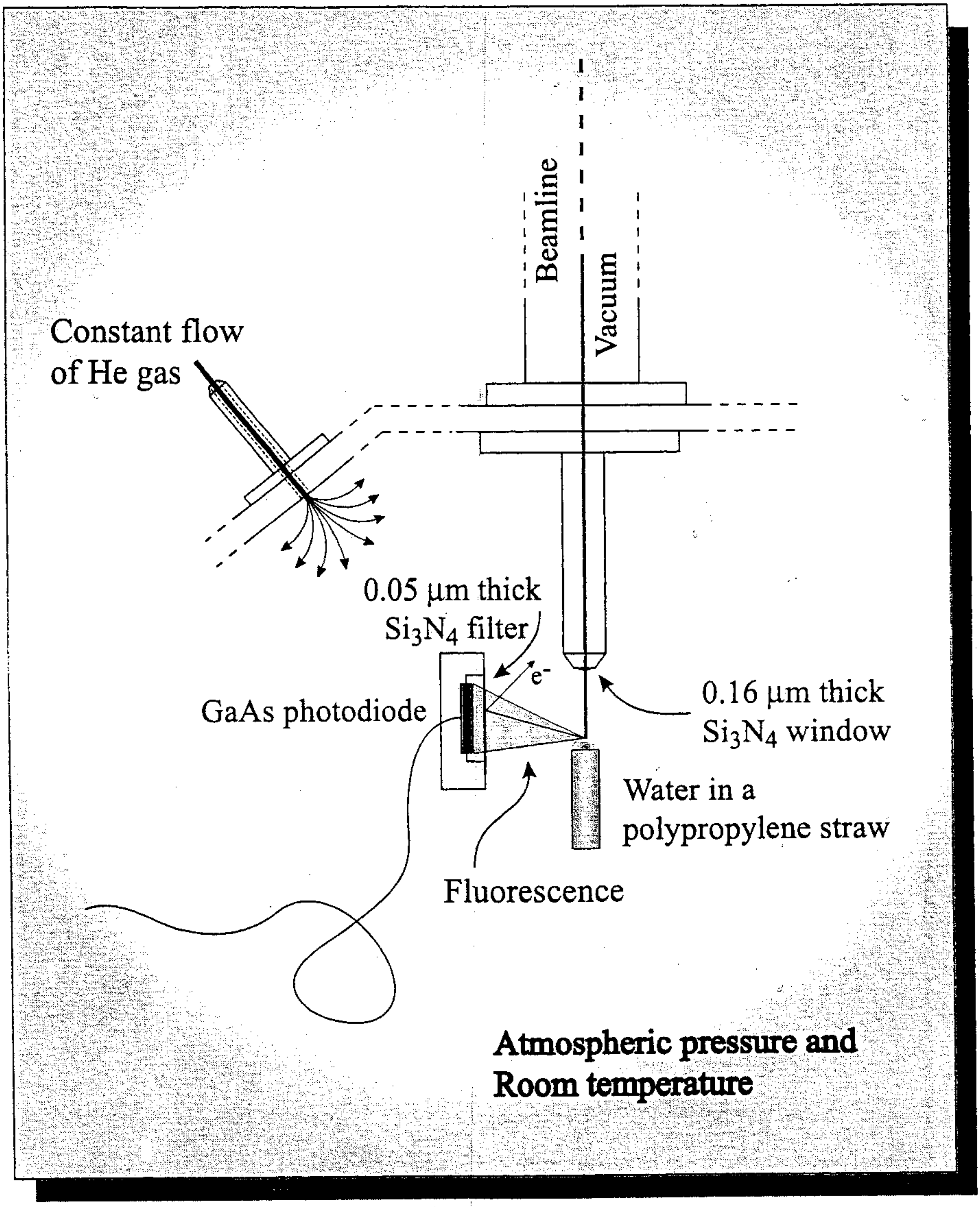




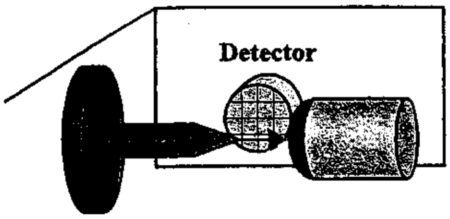
J. Stöhr Nexafs Spectroscopy

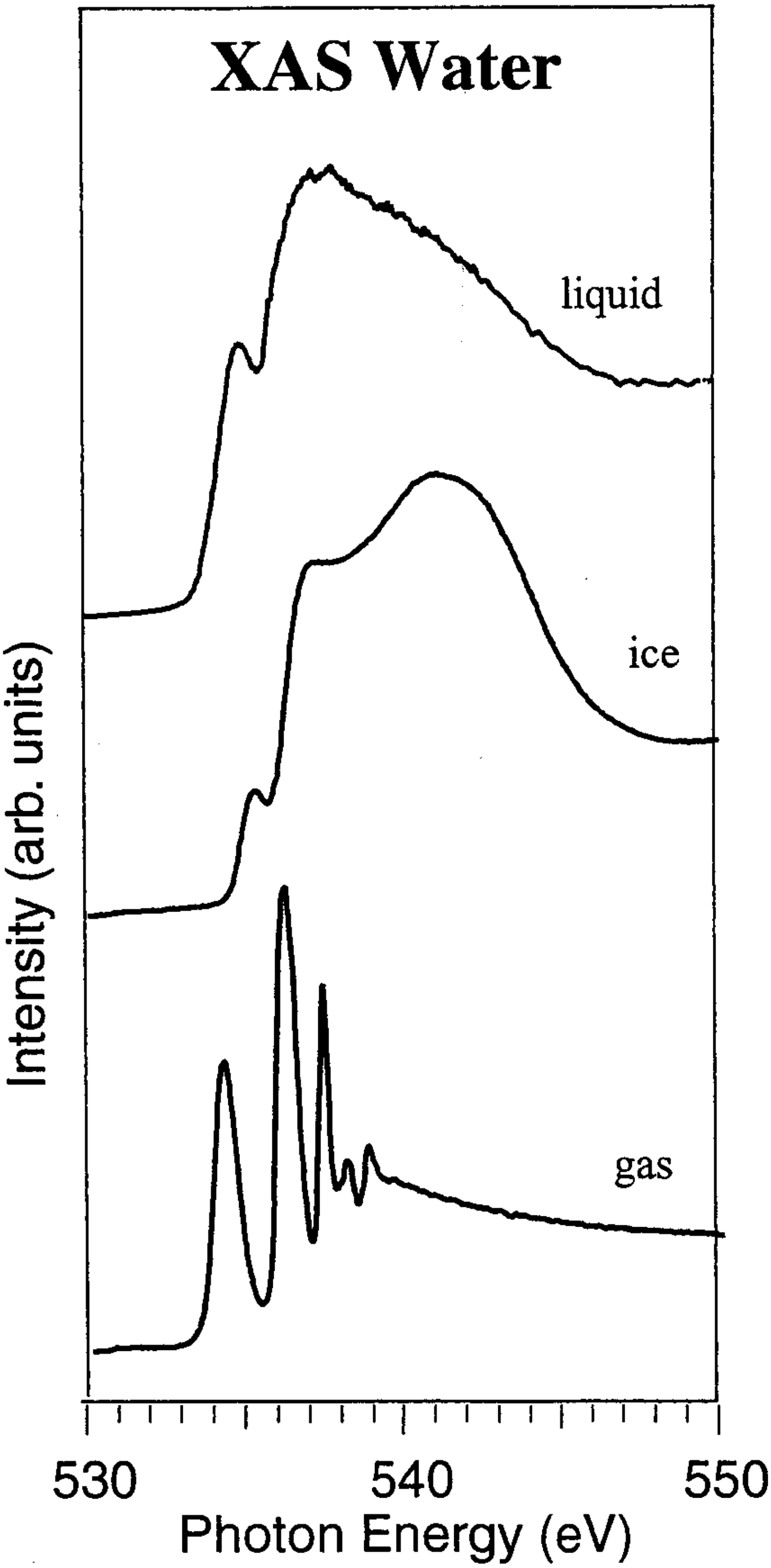


Experimental Setup

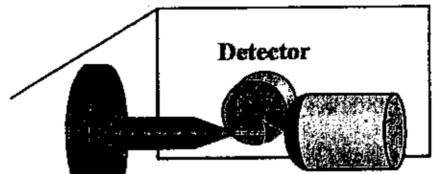


O1s XAS of Water in Helium Atmosphere

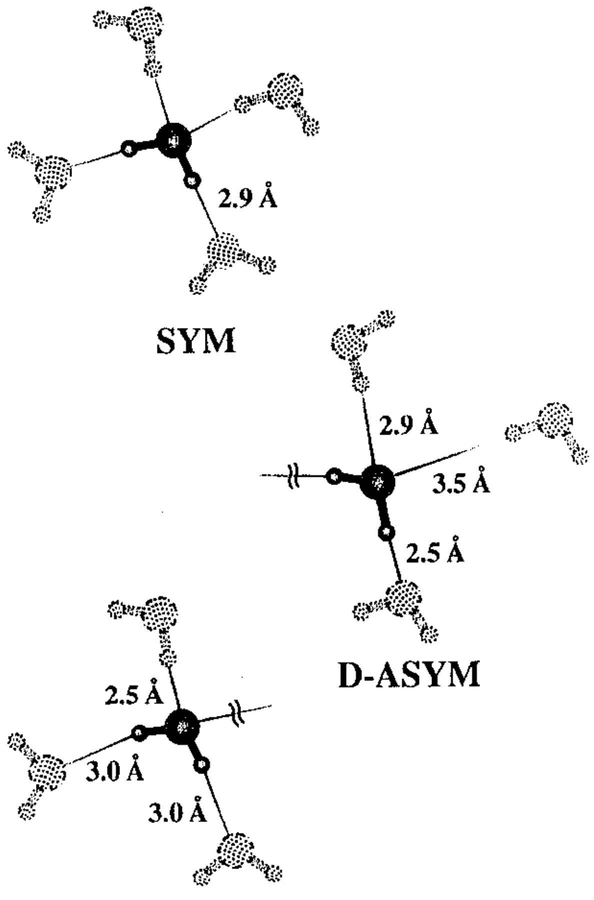


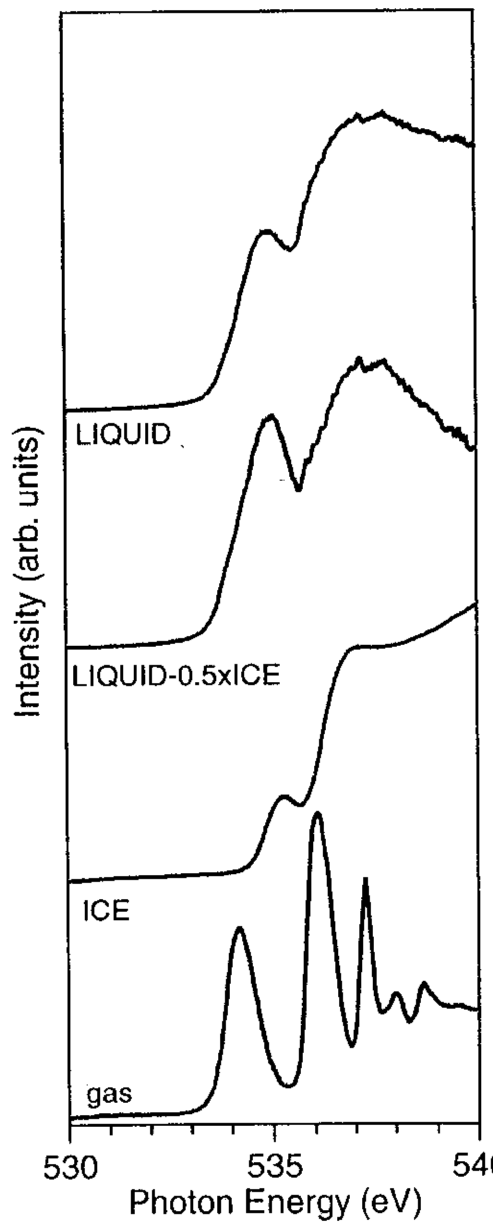


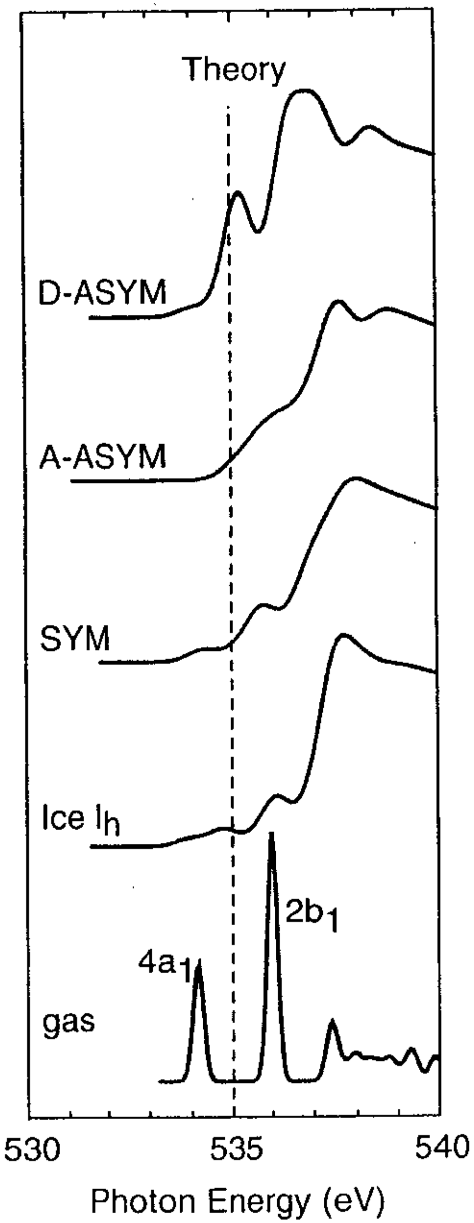
Spectroscopic Evidence of Unique Hydrogen Bonding in Water



