Core level photoelectron spectroscopy

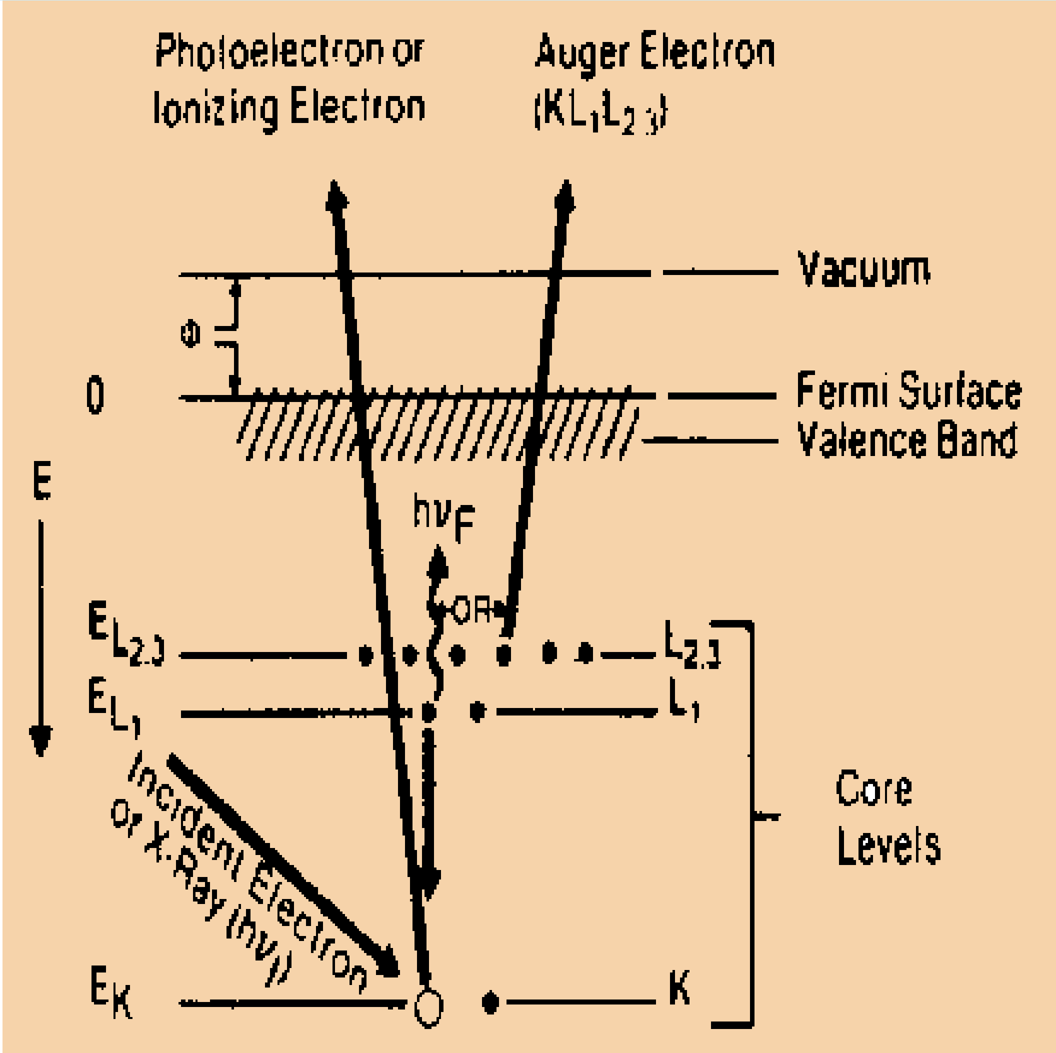
General features

Surface sensitivity

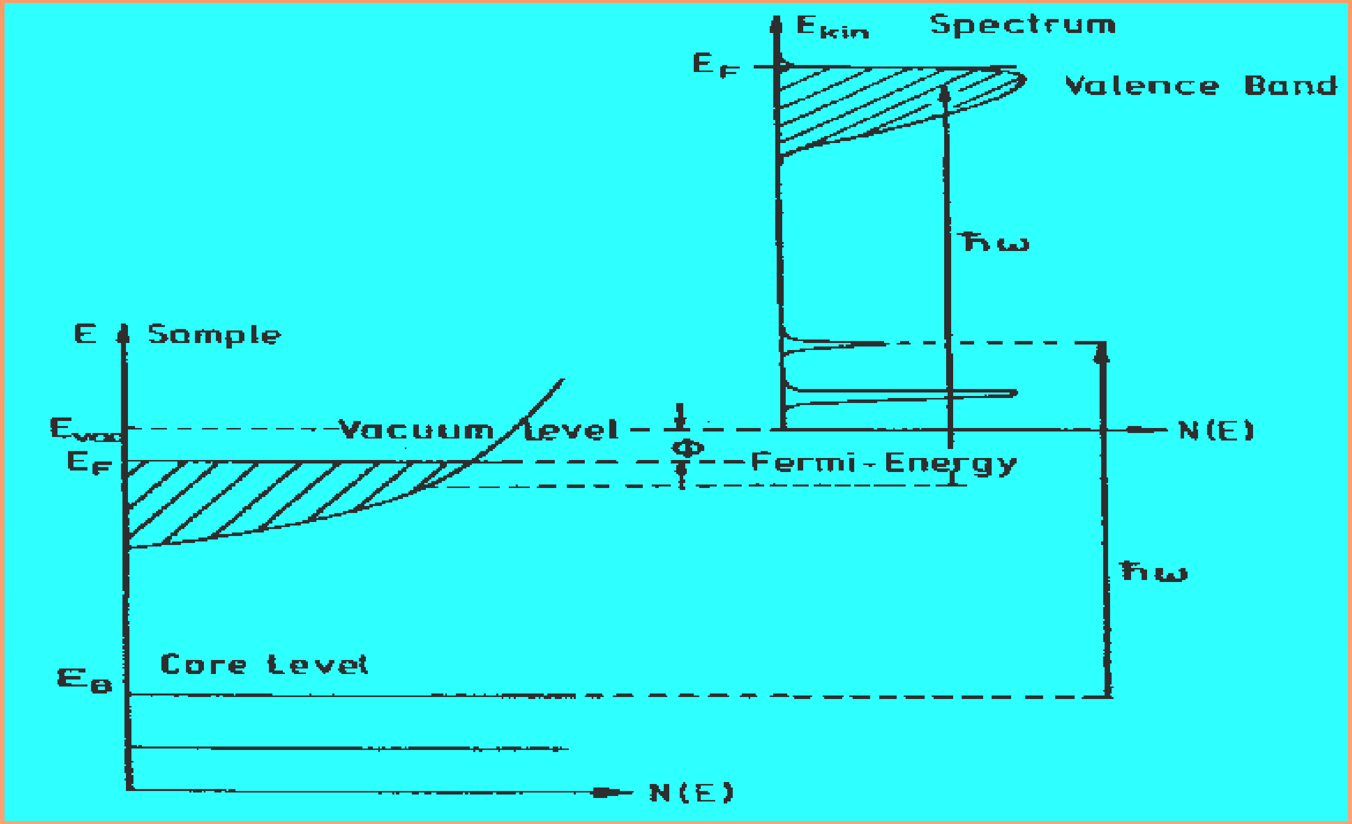
Final state effects

Applications

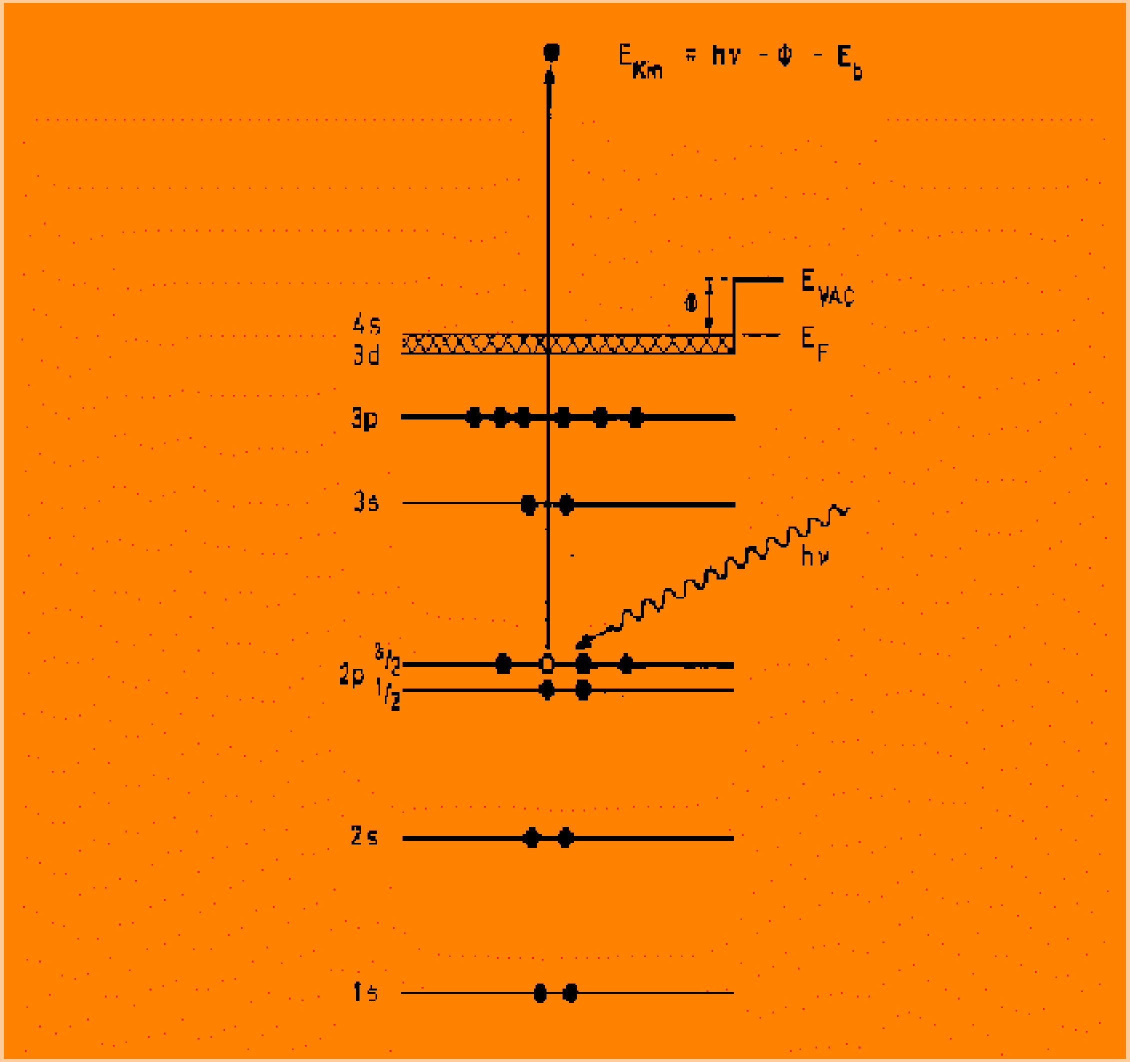
General Features



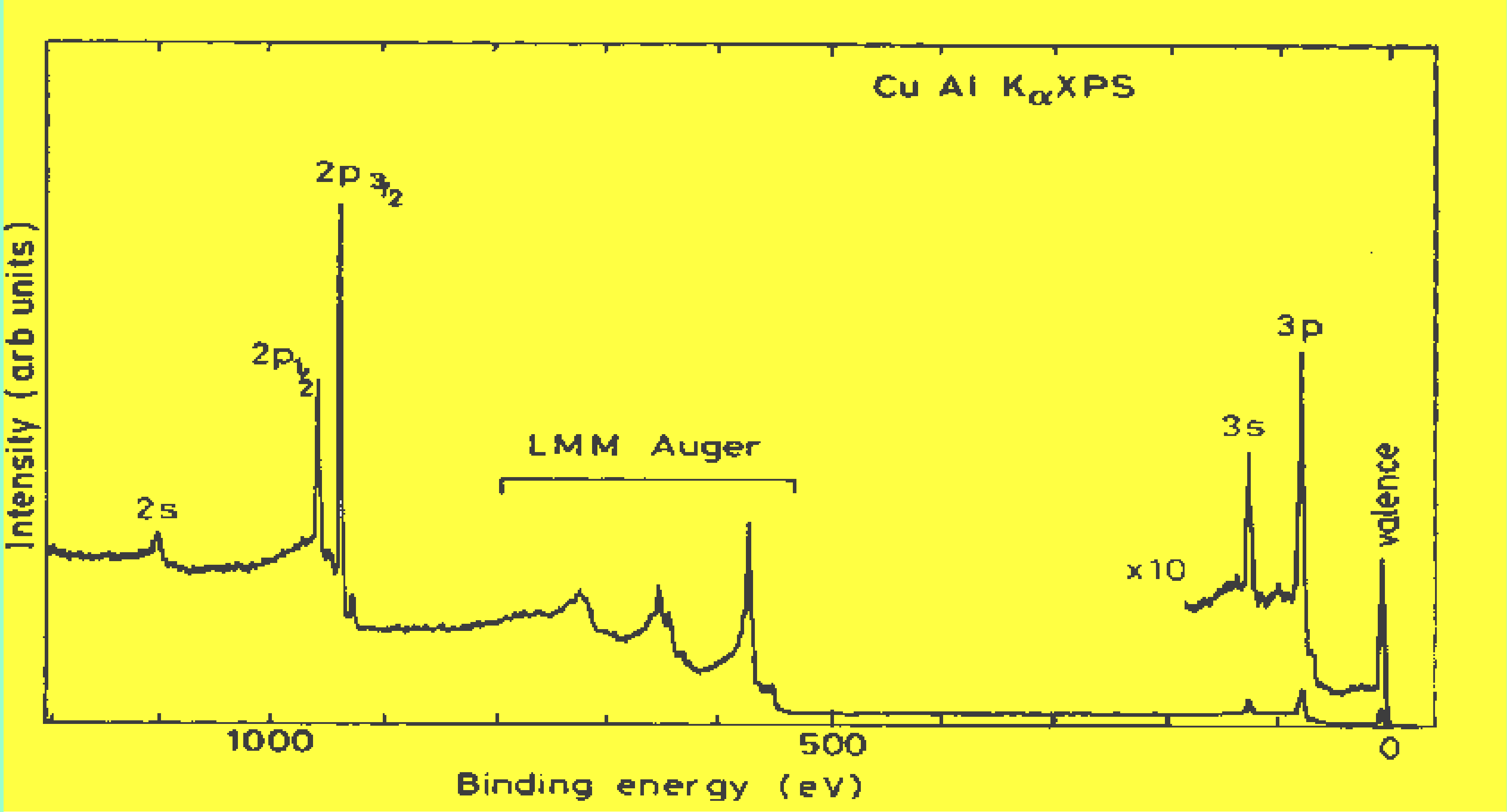
Energy level diagram for XPS/AES/X-ray fluorescence.



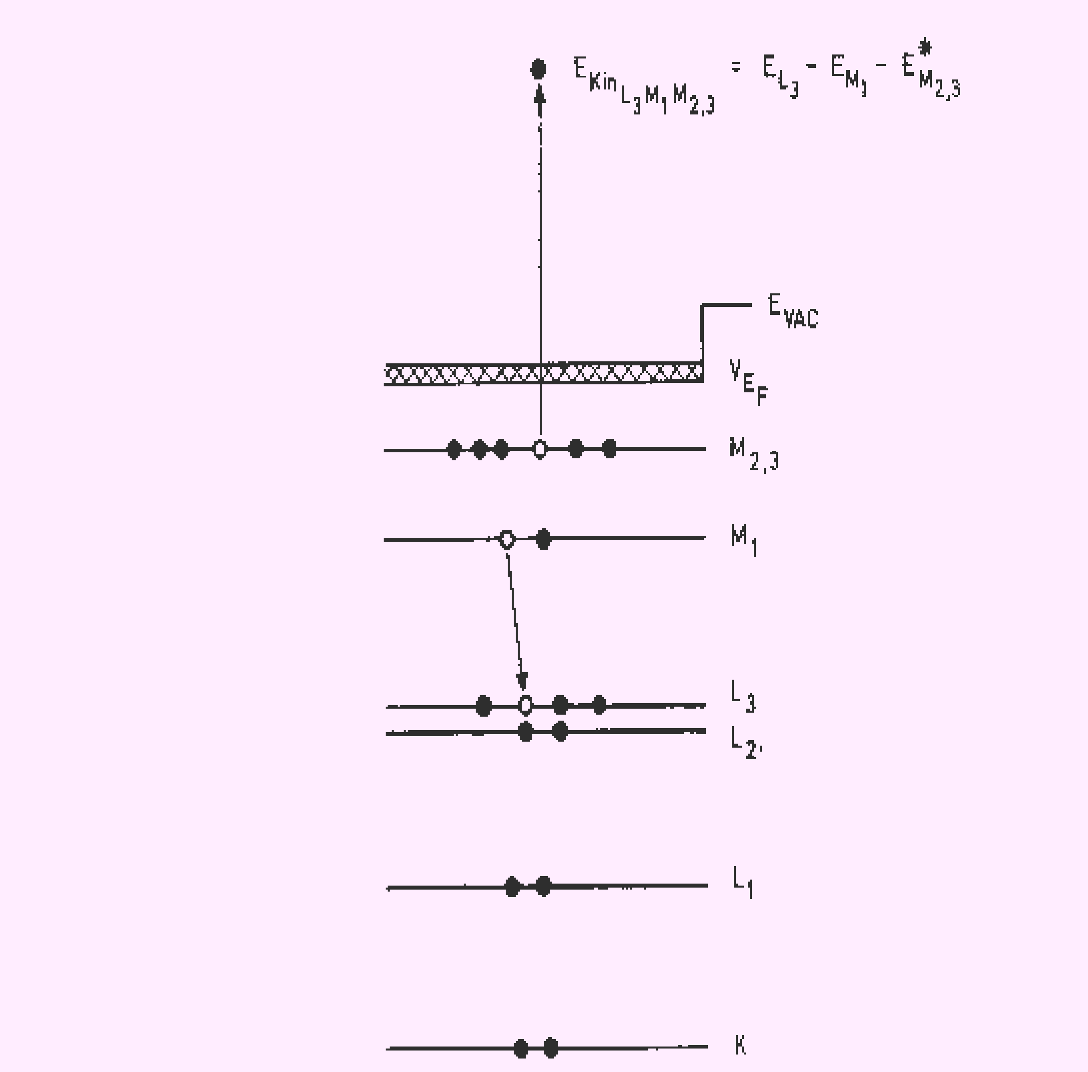
Energy levels in a solid and the electron energy distribution produced by photons of energy $h/_{2\pi}\omega$ (from S. Hüfner).



