UNITED NATIONS EDUCATIONAL, SCIENTIFIC AND CULTURAL ORGANIZATION
INTERNATIONAL ATOMIC ENERGY AGENCY
INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
I.C.T.P., P.O. BOX 586, 34100 TRIESTE, ITALY. CABLE: CENTRATOM TRIESTE

H4.SMR/1013-27

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

3 November - 5 December 1997

Miramare - Trieste, Italy

Core Level Spectroscopy

A. Nilsson
University of Uppsala
Sweden

Core Level Spectroscopies

Anders Nilsson
Department of Physics
Uppsala University, Sweden
and
Advanced Light Source
Berkeley, USA

Outline

- Comparing XPS, XAS, RES and XES
- Instrumentation

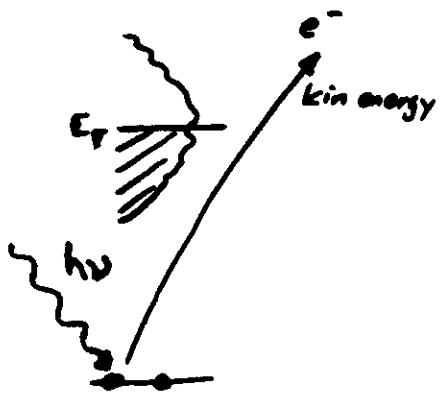
XPS
- Chemical shifts, general
  Koopmans ⇔ total Energy
- dynamic response to ionization

XAS
- dipole selection rules and Polarization
- Initial and Final state rules
- Unoccupied density of states

XES and RES
- Different final states
- Occupied density of states

Resonant process
- Autoionization
- Resonant PES
- Inelastic scattering XES

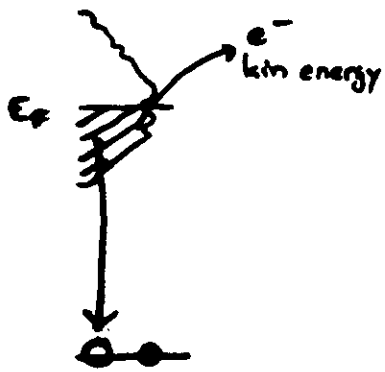
a) creation of core holes



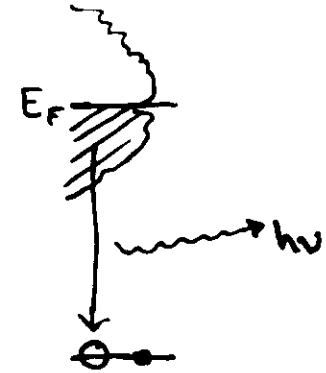
Ionization
(XPS or ESCA)

Excitation
(XAS or NEXAFS)

b) core hole decay

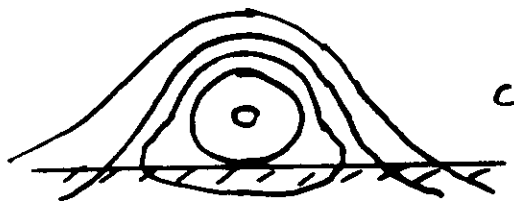


Autoionization
or
Auger decay



X-ray emission

Why core level ?



local Probing!

core hole effects?

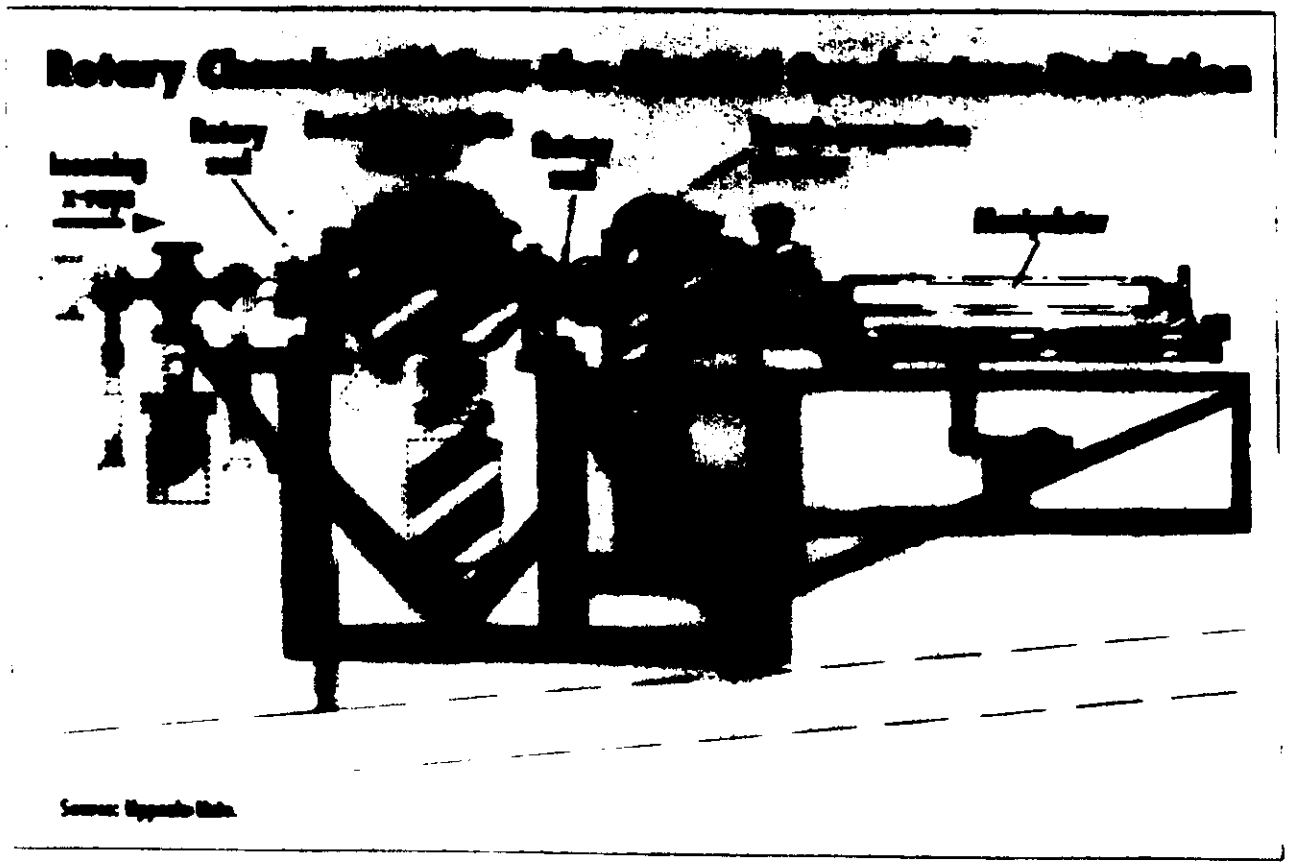
What can we hope to learn ?

- Chemical Information:
  Chemical state, different functional groups
  composition etc.

- Geometric Structure information
  atomic site distribution
  molecular orientation
  bond length correlation

- Electronic Structure information
  the nature of the chemical bond
  density of states

- Dynamic repose
  sudden creation of charge
  time evolution on femtosecond scale



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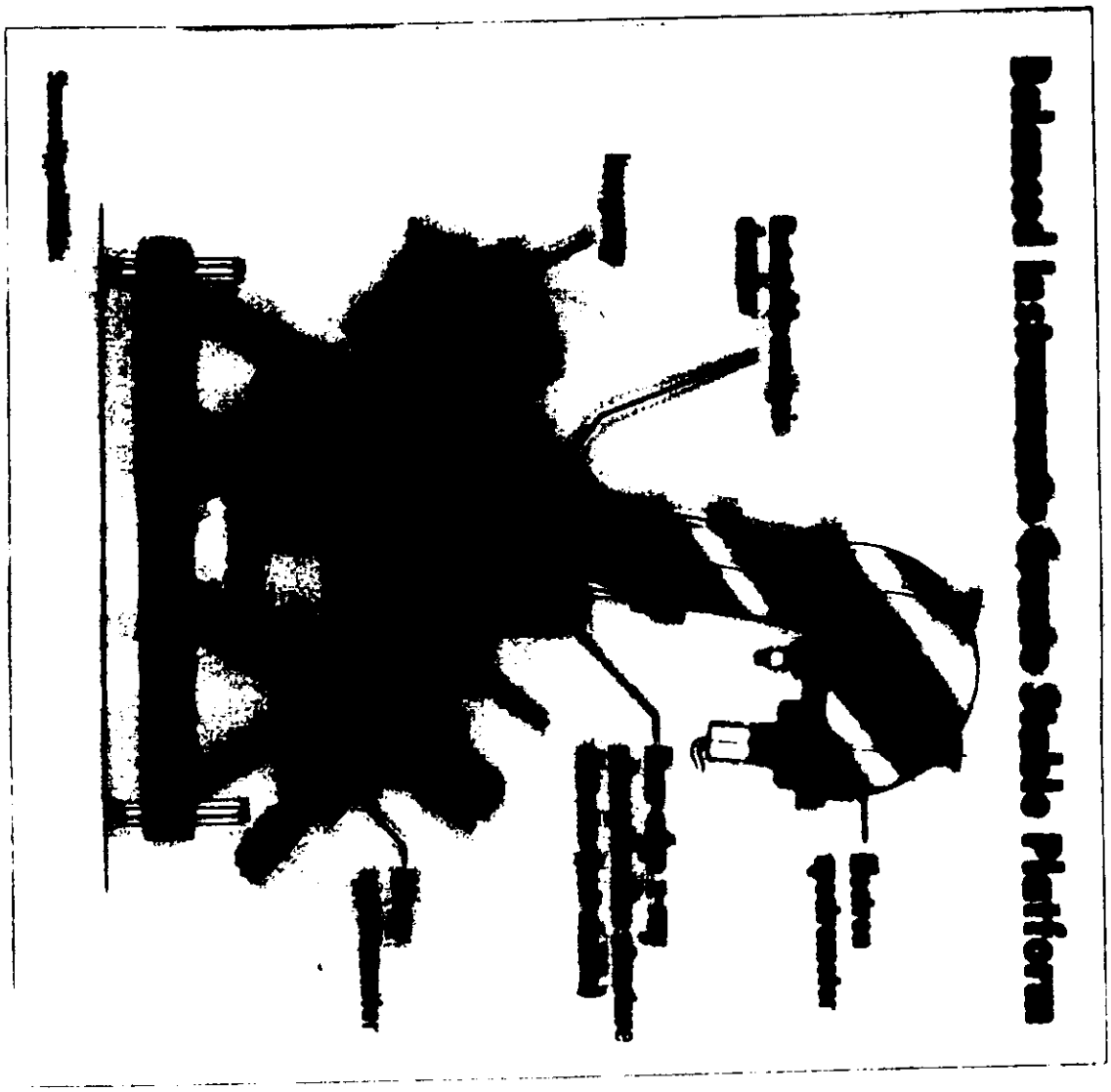
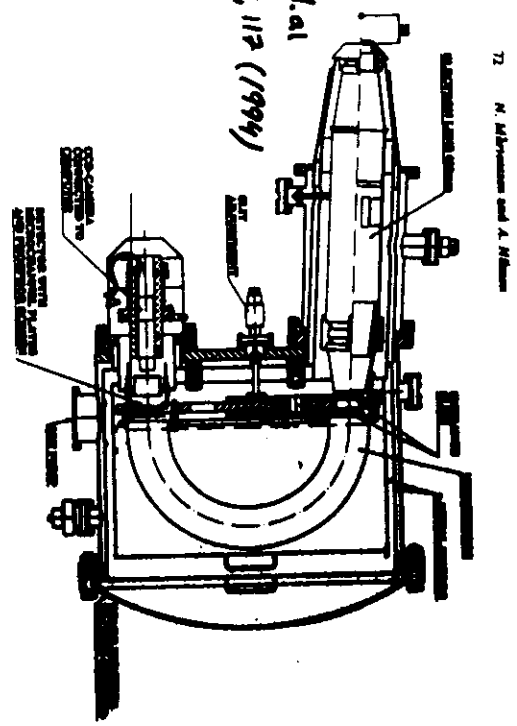


Scienta - upgrade
Electron spectrometer

Mårtensson et al.
J. El. spec. 70, 117 (1994)



200 mm mean radius
ΔE 2.7 meV at 21 eV pass energy
Angular resolution 0.2°
multidetection

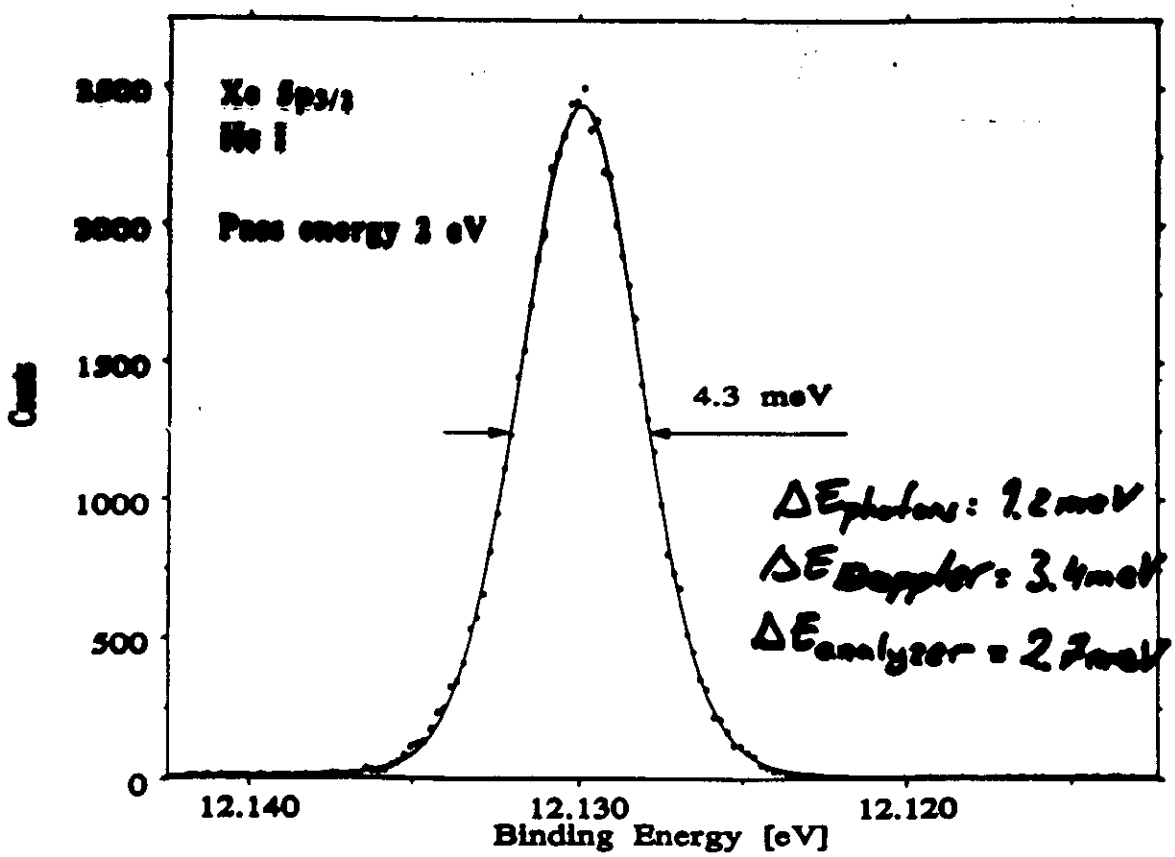
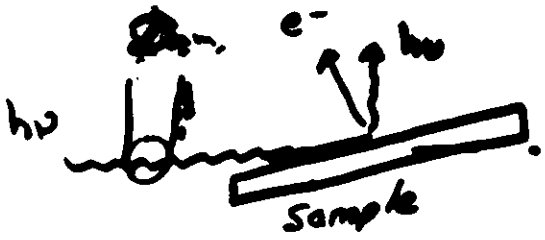
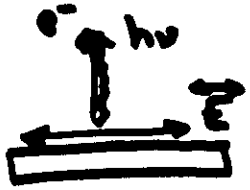


Fig 4





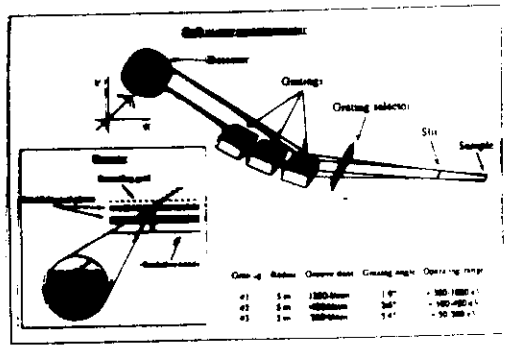
along beam

along beam

X-ray Spectrometer

J. Nordgren and N. Wassdahl
Rev. Sci. Instrum. 60 (1989) 1690

99.9% Decay Auger



grazing incidence ⇒ surface sensitivity
3 - 5°

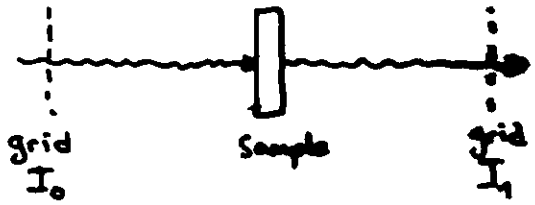
ΔE ~ 0.5 eV C, N, O 1s
1.0 Cu 2p

ALS and SSRL

photon flux ~ 10^{13} photons/sec
undulators

X-ray Absorption measurements:

- transmission

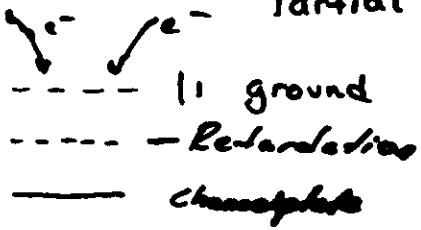


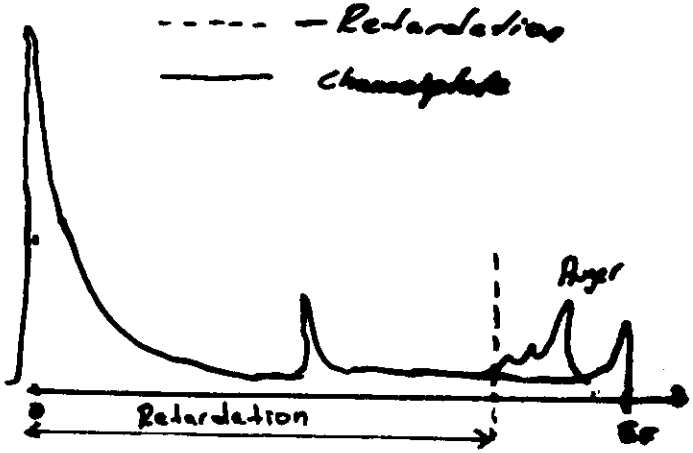
- number of core holes created

electron yield ⇒ Auger Processes

fluorescence yield ⇒ x-ray emission

Partial yield detection

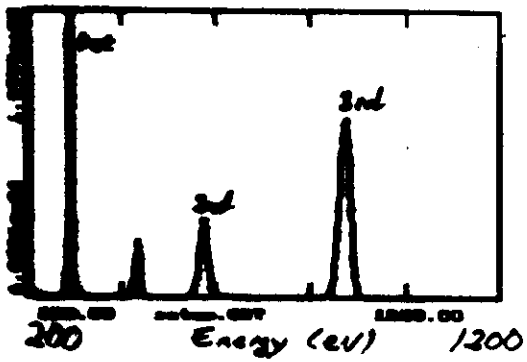


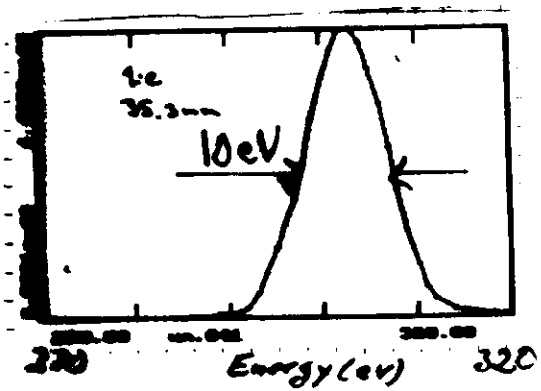


Undulator 5cm period

SGM 380 ℓ/mm

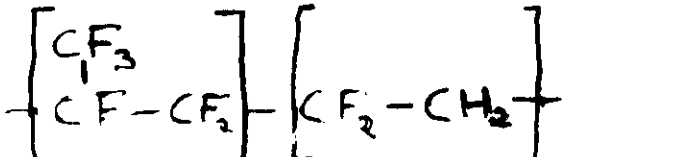
1.6 GeV

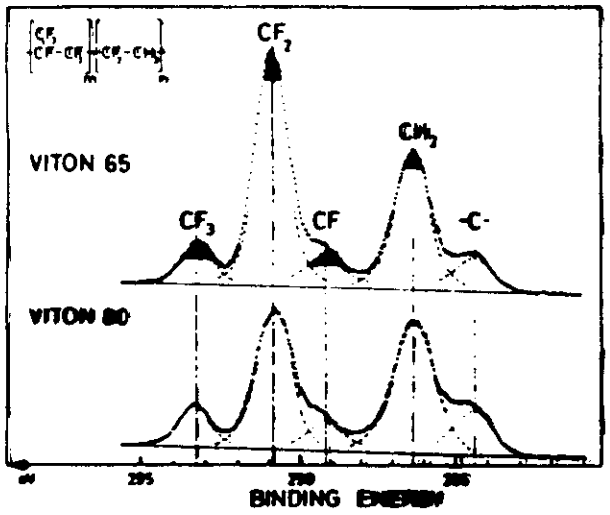


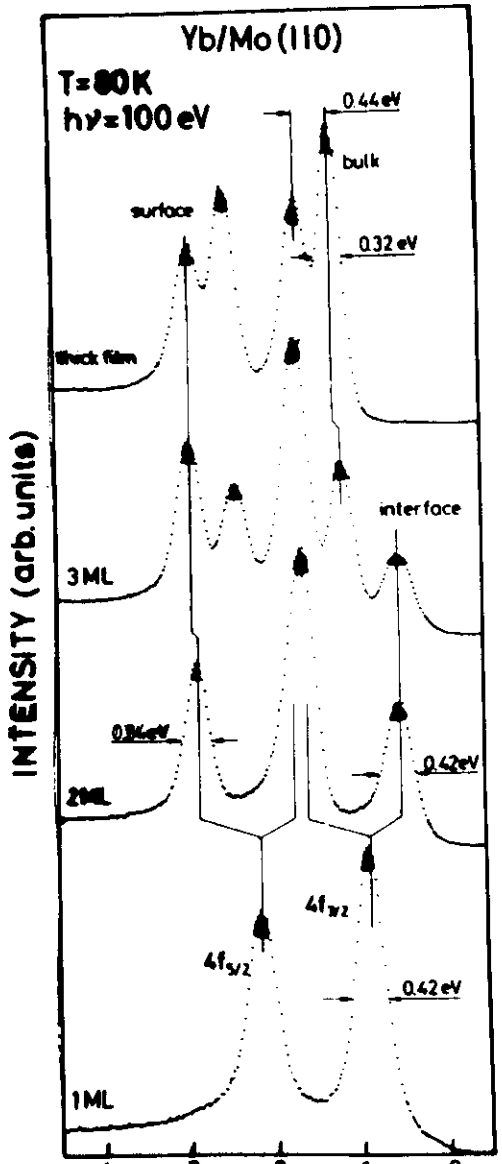


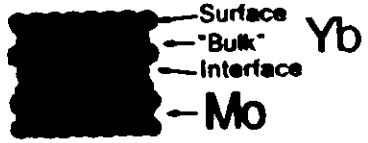
Chemical shifts in XPS

Viton Polymers









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

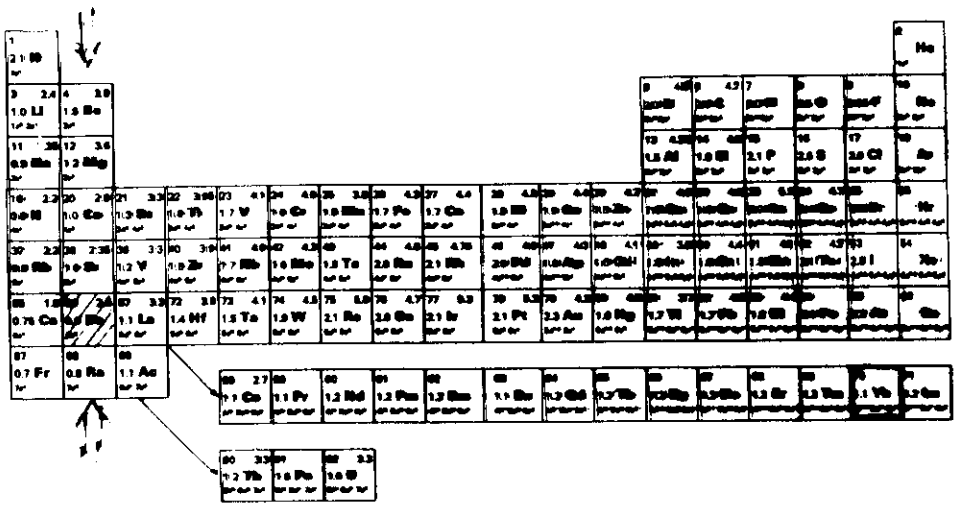
Yb Rare Earth metal

Divalent $4f^{14}$ [$6s^2$]

chemical properties like Ba

Electropositive ⇔ alkali metals

Divalent



How to use chemical shifts

i) Chemical Analysis using knowned Binding Energies of metal compounds

ii) Intensity variation of shirtal compound

Photo electron Diffraction i.e. holley

Time evolution, chemical reaction

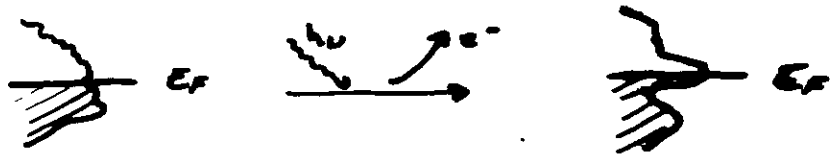
iii) Basic Understanding of the origin of the shifts

Chemical, Electronic and structure information

COMPLICATED

Two Descriptions of Chemical Shifts

a) Differences in Total Energy



1s

E^I_{TOT} (Initial or ground state)

1s

E^F_{TOT} (Final state)

$$E_{B(1s)} = E^I_{TOT} - E^F_{TOT}$$

b) Koopmans or orbital eigenvalues

H-F eigenvalues ε_i

$\varepsilon_{valence}$

1s $\quad \varepsilon_{1s}$

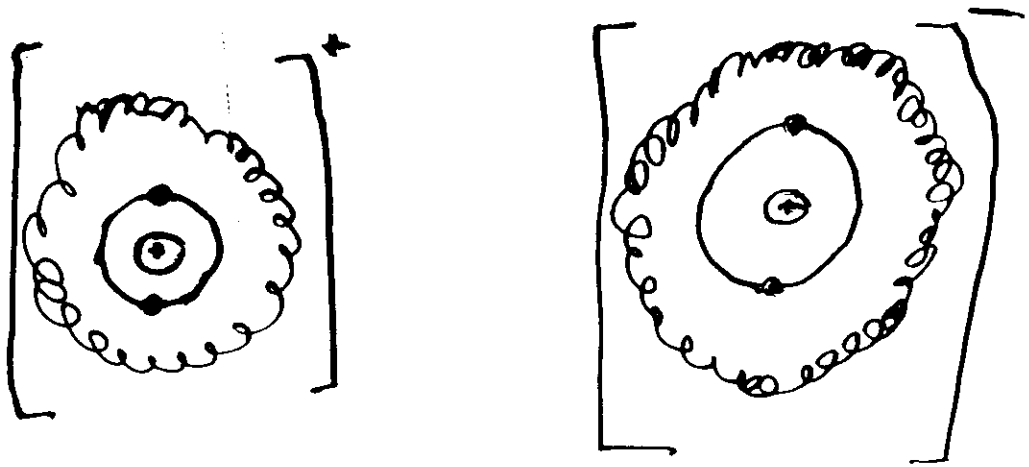
$E_B(1) = \varepsilon_{1s}$ Koopmans theorem

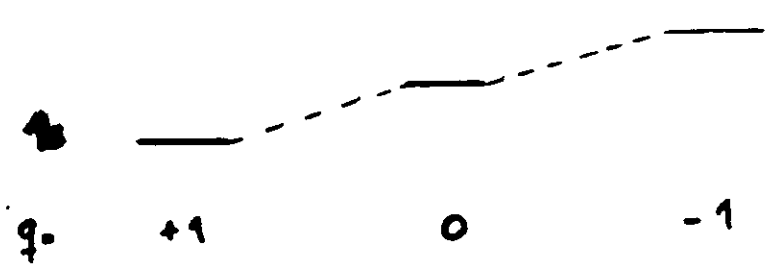
With Final state relaxation

$E_B(1) = \varepsilon_{1s} + \varepsilon_{relaxation} + \varepsilon_{correlation}$

Koopmans Energies

Ground state Potential model





$\Delta E_B \propto k\,q$

q: charge on ionized atom in the ground state

Koopmans Energies

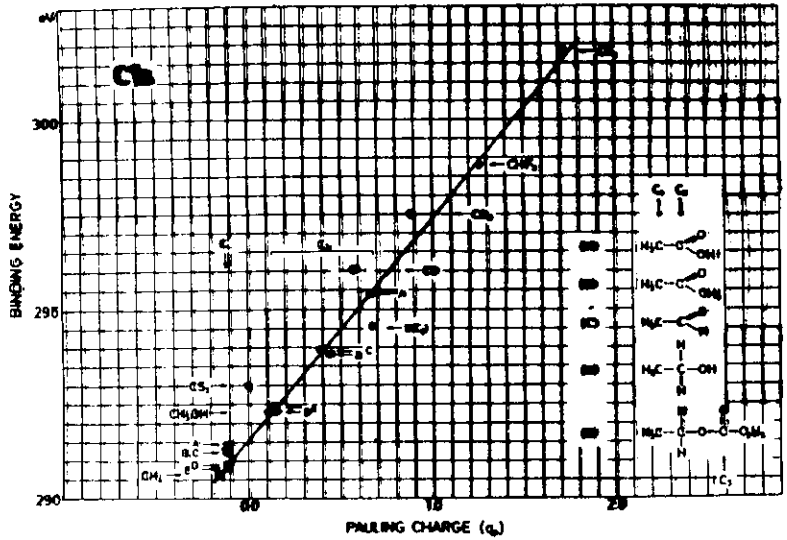
Ground state Potential model

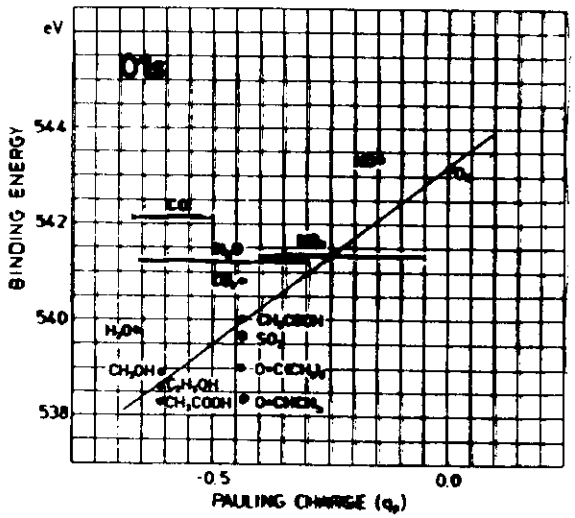
E_{vac}

$\Delta E_B \propto kq$

q: charge on ionized atom in the ground state

-1 0 +1



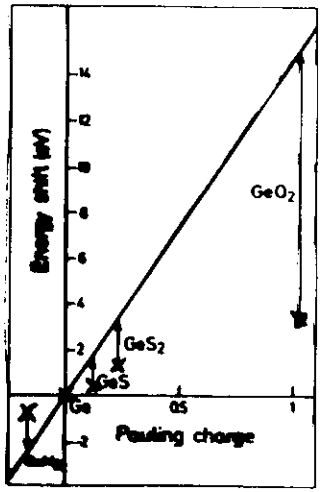


Straight line almost exactly equivalent to free molecules

Ionic and Covalent solids

$\Delta E_B = kq + V$

$V = \sum_{i \neq j} \frac{q_j}{R_{ij}}$

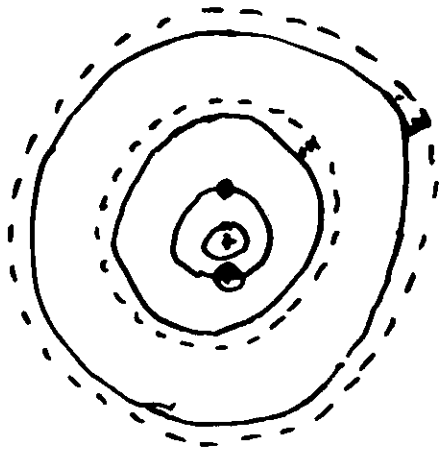


Hollinger et al.