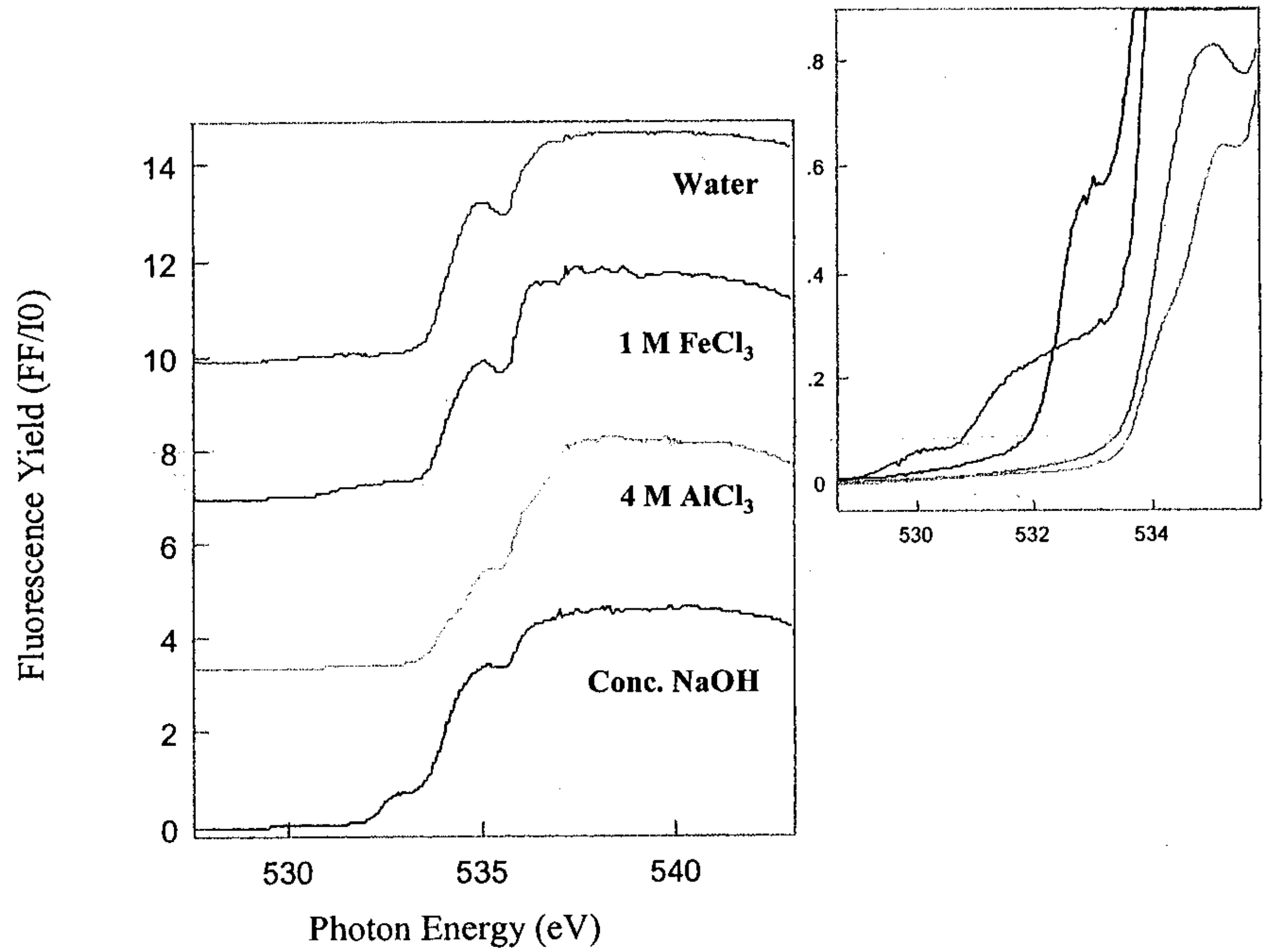
O1s XAS of Water in Helium Atmosphere



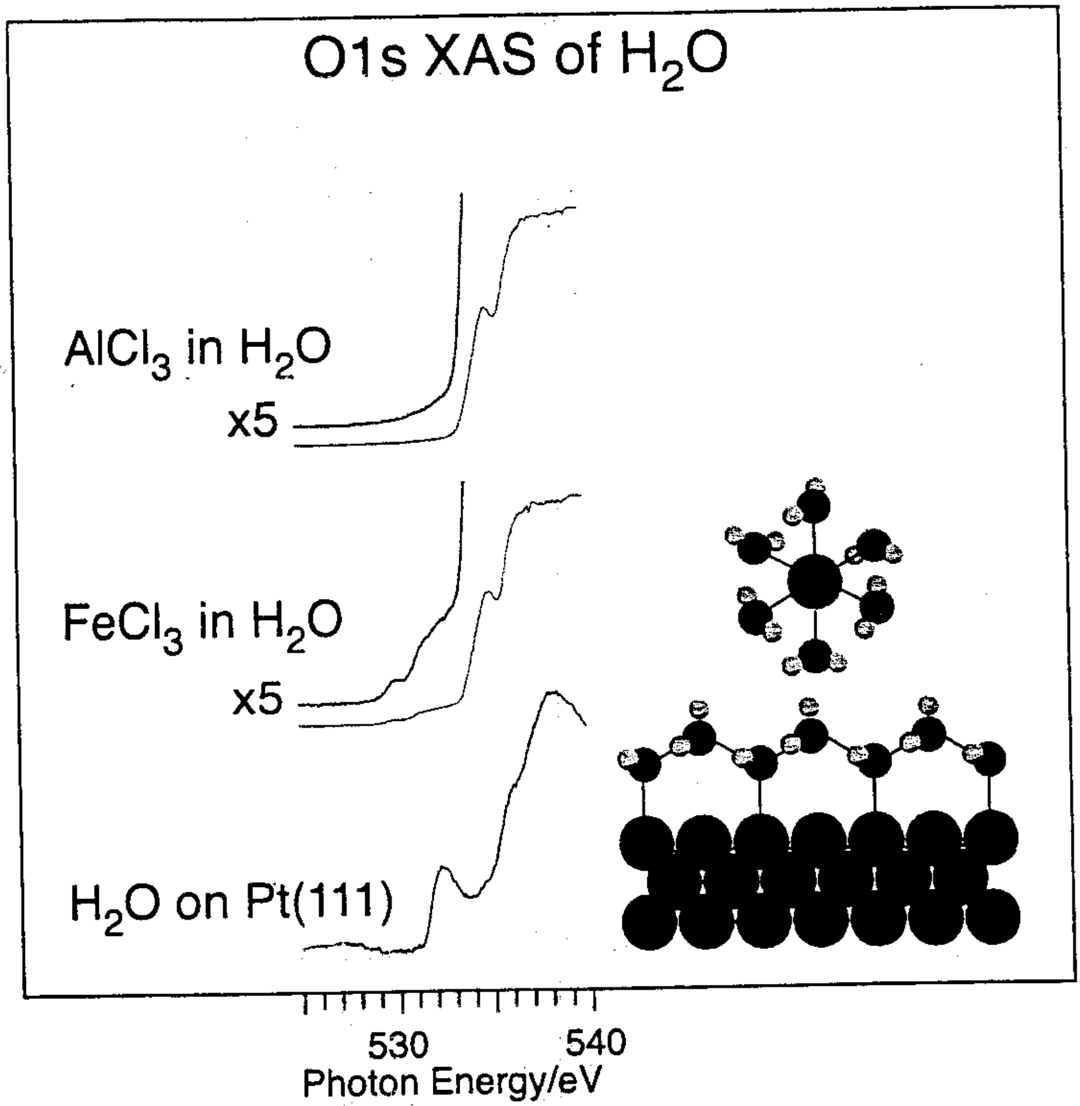


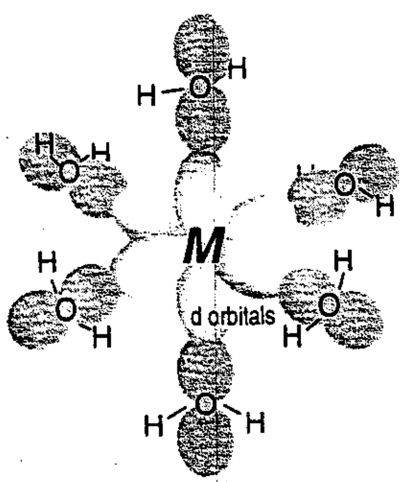


Influence of Cation Complexation on H-bonding in Water



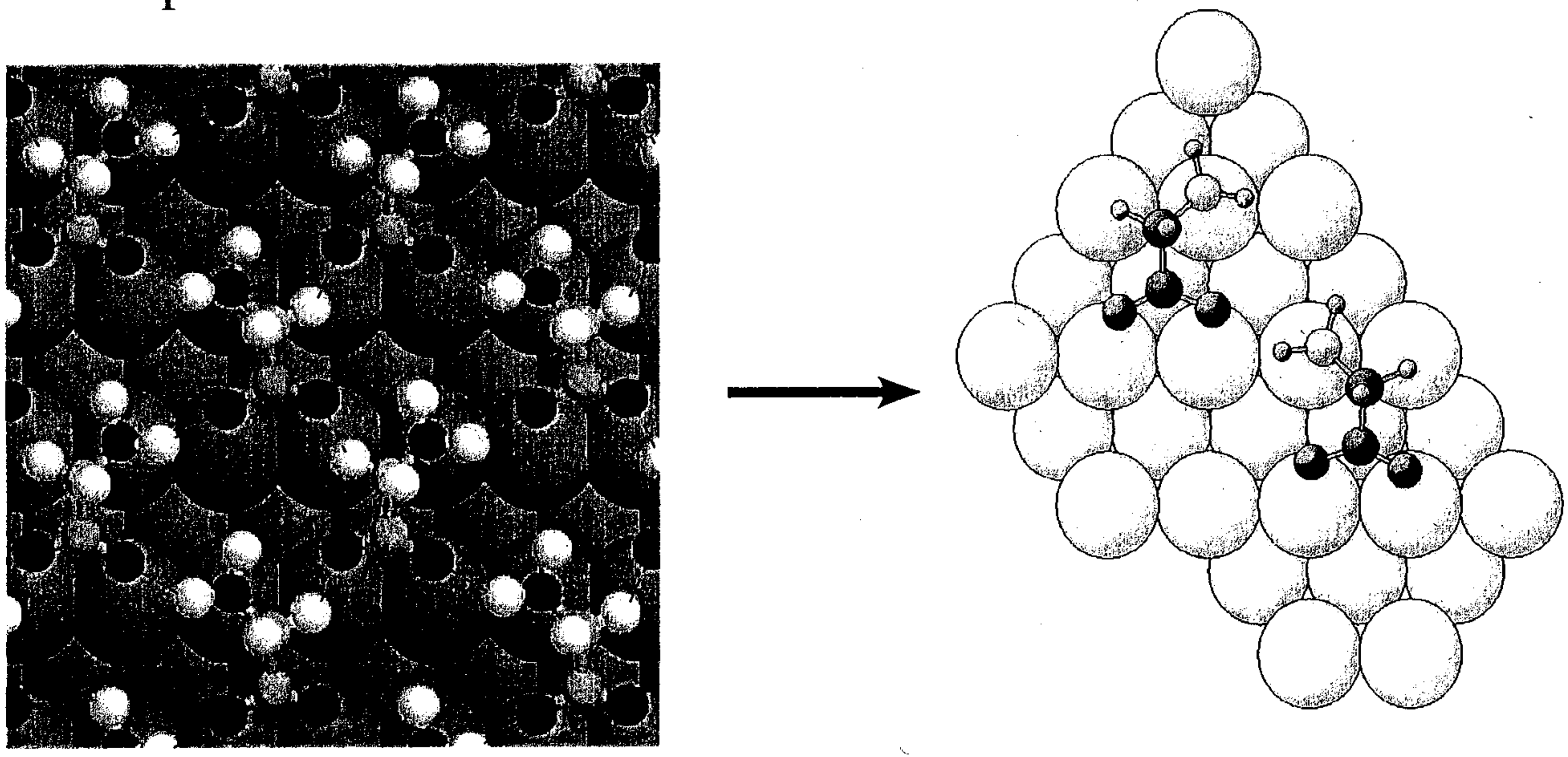
Covalent Bonding of Water



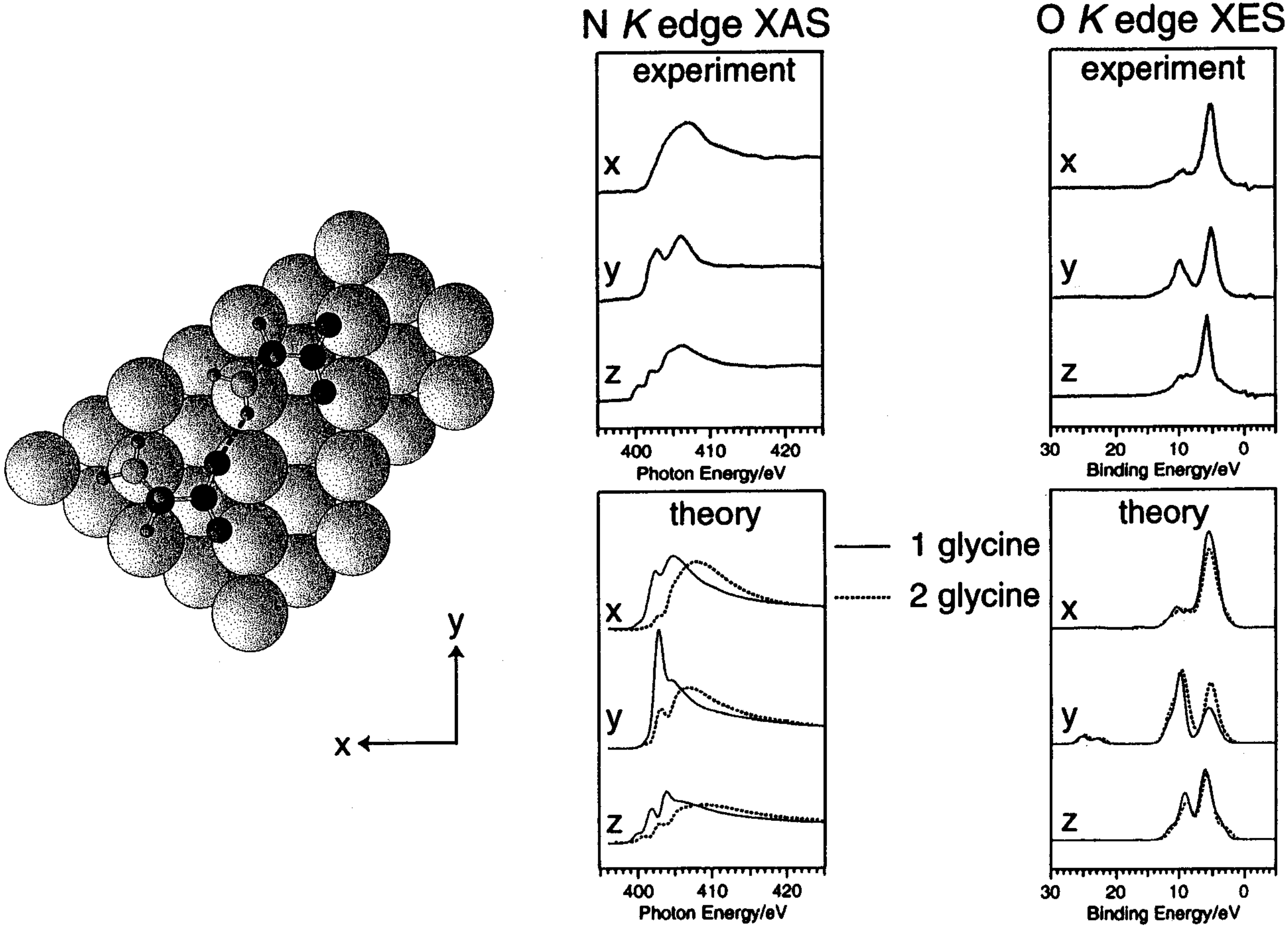


Cluster modelling of surfaces

- Cut out a small piece of the surface, up to about 50 atoms
- Adsorbate–adsorbate interactions often neglected, frozen metal atom positions.

