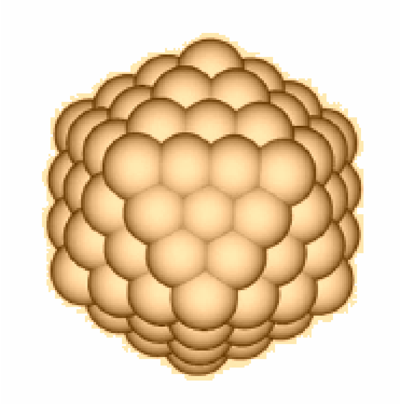
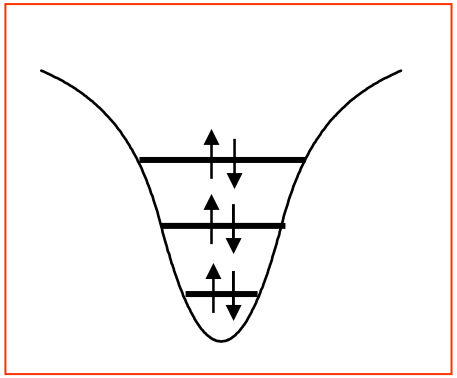
Photoelectron spectroscopy on simple metal clusters

B.v.Issendorff

What is the correct description of a simple metal nanoparticle?

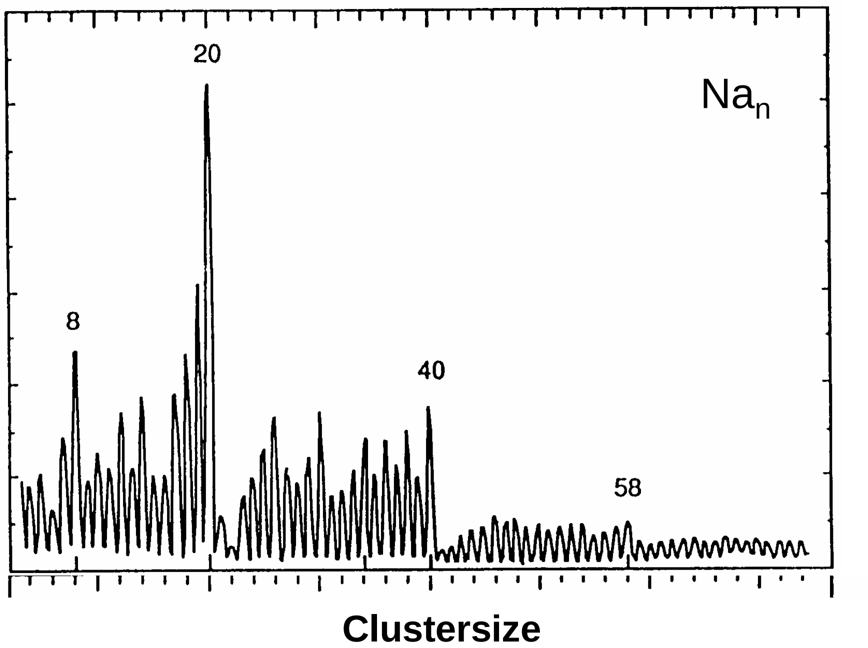


High or low symmetry
Supermolecule

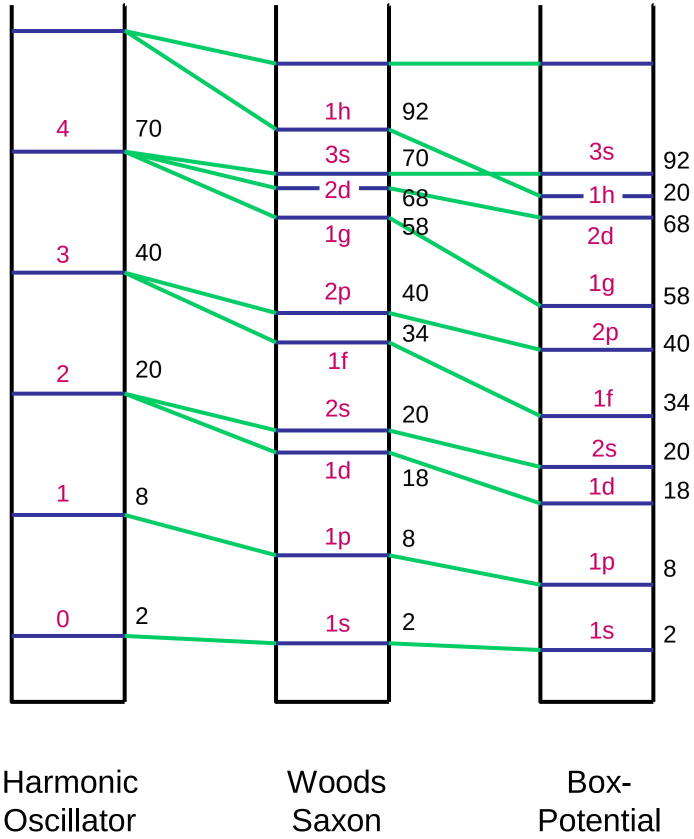


Trapped Fermi gas
(parabolic trap filled
with electrons)

Electron shells: spherical box model

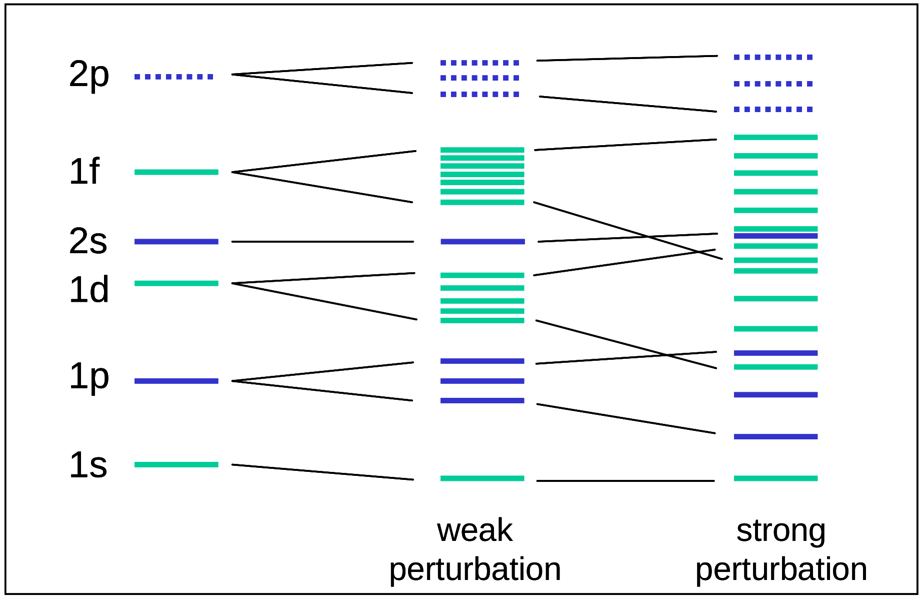


Knight, de Heer, 1984



Electron levels in different spherical model potentials

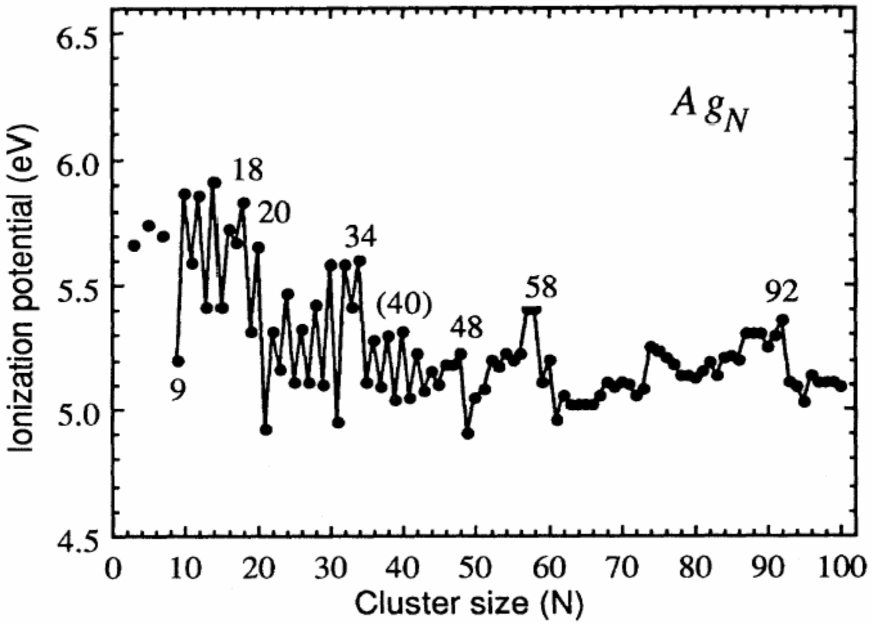
Shell structure in a real cluster



The atomic structure perturbs the electron angular momentum eigenstates

Ideal probe: Photoelectron-spectroscopy (Lineberger, Bowen, Smalley, Cheshnovsky, Meiwes-Broer...)

Ionization potentials of silver clusters: evidence for perturbed shell structure



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

Program

Experiment
Photoelectron spectroscopy
cluster thermalization

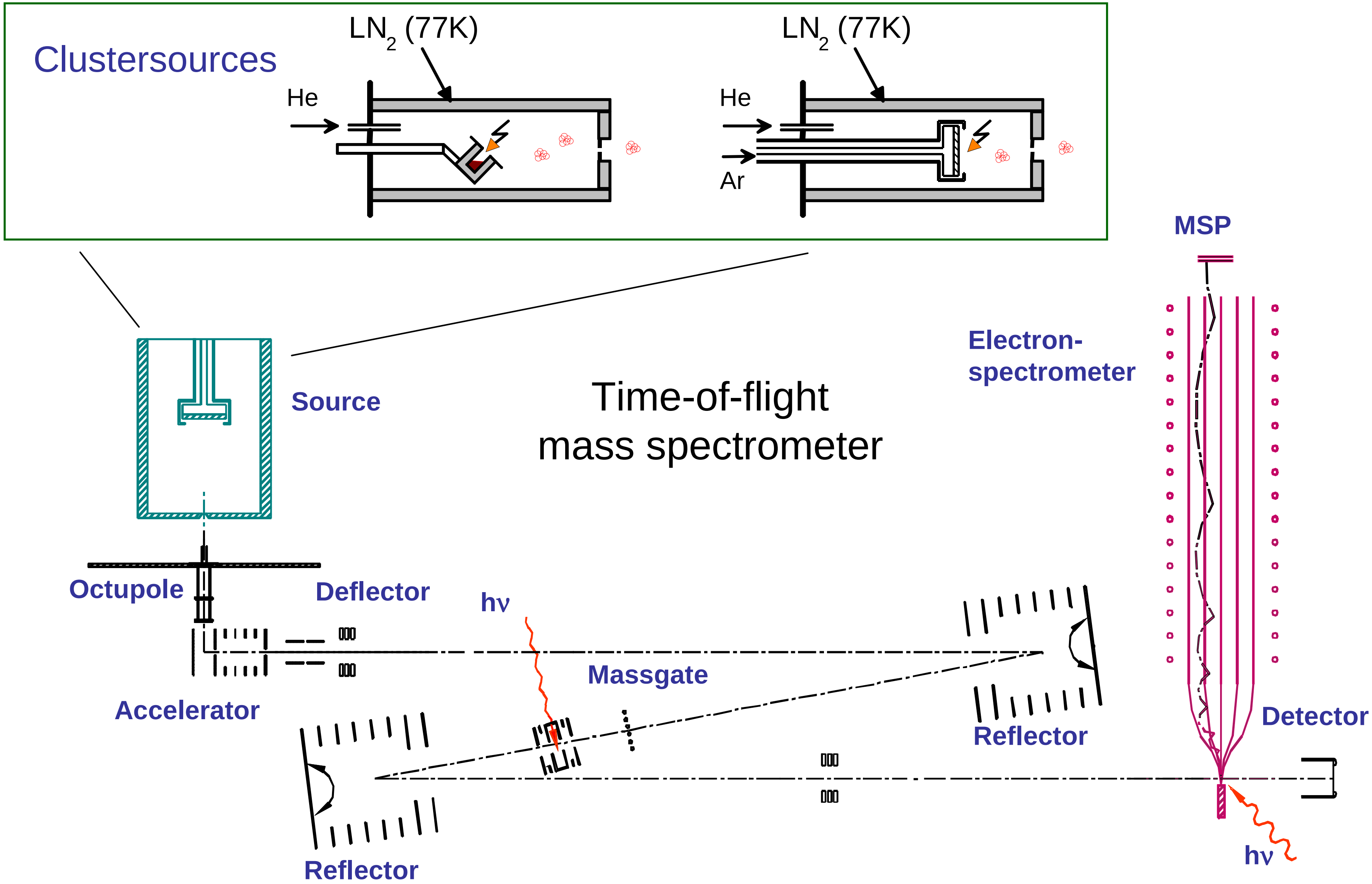
Sodium clusters
Electronic shell structure
Interaction with geometric structure
Cluster shapes: comparison to simple models
Structure of larger clusters
Comparison with potassium clusters

Noble metal clusters
Electronic structure
Geometrical structure
special case: gold clusters
Comparison Na, Cu, Ag, Au

