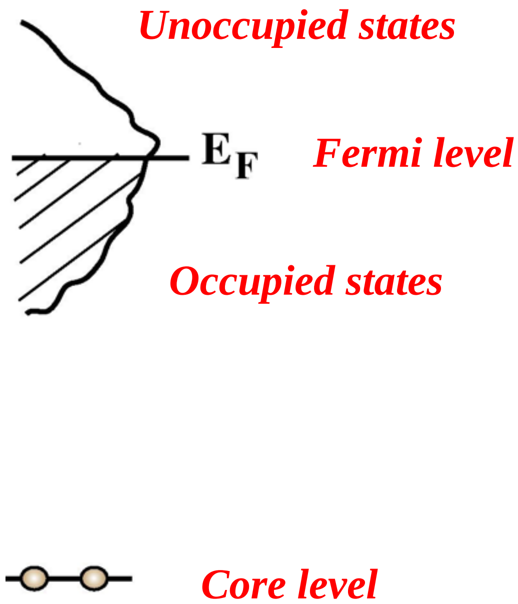
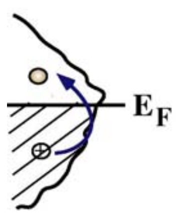
Core Level Spectroscopy

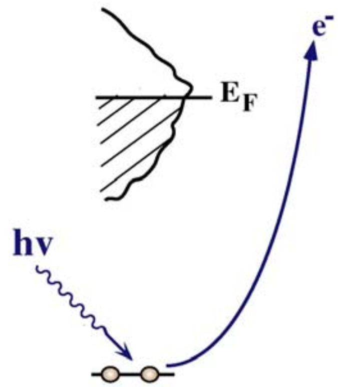


Laser spectroscopy

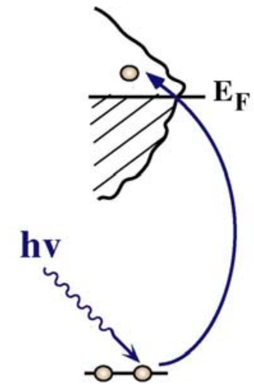


Excitations of valence electrons

Creation of core holes

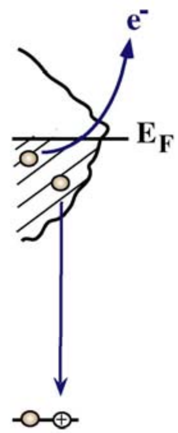


Ionization
X-ray Photoelectron Spectroscopy (XPS)

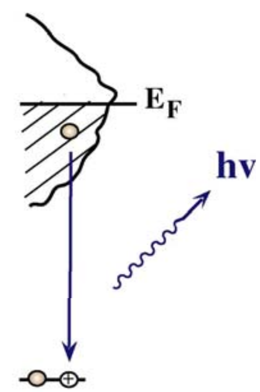


Excitation
X-ray Absorption Spectroscopy (XAS)

Decay of core holes



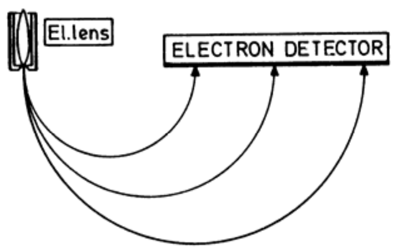
Non Radiant
Auger Electron Spectroscopy (AES)

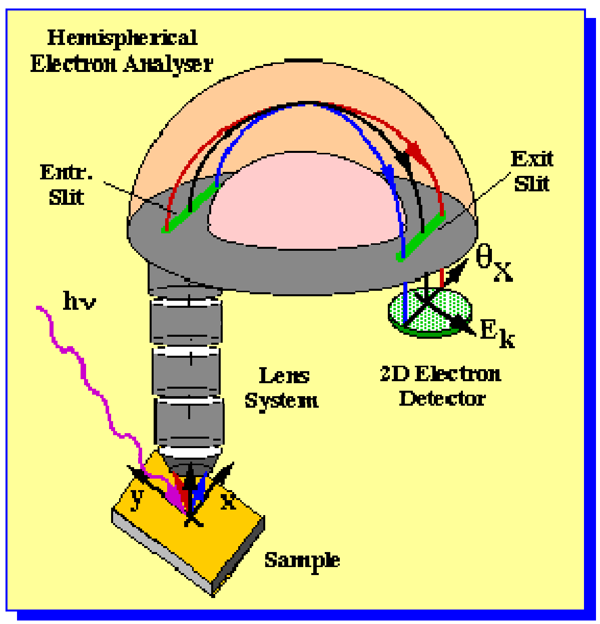


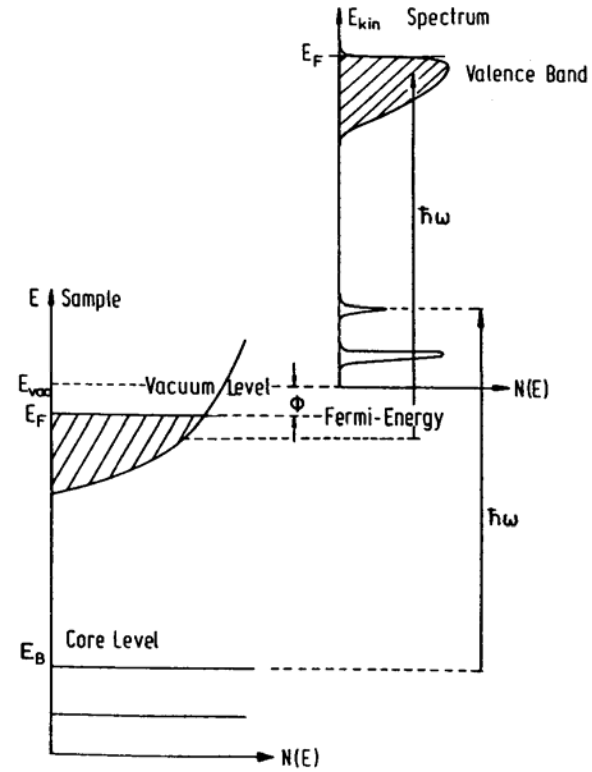
Radiant
X-ray Emission Spectroscopy (XES)

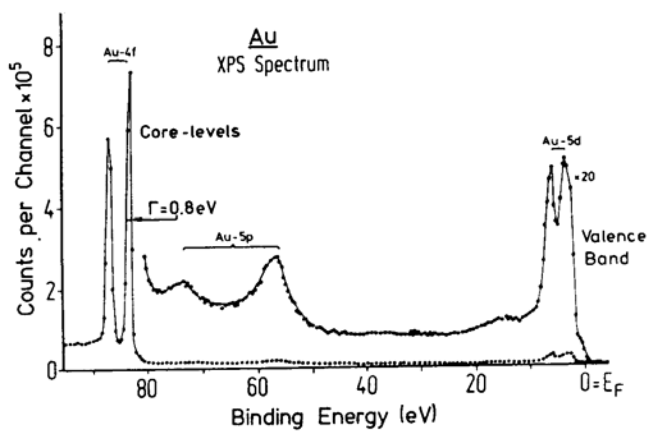
Photoelectron Spectroscopy

$$E_b = h\upsilon - E_{kin}$$



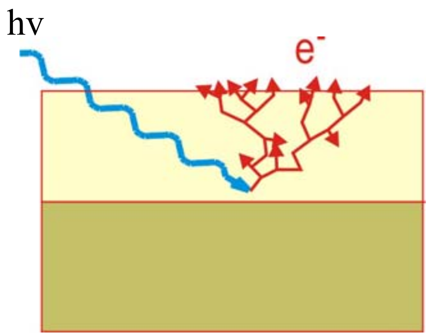






Hufner, Photelectron Spectroscopy

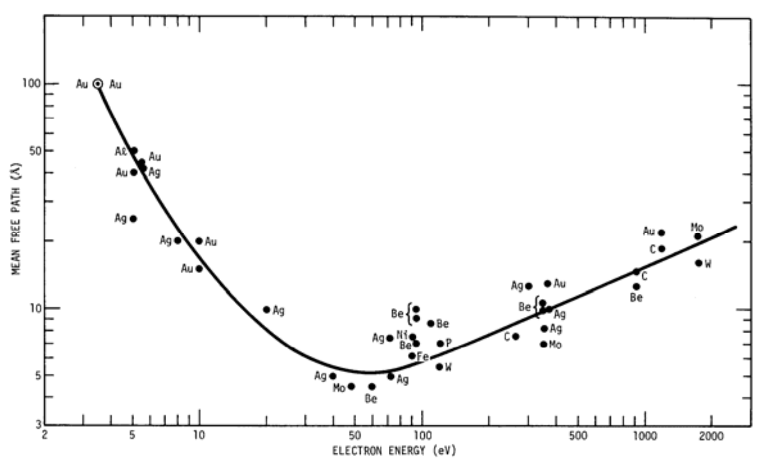
Core Level Electron Spectroscopy



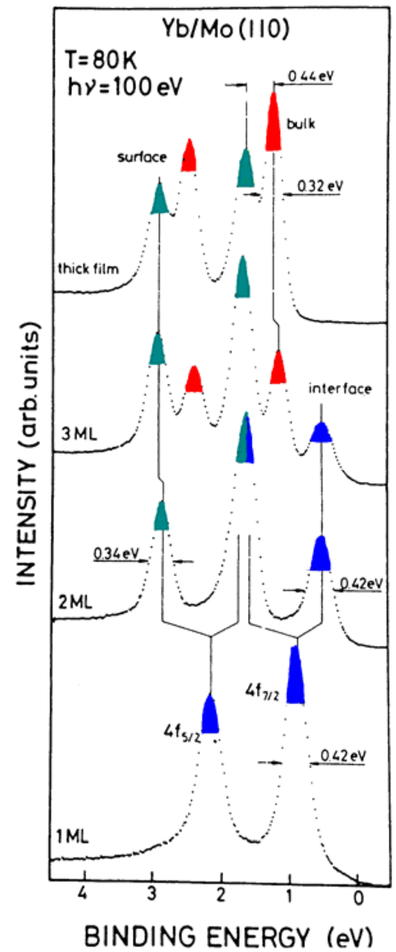
Electrons interact strongly

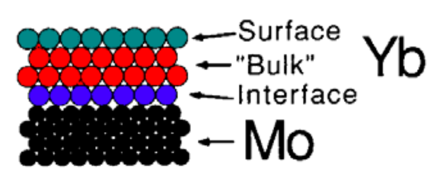
Surface Sensitivity

5-20 Å



Dependent on electron kinetic energy





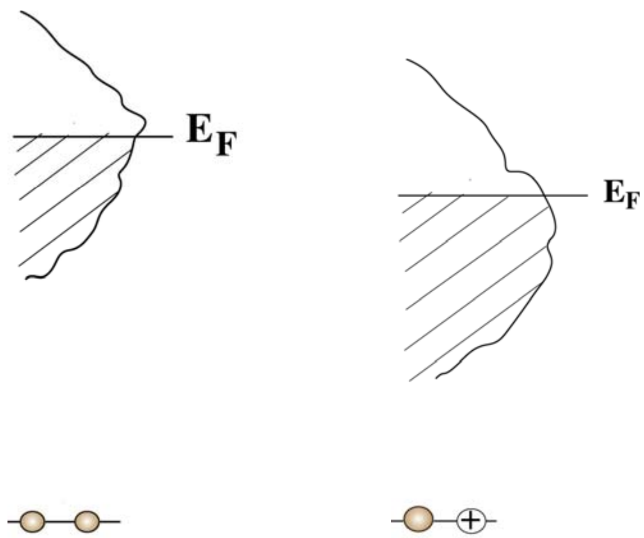
Mårtensson et. al. Phys. Rev. Lett. 60, 1731 (1988)

