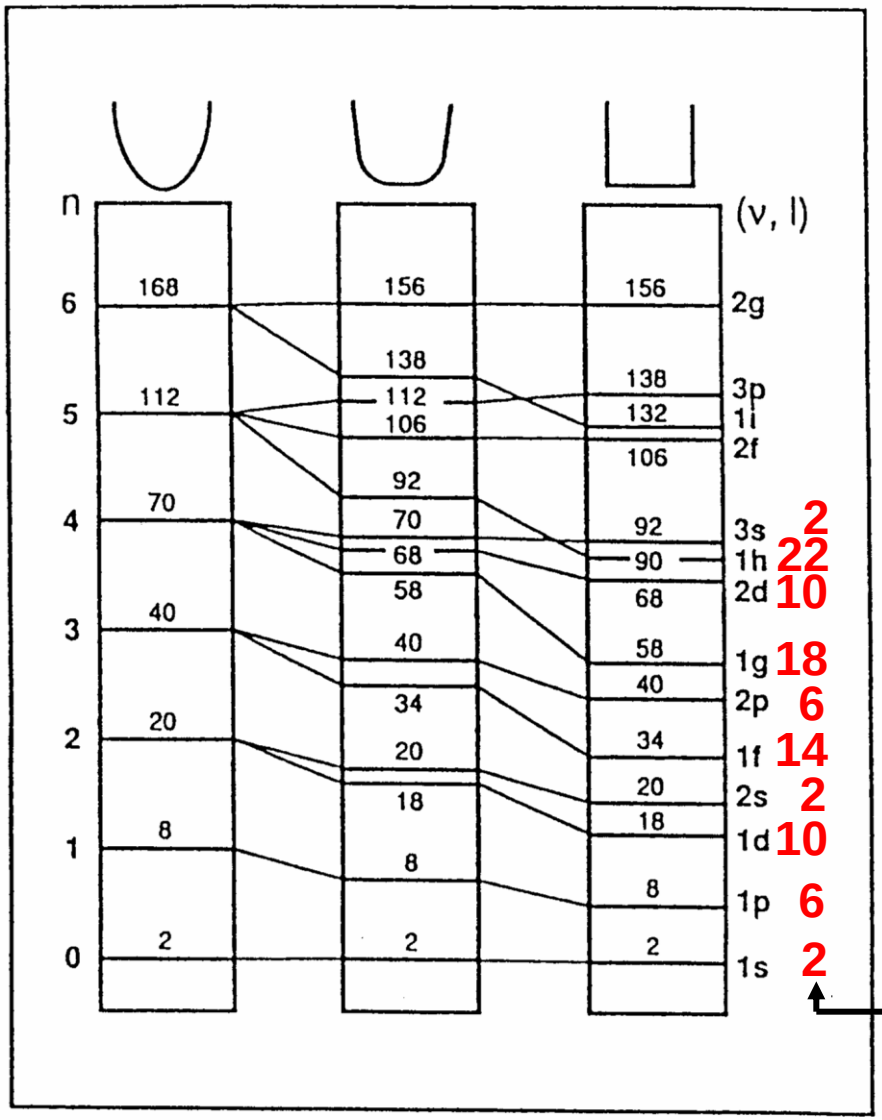
lecture 19.1.2012
we had so far:

- binding in clusters and their appearances in mass spectra
  d) metallic bonding

today

- more to metallic bonding
- photoelectron spectroscopy
- trends in photoionization and detachment energies

The spherical jellium model: role of the potential like in *nuclear physics*



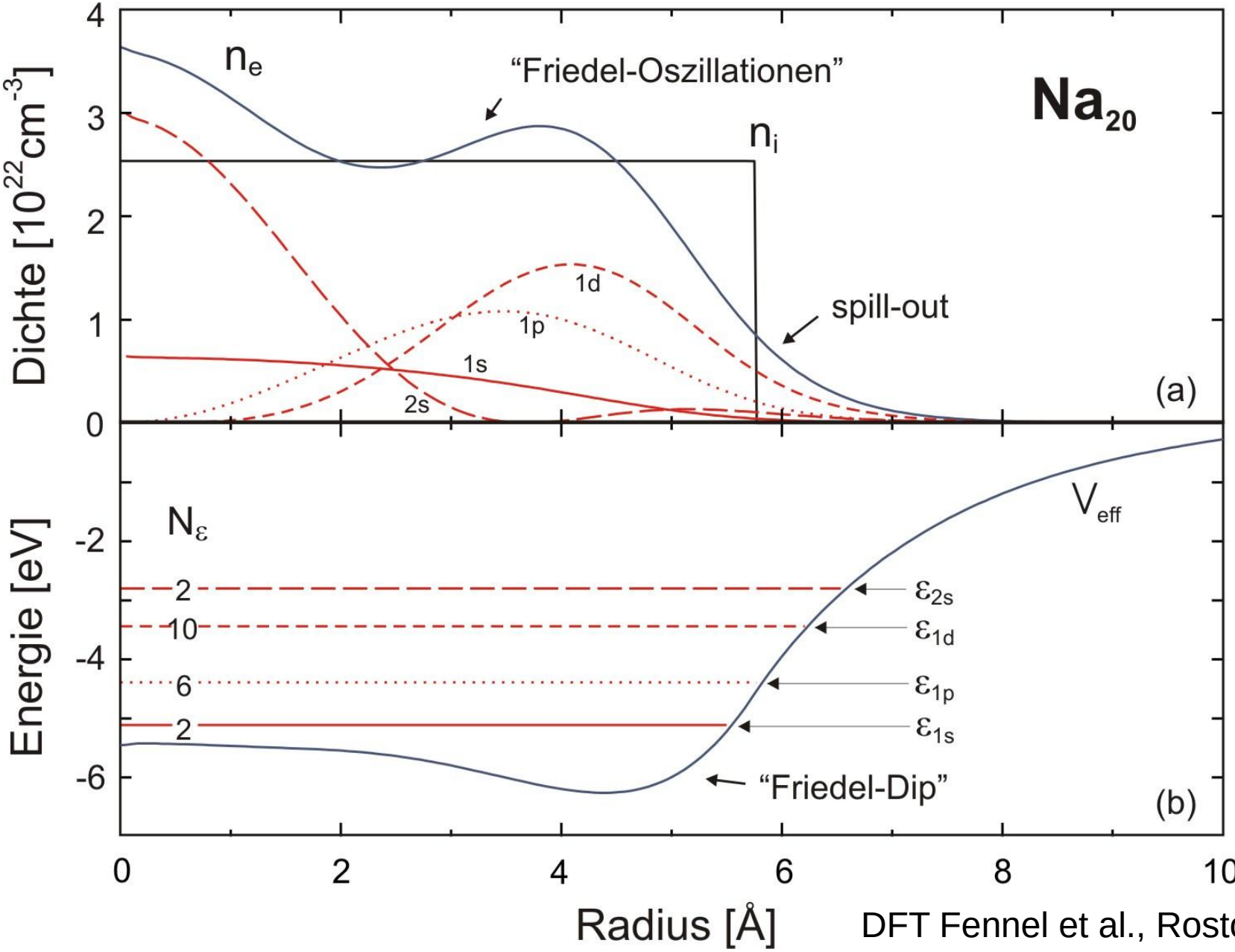
Explains the magic numbers of neutral alkali clusters :
2, 8, 20, 40, 58, 70, 92 ...

Also explains the magic numbers for divalent metals such as zinc or cadmium, at 4,9,10,17,20,29 ... atoms.

$2(2l+1)$ electrons

After: Mayer-Kuckuk, Kernphysik

the jellium model

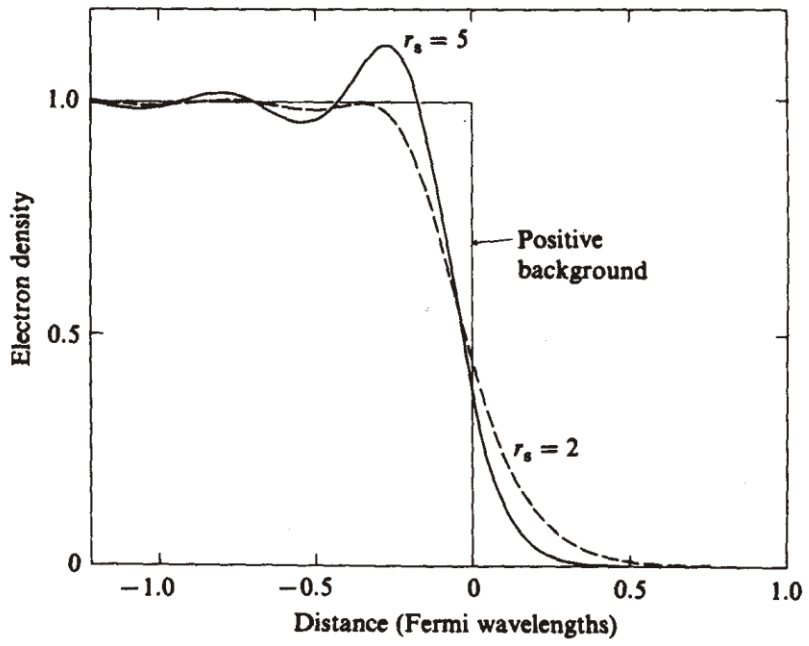


DFT Fennel et al., Rostock

compare: metal surfaces - resulting electron density

- electron density n(z) shows oscillations (Friedel oszillations)
- n(z) spills out beyond the ionic charge (electron spill-out)
- spill-out produces a surface dipole

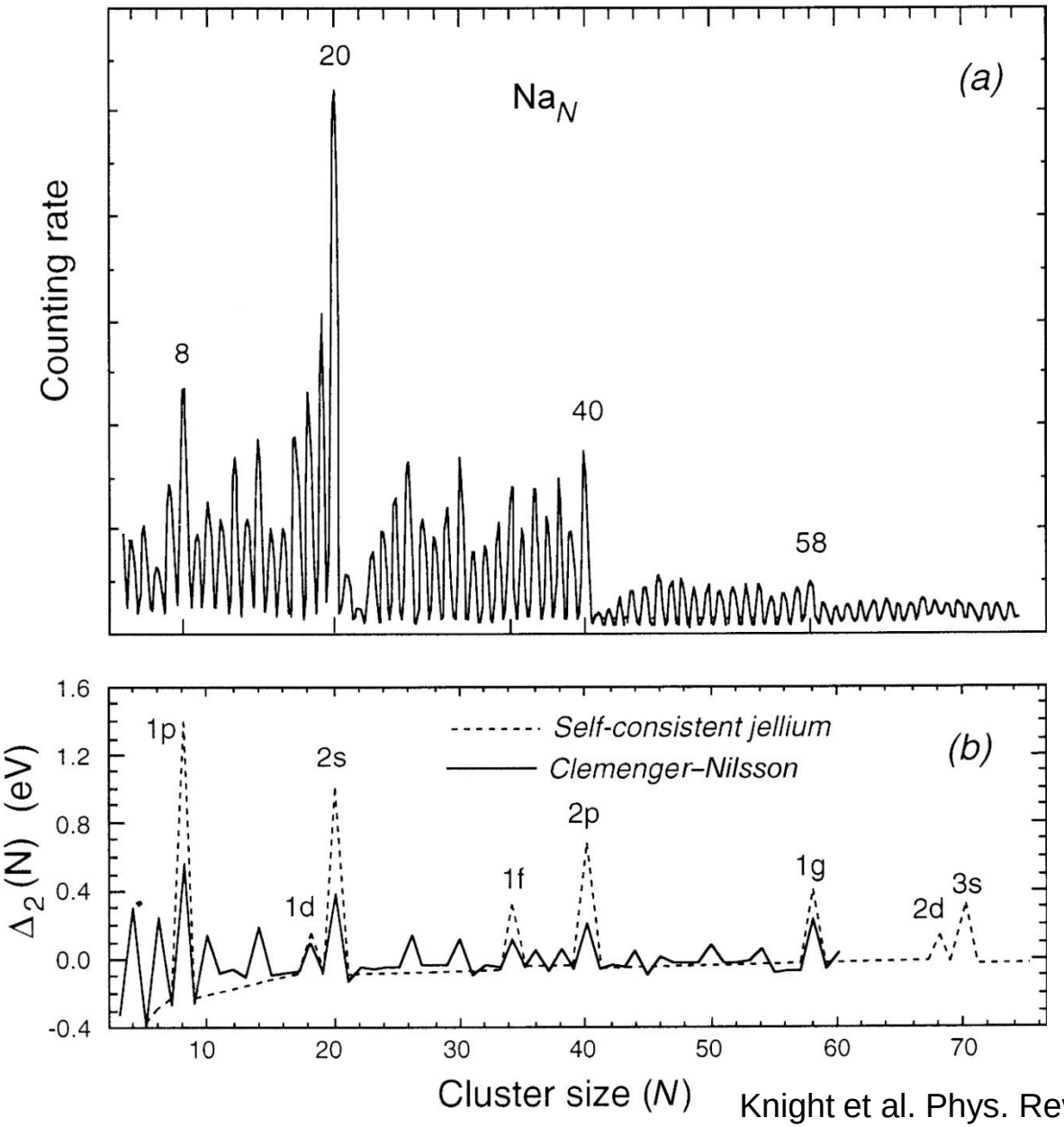
Fig. 4.2. Electron density profile at a jellium surface for two choices of the background density, r_s (Lang & Kohn, 1970).



