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Advancing Frontiers of Condensed Matter Physics

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High resolution metal cluster photoelectron spectroscopy

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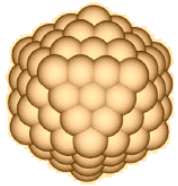
D-79104 Freiburg im Breisgau
GERMANY

High resolution metal cluster photoelectron spectroscopy

B.v.Issendorff



Why clusters?

Study of the size dependence of bulk properties

- crystal structure
- electronic structure
- optical, magnetic, chemical properties
- ...

Model systems

- simple metal clusters: finite electron gas in a parabolic trap
- study of few particle dynamics, finite system thermodynamics, ...
- test for theory

Program

Introduction — free electron model

Experiment — Photoelectron spectroscopy on size selected clusters

Results

Simple metals: electronic and geometric structure

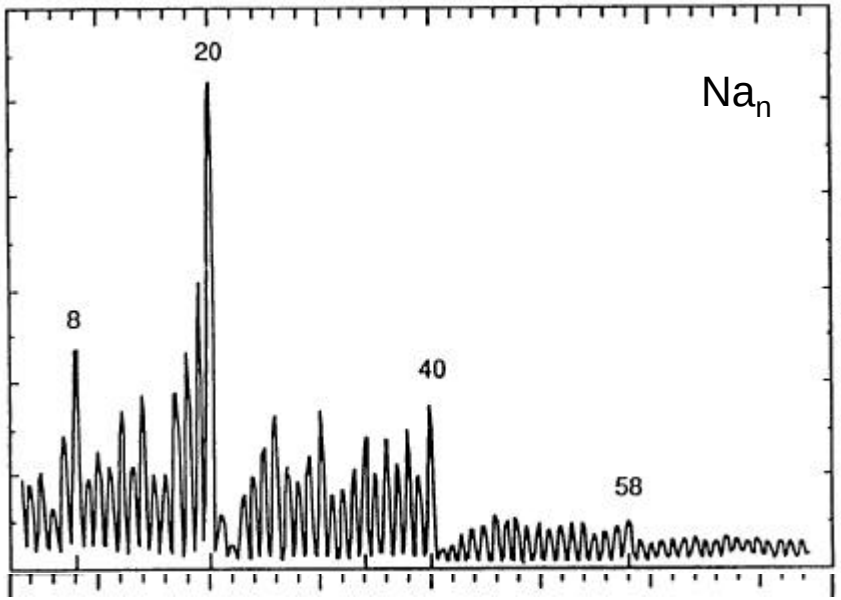
- Sodium
- Noble metals

Divalent metals: nonmetal/metal transitions

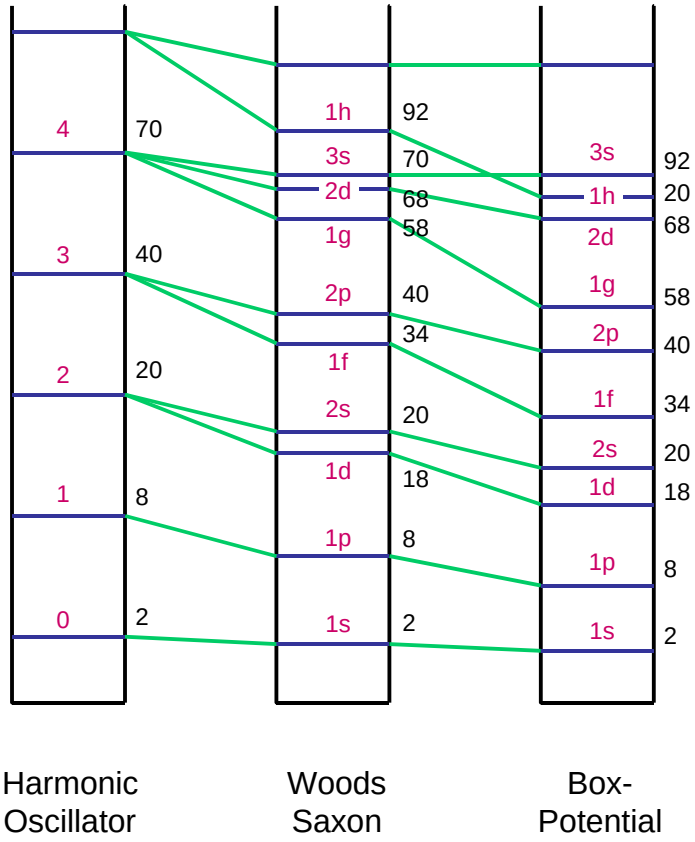
- Introduction: Mercury
- Zinc
- Strontium

Summary

Electron shells: spherical box model

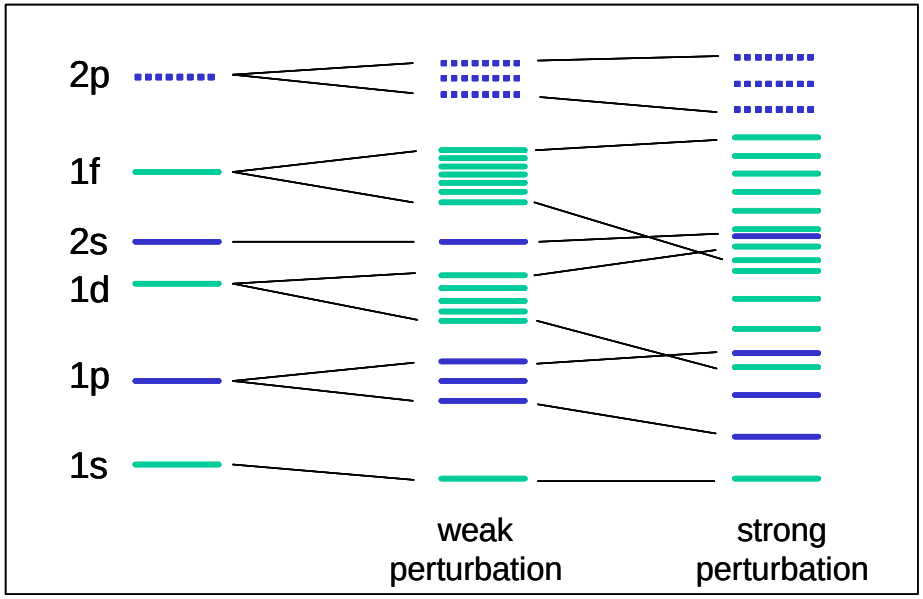


Knight, de Heer, 1984



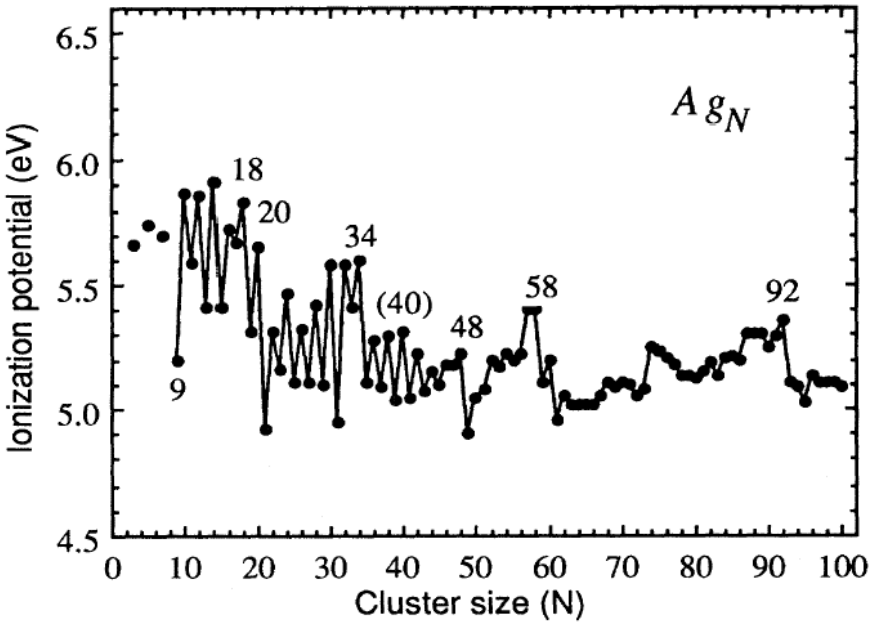
Electron levels in different spherical model potentials

Shell structure in a real cluster



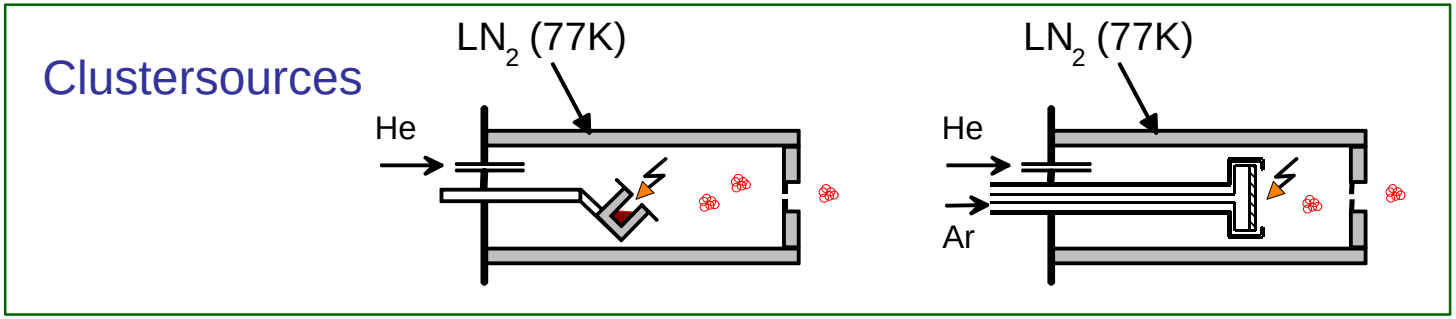
The atomic structure perturbs the electron angular momentum eigenstates

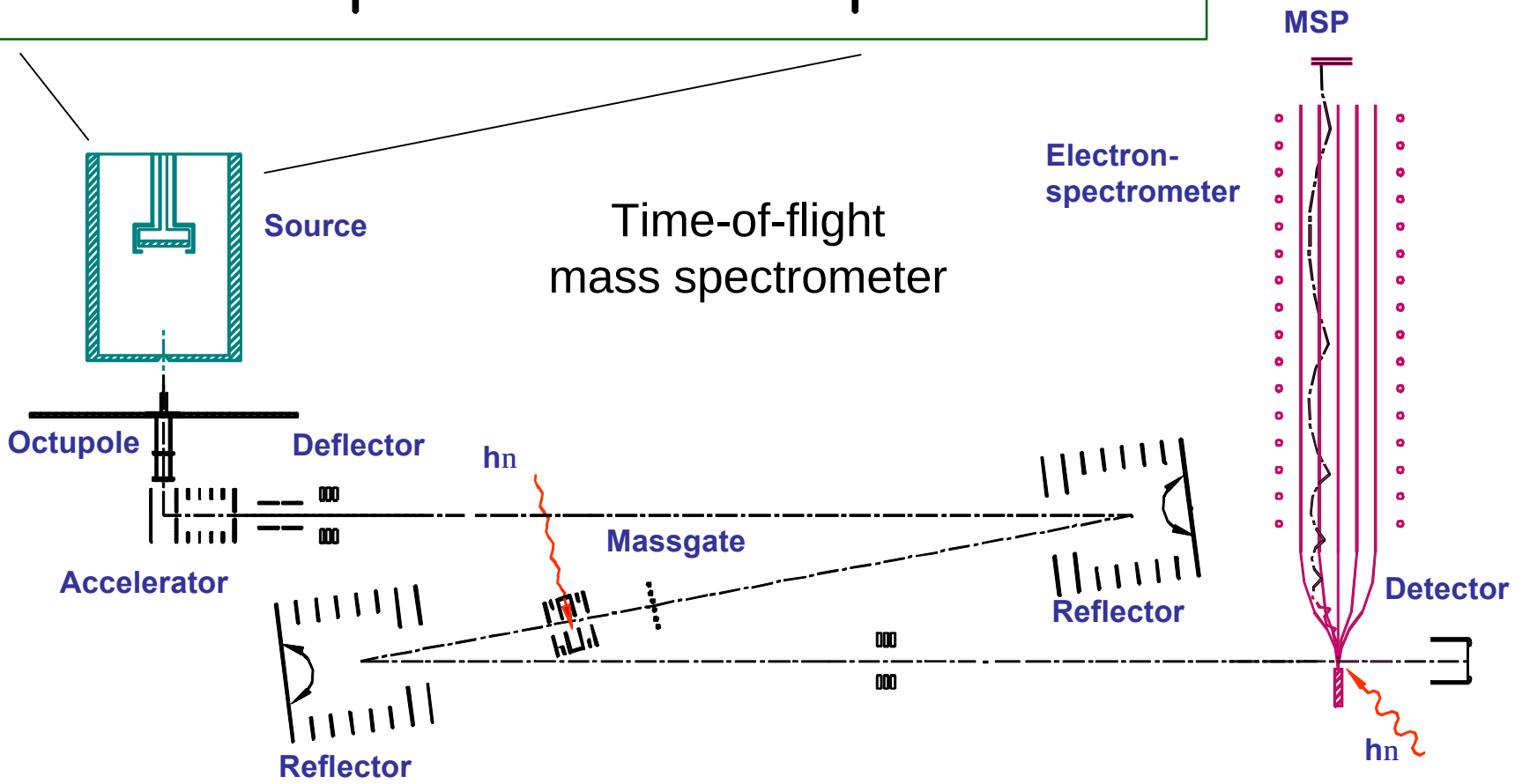
Ionization potentials of silver clusters: evidence for perturbed shell structure



