UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL ATOMIC ENERGY AGENCY
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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H4.SMR/1013-30

SCHOOL ON THE USE OF SYNCHROTRON RADIATION IN SCIENCE AND TECHNOLOGY:
"John Fuggle Memorial"

3 November - 5 December 1997

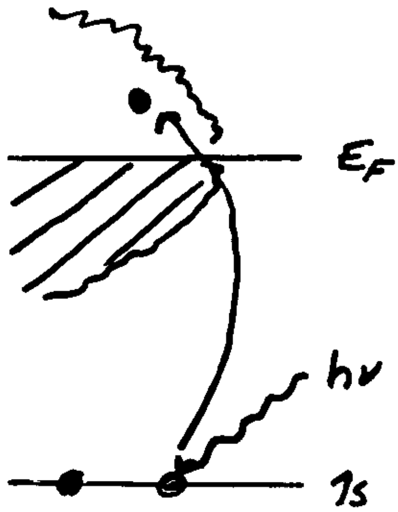
Miramare - Trieste, Italy

Core Level Spectroscopies II

A. Nilsson
University of Uppsala
Sweden

MAIN BUILDING STRADA COSTIERA, 11 TEL. 2240111 TELEFAX 224163 TELEX 460392 ADRIATICO GUEST HOUSE VIA GRIGNANO, 9 TEL. 224241 TELEFAX 224531 TELEX 460449
MICROPROCESSOR LAB VIA BEIRUT, 31 TEL. 2249911 TELEFAX 224600 TELEX 460392 GALILEO GUEST HOUSE VIA BEIRUT, 7 TEL. 2240311 TELEFAX 2240310 TELEX 460392
ENRICO FERMI BUILDING VIA BEIRUT, 6 (TELEPHONE, FAX AND TELEX THROUGH MAIN BUILDING)

XAS or NEXAFS



Probing unoccupied states

Dipole selection rule

$$\langle \Psi_i | \vec{r} | \Psi_f \rangle$$

one center approximation $\Rightarrow$

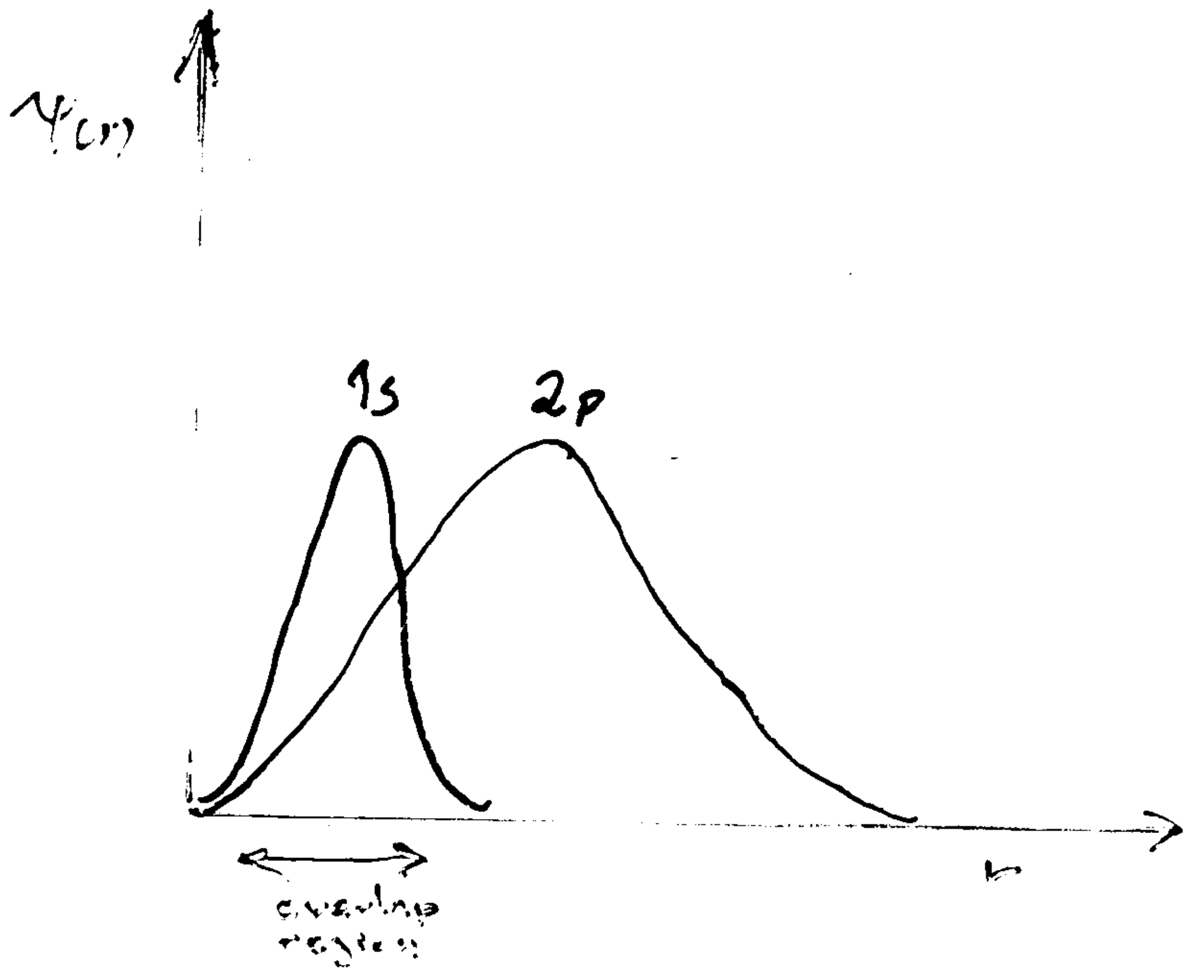
atomic orbitals selection rule

1s $\rightarrow$ 2p

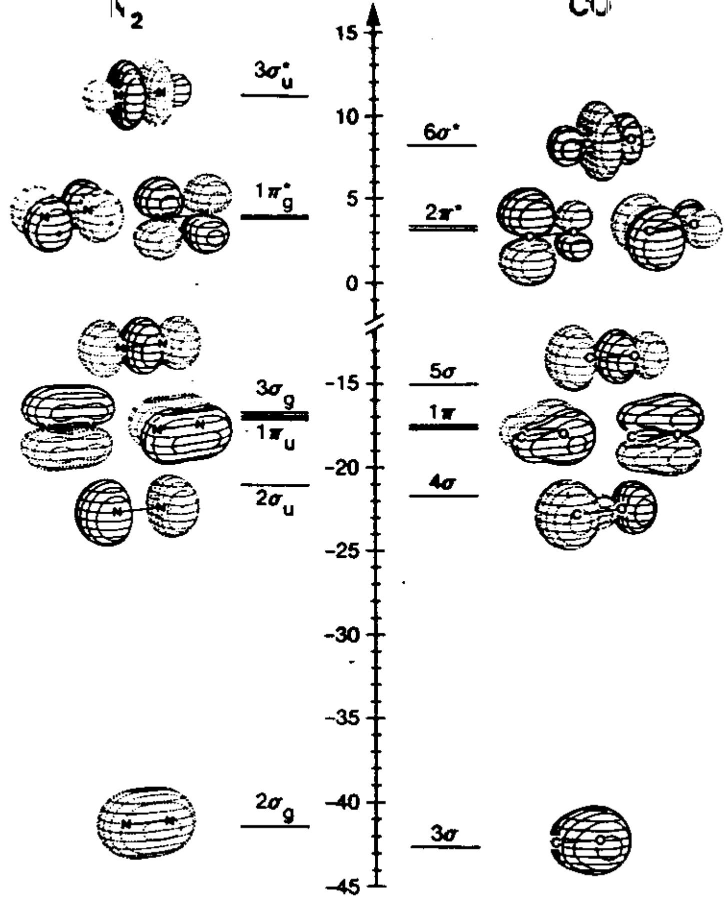
2p $\rightarrow$ 3d, 4s

etc.

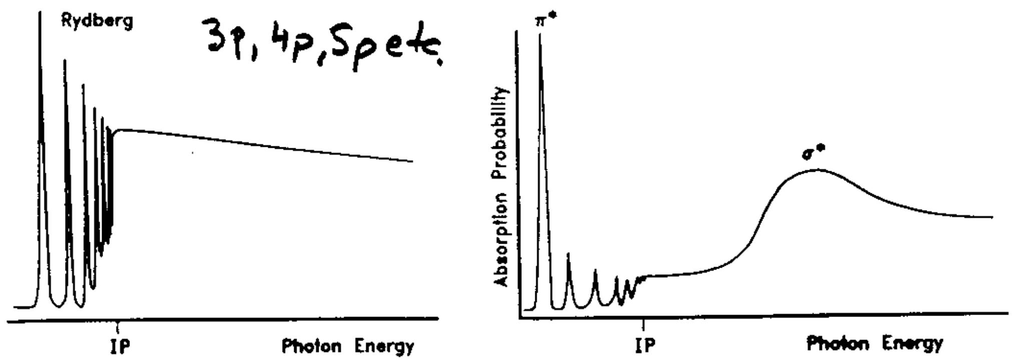
X-ray spectroscopy



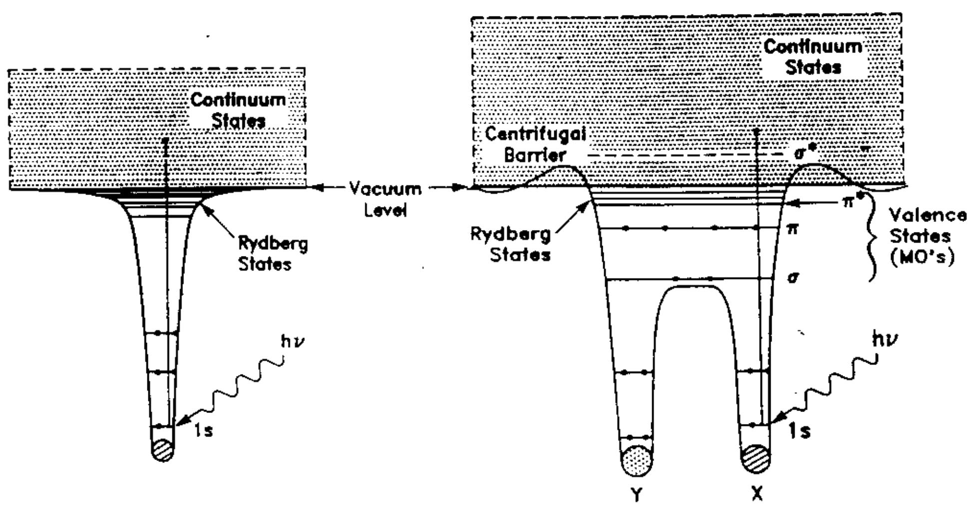
Matrix element ⇒ constant
atomic cross section



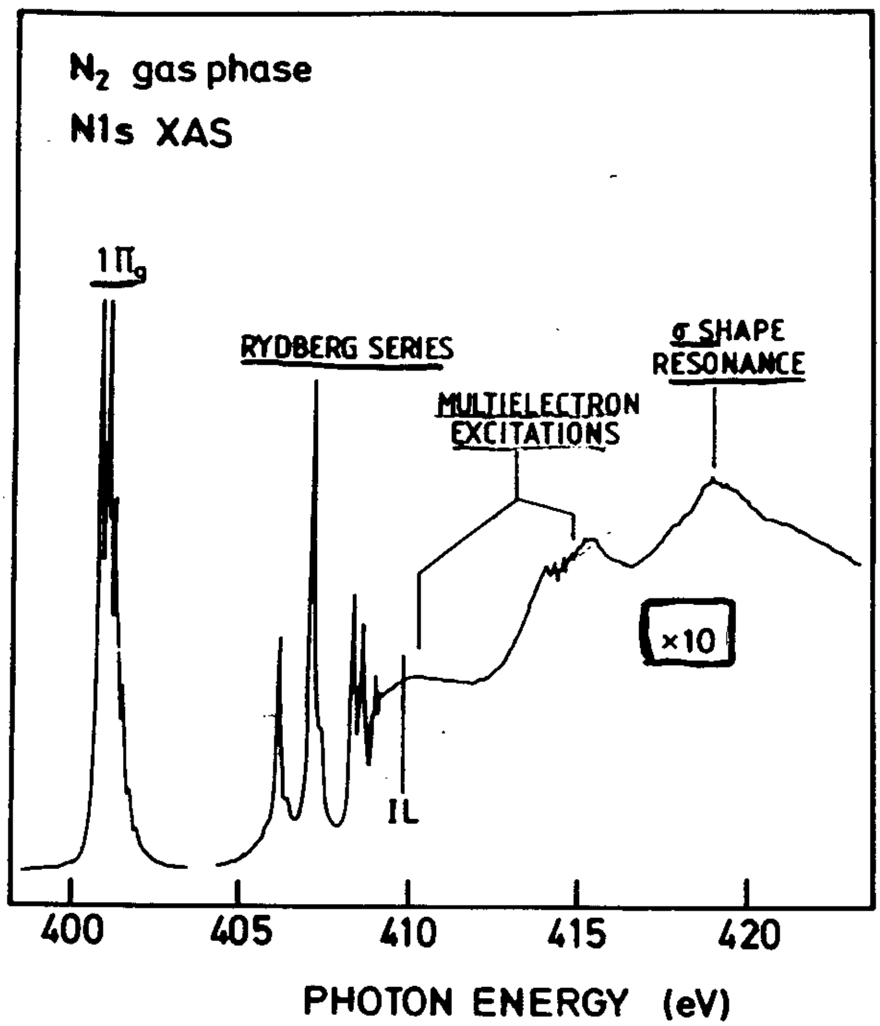
N2
CO
15
10
5
0
-15
-20
-25
-30
-35
-40
-45
$3\sigma_u^*$
$1\pi_g^*$
$3\sigma_g$
$1\pi_u$
$2\sigma_u$
$2\sigma_g$
$6\sigma^*$
$2\pi^*$
5σ
1π
4σ
3σ



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



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

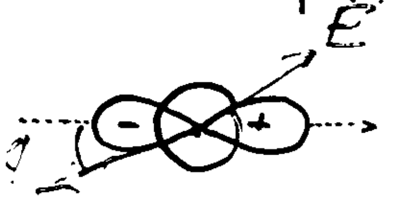


Ma et al Phys. Rev. A44, 1848 (1991)

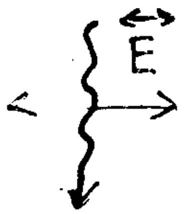
Moleculor orbitals

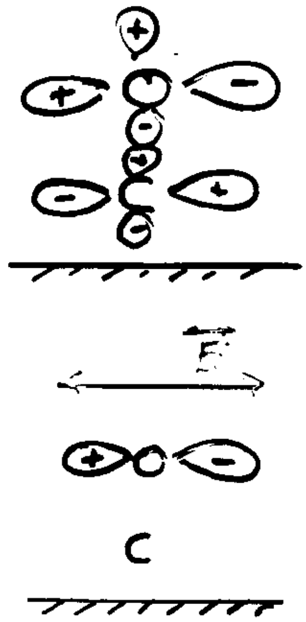
Rydberg states: extended atomic like states

$1s \rightarrow 2p$

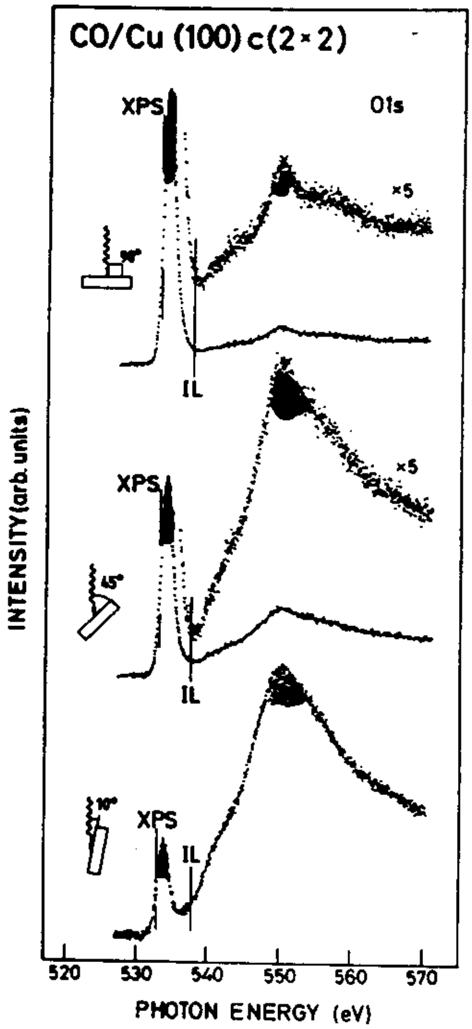


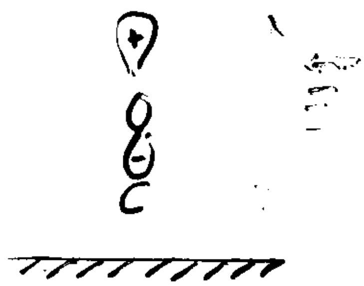
$I \propto \cos^2\theta$





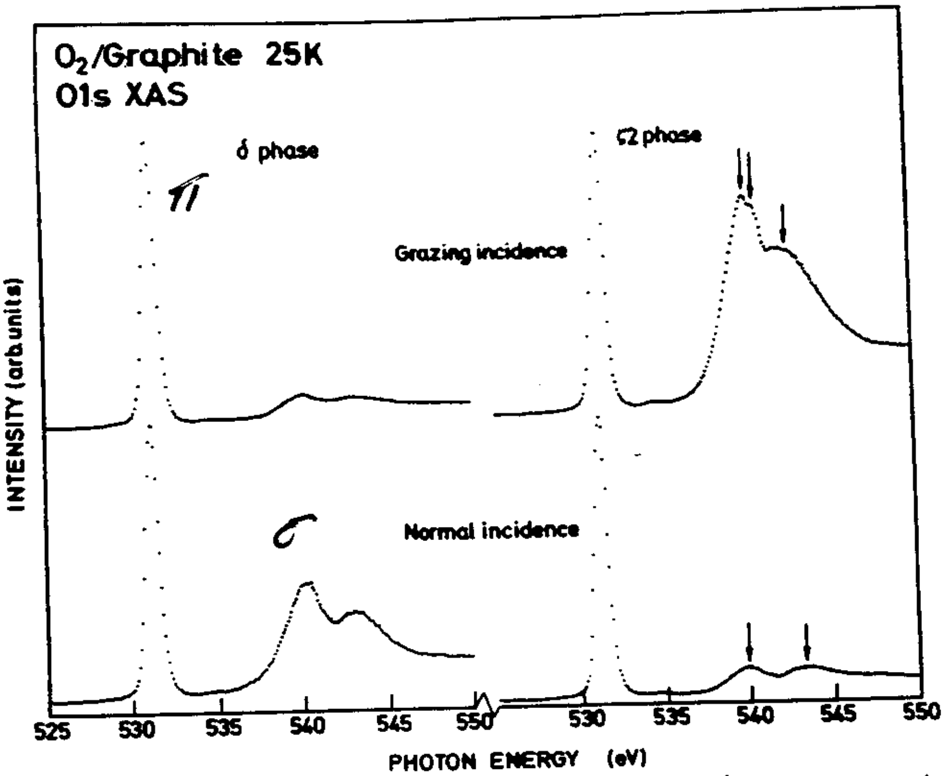
π-states



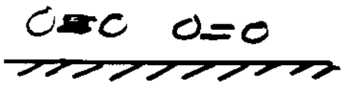


σ-states

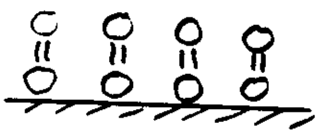
Bjøreholm et.al. Phys. Rev. B47, 2308 (1993)



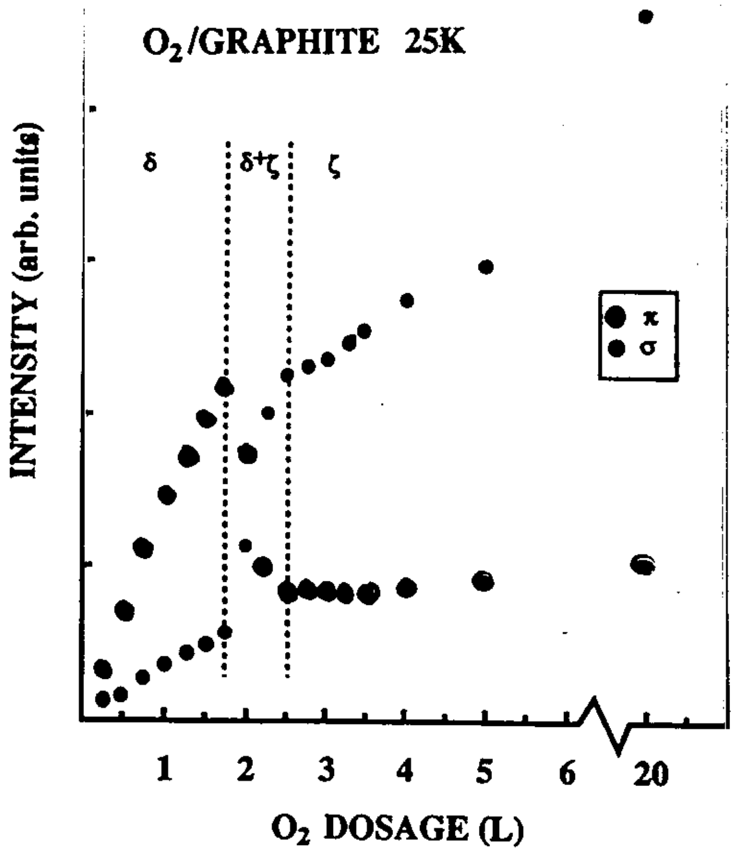
Guest et al. Surf. Sci. 269/270, 432 (1992)

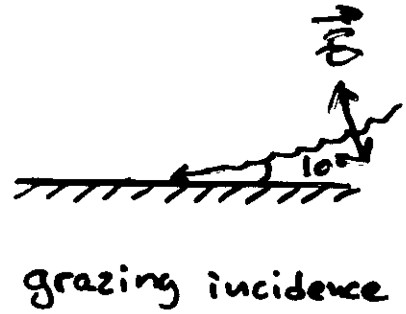


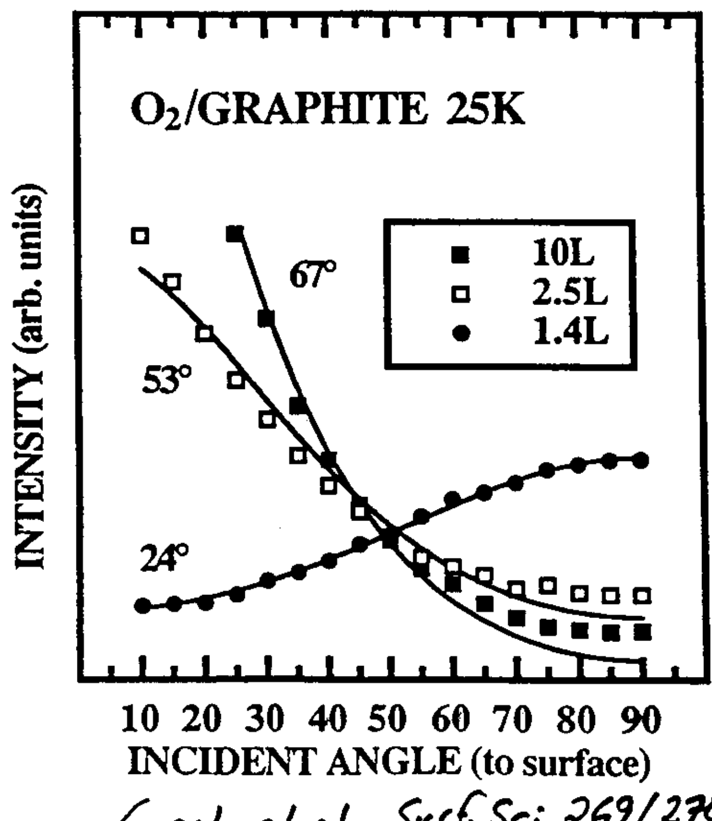
δ-phase



ε2-phase

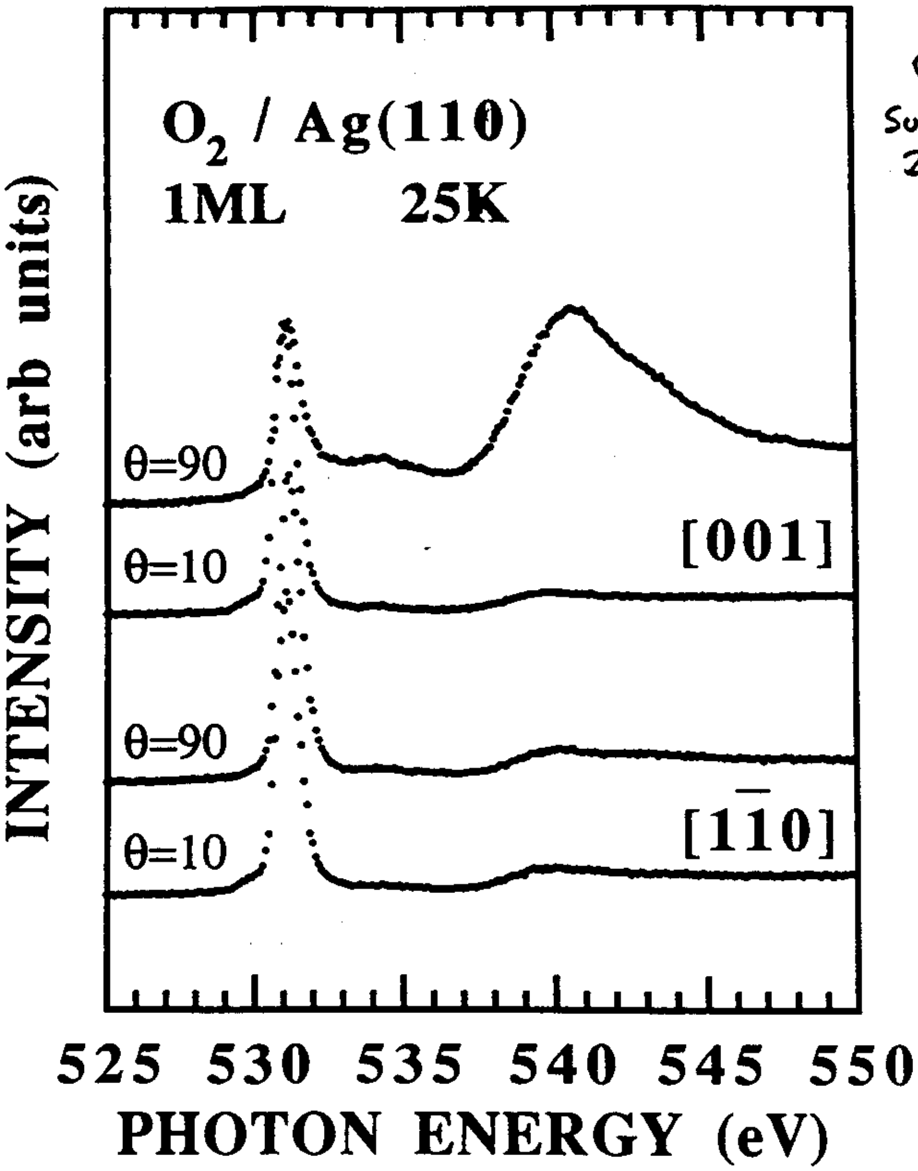


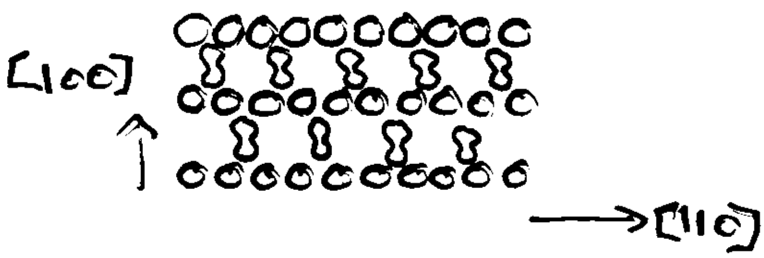




Guest et.al Surf. Sci. 269/270, 432 (1992)