Angle resolved photoelectron spectroscopy
Basics
Results on Na, Ag, Cu

Universität Freiburg

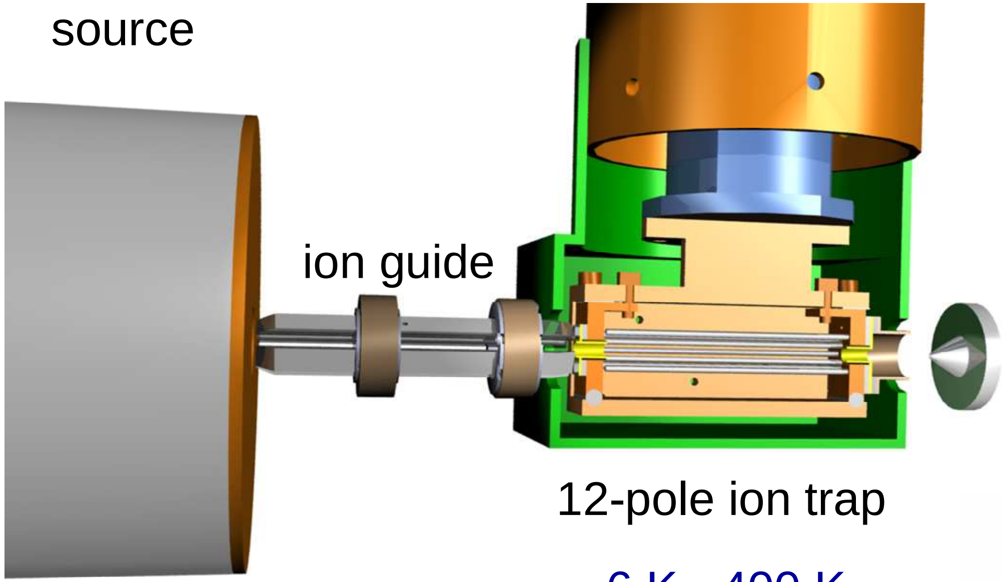
Experiment



Cluster Thermalization

source

ion guide

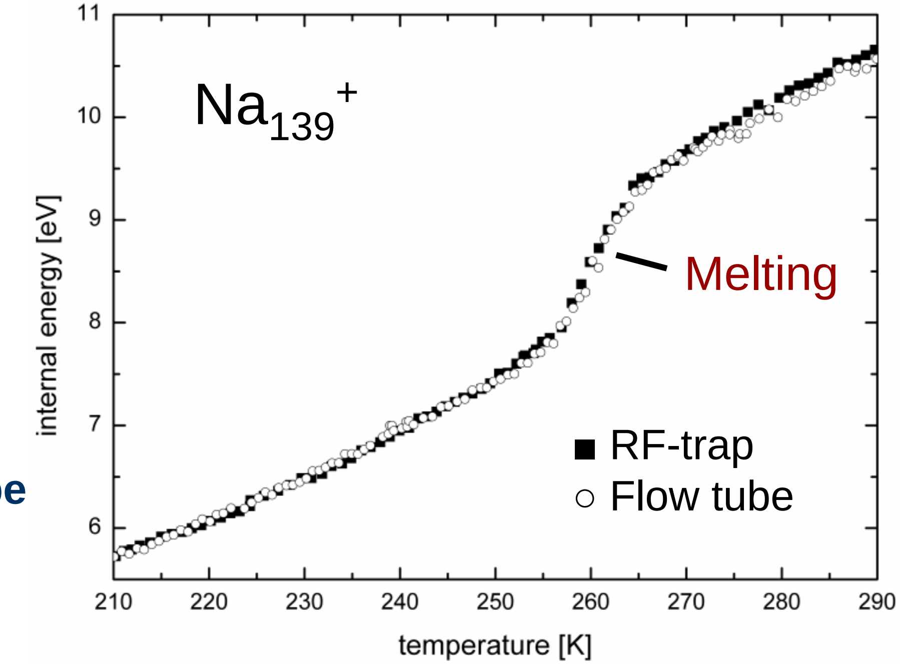


12-pole ion trap

6 K - 400 K

Linear RF-Trap for cluster thermalization after production

Caloric Curve

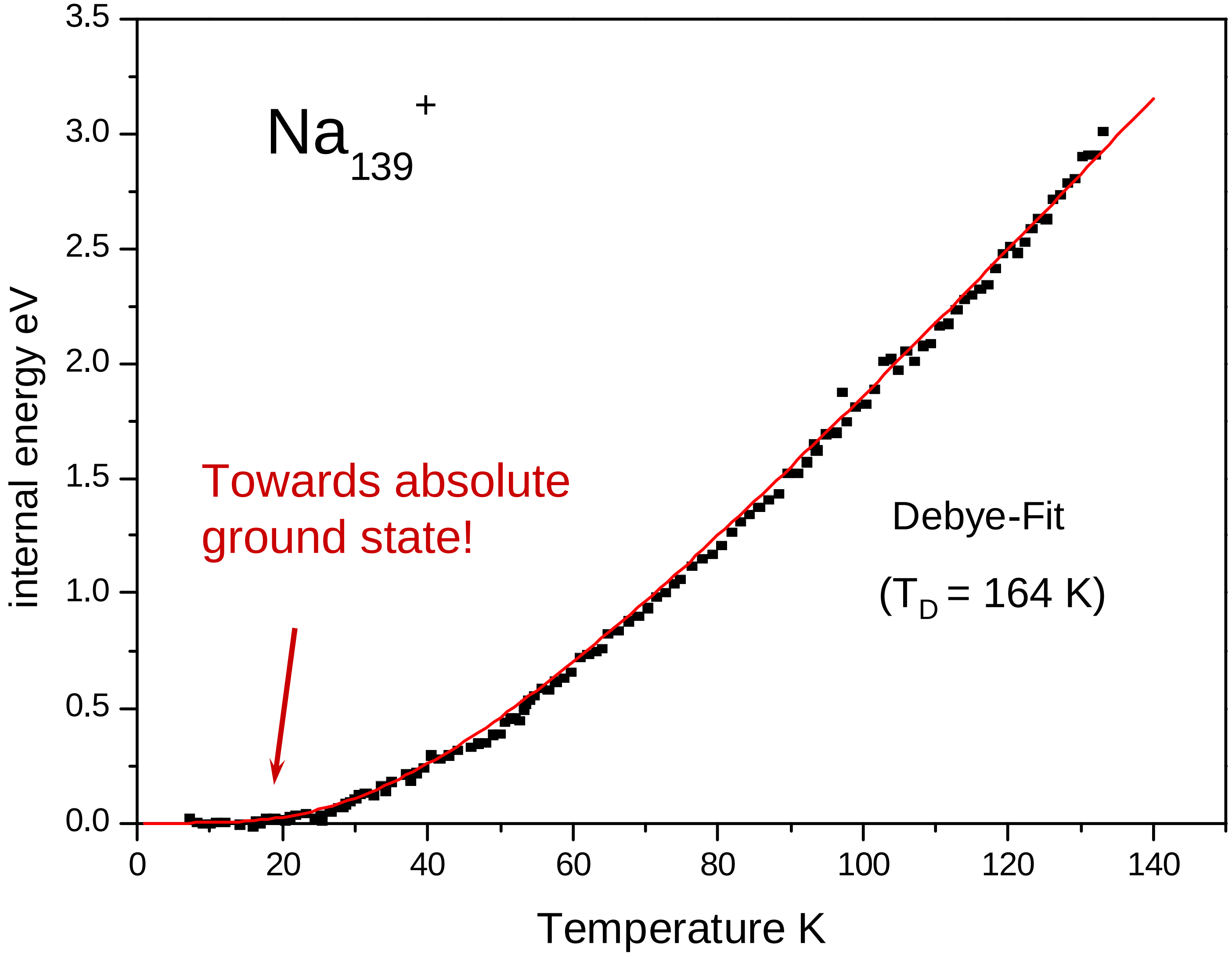


Check of temperature: Comparison with flow tube thermalization

Universität Freiburg

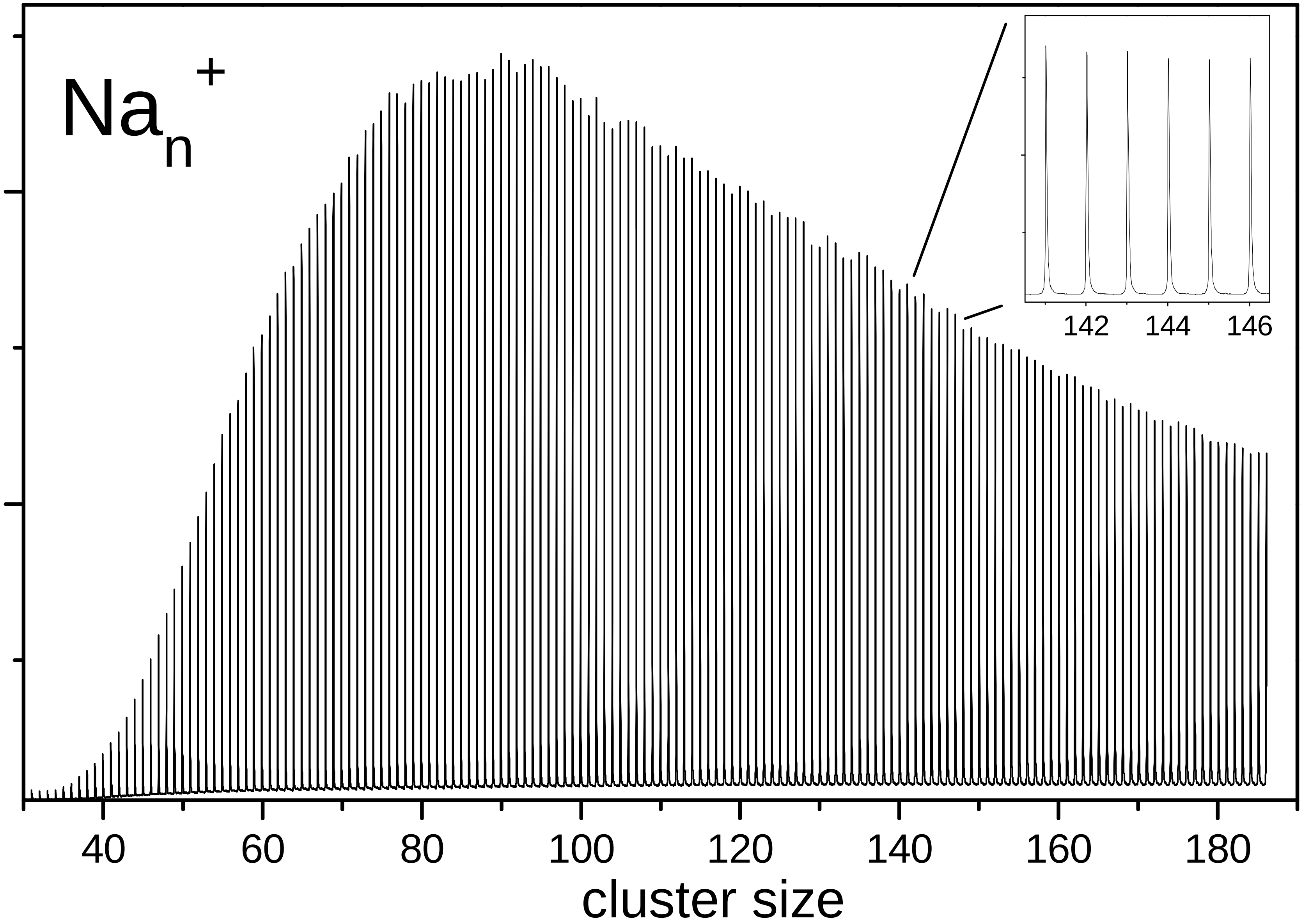
Very low temperatures

Caloric curve of clusters thermalized in RF-Trap

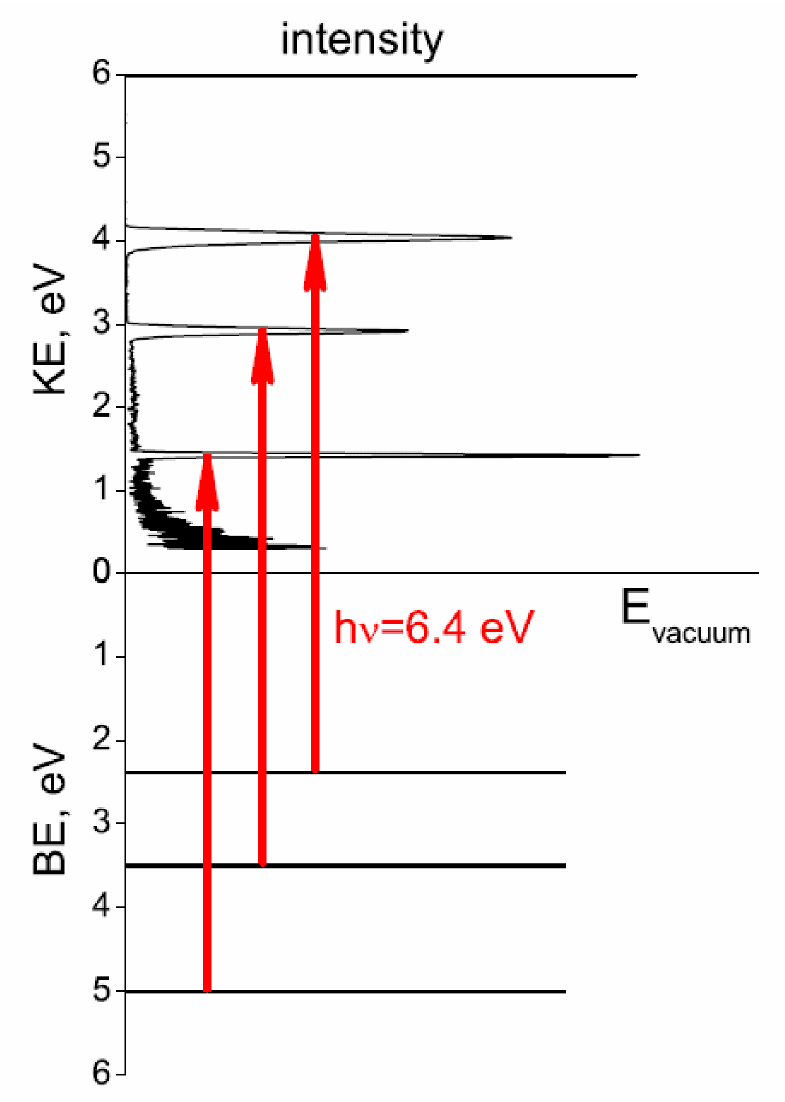


Universität Freiburg

Mass spectrum of sodium clusters



Photoelectron spectroscopy: principle



Photoeffect:

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

broadening effects:

- **vibrational (de)excitation**
- **hole lifetime**

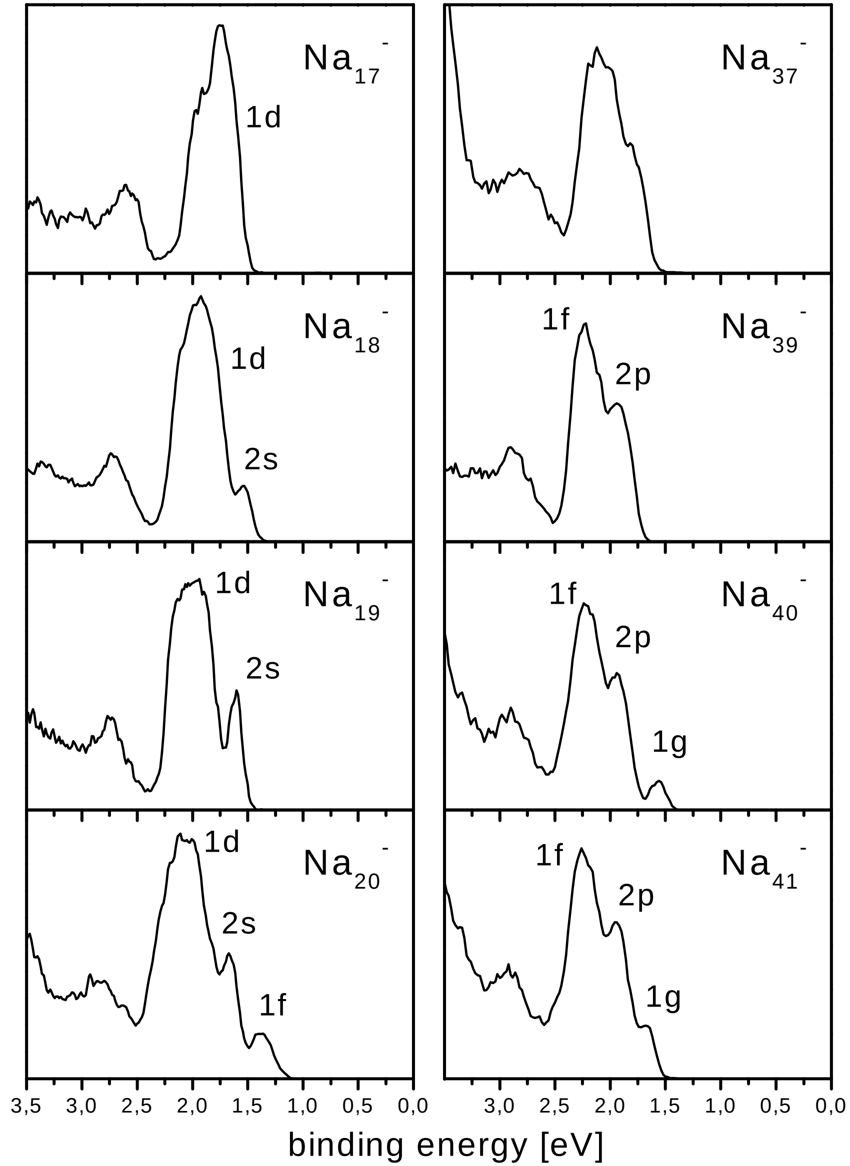
PES on hot sodium clusters

Universität Freiburg

Jellium levels:

1s	1p	1d	2s	1f	2p	1g
2	8	18	<u>20</u>	34	<u>40</u>	<u>58</u>

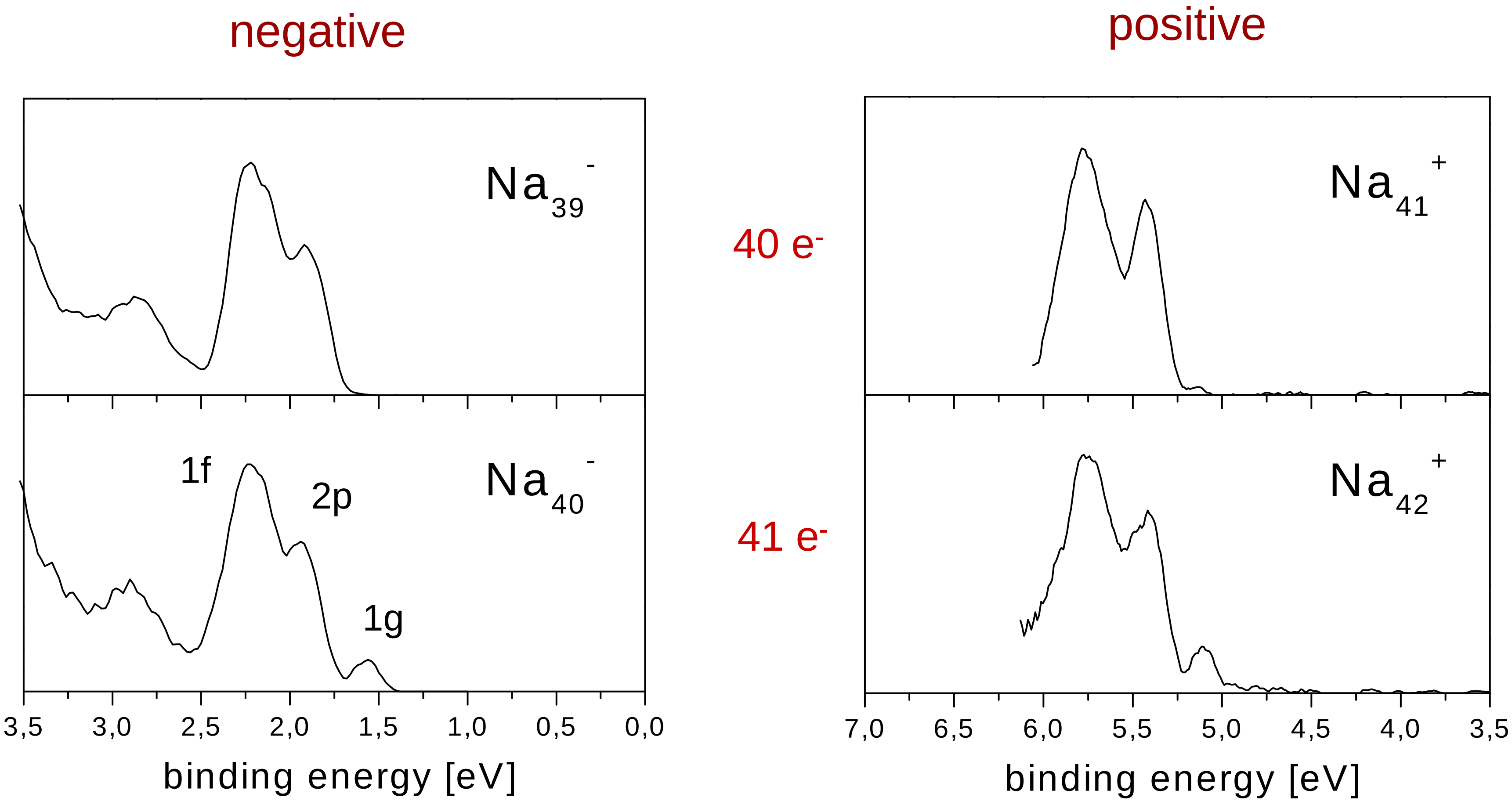
ideal electron shell structure!



BvI, O. Cheshnovsky
Annu. Rev. Phys. Chem. 56, 549 (2005)

Comparison of cluster anions and cations

Universität Freiburg



Identical DOS despite different geometrical structures!

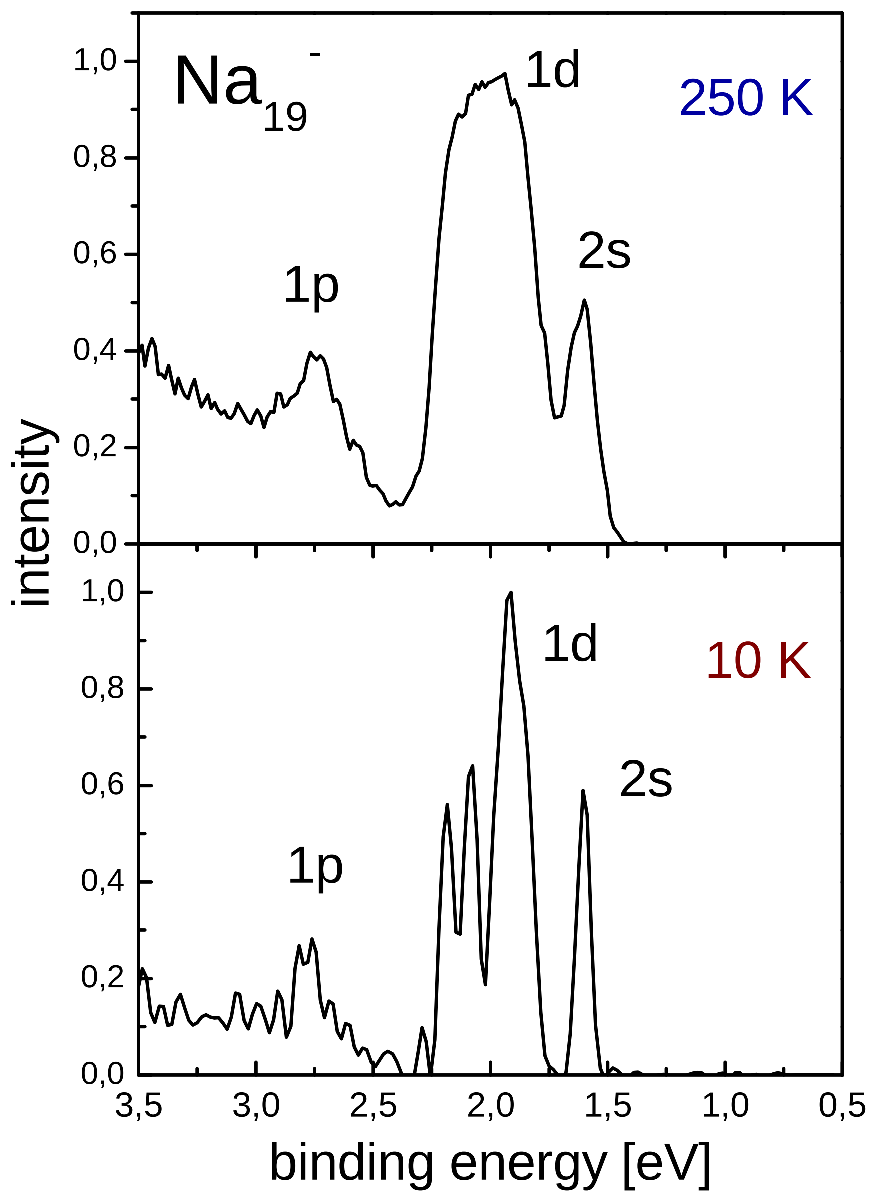
Universität Freiburg

Temperature dependence of PES

20 valence electrons:
spherical shape

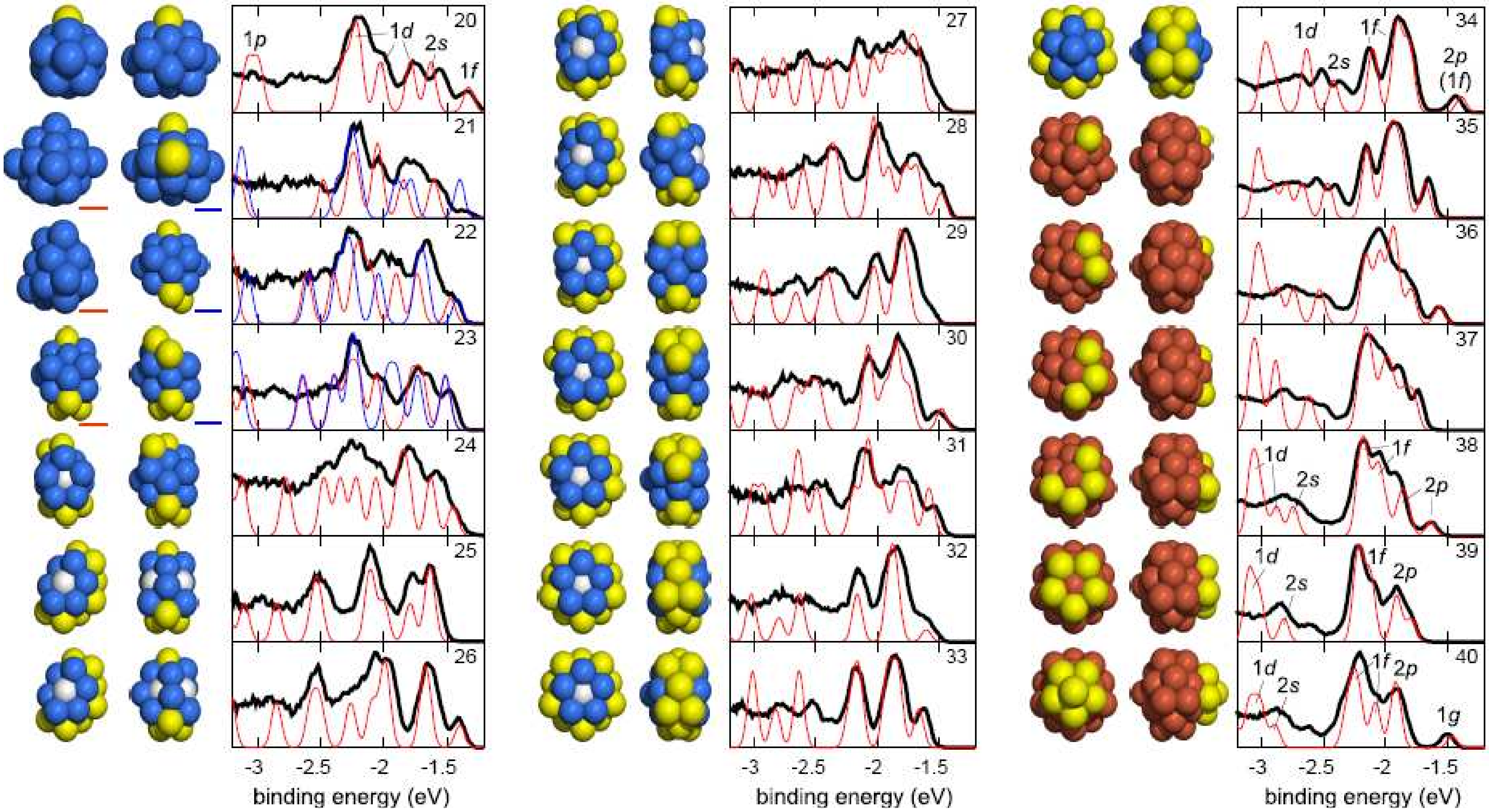
Strong splitting
of d-state:

electron-lattice
interaction!



