united nations
educational, scientific
and cultural
organization

international atomic
energy agency

the
abdus salam
international centre for theoretical physics

SMR/1270-38

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

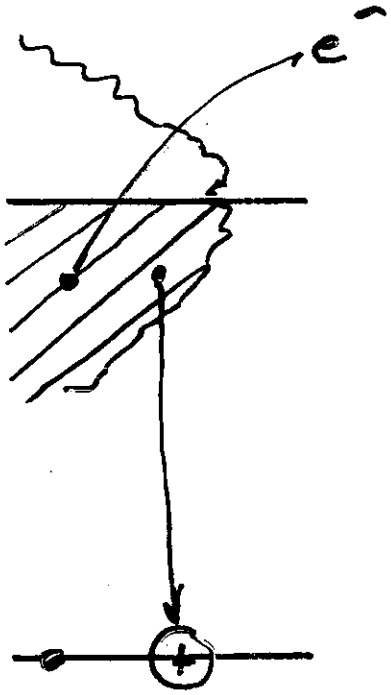
Co-sponsors: Sincrotrone Trieste, Società Italiana di Luce di Sincrotrone (SILS) and the Arab Fund for Economic and Social Development

Angle-Resolved Photoemission from Three-Dimensional Systems – Including Magnetism

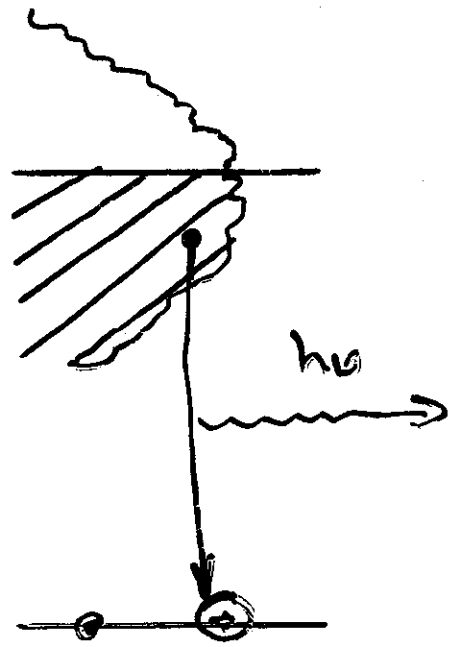
Juerg Osterwalder
Universitaet Zuerich-Irchel
Zurich, Switzerland

Core hole Decay

after ionization

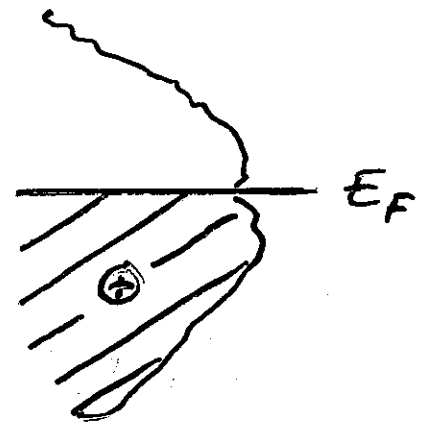


electron emission
Auger spectroscopy (AES)



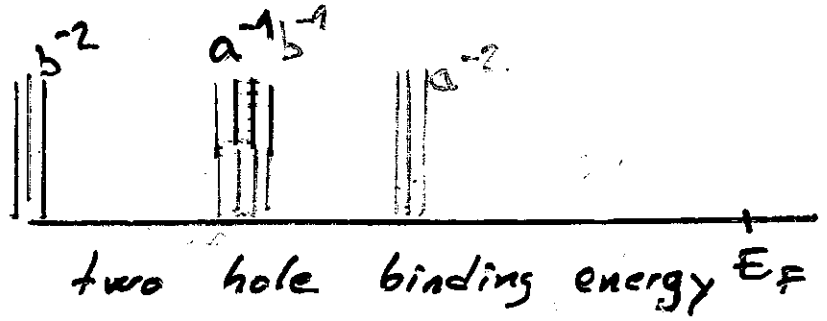
photon emission
X-ray Emission Spectroscopy (XES)

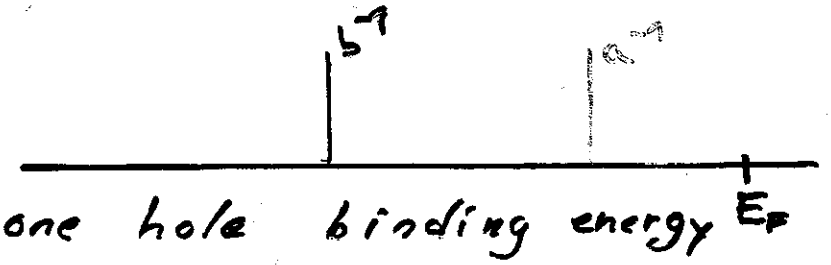
Different Final states

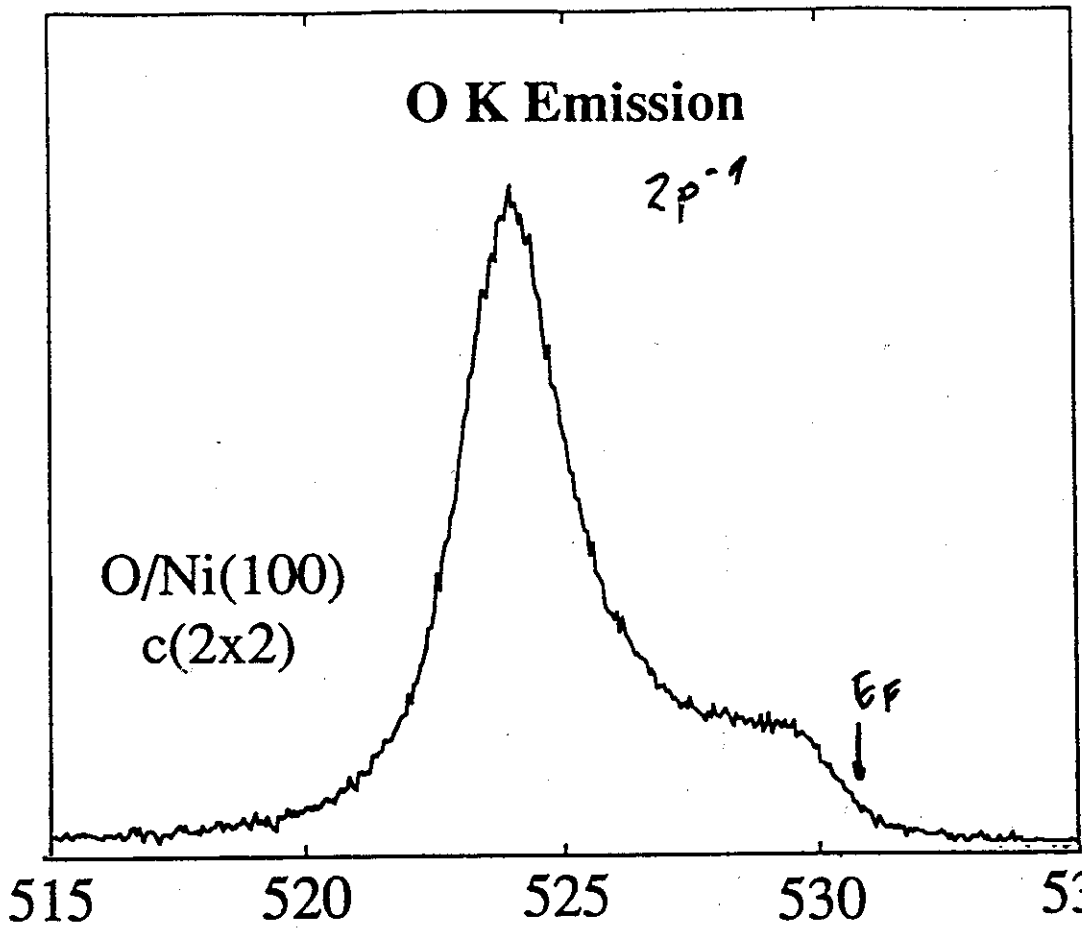


AES
two holes

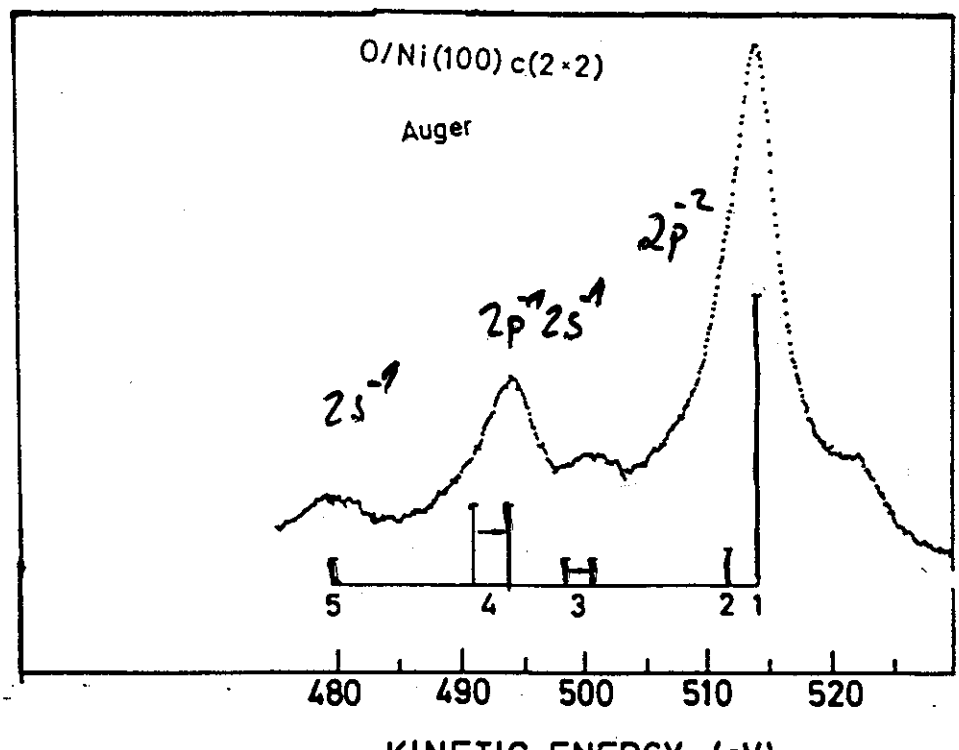
XES
one hole







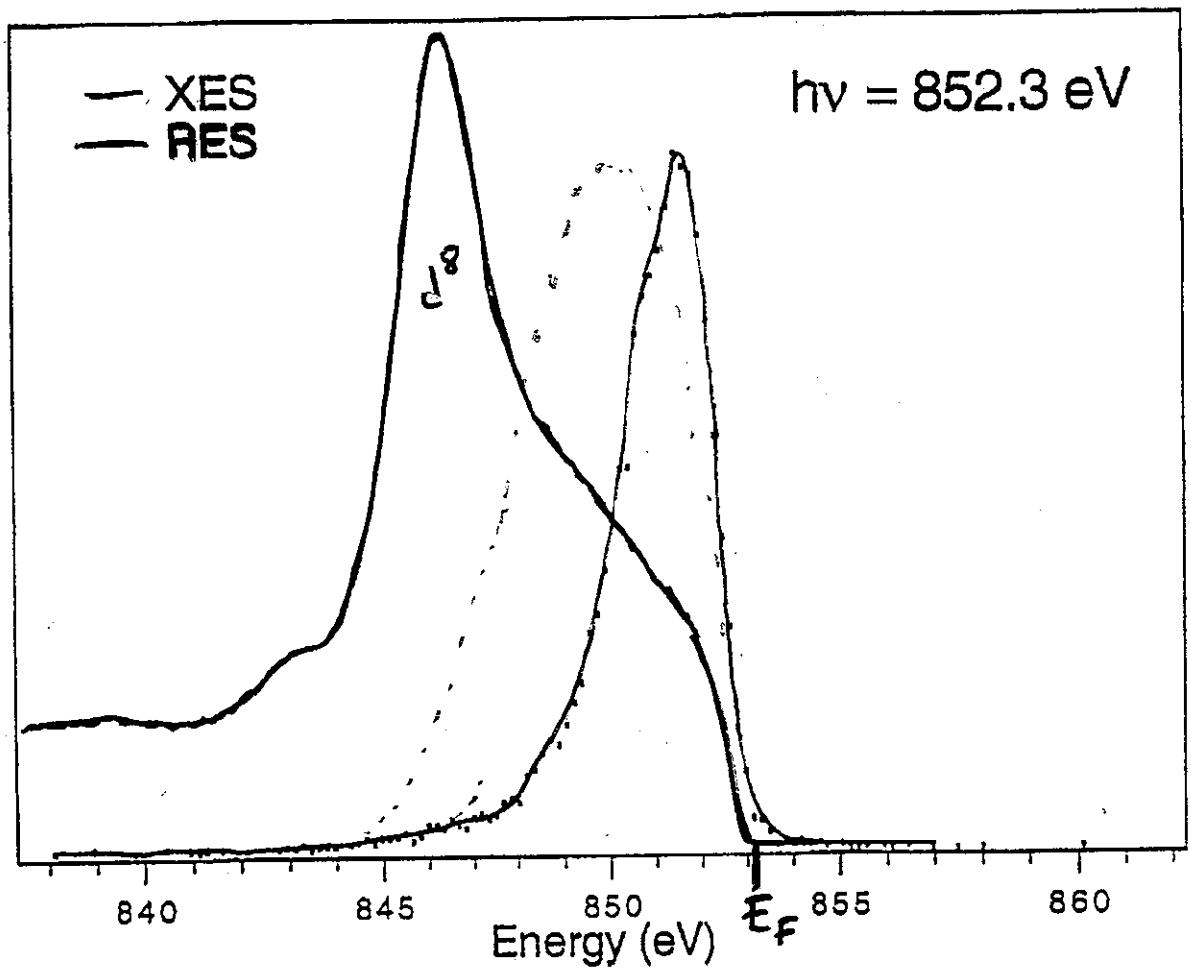
localized $2p^{-2}$
Strong hole hole
Interaction



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

A. Sandell Phys Rev. B48, 4367 (1993)

Comparing RES and XES final states

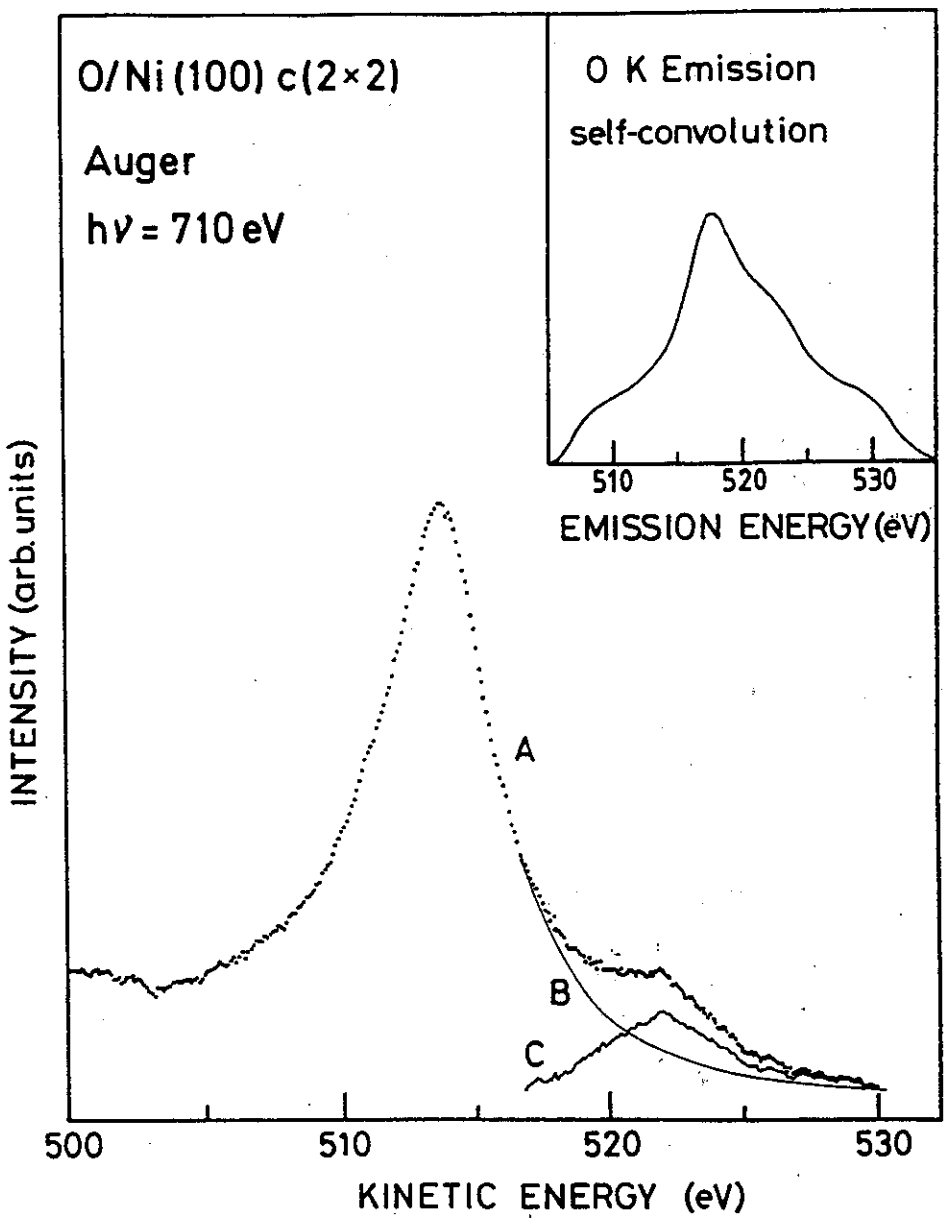


two hole - self convolution

RES still different

hole-hole interaction

way of study correlation



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

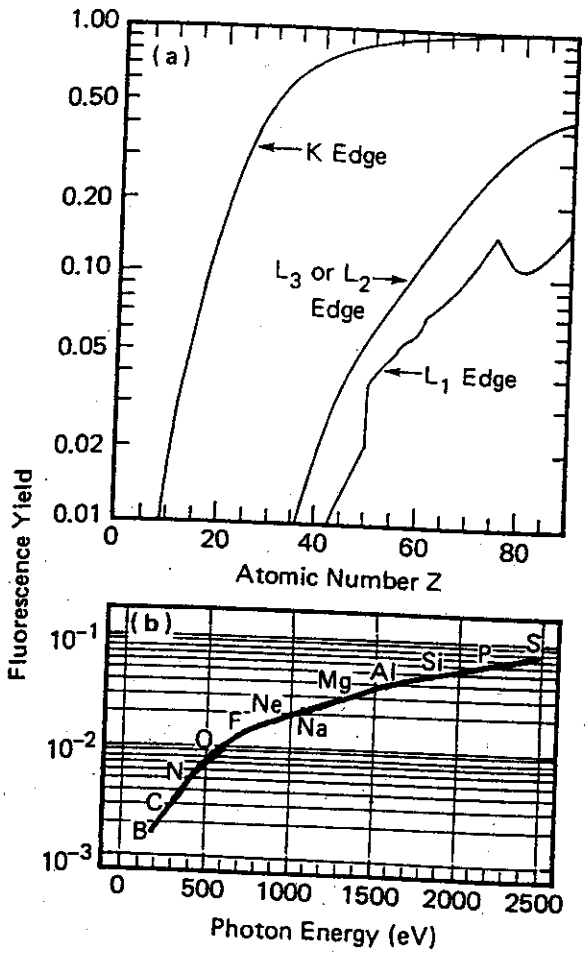
Life time of core hole $\Gamma = \Gamma_{Aug} + \Gamma_{x\text{-ray}}$

$\frac{1}{\Gamma_{Aug}} \propto R_{Aug} \propto \sum_f \langle \psi_i | \frac{1}{r} | \psi_f \rangle$ 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 $(\frac{1}{r})$.