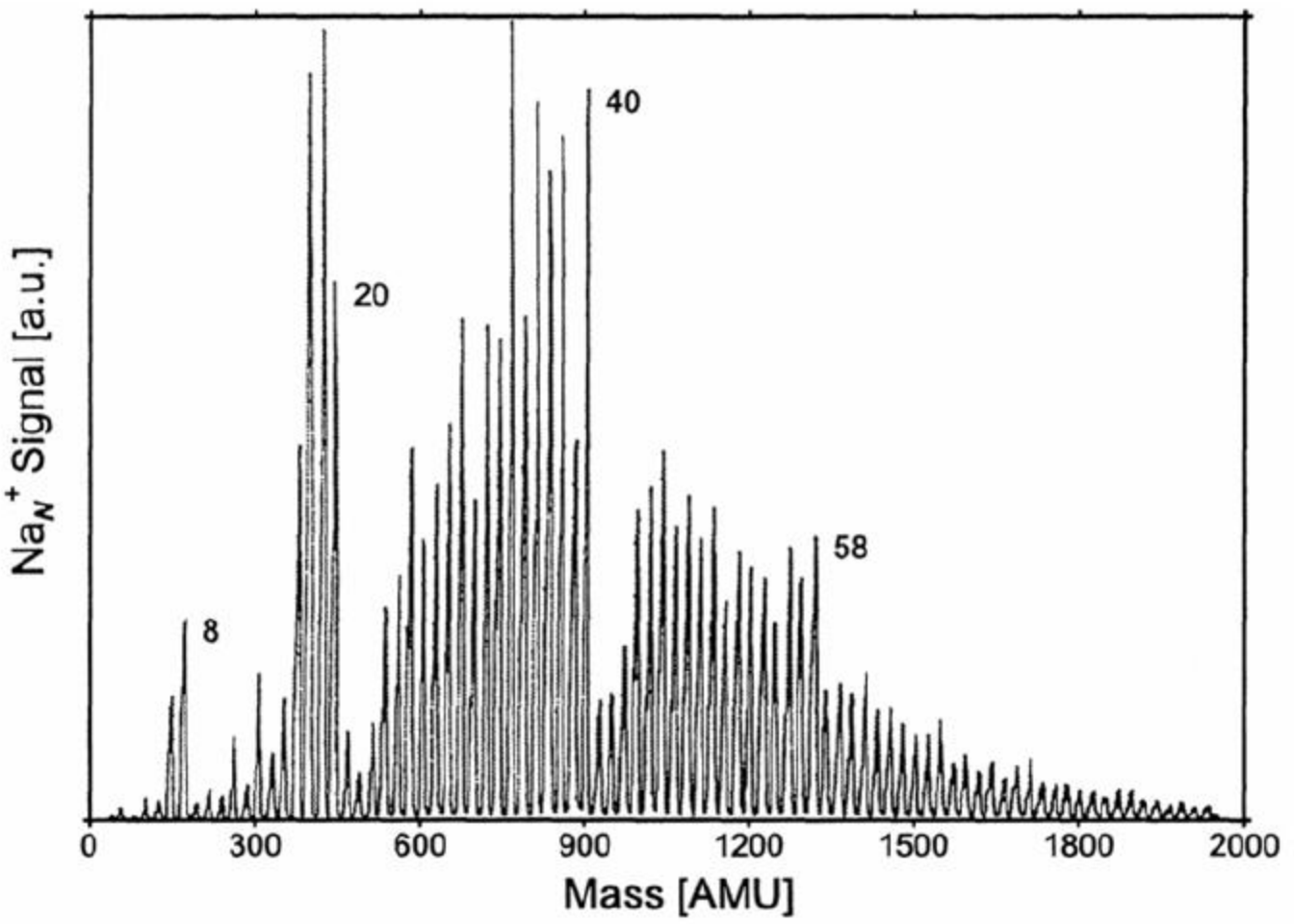
Ursache der Oszillation:
Elektronen mit festen Wellenvektor versuchen pos. Hintergrundladung abzuschirmen; hieraus folgen leichte Verschiebungen der einzelnen Atom-lagen im Bereich der Oberfläche

Zangwill, page 58

jellium fingerprint in the mass spectra

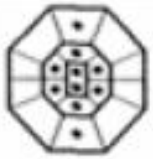
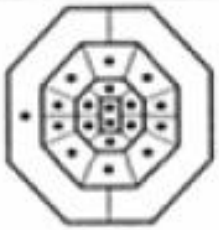
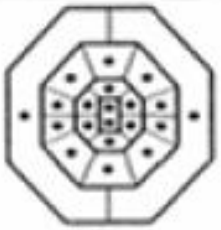


Knight et al. Phys. Rev. Lett. 52, 2141 (1984)



M. Kappes, R. W. Kunz, und E. Schumacher,
Chem. Phys. Lett. 91, 413(1982)

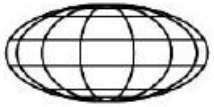
like a periodic table: the shell model for Na clusters

Shell	Monovalent				Closed shells
1*s*	 Na				 Na_2
1*p*	 Na_3	 Na_4	—··—▶	 Na_7	 Na_8
1*d*	 Na_9	 Na_{10}	—··—▶	 Na_{17}	 Na_{18}
2*s*	 Na_{19}				 Na_{20}

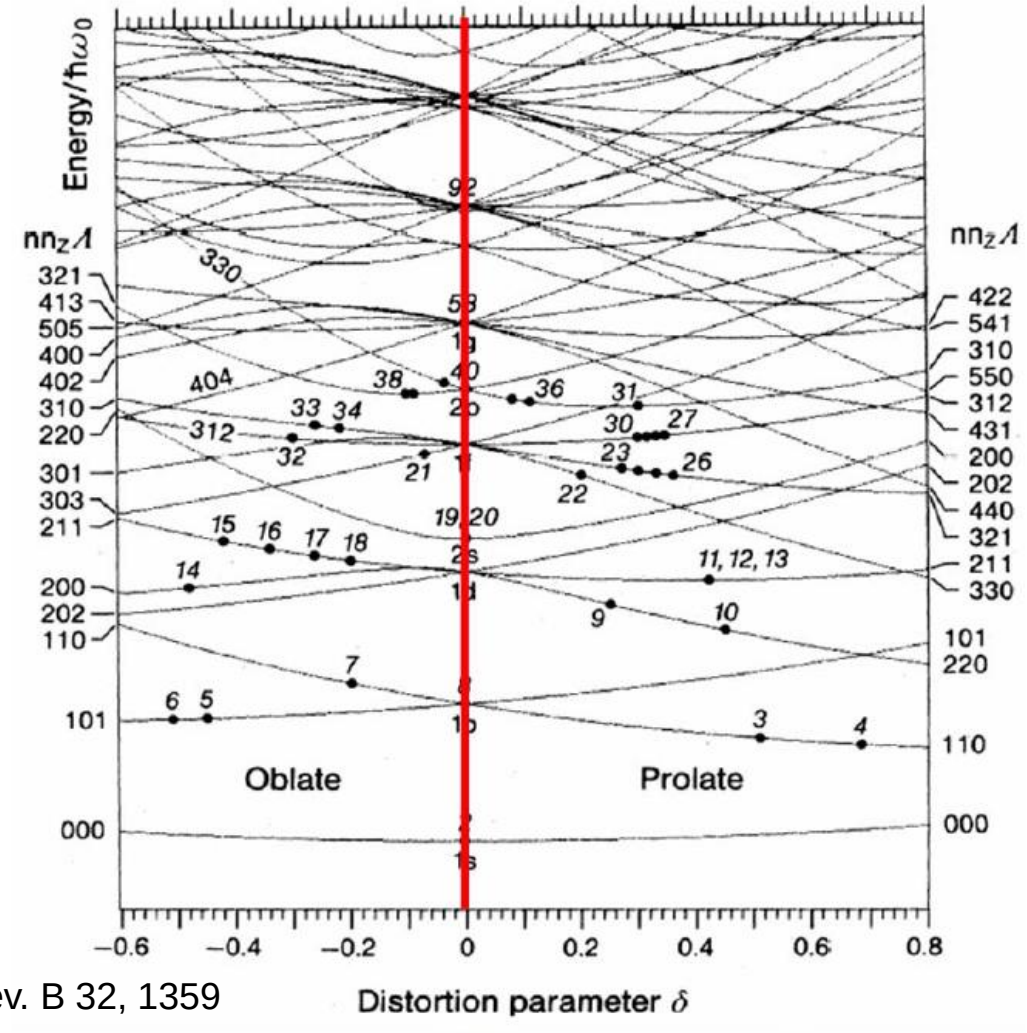
in *Metal Clusters at Surfaces*, KH Meiwes-Broer, Springer 2000

sub shells through distortion: the Clemenger-Nielsson model

oblate deformation

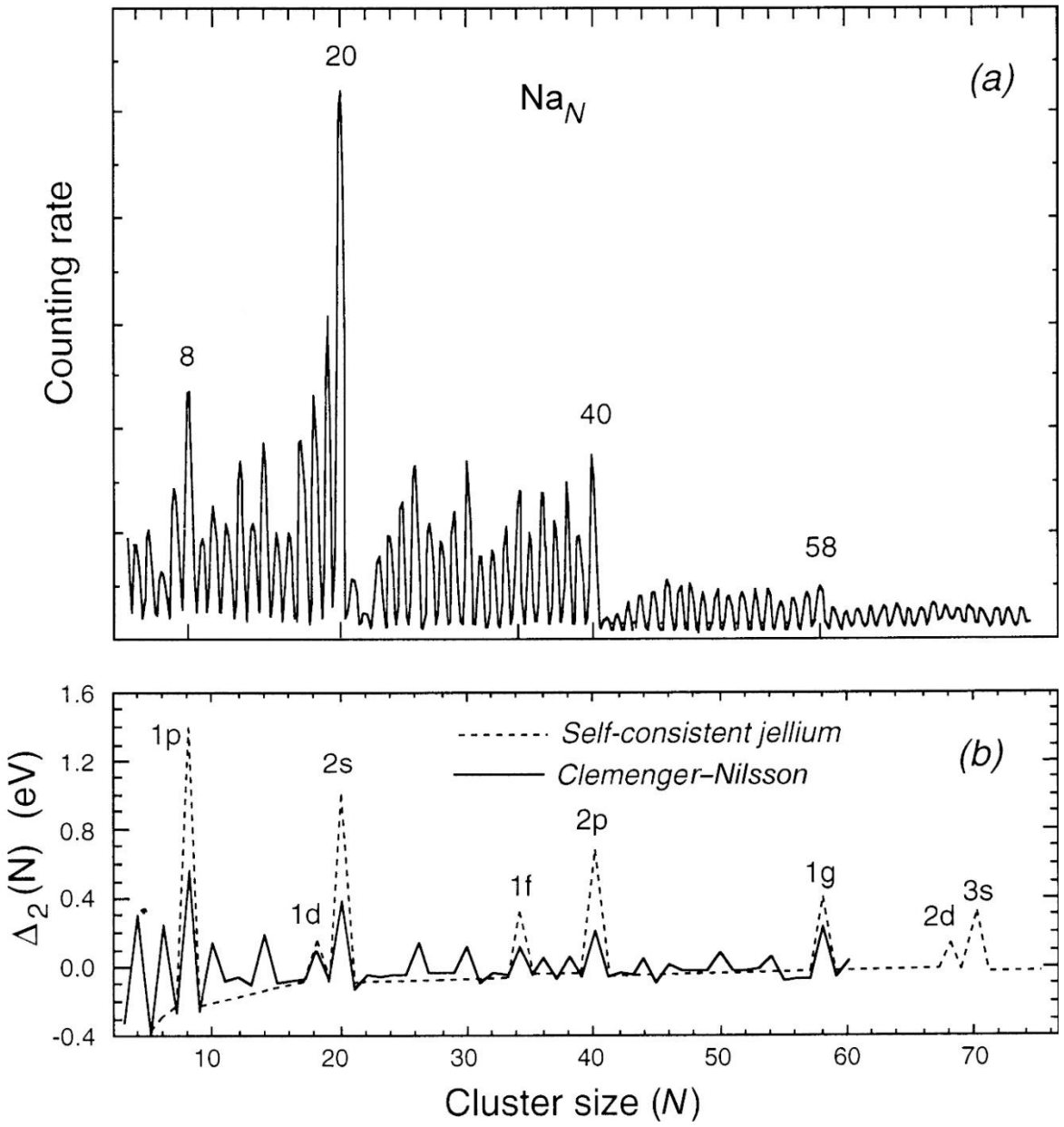


prolate deformation



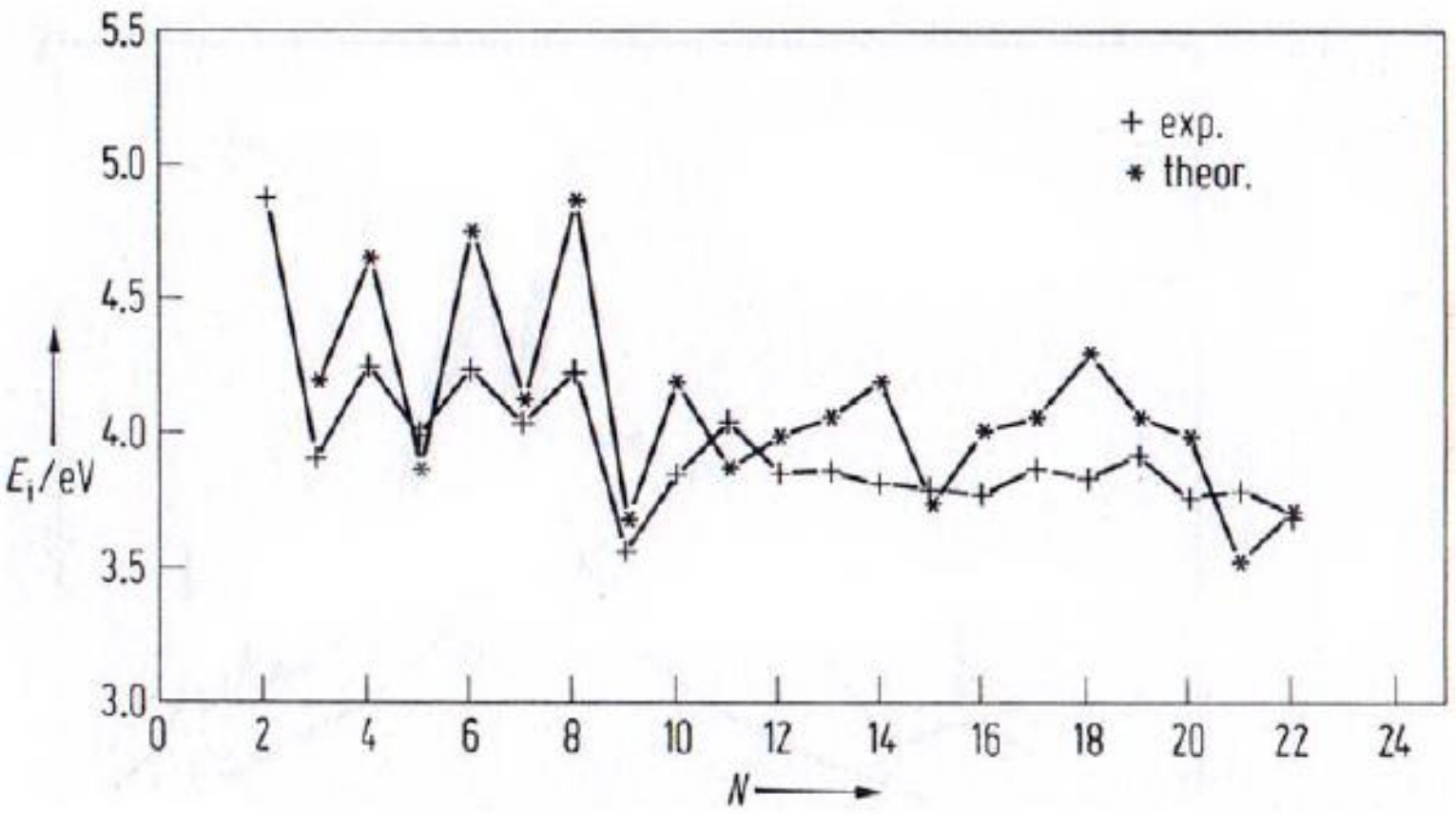
K. Clemenger, Phys.Rev. B 32, 1359 (1985)

