lecture 20.1.2011

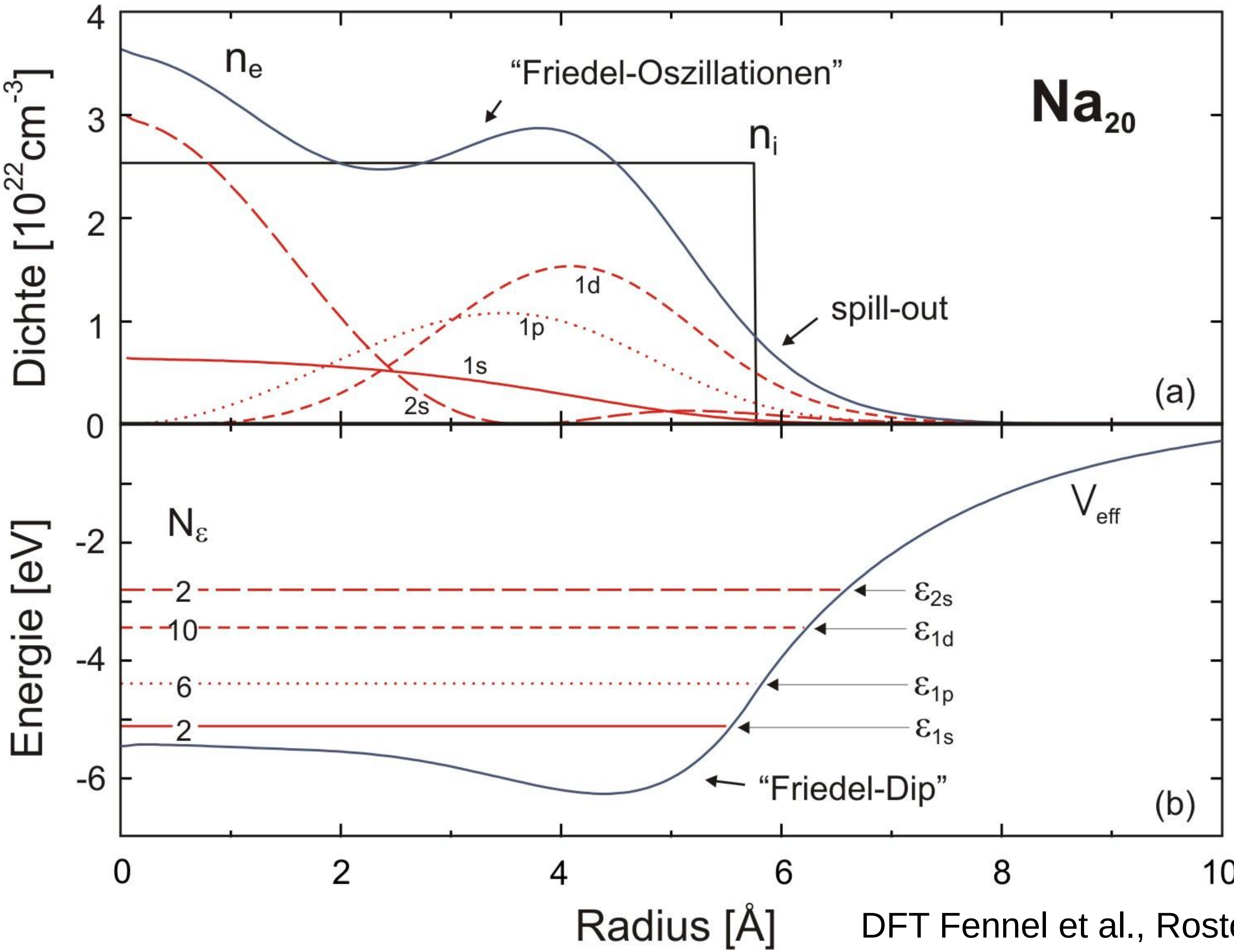
we had so far:

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

today

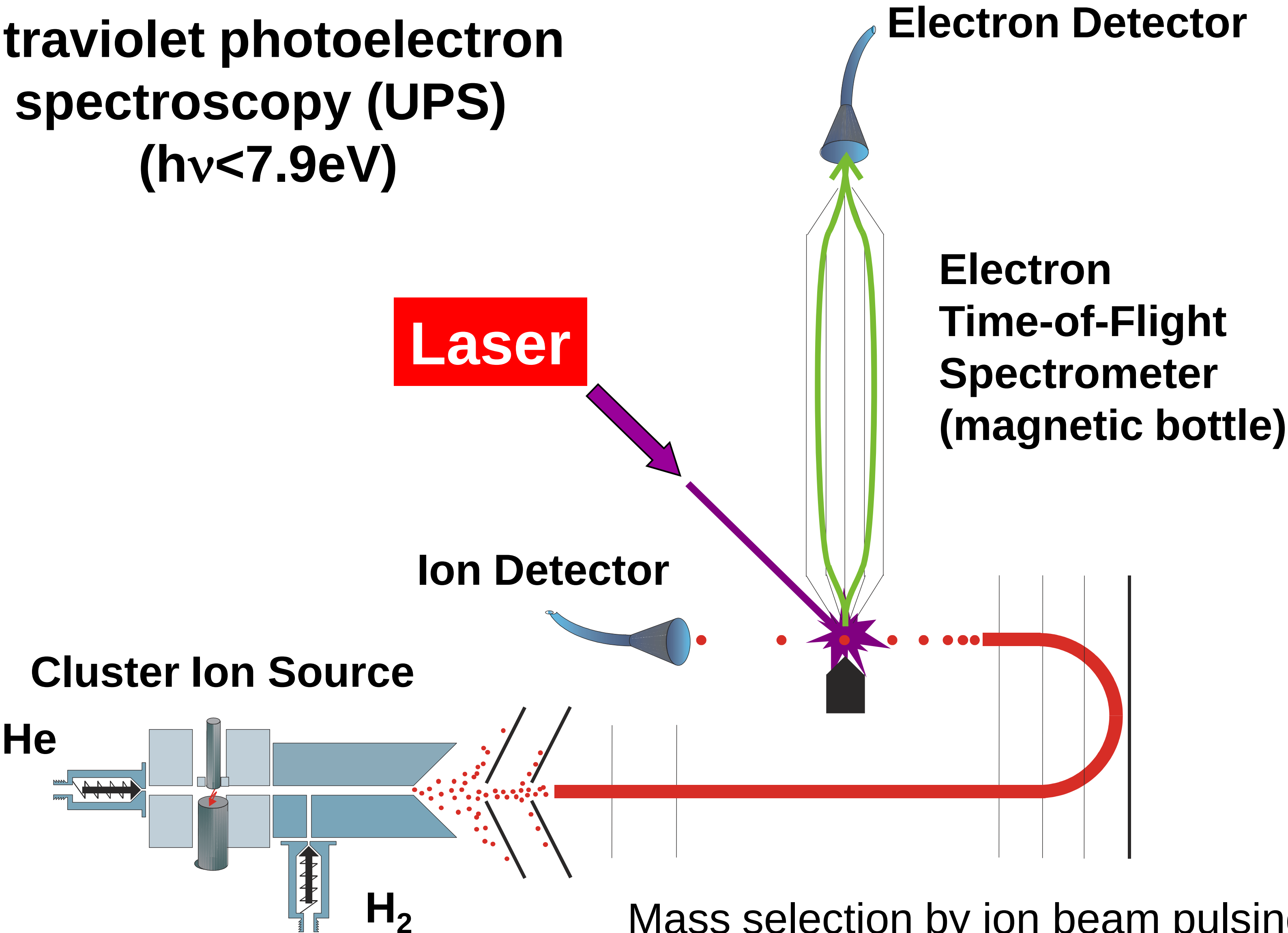
- more photoelectron spectroscopy
- optical properties of metal (jellium) clusters

the jellium model



DFT Fennel et al., Rostock

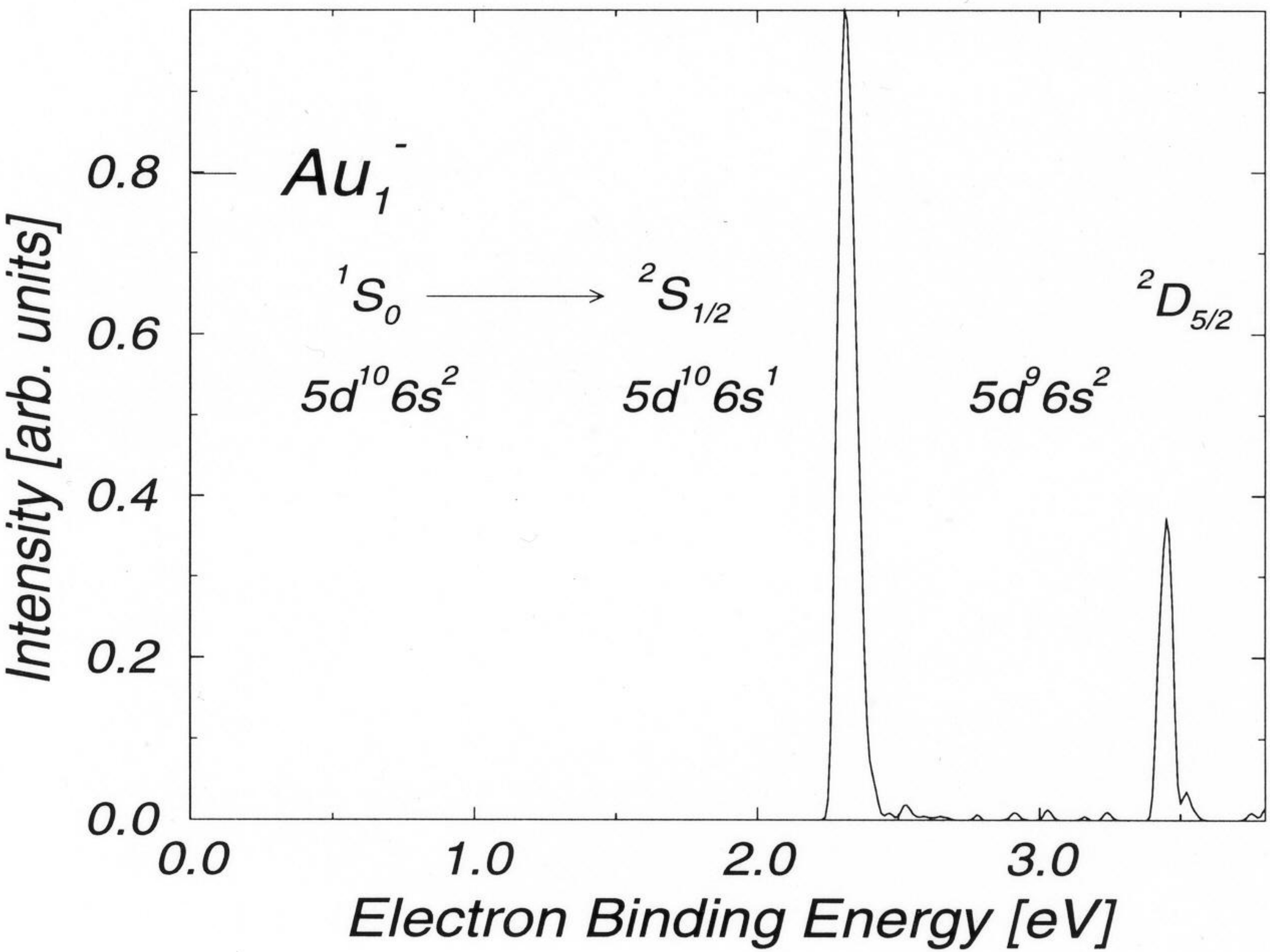
ultraviolet photoelectron spectroscopy (UPS) ($h\nu<7.9$eV)



