

*Core level
photoelectron
spectroscopy*

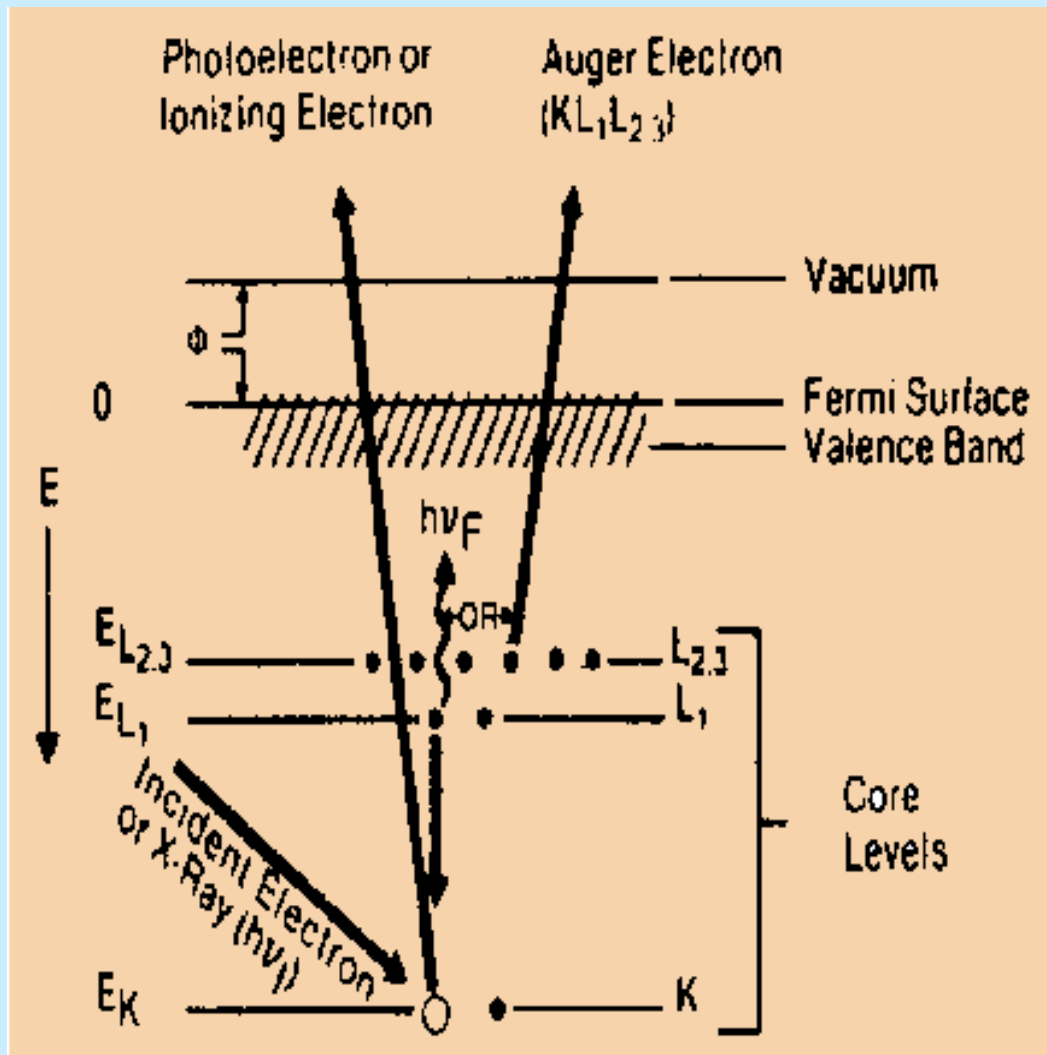
General features

Surface sensitivity

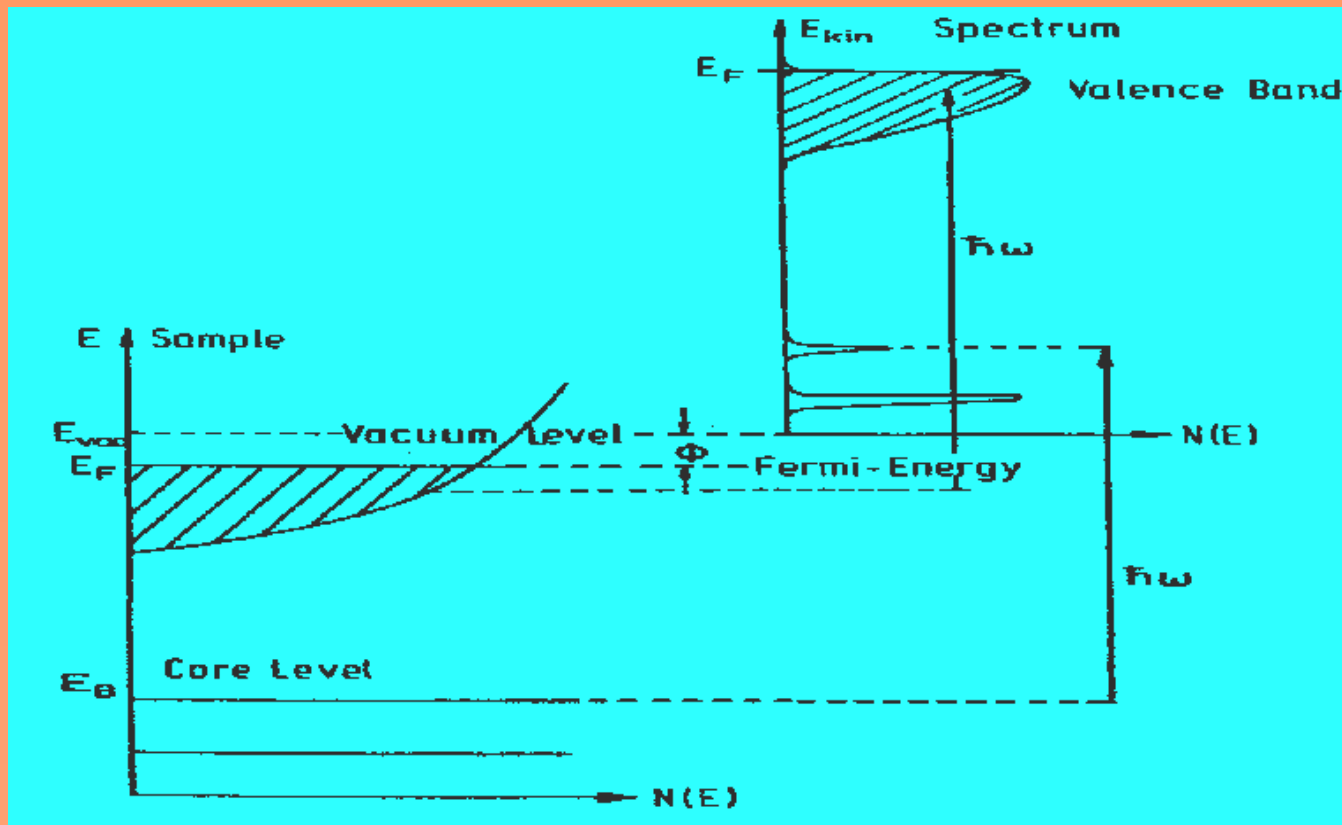
Final state effects

Applications

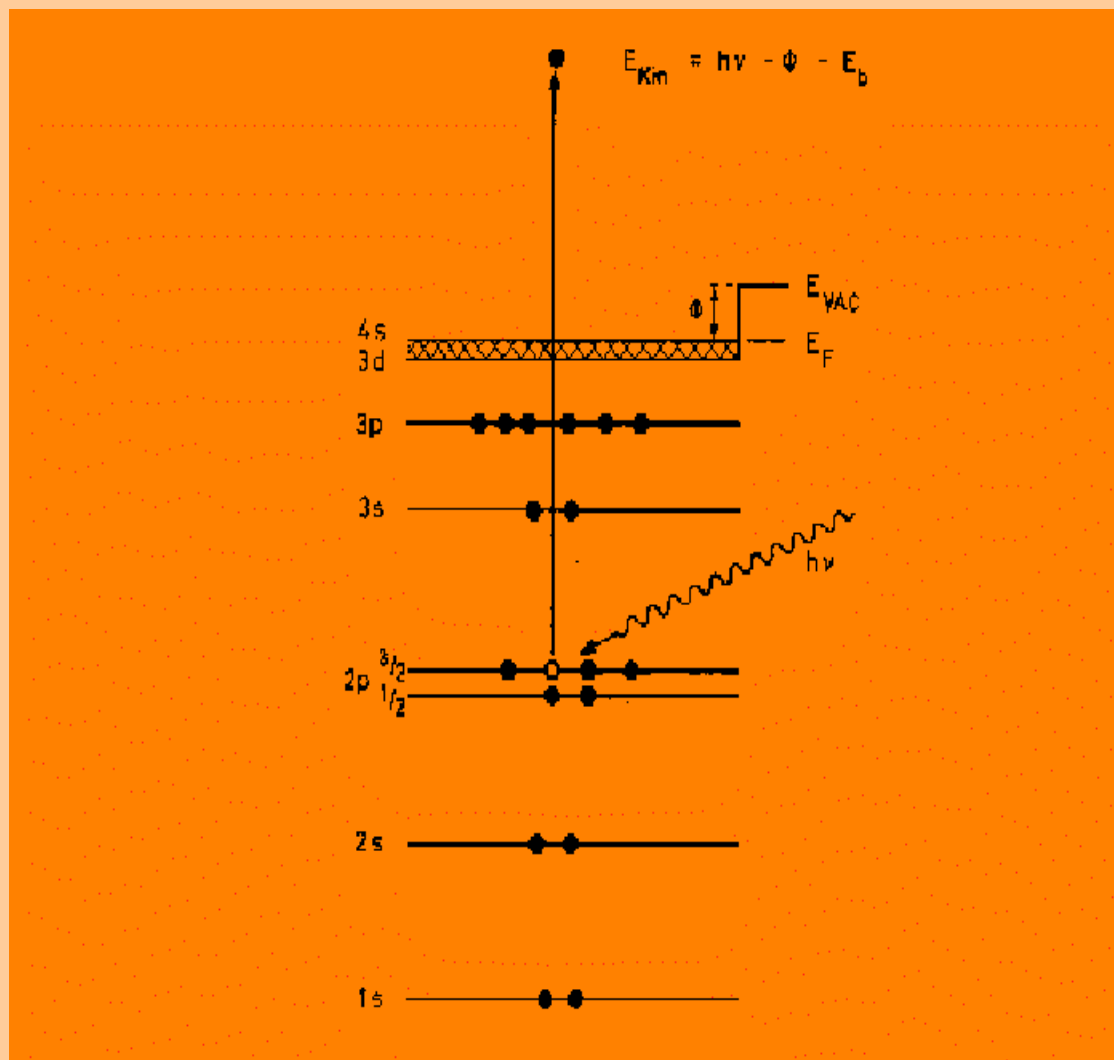
General Features



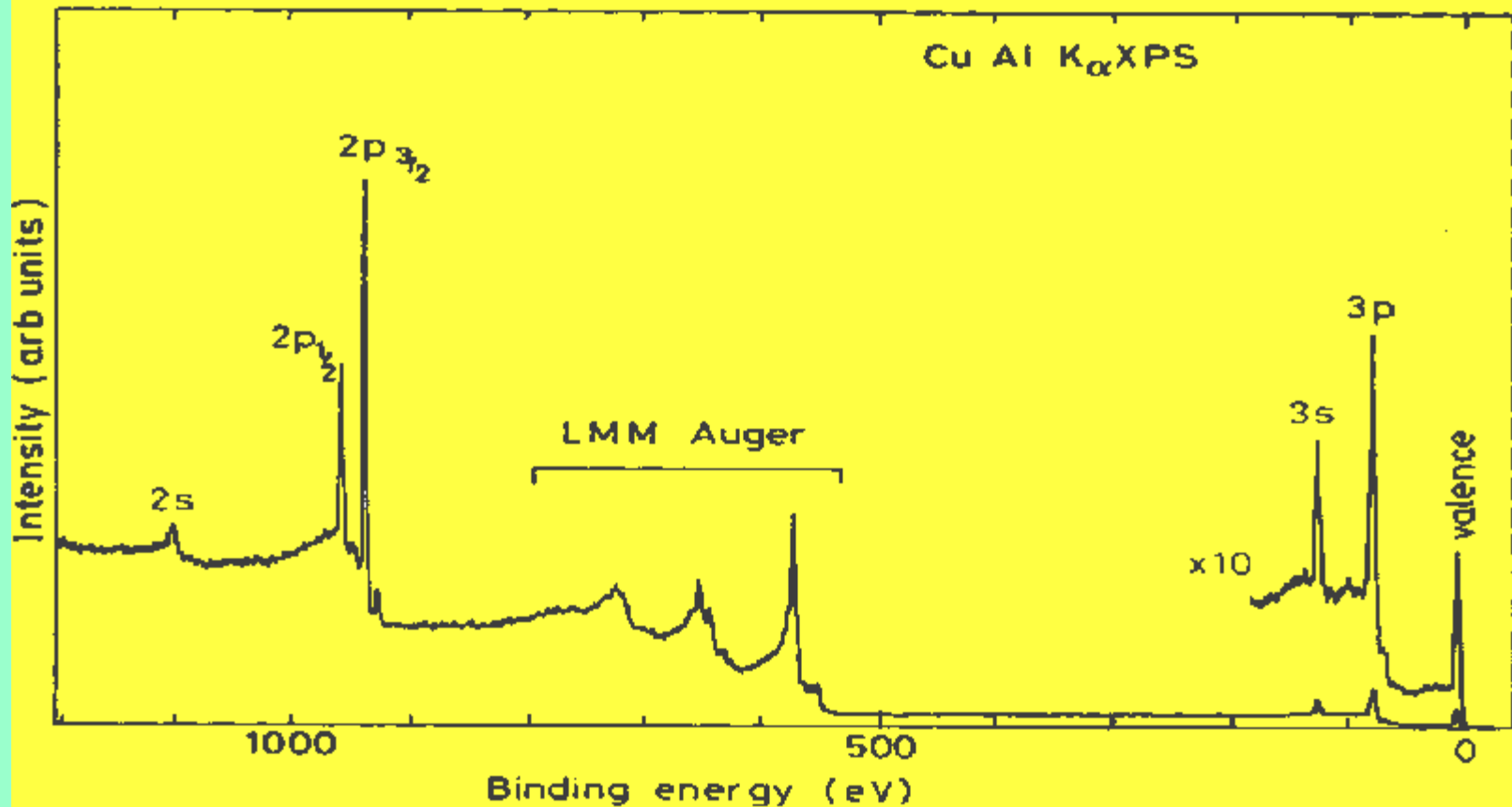
Energy level diagram for XPS/AES/X-ray fluorescence.



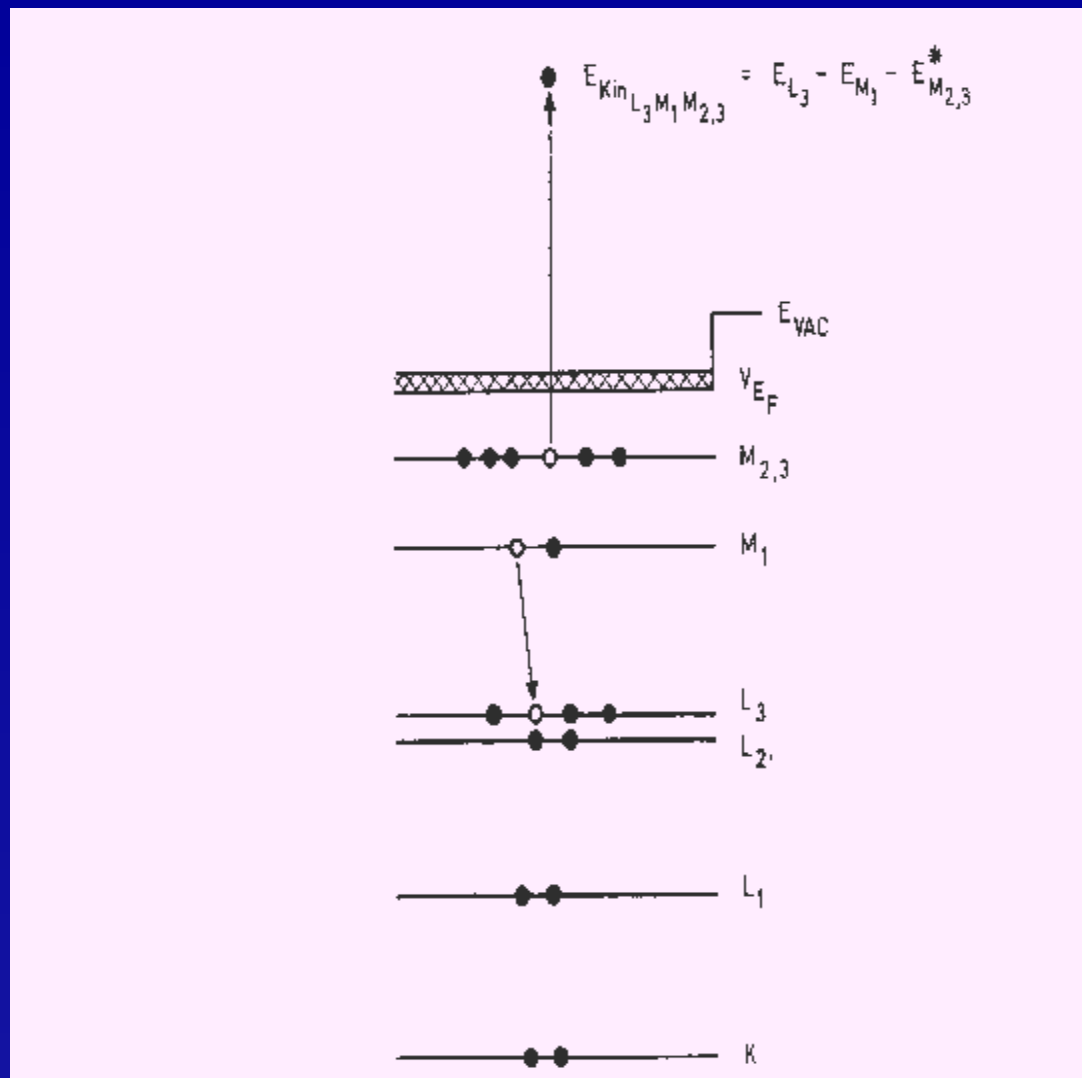
Energy levels in a solid and the electron energy distribution produced by photons of energy $h/_{2\pi}\omega$ (from S. Hüfner).