deformations explain the sub-shell closings



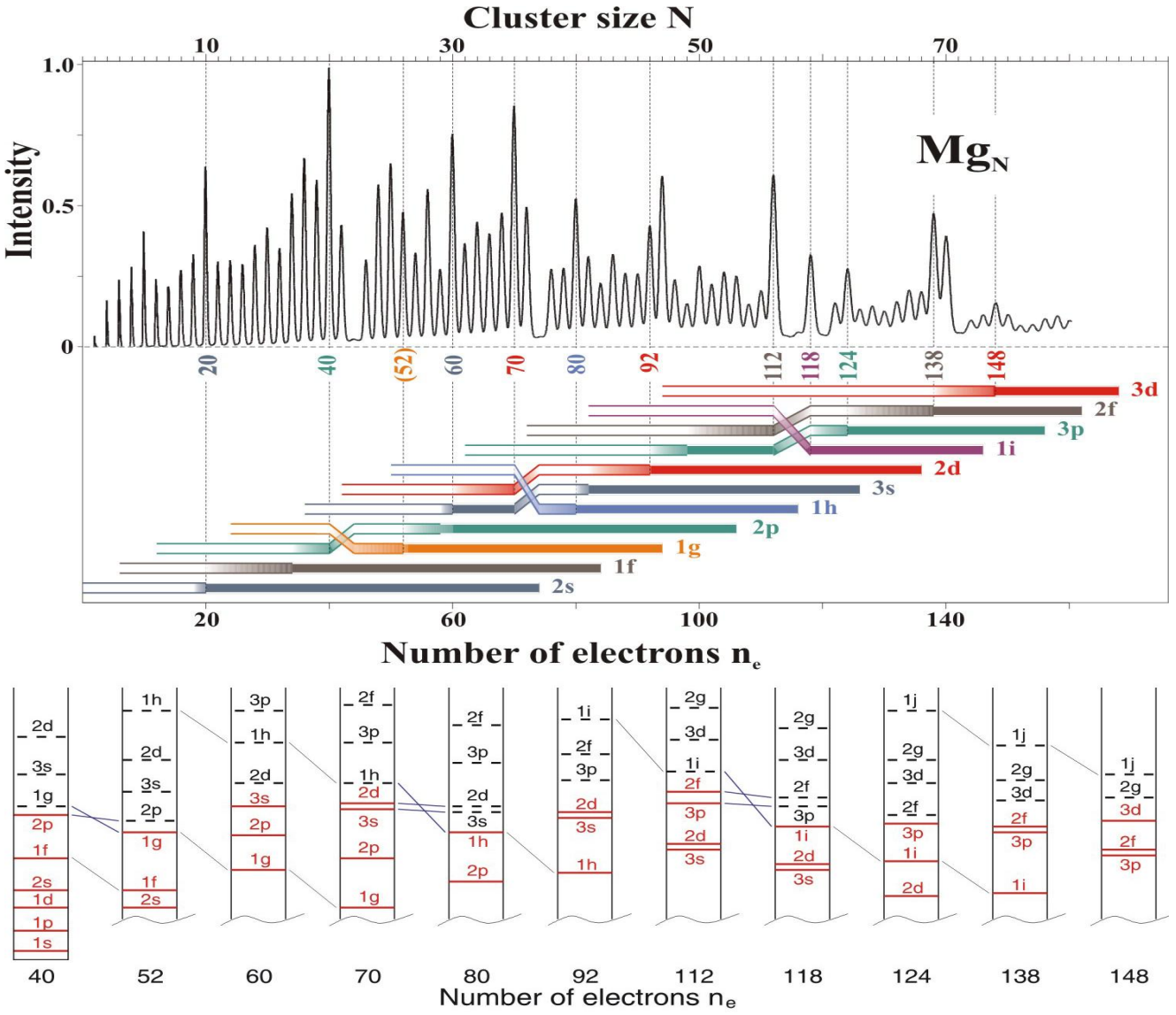
Knight et al.

early direct evidence for electronic shells: ionization energies of Na clusters

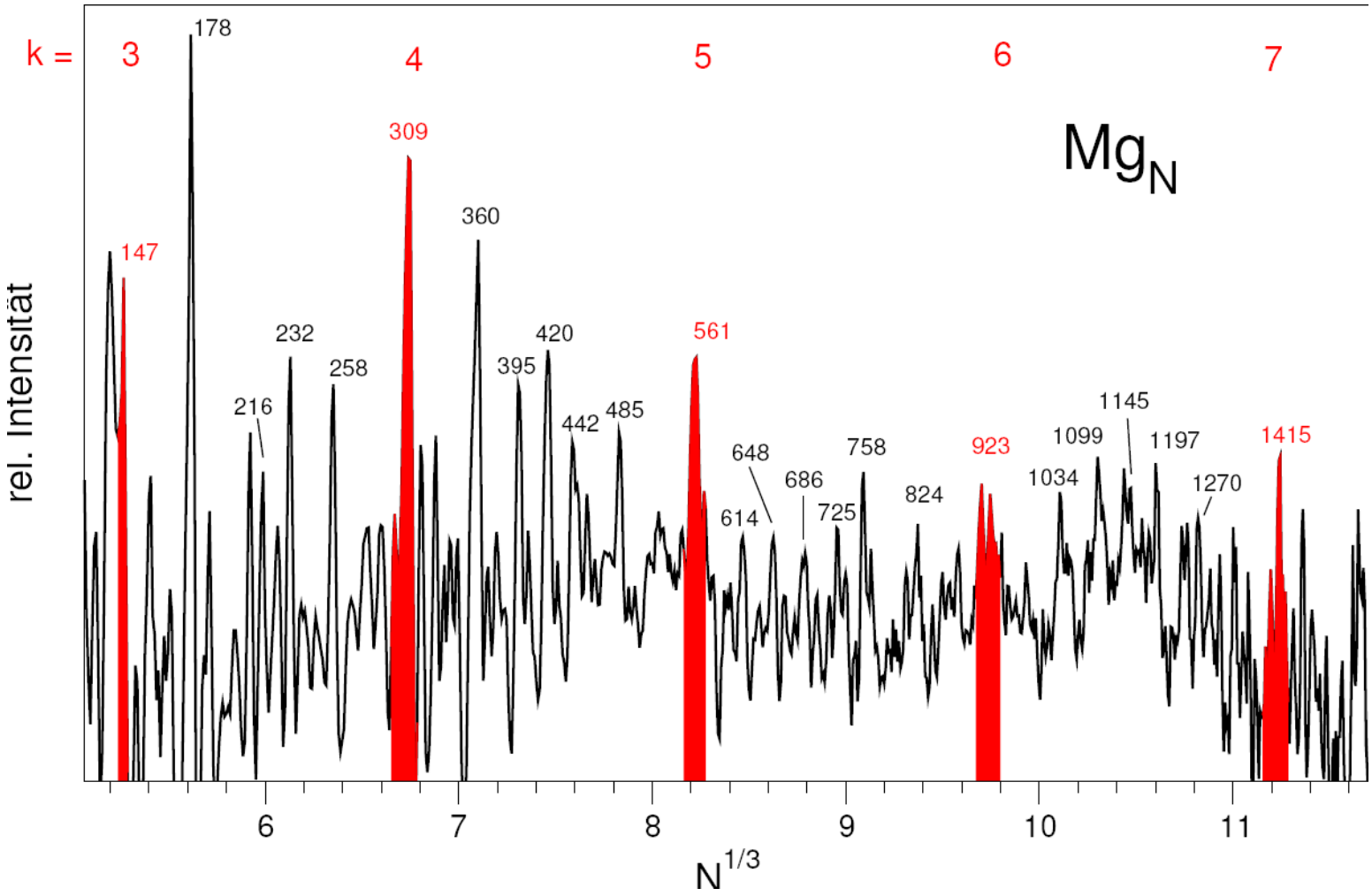


H. Haberland: Cluster. in *Lehrbuch der Experimentalphysik, W. Raith, de* Gruyter, 1992

Small Magnesium clusters as another example for a jellium system.
Now each atom contributes with two electrons

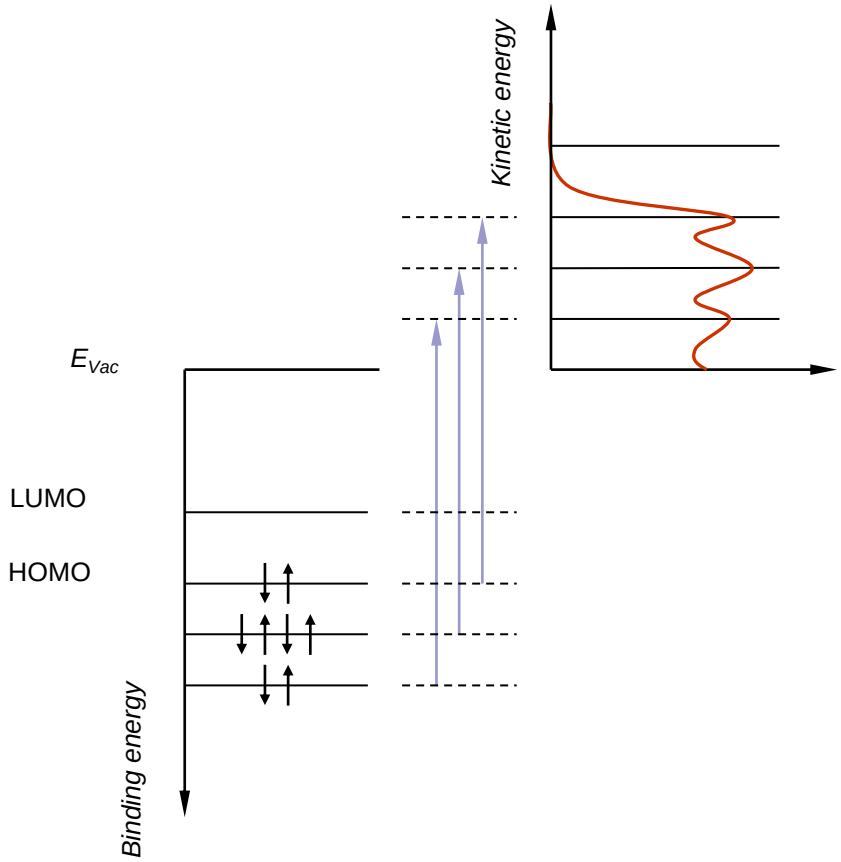


Electronic vs. geometrical shell
Example: large Mg_N show both, electronic and geom. shells



Diederich et al., Rostock

how to measure the electronic structure?
by photoelectron spectroscopy



$$E_{kin} = h\nu - E_B$$

technical challenge: extremely low target density as it is necessary to work with a *charged* cluster beam. Only charged clusters can be mass selected

Magnetic bottle electron spectrometer

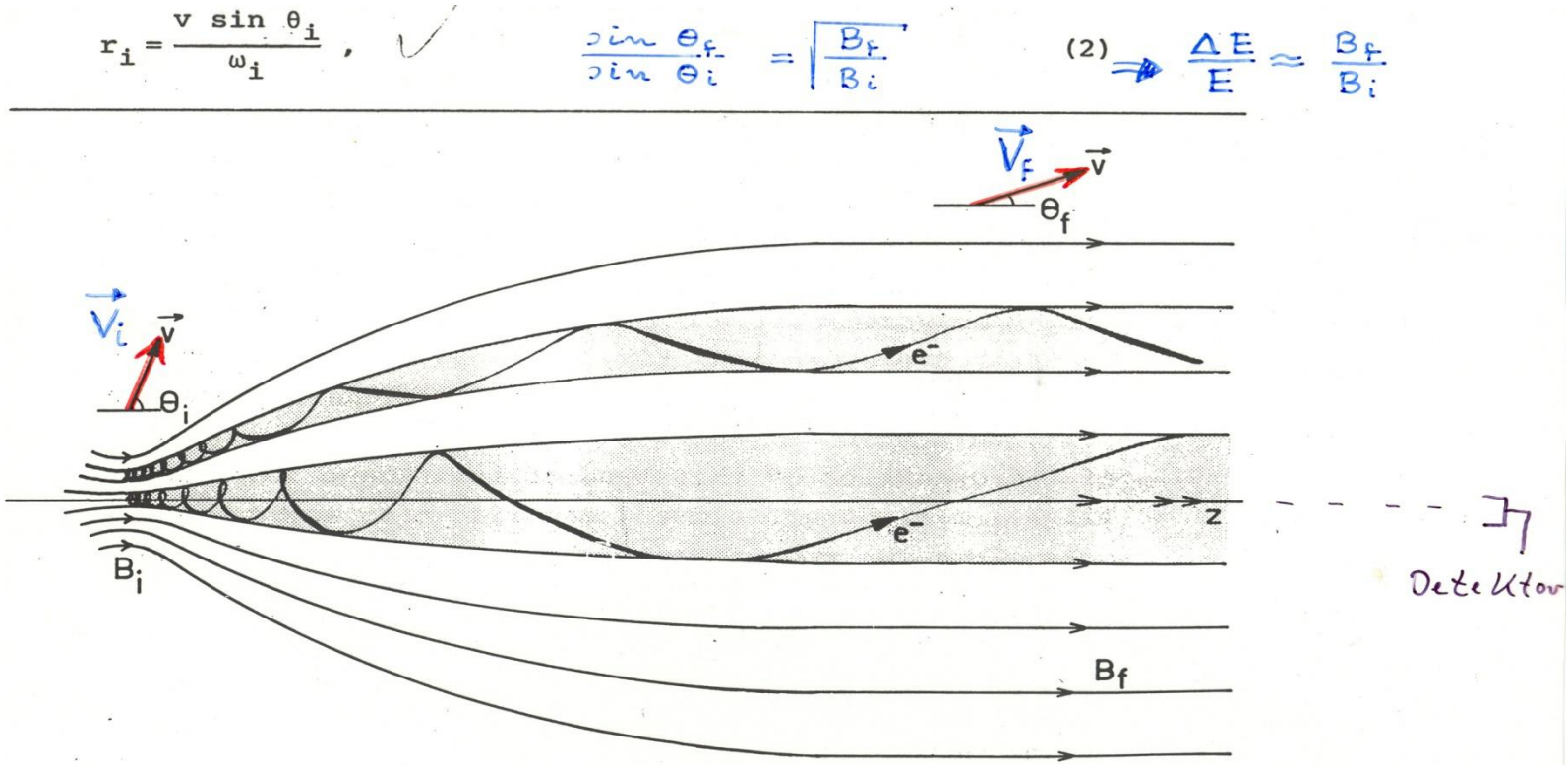


Figure 1

Schematic diagram showing the helical motion of an electron moving in a magnetic field that changes gradually from a strong field B_i to a weaker uniform field B_f.