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





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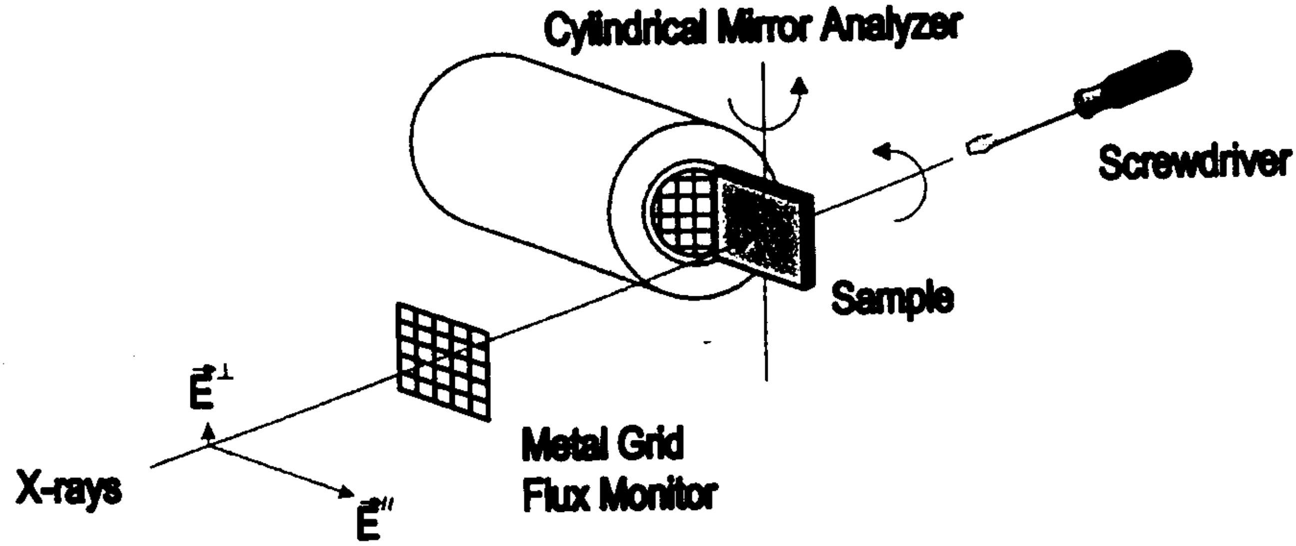
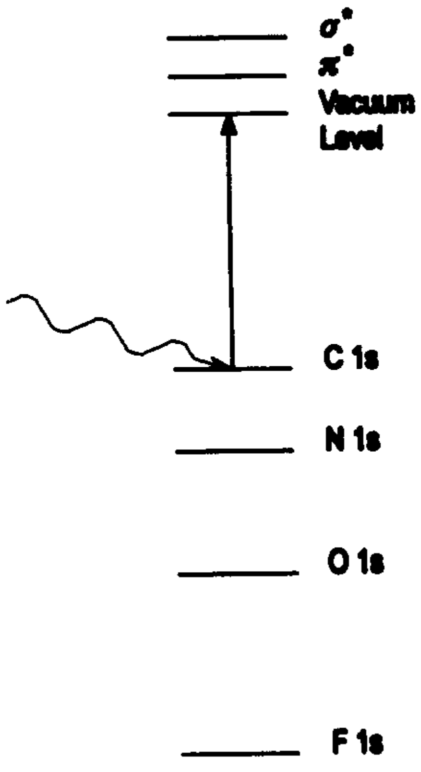
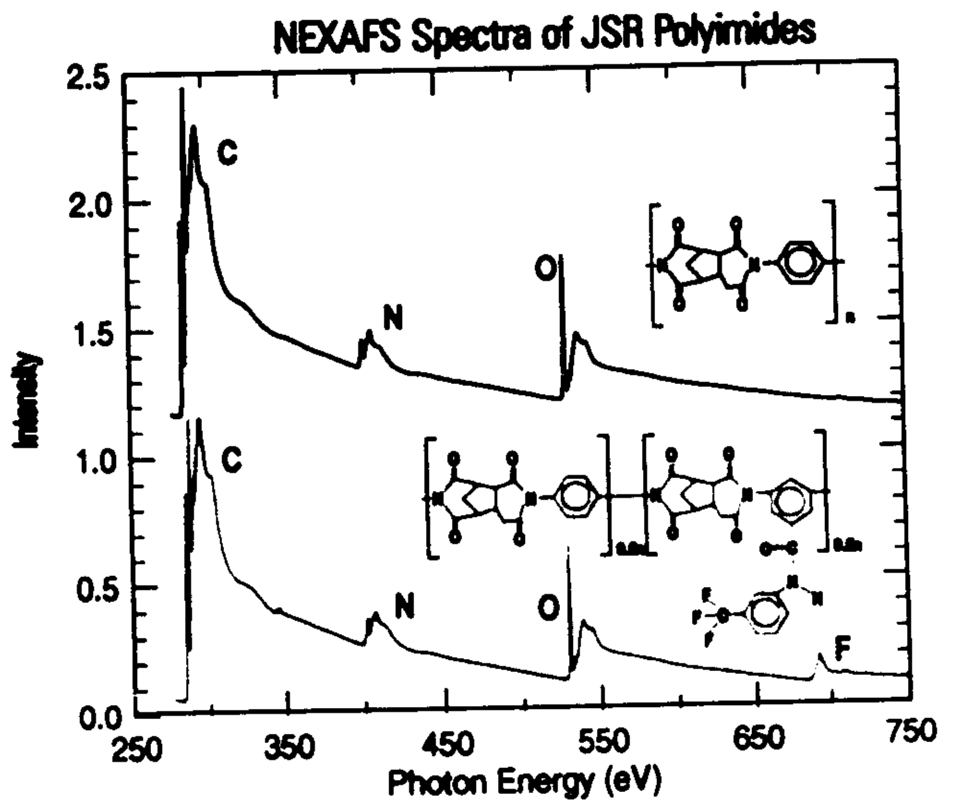


NEXAFS is element specific





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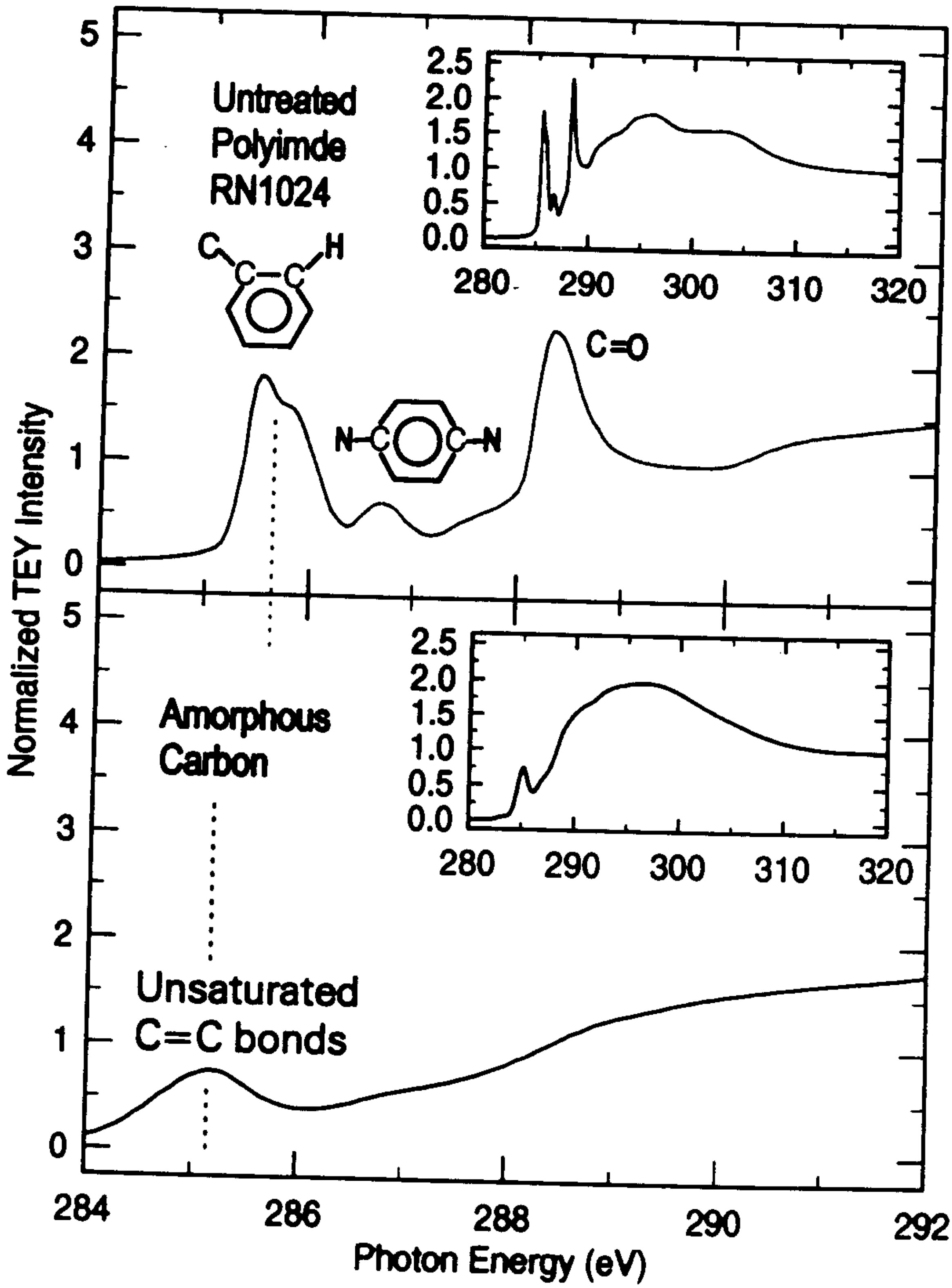
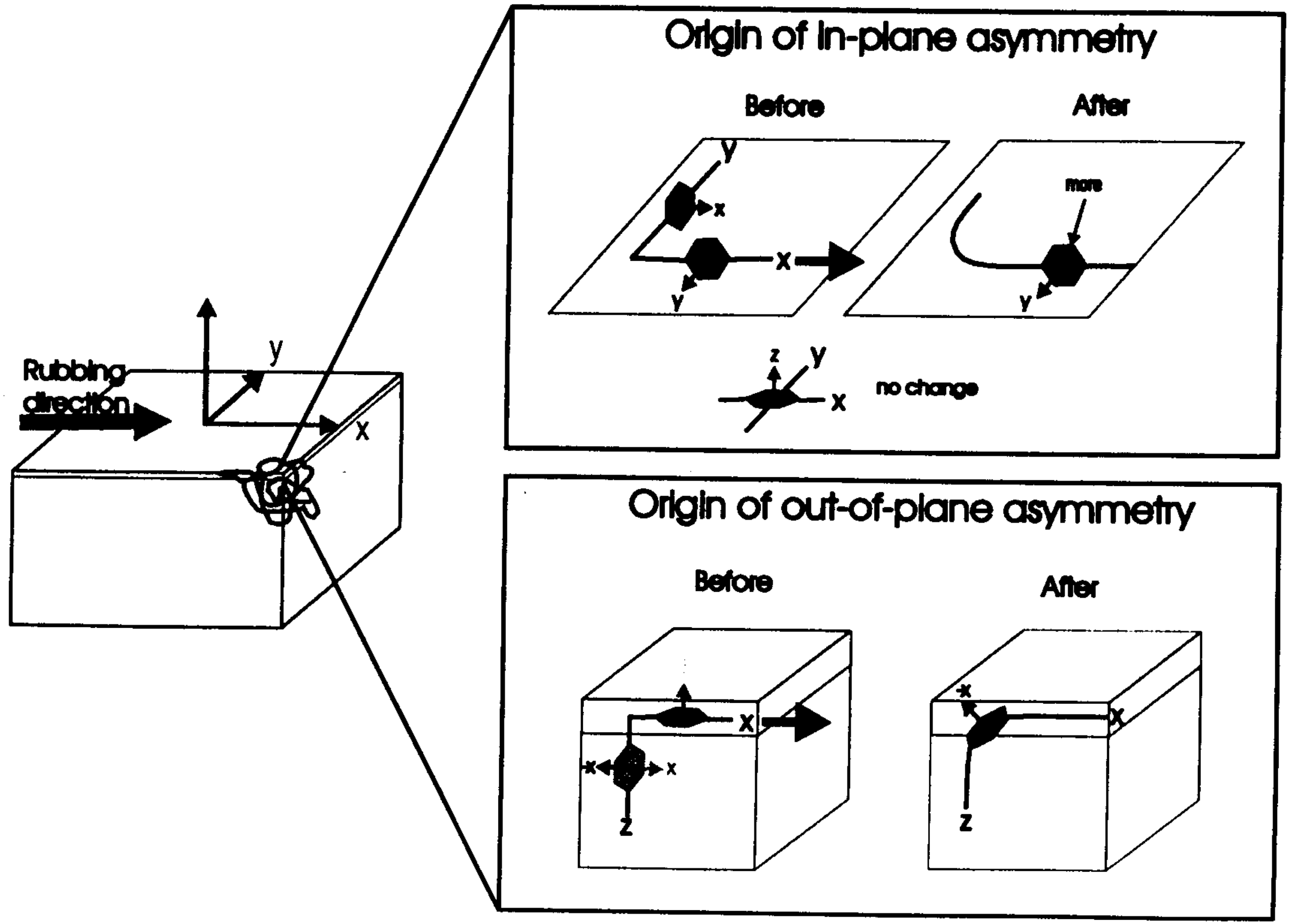


ibnexafs.cdr

IBM Almaden

[redacted]

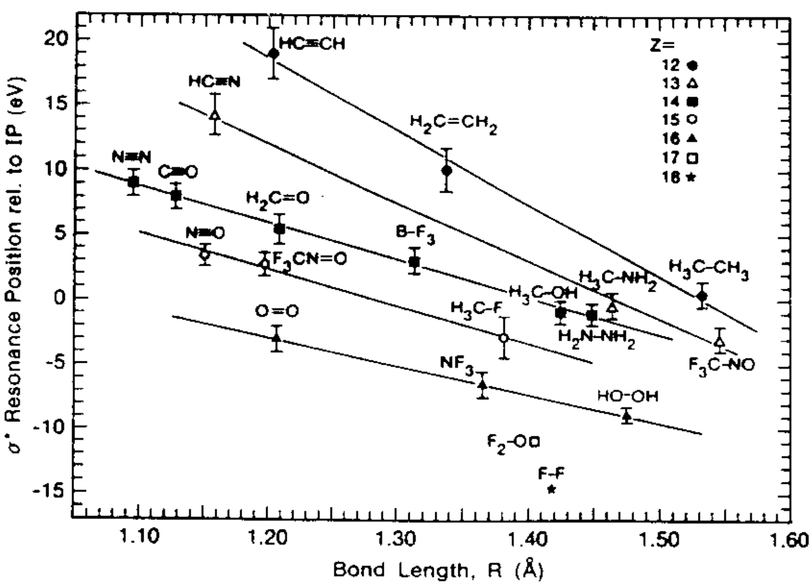


Origin of in-plane asymmetry
Before
After
more
no change
Origin of out-of-plane asymmetry
Before
After
Rubbing direction
x
y
z

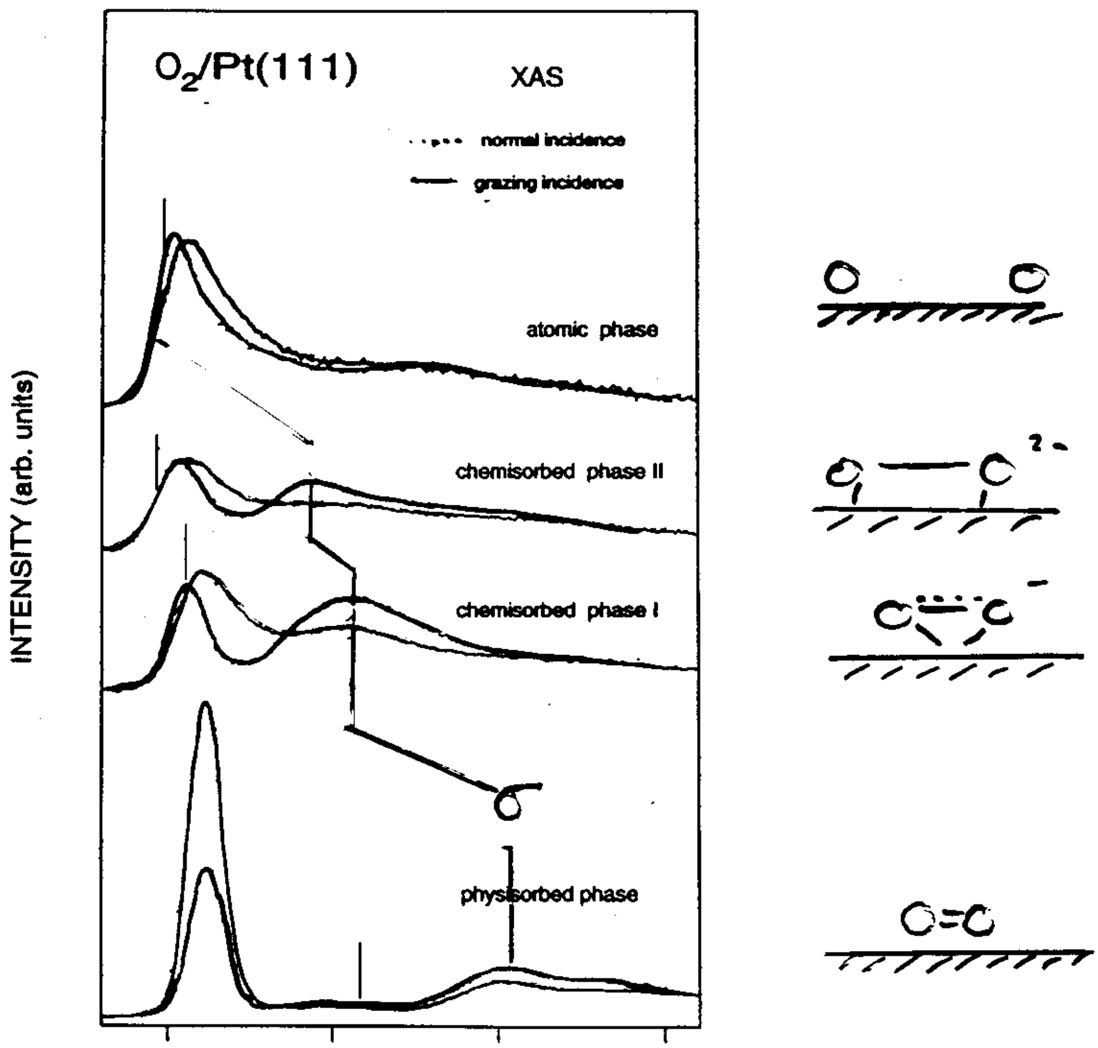
σ - resonance ⇔ bond length

multiple scattering in molecular potential

bonding ⇔ antibonding



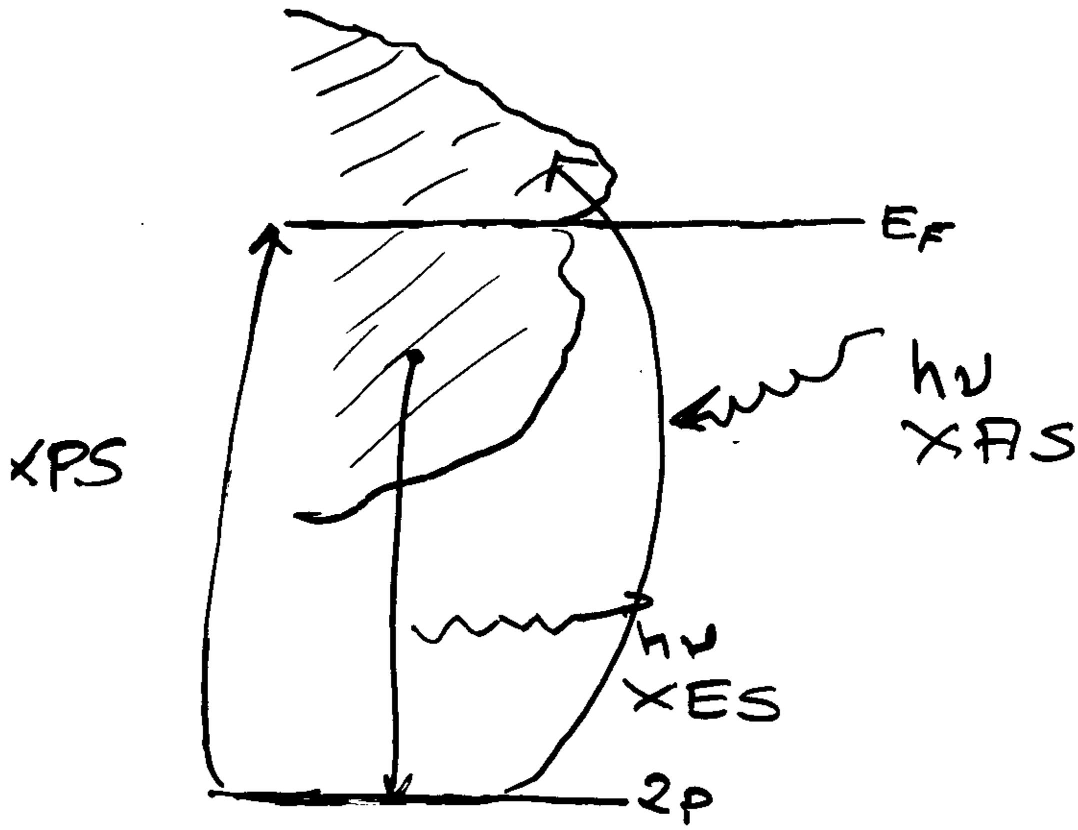
Stöhr, "NEXAFS spectroscopy"



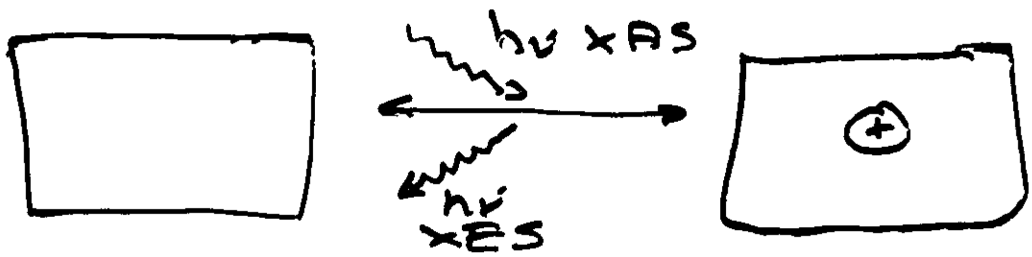
Puglia, etal Surf. sci. in press

X-ray transitions

Initial and Final state rules

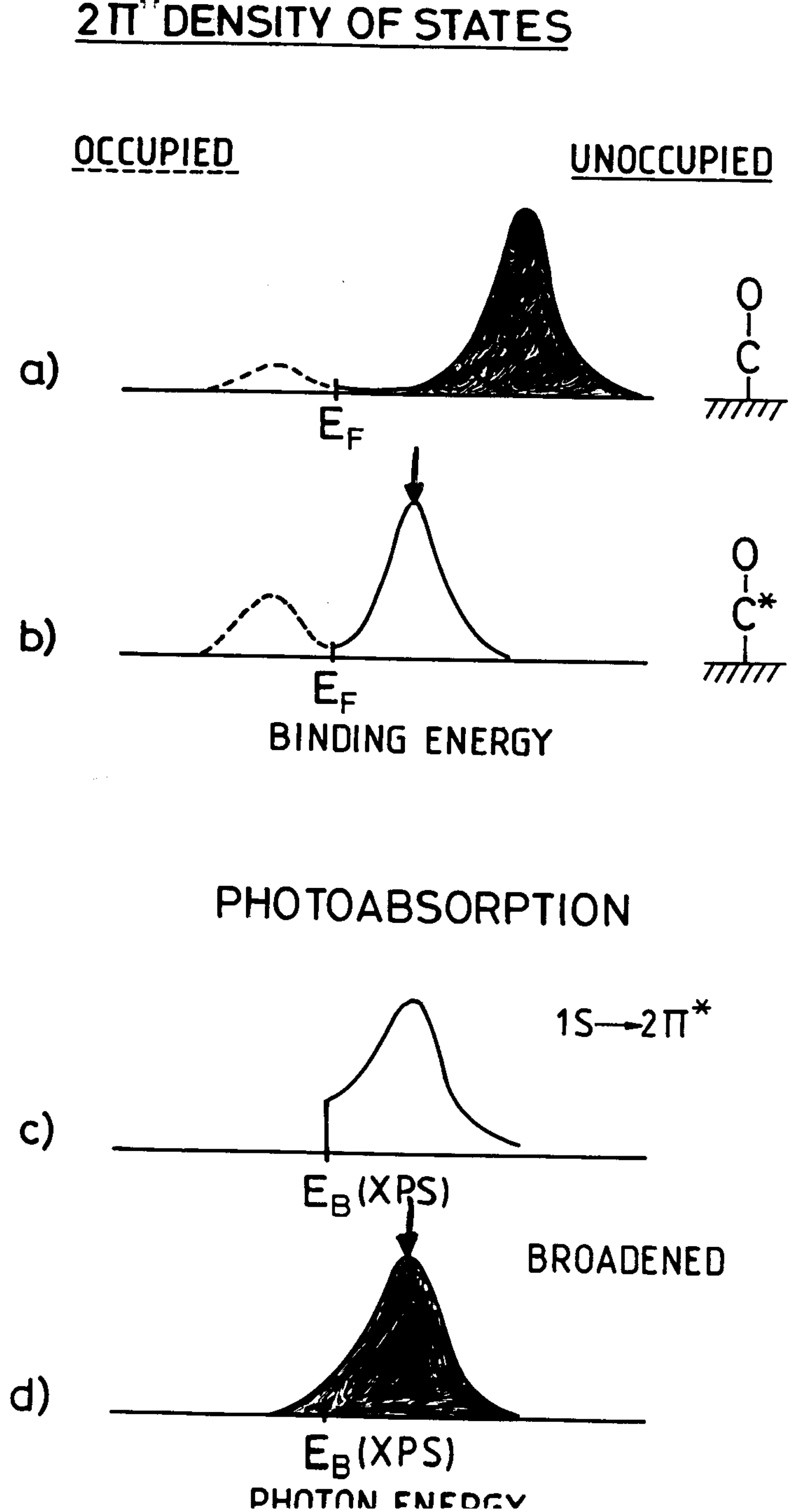


X-ray Emission Spectroscopy XES
X-ray Absorption Spectroscopy XAS

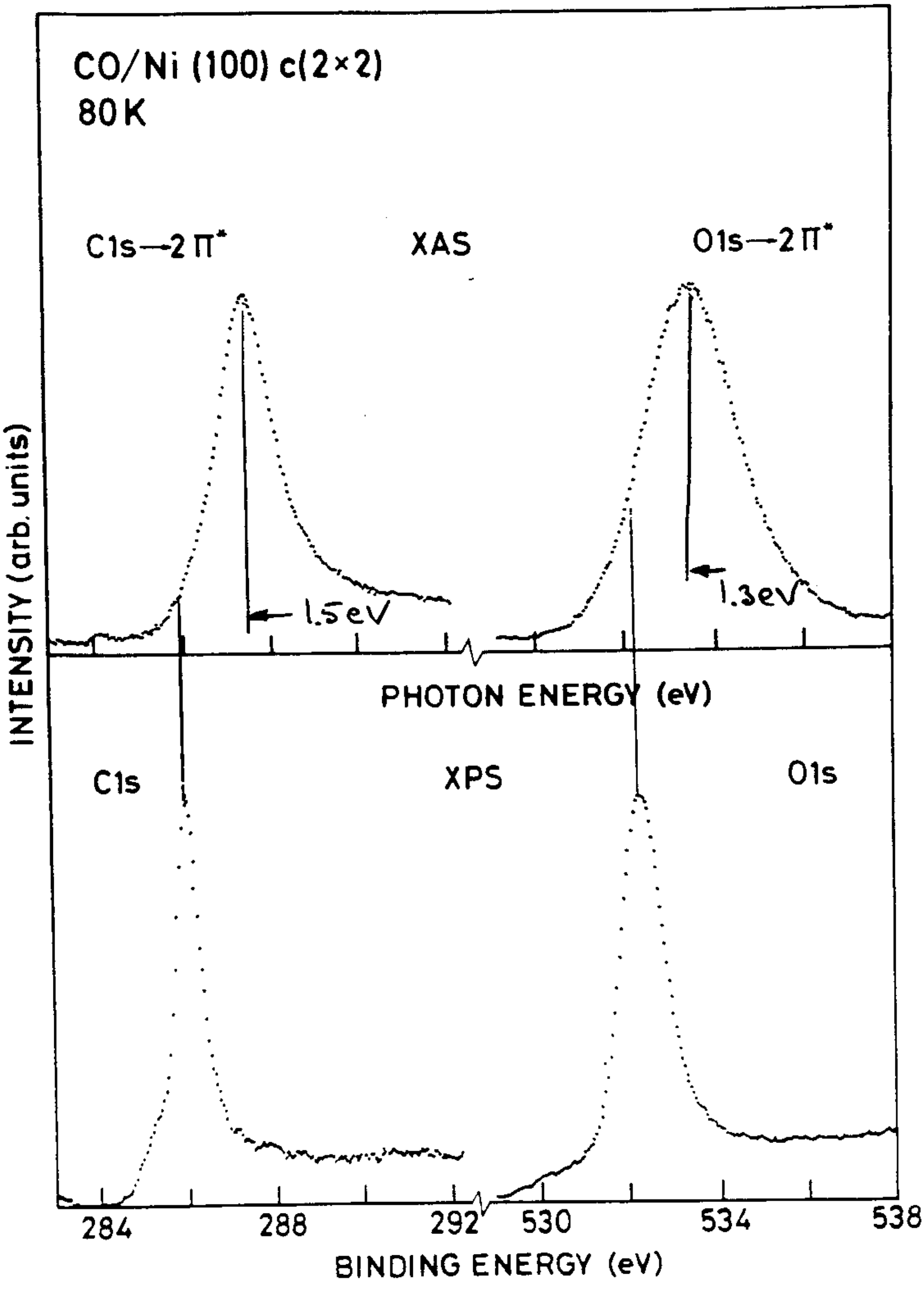


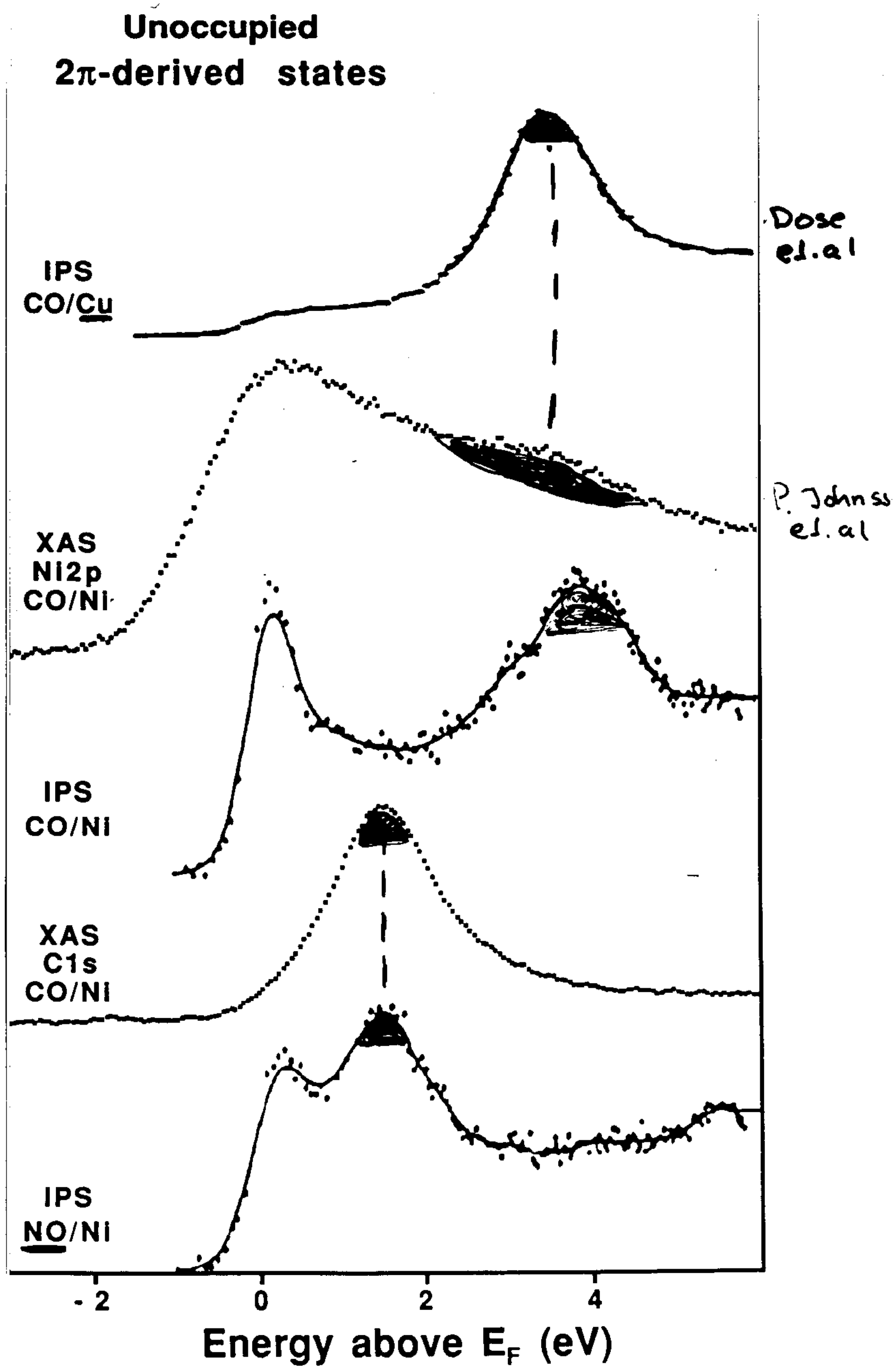
Final state ⇒ Energy position
Initial state ⇒ Intensity