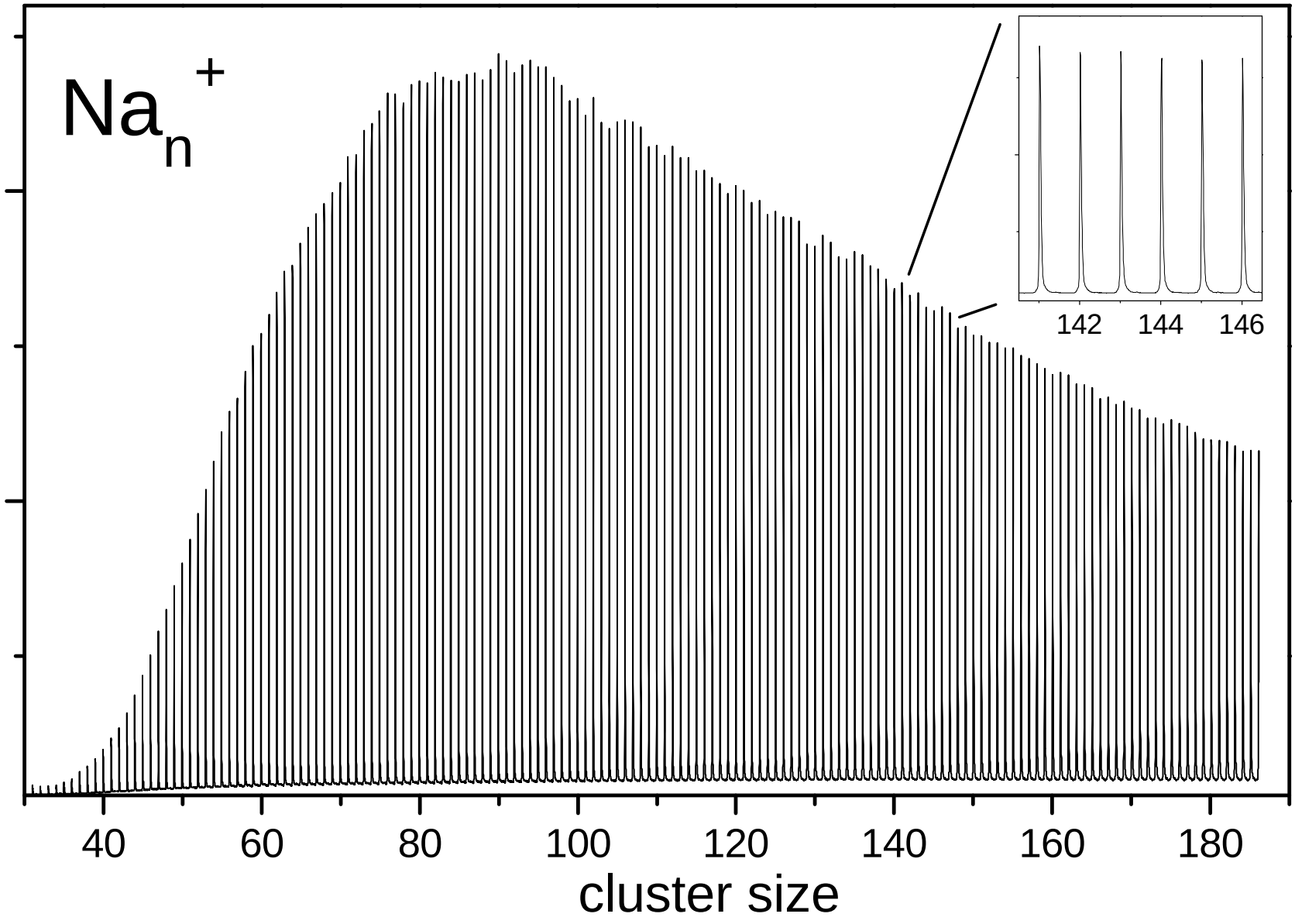
Alameddin et al.
Chem.Phys. Lett. 192, 122 (1992)

Experiment


Clustersources
LN2 (77K)
He
LN2 (77K)
He
Ar


Source
Time-of-flight
mass spectrometer
MSP
Electron-
spectrometer
Octupole
Deflector
hn
Massgate
Accelerator
Reflector
Detector
Reflector
hn

Mass spectrum of sodium clusters

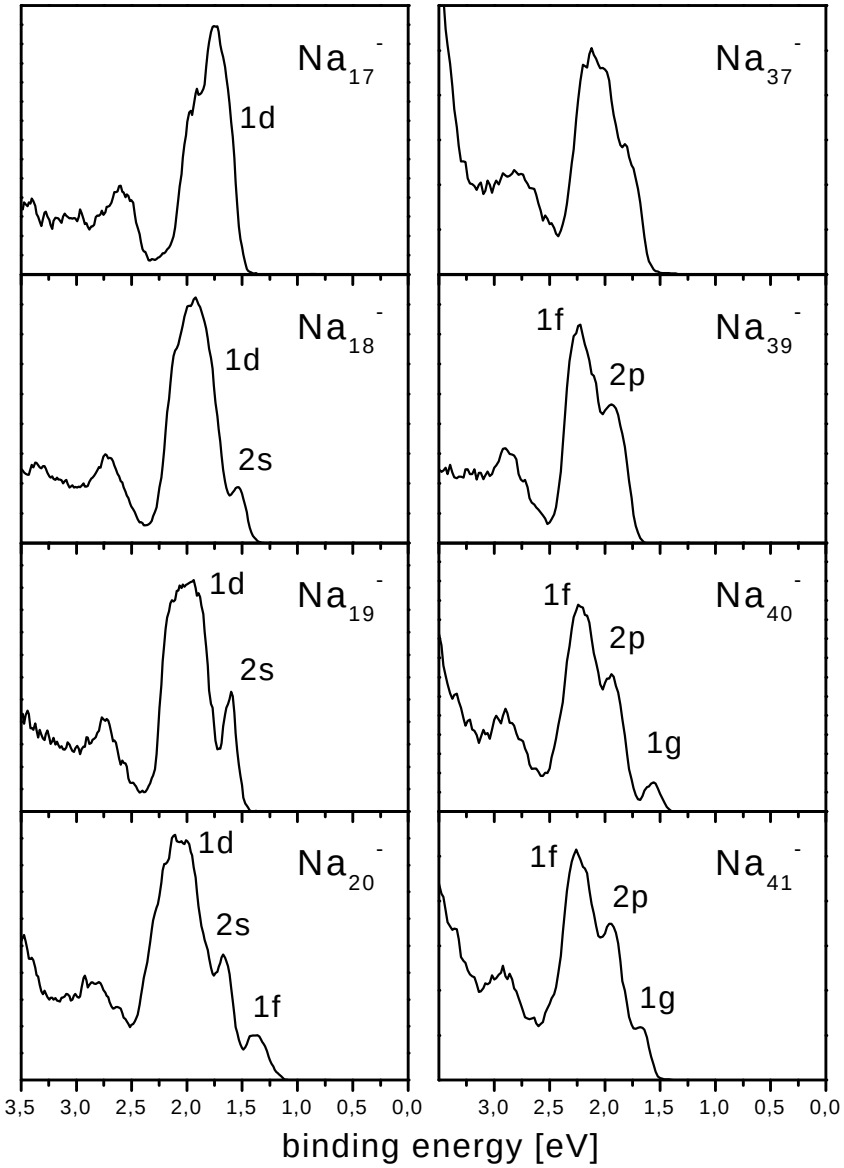


PES on hot sodium clusters

Jellium levels:

1s	1p	1d	2s	1f	2p	1g
2	8	18	20	34	40	58

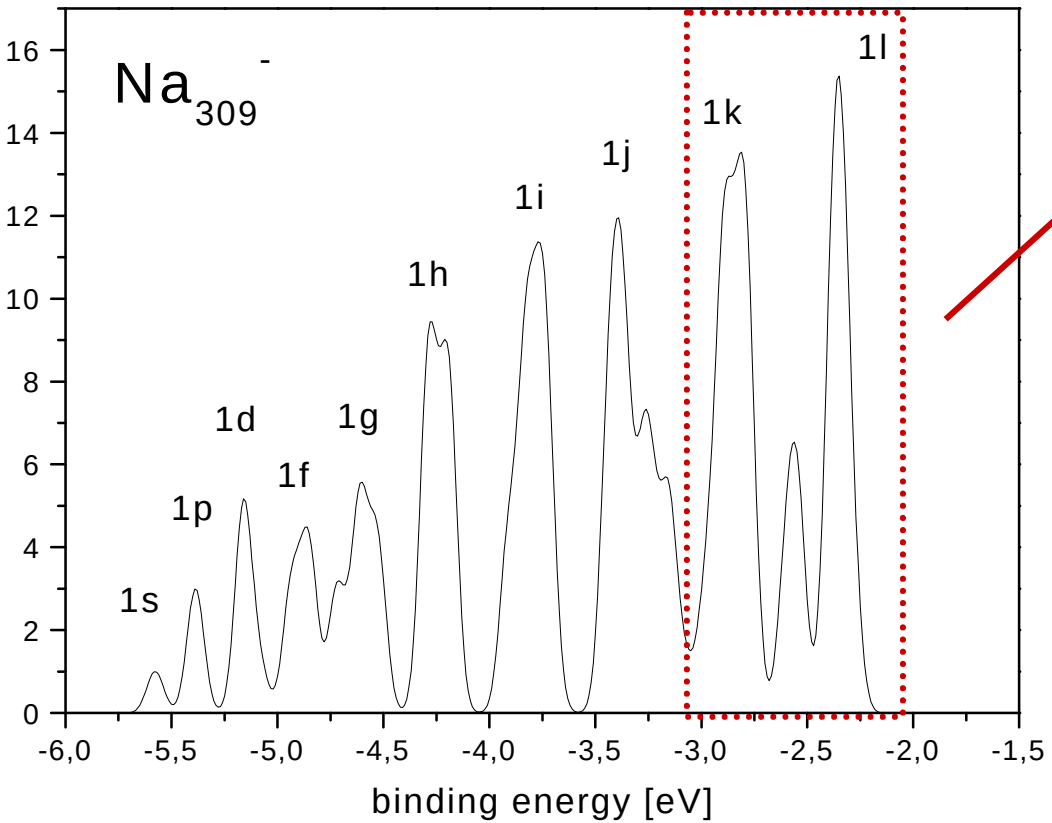
ideal electron shell structure!

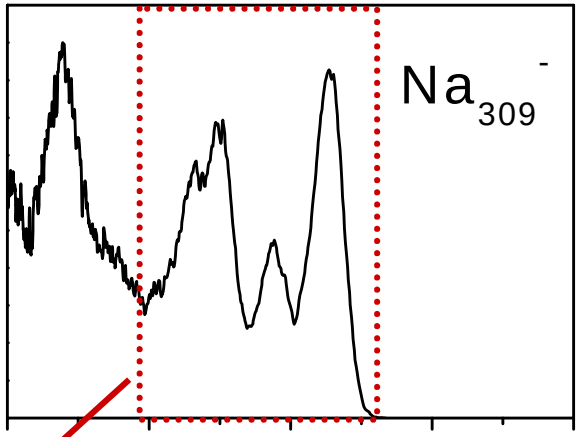


Annu. Rev. Phys. Chem. 56, 549 (2005)