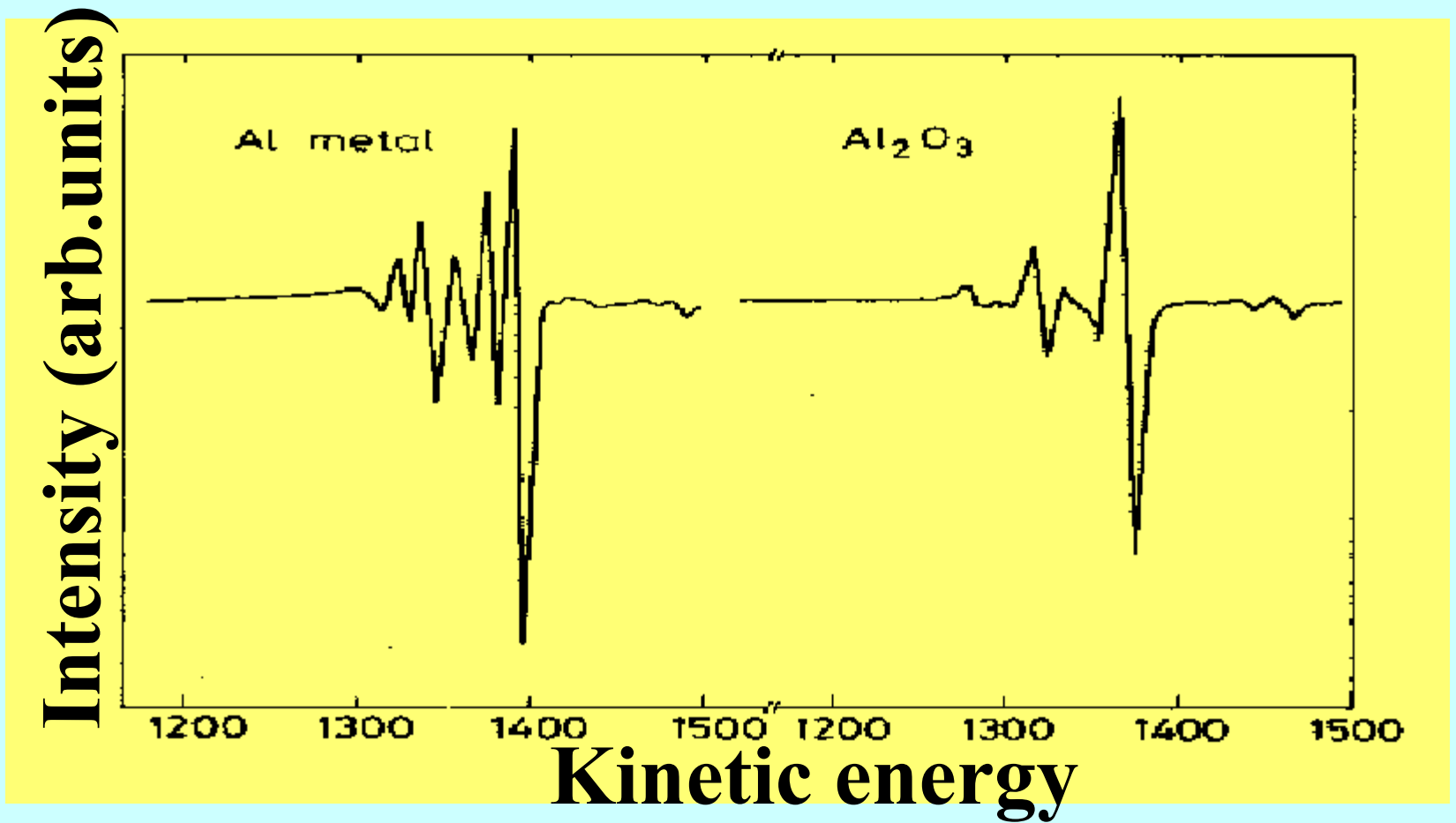
The electronic transition involved in the $2p_{3/2}$ emission of copper.



The XPS of a clean copper surface (from Chapter 2 of G. C. Smith).



LMM Auger transition of Cu
(from Chapter 2 of G. C. Smith).



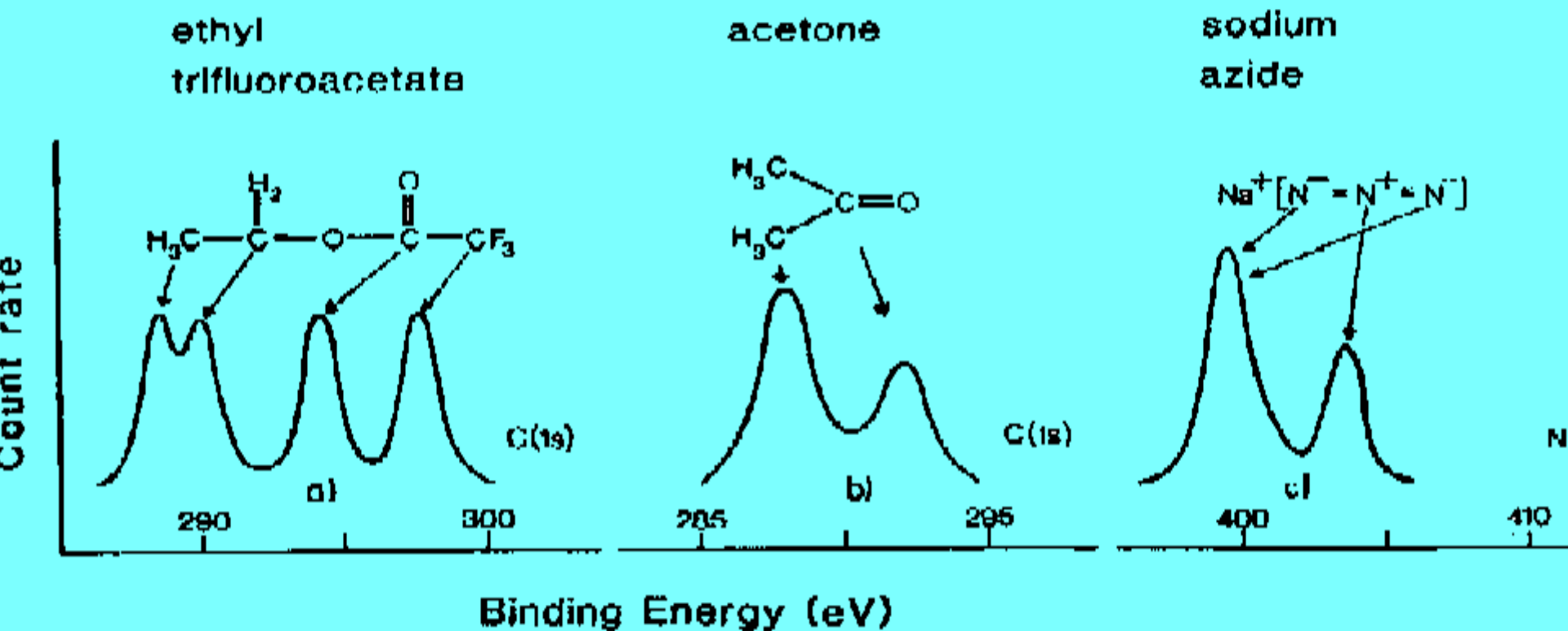
Differential Auger spectra from Al in the metallic and oxide states (from Chapter 2 of G. C. Smith).

	1s _{1/2} K	2s _{1/2} L _I	2p _{1/2} L _{II}	2p _{3/2} L _{III}	3s _{1/2} M _I	3p _{1/2} M _{II}	3p _{3/2} M _{III}	3d _{5/2} M _{VI}	3d _{3/2} M _V
1 H	14								
2 He	25								
3 Li	55								
4 Be	111								
5 B	188		5						
6 C	284		7						
7 N	399		9						
8 O	532	23	7						
9 F	686	31	9						
10 Ne	867	45	18						
11 Na	1072	63	31		1				
12 Mg	1305	89	52		2				
13 Al	1560	118	74	73	1				
14 Si	1839	149	100	99	8		3		
15 P	2149	189	136	135	16		10		
16 S	2472	229	165	164	16		8		
17 Cl	2823	270	202	200	18		7		
18 Ar	2303	320	247	245	25		12		
19 K	3608	377	297	294	34		18		
20 Ca	4038	438	350	347	44		26		5
21 Sc	4493	500	407	402	54		32		7
22 Ti	4965	564	461	455	59		34		5
23 V	5465	628	520	513	66		38		2
24 Cr	5989	695	584	575	74		43		2
25 Mn	6539	769	652	641	84		49		4
26 Fe	7114	846	723	710	95		56		6
27 Co	7769	926	794	779	101		60		3
28 Ni	8333	1008	872	855	112		68		4
29 Cu	8979	1096	951	931	120		74		2
30 Zn	9659	1194	1044	1021	137		87		9

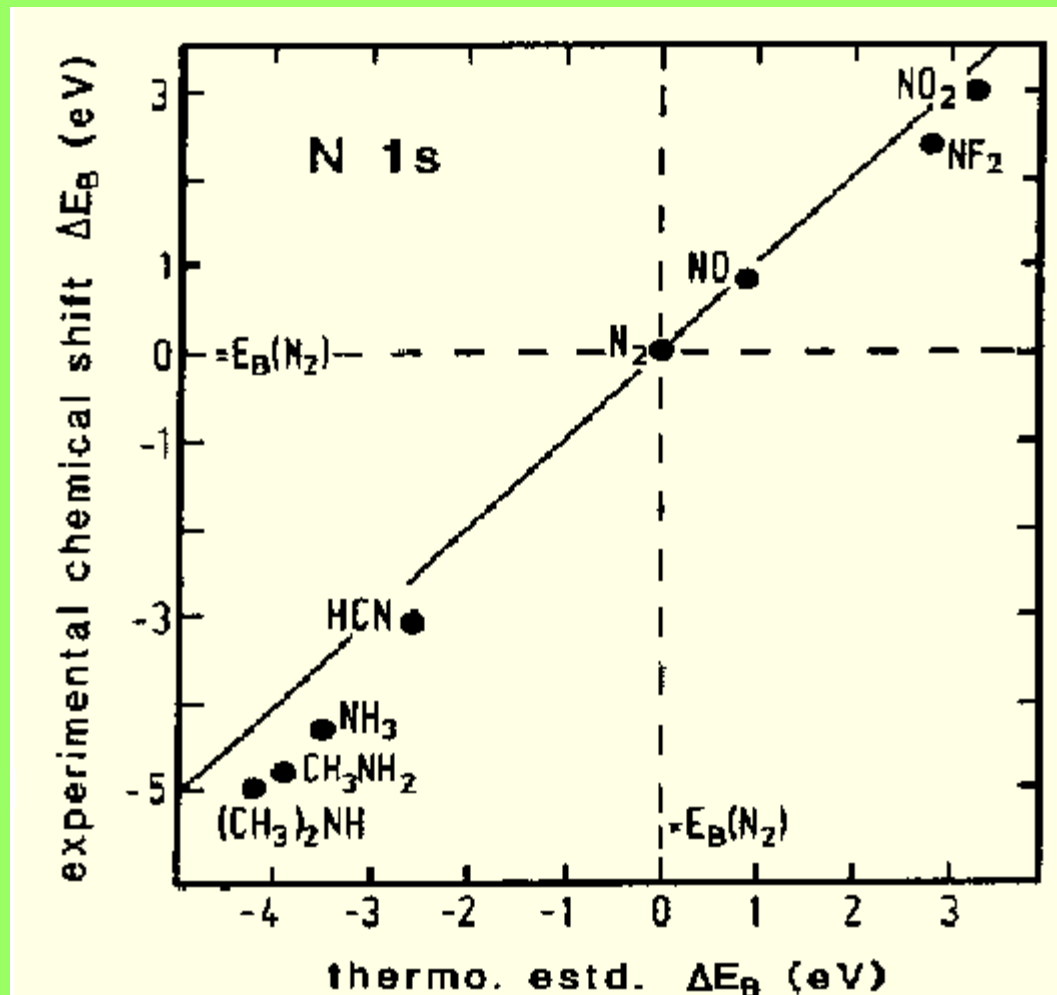
Binding

energy

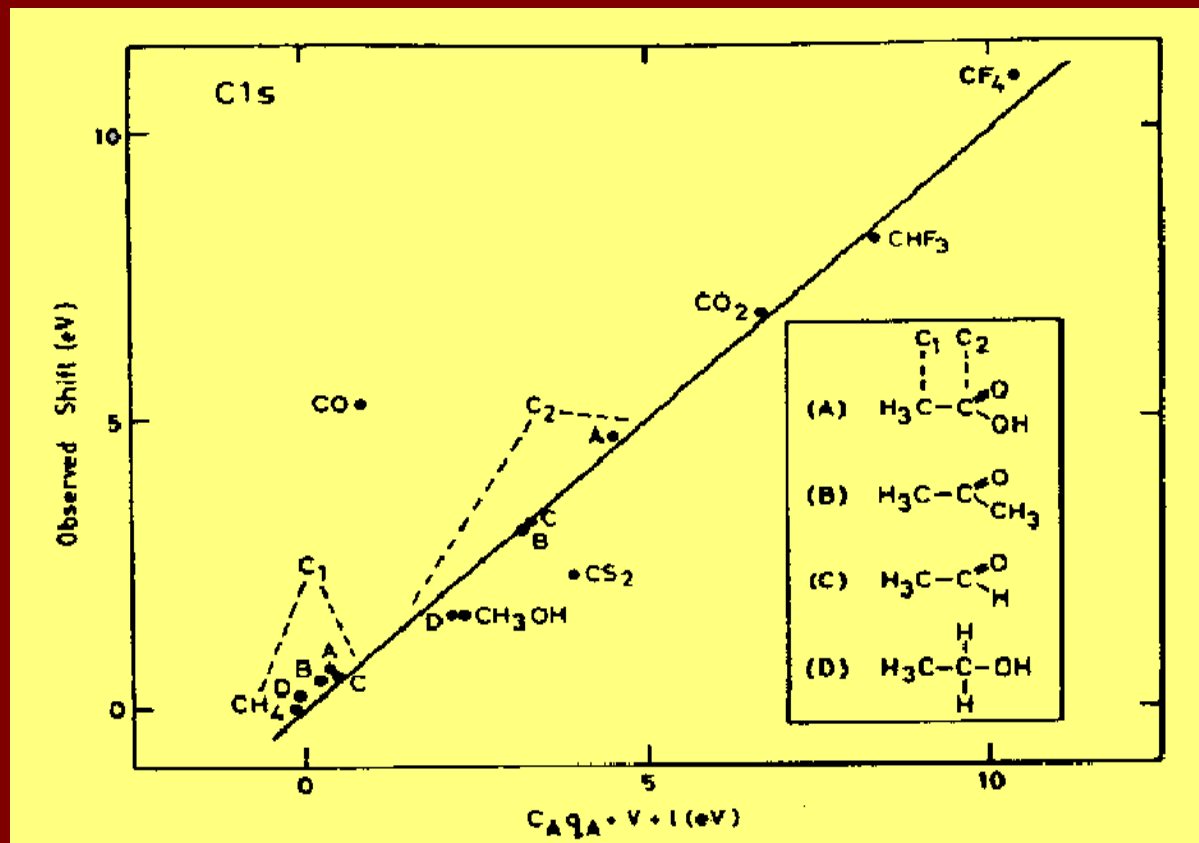
shifts



C 1s spectra of ethyl trifluoroacetate (a), acetone (b), and the N 1s spectrum of sodium azide (from S. Hüfner).

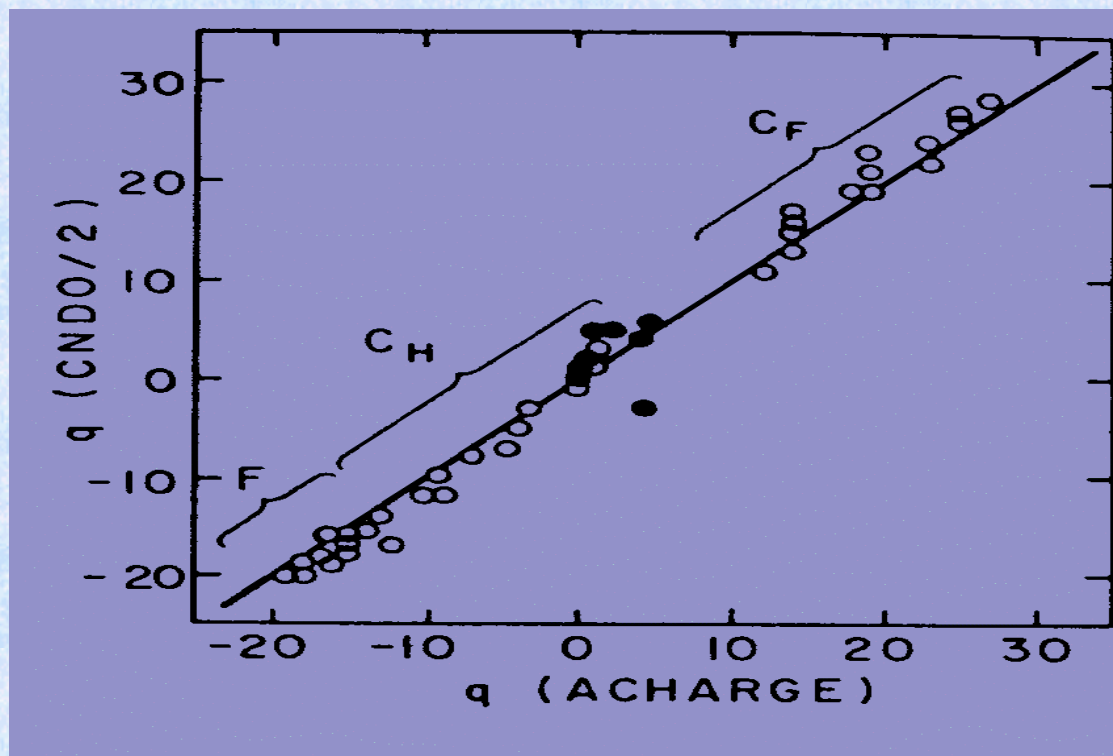


N 1s BEs (relative to N_2) versus values calculated from thermodynamic data (from S. Hüfner).