Ground state Energy XES
(without corehole) Intensity XAS

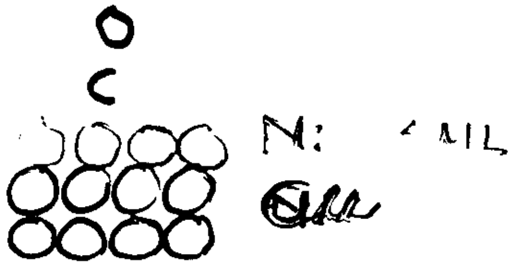

2π* DENSITY OF STATES
OCCUPIED
UNOCCUPIED
a)
E_F
O
C
b)
E_F
BINDING ENERGY
O
C*
PHOTOABSORPTION
1S→2π*
c)
E_B(XPS)
BROADENED
d)
E_B(XPS)
PHOTON ENERGY

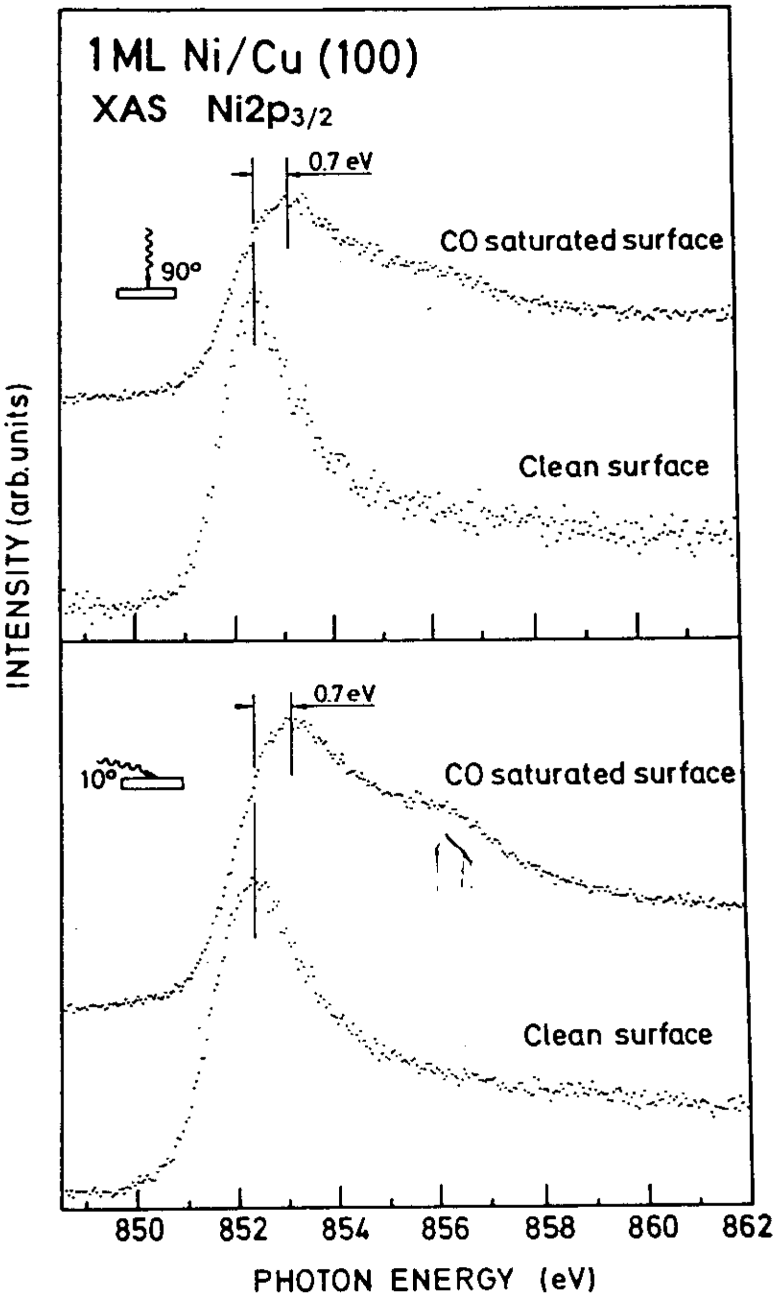
Unoccupied states





Nilsson el.al. Physica B208 & 209

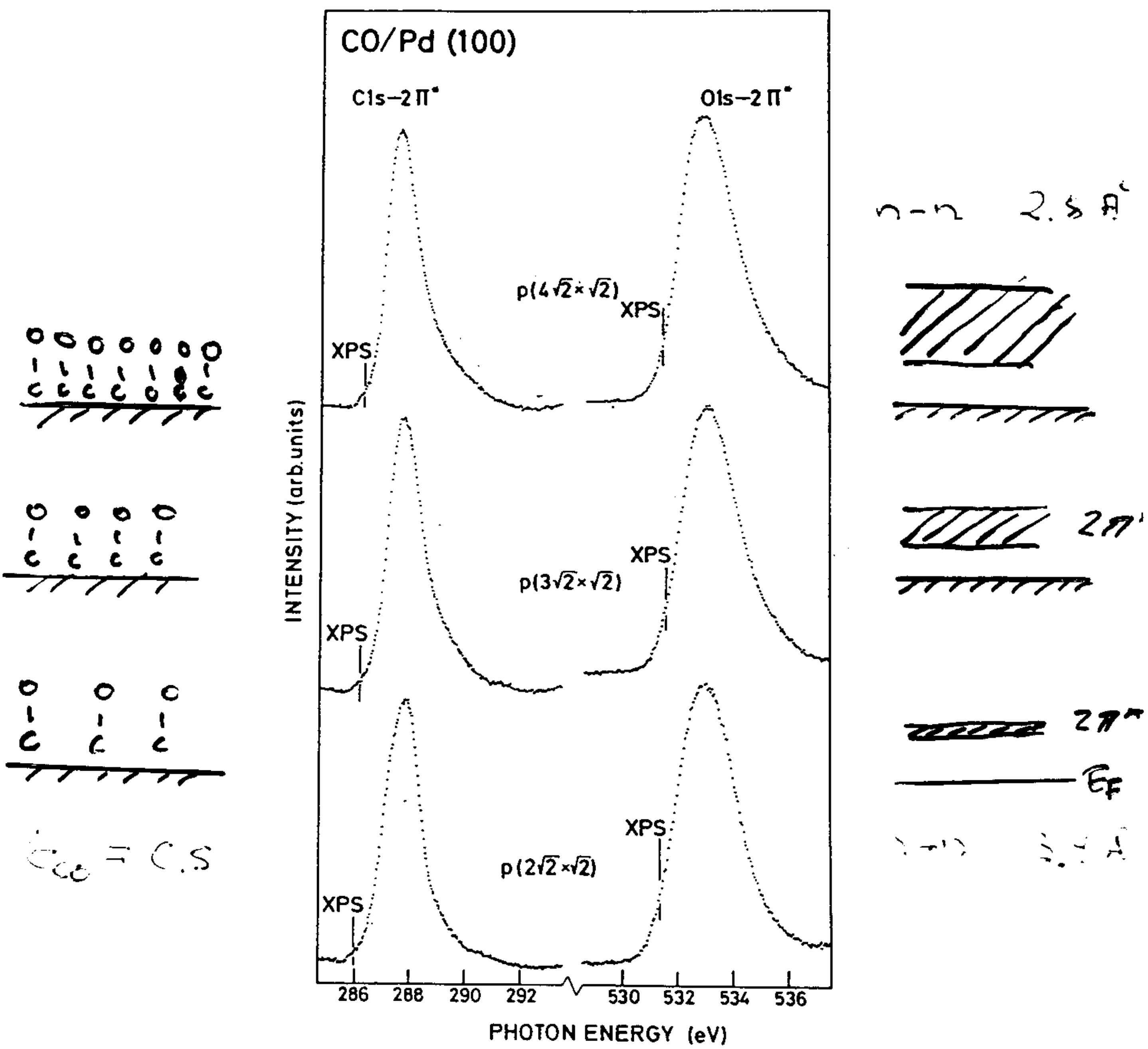




Hernnäs et.al. Phys. Rev. B47, 16052 (1993)

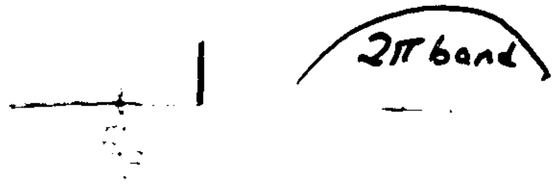
Bridge sites

CO–CO interaction

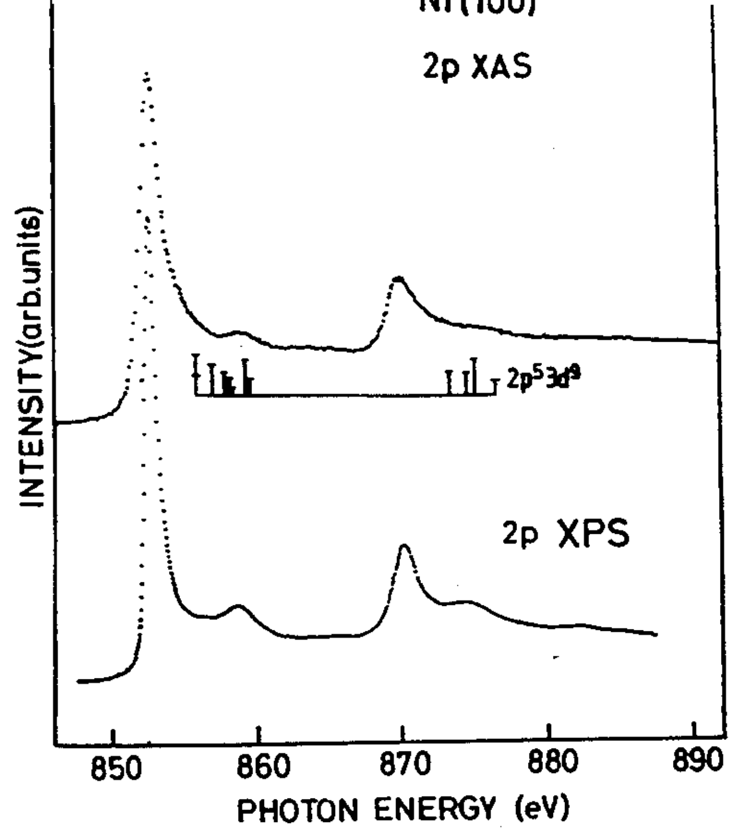


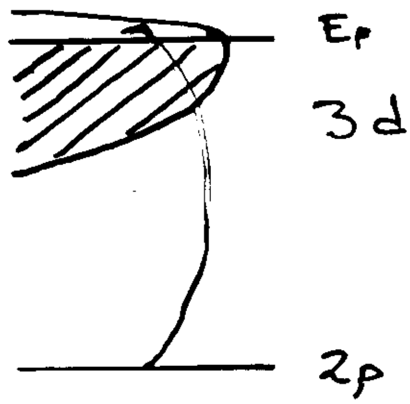
Björneholm et.al. Phys. Rev. B46, 10353 (1992)

core hole

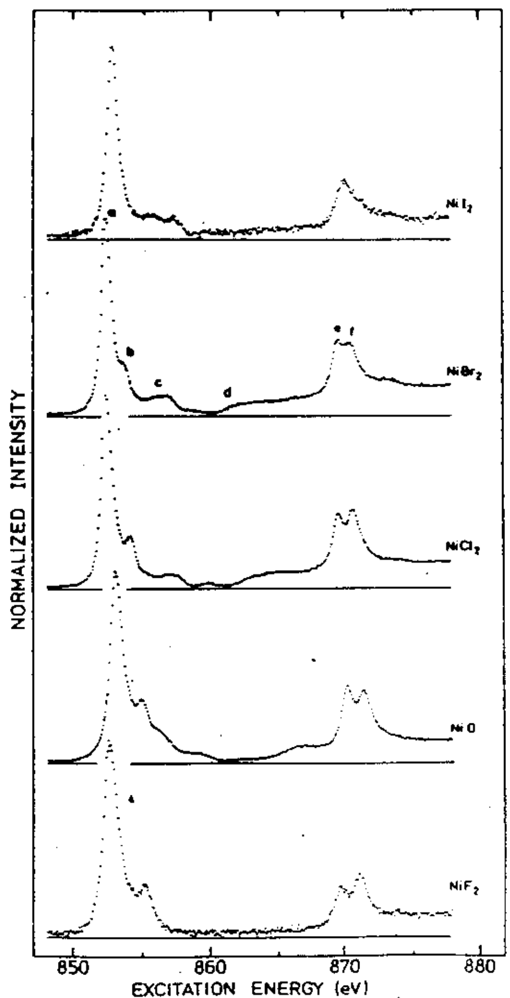


2632 (1993





$2p^6\,[3d^9] \rightarrow 2p^5\,[3d^{10}]$



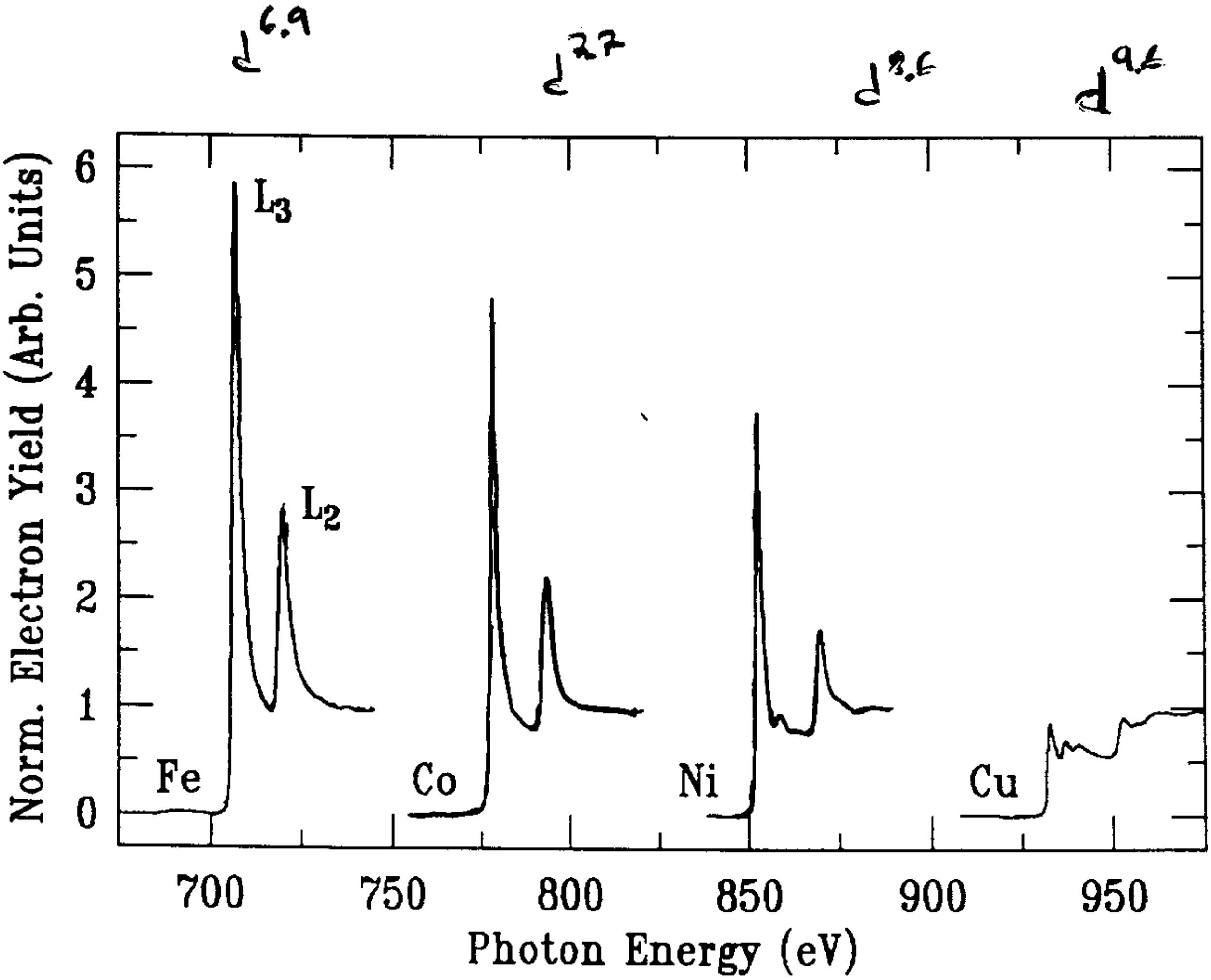
Ni compounds

$2p^6\,3d^8 \rightarrow 2p^5\,3d^9$

multiplets

Van der Laan et al. Phys. Rev. B33, 4253 (1986)

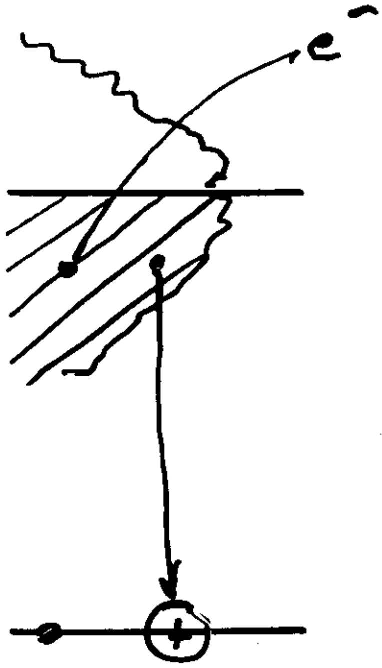
Initial State Rule in XAS

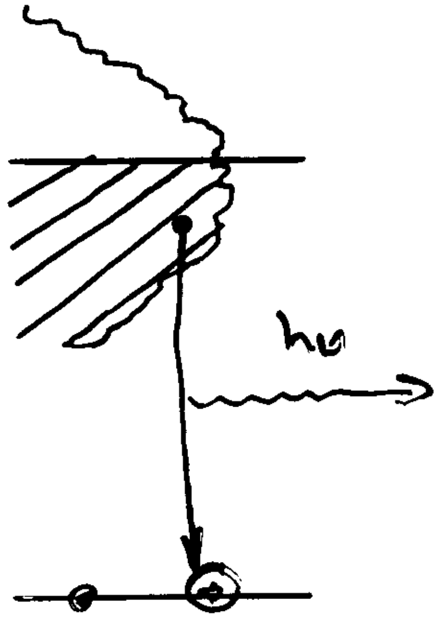


Stohr 3dexp.eng 08/17/94 11:52

Core hole Decay

after ionization





electron emission
Auger spectroscopy (AES)

photon emission
X-ray Emission
Spectroscopy (XES)

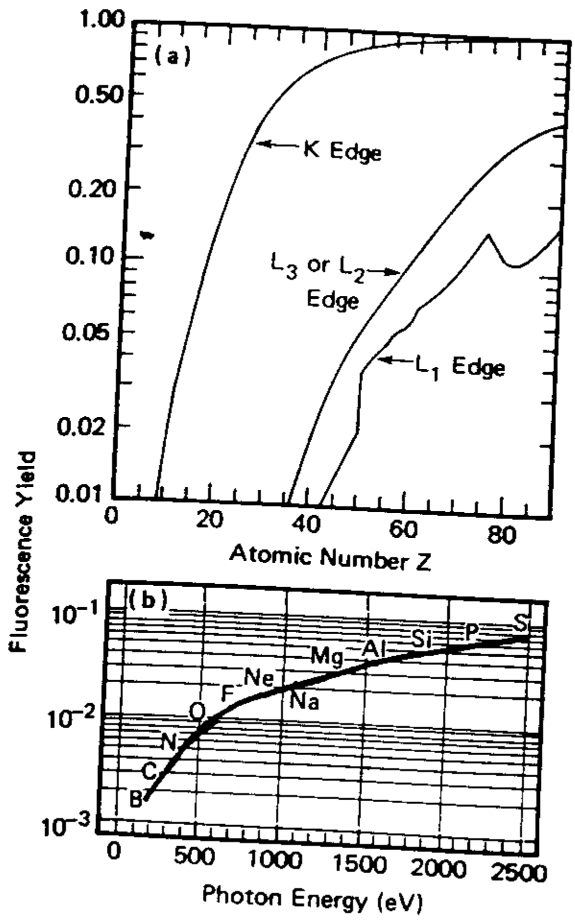
Life time of core hole $\Gamma = \Gamma_{Aug} + \Gamma_{x\text{-}ray}$

$\frac{1}{\Gamma_{Aug}} \propto R_{Aug} \propto \sum_f \langle \psi_i | \frac{1}{r} | \psi_f \rangle$ Coulomb op

$\frac{1}{\Gamma_{x\text{-}ray}} \propto R_{x\text{-}ray} \propto \sum_f \langle \psi_i | r | \psi_f \rangle$ Dipole

Auger fast when the involved electrons are close in space ($\frac{1}{r}$).

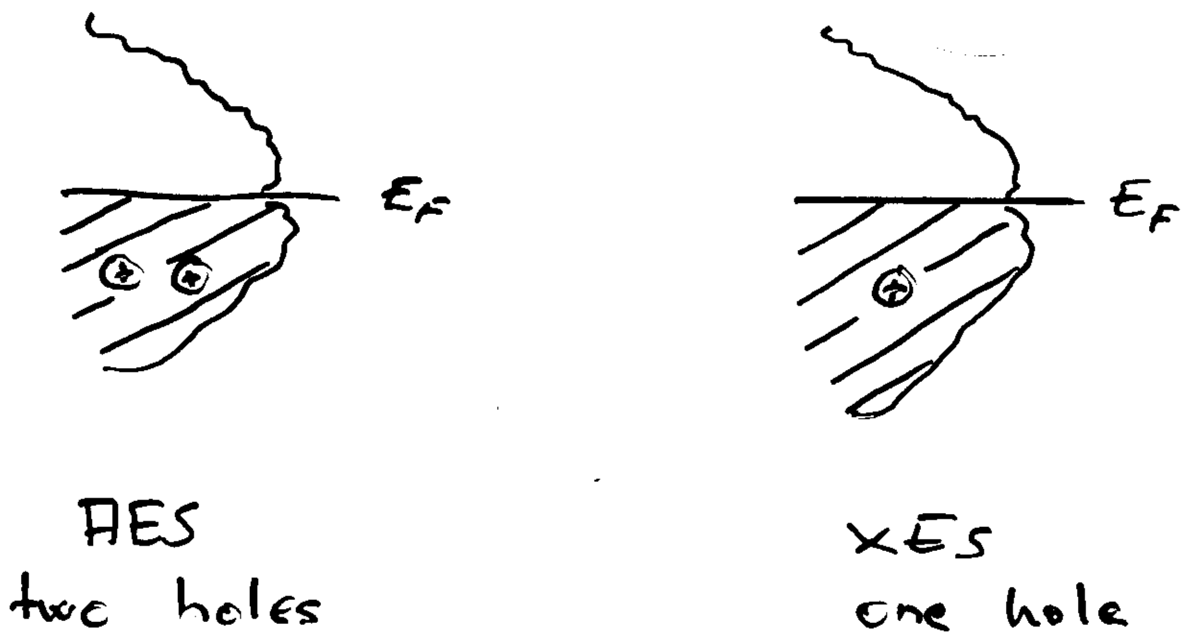
Coster-Kronig : Auger in the same shell very fast.

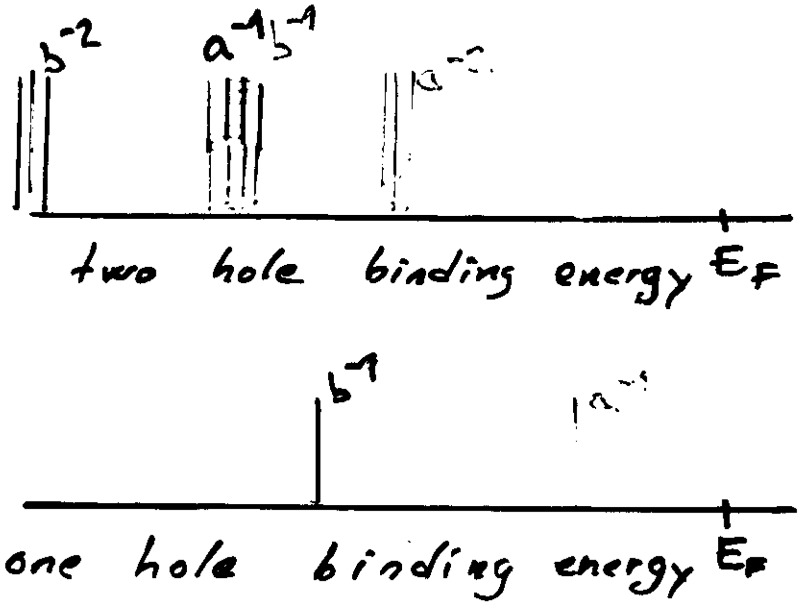


Fluorescence yield

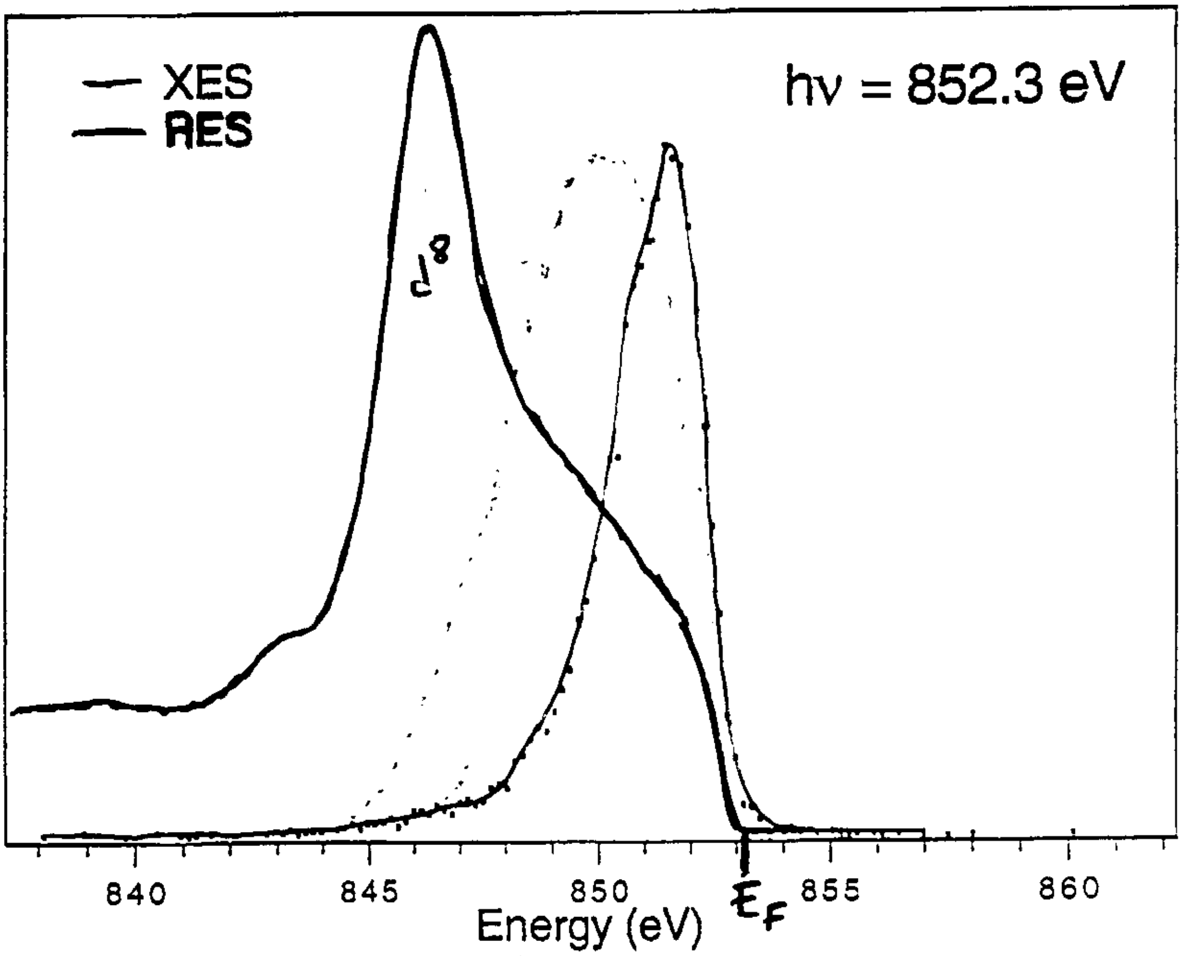
$$= \frac{R_{x\text{-}ray}}{R_{Auger} + R_{x\text{-}ray}}$$