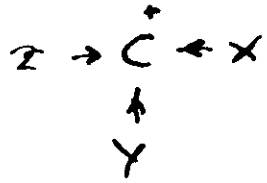
J. El. spec. 5, 23 (1974

Relaxation

Intra atomic : within the atom



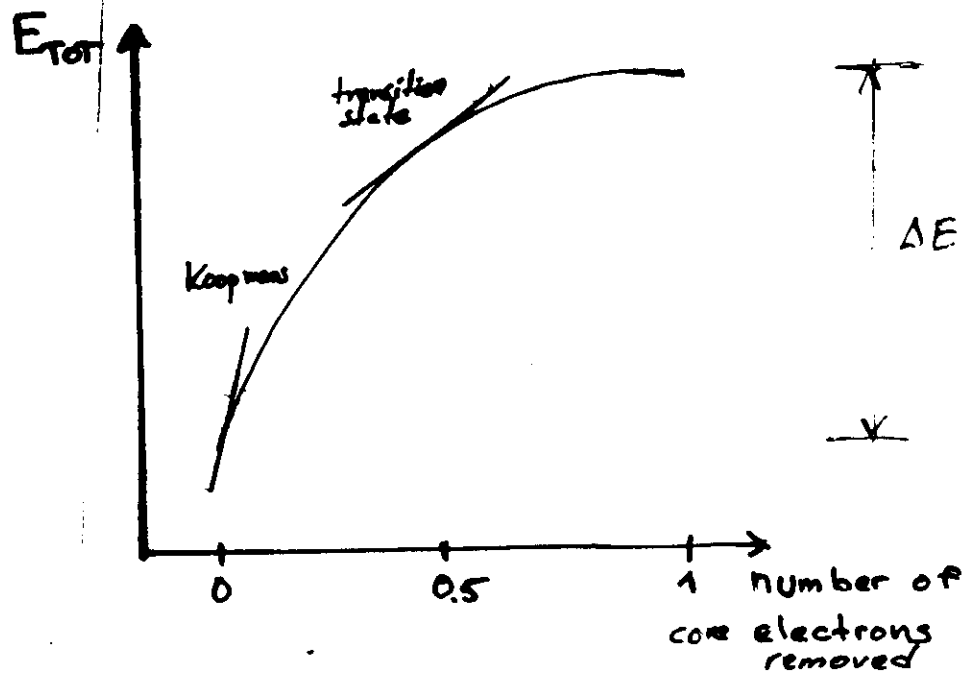
Inter atomic : between atoms



Relaxation

O1s shift between H_2O and

Exp	−0.8 eV
Koopmann	+1.7 eV
Transition state	−0.4 eV



(i) The true binding energy from difference in total energy

(ii) eigenvalue of core electron slop at zero removal

(iii) Transition state model E_i at ½ electron incorporates aspects both from ground and core ionised state

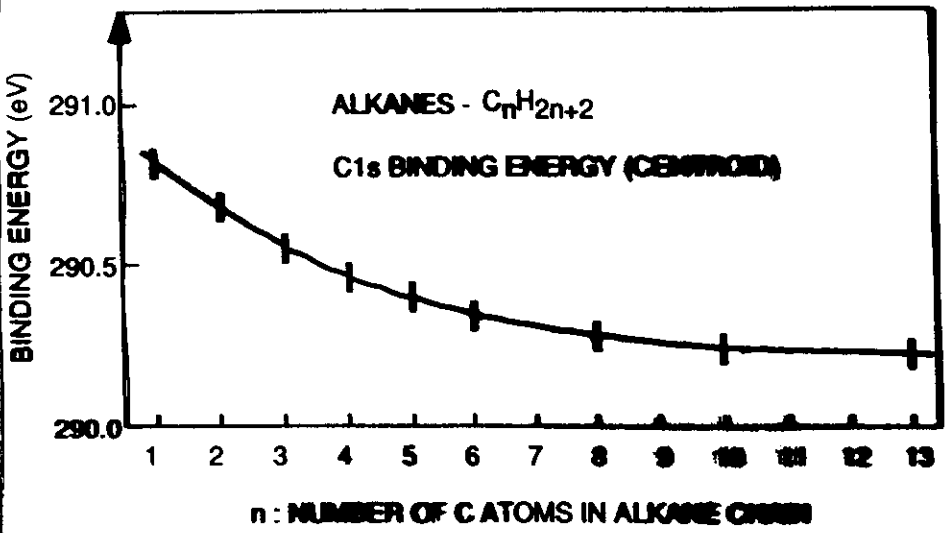
Long range relaxation or screening

$CH_3-CH_2-CH_2-\overset{+}{C}H_2-CH_2-CH_2-CH_3$

F.e shift without ground state charge

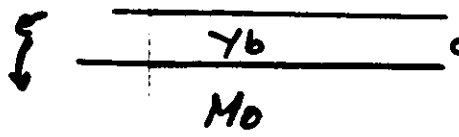
The same in C1s π-system

$O=CHCH_3$
$O=C(CH_3)_2$
CC, CC_2 etc

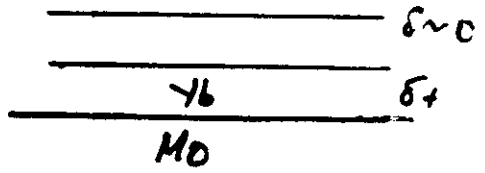


Koopmans Energies in Metals ?

Yb on Mo(110) similar to alkali's



1ML



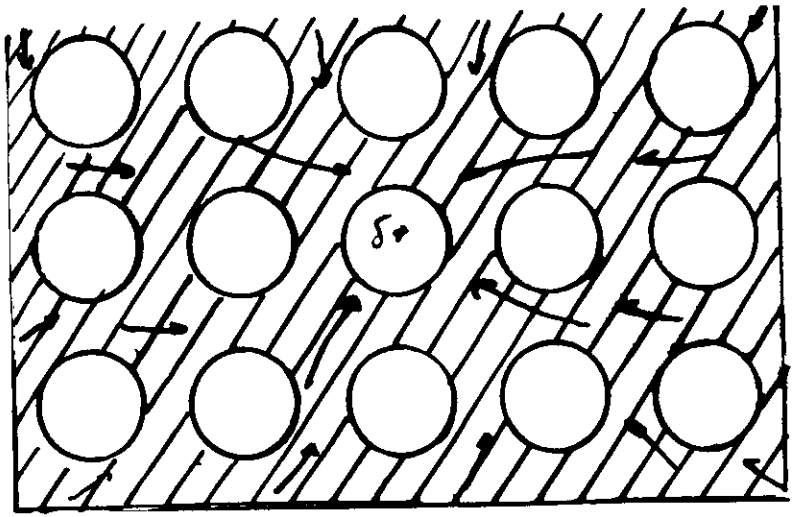
2ML

1ML Yb and Interface $\delta+$ ⇒ higher B.e

It shifts to lower B.e

! Potential model do not work for metals

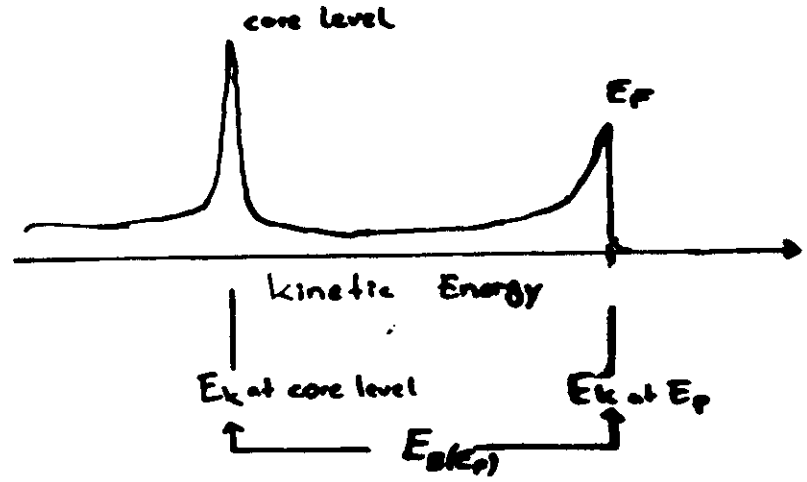
Metalic screening

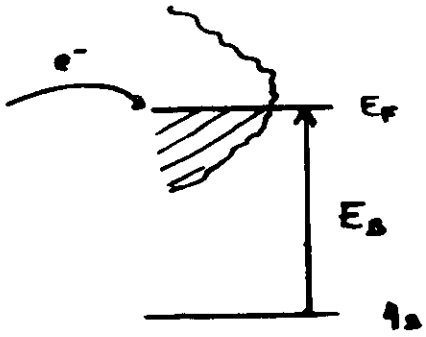


Metallic screening ⇒ lowest core hole state

Compare XPS with XAS

Binding Energy at XAS threshold





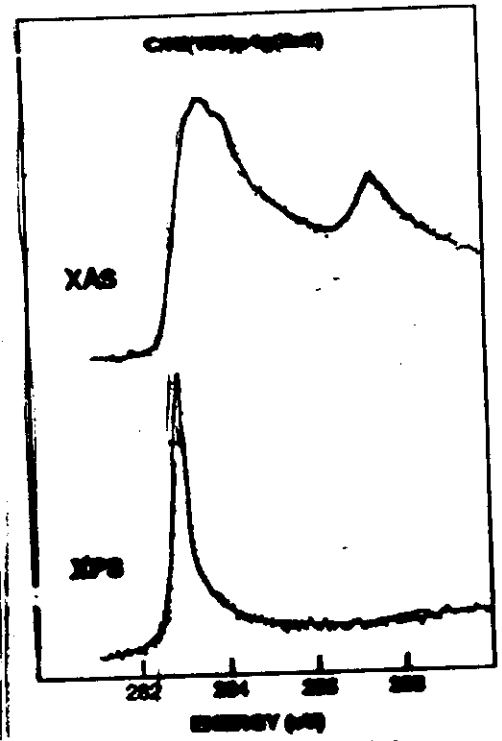
Metallic system

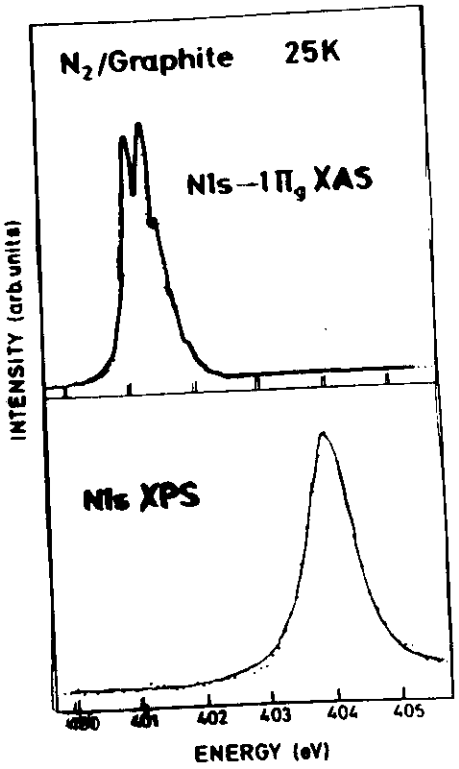
$N \sim N-1$

when $N \sim 10^{26}$

Metallic Screening

non metallic screening





Mårtensson et.al IEL spec. in press

Screening by Polarization of charge

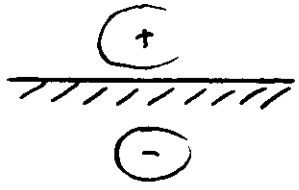
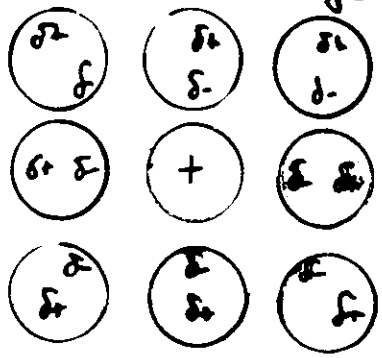


Image Potential



> Polarization

Why do the Potential model work in some systems ?

Strong Relaxation it do not work

Metallic screening !

TOTAL ENERGY CONCEPT

$E_B = E_{final} - E_{initial}$

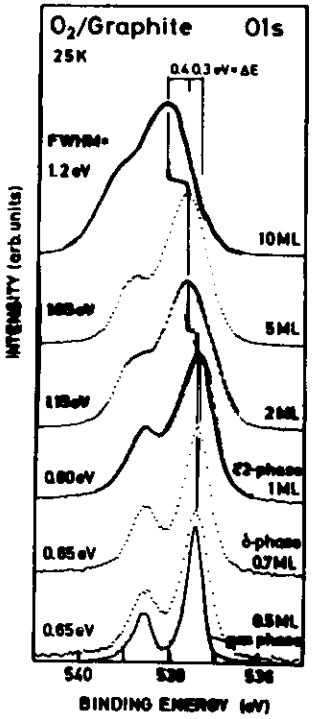
Final state Z+1 Approximation

Z Z+1

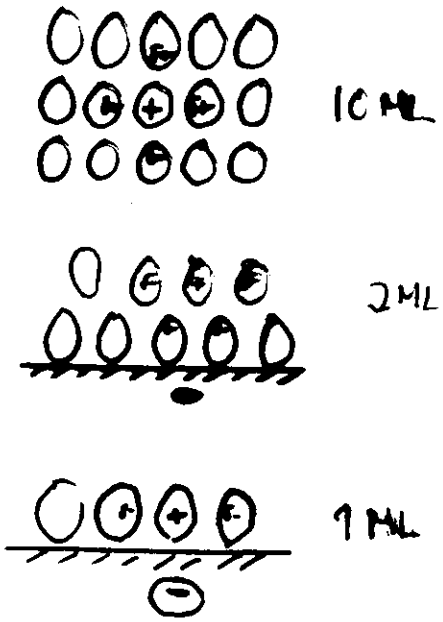
$CO^* = NO = NN^*$

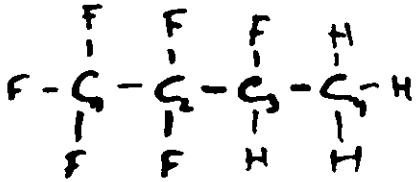
$CO^* = CF$

$Ni^* = Cu$

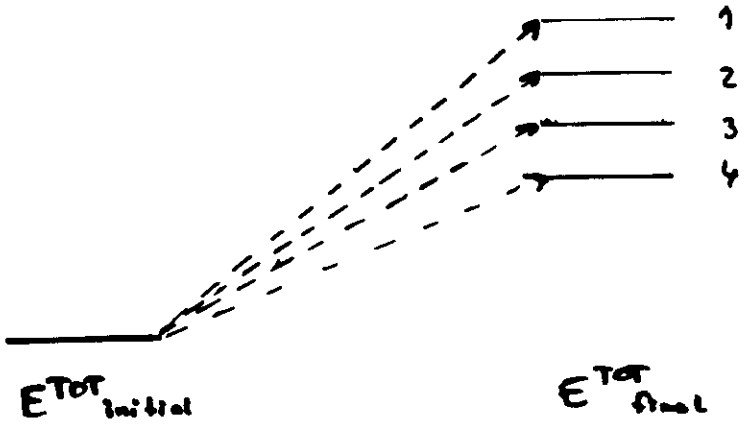


Tillborg et.al Surf. Sci. 295, 1 (1993)





$$E_B = E_{final} - E_{initial}$$



Chemical shifts: **different energetics in initial and final state**

within the same molecule:
only consider different energetics in final state

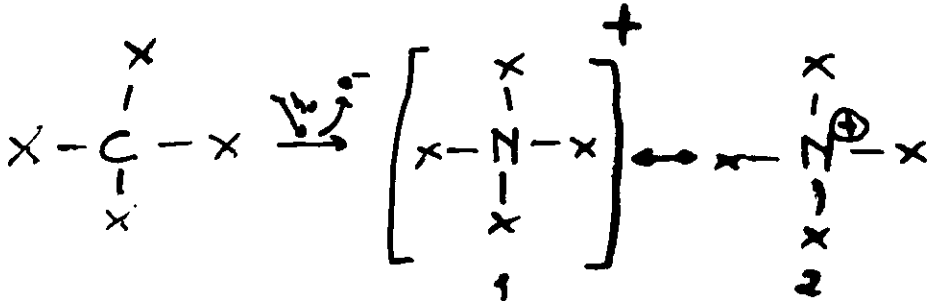
Chemical bond

Covalent bond

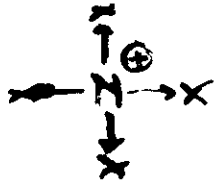
$N \equiv N$ > $C^{\delta+} \equiv C^{\delta-}$

non poler bond stronger than poler bond

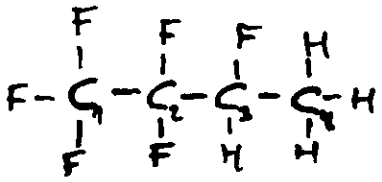
Correlation charge and shifts in Final state

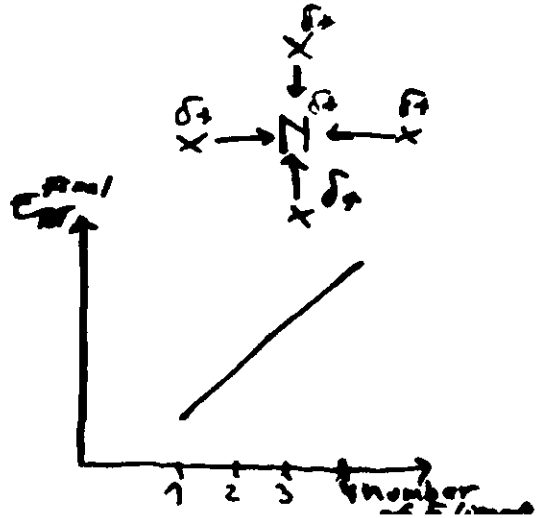


if X electronegative charge on N
strong polarized ionic bond
high E_{TOT}^{Final}



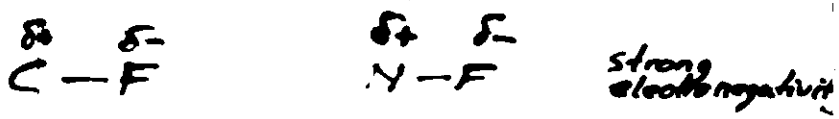
if X electropositive charge on the ligands
delocalized and covalent bond
low E_{TOT}^{Final}