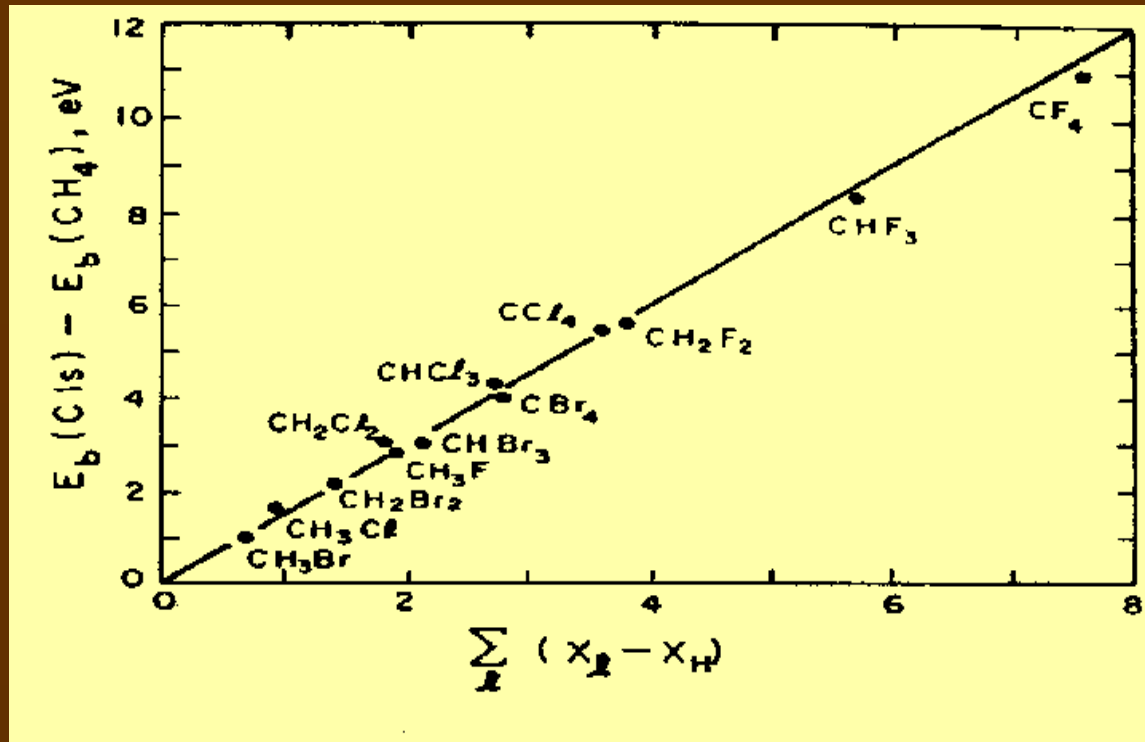
C1s BEs (relative to CH_4) vs. shifts calculated using a potential model.

Fit gives $C_A = 21.9$ eV/charge and $I = 0.80$ eV (from K. Siegbahn, et. al.).

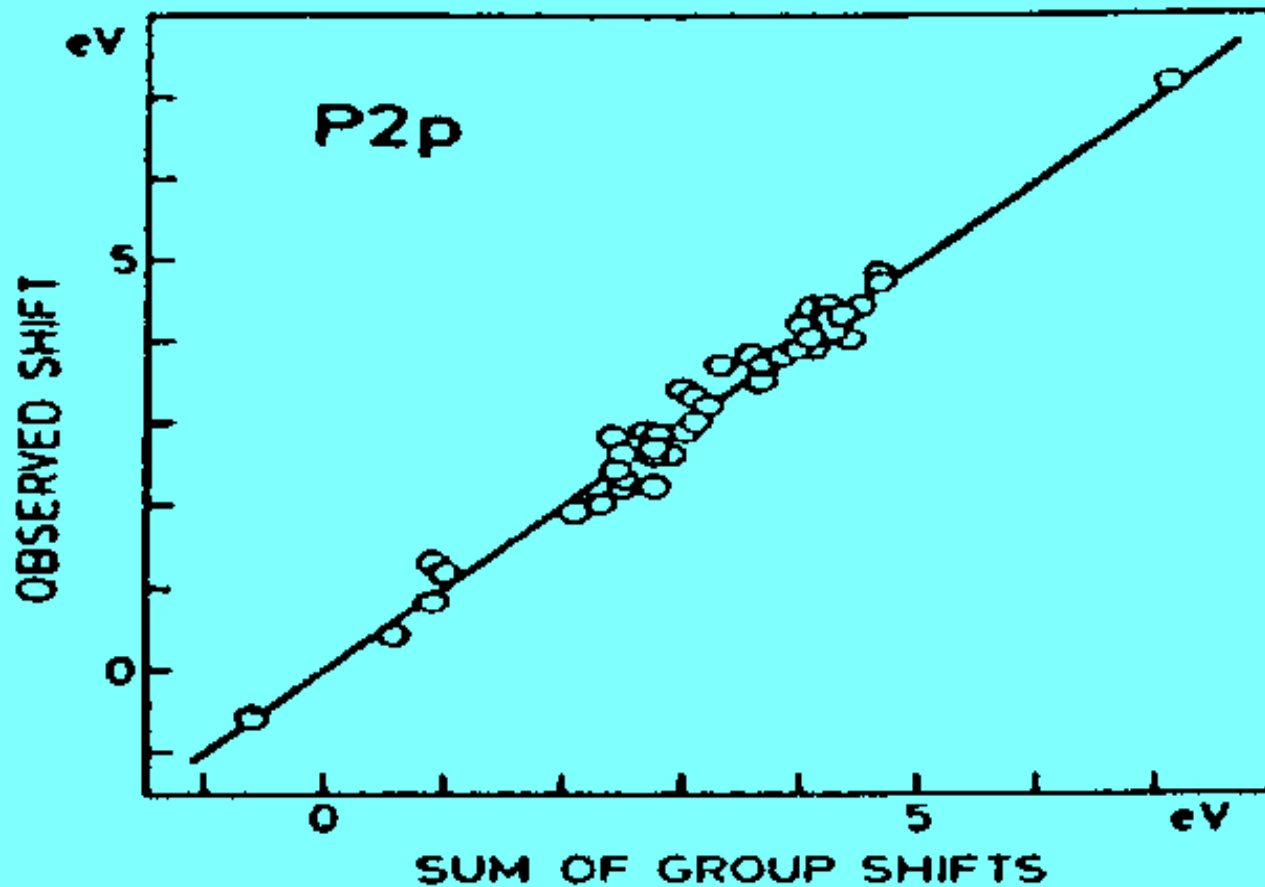


CNDO/2 atomic charges of fluobenzenes Vs. derived experimentally from XPS

(from D.W. Davis, D.A. Shirley, and T.D. Thomas, *J. Chem. Phys.*, 56, 671, 1972).



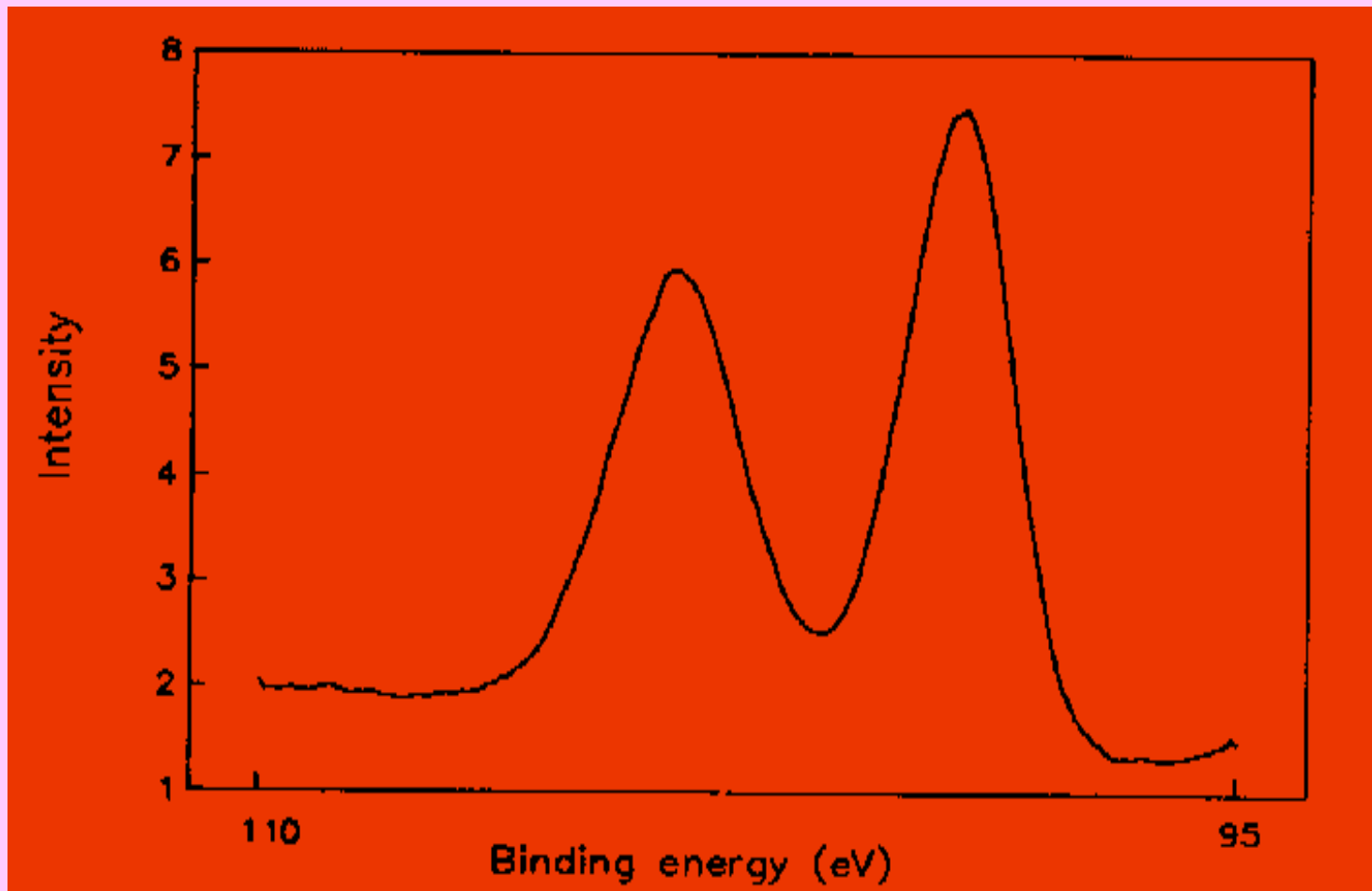
C1s BEs halomethanes (relative to CH₄) Vs. electronegativity differences (from T. D. Thomas, *J. Am. Chem. Soc.*, 92, 4184, 1970).



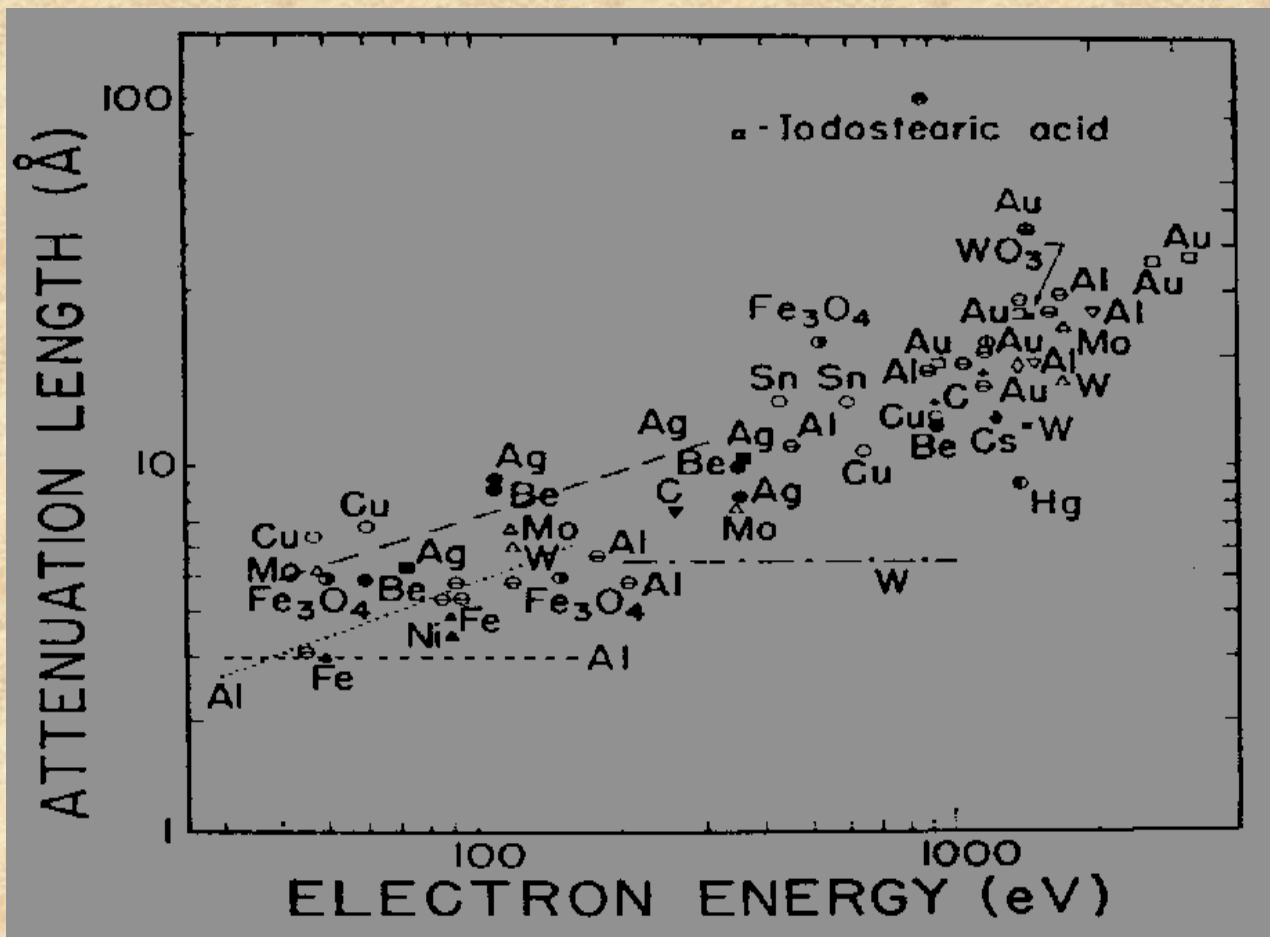
P2p chemical shifts with those calculated using the group shift model.

(from J. Hedman, M. Klasson, B. J. Lindberg, and C. Nordling in "Electron Spectroscopy", D. A. Shirley, ed.. North-Holland, Amsterdam, 1972, p.681).

