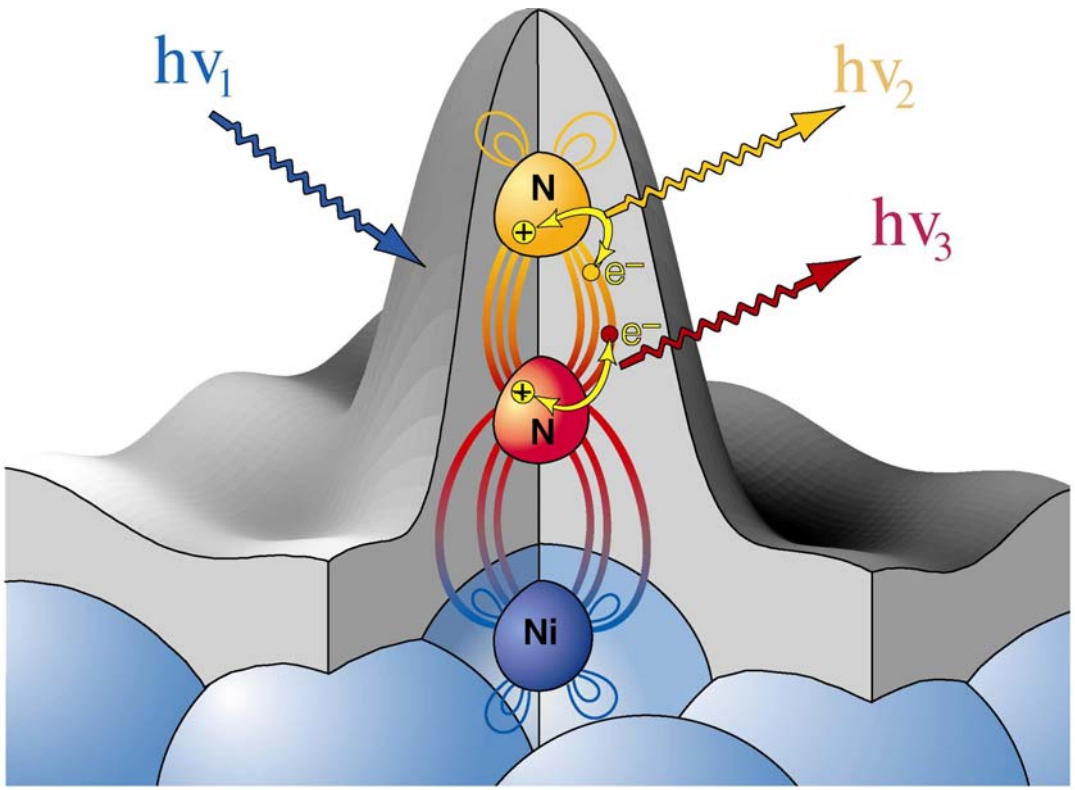
X-ray Spectroscopy

Probing of Valence Electrons with X-rays

Anders Nilsson
SSRL and Stockholm University



Excitations involving valence electrons

Atom specific

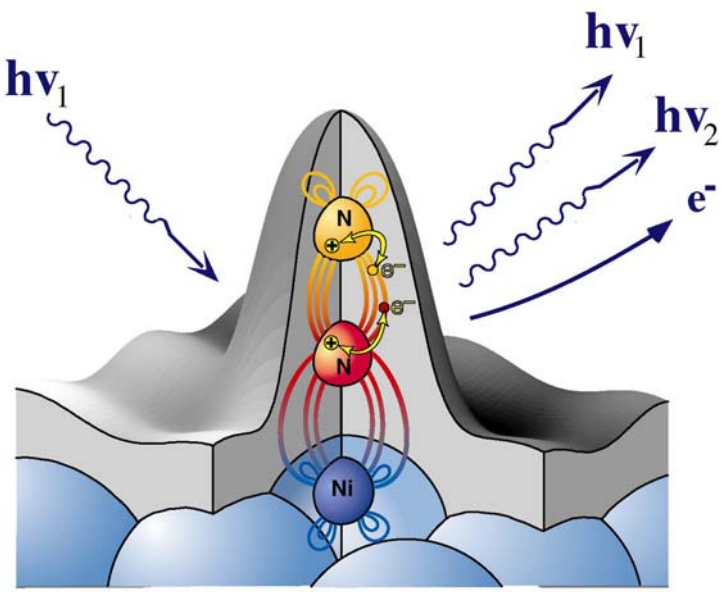
Local probing allows complex systems

Spin and Charge distributions

Could we probe the valence electrons during an ultrafast process?

Photon Interaction

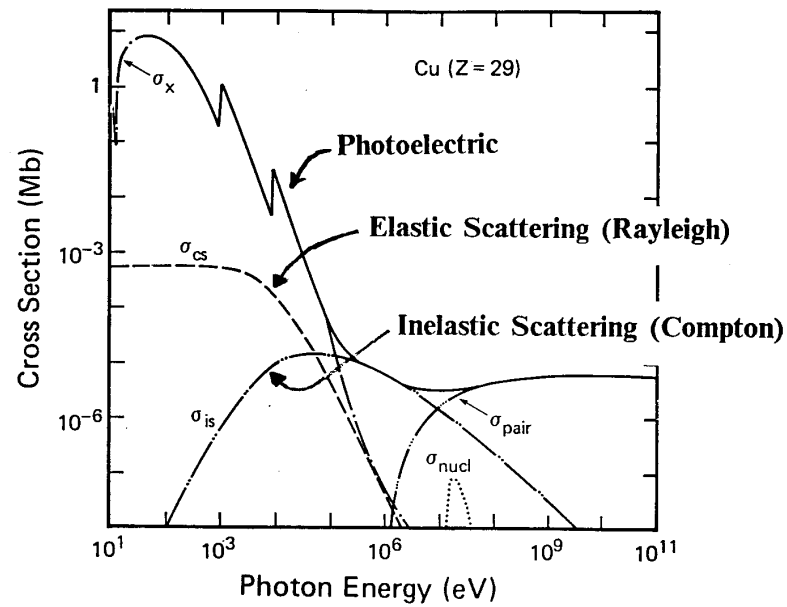
Incident photon interacts with electrons
Core and Valence