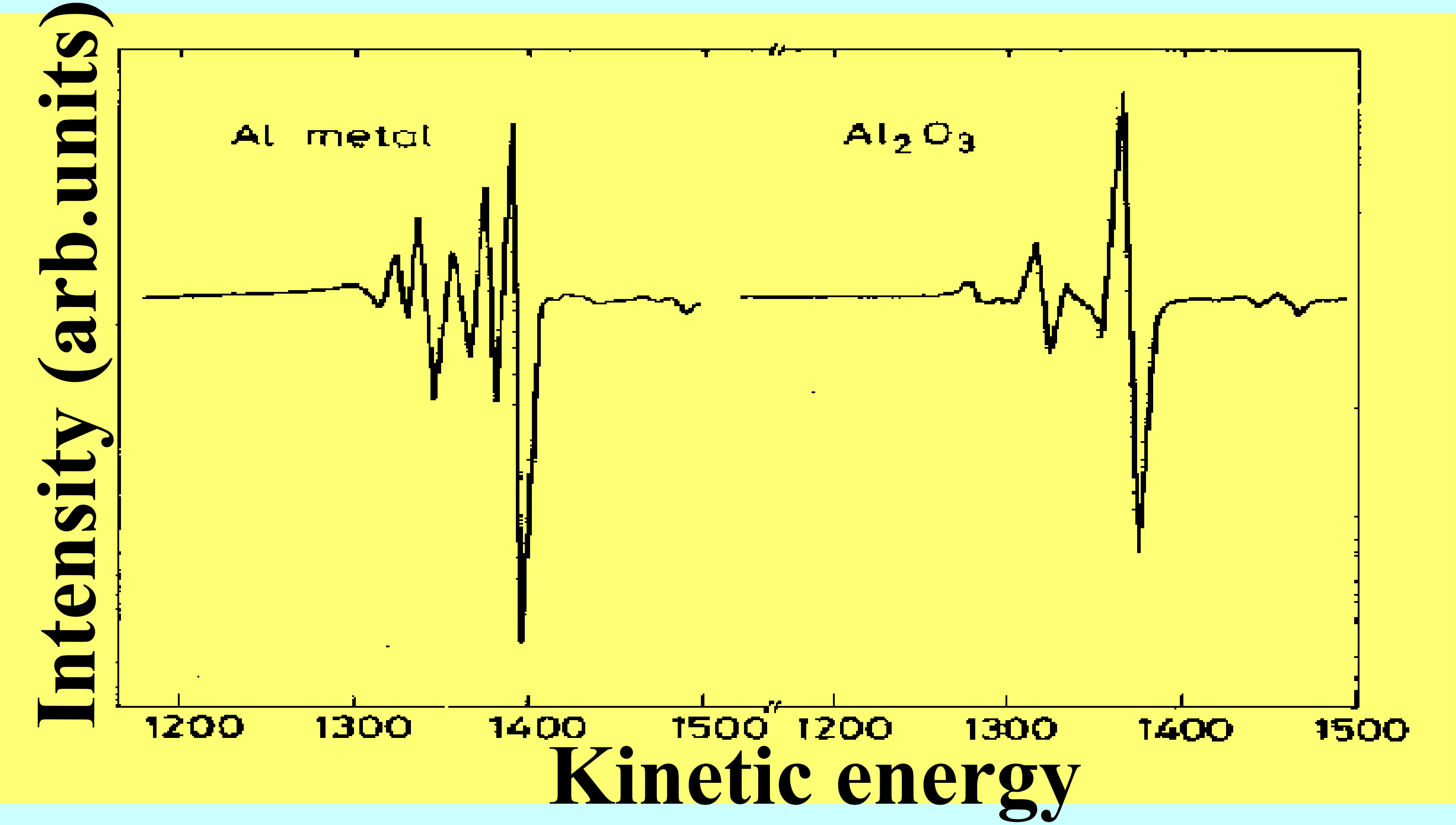
The electronic transition involved in the 2$p_{3/2}$ emission of copper.



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).

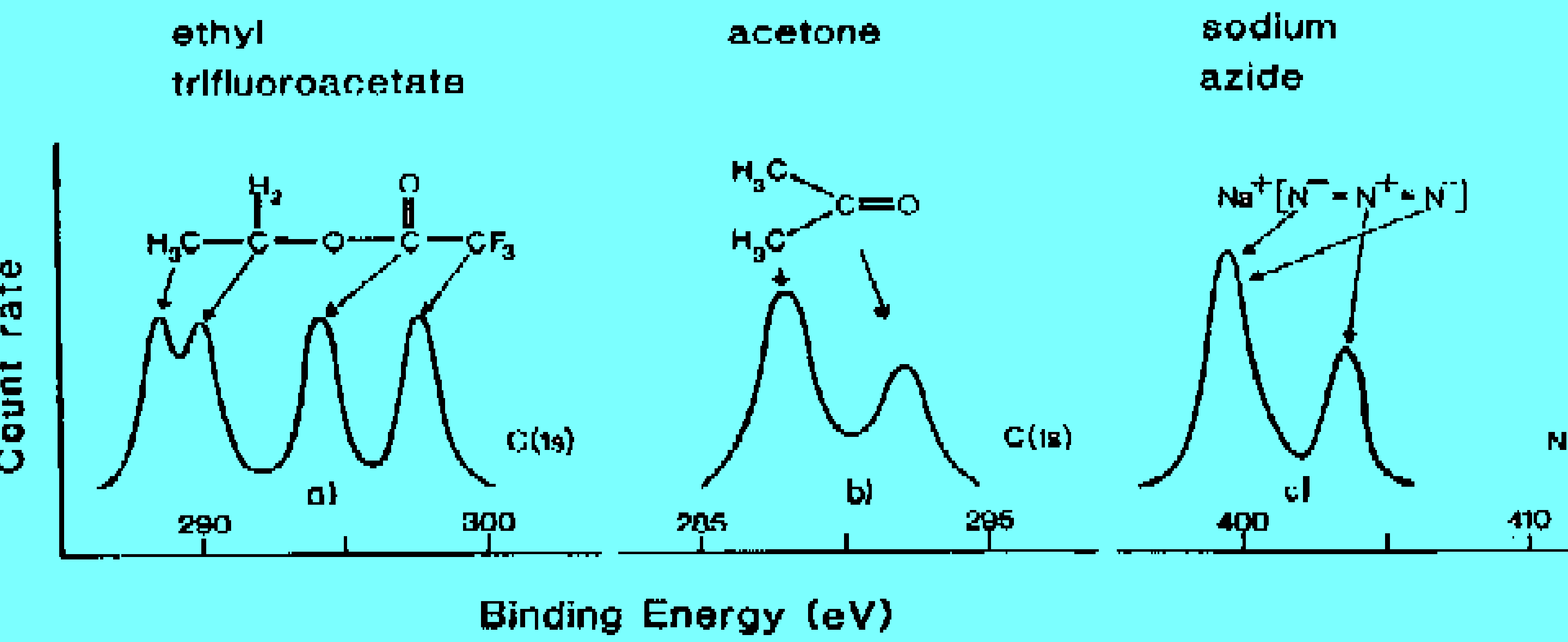


Differential Auger spectra from Al in the metallic and oxide states

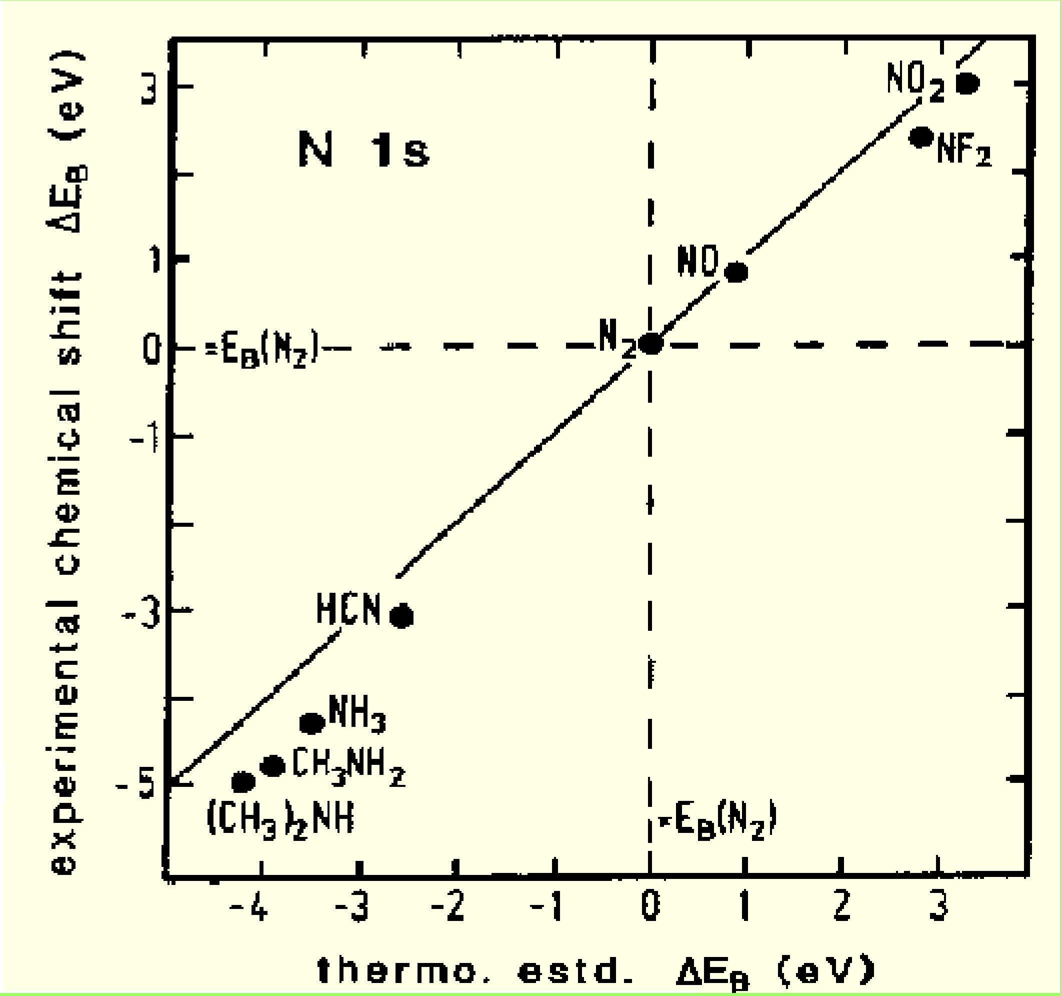
(from Chapter 2 of G. C. Smith).

	1s1/2	2s1/2	2p1/2		2p1/2	3s1/2	3p1/2		3p3/2	3d5/2		3d5/2
	K	L_{I}	L_{II}		L_{III}	M_{I}	M_{II}		M_{III}	M_{VI}		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 Se	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	

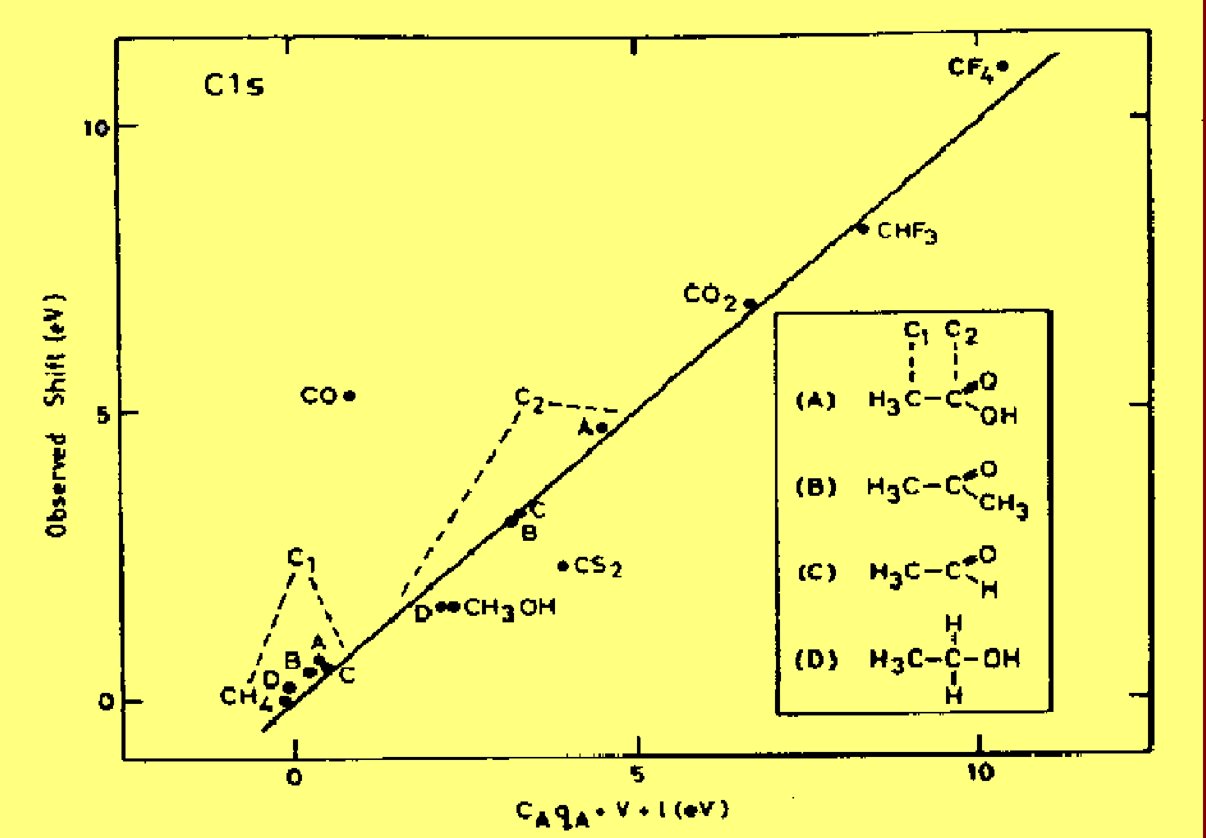
Binding energy shifts



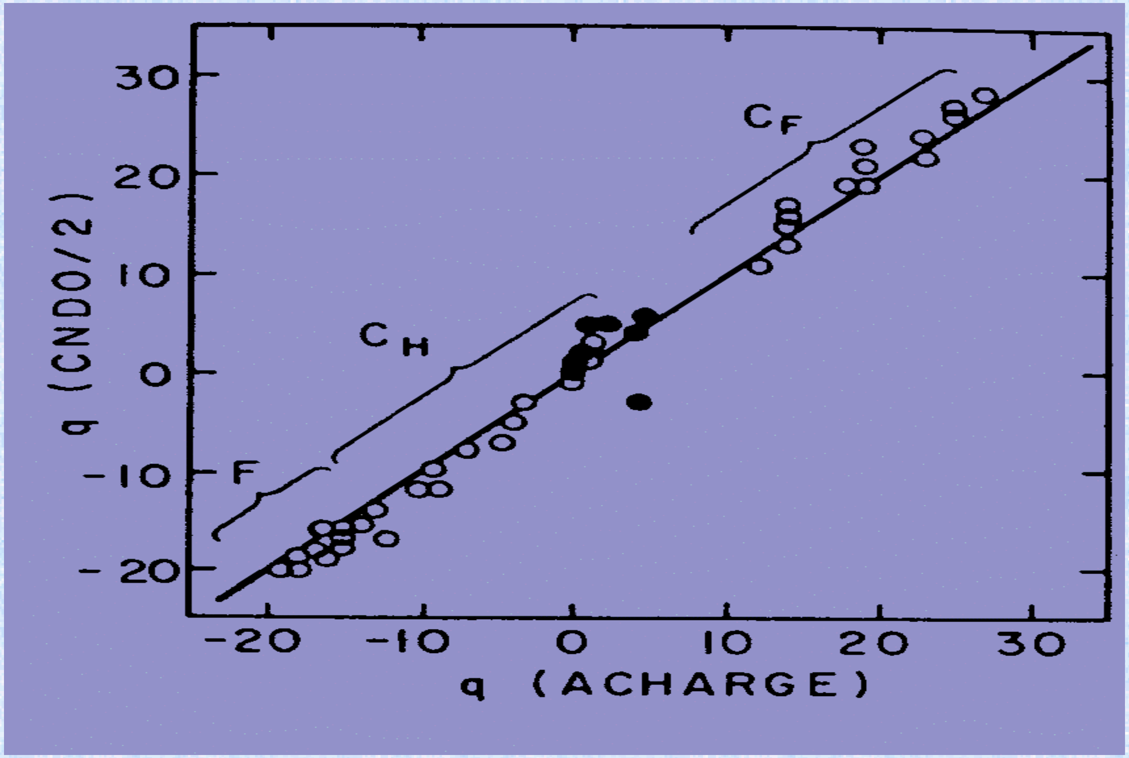
C 1s spectra of ethyl trifluoroacetate (a), acetone (b), and the N ls spectrum of sodium azide (from S. Hüfner).



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

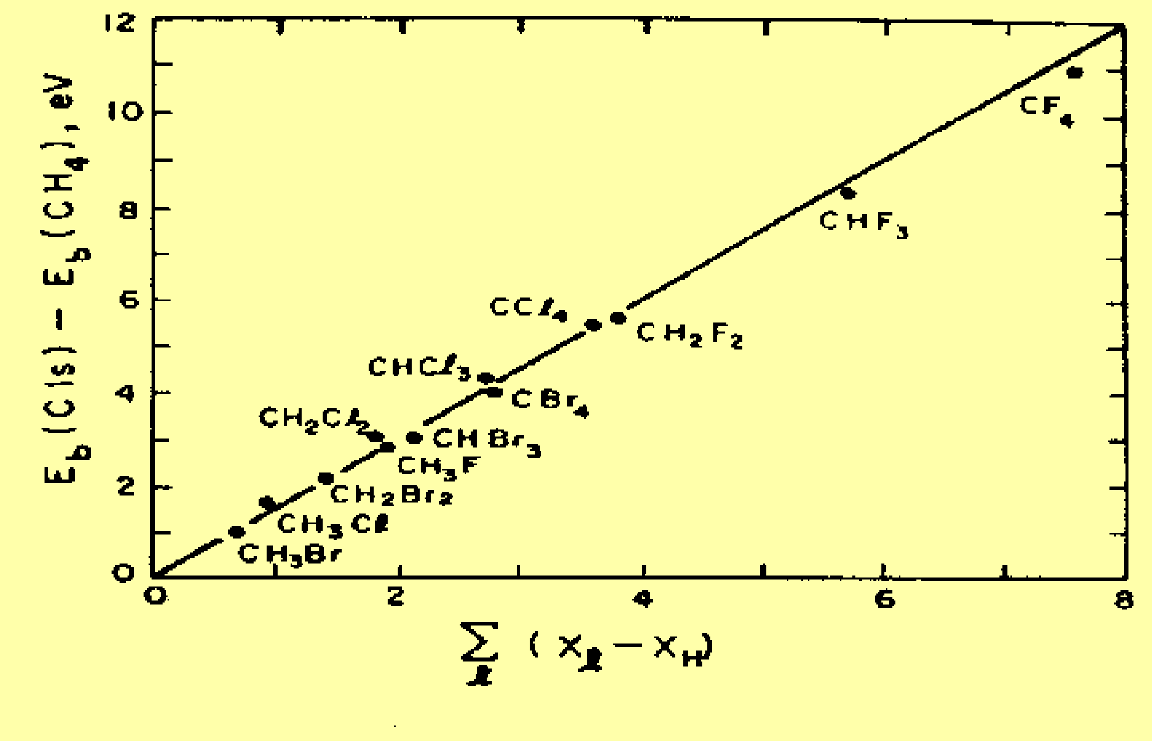


C1*s* BEs (relative to CH_4) vs. shifts calculated using a potential model. Fit gives C_A=21.9 eV/charge and l=0.80 eV (from K. Siegbahn, et. al.).