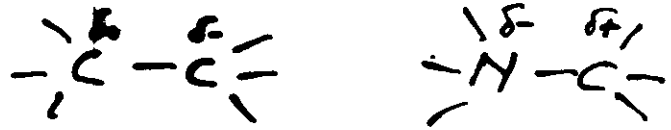


It reflects the charge distribution in Final state

We find correlation when

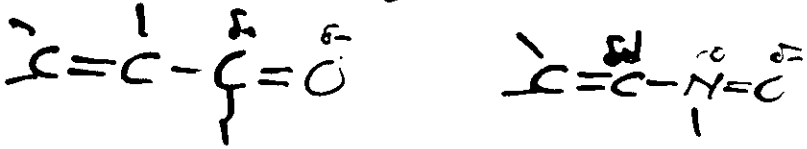


but when

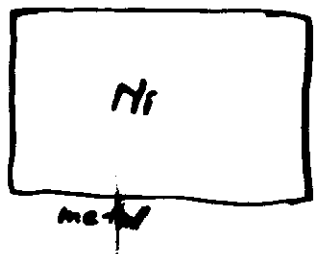


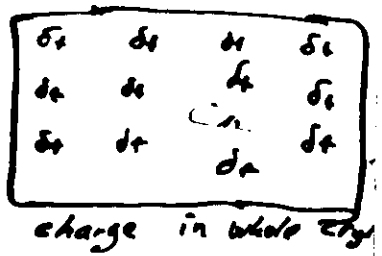
it will not work

or



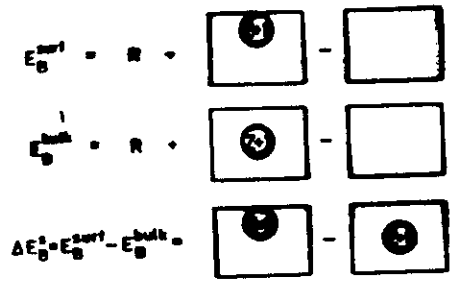
π-bonded and delocalized system
it will not work





Ionic contribution to cohesive energy in metals small
it will not work

Surface Core Level shift



Johansson et al
Phys. Rev. B 21, 4427 (1980)

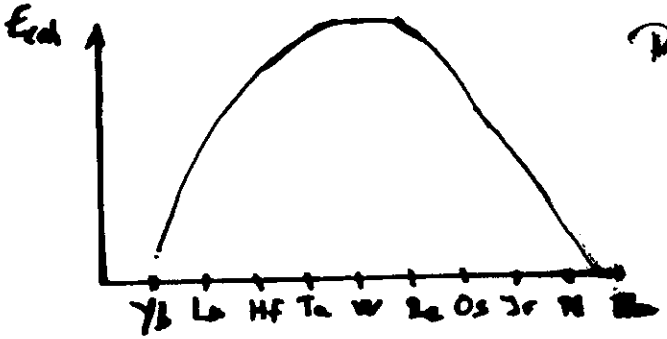
Surface segregation energies

Through Born–Haber cycle

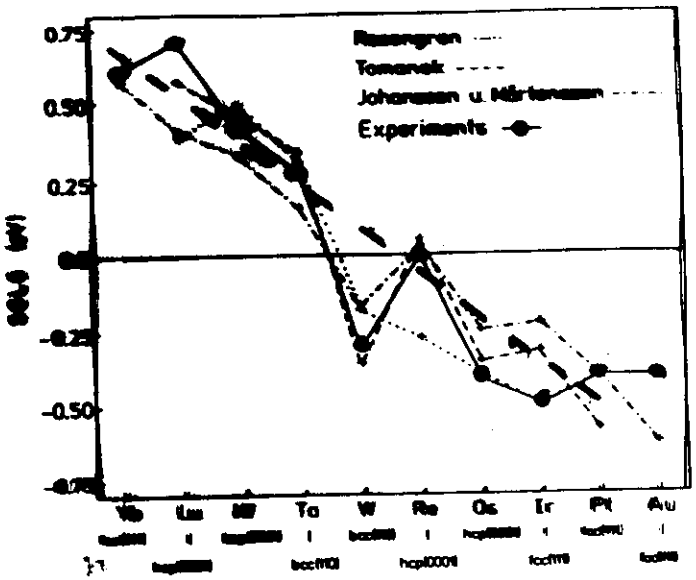
$$\Delta E_B^S = \gamma^{2nn} - \gamma^{B} \sim 0.25\,(E_{coh}^{2nn} - E_{coh}^{B})$$

γ : surface Energy

E_{coh} : cohesive Energy



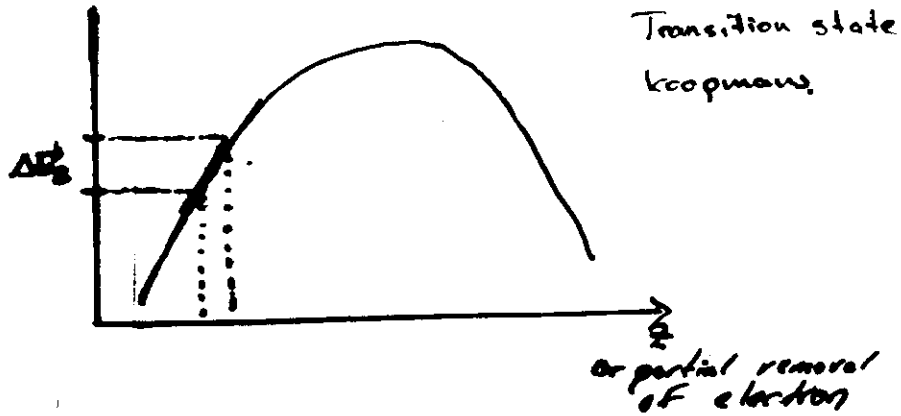
Parabola
positive shift in beginning
and negative at end.
zero in between



Mårtensson et al.
Phys. Rev. B39, 8181 (1989)

Ground state calculations of koopmans energies gives a similar trend.

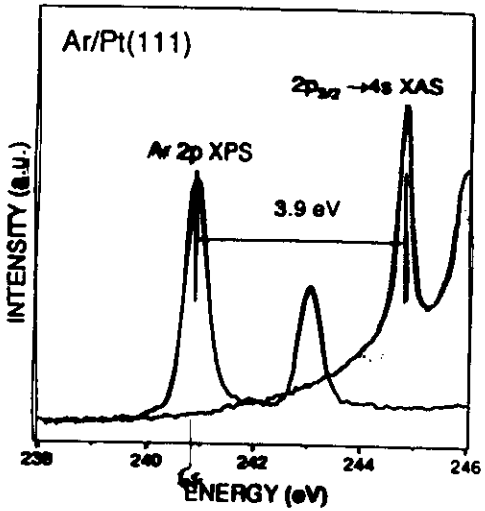
Coincidence!



Transition state koopmans.

or partial removal of electron

Amount of transferred charge

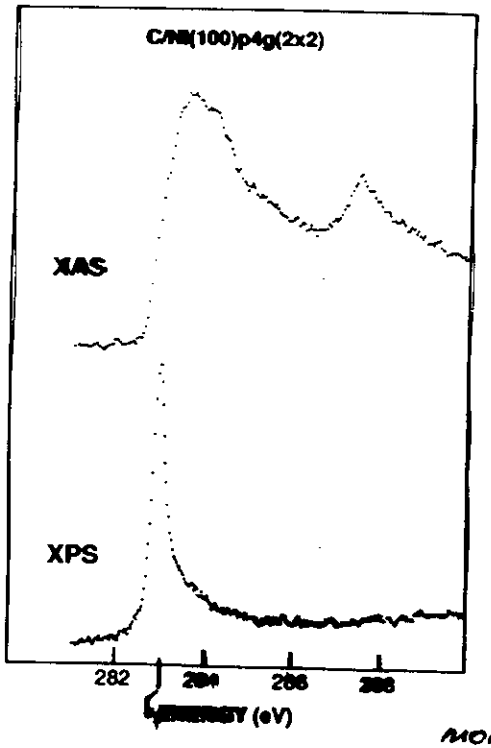


Z+1

Ar → K

K^+ ionic

metallic screening
no transfer of charge
lowest final state ionic



Z+1

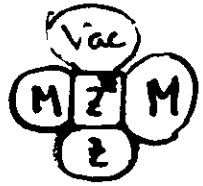
C → N

N higher el neg c
more than 1 electron
transfered

$C^{\delta-}$ → $N^{\delta+}$

metallic screening
more than 1 electron
transferred
lowest final state
more ionic than initial state

Partial shifts in alloys, intermetallic compounds etc.



Vac : surface
M: alloy metall
Z: metal of same kind

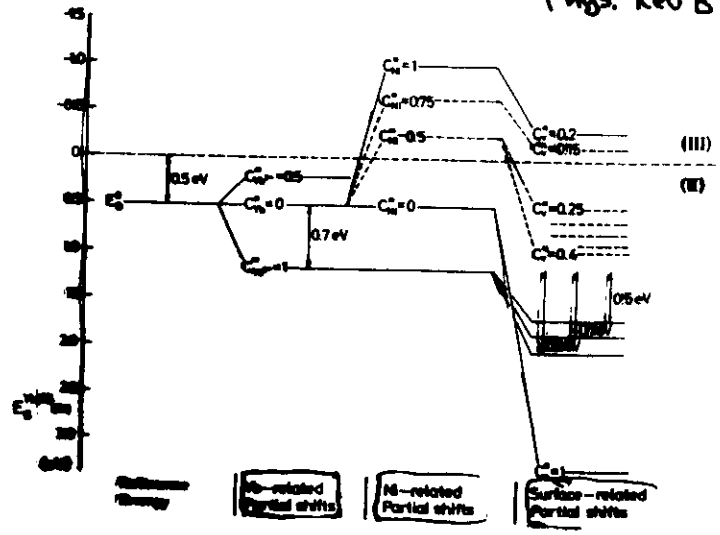
$$E_B^Z - E_B^\circ + C_Z^* \Delta E_Z + C_M^* \Delta E_M + C_V^* \Delta E_V$$

C^* : effective concentration parameters

ΔE partial shifts

E_B° : reference level

Yb-Ni Nilsson et.al Phys. Rev B 38, 10357 (1988)

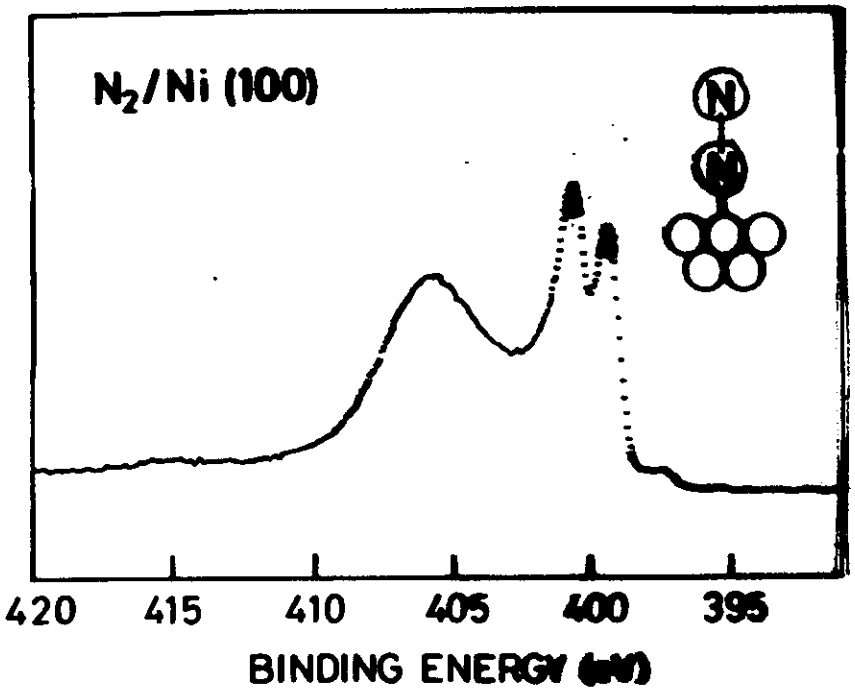


Chemical shifts

Different atoms within an molecule

standing up configuration

Nilsson et.al. Phys Rev Lett 47, 1495 (1981)



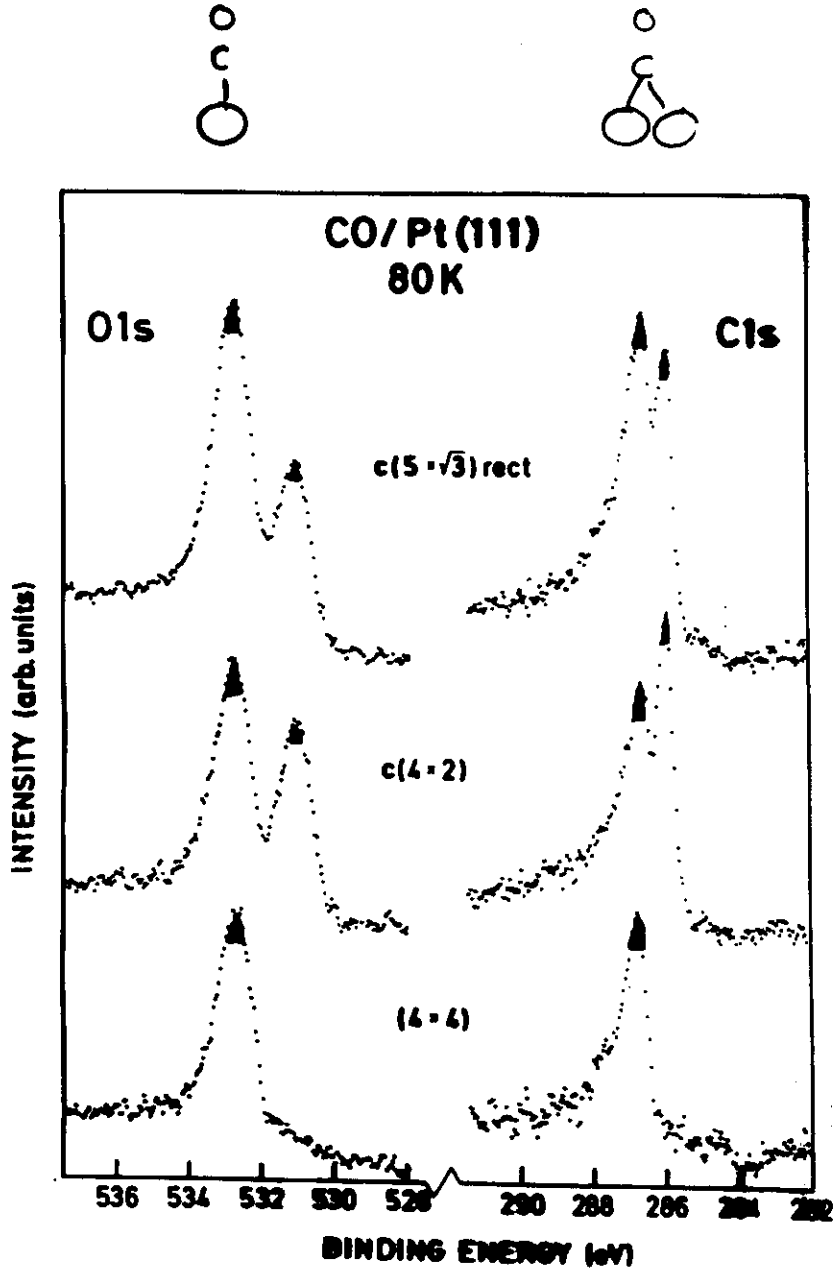
CO adsorption

on top > bridge > hollow

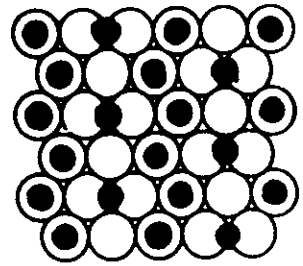
O 1s > C 1s

lowest energy for maximum coordination

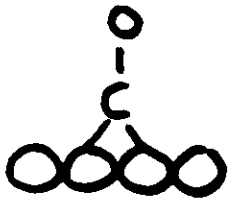
CO on Pt(111)

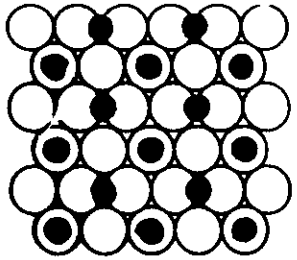


Björneholm Surf. Sci. 315, L903 (1994)

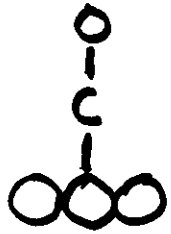


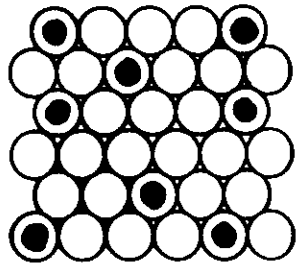
c(5√3 × √3)