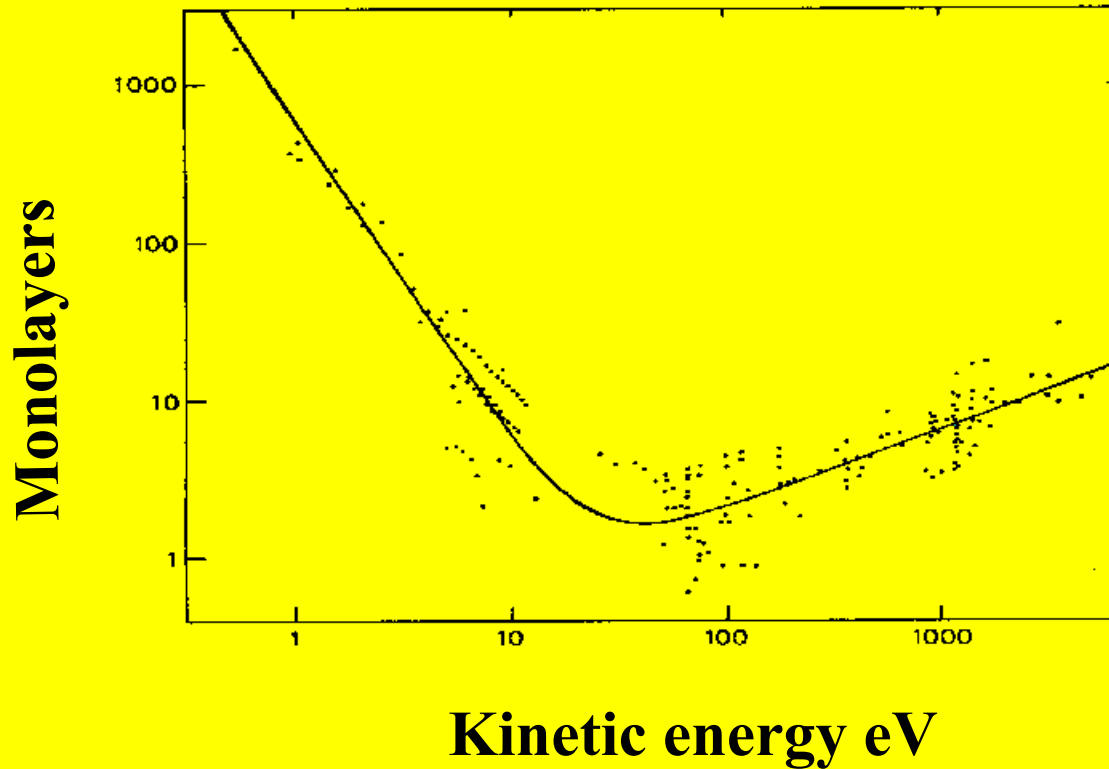
*Surface
sensitivity*



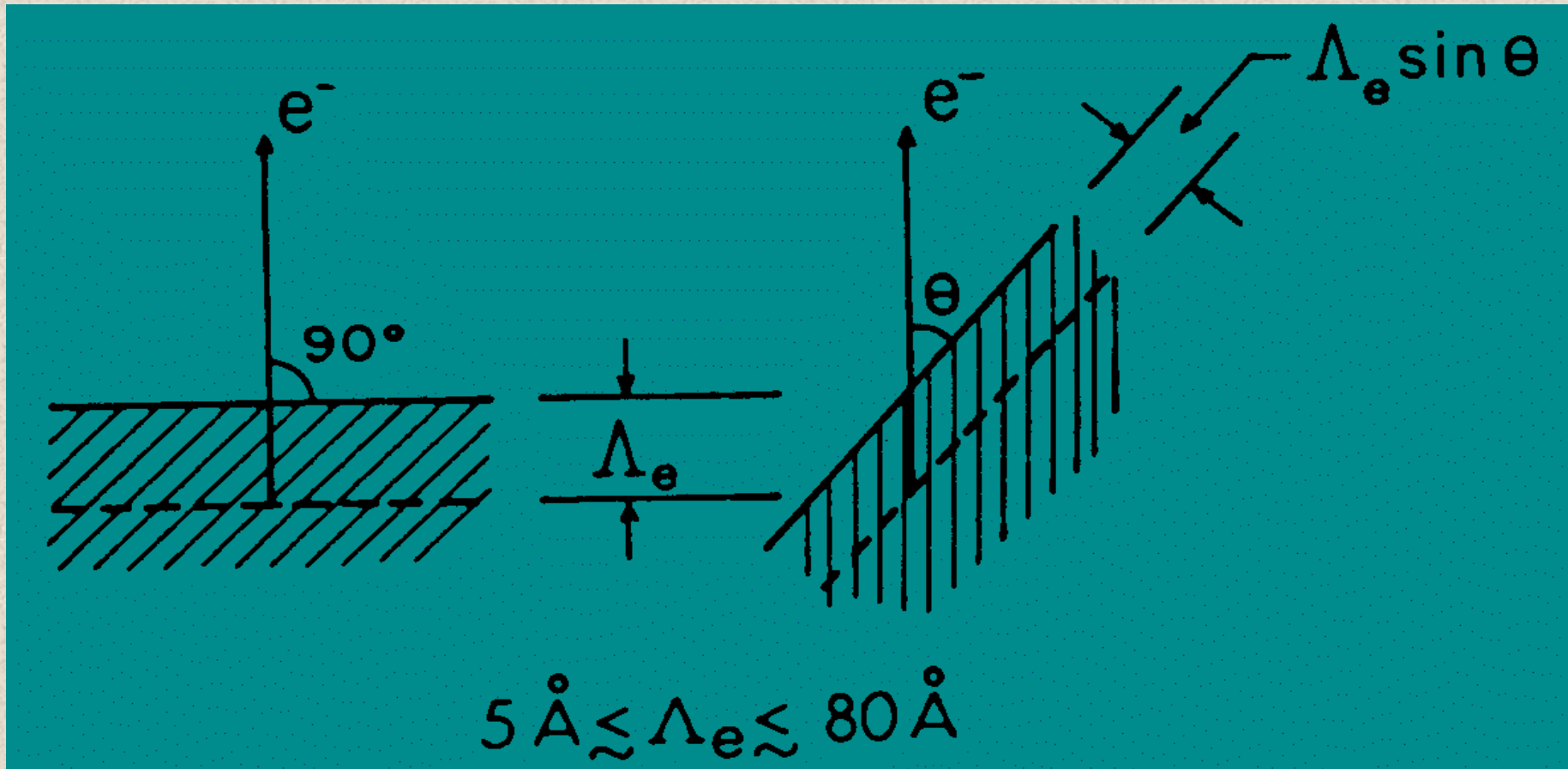
XPS of Si (100) (from Chapter 2 of G. C. Smith).



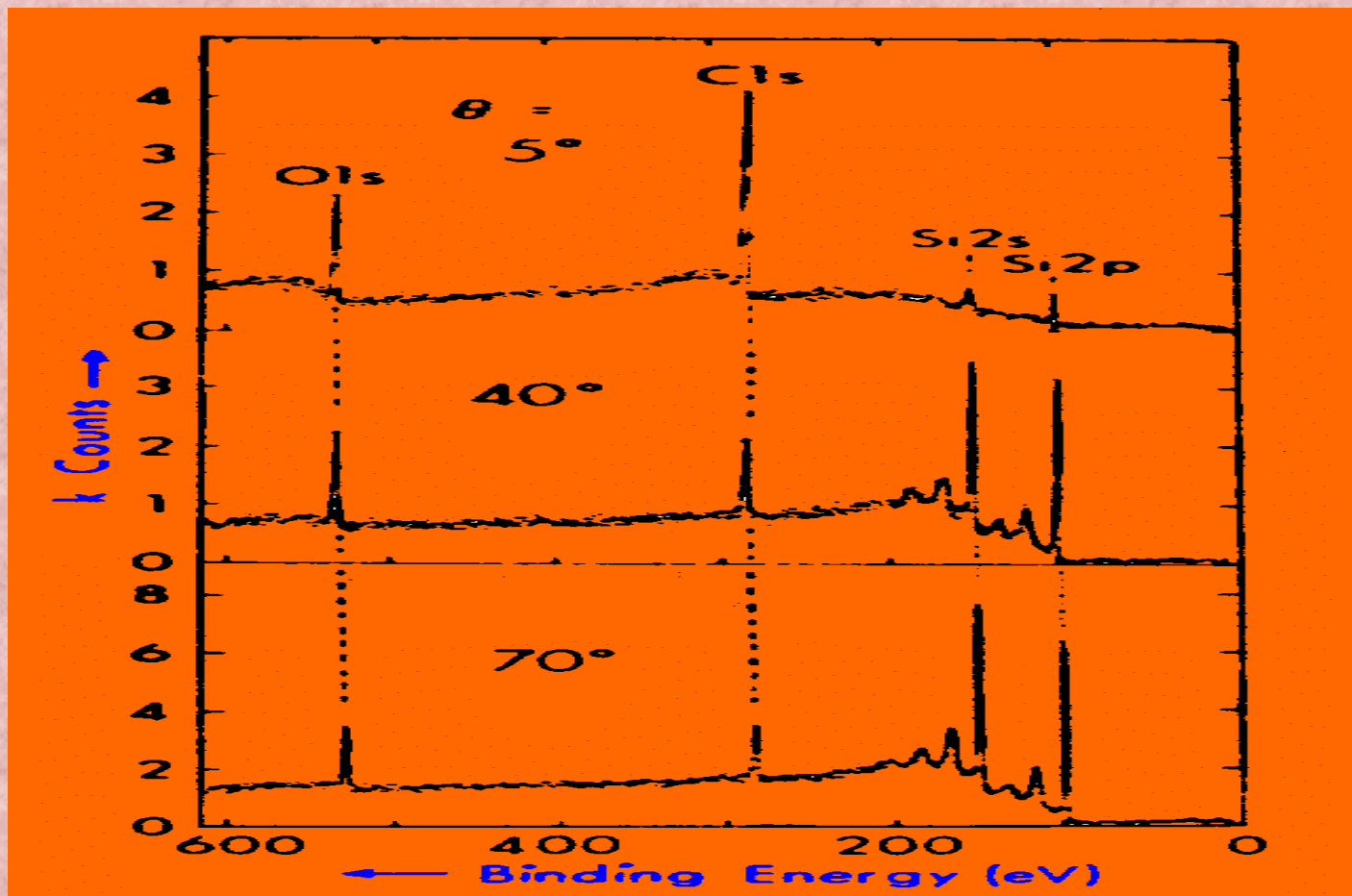
Electron inelastic attenuation length Λ_e (from C. J. Powell, *Surf. Sci.* 44, 29, 1974).



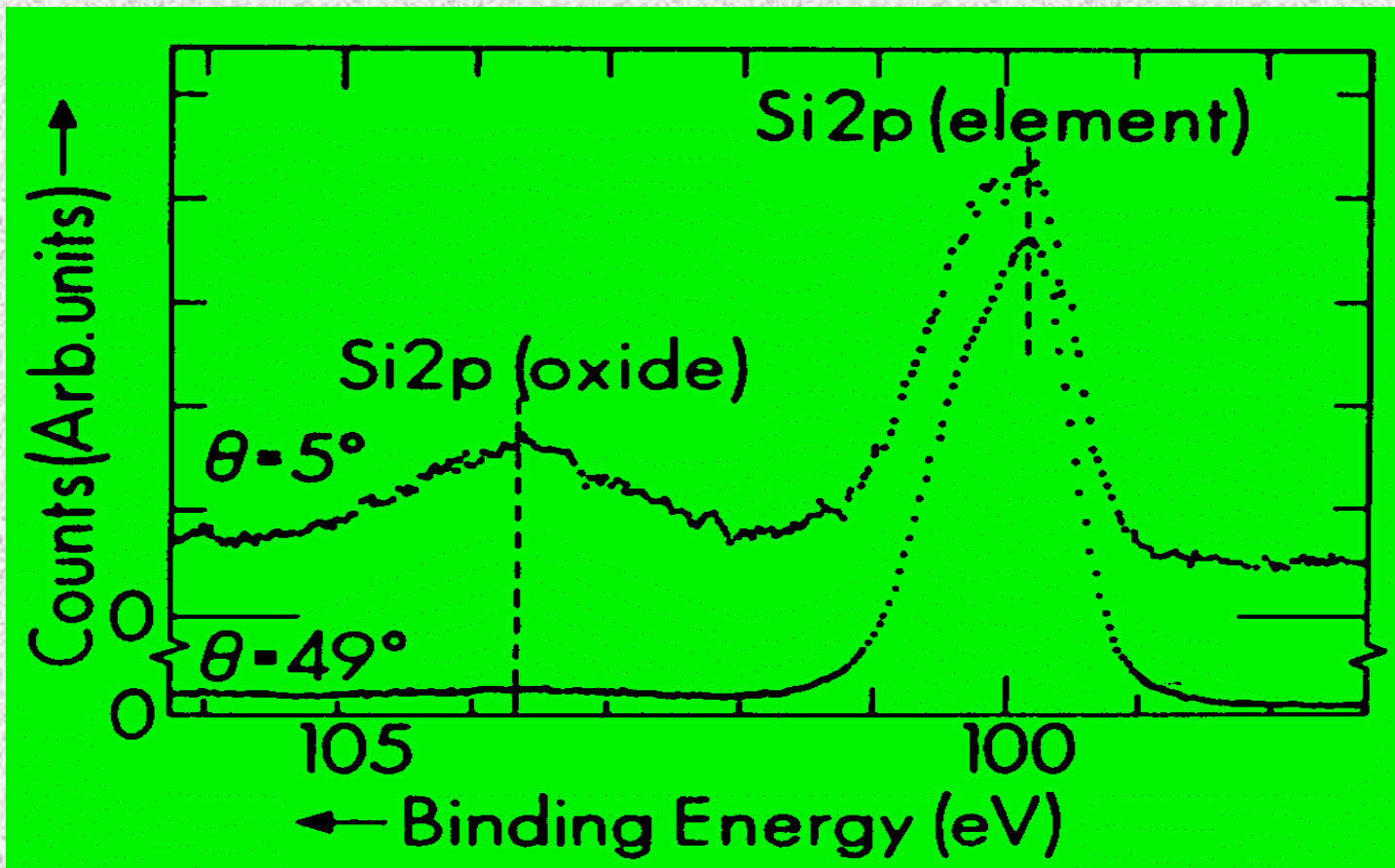
**Attenuation length data
with a best parametric fit
(from Chapter 2 of G. C. Smith).**



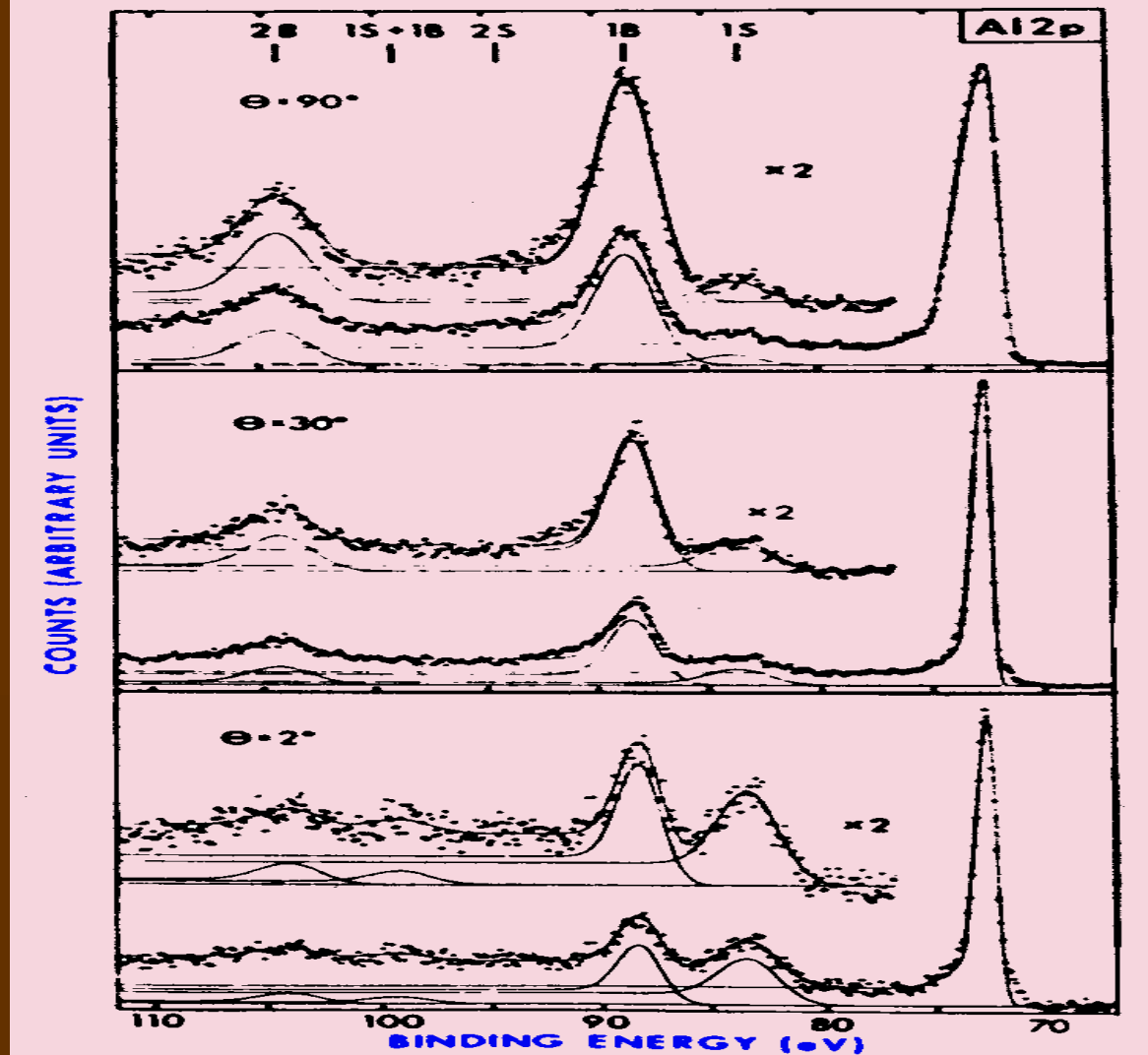
Surface sensitivity enhancement
(from C.S. Fadley, in Vol.. 2 of C.R.
Brundle and A.D. Baker).



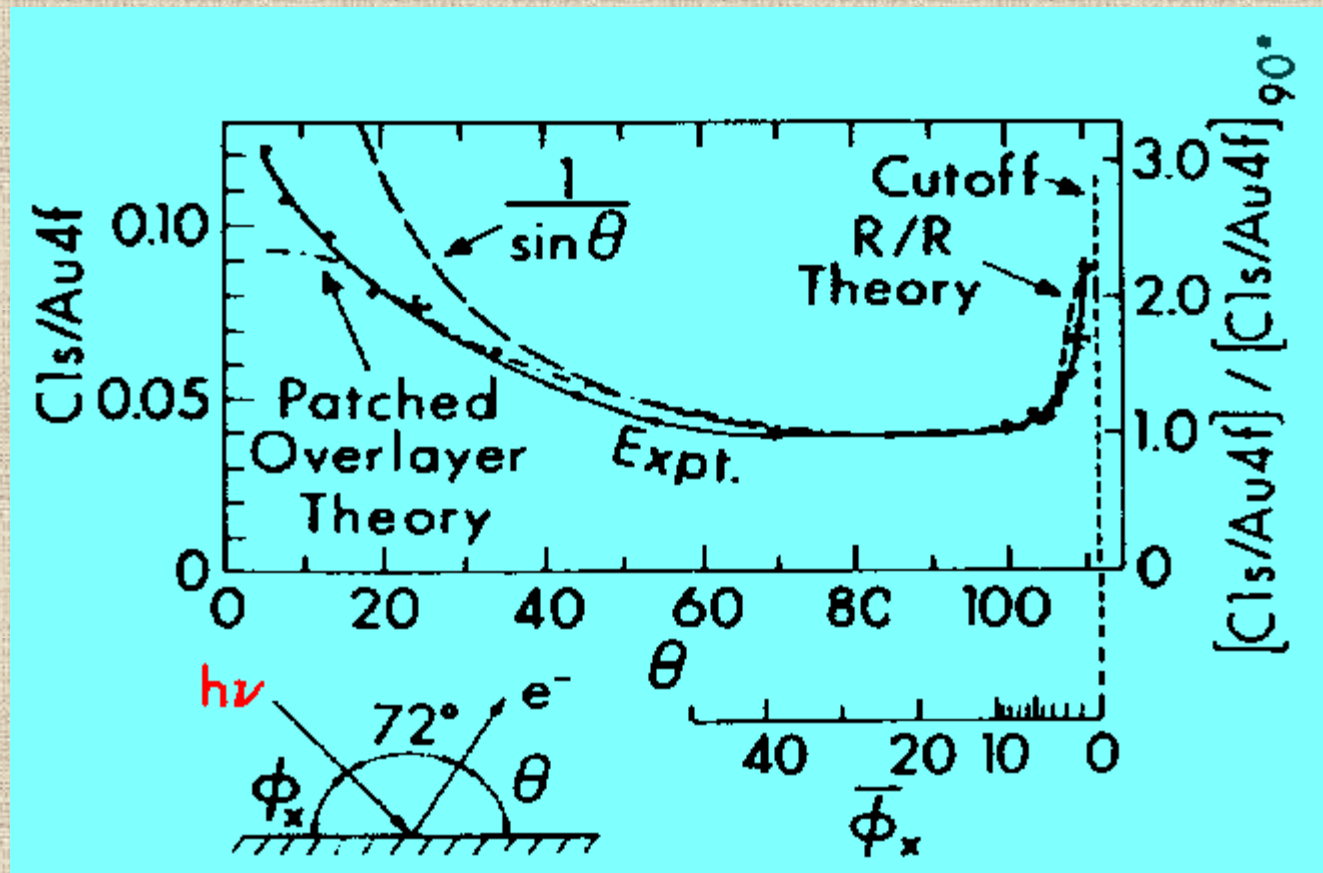
XPS at low and high exit angles for a Si surface (from C.S. Fadley, *Prog.Sol. St. Chem.*, 11, 265, 1976).