Core Level Binding Energy

Difference in total energy

$$E_b = E_{TOT}^{Ground} - E_{TOT}^{Final}$$

total energy of the whole system including all interacting atoms

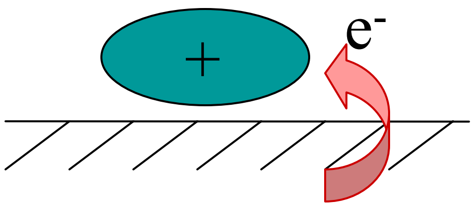


Relaxation

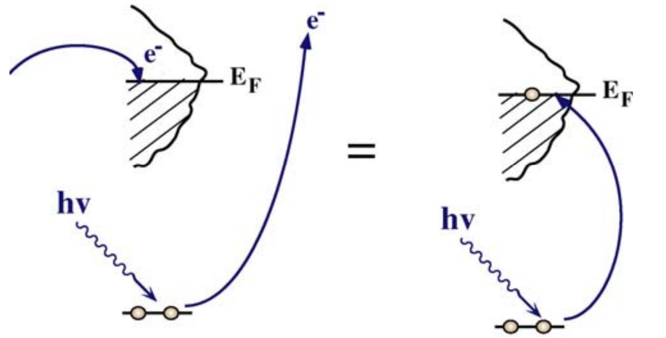
Change of valence electrons

Relaxation

Metallic screening



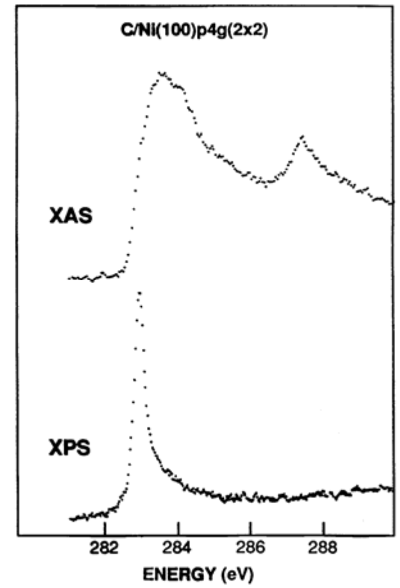
Electron transfer



When N (electrons) are $\simeq 10^{23}$

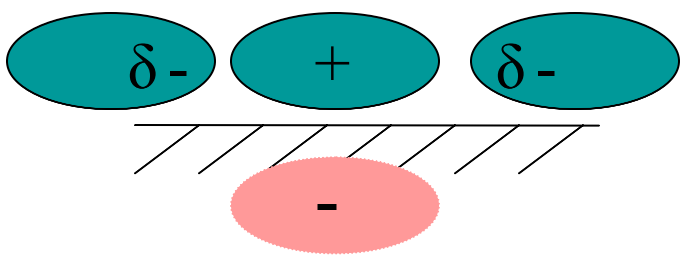
δ -

XPS binding energy is onset for XAS



Chemisorbed C on Ni

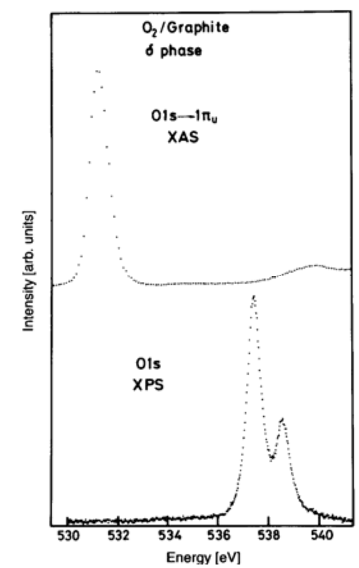
Image screening or polarization



Electrostatic

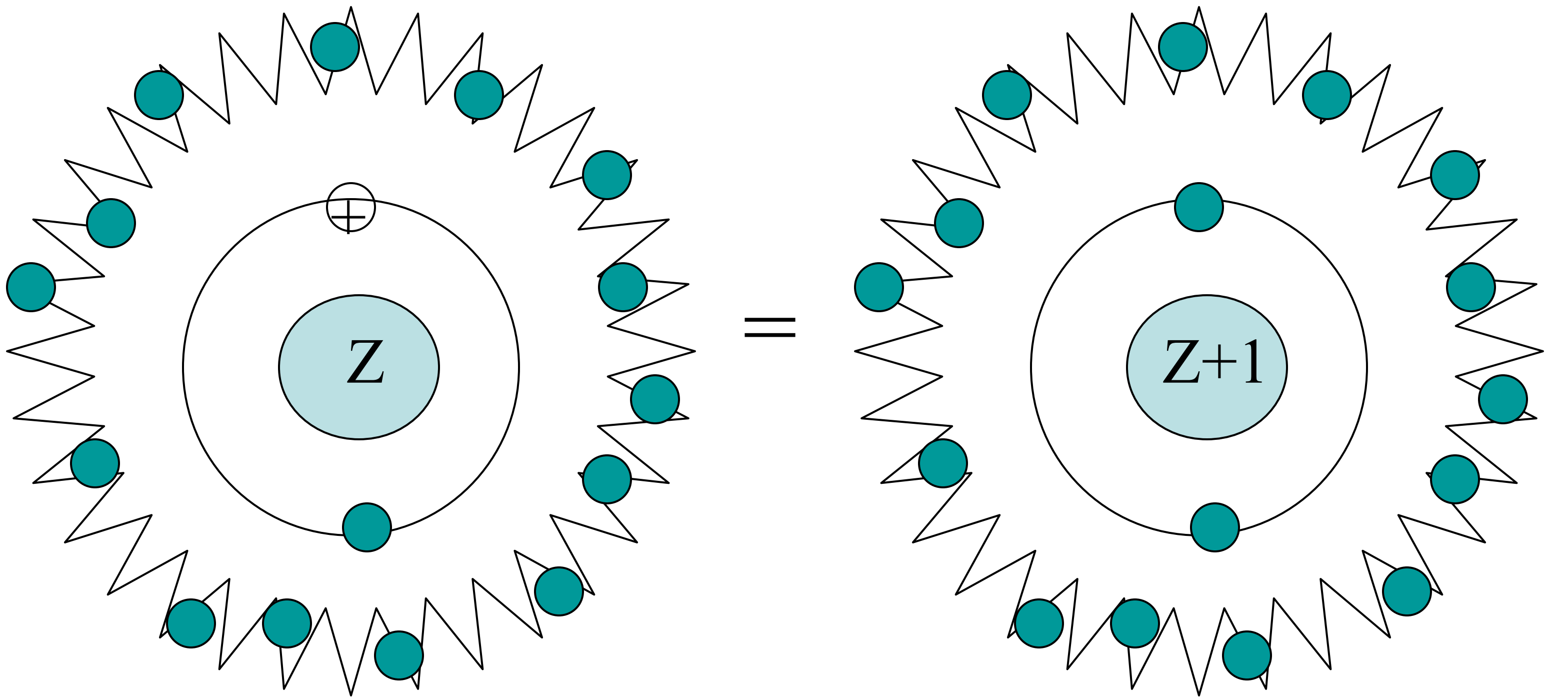
No mixing of electrons between ionized atom and surroundings

No relationship between XPS and XAS



Physisorbed O_2 on graphite

Z+1 Approximation



The valence electrons can not approximately distinguish
an extra charge in the core region or in the nucleus

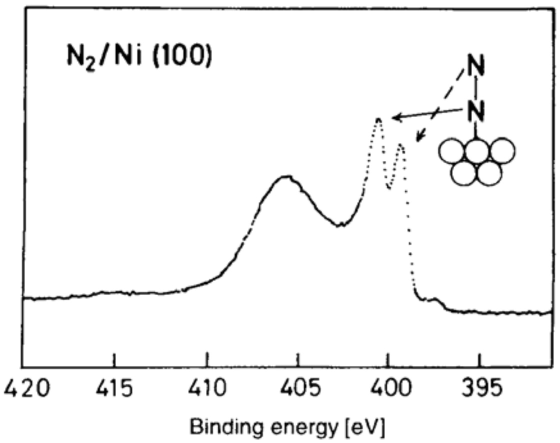
Core ionized final states

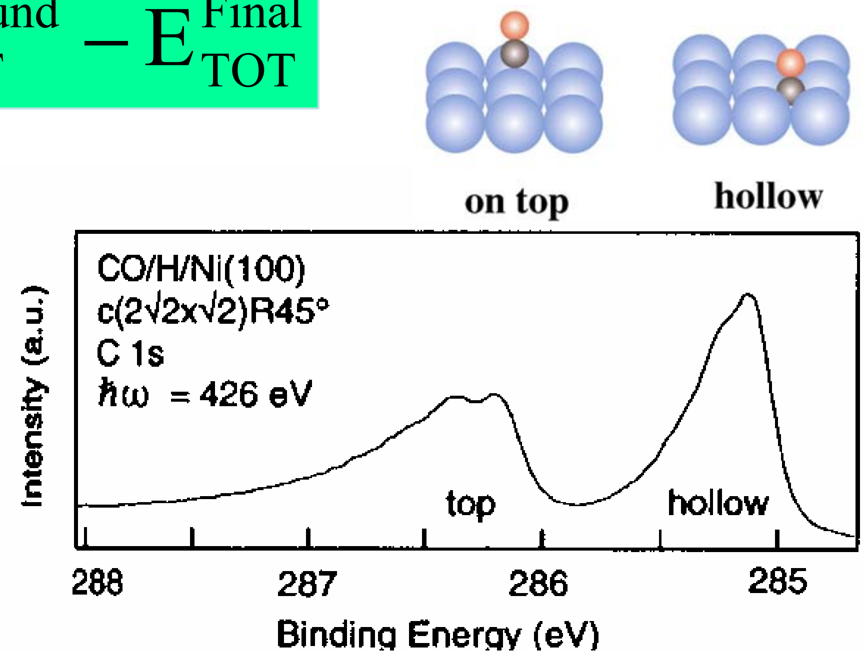
C*O = NO

Ni* = Cu

N_2 and CO on Ni(100)

$$E_b = E_{TOT}^{Ground} - E_{TOT}^{Final}$$

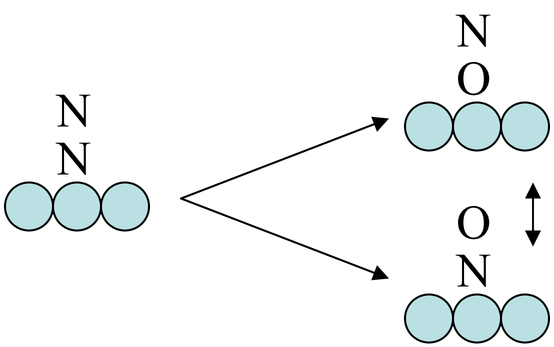




Two different N atoms

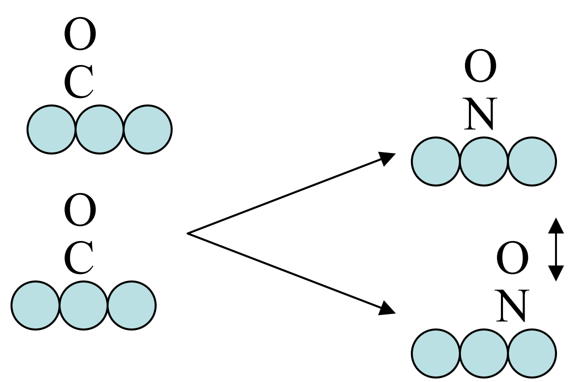
1.5 eV binding energy shift

The same ground state for both atoms



ΔE=1.5 eV

Difference in Adsorption energies



ΔE=1eV

Similar ground state energy

Vibrations Core Levels

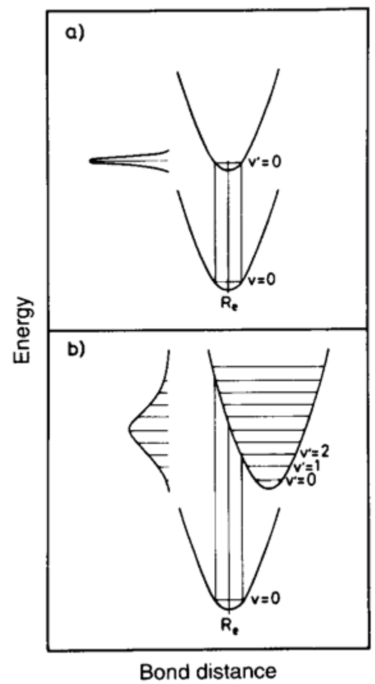
Frank Condon Principle

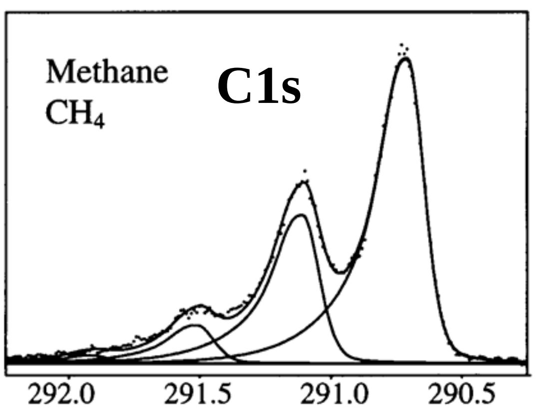
Core levels are non bonding orbitals

No vibrational excitations expected?