Electron shell structure in a large cluster

Total calculated DOS of the icosahedral cluster



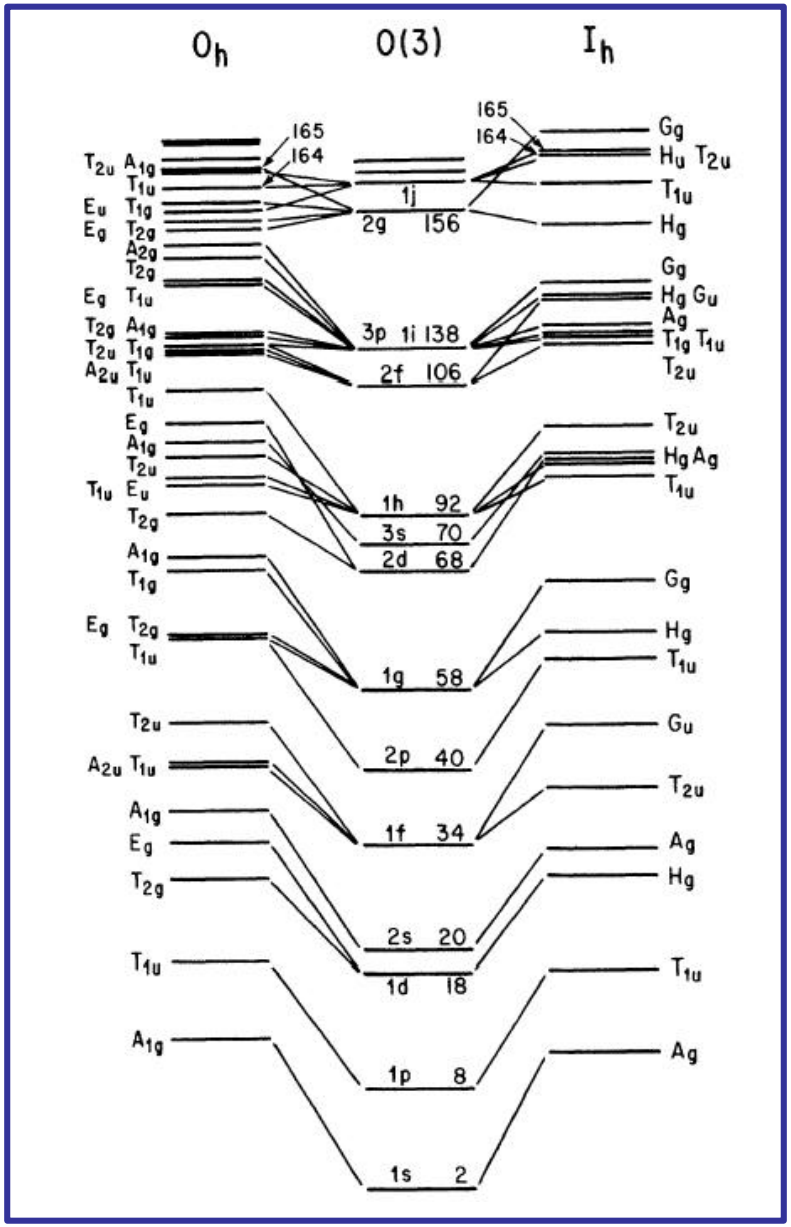


measured photoelectron spectrum

DFT- calculations by M. Moseler and B. Huber, Freiburg

Crystal field splitting in clusters

Splitting of angular momentum eigenstates



octahedral symmetry

icosahedral symmetry

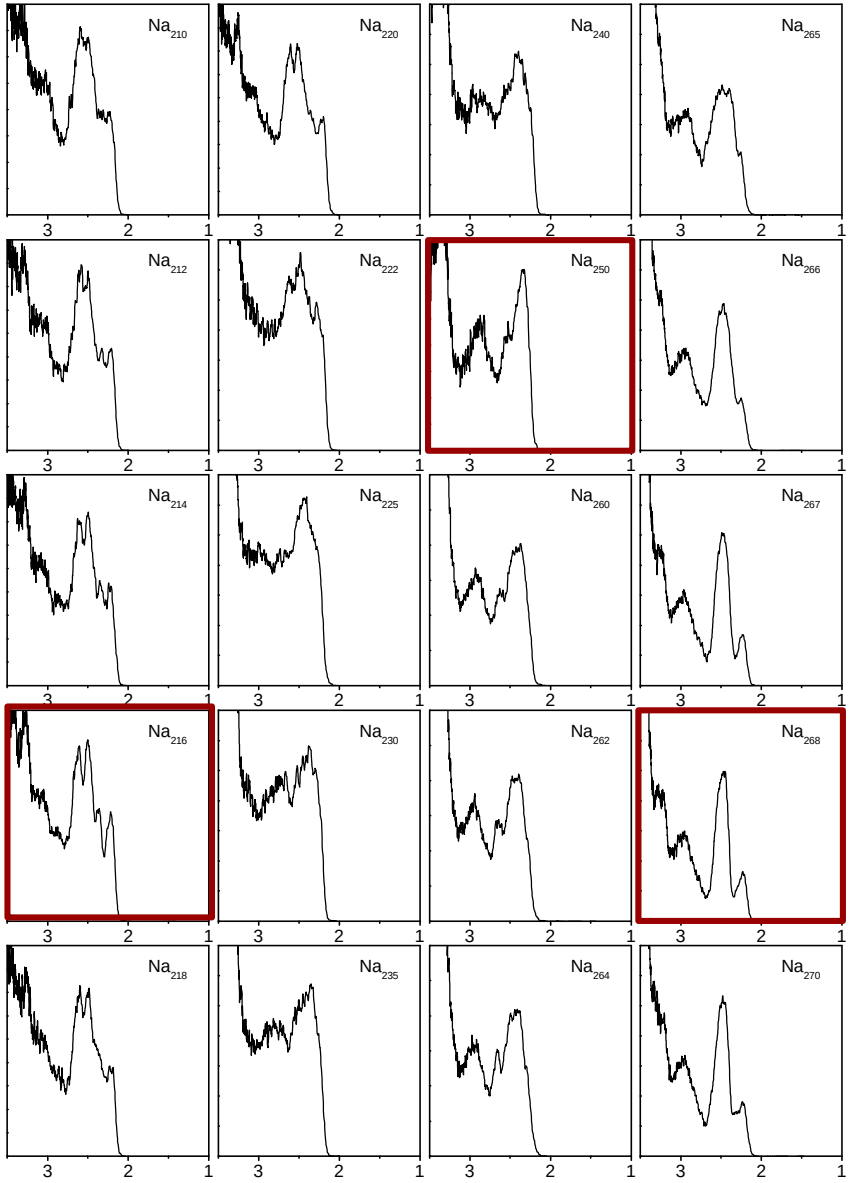
higher degeneracy!

Size dependence of spectra

Spectra of Na_n^- with n=210-270:

strong variation with size

highly structured spectra indicate high symmetry!



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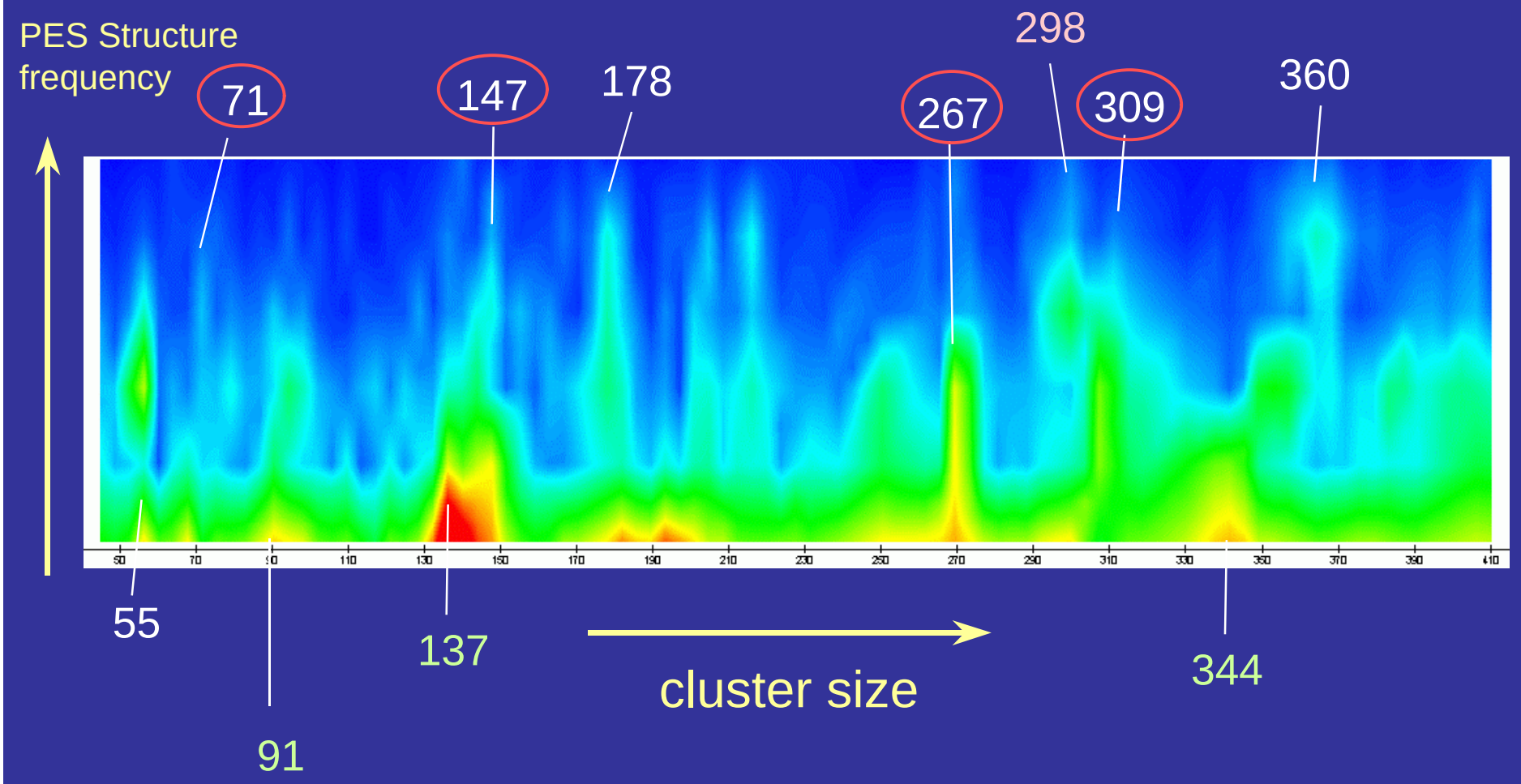
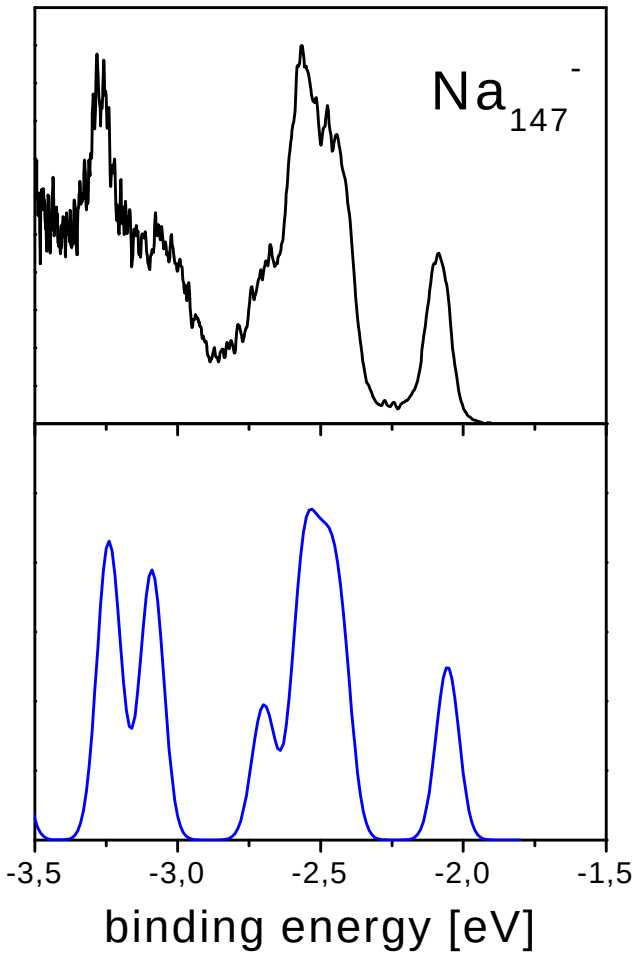
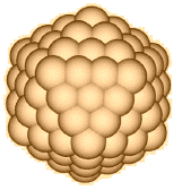
Fourier Transform PES