- Photon is
- Adsorbed
- Elastic Scattered
- Inelastic Scattered

- Electron is
- Emitted
- Excitated
- Dexcitated

Cross Sections



Stöhr, NEXAPS spectroscopy

Below 100 keV

Photoelectric cross section dominates

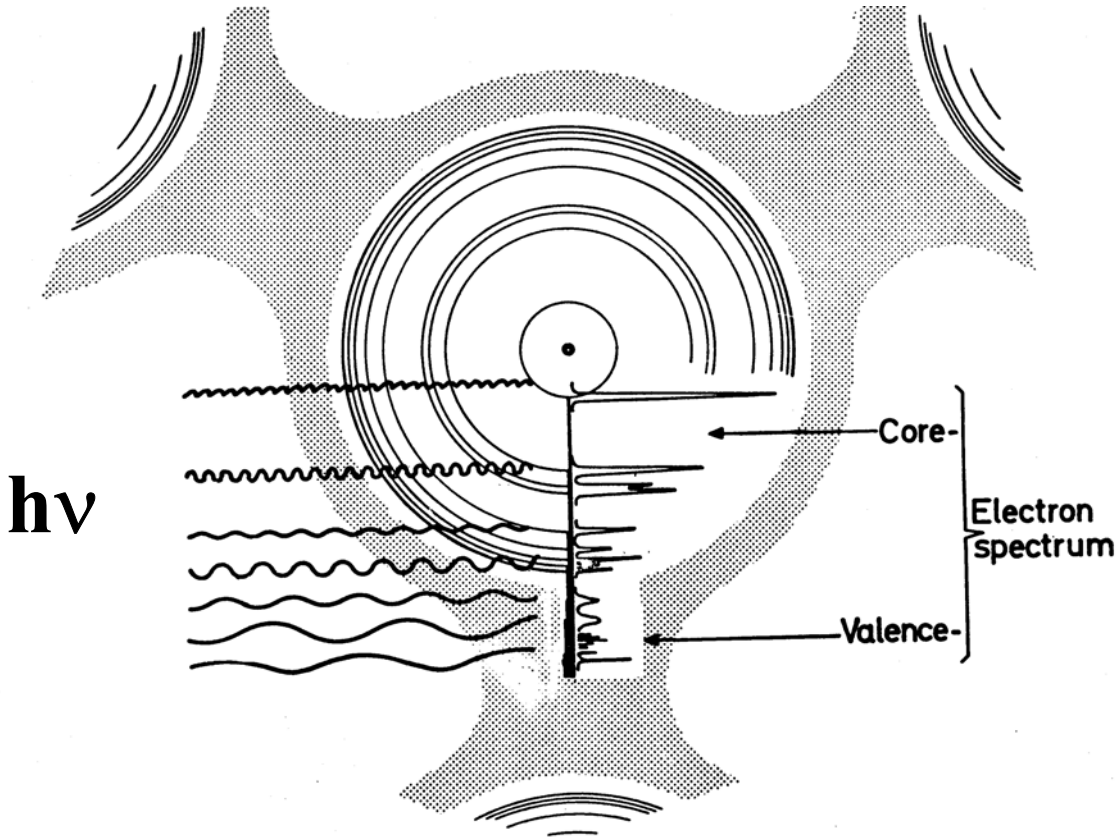
Spectroscopy

Spectroscopy

Valence electrons → Chemical Bonding

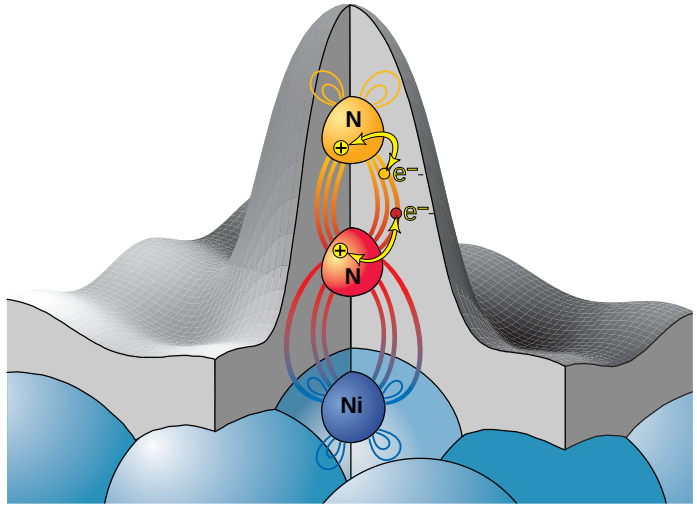
Core electrons → Non interacting

Ionization → Photoelectron Spectroscopy

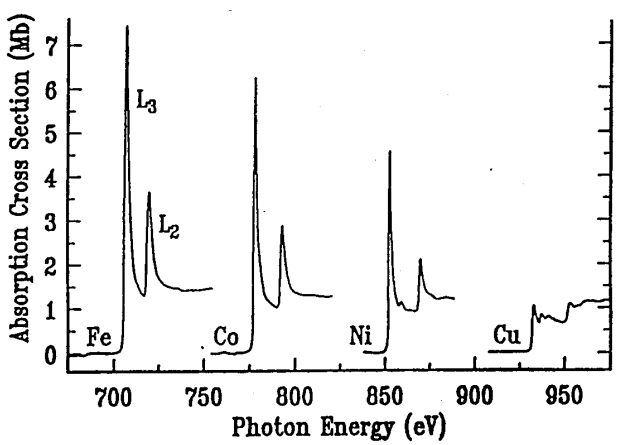


Core Levels-Atom Specific Information

X-rays probes core levels

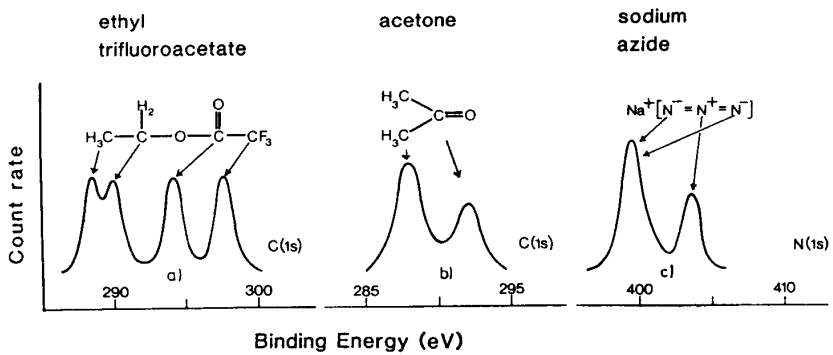


Element Sensitive



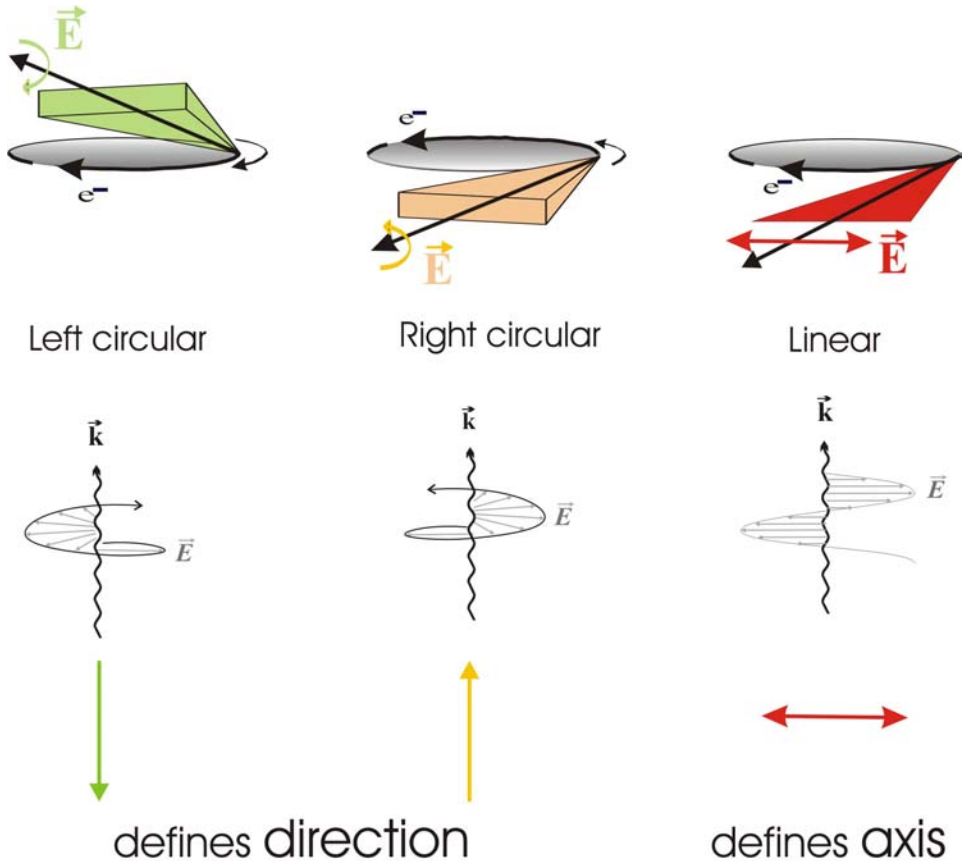
Stöhr et.al

Chemical Shifts



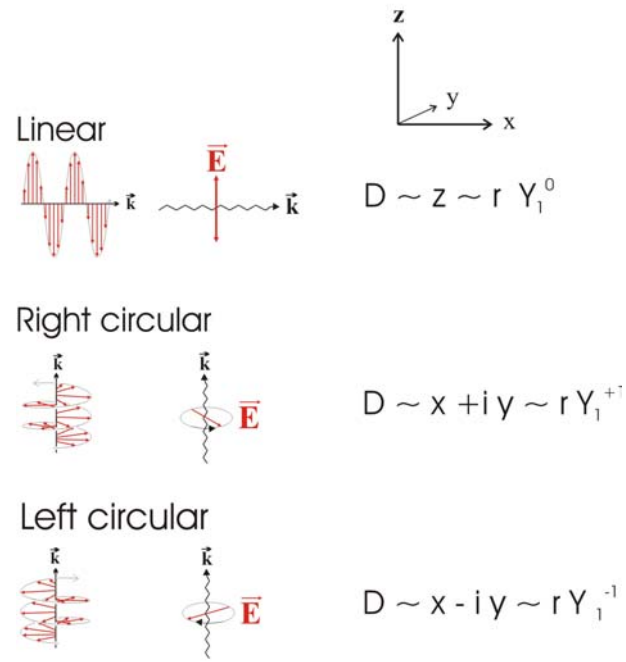
Hufner, Photoelectron Spectroscopy

Polarized X-rays Orientations and Directions



Absorption Intensity ~ $|\langle f | \mathbf{D} | i \rangle|^2$

$\mathbf{D} = \mathbf{E} \cdot \mathbf{r}$ is dipole operator

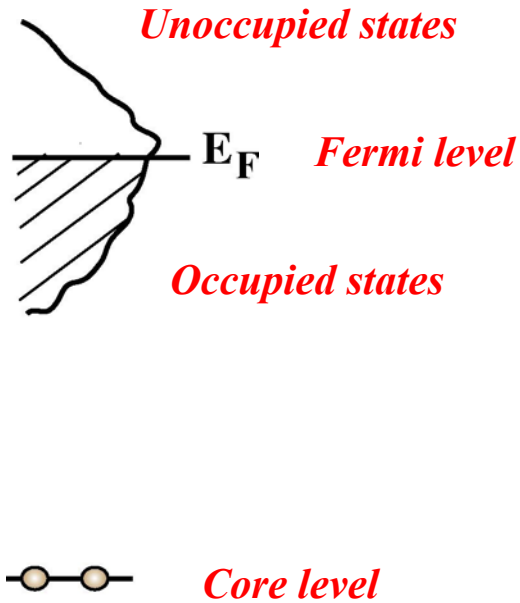


Selection rules:

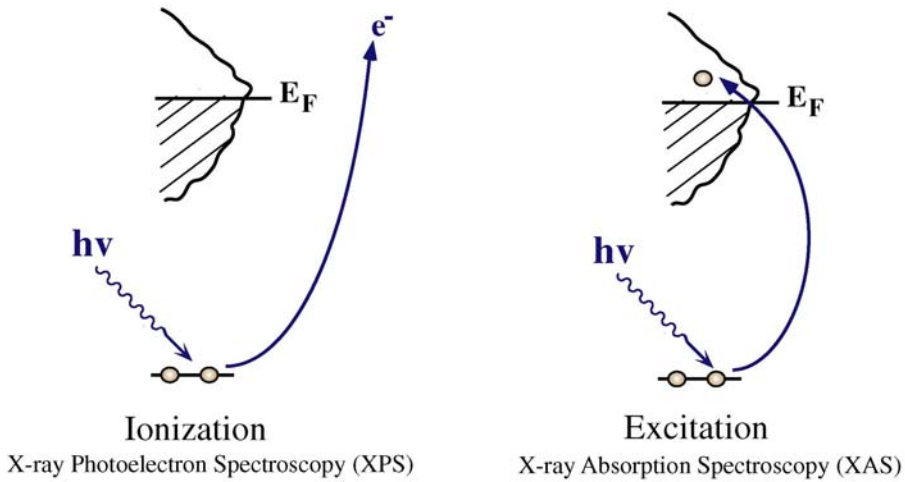
$\Delta l = \pm 1,\ \Delta s = 0,\ \Delta j = 0, \pm 1$

Probing Charge orientations and Spin directions

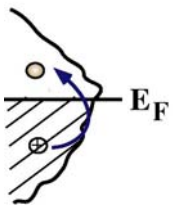
Core Level Spectroscopy



Creation of core holes

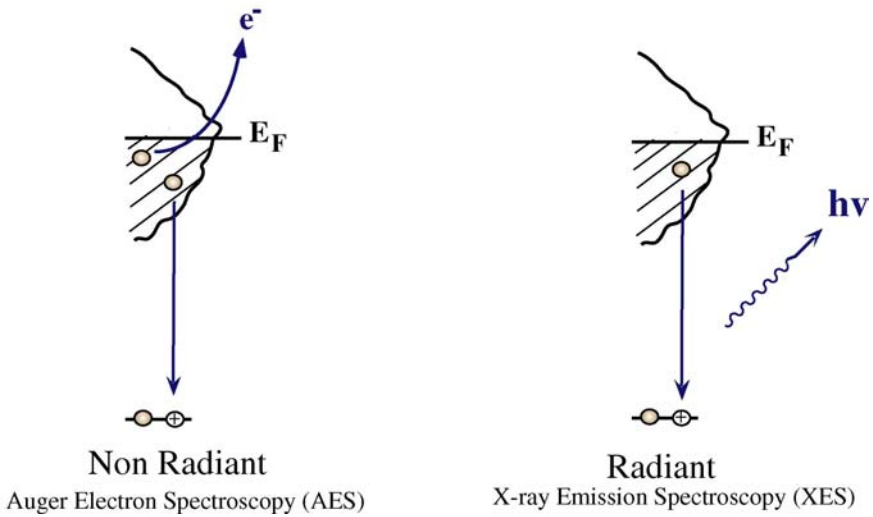


Laser spectroscopy



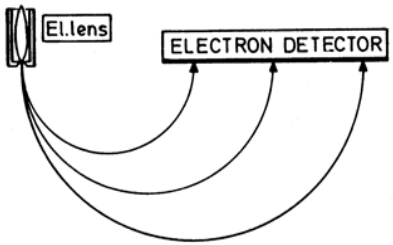
Excitations of valence electrons

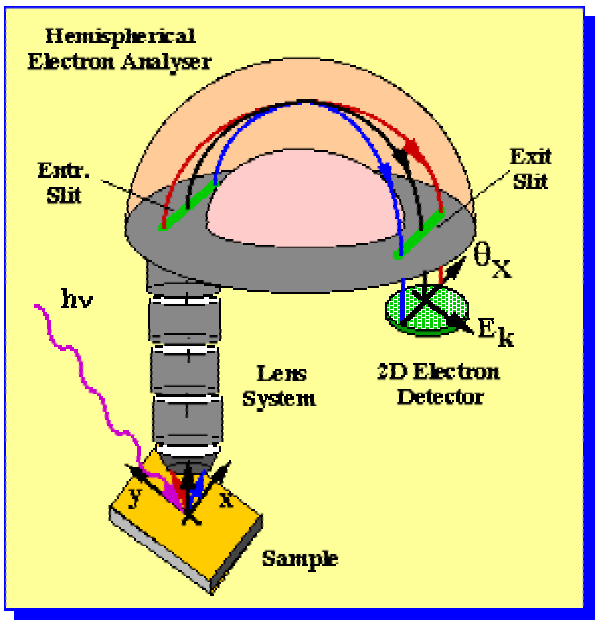
Decay of core holes

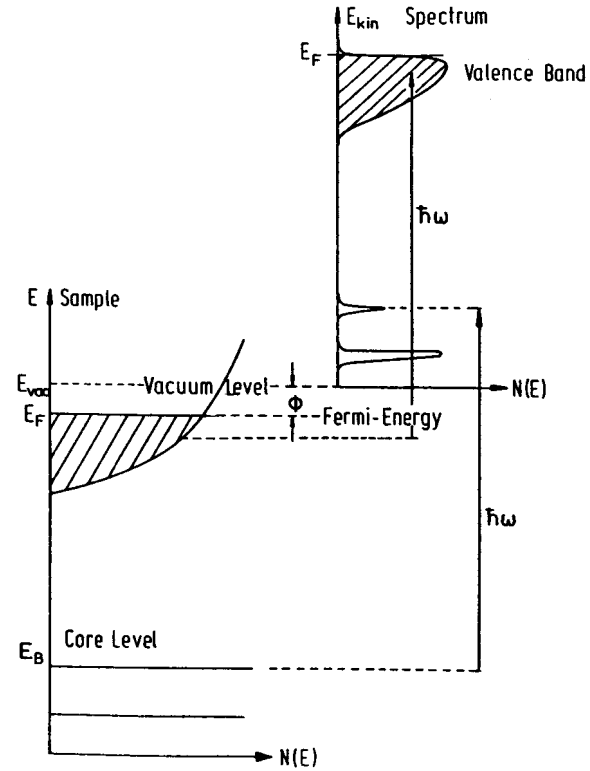


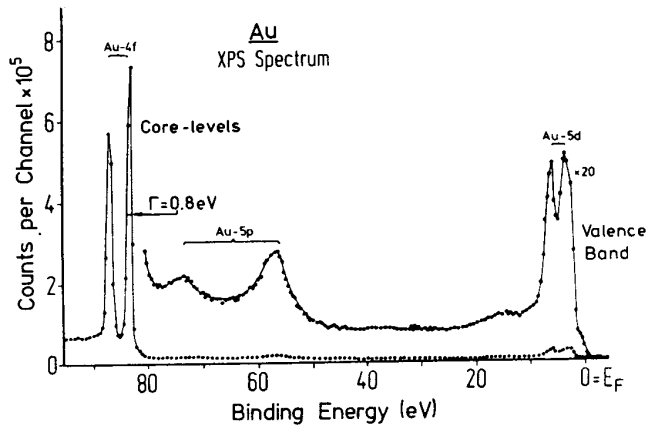
Photoelectron Spectroscop

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



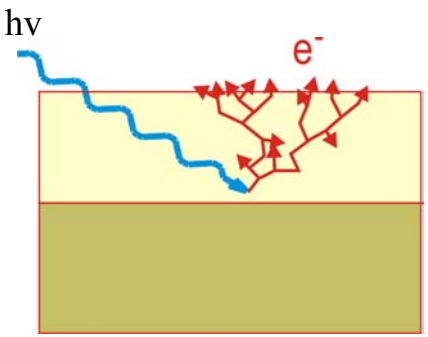






Hufner, Photelectron Spectroscopy

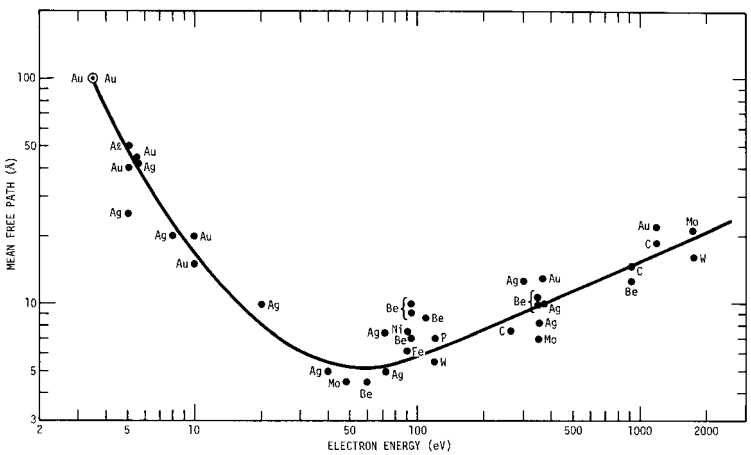
Core Level Electron Spectroscopy



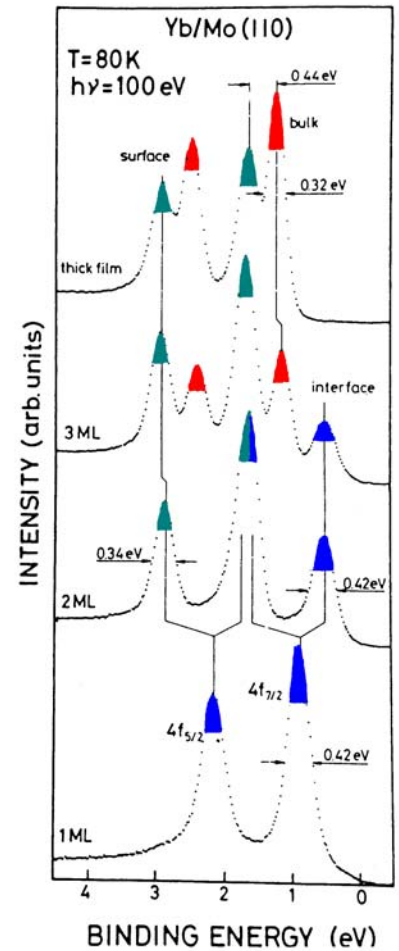
Electrons interact strongly

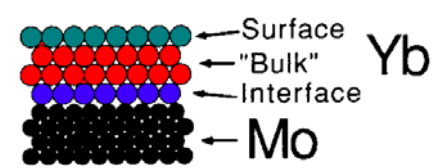
Surface Sensitivity

5-20 Å



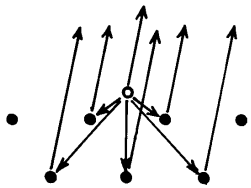
Dependent on electron kinetic energy

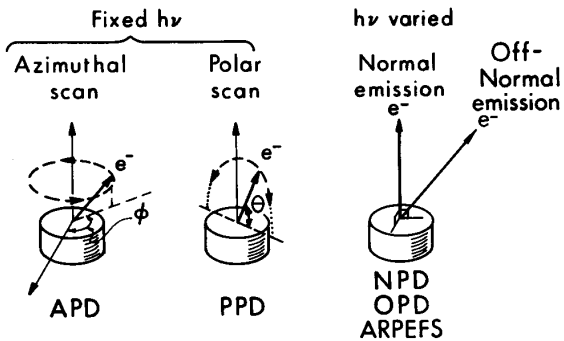


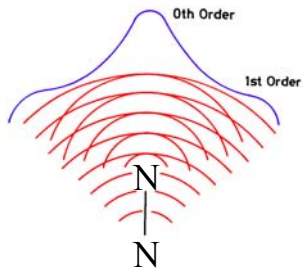


Mårtensson et. al. Phys. Rev. Lett. 60, 1731 (1988)