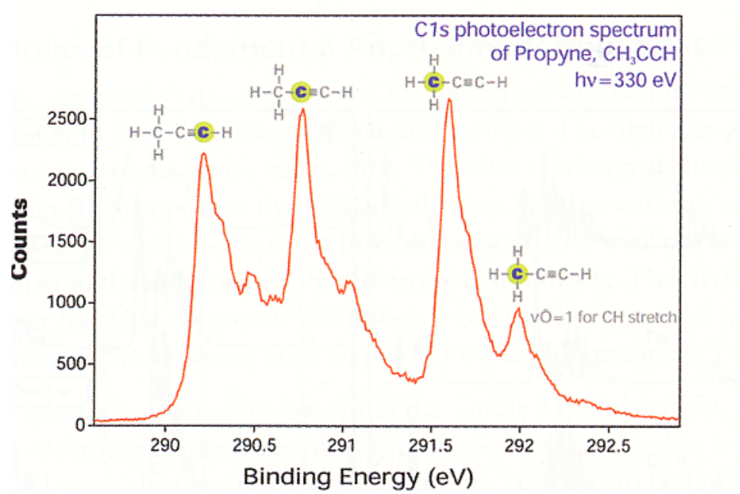
Relaxation in the ionized state

Different potential energy curves

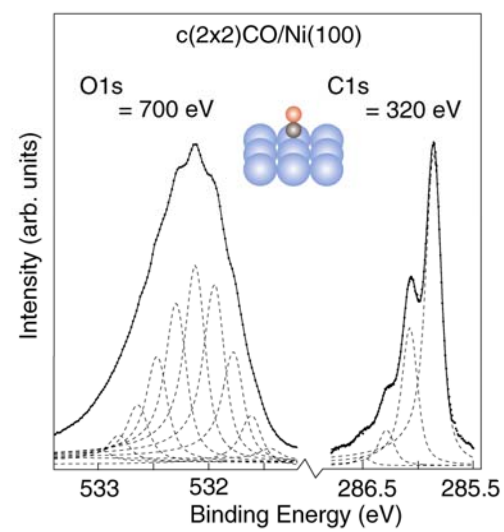




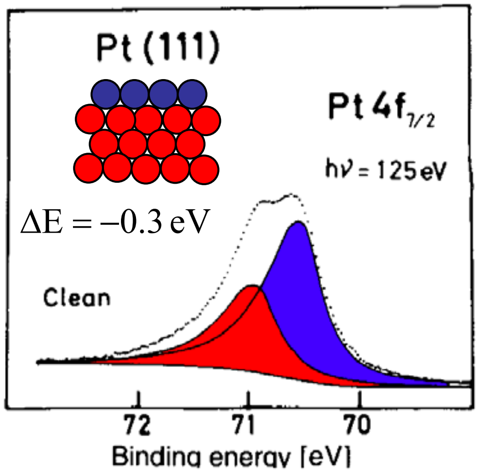
Chemical shifted components



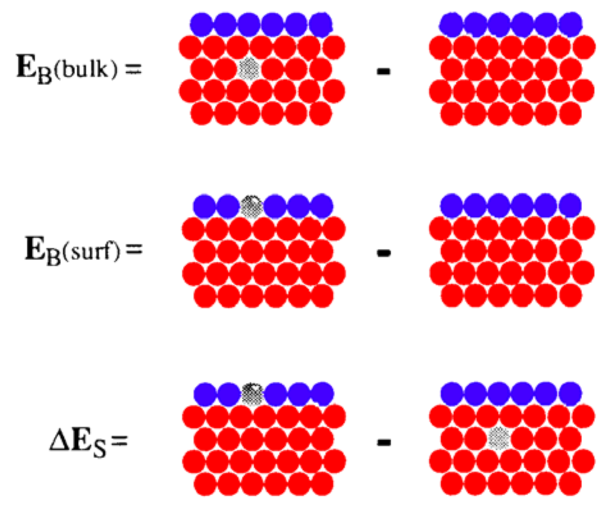
Adsorbed CO on Ni

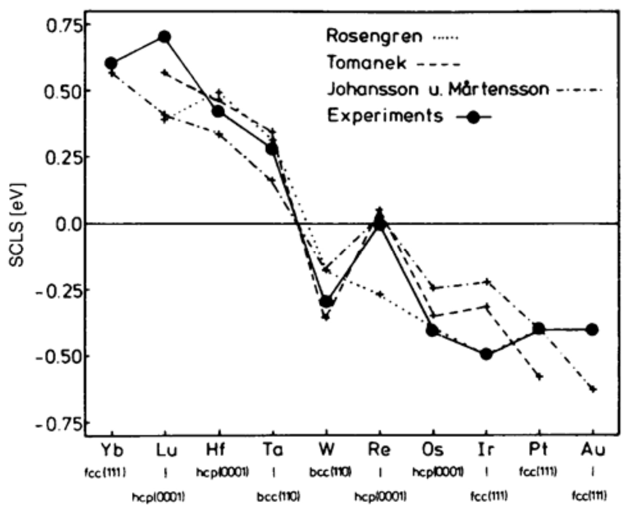


Surface Core Level Shift (SLCS)



$$E_b = E_{TOT}^{Final} - E_{TOT}^{Ground}$$





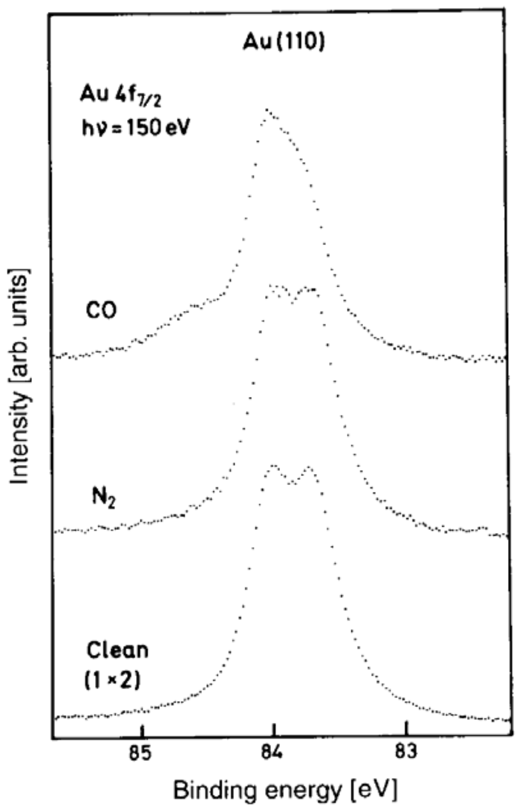
Variation across the 5d series

ΔE_S Surface segregation energy for Z+1 impurity in Z metal

We have a lower binding energy for Au at the surface than in bulk for Pt (111)

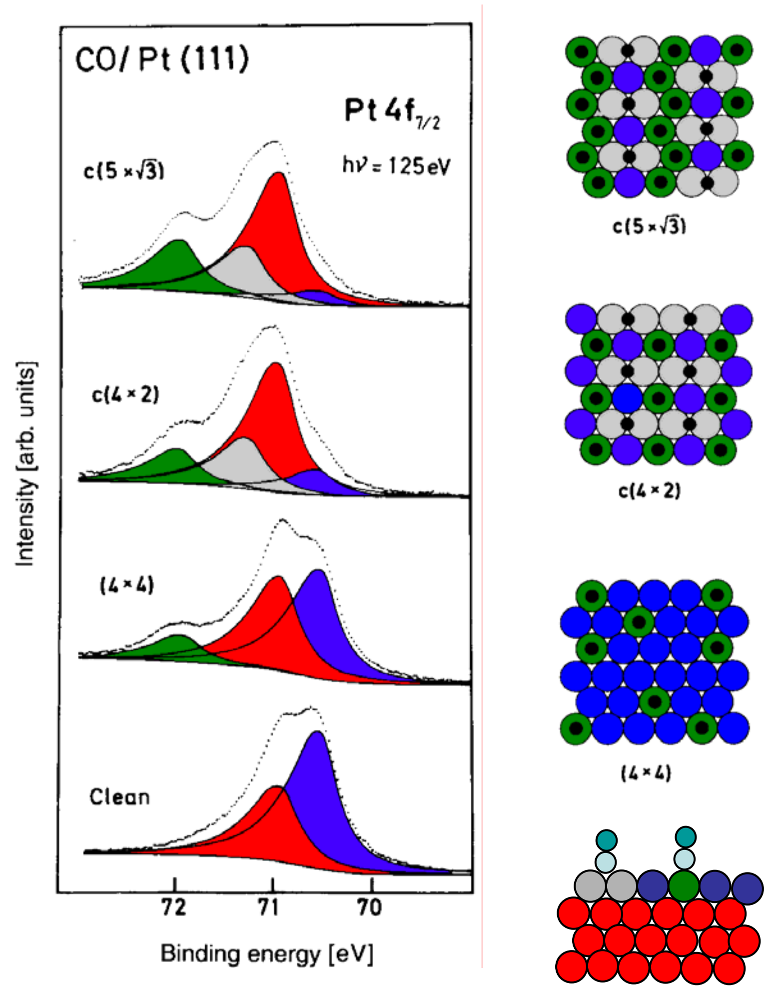
The more open surfaces have a larger ΔE_S

Adsorbate Induced Shift



N2 is physisorbed on Au

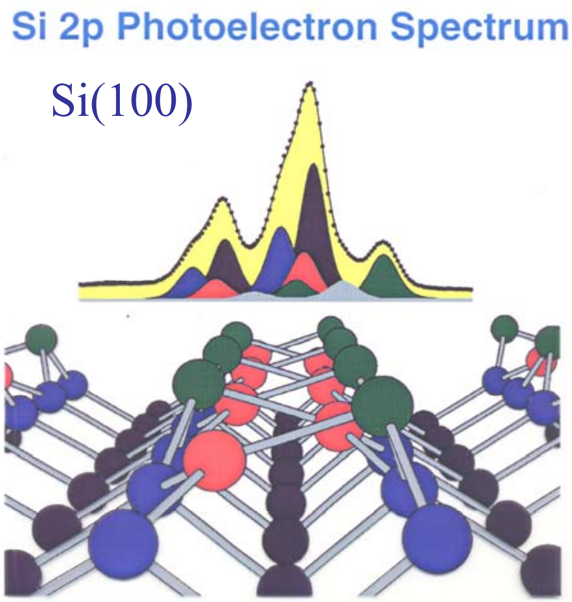
CO is chemisorbed



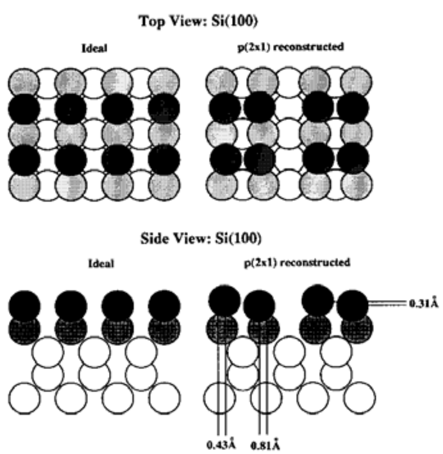
Pt is segregated to the surface in presence of CO

CO forms stronger bonds to Pt compared to Au

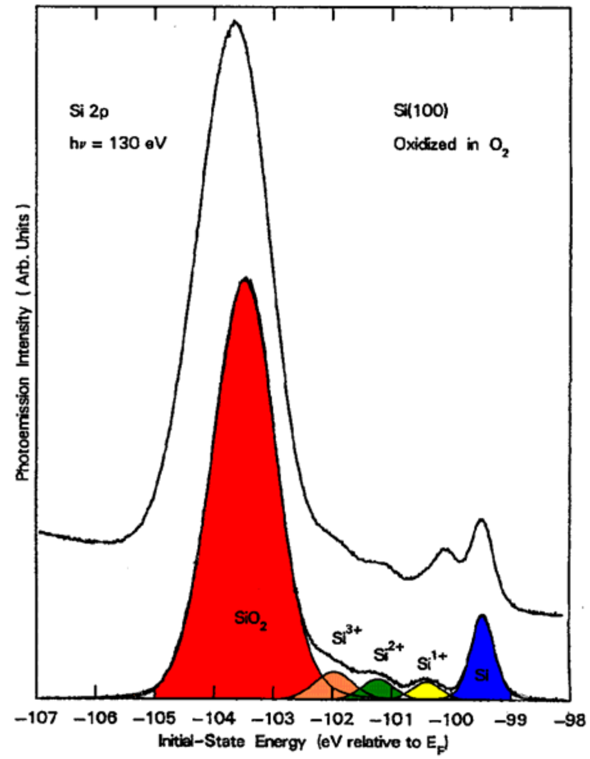
Semiconductor Core Level Shifts



Surface reconstruction

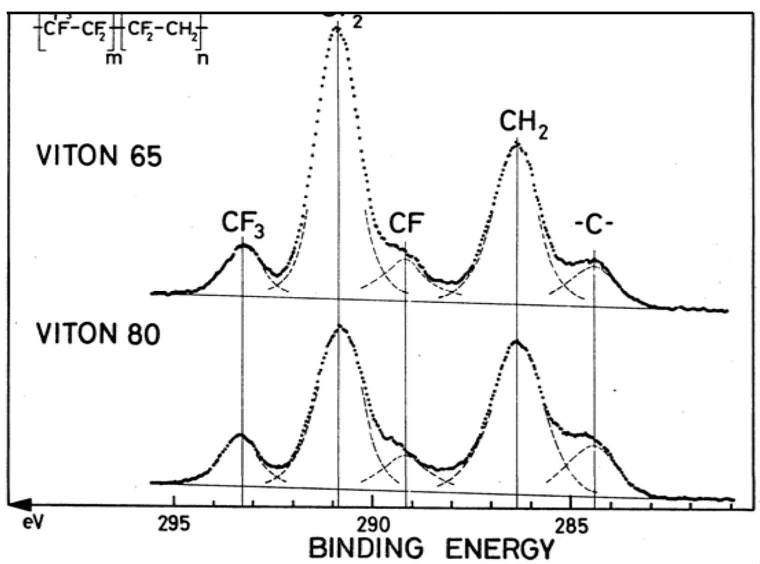


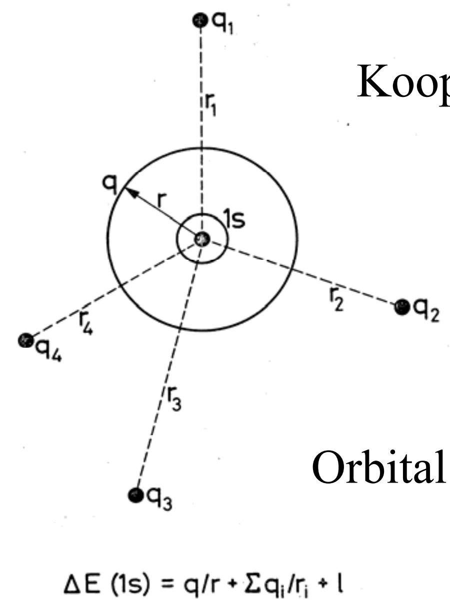
Oxidation of Si   Si/SiO_2 interface



Si2p chemical shift due to local charge on Si atom

Electrostatic effects on Shifts





Koopmans teorem

Orbital eigenvalue

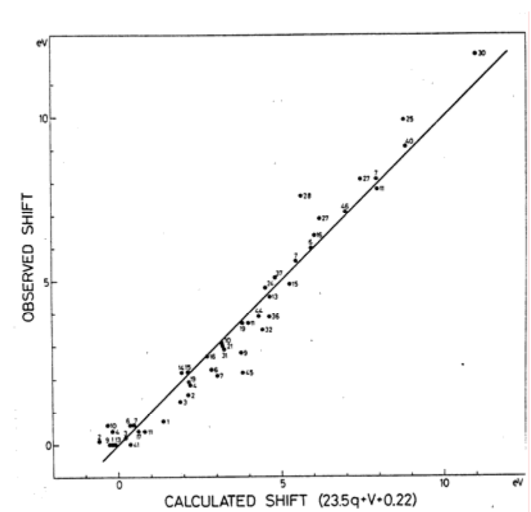
Correlation between local charge on ionized atom and binding energy shifts