Comparison with theory

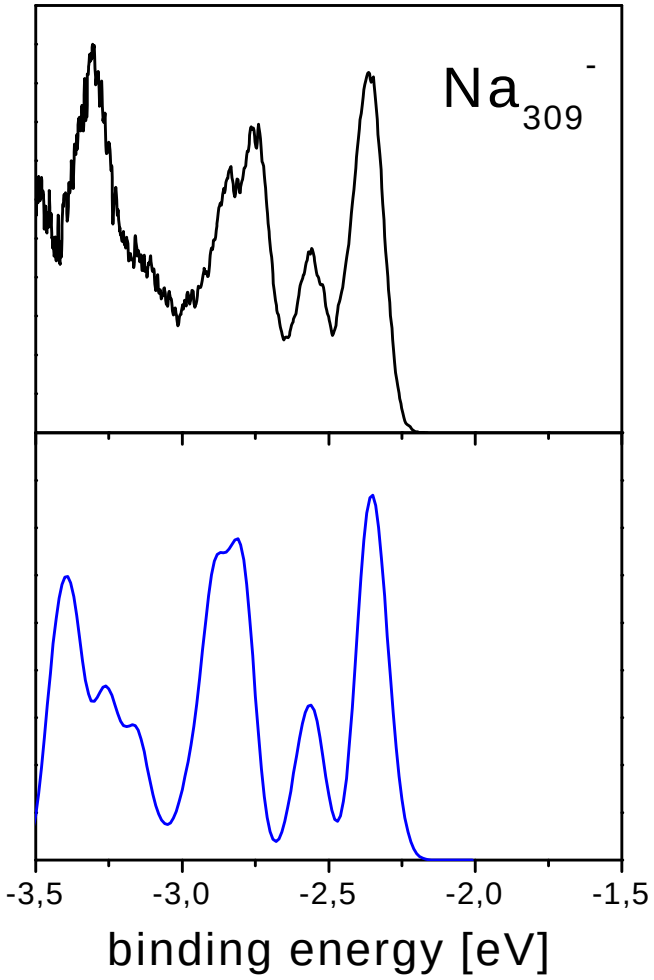


Experiment



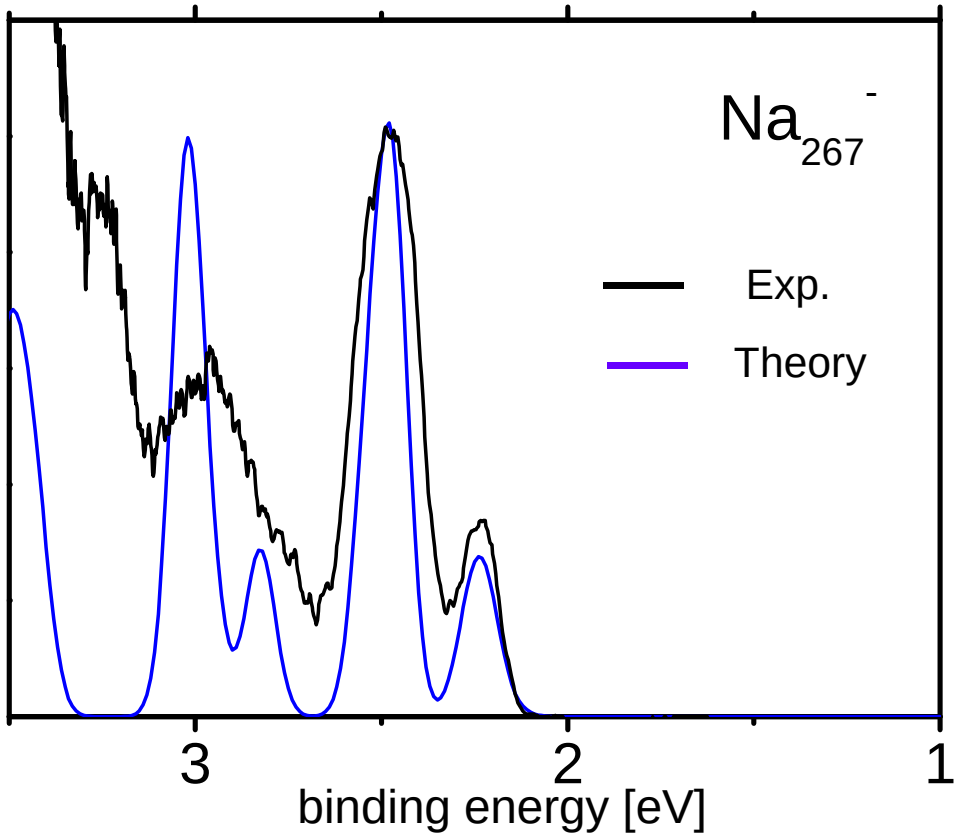
Theory

calculations by
M. Moseler
and B. Huber,
Freiburg



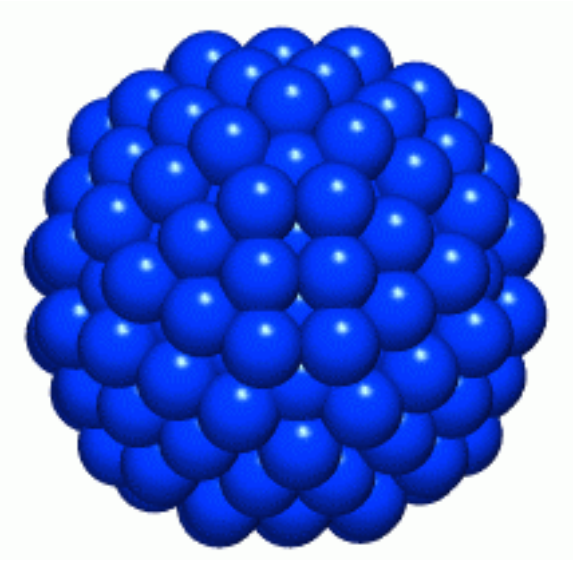
Closed shell icosahedral stuctures!

Double magic cluster



268 electrons

&



Closed anti-Mackay-shell
on 147 atom icosahedron

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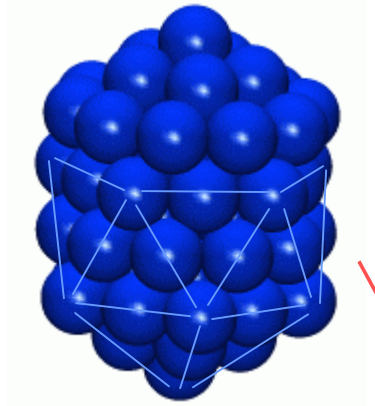
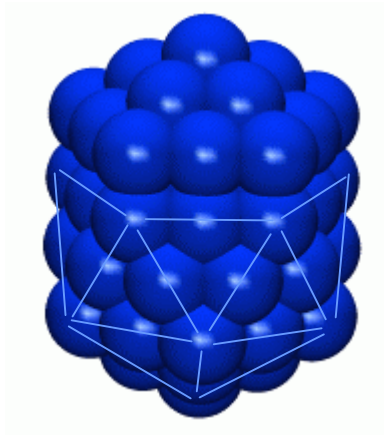
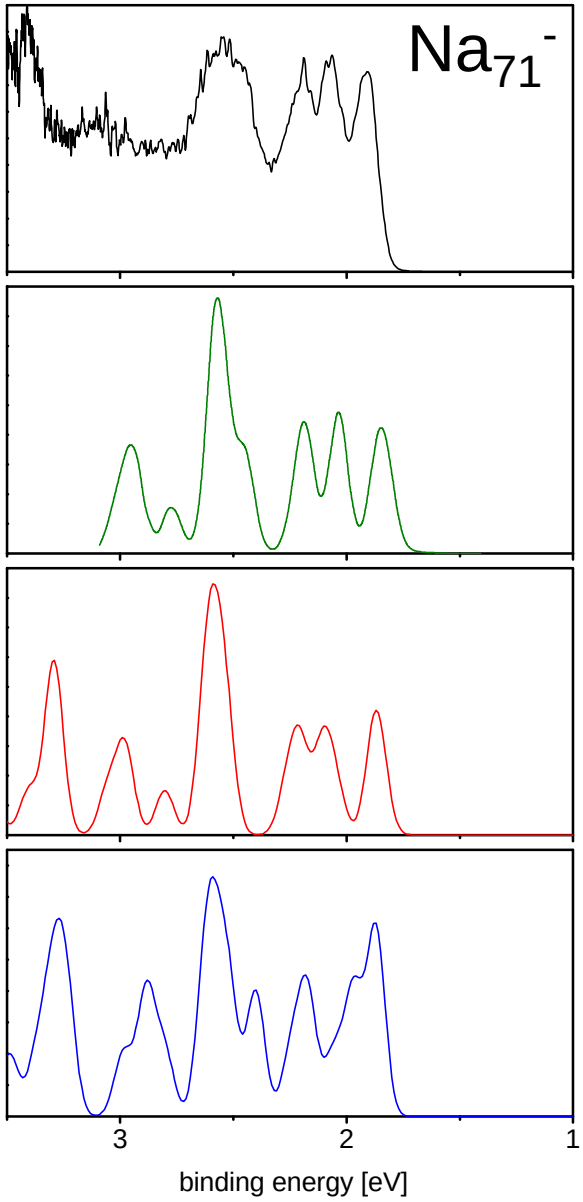
Sodium: Mackay / anti-Mackay stacking



55 atom icosahedron
with anti-Mackay-cap



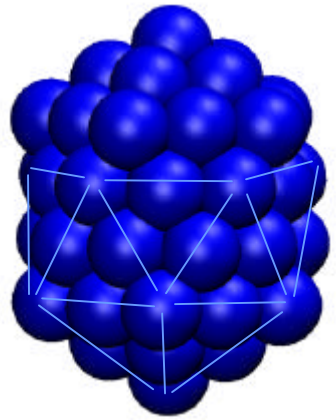
55 atom icosahedron
with Mackay-cap



Experiment

Calculated DOS

(M.Moseler, IWM Freiburg)



55 atom icosahedron
with twisted cap

(Noya et al., cond-mat/0506329)

Program

Introduction — free electron model

Experiment — Photoelectron spectroscopy on size selected clusters

Results

Simple metals: electronic and geometric structure

- Sodium
- Noble metals

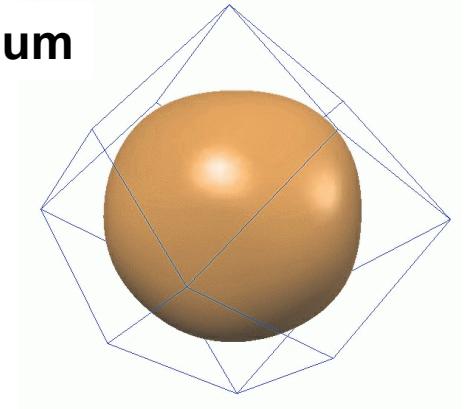
Divalent metals: nonmetal/metal transitions