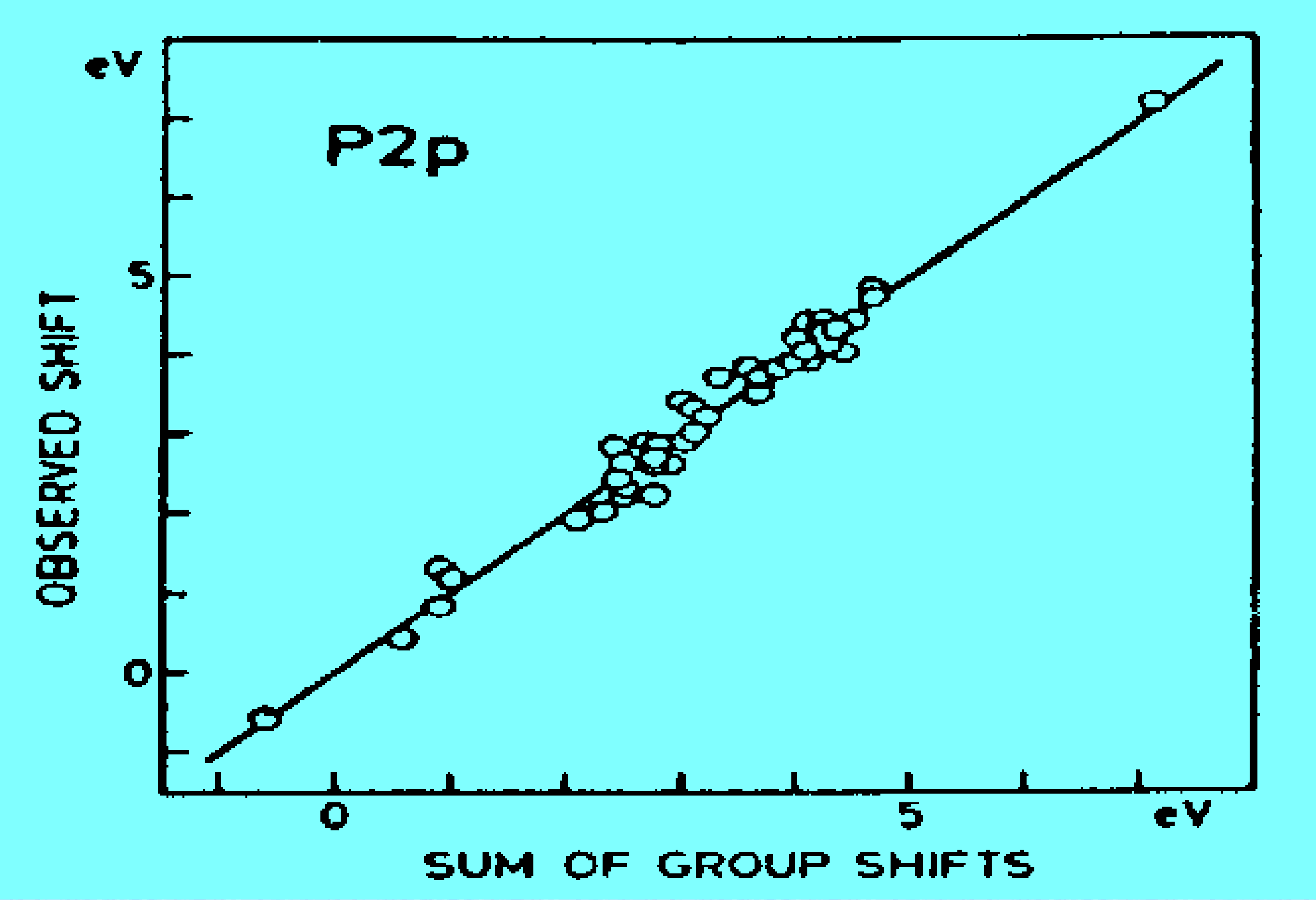


CNDO/2 atomic charges of fluobenzenes Vs. derived experimentally fromXPS

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



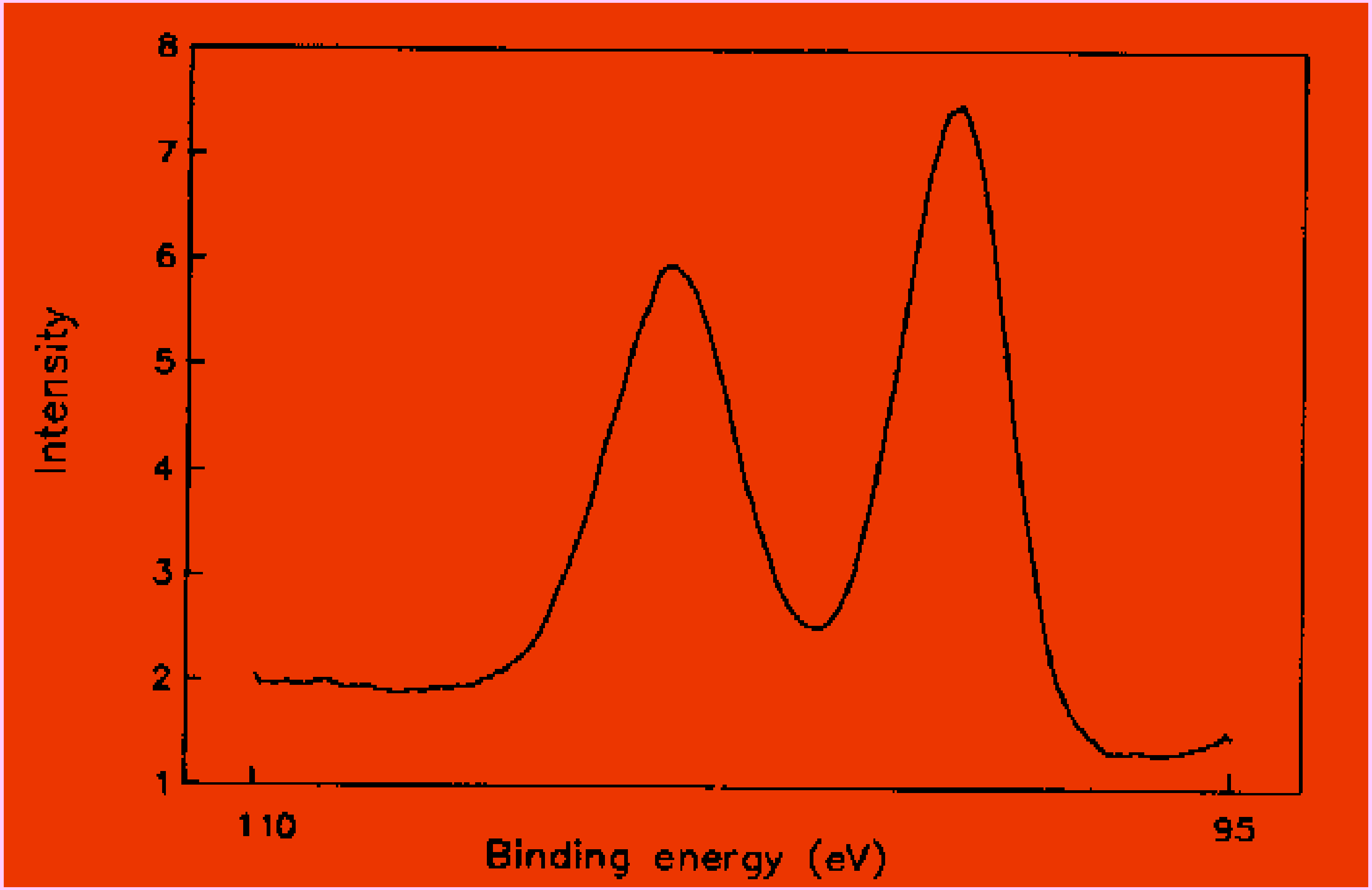
C1*s* BEs halomethanes (relative to CH_4) Vs. electronegativity differences (from T. D. Thomas, *J. Am. Chem. Soc.*. 92, 4184, 1970).



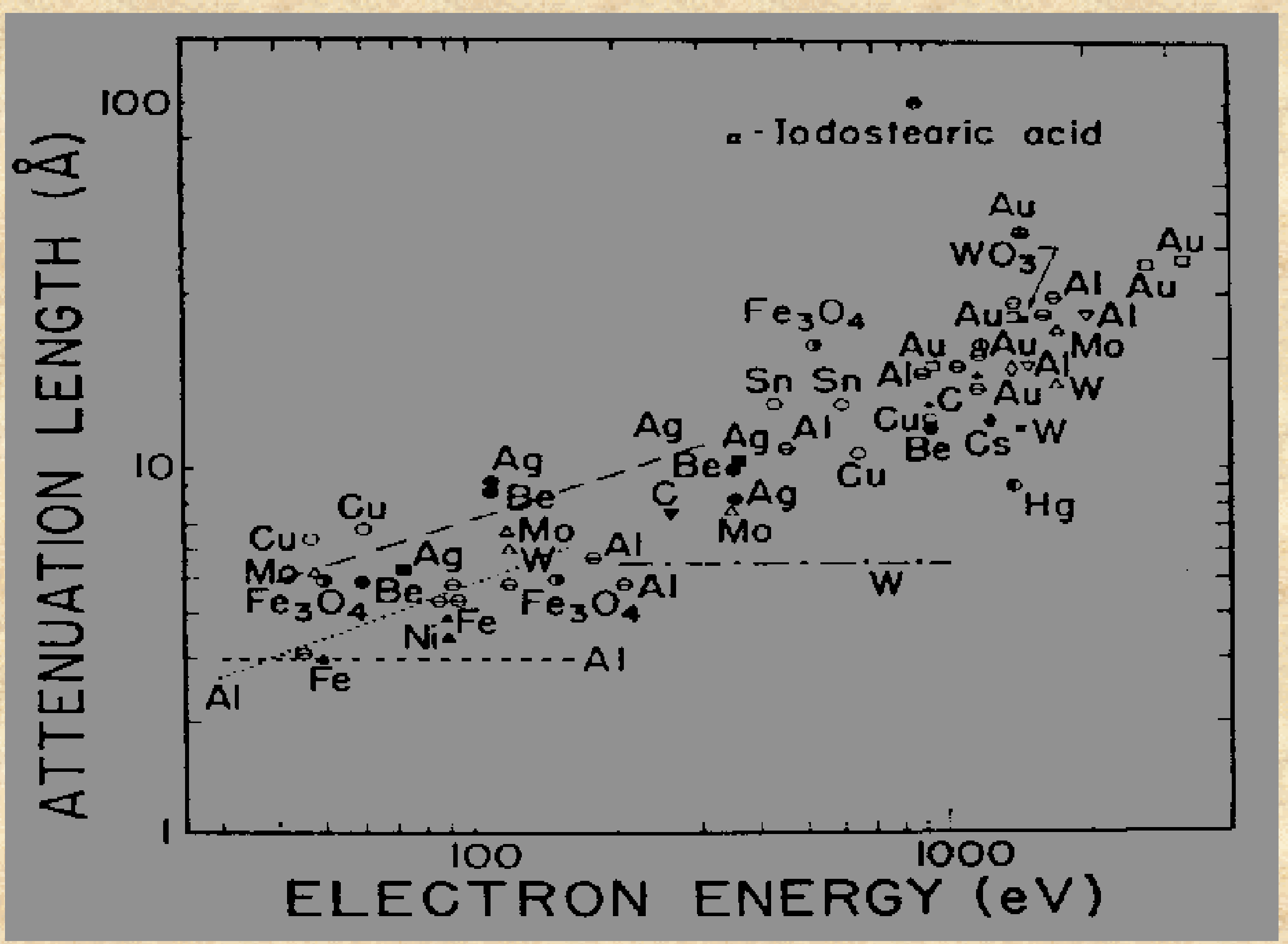
P2*p* chemical shifts with those calculated using the group shift model.

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

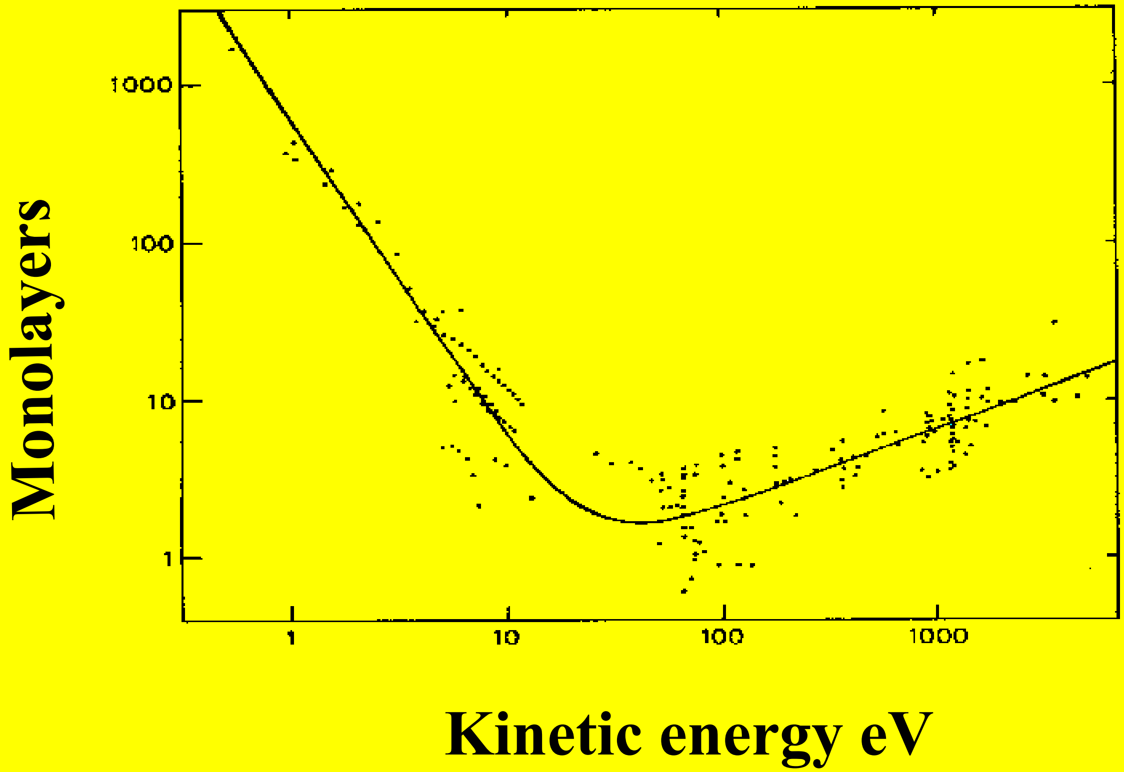
Surface sensitivity



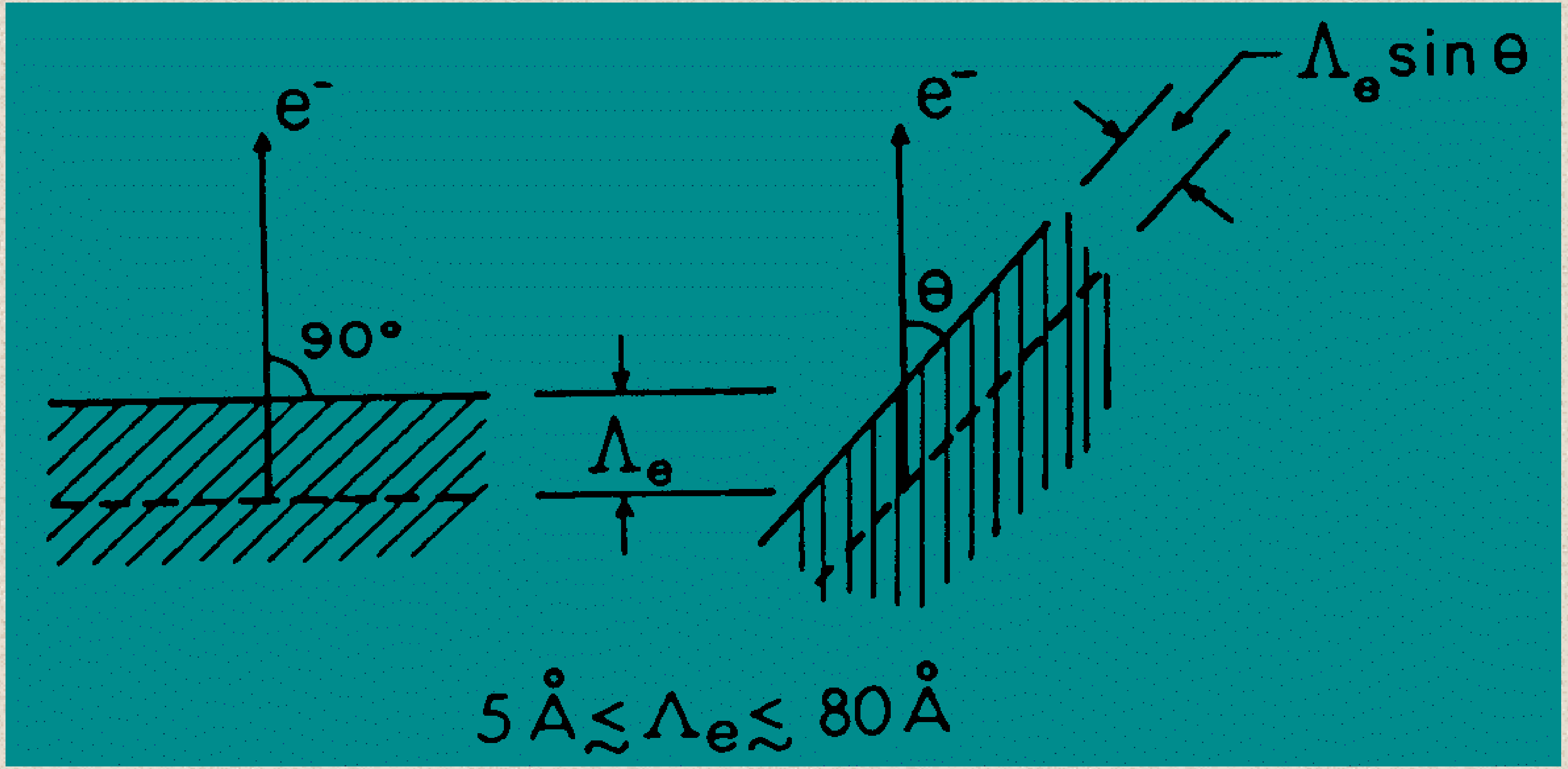
XPS of Si (100) (from Chapter 2 of G. C. Smith).