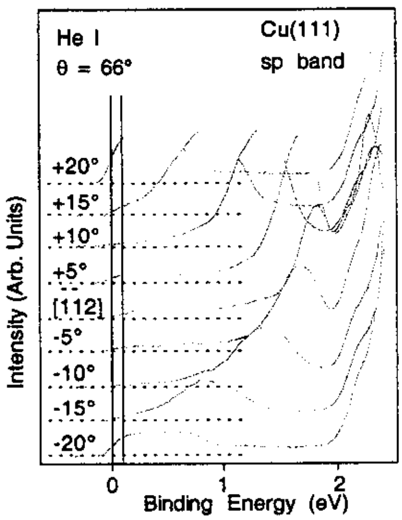


Hydrogen bonding in glycine

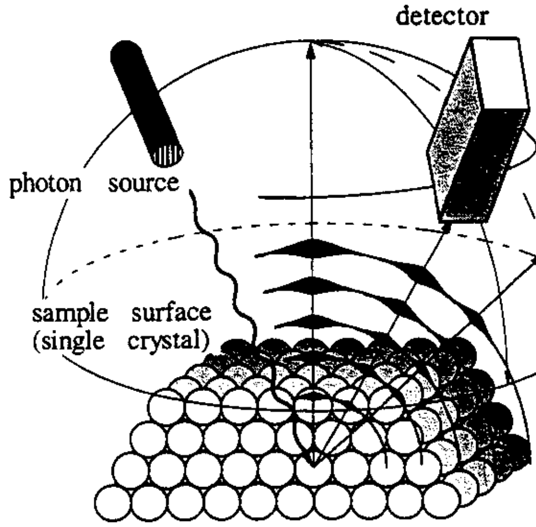


Fermi Surface Mapping

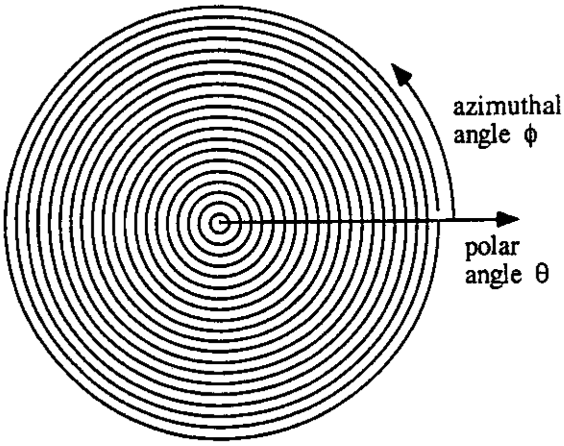
Record intensity at the Fermi energy



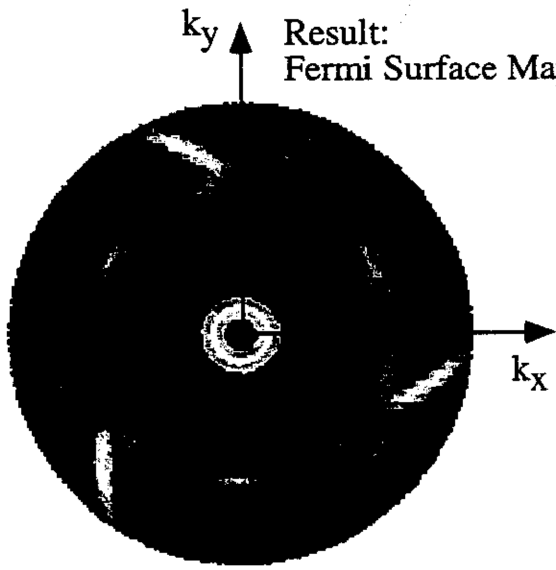
Map the hemisphere above a sample



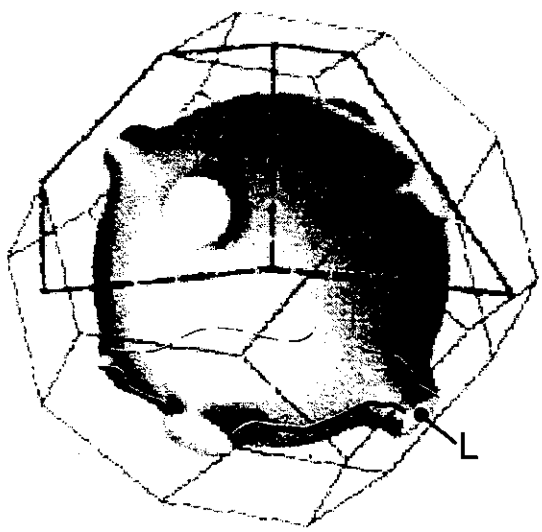
Mapping procedure



Result:
Fermi Surface Map



What we see:

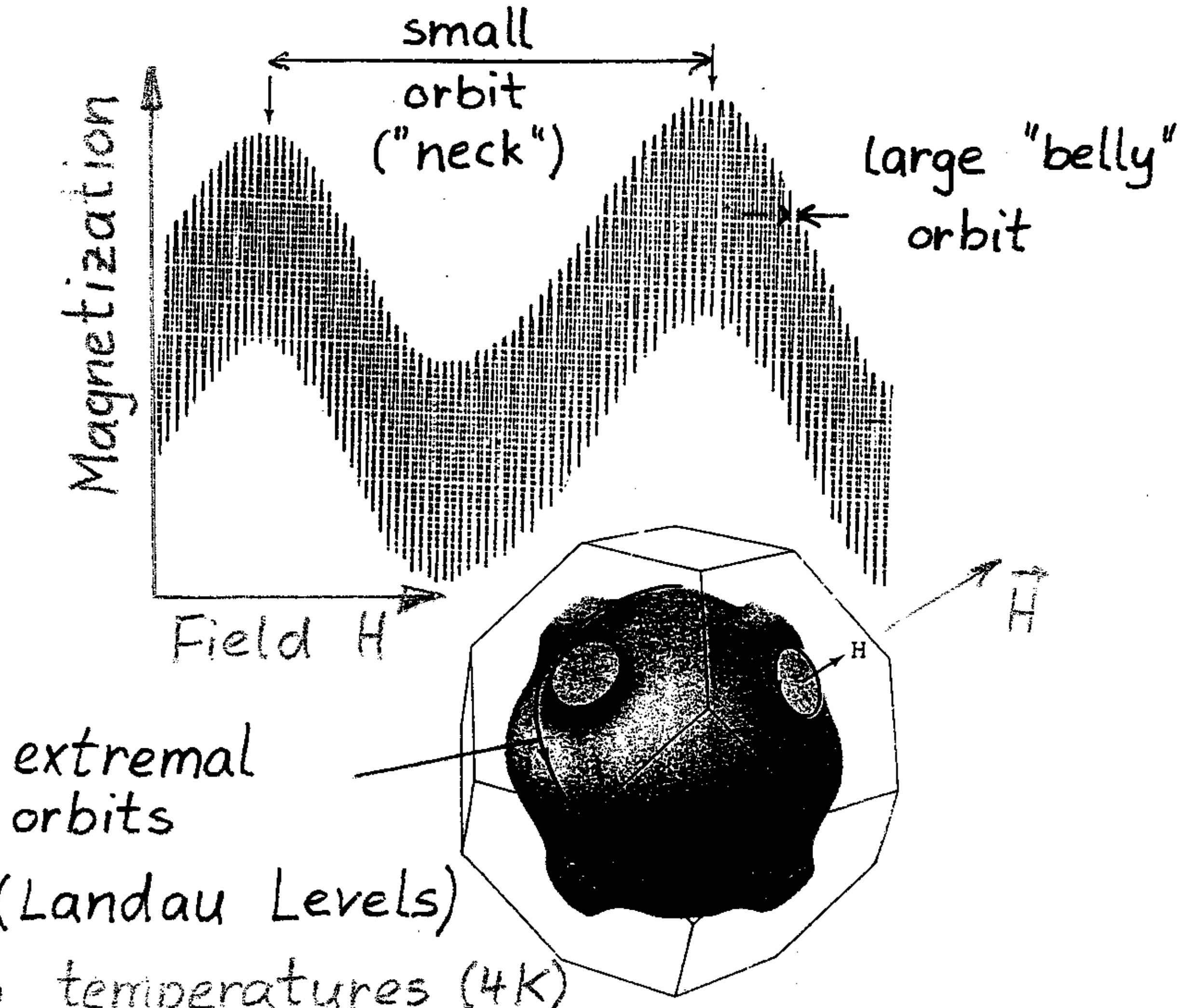


parallel projection
($k_{||}$ mapping)

Solid State Physics

Neil W. Ashcroft
N. David Mermin
Cornell University

Measuring the Fermi Surface by De Haas van Alphen Effect

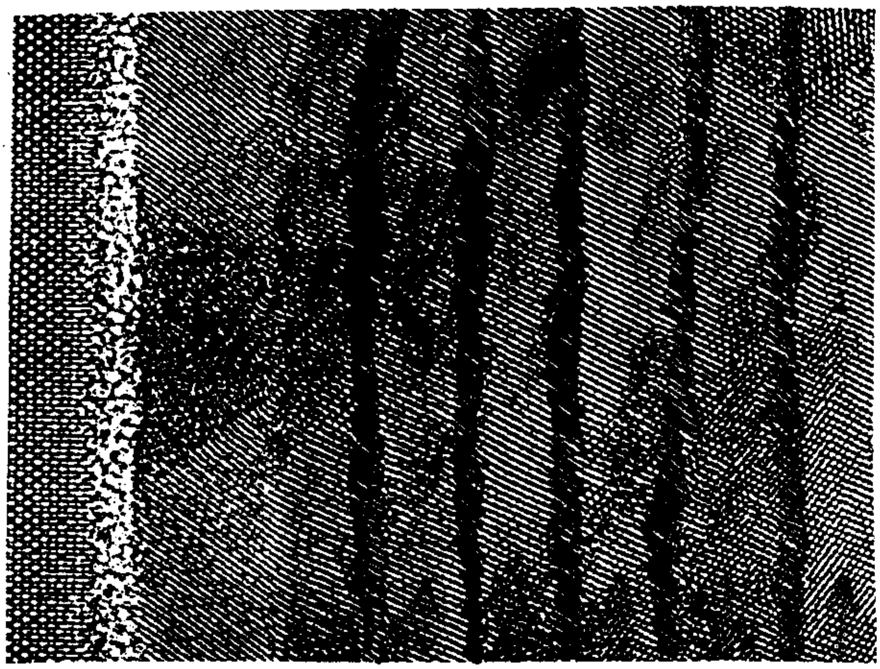


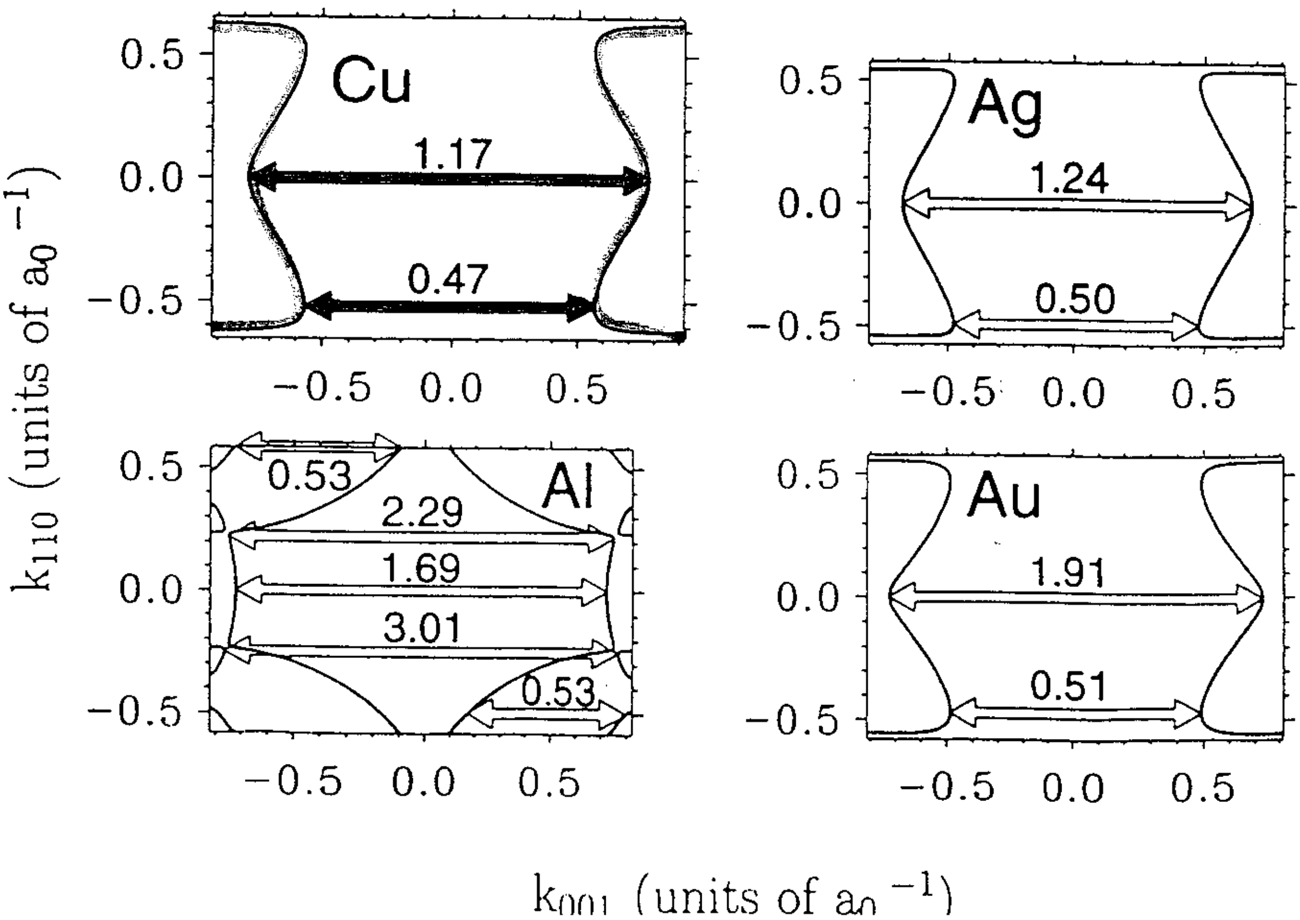
- low temperatures (4K)
- ultrapure samples
- 3D bulk