Only special cases with ligands with large difference in electronegativity

Do not work for metallic systems

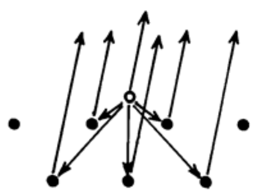
RELAXATION changes the picture

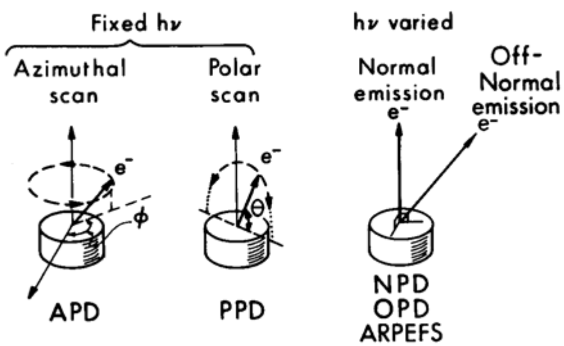
Difference in total energy is the correct approach

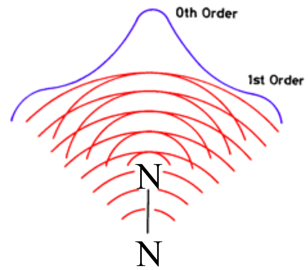


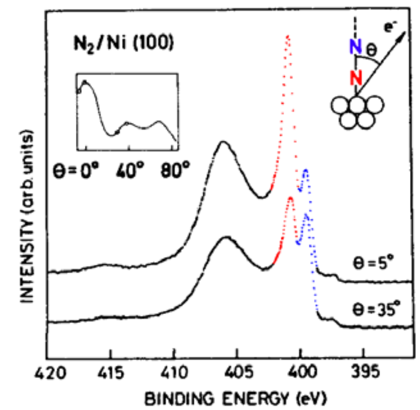
C1s shifts for different compounds

Photoelectron Diffraction



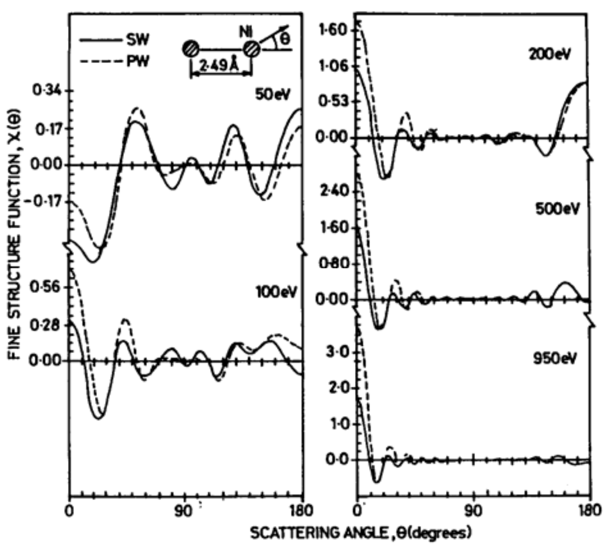






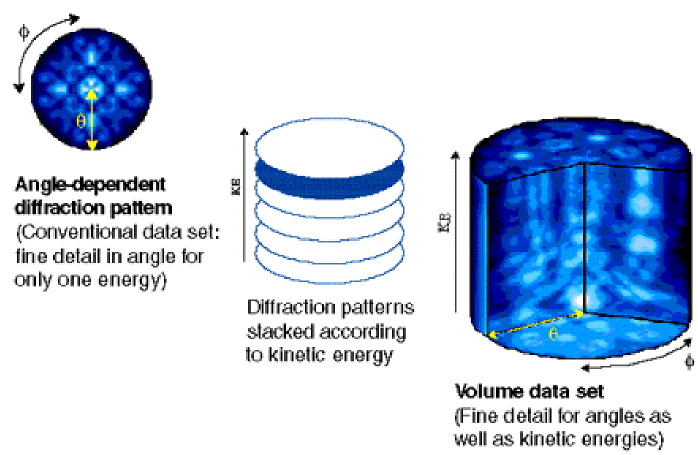
Forward scattering zero order diffraction

Molecular orientations



Scattering angles at different energies

X-Ray Photoelectron Diffraction of Copper (100): Volume Data Set

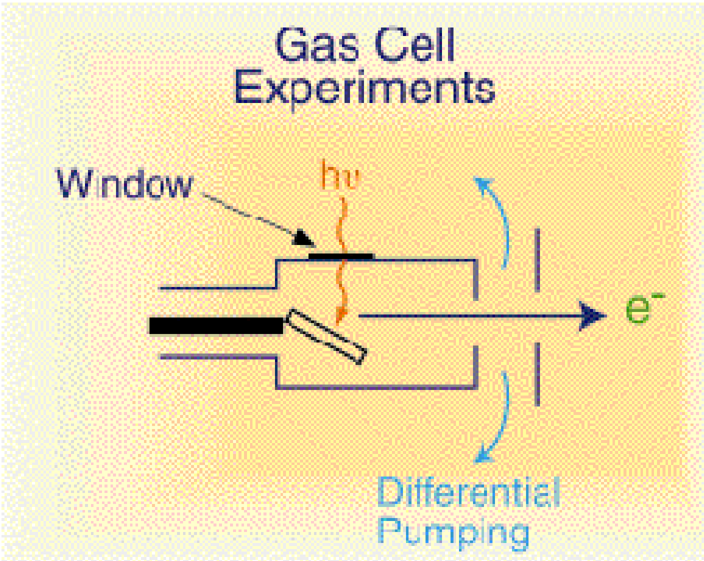


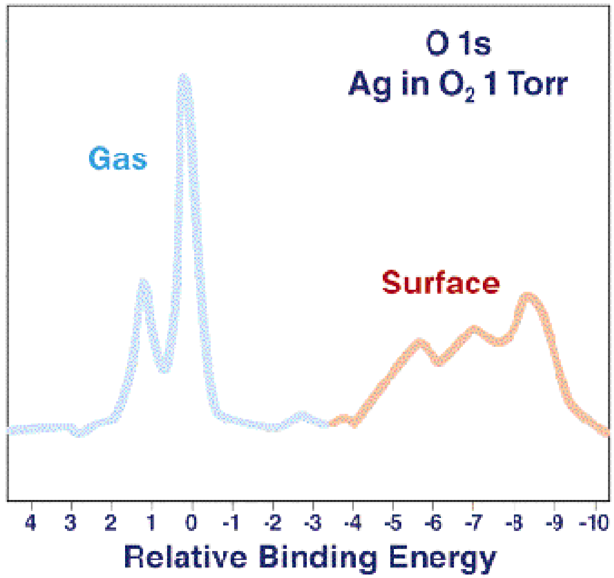
Beamline 7.0.1: U. of Wisconsin-Milwaukee, U. of Oregon, LBNL

For a full structure determination

Energy dependent diffraction together with multiple scattering calculations

High Pressure XPS

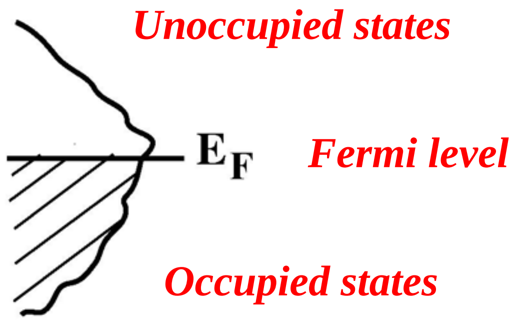


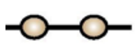


New development of XPS at intermediate pressures

Catalysis, solid/liquid interfaces etc.

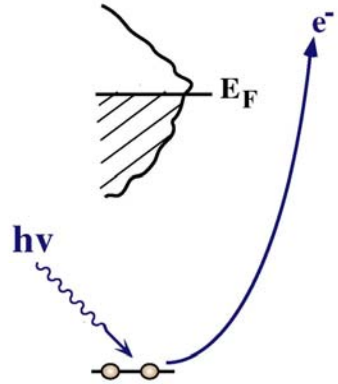
Core Level Spectroscopy



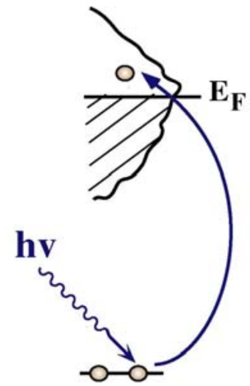


Core level

Creation of core holes

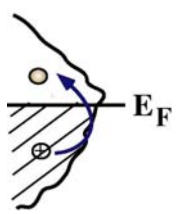


Ionization
X-ray Photoelectron Spectroscopy (XPS)



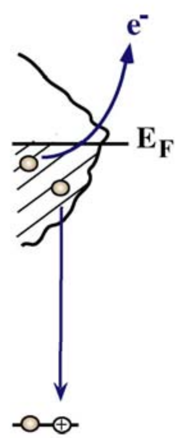
Excitation
X-ray Absorption Spectroscopy (XAS)

Laser spectroscopy

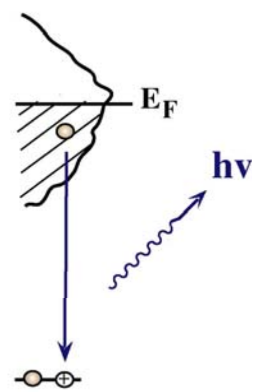


Excitations of valence electrons

Decay of core holes



Non Radiant
Auger Electron Spectroscopy (AES)

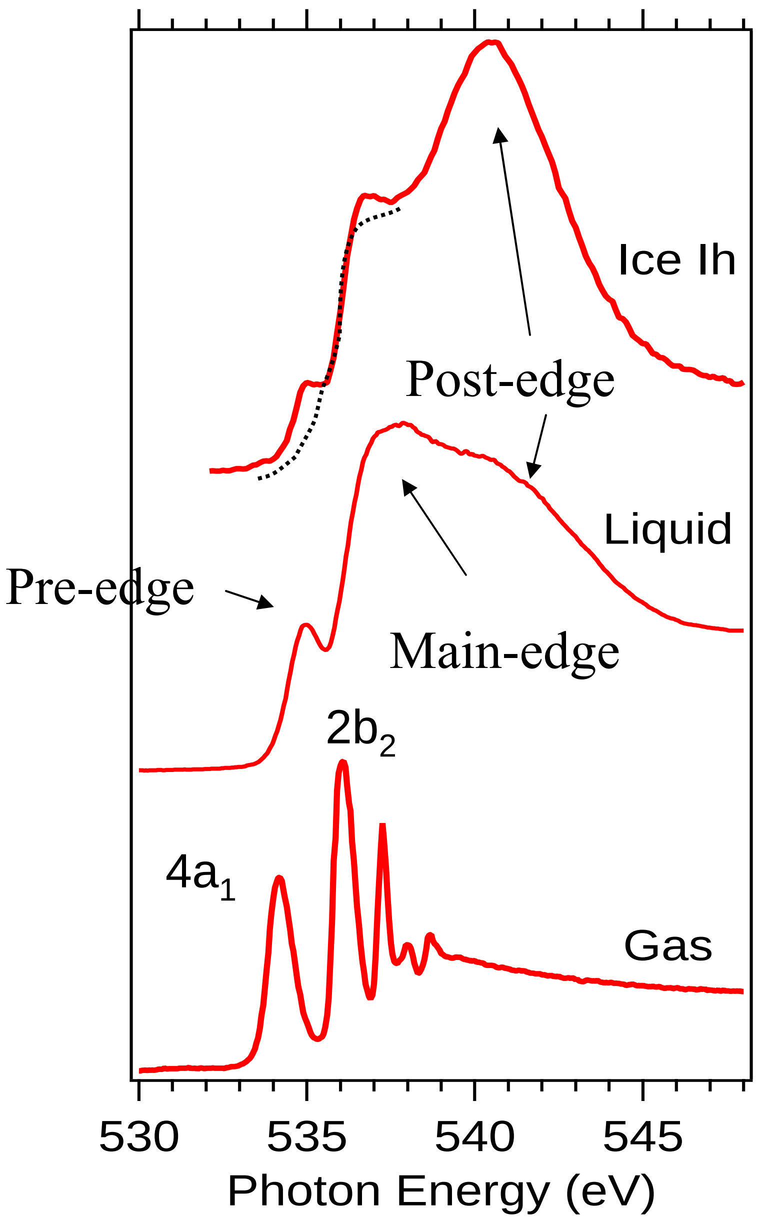


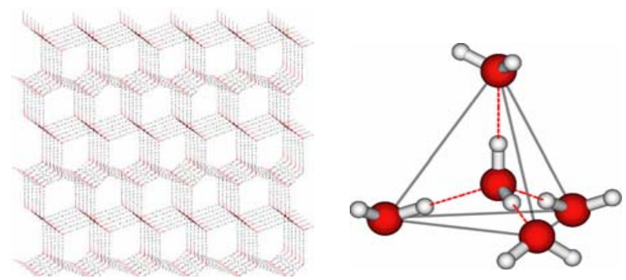
Radiant
X-ray Emission Spectroscopy (XES)