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

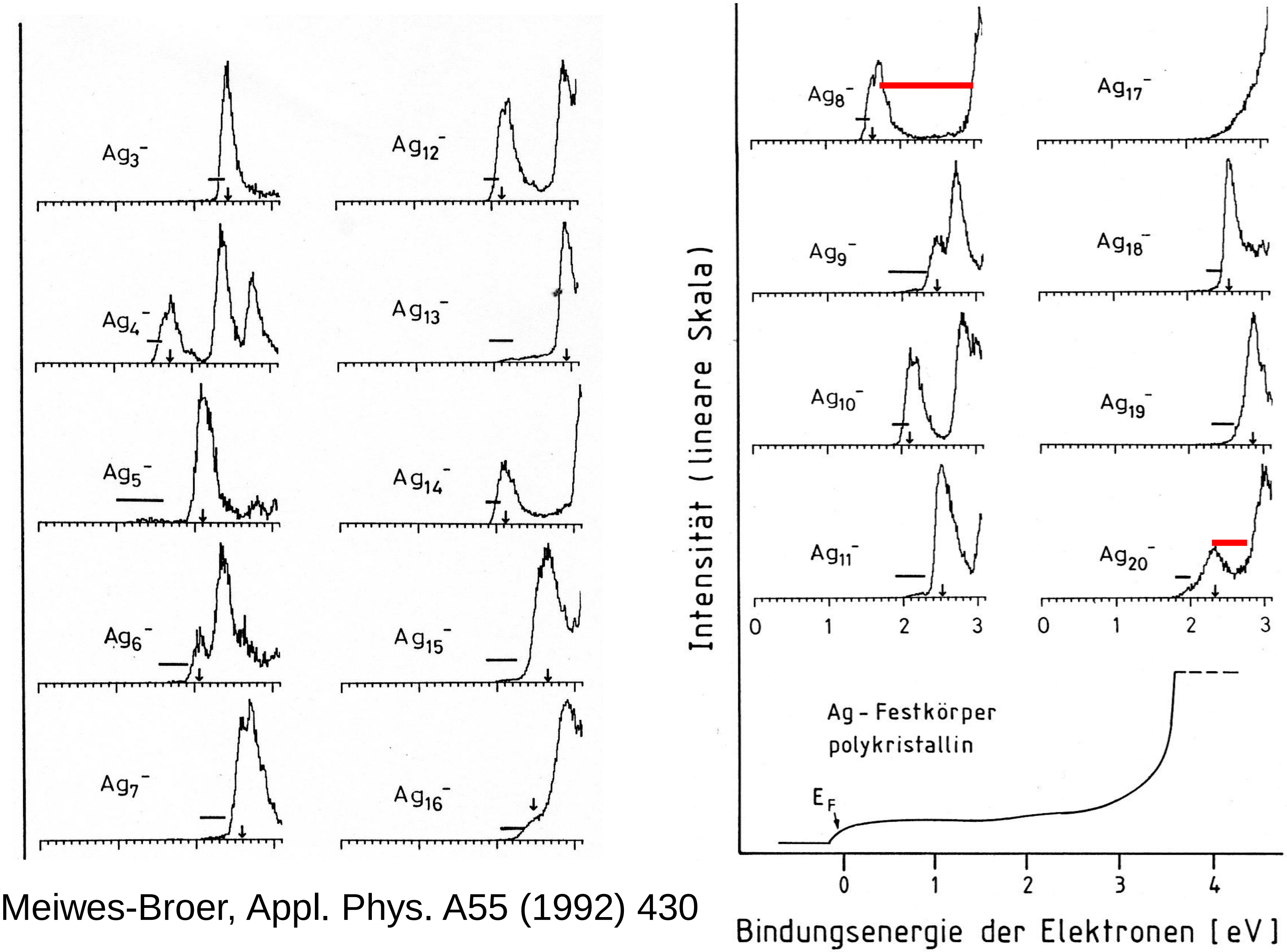
Setup Ganteför group, Konstanz

calibration magnetic bottle spectrometer with Au_1^-



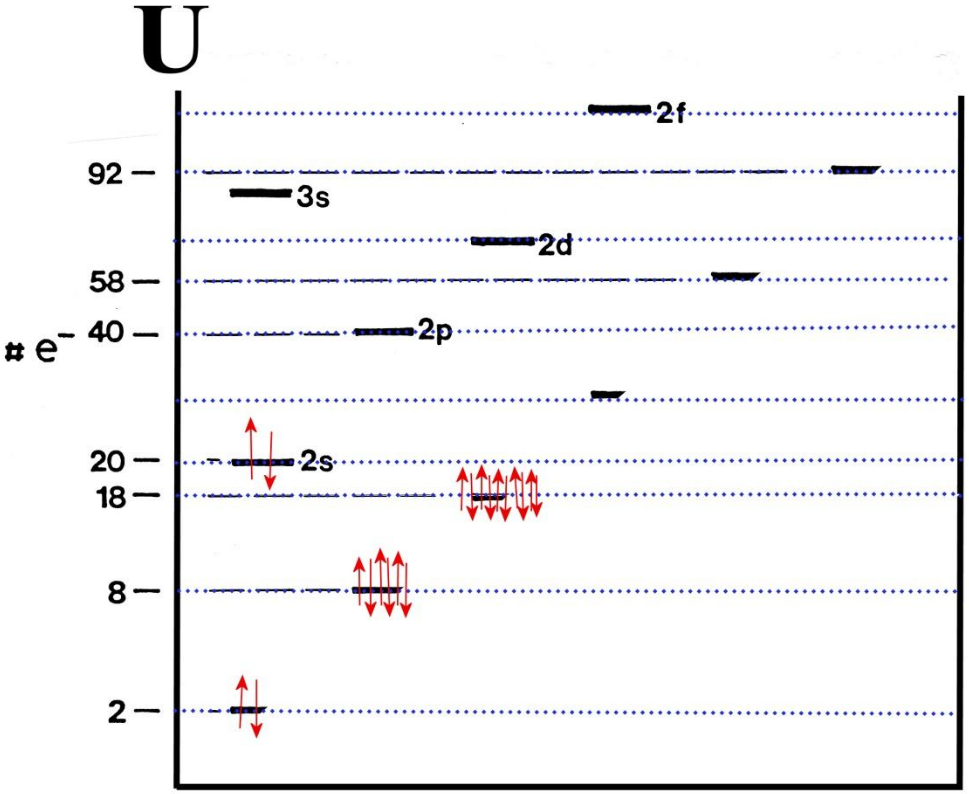
Group Meiwes-Broer, Rostock

photoelectron spectra from Ag_N^-



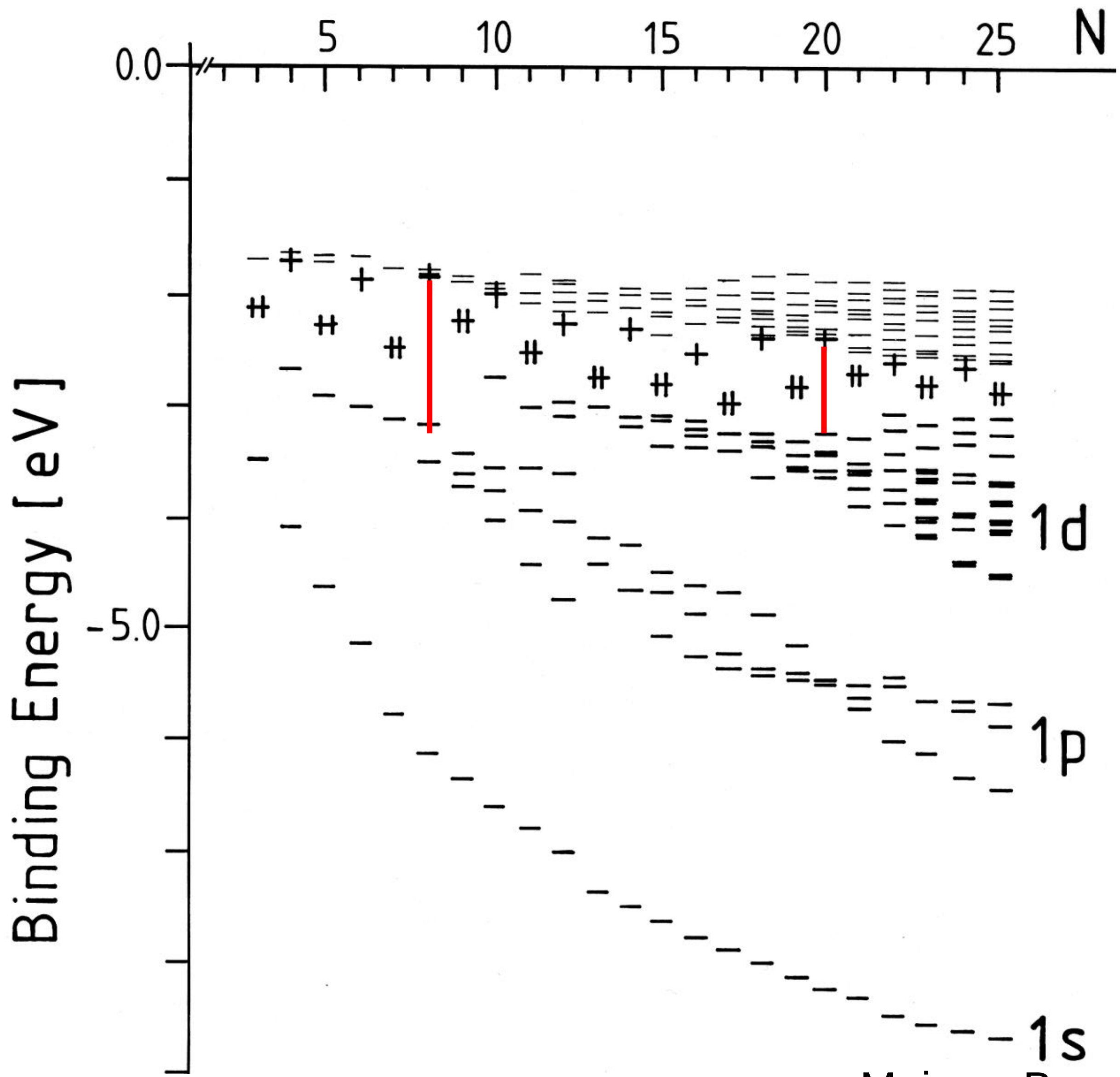
Meiwes-Broer, Appl. Phys. A55 (1992) 430

comparison with the jellium model



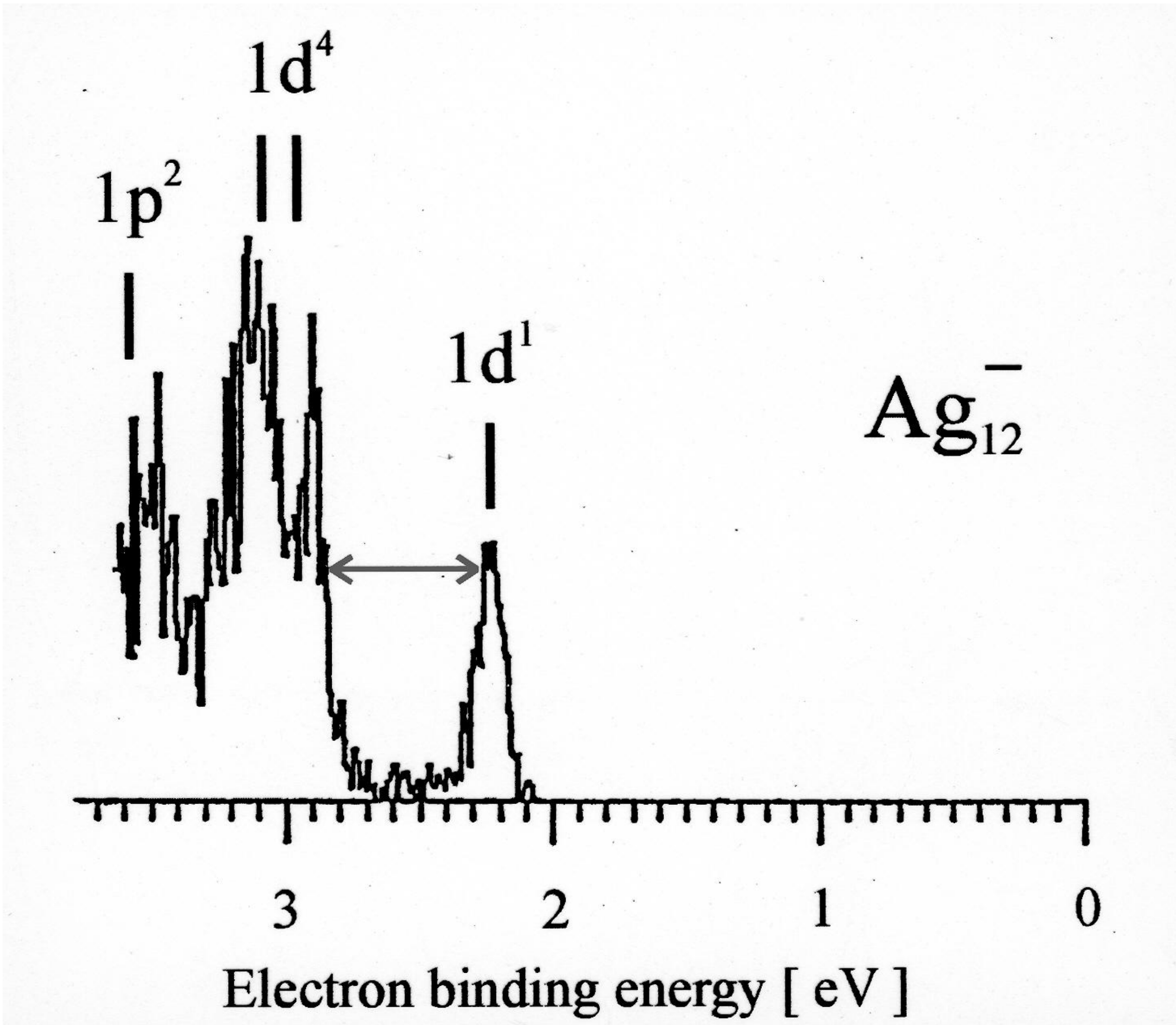
pronounced energy gaps after 8 and 20 electrons, but there are more gaps due to lifting of degeneracy

Ag_N^- effective medium theory



<u>Better theory</u>:
One-electron energy levels of An_{N^-} by tight-binding calculations within the effective medium theory