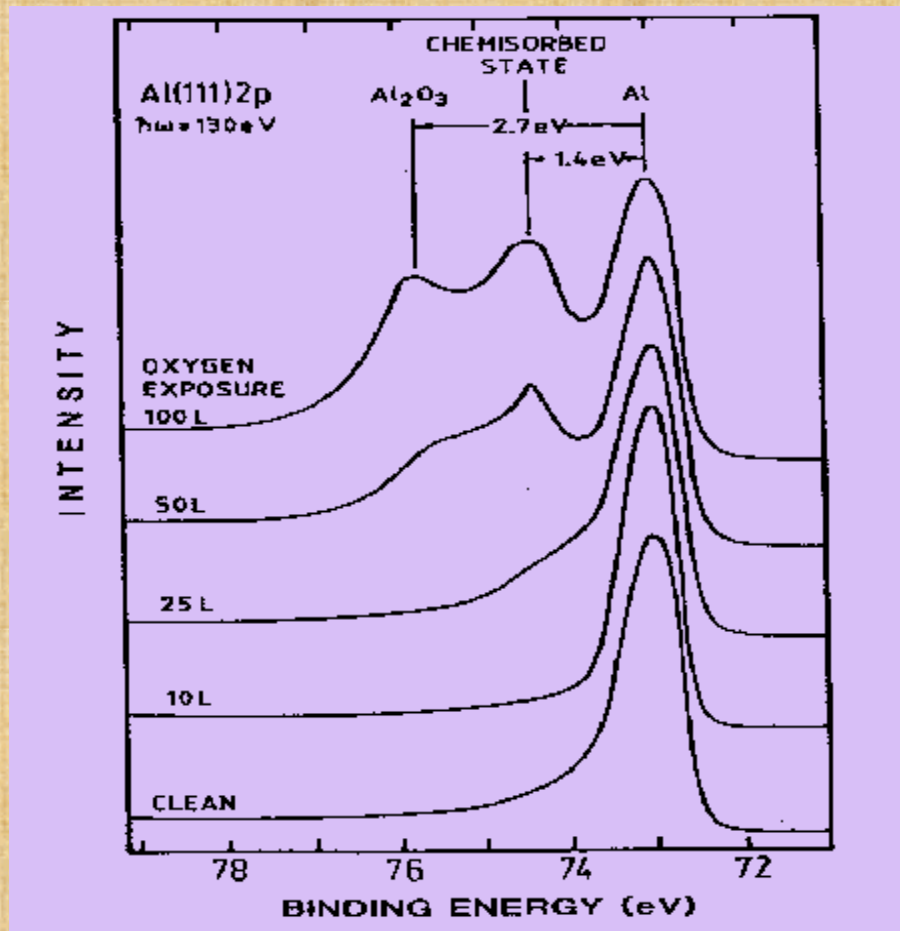
**Si2p core spectra at $\theta = 5^\circ$
and 49° of an oxide covered
Si (from C.S. Fadly, *Prog. Sol. St.
Chem.* 11, 265, 1976).**



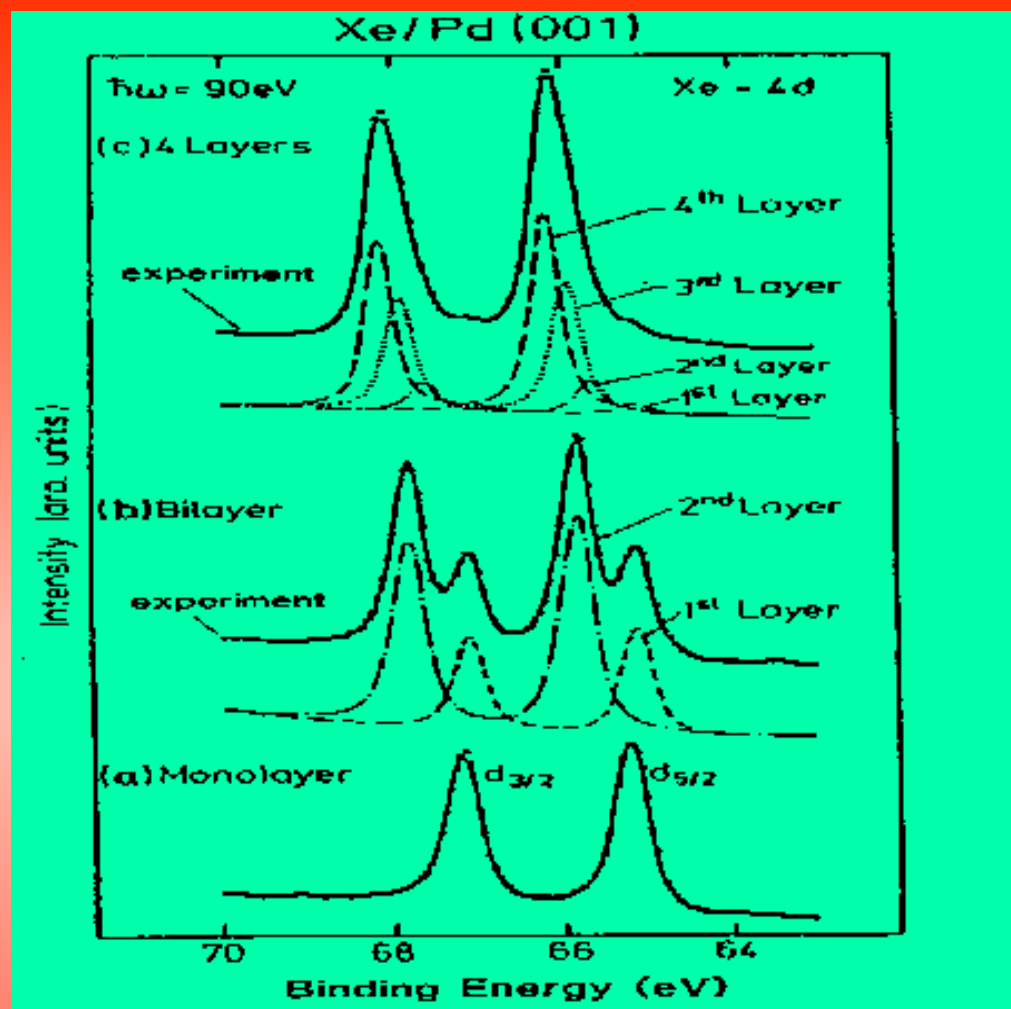
Al 2p plasmons from poly-crystalline Al (from R.J Baird et. al., *Surf. Sci.* 72, 495, 1978).



Angular dependence of the C1s/Au4f intensity ratio for a carbon covered gold (from M. Mehta and C.S.Fadley, *Phys. Lett. A*55, 59, 1975).



**Oxidation of Al (111)
monitored via the Al 2p with
 $h/2\pi\omega = 130 \text{ eV}$ (from S. Hüfner).**



Xe 4d XPS of (a) one, (b) two and (c) four layers of Xe on Pd(001) (from S. Hüfner).