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

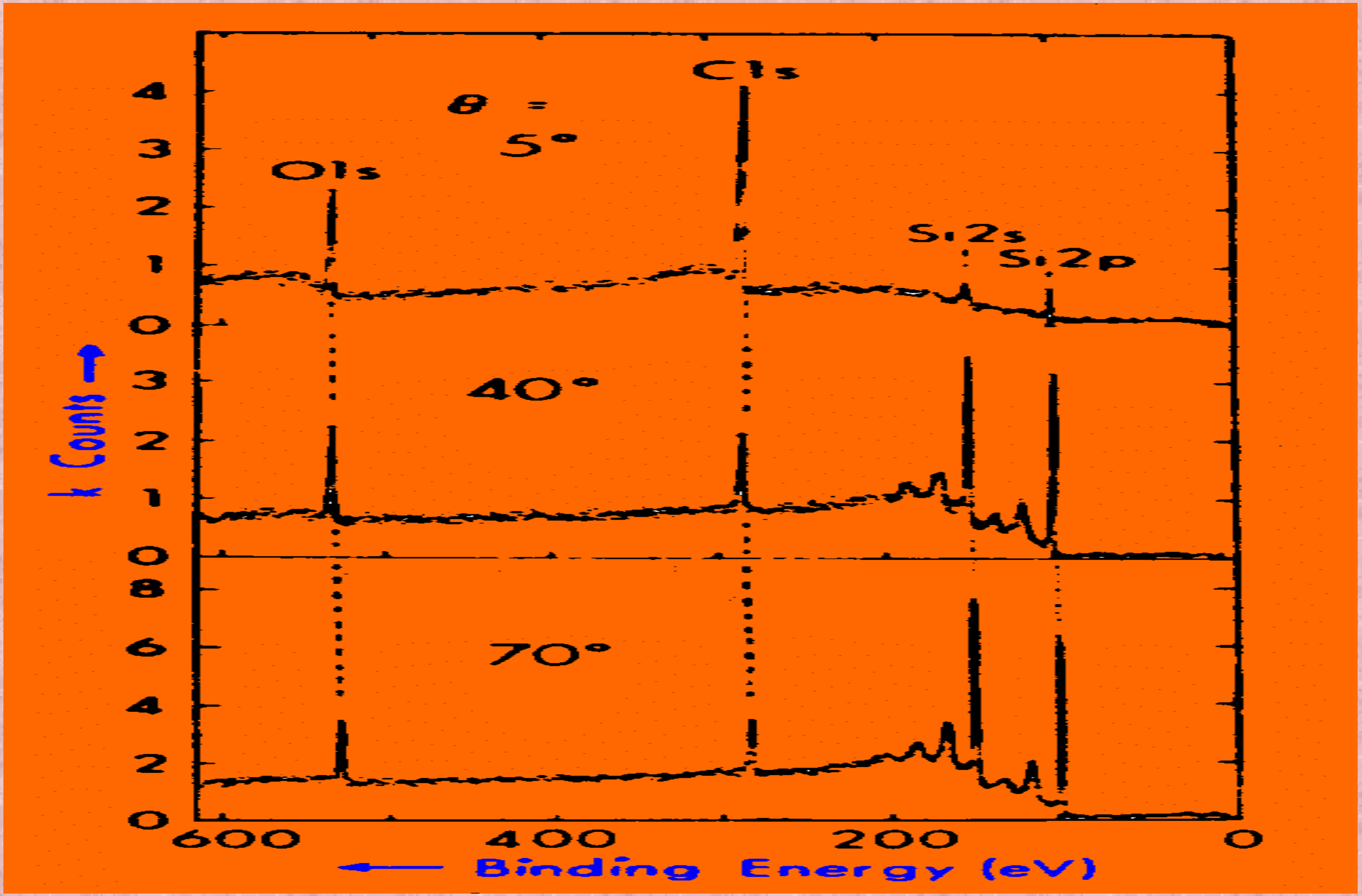


Attenuation length data with a best parametric fit (from Chapter 2 of G. C. Smith).

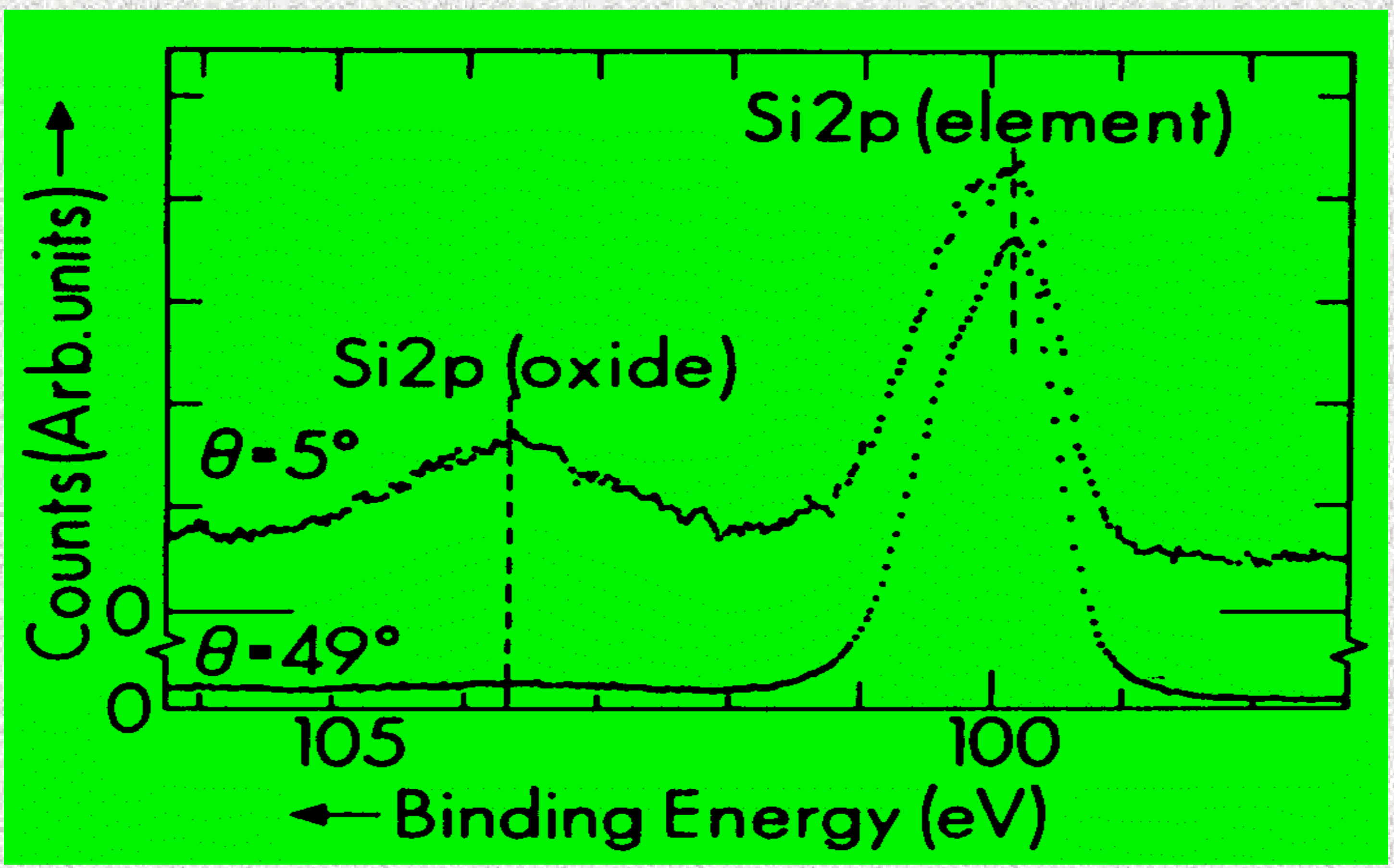


Surface sensitivity enhancement

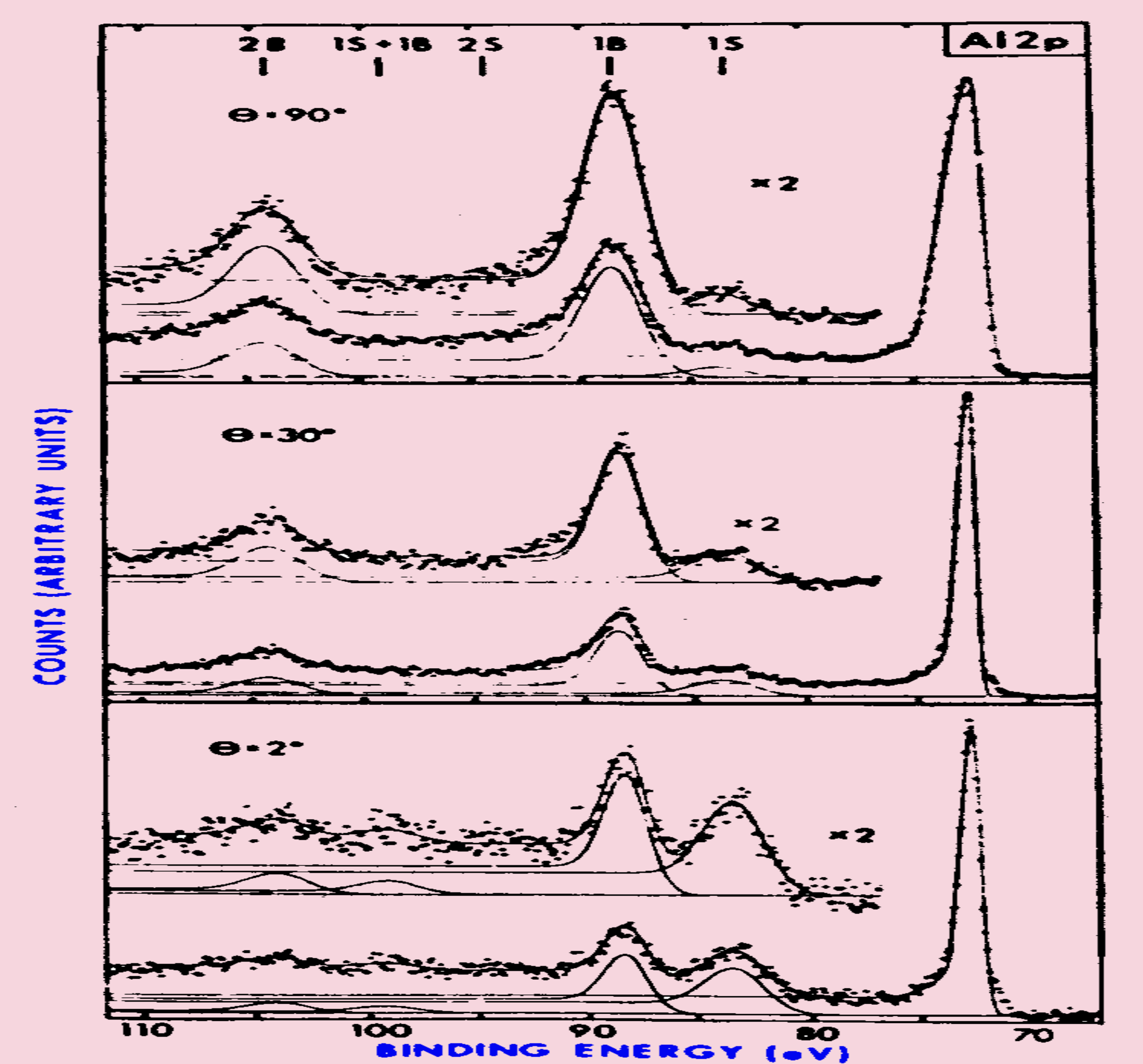
(fromC.S. Fadley, in Vol.. 2 of C.R. Brundleand A.D. Baker).



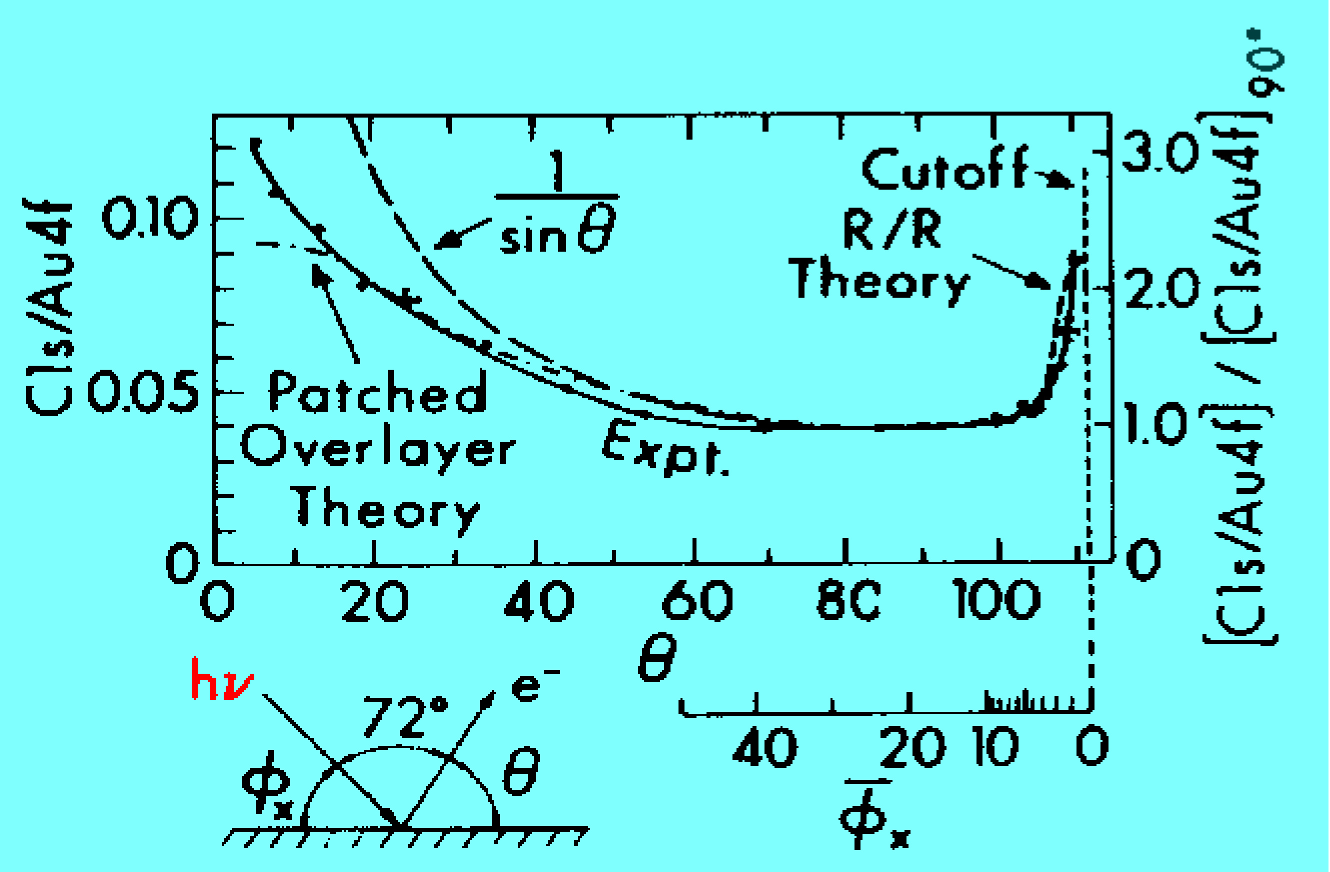
XPS at low and high exit angles for a Si surface (from C.S. Fadley, *Prog.Sol. St. Chem.*, 11, 265, 1976).



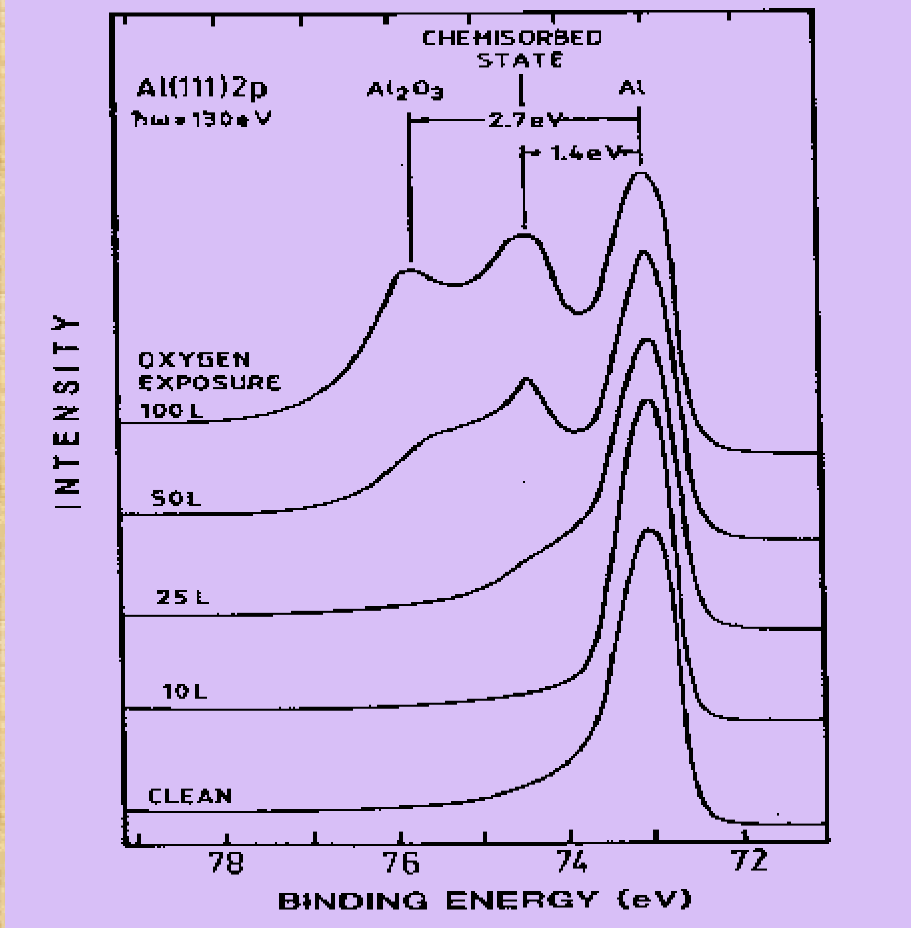
Si2*p* core spectra at $\theta = 5^\circ$ and 49° of an oxide covered Si (from C.S. Fadly, *Prog. Sol. St. Chem.* 11, 265, 1976).