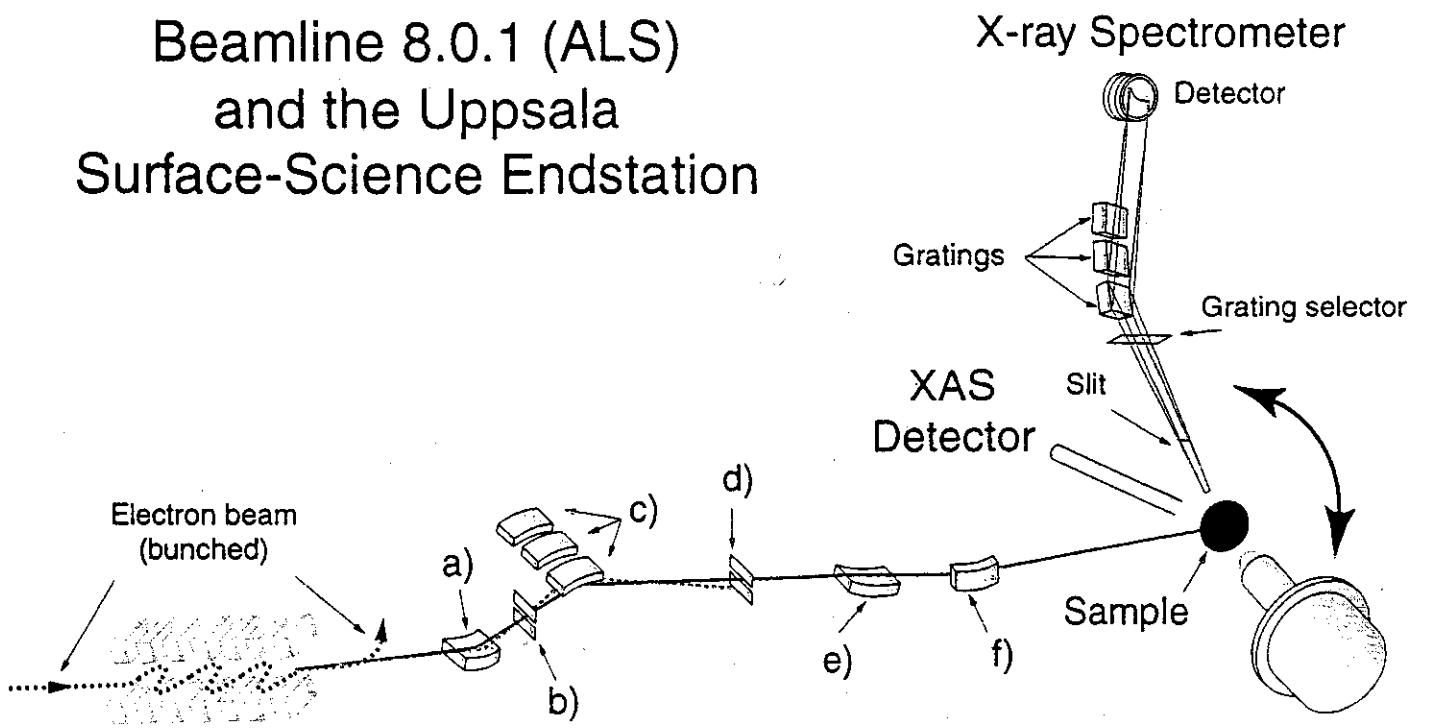
Coster-kronig : Auger in the same shell very fast.



Fluorescence yield

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

Beamline 8.0.1 (ALS) and the Uppsala Surface-Science Endstation



U5 Undulator

Hemispherical Electron Analyzer

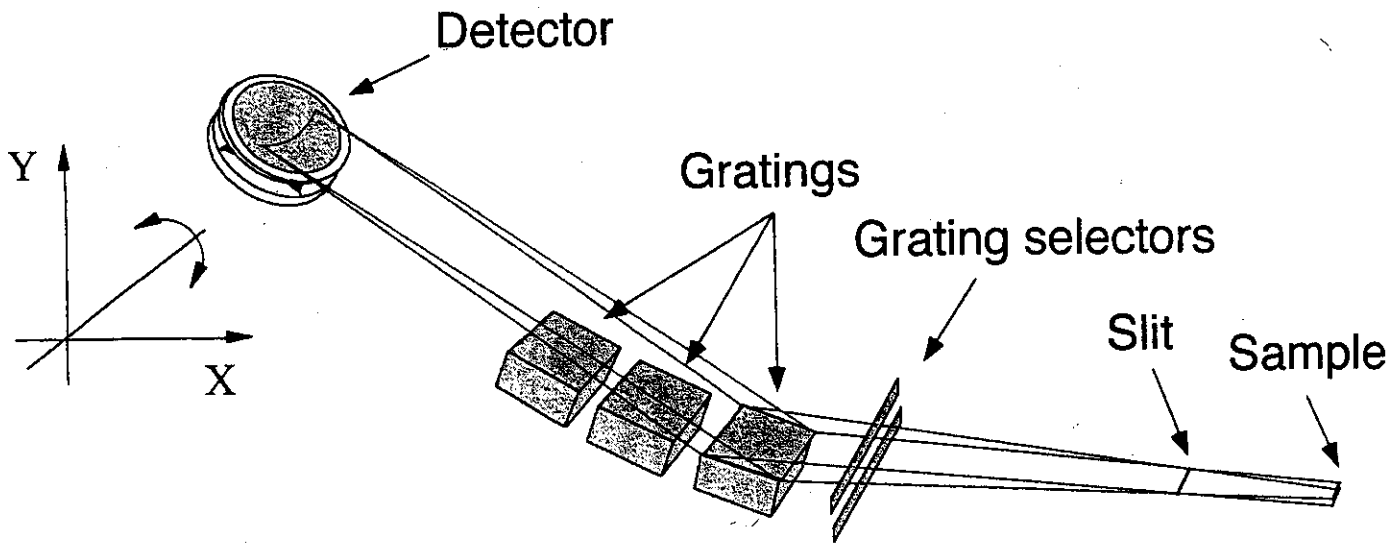
Optical Elements

Monochromator:
- a) Vertical Condenser
- b) Entrance slit (fixed)
- c) Spherical Gratings (3)
- d) Exit slit (translating)

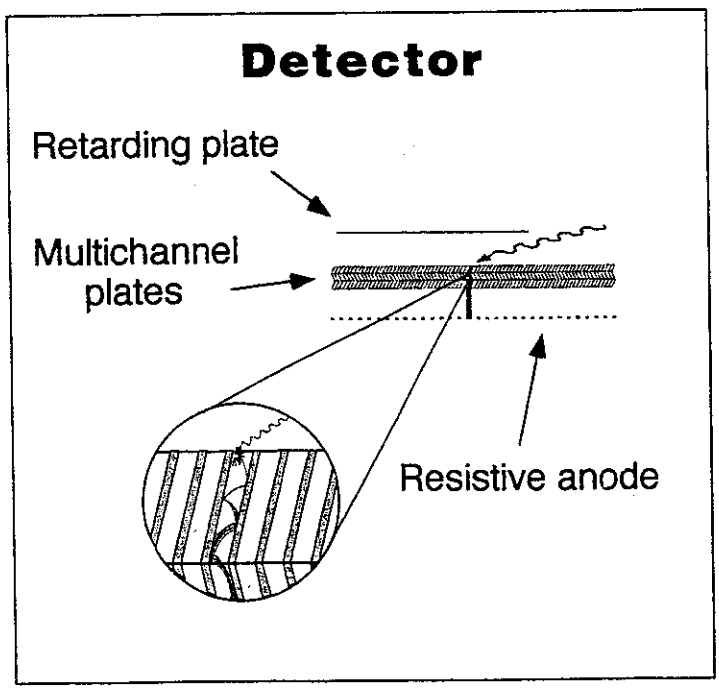
Refocusing Optics:
- e) Vertical
- f) Horizontal

Soft X-ray Emission Spectrometer

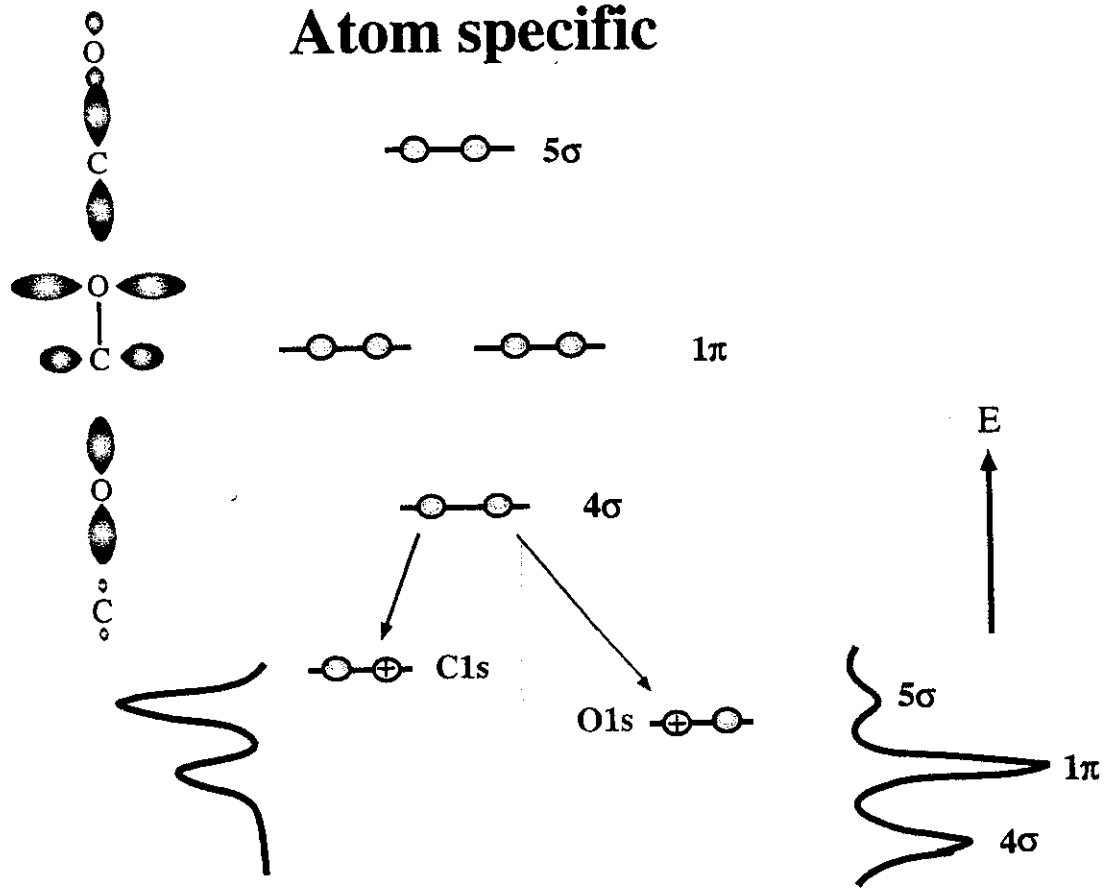
XES 300

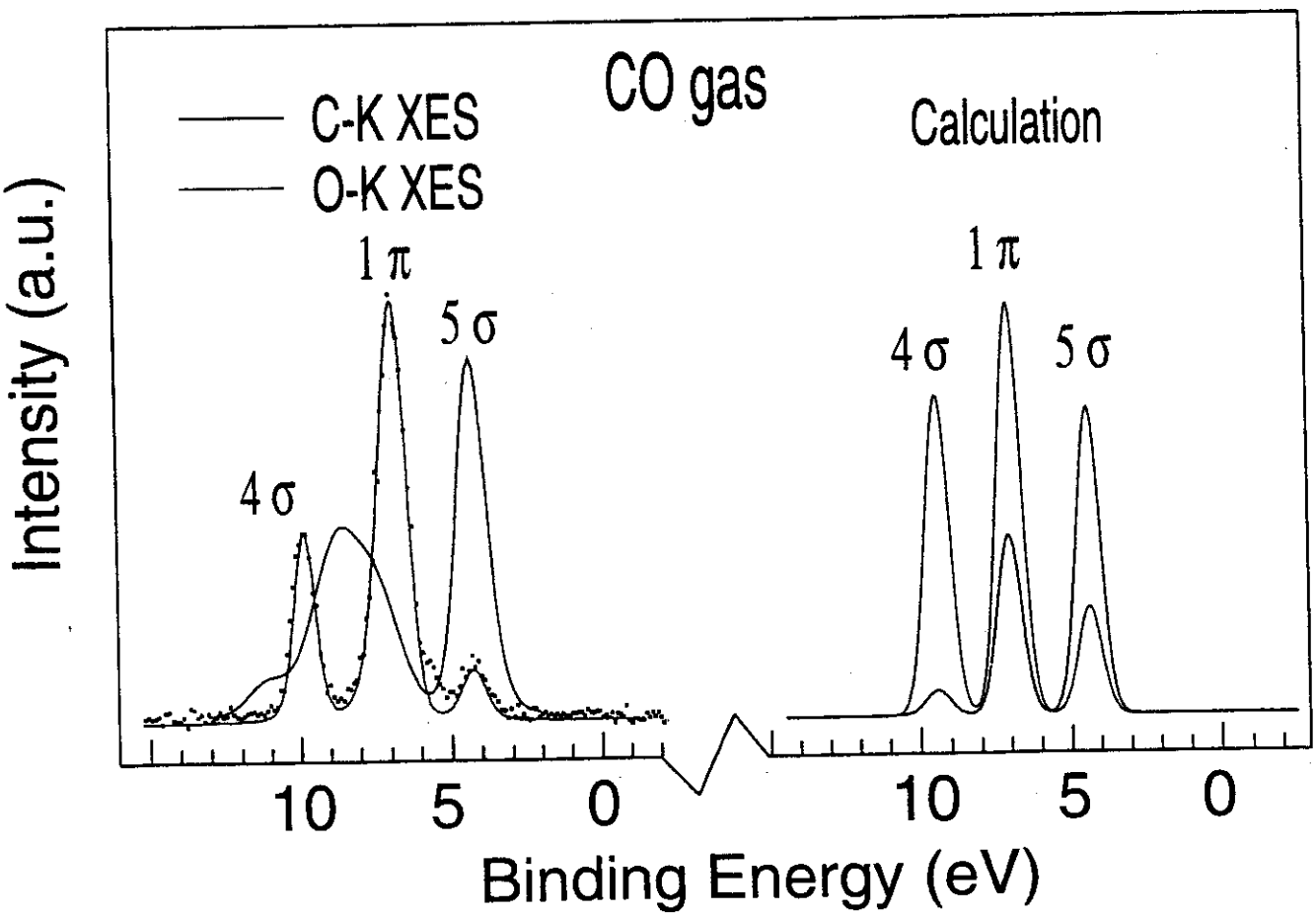


Grating	Radius	Grooves	Angle	Range
#1:	5 m	1200 l/mm	1.9°	≈ 300 - 1000 eV
#2:	5 m	400 l/mm	2.6°	≈ 100 - 450 eV
#3:	3 m	300 l/mm	5.4°	≈ 50 - 200 eV

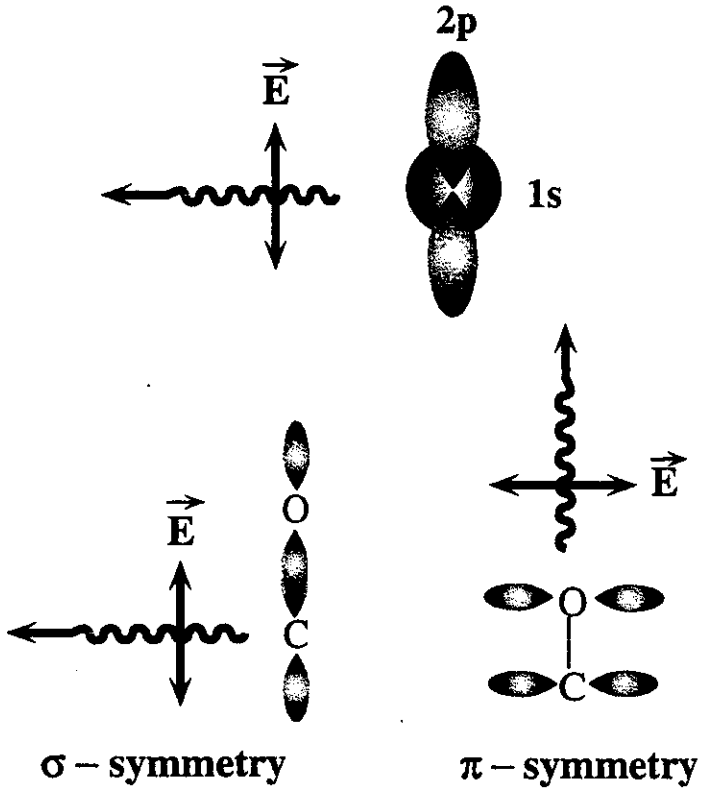


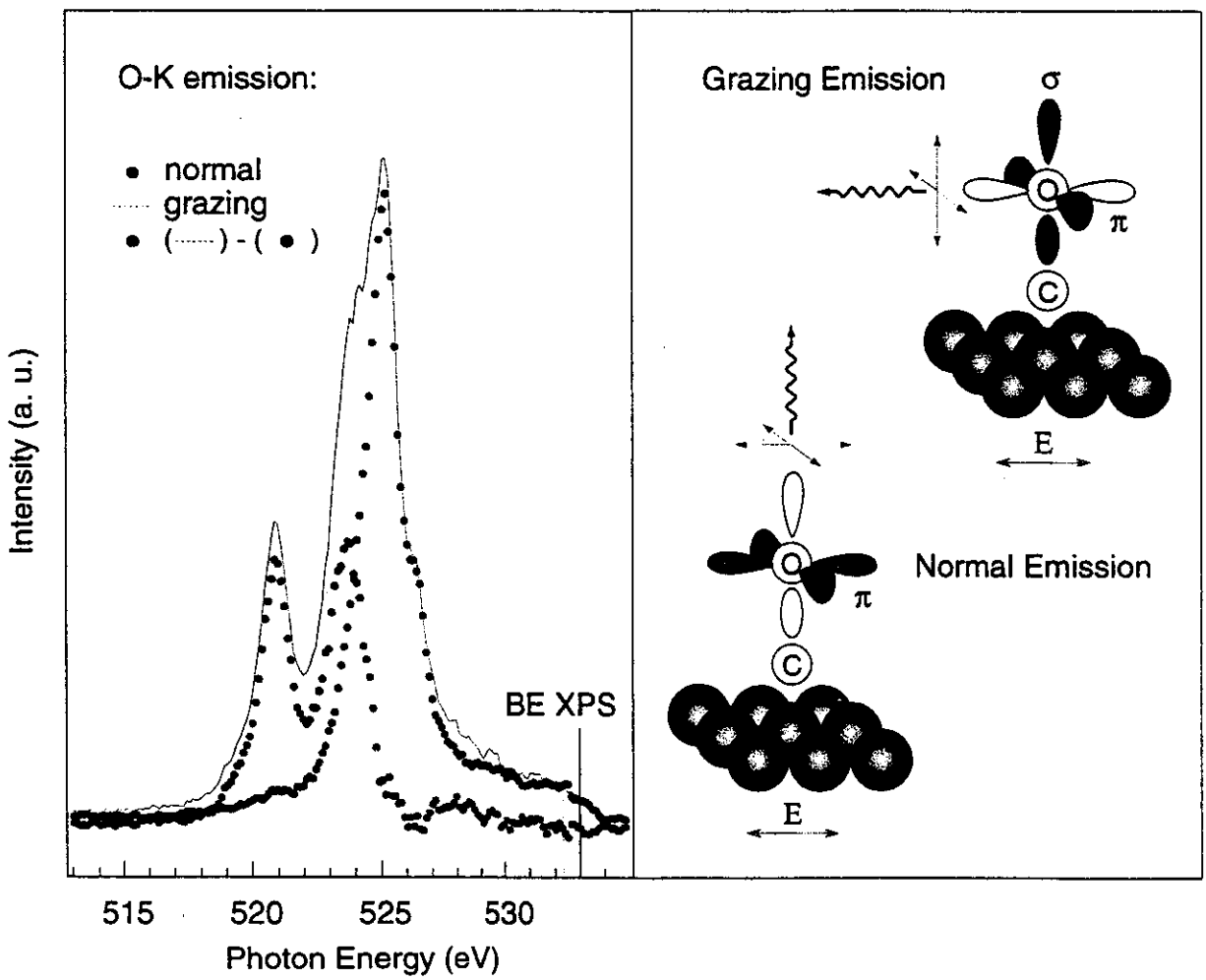
Nordgren et.al


Atom specific
O
C
O
C
O
C
5σ
1π
4σ
C1s
O1s
E
5σ
1π
4σ

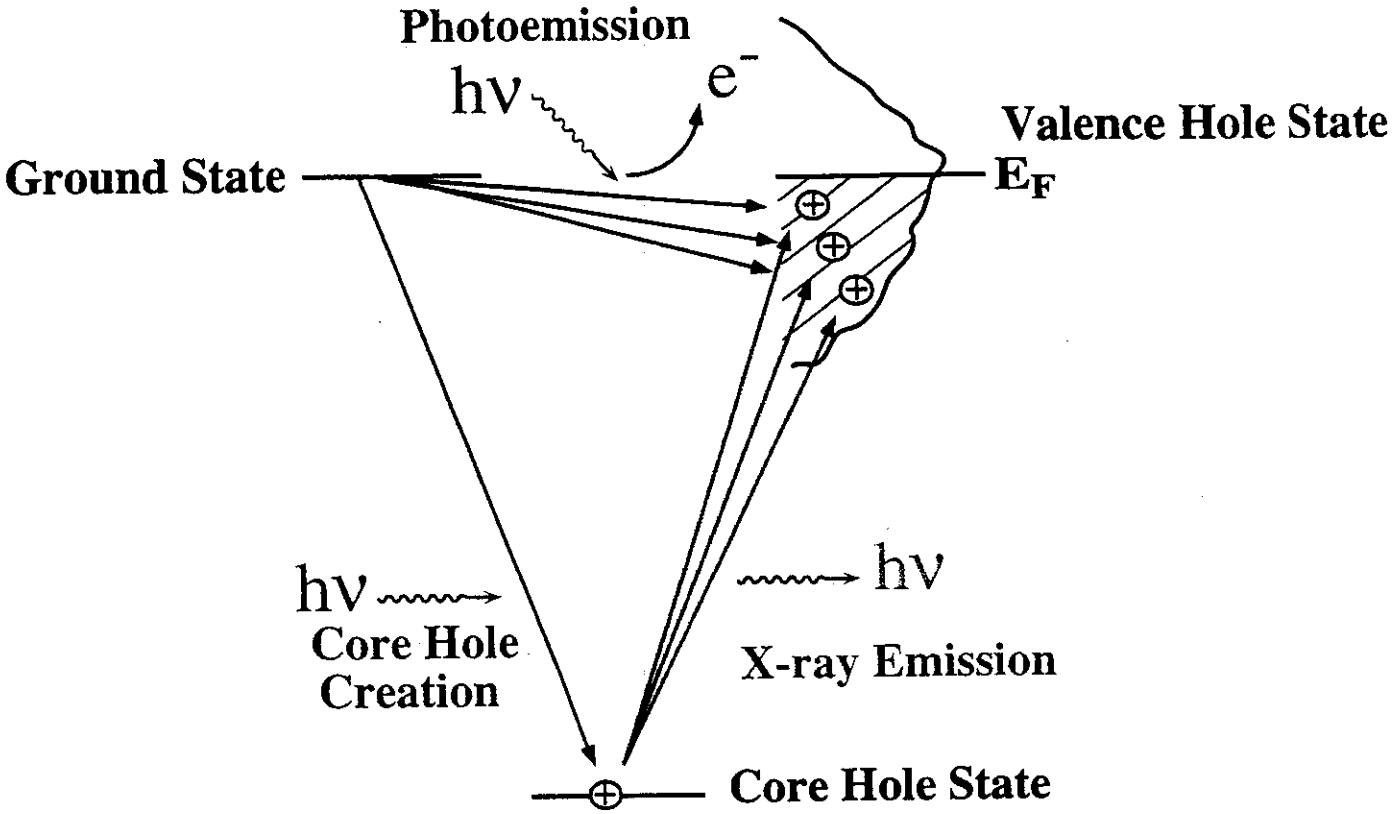

CO gas
C-K XES
O-K XES
Calculation
1 π
5 σ
4 σ
1 π
4 σ
5 σ
Intensity (a.u.)
10
5
0
10
5
0
Binding Energy (eV)