Photoelectron Diffraction

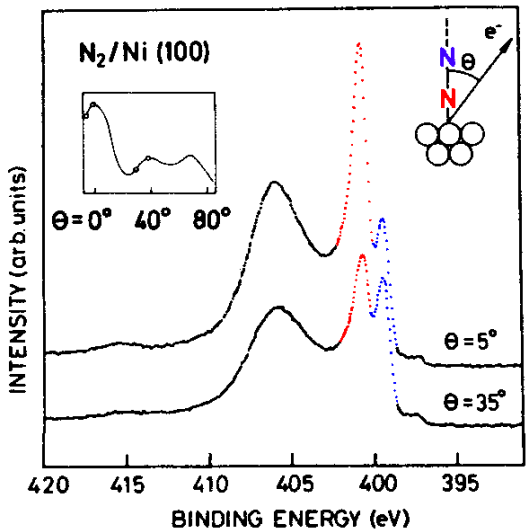






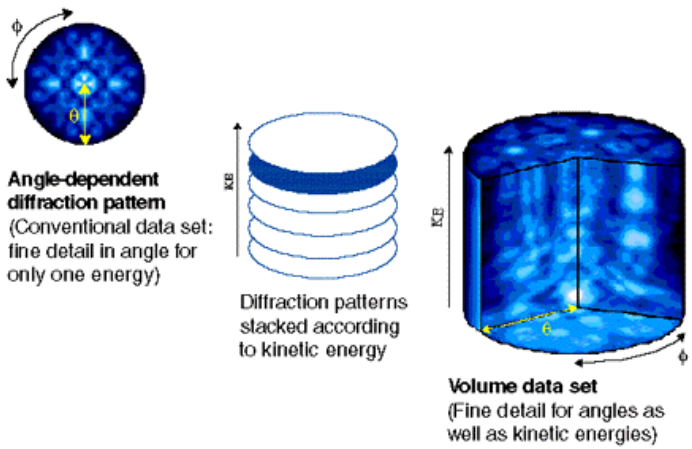
Forward scattering zero order diffraction

Molecular orientations



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

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



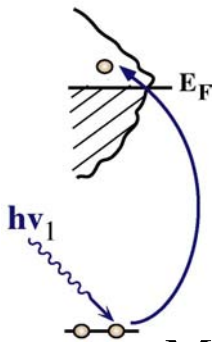
Beamline 7.0.1: U. of Wisconsin-Milwaukee, U. of Oregon, LBNL

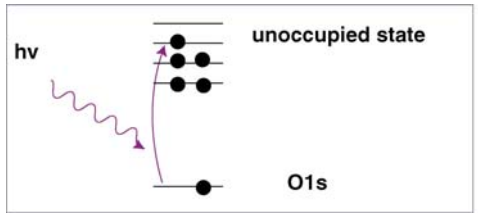
For a full structure determination

Energy dependent diffraction together with multiple scattering calculations

Tonner et. al. ALS web page

X-ray Absorption Spectroscopy

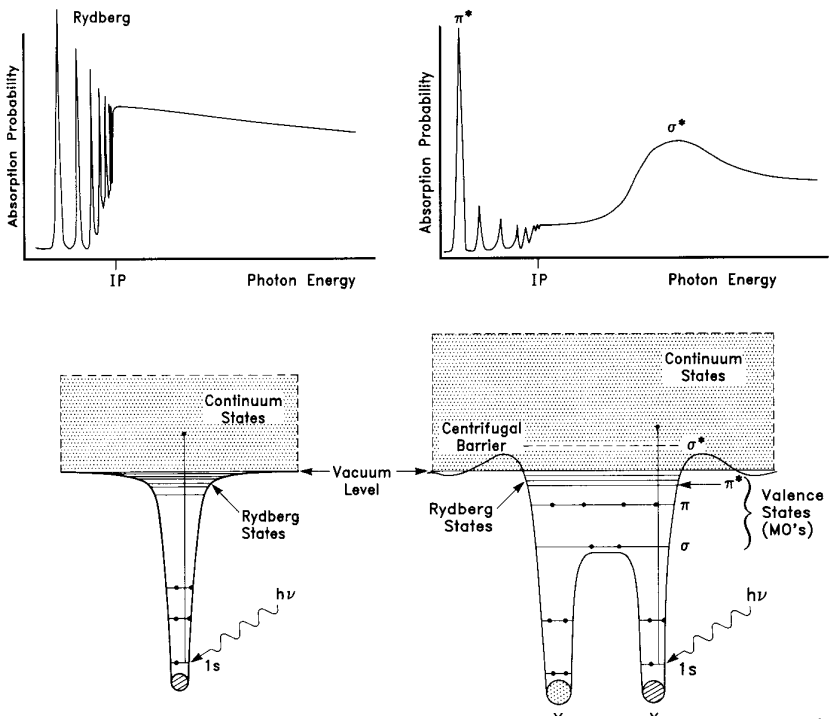


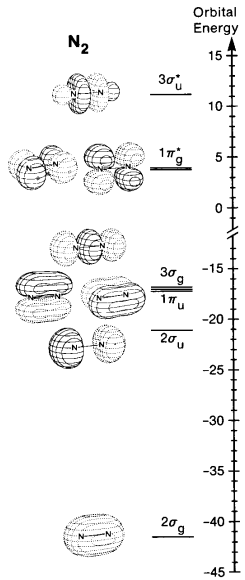


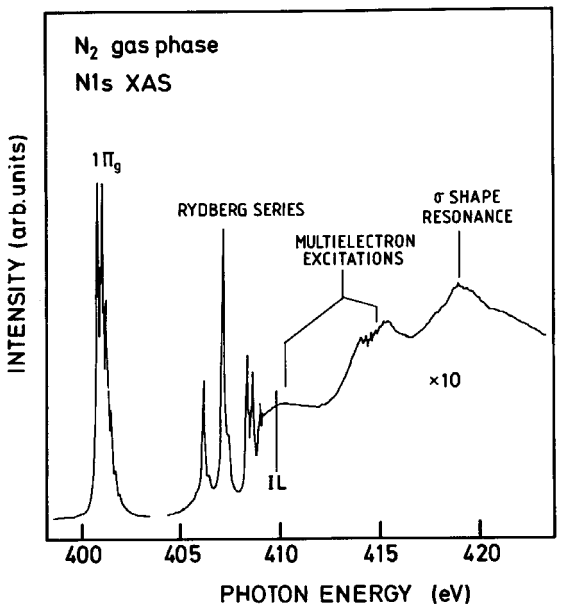
Dipole selection rule $\Delta l = \pm 1$

$1s \rightarrow 2p$

Molecular orbital or scattering picture





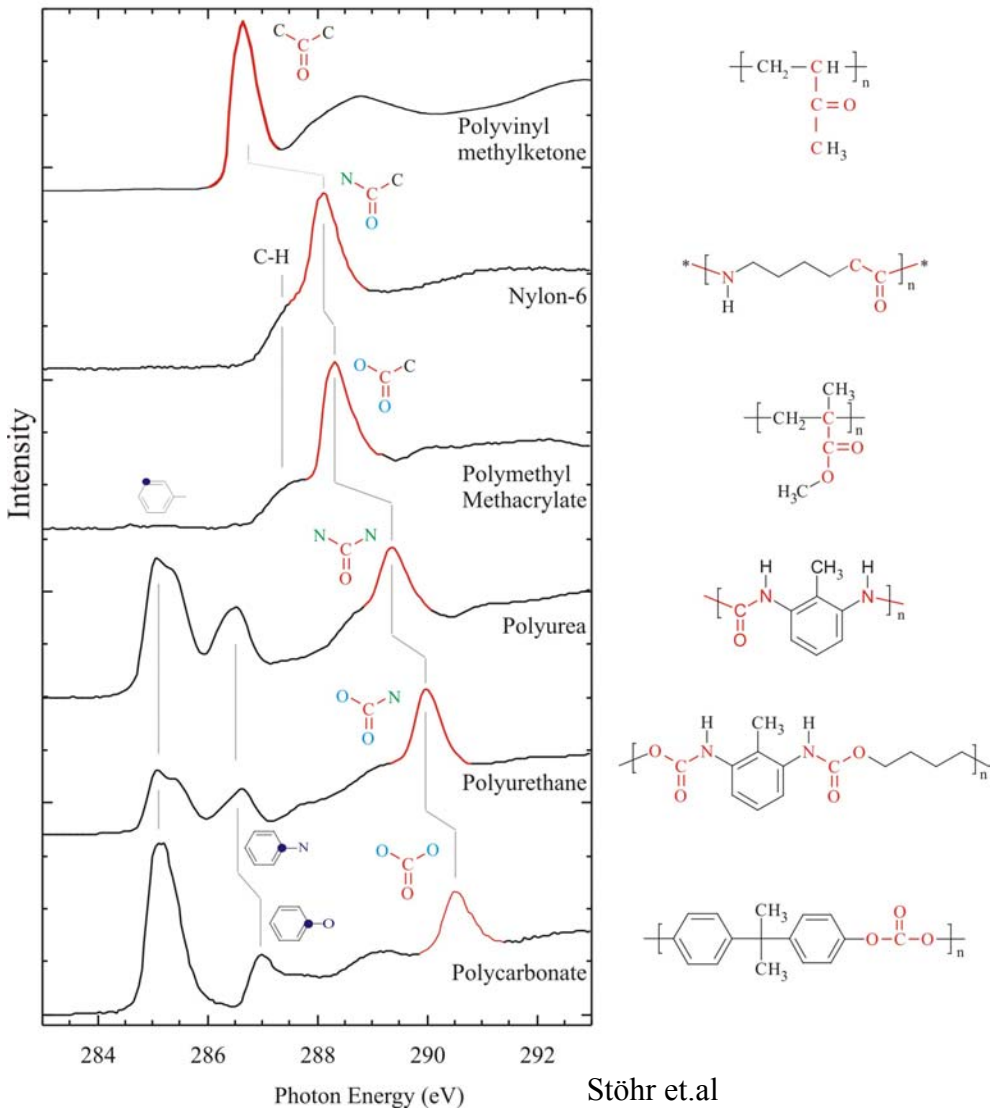


Ma et.al. Phys. Rev. A44, 1848 (1991)

Stöhr, NEXAFS spectroscopy

Chemical Sensitivity

Chemical Shift of C=O π Resonance



Stöhr et.al

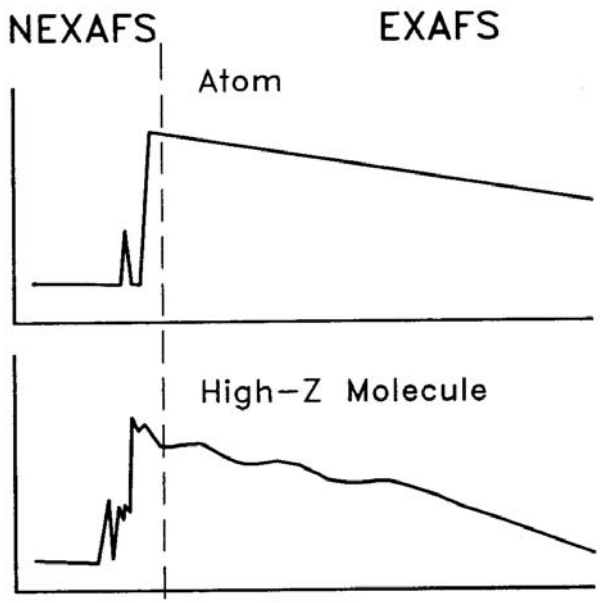
Core level shifts

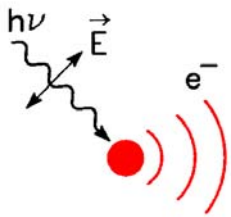
and

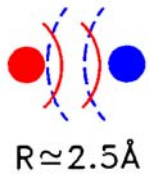
Molecular orbital shifts

EXAFS

Extended X-ray Absorption Fine Structure



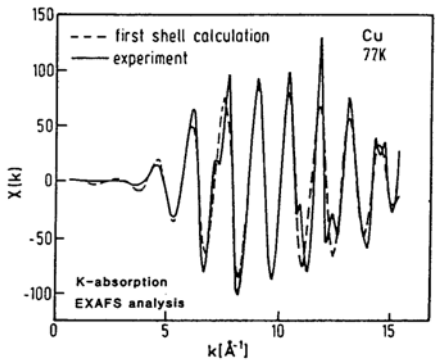


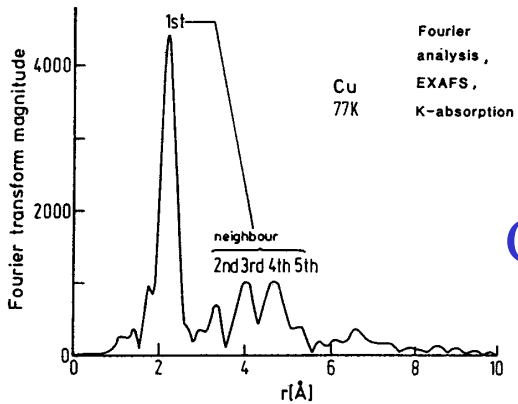


Interference of outgoing photoelectron and scattered waves

$$\chi(k) = (-1)^l \sum_i A_i(k) \sin\left[2kr_i + \beta_i^l(k)\right]$$

Nearest neighbor distance





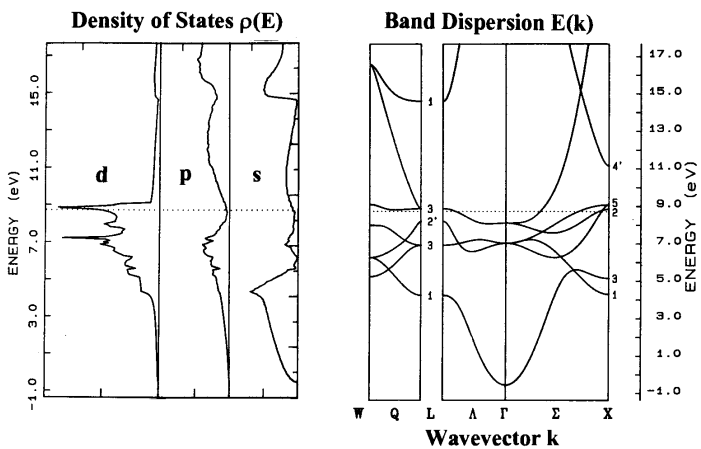
Coordination shells

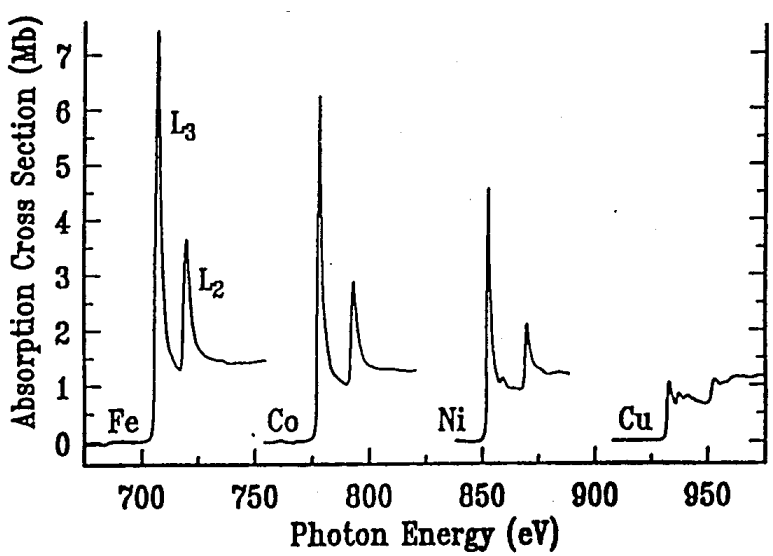
Transition Metals

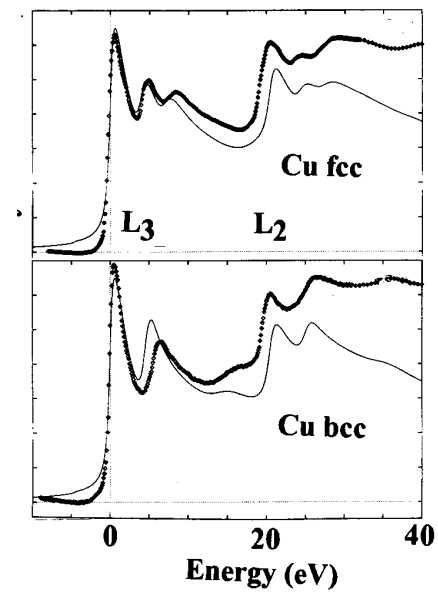
Dipole selection rule $\Delta l = \pm 1$