Final state

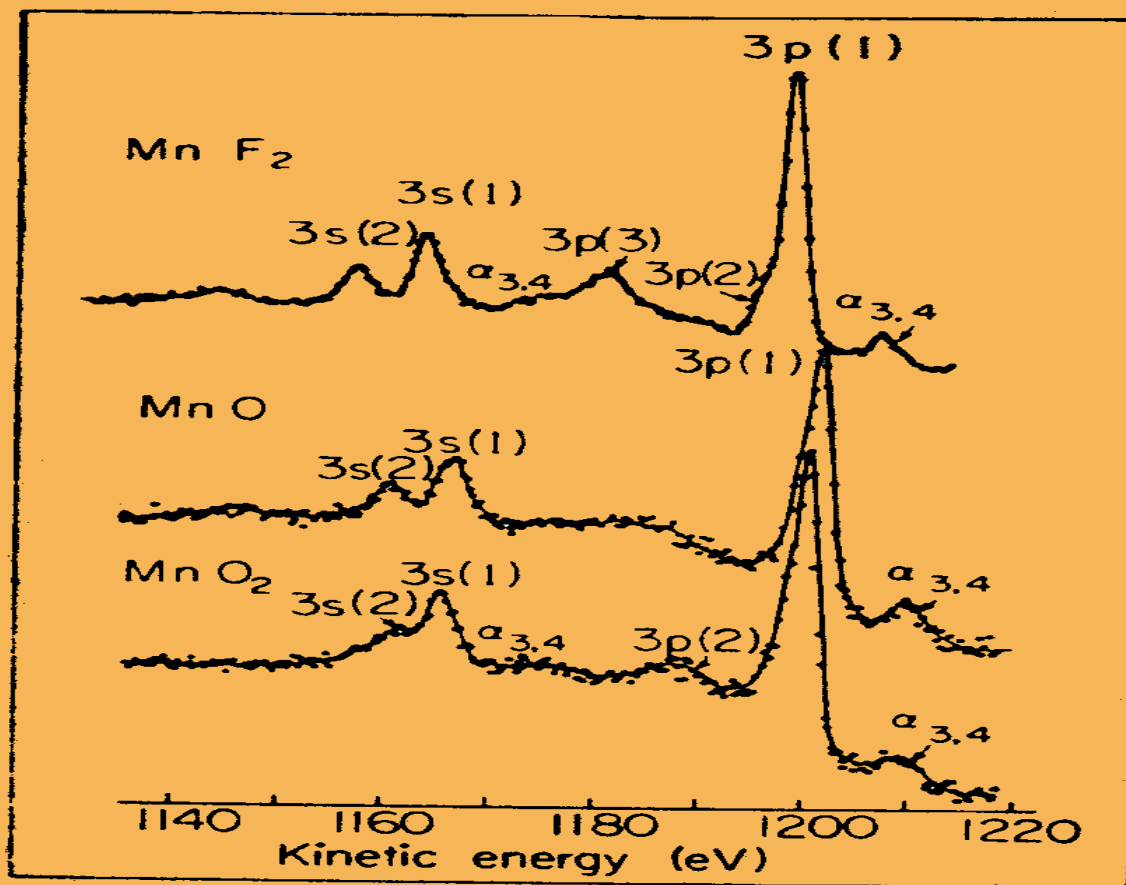
Multiple scattering
effects

Multielectron excitations

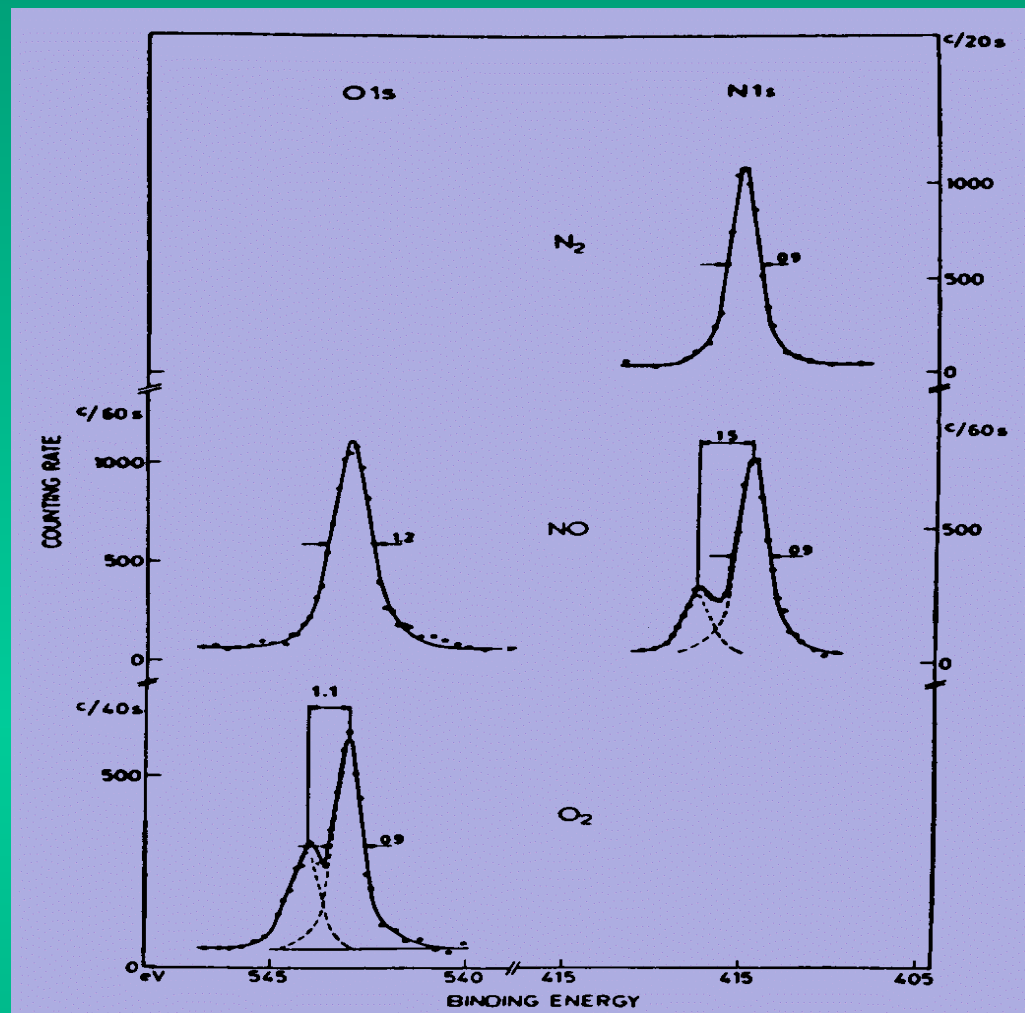
Shake-up, Shake-off, metals, satellites

Other many body effects

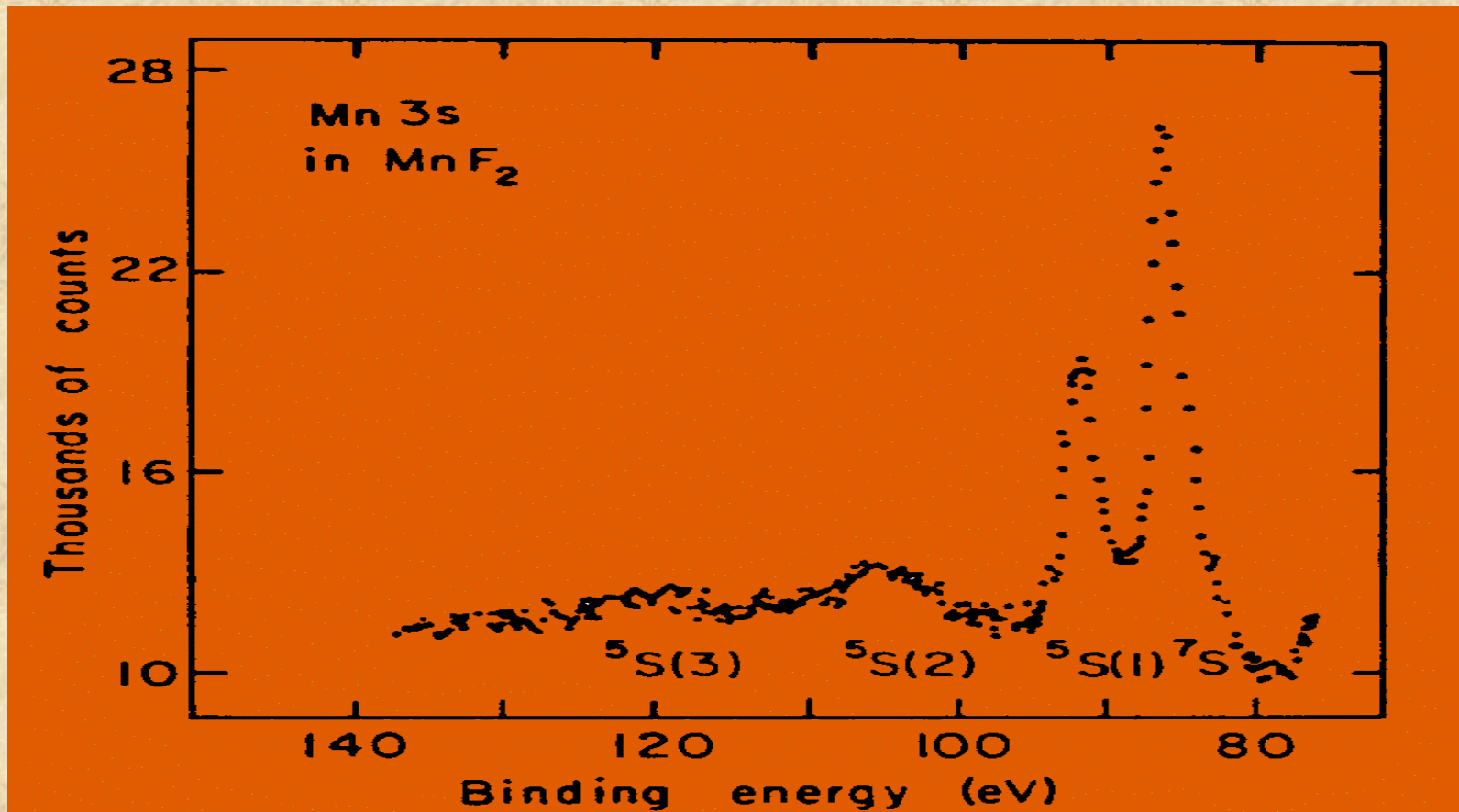
Vibrational structure



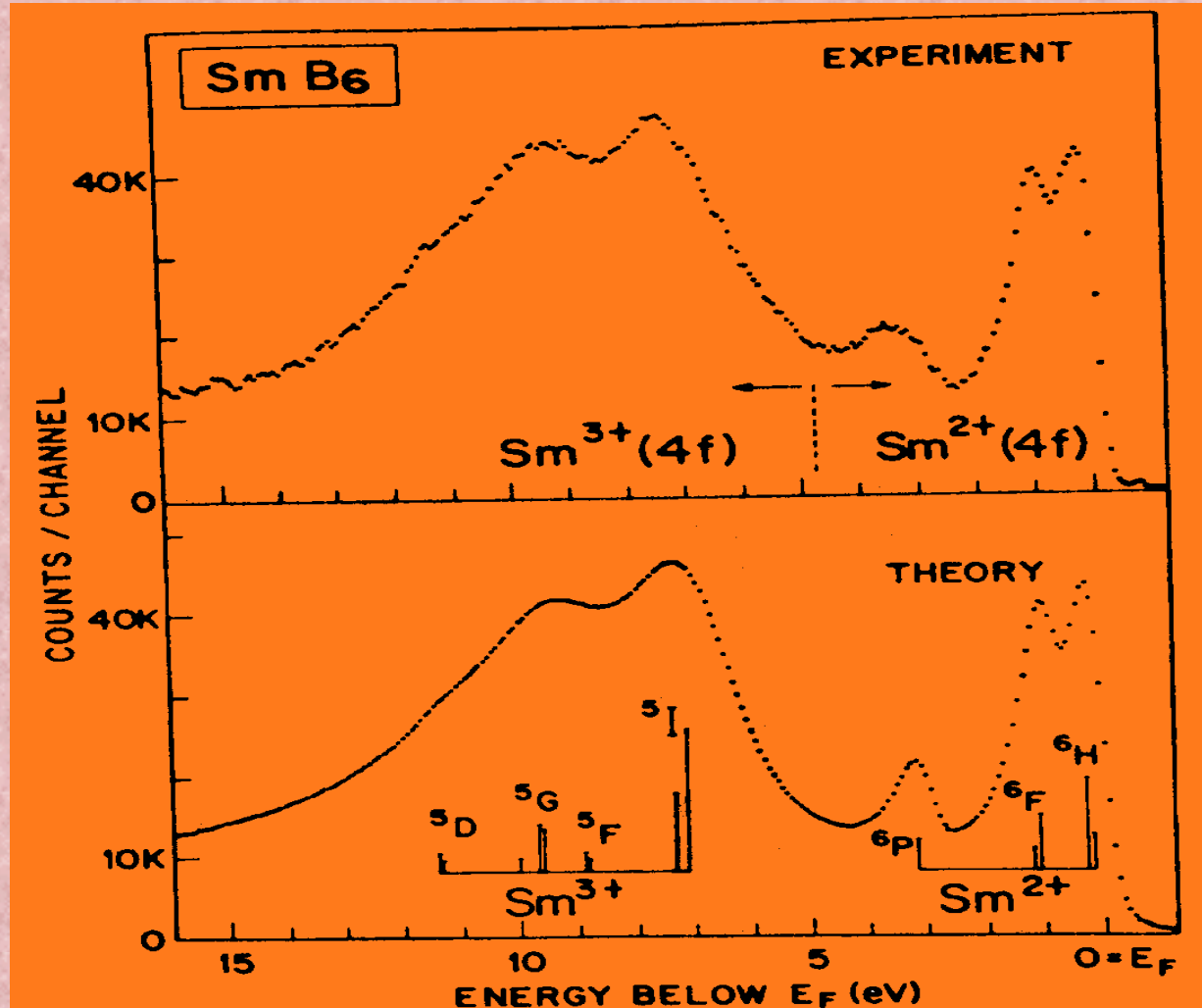
Mn 3s and 3p XPS. Initial states are $\text{Mn}^{+2}3d^5$ (MnF_2 , MnO) and $\text{Mn}^{+4}3d^3$ (MnO_2) (from C. S. Fadley and D.A. Shirley, *Phys. Rev. A*2, 1109, 1970).



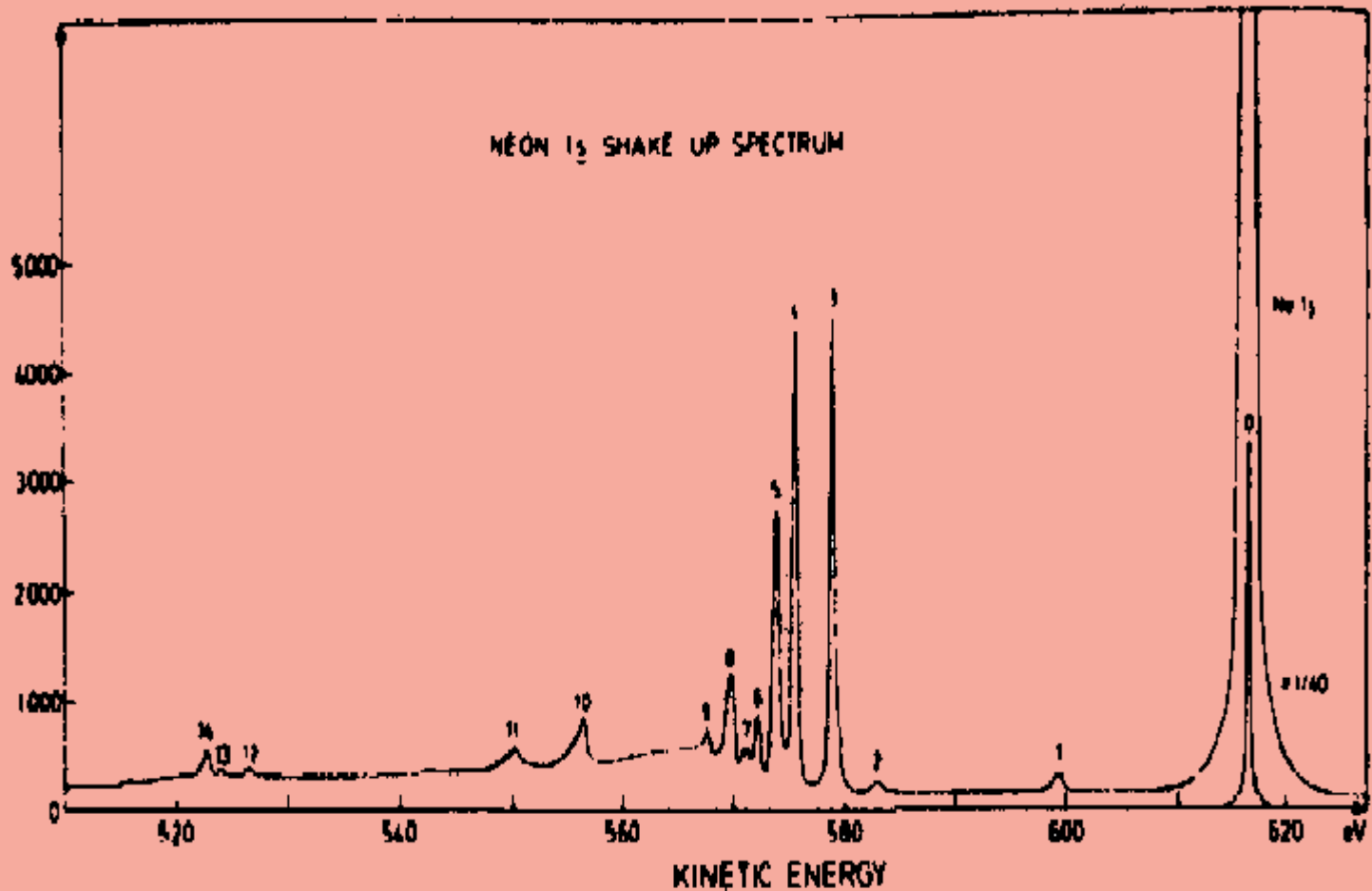
1s XPS of N_2 , NO and O_2 . Peaks of NO and O_2 are split due to final-state multiplets. (from K.Siegbahn).



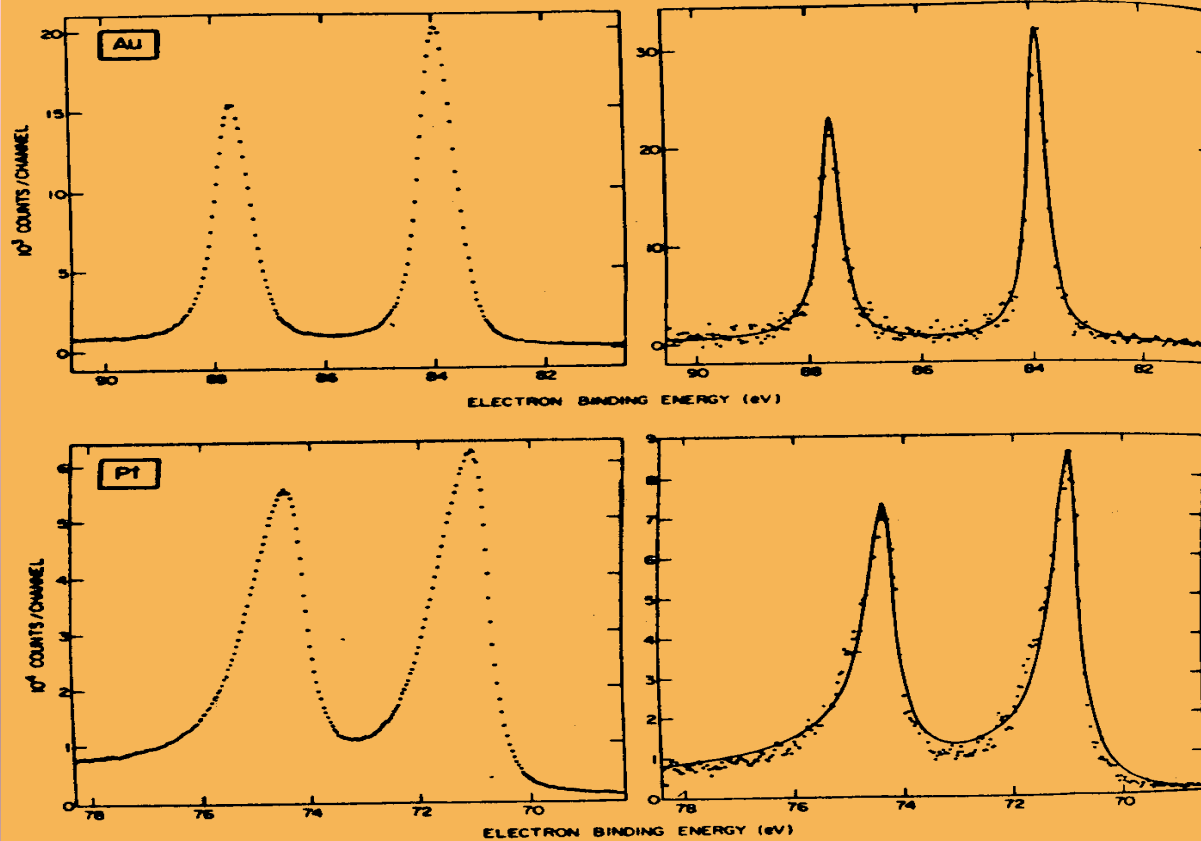
Mn3s of MnF₂. $^5S(2)$ and $^5S(3)$ are due to CI (from S.P. Kowalczyk et. al., *Phys. Rev. B*7, 4009, 1973).



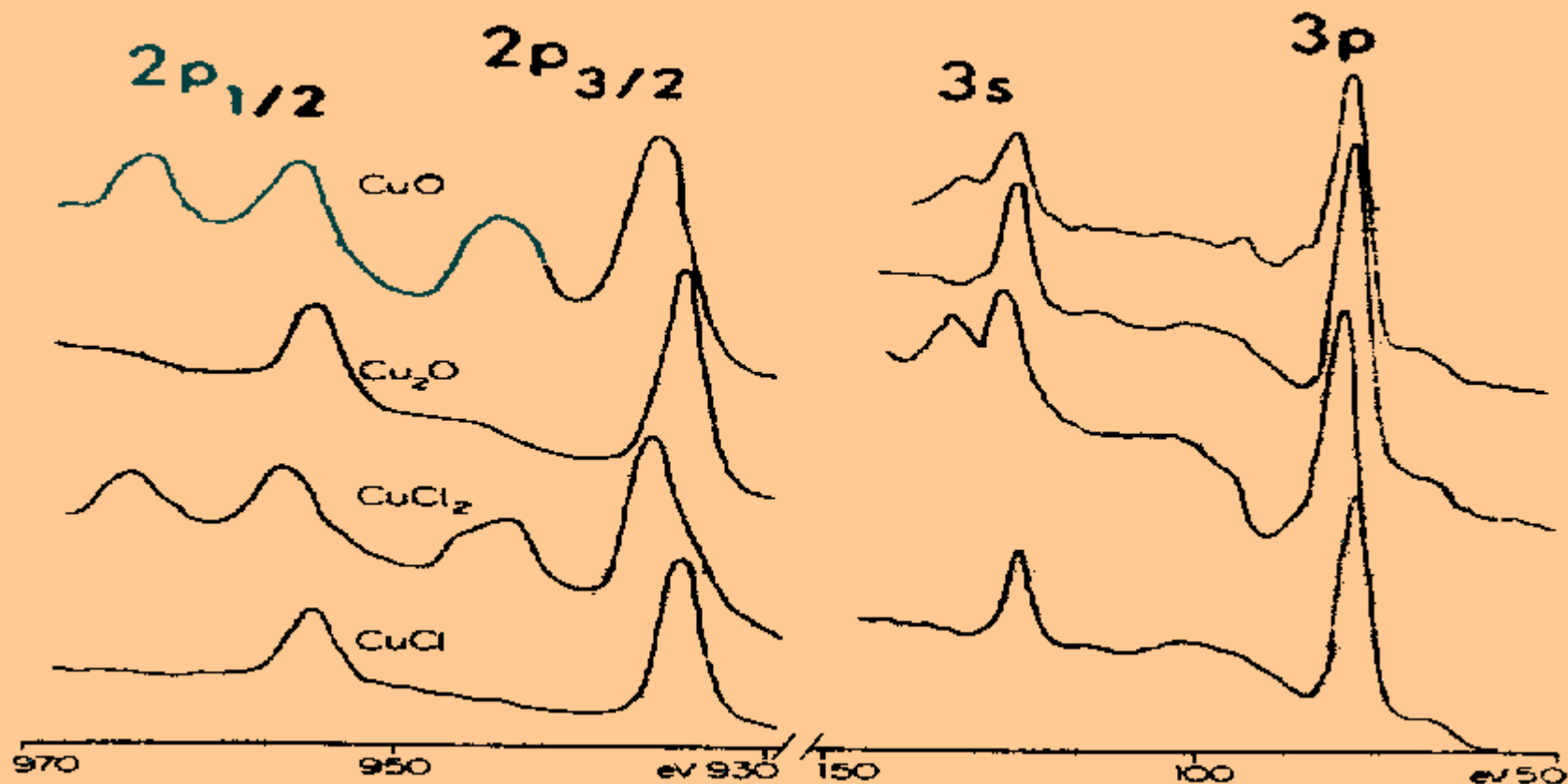
4f valence spectrum of “mixed-valence” SmB₆ (from J.N. Chazalviel, et. al., *Phys. Rev. B*10, 4586, 1976).



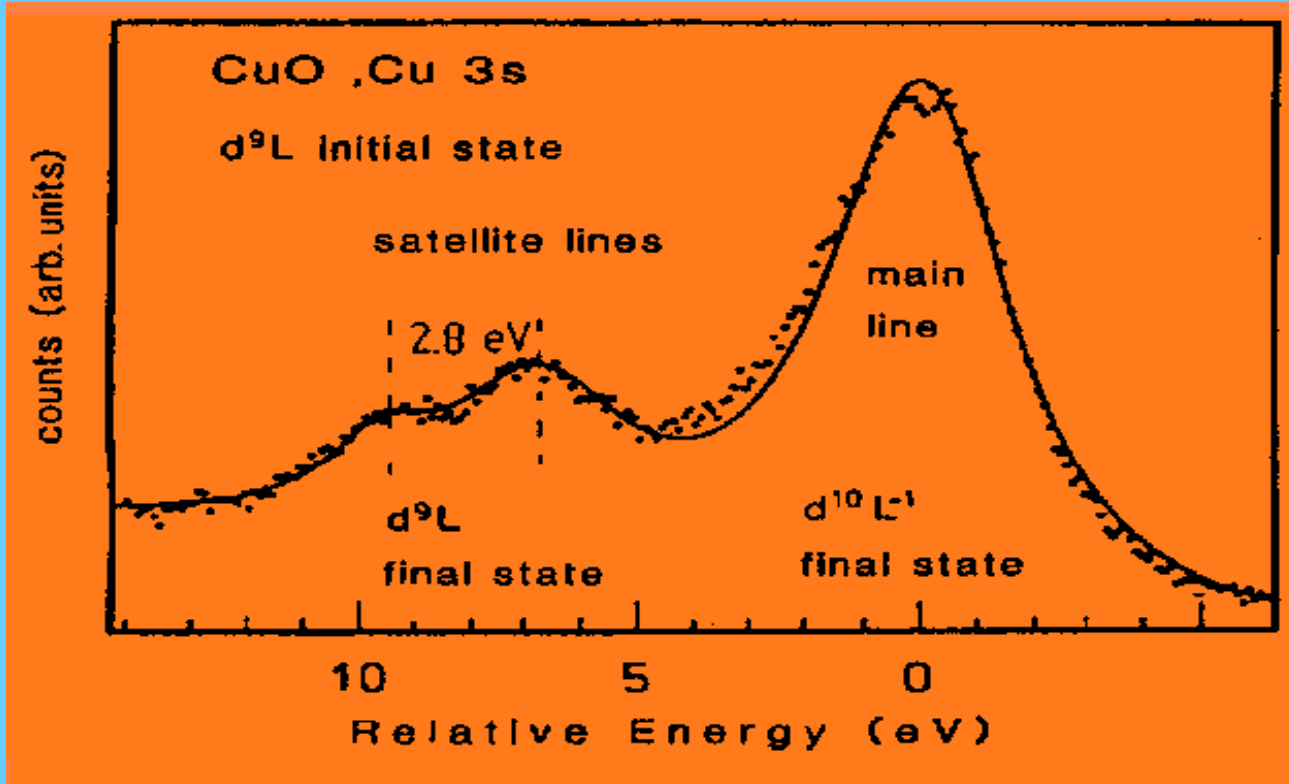
Shake-up of Ne 1s (from U. Gelius, *J. Electr. Spectr.* 5, 611, 1974).