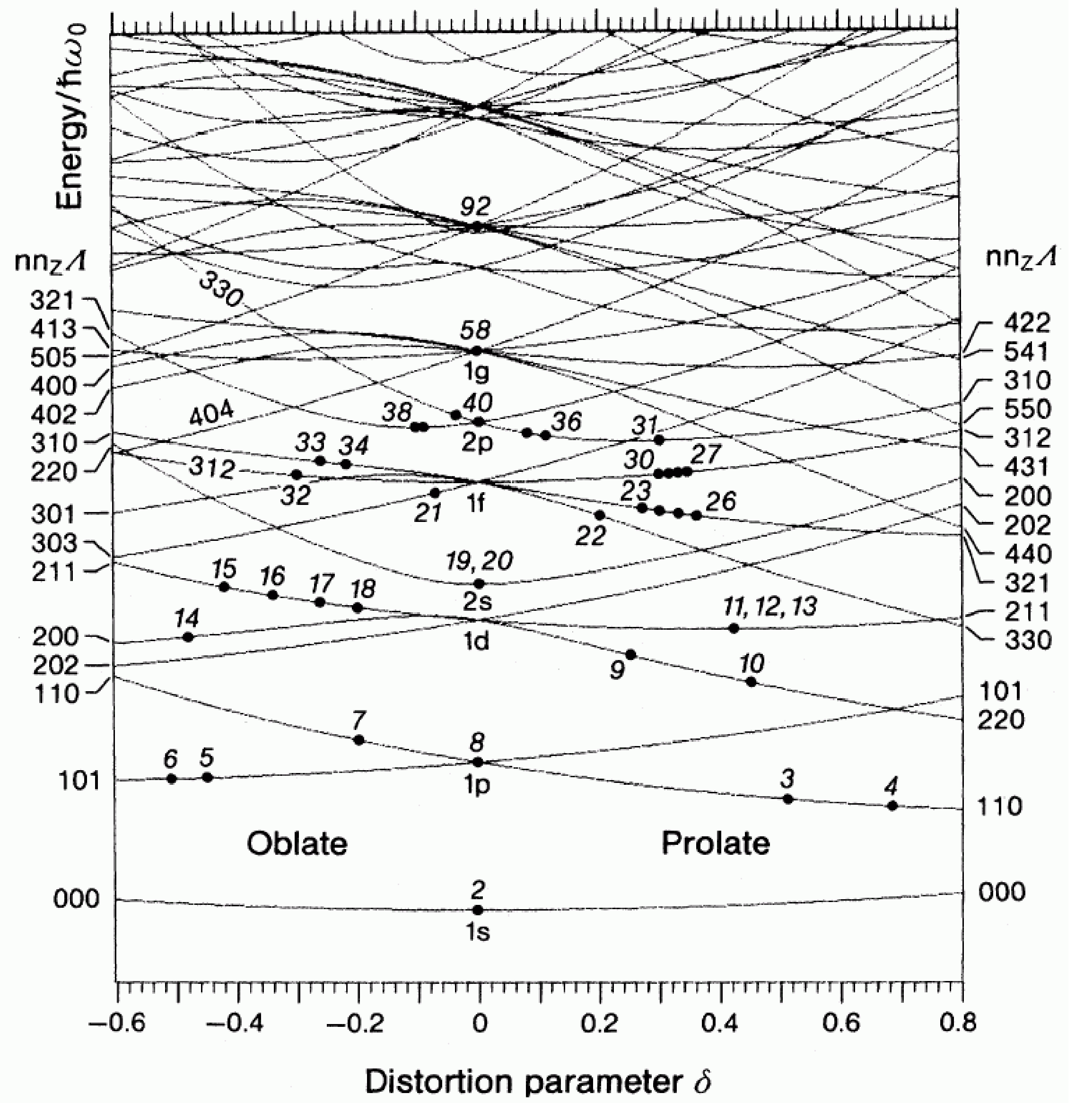
PES of Na_n^- : n = 20-40

T = 100 K



DFT- calculations by
M. Moseler and B. Huber

Cluster deformation: Clemenger-Nilsson-model

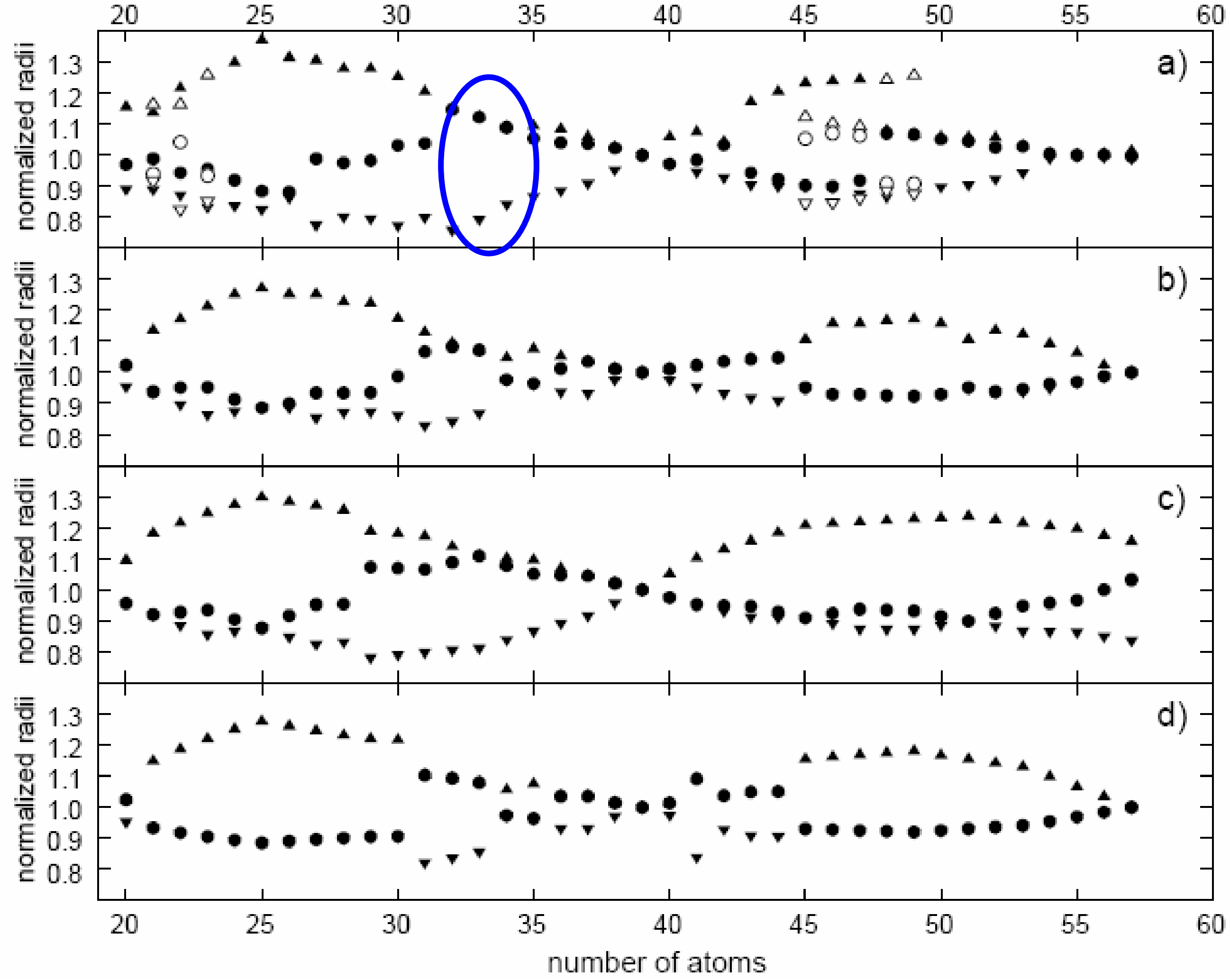


Spherical shape only for closed shell sizes (electron numbers 8, 20, 40, 58, 92..)

Deformation: comparison to simple models

Radii as derived from moment of inertia

34 electrons: closed shell!



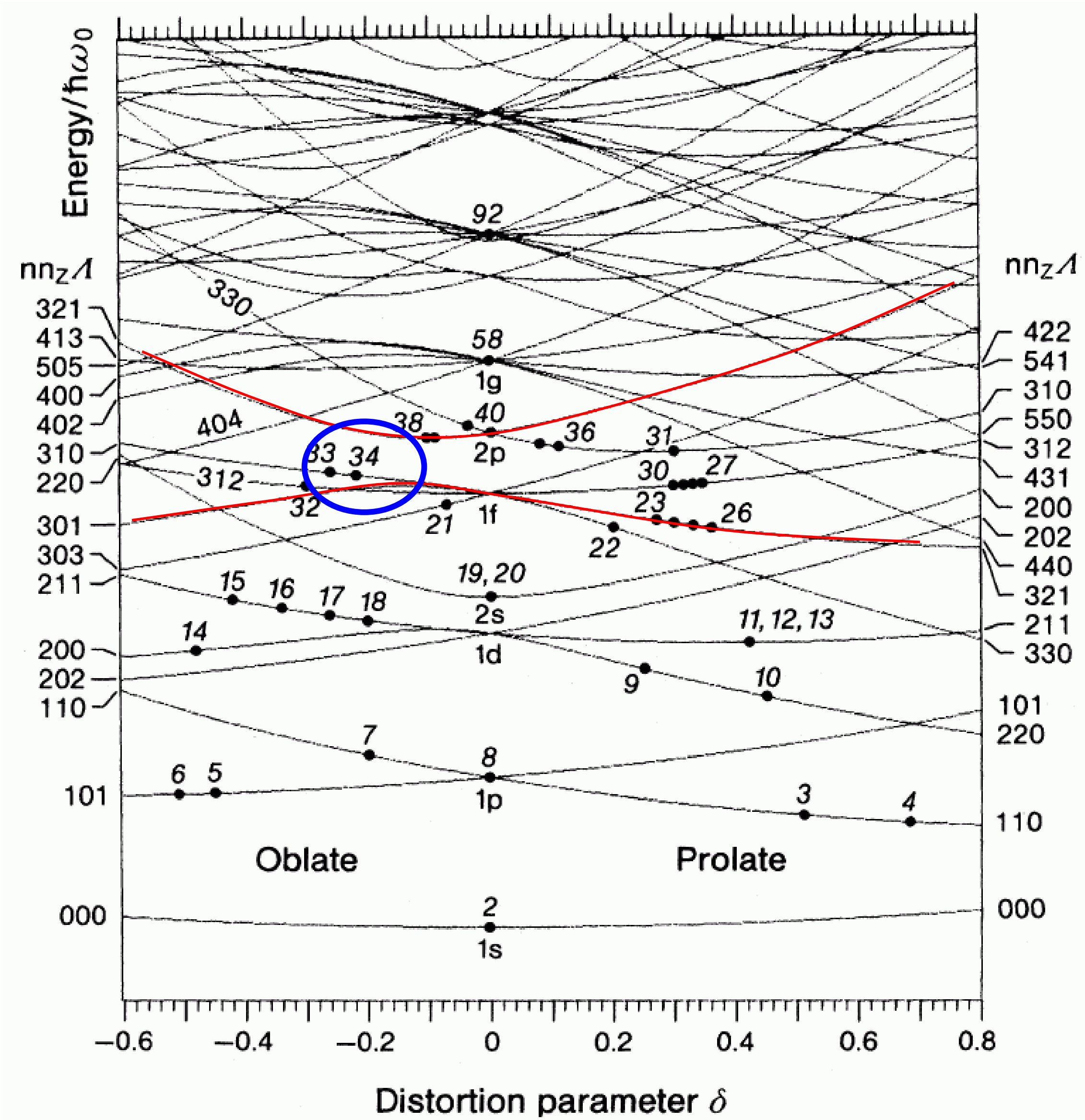
Experiment + DFT

Triaxial Jellium

Triaxial harmonic Oscillator

Clemenger/ Nilsson

Deformation: avoided crossings



Clemenger-Nilsson-model

Quadrupole deformation:

Perturbing potential

$$V(r,\theta,\varphi) = f(r)\, Y_{20}(\theta,\varphi)$$

⇒ mixing of states with $\Delta l=2$

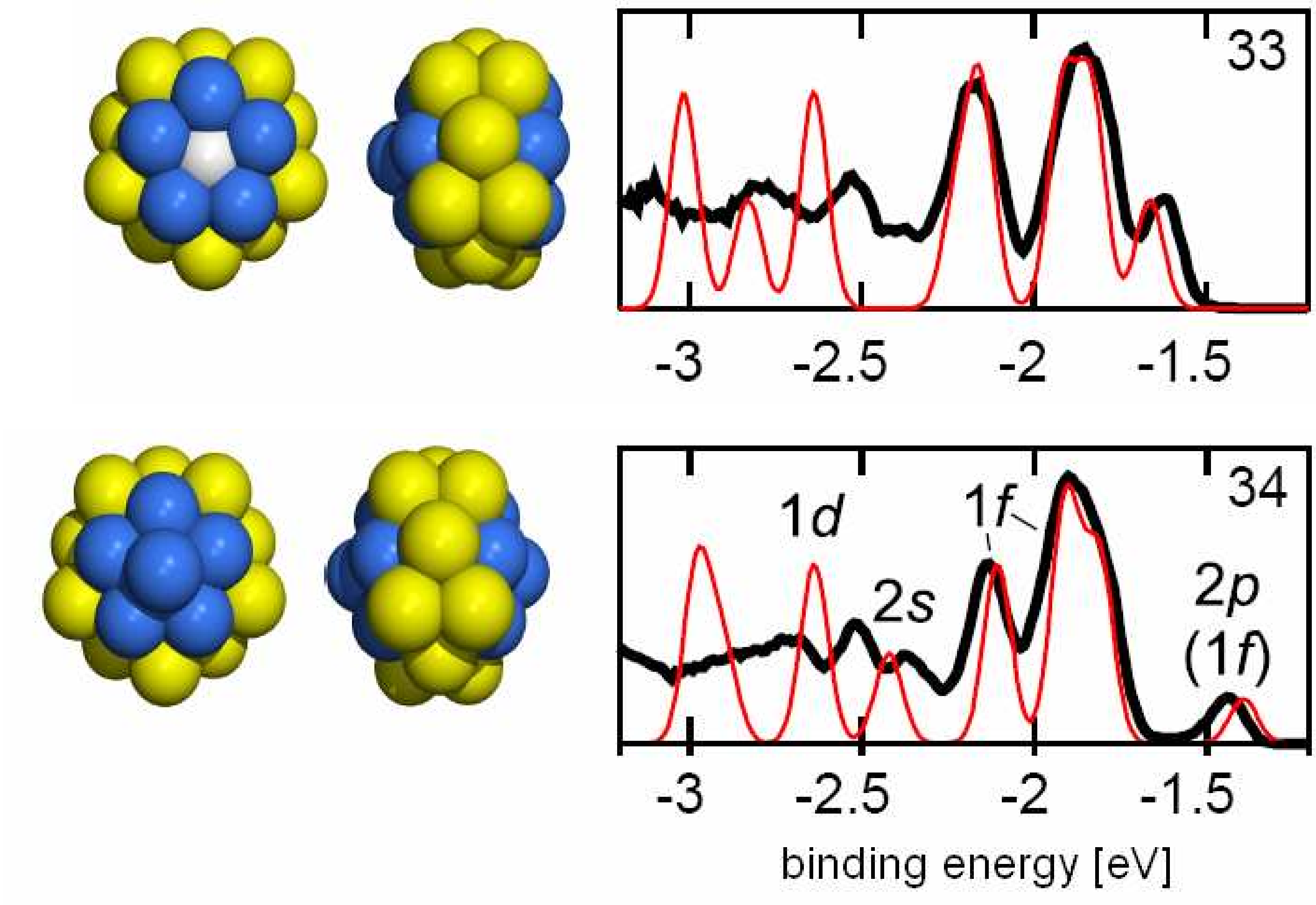
⇒ avoided crossing between 1f and 2p

⇒ stabilization of deformation

Deformation: the 34 electron case

Prolate (quadrupole) deformation: mixing between 1f and 2 p stabilizes nonspherical shape of closed shell structure

Oblate!

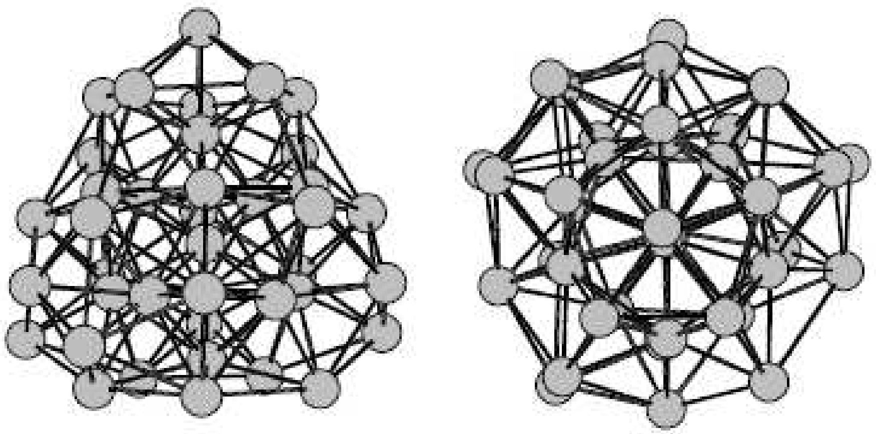


Deformation: the 40 electron case

Octupole deformation mixes 2p and 1g (ΔI=3):

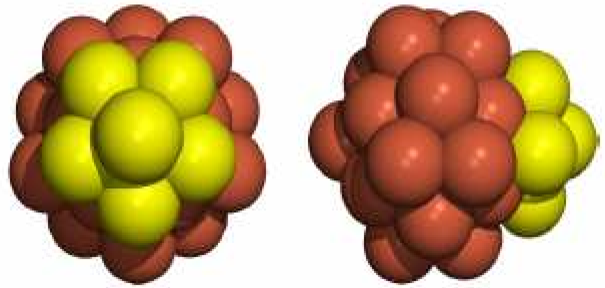
Stabilization of deformation

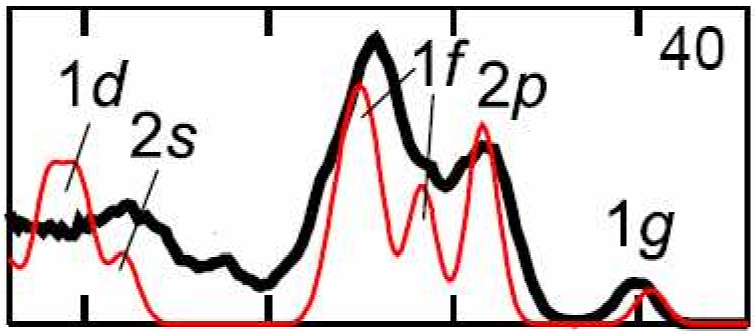
Simulated structure of hot Na_{40}



A.Rytkönen et al., PRL 80, 3940 (1998)

Experiment/DFT





Program

Experiment

Photoelectron spectroscopy
cluster thermalization

Sodium clusters

Electronic shell structure
Interaction with geometric structure
Cluster shapes: comparison to simple models
Structure of larger clusters
Comparison with potassium clusters

Noble metal clusters

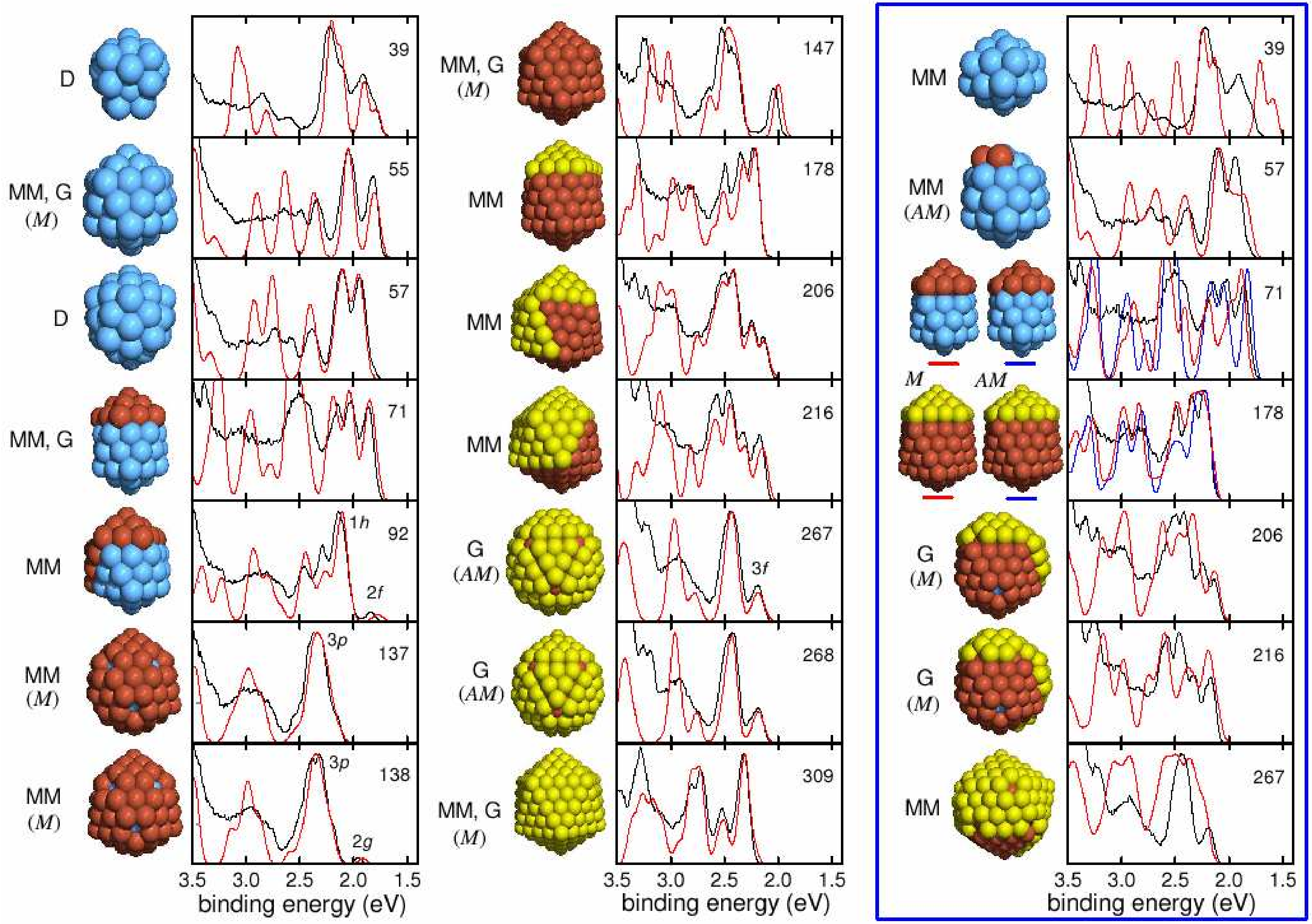
Electronic structure
Geometrical structure
special case: gold clusters
Comparison Na, Cu, Ag, Au

Angle resolved photoelectron spectroscopy

Basics
Results on Na, Ag, Cu

Universität Freiburg

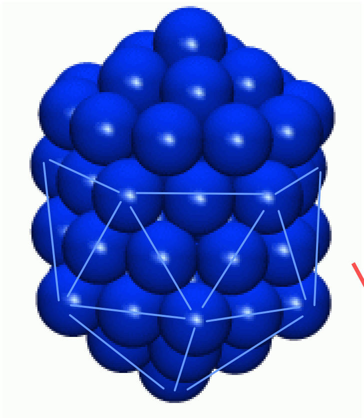
PES of Na_n^- : n = 39-309



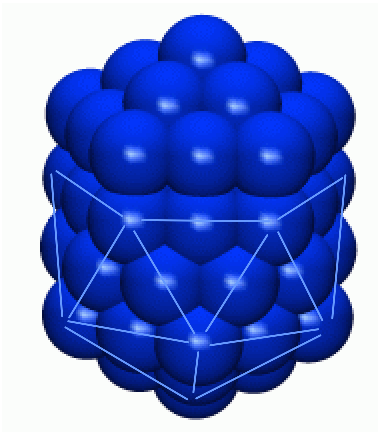
O. Kostko, B. Huber, M. Moseler, and BvI, Phys. Rev. Lett. 98, 043401 (2007)