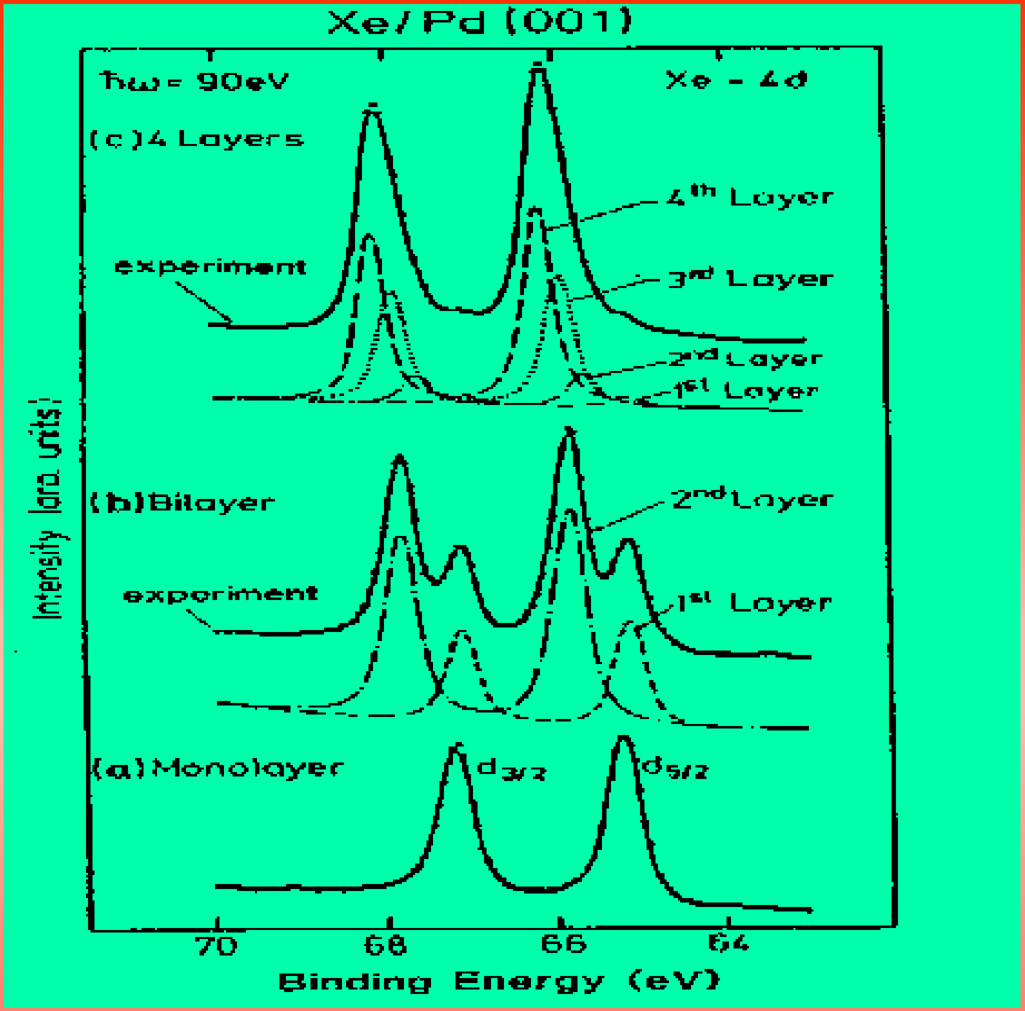
A12*p* plasmons from poly-crystalline Al (from R.J Baird et. al.,*Surf. Sci*. 72, 495, 1978).



Angular dependence of the C1*s*/Au4*f* intensity ratio for a carbon covered gold (from M. Mehta and C.S.Fadley,*Phys. Lett.* A55, 59, 1975).



Oxidation of Al (111) monitored via the Al 2p with $h/_{2\pi}\omega$ = 130 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 effects

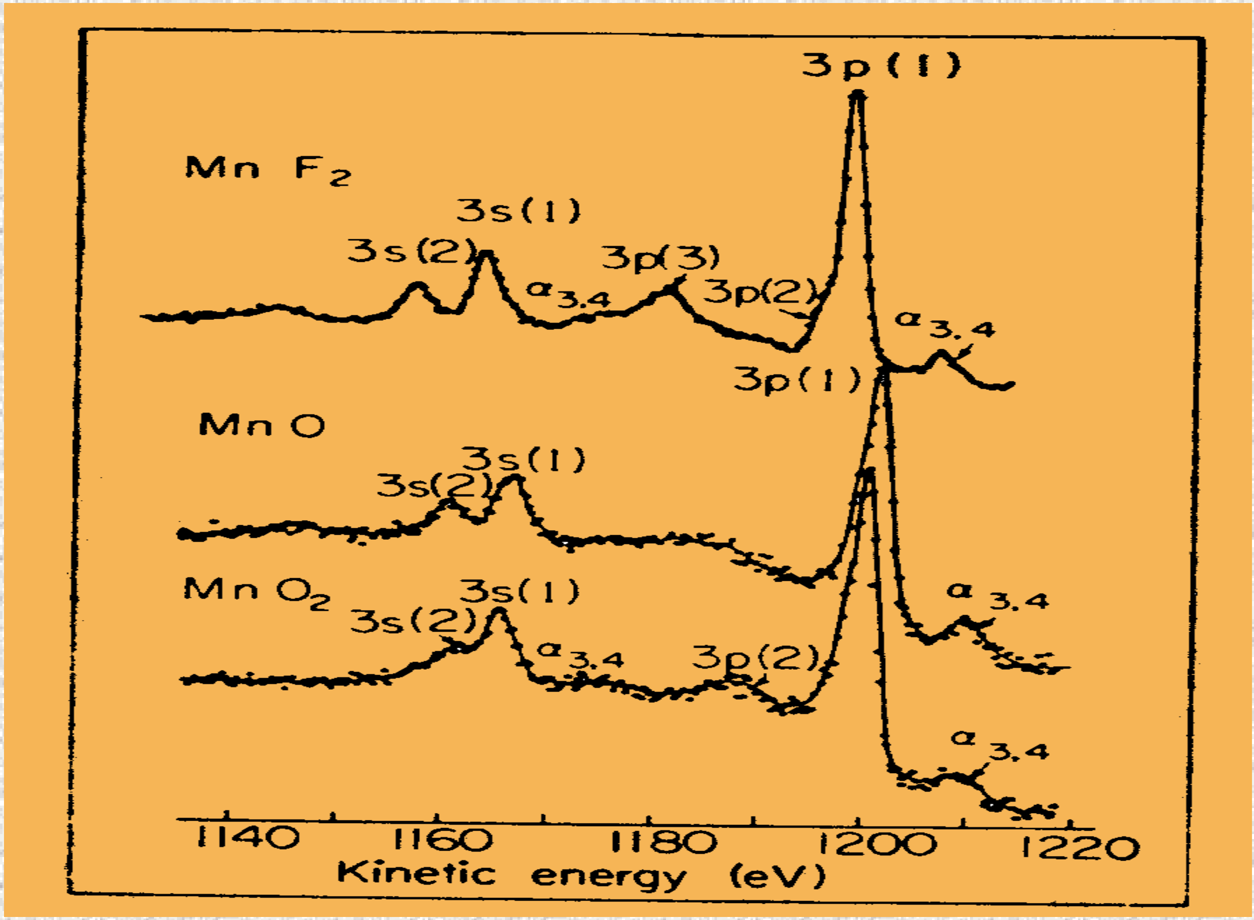
Multiplet splitting

Multielectron excitations

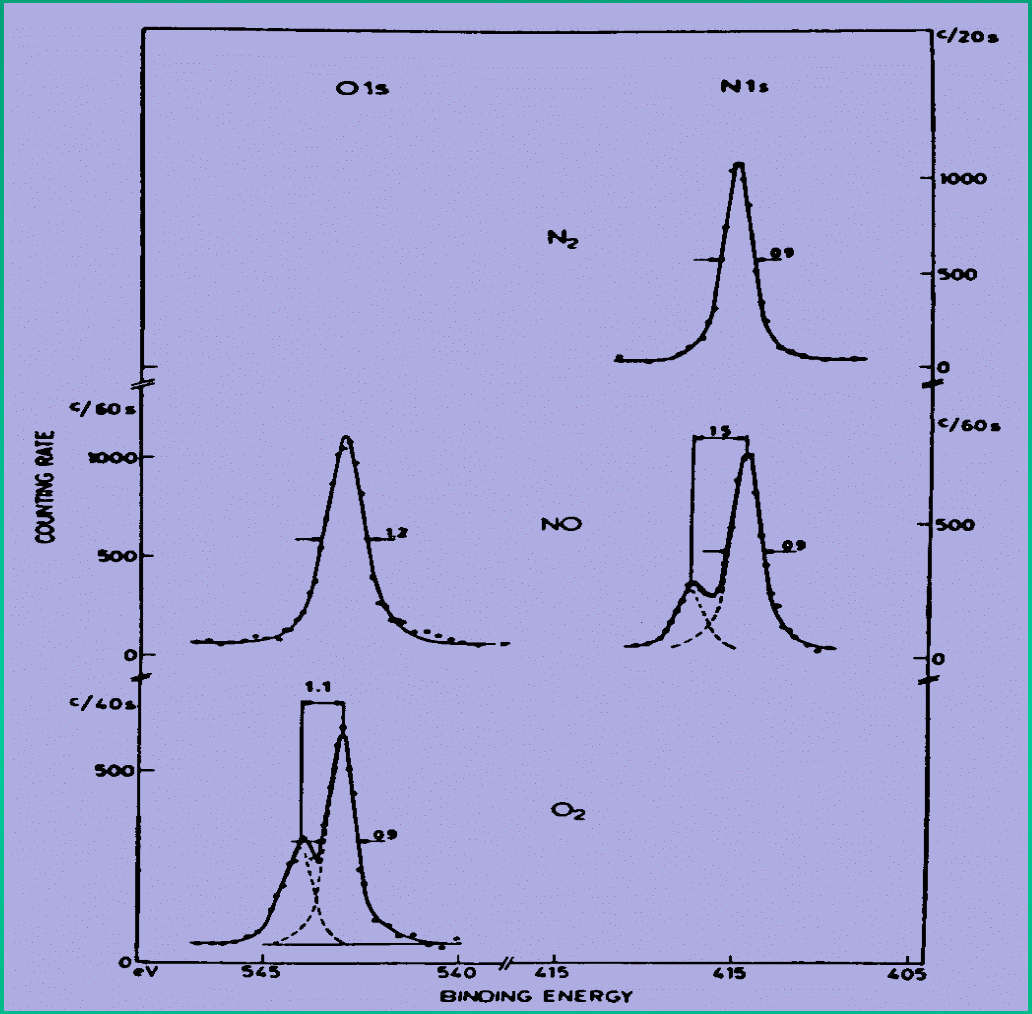
Shake-up, Shake-off, metals, satellites

Other many body effects

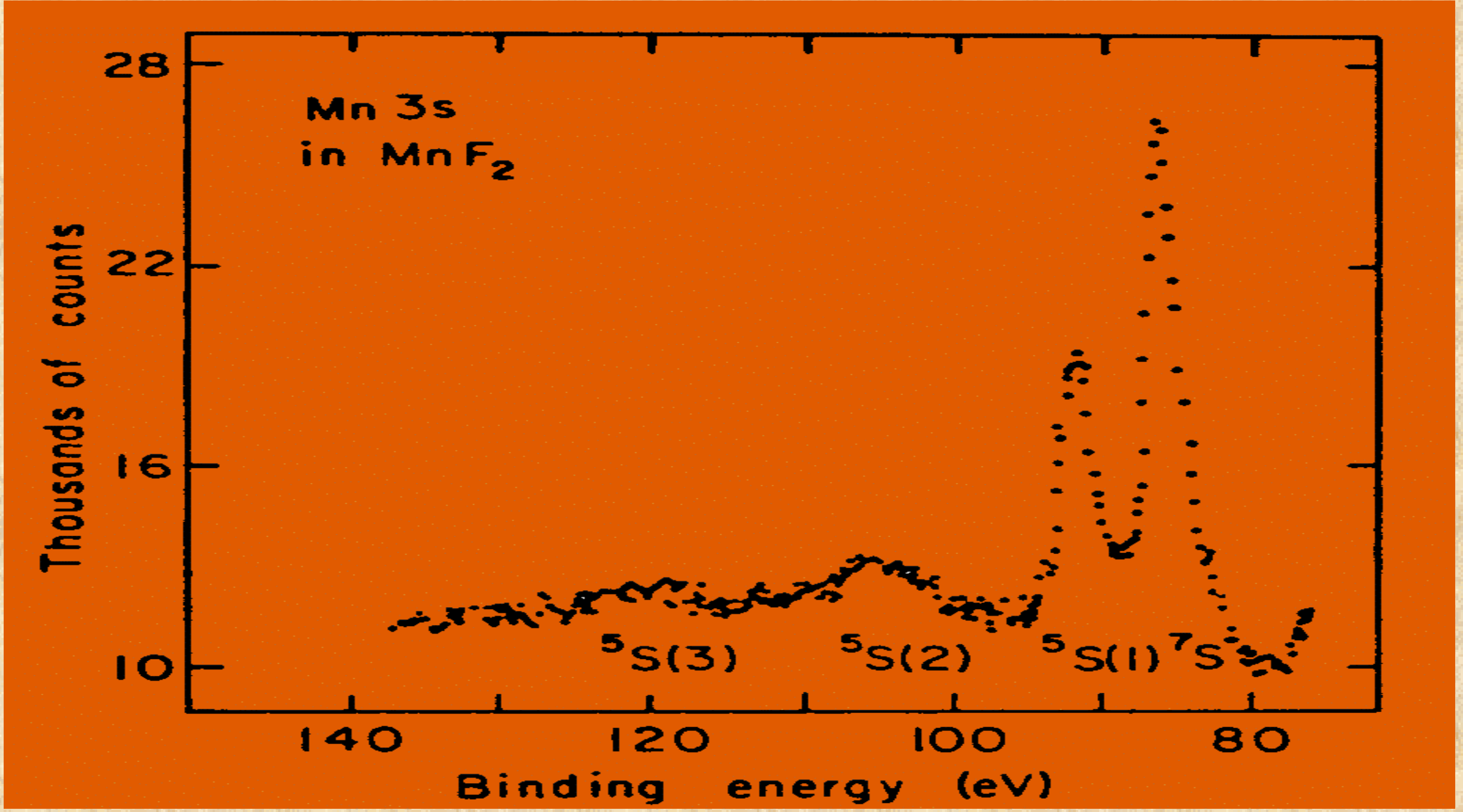
Vibrational structure



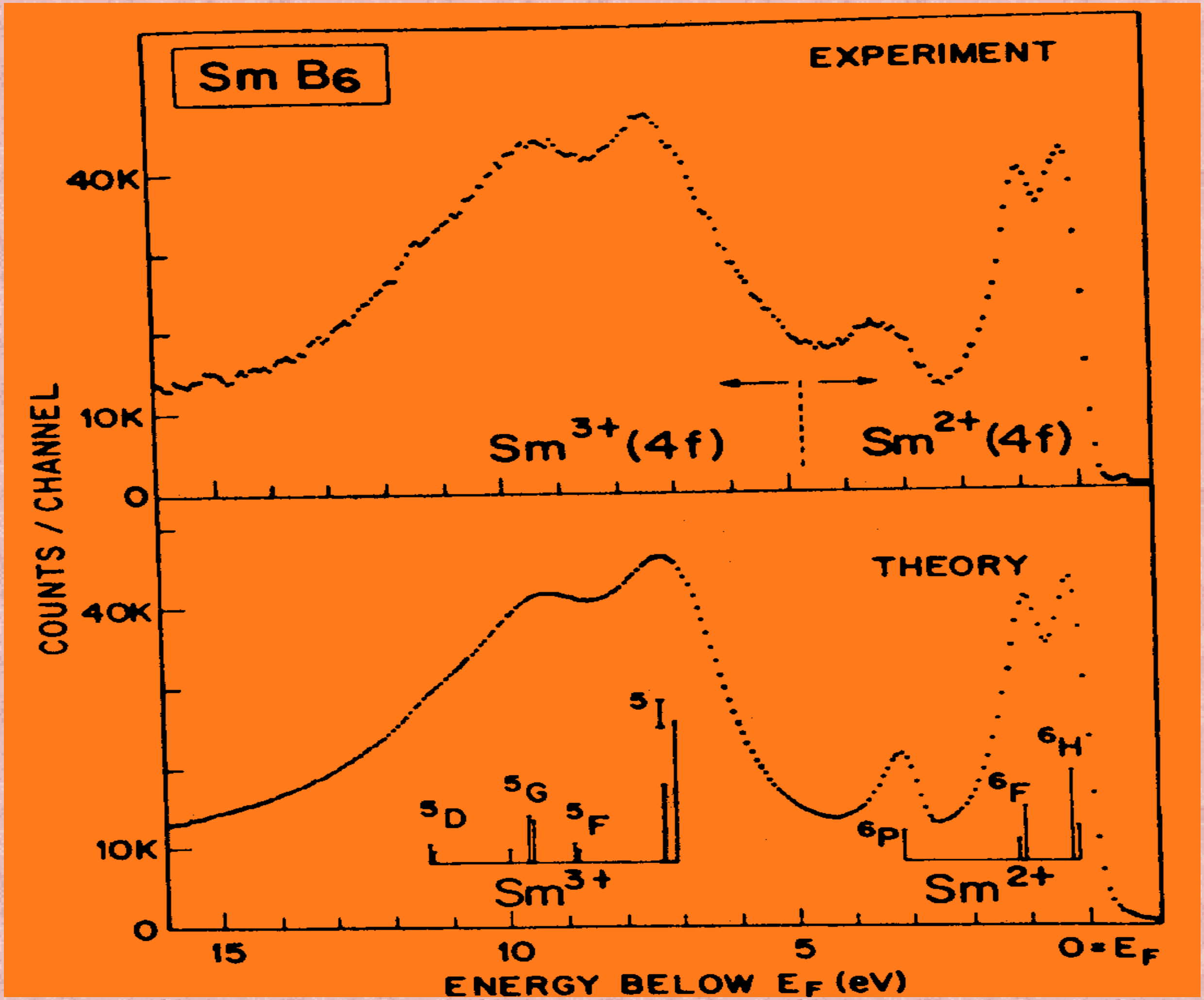
Mn 3*s* and 3*p* XPS. Initial states are Mn^{+2}3d^5 (MnF$_2$, MnO) and Mn^{+4}3d^3 (MnO$_2$) (from C. S. Fadley and D.A. Shirley, *Phys. Rev.* A2, 1109, 1970).