Kruit, Read

in the limit of a strong gradient and a long drift area, the flight times of electrons with the same energy are independent of the emission angle.
detection efficency of about 50 %

technical realization of a magnetic-bottle electron spectrometer

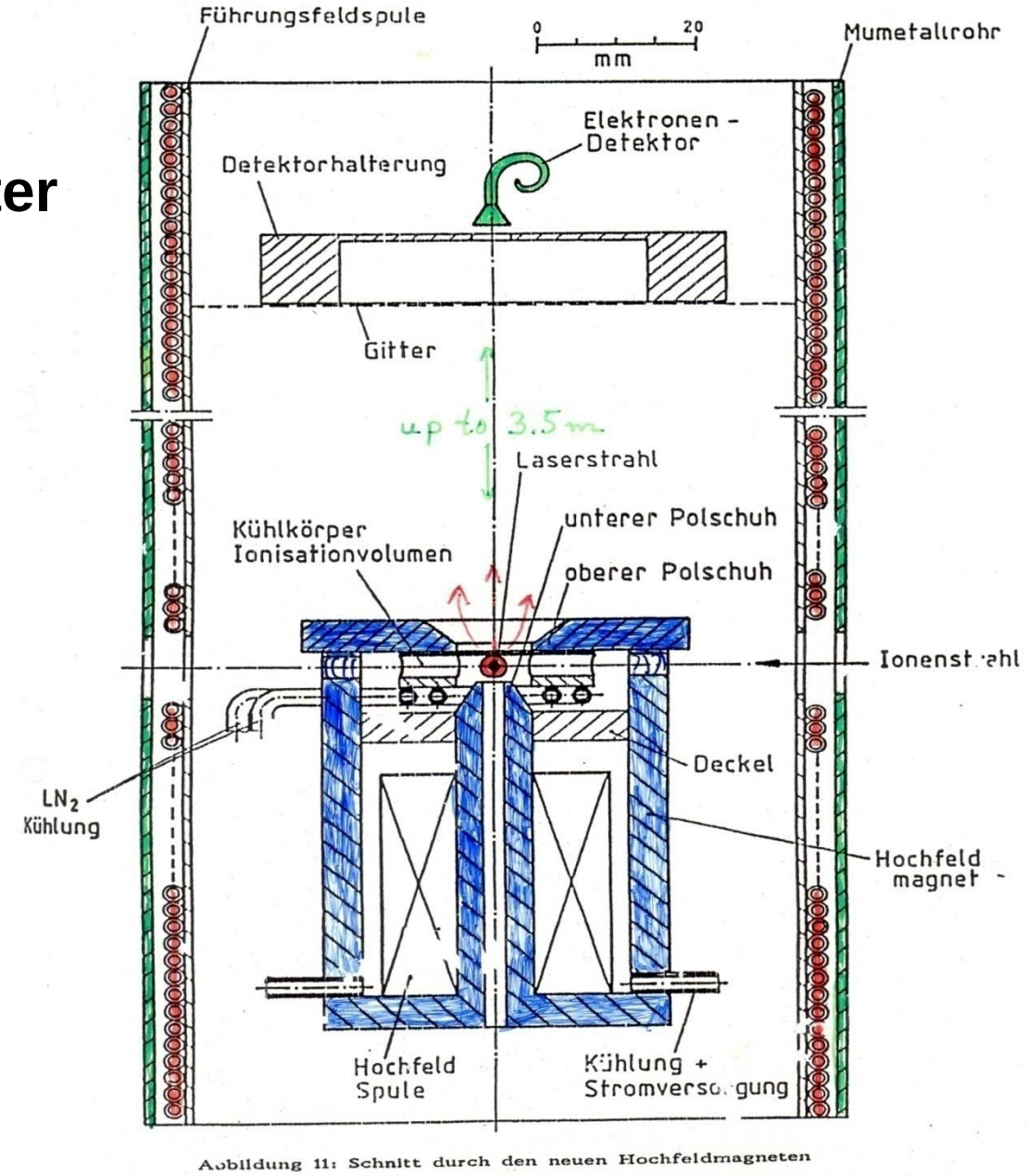
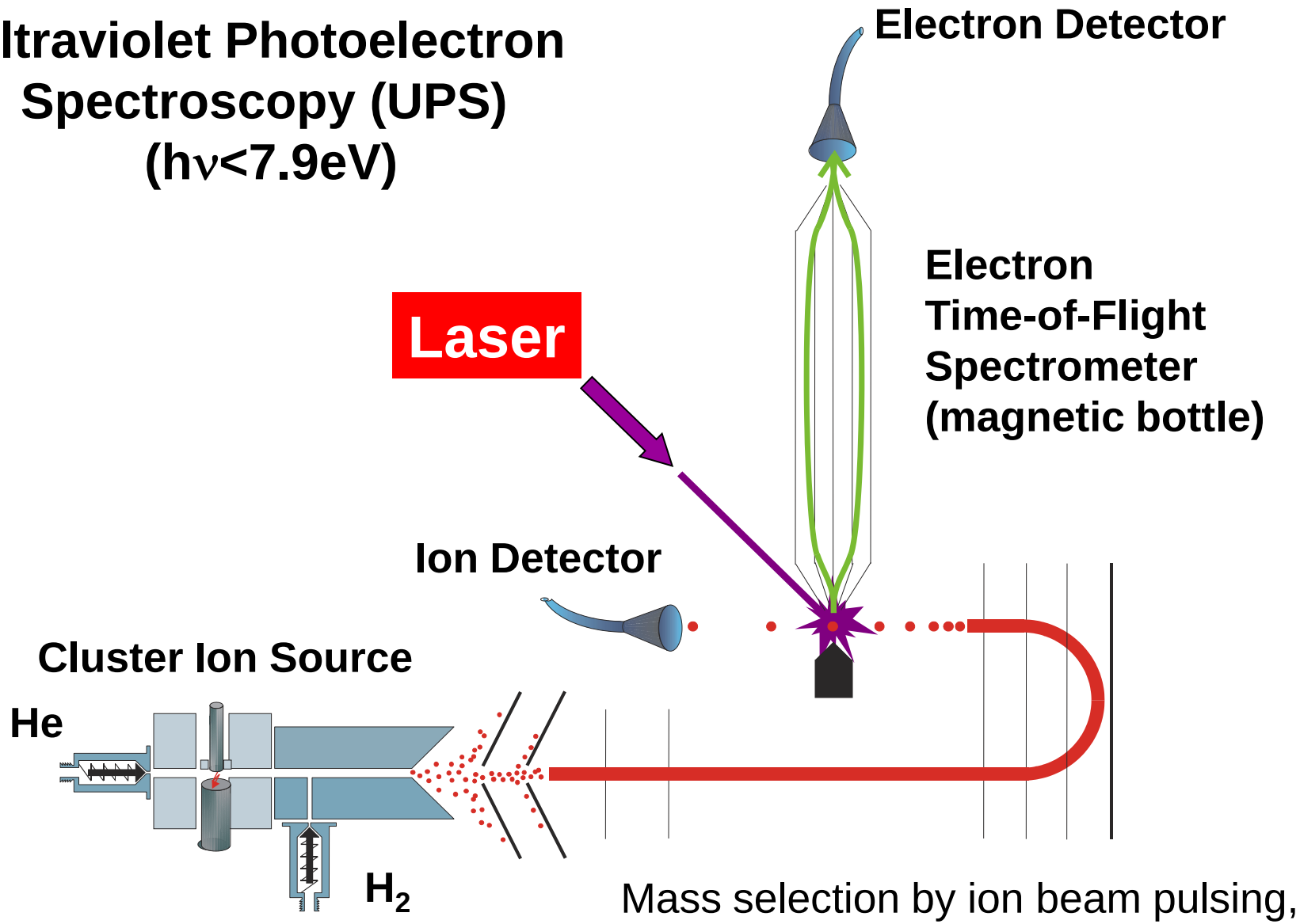


Abbildung 11: Schnitt durch den neuen Hochfeldmagneten

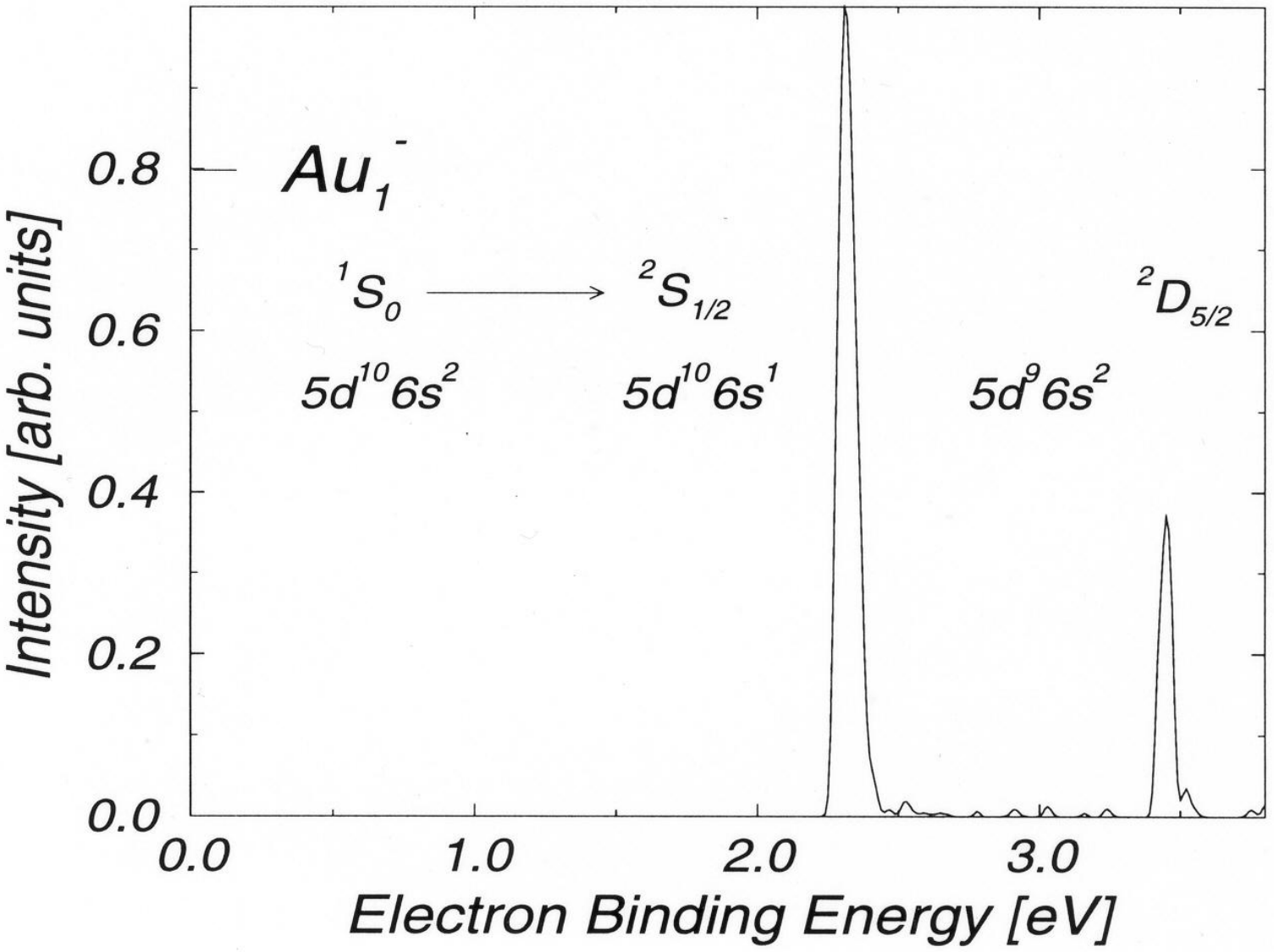
Ultraviolet Photoelectron Spectroscopy (UPS) ($h\nu$<7.9eV)