$2p \rightarrow 3d$

$2p \rightarrow 4s$



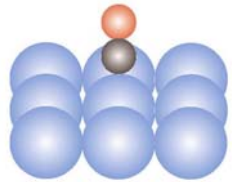


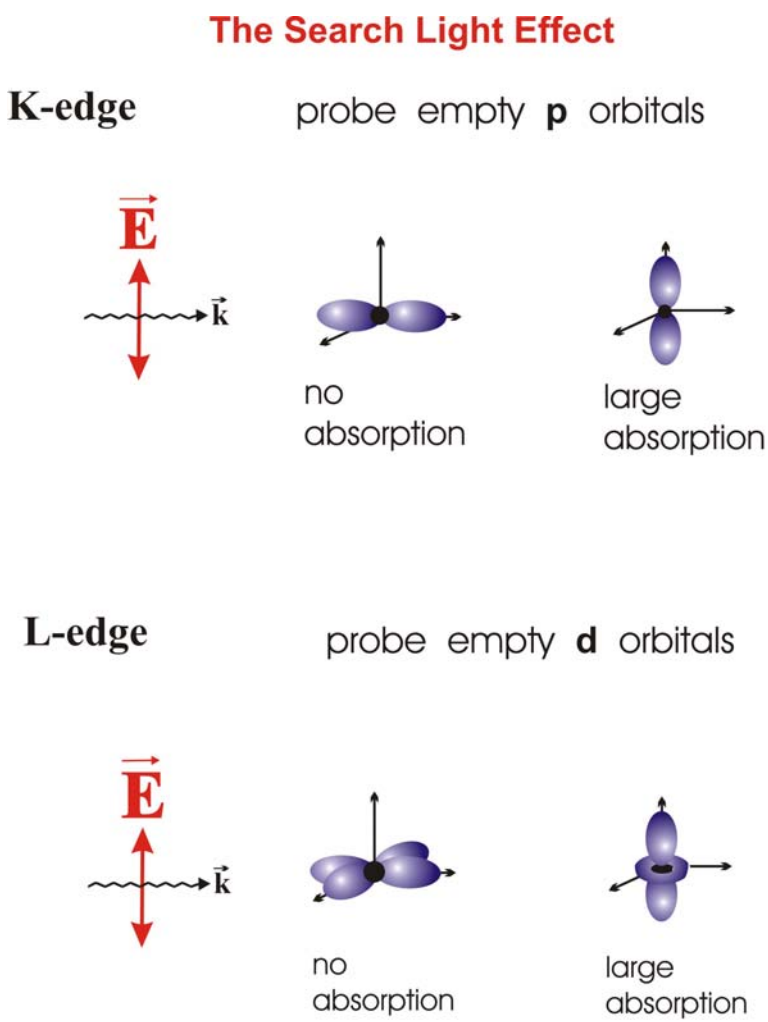


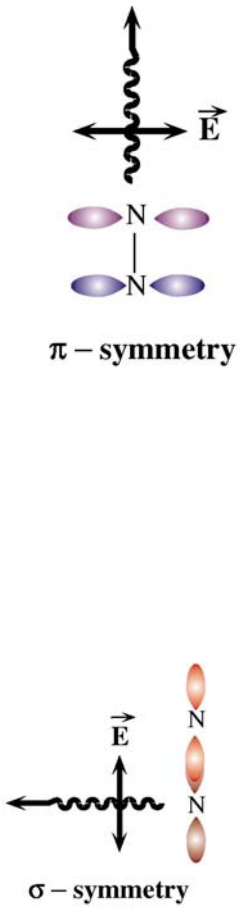
Ebert et. al. Phys. Rev. B 53, 16067 (1996).

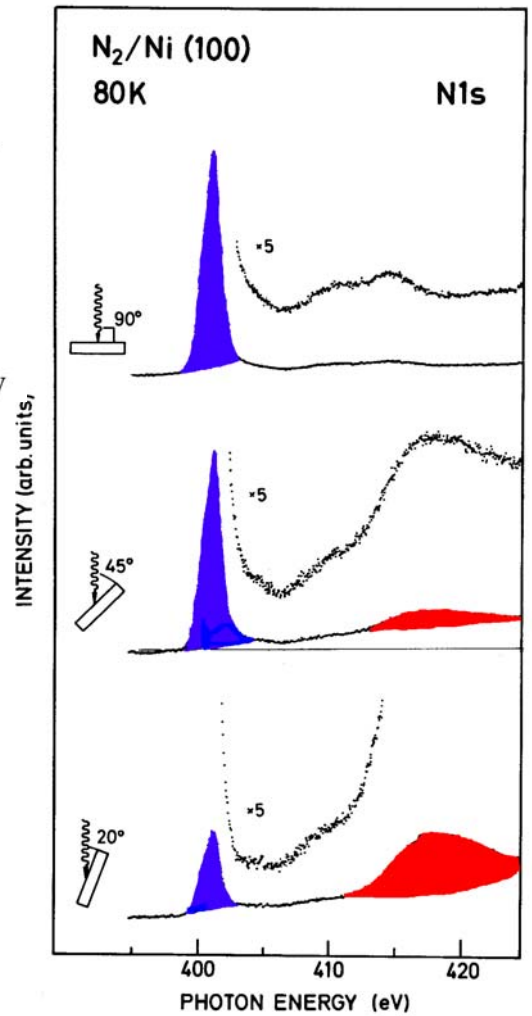
Total intensity reflect number of empty holes

Linear Dichroism









Molecular Orientations

Surfaces, Polymers etc.

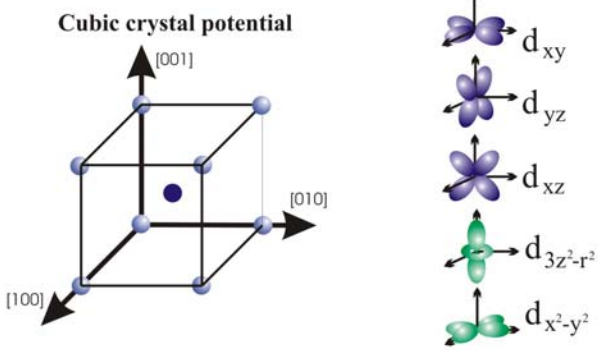
Stöhr NEXAFS Spectroscopy

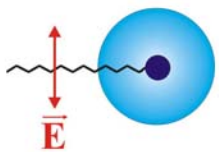
Björneholm et.al. Phys. Rev. B47, 2308 (1993)

Magnetic Linear Dichroism

Polarization with charge and spin

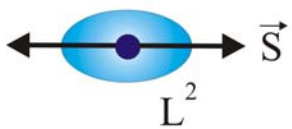
Non-magnetic state





d electron charge density is isotropic
no polarization dependence

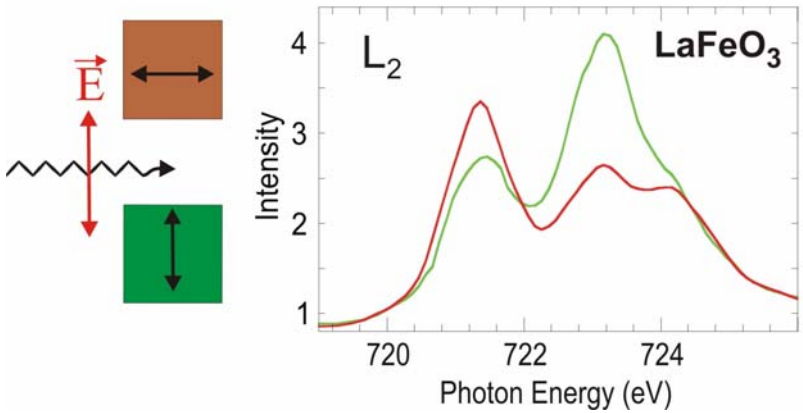
Magnetic state - preferred spin axis



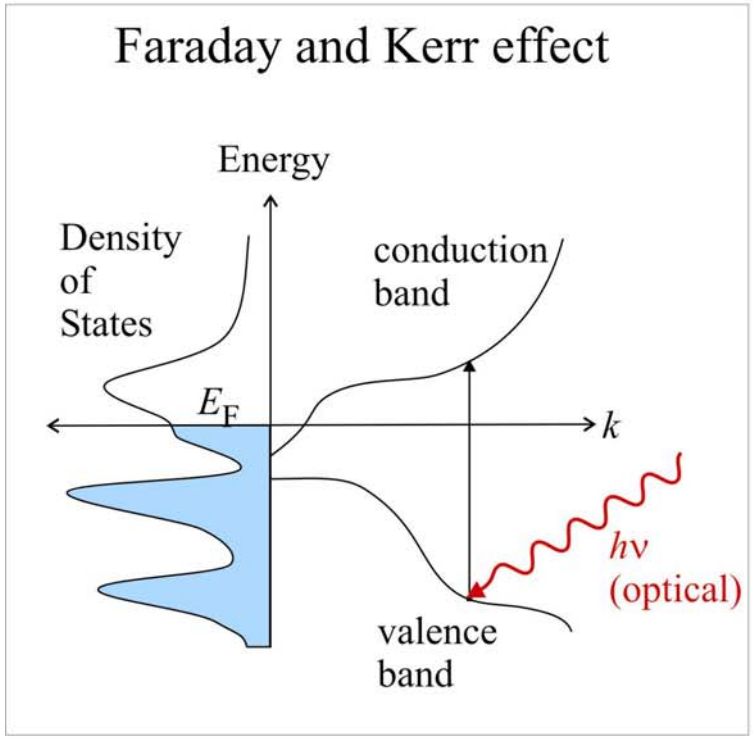
spin-orbit coupling distorts charge
creates polarization dependence

X-ray Magnetic Linear Dichroism

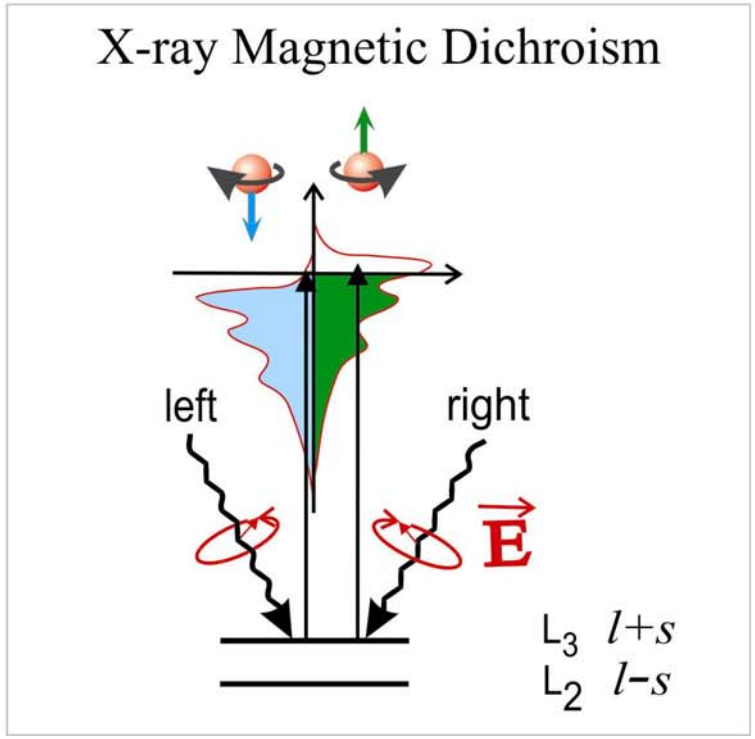
Van der Laan *et al.*, Phys. Rev. B **34**, 6529 (1986)



Magnetic Circular Dichroism



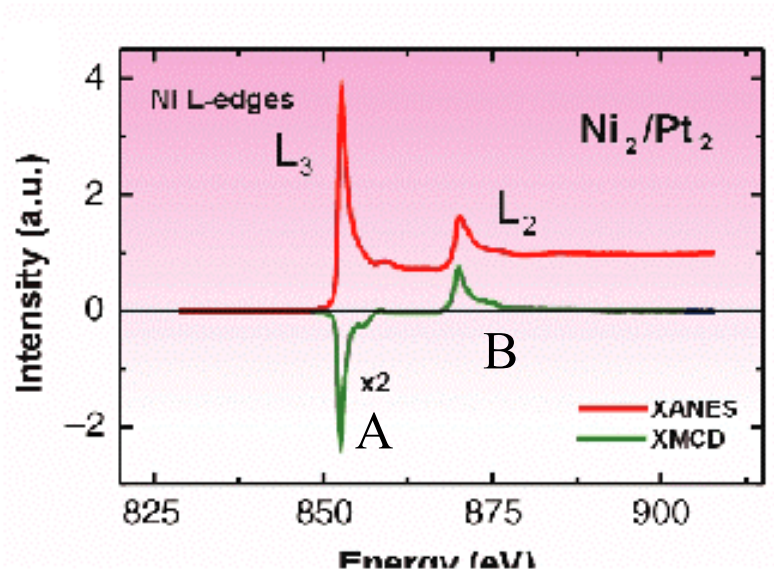
Magneto-optical response:
weak, k-dependent



X-ray response:
strong, k-integrated quantities
number of holes, spin monent, orbital moment

Spin and orbital moment

- X-ray magnetic circular dichroism (XCMD)
- Element specific
- Spin and orbital moments
- Magnetic Information



Ni L edge XAS spectrum and XMCD effect of Pt-Ni multilayer sample

Difference spectra of Right versus Left

$$M_{spin} = C(A - 2B)$$ Spin moment

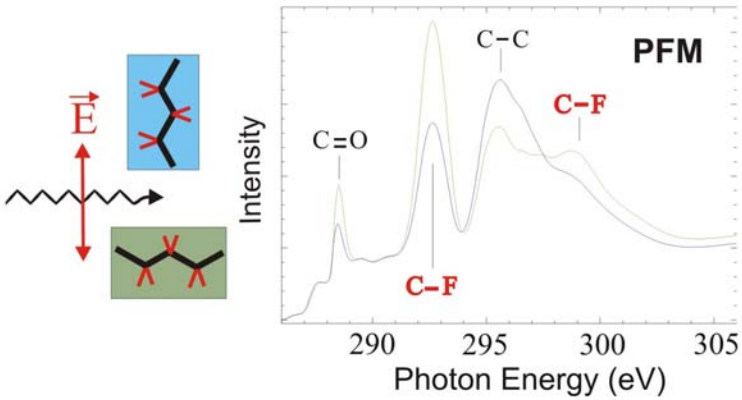
$$M_{orb} = C(A + B)$$ Orbital moment

C total intensity (number of d-holes)