PHYSICAL REVIEW B VOLUME 48, NUMBER 10 1 SEPTEMBER 1993-II

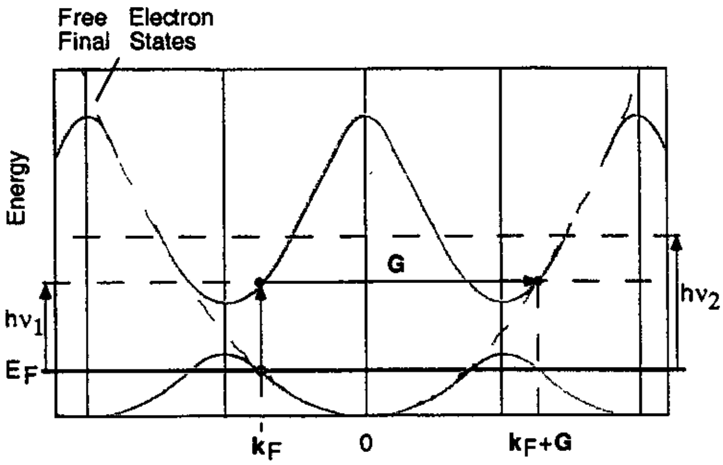
Exchange coupling in magnetic heterostructures

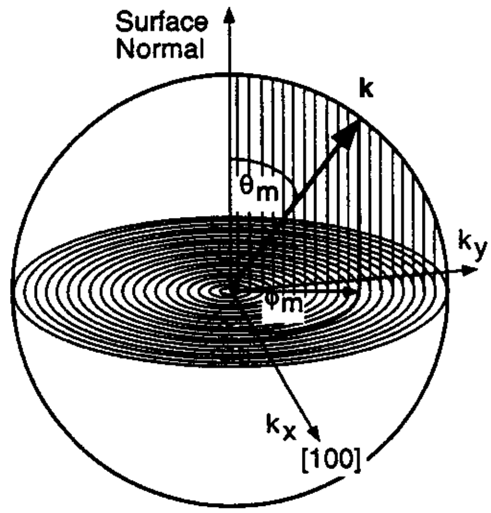
M. D. Stiles
National Institute of Standards and Technology, Gaithersburg, Maryland 20899
(Received 3 May 1993)





Direct Transitions from the Fermi Surface





$$E_{kin}^{m} = h\nu - \Phi - E_B$$

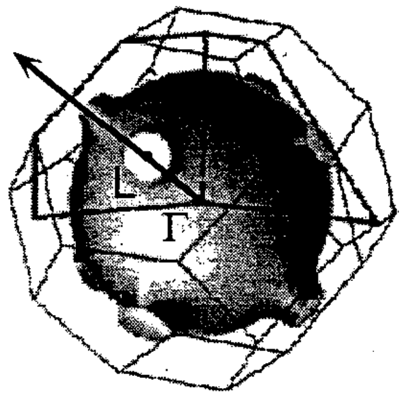
$$\left|\vec{k}_{\parallel}\right| = \frac{1}{\hbar}\sqrt{2mE_{kin}^{m}}\sin\theta_m$$

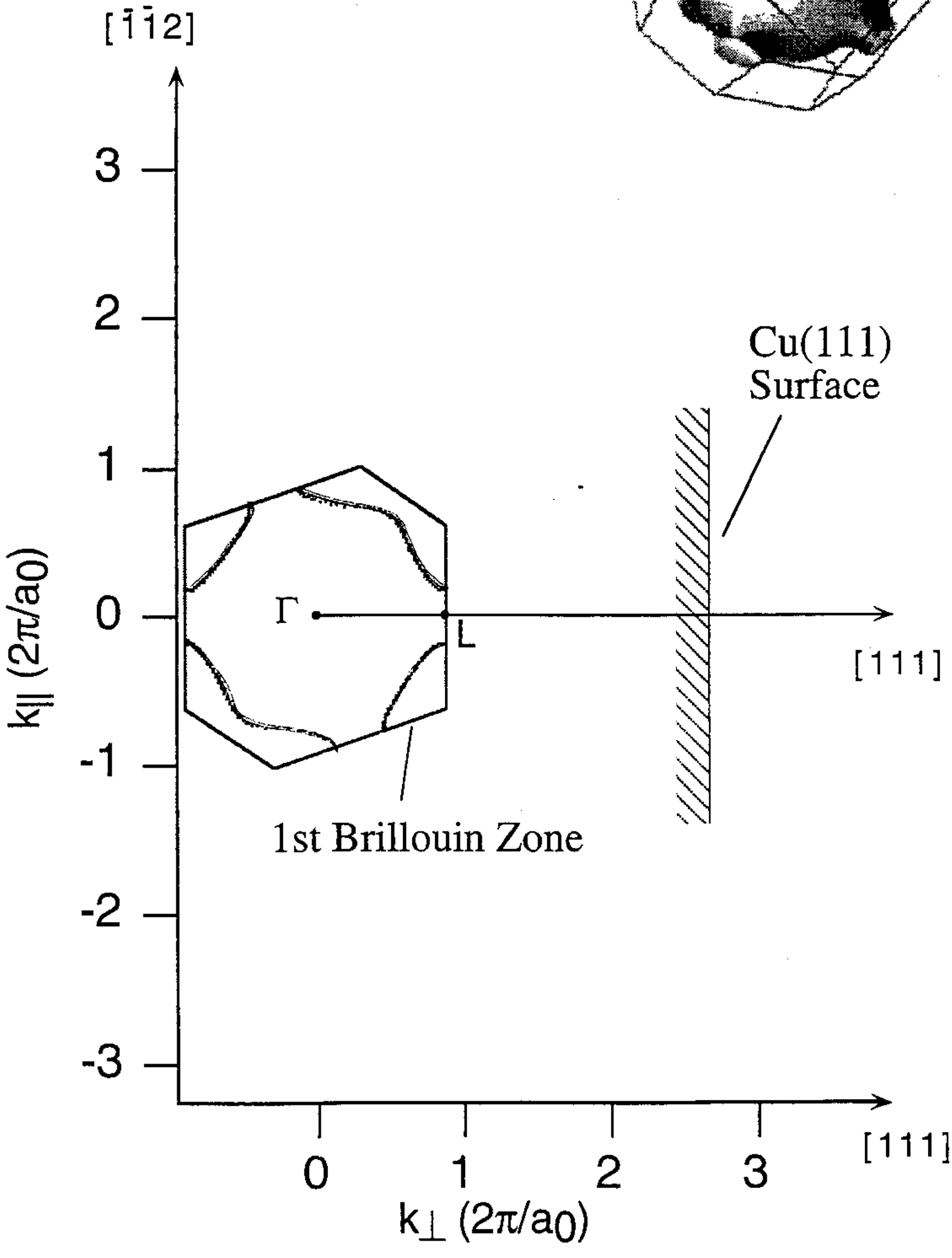
$$k_{\perp} = \frac{1}{\hbar}\sqrt{2m(E_{kin}^{m} + V_0)}\cos\theta$$

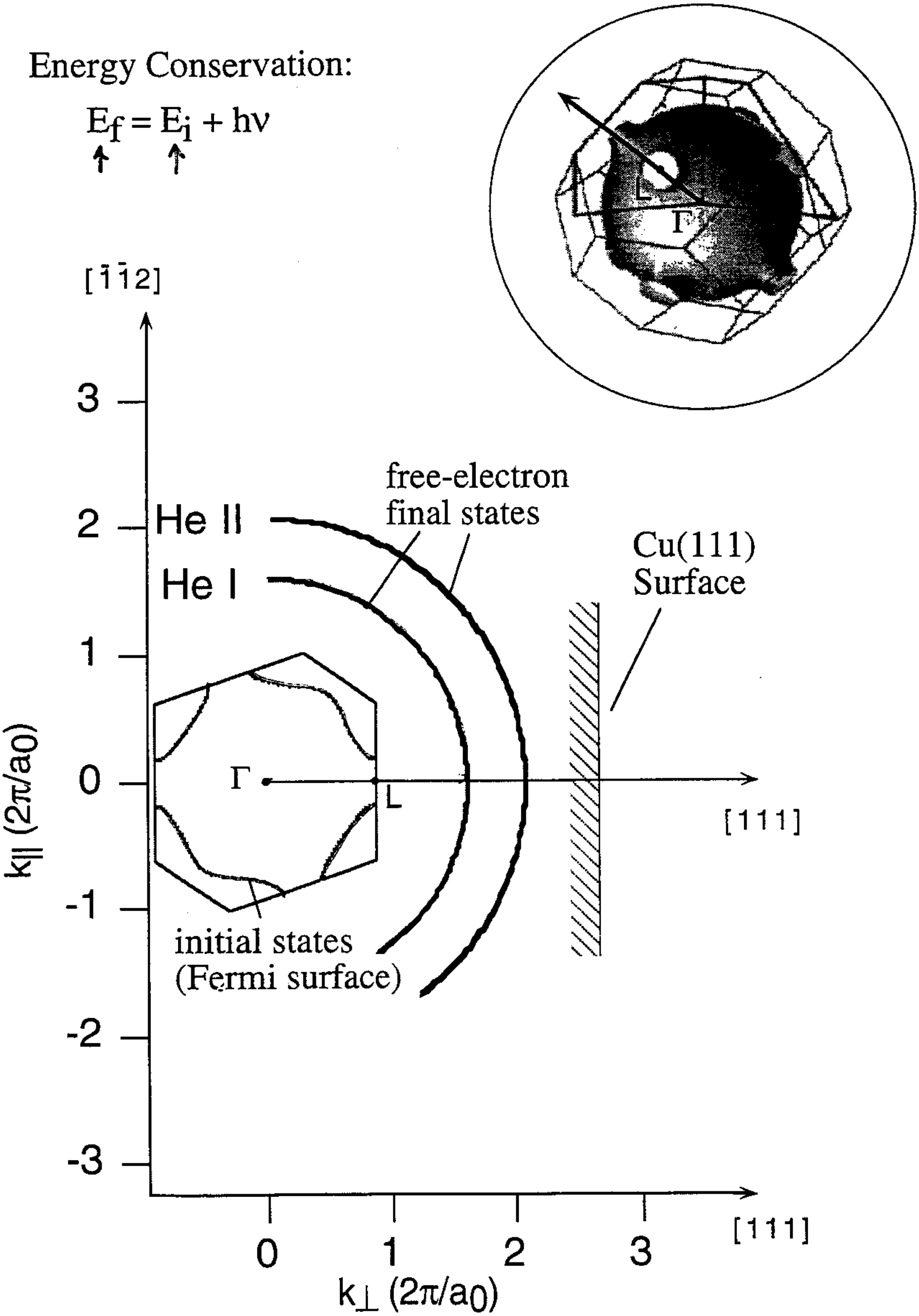
$$\sin\theta = \sin\theta_m \sqrt{\frac{E_{kin}^{m}}{E_{kin}^{m} + V_0}} \qquad \text{(Refraction)}$$