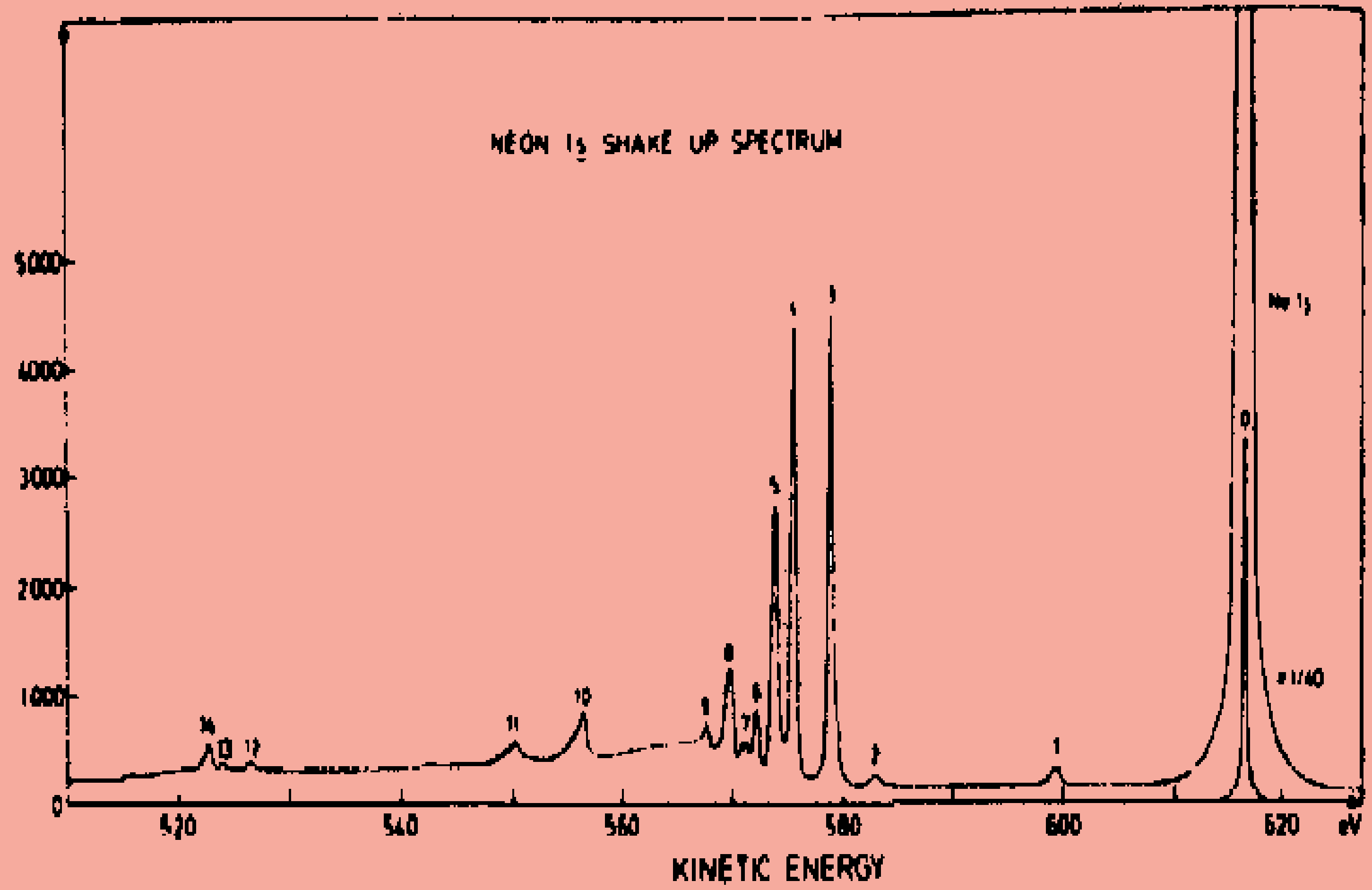
1*s* XPS of N_2, NO and O_2. Peaks of NO and O_2 are split due to final-state multiplets. (from K.Siegbahn).



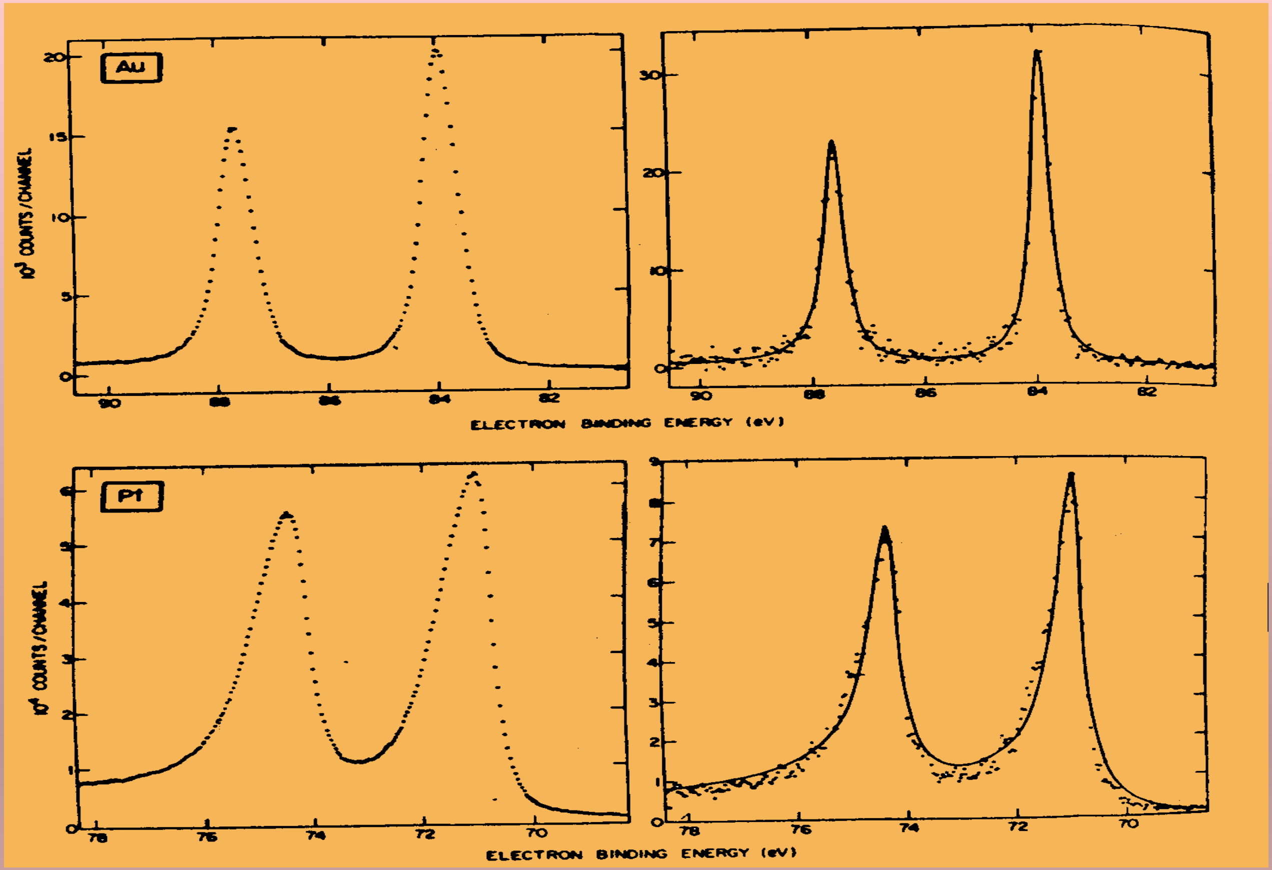
Mn3*s* of MnF_2. $^5S(2)$ and $^5S(3)$ are due to CI (from S.P. Kowalczyk et. al., *Phys. Rev.* B7, 4009, 1973).



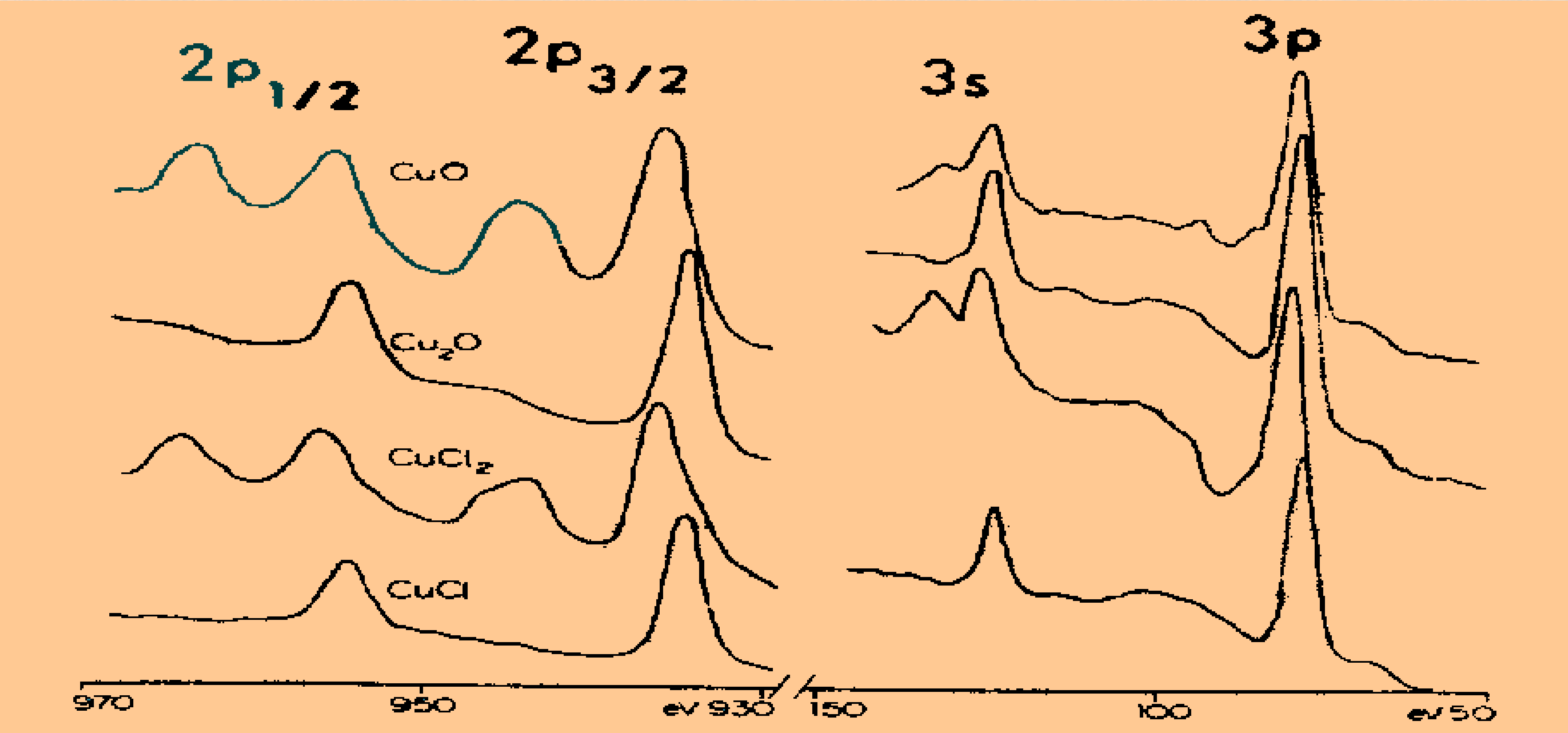
4f valence spectrum of "mixed-valence" SmB_6 (from J.N. Chazalviel, et. al., *Phys. Rev.* B10, 4586, 1976).



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

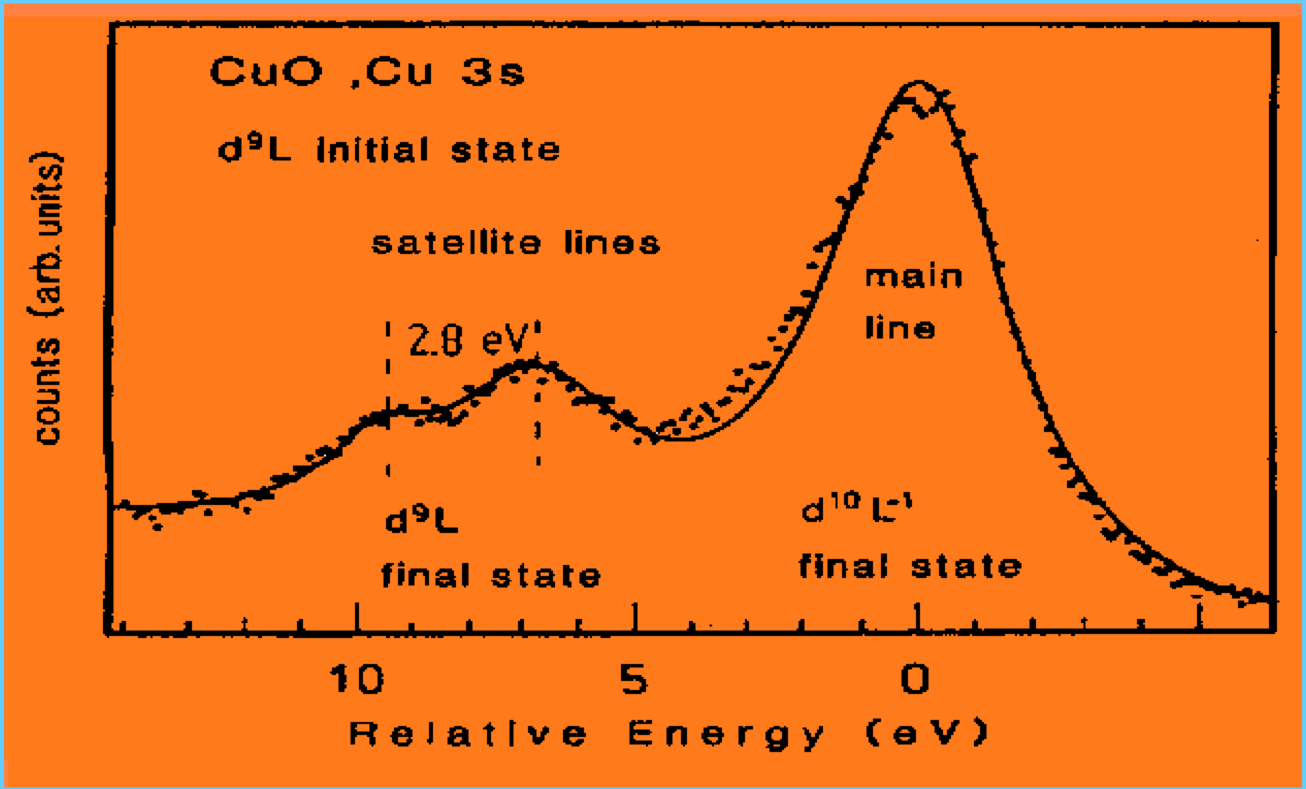


4f core spectra of Au and Pt and data corrected for instrumental line shape(from S.Hüfner and G.K.Wertheim, *Phys.Rev.* B11, 678, 1975; B11, 5197, 1975; *Phys. Rev. Lett.* 35, 53, 1975).

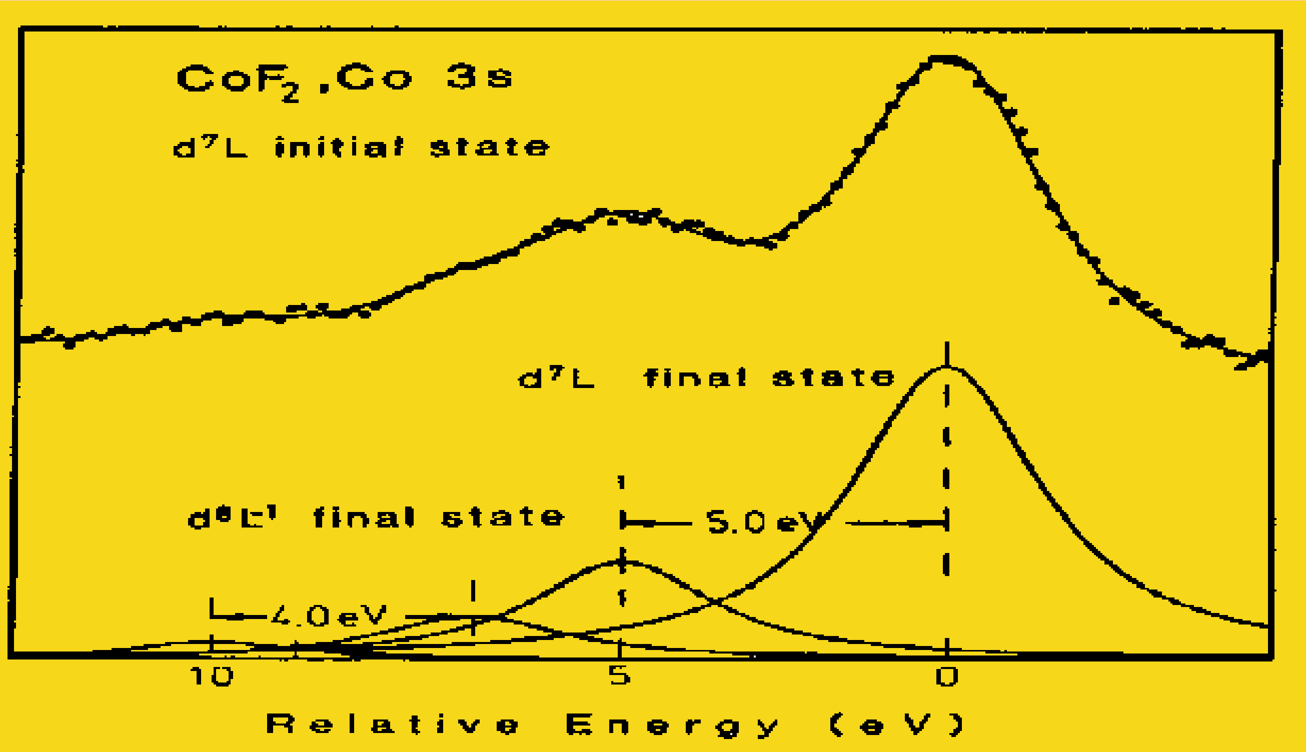


Cu 2*P*, 3*S* and 3*P* XPS of CuO, Cu_2O, $CuCl_2$, and CuCl.