Sodium: Mackay / anti-Mackay stacking

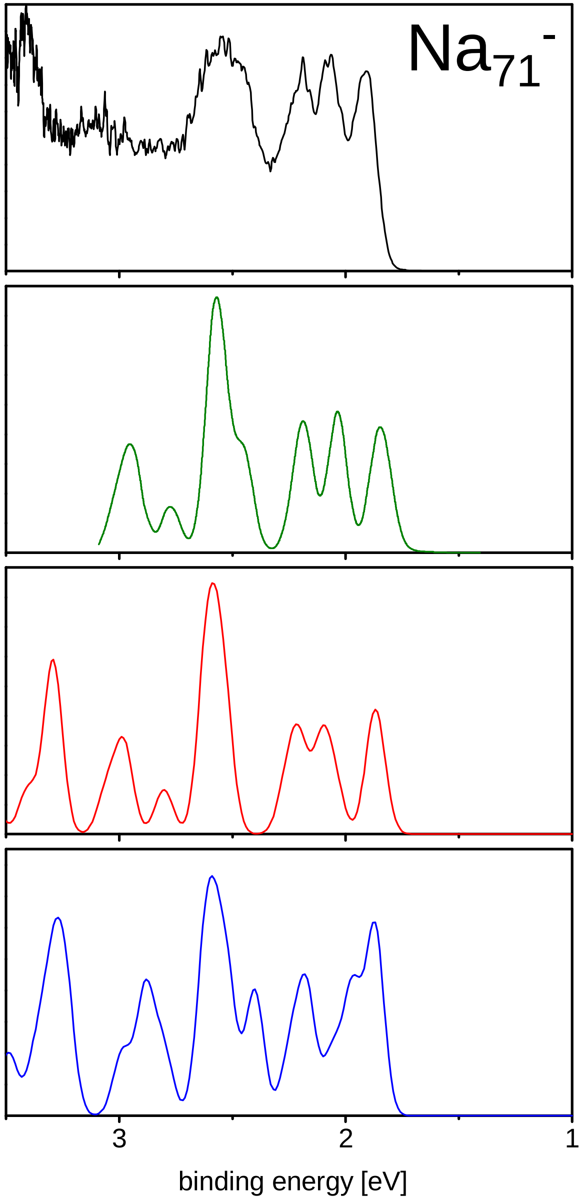
Universität Freiburg



55 atom icosahedron
with anti-Mackay-cap



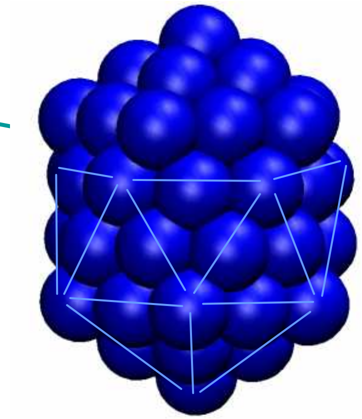
55 atom icosahedron
with Mackay-cap



Experiment

Calculated DOS

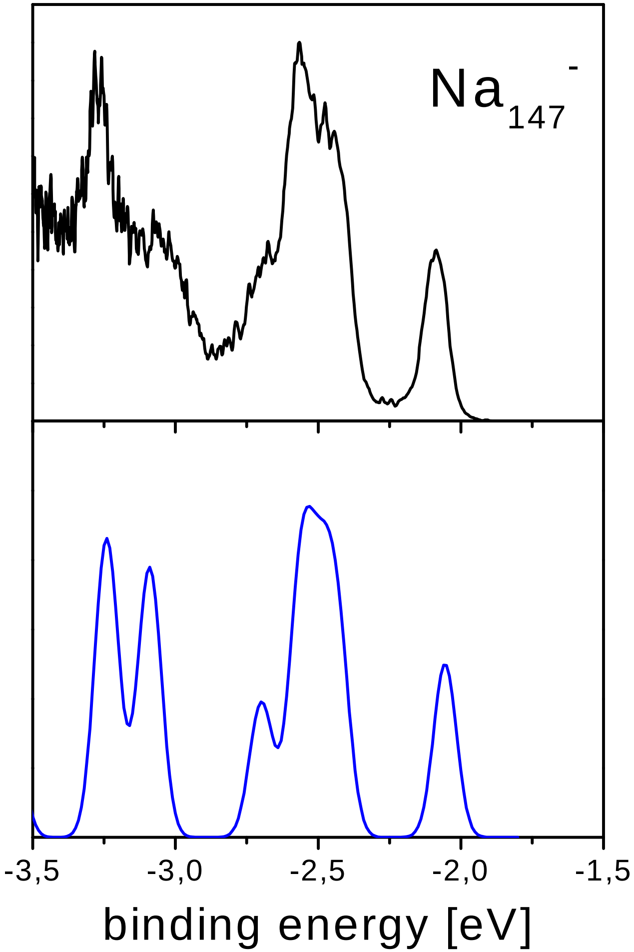
(M.Moseler, IWM Freiburg)



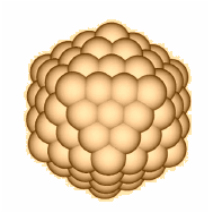
55 atom icosahedron
with twisted cap

(Noya et al., EPJD 43, 57 (2007)

Comparison with theory

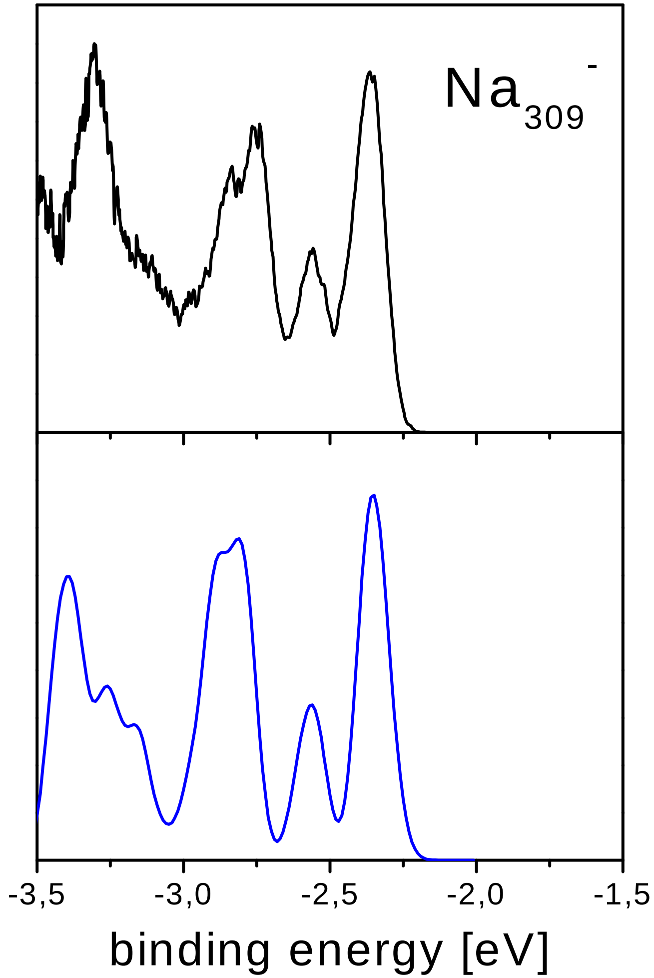


Experiment



Theory

calculations by
M. Moseler
and B. Huber,
Freiburg

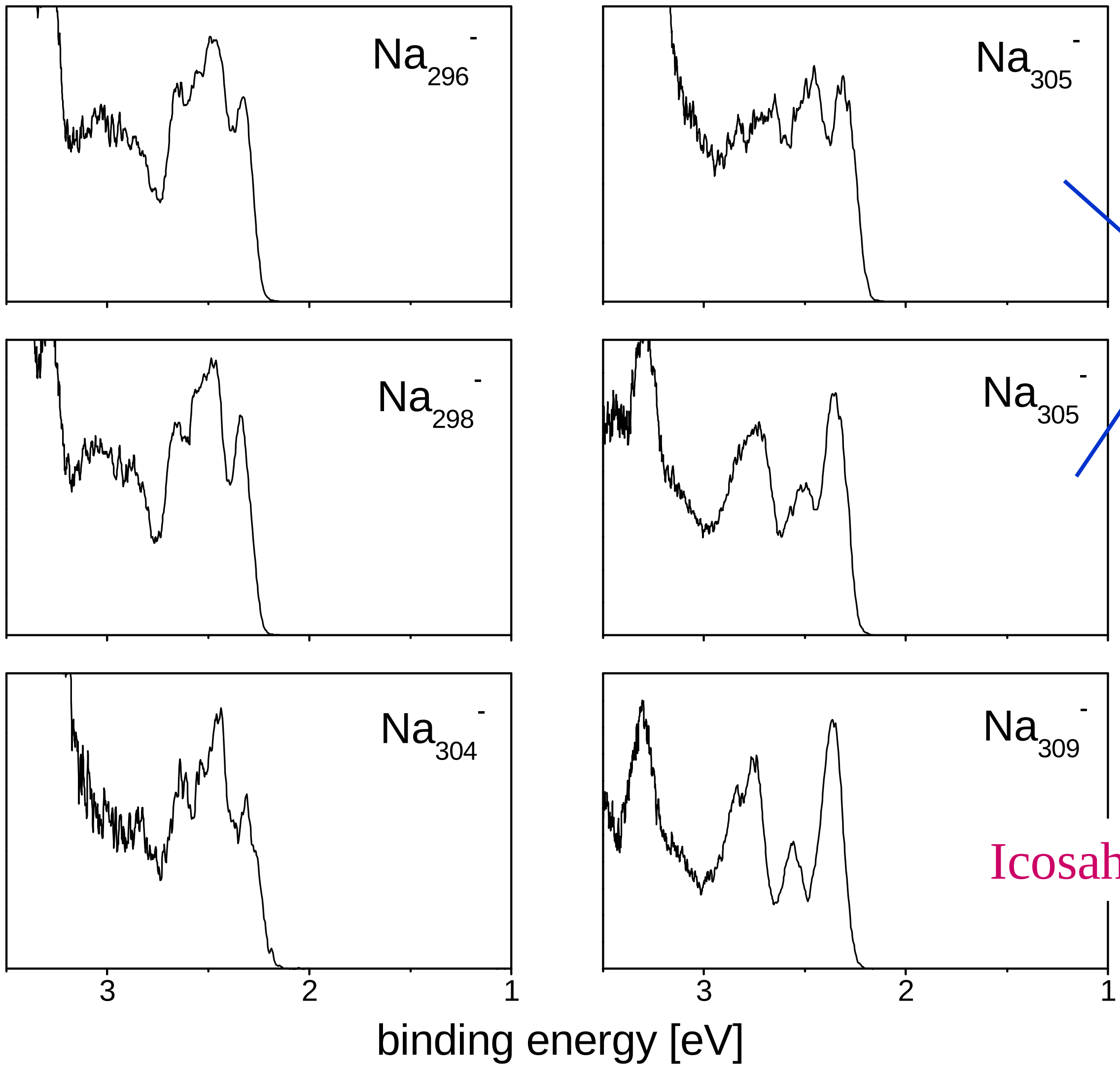


Closed shell icosahedral stuctures!

Universität Freiburg

Abrupt structure change at size 305

Unknown Structure!



T=150 K

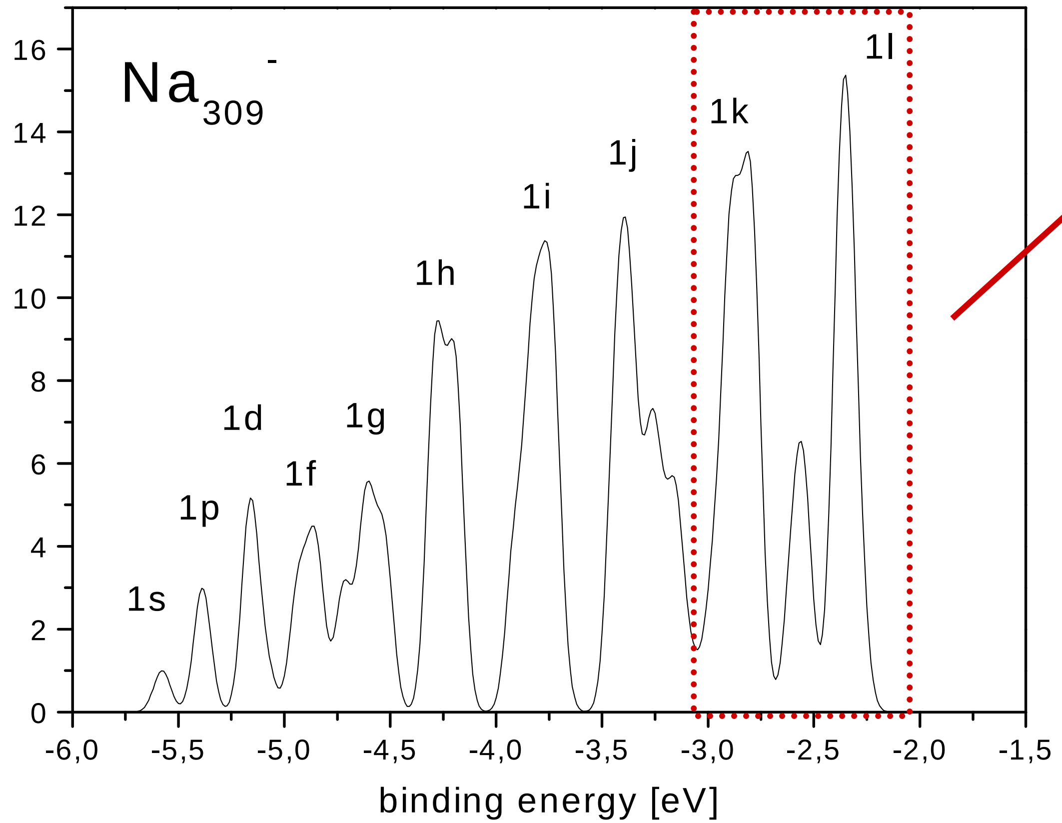
Same size!

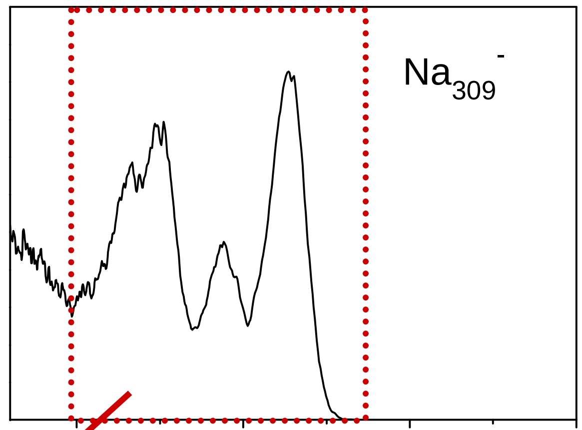
T=100 K

Universität Freiburg

Electron shell structure in a large cluster

Total calculated DOS of the icosahedral cluster



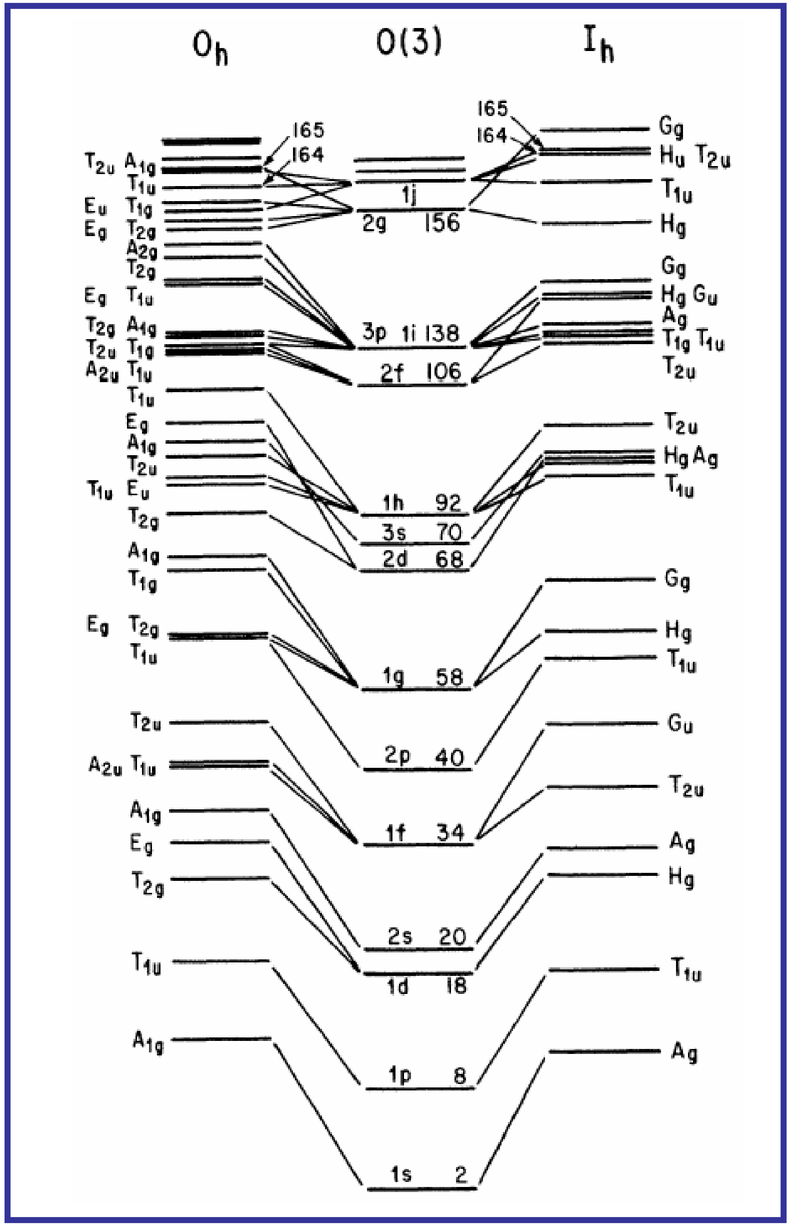


measured photoelectron spectrum

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!