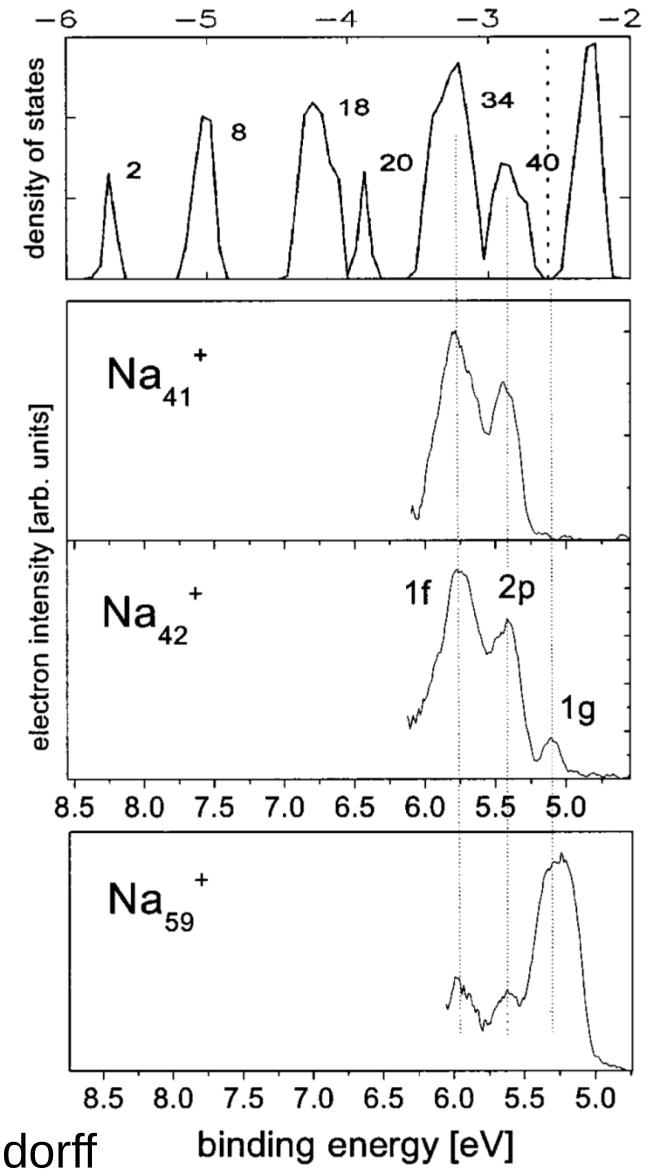
Meiwes-Broer, Appl. Phys. A55 (1992) 430



fine details of the electronic structure can be resolved

comparison PES with jellium calculations

Density of states from KS single-particle energy eigenvalues

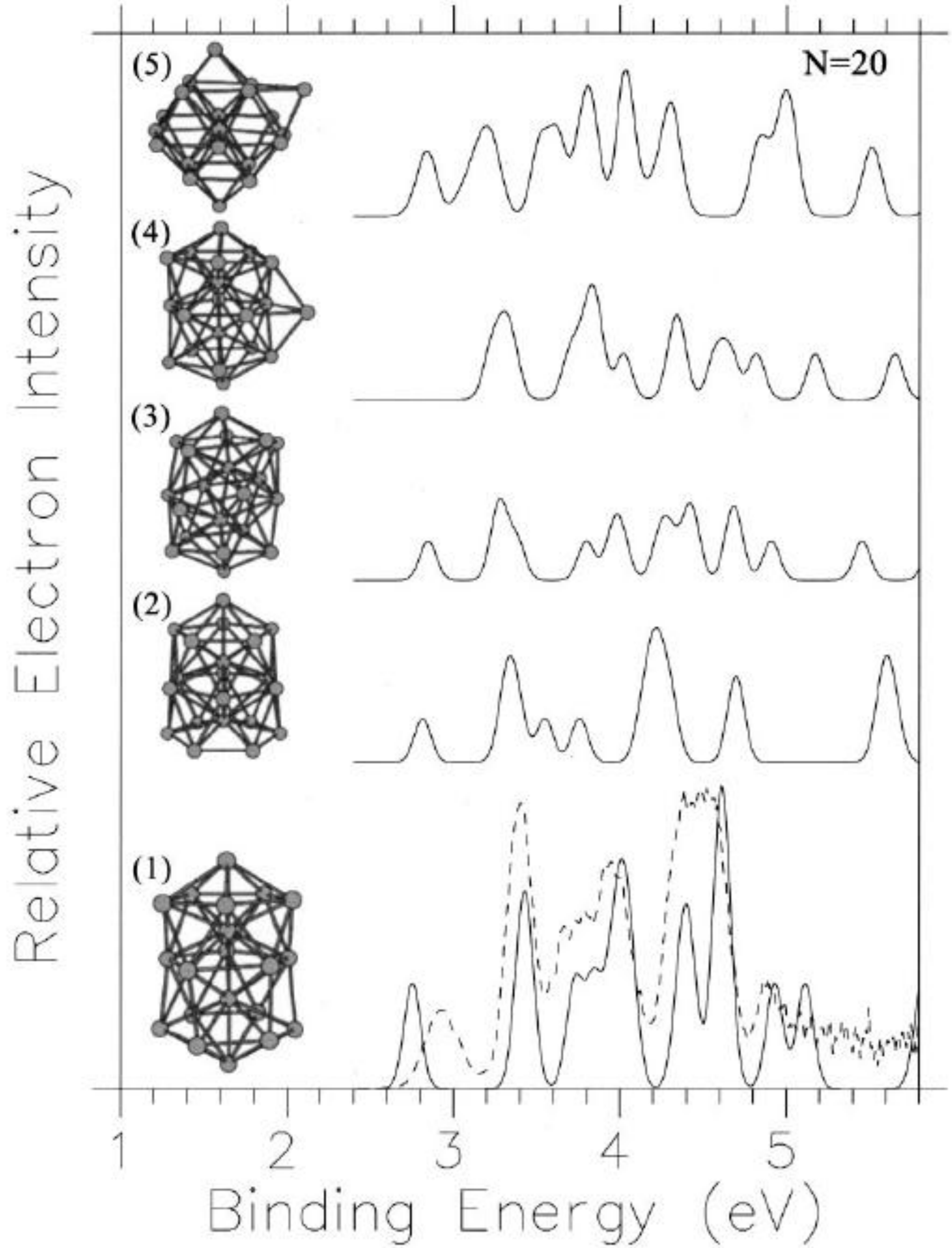


G. Wrigge, M. Astruc Hoffmann, and B. v. Issendorff PRA65, 063201(2002)

Al_{20} PES *vs.* calc.

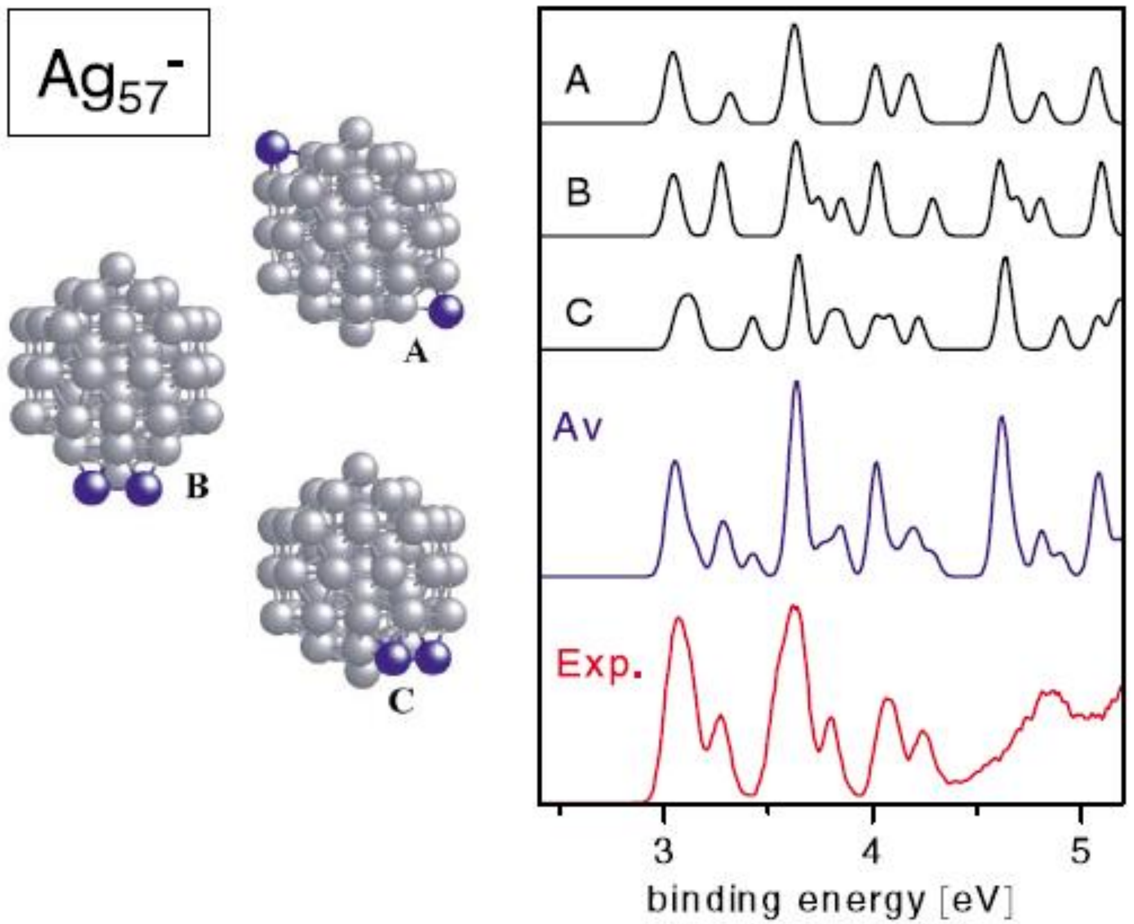
in this case:
mainly one isomer contributes

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

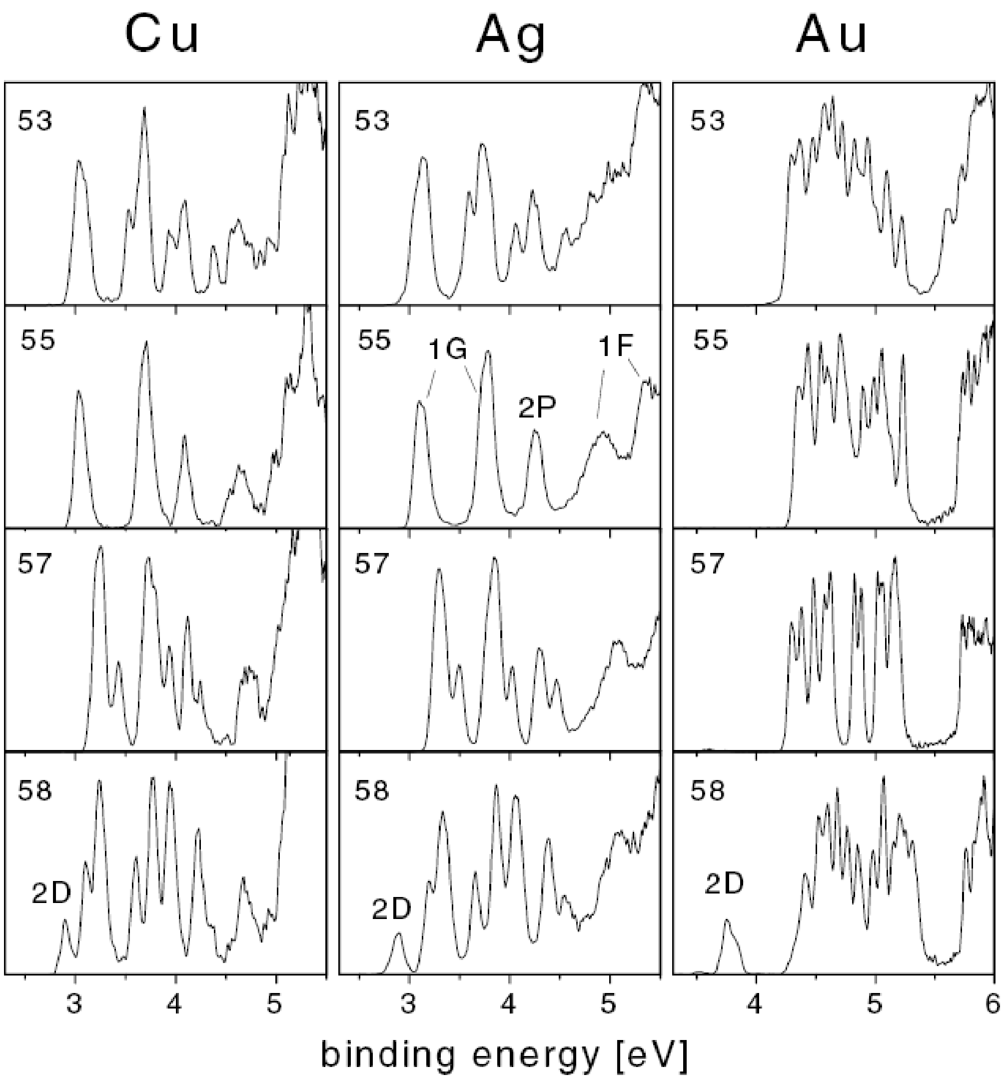
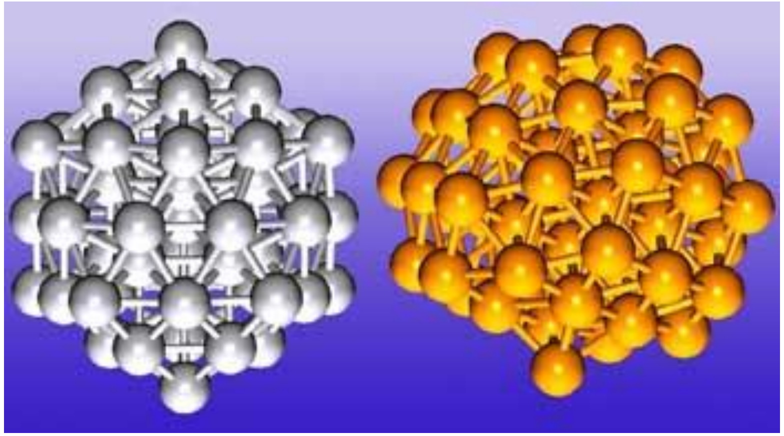


FIG. 1. Photoelectron spectra of Cu_n^-, Ag_n^-, and Au_n^- ($n =$ 53, 55, 57, 58) obtained at a photon energy of 6.42 eV.