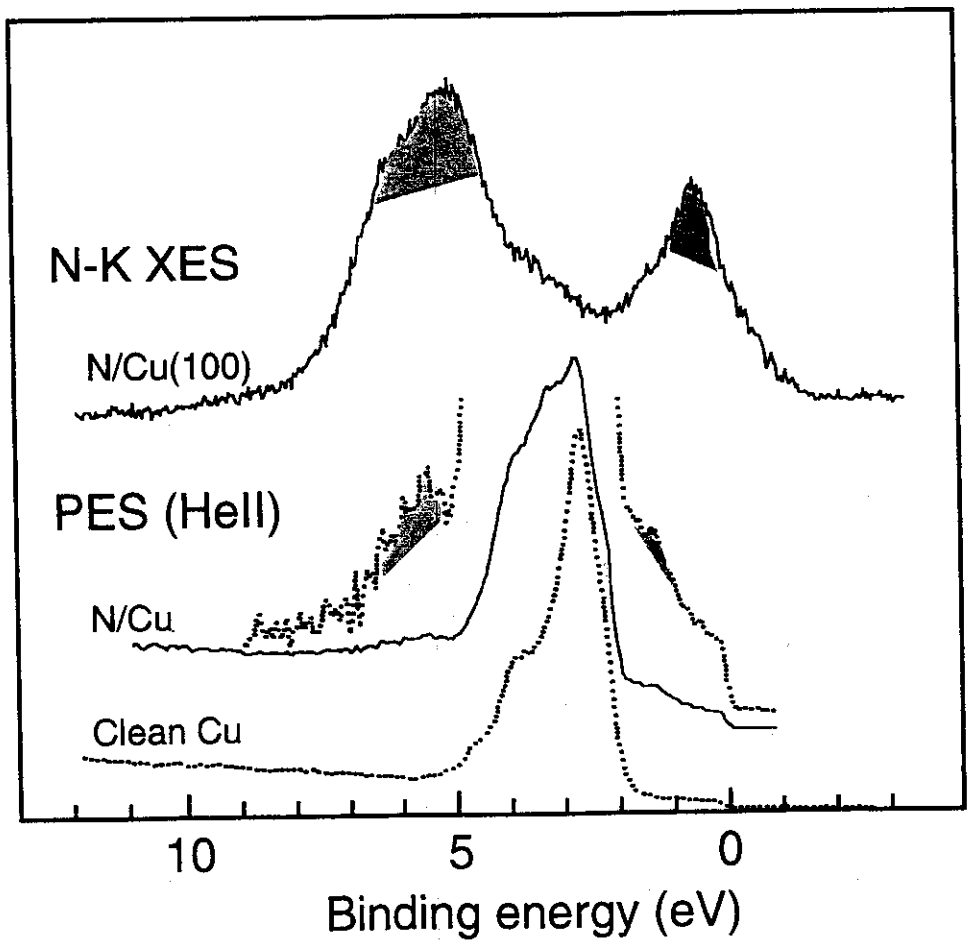
Orbital symmetry selective





XES and PES, the same final state

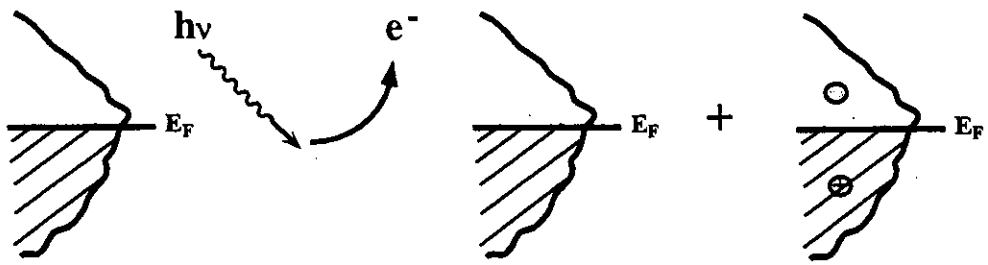


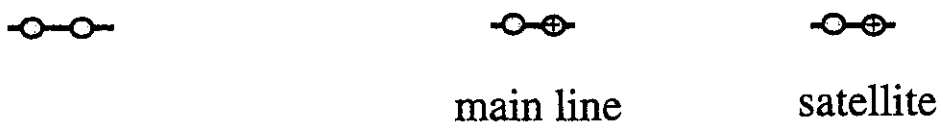


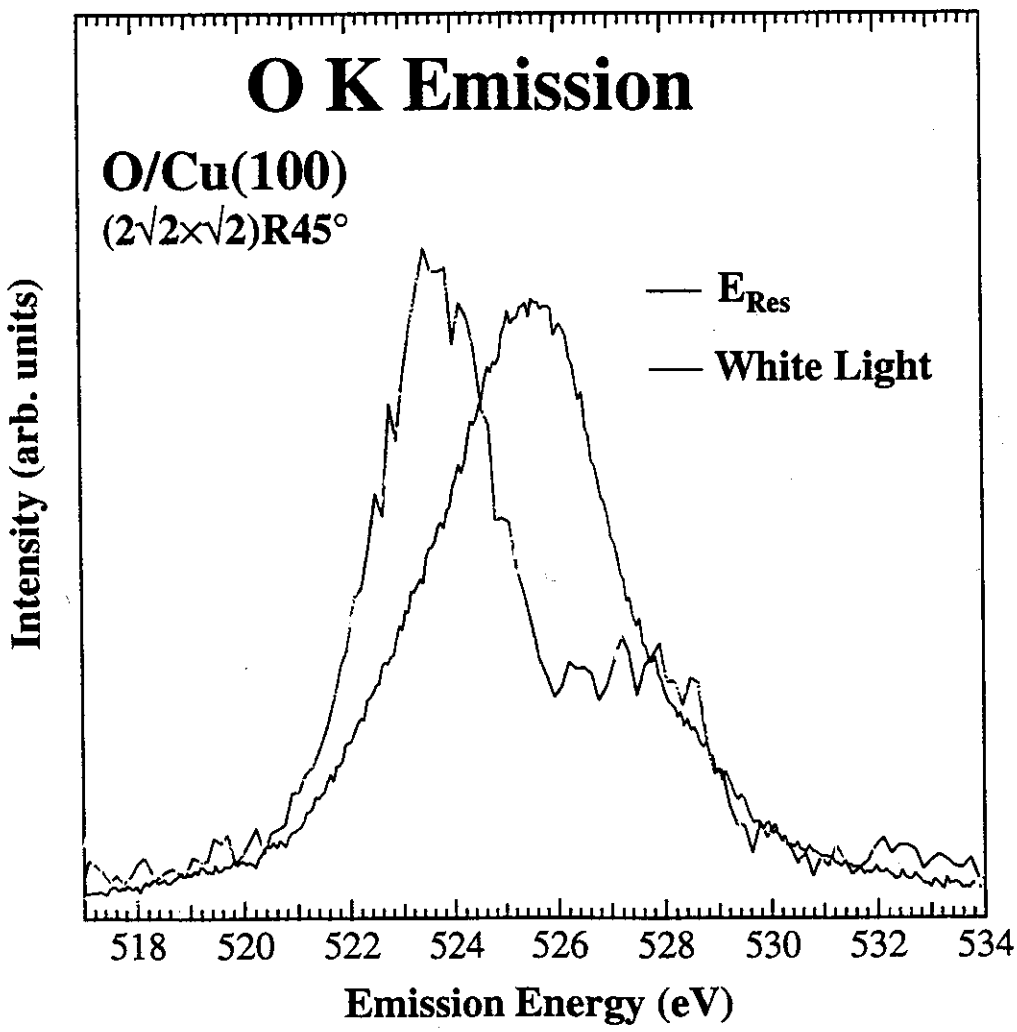
T. Wiell et al. Surf. Sci, 304, L451 (1995)

Why synchrotron radiation

- clean core hole states

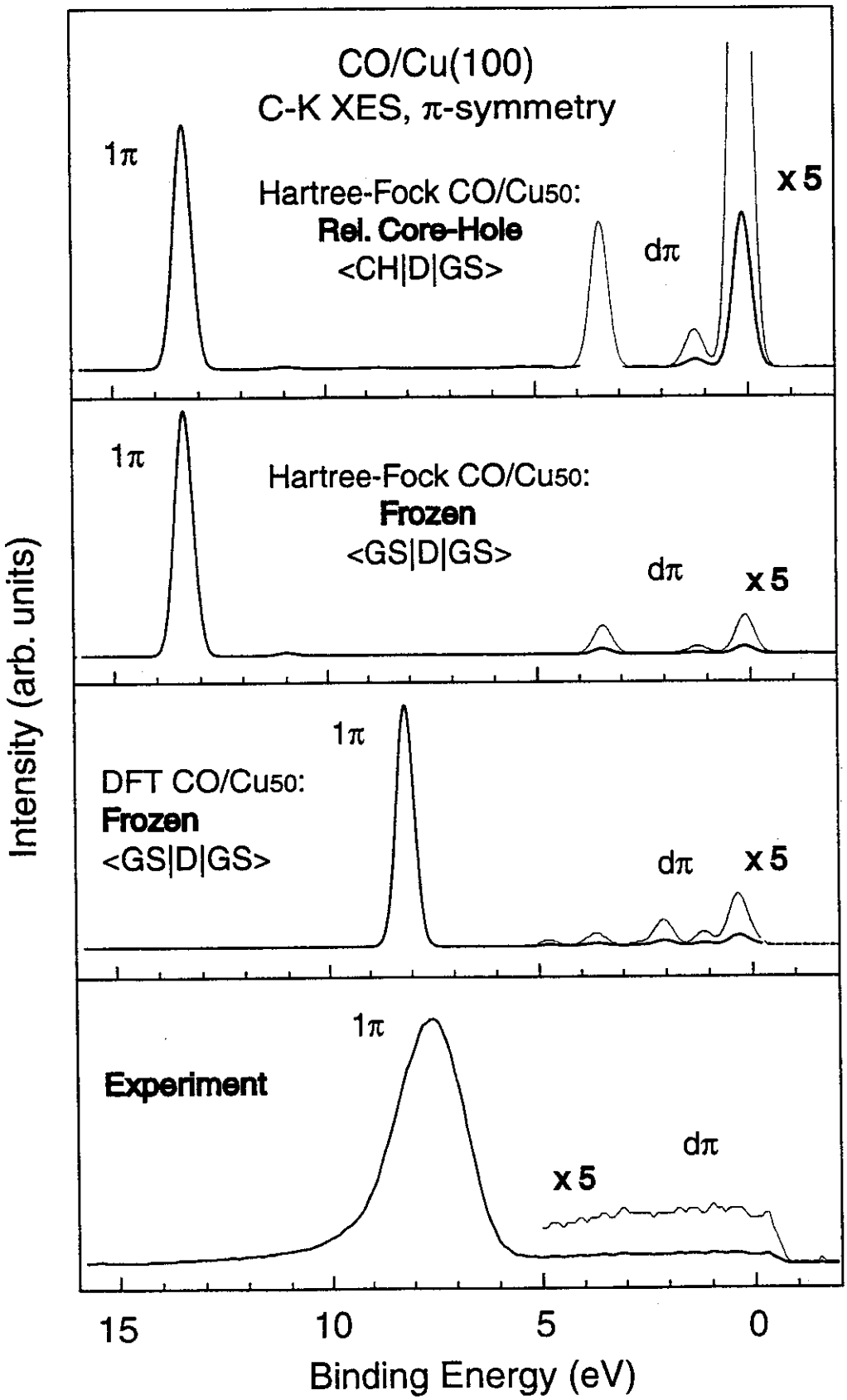






Core Hole Effects

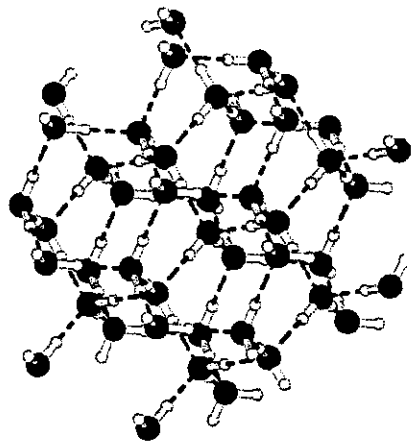
Intensities close to ground state discreption



Hydrogen bond of Water in I_h Ice

Hydrogen bond energy: 0.29 eV

Covalent bond energy: 4.8 eV



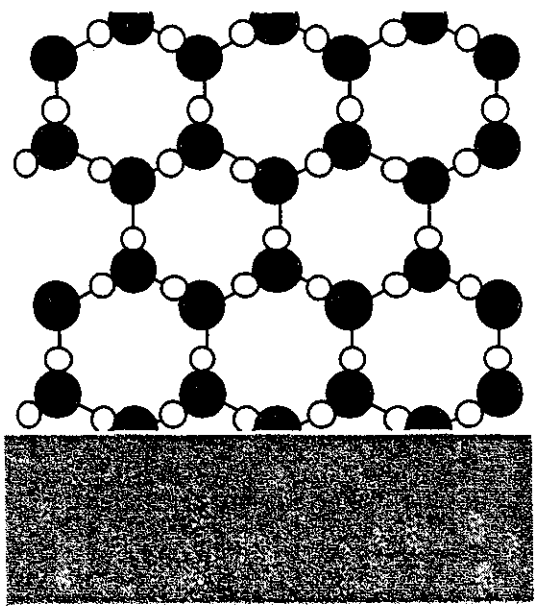
60% higher dipole moment of condenced water

PRL **82**, p3308 (1999)

Substantial covalent nature of hydrogen bond

PRL **82**, p600 (1999)

ice Ih film on Pt(111)



beamline I511

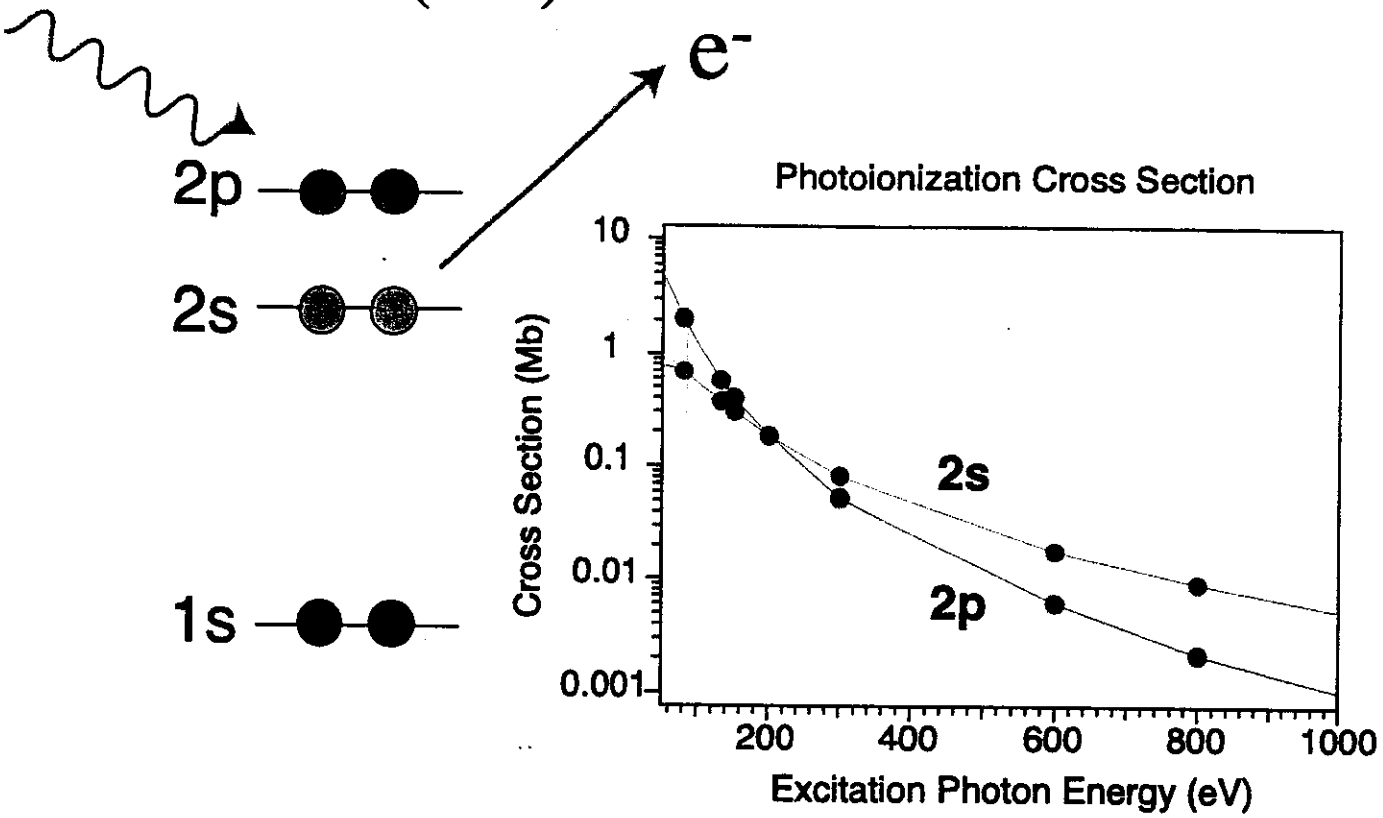
UHV Surface Science

PES, XAS and XES station

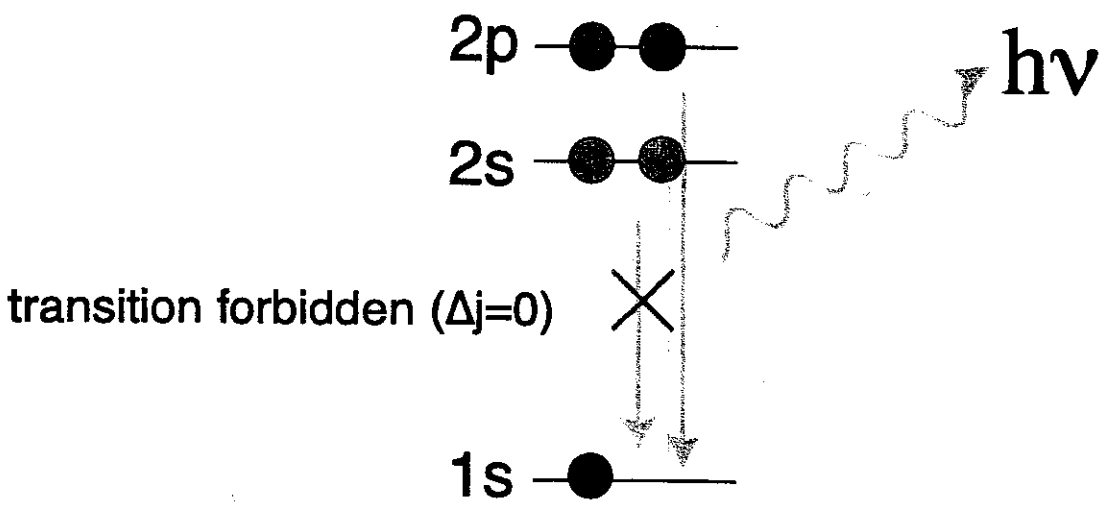
MAX-2

XES and PES

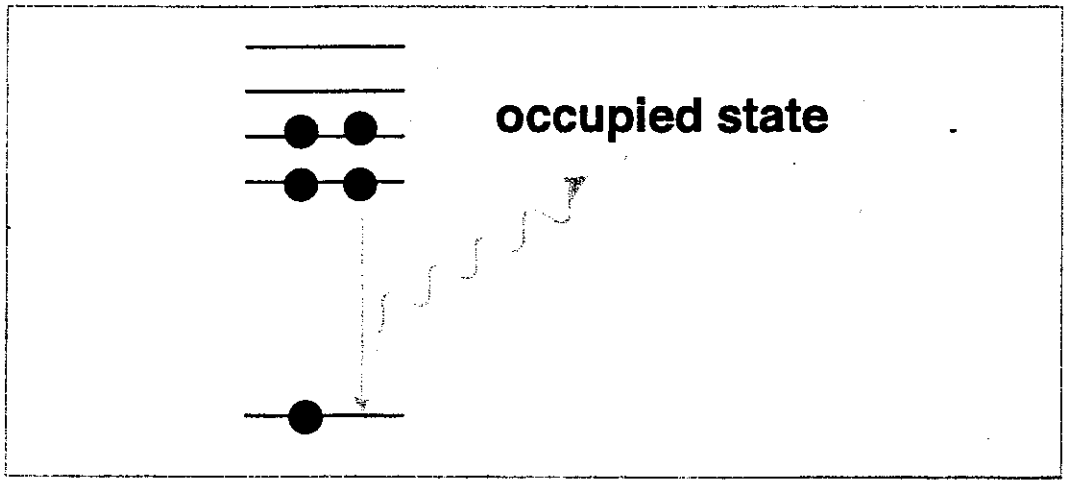
Photoemission (PES)