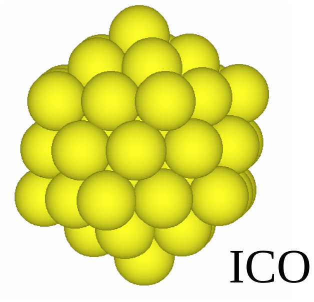
Symmetry perturbation

2p-shell

minus 2 atoms: oblate

p_z

p_x p_y

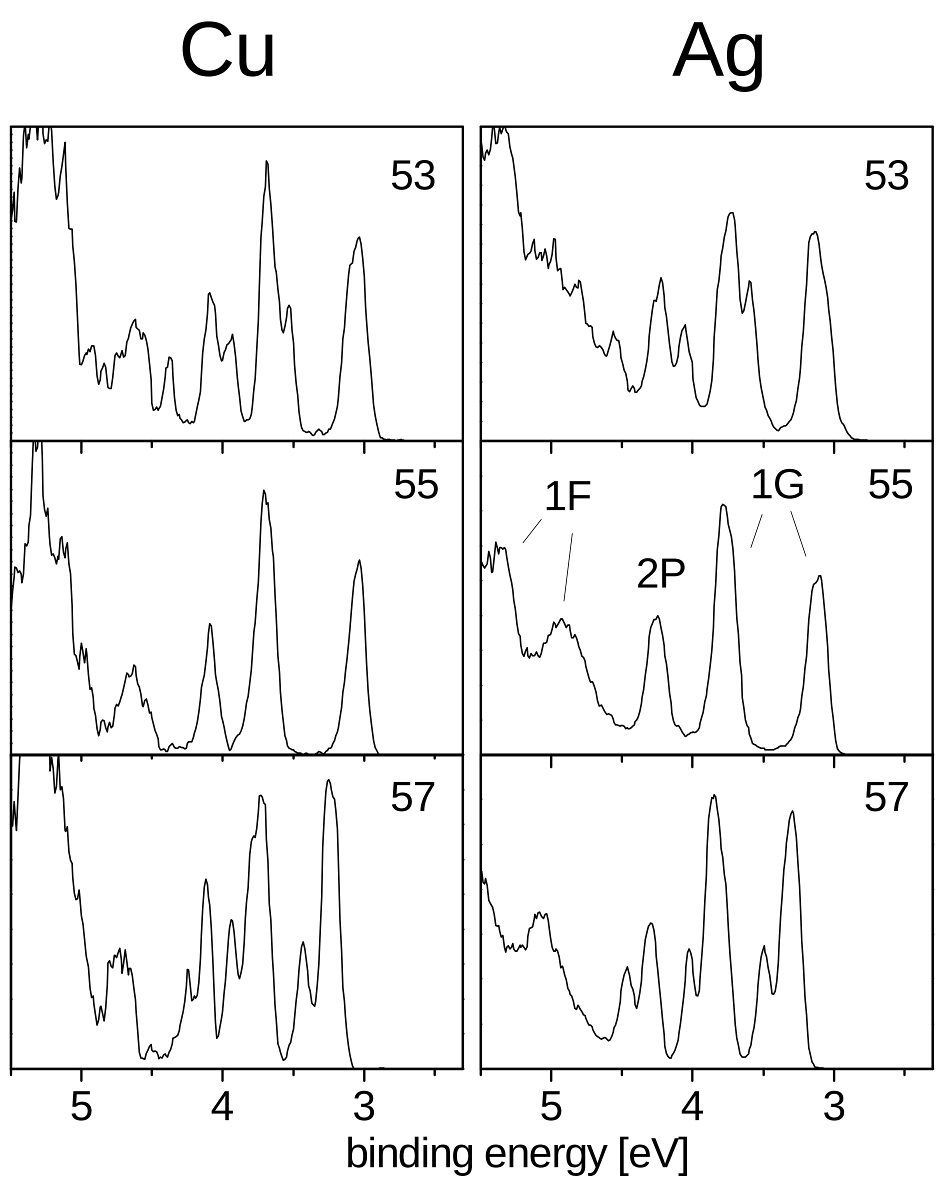


p_x p_y p_z

plus 2 atoms: prolate

p_x p_y

p_z



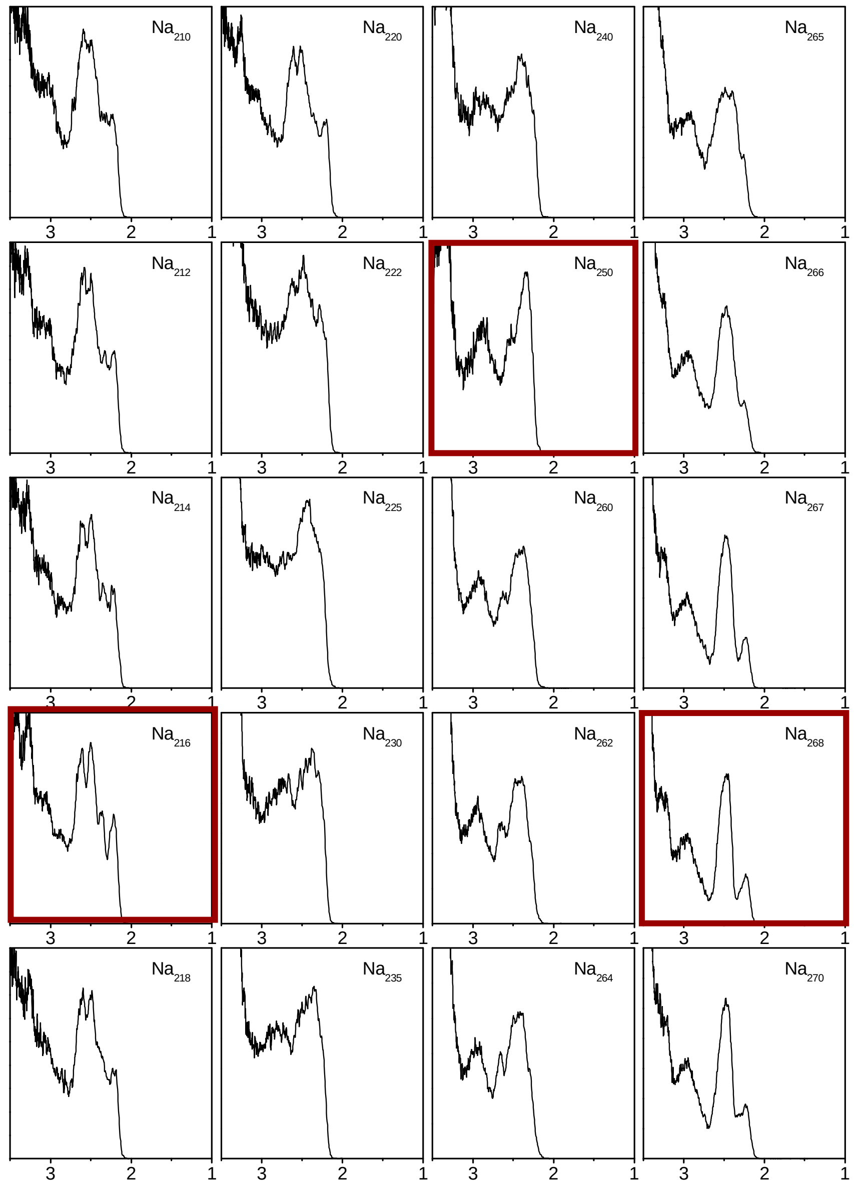
Universität Freiburg

Size dependence of spectra

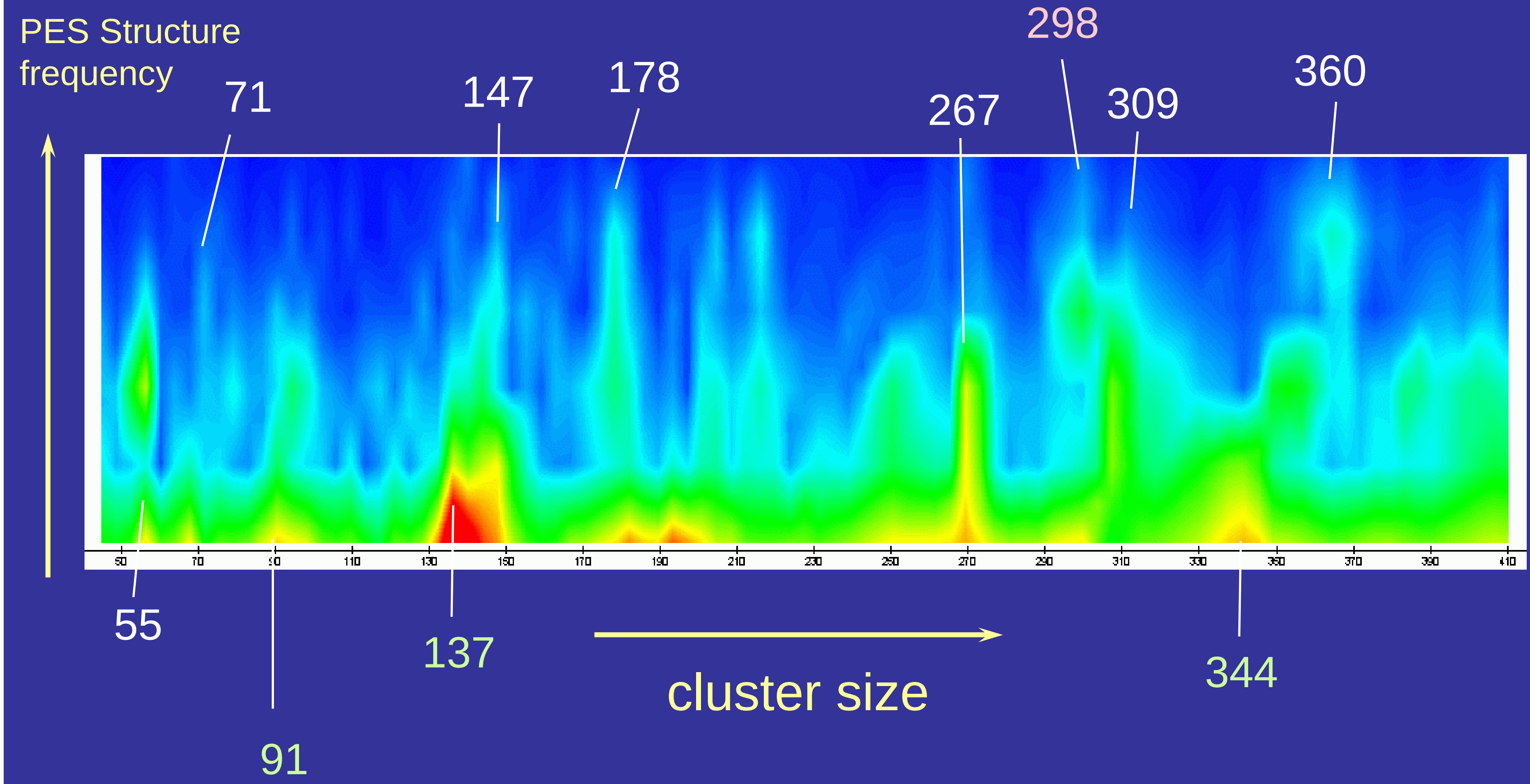
Spectra of Na_n^- with n=210-270:

strong variation with size

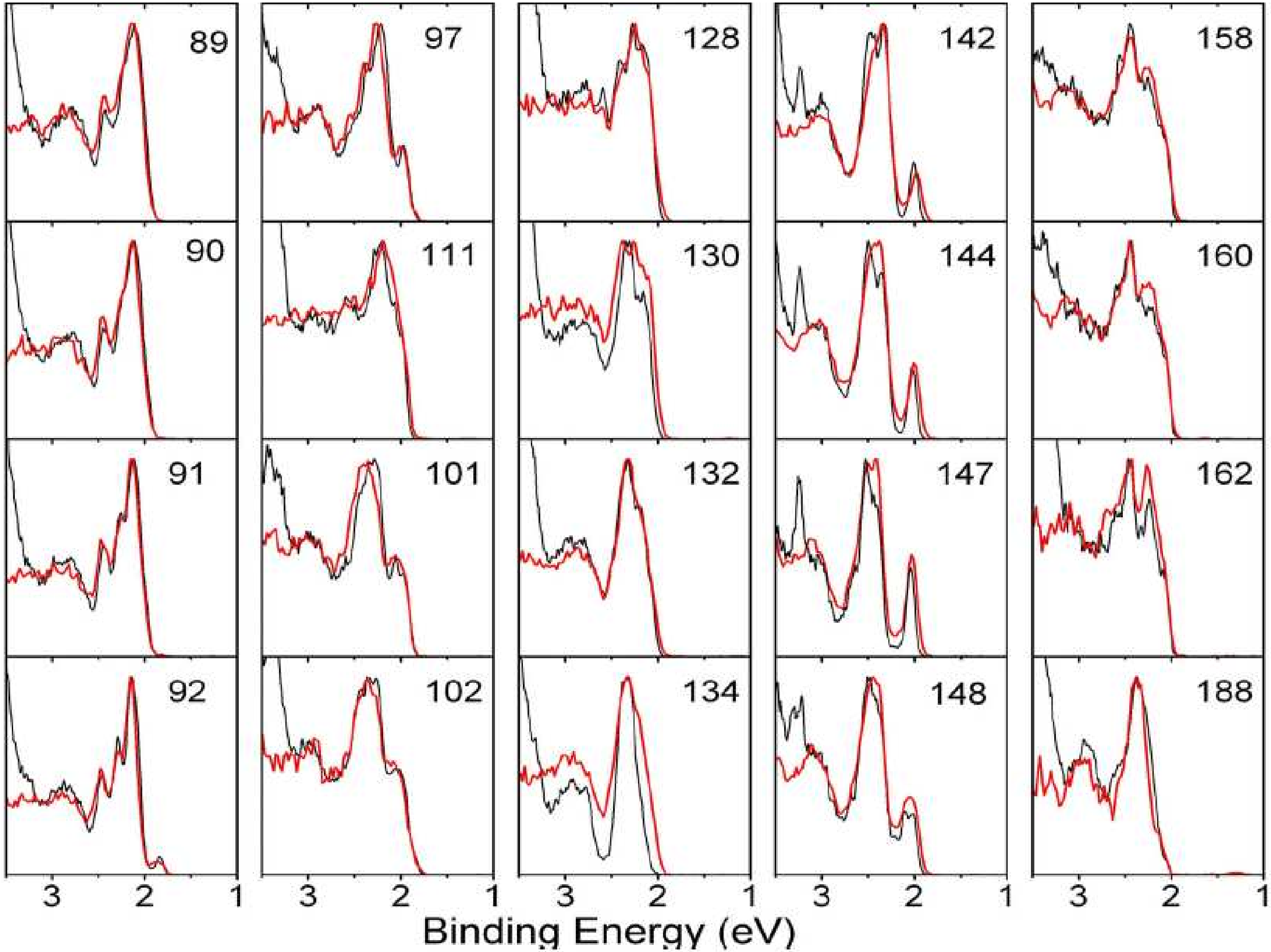
highly structured spectra indicate high symmetry!



Fourier Transform PES



Comparison with potassium clusters



K_n^-

Na_n^-

Energy axis scaled by Fermi energy

Program

Experiment
Photoelectron spectroscopy
cluster thermalization

Sodium clusters
Electronic shell structure
Interaction with geometric structure
Cluster shapes: comparison to simple models
Structure of larger clusters
Comparison with potassium clusters

Noble metal clusters
Electronic structure
Geometrical structure
special case: gold clusters
Comparison Na, Cu, Ag, Au

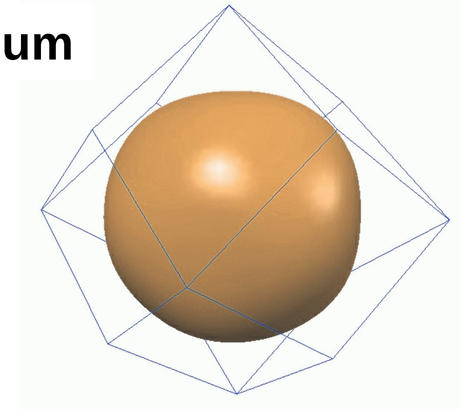
Angle resolved photoelectron spectroscopy
Basics
Results on Na, Ag, Cu

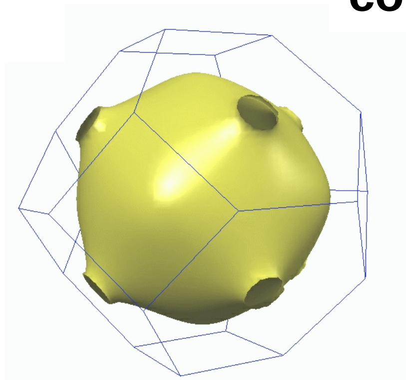
Universität Freiburg

Comparison of alkali and noble metals

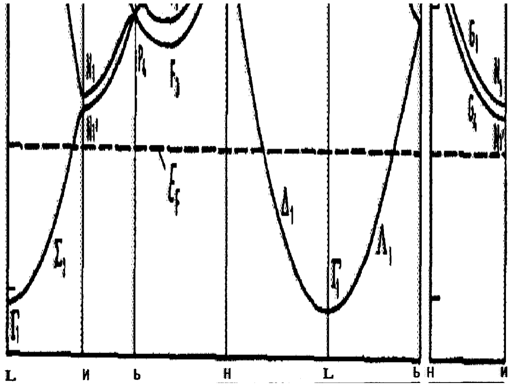
sodium | **copper**

Fermi surfaces

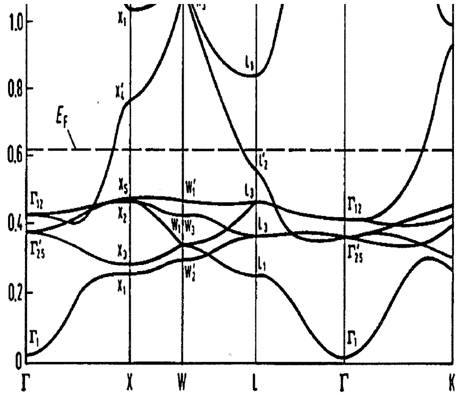




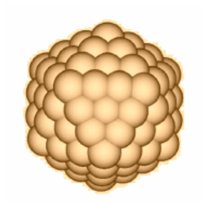
Band structures



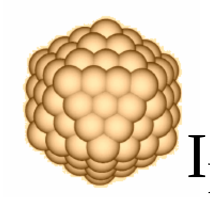
d-Band



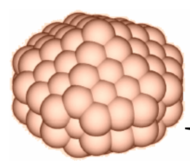
Predicted cluster geometries



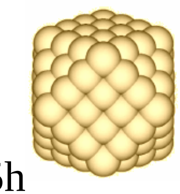
I_h



I_h



D_{5h}



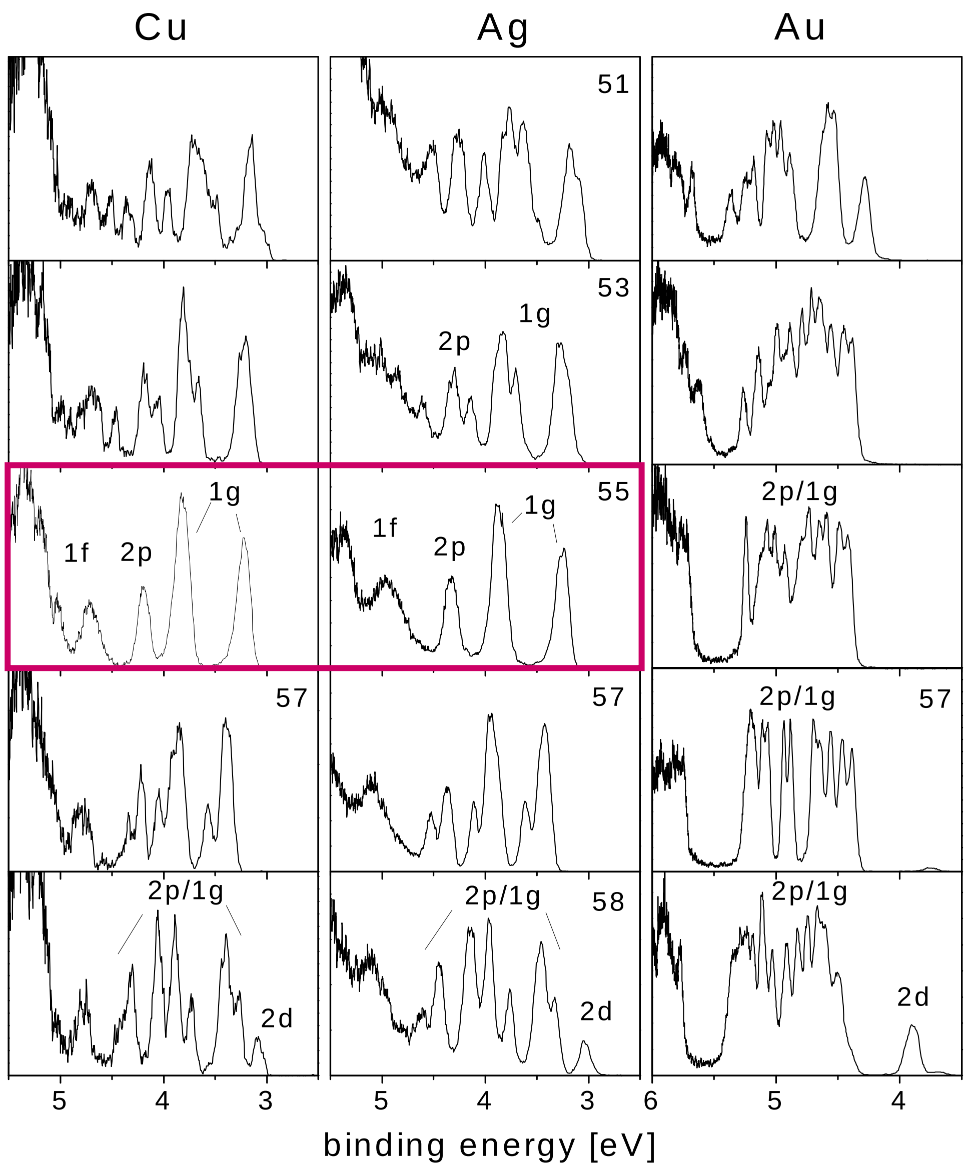
O_h

PES of noble metal cluster anions

Universität Freiburg

size 55:
highly degenerate states for copper and silver!

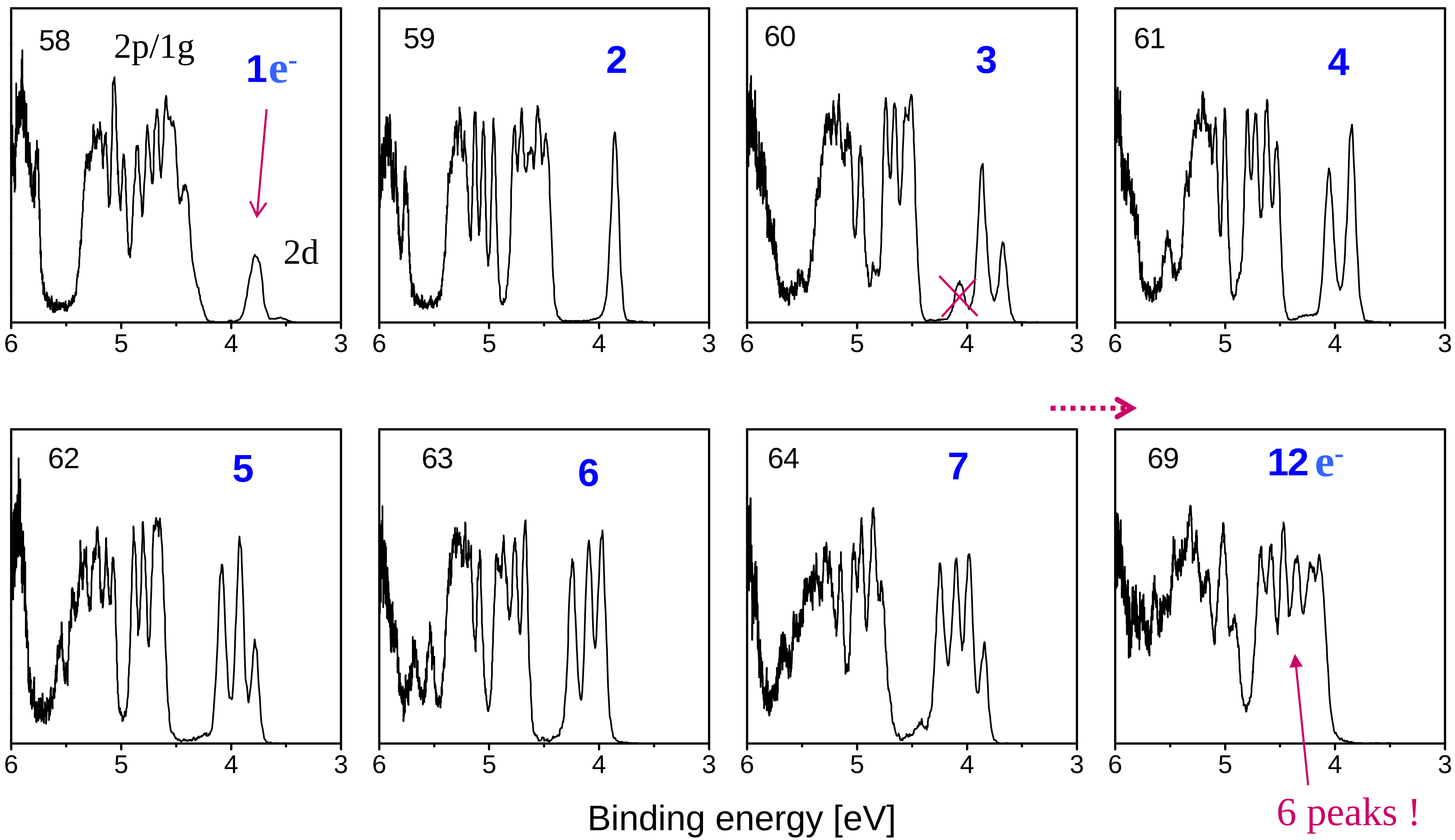
size 58:
appearance of a new shell (2d)