Principles of
Fermi Surface Mapping

Section along $(\bar{1}10)$ plane
in reciprocal space

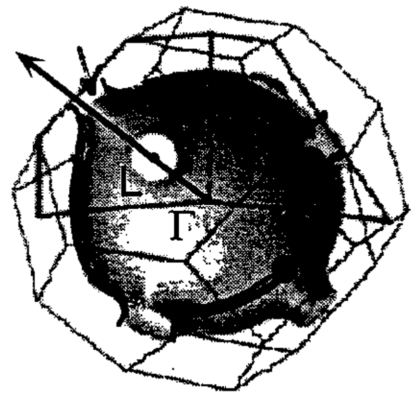


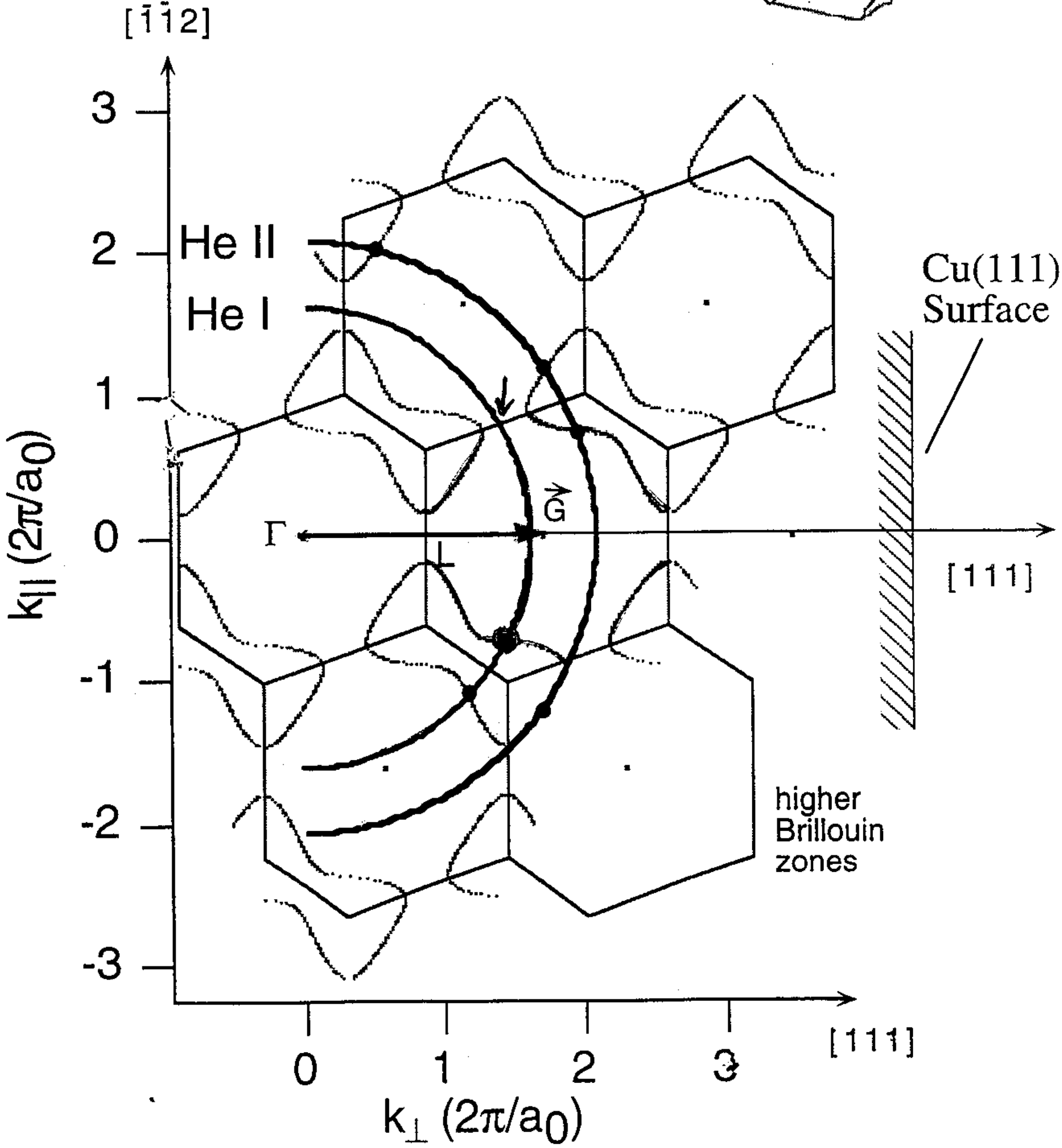


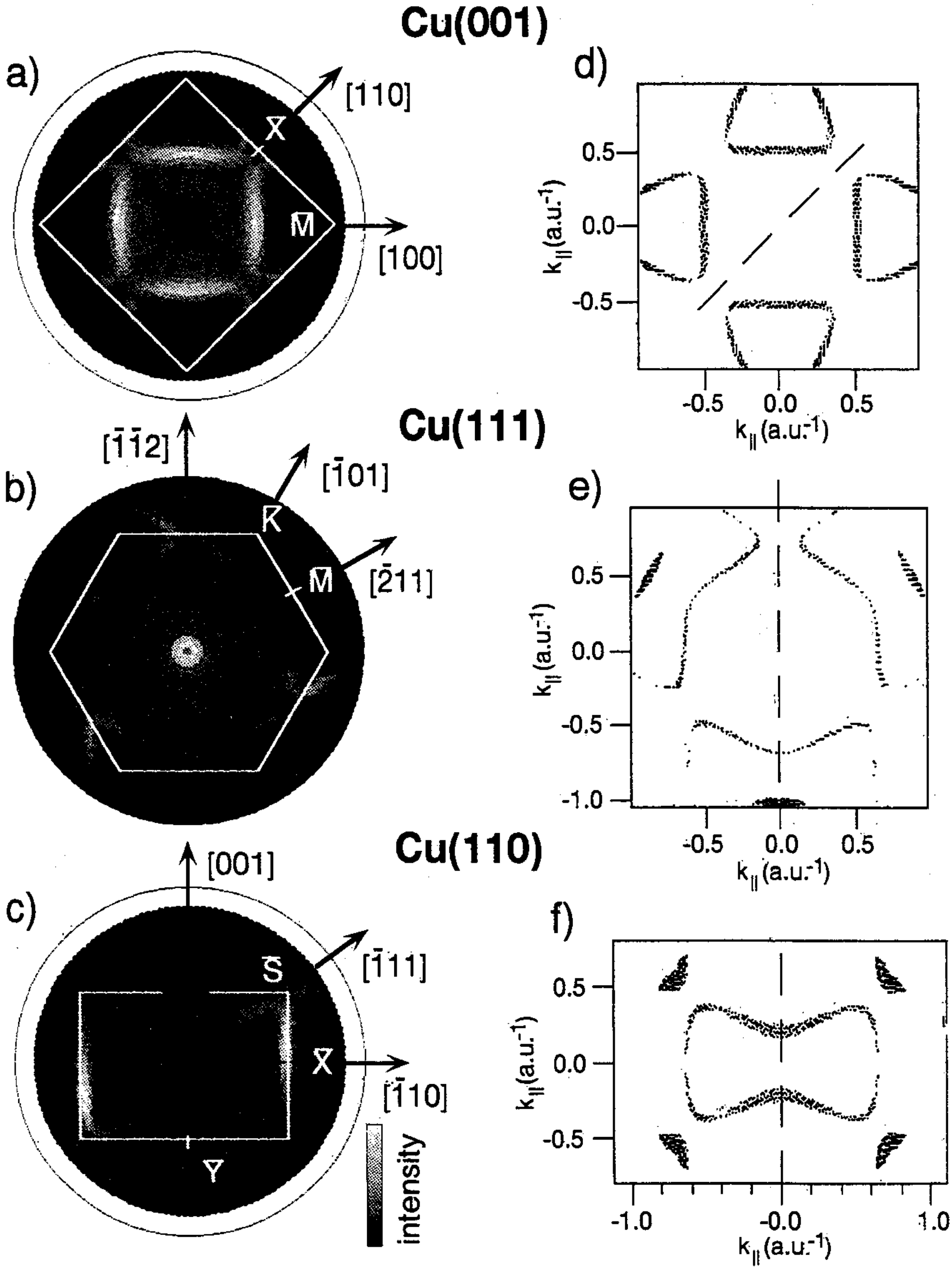

Energy Conservation:
$E_f = E_i + h\nu$
$[\bar{1}\bar{1}2]$
$k_{\parallel}$ $(2\pi/a_0)$
3
2
1
0
-1
-2
-3
He II
He I
free-electron
final states
Cu(111)
Surface
Γ
L
[111]
initial states
(Fermi surface)
0
1
2
3
[111]
$k_{\perp}$ $(2\pi/a_0)$

Momentum Conservation:

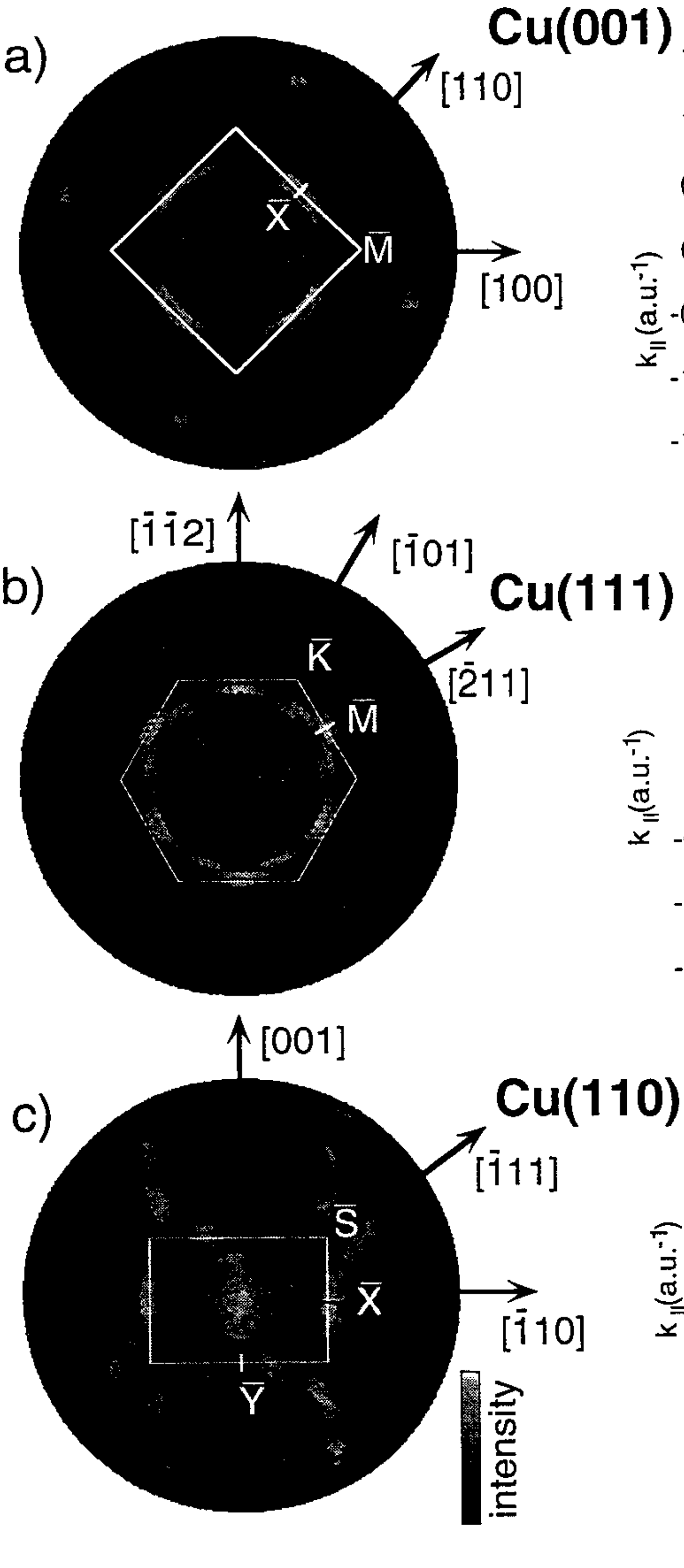
$$\vec{k}_f = \vec{k}_i + \vec{k}_{h\nu} + \vec{G}$$





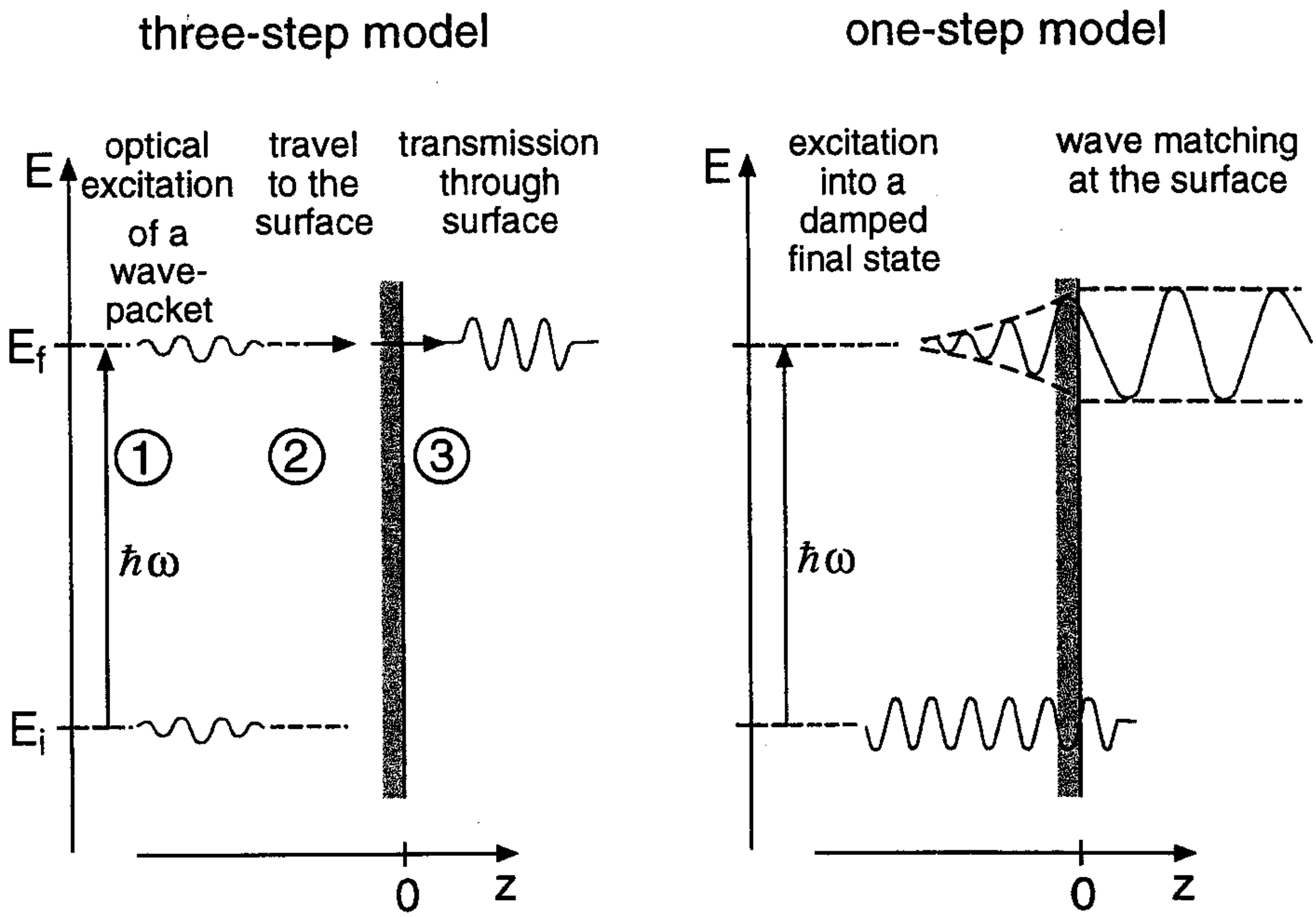


Cu(001)
a)
[110]
X̄
M̄
[100]
d)
0.5
0.0
-0.5
k∥(a.u.⁻¹)
Cu(111)
[1̄1̄2]
b)
[1̄01]
K̄
M̄
[2̄11]
e)
-1.0
Cu(110)
[001]
c)
S̄
[1̄11]
X̄
[1̄10]
Ȳ
intensity
f)
1.0
-0.0



a)
Cu(001)
[110]
X
M
[100]
d)
b)
[1̄1̄2]
[1̄01]
Cu(111)
K
M
[2̄11]
e)
c)
[001]
Cu(110)
[1̄11]
S
X
[1̄10]
Y
intensity
f)
k∥ (a.u.⁻¹)

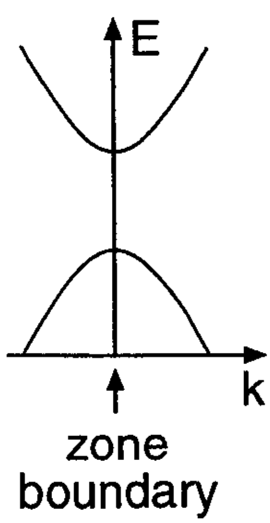
Comments on the Free Electron Final State



Excited State:

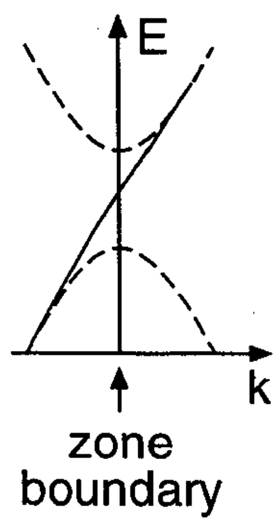
Bloch state of the 3D crystal

→ band gaps



Evanescent wave at the surface

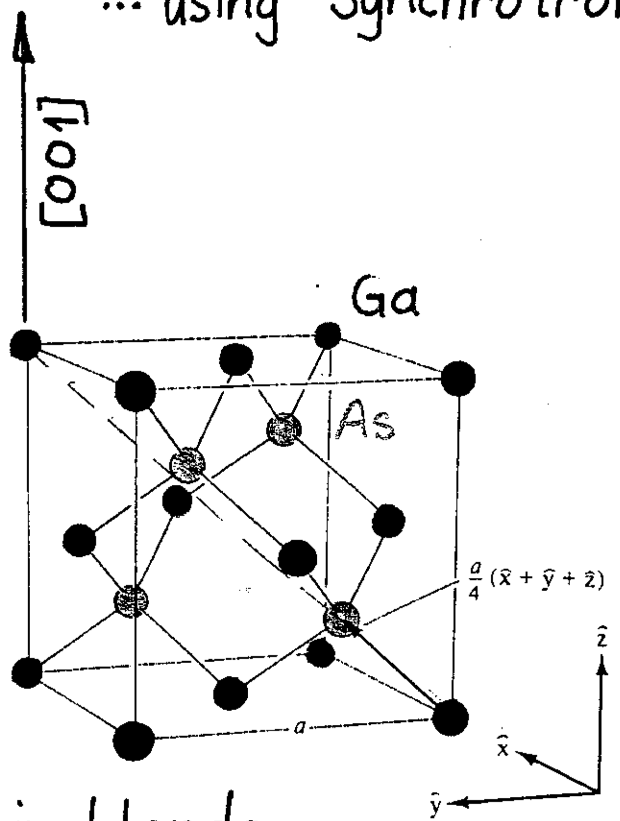
→ exists in band gaps



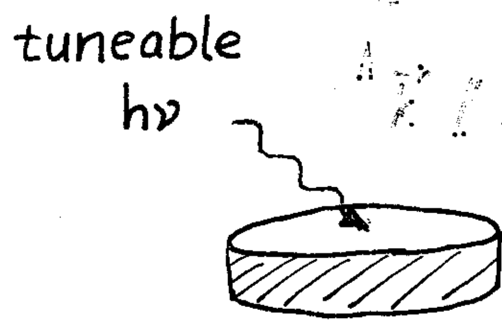
→ free electron like

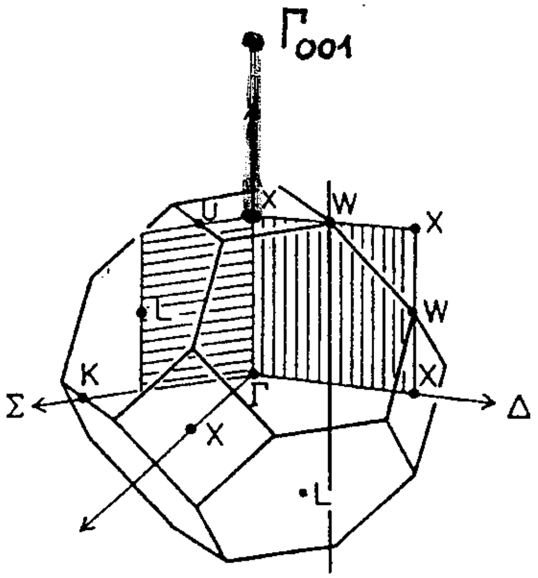
Mapping the Bands of GaAs

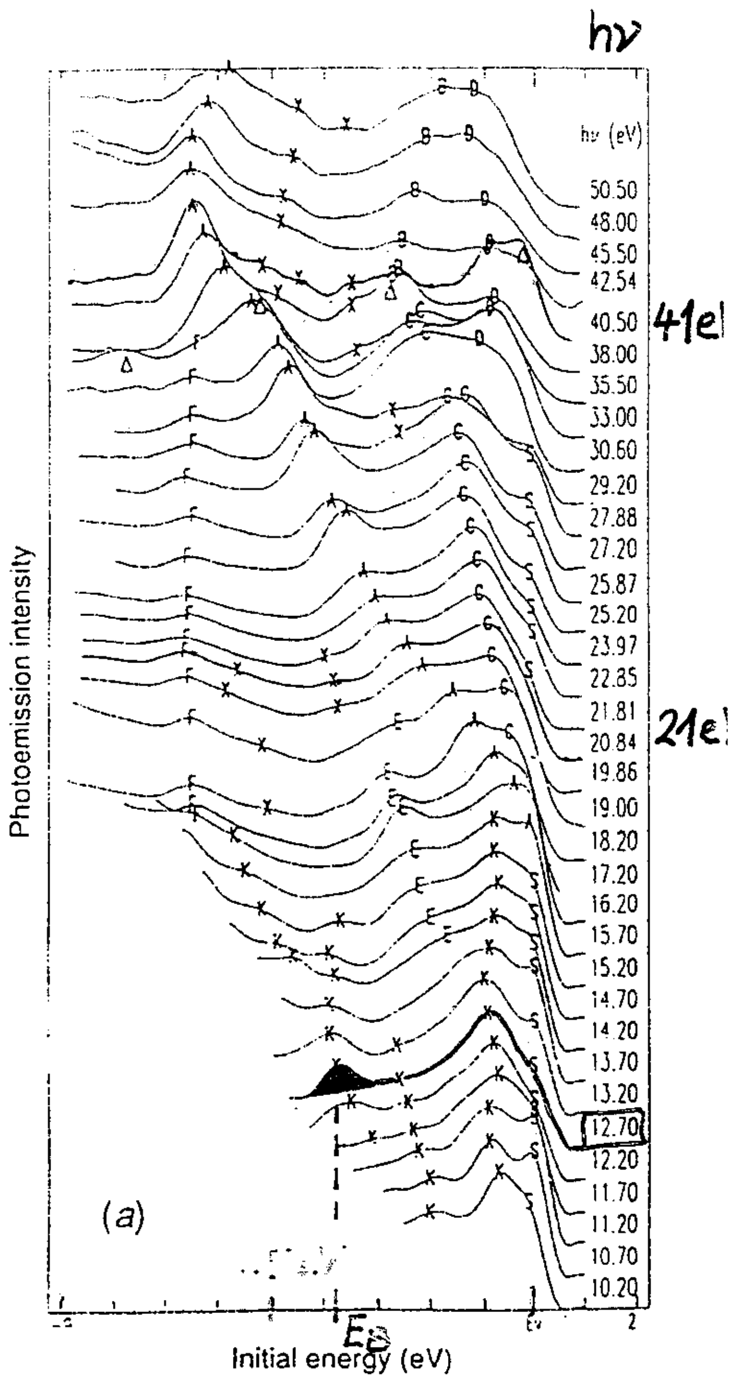
... using Synchrotron Radiation



zincblende structure (fcc)





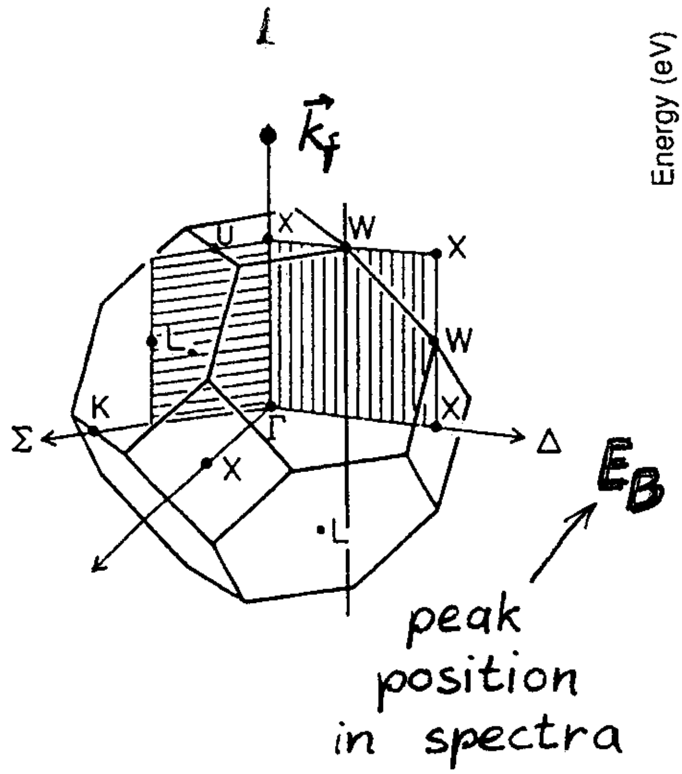


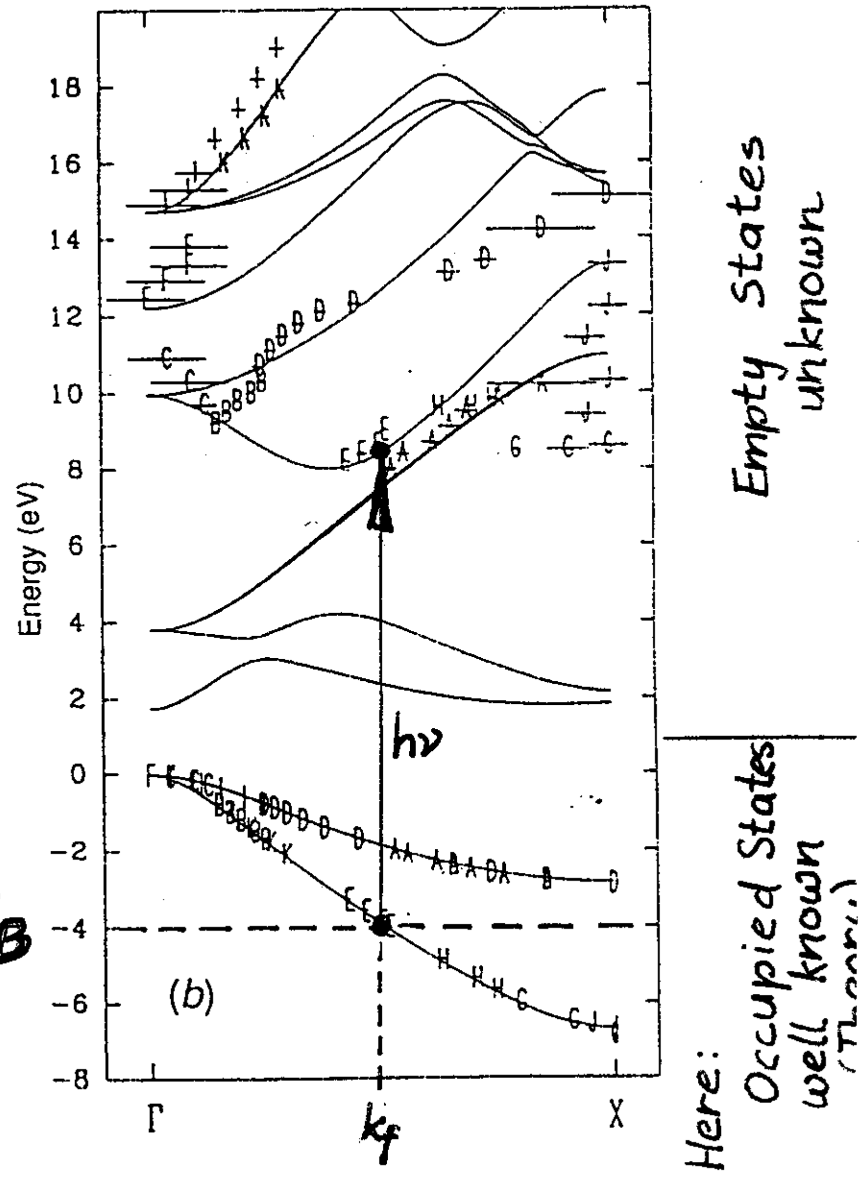
Result

- Normal emission $\Rightarrow$ $k_\parallel = 0$

procedure
- Free electron final state
  $\Rightarrow$ $k_\perp = \frac{1}{\hbar}\sqrt{2m(h\nu - E_B - \Phi + V_0)}$
  $\Rightarrow$ $\boxed{E_B(k_\perp)}$ measured!

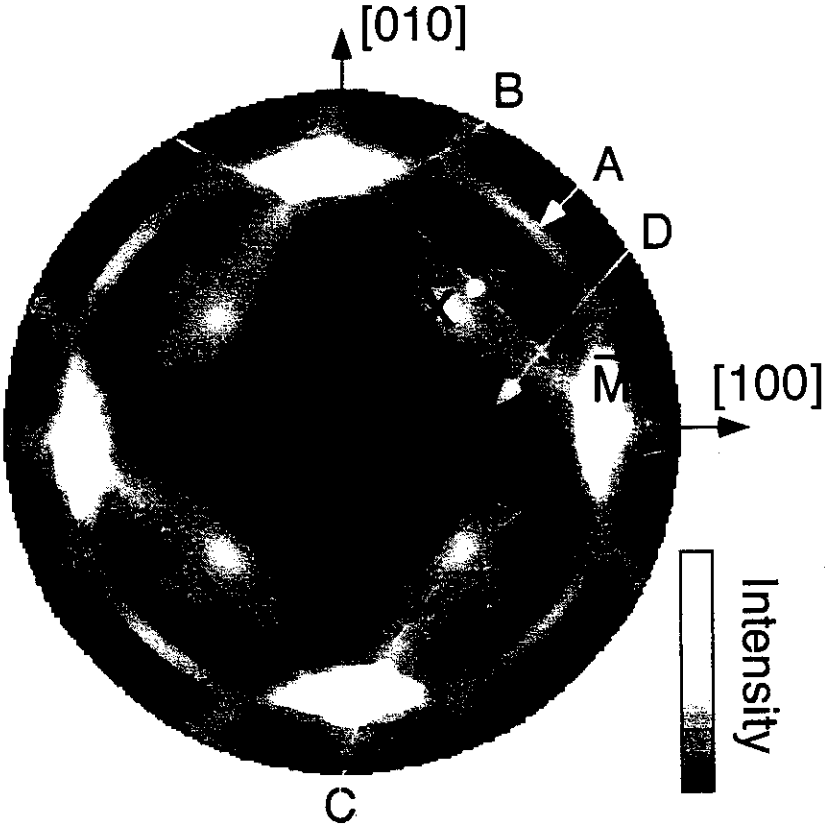
special
- Or, as here, if $E_B(k)$ is known, the excited states bandstructure can be measured!





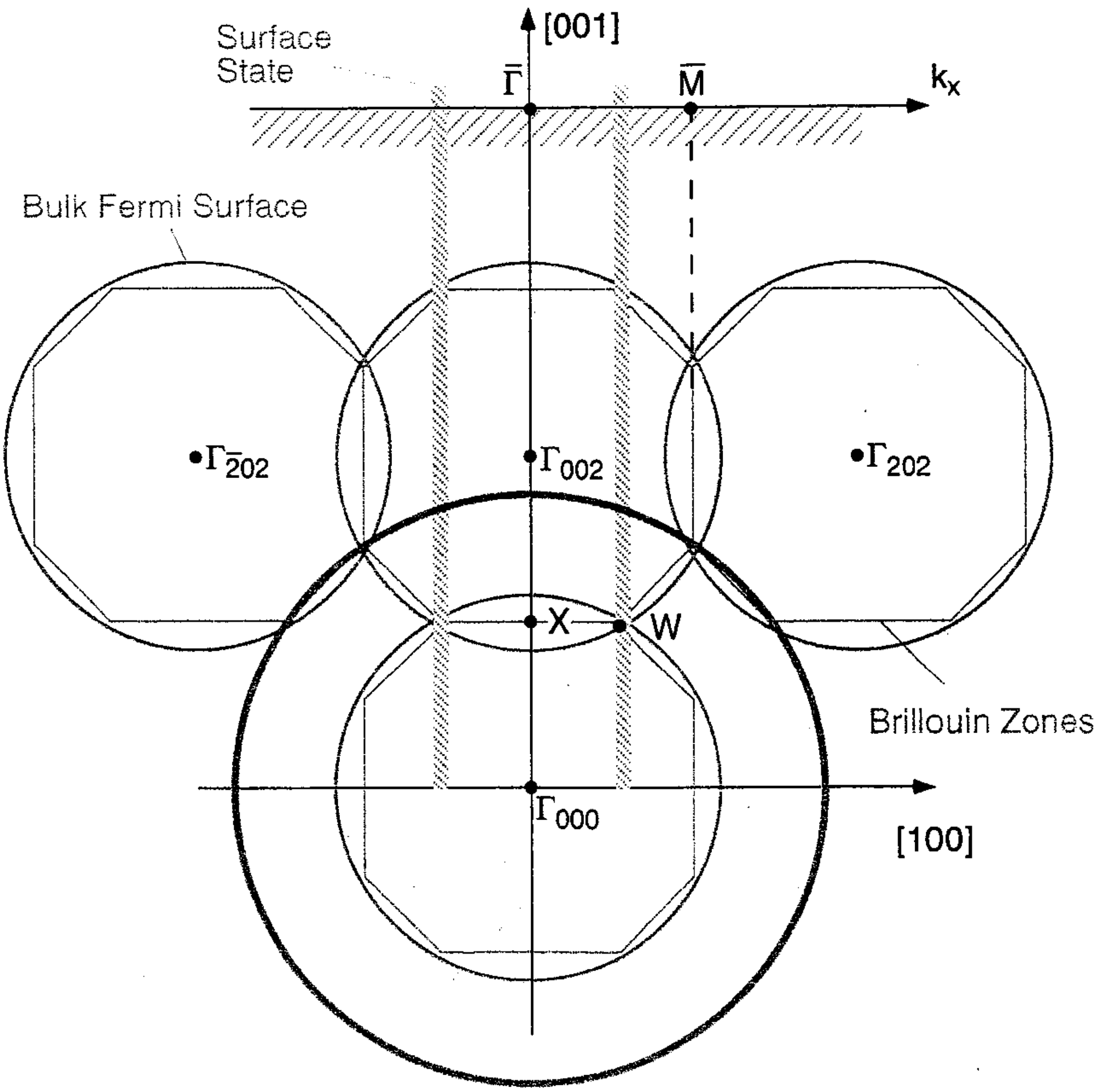
Fermi Surface Map of Al(001)