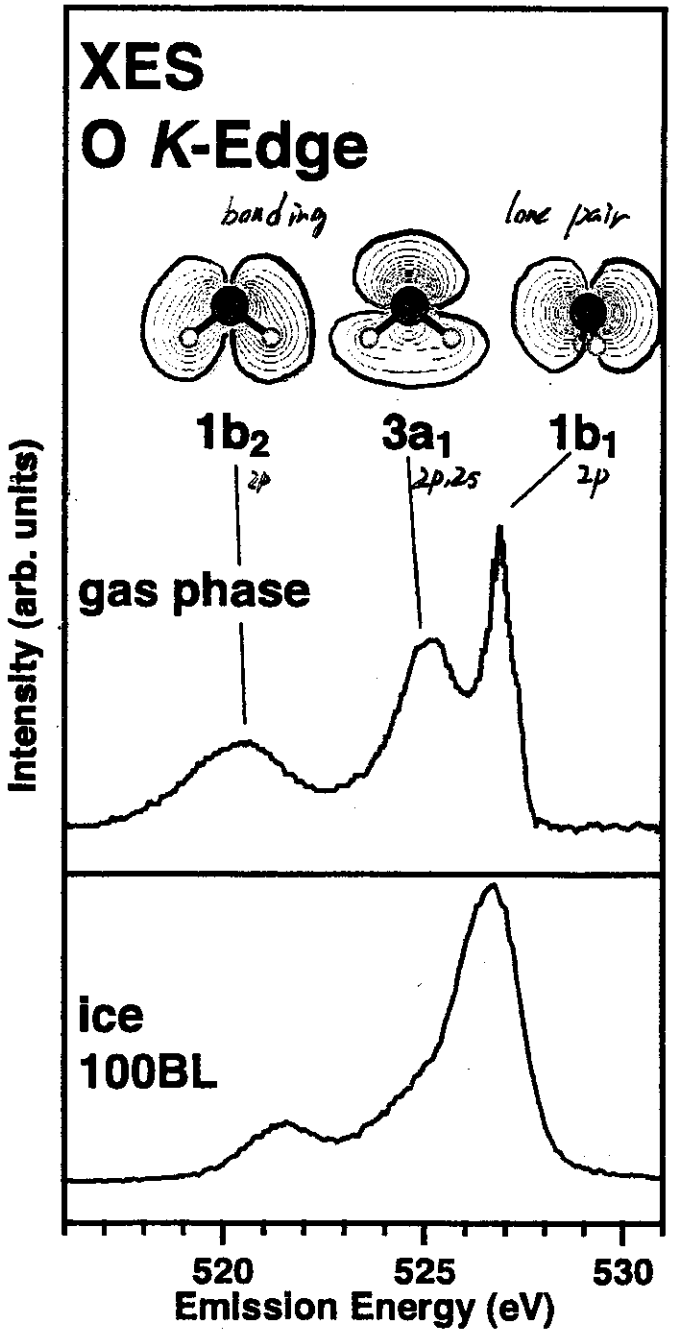


X-ray emission (XES)

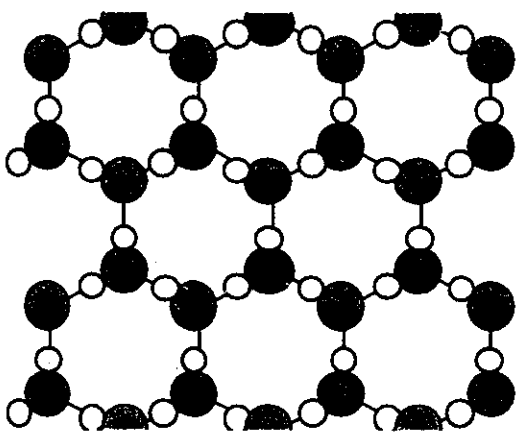


X-ray emission spectra of water

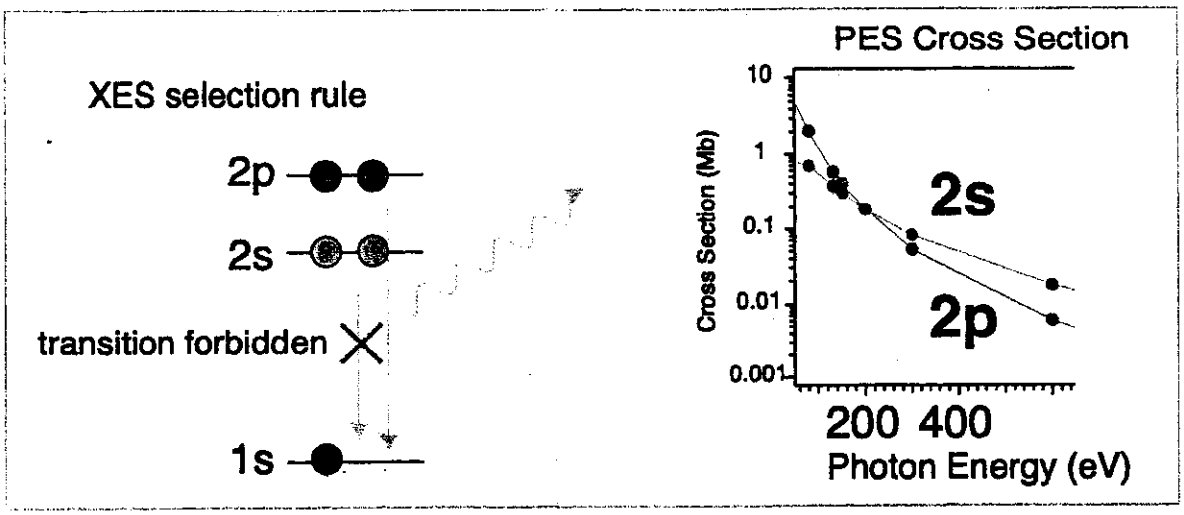


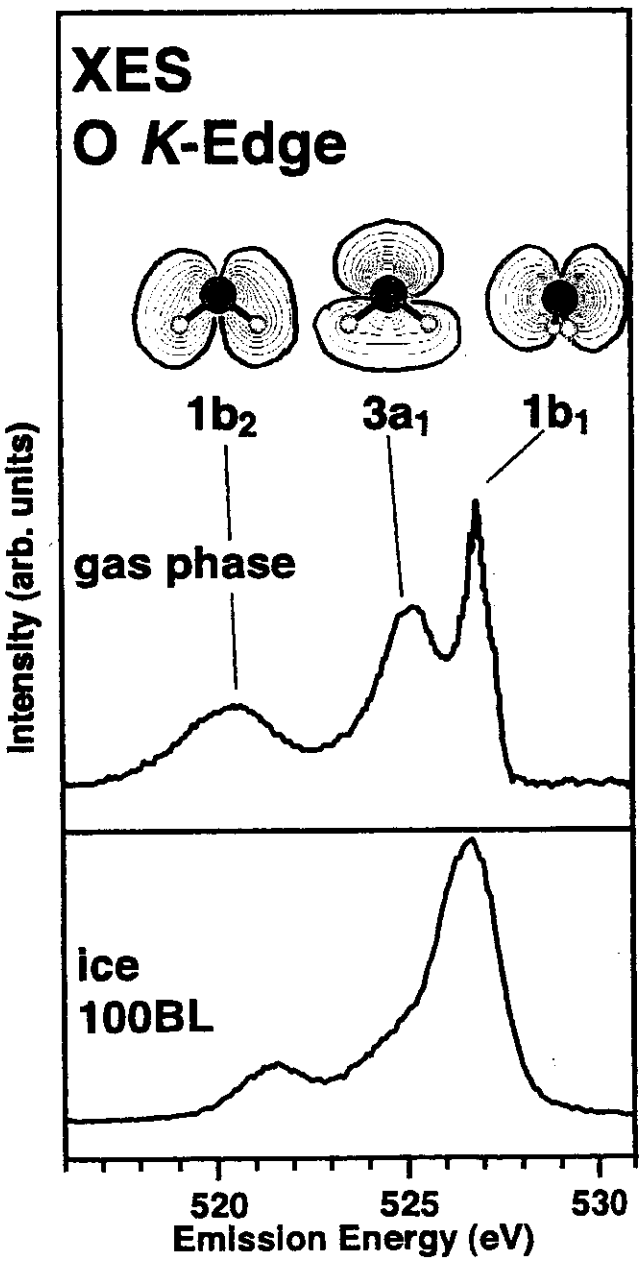


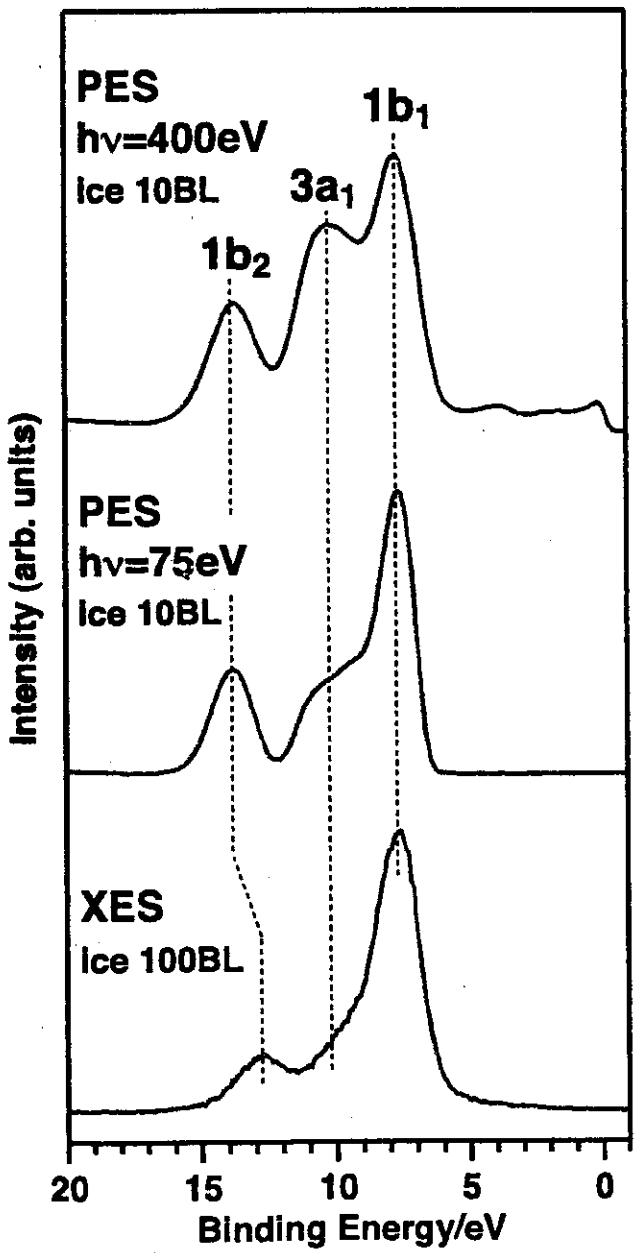
ice Ih film on Pt(111)



XES and PES spectra of water

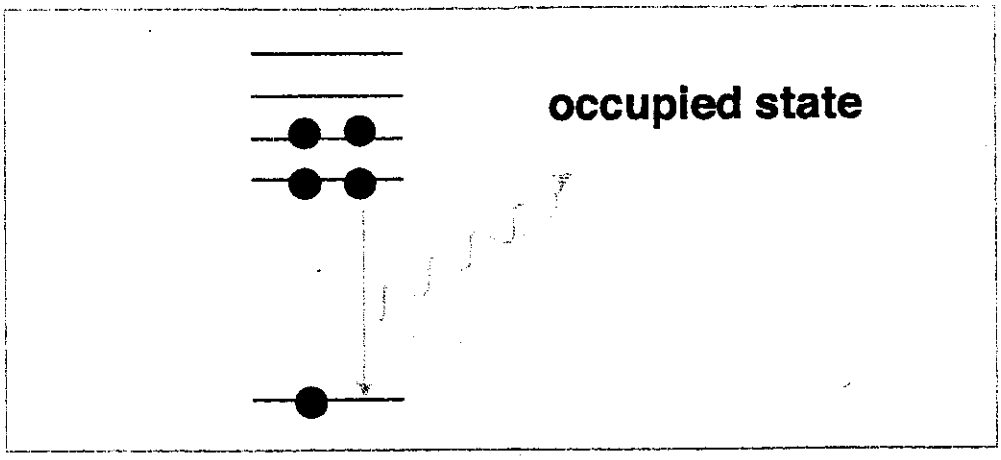


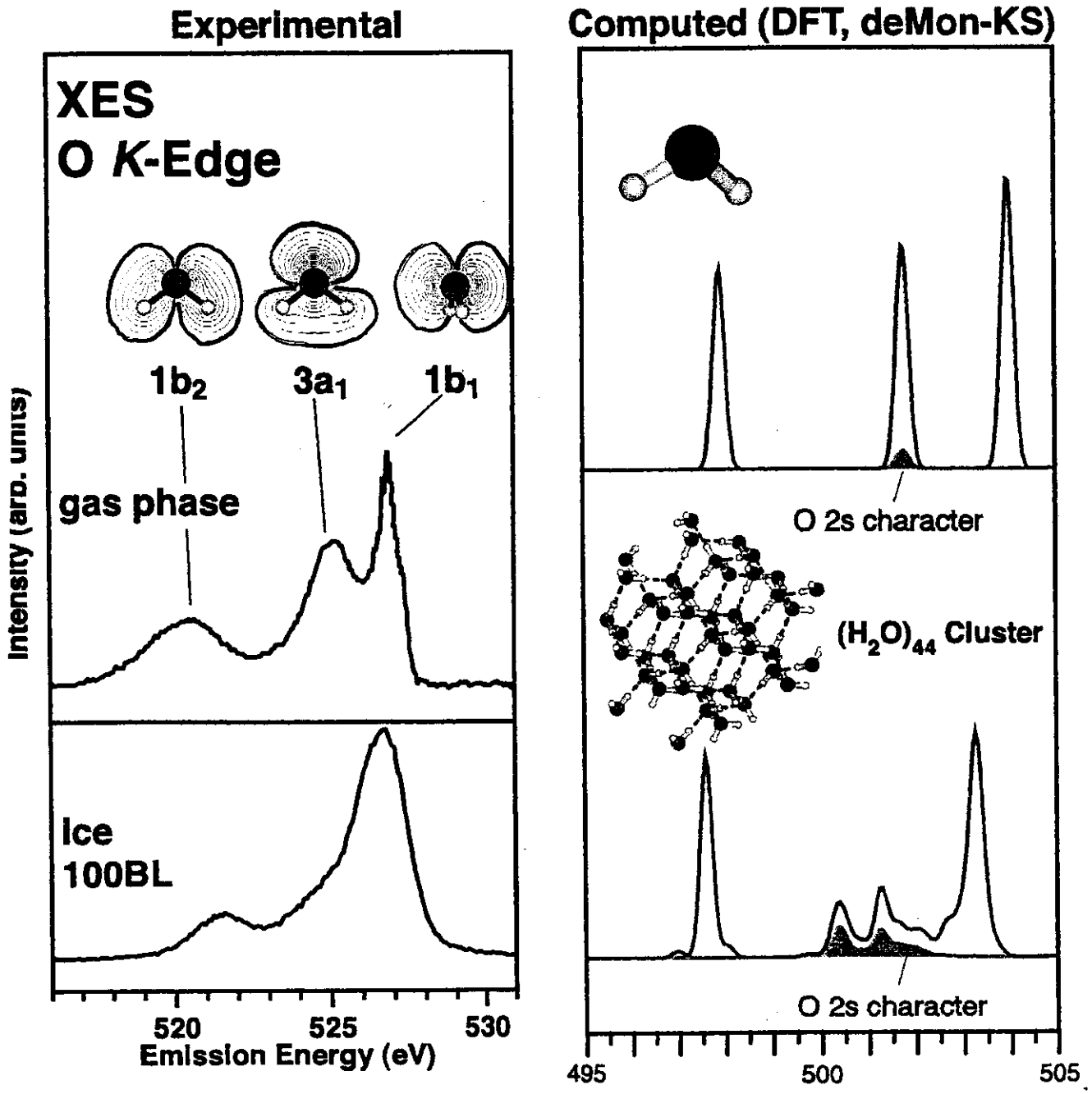




XES, selection rule, why orthogonal

X-ray emission spectra of water





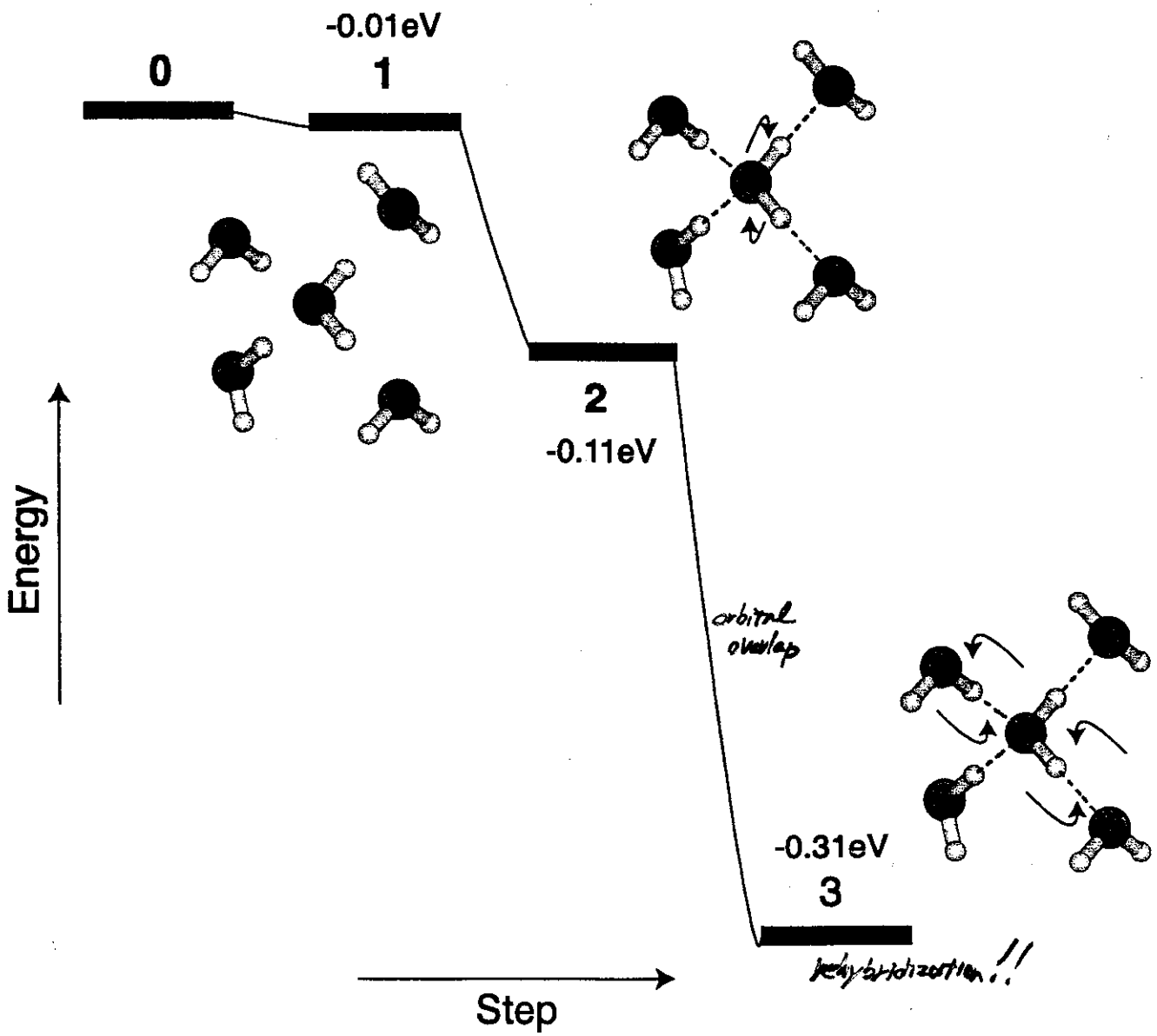
binding effects, origin of

CSOV analysis

Constrained space orbital variation calculation for water pentamer as a model of ice

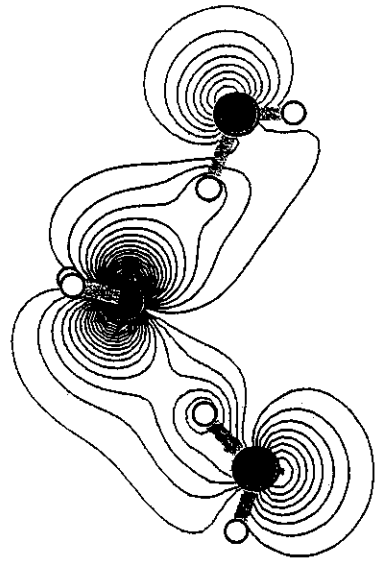
Bond energy in different configuration

0 Separate
1 Initial repulsion
2 Internal polarization
3 Charge transfer



Molecular Orbitals shows overlap

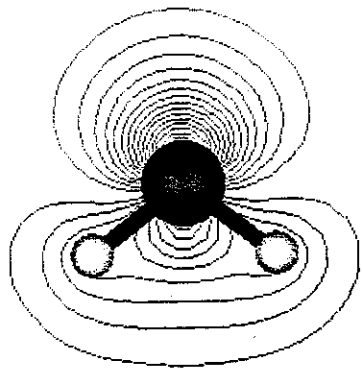
Covalency ?