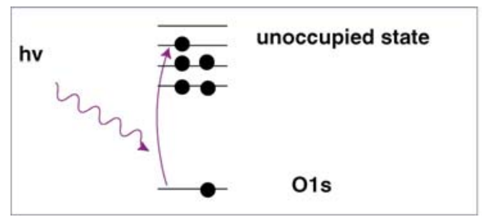
Water

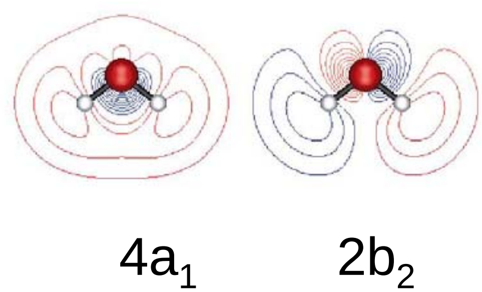
Wernet et al. Science 304, 995 (2004)

X-ray Absorption Spectroscopy of Water



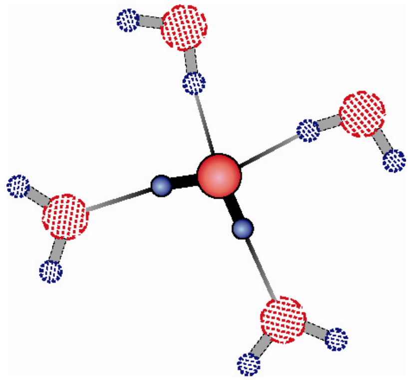






Myneni et.al. *J. Phys. Condens. Matter* **14** (2002) 213

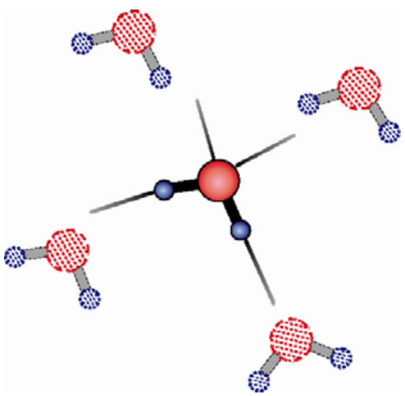
Distortions



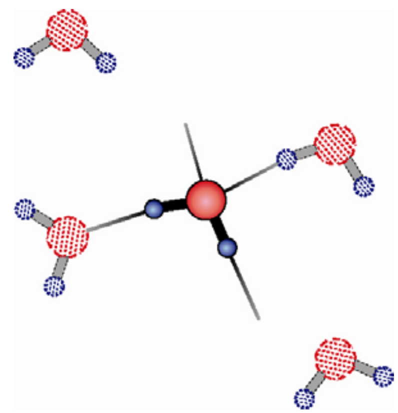
Ice

Tetrahedral
Coordination

Energy



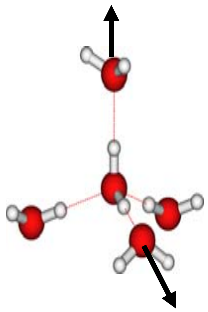
Water



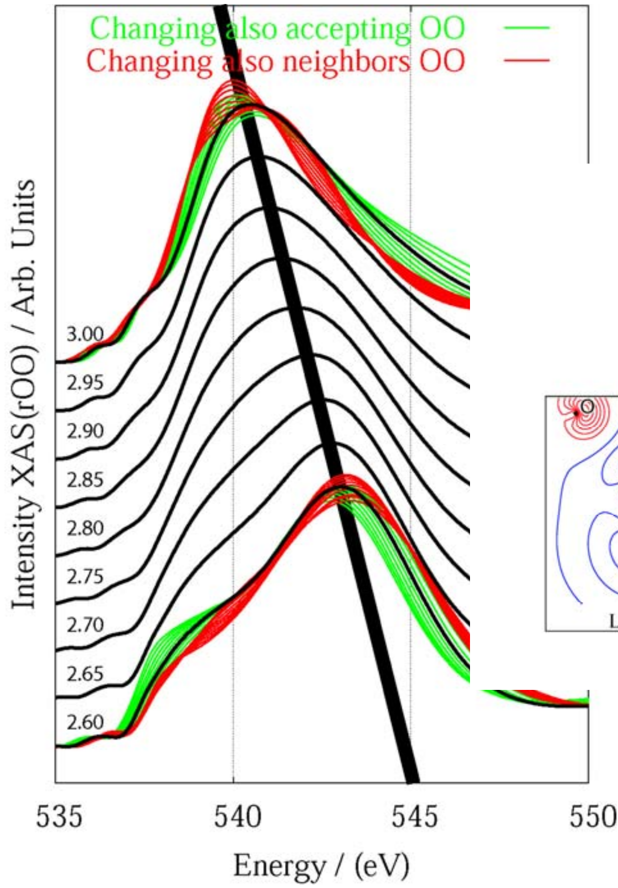
Symmetrical distortions

Asymmetrical distortions

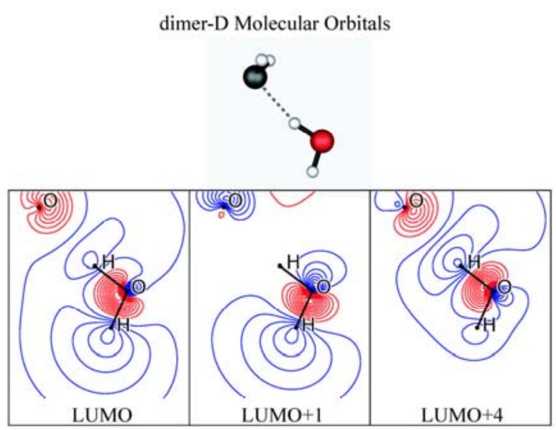
Unequal distortions of H-bonds



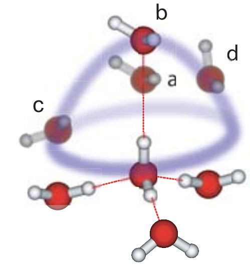
Symmetrical distortions



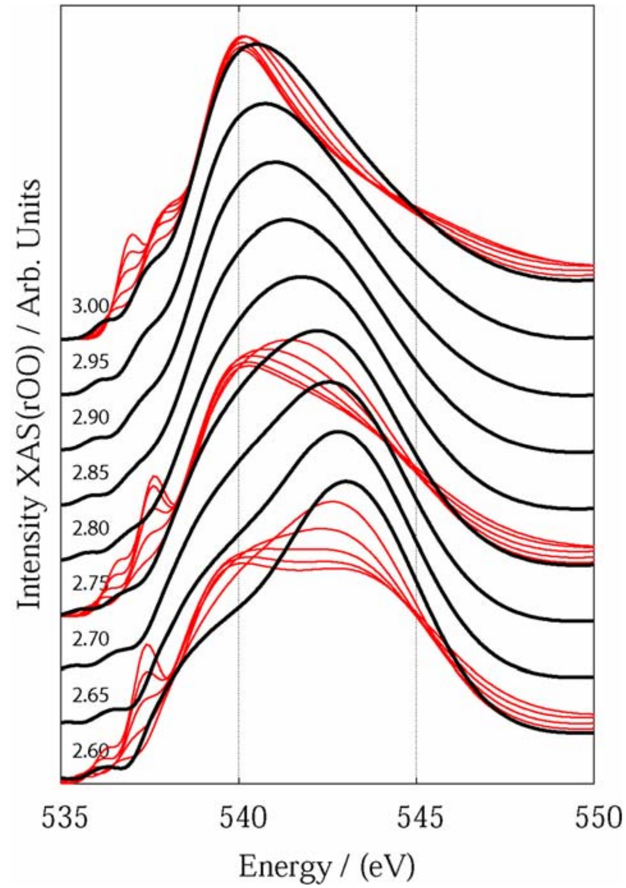
XAS sensitive
to asymmetry
in H-bonding



Odelius et. al. unpublished

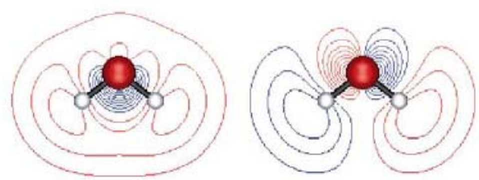


Asymmetrical distortions

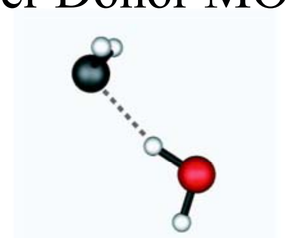


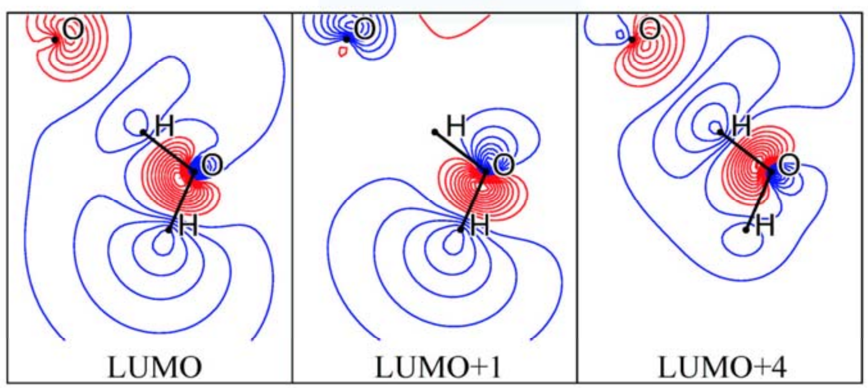
Localized Orbitals