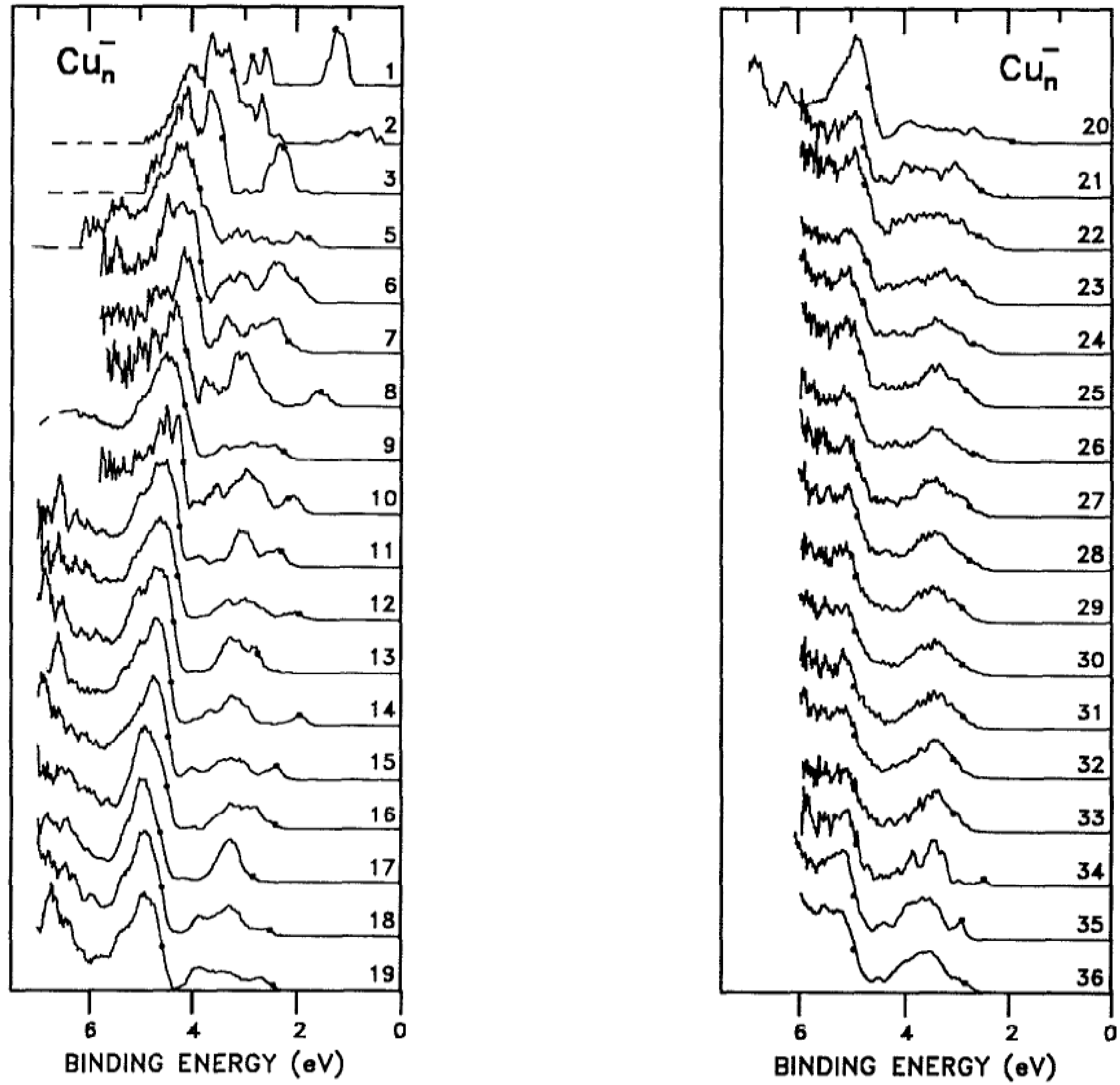
chemically similar systems may have similar PE spectra.
Exception: Gold, due to relativistic effects

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

Trends in photoemission threshold energies

N-dependent trends in photoemission

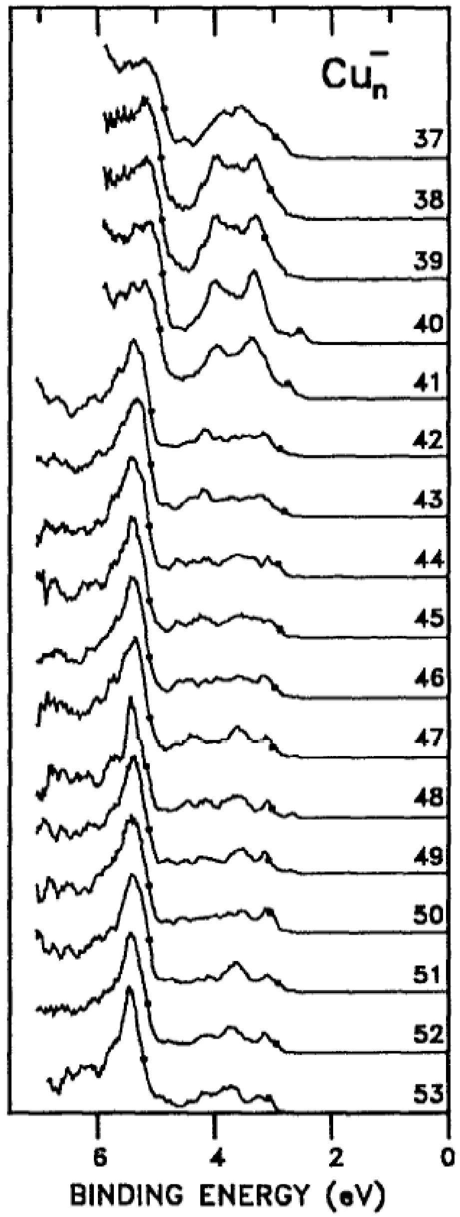
Cu_N^- PE threshold rises with increasing cluster size

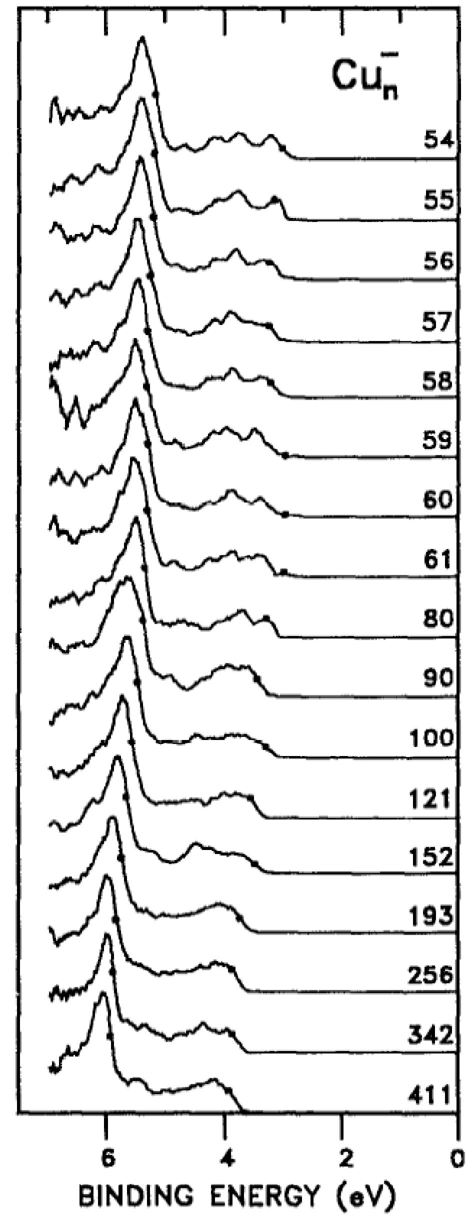


Taylor, Smalley, et al., JCP 96, 3319 (1992)

Cu_N^- PES

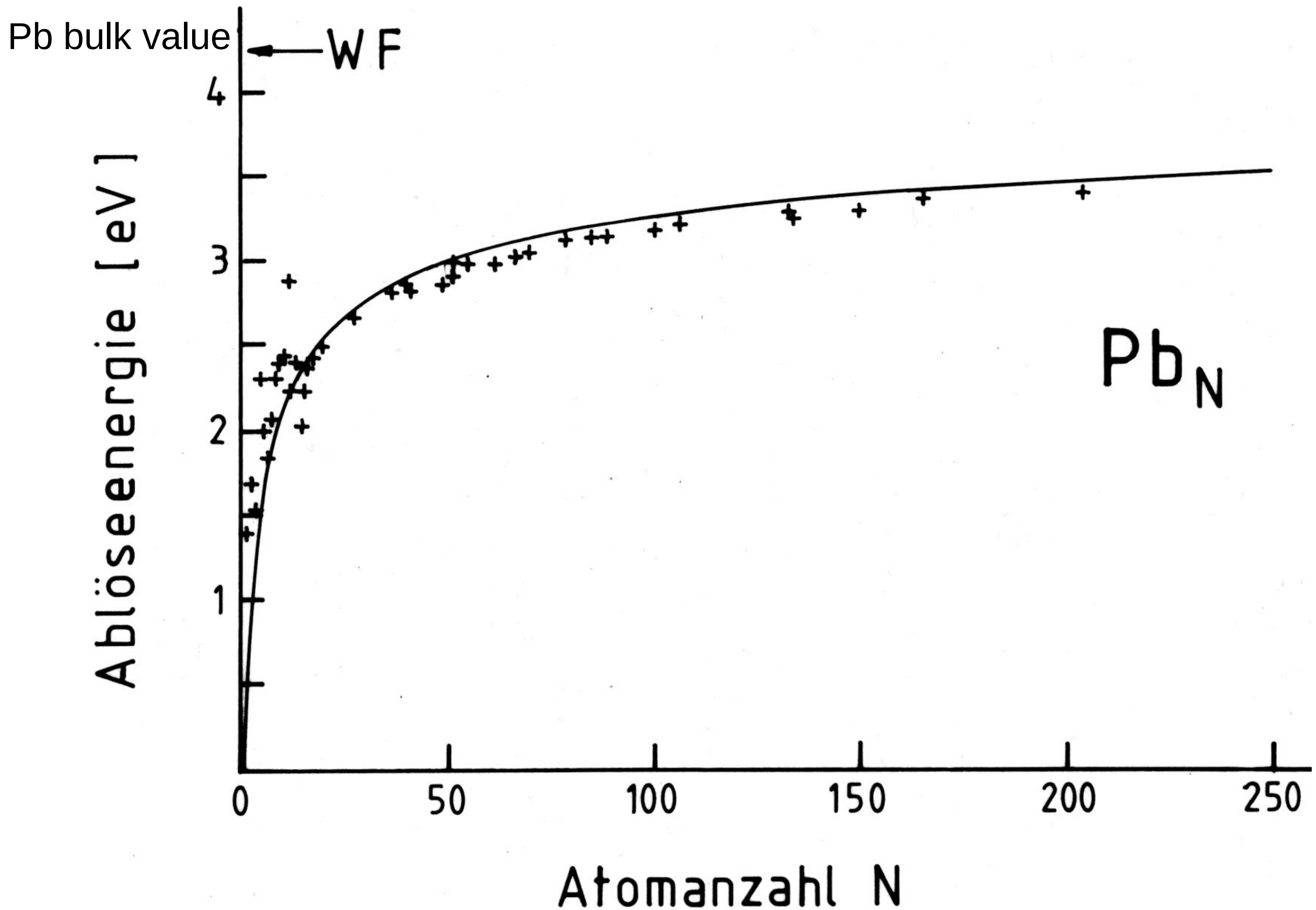
threshold energies increase with N



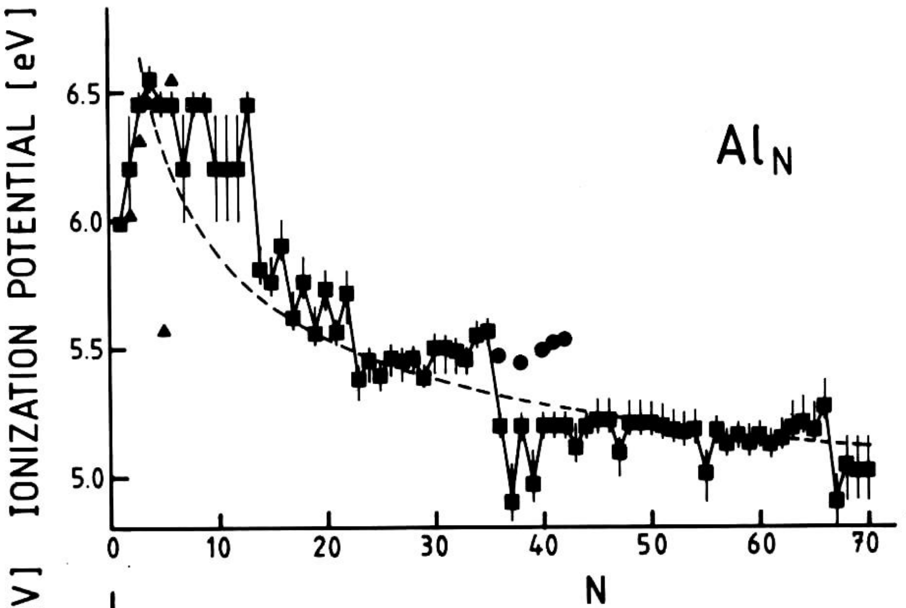


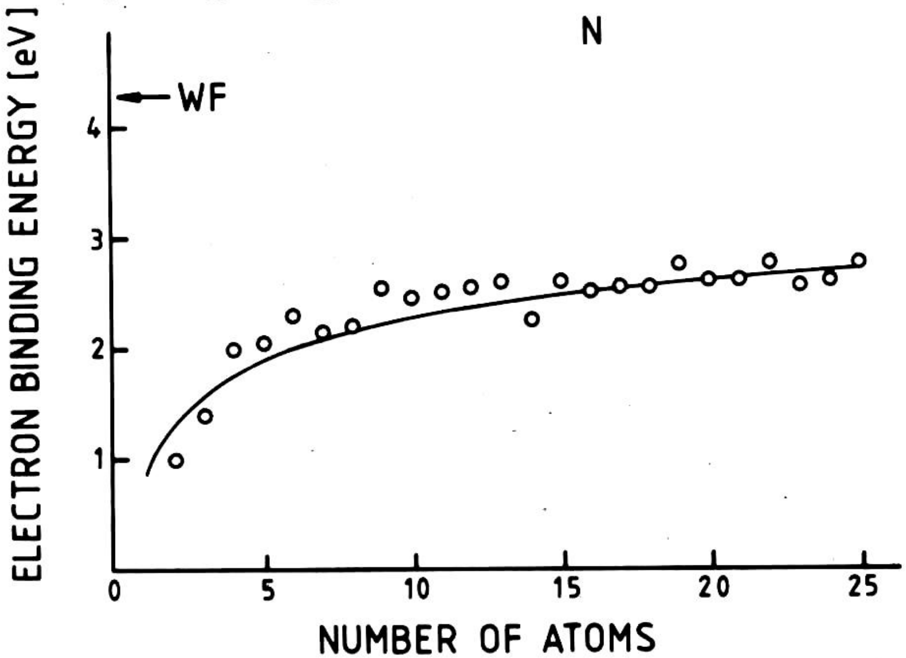
Taylor, Smalley, et al., JCP 96, 3319 (1992)

threshold energies: electron detachment



Gausa, Hector, Lüder, Meiwes-Broer





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

generally:

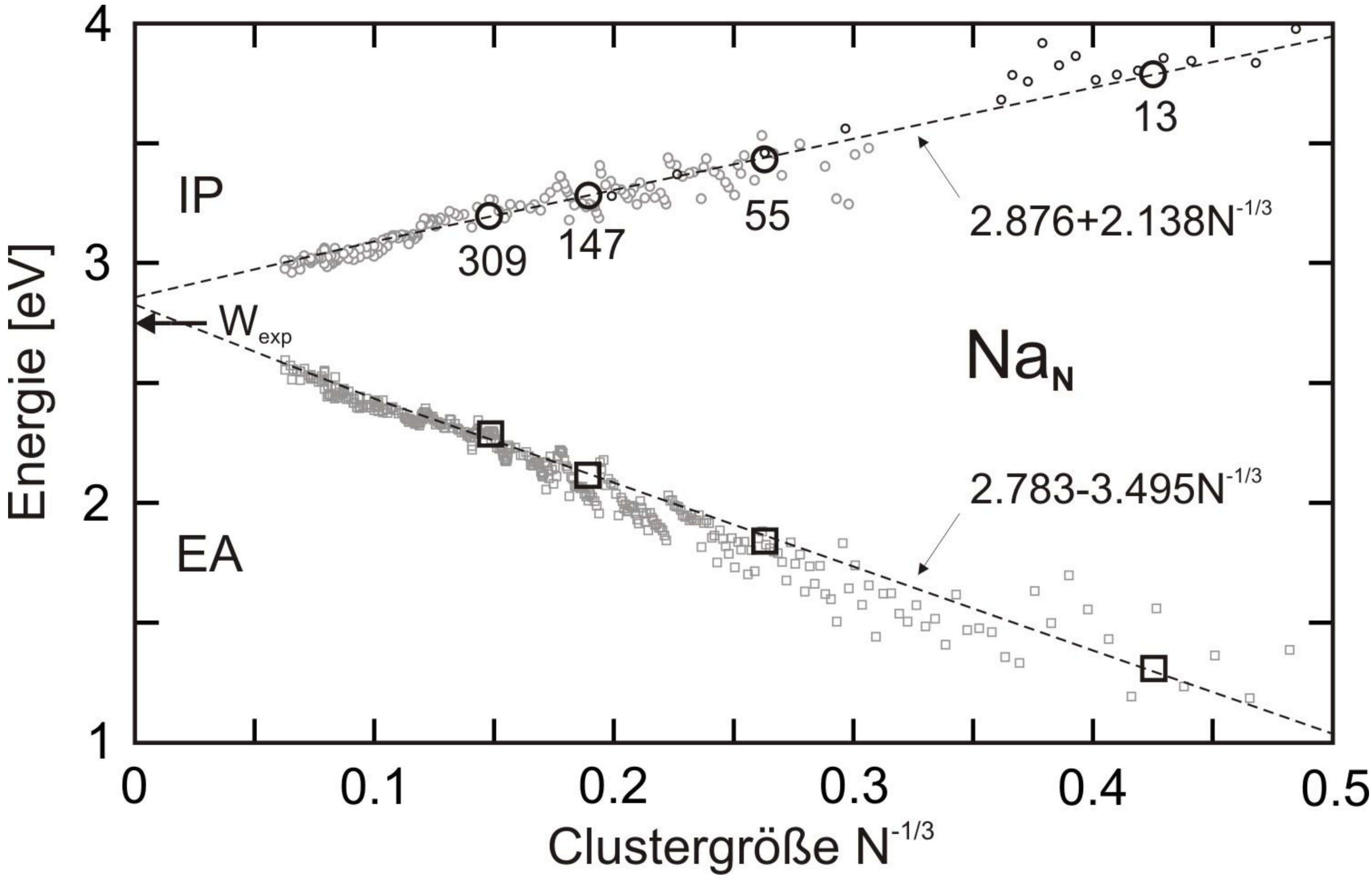
- the IPs <u>decrease</u> with increasing N
- the EAs <u>rise</u> with increasing N

Parametrization:

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

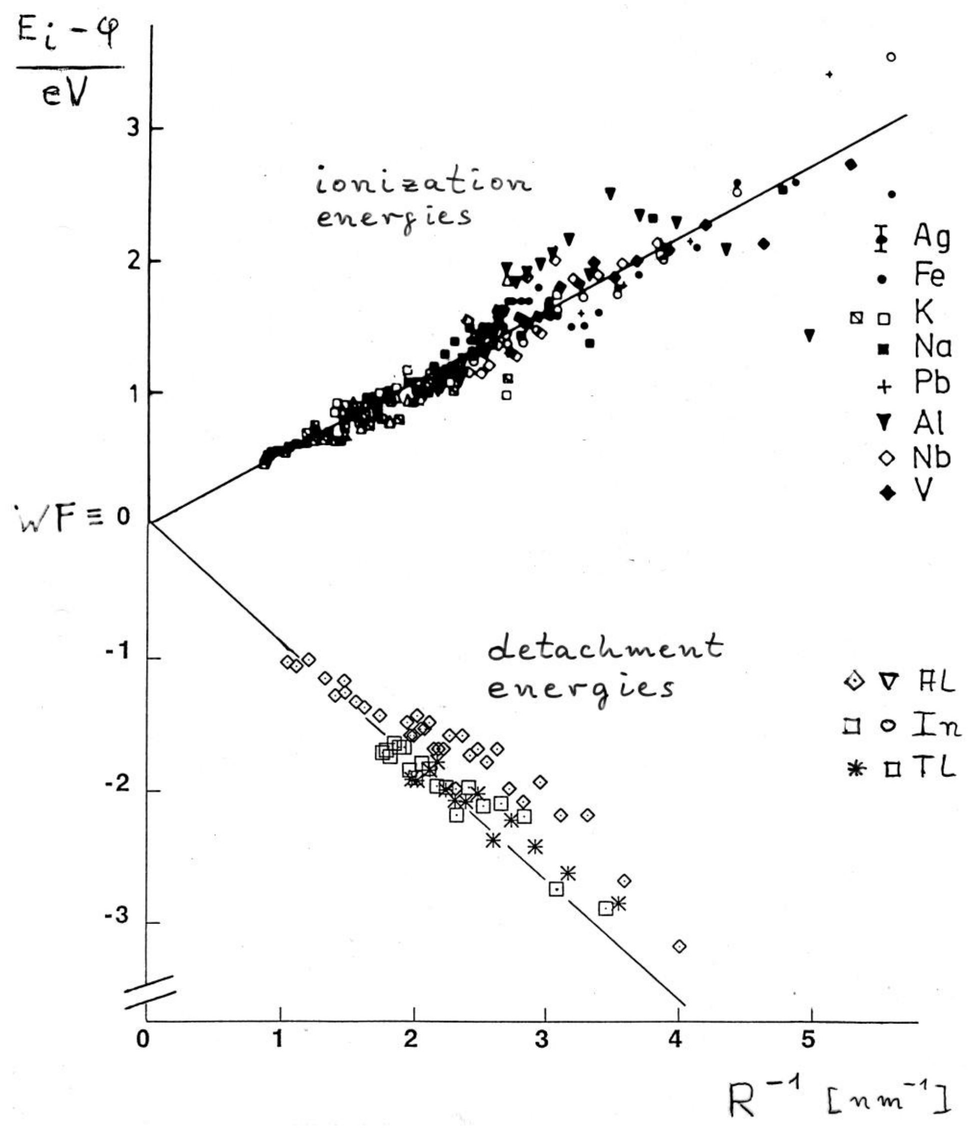
$$EA(R) = WF - \beta \frac{e^2}{R}$$ with β = ½ 5/8

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



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

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

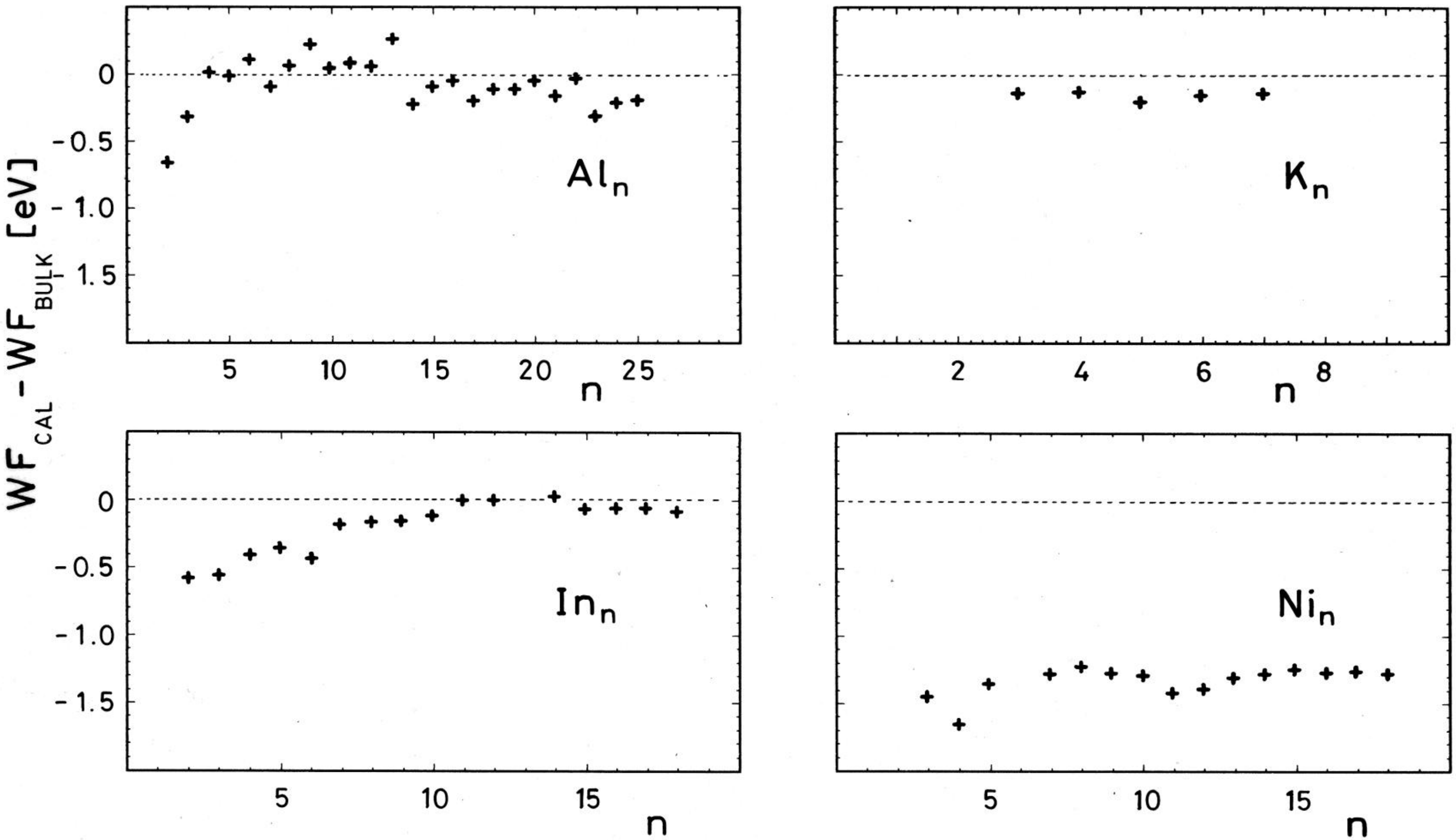
α - β is small

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 !

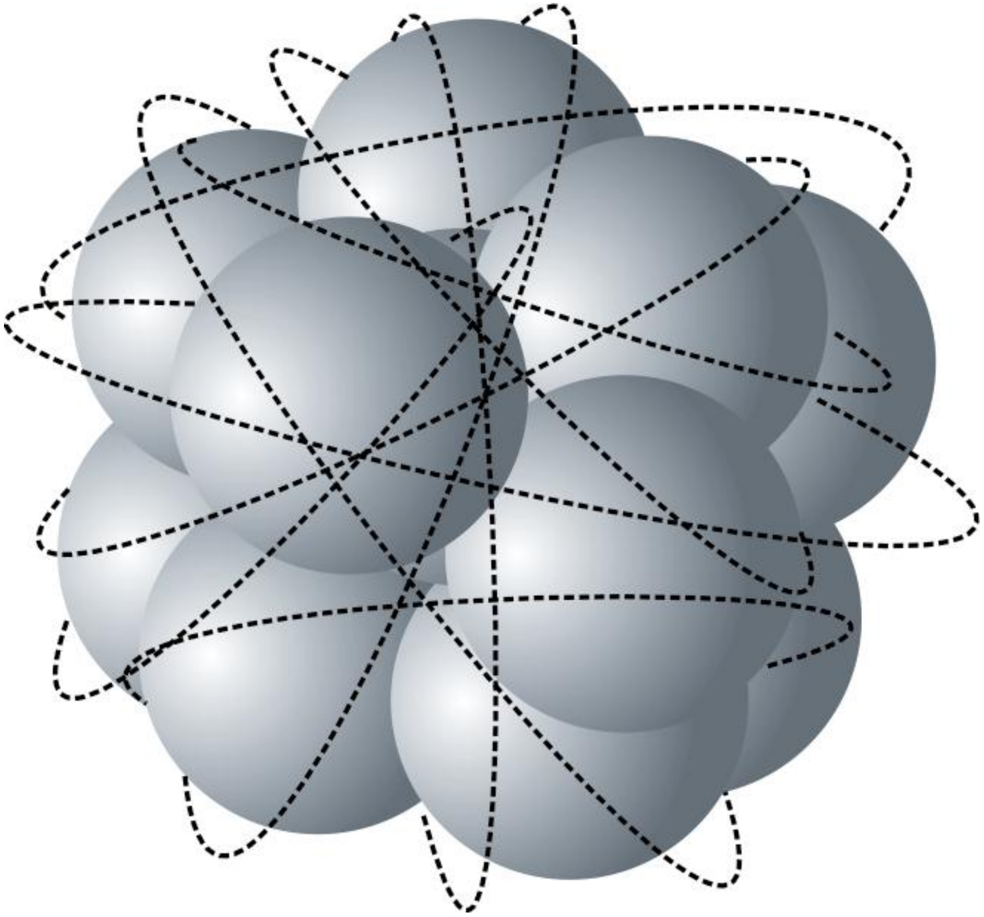
differences between measured IP and EA and bulk values