Formation of Bandstructure

Occupation of both bonding and antibonding orbitals ?

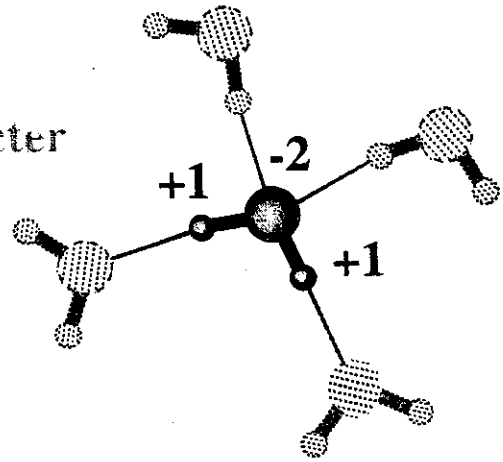
Rehybridization of $3a_1$



More 2s

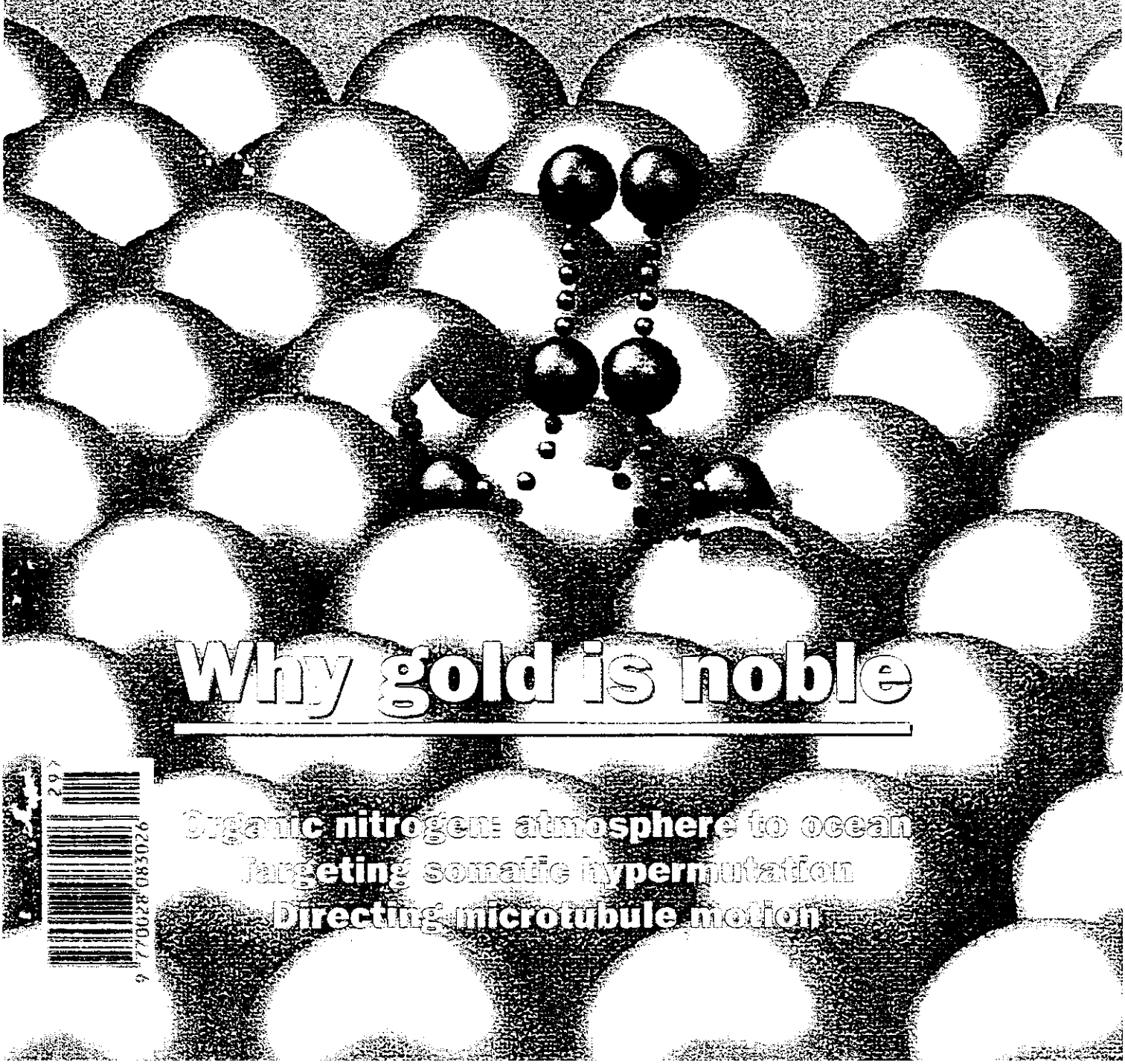
increased lone pair character

weakend O-H bond



nature

INTERNATIONAL WEEKLY JOURNAL OF SCIENCE



Why gold is noble

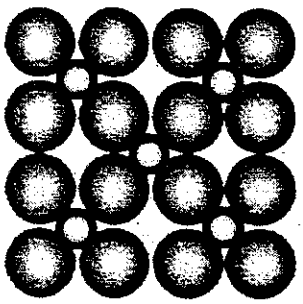
Organic nitrogen: atmosphere to ocean

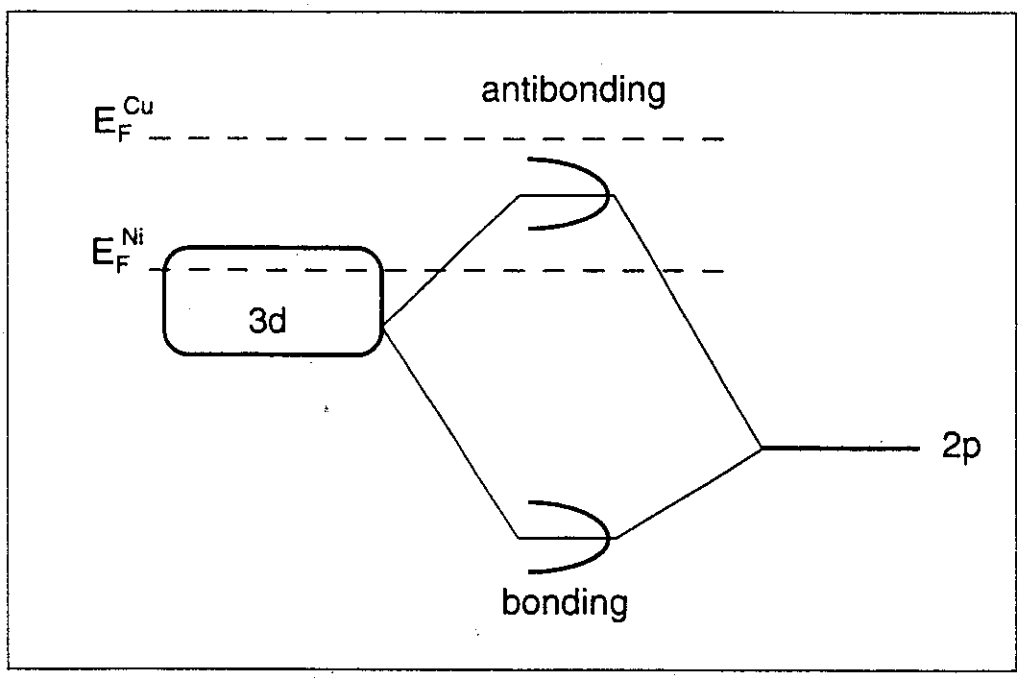
Targeting somatic hypermutation

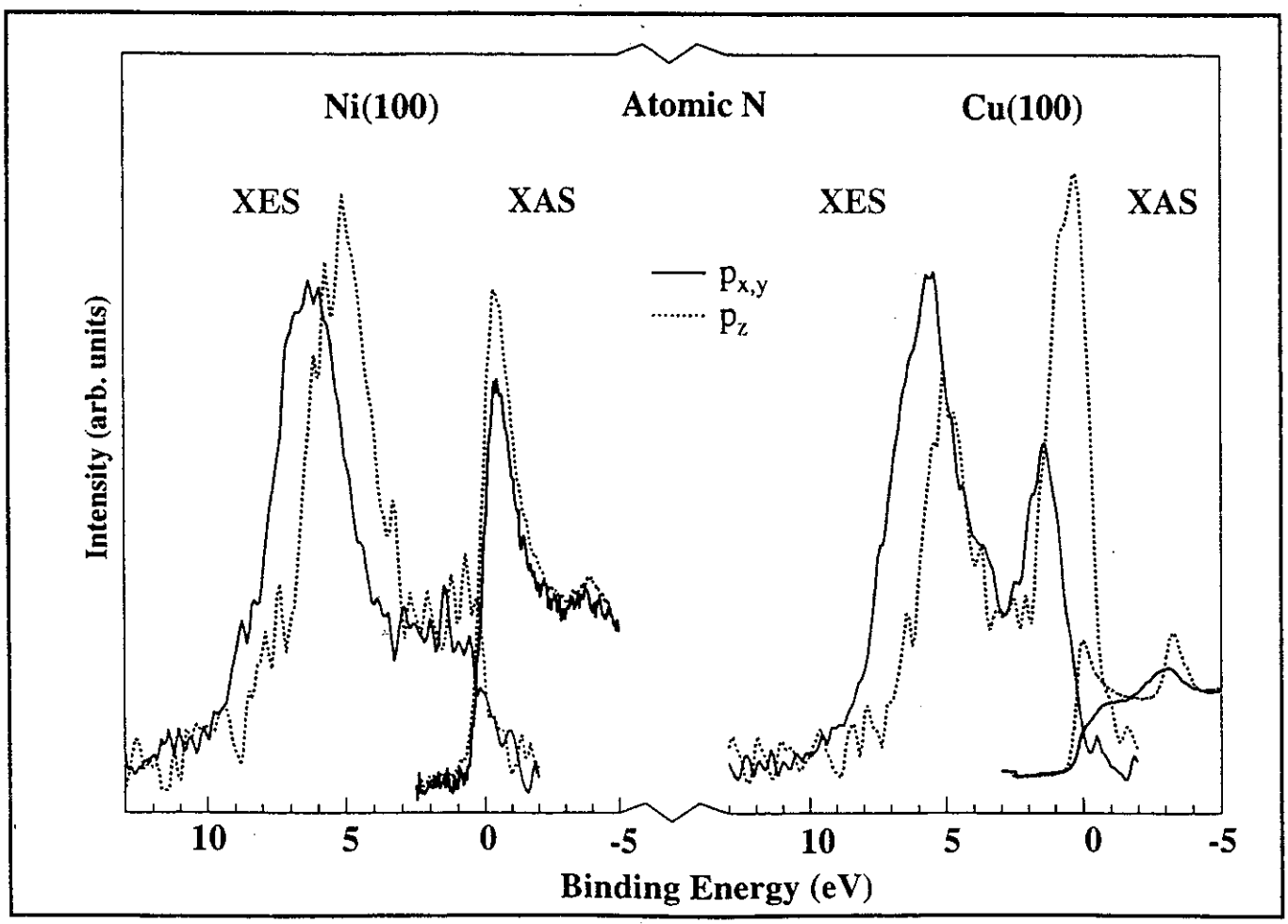
Directing microtubule motion

9 770028 083026

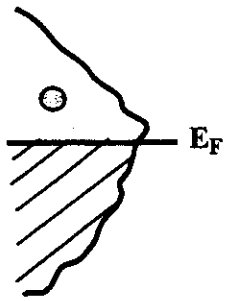
ATOMIC ADSORBATES
C, N and O on Ni and Cu

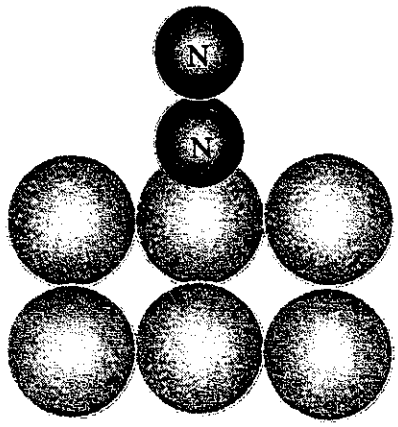




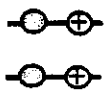


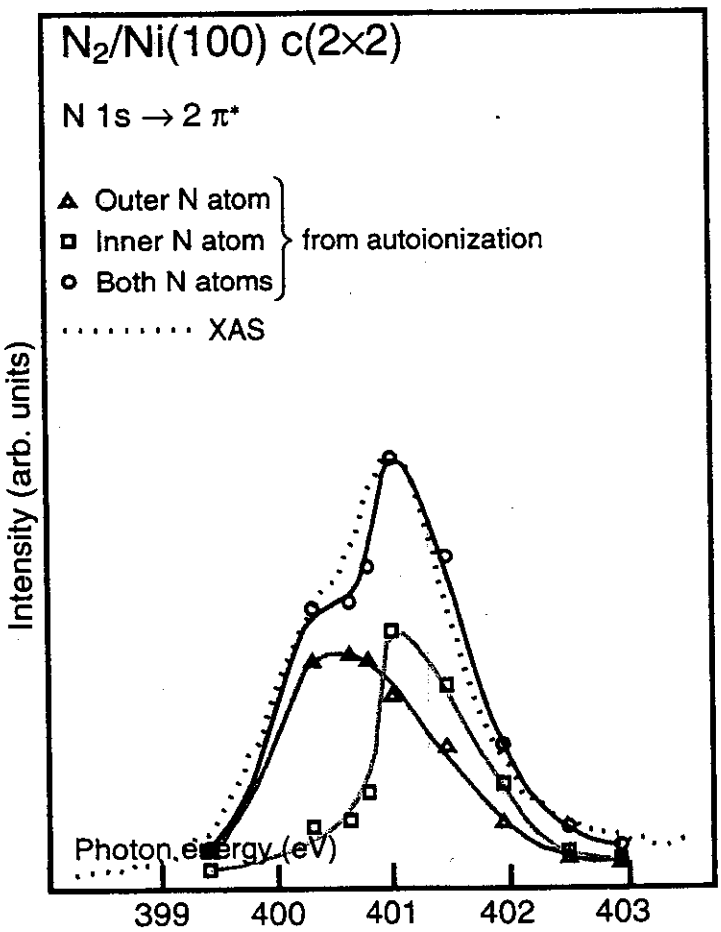
Atom Selective Excitation
Chemical Shift