- Introduction: Mercury
- Zinc
- Strontium

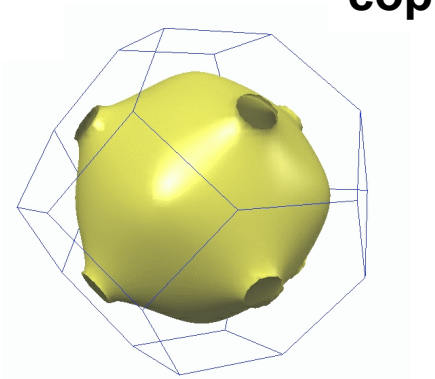
Summary

Comparison of alkali and noble metals

sodium

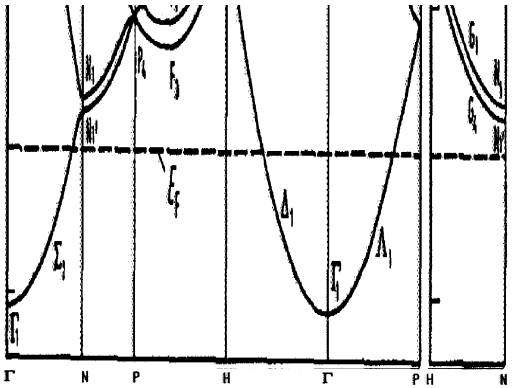


copper

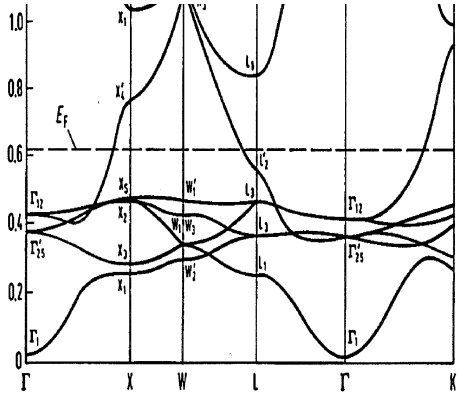


Fermi surfaces

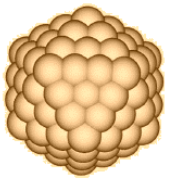
Band structures



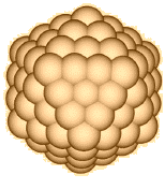
d-Band



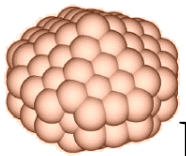
Predicted cluster geometries



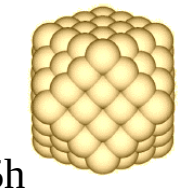
I_h



I_h



D_{5h}

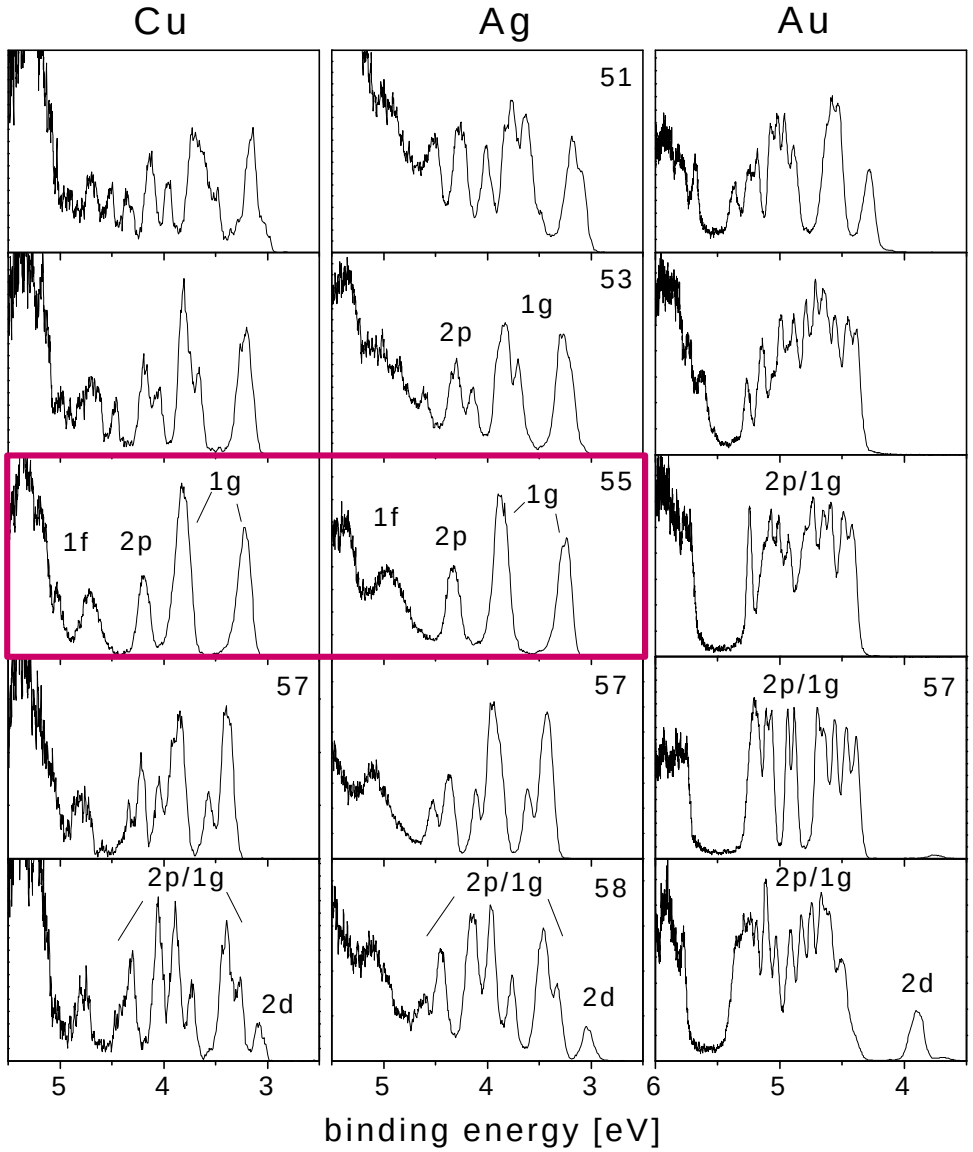


O_h

PES of noble metal cluster anions

size 55:
highly degenerate states
for copper and silver!

size 58:
appearance of a
new shell (2d)



PRL 93, 093401 (2004)

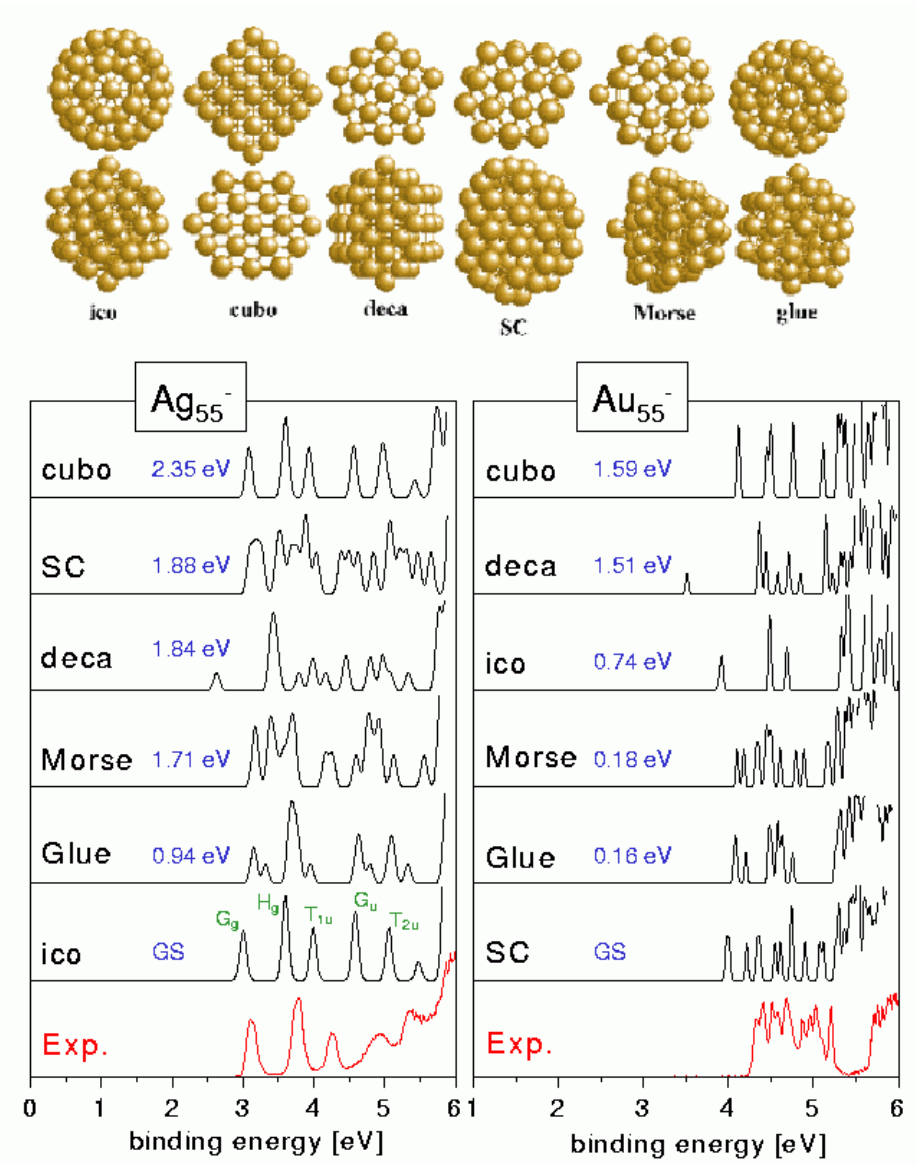
Comparison with theory

selected cluster structures

calculated DOS (M.Moseler, H.Häkkinen)

Program by Landman/Barnett

Experiment



PRL 93, 093401 (2004)

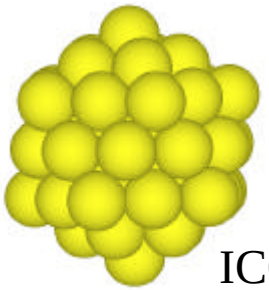
Symmetry perturbation

2p-shell

minus 2 atoms:
oblate

p_z

p_x p_y



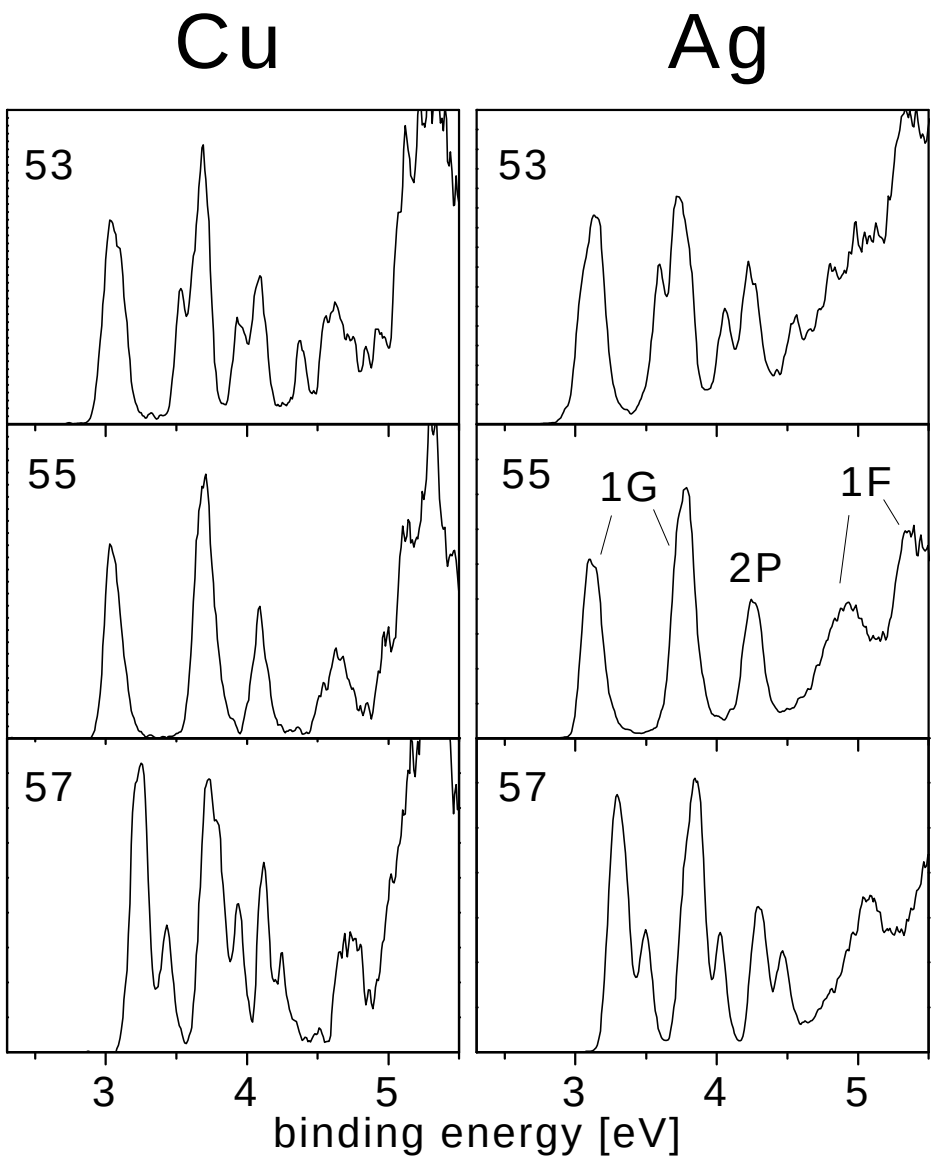
ICO

p_x p_y p_z

plus 2 atoms:
prolate

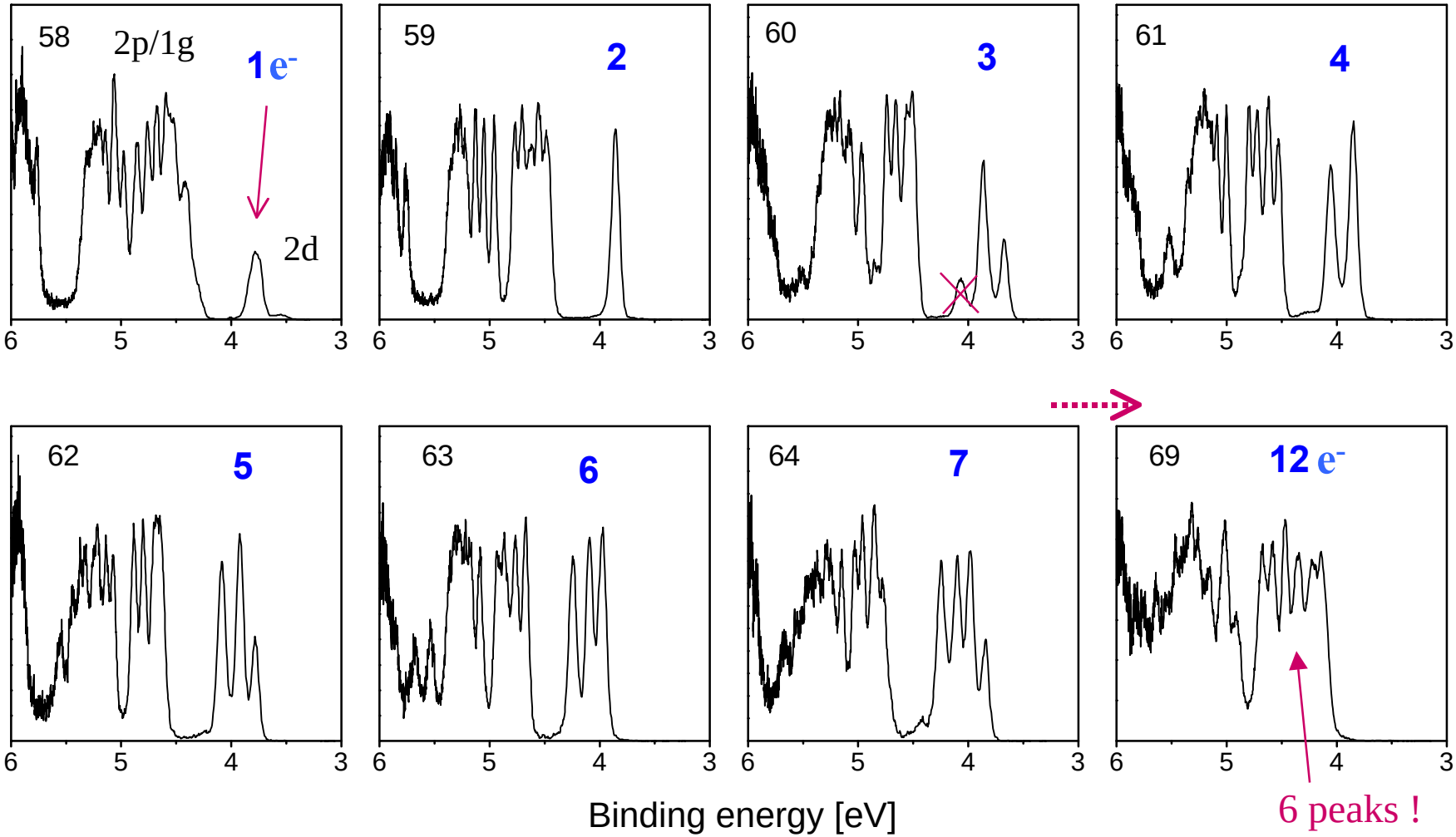
p_x p_y

p_z



Counting electrons: gold clusters

PES of Au_n^-, n = 58-69



Program

Introduction — free electron model

Experiment — Photoelectron spectroscopy on size selected clusters

Results

Simple metals: electronic and geometric structure

- Sodium
- Noble metals

Divalent metals: nonmetal/metal transitions

- Introduction: Mercury
- Zinc
- Strontium

Summary

Development of the electronic bands of metal clusters

Monovalent:

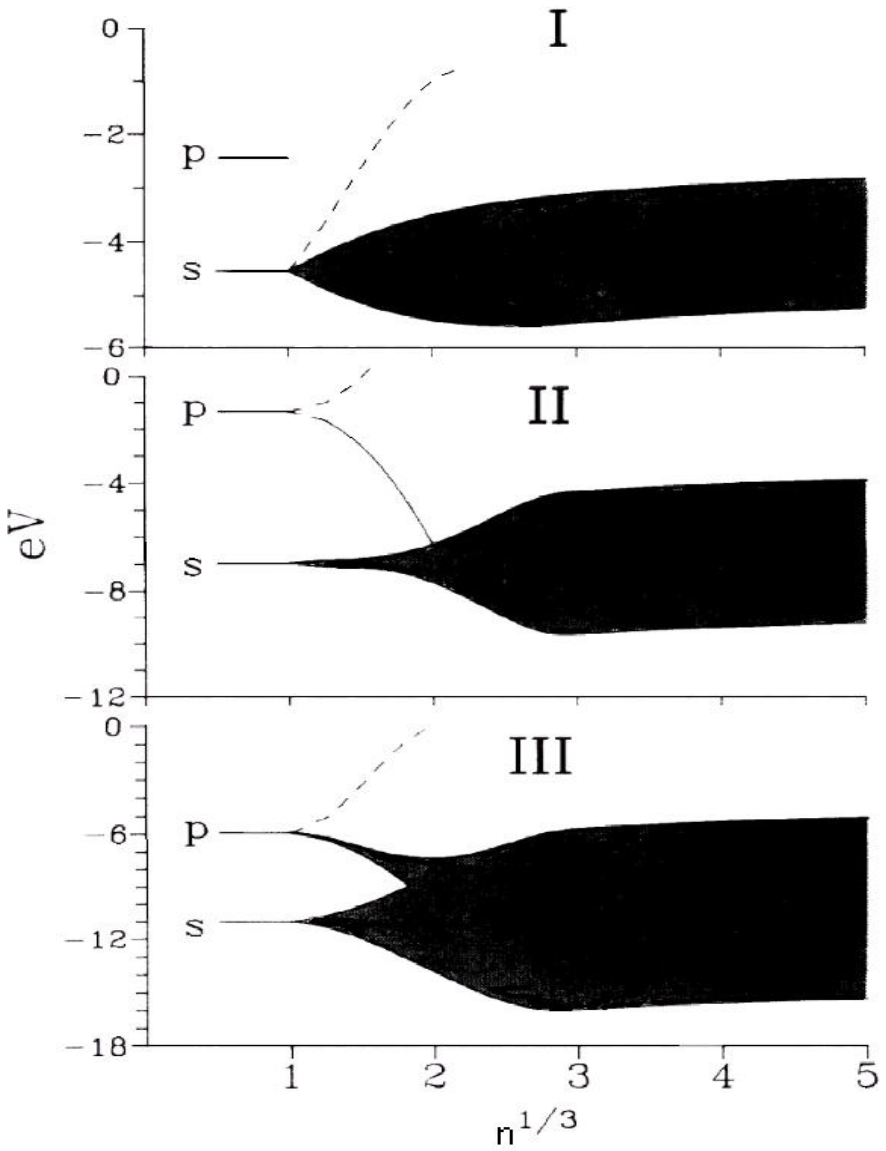
Sodium

Divalent:

Zinc

Trivalent:

Aluminum



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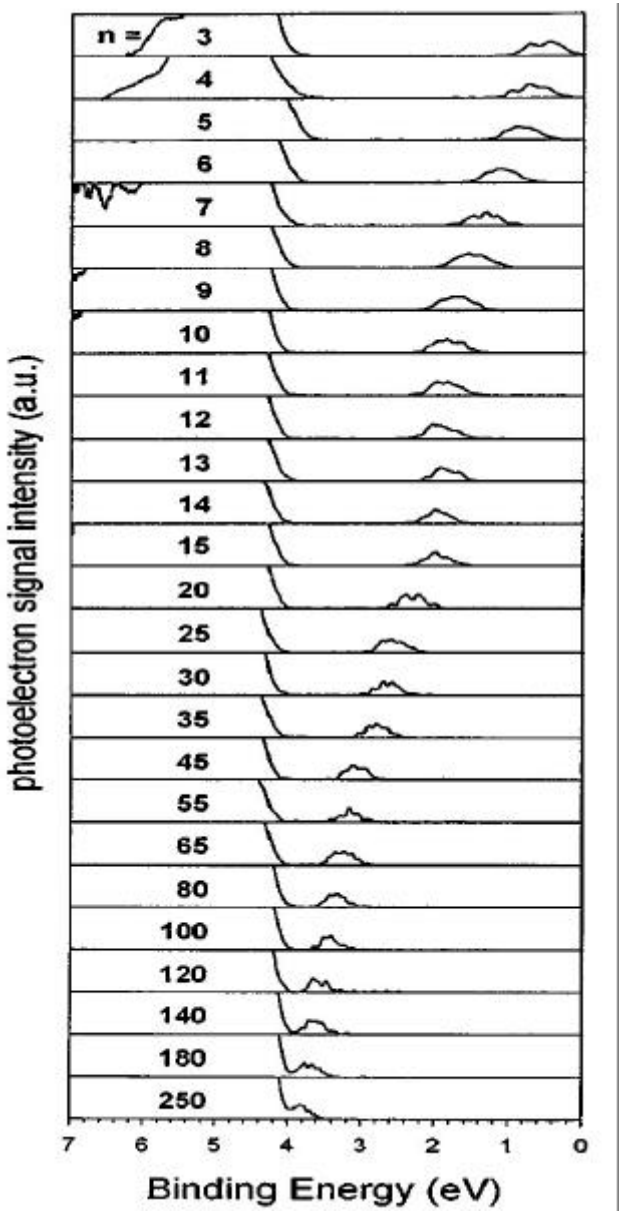
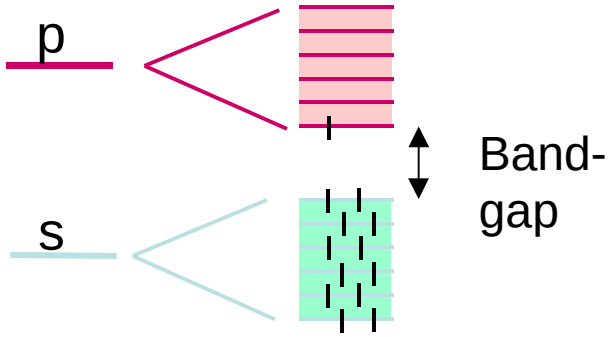
Photoelectron spectroscopy on Hg_n^--clusters: Nonmetal-metal-transition

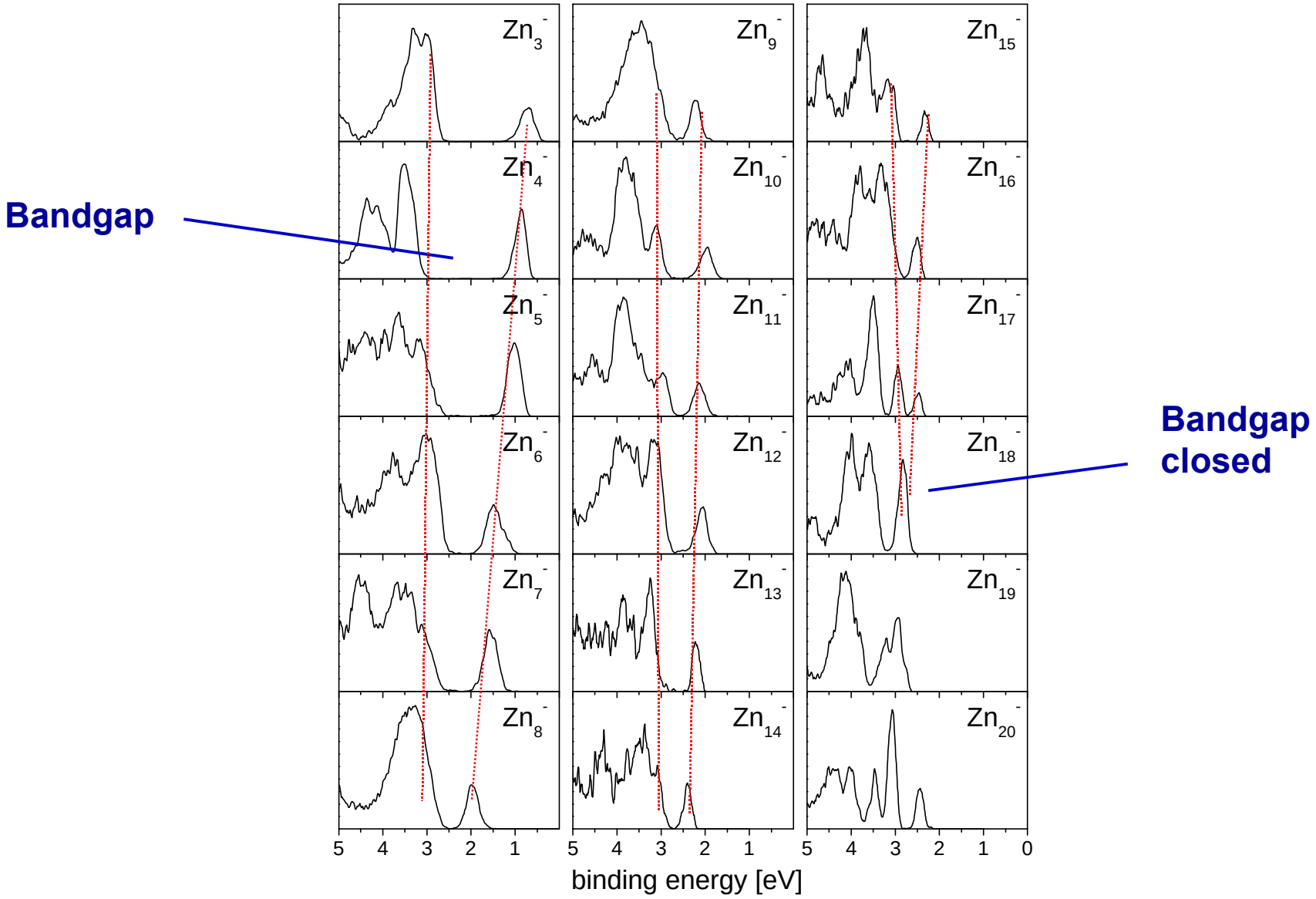


Cluster anions:
1 electron in p-band



Busani, Folkers, Cheshnovsky,
PRL 81, 3836 (1998)

Photoelectron spectroscopy on small Zn^--clusters

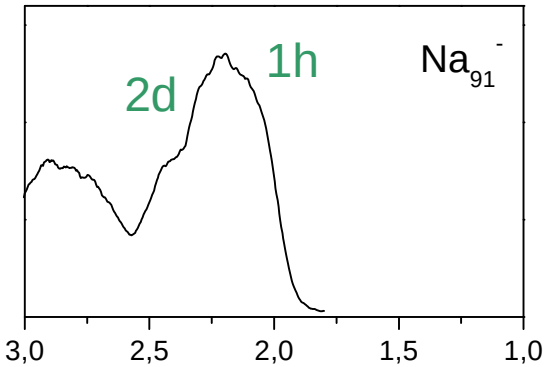


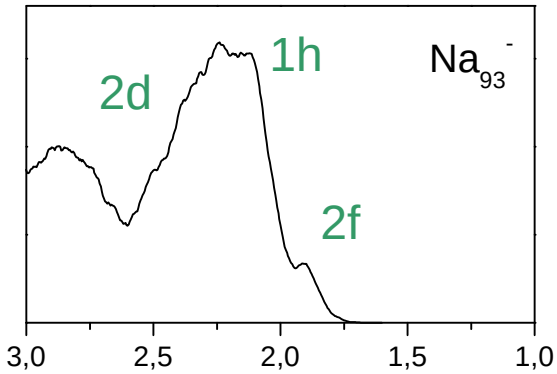
Free electron shells in larger Zn clusters