Mass selection by ion beam pulsing, i.e. by timing

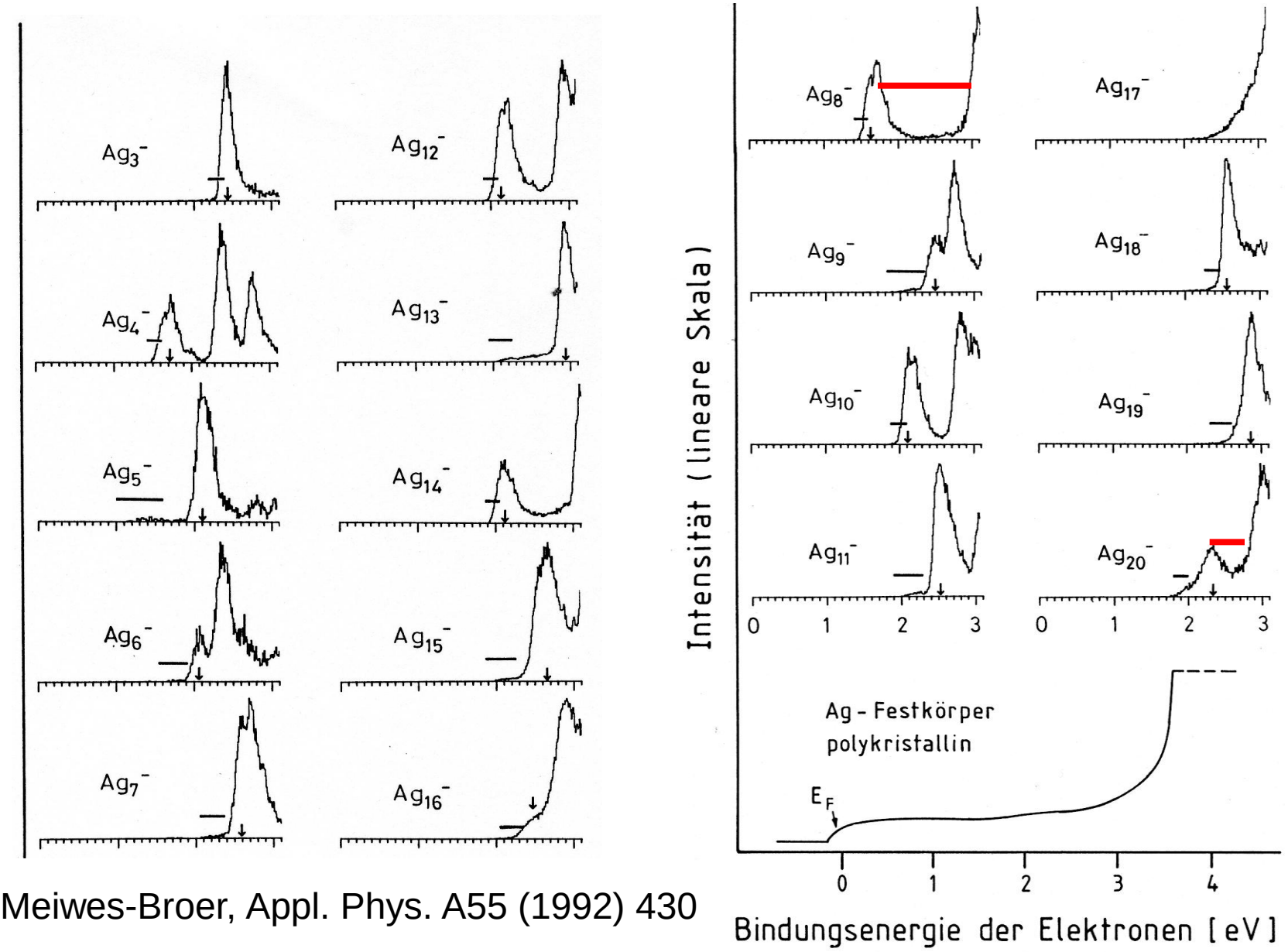
Setup Ganteför group, Konstanz

Calibration mag. bottle spectrometer with Au_1^-



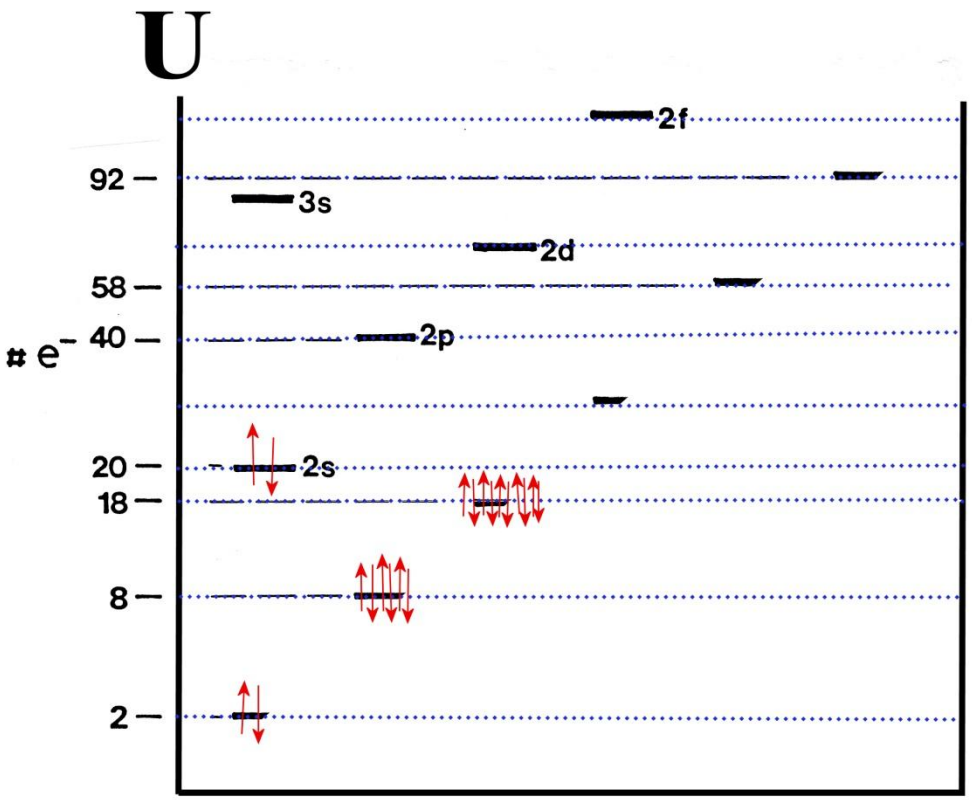
Group Meiwes-Broer, Rostock

photoelectron spectra from Ag_N^-



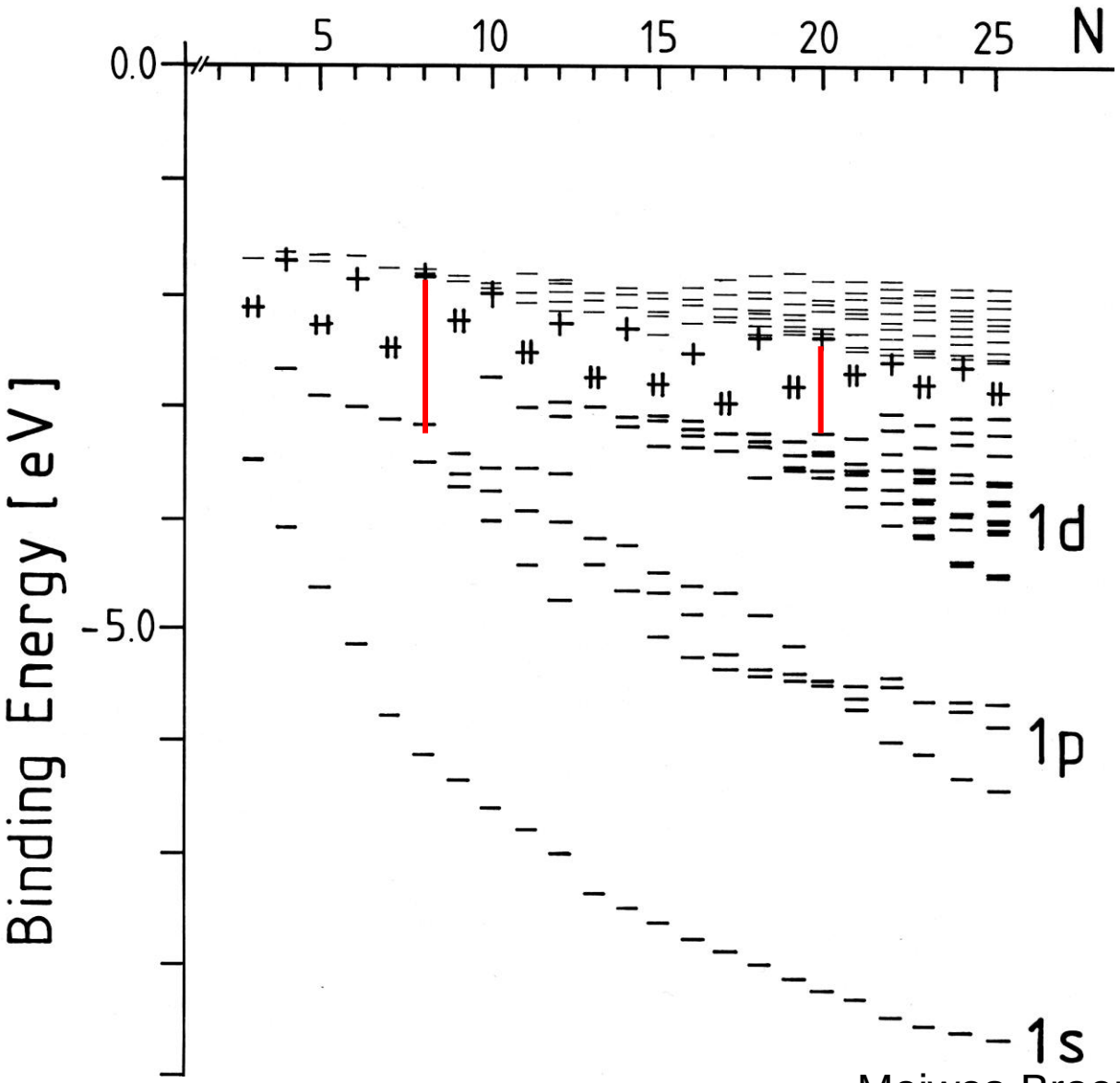
Meiwes-Broer, Appl. Phys. A55 (1992) 430

comparison with the jellium model



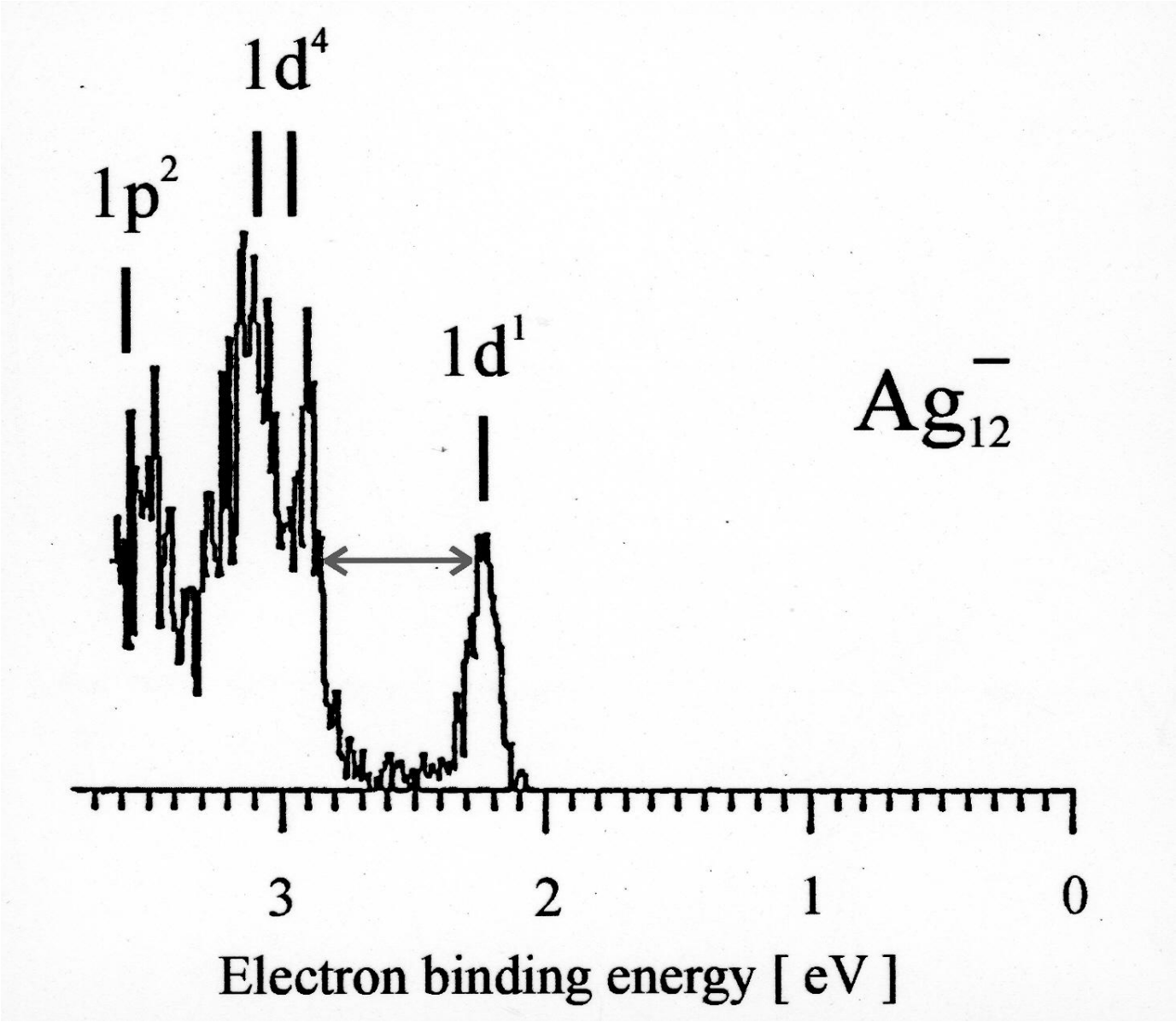
pronounced energy gaps after 8 and 20 electrons, but there are more gaps due to lifting of degeneracy

Ag_N^- effective medium theory



Better theory:
One-electron energy levels of An_N^- by tight-binding calculations within the effective medium theory

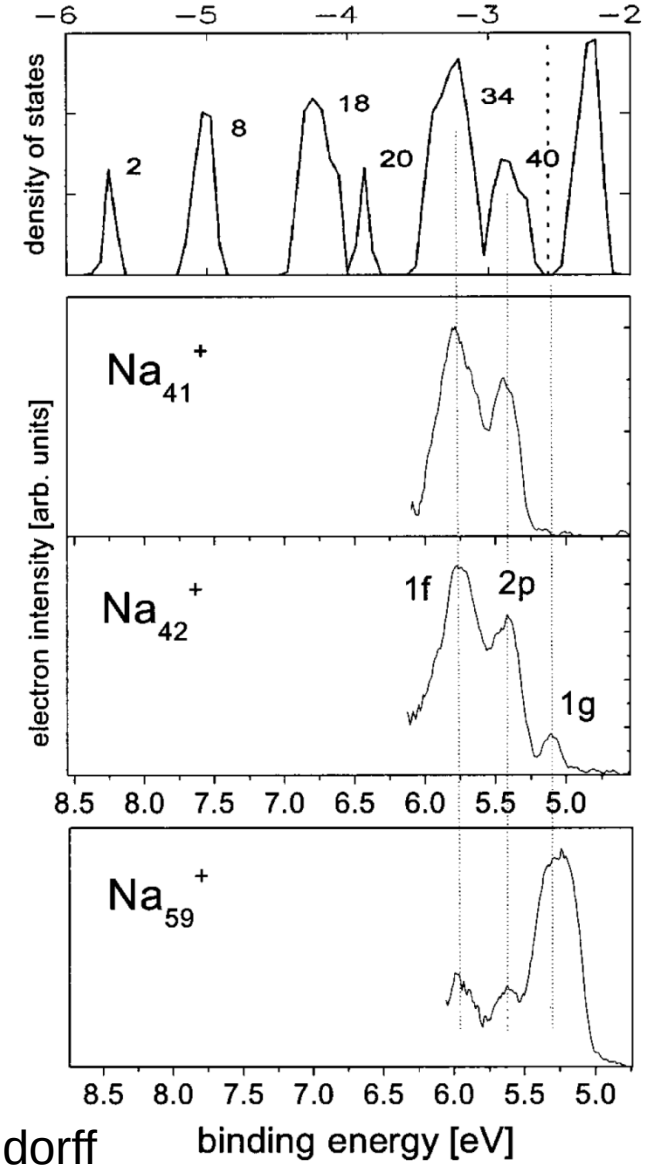
Meiwes-Broer, Appl. Phys. A55 (1992) 430



fine details of the electronic structure can be resolved

comparison PES with jellium calculations

Density of states from KS single-particle energy eigenvalues

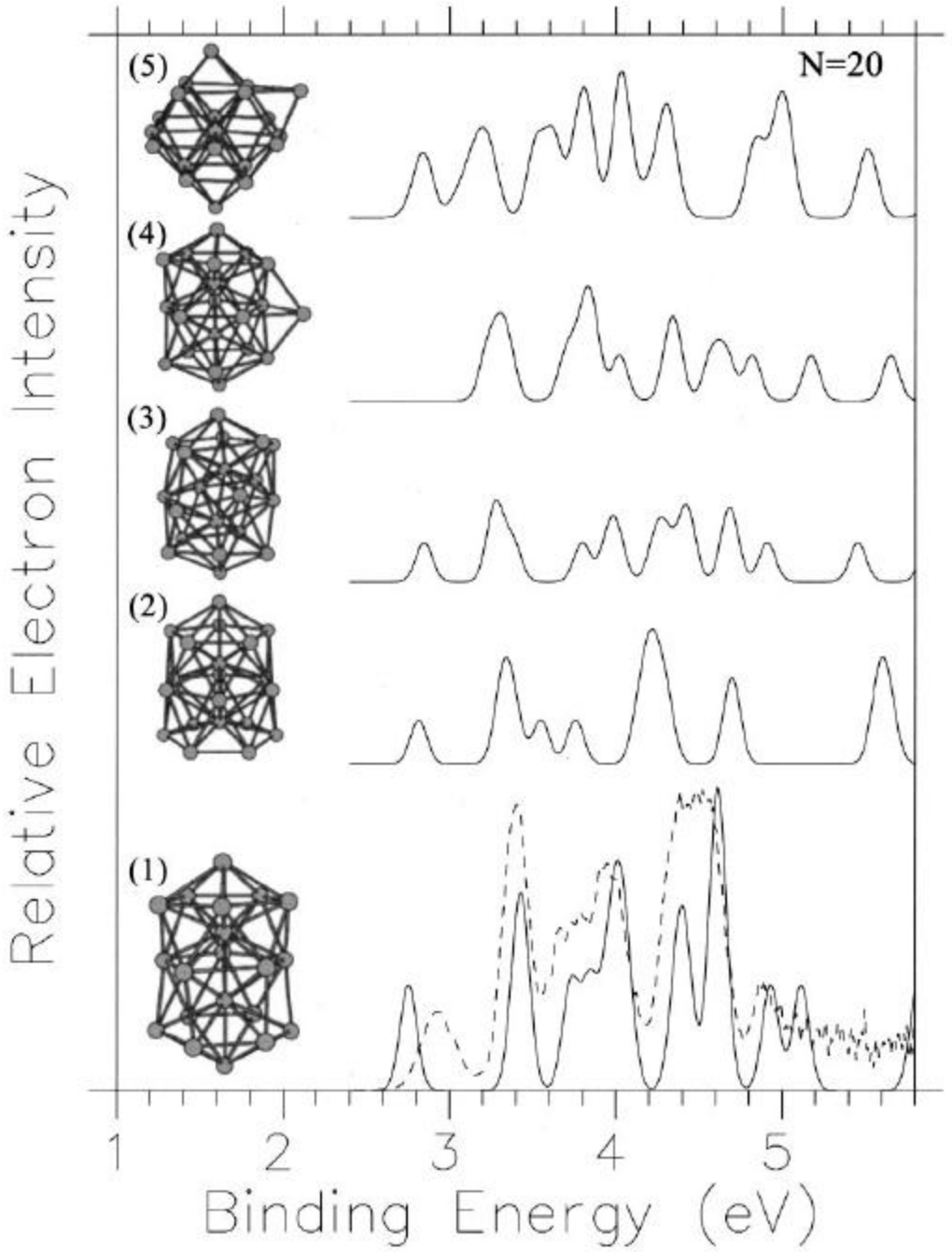


G. Wrigge, M. Astruc Hoffmann, and B. v. Issendorff
PRA65, 063201(2002)

Al_{20} PES *vs.* calc.