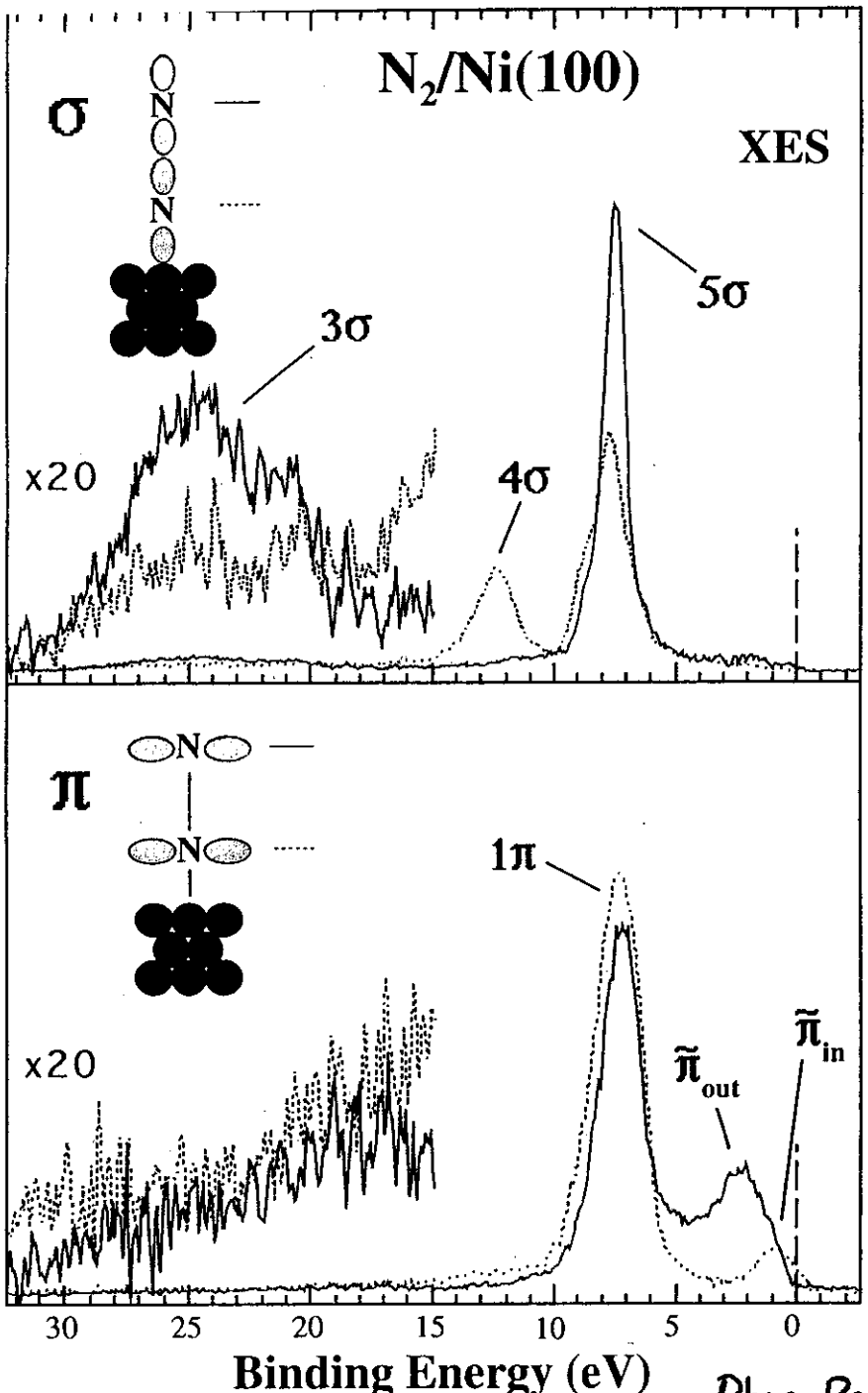




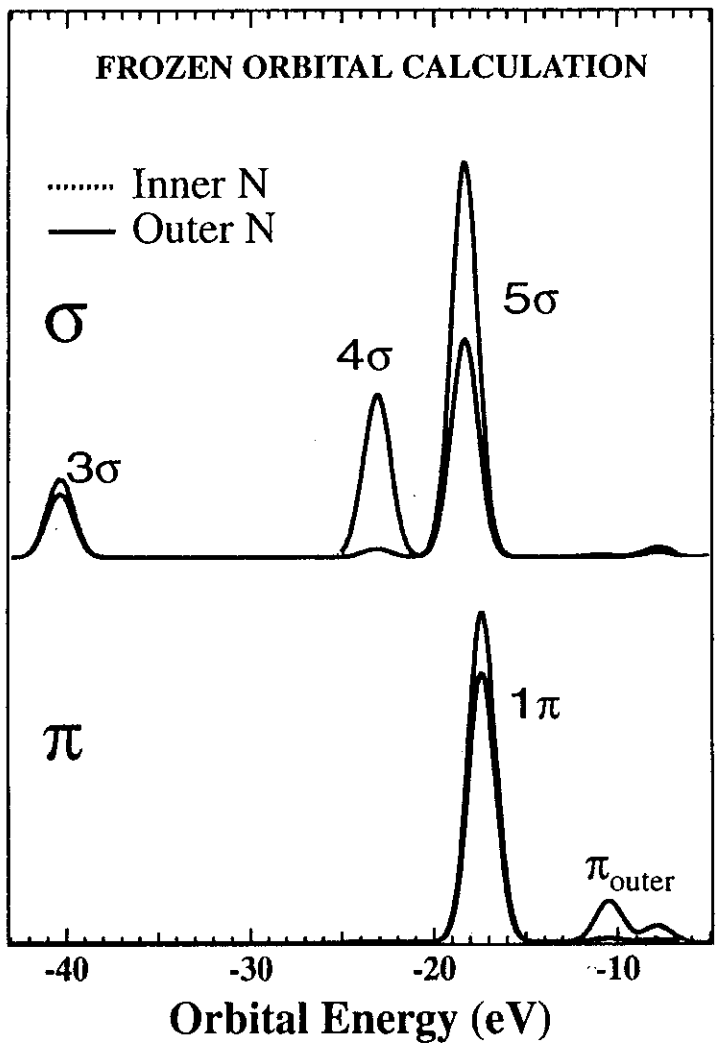
ΔE=1.5 eV





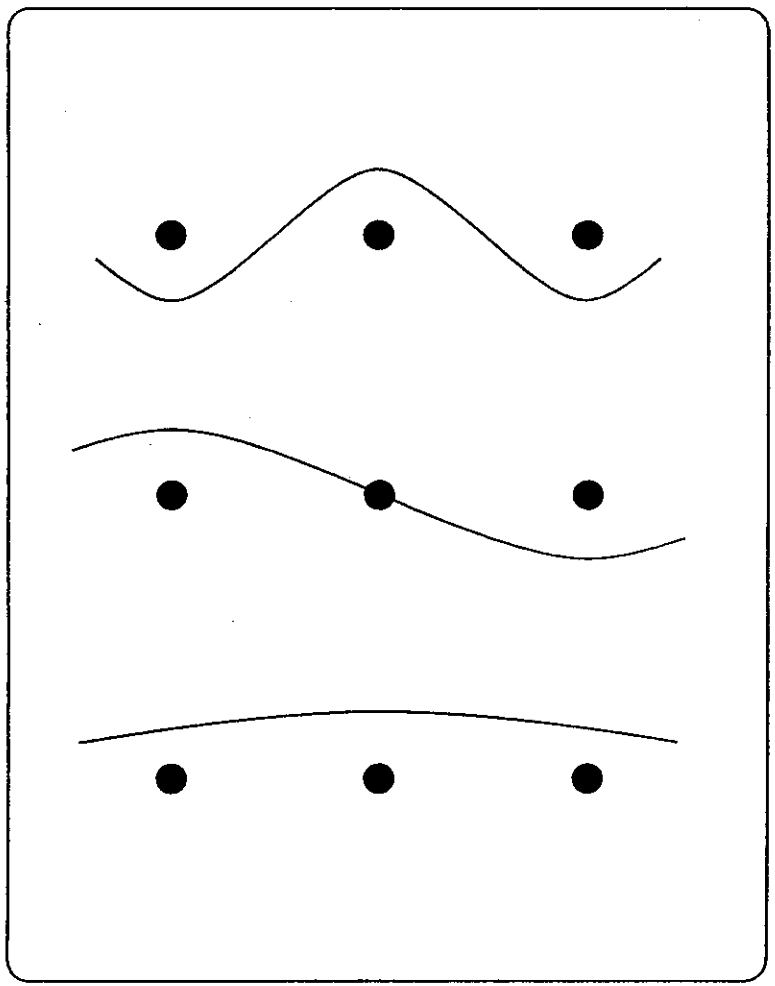


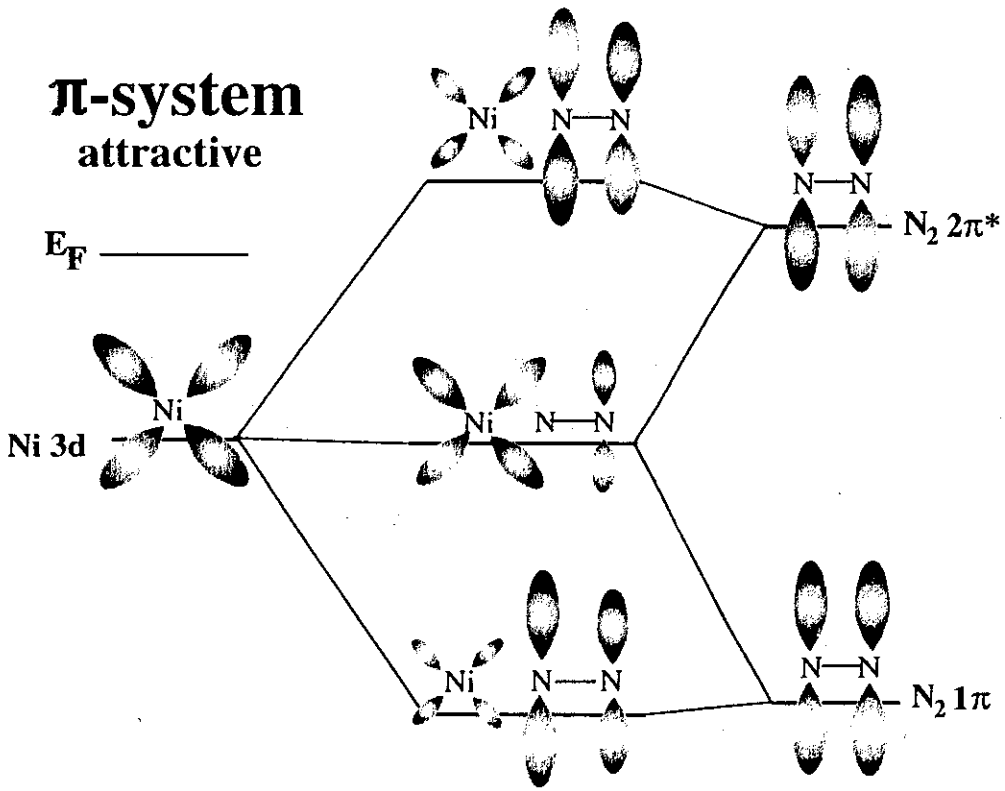
Theory

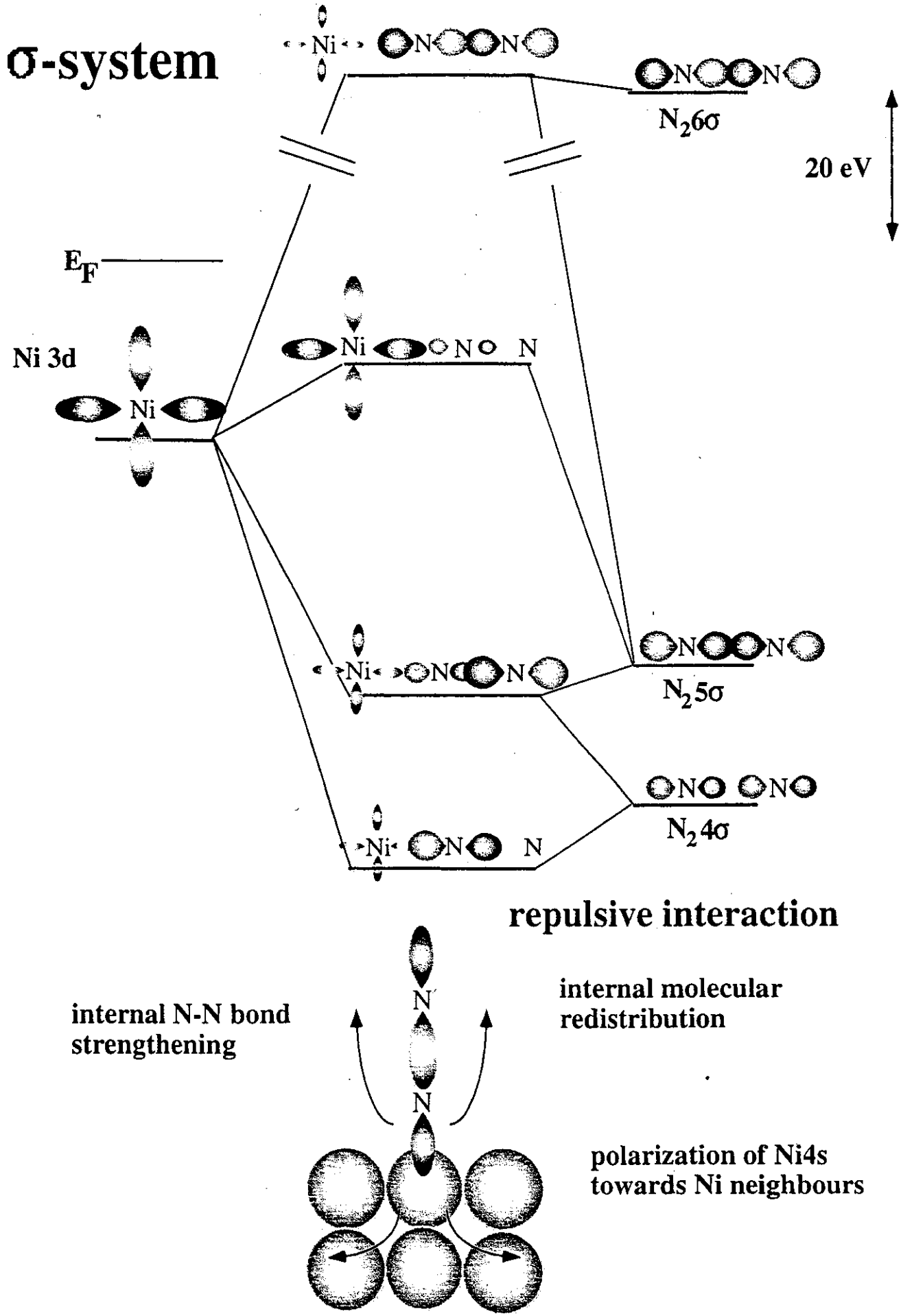


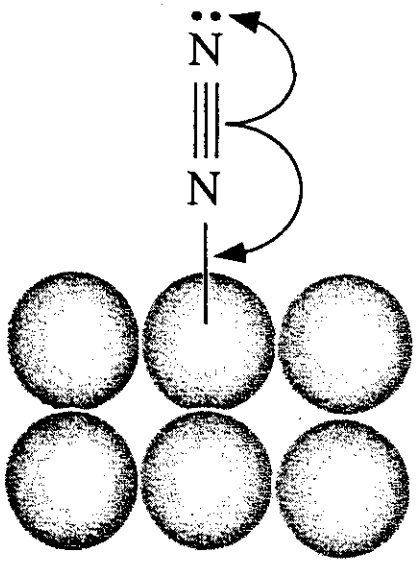
Phys. Rev. Lett 78, 2847 (1997)
Phys. Rev. B 57, 9275 (1998)

Allylic Configuration
π-Orbital structure of 3 atoms





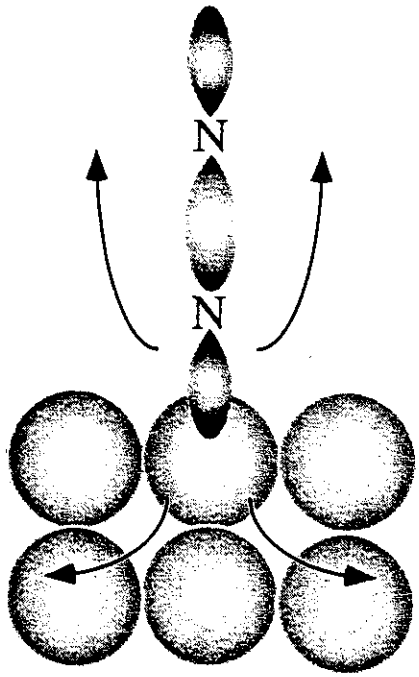

σ-system
Ni
N
N
N2 6σ
20 eV
EF
Ni 3d
Ni
Ni
N O N
N2 5σ
N2 4σ
repulsive interaction
internal N-N bond strengthening
internal molecular redistribution
polarization of Ni4s towards Ni neighbours