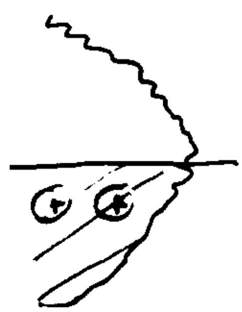
Different Final states



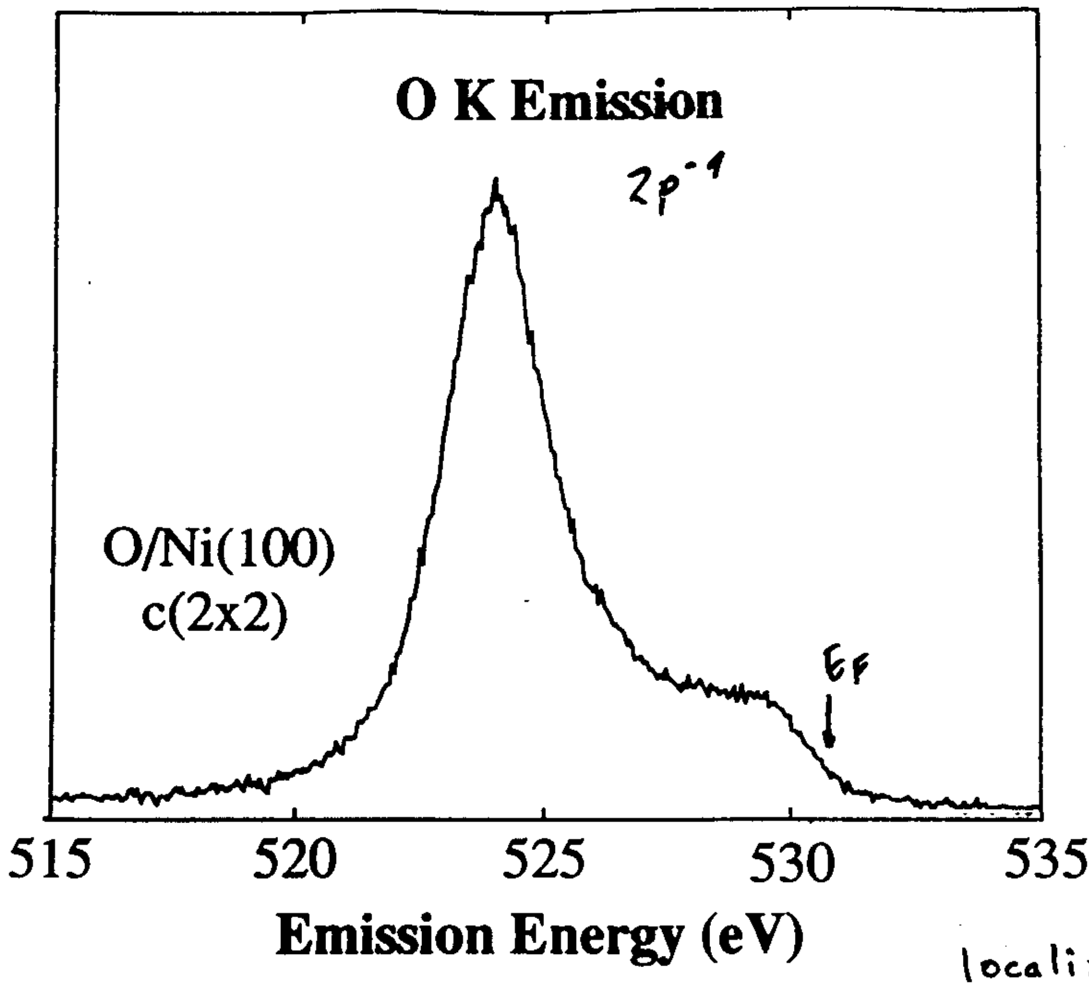


Comparing AES and XES final states

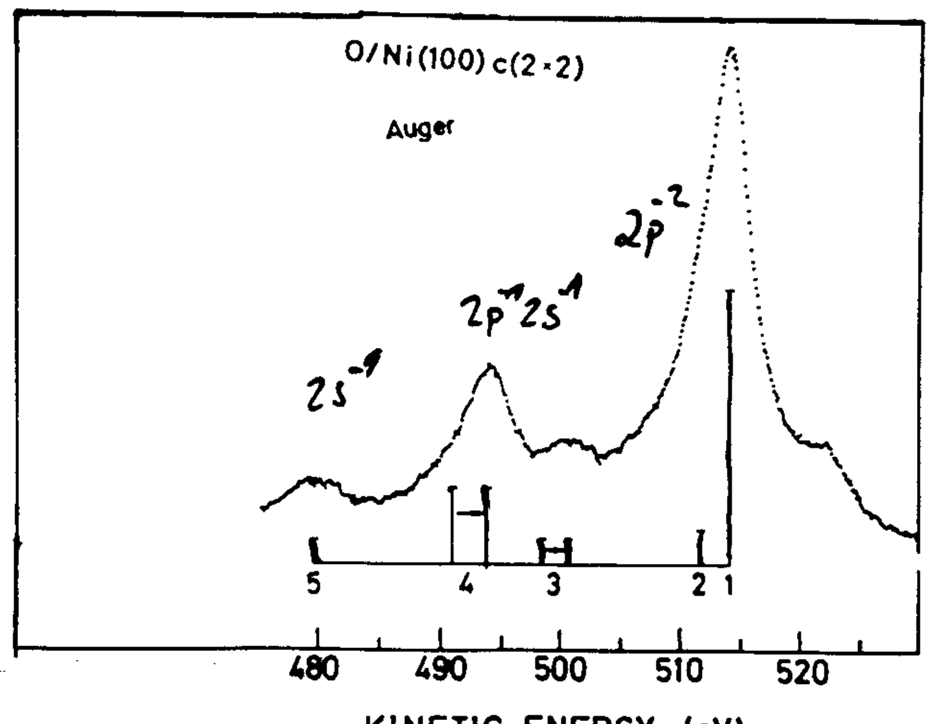




way of study correlation

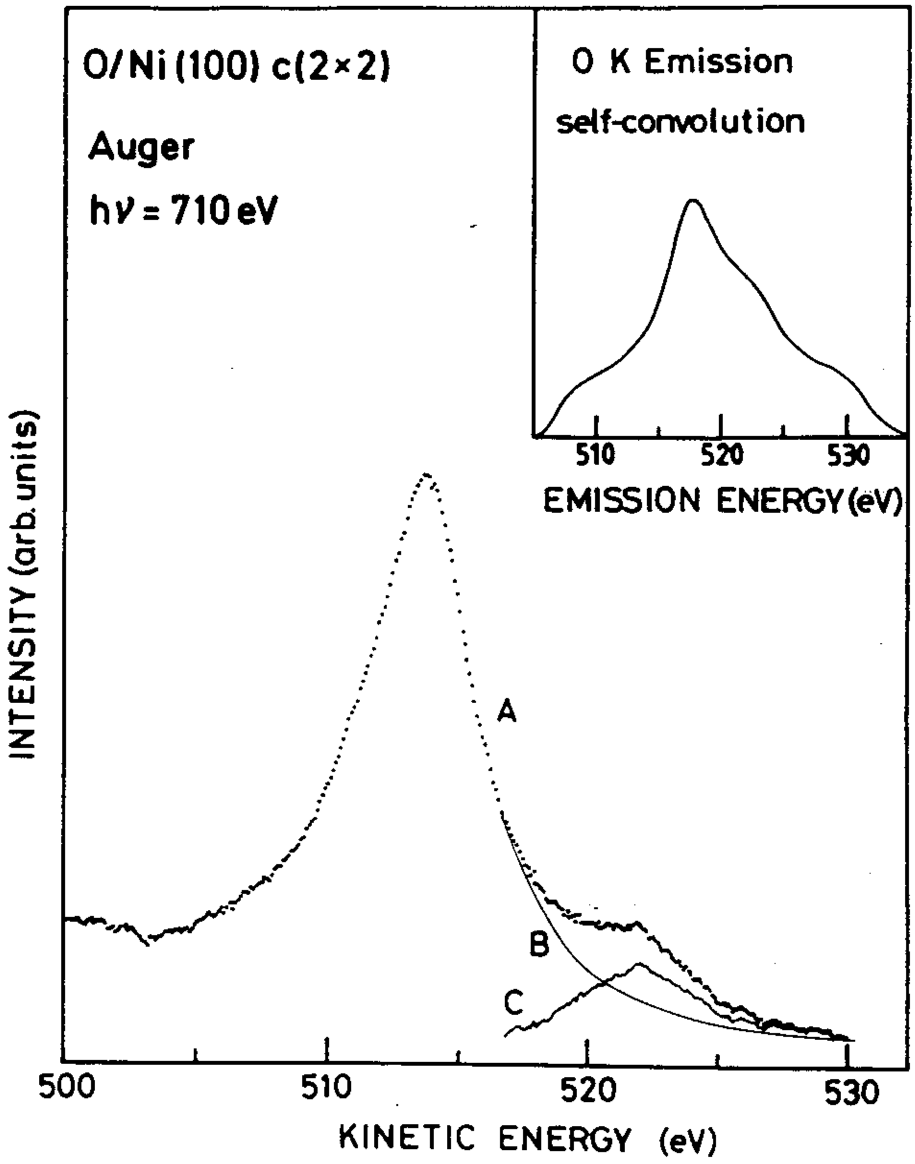


localized $2p^{-2}$
strong hole hole
interaction



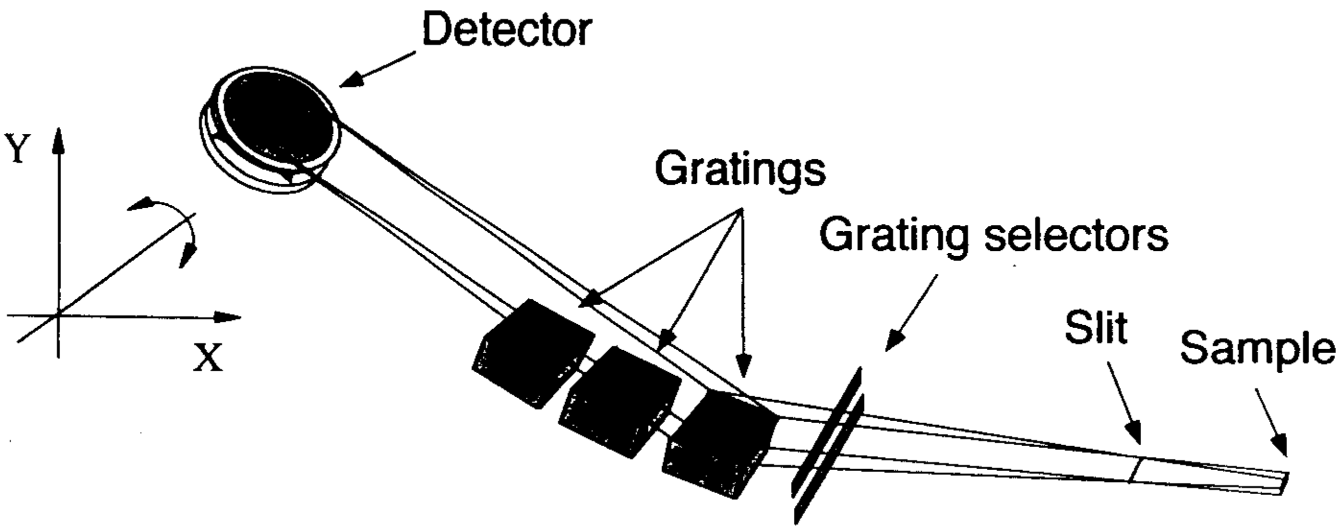
Multiplets
in Ne^{-2}
$2p^4$

A. Sandell Phys. Rev. B48, 4347 (1993)

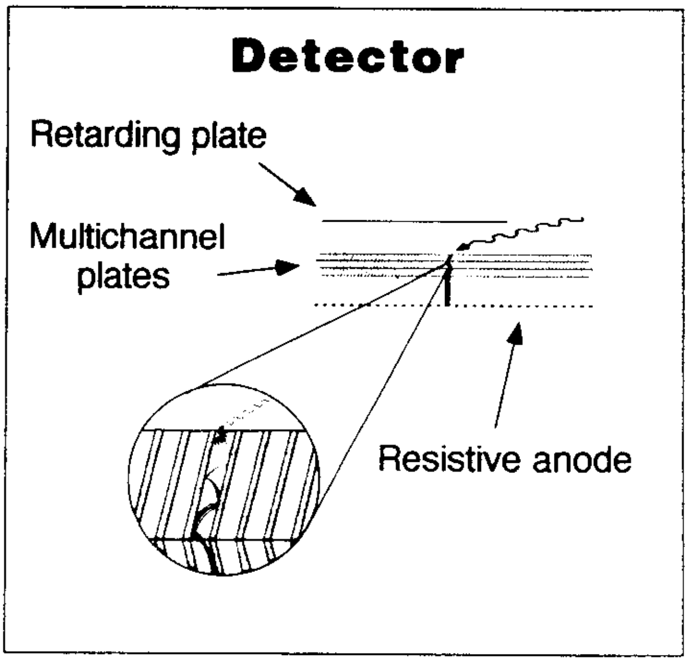


Sandell et. al. Phys. Rev. B48, 11347 (1993)

Soft X-ray Emission Spectrometer
XES 300



Grating	Radius	Grooves	Angle	Range
#1:	5 m	1200 l/mm	1.9°	≈ 300 - 1000 eV
#2:	5 m	400 l/mm	2.6°	≈ 100 - 450 eV
#3:	3 m	300 l/mm	5.4°	≈ 50 - 200 eV



GAMMADATA

- [illegible]ounted
- [illegible]
- [illegible]
- Wide energy range
- Multichannel detection

Applications:

- Synchrotron radiation
- In-situ characterisation
- Materials Science
- Surface Science
- Gas-phase studies

The *XES 300* spectrometer is a state-of-the-art soft x-ray emission spectrometer covering a large energy range, 50 ->1000 eV at high resolution and sensitivity.*

The design makes a very compact instrument that is flange-mounted and thereby easily adapted to various vacuum chambers, even to rotatable chambers for angular resolved studies. The instrument uses multiple spherical gratings with different groove densities and radii, which facilitates customized performance optimization.

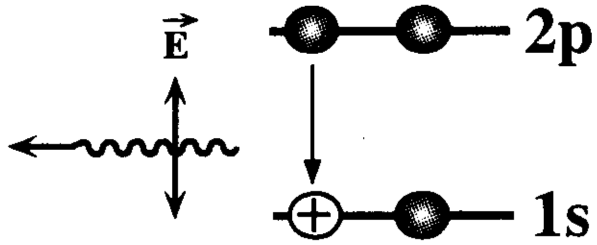
The spectrometer [illegible] UHV systems, [illegible] with relatively [illegible] tems, like [illegible] Applications [illegible] characterization [illegible] Charging problems [illegible] electron [illegible] samples [illegible] cause [illegible]

Soft x-ray emission [illegible] detailed information [illegible]

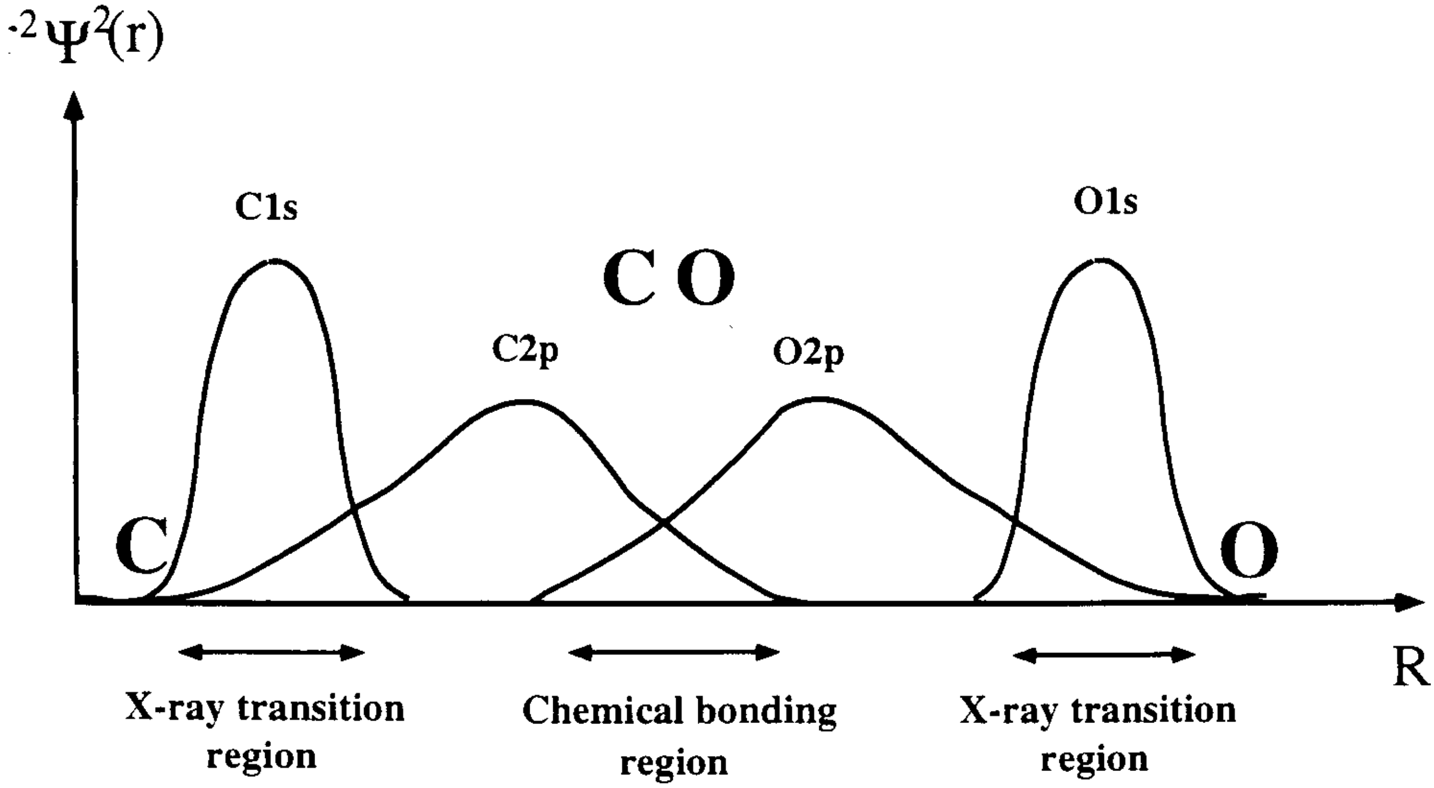
P.O. Box 15120 • S-750 15 UPPSALA, SWEDEN [illegible]
e-mail: [illegible]

X-ray Emission Spectroscopy (XES)

Dipole selection rule

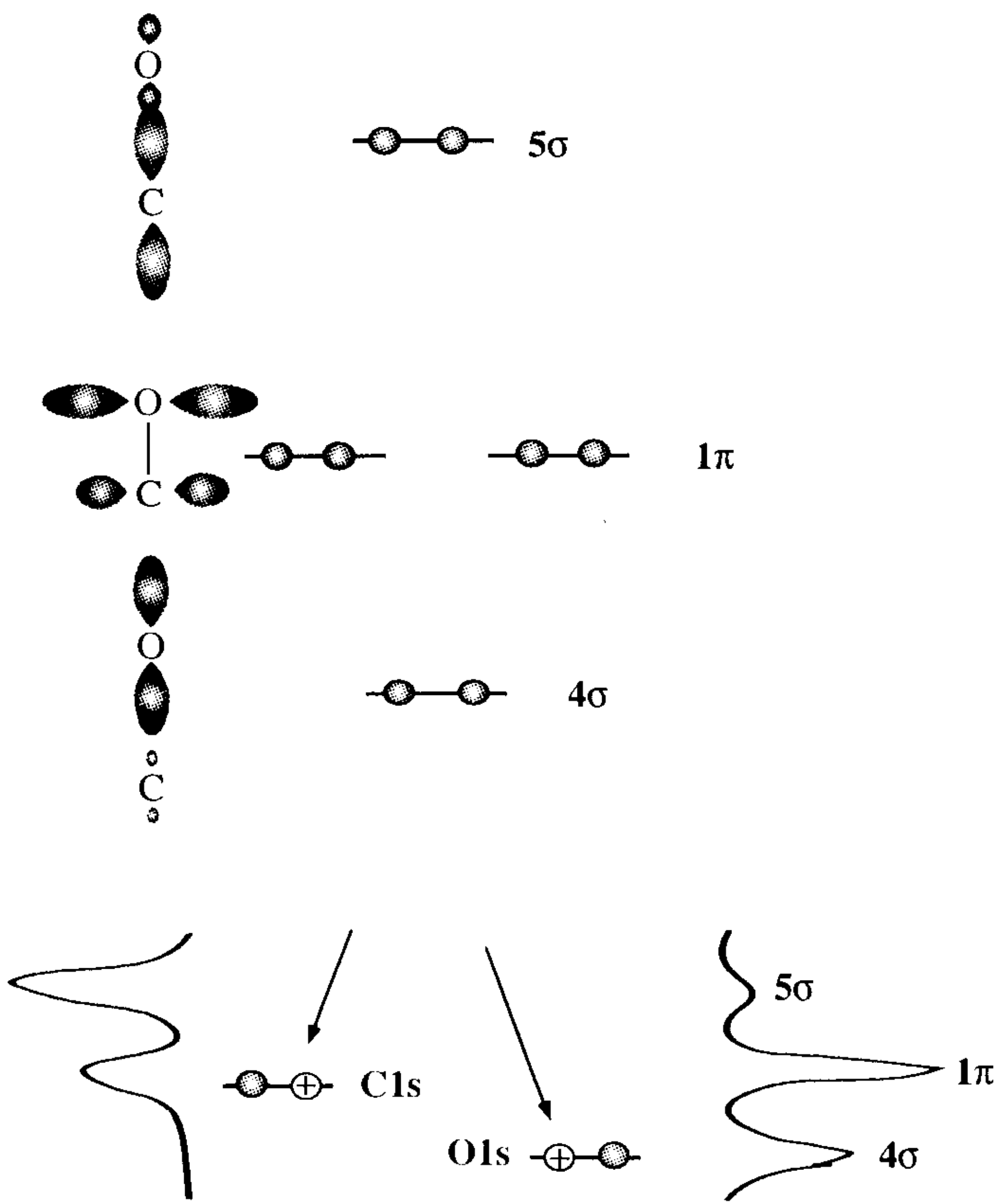


One center approximation

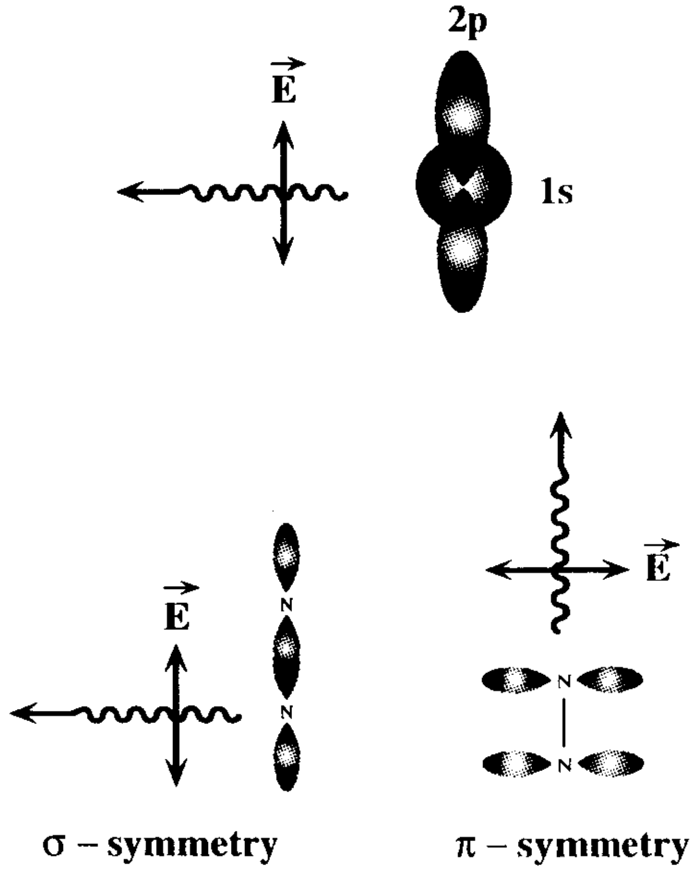


X-ray Emission Spectroscopy (XES)