92 (91) electrons

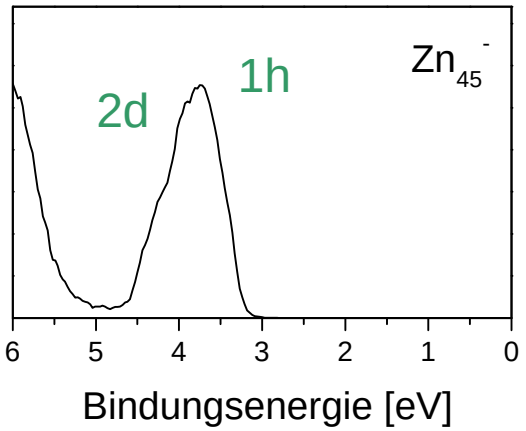
94 (93) elektrons

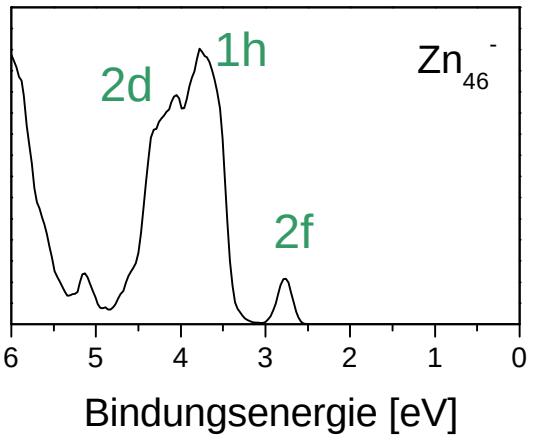
Comparison with spectra of sodium clusters





Energy axis scaled according to Fermi energies
Na: 3.1 eV
Zn: 9.5 eV



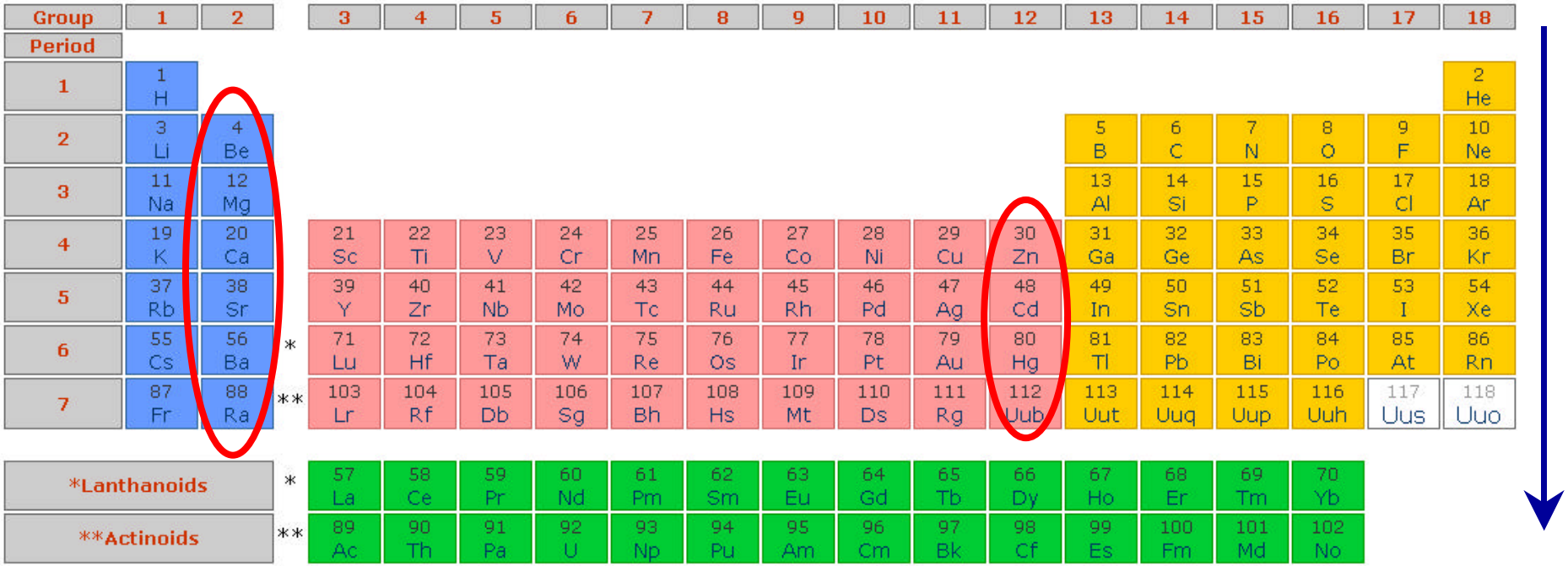


J. Chem. Phys. **123**, 221102 (2005)

Other divalent metals

Increasing elativistic effects

IIA **IIB**

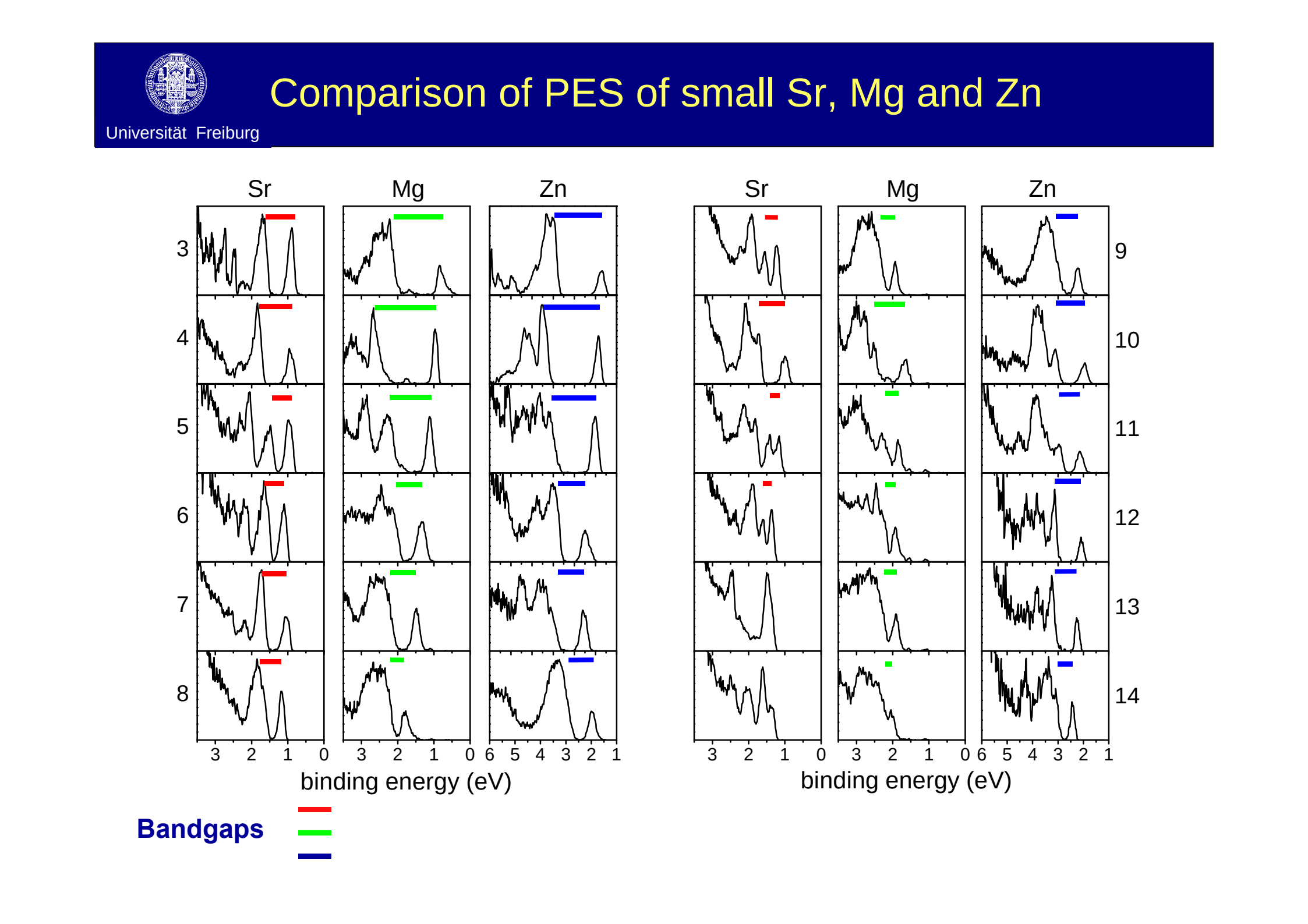


Mg [Ne]$3s^2 3p^0$

Zn [Ar]$3d^{10} 4s^2 4p^0$

Sr [Kr]$5s^2 5p^0 4d^0$

Hg [Xe]$4f^{14} 5d^{10} 6s^2 6p^0$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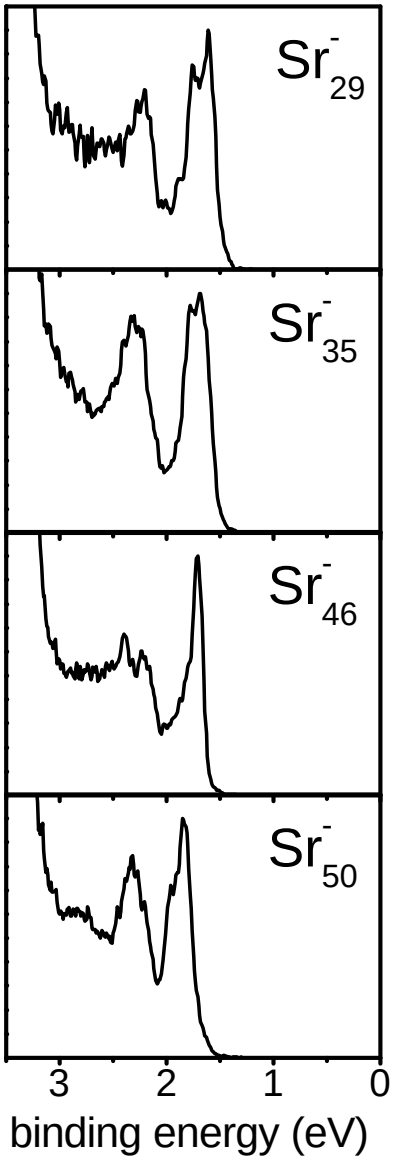
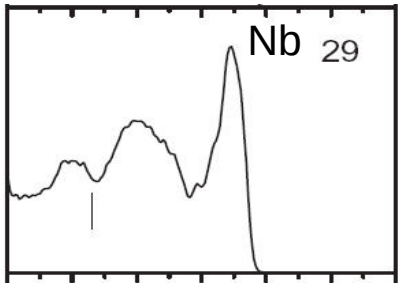
Comparison of PES of small Sr, Mg and Zn
Sr
Mg
Zn
3
4
5
6
7
8
9
10
11
12
13
14
3 2 1 0
6 5 4 3 2 1
binding energy (eV)
Bandgaps

PES of big Sr clusters

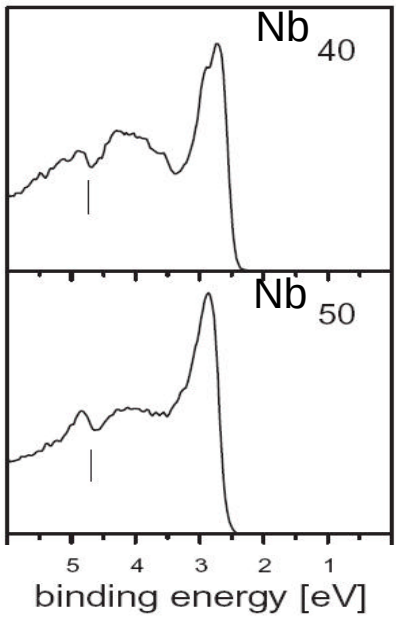
Electronically magic sizes:

No bandgap!