Free molecule MO

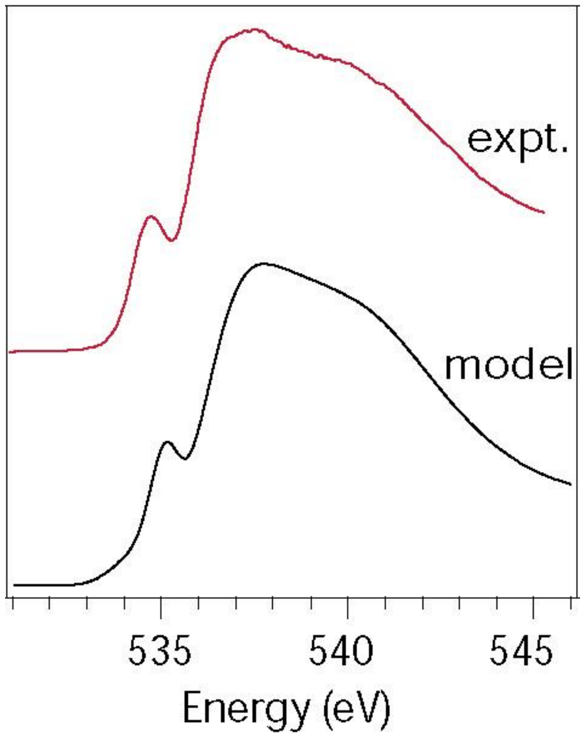


Dimer Donor MO

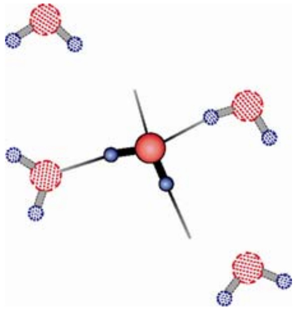


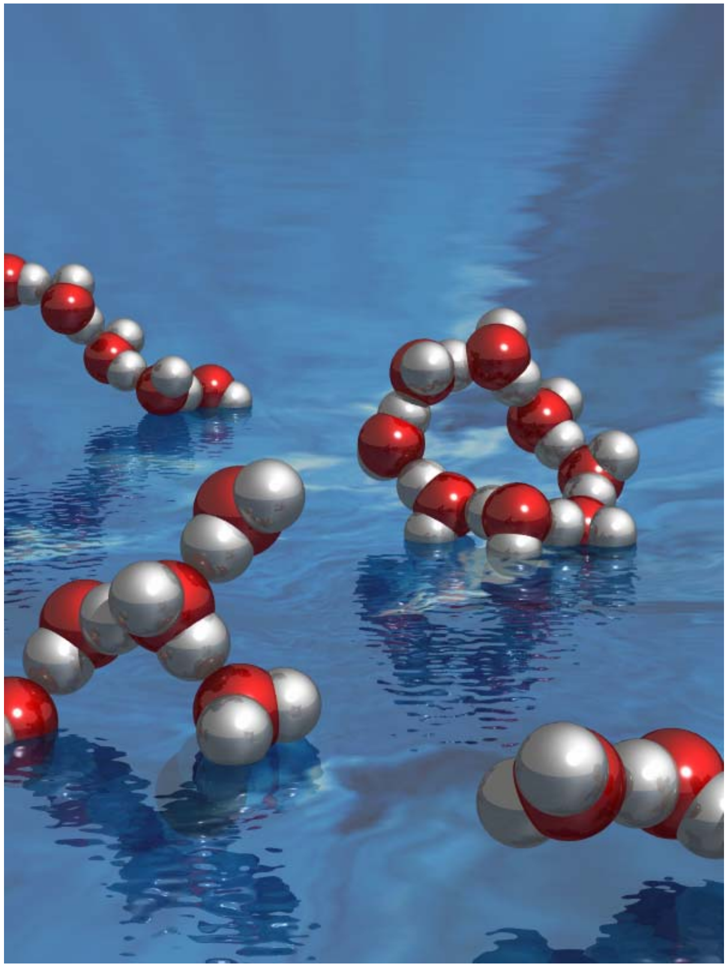


Water structure



85%

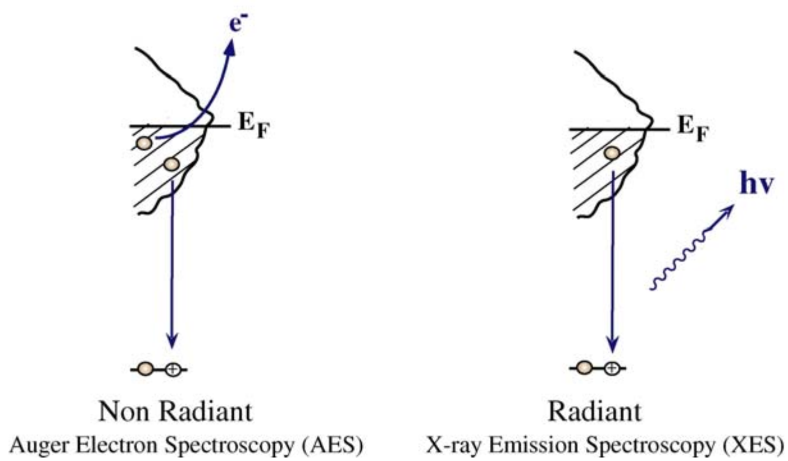




Opposite results to MD Simulations

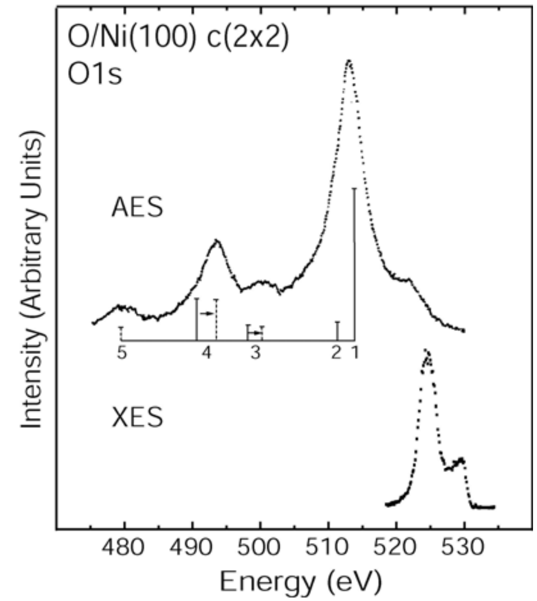
Strong debate

Core Hole Decay

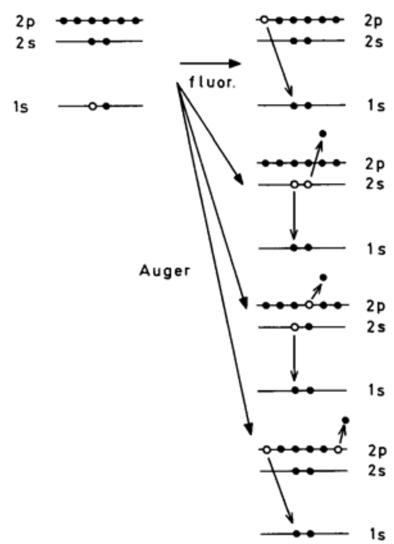


XES one electron picture

AES two electron interaction; complex Correlation effects



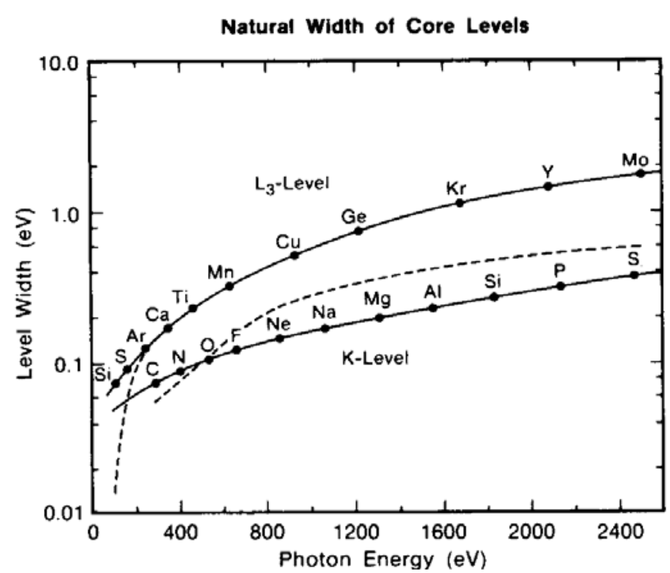
Sandell et. al. Phys. Rev. B48, 11347 (1993)



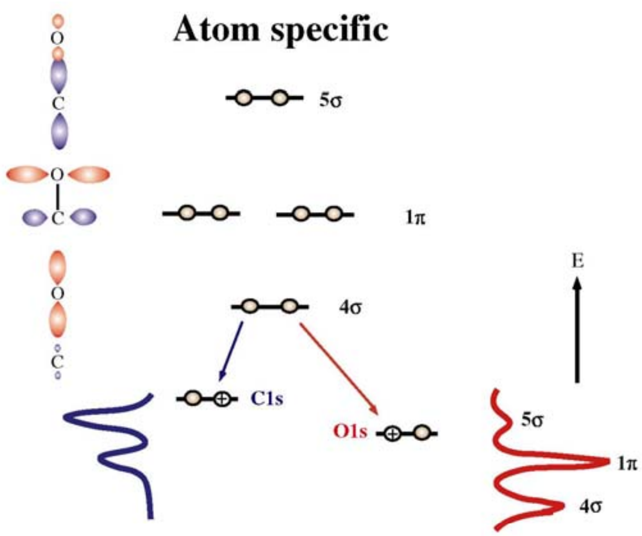
Core hole life time

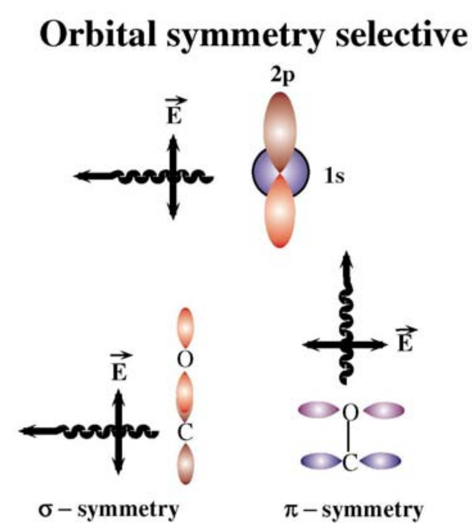
Sum of all decay channels

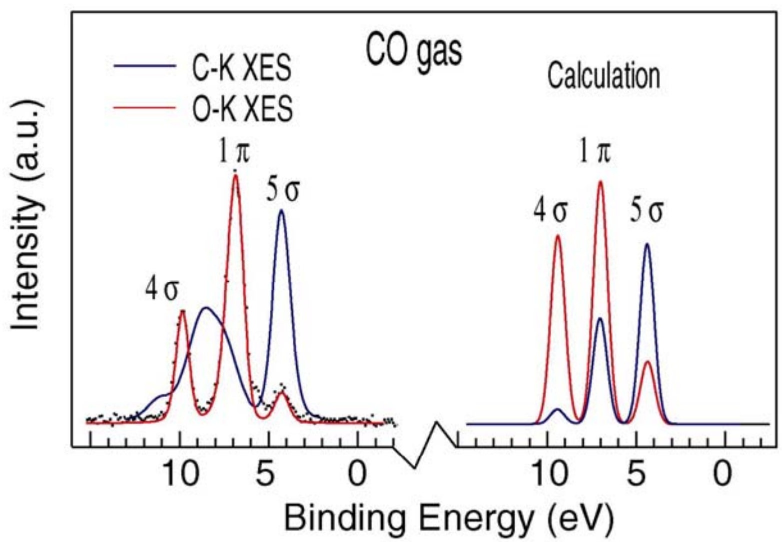
$$\Gamma = \Gamma_{aug} + \Gamma_{fluo}$$

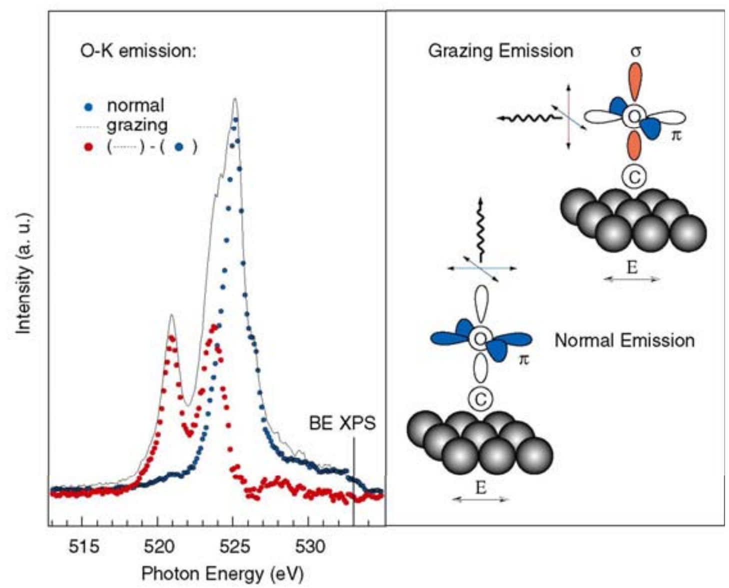


X-ray Emission Spectroscopy







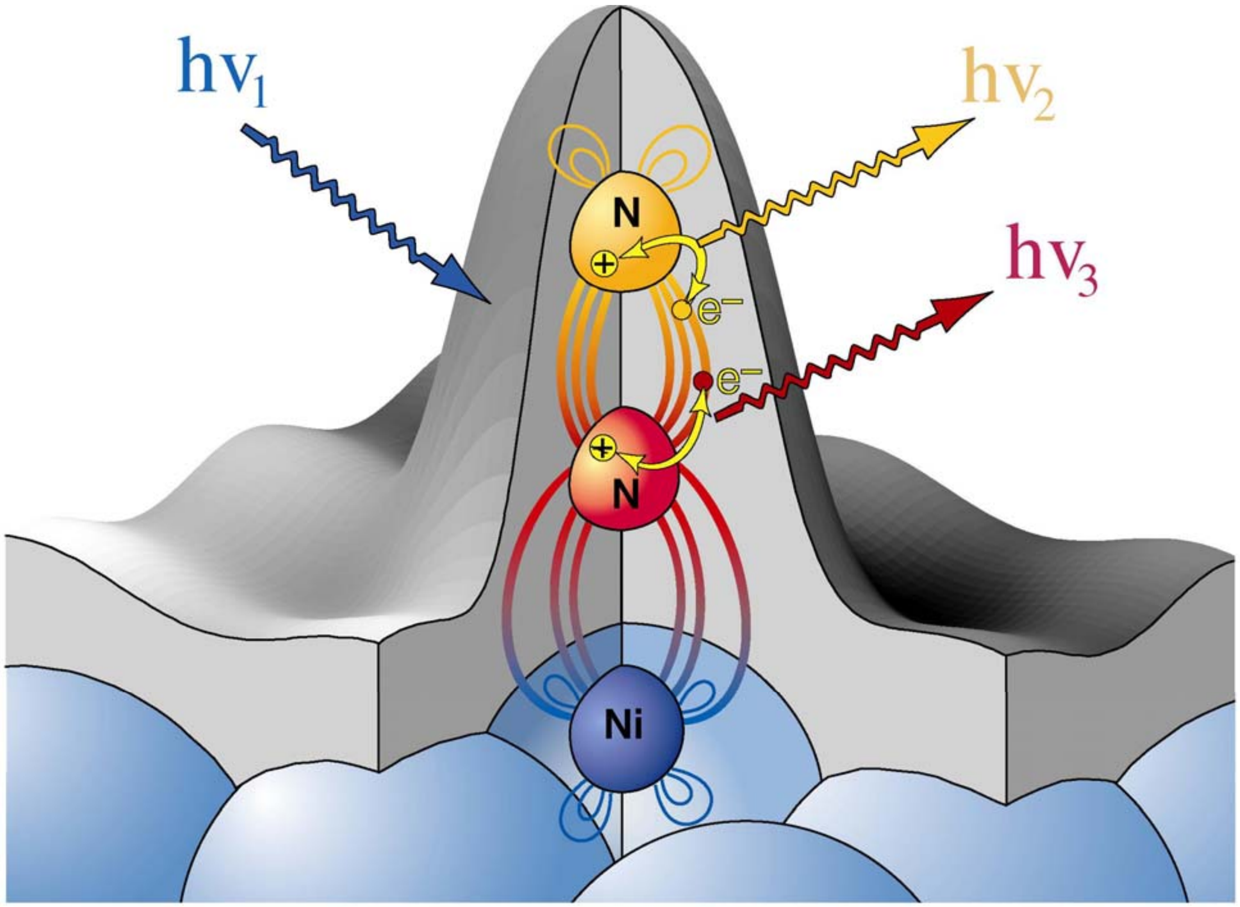


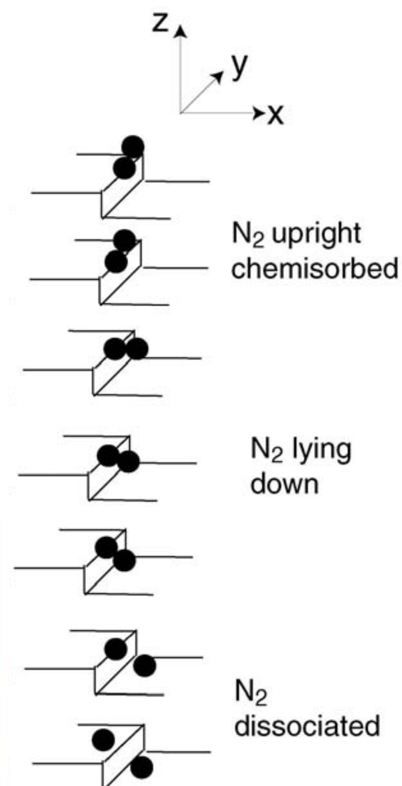
A. Nilsson et.al. J. Electron Spectr. 110-111, 12 (2000)