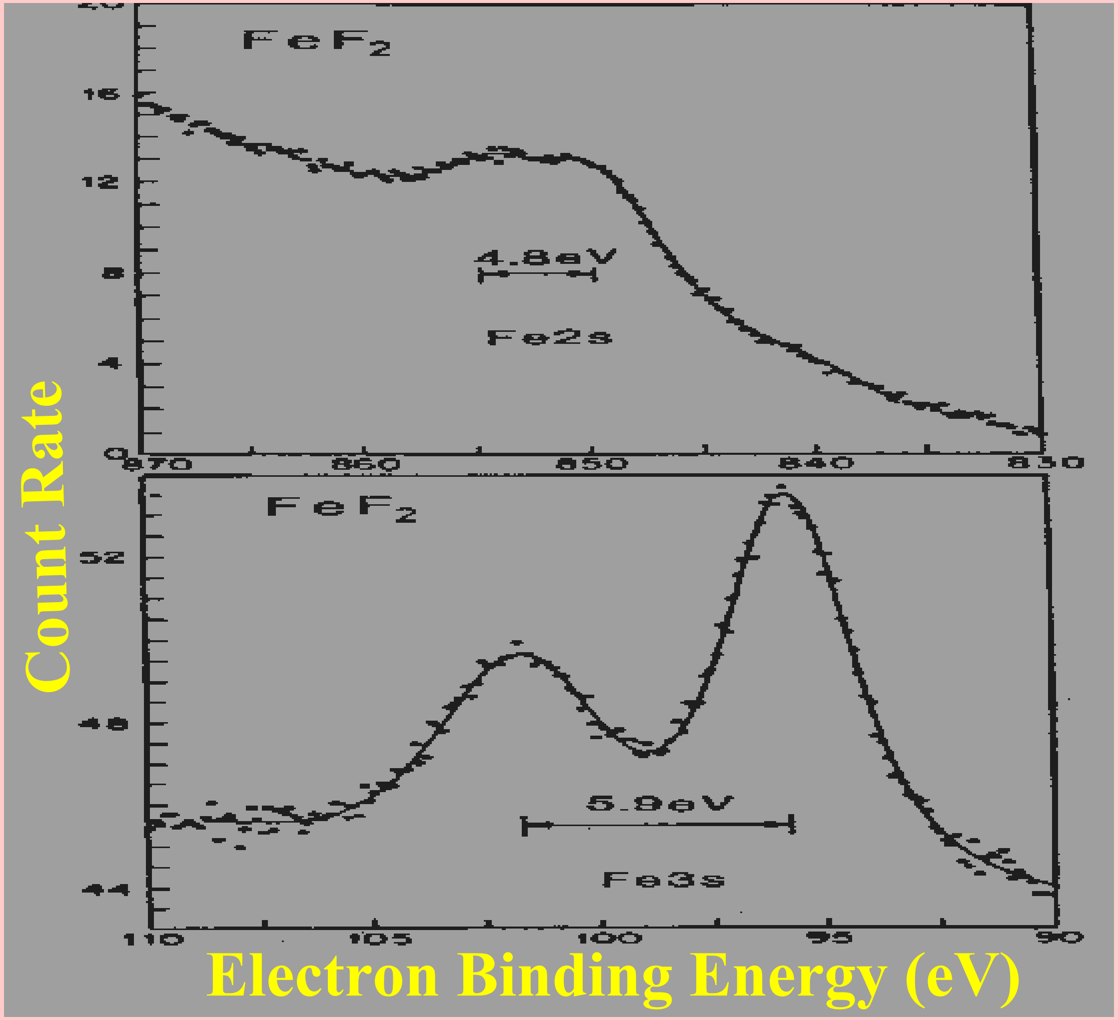
(from D.C. Frost, et. al., *Mol. Phys.* 24, 861, 1972).



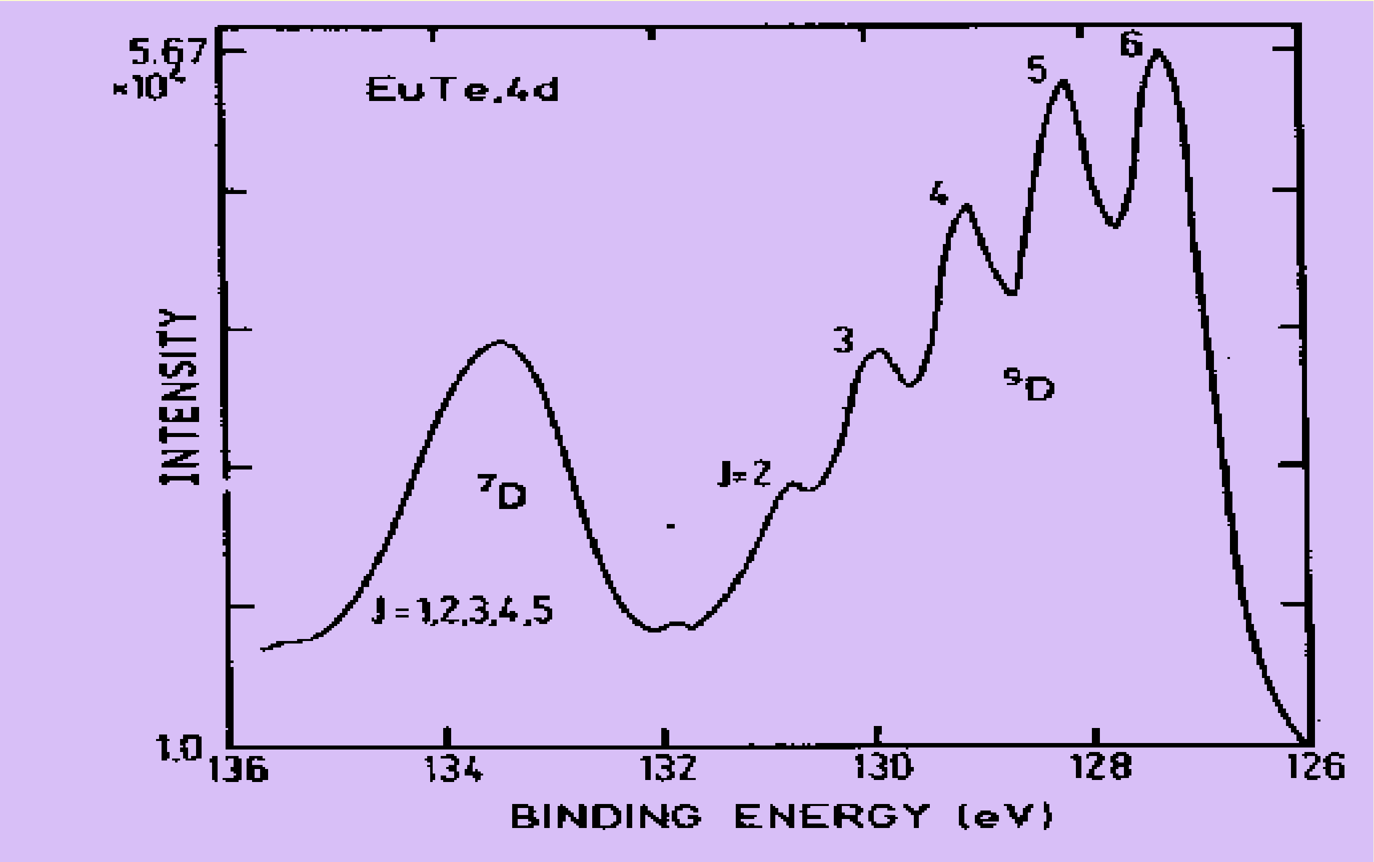
3s core line in CuO. Main line ($d^{10}L^{-1}$) has no exchange interaction but satellite (d^9L) shows it (from S. Hüfner).



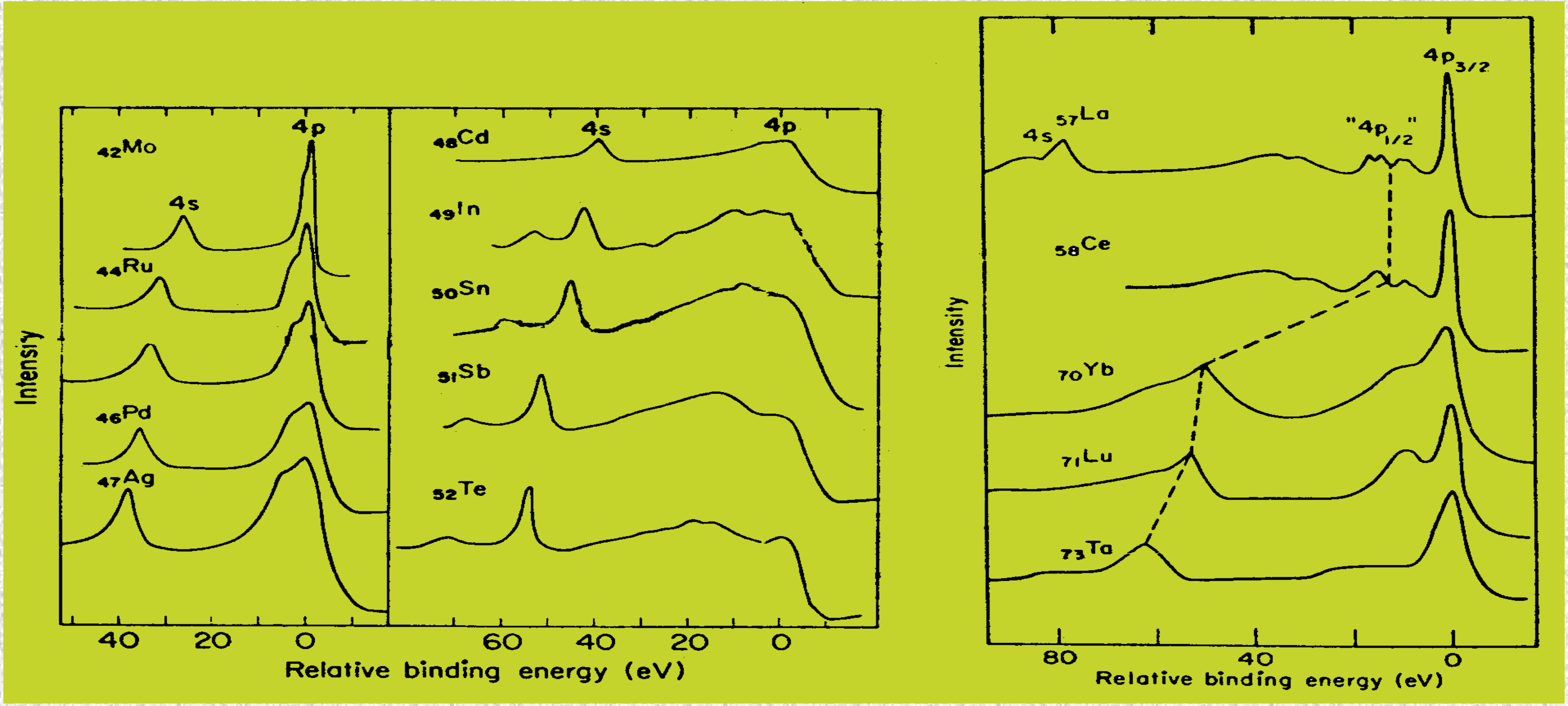
3s XPS of CoF_2. Larger exchange splitting for the main line than the satellite indicates that the main line is d^7L and the satellite is d^8L^{-1}(from S. Hüfner).



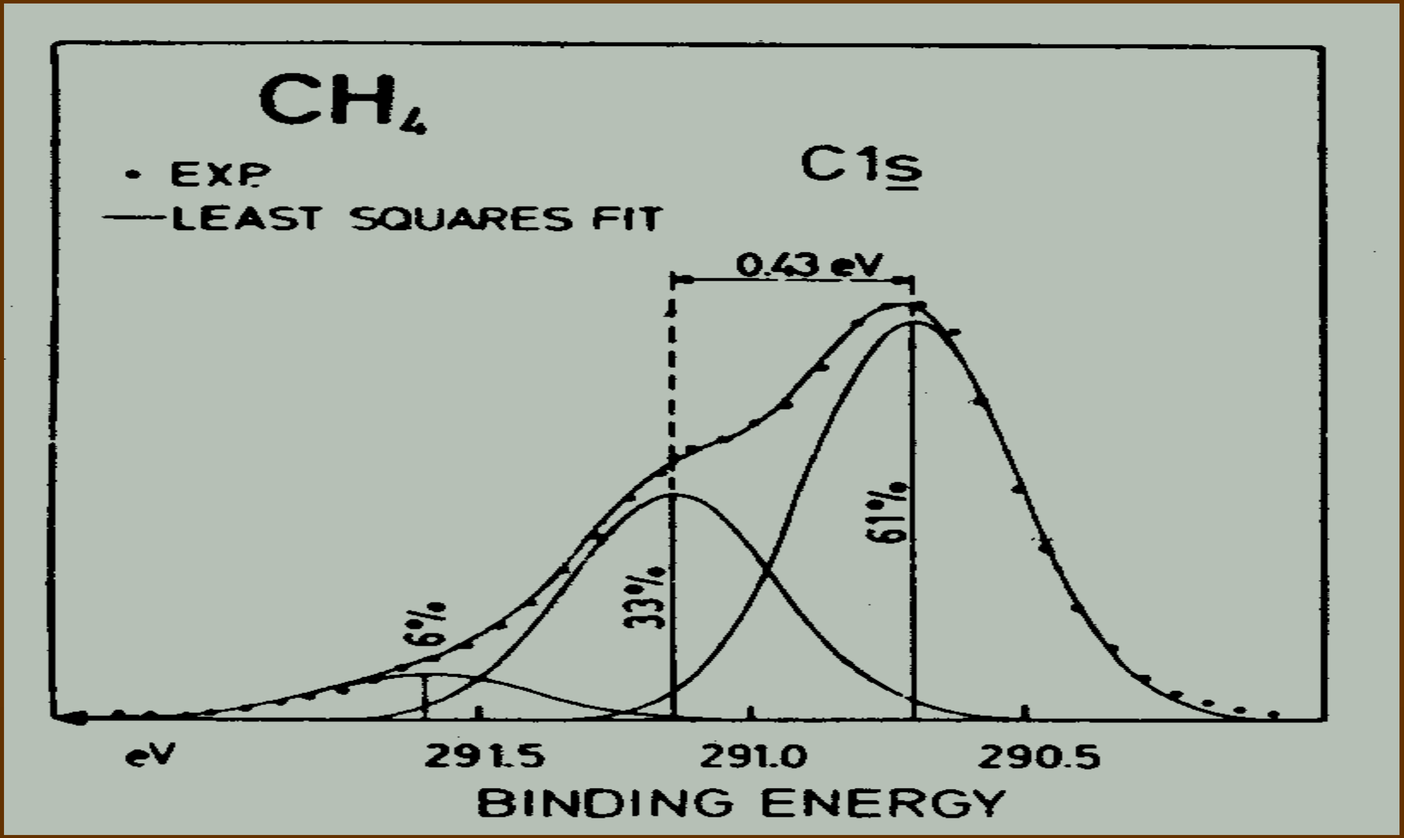
FeF$_2$ 2s and 3s core lines (from S. Hüfner).



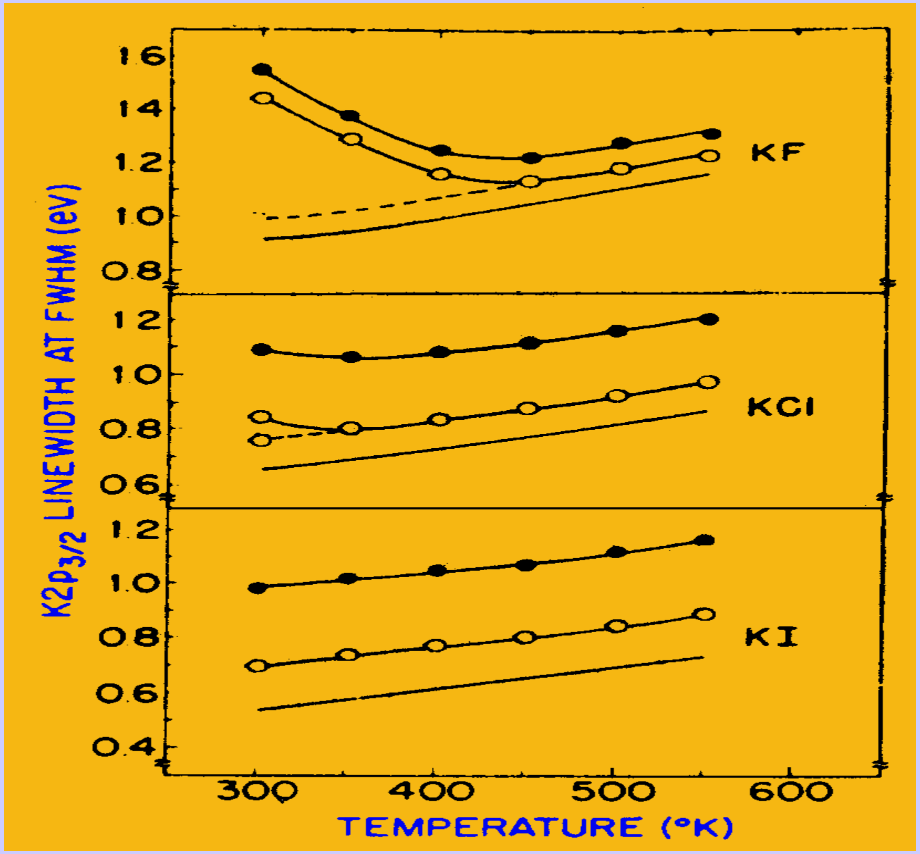
4d XPS of Eu in EuTe (Eu^{2+}). $^2d_{3/2}$ and $^2d_{5/2}$ couple to the $^8S_{7/2}$ of 4f yielding $^7D_{1\ldots5}$ and $^9D_{2\ldots6}$ multiplets (from S. Hüfner).



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



A C1*s* XPS of gaseous CH_4 showing vibrations (from U. Gelius, *J. Electr. Spectr.* 5, 985, 1974).



K2*p*3/2 FWHM withT.—●—●— 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).