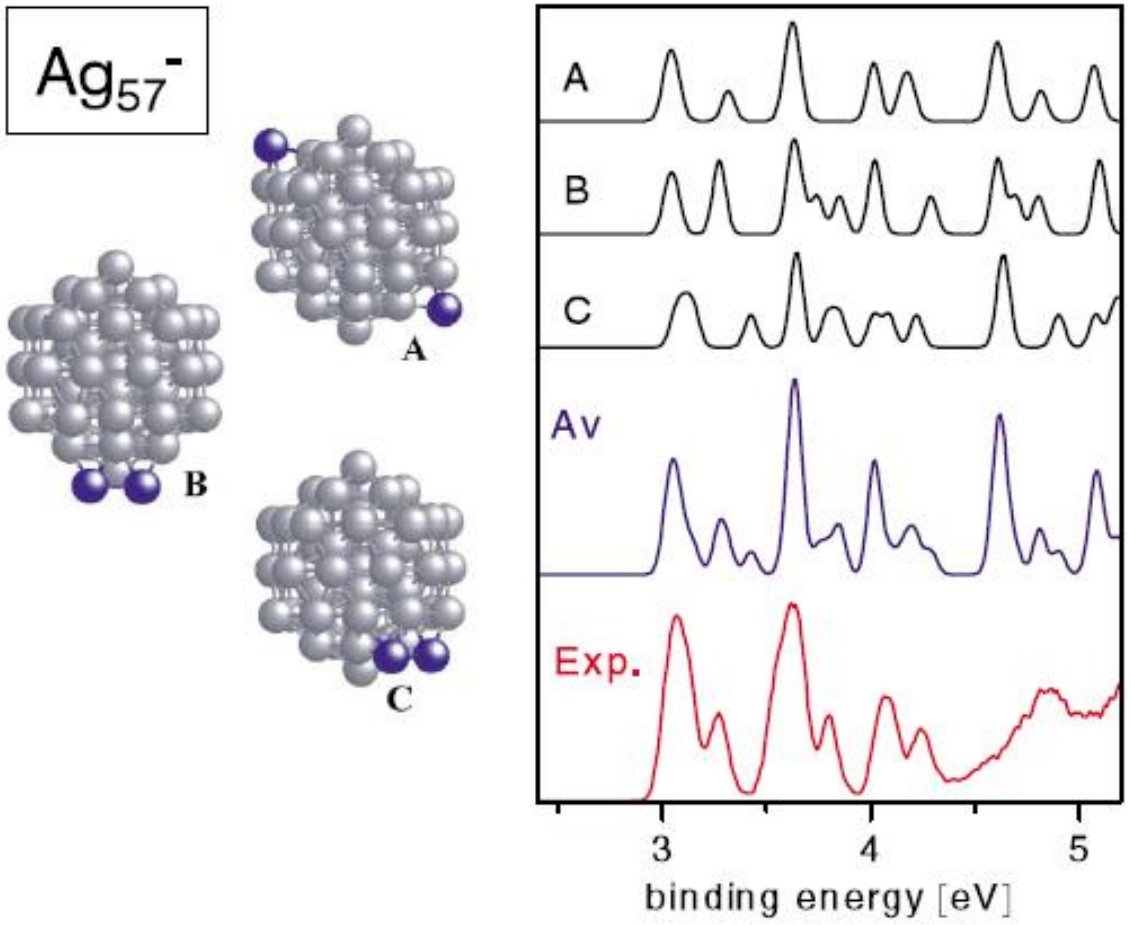
in this case:
mainly one isomer contributes

dashed curve: measured spectrum



Akola et al., PRB 62, 13 216 (2000)

close-lying isomers



here: all three isomers contribute to the experimental spectrum

PES on coinage metal clusters

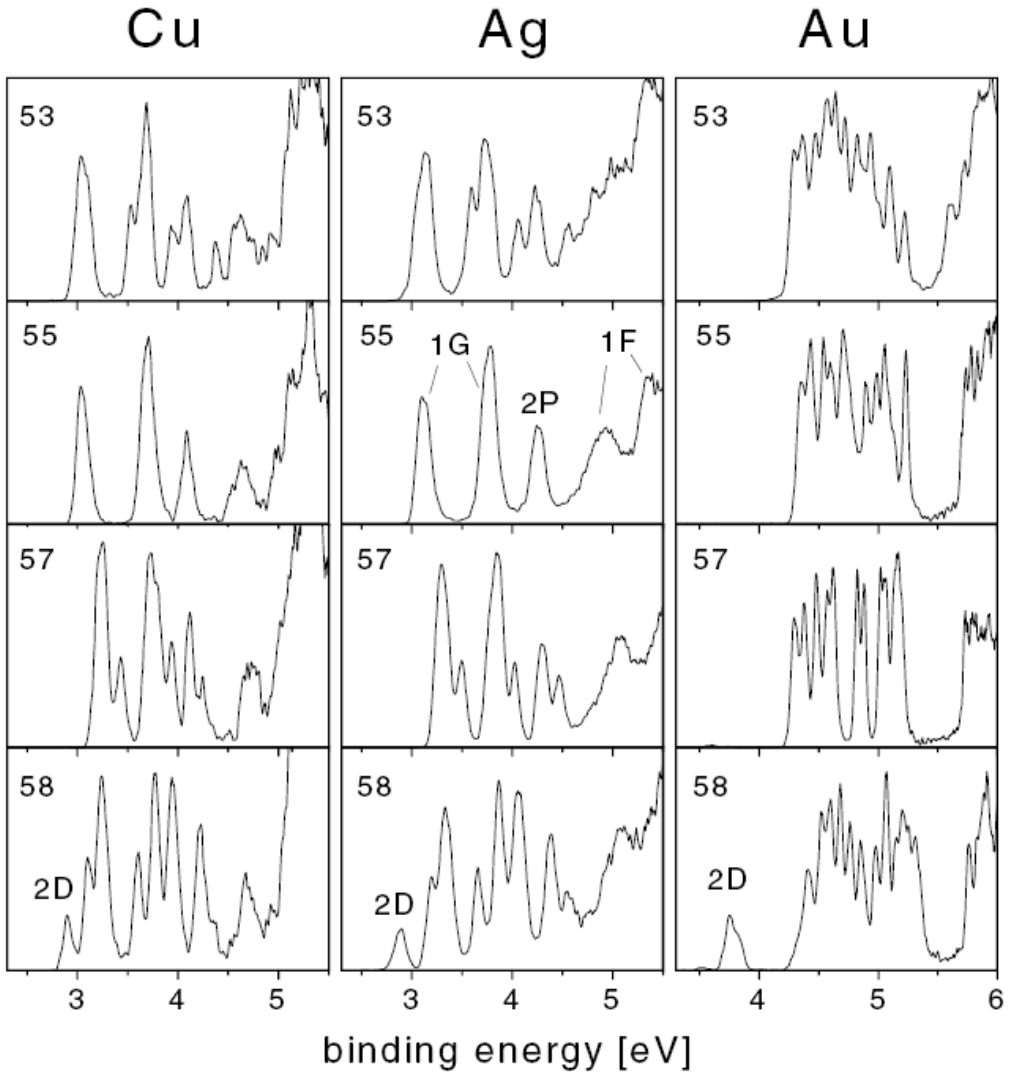
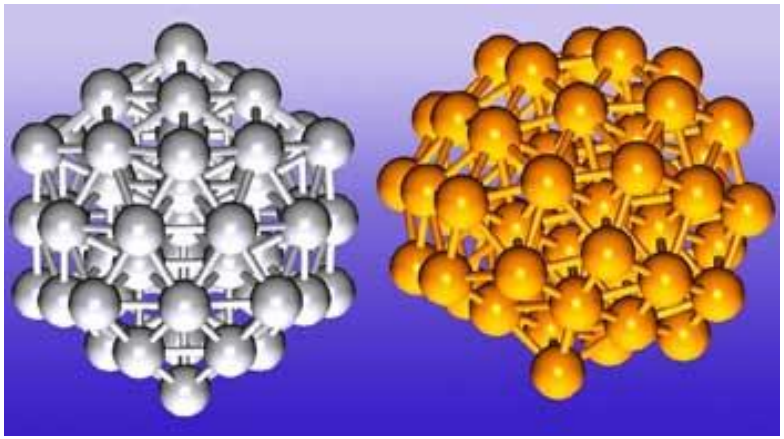


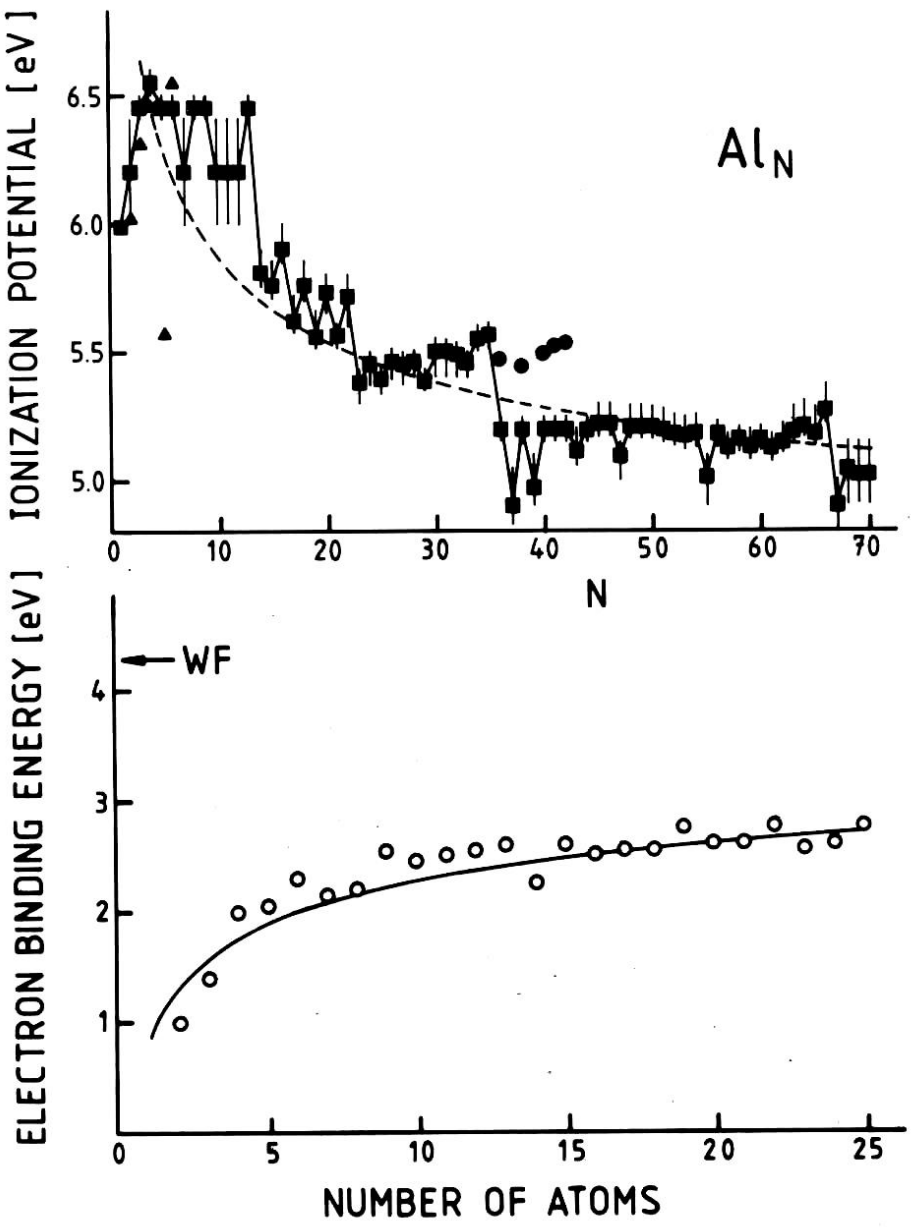
FIG. 1. Photoelectron spectra of Cu_n^-, Ag_n^-, and Au_n^- (n = 53, 55, 57, 58) obtained at a photon energy of 6.42 eV.



chemically similar systems may have similar PE spectra.
Exception: Gold, due to relativistic effects

Hannu Hakkinen, Michael Moseler, Oleg Kostko, Nina Morgner, Margarita Astruc Hoffmann, and Bernd v. Issendorff, PRL 93 093401(2004)