Chemical Bonding and Catalysis

Haber-Bosch

$$N_2 + 3H_2 \rightarrow 2NH_3$$



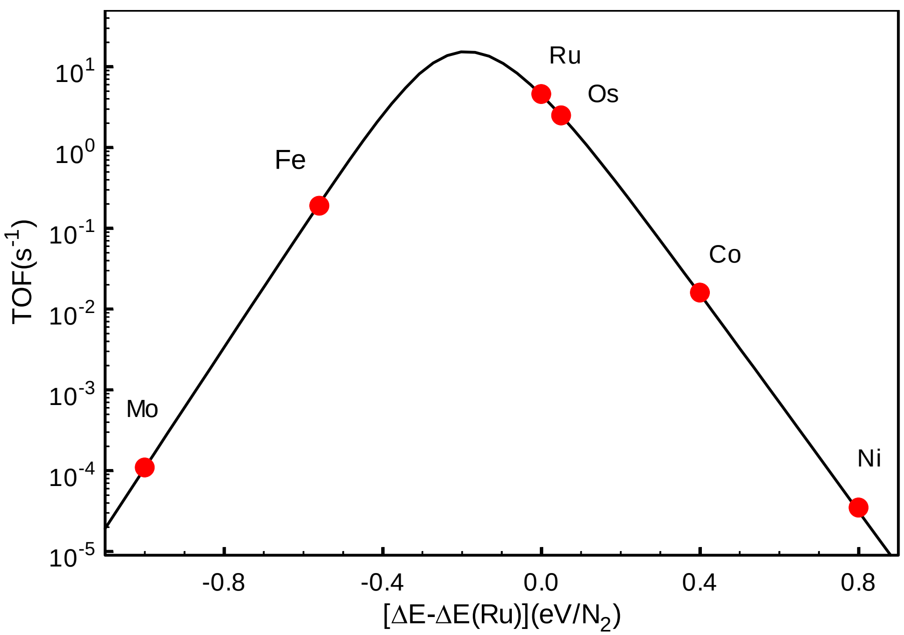


Surf. Sci. Reps. **55** (2004) 49.

Ammonia synthesis

Haber-Bosch

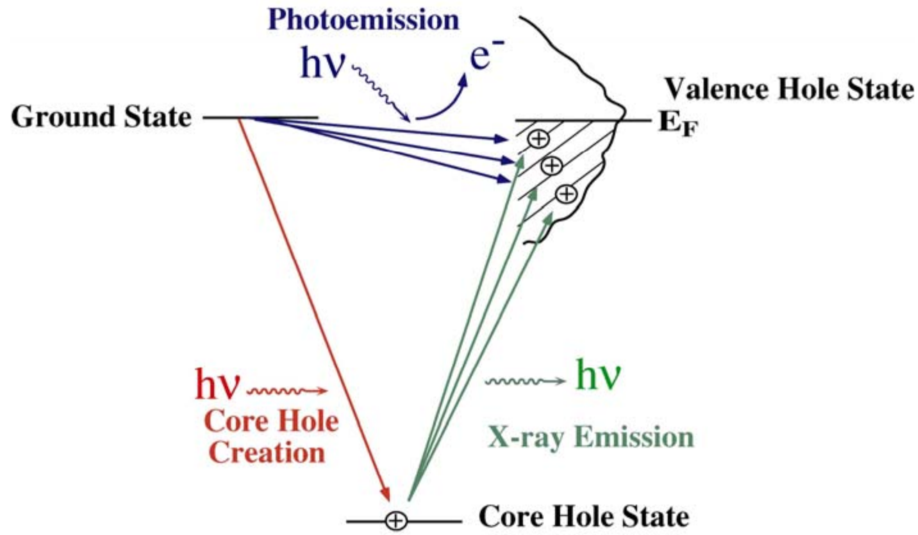
$$N_2 + 3H_2 \rightarrow 2NH_3$$

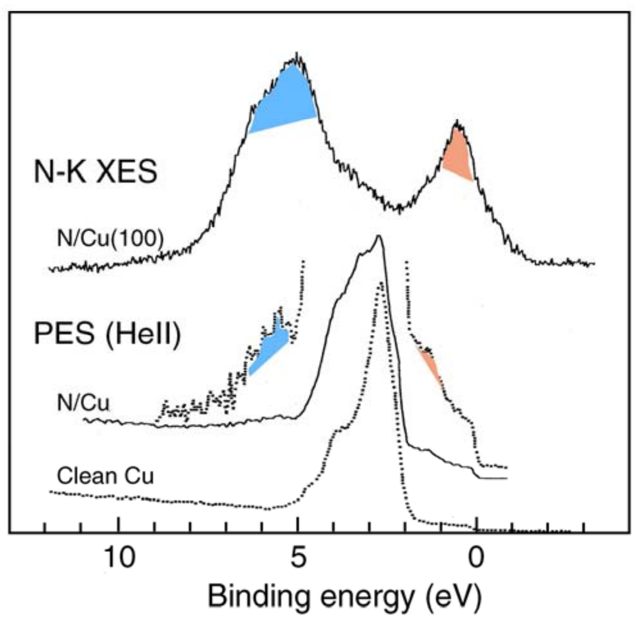


Reaction rate versus N-metal adsorption energy

X-ray Emission and Photoemission

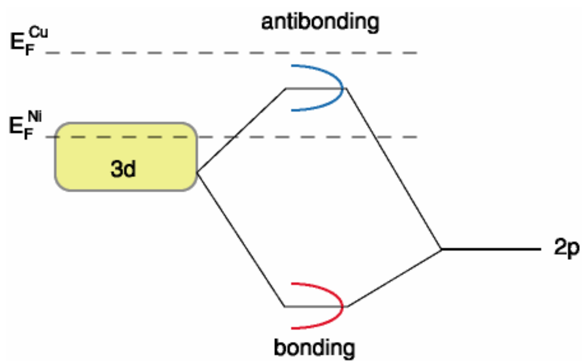
XES and PES, the same final state

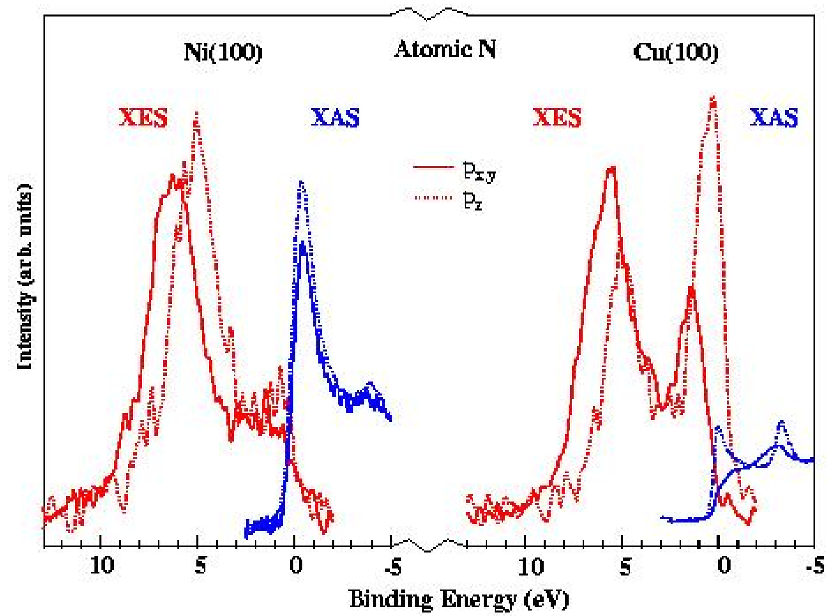


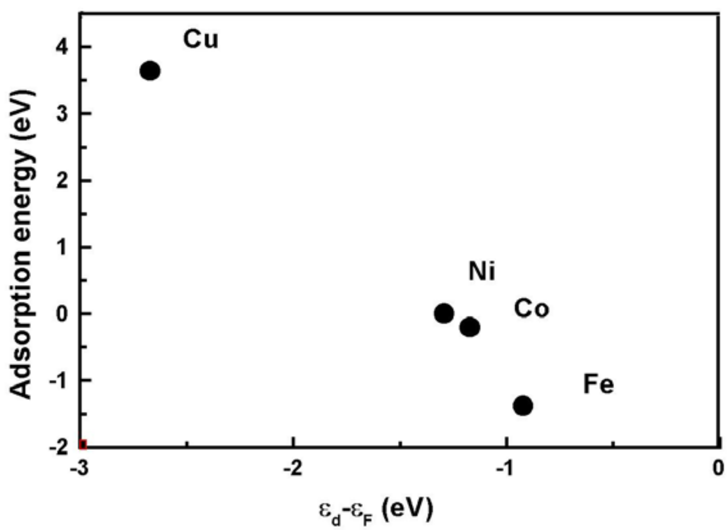


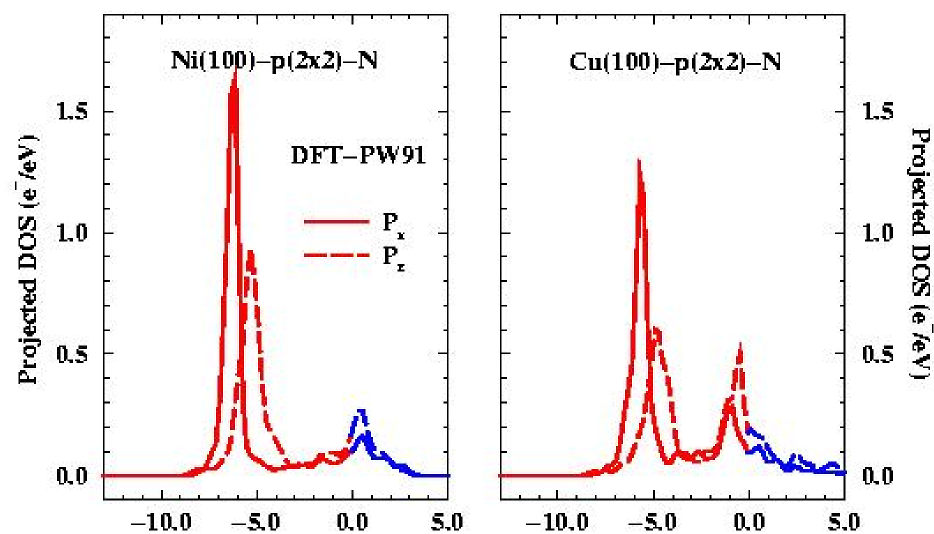
T. Wiell et al. Surf. Sci, 304, L451 (1995)

Electronic Effect in Catalysis





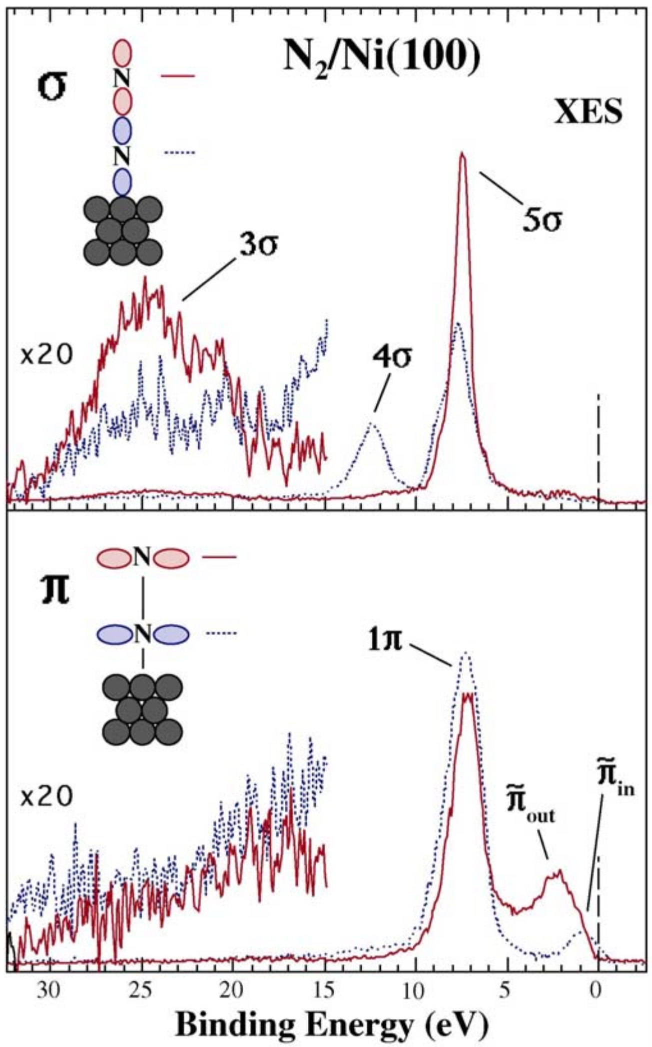




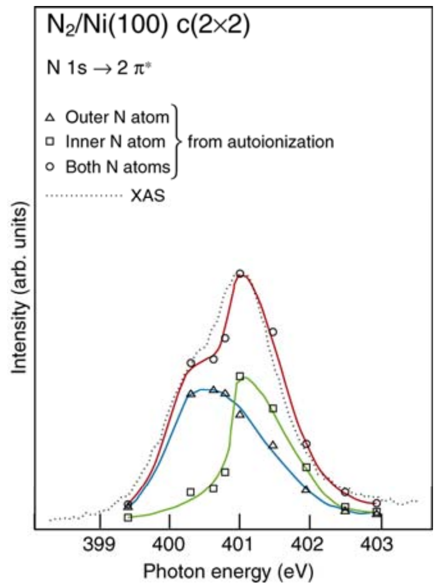
A. Nilsson et.al. to be published

Atom Selectivity

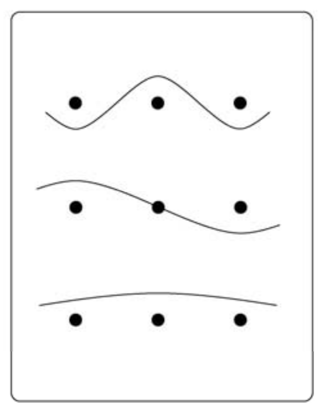
Selective excitation of inner and outer nitrogen atoms