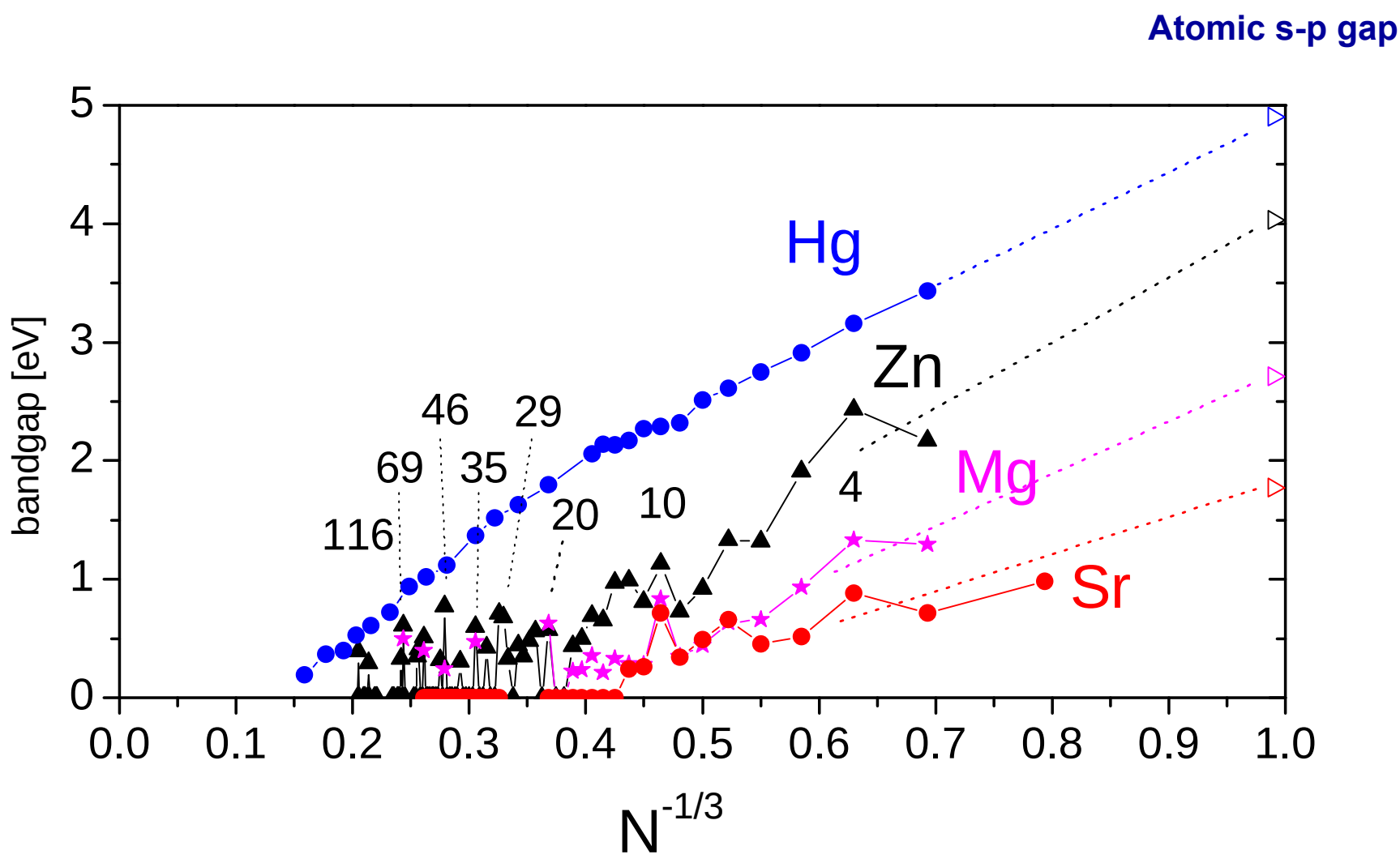
G.Wrigge et al.
Eur. Phys. J. D **24**, 23 (2003)



Spectra similar to open d-band transition metals!

Sr develops into a transition metal!

Bandgaps of Hg, Zn, Mg and Sr

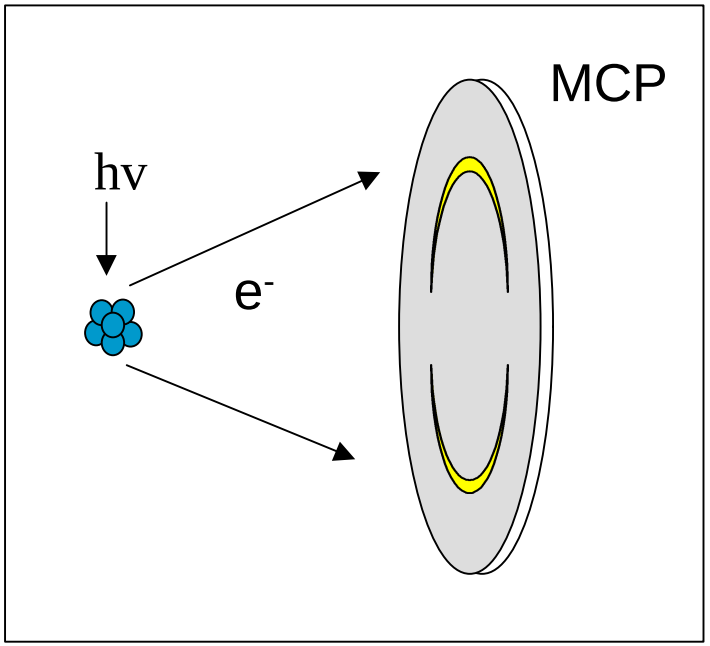


Outlook: angular resolved PES

Imaging Photoelectron Spectrometer:

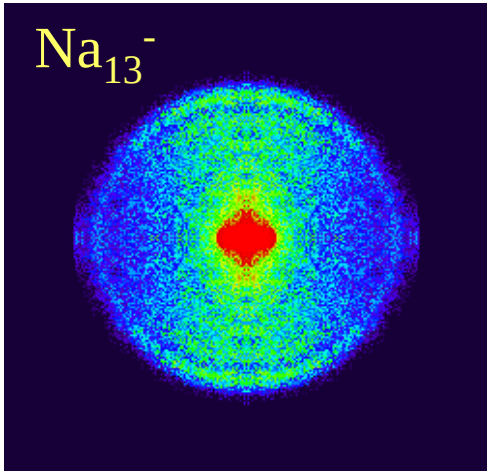
Measurement of angular and kinetic energy distribution

„Superatom“ behaviour ?

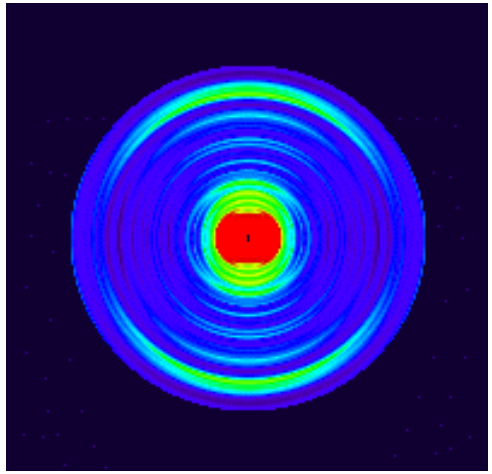


Na_{13}^-

$1s^2\ 1p^6\ 1d^6$



raw data



„Abel“ transform

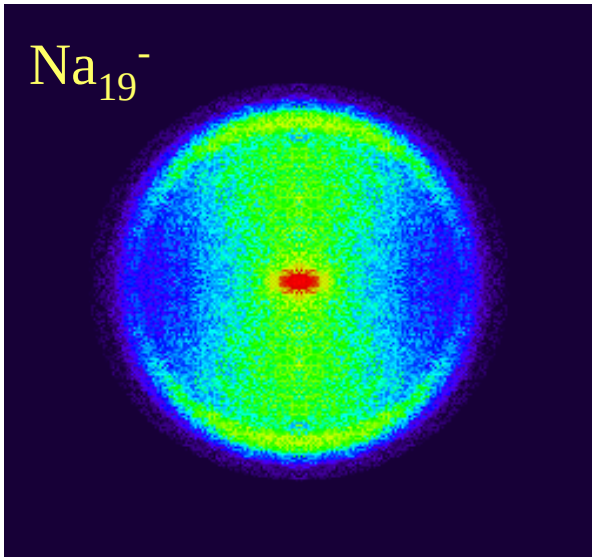
308 nm

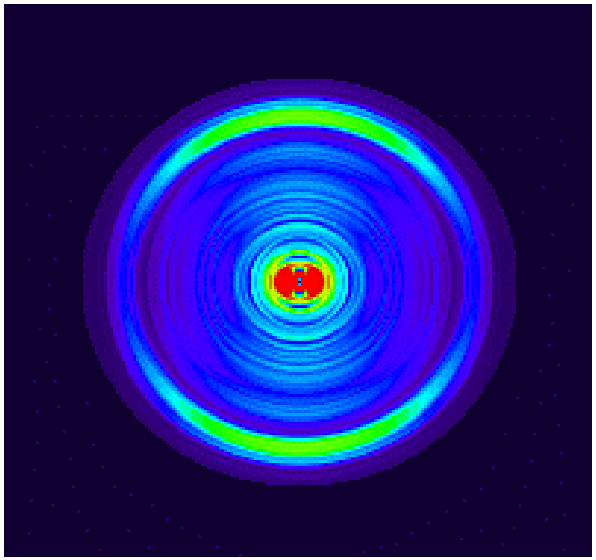
laser polarization

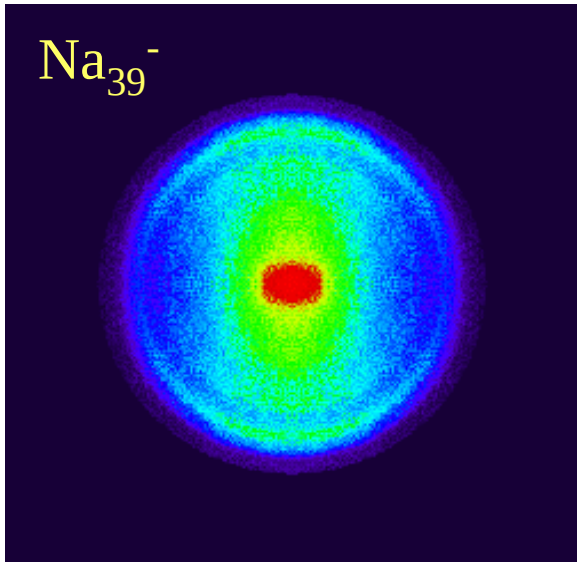
Angular resolved PES

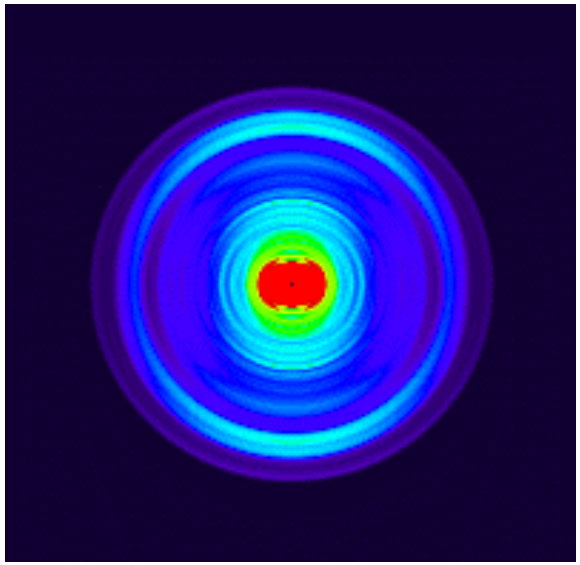
nanosecond laser pulse 308 nm

laser polarization







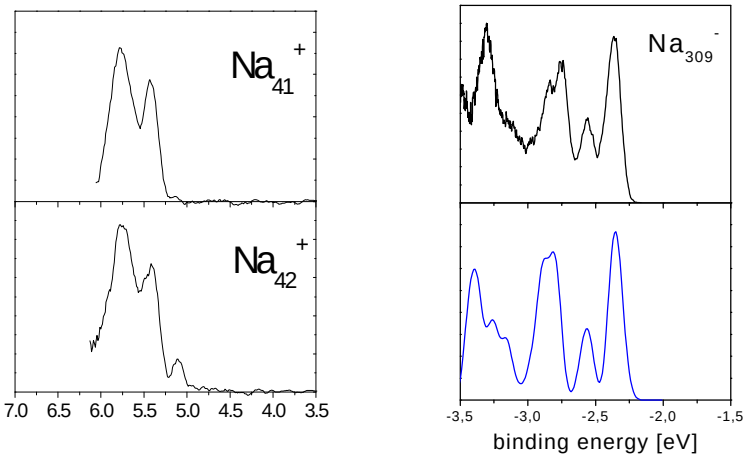


p-character of outgoing electron wave in all cases !

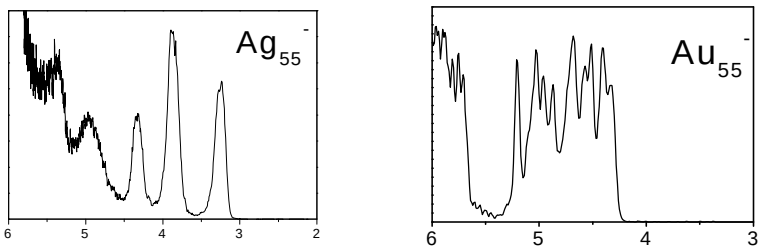
Atomic s-character visible?

Summary

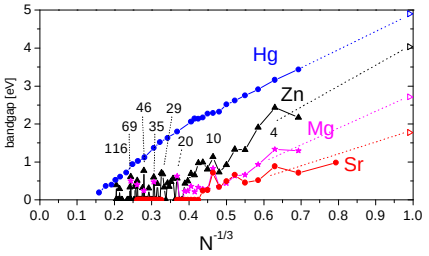
Sodium clusters:
perfect shell structure
(only) for liquid clusters



Noble metal clusters:
strongly perturbed shell structure;
high degeneracy only for high symmetry.
And:
Gold is different!



Divalent metals:
Nonmetal/metal transition as a function of size
Hg and Sr are special!



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