Polarization Effects in X-ray Absorption

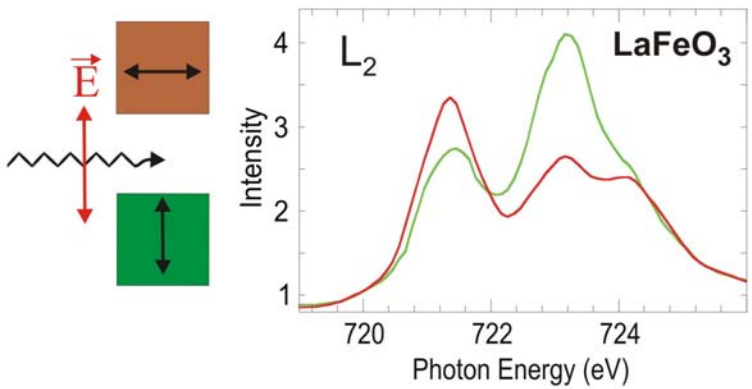
X-ray Linear Dichroism

Stöhr *et al.*, Phys. Rev. Lett. **47**, 381 (1981)



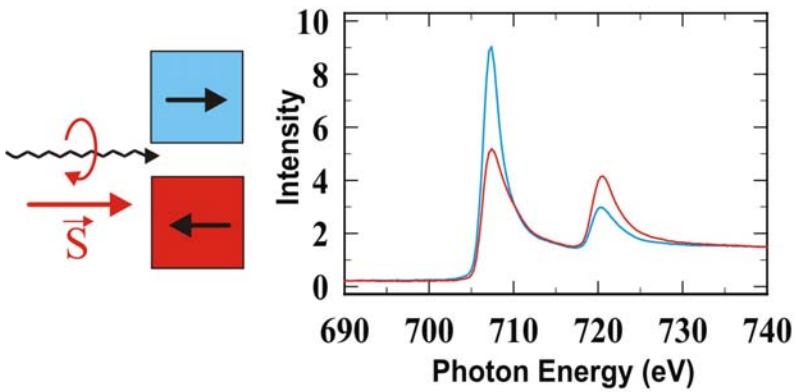
X-ray Magnetic Linear Dichroism

Van der Laan *et al.*, Phys. Rev. B **34**, 6529 (1986)



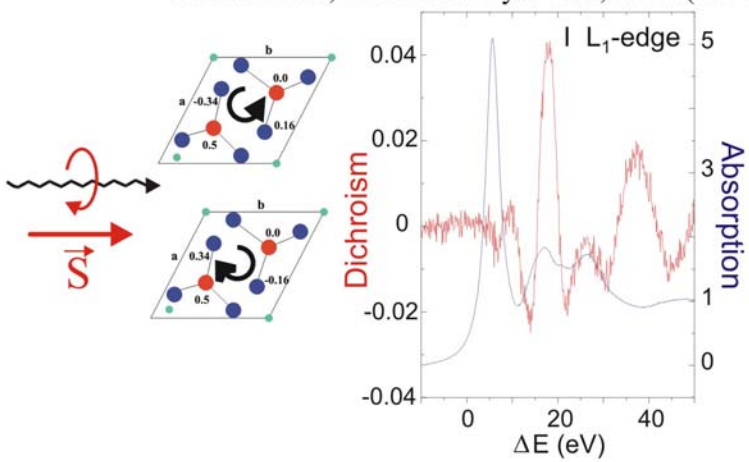
X-ray Magnetic Circular Dichroism

Schütz *et al.*, Phys. Rev. Lett. **58**, 737 (1987)

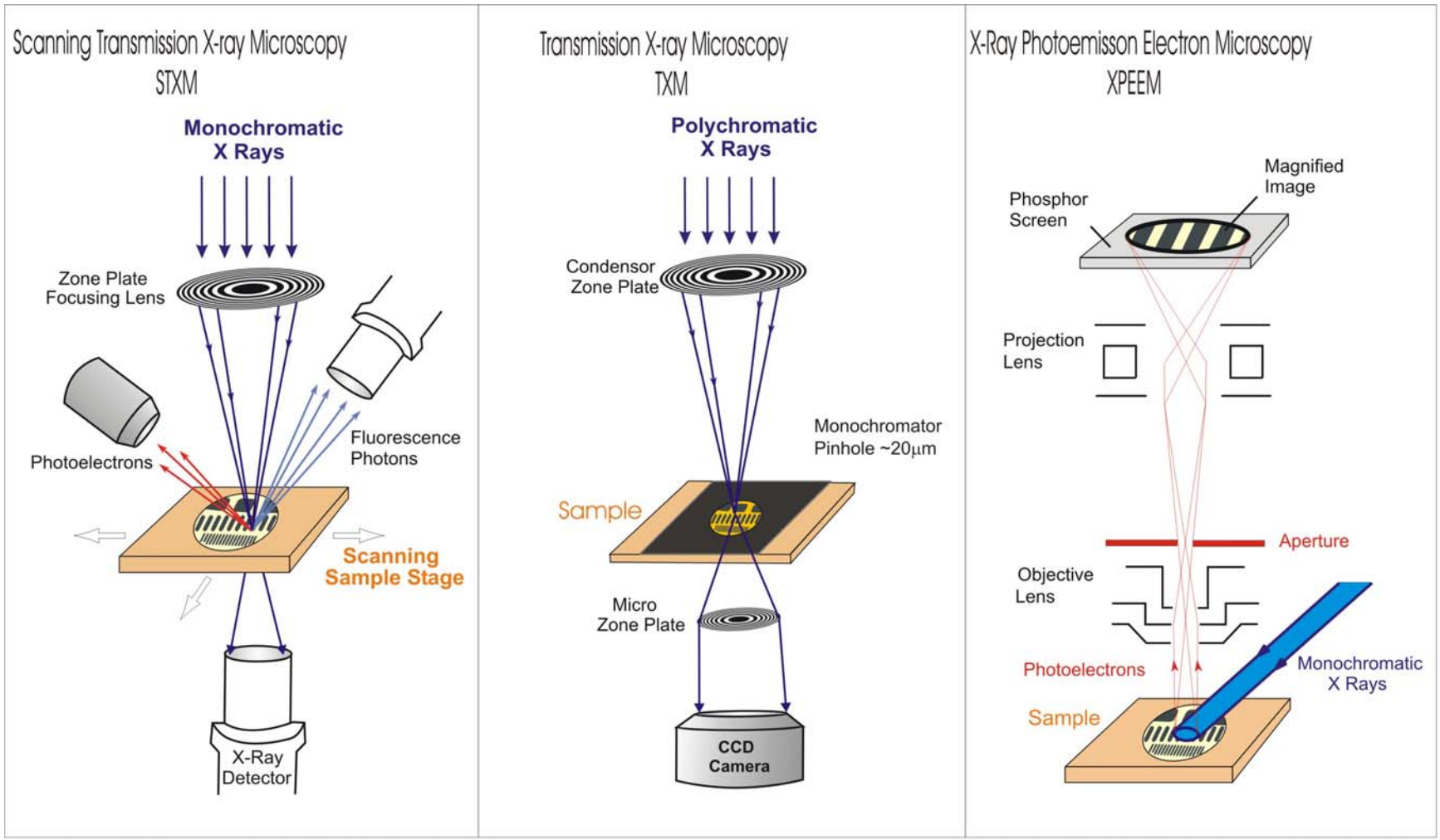


X-ray Natural Circular Dichroism

Goulon *et al.*, J. Chem. Phys. **108**, 6394 (1998)



X-ray Microscopy



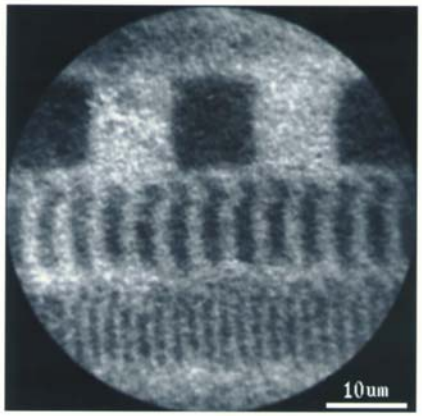
Present resolution in the 20 - 40 nm range

mic-3-meth.cdr

Polarization Dependent Imaging with X-Rays

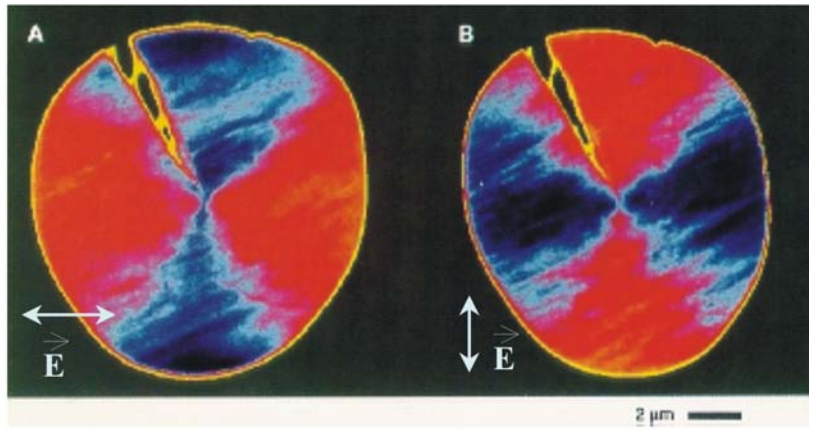
X-Ray Magnetic Circular Dichroism

Stöhr *et al.*, Science **259**, 658 (1993)



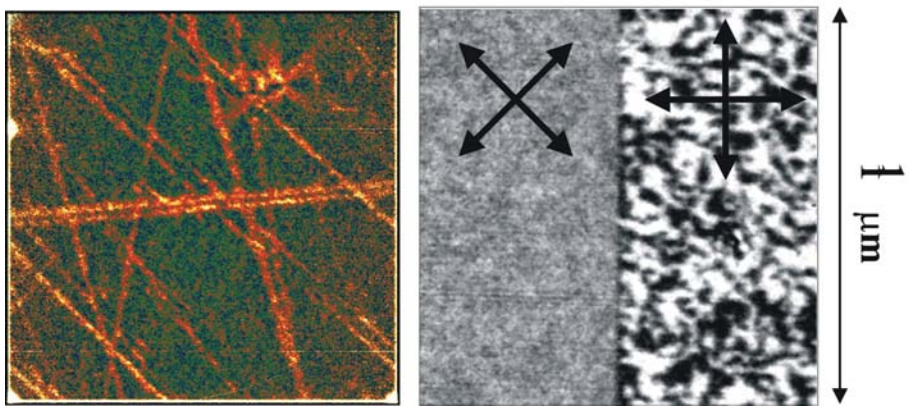
X-Ray Linear Dichroism

Ade and Hsiao., Science **262**, 1427 (1993)



X-Ray Magnetic Linear Dichroism

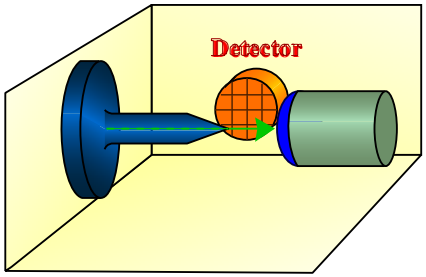
Stöhr *et al.*, Phys. Rev. Lett. **83**, 1862 (1999)
Scholl *et al.*, Science **287**, 1014 (2000)



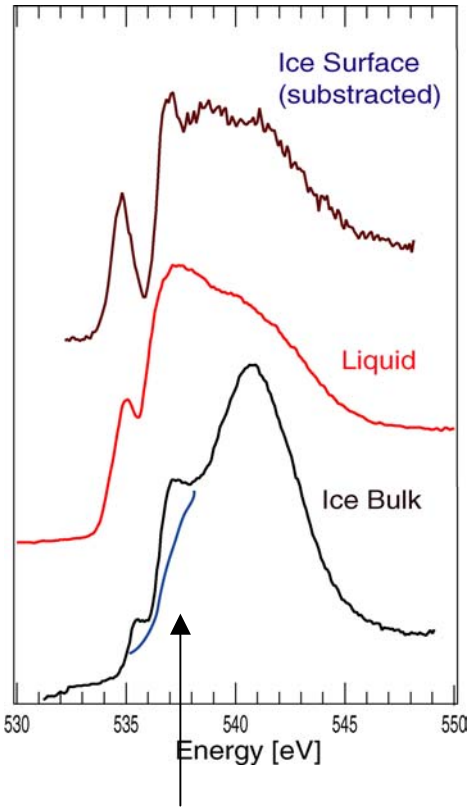
X-Ray Circular Dichroism

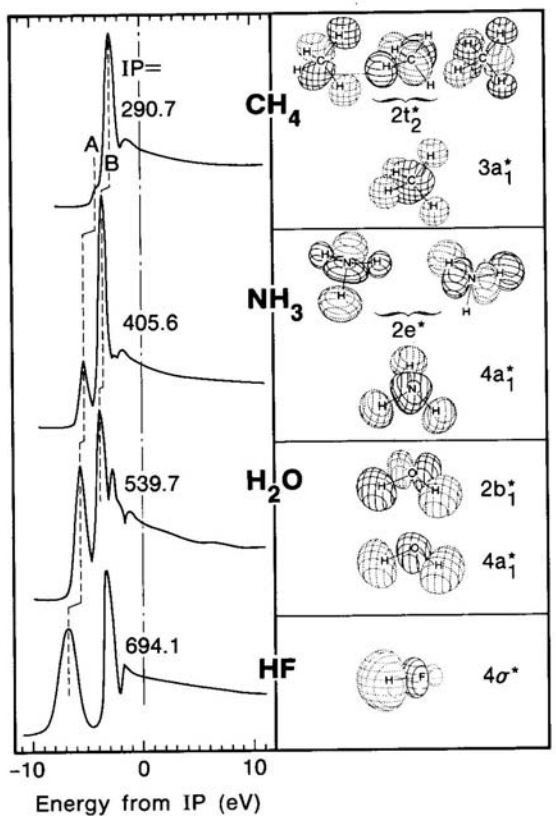
?