Trends in photoemission threshold energies

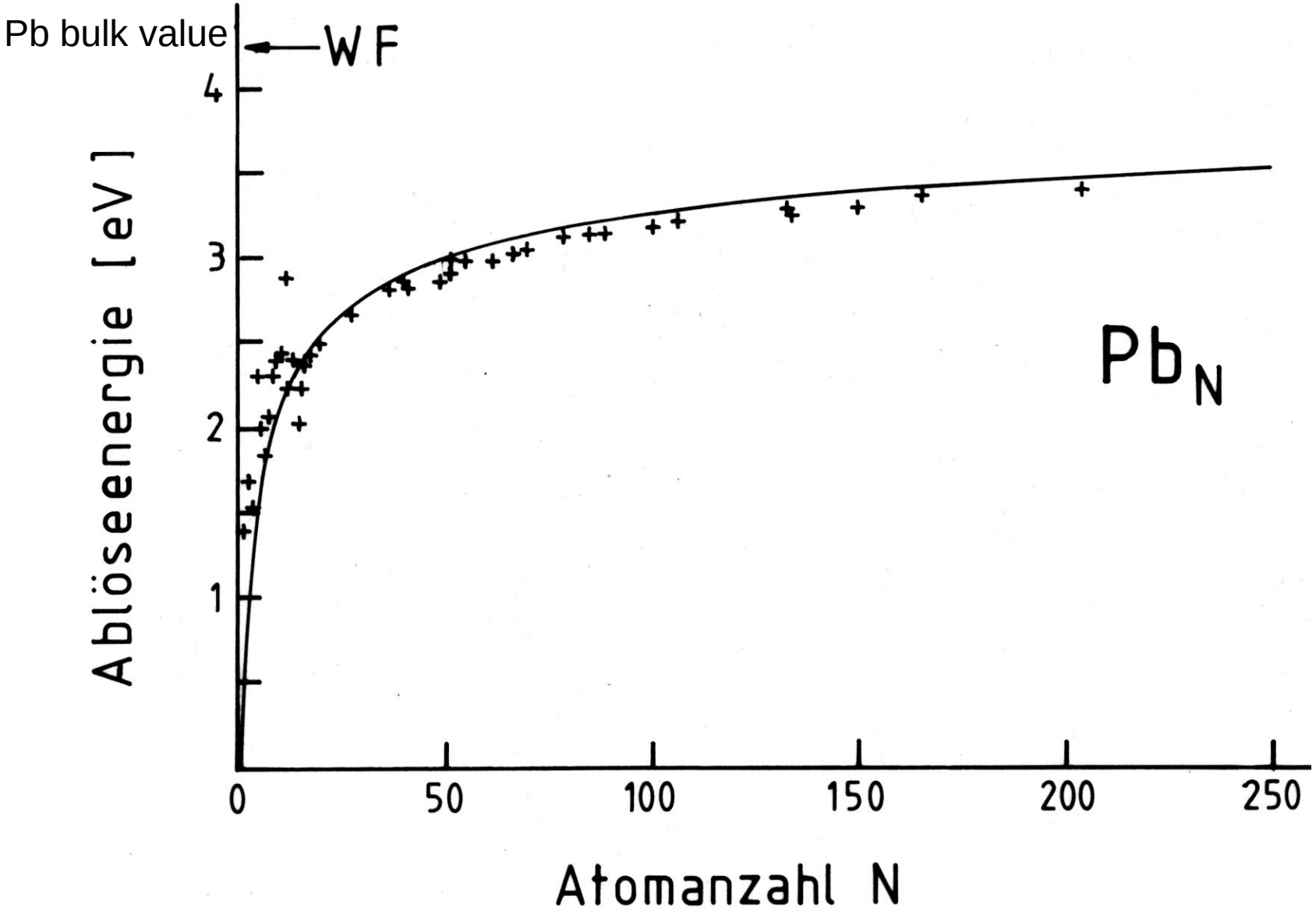


generally:

- **IPs <u>decrease</u> with increasing N**
- **electron detachment en. or EAs <u>rise</u> with increasing N**

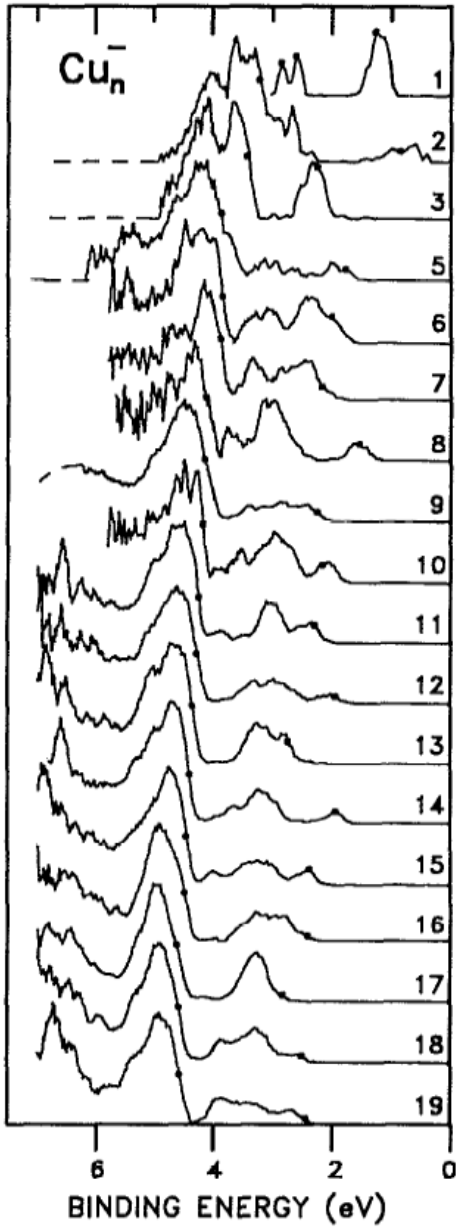
Ionization potentials (top, by R. Whetten) and electron affinities (bottom, Meiwes-Broer group) of Aluminium clusters

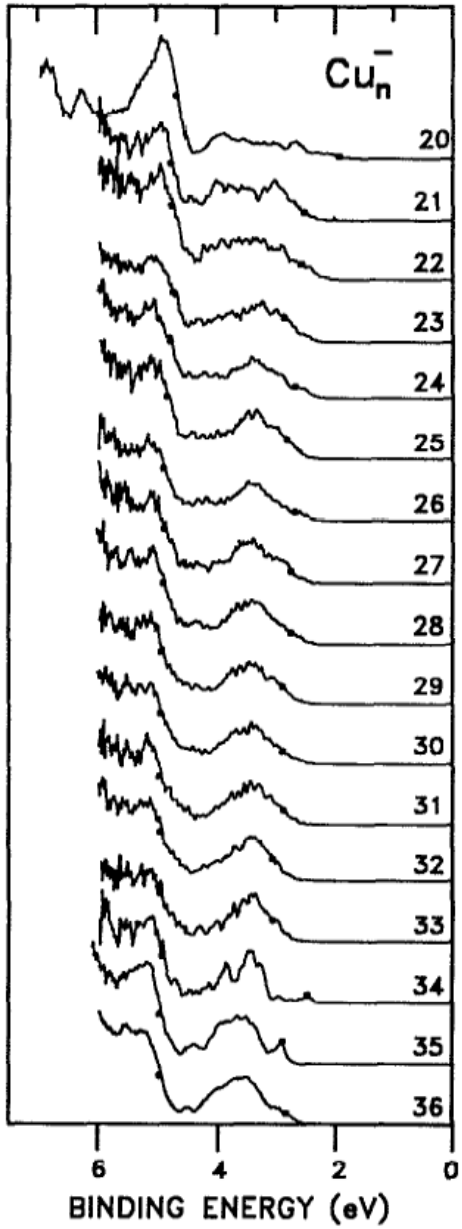
threshold energies: electron detachment



Gausa, Hector, Lüder, Meiwes-Broer

Cu_N^- PE thresholds rise with increasing cluster size

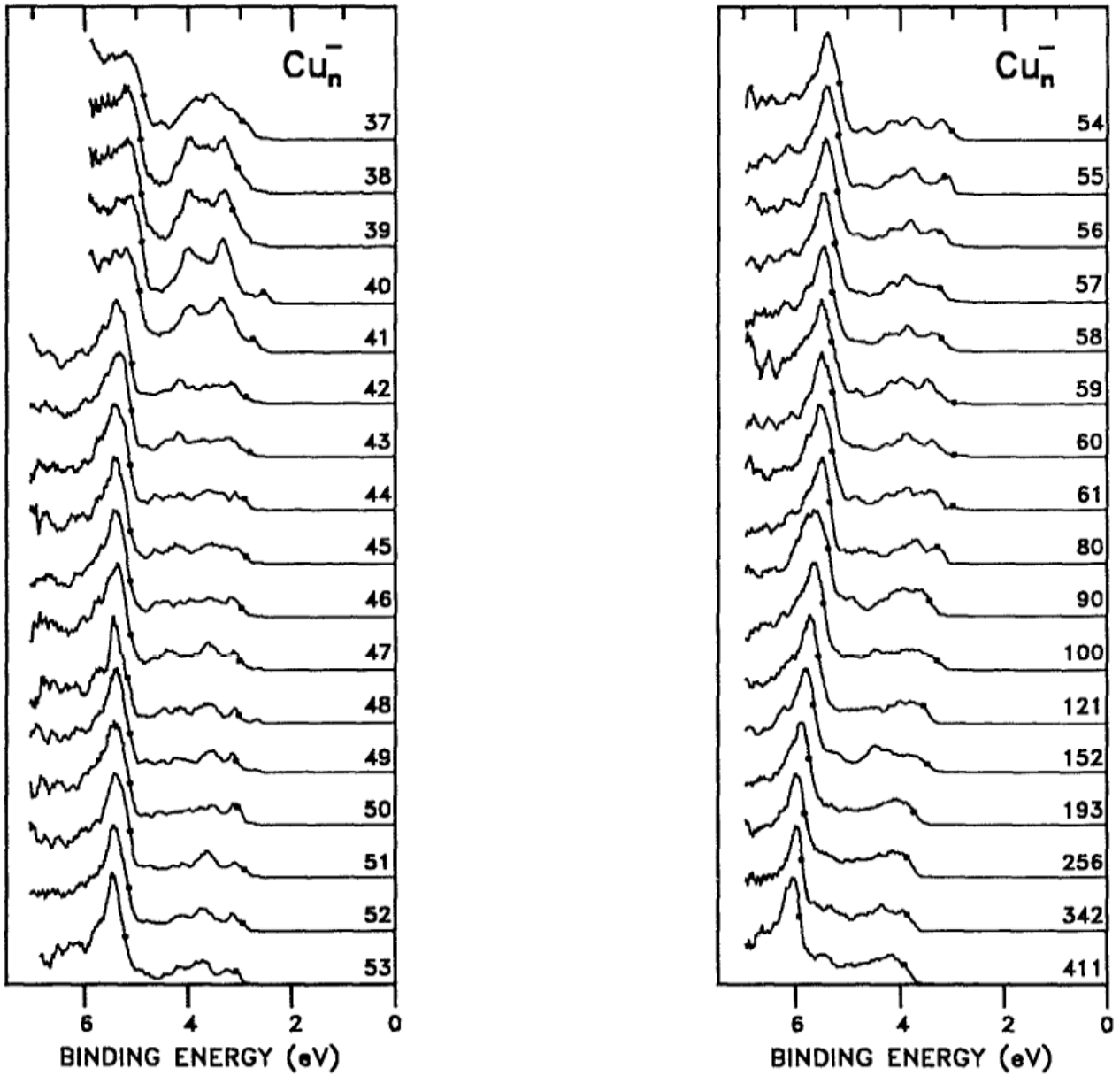




Taylor, Smalley, et al., JCP 96, 3319 (1992)

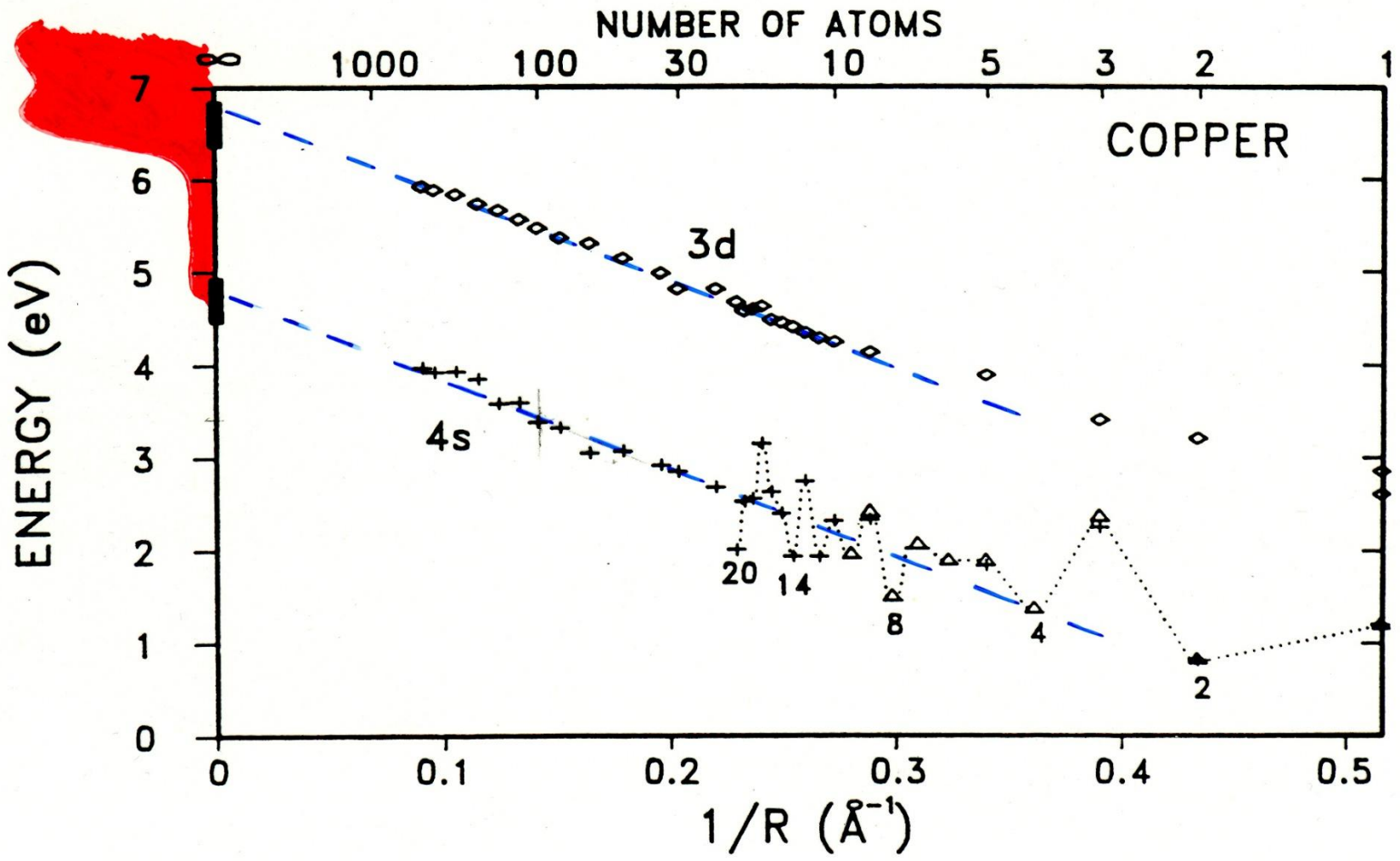
Cu_N^- PES

threshold energies increase with N



Taylor, Smalley, et al., JCP 96, 3319 (1992)