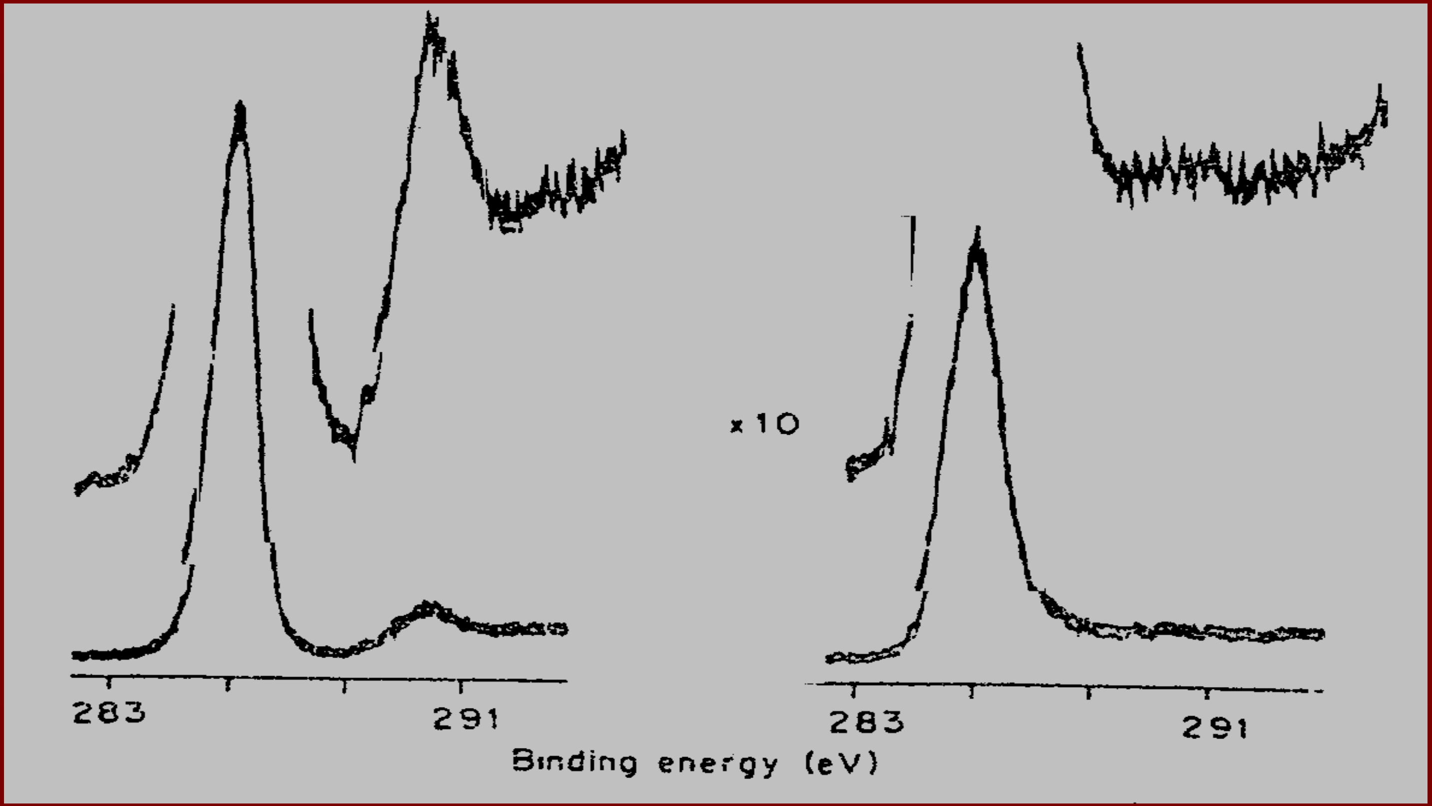
General Uses

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

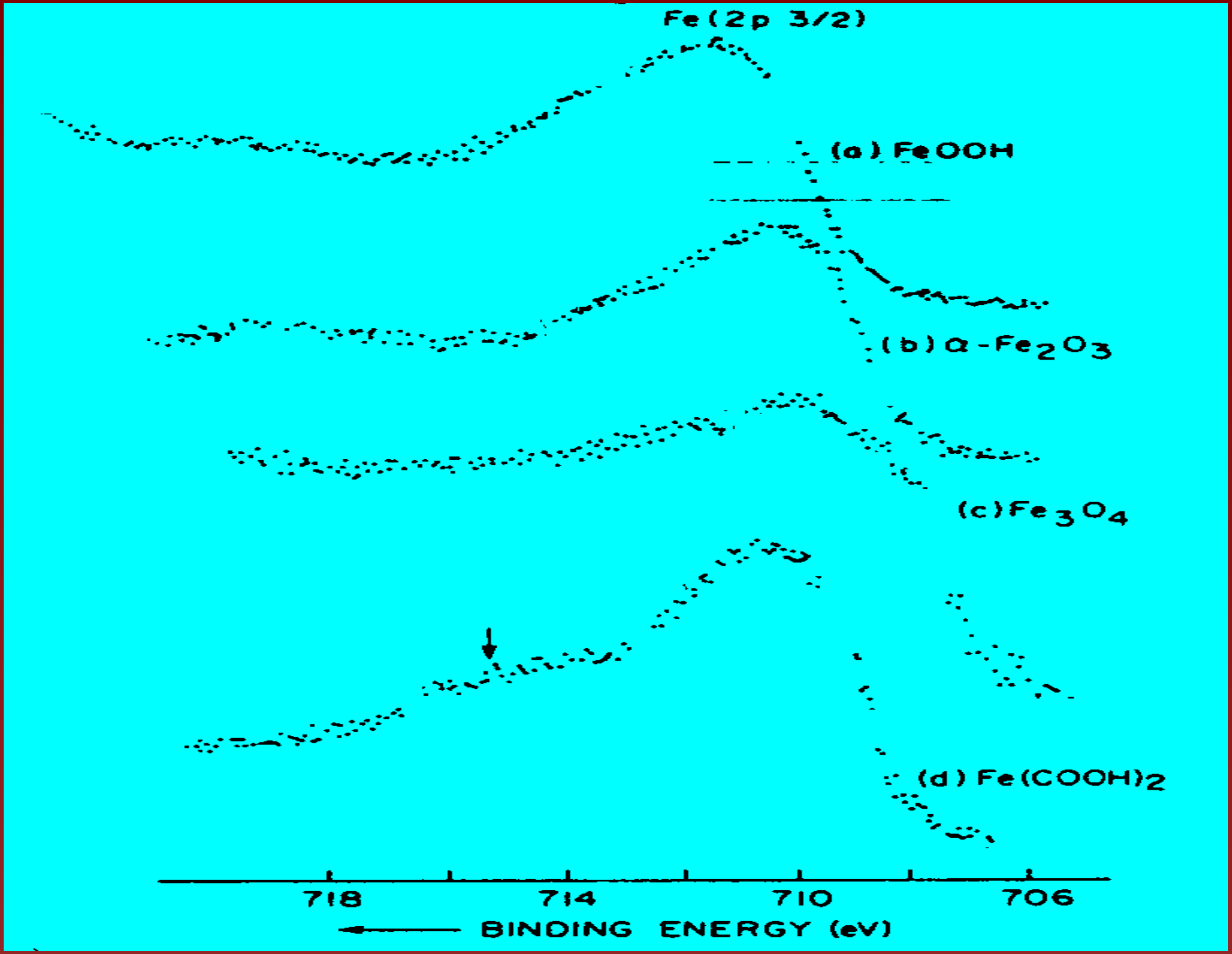
- *Phenomena such as adsorption, desorption, and surface segregation*

- *Determination of chemical states of elements*

- *In situ analysis to determine the chemical reactivity at surface*



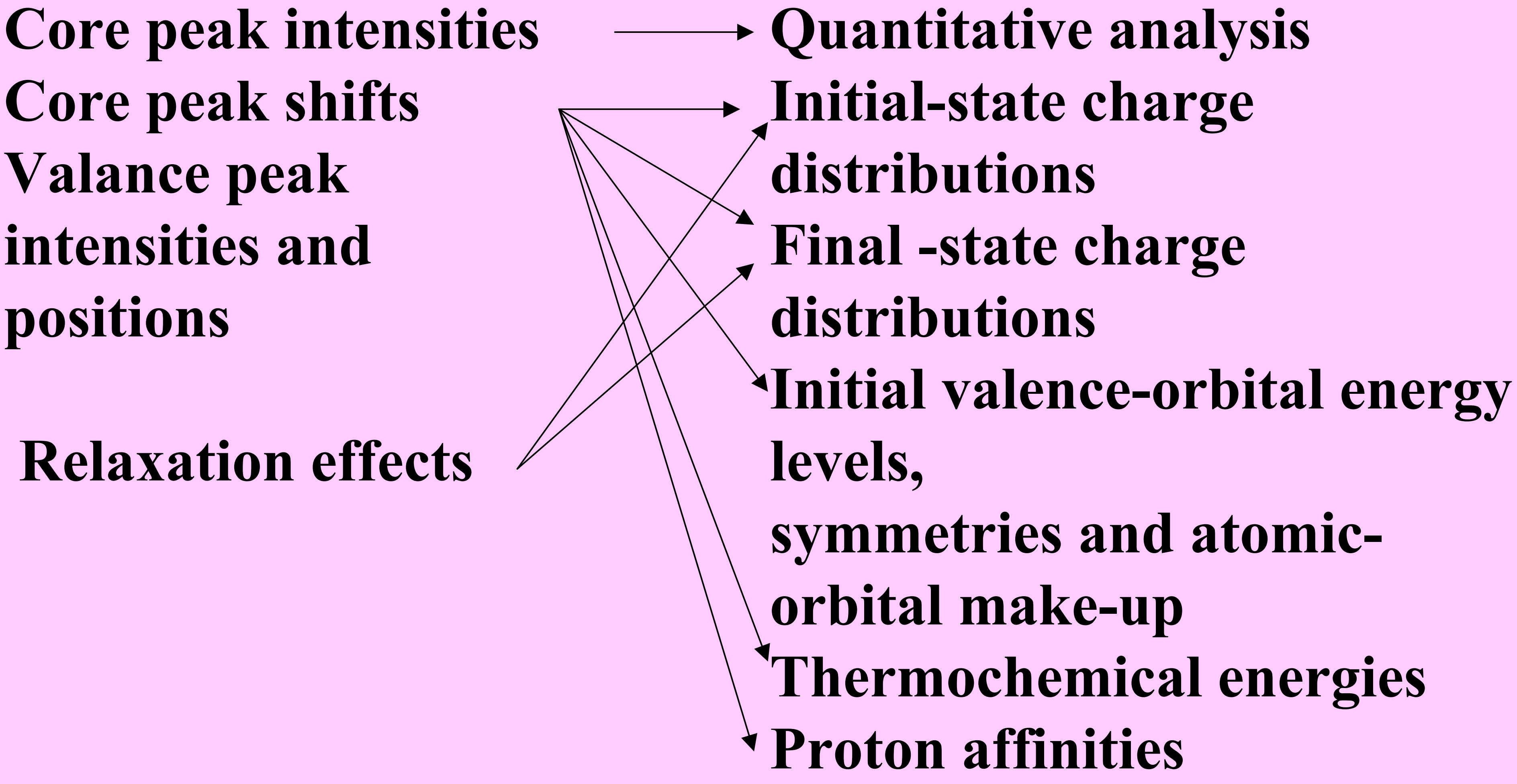
$\pi \rightarrow \pi^*$ shape-up of C1s of polystyrene and its absence after argon ion tching(Briggs and Wootton, Surf. Interfac Anal. 4 (1982) 109.



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

Core peak shifts

Valance peak intensities and positions

Relaxation effects

Quantitative analysis

Initial-state charge distributions

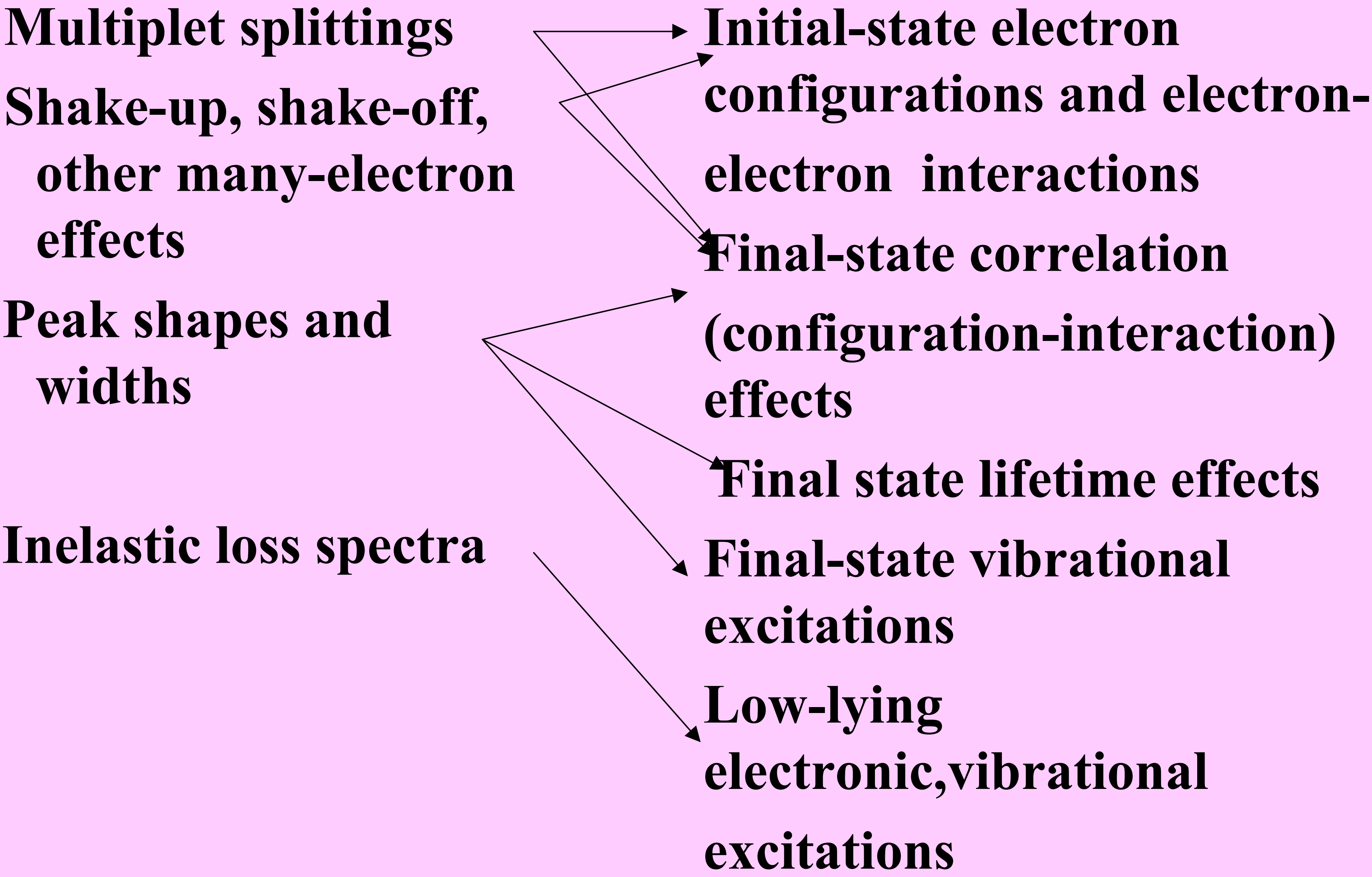
Final -state charge distributions

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

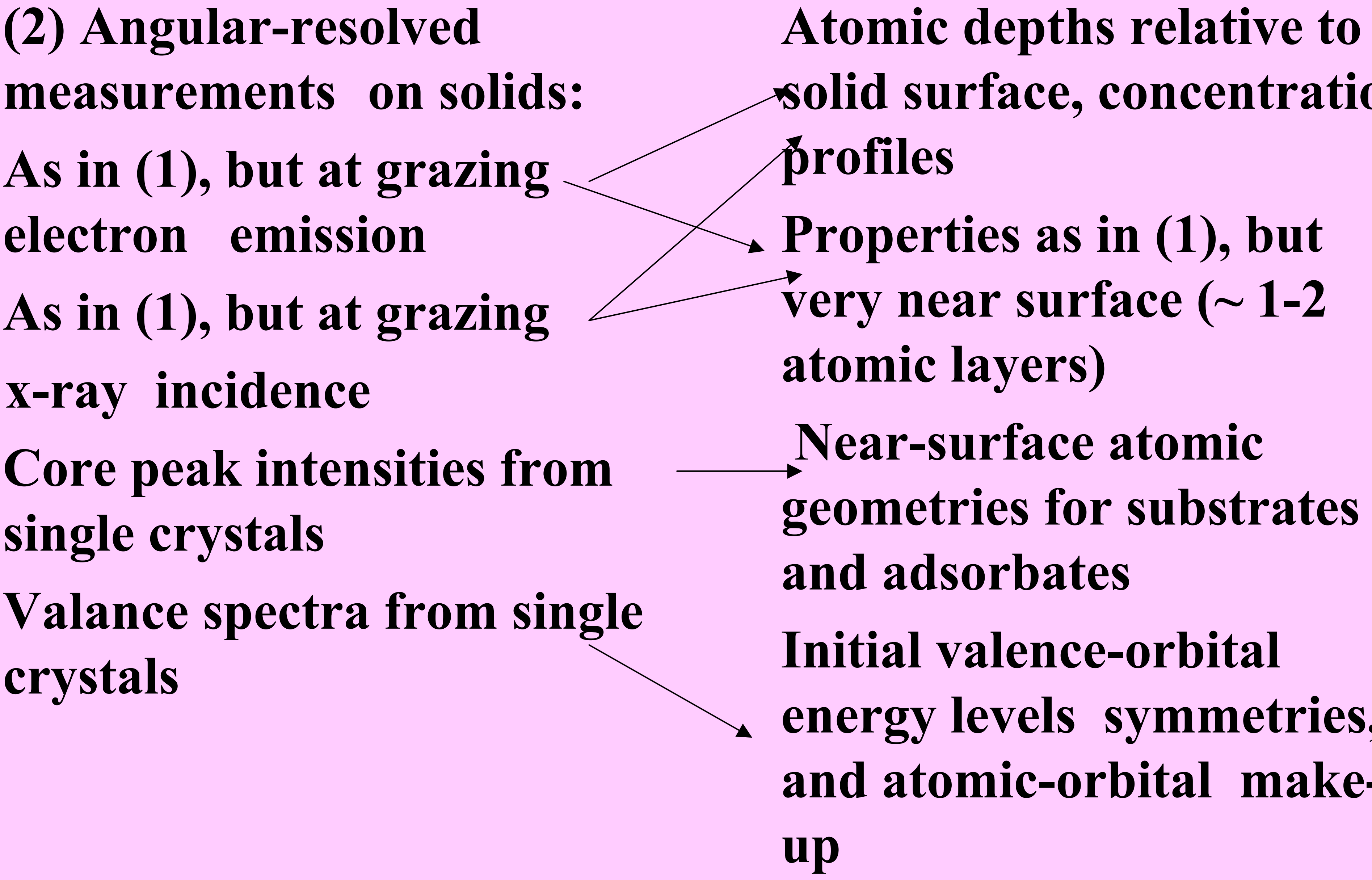
Final-state correlation (configuration-interaction) effects

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, concentratio 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