HeI (21.2 eV)



R. Fasel et al.

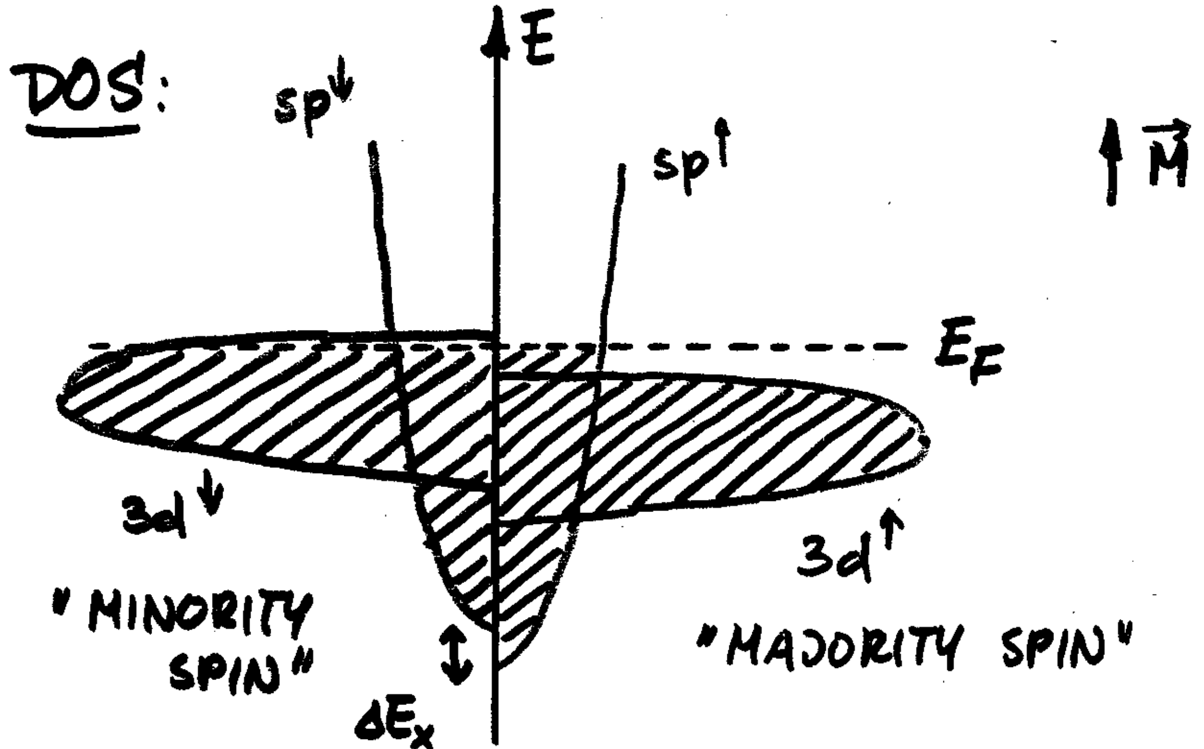
k-Space Section for Al(001)



FERMI SURFACE OF Ni

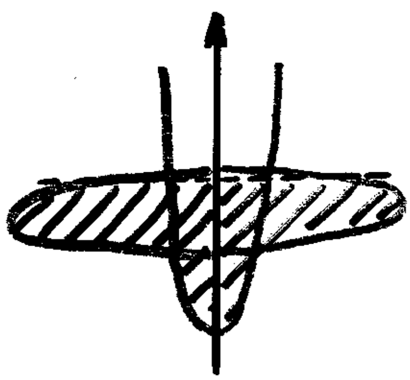
$T < T_c$ (631 K): ITINERANT FERROMAGNET

DOS:

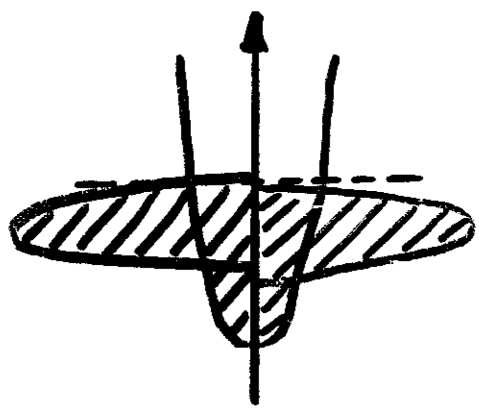


⇒ 2 FERMI SURFACES: < 3d↓, sp↑ (de Haas-van Alphen!)

$T > T_c$:

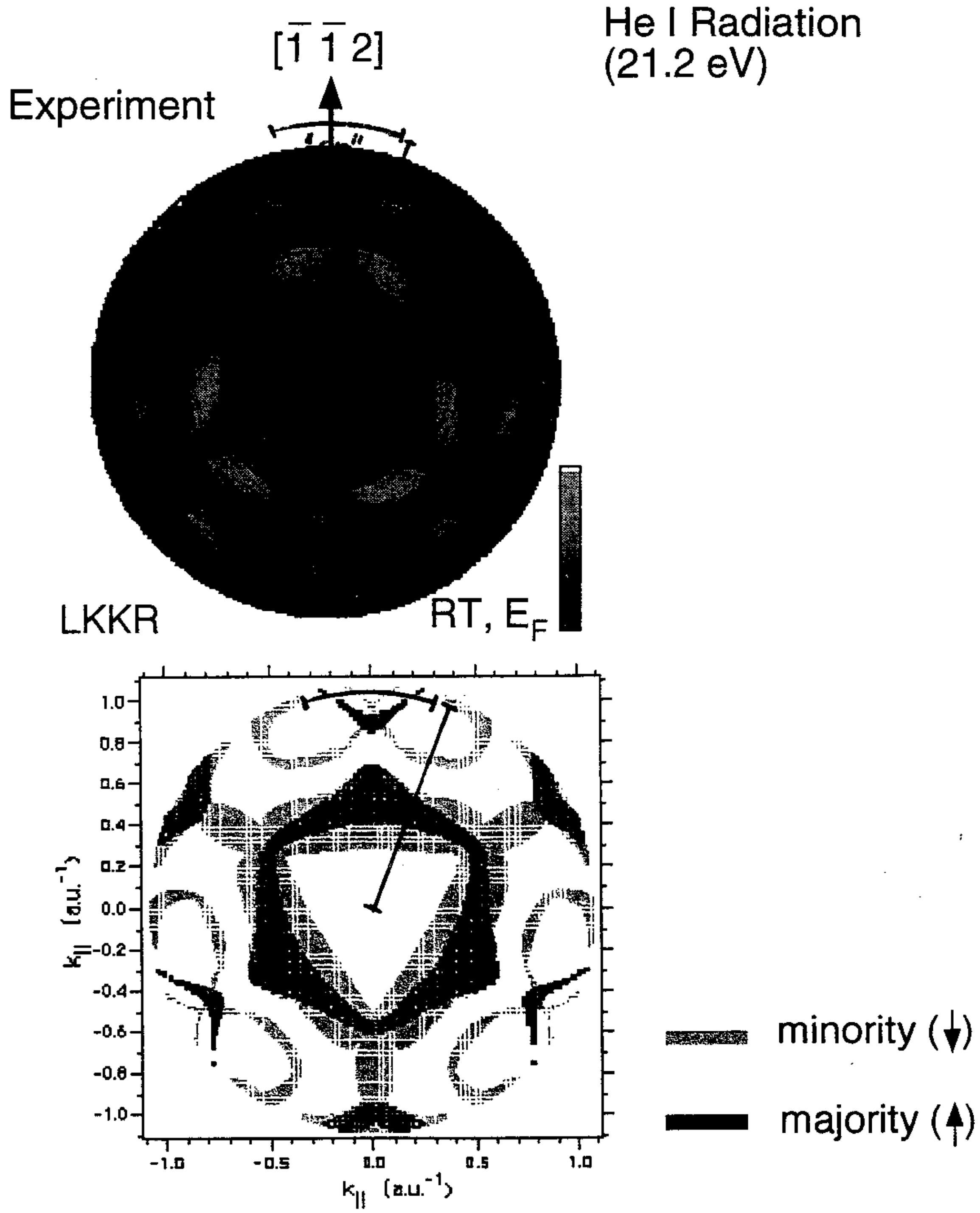


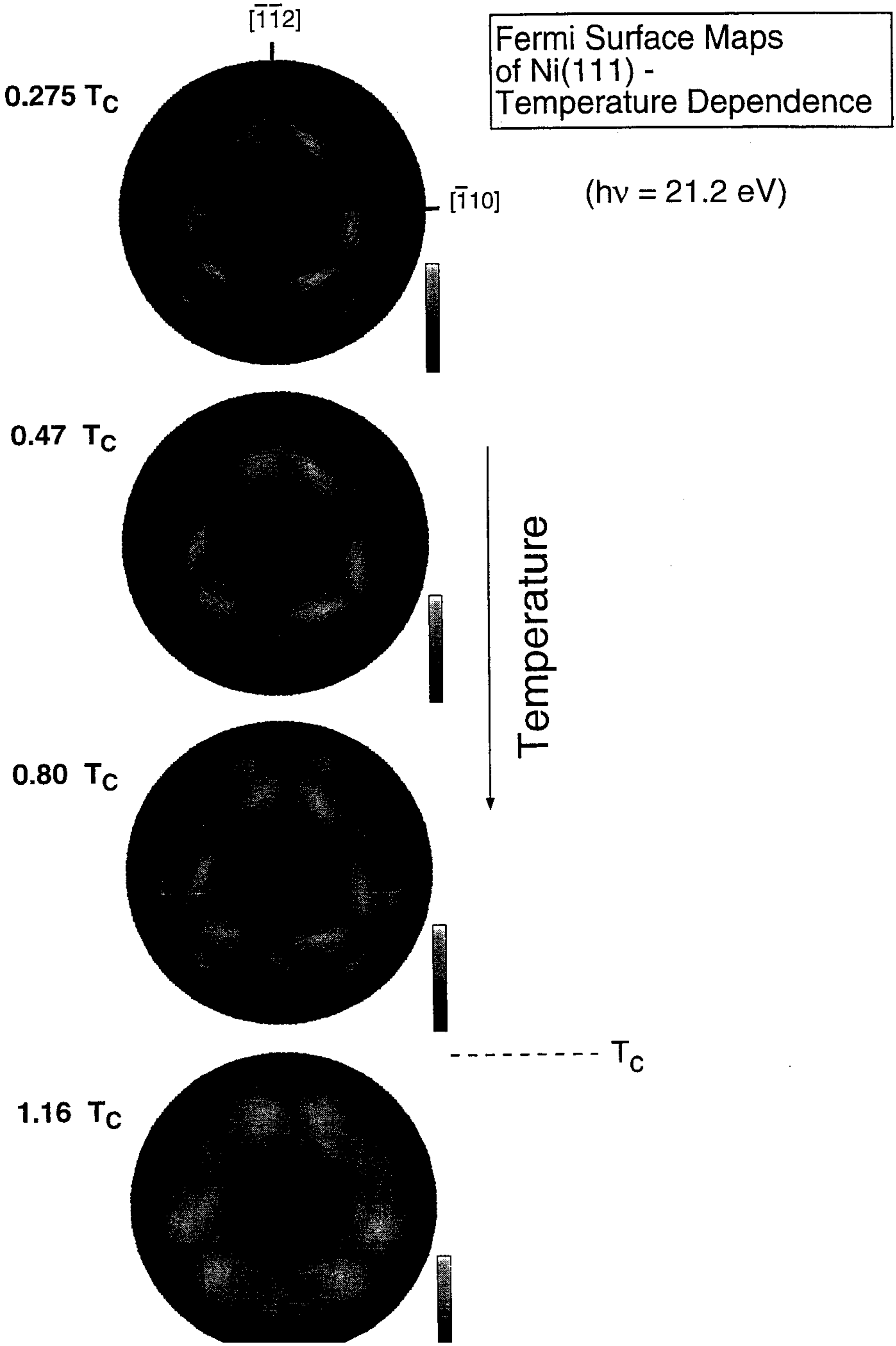
OR ?