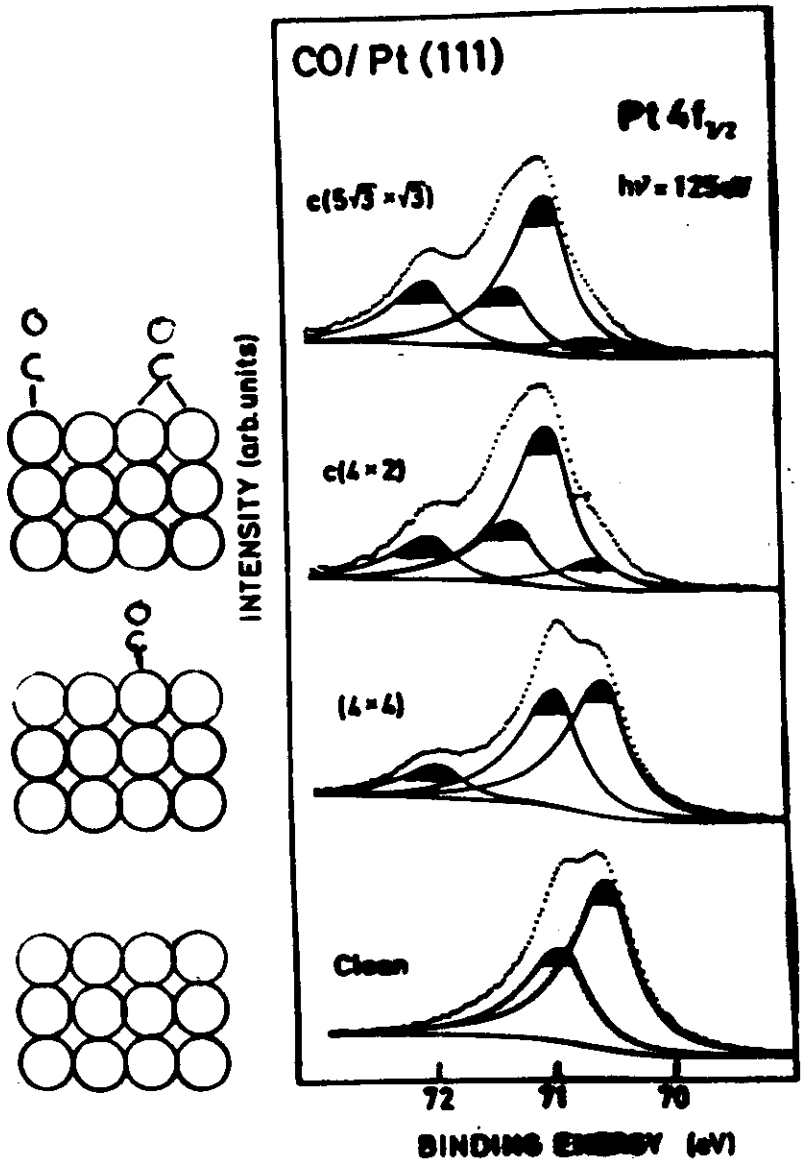
c(4 × 2)

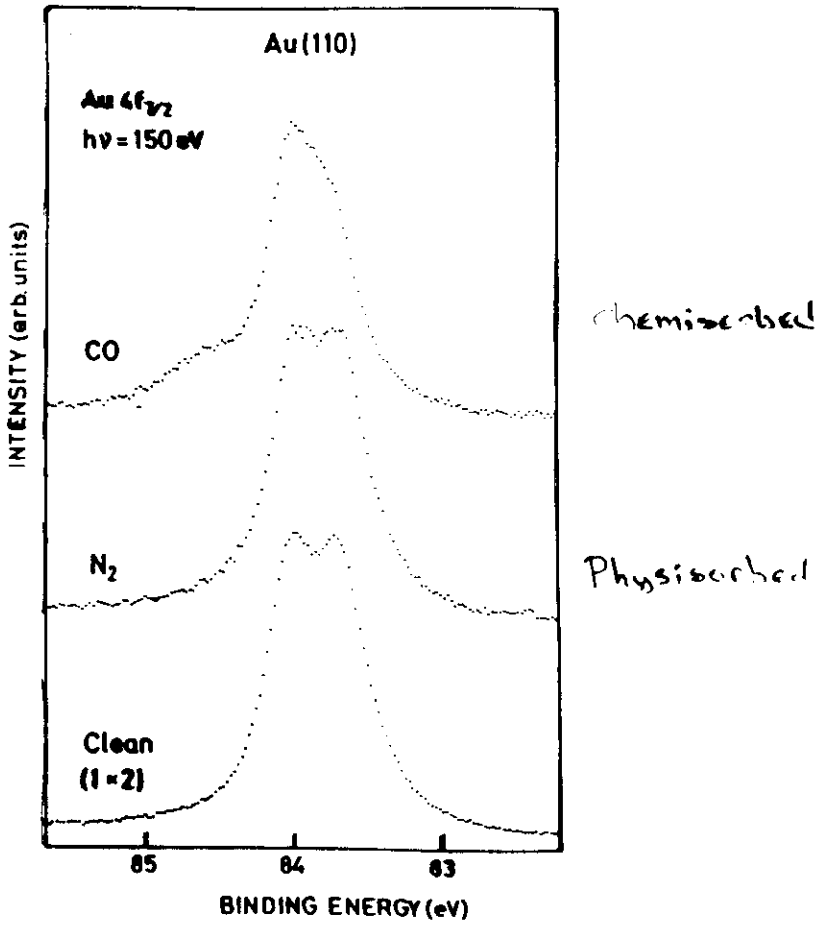




(4 × 4)

Pt Z+1 Au

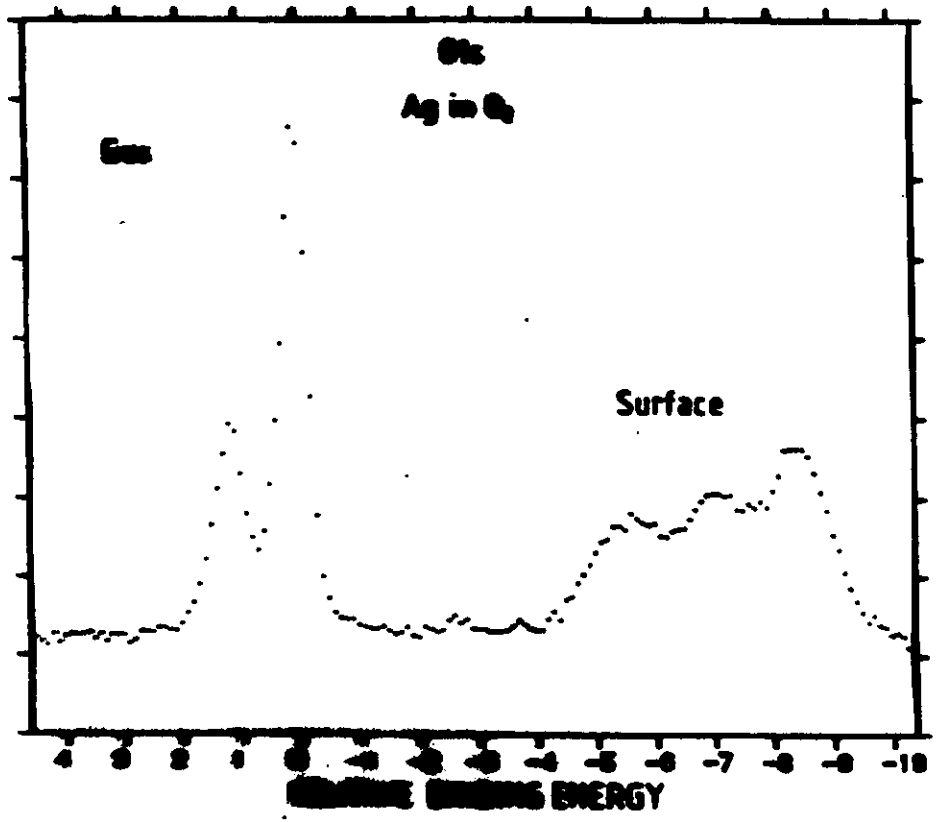




Björneholm et al Surf. Sci 315, L983 (1994).

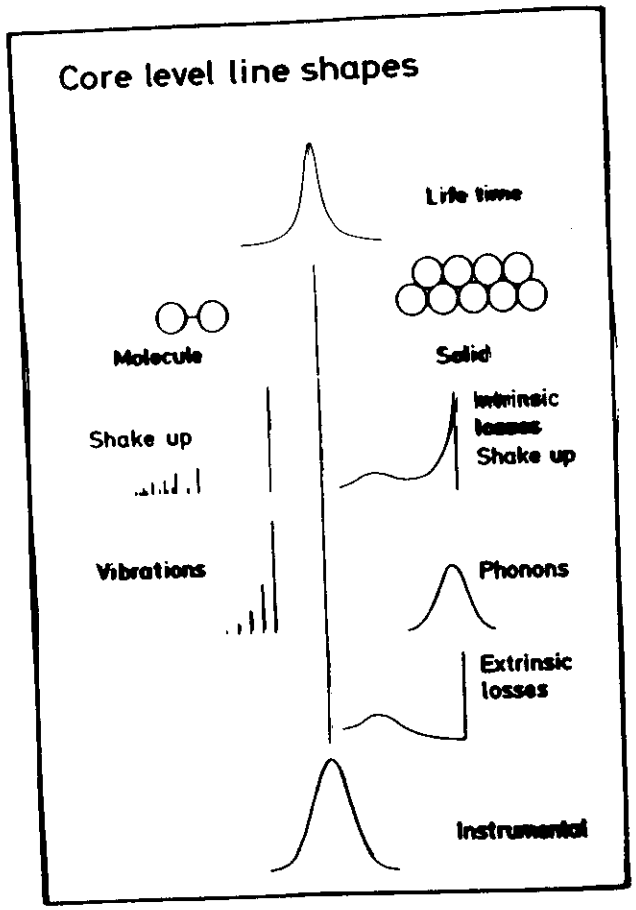
Gas cell experiments

1 torr O_2



Vibrational and Multielectron excitations

Line shapes in core level spectra and satellites



Metallic screening

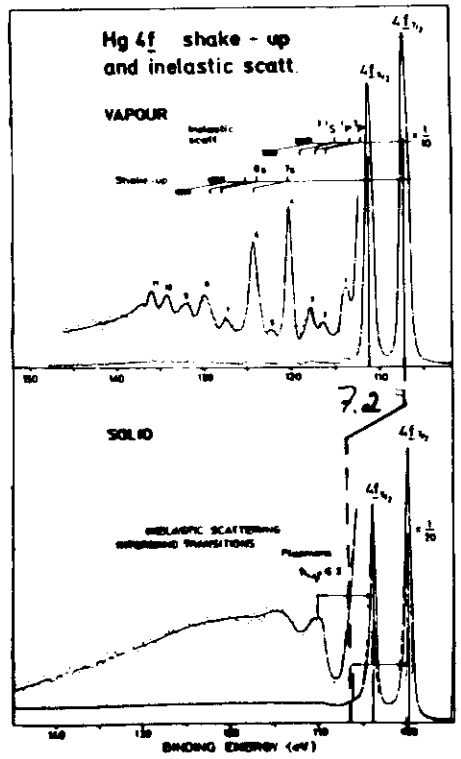
ΔE_B^{Hg} (free atom − solid) = 7.2 eV

Two different reference levels
E_{vac} and E_F

ΔE at the same ref level = 2.7 eV

ref to E_{vac}

ref to E_F



Svensson et. al
J. El. spec 9, 51 (1976)

Sudden Approximation

removal of core electron test at high kinetic energies

INITIAL STATE (N electrons)

a) $\Psi_i(N-1), \varphi(1)$ H(N)

FINAL STATES (N-1 electrons)

b) Frozen Orbitals $\Psi_j(N-1)$ — Koopmans energy ε_k

Charge distribution as in initial state but a new N-1 hamiltonian

c) Relaxed Orbitals $\Psi_j(N-1)$ H(N-1)

$\Psi_f = \sum_j c_{jk} \Psi_j$

$c_j = \langle \Psi_j | \Psi_f \rangle$

$E_k = \sum_j |c_{jk}|^2 \varepsilon_j$

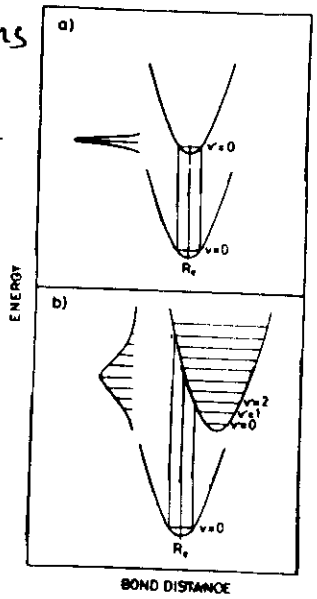
Some rule: Koopmans rule

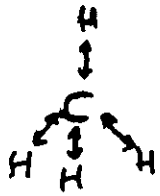
The different Ψ_f must have the same symmetry : monopole rule

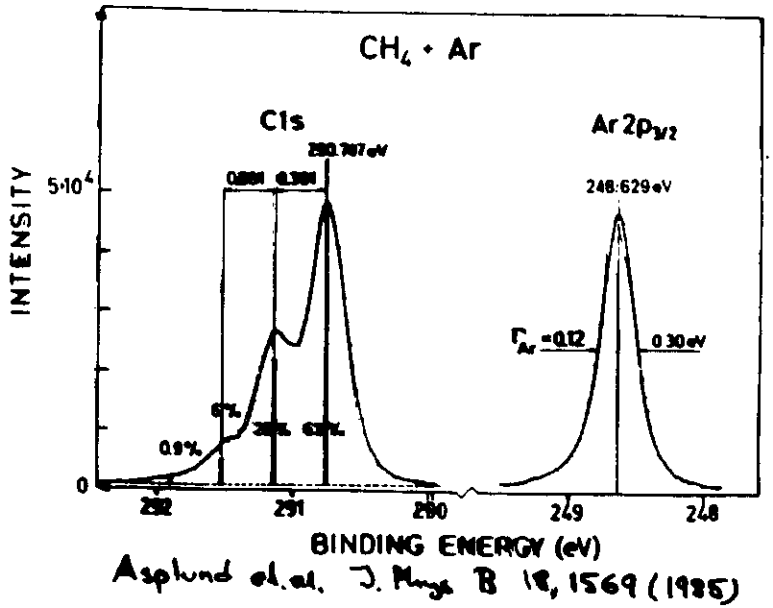
Vibrational excitations

Frank-Condon principle

Ionization much faster than atomic motion







Asplund et al. J. Phys. B 18, 1569 (1985)

Atomic Adsorbates

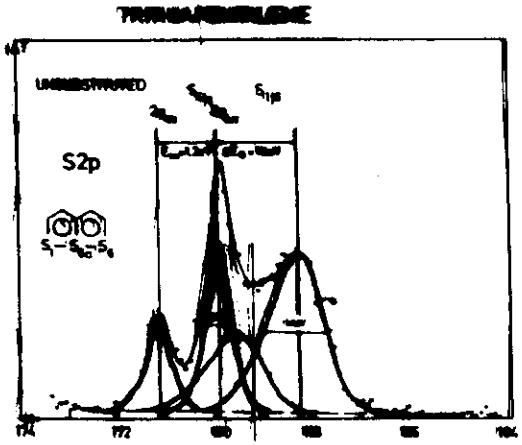
$C^4 - N$

$N^4 - O$

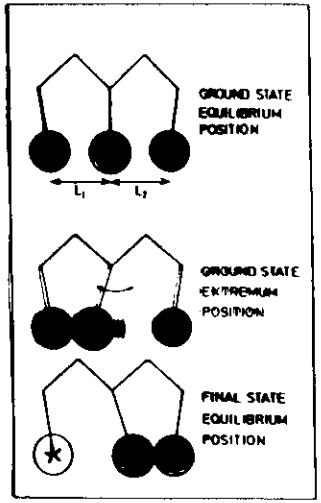
$O^4 - F$

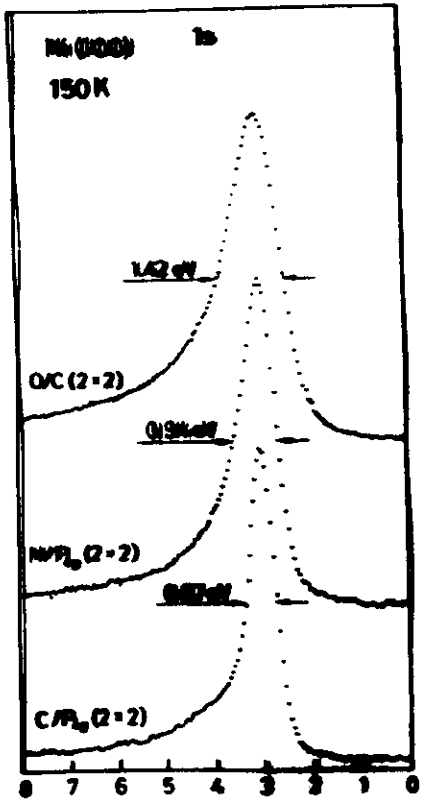
C, N, O Geometry known
Vib energy known

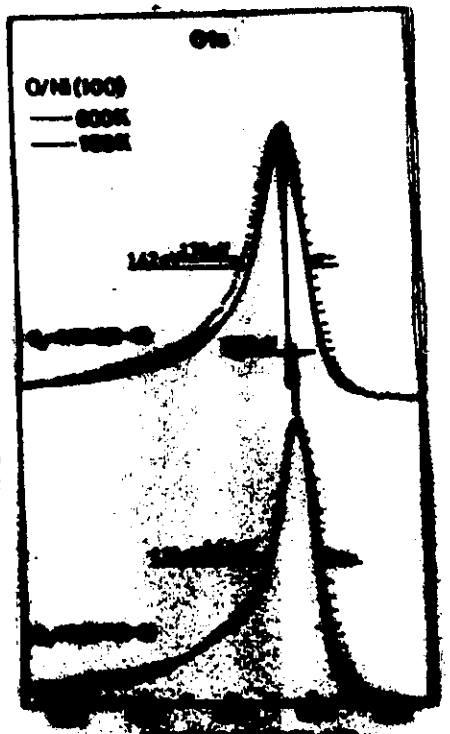
Lifetime broadening ~ 0.1–0.2 eV



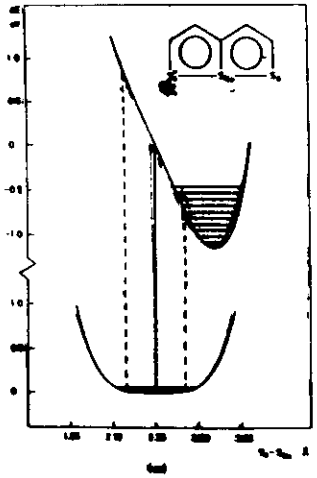
Sanfilippo et al. Chem. Phys. 30, 431 (1978)