Universität Freiburg

Counting electrons: gold clusters

PES of Au_n^-, n = 58-69



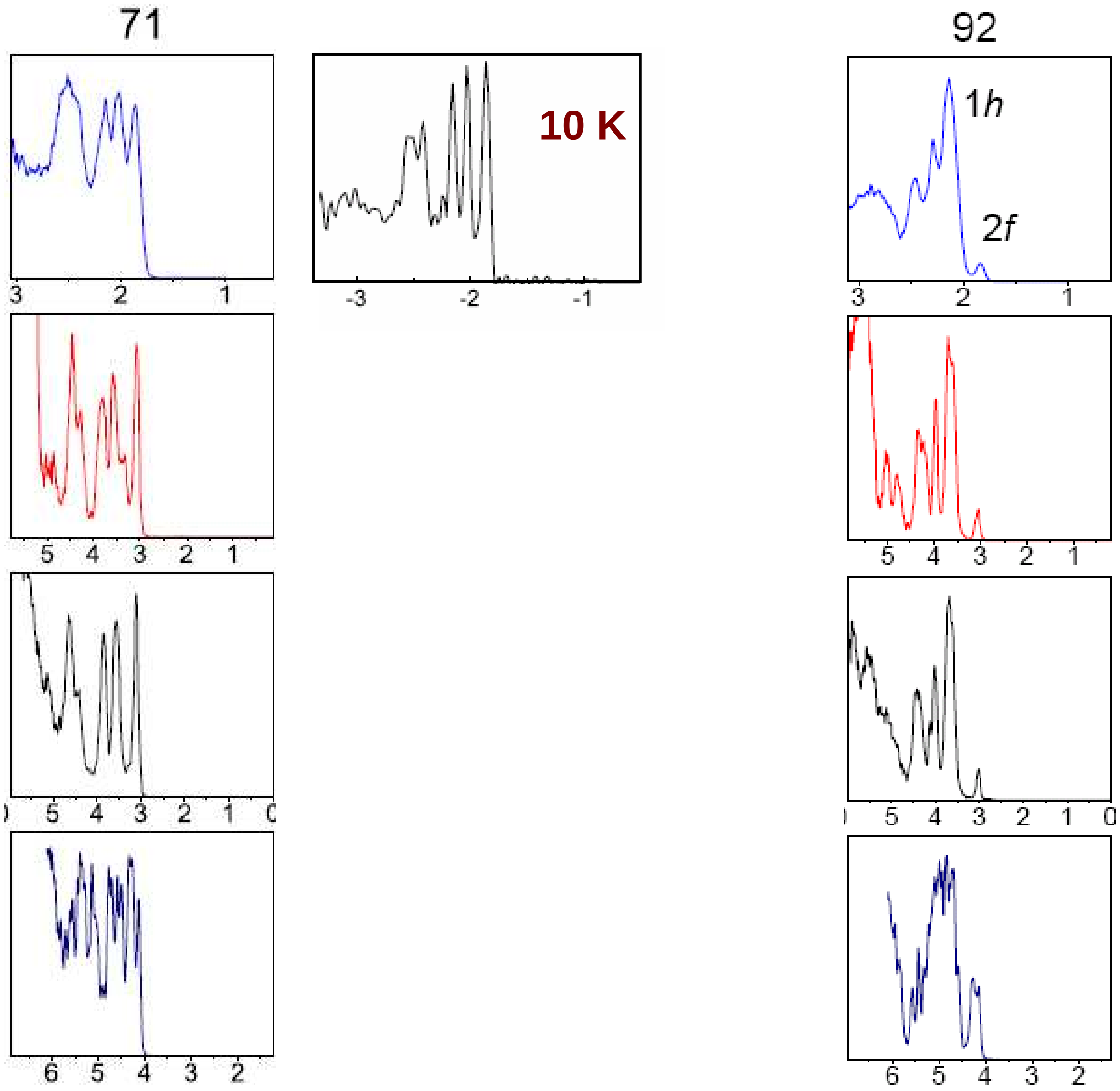
Comparison Na-Cu-Ag-Au

Na

Cu

Ag

Au



Very similar !

Strong deviation only for gold clusters!

Program

Experiment
Photoelectron spectroscopy
cluster thermalization

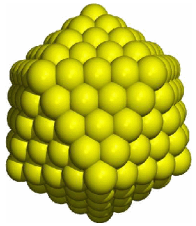
Sodium clusters
Electronic shell structure
Interaction with geometric structure
Cluster shapes: comparison to simple models
Structure of larger clusters
Comparison with potassium clusters

Noble metal clusters
Electronic structure
Geometrical structure
special case: gold clusters
Comparison Na, Cu, Ag, Au

Angle resolved photoelectron spectroscopy
Basics
Results on Na, Ag, Cu

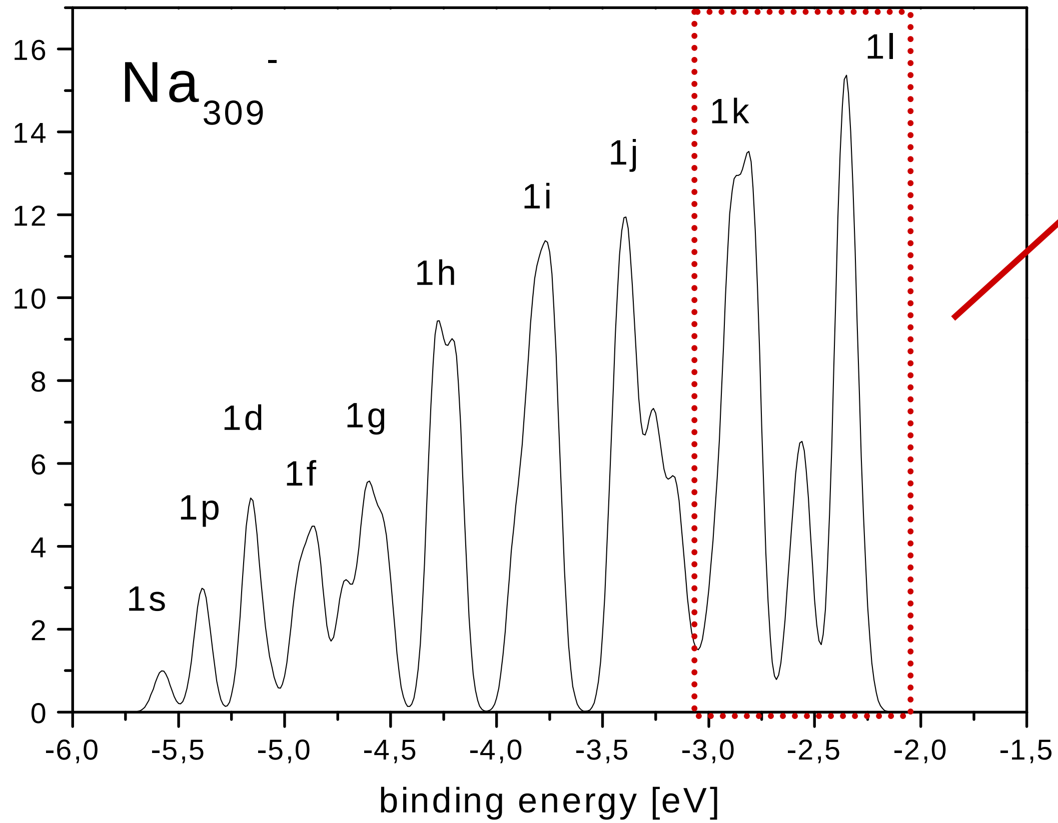
Universität Freiburg

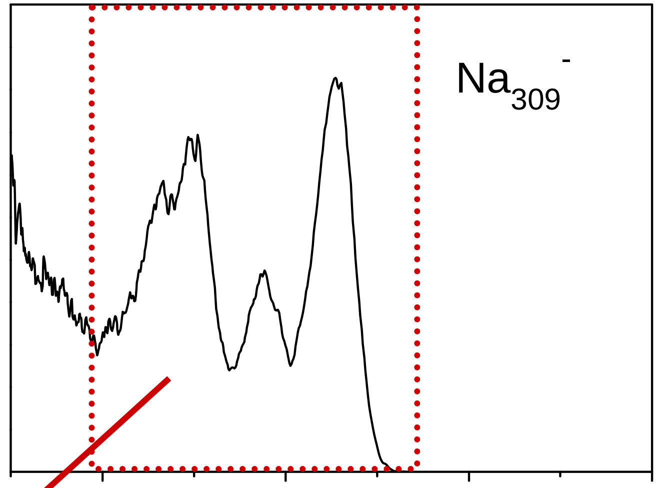
Electron shell structure in a large cluster



Icosahedral symmetry!

Calculated DOS





measured photoelectron spectrum

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

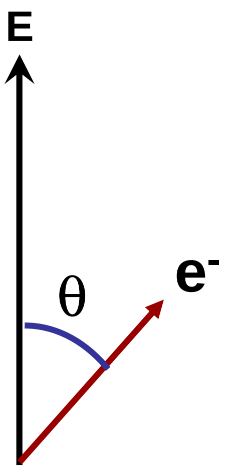
Universität Freiburg

Basics of angular resolved PES

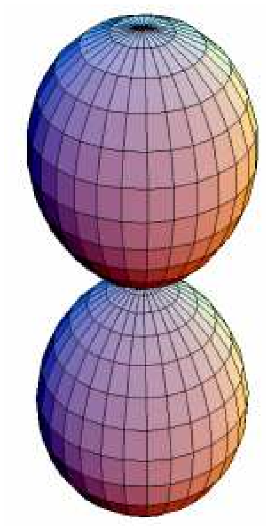
Single photon effect on atoms, molecules or clusters:
angular distribution of photoelectrons can be described by „ß-parameter“

$$f(\theta) = 1 + \beta\left(\frac{3}{2}\cos^2\theta - \frac{1}{2}\right)$$

Light Polarization

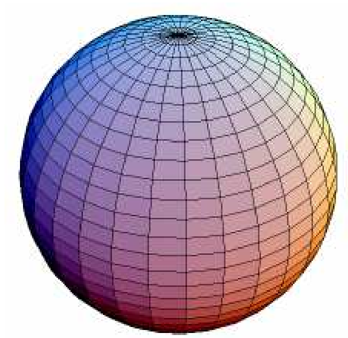


$\beta = 2$



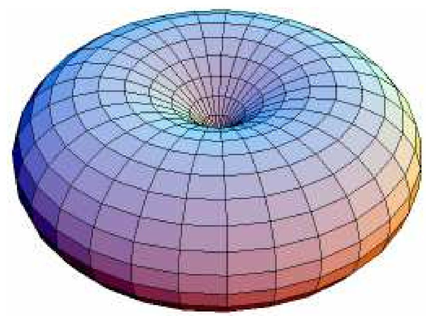
parallel

$\beta = 0$



isotropic

$\beta = -1$



perpendicular

Cooper-Zare formula

Calculation of ß for ionization out of an angular momentum eigenstate (averaged over m_l)

$$\beta = \frac{l(l-1)\sigma_{l-1}^{\ 2} + (l+1)(l+2)\sigma_{l+1}^{\ 2} - 6l(l+1)\sigma_{l-1}\sigma_{l+1}\cos(\delta_{l+1}-\delta_{l-1})}{(2l+1)[l\sigma_{l-1}^{\ 2} + (l+1)\sigma_{l+1}^{\ 2}]}$$

l : angular momentum

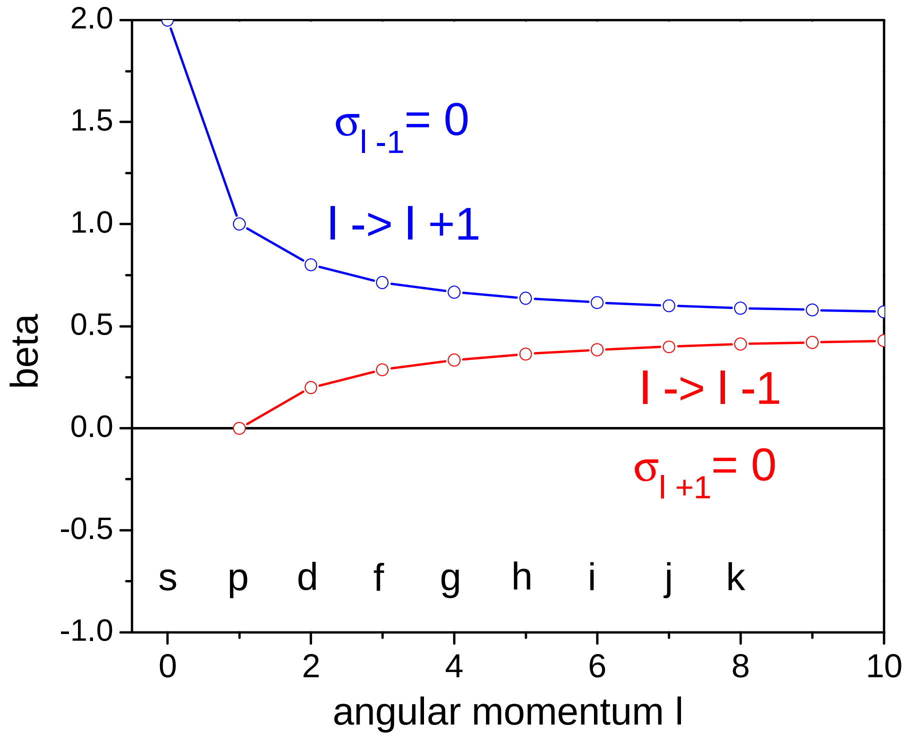
$\delta_{l\pm1}$: phase shift of outgoing (l ±1) wave

$\sigma_{l\pm1}$: radial dipole matrix element

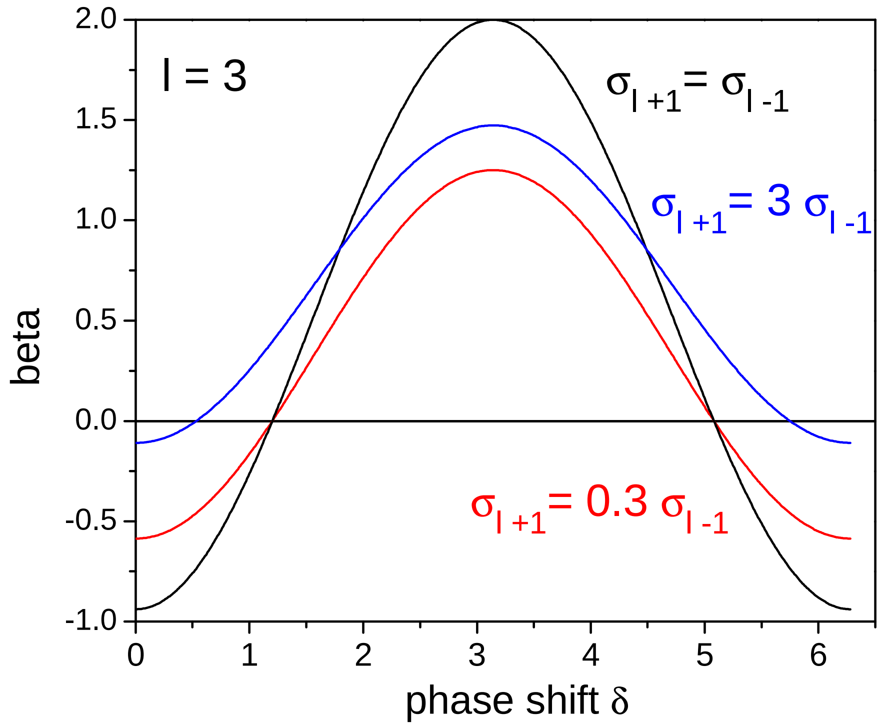
$$\sigma_{l\pm1} = \int_0^\infty R_{il}(r)\, r\, R_{f(l\pm1)}(r)\, dr$$

J. Chem. Phys. 48, 942 (1968)

Variation of ß with l and δ



Emission only into either l+1 or l -1 :
⇒ ß always positive!

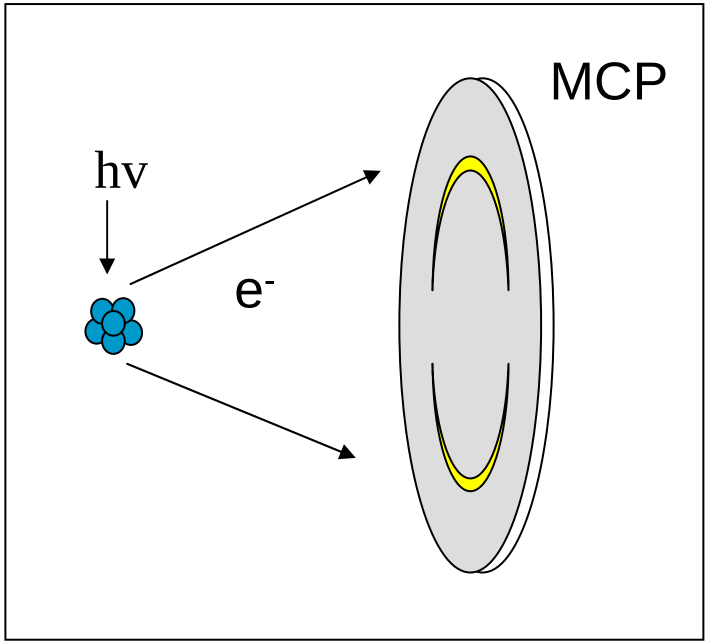


Negative values of ß only if both partial waves interfere, i.e. if

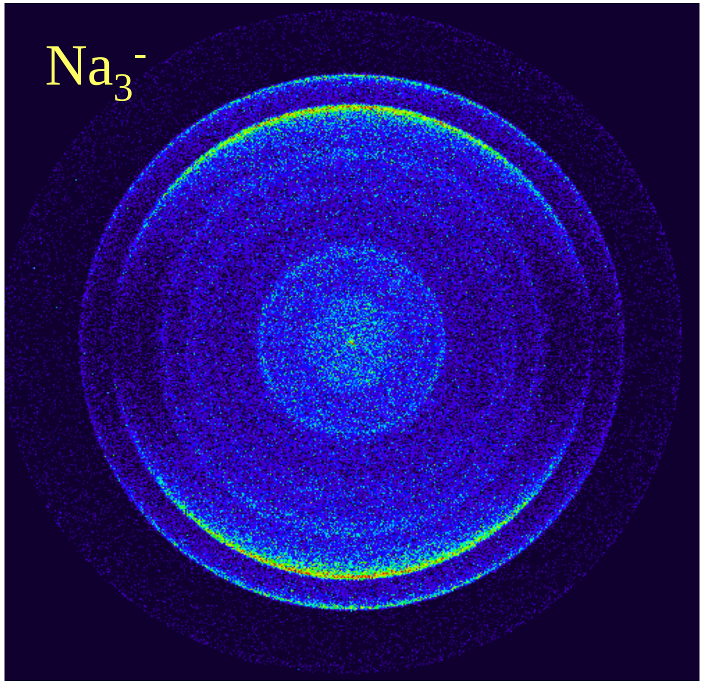
$$\sigma_{l+1} \approx \sigma_{l-1} \quad \textbf{and} \quad \delta \approx 0$$

Imaging PES: principle

Projection of emitted photoelectron onto MCP:



Measurement of angular and kinetic energy distribution



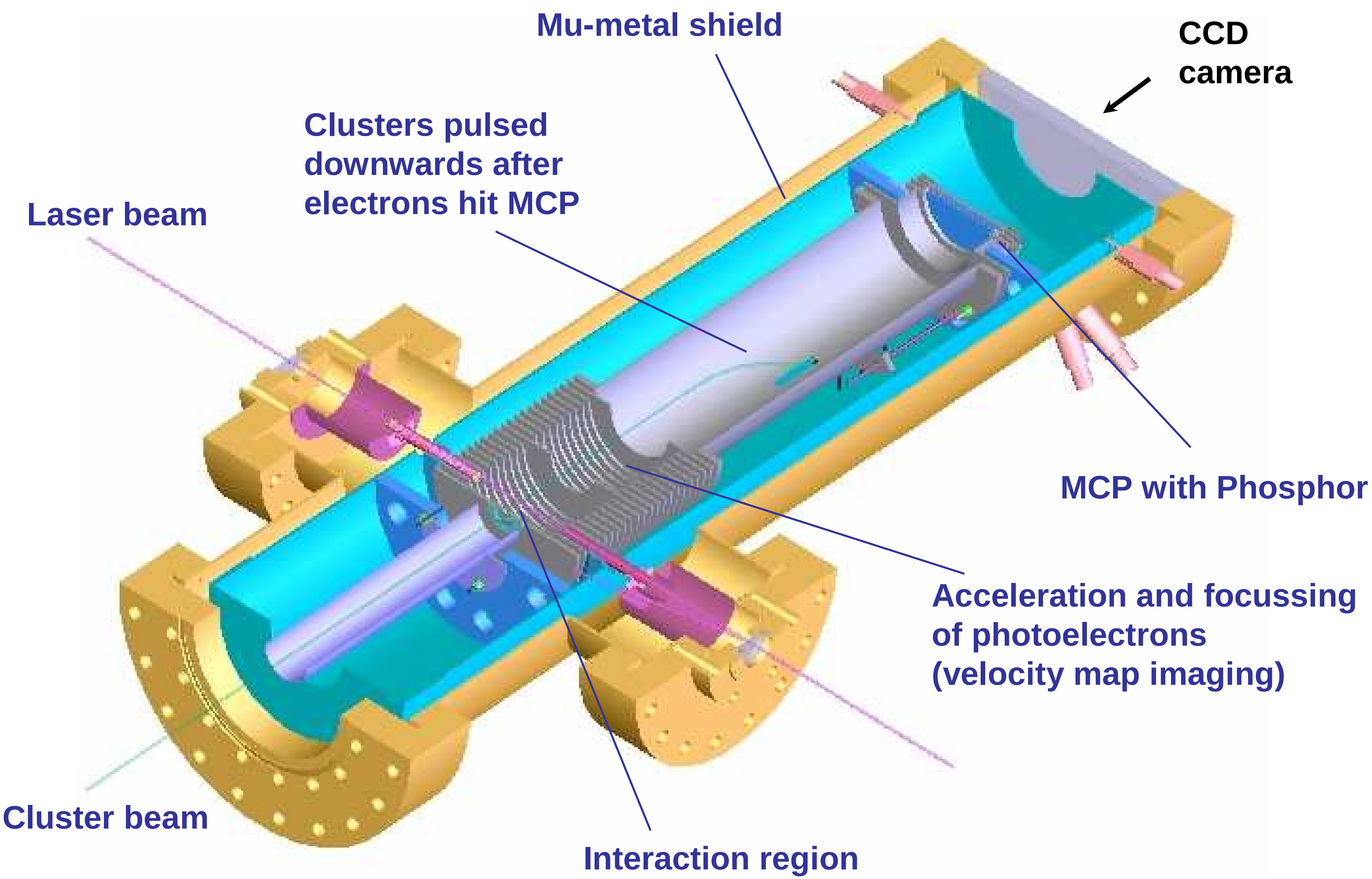
laser polarization

308 nm

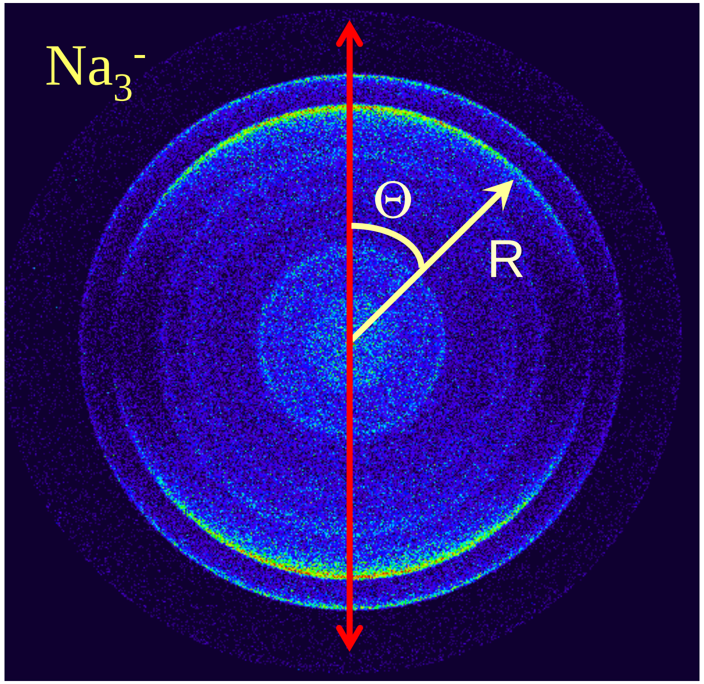
raw data

Universität Freiburg

Imaging spectrometer

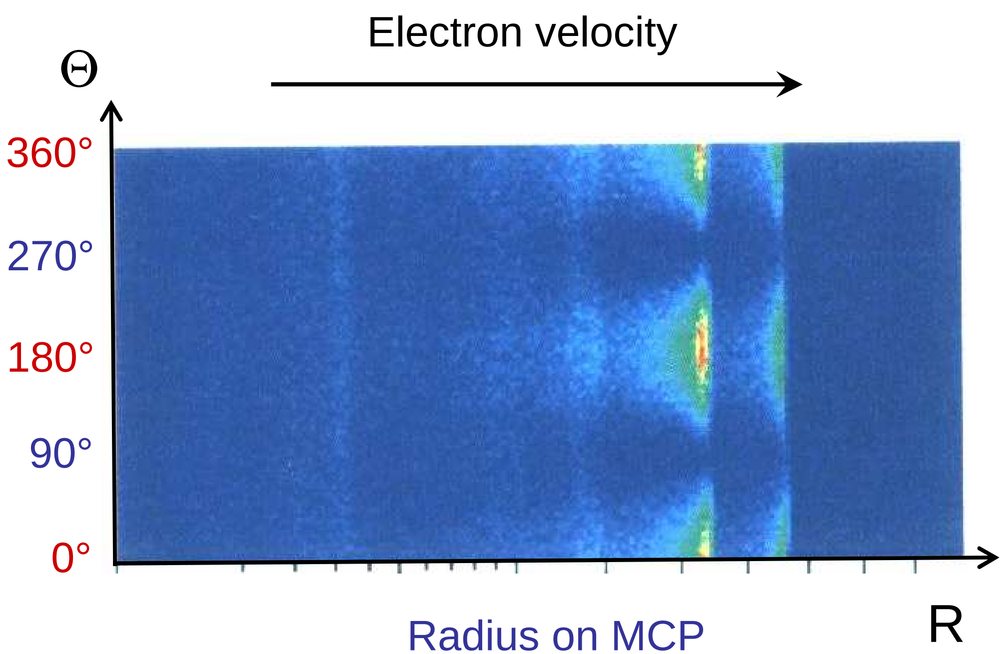


Presentation of the results: projection



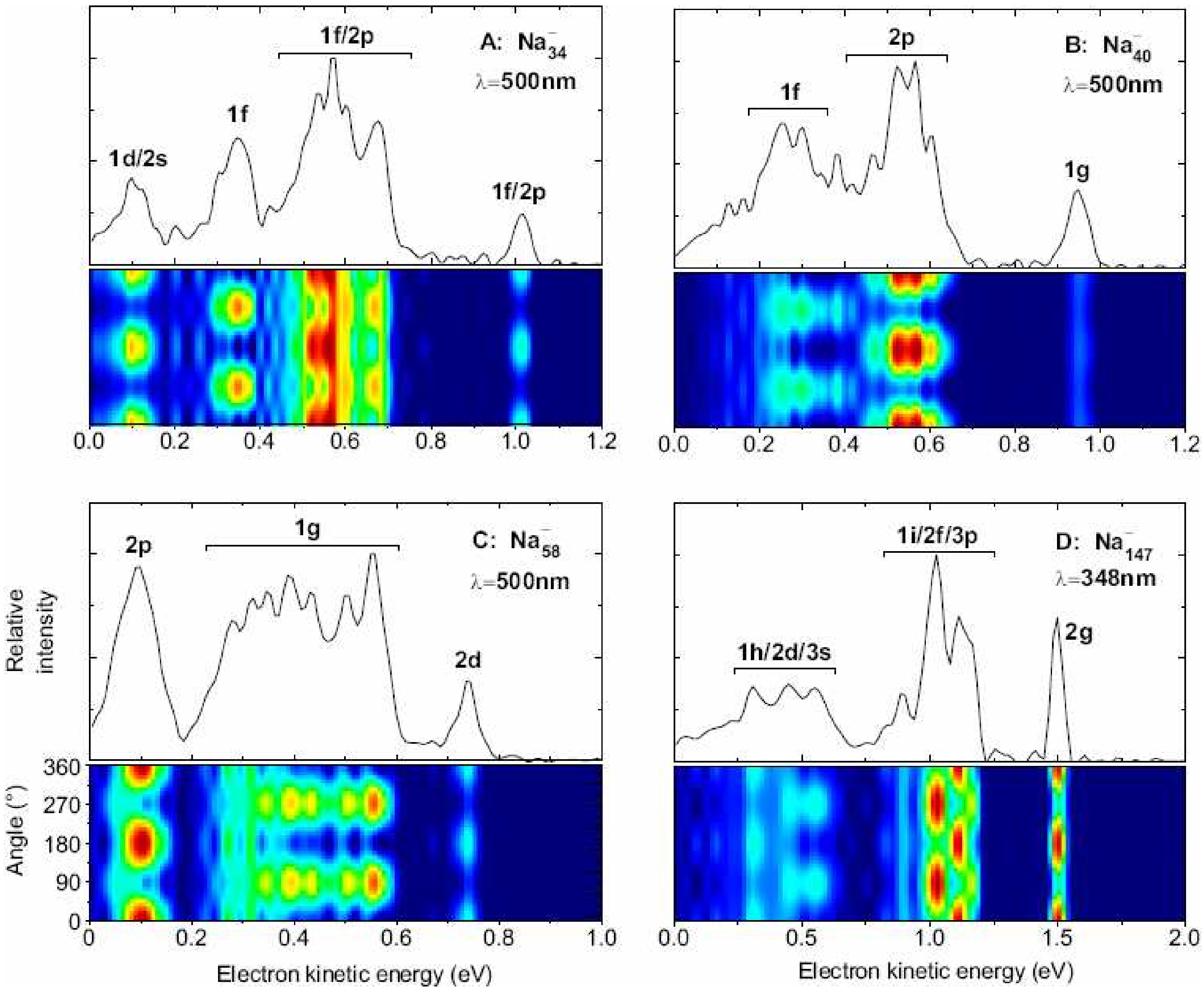
Laser polarization

Presentation of spectra as (R, Θ) - Graphs



Angular distribution of electron shells

p-Basex
deconvolution

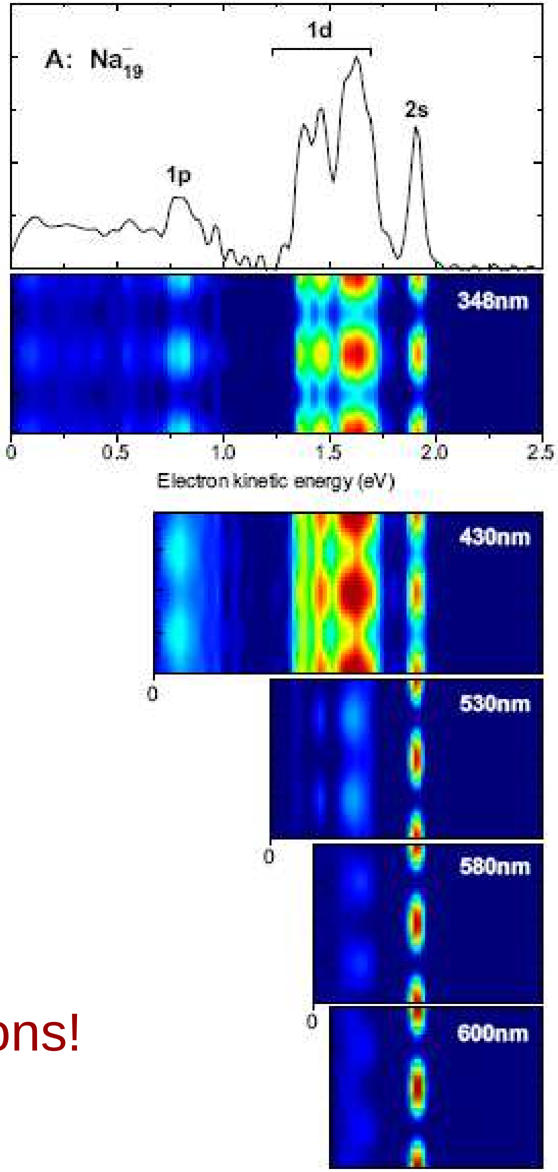


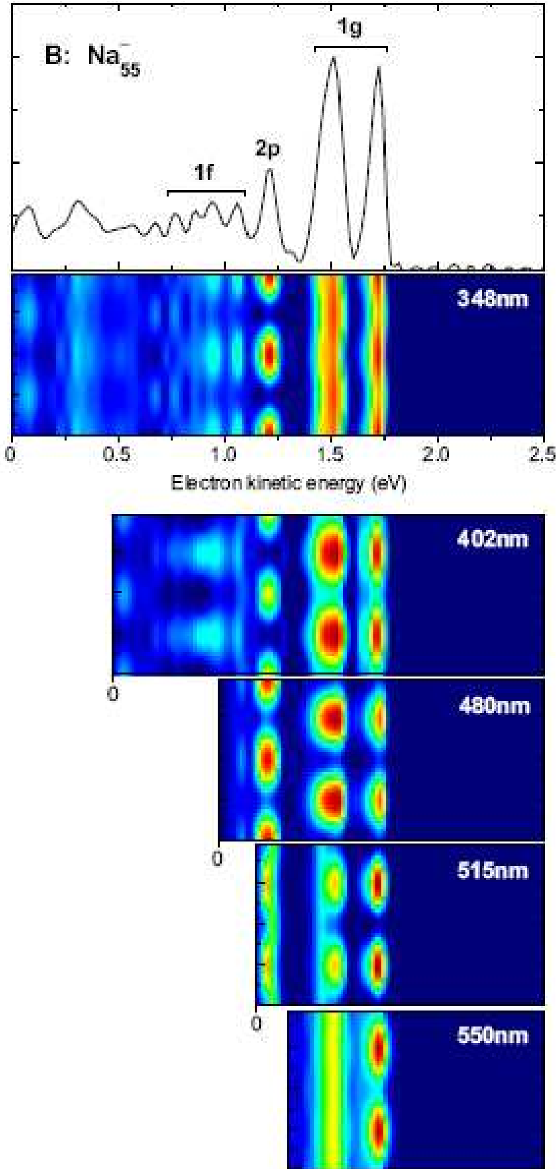
Universität Freiburg

Photon energy dependence

Na_{19}^-

electronic
closed shell



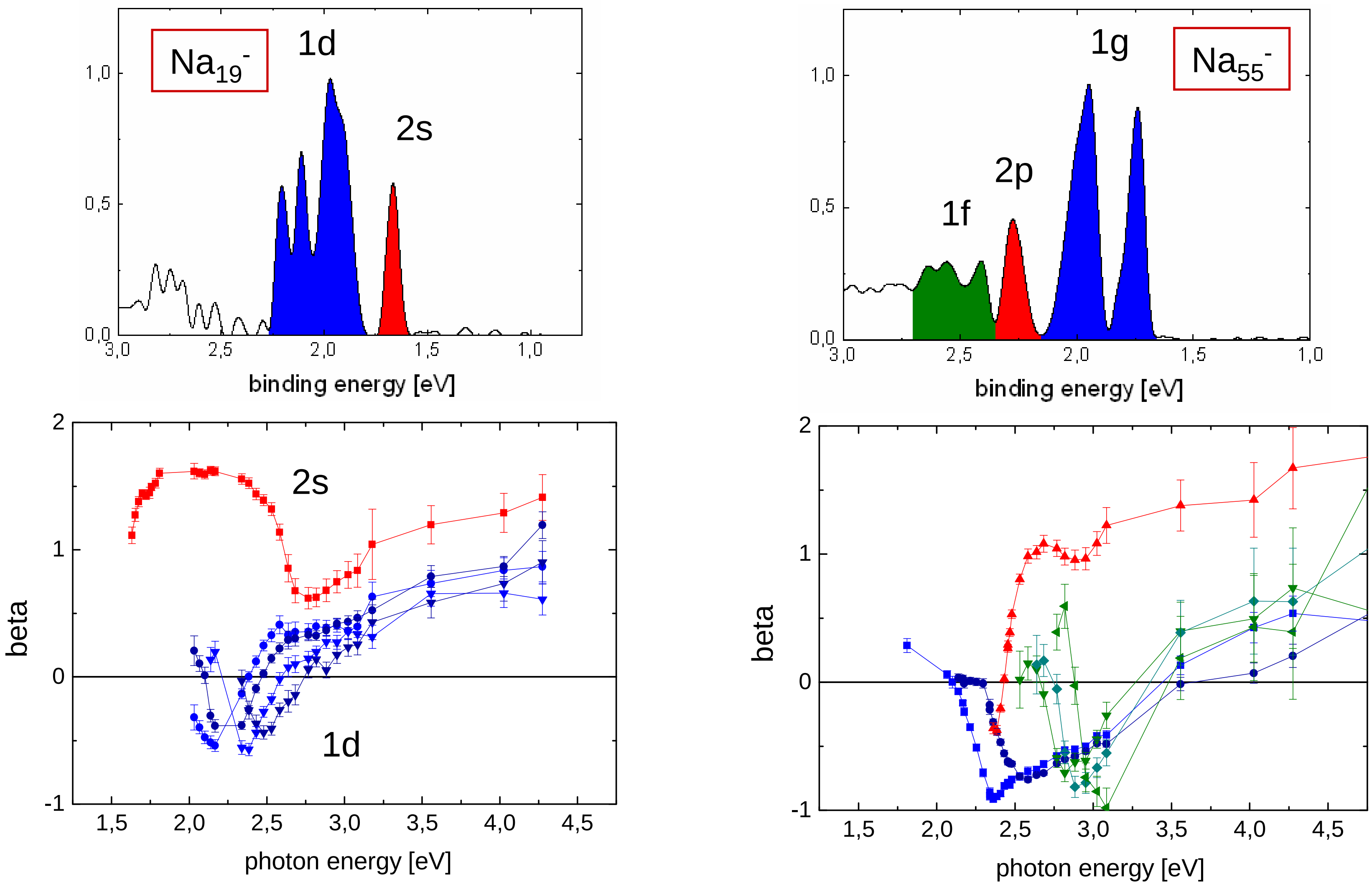


Na_{55}^-

atomic
closed shell

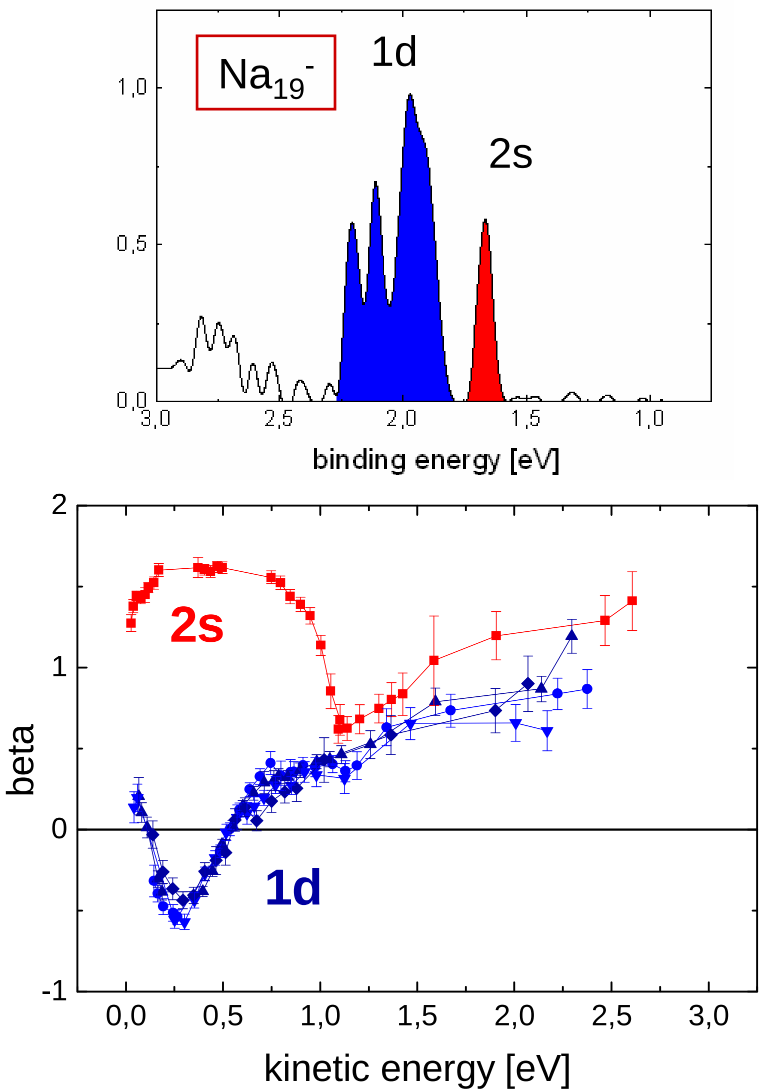
strong
variations!

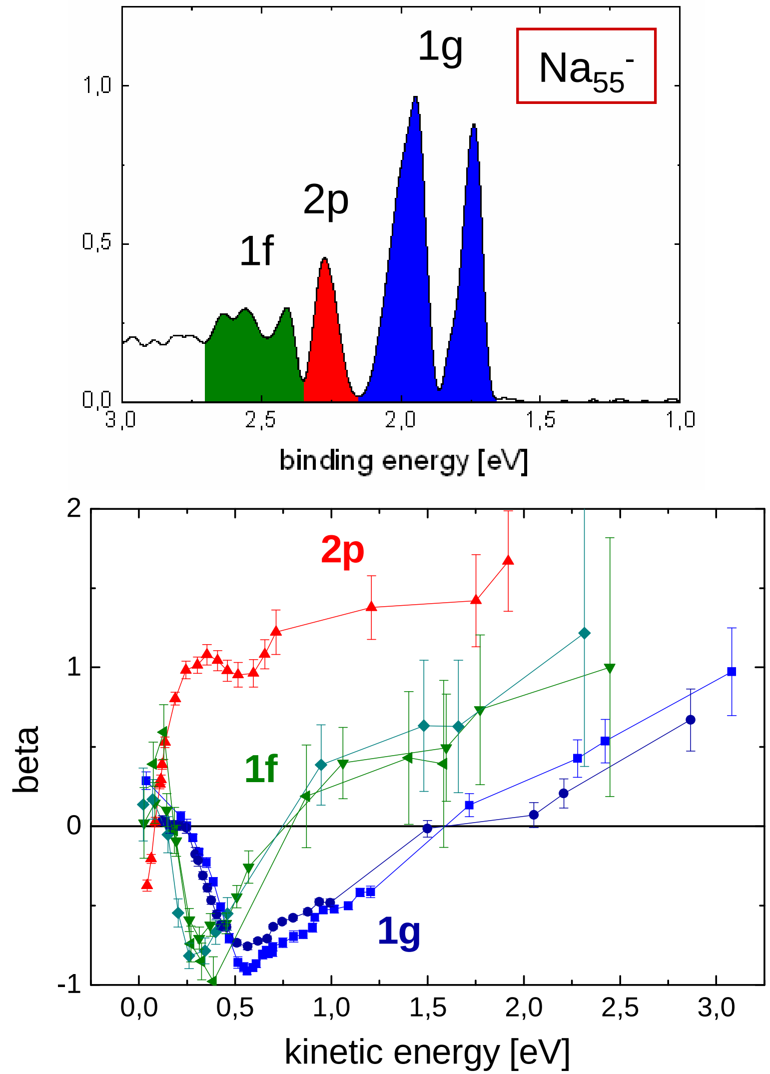
Extracted beta parameters



Universität Freiburg

Extracted beta parameters

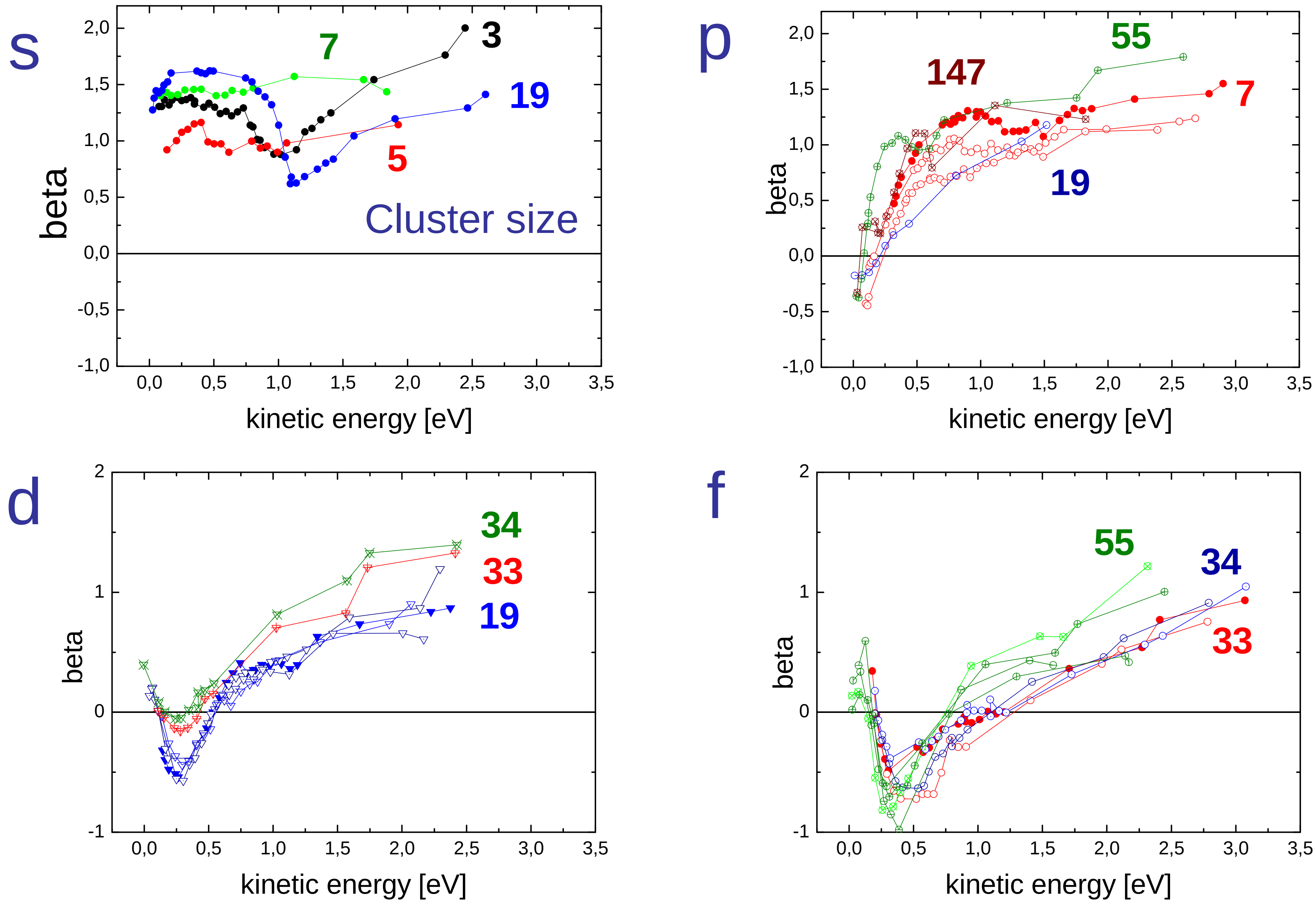




Science **102**, 1323 (2009)