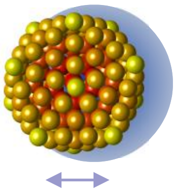
Small or no differences hint at free electron (or: ideal metal droplet) behaviour

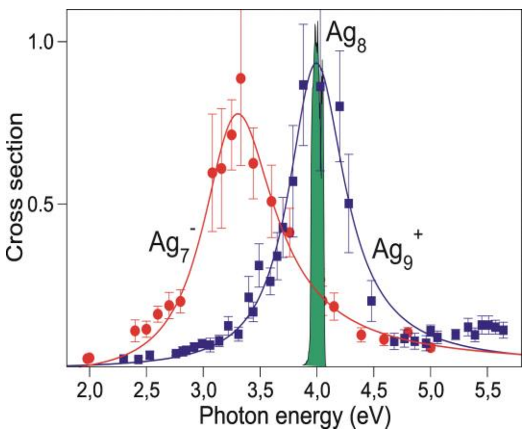
Meiwes-Broer in *Advances in Metal and Semiconductor Clusters, Vol. 1*
M. Duncan, Ed., JAI Press Inc., 1993

optical properties through confined electrons



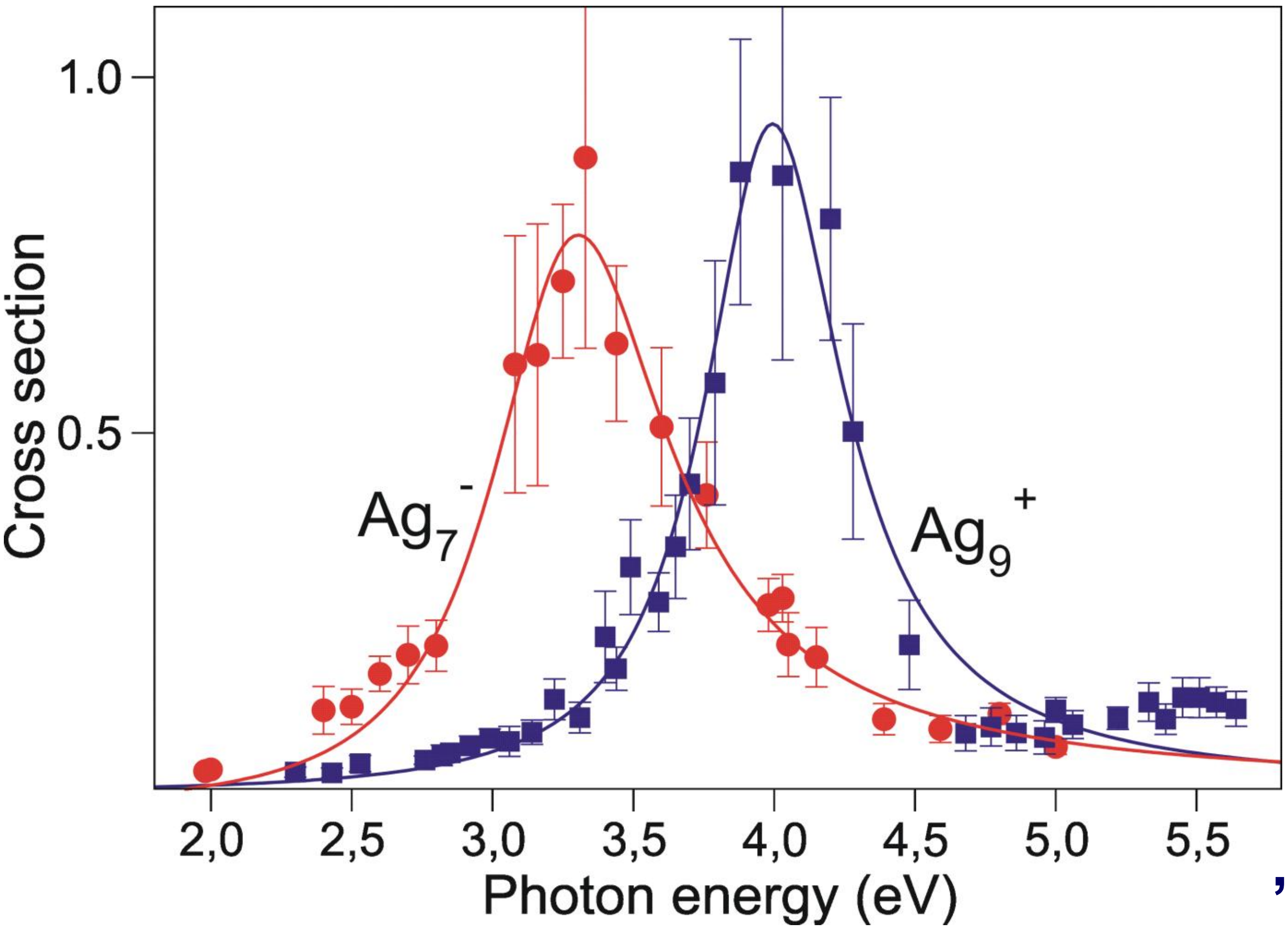
... schwingen gemeinsam im Laserlicht wie ein angetriebenes Pendel

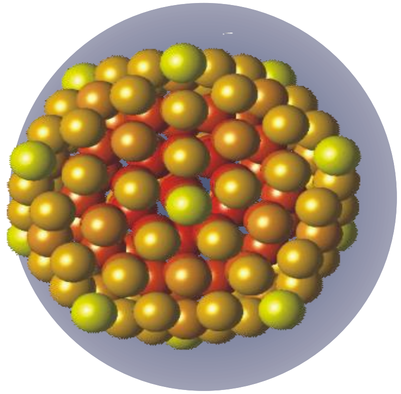




Jellium artwork

photofragment spectroscopy on mass-selected silver clusters





„cold plasmon“

only in metals with delocalized electrons

Tiggesbäumker et al., Phys. Rev. A 48, R1749 (1993); Chem. Phys. Lett. 260, 428 (1996)

also see: Kreibig and Volmer, Springer

similar:
Giant resonances in spherical nuclei

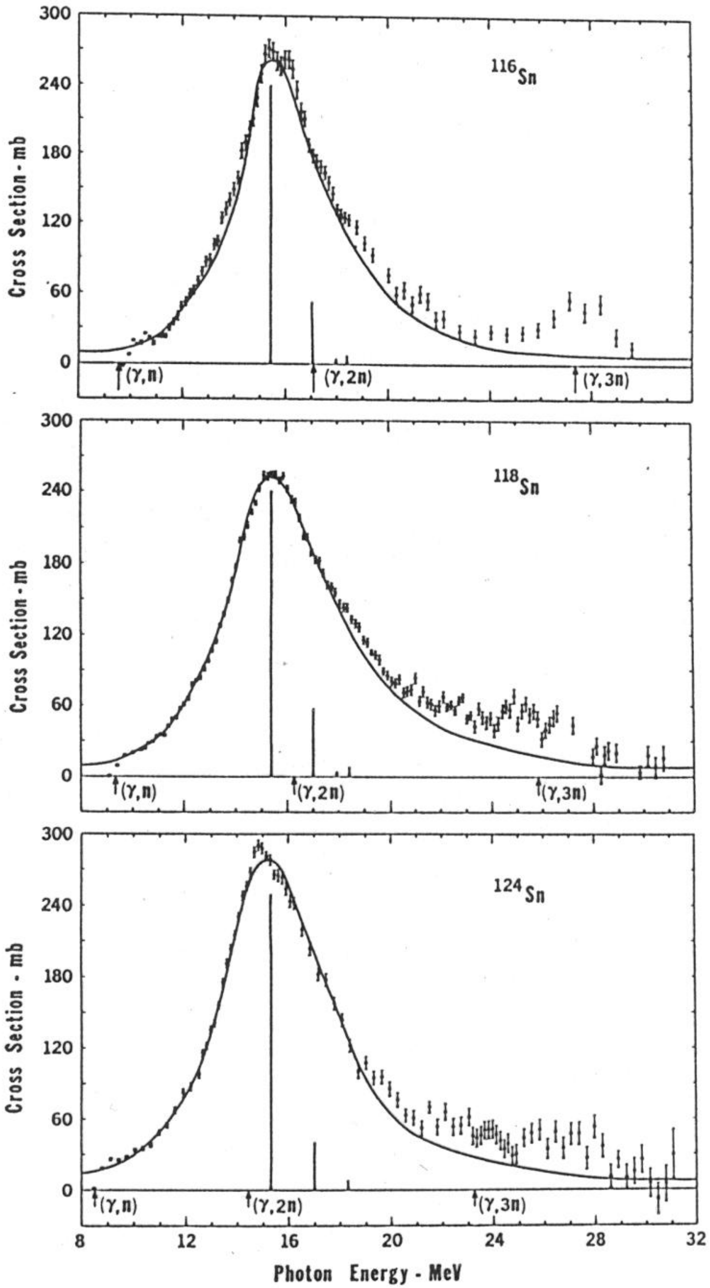


Fig. 1: Showing total photoneutron cross sections for different isotopes of tin, together with theoretical fits based on a dynamical collective model. (After reference 5)

- **electrons in metal clusters and the nuclear particles are fermions. Both oscillate in the confining potential**

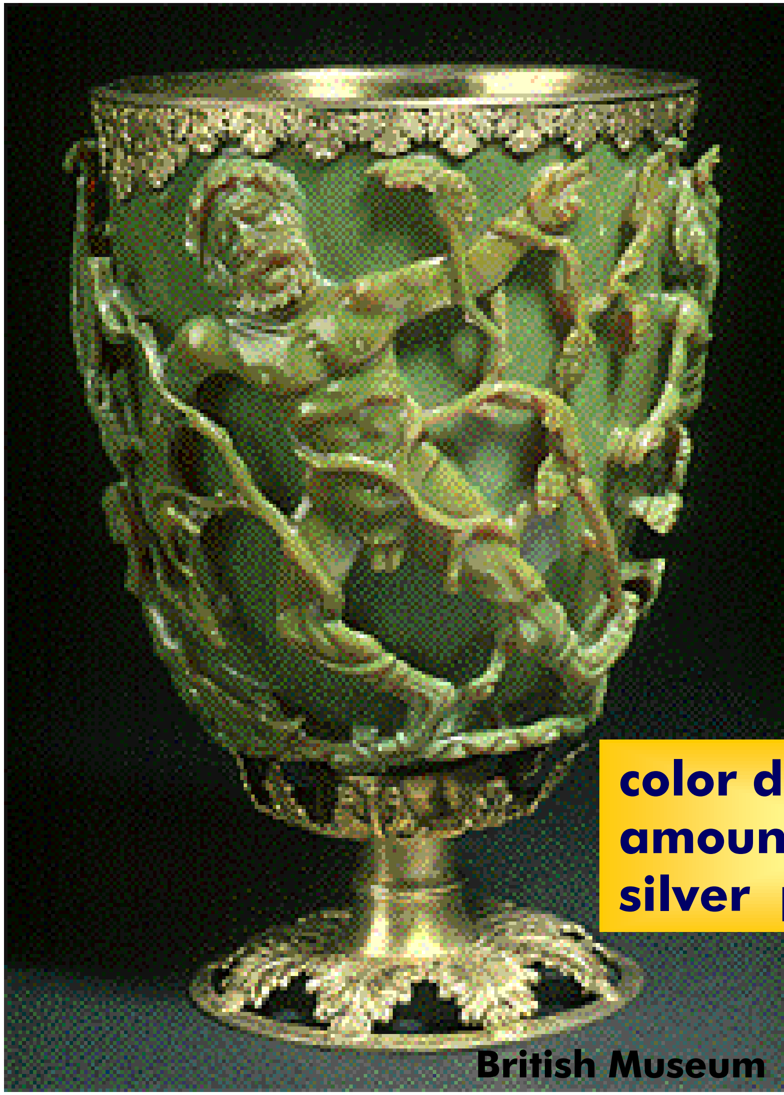
- **therefore the same model can be used in order to describe the optical properties, e.g. the random phase approximation (RPA)**

- **closed-shell nuclei also show only a single absorption**

- **in the nuclei however the excitation energies are much higher, i.e., in the MeV range**

Lycurgus cup (400 AD)

Optical properties of small particles



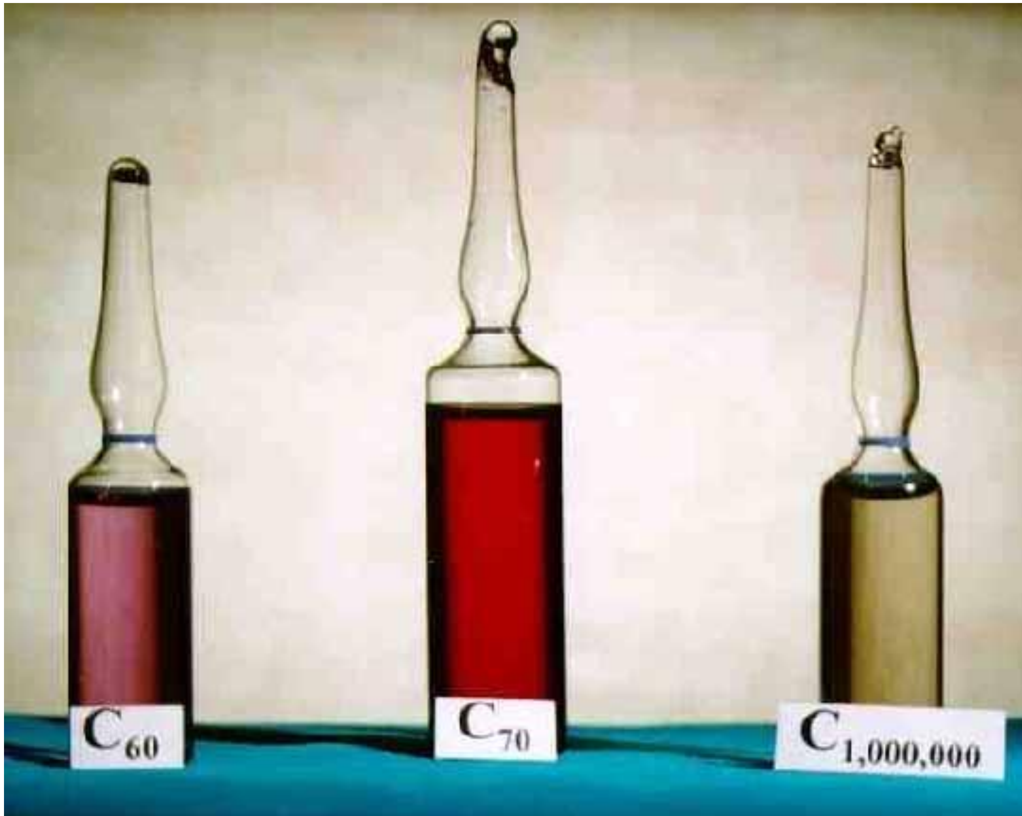
King Lycurgus is dragged into the underworld by Ambrosia

color due to a small amount of gold and silver particles

“Labors of the Months” (Norwich, England, ca. 1480).