$\Delta E_x \rightarrow 0$ (STONER) NO LOCAL MOMENTS	$\Delta E_x(T) = f(T, \vec{k})$ LOCAL MOMENTS

Fermi Surface Map of Ni(111)

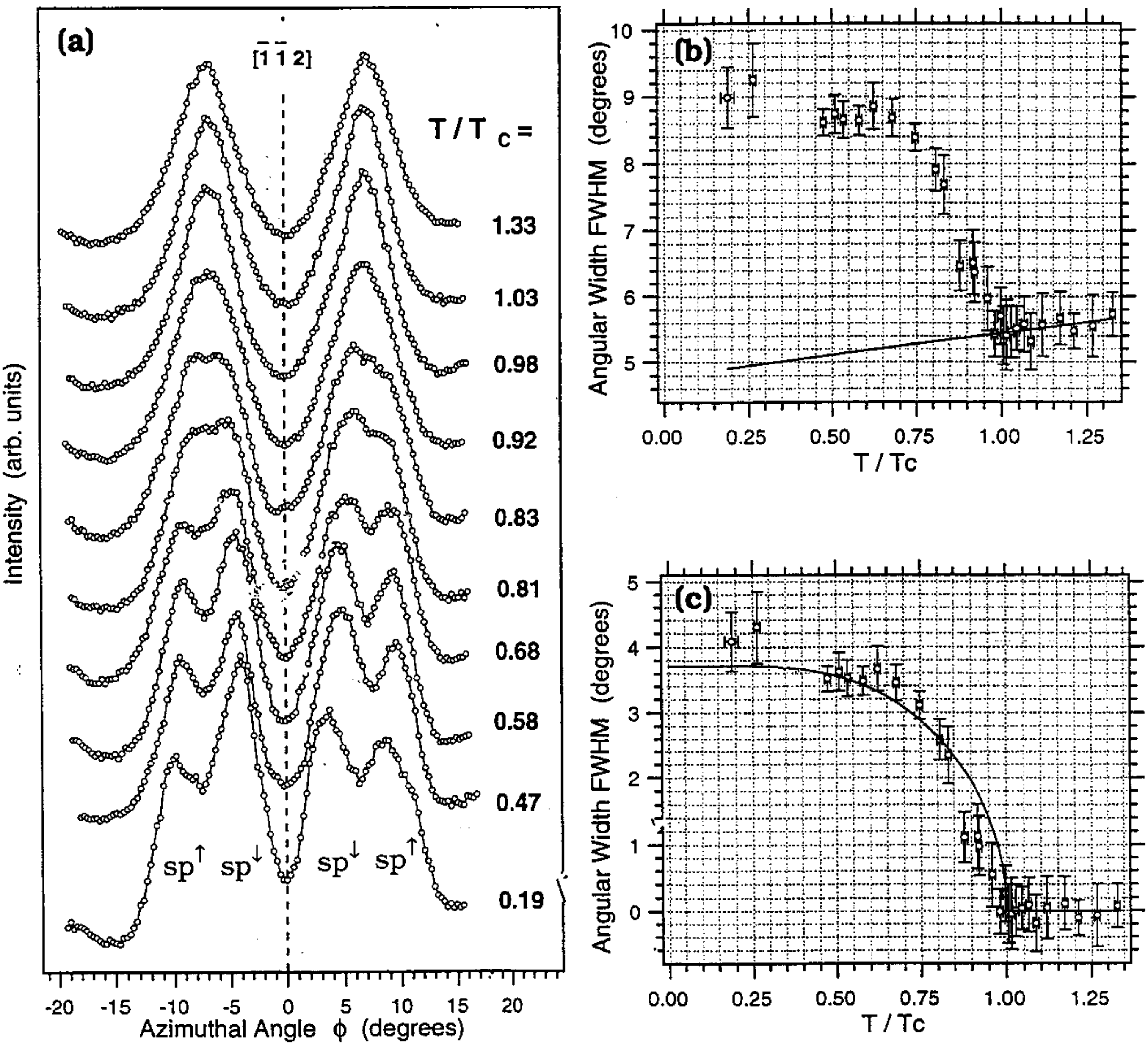




[$\bar{1}\bar{1}2$]
Fermi Surface Maps of Ni(111) - Temperature Dependence
0.275 T_C
[$\bar{1}10$]
(hν = 21.2 eV)
0.47 T_C
Temperature
0.80 T_C
T_C
1.16 T_C

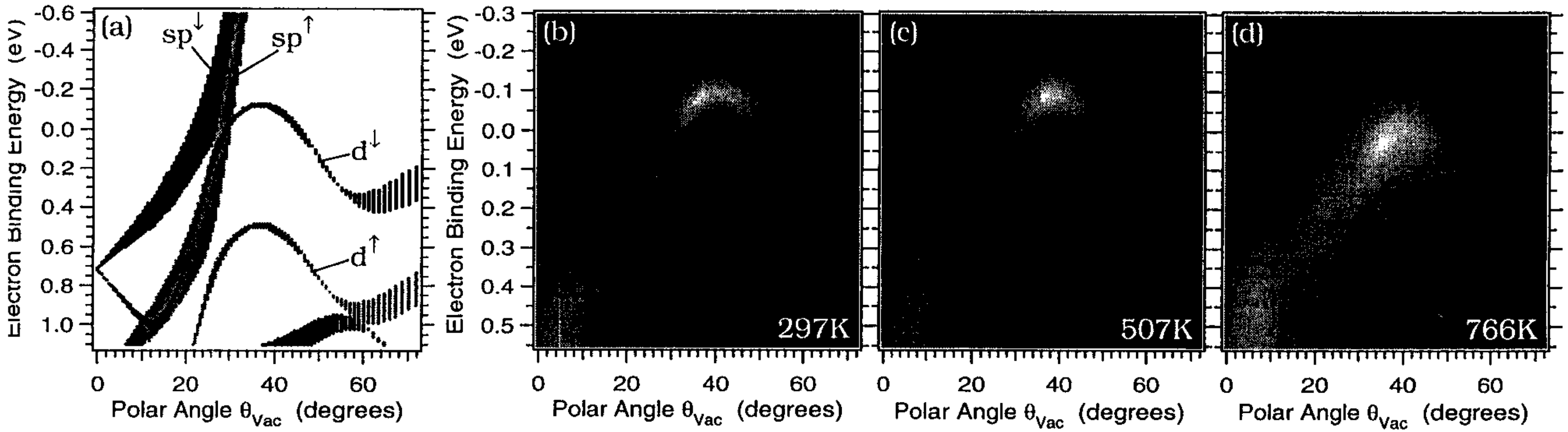
TEMPERATURE - DEPENDENT ANGULAR EXCHANGE SPLITTING OF *sp* - BANDS

from Angular Distribution Curves at the Fermi Level



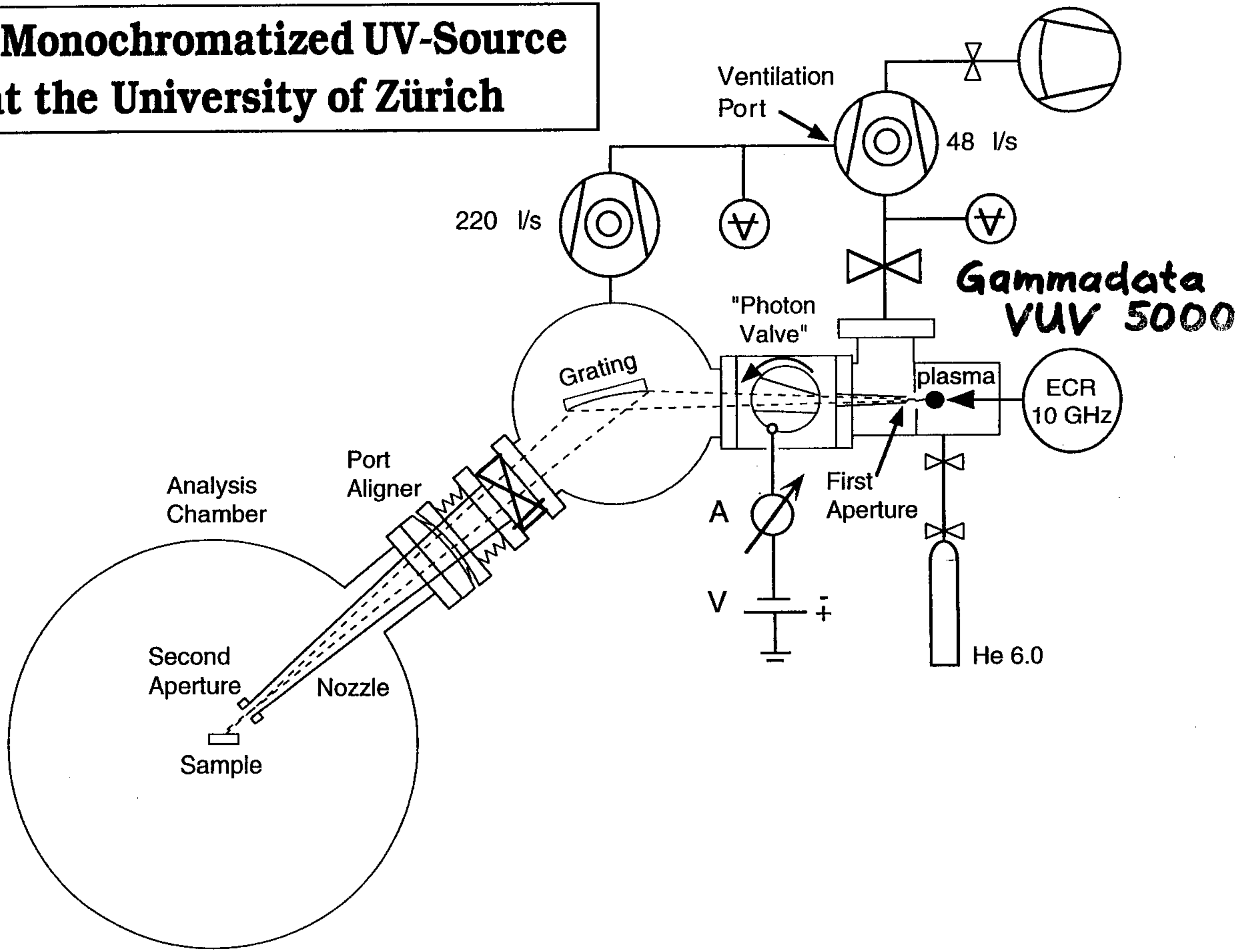
(a) Raw Data

(b) Full Width at Half Maximum / (c) after Offset Subtraction

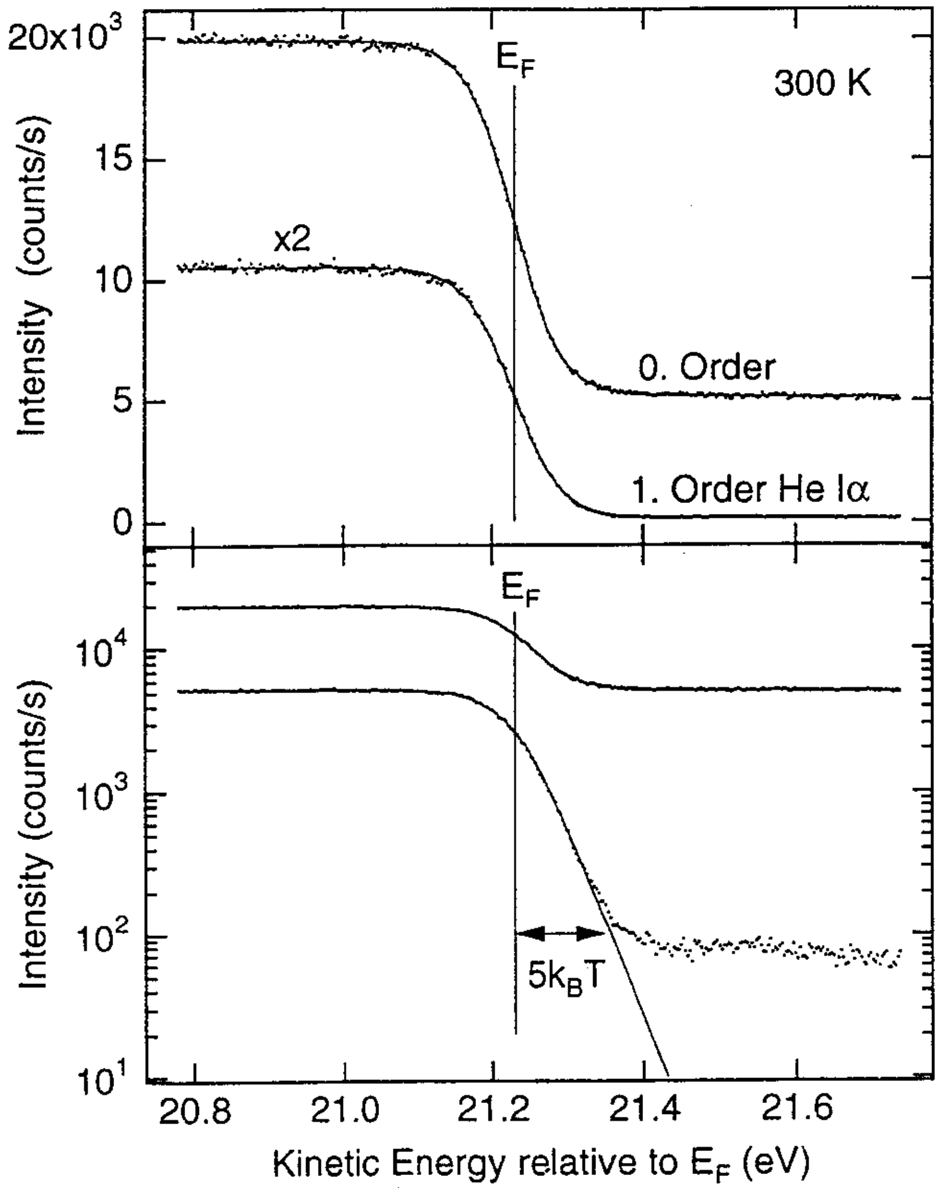


T.Greber, T.J.Kreutz, J.O., PRL 79, 4465 ('97)

The Monochromatized UV-Source at the University of Zürich

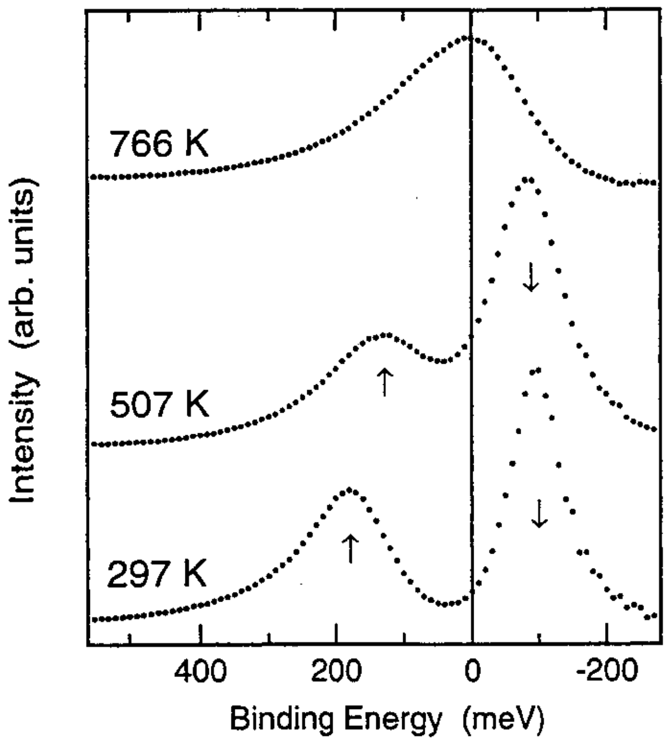


Fermi edge of polycrystalline Ag



T = 300 K

ΔE = 50 meV



766 K
507 K
297 K
Intensity (arb. units)
400
200
0
-200
Binding Energy (meV)

The Magnetic Phase Transition
of Nickel - Photoemission Results

We conclude that ...

... we can measure the Fermi surface
of an itinerant ferromagnet
at various temperatures.

... we can identify majority and minority bands
by comparison to band structure calculations.

... all bands observed (d and sp) show a collapse
of the exchange splitting at T_C.

... one sp band crosses the top of the d band
very near to E_F.

=> reduction of the Stoner gap
sp -> d scattering.

... the top of the d band collapses right at E_F.

=> magnetic moments can be formed
with low excitation energies above T_C
(n-scattering sees spin waves above T_C).

Correlation Effects in
Photoemission from Nickel near E_F ...

... cause a spin- and band-dependent renormalization
of the energy scale.

... can explain the rapid increase of the photoemission
line widths away from E_F.