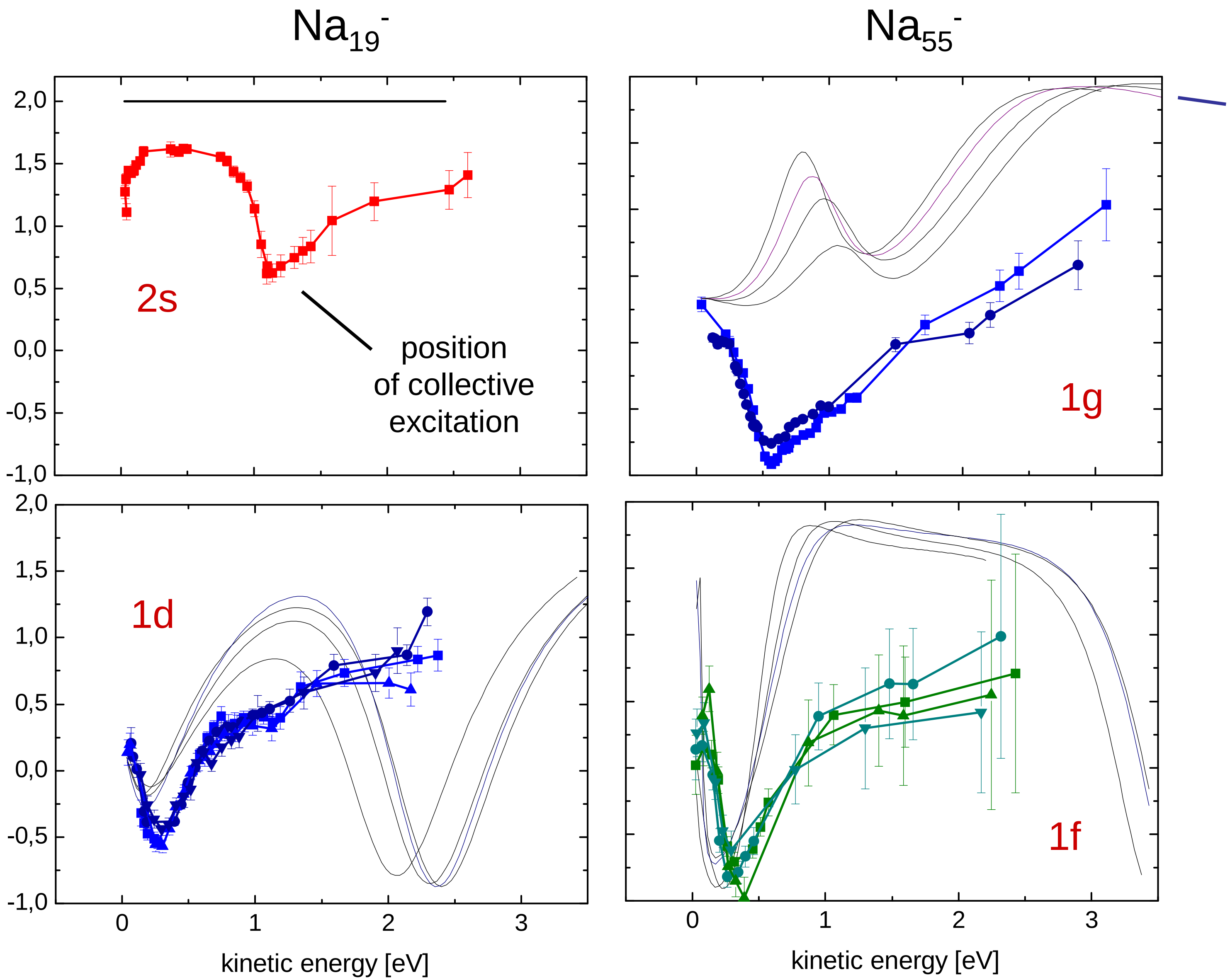
Universität Freiburg

Universal behaviour of l-states



Comparison with model calculations

Universität Freiburg

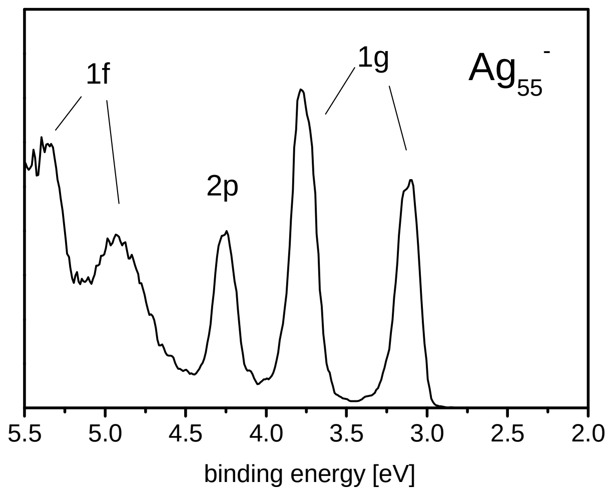


Single
particle
in Wood
Saxon-Pot.

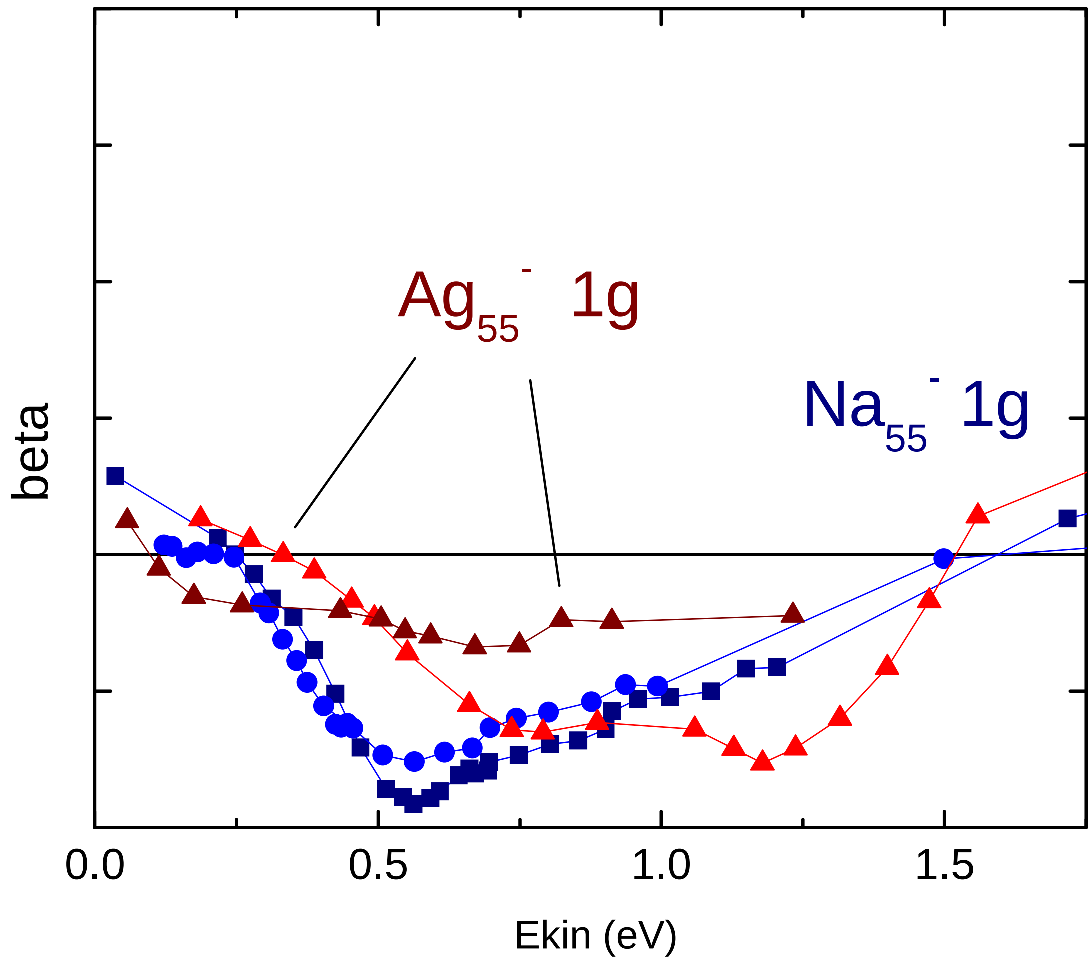
Silver clusters: angular distributions

Universität Freiburg

Photoelectron spectrum



Beta parameter

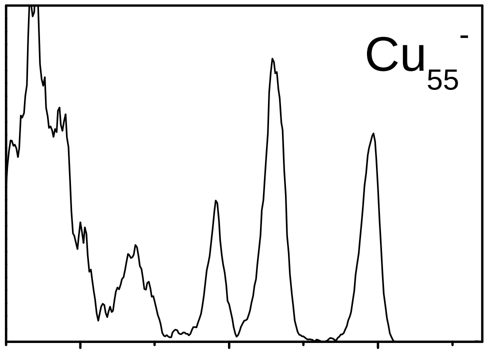


Different behaviour for the two 1-g states!

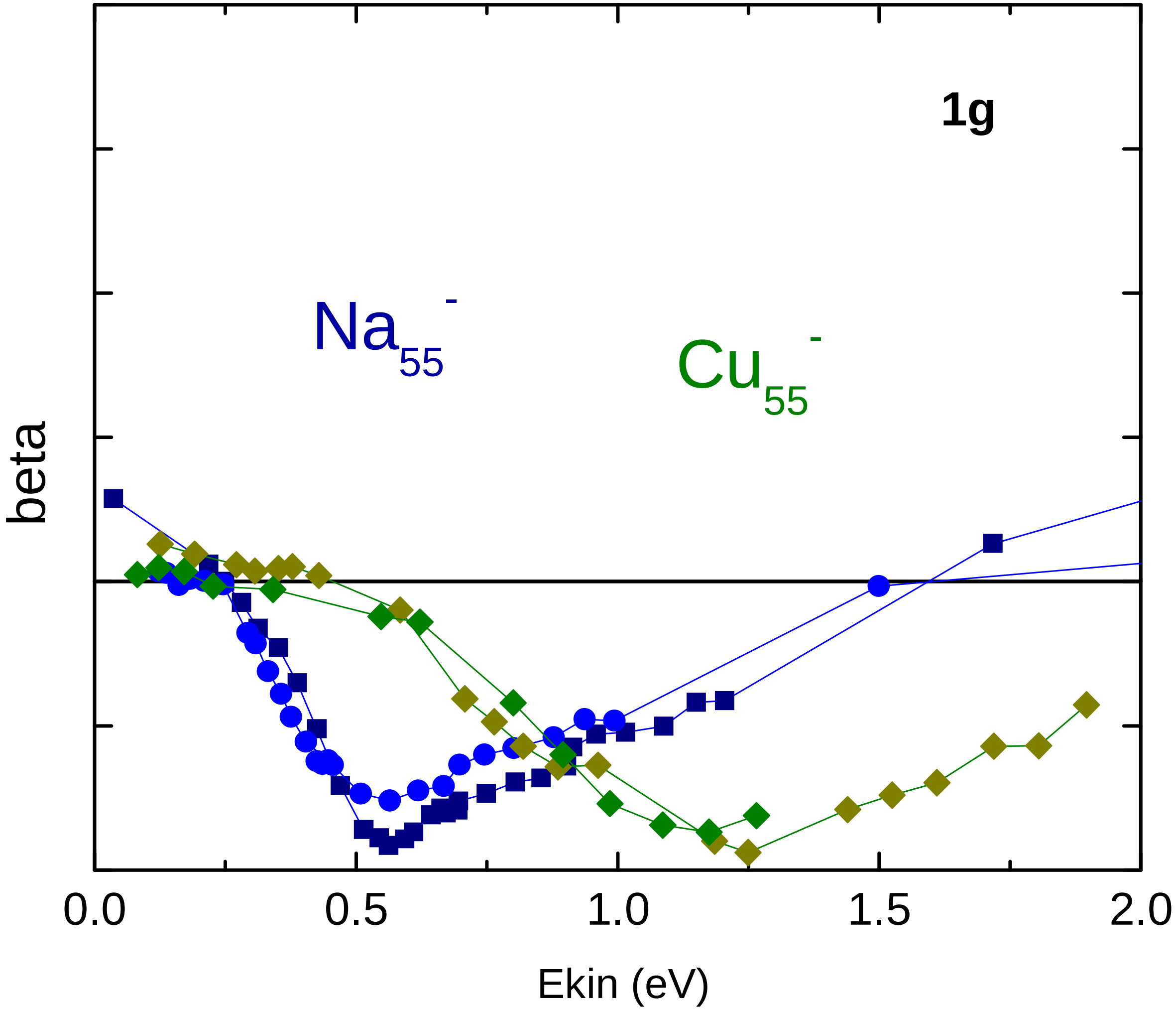
Strong perturbation of s-band by hybridization with d-band?

Copper clusters: angular distributions

Photoelectron spectrum



Beta parameter



Very similar behaviour!

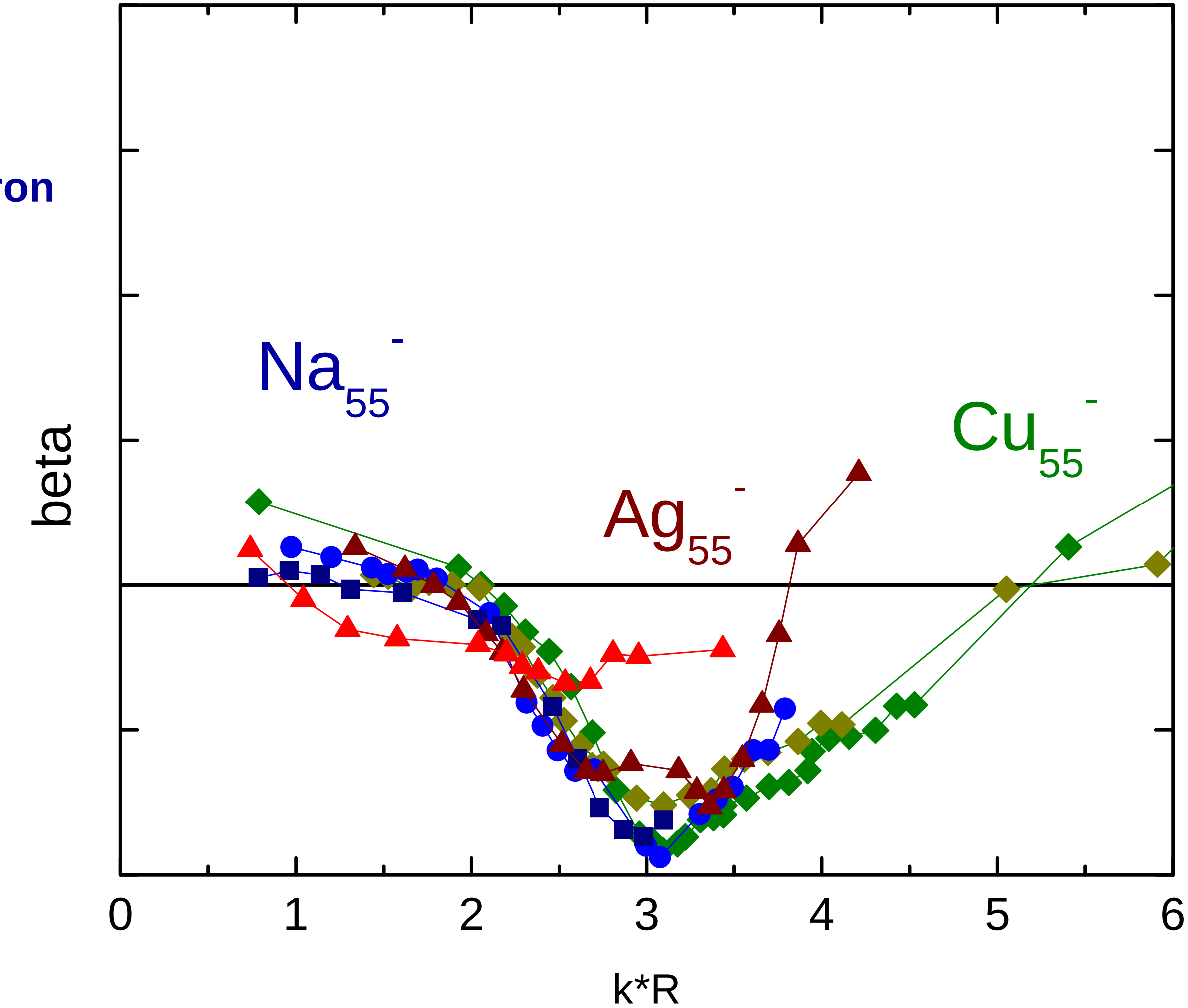
Comparison sodium, copper, silver

Scaled to

$k * R$

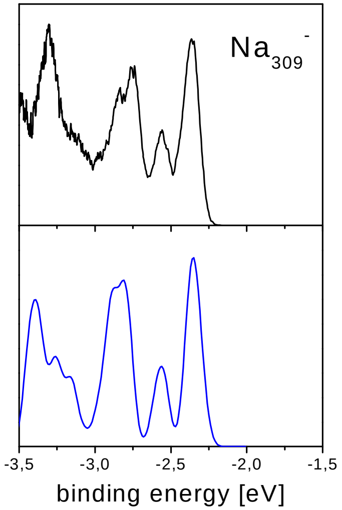
***k*: wavevector free electron**
***R*: cluster radius**

Universal behaviour!

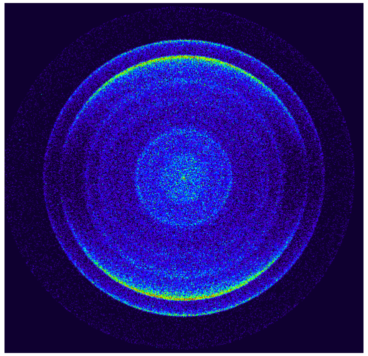


Summary

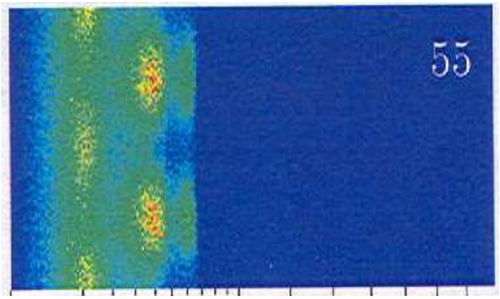
Sodium clusters:
„perfect“ shell structure



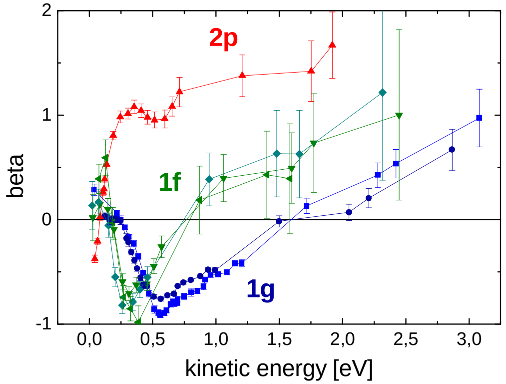
Imaging spectroscopy:
angular resolved
PES of clusters



Perpendicular distributions:
indicate destructive
interference of outgoing
partial waves



Energy dependence:
clear reminiscence of
angular momentum state



Universität Freiburg

Acknowledgment

Thanks to

Oleg Kostko: PES

Christof Bartels: ARPES

Christian Hock: caloric curves/ ARPES

Raphael Kuhnen
Adam Piechaczek
ARPES

Jan Huwer: ARPES

€€: DFG