Atom specific

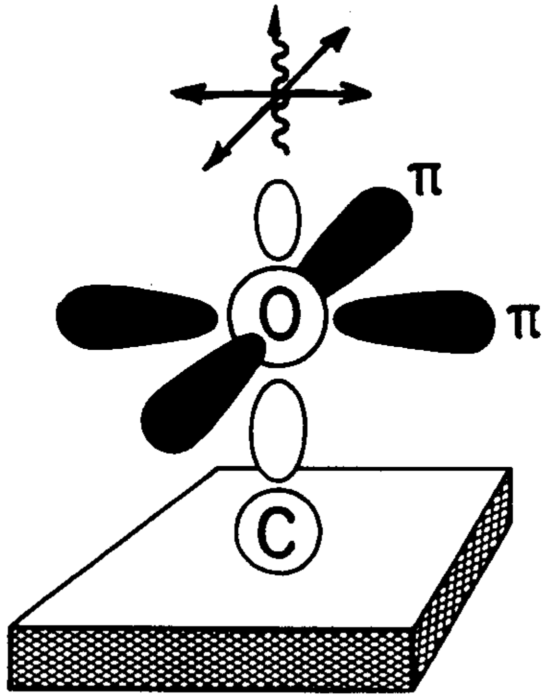


Orbital symmetry selective

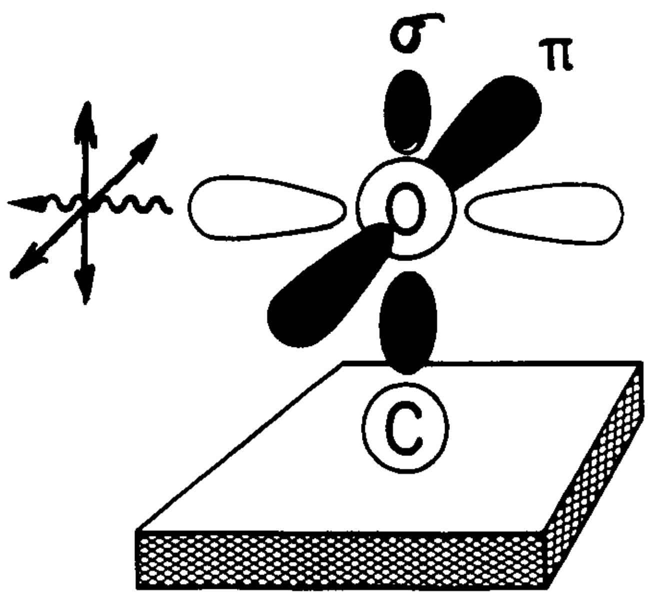


X-ray Emission

Normal Emission



Grazing Emission

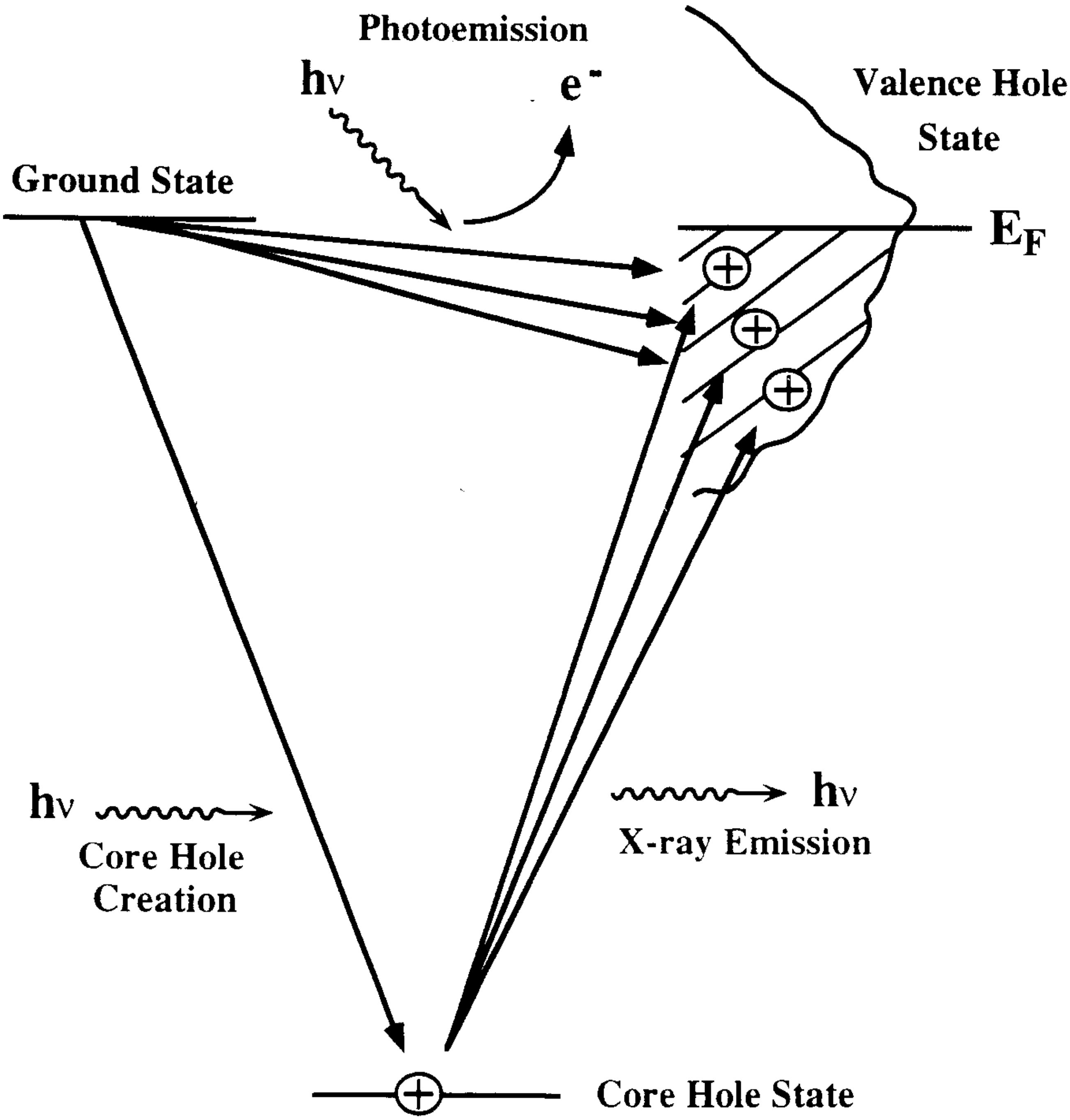


Valence band Photoemission

↕

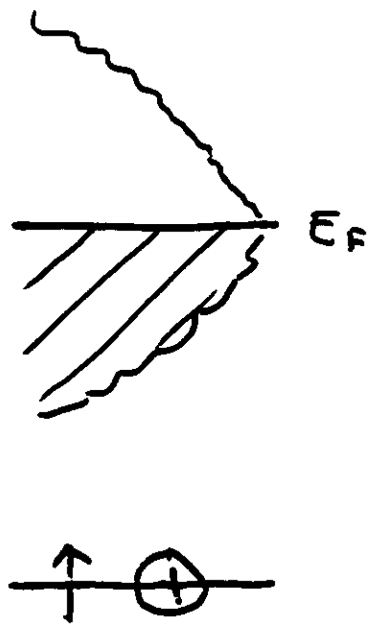
X-ray Emission

the same final state

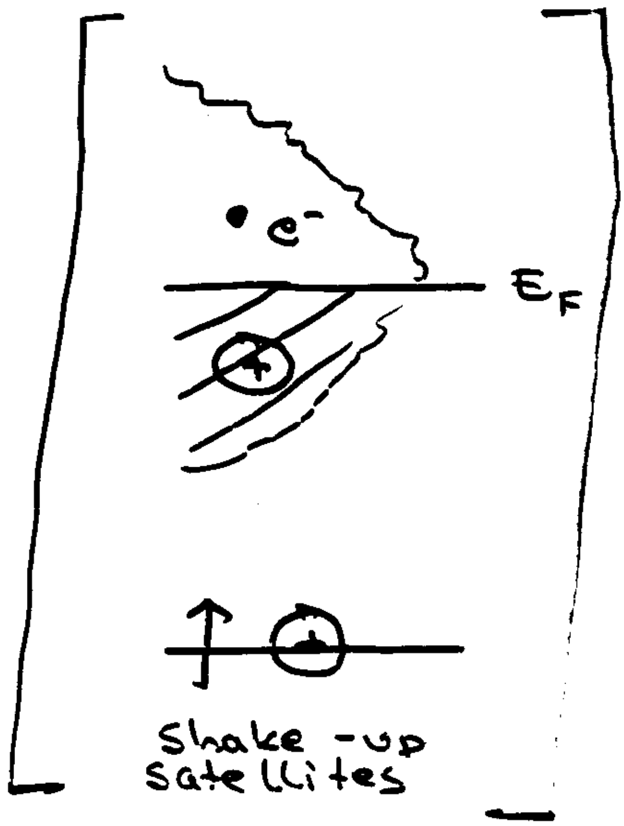


X-ray Emission Spectroscopy

Clean Initial core hole state



lowest core hole state



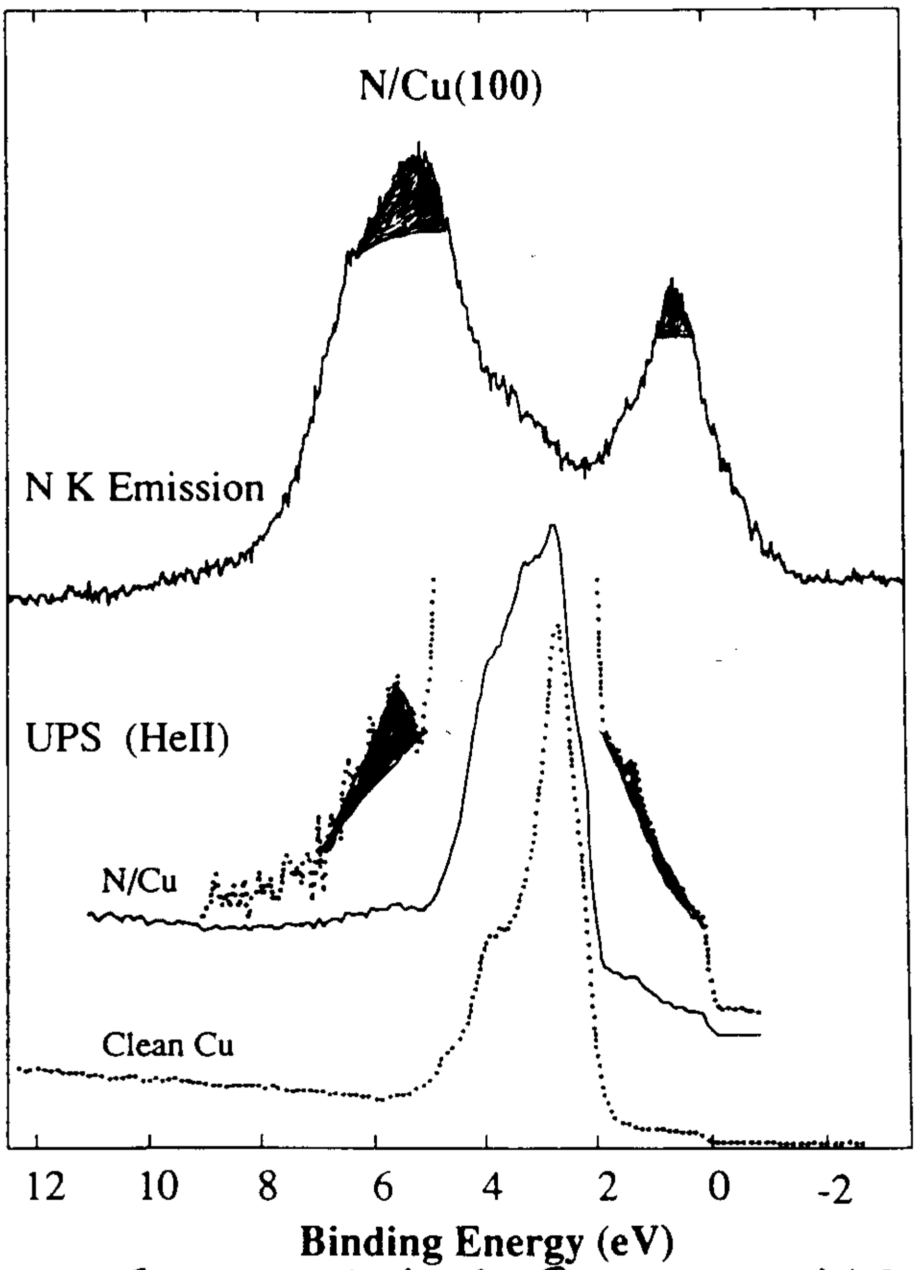
shake-up satellites

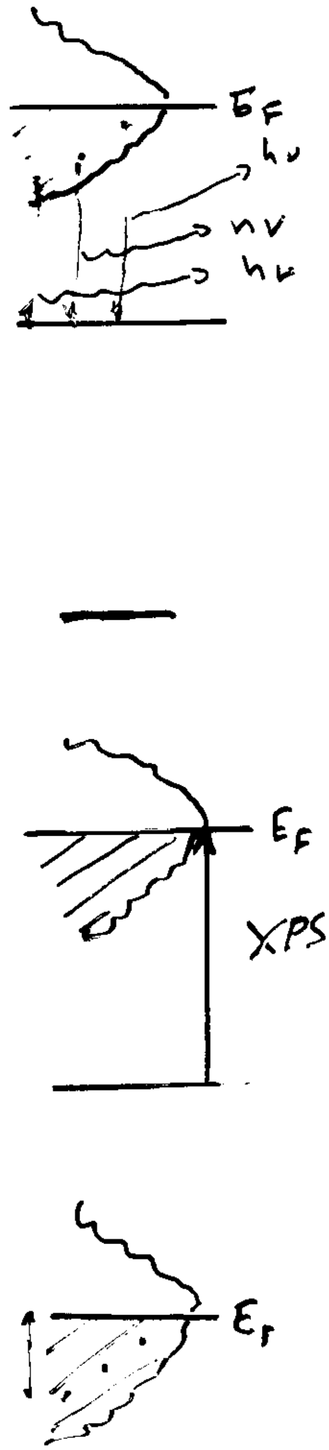
Threshold excitations

core excited state
(XAS final state)

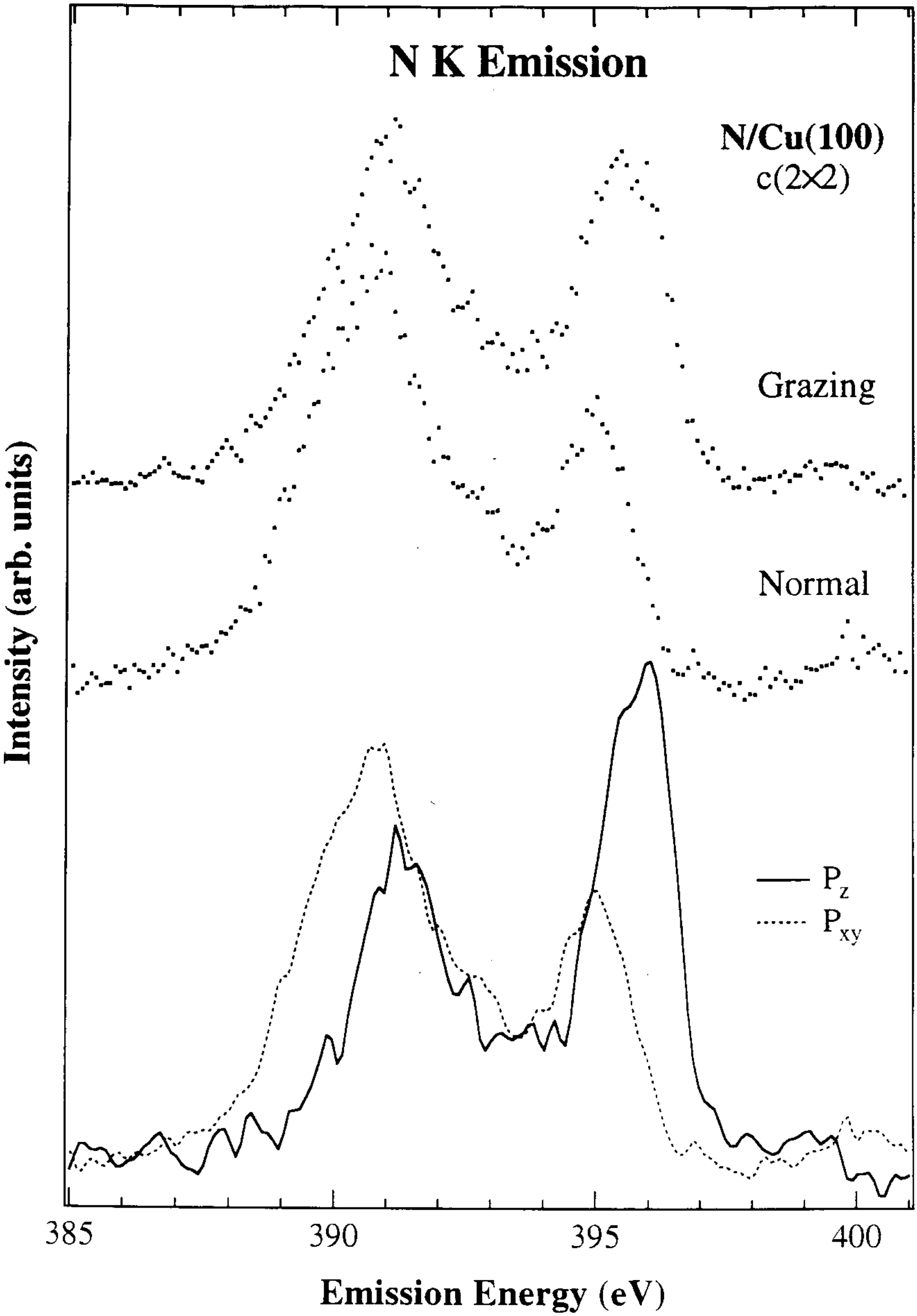
excited electron delocalizes before x-ray decay

XES and PES, the same final state

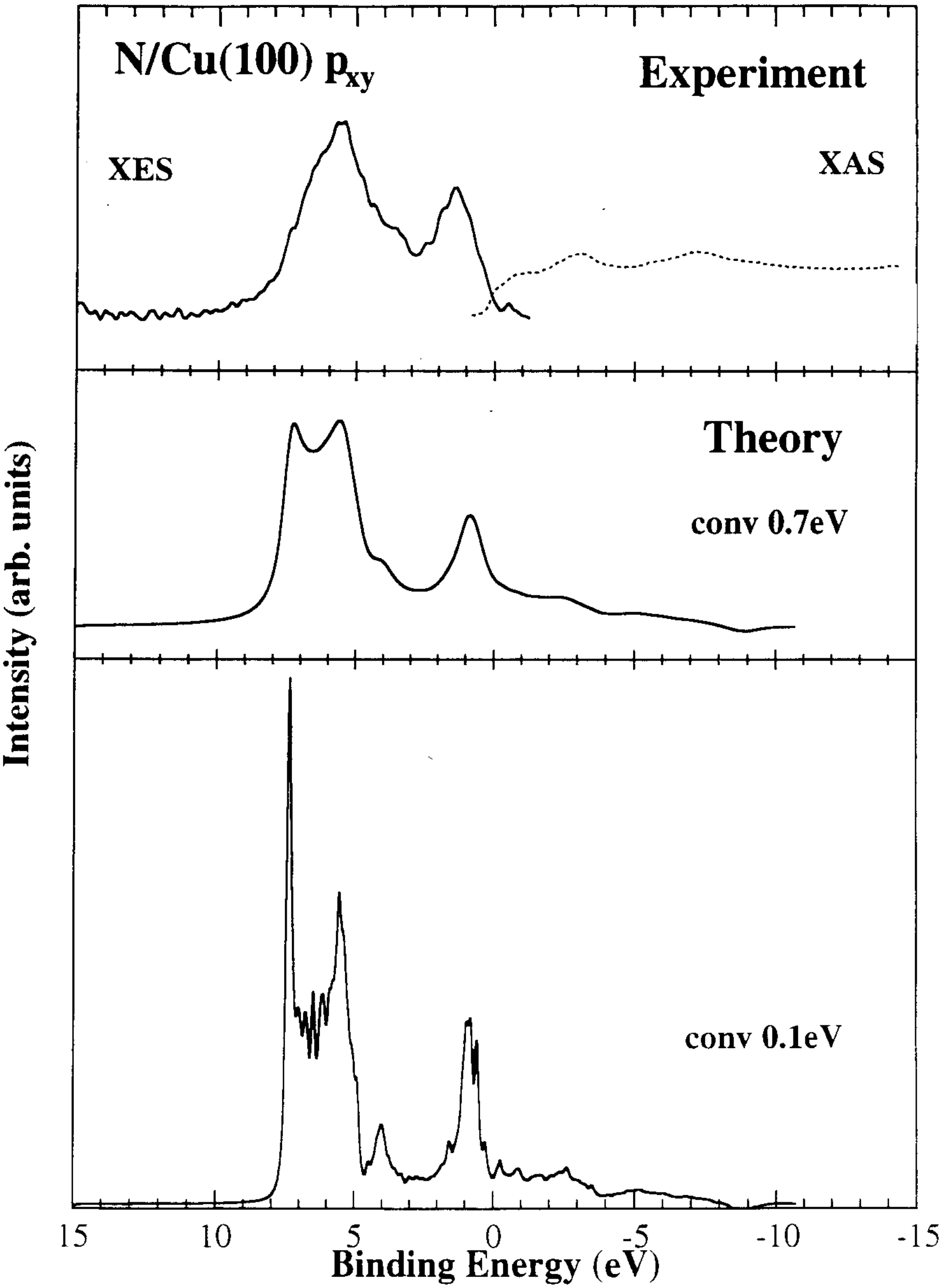




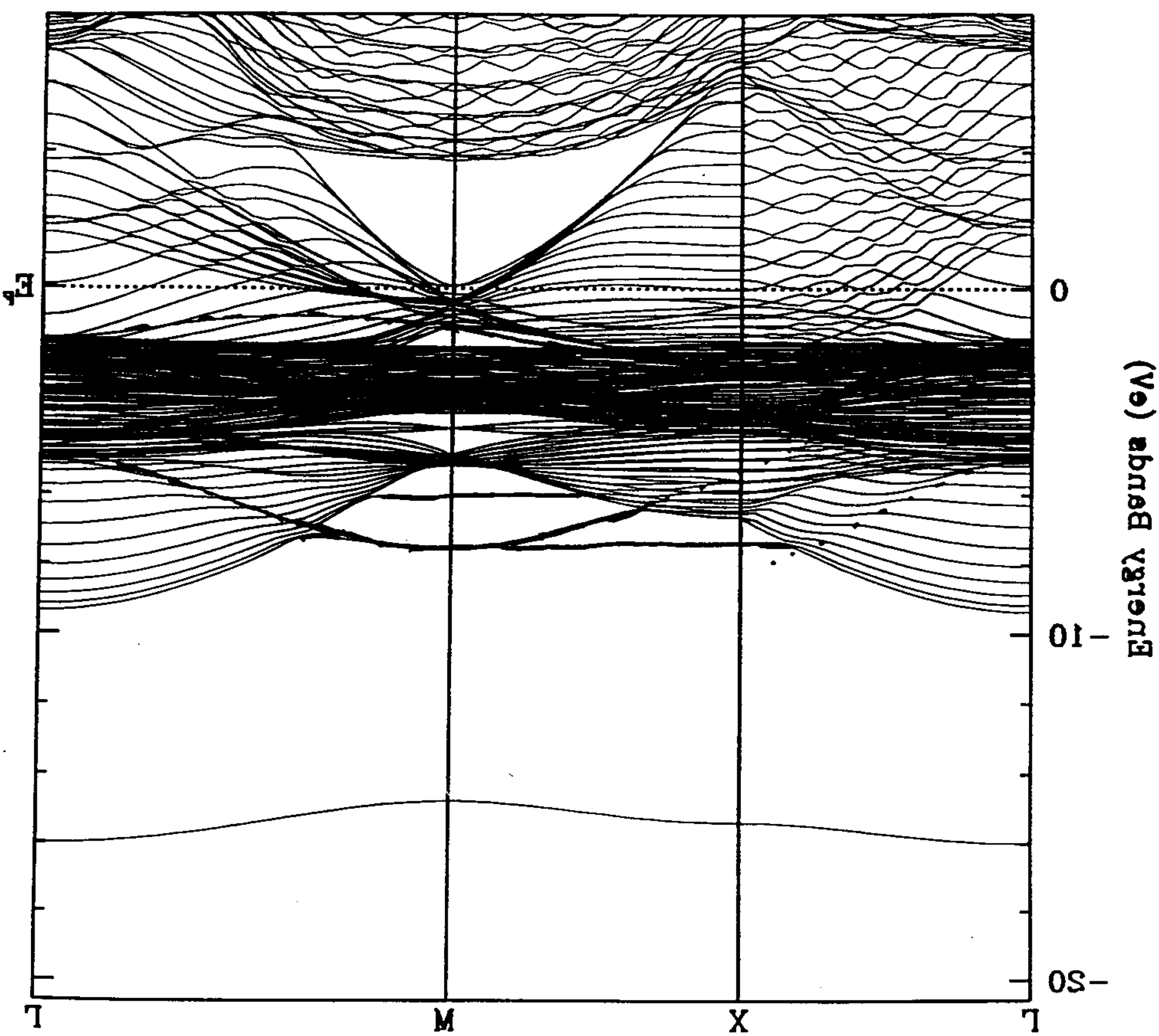
T. Wiell et al. Surf. Sci. 304, L451 (1994)



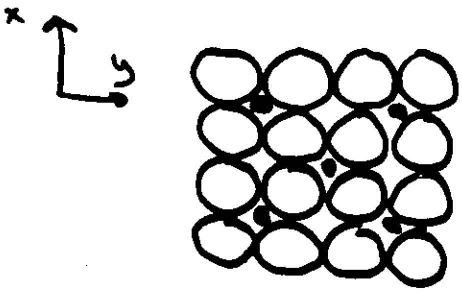
N K Emission
N/Cu(100)
c(2×2)
Grazing
Normal
P_z
P_xy
Intensity (arb. units)
385
390
395
400
Emission Energy (eV)


N/Cu(100) p$_{xy}$
Experiment
XES
XAS
Theory
conv 0.7eV
conv 0.1eV
Intensity (arb. units)
15
10
5
0
-5
-10
-15
Binding Energy (eV)

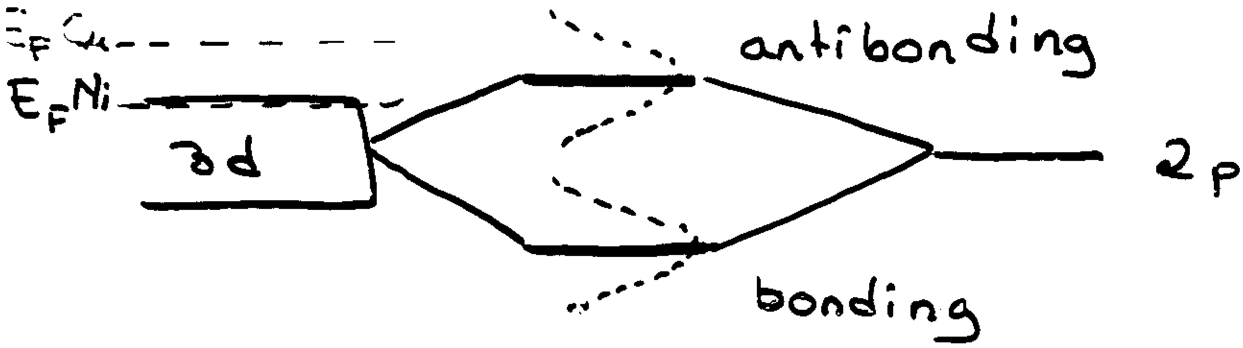
1/2 ML N on Cu (001)-c(2x2)

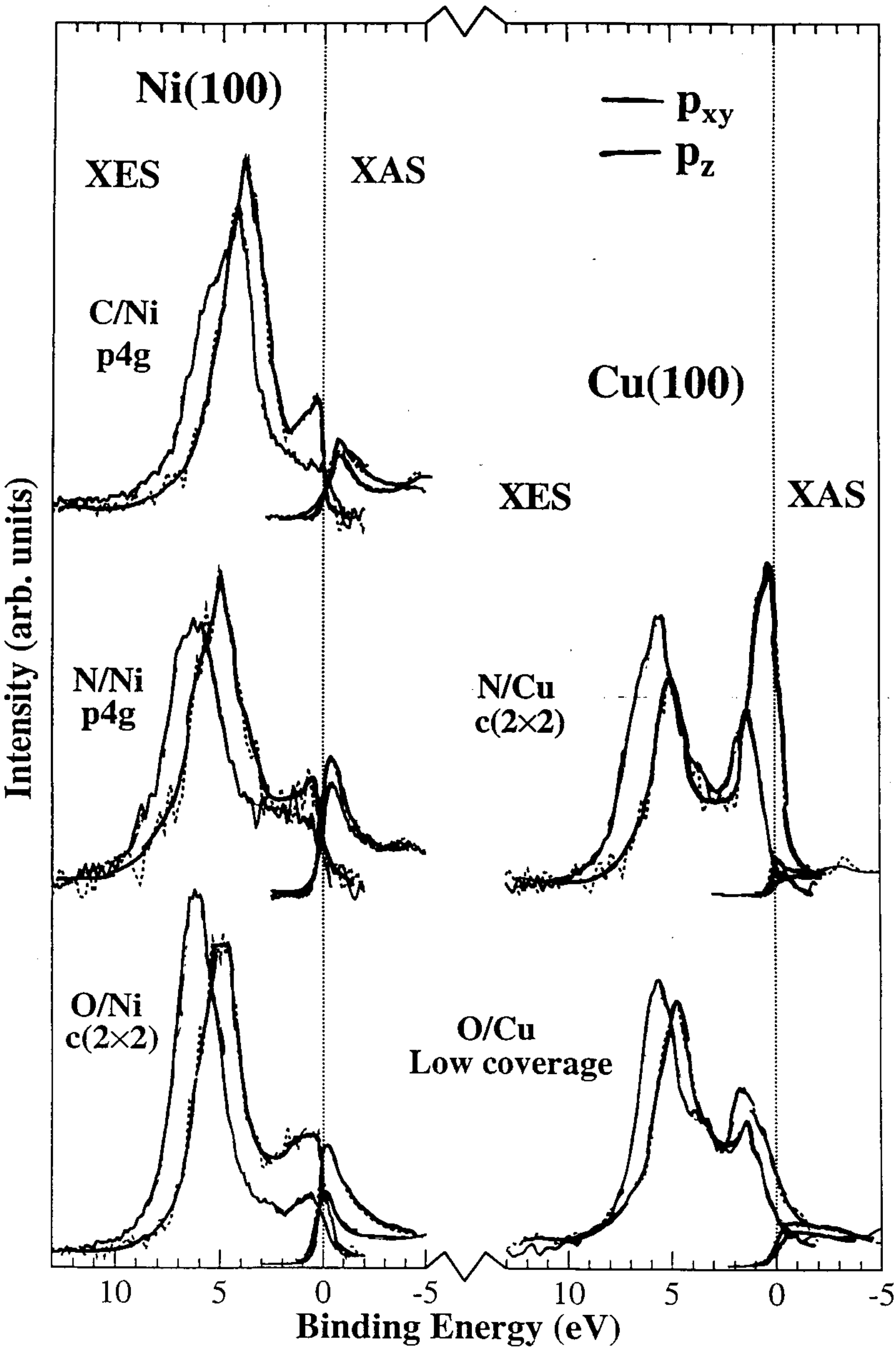


Atomic adsorbates C, N, O



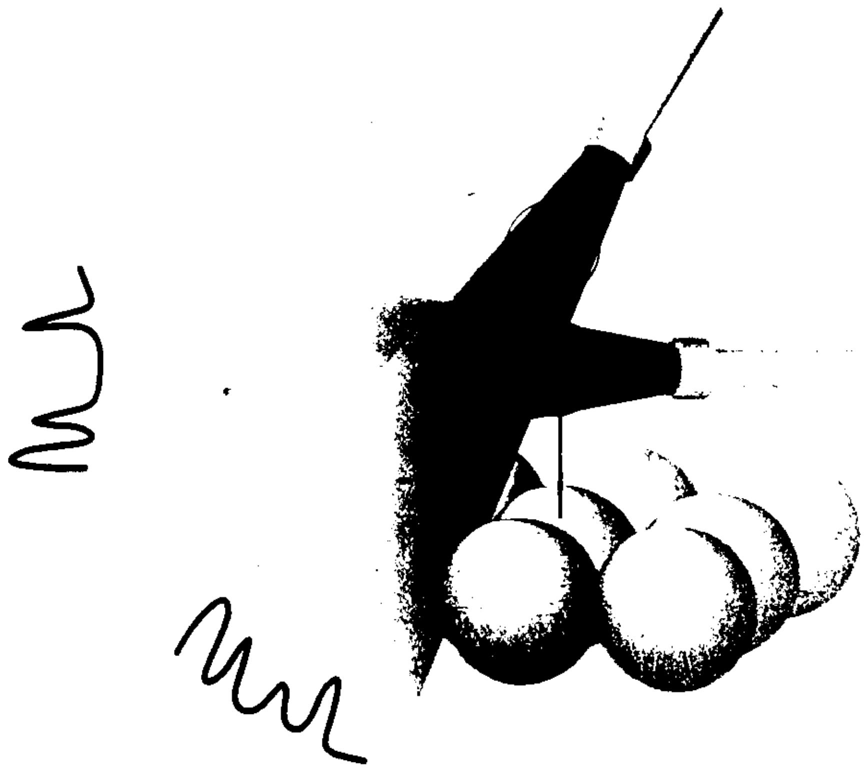
c(2x2) like structure





Ni(100)
XES
XAS
p_xy
p_z
C/Ni
p4g
N/Ni
p4g
O/Ni
c(2×2)
Cu(100)
XES
XAS
N/Cu
c(2×2)
O/Cu
Low coverage
Intensity (arb. units)
10
5
0
-5
10
5
0
-5
Binding Energy (eV)

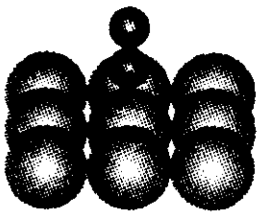
Local Probing of the Chemical Bond



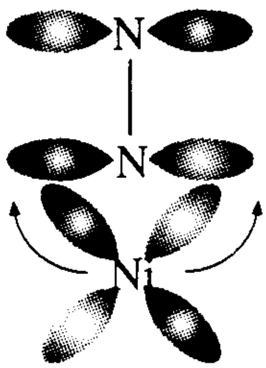
- Atom specific
- Orbital symmetry selective

X-ray Emission Spectroscopy (XES)

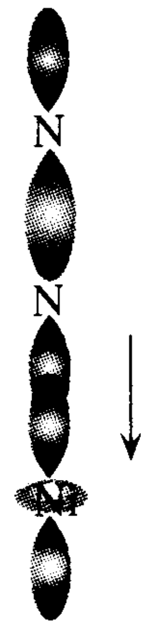
Classical Textbook Picture
the BLYHOLDER MODEL



CO and N_2 on Ni(100)