π-system

attractive interaction

N-N bond weakening



σ-system

repulsive interaction

N-N bond strengthening

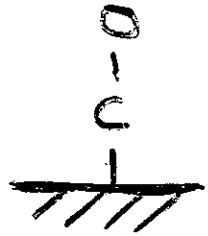
COMPENSATION EFFECTS

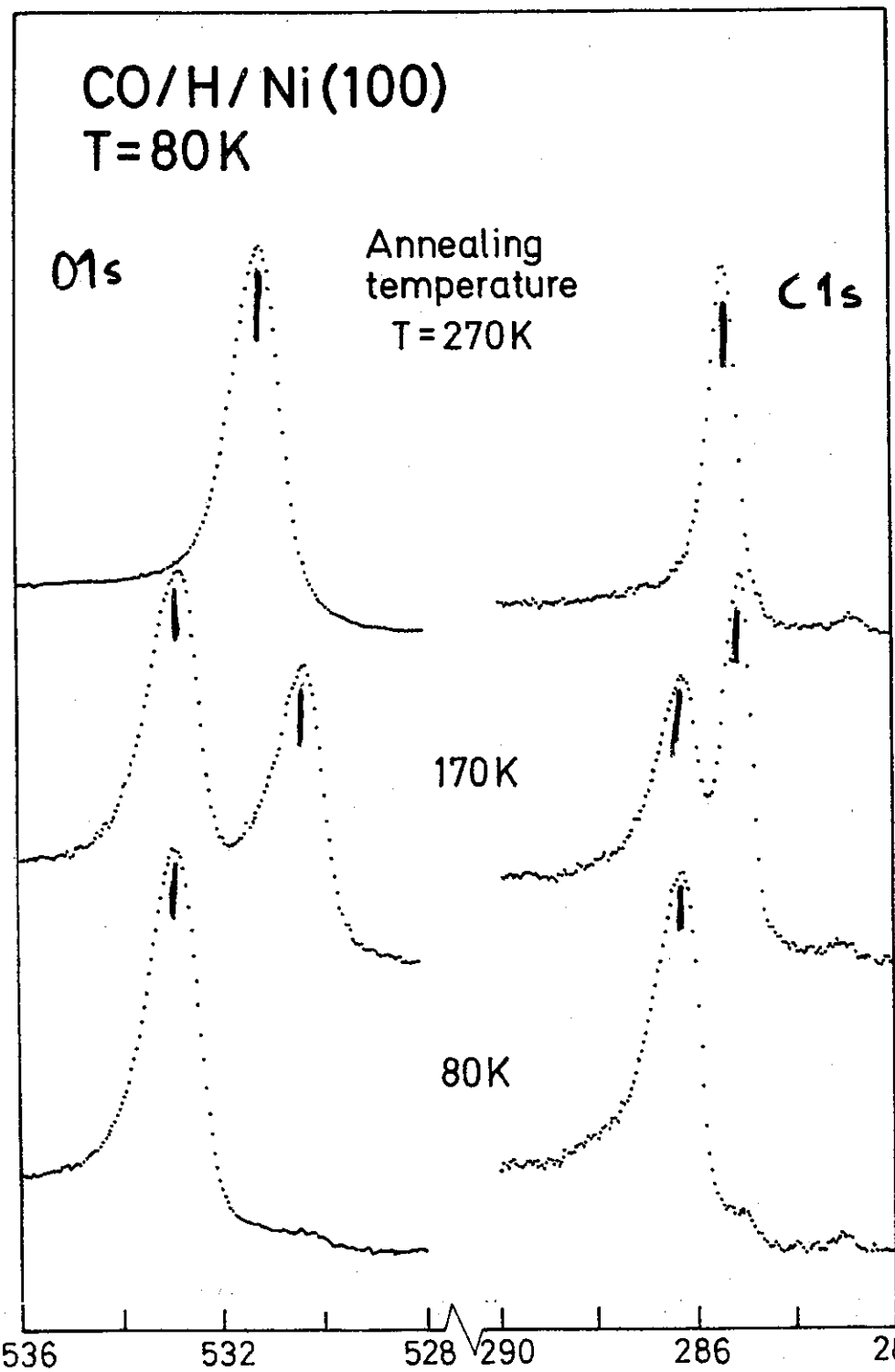
ADSORPTION ENERGY

N-N BOND ENERGY

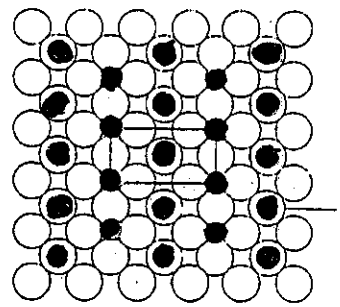
Different adsorption sites

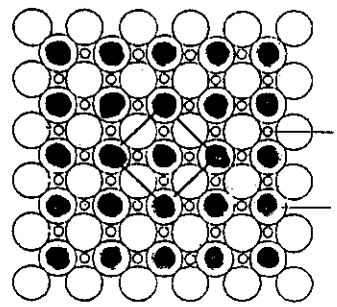
XPS





Disordered bridge

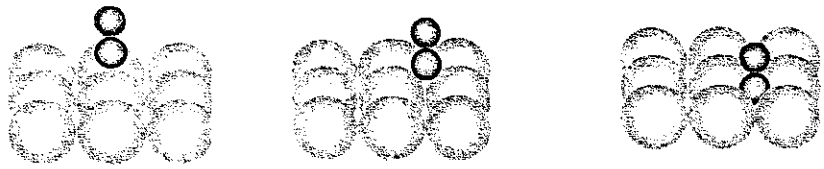




Δ O1s 2.5ev Δ C1s 1.1 eV

Antonsson et. al J. El. spec. 54/55, 601

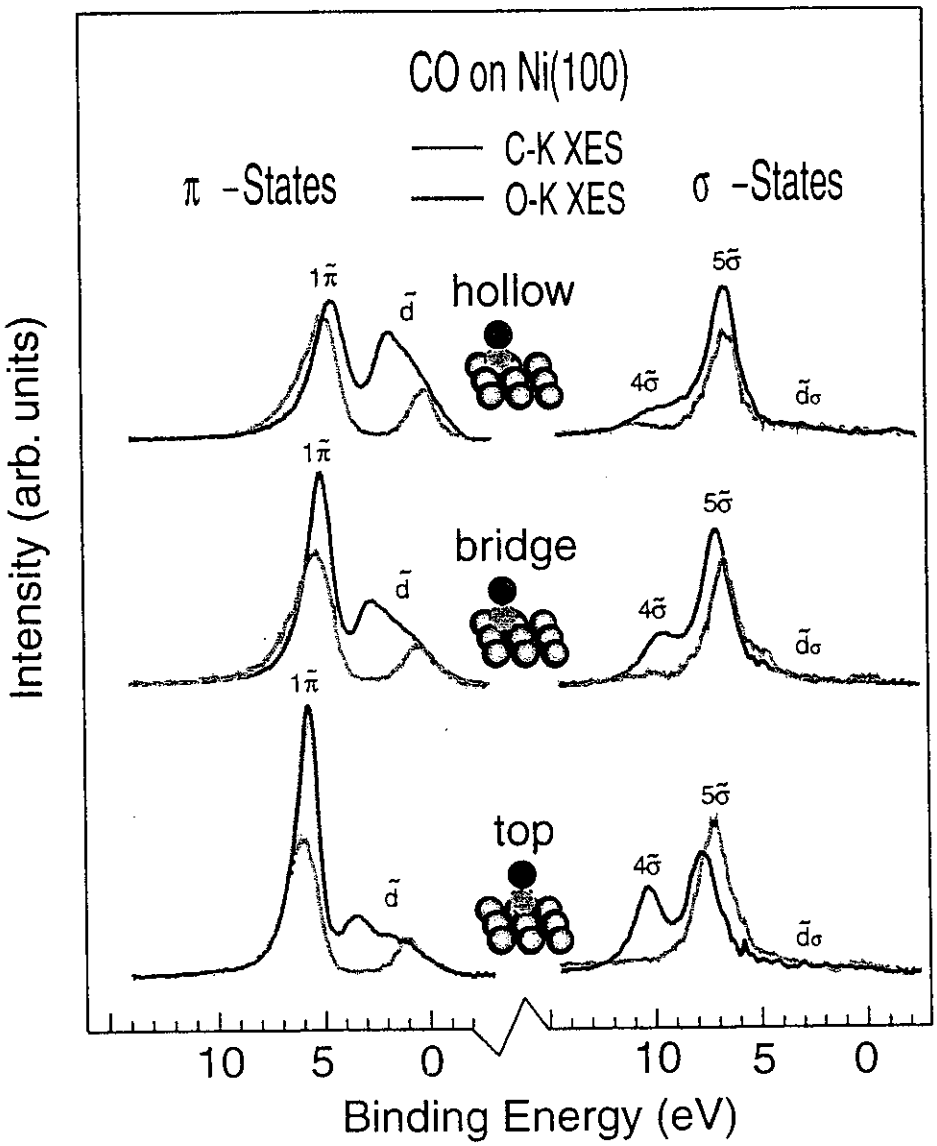
Site Dependent Adsorption of CO



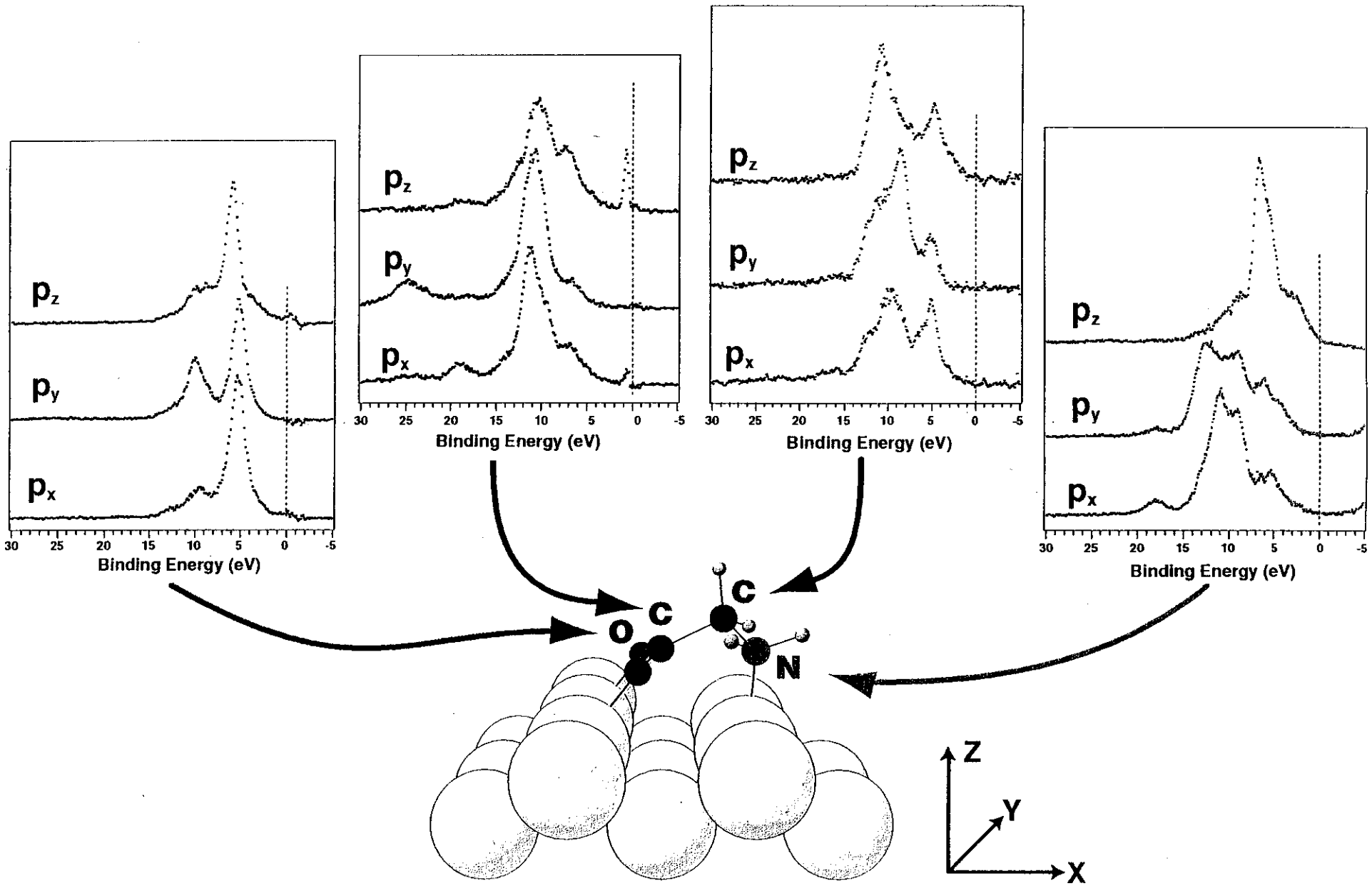
on top **bridge** **hollow**

small differences in adsorption energetics

rich chemistry with many different phases



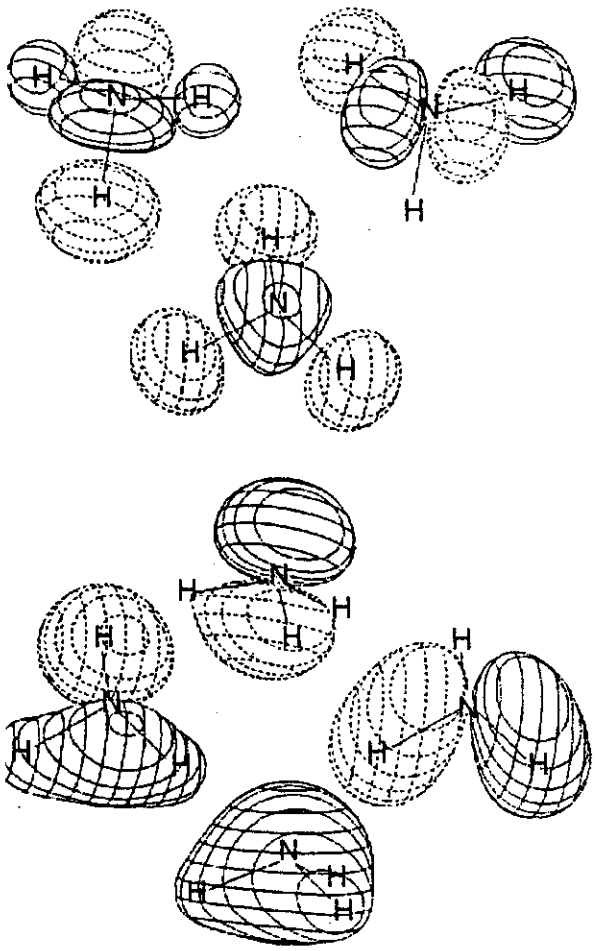
Phys. Rev. Lett. 85, 3309 (2000)

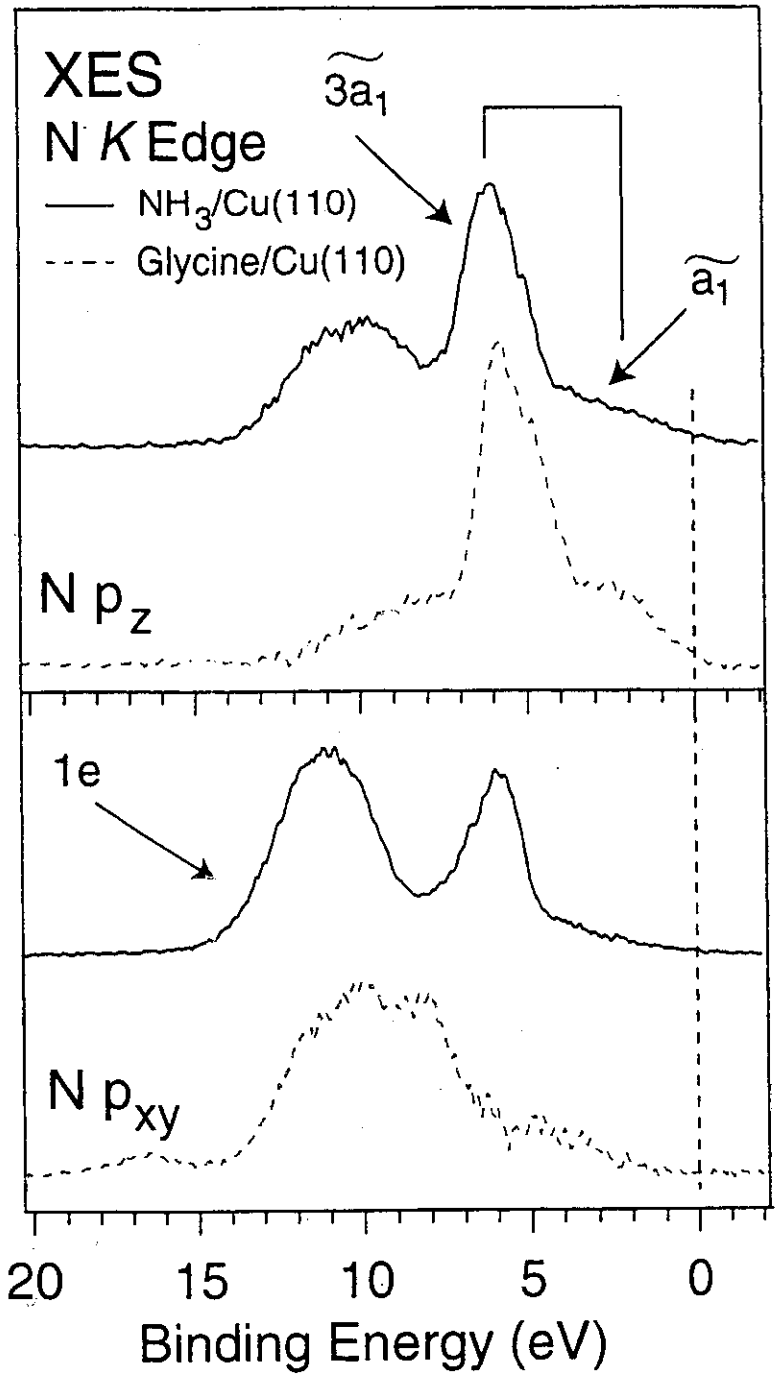


Glycine Cu(1$\bar{1}$0)

J. Chem. Phys. 112, 1946 (2000)

Comparision Ammonia/Glycine on Cu(110)





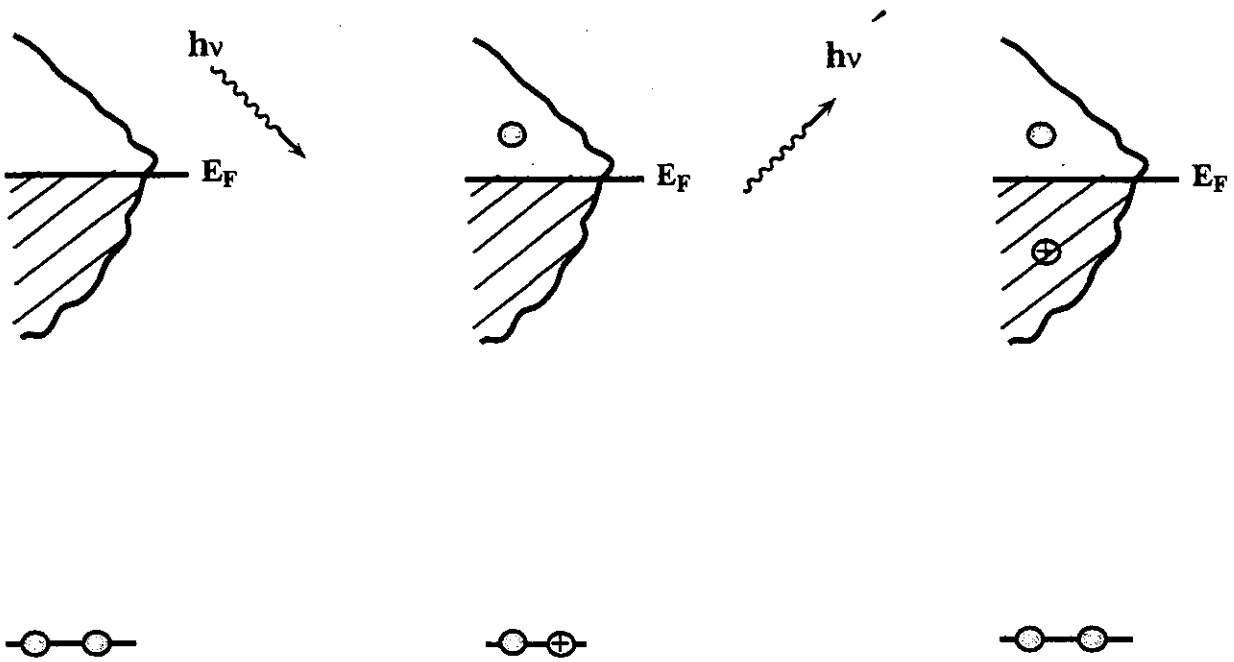
* The glycine "1e" type MOs are broadened

* Perpendicular adsorption geometry of the amino-group of glycine

→ Maximize metal overlap of frontier (σ) type orbitals

* A larger signature of substrate hybridization is found for glycine

Resonant Inelastic X-ray Scattering (RIXS)



Final state e-h pair

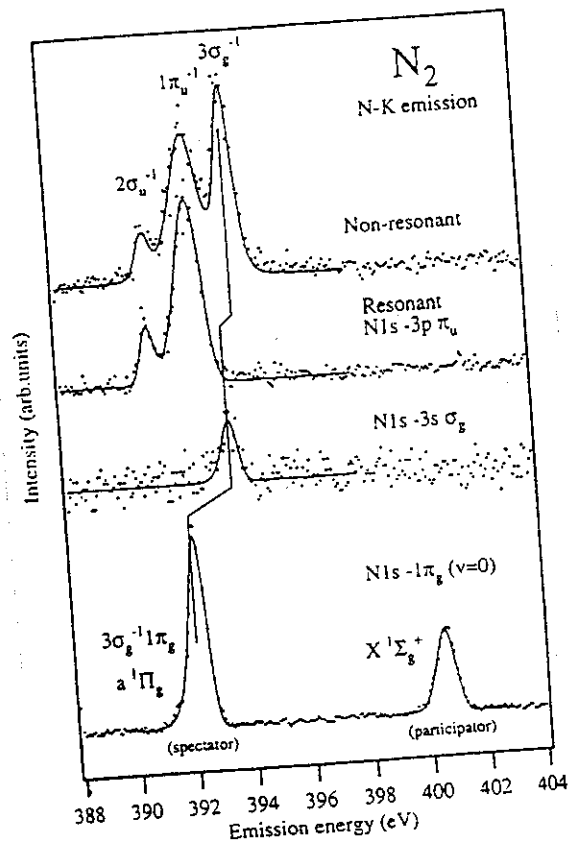
Two dipole excitations

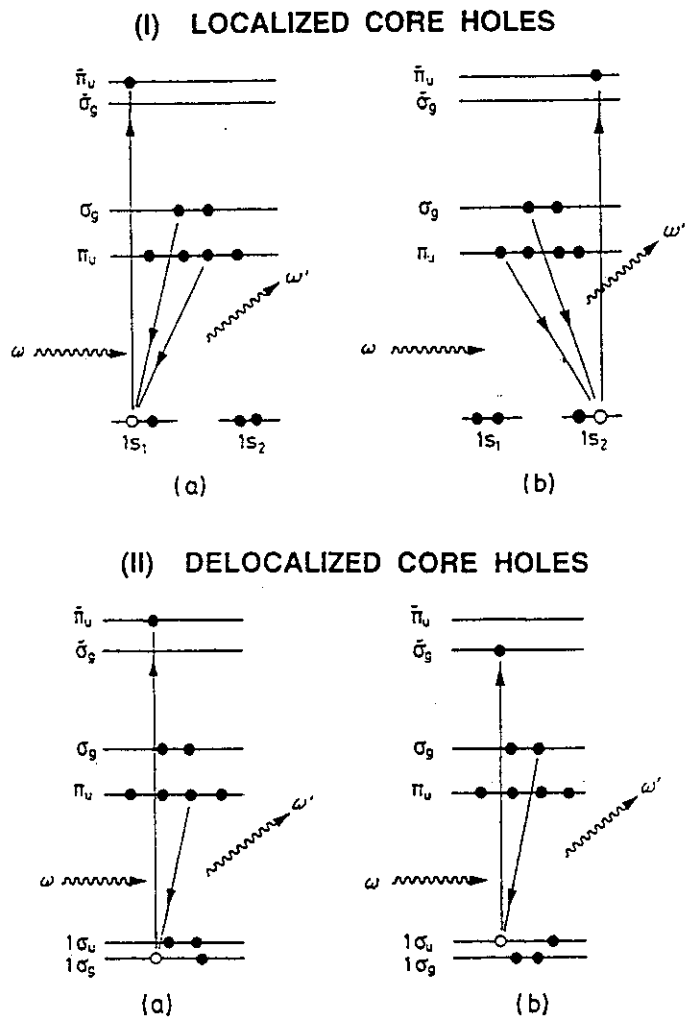
Free molecules
parity selection rules
g--u excitations (inversion symmetry)

Solids
momentum conservation (k-vector)

Free Molecules

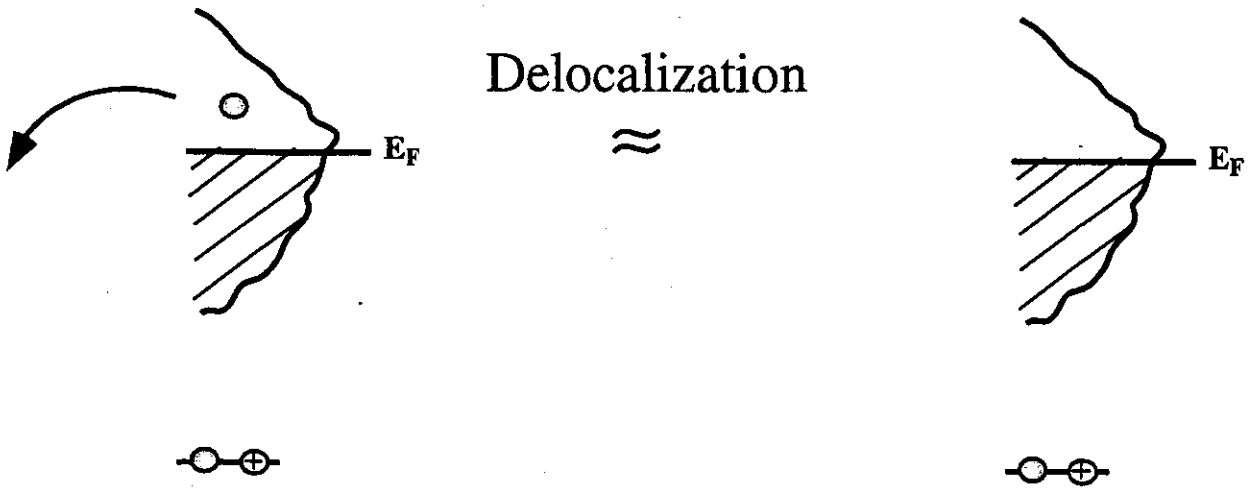
parity selection rule





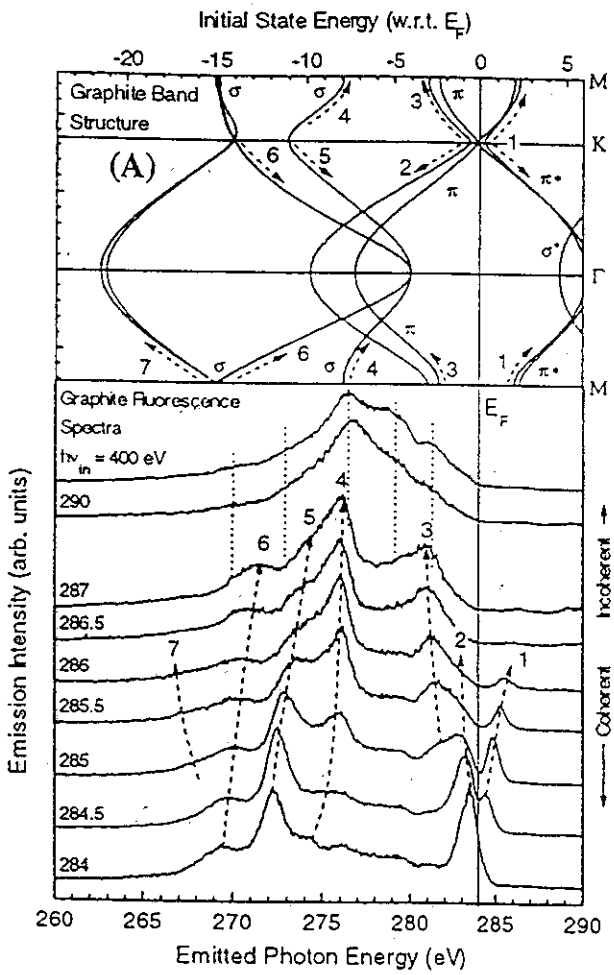
P.Glans et.al. J. El. Spec.Rel. Phen. 82, 1993 (1996)