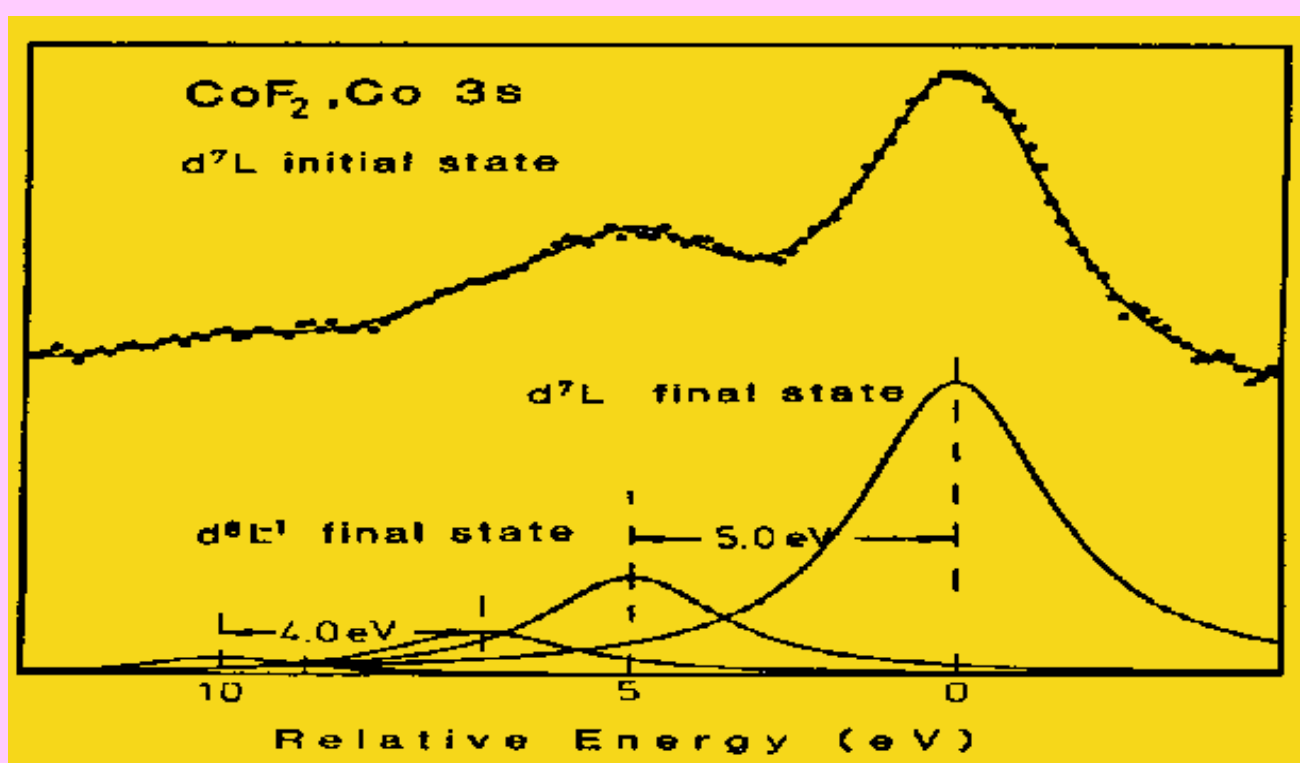
4f core spectra of Au and Pt and data corrected for instrumental line shape(from S.Hüfner and G.K.Wertheim, *Phys.Rev.* B11, 678, 1975; B11, 5197, 1975; *Phys. Rev. Lett.* 35, 53, 1975).



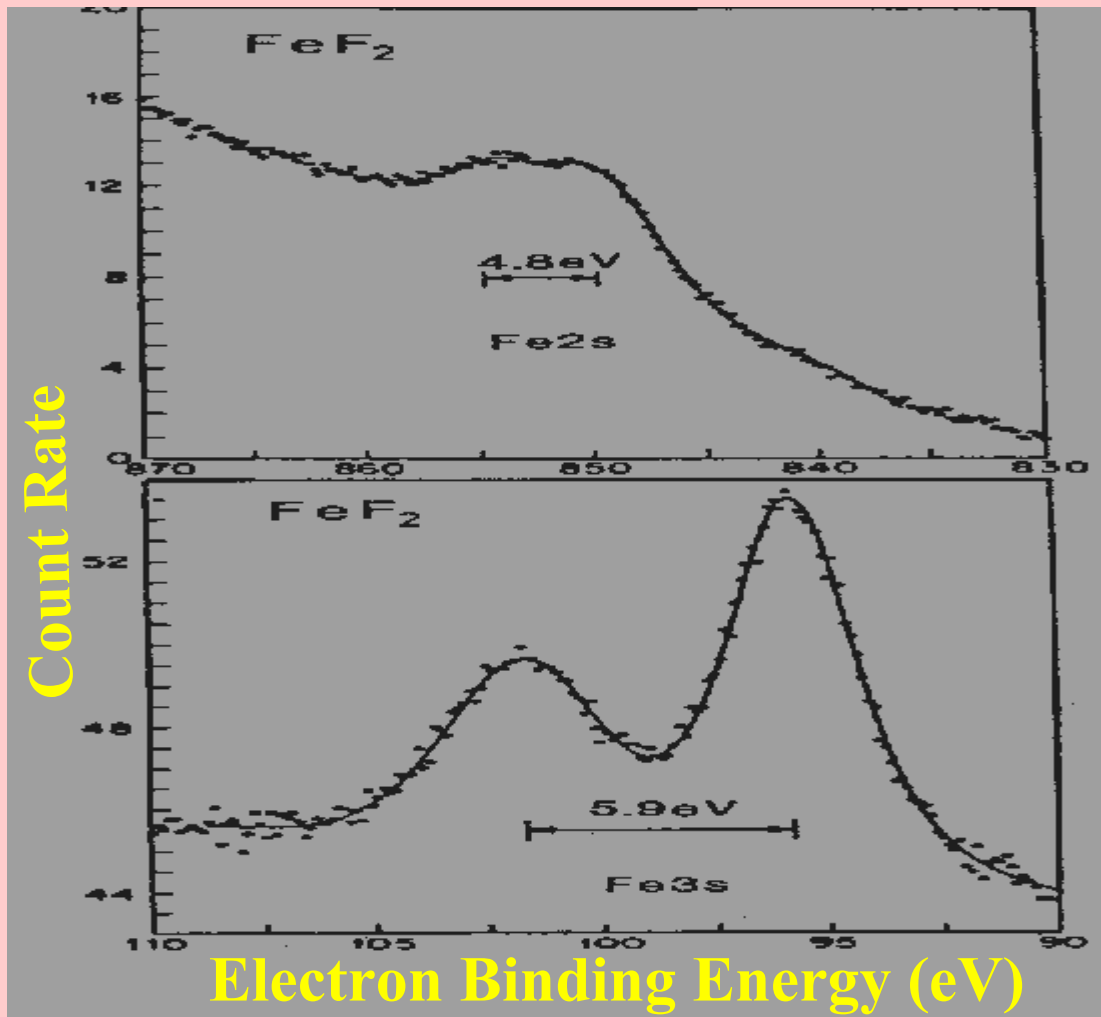
**Cu 2P, 3S and 3P XPS of CuO,
Cu₂O, CuCl₂, and CuCl.
(from D.C. Frost, et. al., *Mol.
Phys.* 24, 861, 1972).**



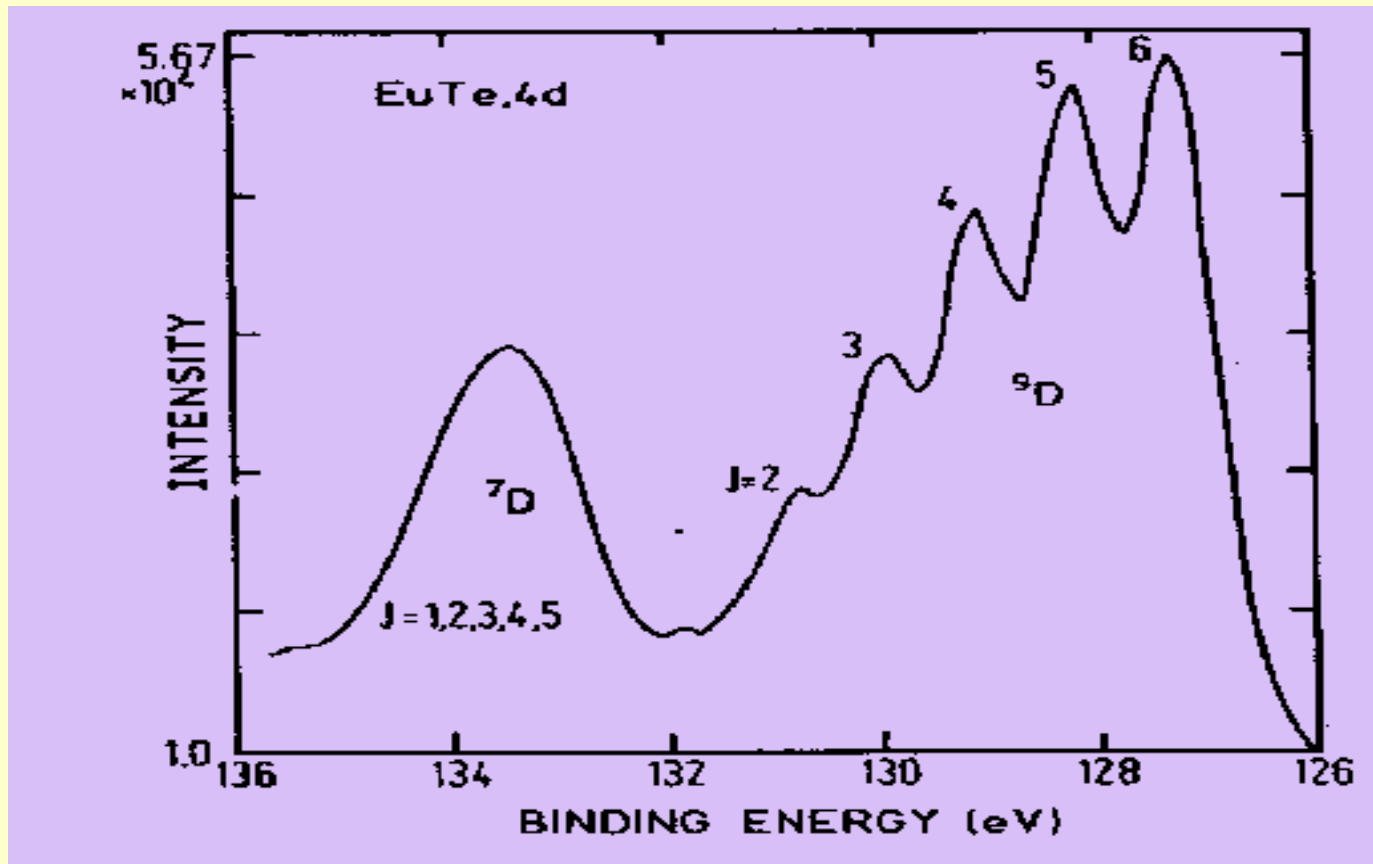
3s core line in CuO. Main line ($d^{10}L^{-1}$) has no exchange interaction but satellite (d^9L) shows it (from S. Hüfner).



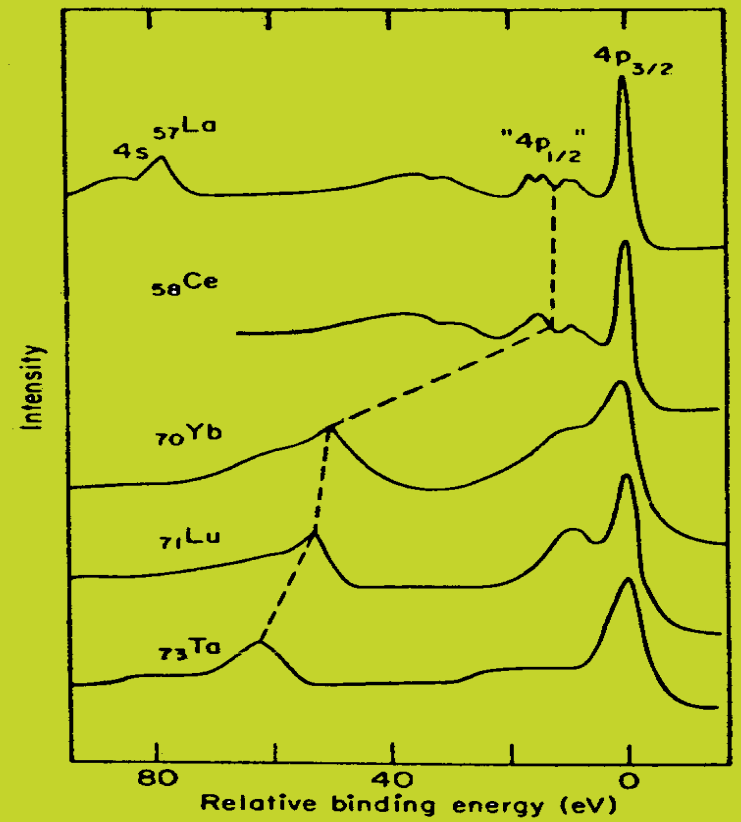
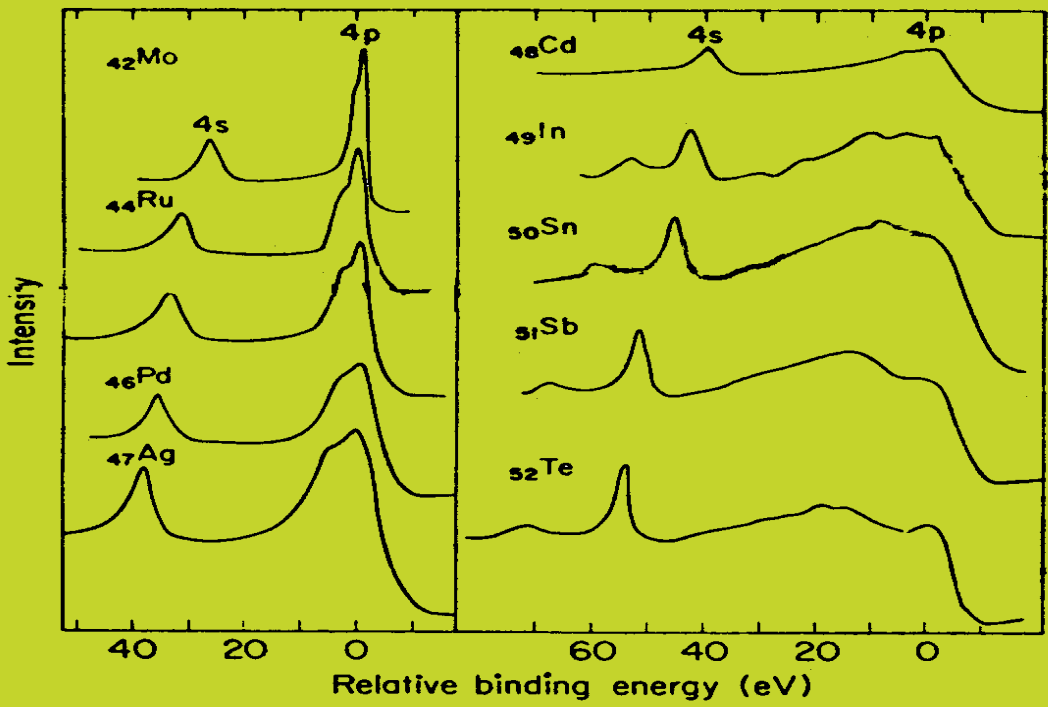
3s XPS of CoF₂. Larger exchange splitting for the main line than the satellite indicates that the main line is d⁷L and the satellite is d⁸L⁻¹ (from S. Hüfner).