The ruby color is probably due to embedded gold nanoparticles

Fullerenes and quantum dots

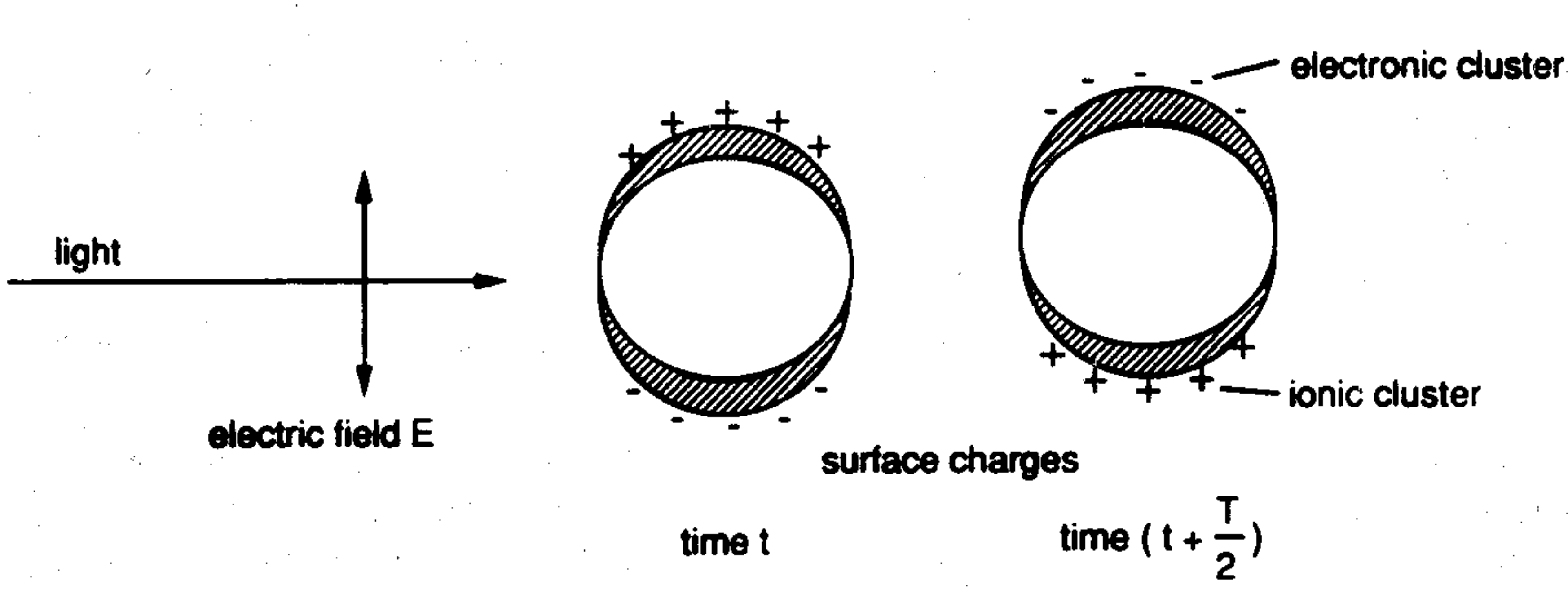


-Such absorption features can also be found in other small particles
- It is therefore not restricted to metal particles but occur also in particles like fullerenes or semiconductor quantum dots
- It turns out that we only need to know the optical properties of the material in order to calculate the optical properties

CdSe

quantum dots

excitation of the electron cloud in a small particle



- Since the ion cores are much heavier than the electrons the positive charges stay more or less at there position when a light field interacts with the particle
- The electric field of the light moves the electron cloud out of the positive background
-Below the resonance the electrons move with the direction of the electric field
- At resonance the movement of the cloud has a p/2 phase difference to the electric field.
- This is called the plasmon resonance
- Above resonance the phase is 180 degrees

Gustav Mie 1868-1957

born in Rostock

Gustav Mie, Beiträge zur Optik trüber Medien, speziell kolloidaler Metallösungen
Ann. Phys. 25, 377 (1908)

absorption and scattering of light by small particles

C.F. Bohren and D.R. Huffman
Wiley, NY 1983

$$\omega_{Mie} = \left(\frac{1}{3} \frac{e^2 n_o}{\varepsilon_o m_e} \right)^{1/2}$$

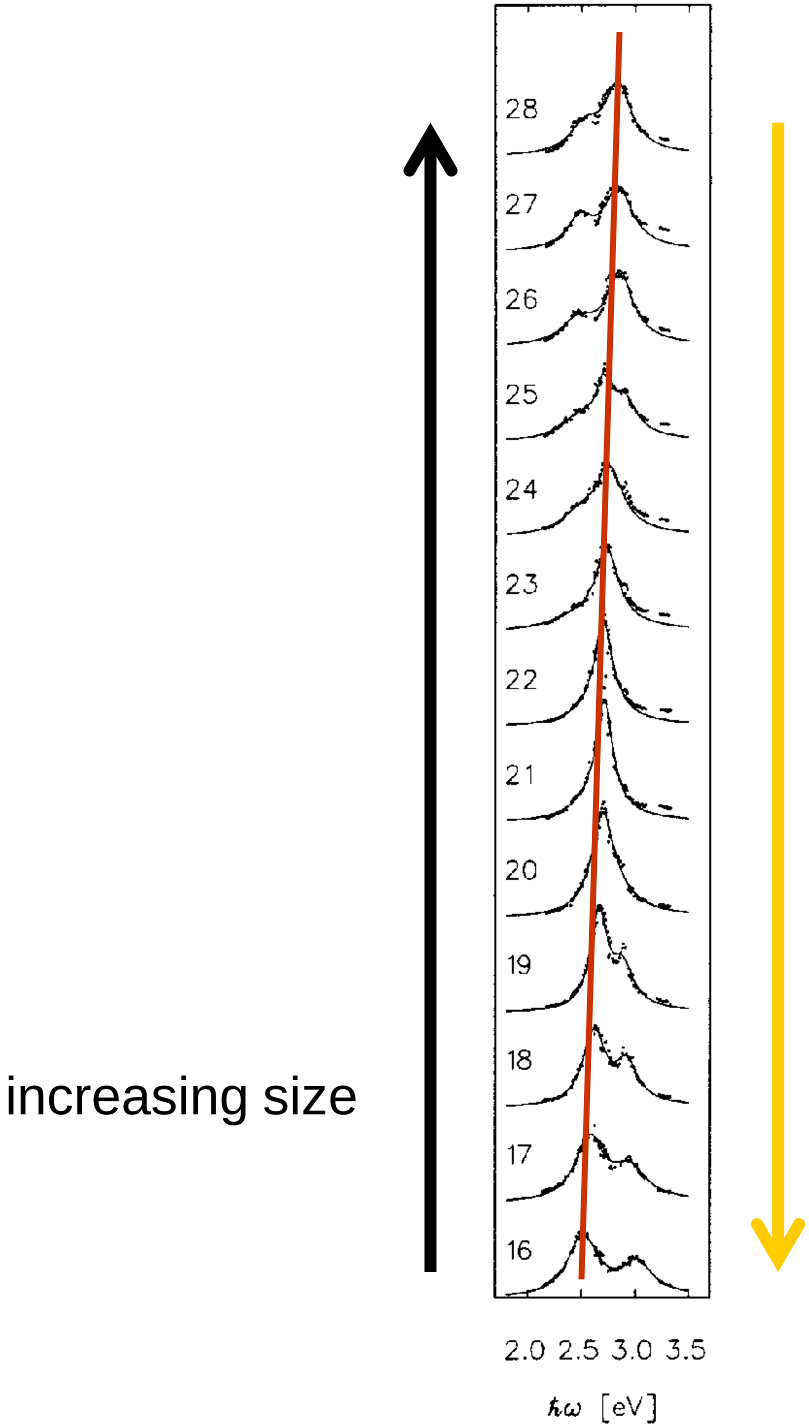
plasmon frequency of a small particle

-Everything gets simplified when the size of the particle is much smaller than the wavelength of the light

- The relevant value is the size R compared to the wavelength λ of the light, i.e. R/ λ

$$\omega_{Mie} = \left(\frac{e^2 N_e}{\alpha \cdot m_e} \right)^{1/2}$$

static polarizability



Trend with small alkalies

For decreasing cluster size the plasmon energy shifts to lower values.
This is called the red-shift.

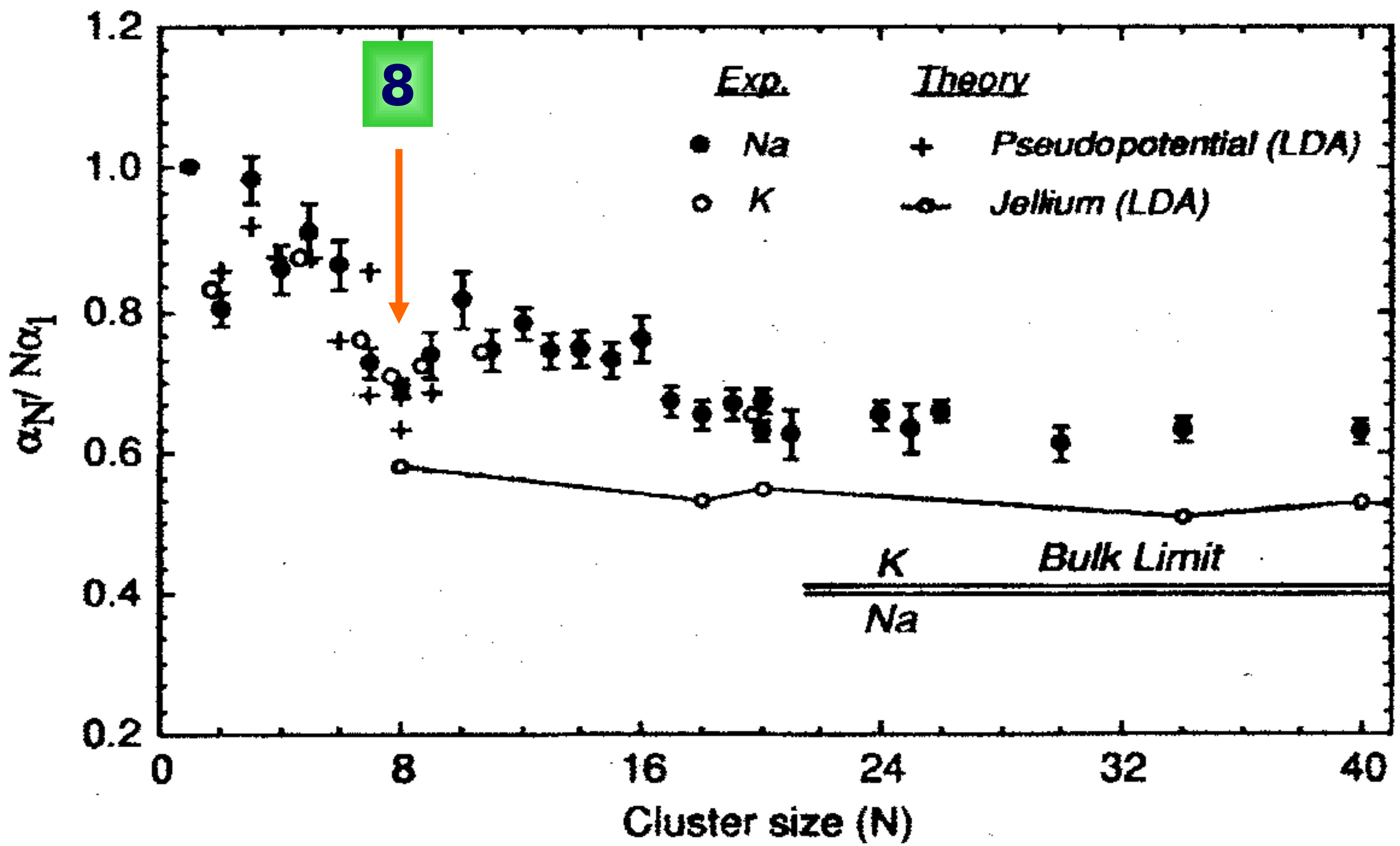
Reason: influence of the spil-out

$$\omega_{Mie} = \sqrt{\frac{n_{bg} e^2}{3 m \varepsilon_o}} = \frac{\omega_p}{\sqrt{3}}$$

Mie – Plasmon

or: increasing polarizability

polarizabilities of alkali clusters



Knight et al. Phys. Rev. B 31, 2539 (1985)

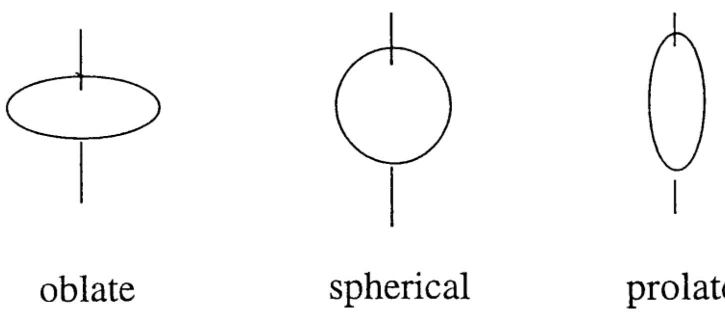
not all clusters are spherical

ellipsoïdal shell model

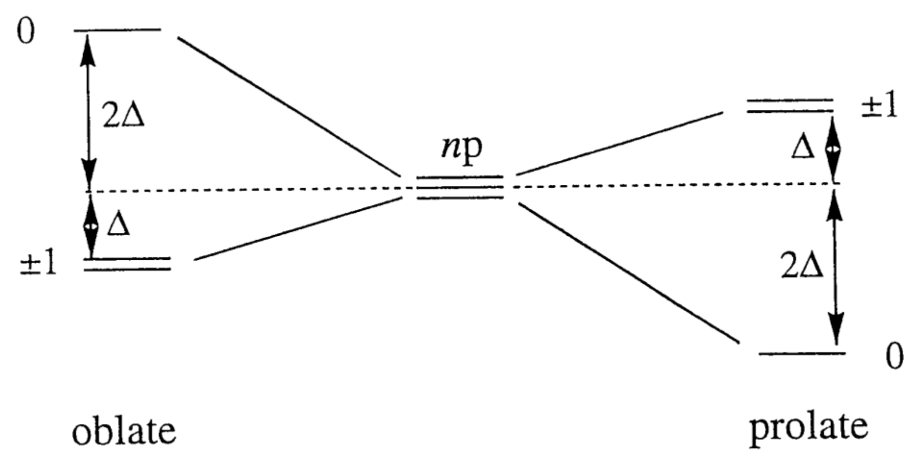
Problems with the spherical jellium model :

- fine structure of mass spectra (even-odd alternation)
- diamagnetism of even-electron clusters with formally open jellium shells (breaking of Hund's rule)

Unlike an atom, the positively charged background can deform !