Rehybridization-Water

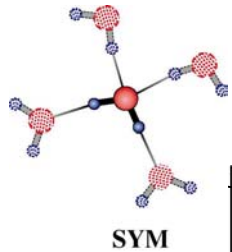


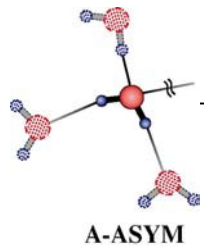
S-p hybridization in MO´s
Only O2p contributions

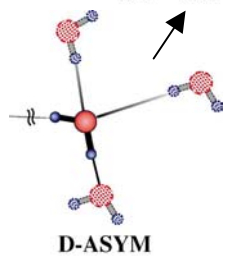


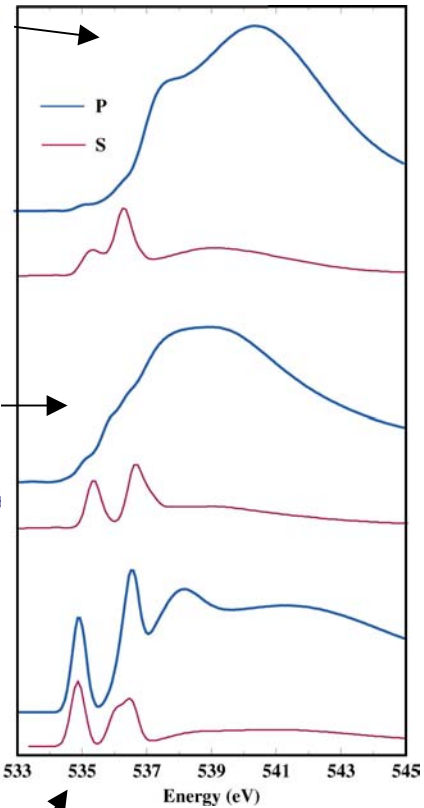


Theory









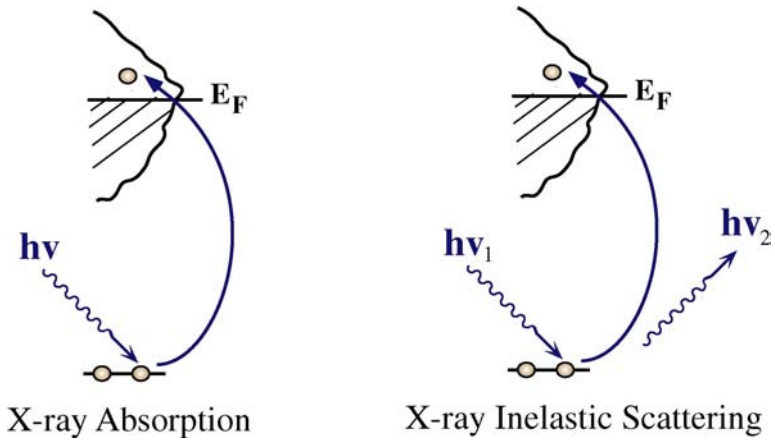
Spectral features from defects

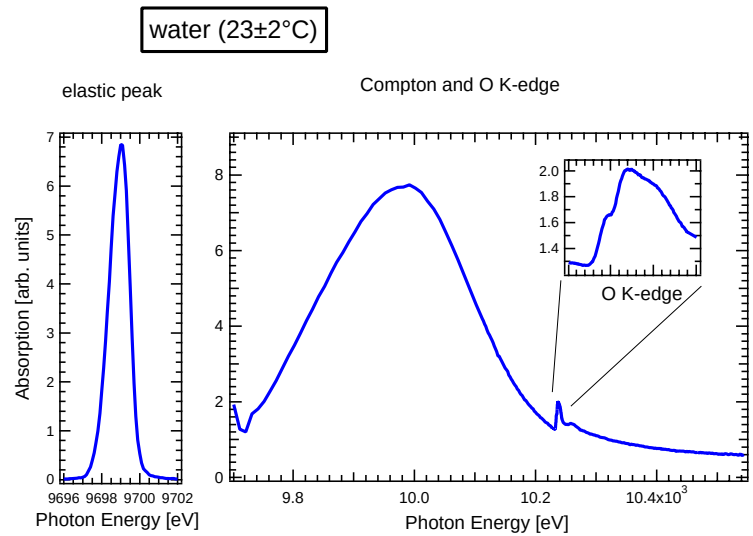
Stöhr NEXAFS spectroscopy

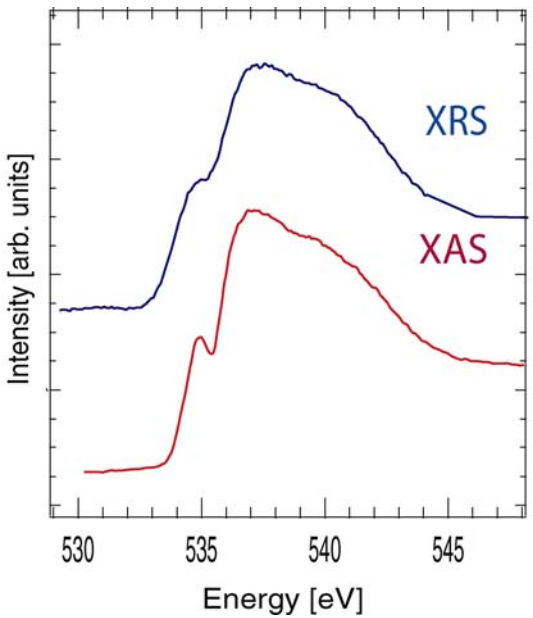
Nilsson et.al. J. Phys. Conden. Matter 14 (2002) 27601

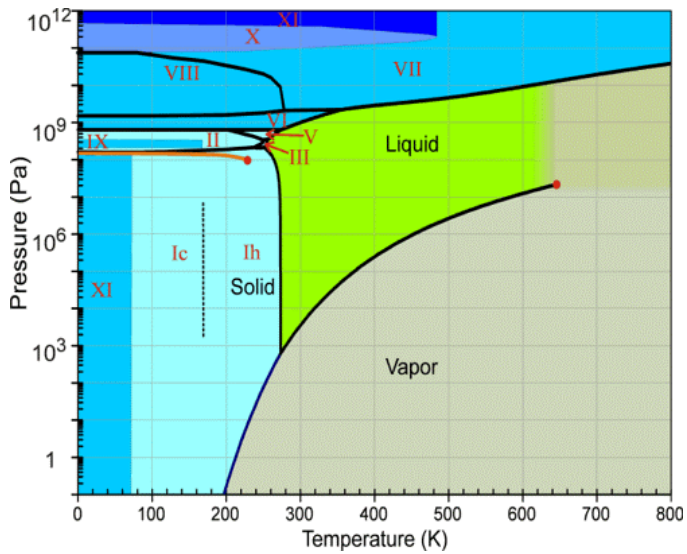
X-ray Raman Spectroscopy

Soft X-ray NEXAFS using hard X-rays

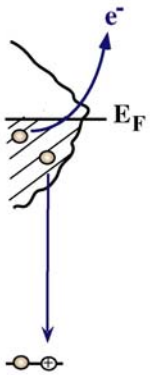




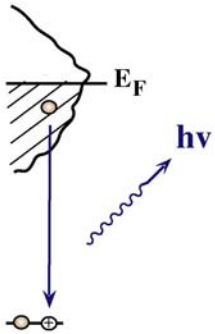




Core Hole Decay



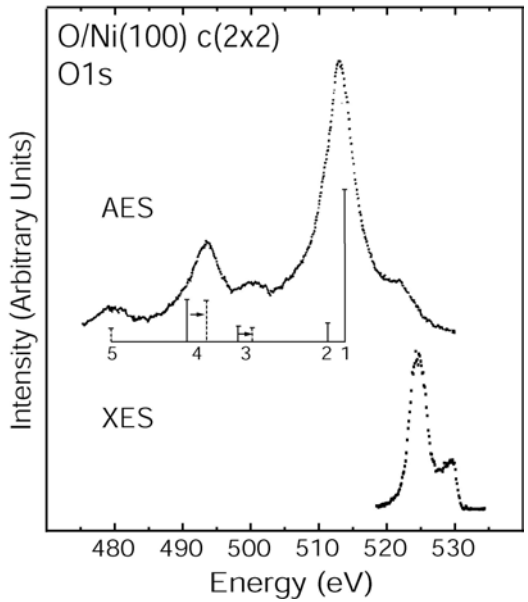
Non Radiant
Auger Electron Spectroscopy (AES)



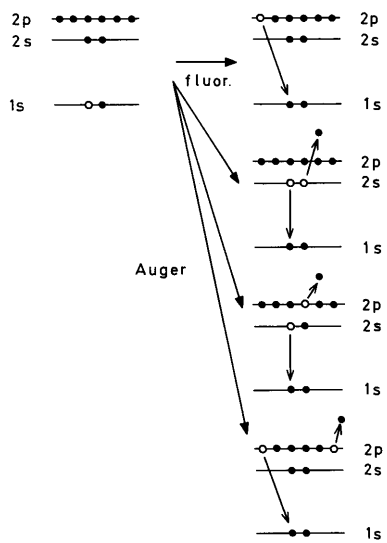
Radiant
X-ray Emission Spectroscopy (XES)

XES one electron picture

AES two electron interaction; complex Correlation effects



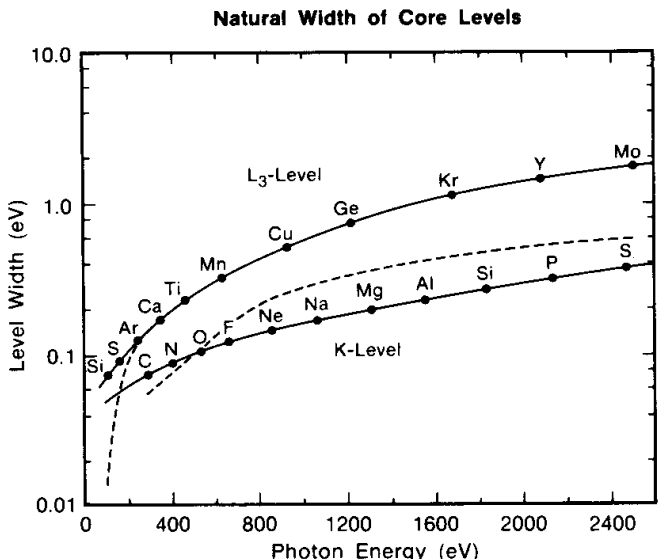
Sandell et. al. Phys. Rev. B48, 11347 (1993)



Core hole life time

Sum of all decay channels

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



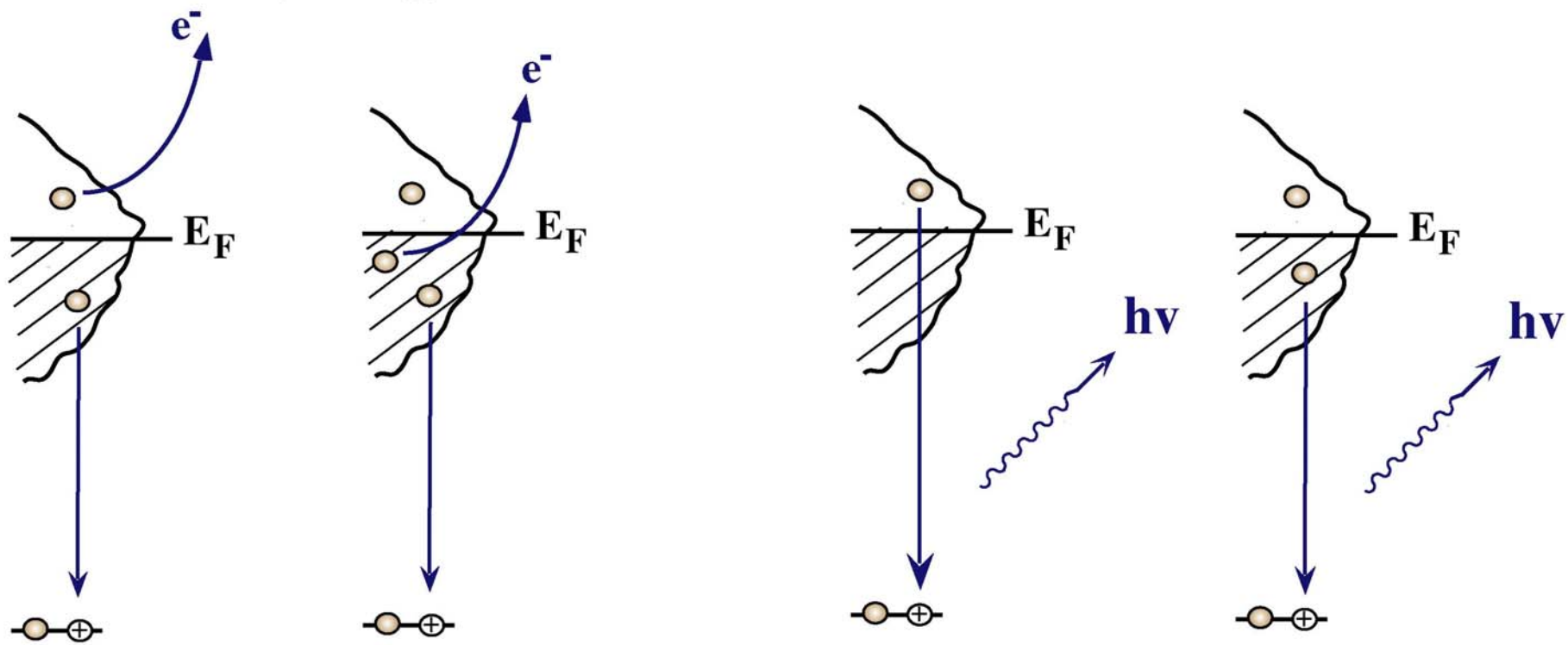
Resonant Processes

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

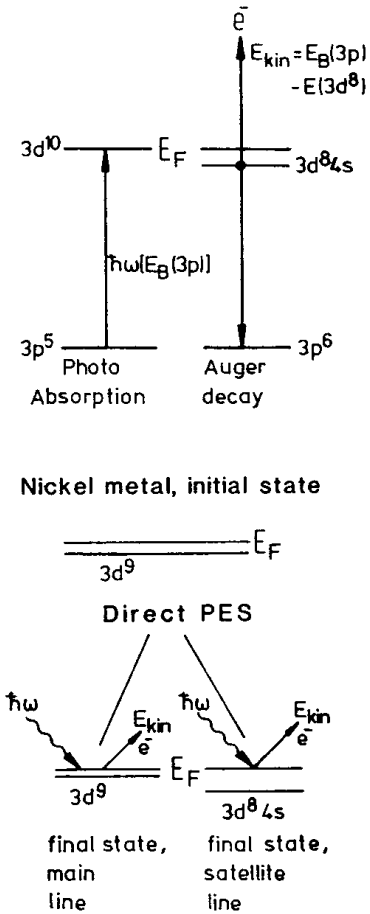
Resonant Photoemission

Valence band features resonant enhanced at core level threshold

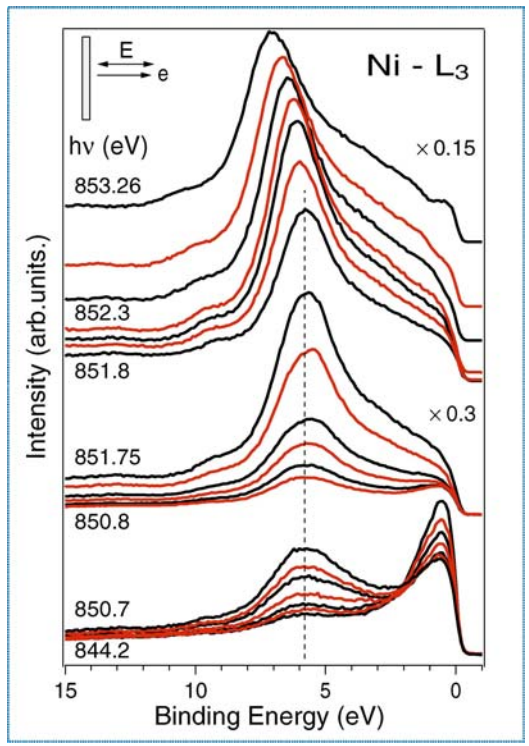
$$I = \left| M_{PES} + M_{Aug} \right|^2$$