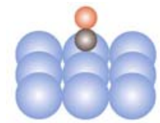


Nilsson et.al. Phys. Rev. Lett. 78, 2847 (1997)
Bennich et. al. Phys. Rev. B57, 9275 (1998)



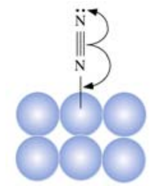
Allylic Configuration
π-Orbital structure of 3 atoms



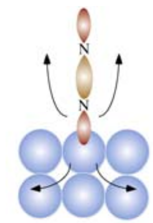


CO and N_2 on Ni(100)

Intramolecular bond 10 eV
Adsorbate-Substrate bond 0.5 eV
Assumed weak perturbation

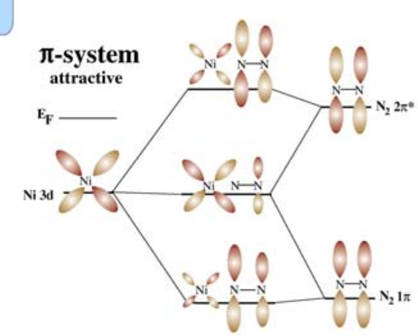


π-system
attractive interaction
N-N bond weakening



σ-system
repulsive interaction
N-N bond strengthening

COMPENSATION EFFECTS
ADSORPTION ENERGY
N-N BOND ENERGY



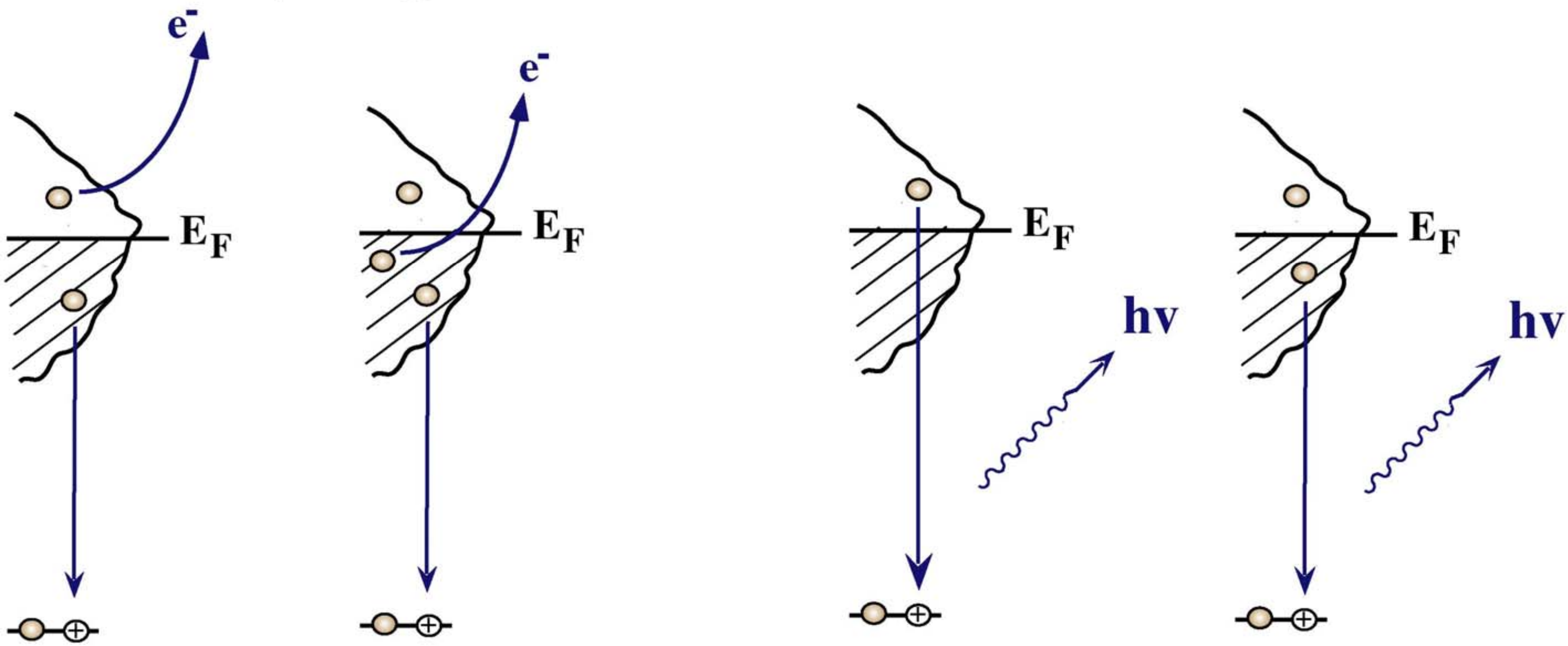
Resonant Processes

Non Radiant

Resonant Photoelectron Spectroscopy (RPES)
Resonant Auger Spectroscopy (RAES)
Autoionization Spectroscopy (AIS)

Radiant

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



Participator decay
one hole final state

Spectator decay
two hole-one electron final state

Participator decay
Recombination process
ground state

Spectator decay
one hole-one electron
final state

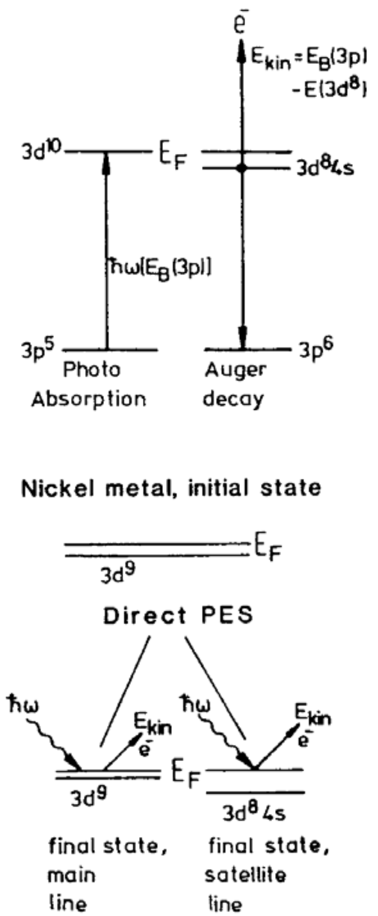
Resonant Photoemission

Valence band features resonant enhanced at core level threshold

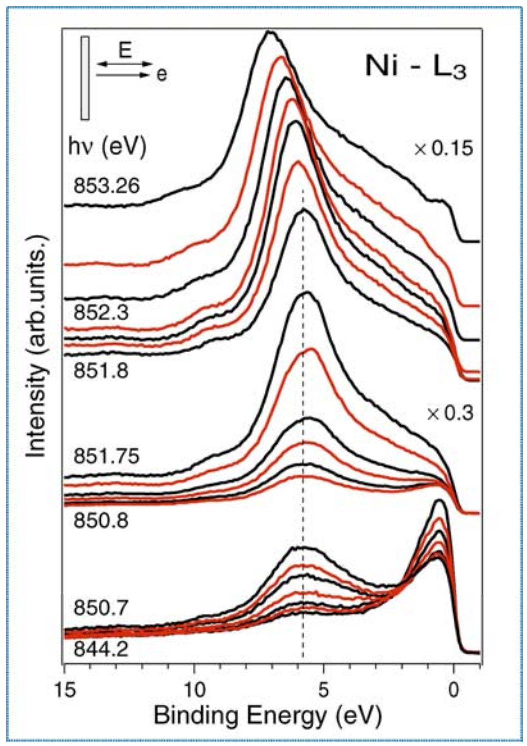
$$I = \left| M_{PES} + M_{Aug} \right|^2$$

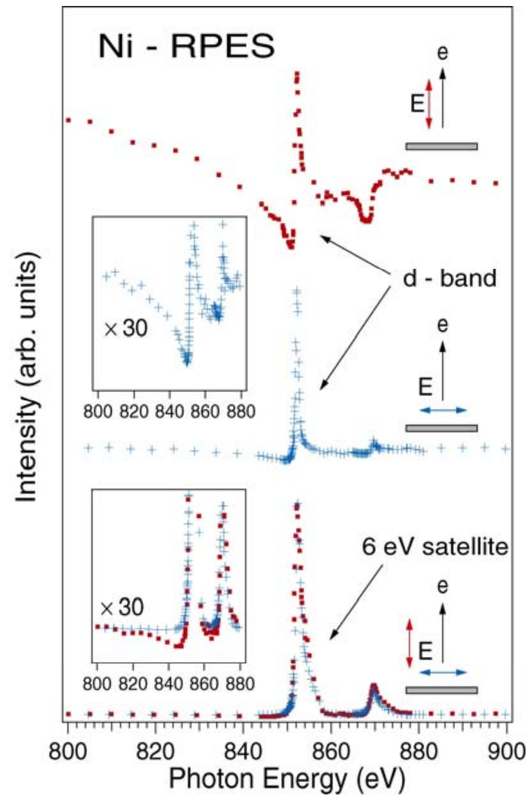
Constructive and destructive interference of direct photoemission and Auger decay

Fano profile



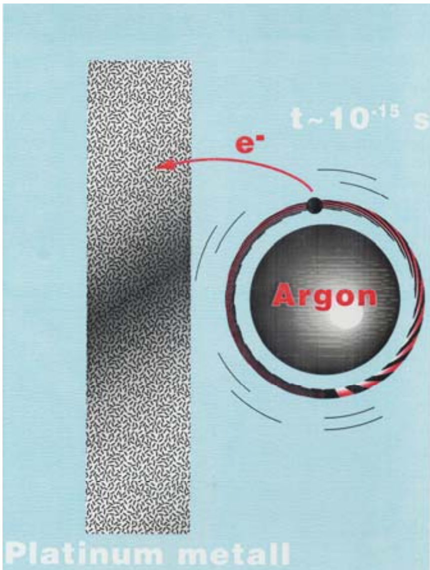
6 eV d-band



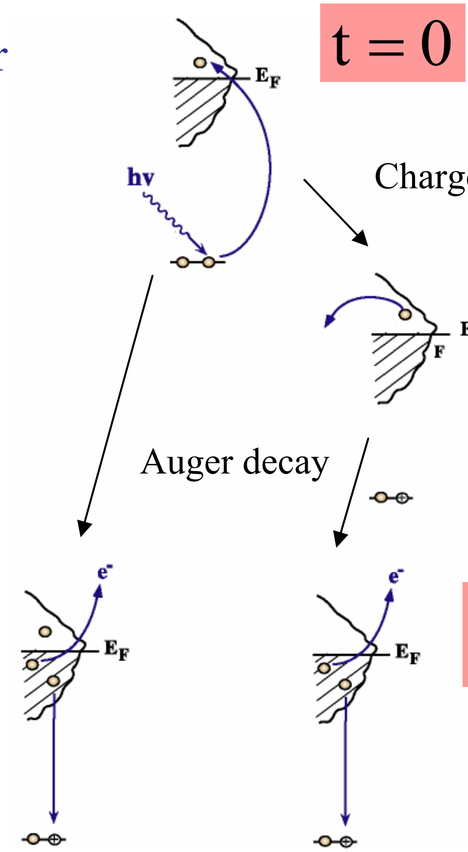


Weinelt et. Al. Phys. Rev. Lett. 78, 967 (1997)

Core Hole Clock Method



Probing charge transfer processes on a femtosecond timescale



$t = 0$

τ_{CT}

$t = \tau$

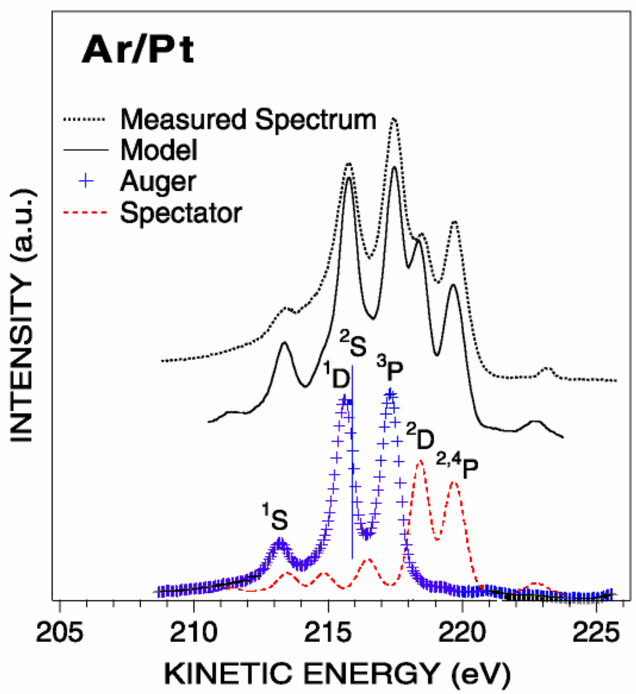
$\tau_{Ar2p} = 5.5x10^{-15}s$

+1 Spectator final state

46%

+2 Auger final state

54%



$$P_{CT} = \left(1 + \tau_{CT} / \tau_{Ar2p}\right)^{-1}$$

$\tau_{CT} = 4.7x10^{-15}s$

Karis et. al. Phys. Rev. Lett. 76, 1380 (1996)

Sandell et. al. Surf. Sci. 429, 309 (1999)