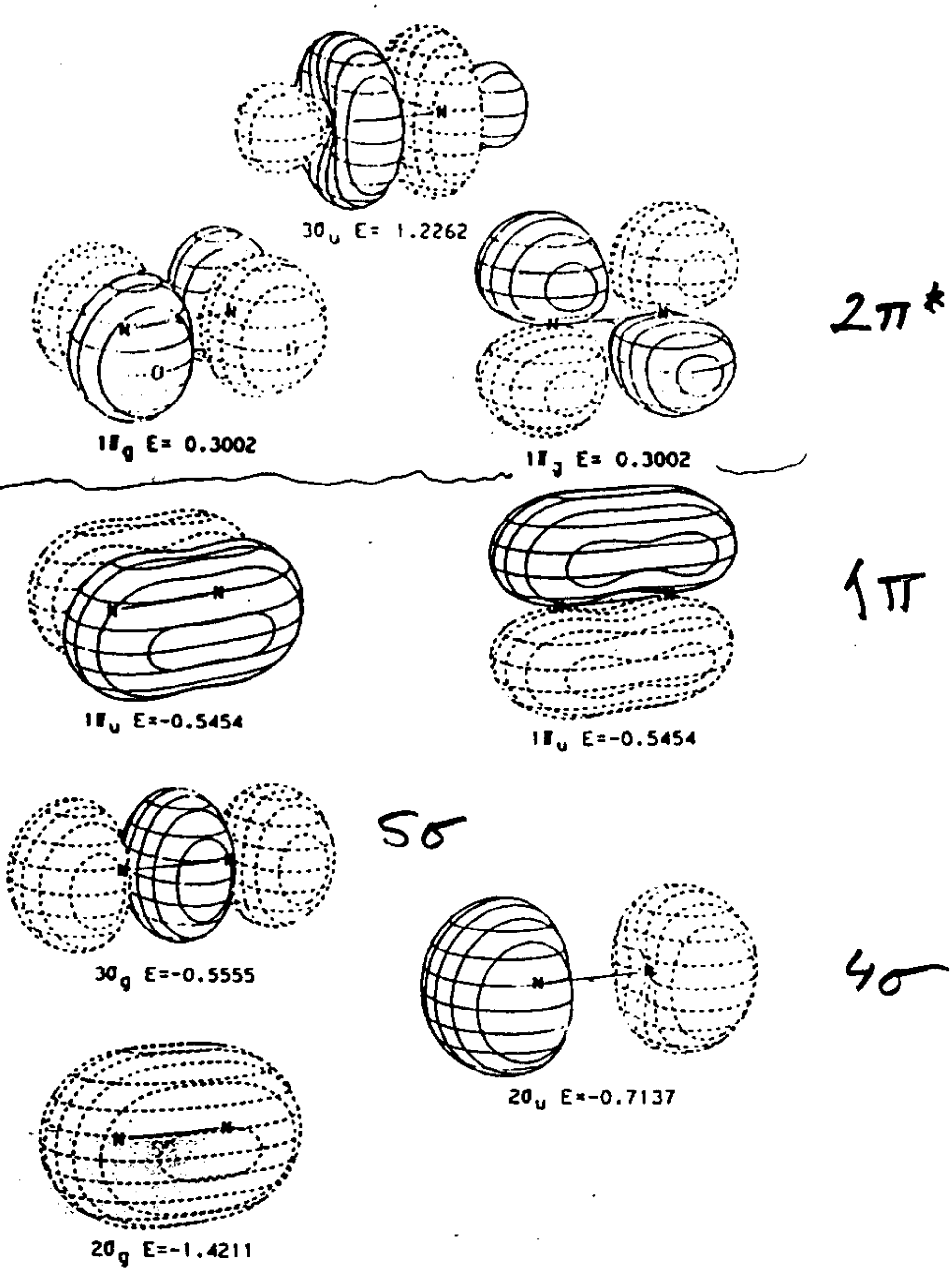


$2\pi^*$ backbonding



5σ donation

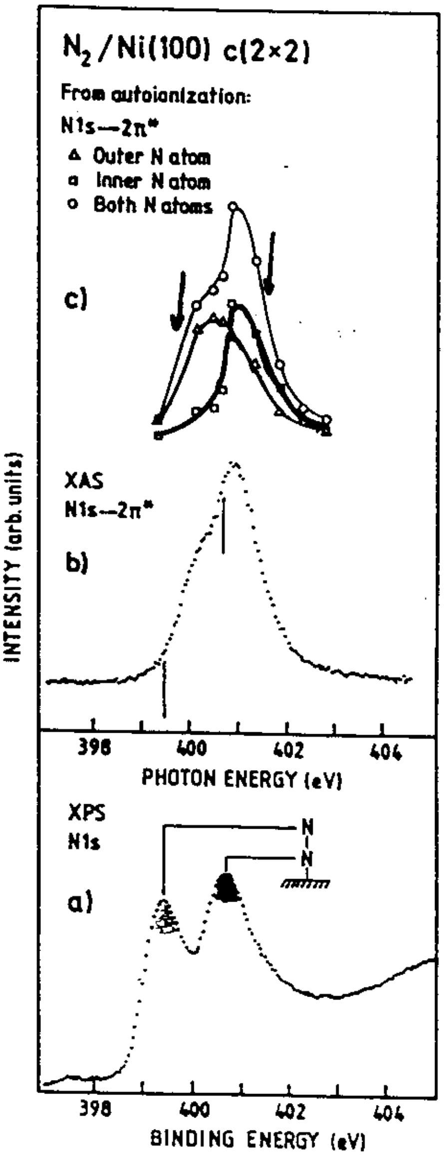
16. Nitrogen Symmetry: $D_{\infty h}$



backbonding
π* - 3d states

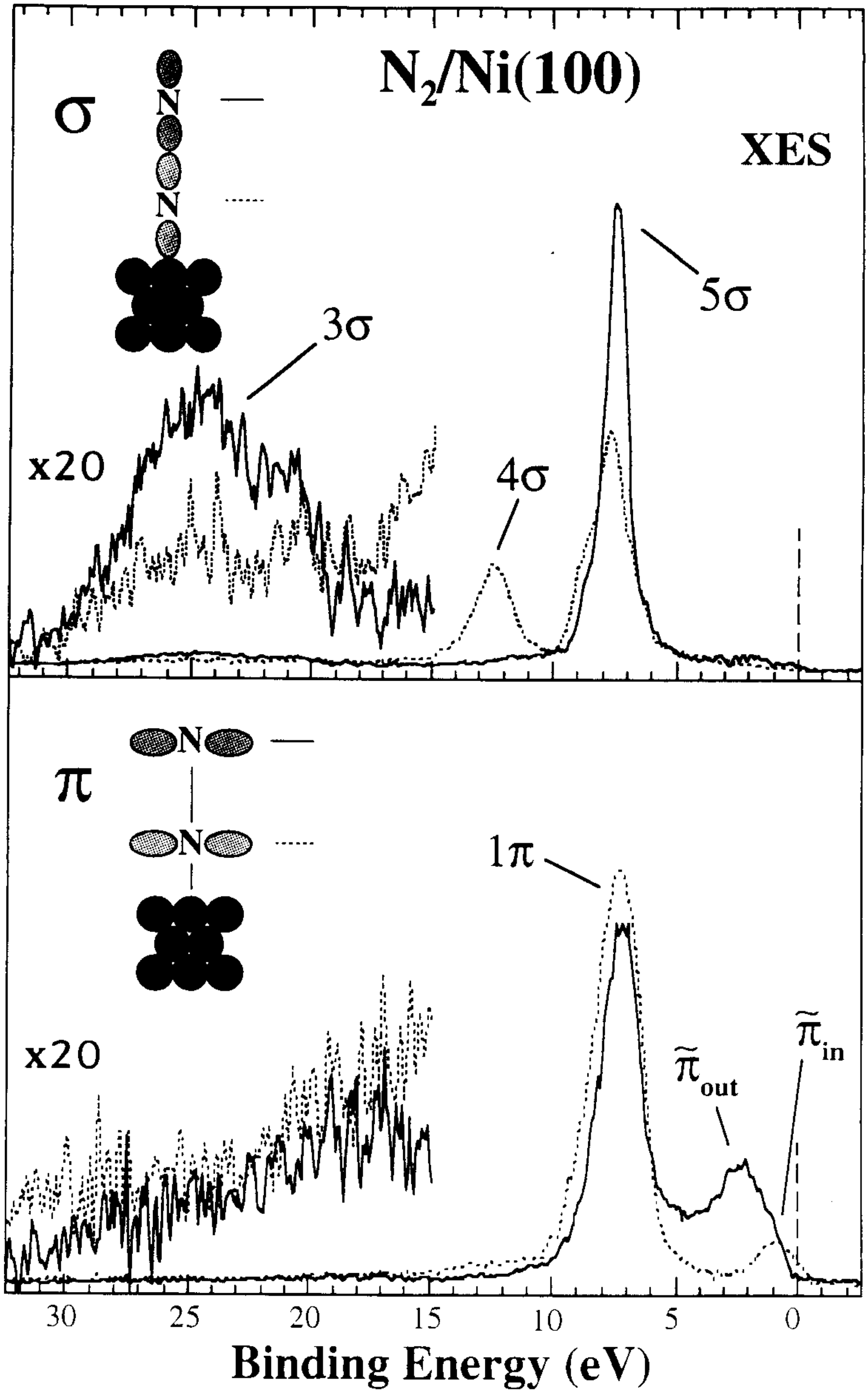
N_2 / Ni (100)

A. Sandell Phys. Rev. Lett. [illegible]

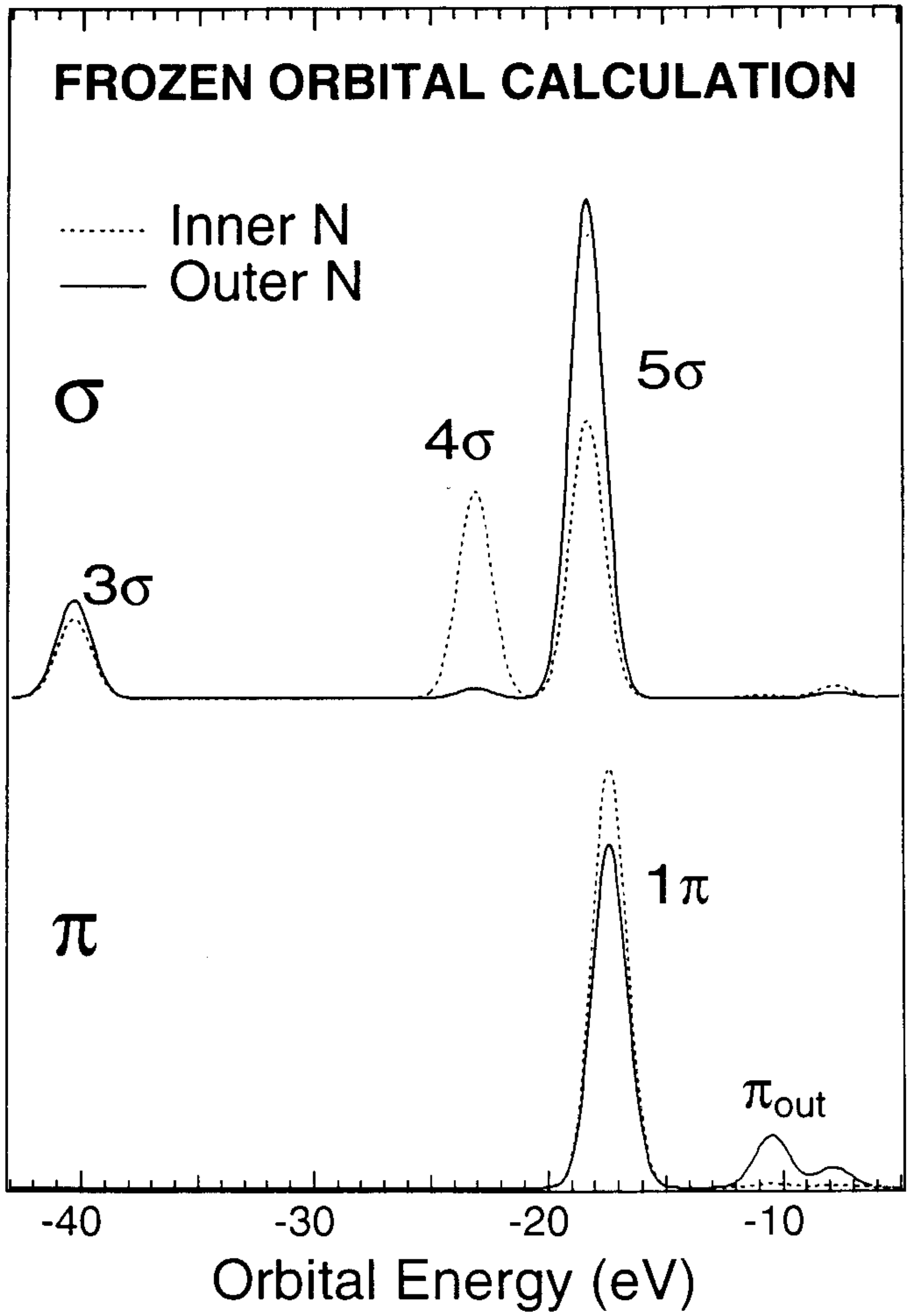


2π total +e⁻

N : N 2 : 1.5



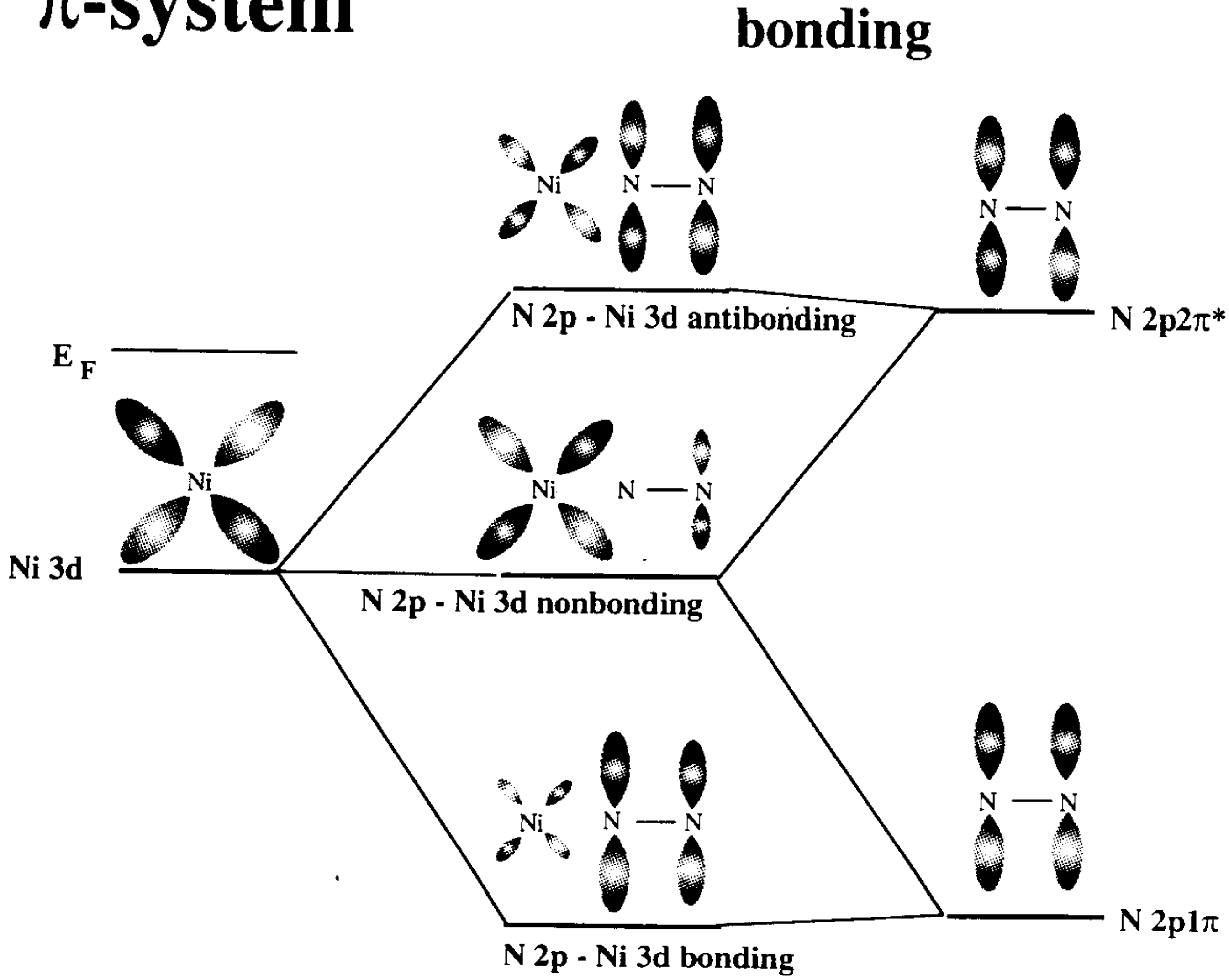
A. Nilsson et al. PRL 78, 2847 (1997)



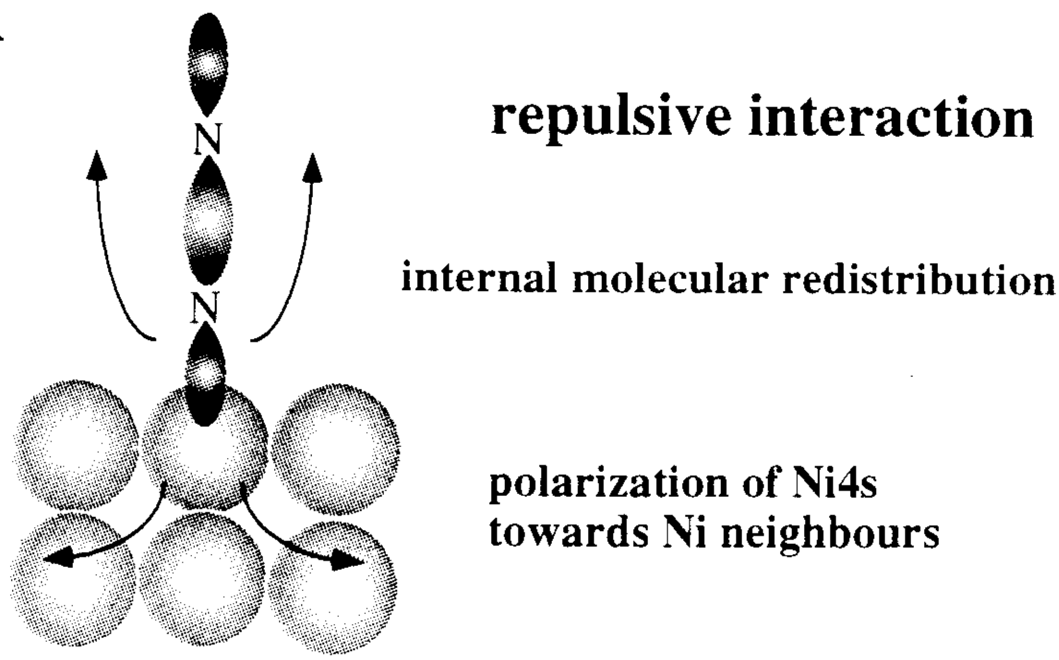
$N_2 Ni_5$ cluster Hartree - Fock

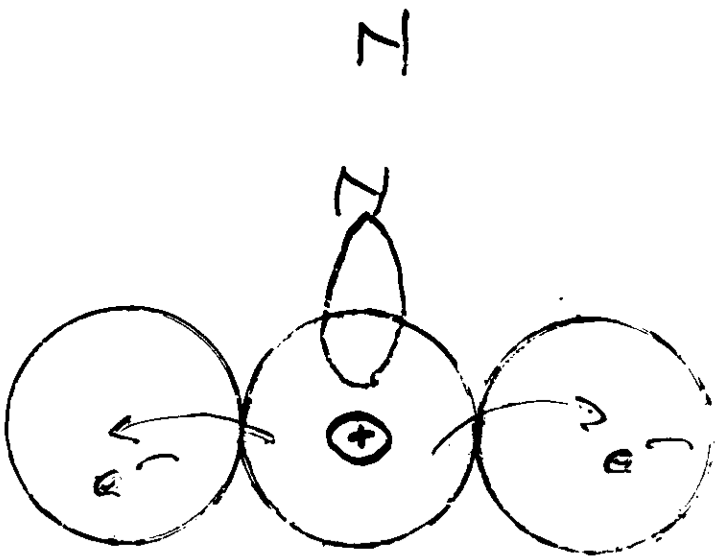
$I = |\langle \psi_i | \vec{r} | \psi_f \rangle|^2$

π-system

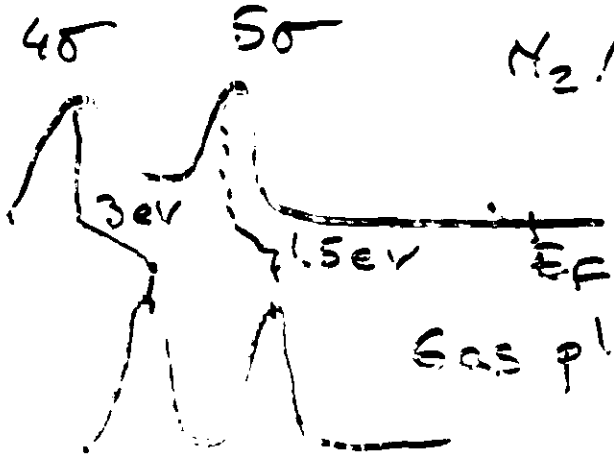


σ-system





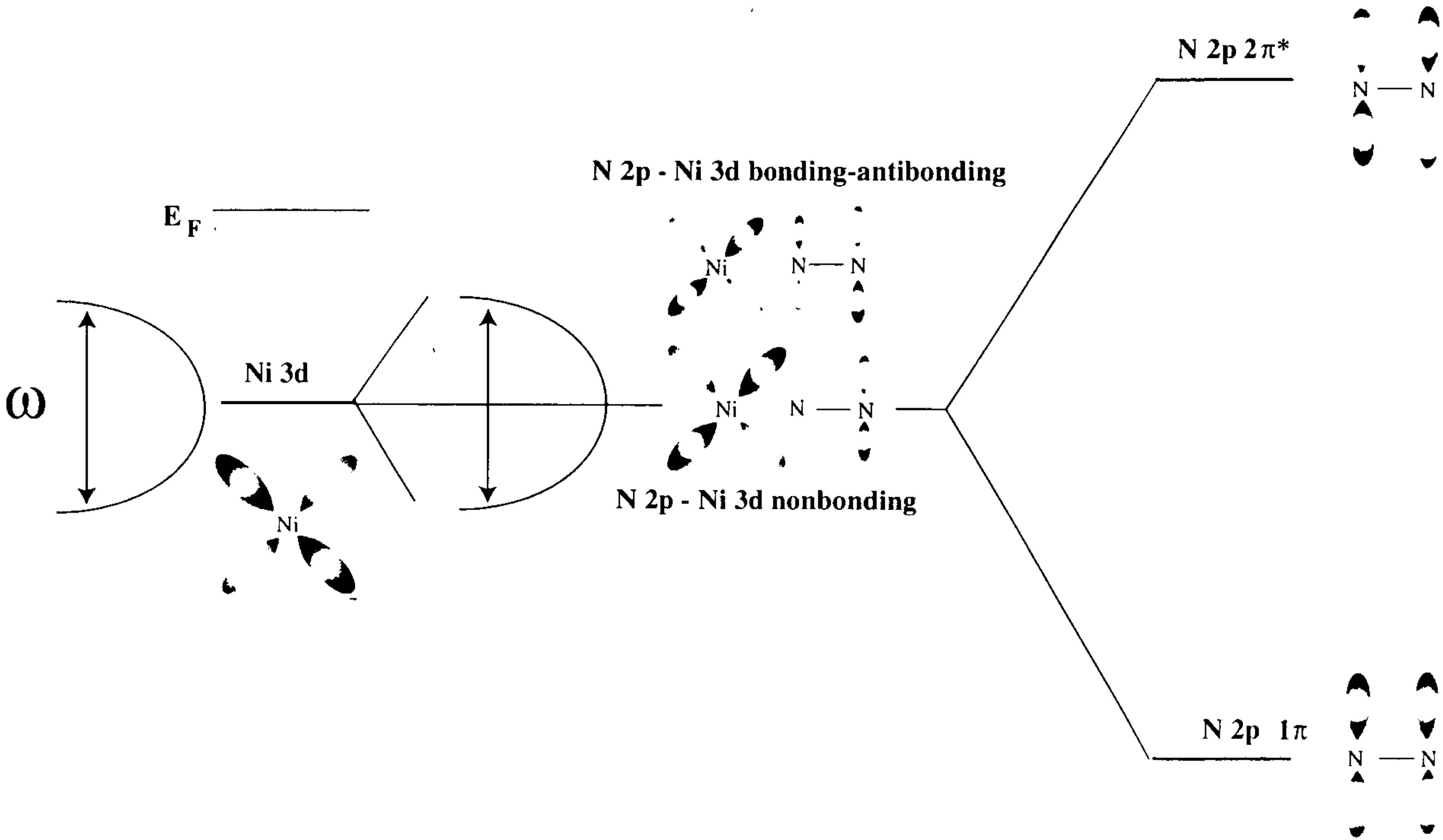
stabilisation of 5σ
attractive interaction with
positive Ni-atom