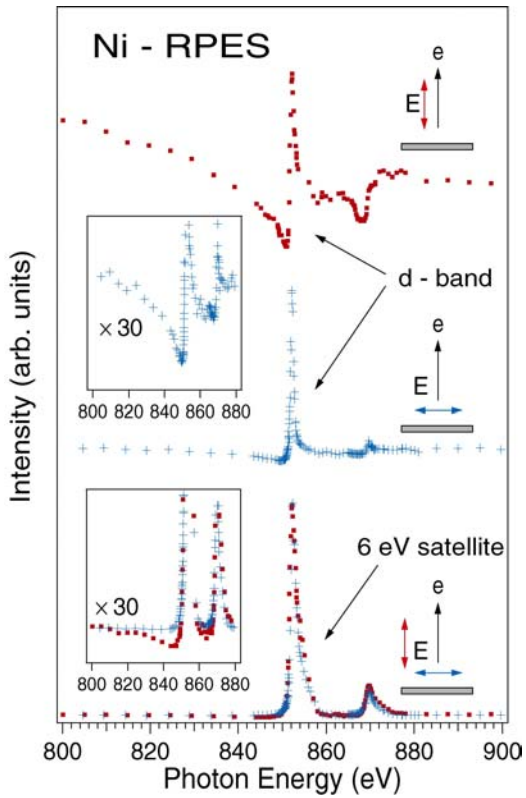
Constructive and destructive interference of direct photoemission and Auger decay

Fano profile



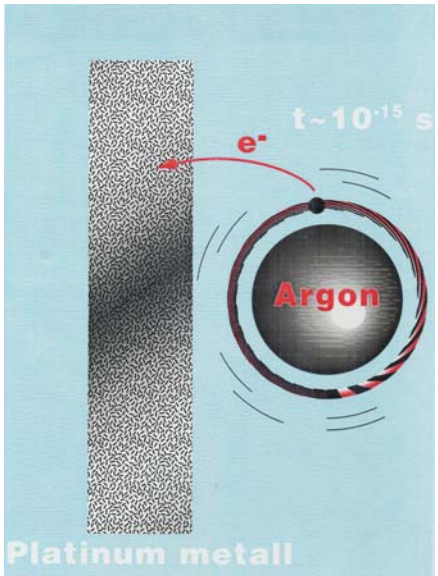
6 eV d-band



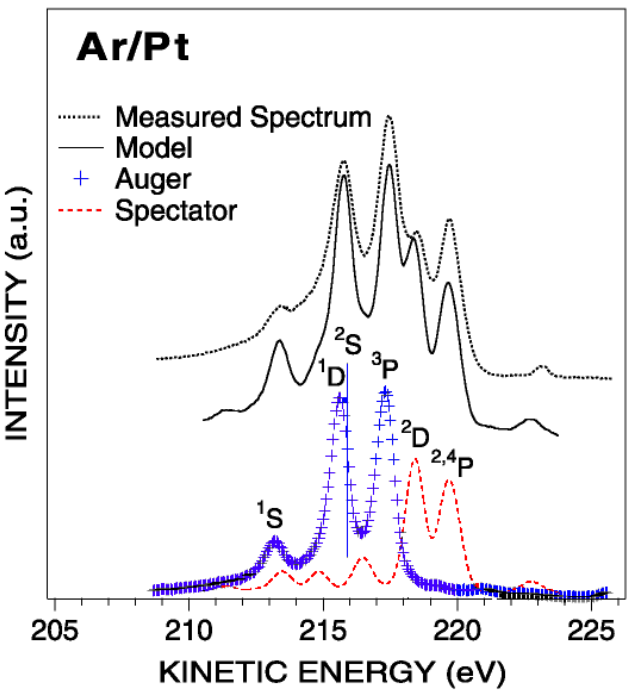


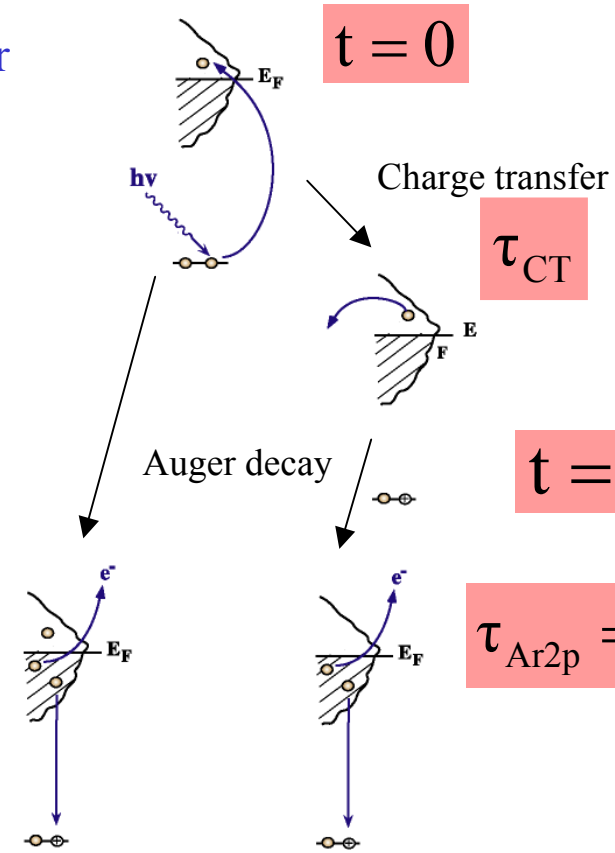
Weinelt et. Al. Phys. Rev. Lett. 78, 967 (1997)

Core Hole Clock Method



Probing charge transfer processes on a femtosecond timescale





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

+1 Spectator final state 46%

+2 Auger final state 54%

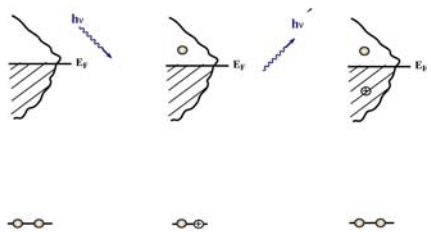
$$P_{CT} = \left(1 + \tau_{CT} / \tau_{Ar2p}\right)^{-1}$$

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

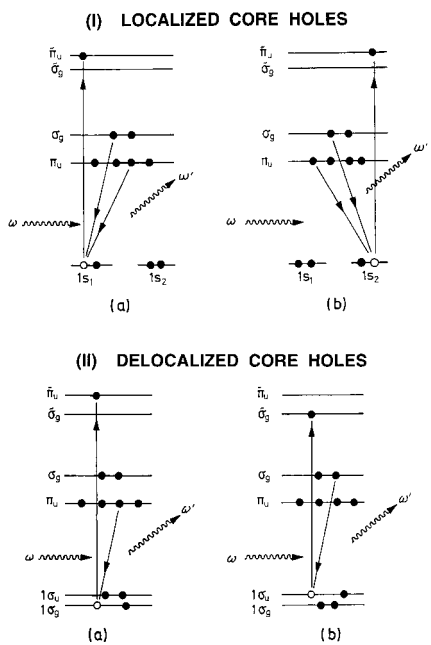
Karis et. al. Phys. Rev. Lett. 76, 1380 (1996)

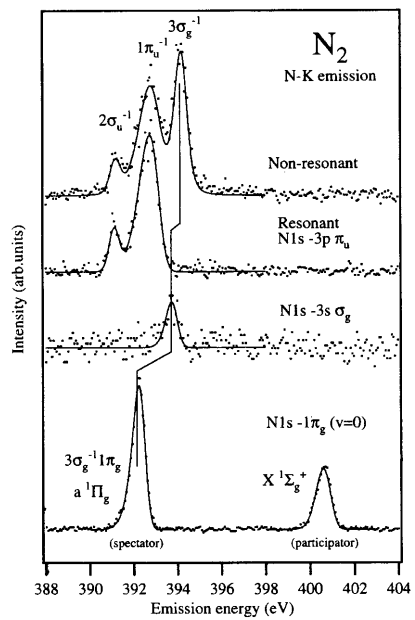
Sandell et. al. Surf. Sci. 429, 309 (1999)

Resonant X-ray Inelastic Scattering



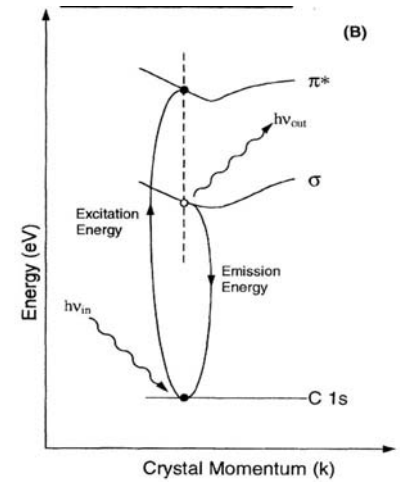
Free molecules





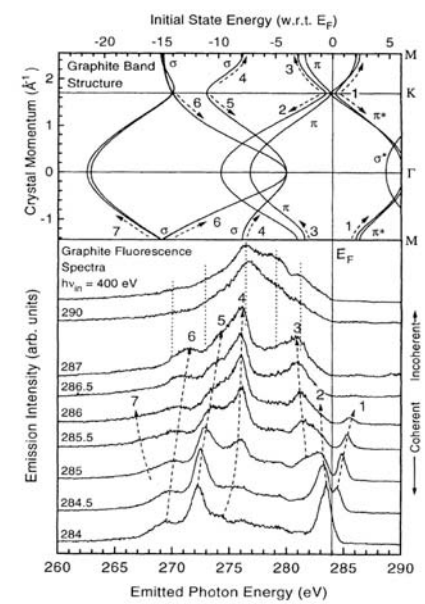
Glans et. al. Phys. Rev. J. El. Spec. 82, 1996 (1993)

Solids



Conservation in k vector

Graphite



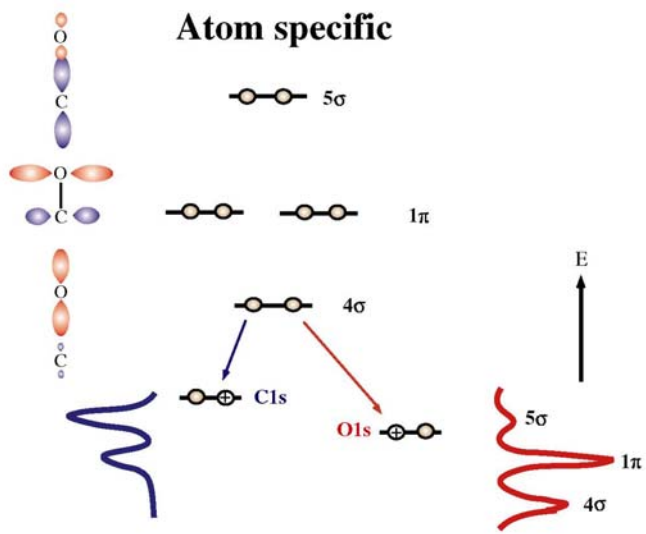
Carlise et. al. Phys. Rev. Lett. 74, 1234 (1995)

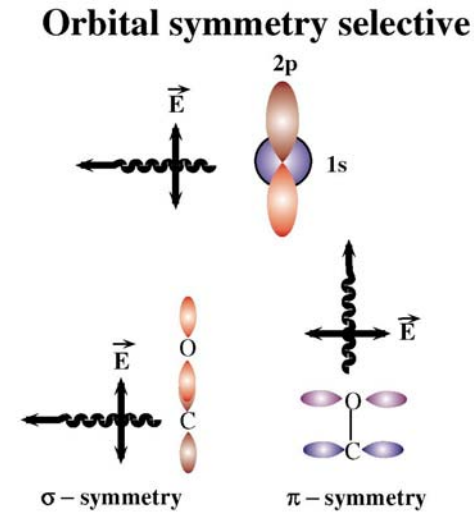
Dipole selection rule:

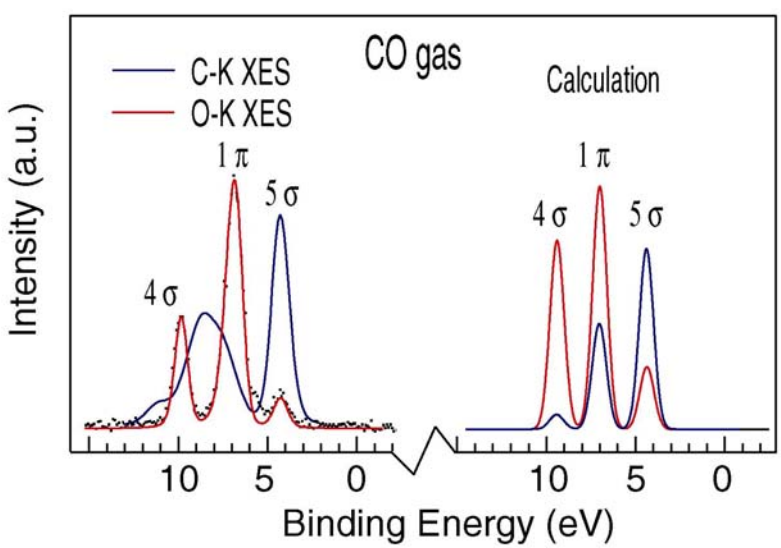
g → u
u → g

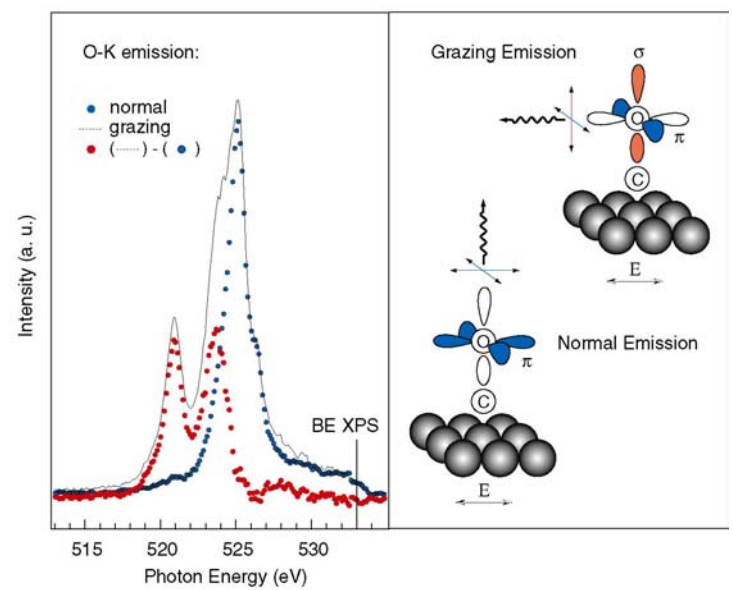
transitions

X-ray Emission Spectroscopy



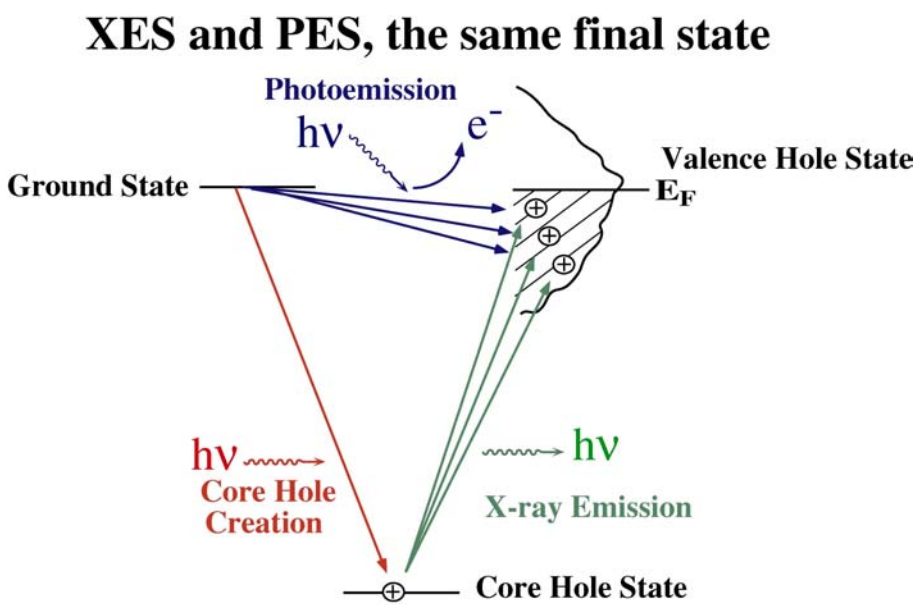


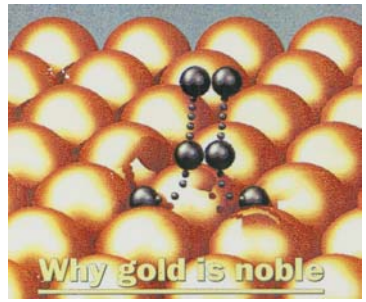




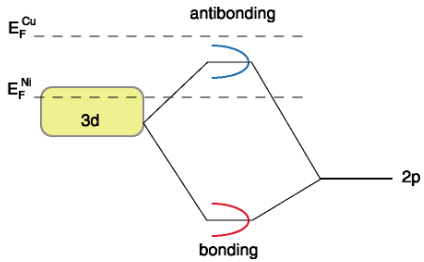
A. Nilsson et.al. J. Electron Spectr. 110-111, 12 (2000)

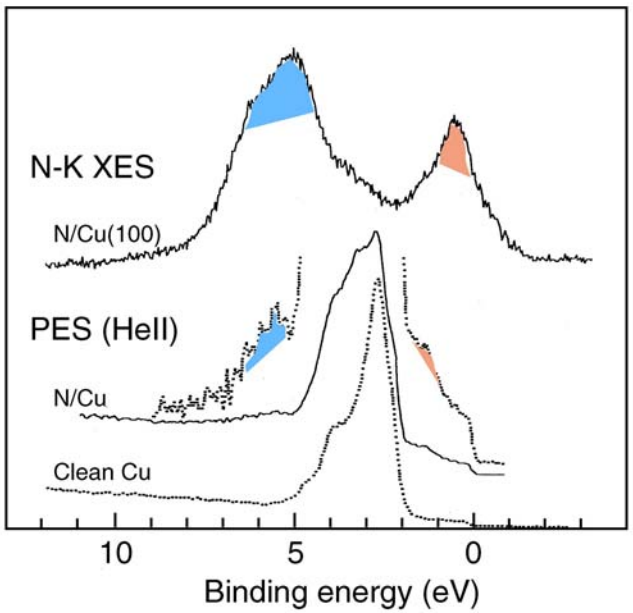
X-ray Emission and Photoemission



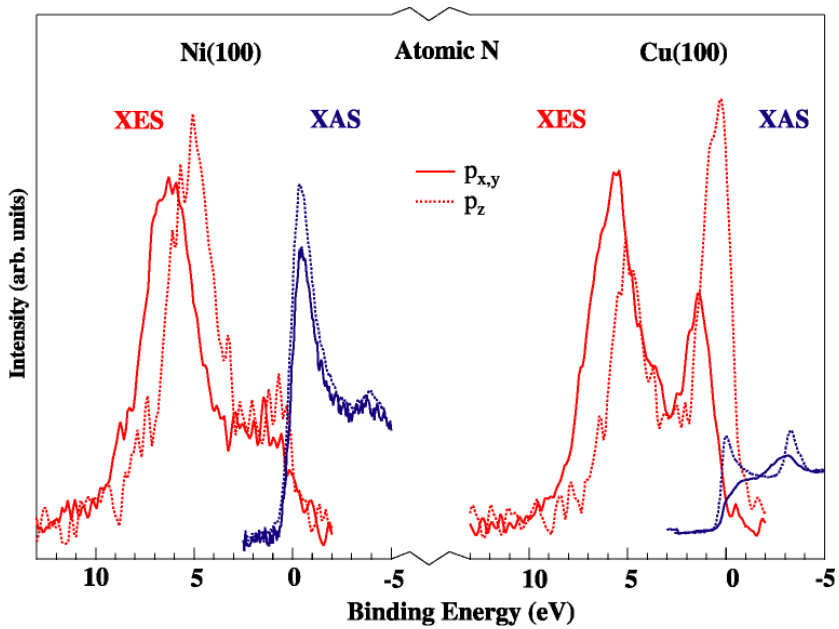


Hammer et. al Nature 376, 238 (1995)





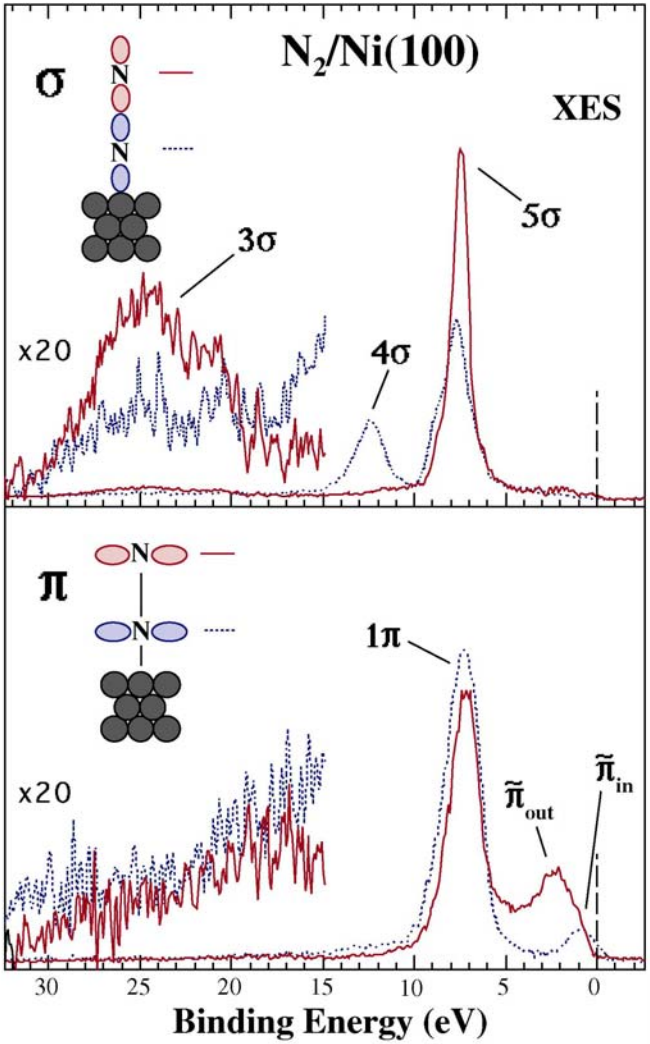
T. Wiell et al. Surf. Sci. 304, L451 (1995)



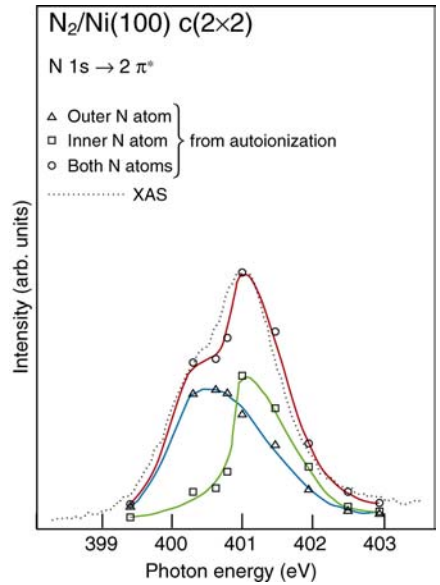
Nilsson et.al. J. El. Spec. 110-111, 15 (2000)

Atom Selectivity

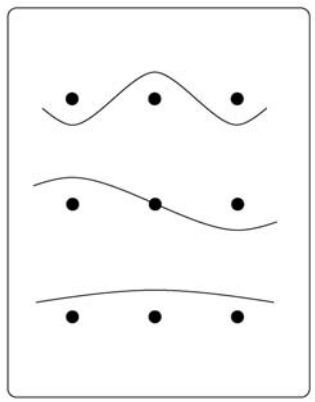
Selective excitation of inner and outer nitrogen atoms

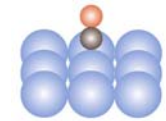


Nilsson et.al. Phys. Rev. Lett. 78, 2847 (1997)
Bennich et. al. Phys. Rev. B57, 9275 (1998)



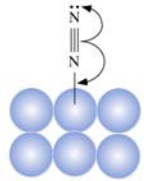
Allylic Configuration
π-Orbital structure of 3 atoms



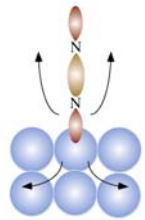


CO and N_2 on Ni(100)

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

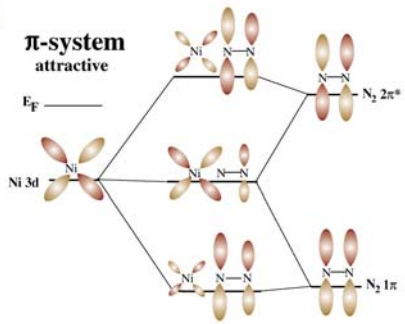


π-system
attractive interaction
N-N bond weakening



σ-system
repulsive interaction
N-N bond strengthening

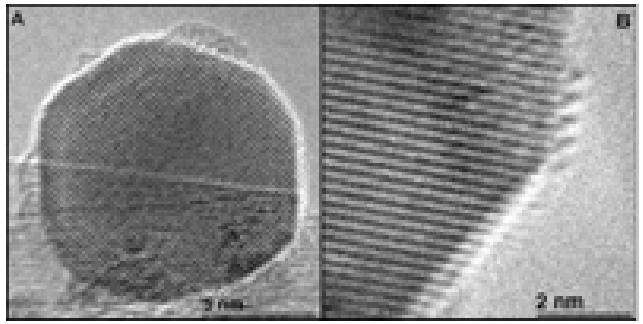
COMPENSATION EFFECTS
ADSORPTION ENERGY
N-N BOND ENERGY



Femtosecond Chemistry

Haber-Bosch

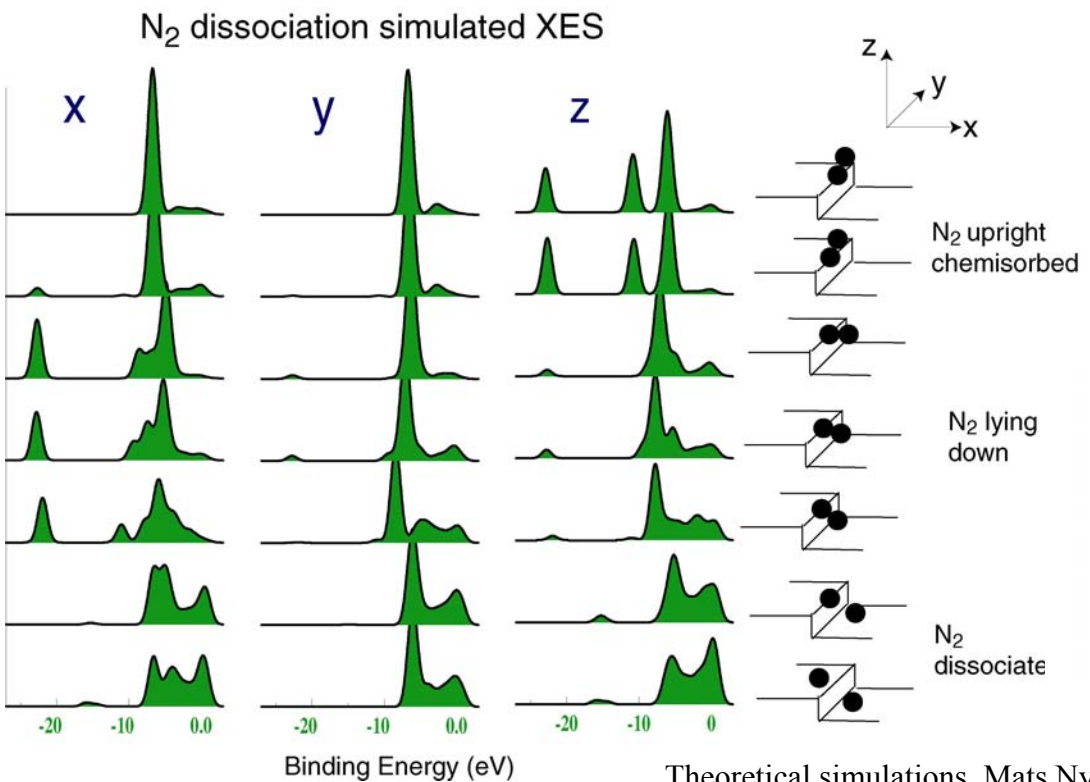
$$N_2 + 3H_2 \rightarrow 2NH_3$$



Hansen et.al. Science 294, 1508 (2001)

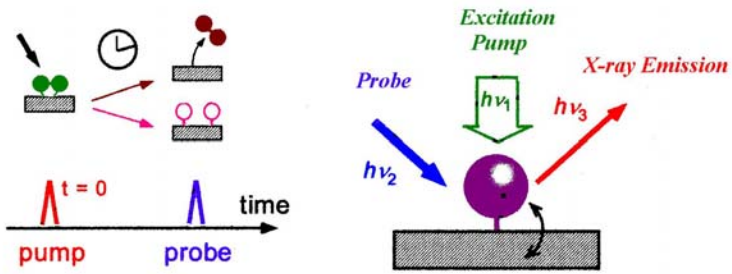
New Ru Catalyst

Active site at steps



Both N atoms

Theoretical simulations, Mats Nyberg, Stockholm University



Probe pulse at different delay time Δt