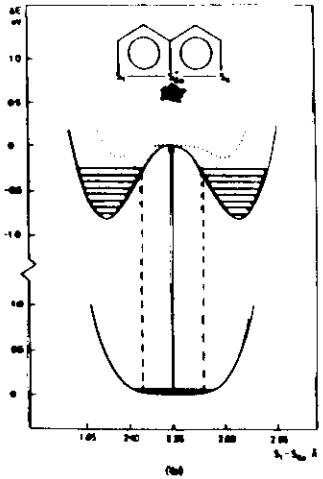




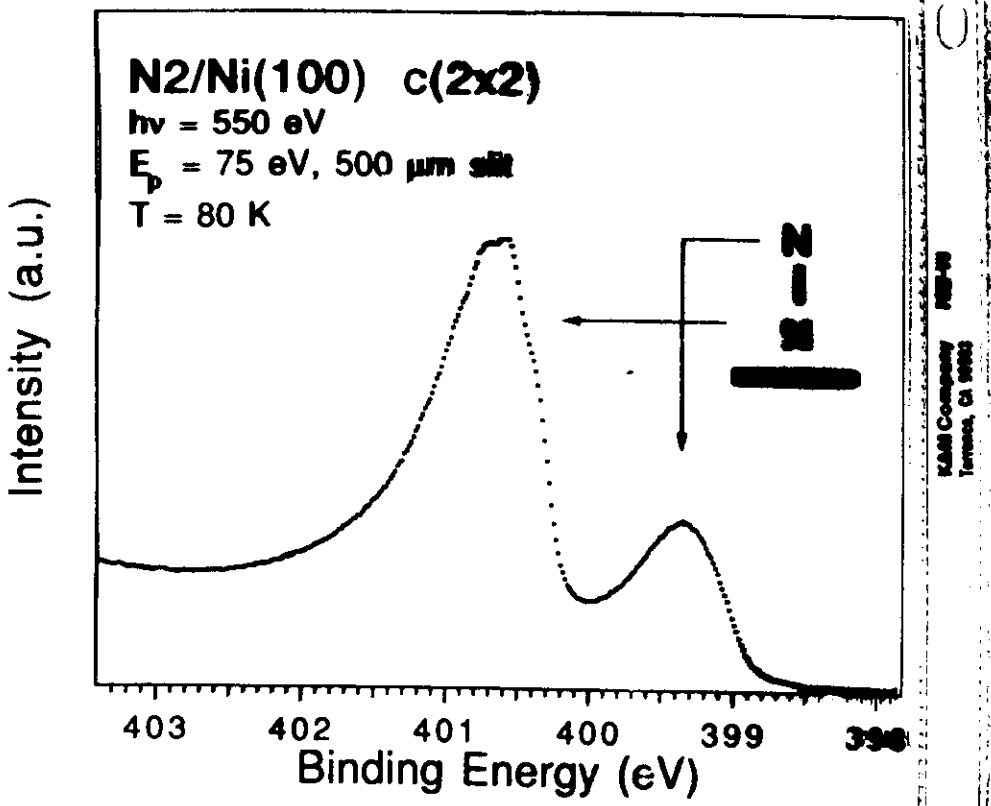


Nilsson et al.