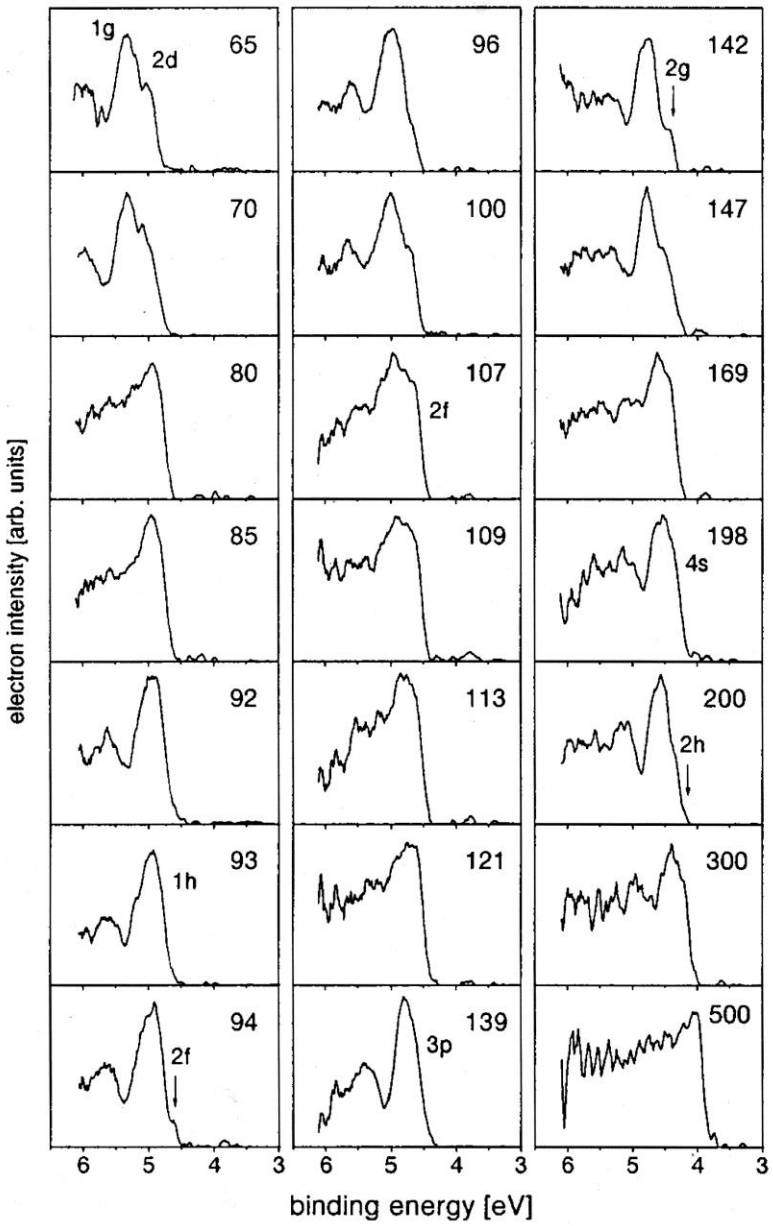
N-dependent shift of low-lying levels: 3d in Cu_N



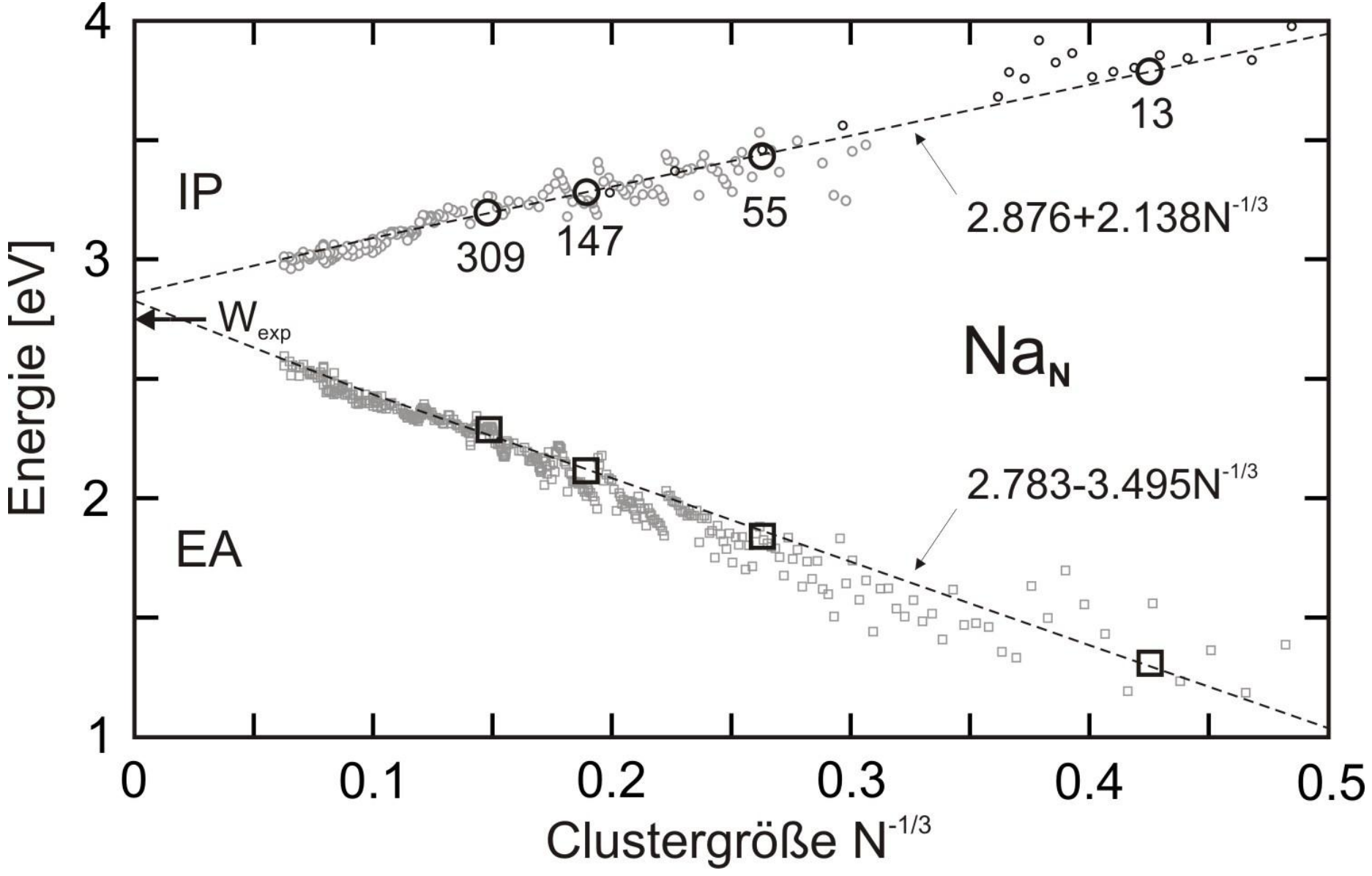
Cheshnovsky, Smalley et al.

photoionization thresholds of neutral clusters

Na^+ photoelectron spectra

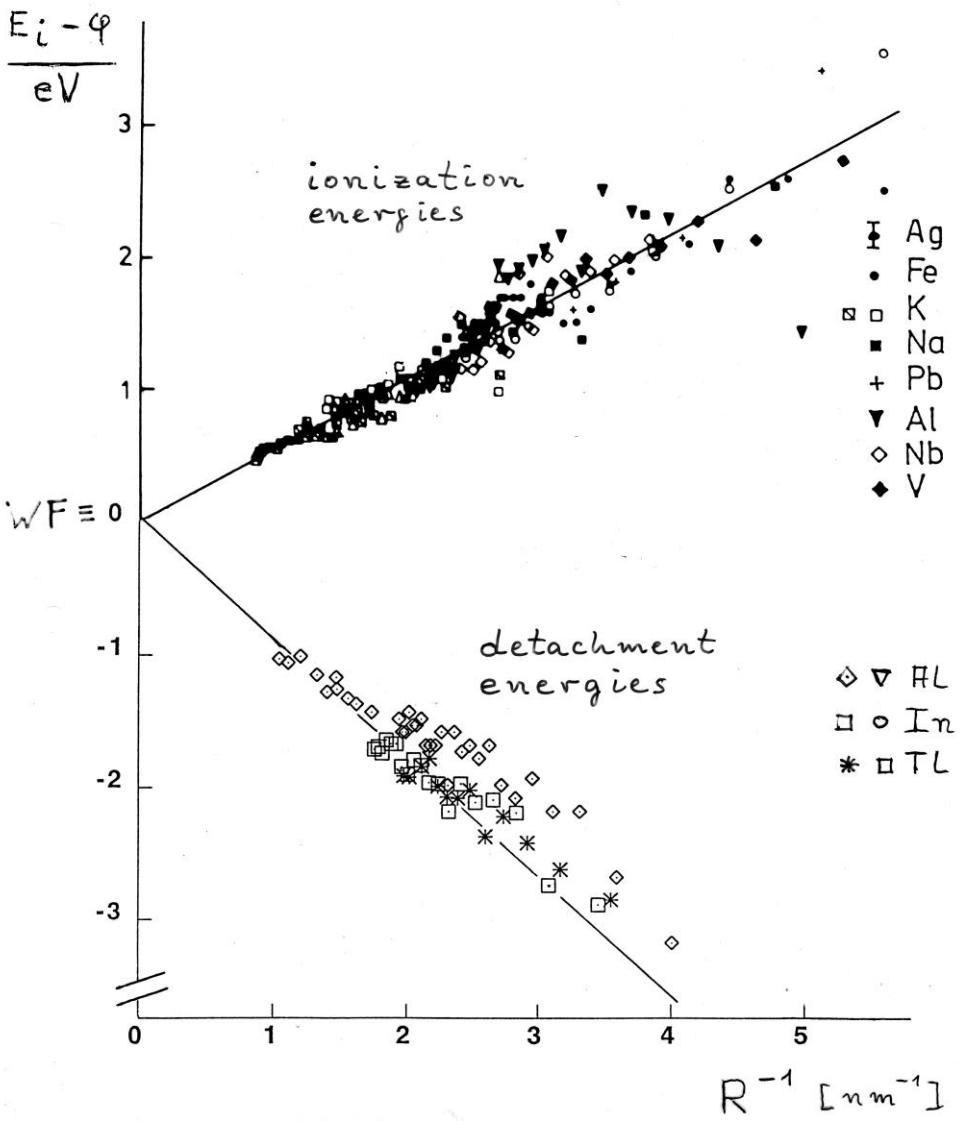


Wrigge et al. PRA, 65, 063201 2002



DFT calculations Fennel et al., Rostock, measurements von Issendorff et al., Freiburg

experimental values for the IP and the EA



Meiwes-Broer, Appl. Phys. A55 (1992) 430; also Bergmann/Schaeffer

generally:
- the IPs decrease with increasing N
- the EAs rise with increasing N

Parametrization:

$$IP(R) = WF + \alpha \frac{e^2}{R}$$ with α = 3/8 .... ½

$$EA(R) = WF - \beta \frac{e^2}{R}$$ with β = ½ 5/8

α = β = ½ corresponds to the charging energy of a jellium sphere, deviations arise from QM exchange and correlation

let us evaluate IP and EA simultaneously

$$IP(R) = WF + \alpha \frac{e^2}{R}$$ with α = 3/8 .... ½

$$EA(R) = WF - \beta \frac{e^2}{R}$$ with β = ½ 5/8

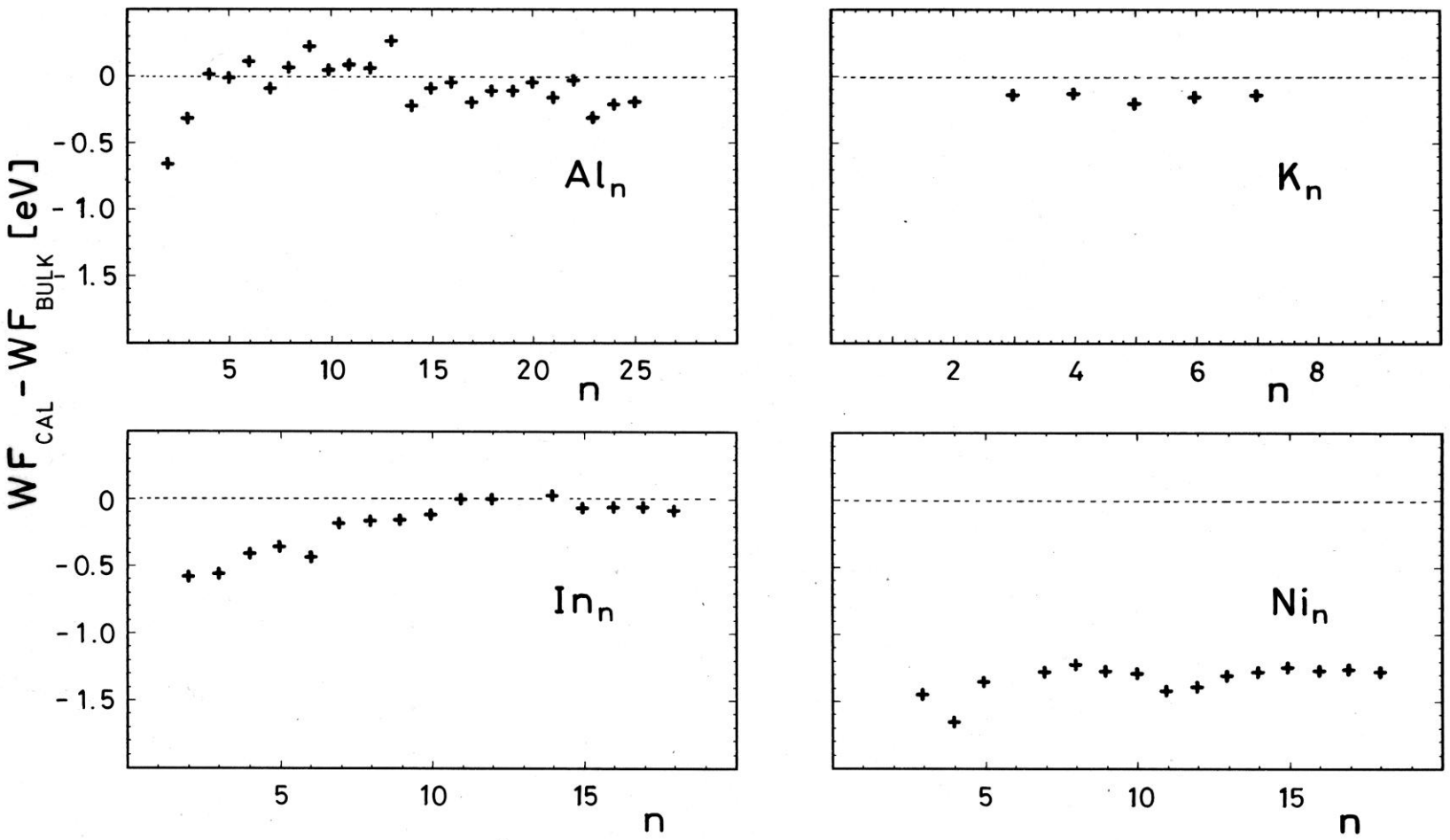
α - β is small

solve for WF: $$WF_{cal} = \tfrac{1}{2}(IP + EA) + \tfrac{1}{2}\frac{e^2}{R}(b - a)$$

$$WF_{cal} \approx \tfrac{1}{2}(IP + EA)$$

thus the work function should be the mean value of IP and EA !

differences between measured IP and EA and bulk values



Small or no differences hint at free electron (or: ideal metal droplet) behaviour

Meiwes-Broer in *Advances in Metal and Semiconductor Clusters, Vol. 1*
M. Duncan, Ed., JAI Press Inc., 1993