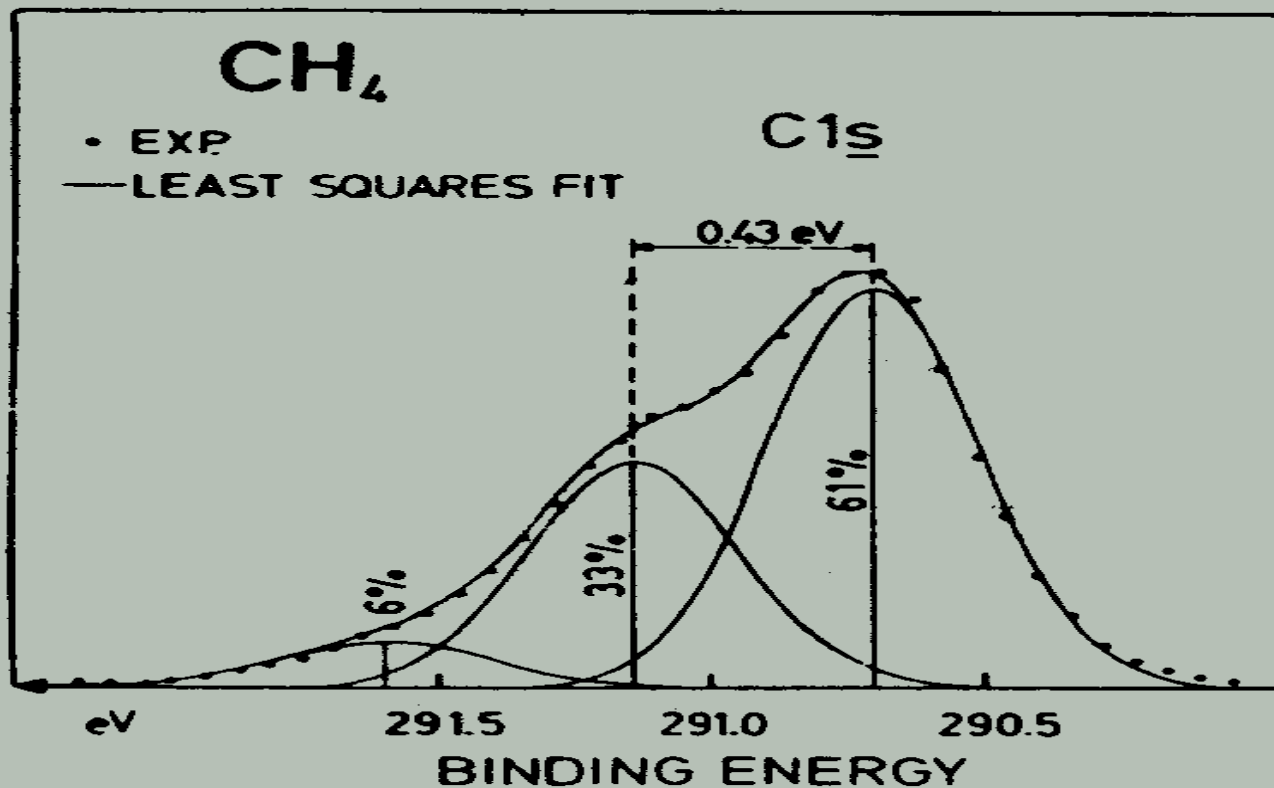
FeF₂ 2s and 3s core lines (from S. Hüfner).



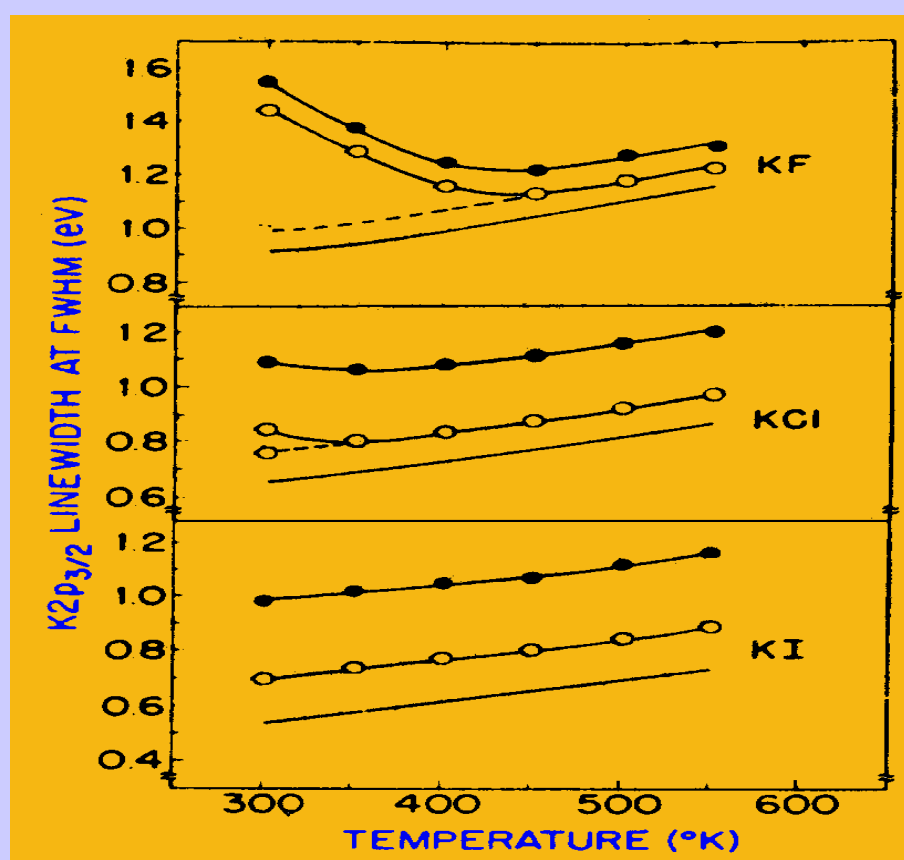
4d XPS of Eu in EuTe (Eu^{2+}).
 ${}^2d_{3/2}$ and ${}^2d_{5/2}$ couple to the ${}^8S_{7/2}$ of
 4f yielding ${}^7D_{1\dots 5}$ and ${}^9D_{2\dots 6}$
 multiplets (from S. Hüfner).



**4s, 4p XPS of Mo ($Z = 42$)
to Ta ($Z = 73$) (from D.A.
Shirley et. al. *Faraday*.
Soc. Disc. No.60, 7, 1975).**



A C 1s XPS of gaseous CH₄ showing vibrations (from U. Gelius, *J. Electr. Spectr.* 5, 985, 1974).

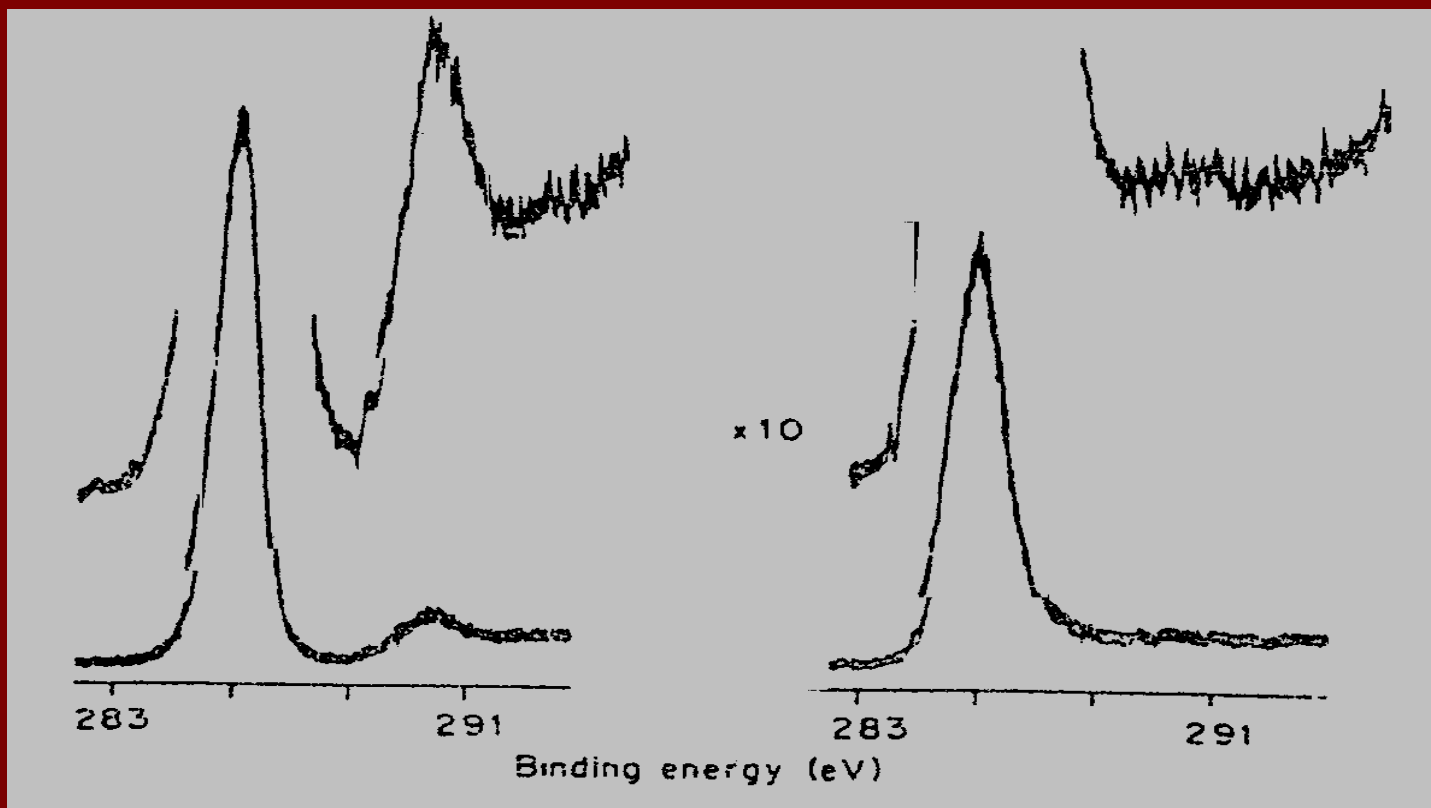


K_{2p_{3/2}} FWHM with T. —●—●— experimental. —○—○— corrected for lifetime and instrumental width. Dotted curves corrected for specimen charging. Solid curves are calculations based on final-state vibrational broadening (from P. H. Citrin, et. al., *Phys. Rev. Lett.* 33, 965, 1974).

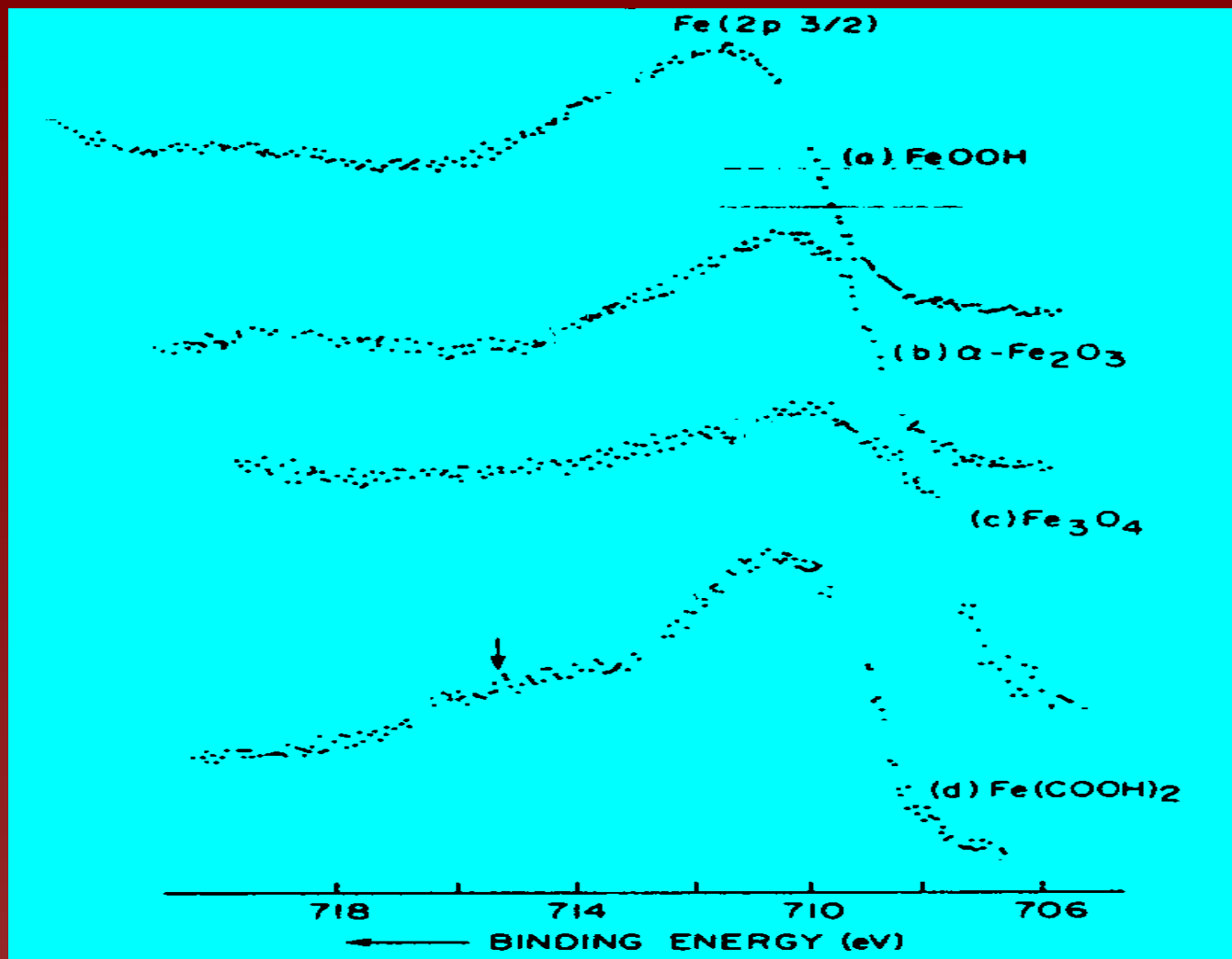
General Uses

- *Identification of elements on surfaces of materials*
- *Quantitative determination of elements on surfaces*
- *Depth profiling by inert gas sputtering*

- *Phenomena such as adsorption, desorption, and surface segregation*
- *Determination of chemical states of elements*
- *In situ analysis to determine the chemical reactivity at surface*



$\pi \rightarrow \pi^*$ shape-up of C1s of polystyrene
and its absence after argon ion
sputtering (Briggs and Wootton, Surf. Interfac
Anal. 4 (1982) 109.



**XPS of iron corrosion compounds
(N. S. McIntyre in Windawi and Ho).**

Special feature or effect

System property derivable

**(1) Fixed-angle
measurements:**

Core peak intensities

—————→ **Quantitative analysis**

Core peak shifts

—————→ **Initial-state charge**

**Valance peak
intensities and
positions**

—————→ **distributions**

—————→ **Final -state charge**

—————→ **distributions**

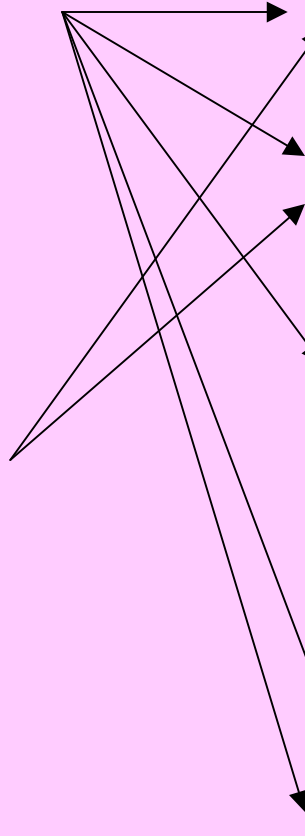
Relaxation effects

—————→ **Initial valence-orbital energy
levels,**

**symmetries and atomic-
orbital make-up**

—————→ **Thermochemical energies**

—————→ **Proton affinities**



Multiplet splittings

**Shake-up, shake-off,
other many-electron
effects**

**Peak shapes and
widths**

Inelastic loss spectra

**Initial-state electron
configurations and electron-
electron interactions**

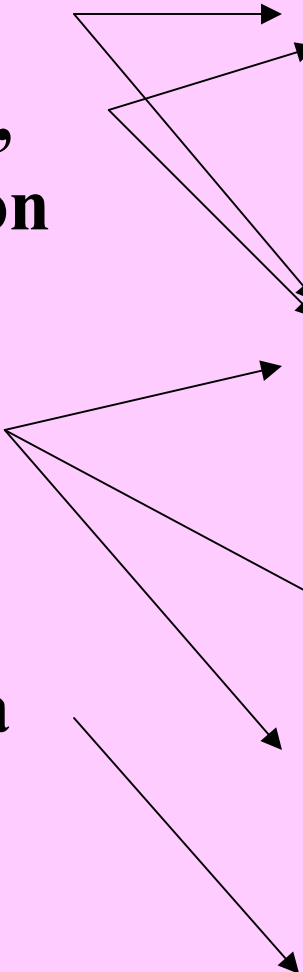
Final-state correlation

**(configuration-interaction)
effects**

Final state lifetime effects

**Final-state vibrational
excitations**

**Low-lying
electronic, vibrational
excitations**



(2) Angular-resolved measurements on solids:

As in (1), but at grazing electron emission

As in (1), but at grazing x-ray incidence

Core peak intensities from single crystals

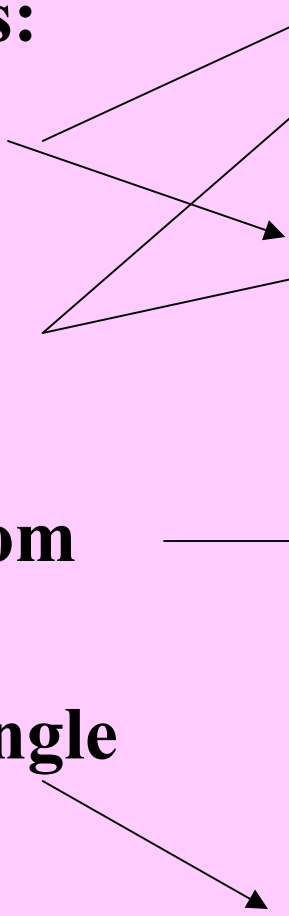
Valance spectra from single crystals

Atomic depths relative to solid surface, concentration profiles

Properties as in (1), but very near surface (~ 1-2 atomic layers)

Near-surface atomic geometries for substrates and adsorbates

Initial valence-orbital energy levels symmetries, and atomic-orbital make-up



Complementary or Related Techniques

X- ray fluorescence

Auger electron spectroscopy

*Rutherford backscattering
spectroscopy*

Secondary ion mass spectrometry