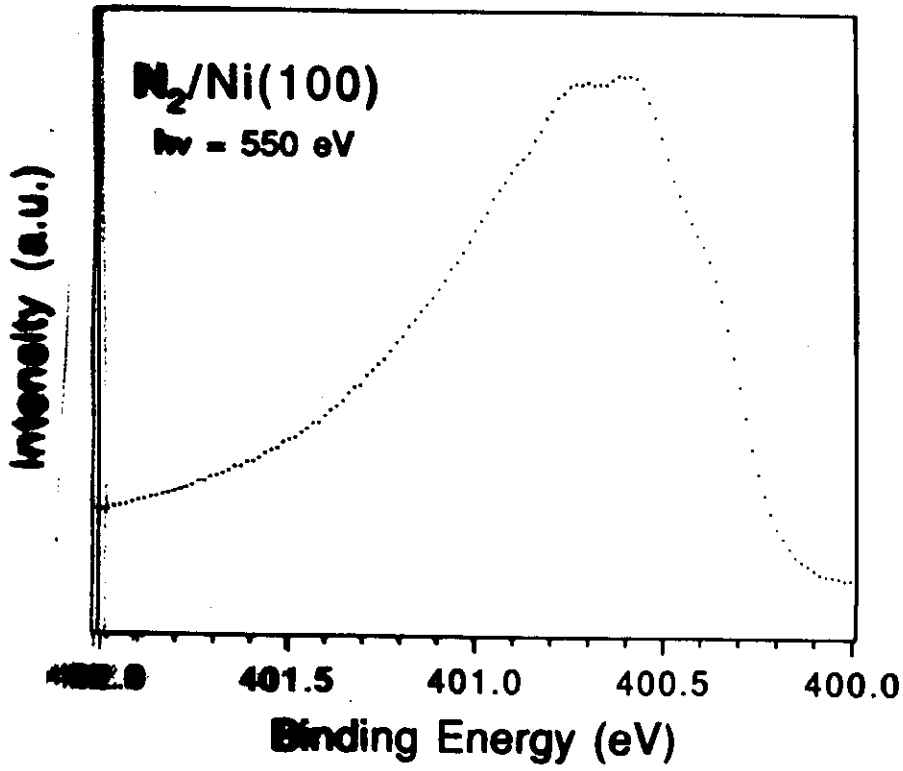




ALS (Advanced Light Source), Berkeley, Cal.
BL 8.0 (IBM)
Scienta SES200 1995



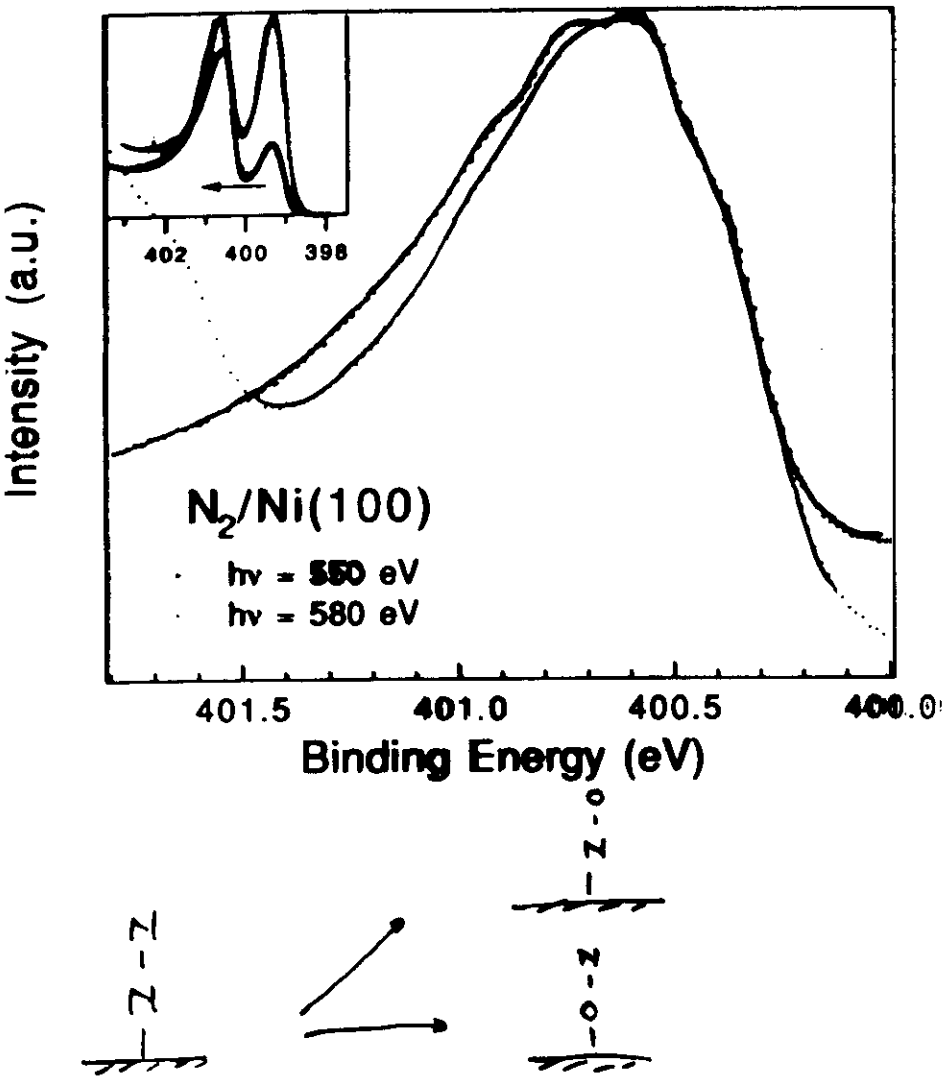
Weinelt and Nilsson, to be published

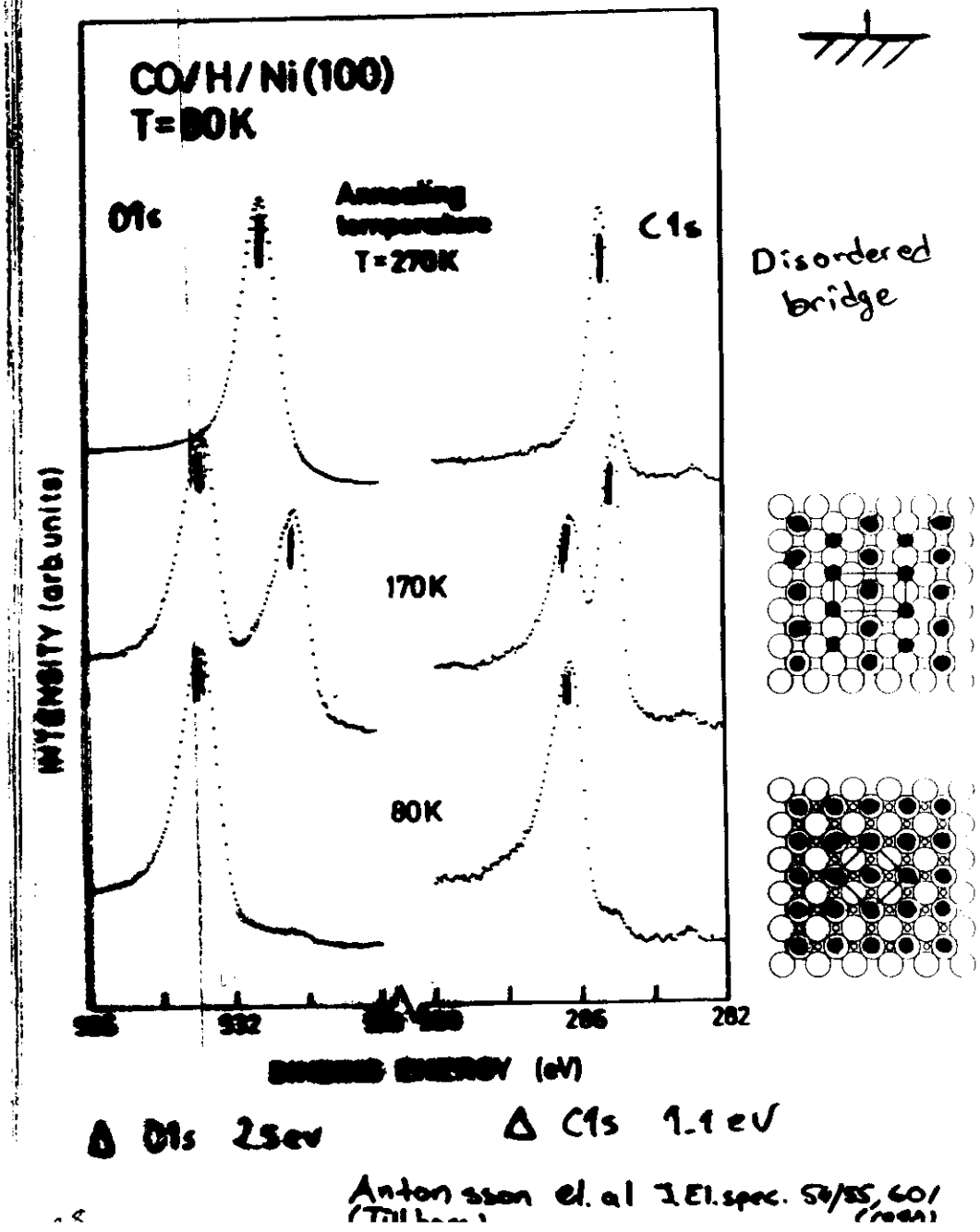


ΔE_{ph} 50 meV
ΔE_{el} 50 meV

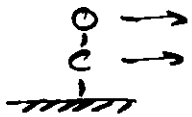
Different adsorption sites

XPS



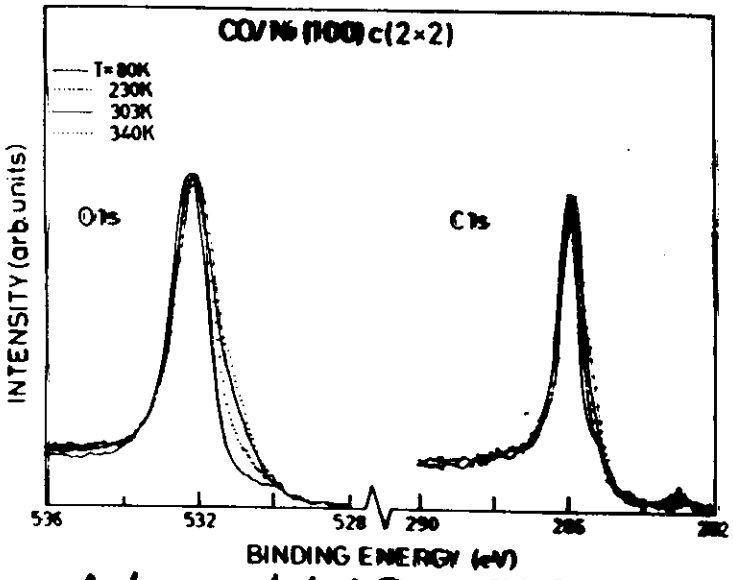


Antonsson et al J.El.spec. 50/55, 601

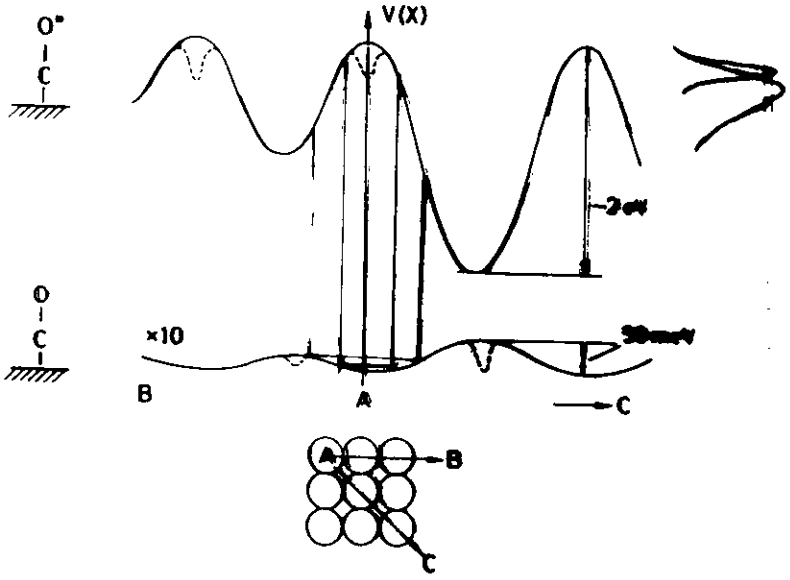


$V \sim 3.5$ meV

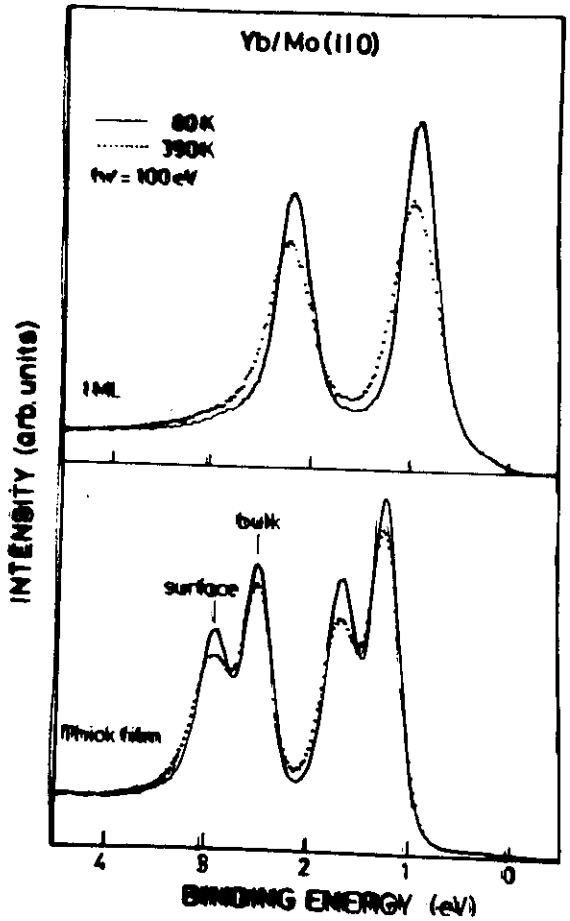
Frustrated Translation mode



Andersson et al. J. El. Spec. 59/55, 601 (1980

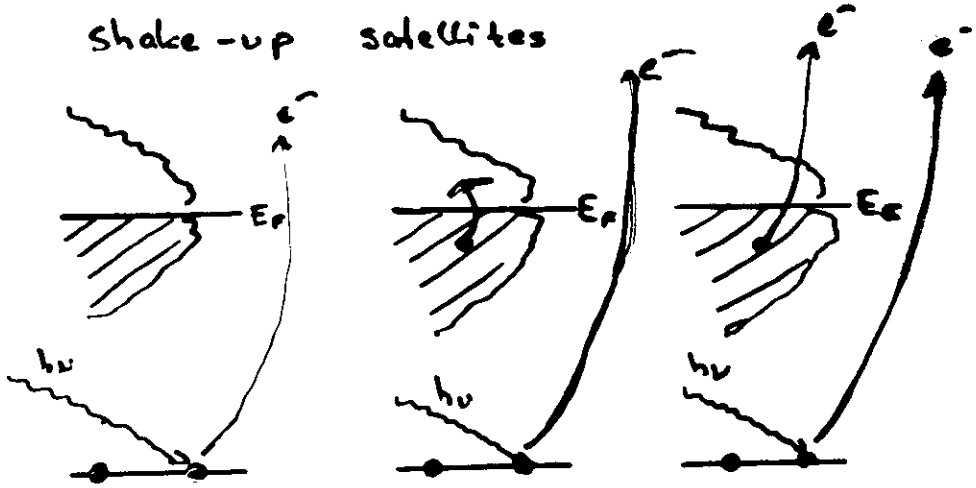


Large width for surface peak at elevated temperature.

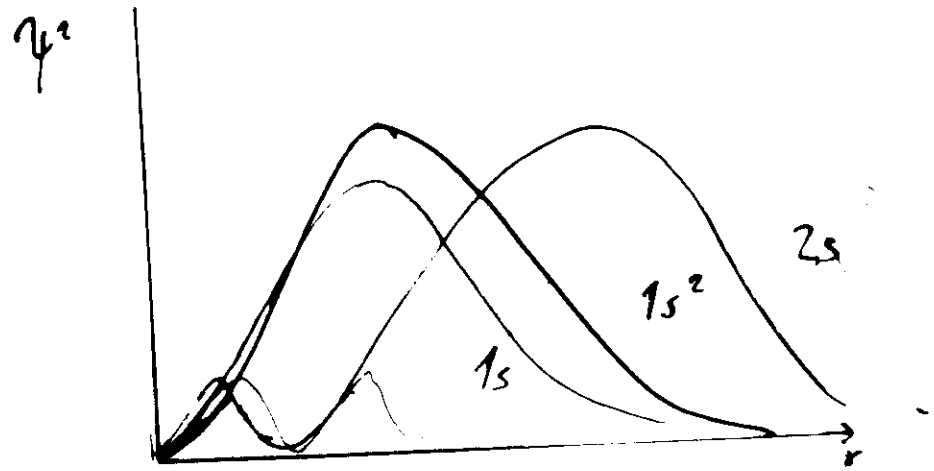


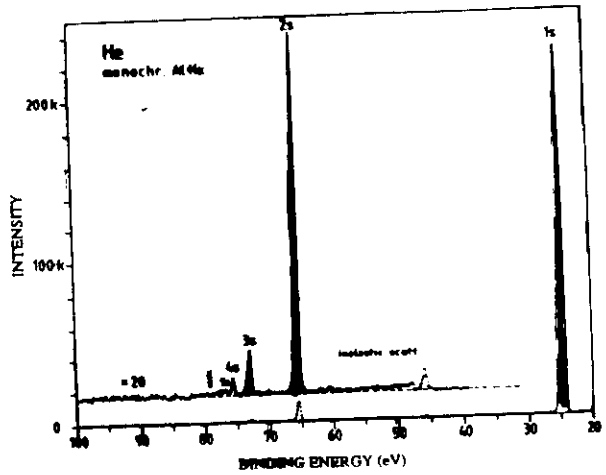
Stenborg et. al unpublished

Multi electron excitations

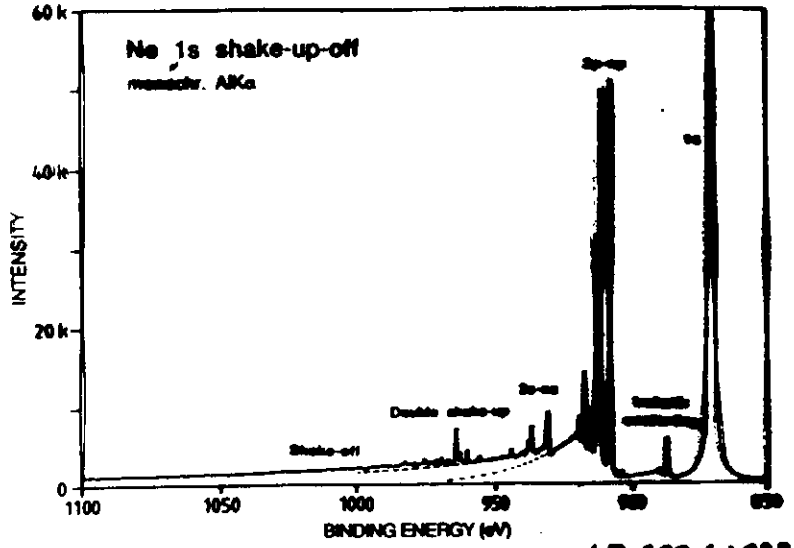


Main line shake-up shake-off
double ionization

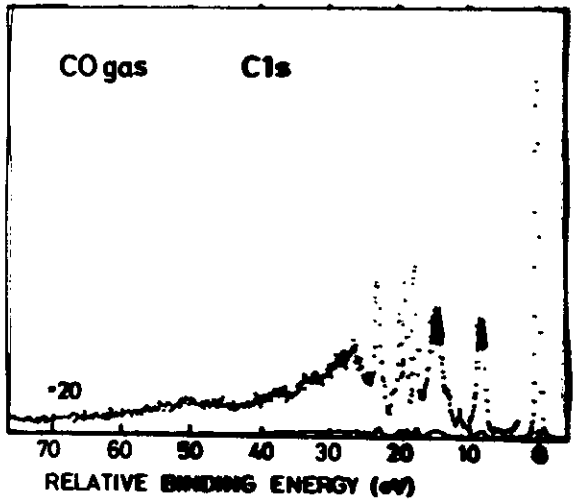




Svensson et. al. J. El. spec. 47, 327 (1988)



Svensson et al. J. El. spec. 47, 327 (1988)



$\pi \rightarrow \pi^*$ shake-up

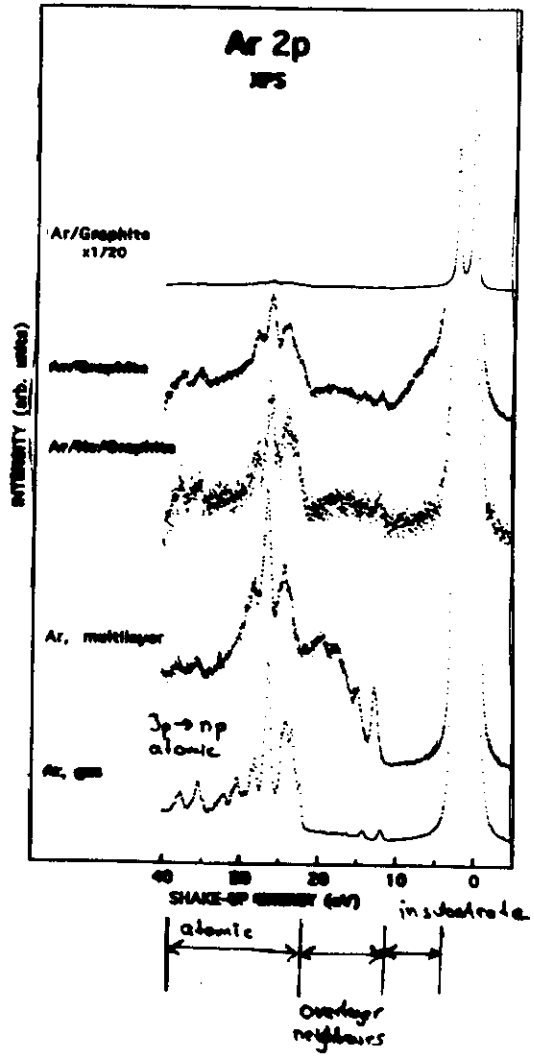
Schirmer et al. J. Phys. B20, 6031 (1987)

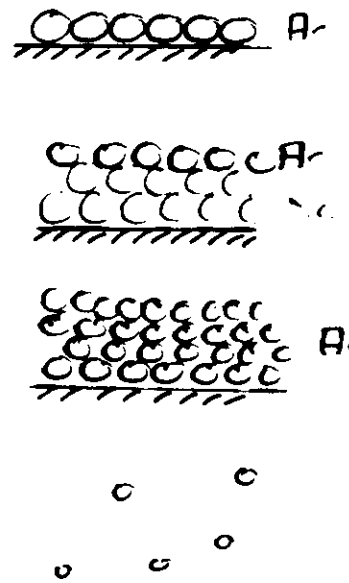
Ar physisorbed on substrate

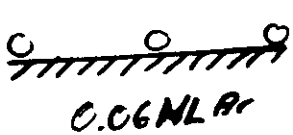
reason due to extra screening

new shake-up ?

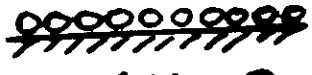
Sundell et al. Phys. Rev. Lett. 72, 2604 (1994)



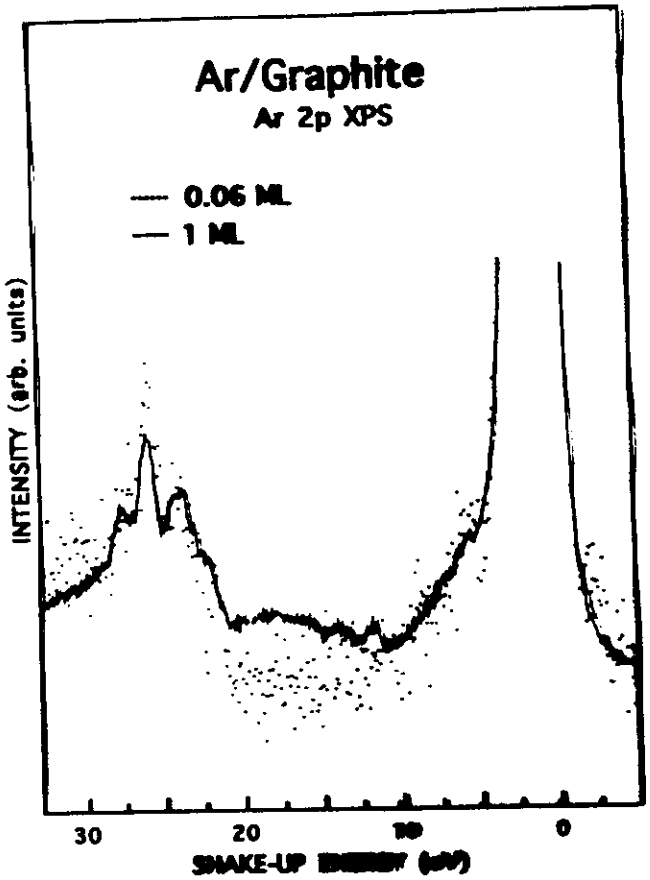


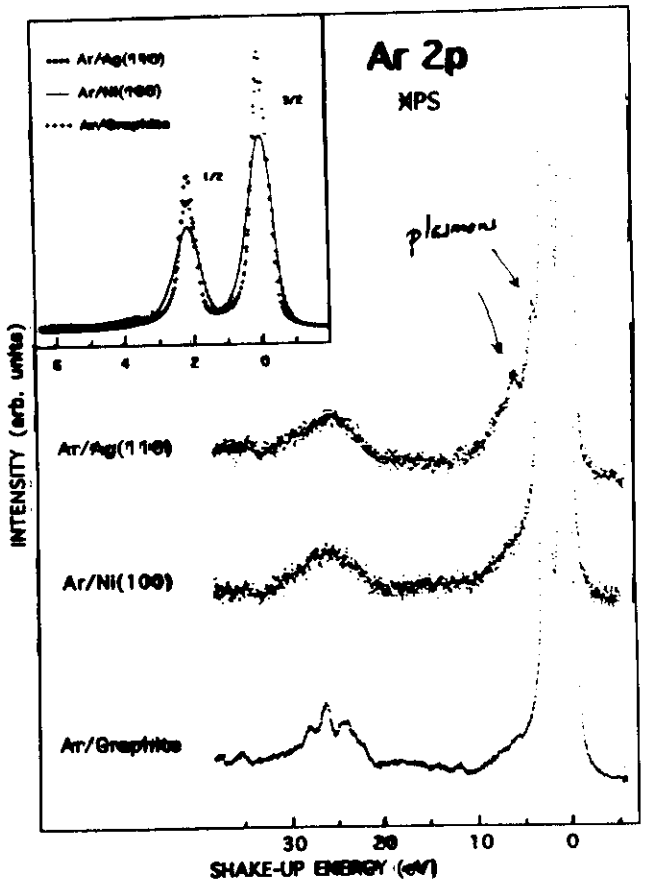


0.06 ML Ar



1 ML Ar





Three regimes of shake-up processes

i) short range screening
local excitations on adsorbate atom
core hole effects

3p → np
monopole

intensities change due to long range screening

ii) long range screening
no core hole effects
similar to extrinsic losses (intrinsic)

a) polarization of neigbour Ar atoms

dipole excitations
3p → 4s

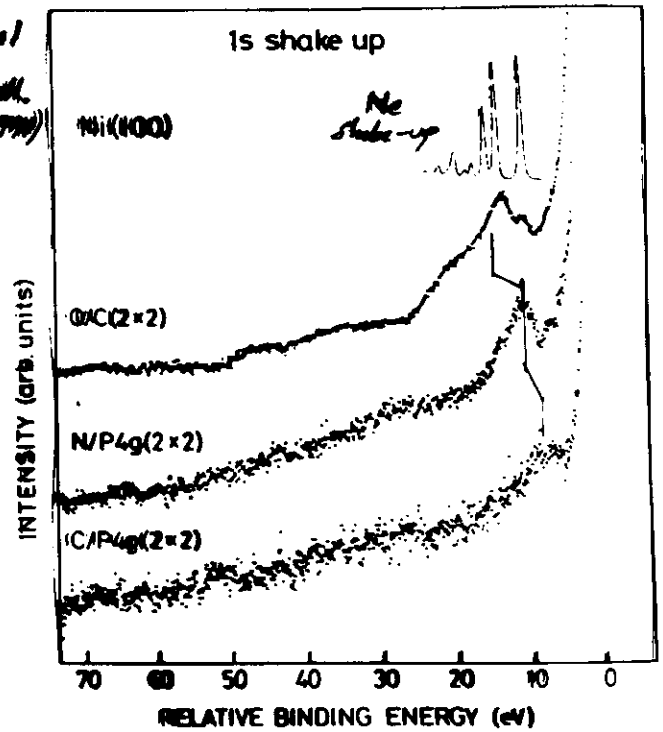
b) image screening from substrate

plasmon excitation

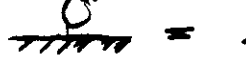
Strong Chemisorption bond
C, N, O on Ni(100)