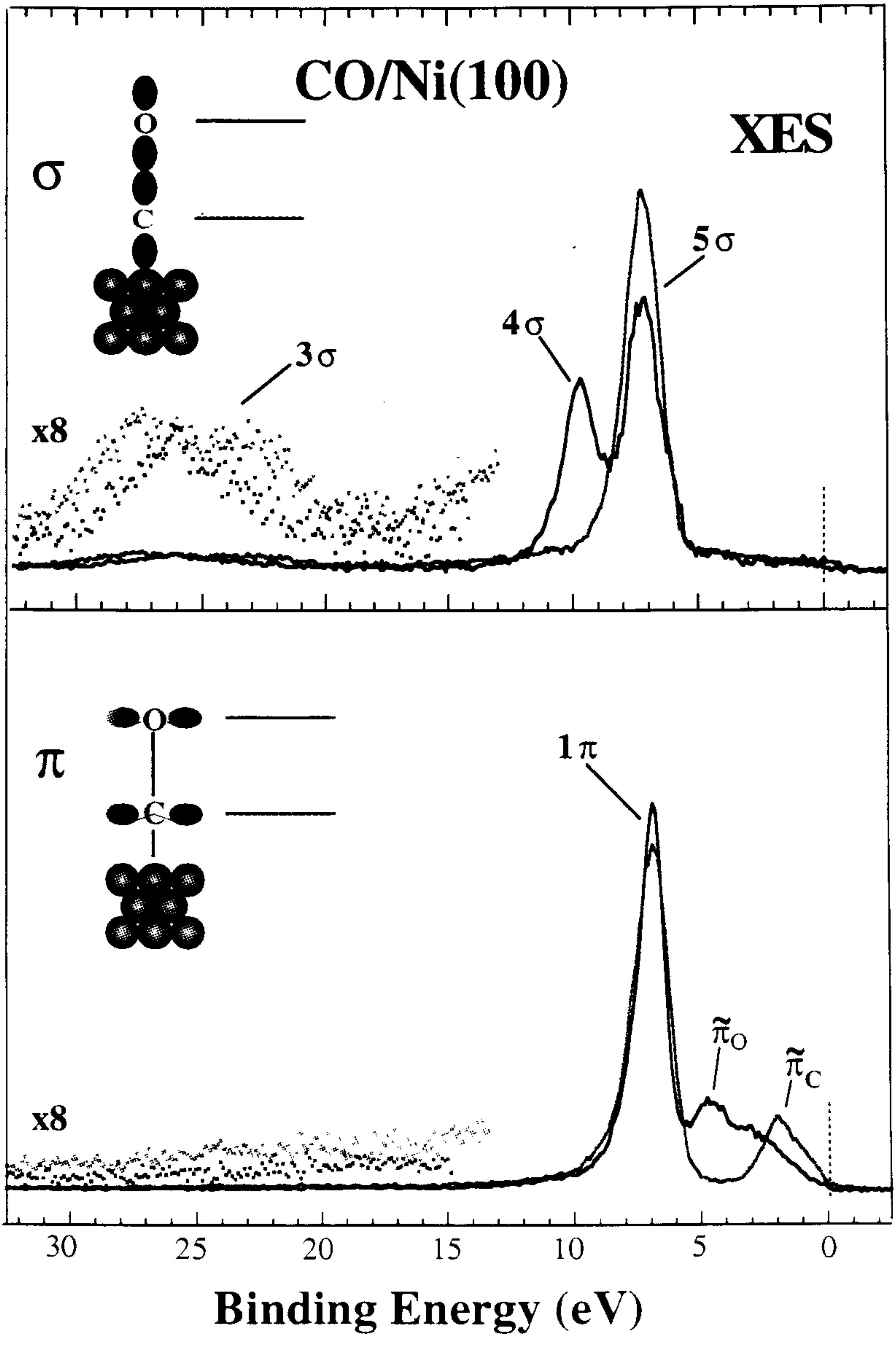


Including polarization of substrat
⇒ Net effect

repulsive interaction

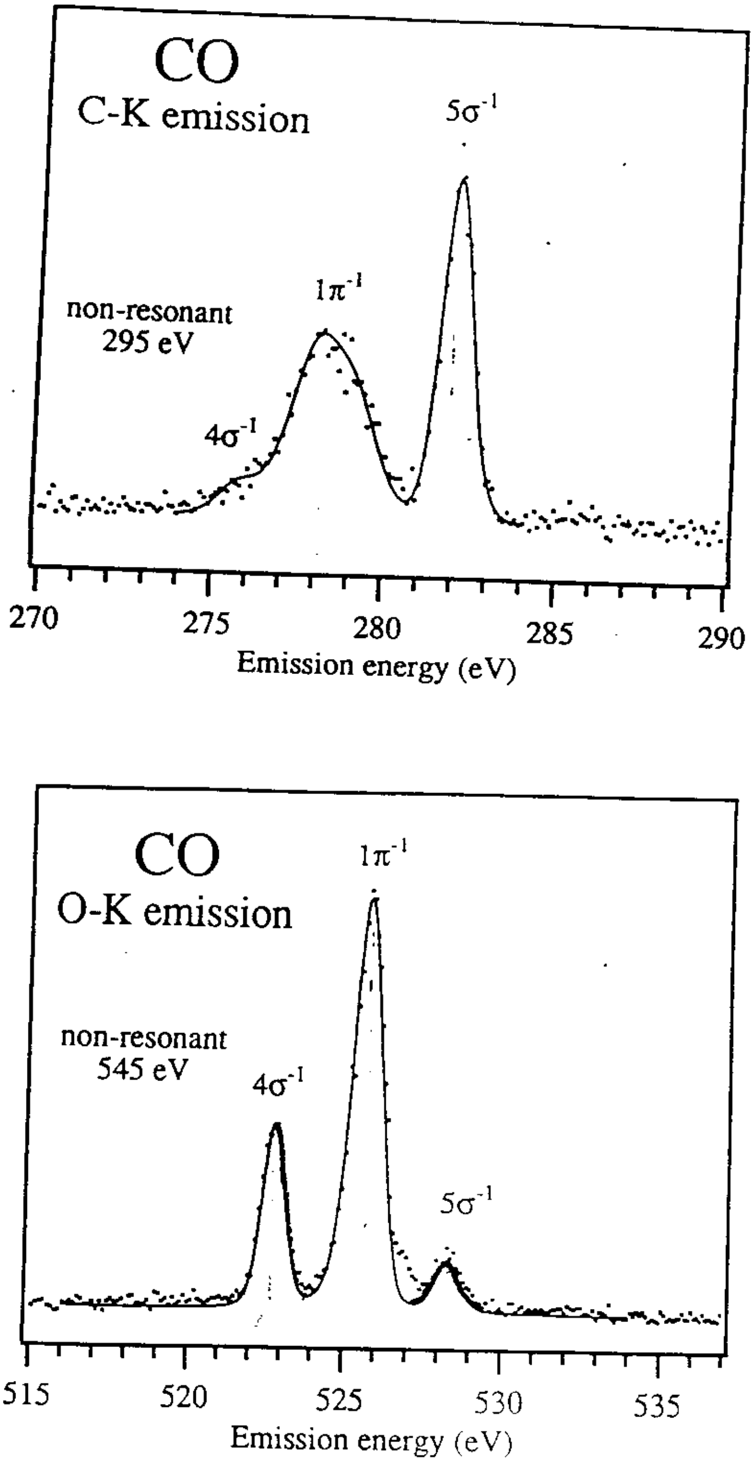
Influence of Bandwidth

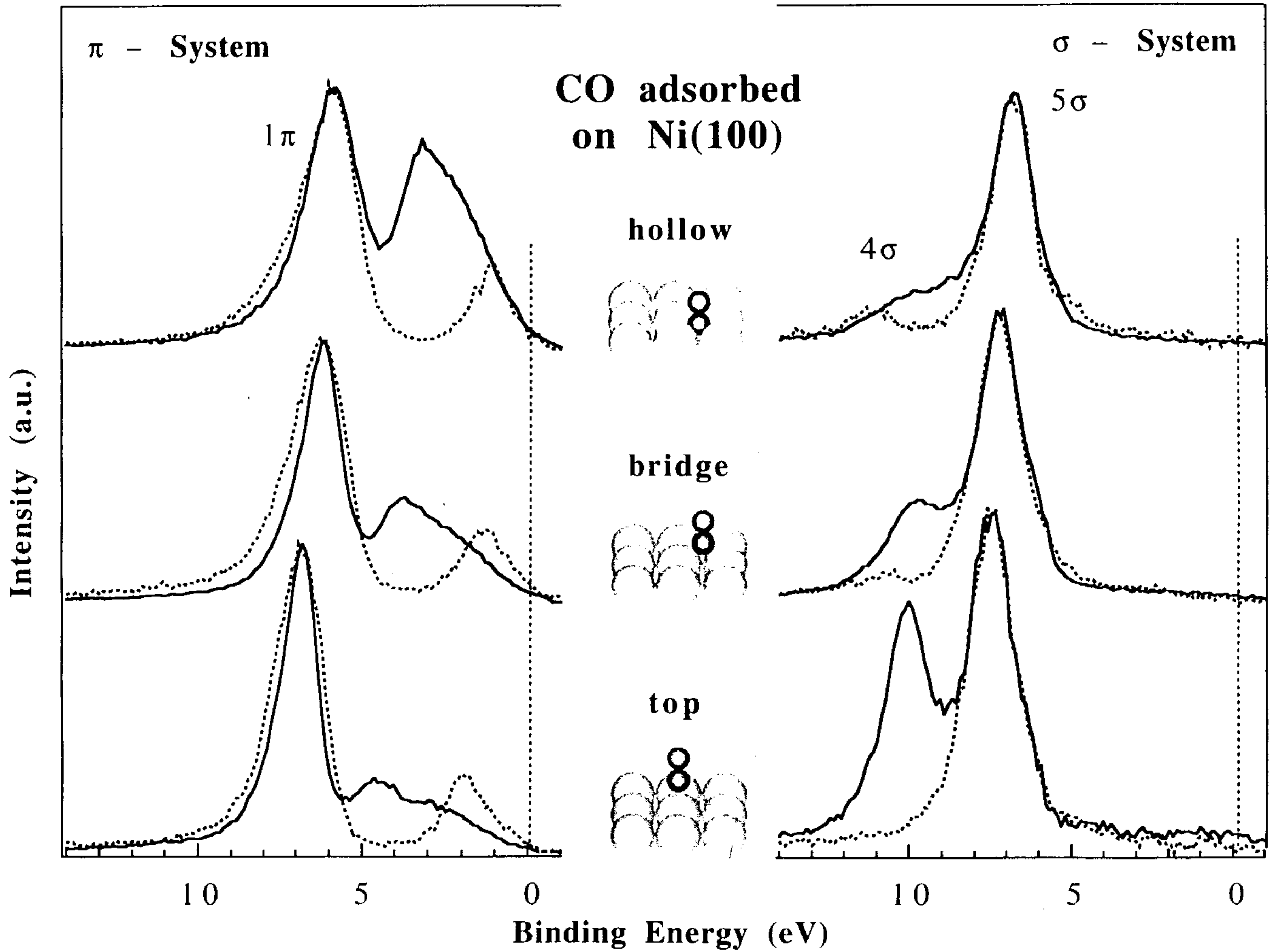


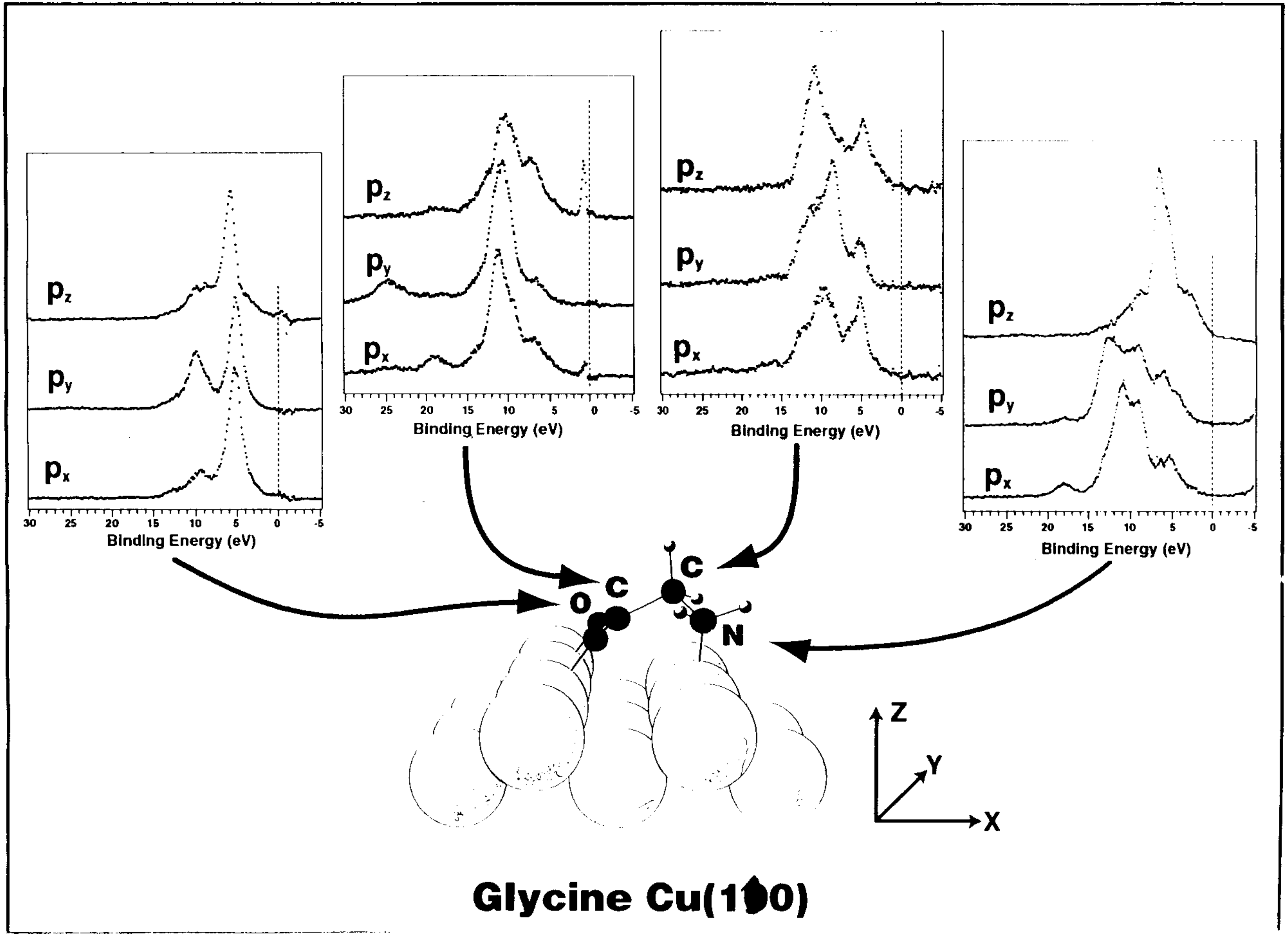


CO/Ni(100)
XES
σ
O
C
5σ
4σ
3σ
x8
π
O
C
1π
$\tilde{\pi}_O$
$\tilde{\pi}_C$
x8
30
25
20
15
10
5
0
Binding Energy (eV)

CO gas phase


CO
C-K emission
non-resonant
295 eV
$4\sigma^{-1}$
$1\pi^{-1}$
$5\sigma^{-1}$
270
275
280
285
290
Emission energy (eV)
CO
O-K emission
non-resonant
545 eV
$4\sigma^{-1}$
$1\pi^{-1}$
$5\sigma^{-1}$
515
520
525
530
535
Emission energy (eV)

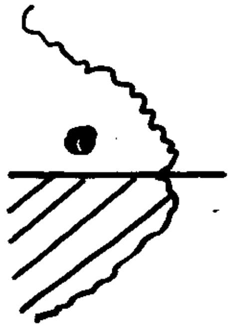

π – System
σ – System
CO adsorbed
on Ni(100)
1π
5σ
4σ
hollow
bridge
top
Intensity (a.u.)
10
5
0
10
5
0
Binding Energy (eV)



p_z
p_y
p_x
Binding Energy (eV)
30 25 20 15 10 5 0 -5
O
C
C
N
Z
Y
X
Glycine Cu(110)

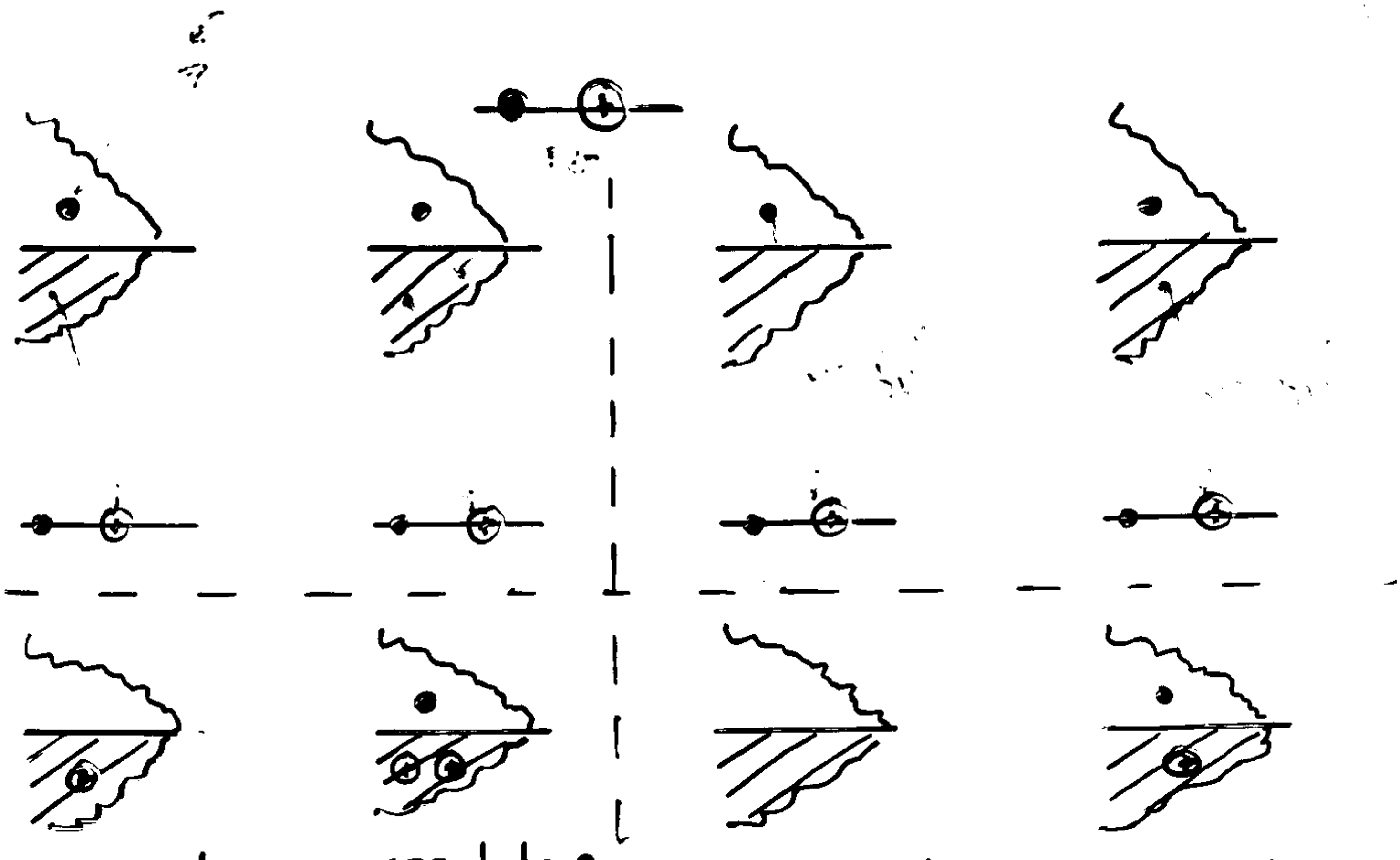
Resonant Processes

Decay from bound core excited states



neutral state

Autoionization | Inelastic x-ray scattering



participator
simiiler to
one hole
valence band

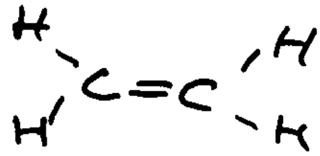
spectator
two hole –
one particle
valence band
shake-up

recombination
ground state

spectator
compare with
optical
excitation

Parity selection rule

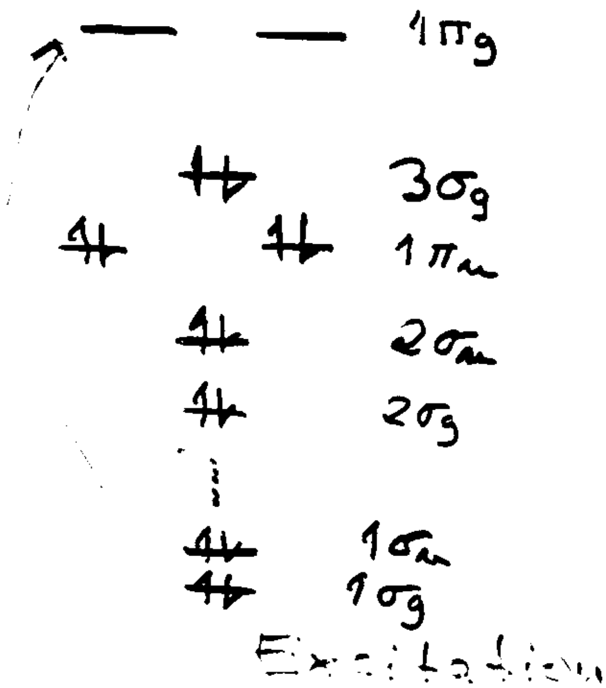
Molecules with inversion symmetry
g and u states

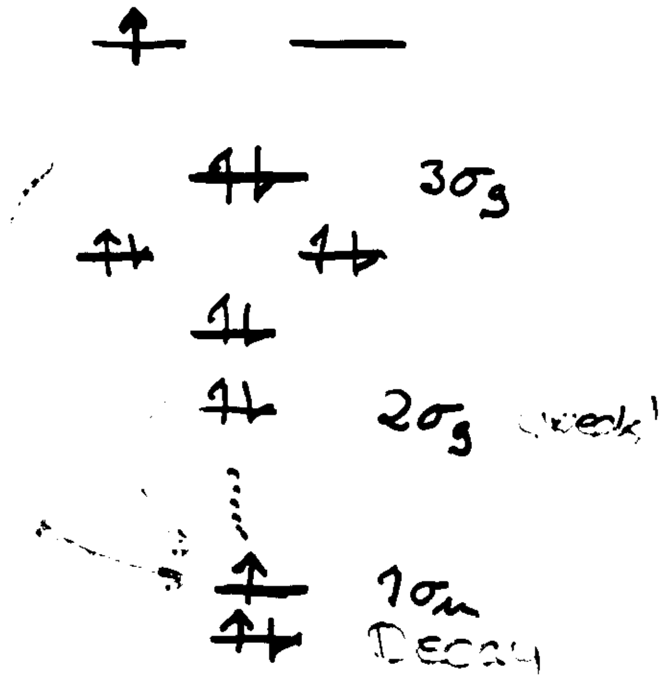
N≡N  

two different core levels $1\sigma_u$ or $1\sigma_g$

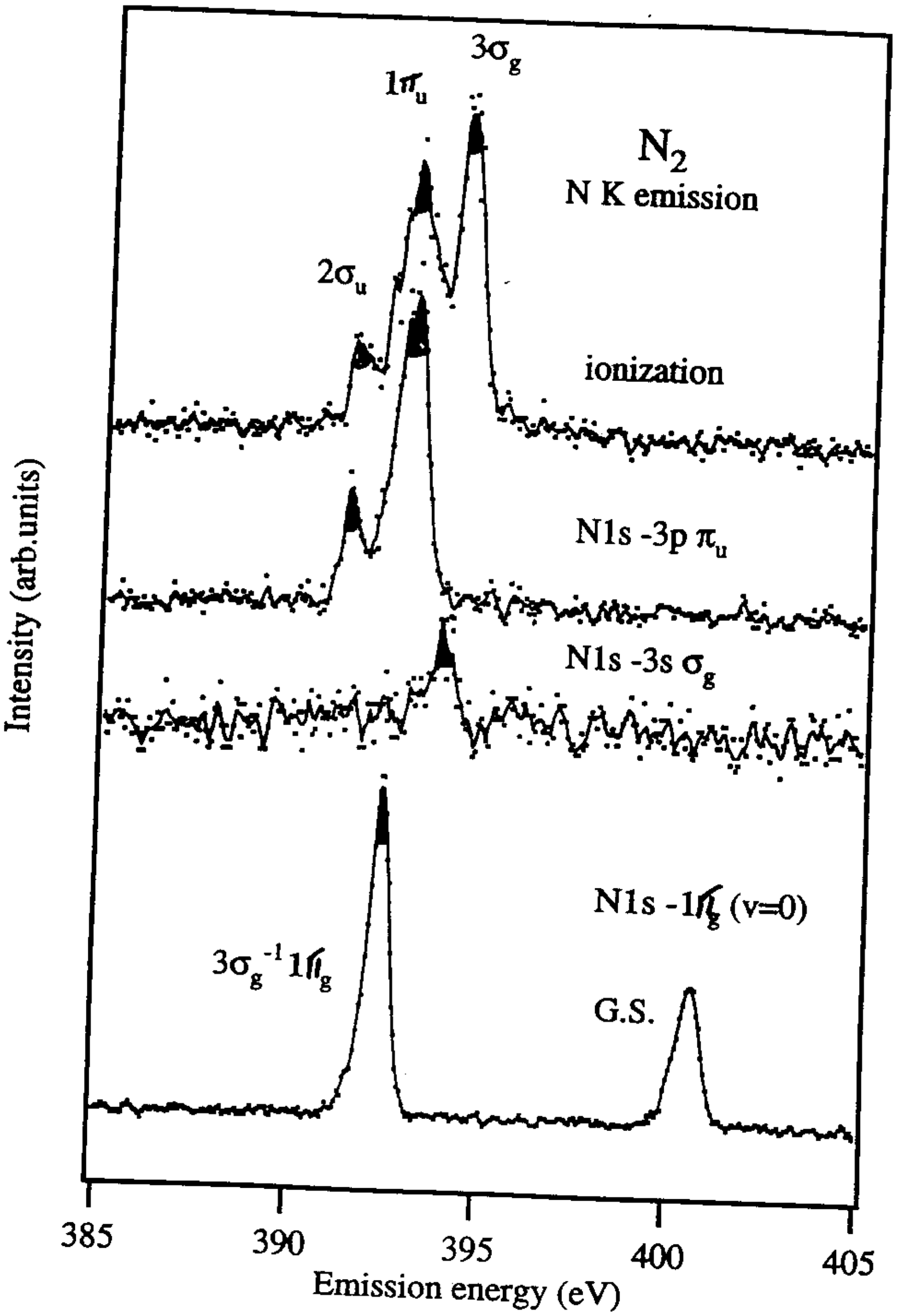
Dipole selection rule $g \rightarrow u$

Ex N_2

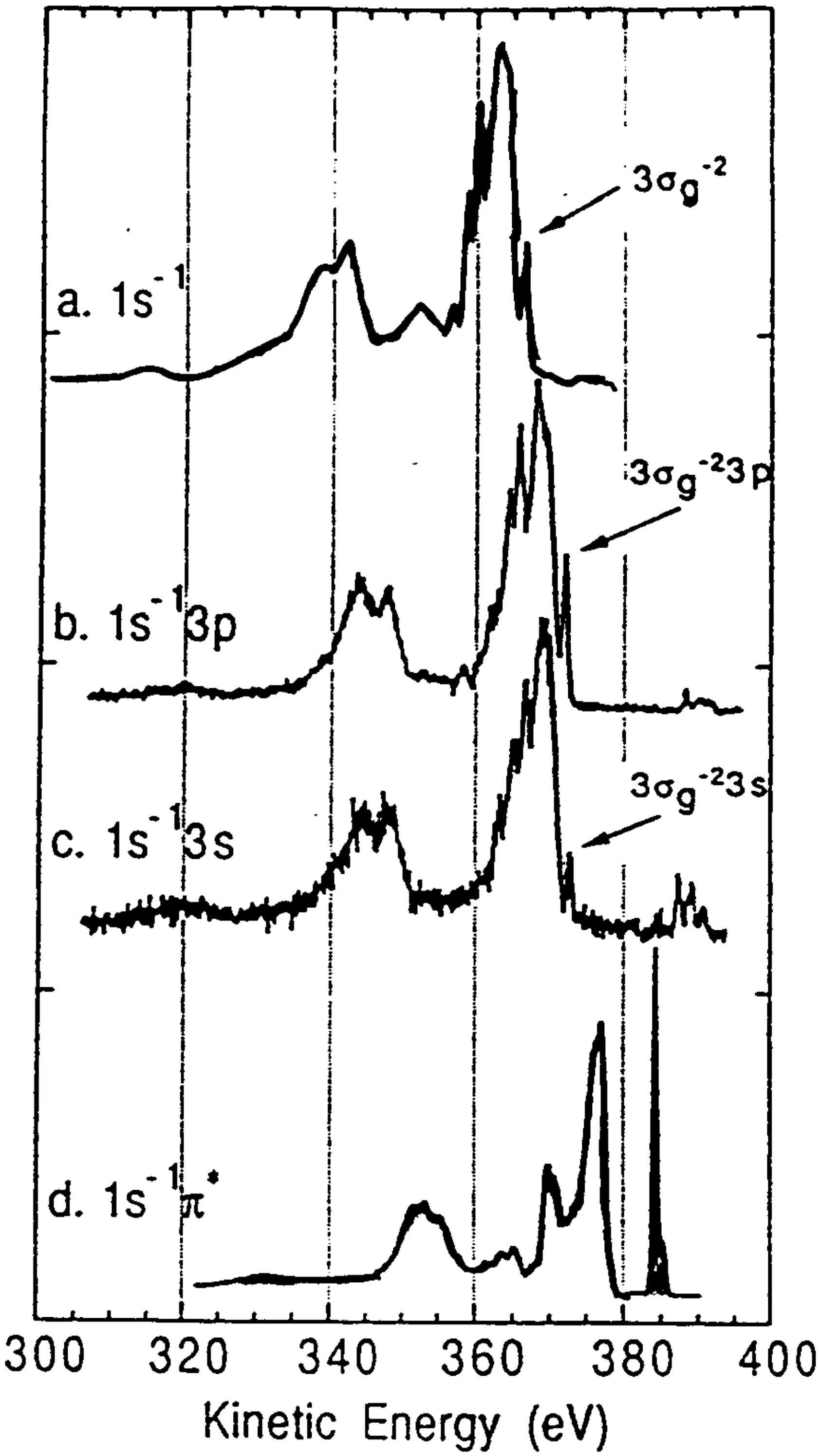




Excitation to g state : core hole u
deexcitation to fill u core hole: g states
No symmetry breaking ⇒ one step process.

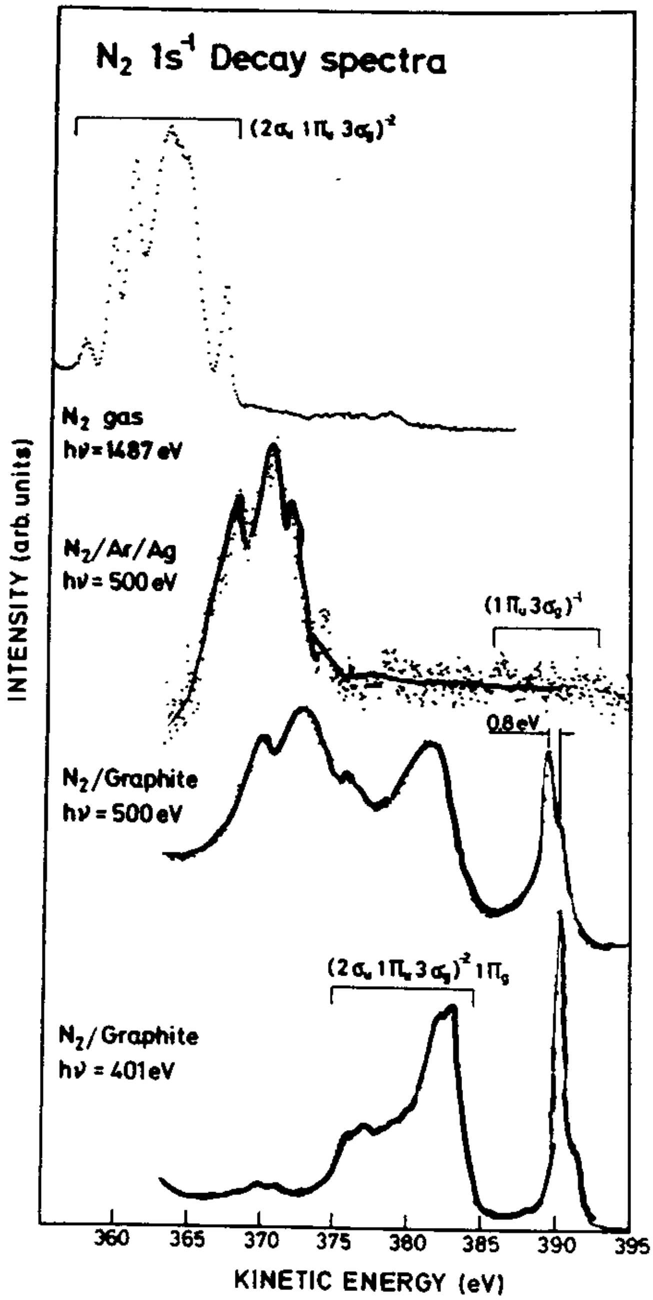


Per skytt et.al unpublished



spectator

Eberhardt et.al Phys. Scr. T41



Björneholm et.al. Phys. Rev. Lett. 68, 1892 (1992)