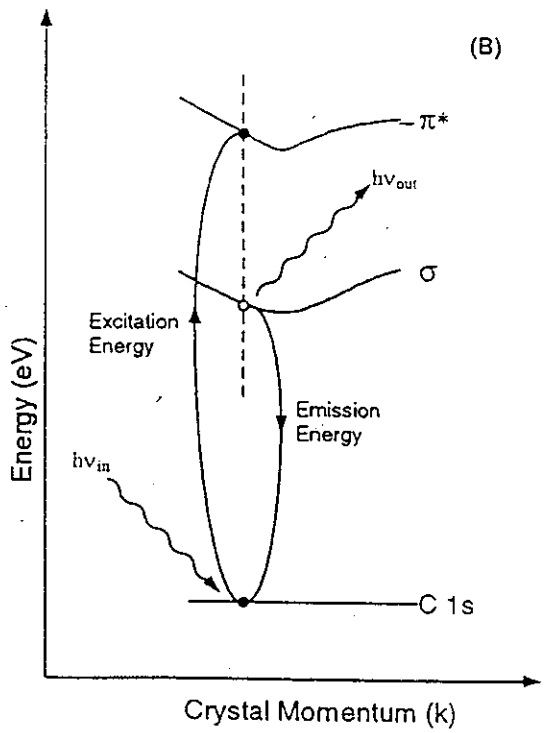
Solids and Surfaces



Final State XES≈RIXS

Excitation prepares symmetry of core hole state

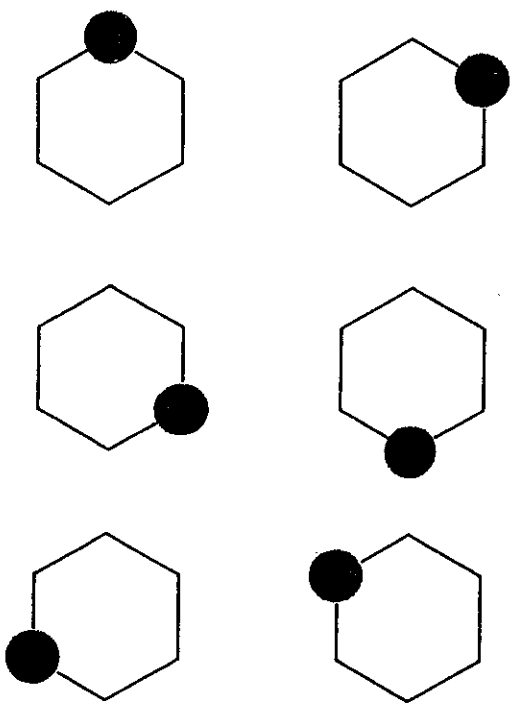


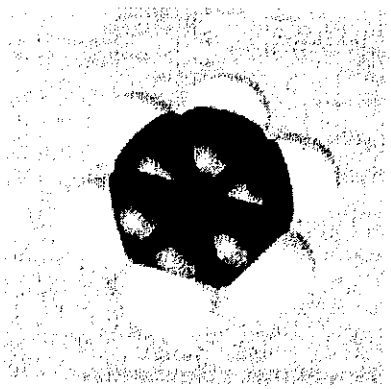


J.A Carlisle et.al. Phys. Rev. Lett. 74, 1234 (1995)

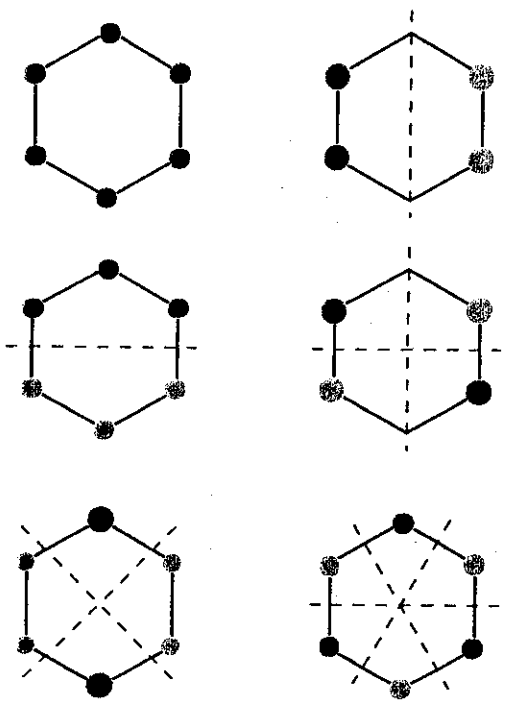
BENZENE: description of the core-levels

a) Localized (C_{2v}):



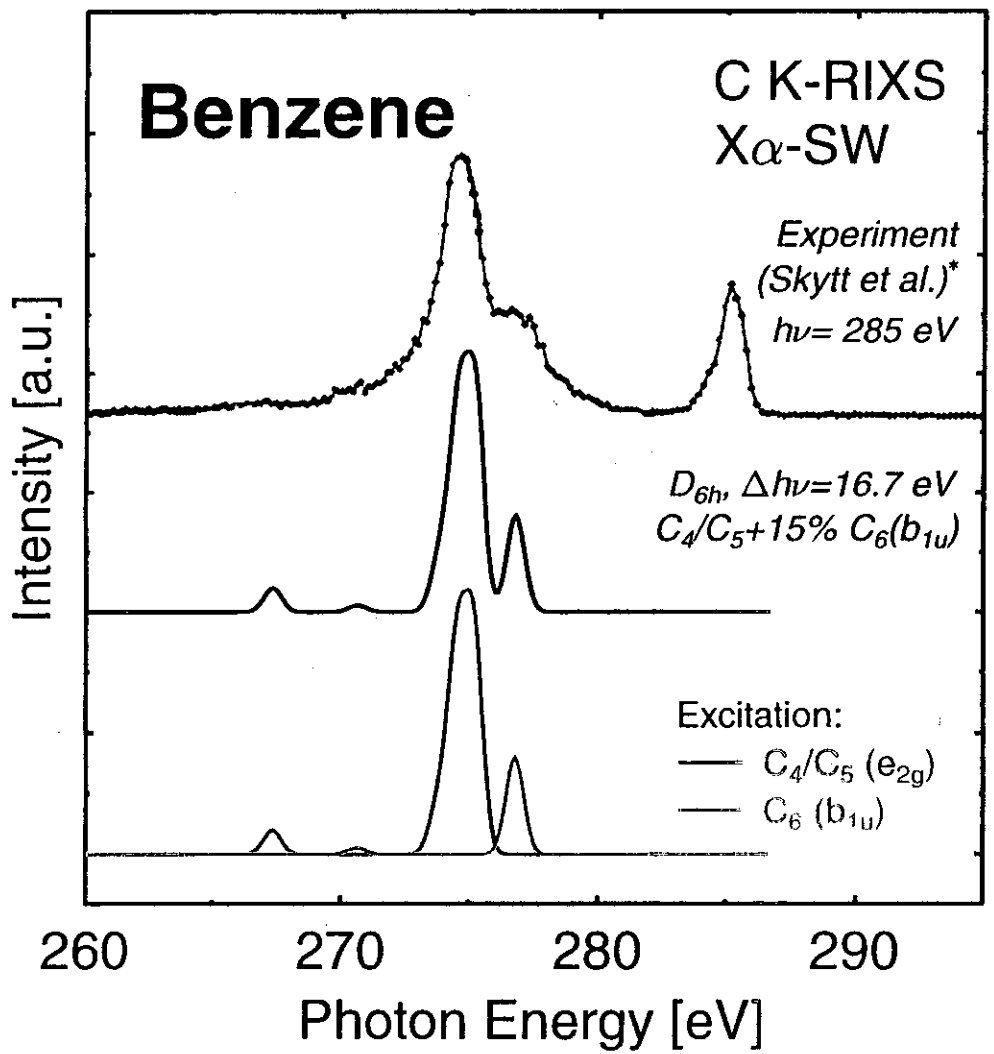


b) Symmetry adapted (D_{6h}):



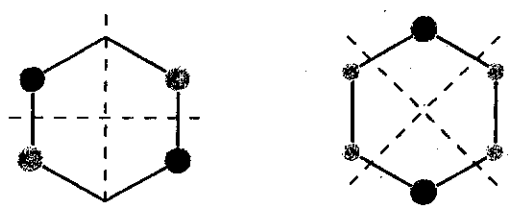
* Both descriptions are equivalent in the ground state
* Equivalence is lifted upon core excitation

BENZENE: x-ray emission (resonant)

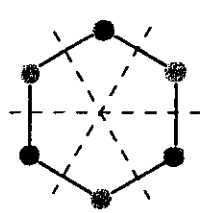


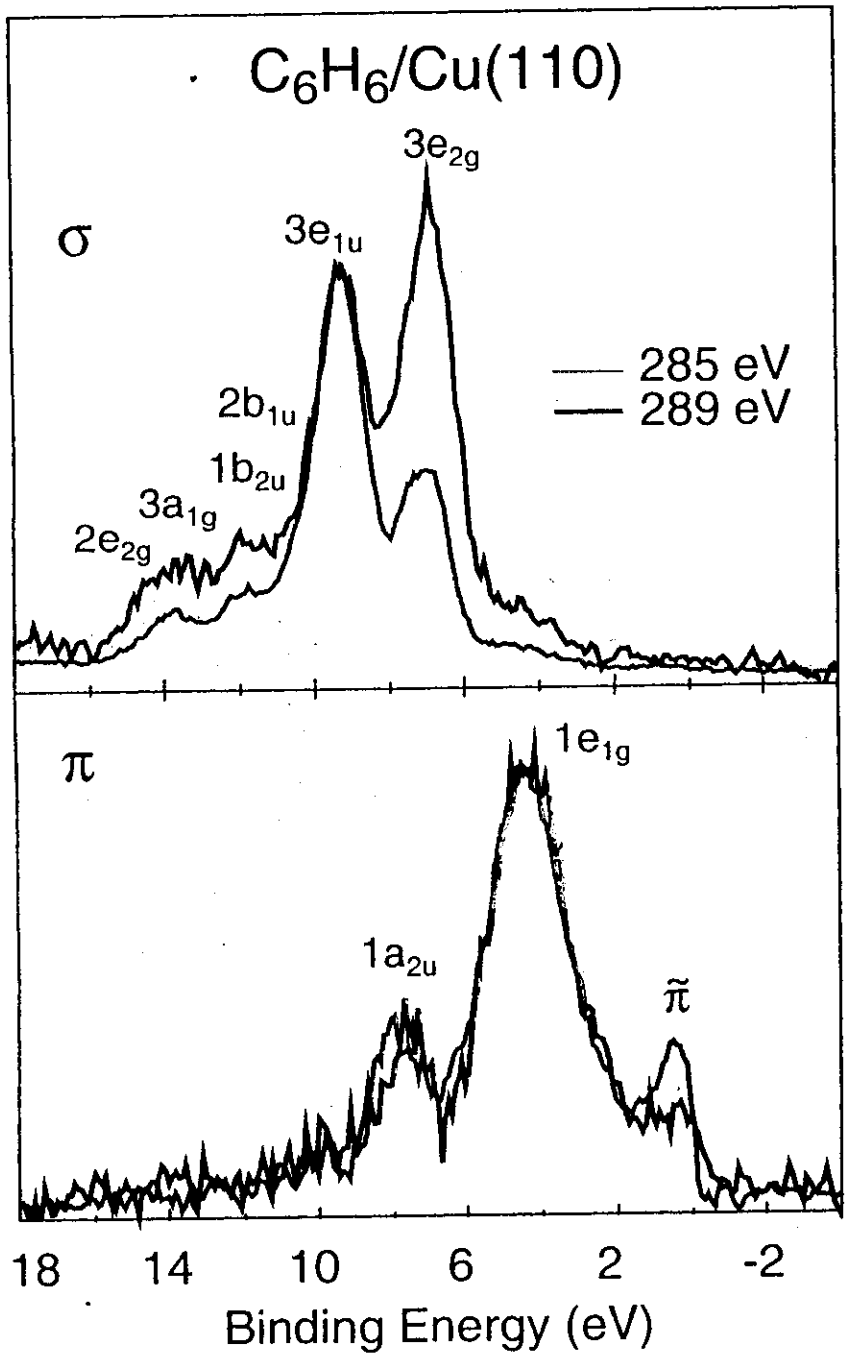
*From: P. Skytt et al., Phys. Rev A, vol. 52(5), 3572 (1995)

- well-defined core-excited state: C 1s $\longrightarrow$ $1e_{2u}$
- very strict symmetry selection rules: only excitation of e_{2g} core levels allowed



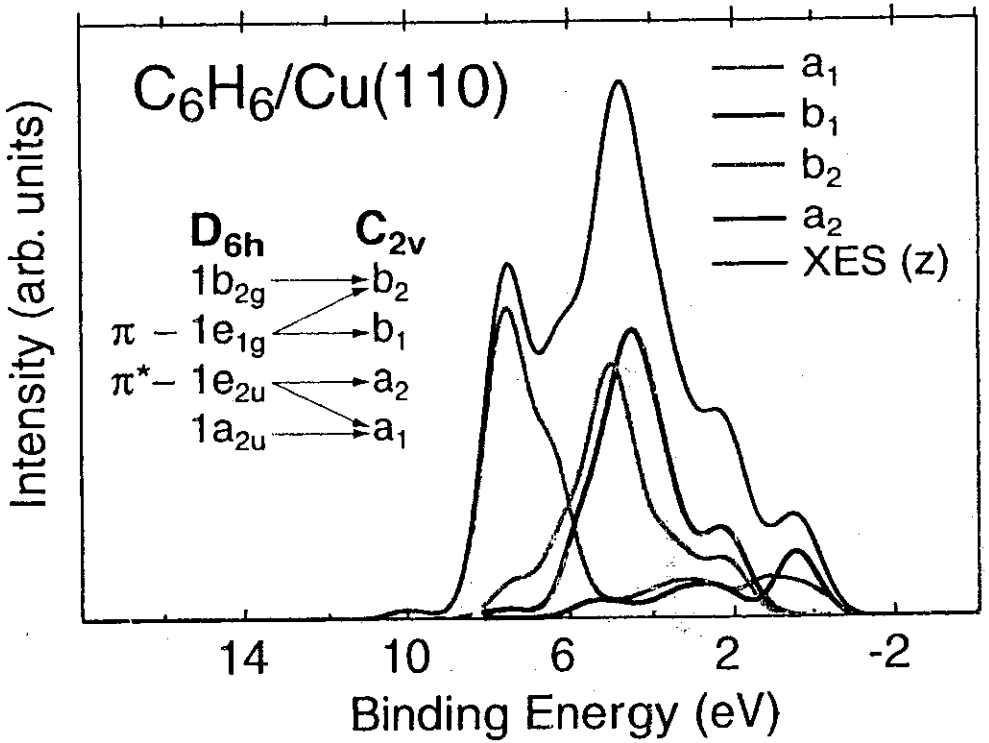
- experimentally also observed: decay of b_{1u} core holes

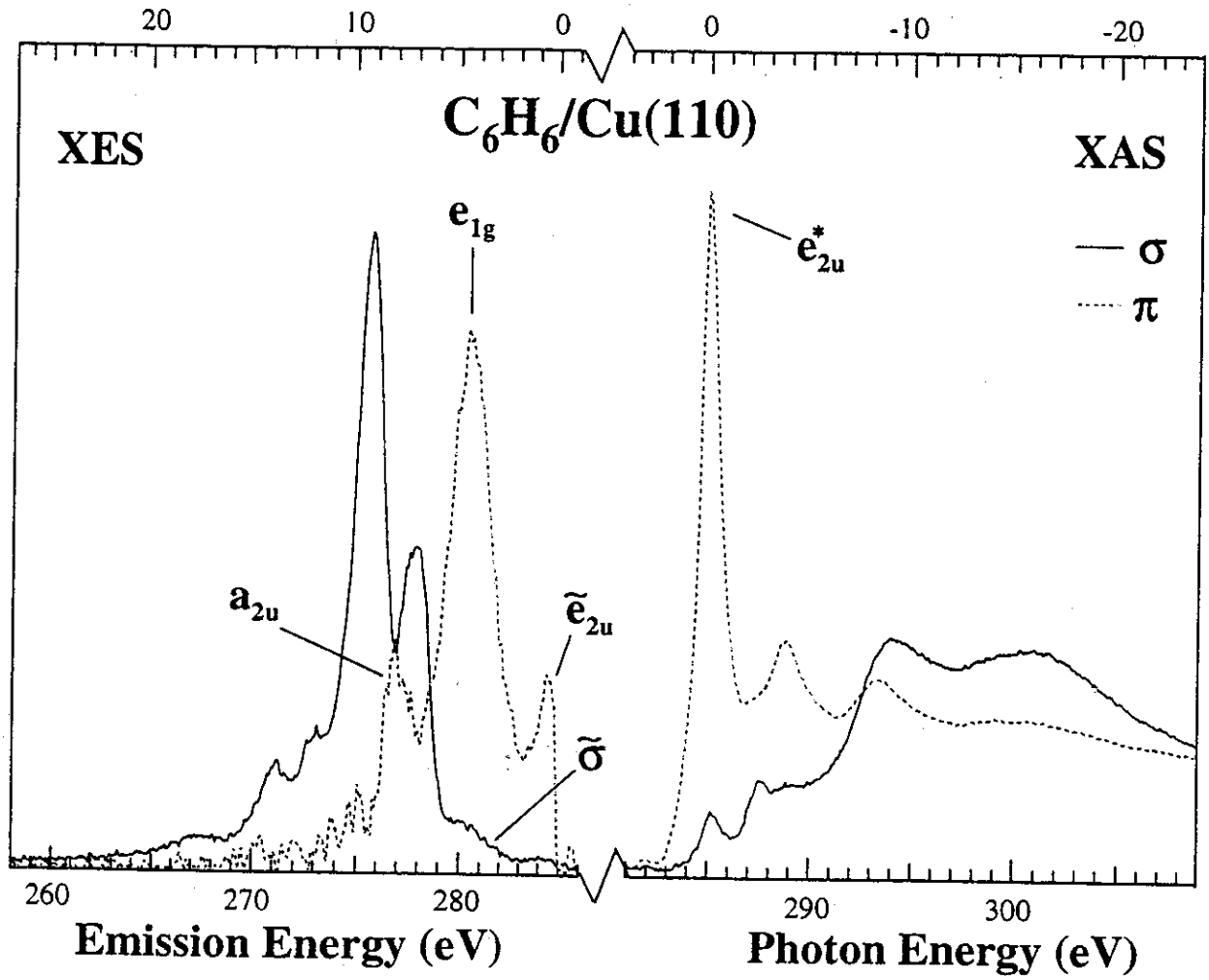


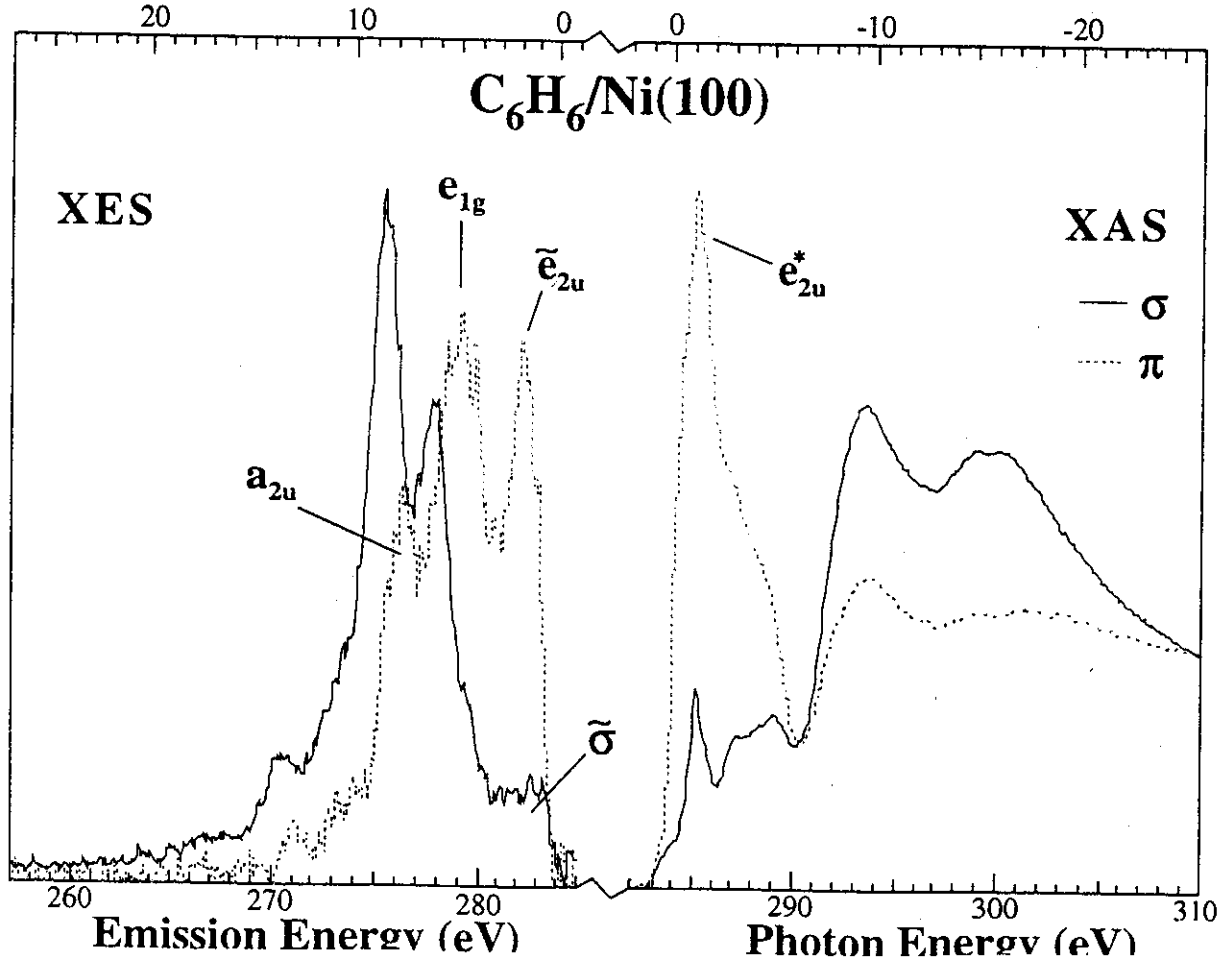


Theory

π system




20
10
0
0
-10
-20
C6H6/Cu(110)
XES
XAS
e1g
e*2u
σ
π
a2u
ẽ2u
σ̃
260
270
280
290
300
Emission Energy (eV)
Photon Energy (eV)


20
10
0
0
-10
-20
C6H6/Ni(100)
XES
XAS
e1g
ẽ2u
e*2u
σ
π
a2u
σ̃
260
270
280
290
300
310
Emission Energy (eV)
Photon Energy (eV)