Changing the 2p states → 2p → 3p, np excitations
local excitations

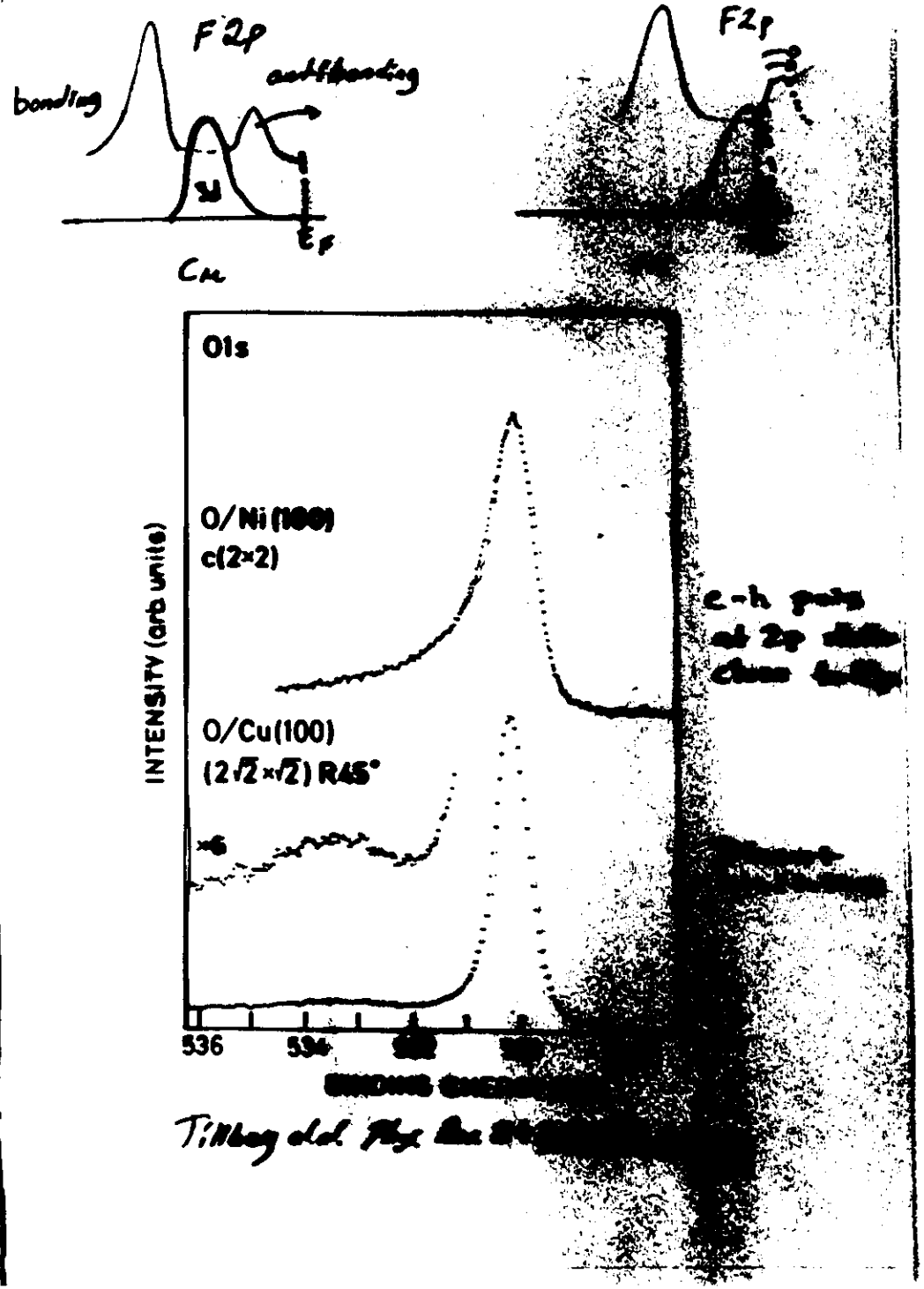
Nilsson et al
(Chem. Physics Lett. 1982, Nilsson (1979))



core hole effects



Fluorin close to F^-
$2p^6$ filled shell ~ Ne
$1s\,2p^6 \rightarrow \underline{1s}\,\underline{2p}^5 3p$ multiplets



Metals

long range screening

DOS

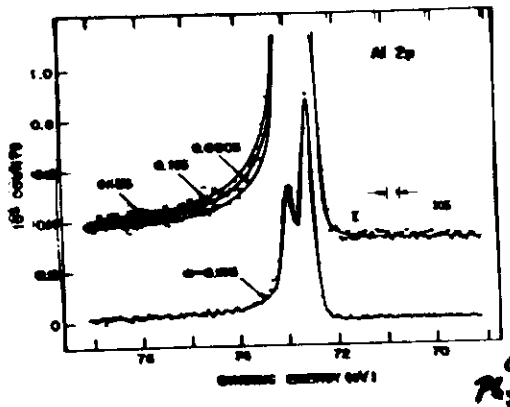
e-h pairs

Doniach-Šunjić
J. Phys. C 3, 285 (1970)

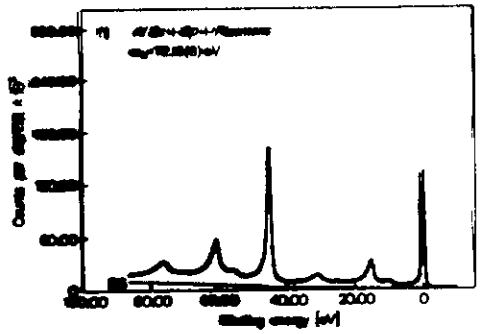
assymetry

$1/E^{1-\alpha}$

α: parameter related to screening charge



Citrin et. al
Phys. Rev. Lett. 35, 985 (1975)



Plasmon excitations

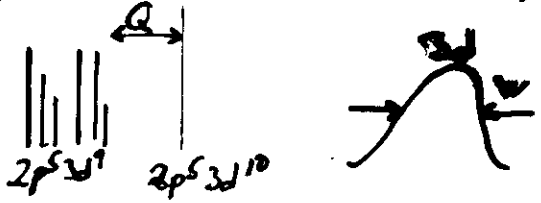
surface and bulk

local excitations Ni 2p satellite

$2p^6[3d^9\underline{s}] \rightarrow 2p^5[3d^{10}\underline{s}]$ main line Cu

$2p^5 3d^9[\underline{s}^2]$ satellite

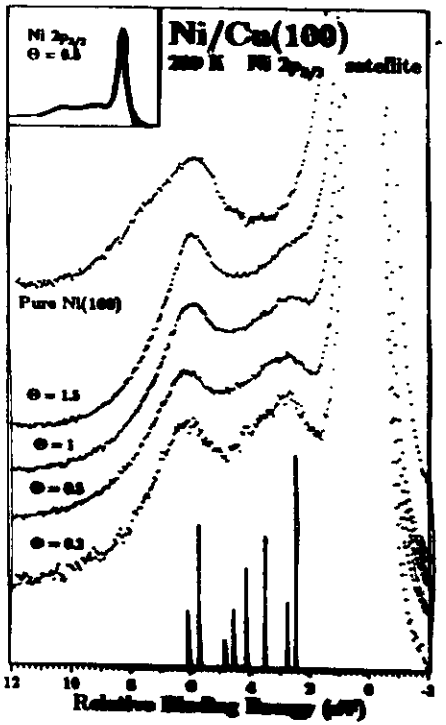
$2p^5 3d^9$ localized d multiplets

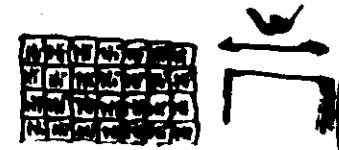


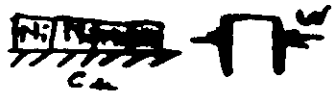
Q: Energy separating between multiplet terms and main line

W: 3d bandwidth

Hermans unpublished







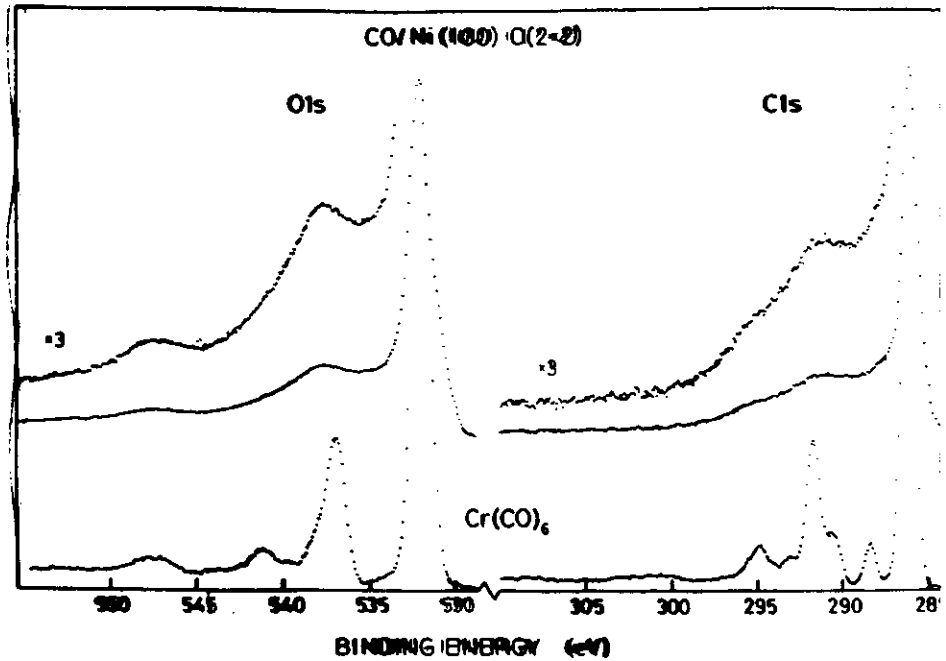
$Q > W$ localized multiplet terms

$Q < W$ delocalized states

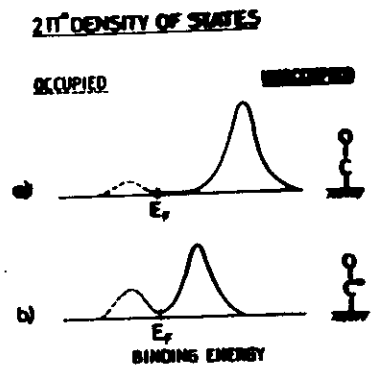
Molecular Adsorption

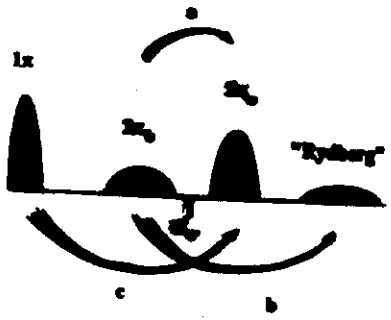
Shake-up local to Adsorbat-Substra complex

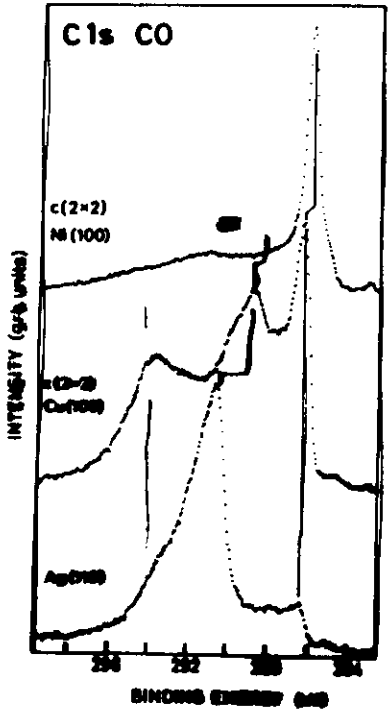
Difference between C1s an C 1s

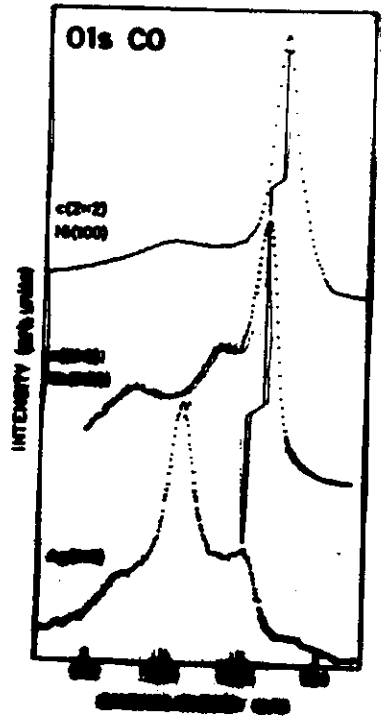


Nilsson et al. Phys. Rev. B 40, 10249 (1989)

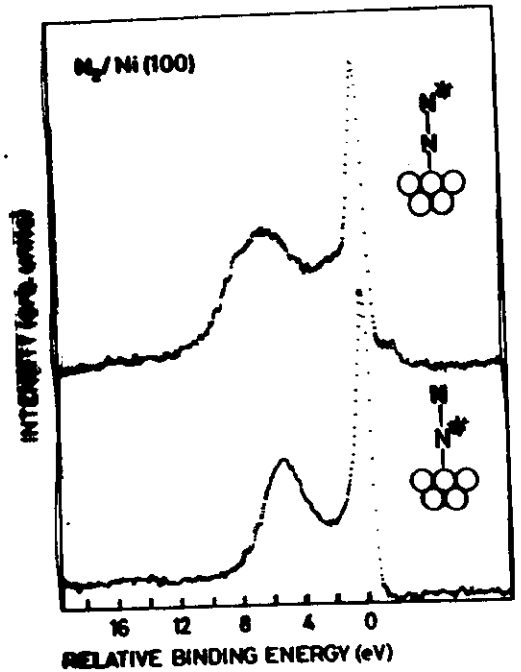


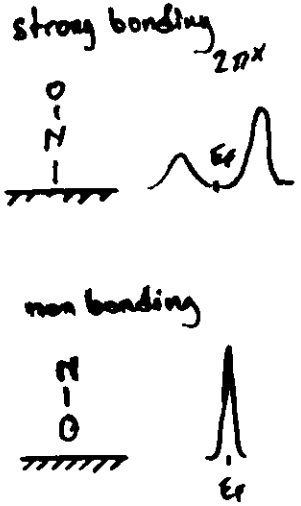


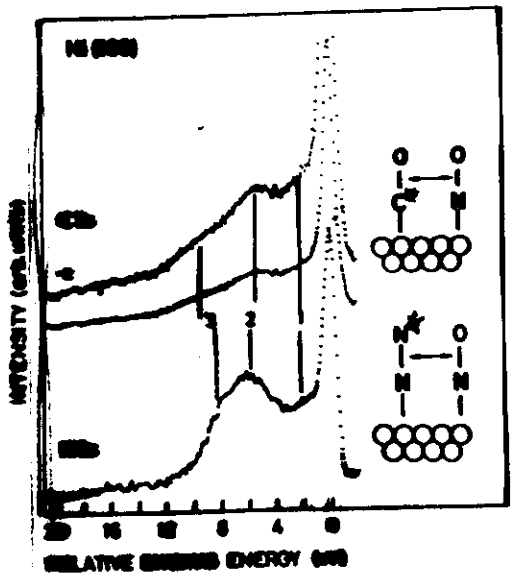




Tillborg et al J. El. spec. 62, 73 (1993)







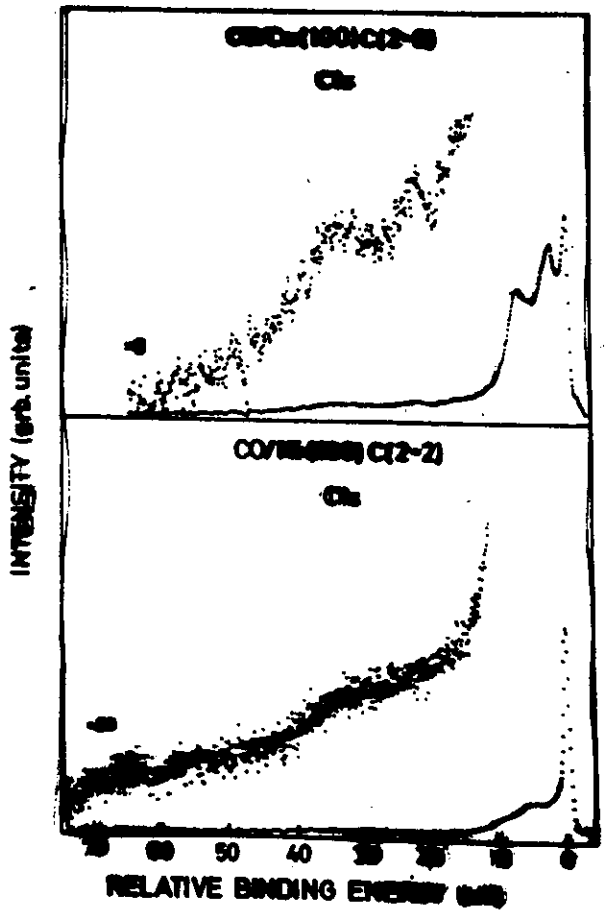
Similar Final states

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

Shake-off

Resonances in continuum

Main line intensity ~ 20-30 %



Tillborg et al. J. El. Spec. 62, 73 (1993)