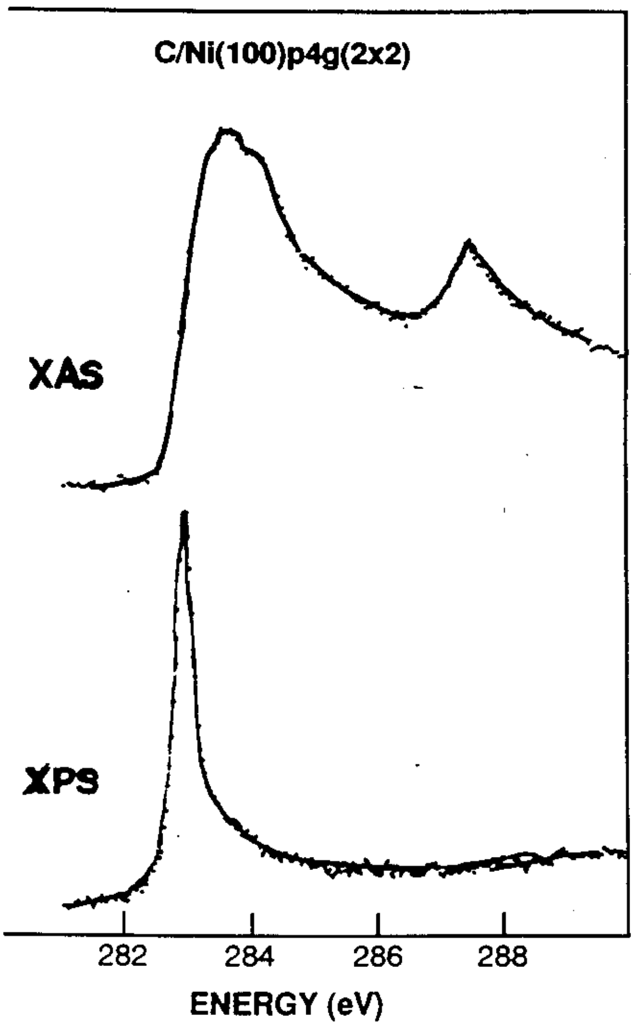
Metallic screening ⇒ lowest

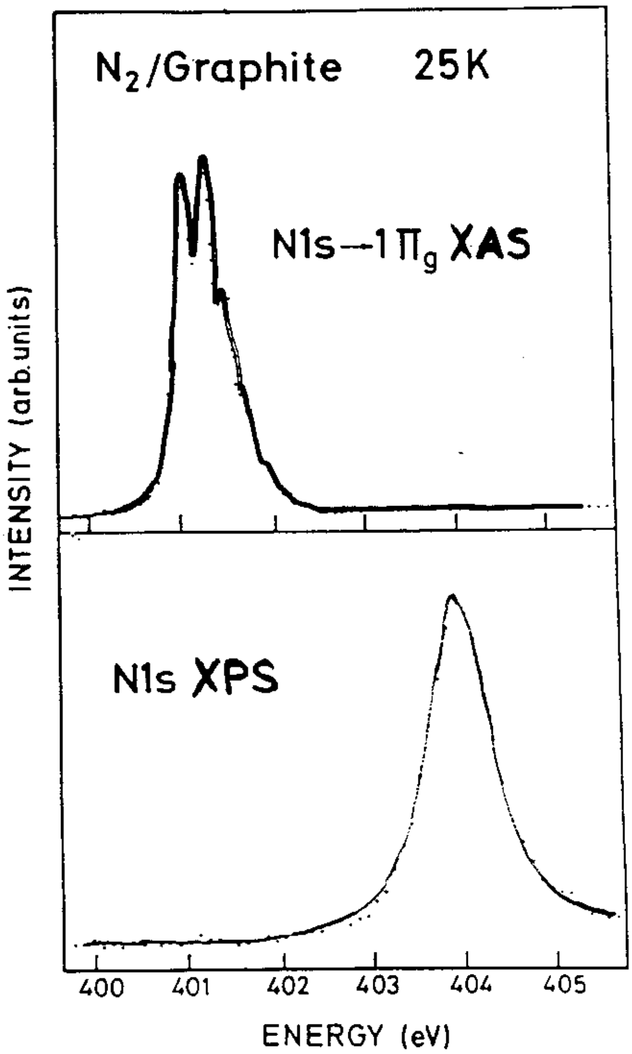
Compare XPS with XAS

Binding Energy at XAS threshold

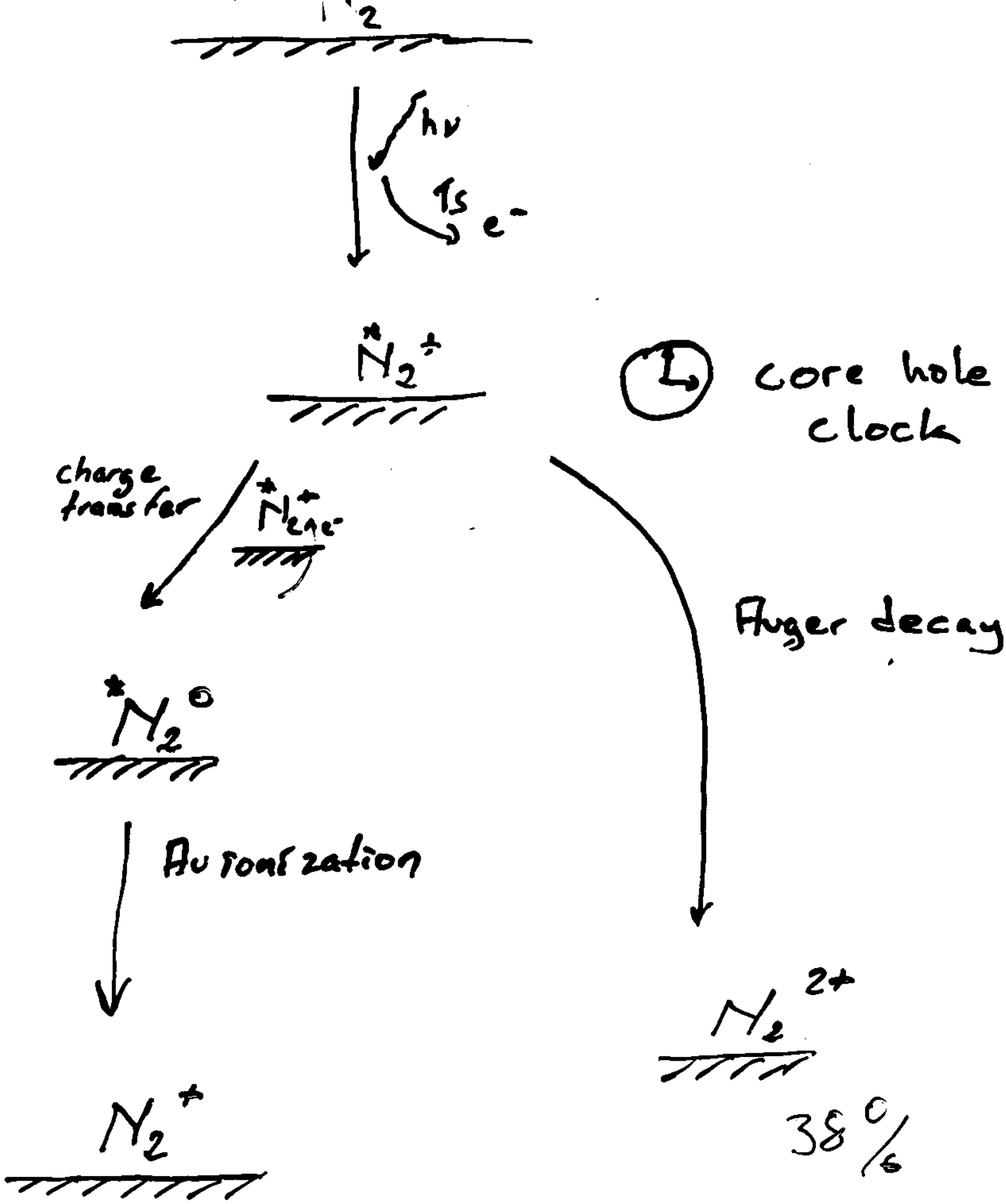
Metallic screening

Non metallic screening





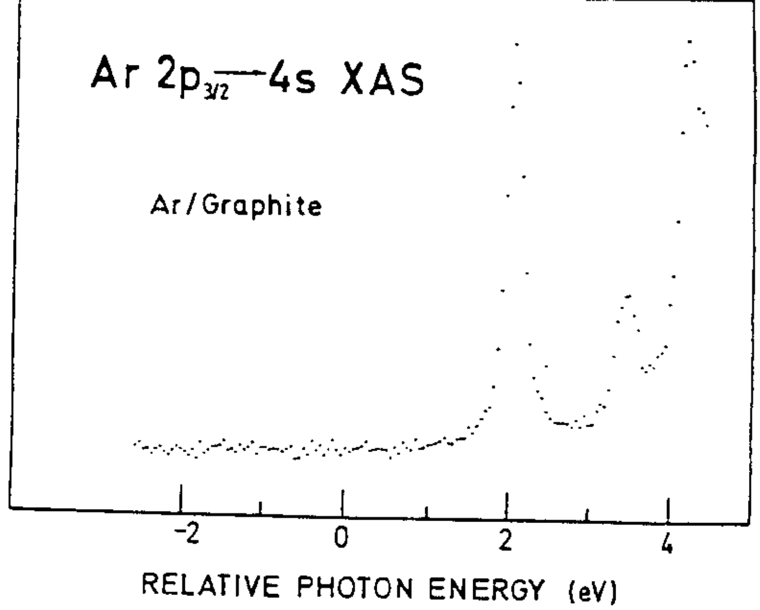
Mårtensson et.al J.El. spec. in press

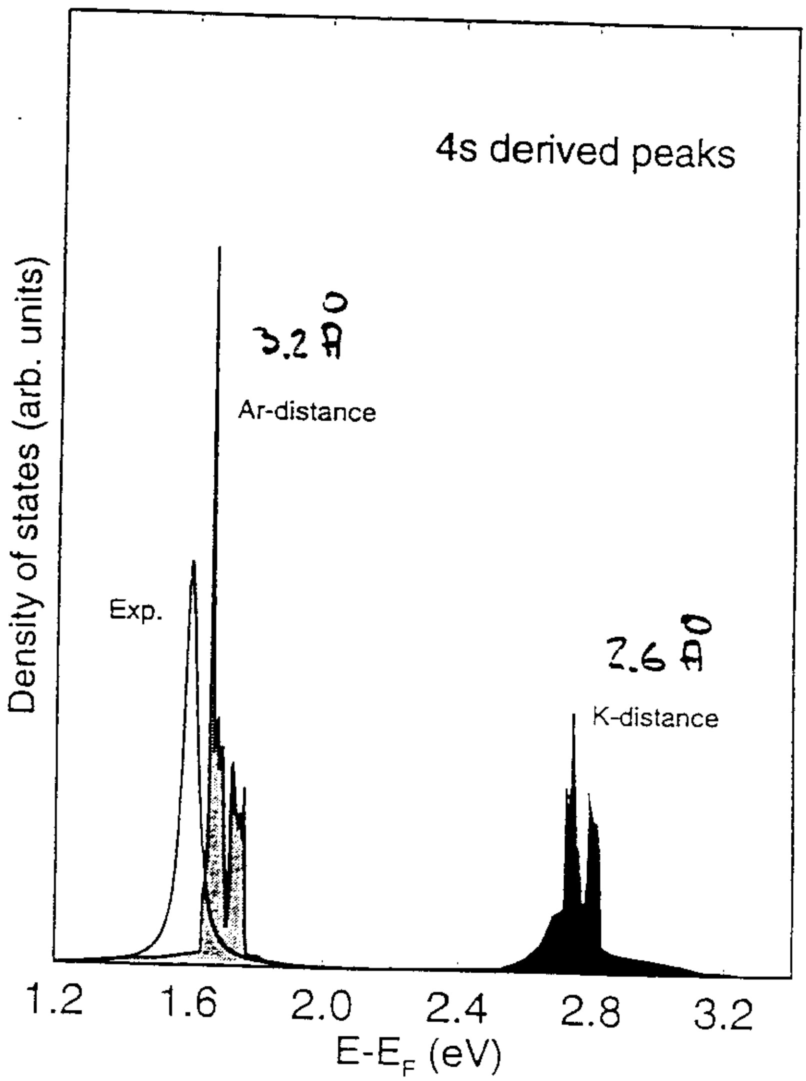


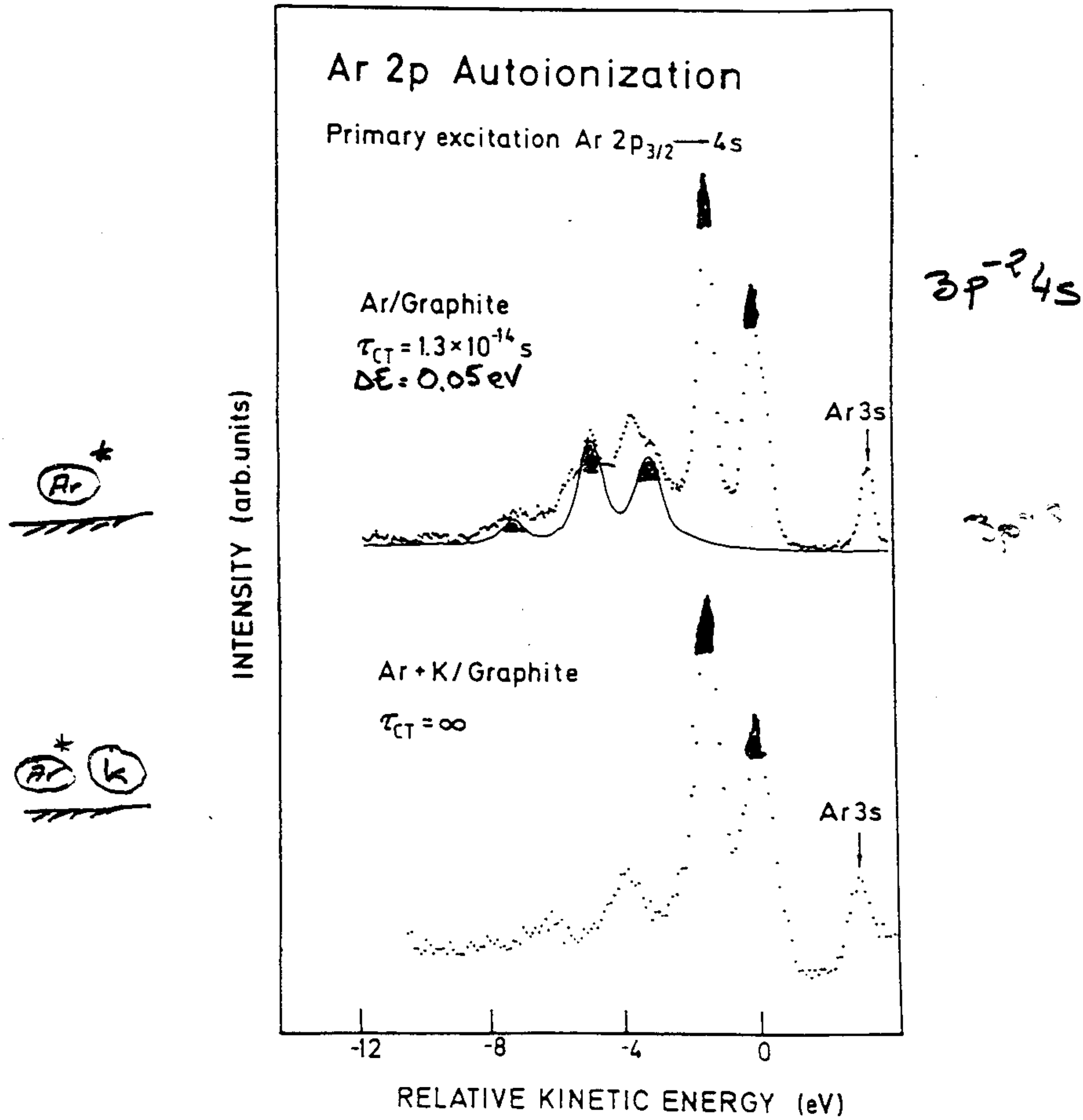
$\Gamma_{1s} = 5.5 \cdot 10^{-15}\, s$

charge transfer time $9 \times 10^{-15}\, s$

$\Delta_{CT} = 0.07\, eV$


Ar 2p3/2—4s XAS
Ar/Graphite
-2
0
2
4
RELATIVE PHOTON ENERGY (eV)


4s derived peaks
Density of states (arb. units)
3.2 Å
Ar-distance
Exp.
2.6 Å
K-distance
1.2
1.6
2.0
2.4
2.8
3.2
E-E_F (eV)



Ar 2p Autoionization
Primary excitation Ar $2p_{3/2}$—4s
Ar/Graphite
$\tau_{CT} = 1.3\times10^{-14}$ s
$\Delta E = 0.05$ eV
Ar 3s
Ar + K/Graphite
$\tau_{CT} = \infty$
Ar 3s
INTENSITY (arb.units)
-12
-8
-4
0
RELATIVE KINETIC ENERGY (eV)
$3p^{-2}4s$
Ar
Ar
K

$\tau_{Ar 2p} = 5.5 \times 10^{-15}$ s

From ratio $\frac{+2}{+1}$ final state

we can derive

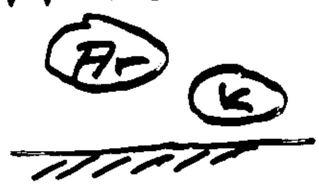
$\tau_{\text{charge transfer}}$ ratio = 1 + [illegible]

Z + 1 approximation

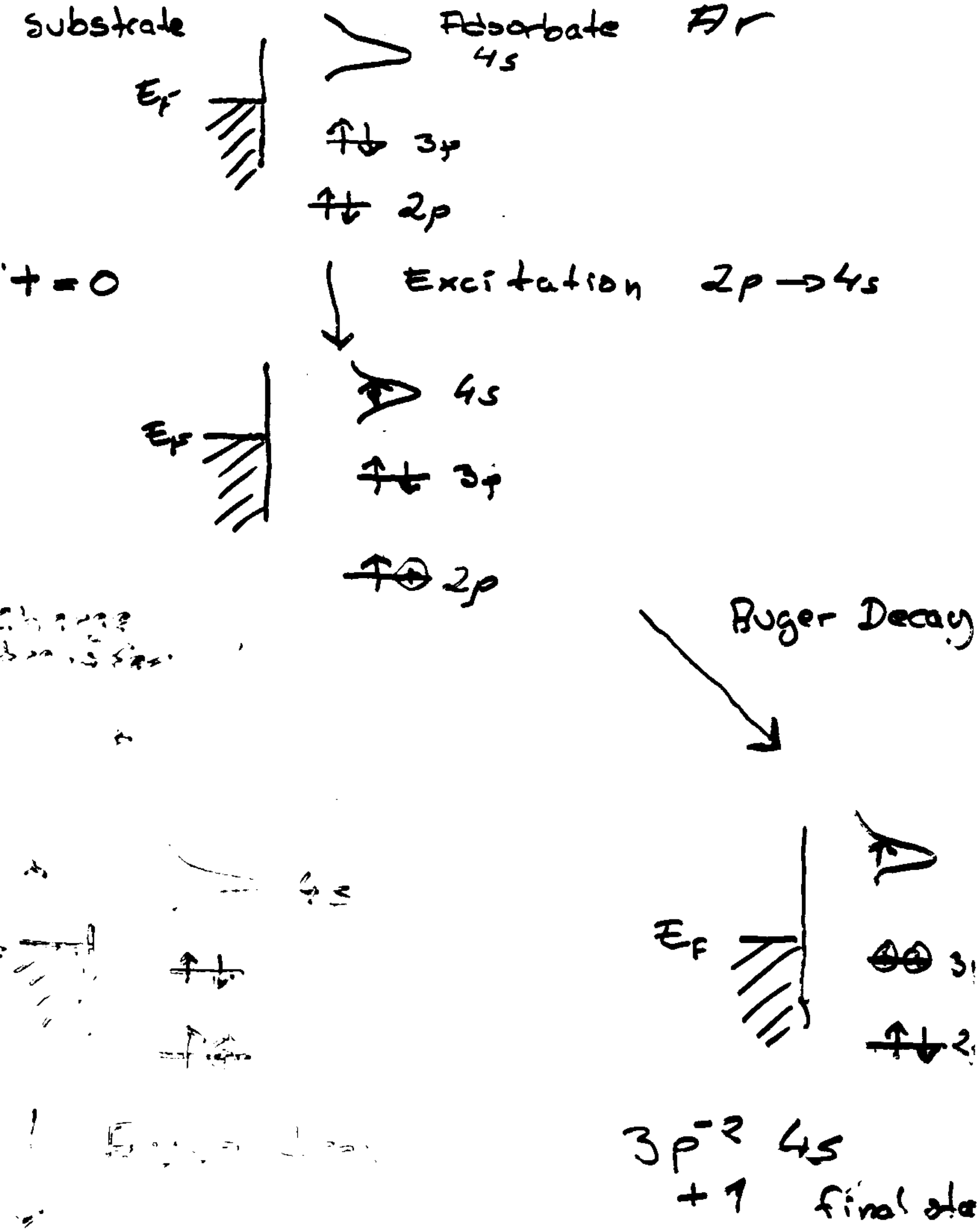
Ar ⟹ K

we can probe K 4s level

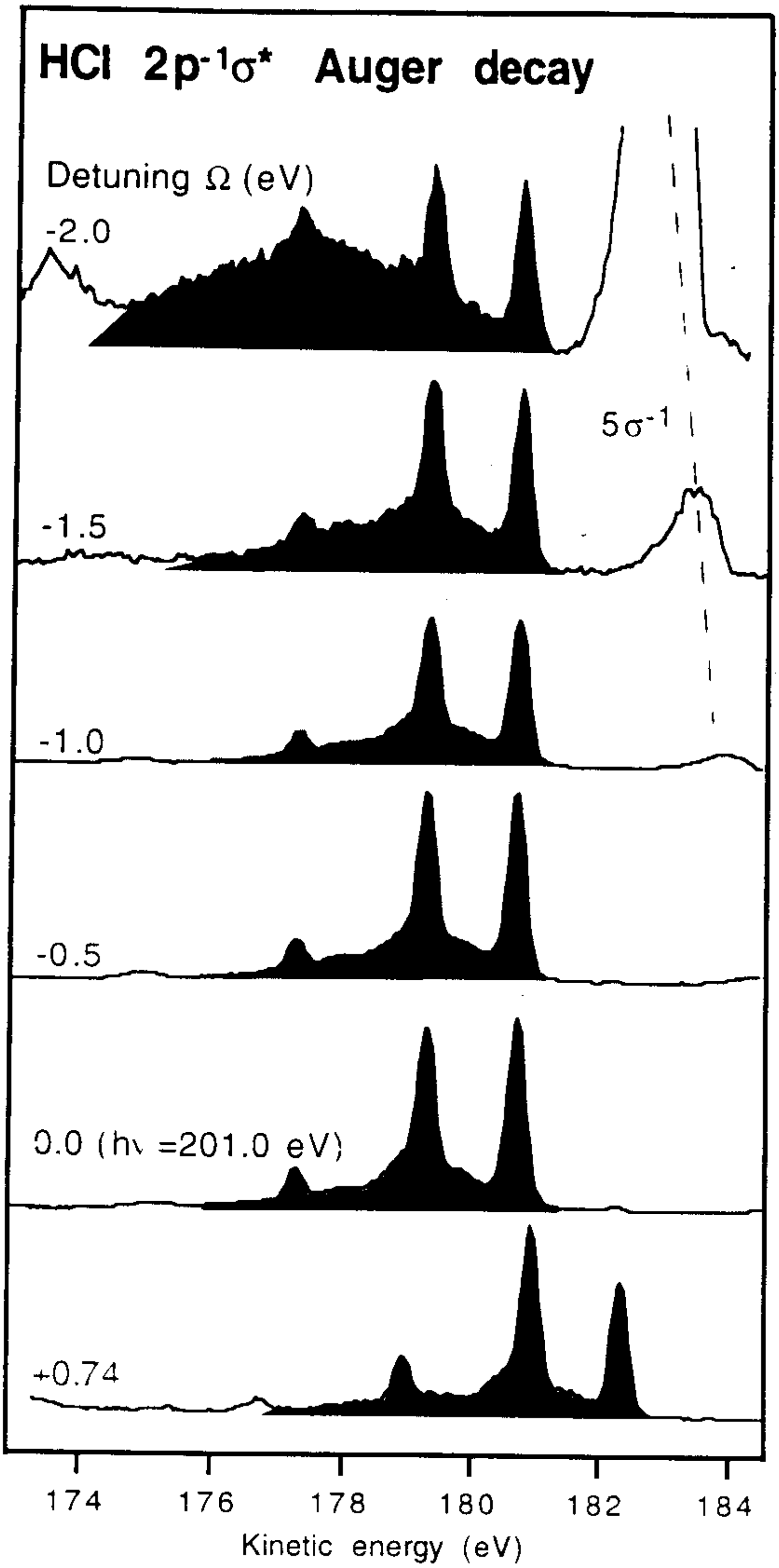
important to correct for bond distance.

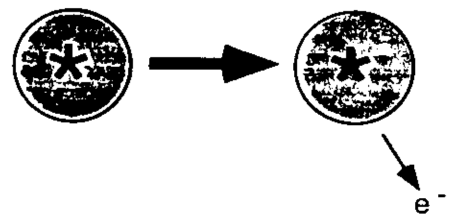


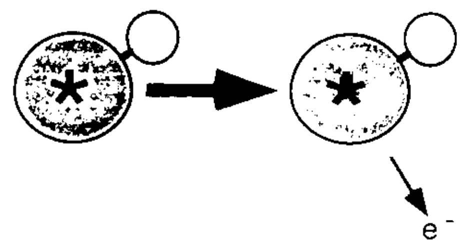
The "Core Hole Clock" method



Experimental Auger spectra

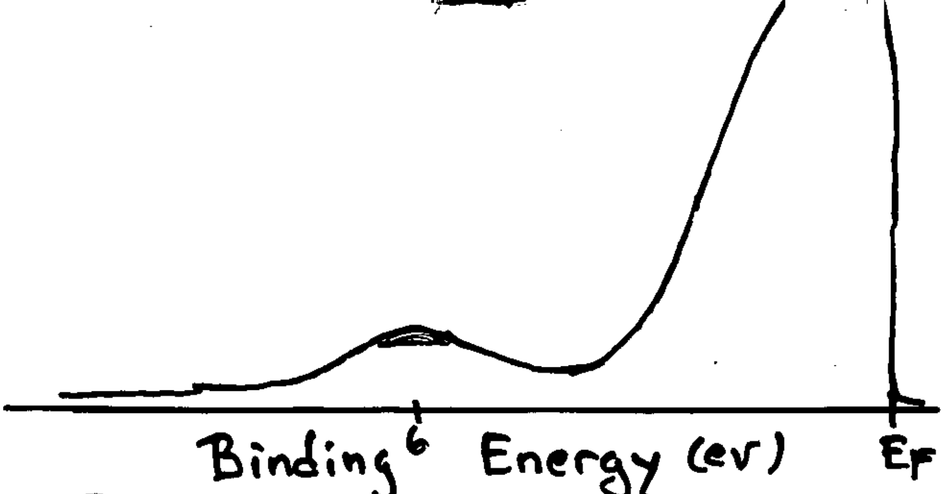






Broad "molecular" features
increase in intensity with Ω
shift in KE

Sharp "atomic" features
decrease in intensity with Ω
have constant KE



PES

Valence band photoemission

$2p^6 [d^9 s] \xrightarrow{e^-} 2p^6 [d^{10}] [\oplus]$ band hole propagation

6 eV satellite

$2p^6 [d^9 s] \xrightarrow{e^-} 2p^6 d^8 [s^2]$

Autoionization

$$2p^6 [d^9 s] \xrightarrow{\times As} \underline{2p^5} [d^{10} s] \begin{cases} \nearrow 2p^6 [d^9 s] [\oplus] \\ \searrow 2p^6 d^8 [s^2] \end{cases}$$

two channel/s

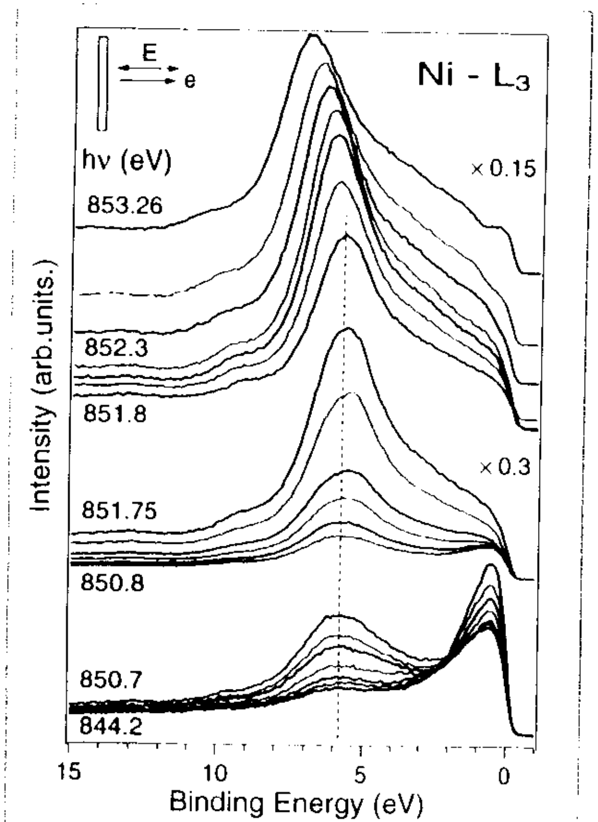
Mixing of PES and Autoionization?

Resonant Raman effects?

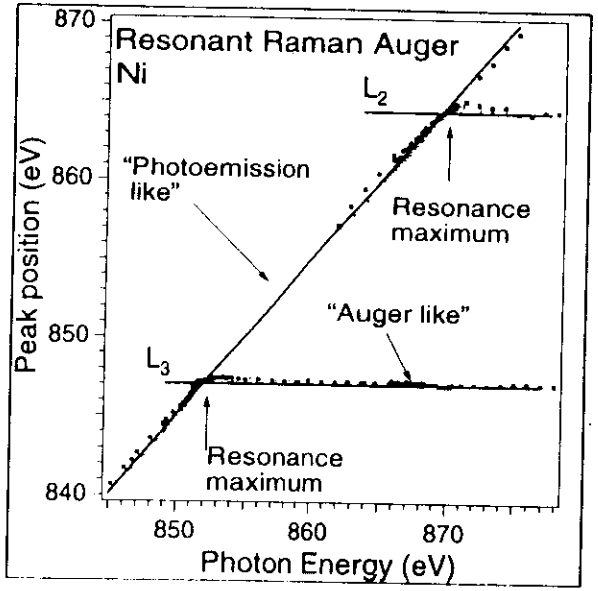
one or two step behaviour?

Ni 2*p* Resonant photoemission

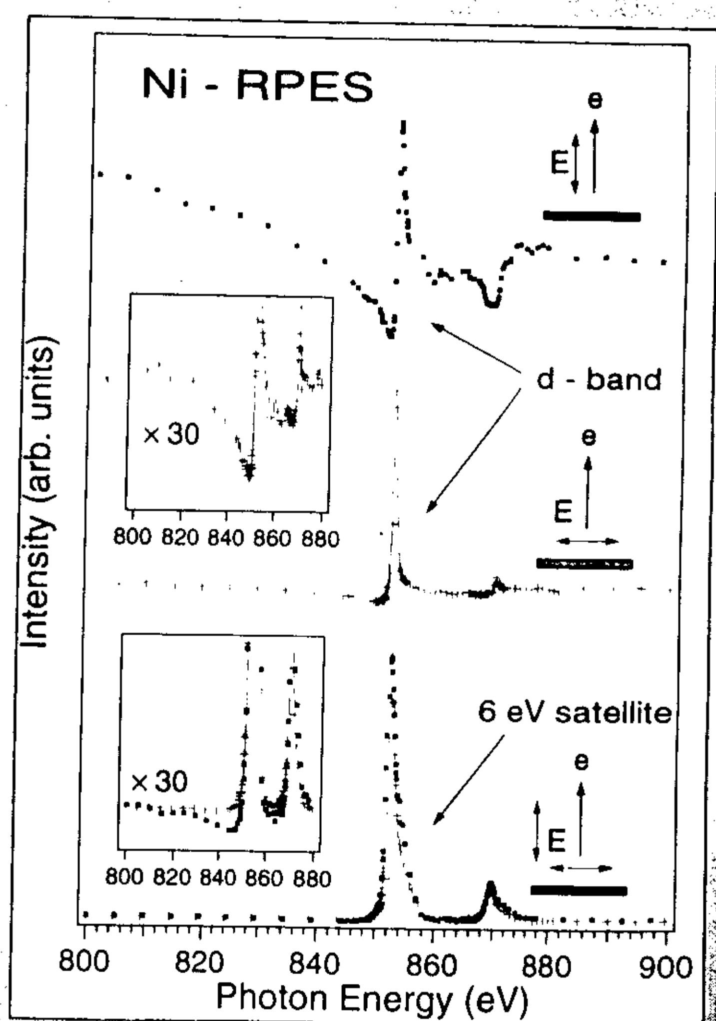
Resonant photoemission - Enhancement of certain spectral features near a core level threshold.
E.g. Ni 2*p*



Rapid transition from coherent to non-coherent regime above threshold.



Interference effects at the d-band and 6 eV satellite. Fano-type profiles.



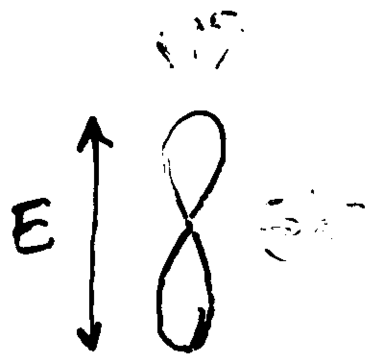
Photoemission mixes with autoionication

constructive and destructive interference

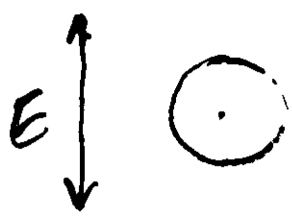
Fano

the two channels has to have similar cross sections

angle Photoemission cross section



Autoionization



isotropic