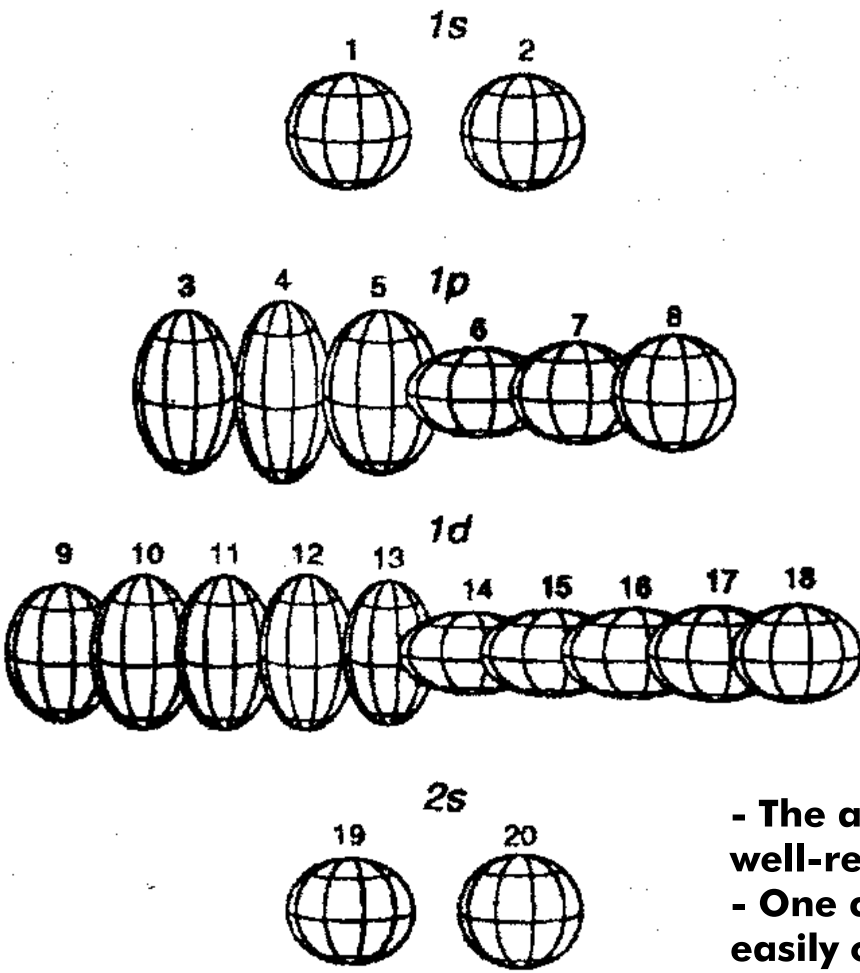
oblate	spherical	prolate
$I_x = I_y < I_z$	$I_x = I_y = I_z$	$I_x = I_y > I_z$
$k_x = k_y < k_z$	$k_x = k_y = k_z$	$k_x = k_y > k_z$



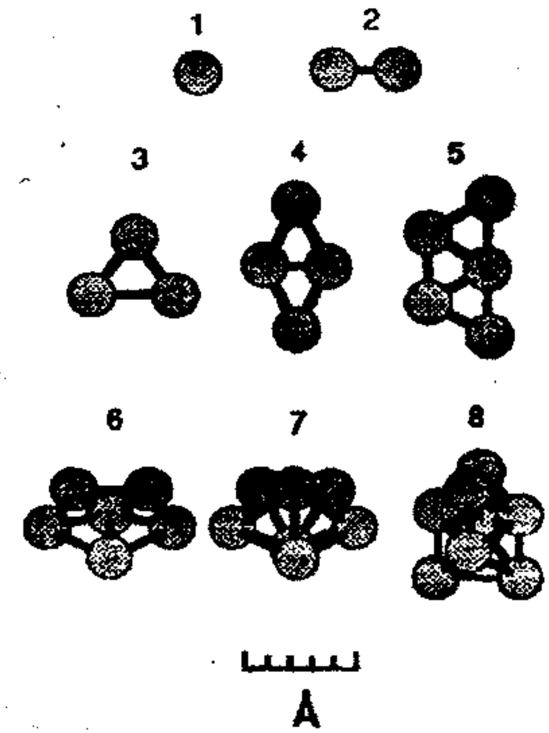
Nielsson model

not all clusters are spherical

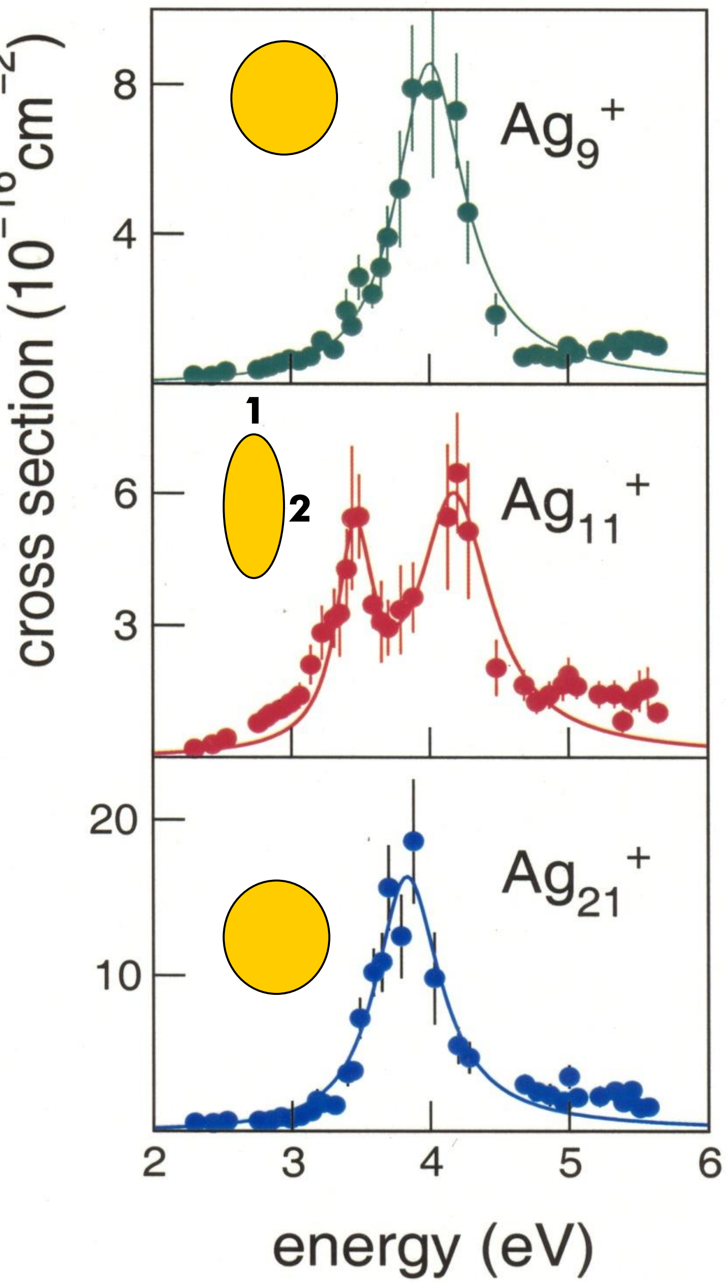
Ellipsoidal shell model



Quantum chemical calculations



- The ab-initio cluster structures are in first order well-reproduced by the ellipsoidal shell model.
- One can calculate the plasmon profiles more easily on the basis of this model.



Tiggesbäumker et al.

role of deformation

-In cluster ions the number of electrons is N-1

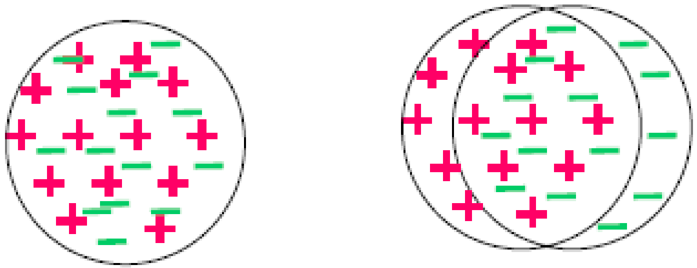
- Closed-shell cluster therefore appear at M_{N+1}^+

- Ag_9^+ and Ag_{21}^+ are closed-shell clusters and only a single absorption line appear in the optical spectra.

- In Ag_{11}^+ the prolate deformation of the particle results in a splitting of the absorption into two components.

- According to the ellipsoidal shell model the lower energy peak should have half the oscillator strength.

Optical response of mass-selected free metallic clusters

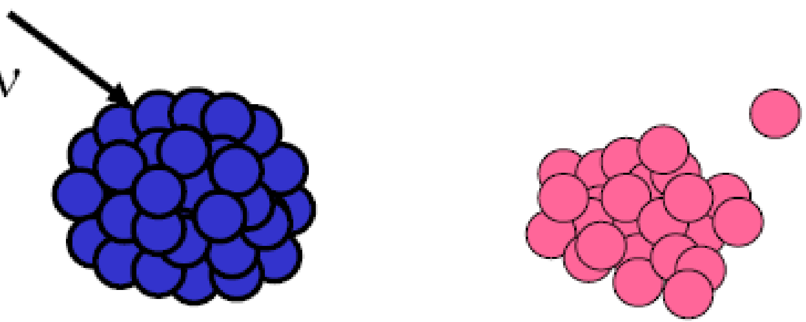


λ>>R

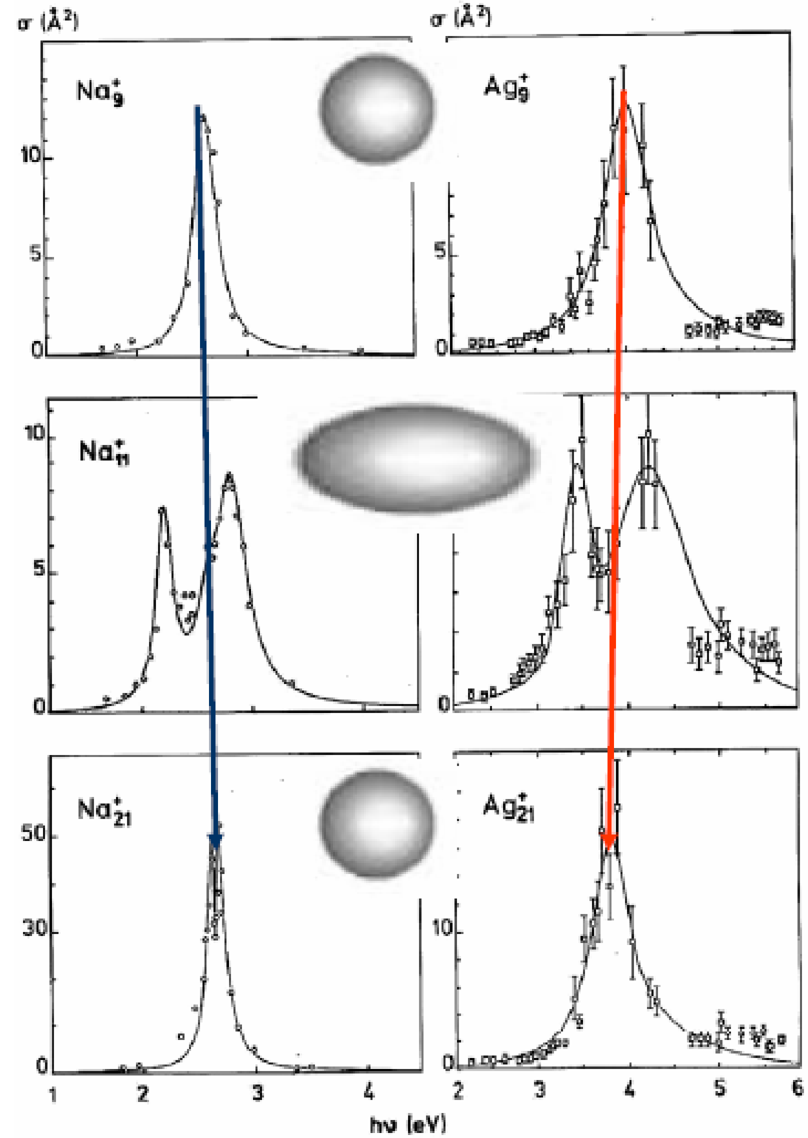
Mie resonance

Photo-absorption depletion spectroscopy

hν



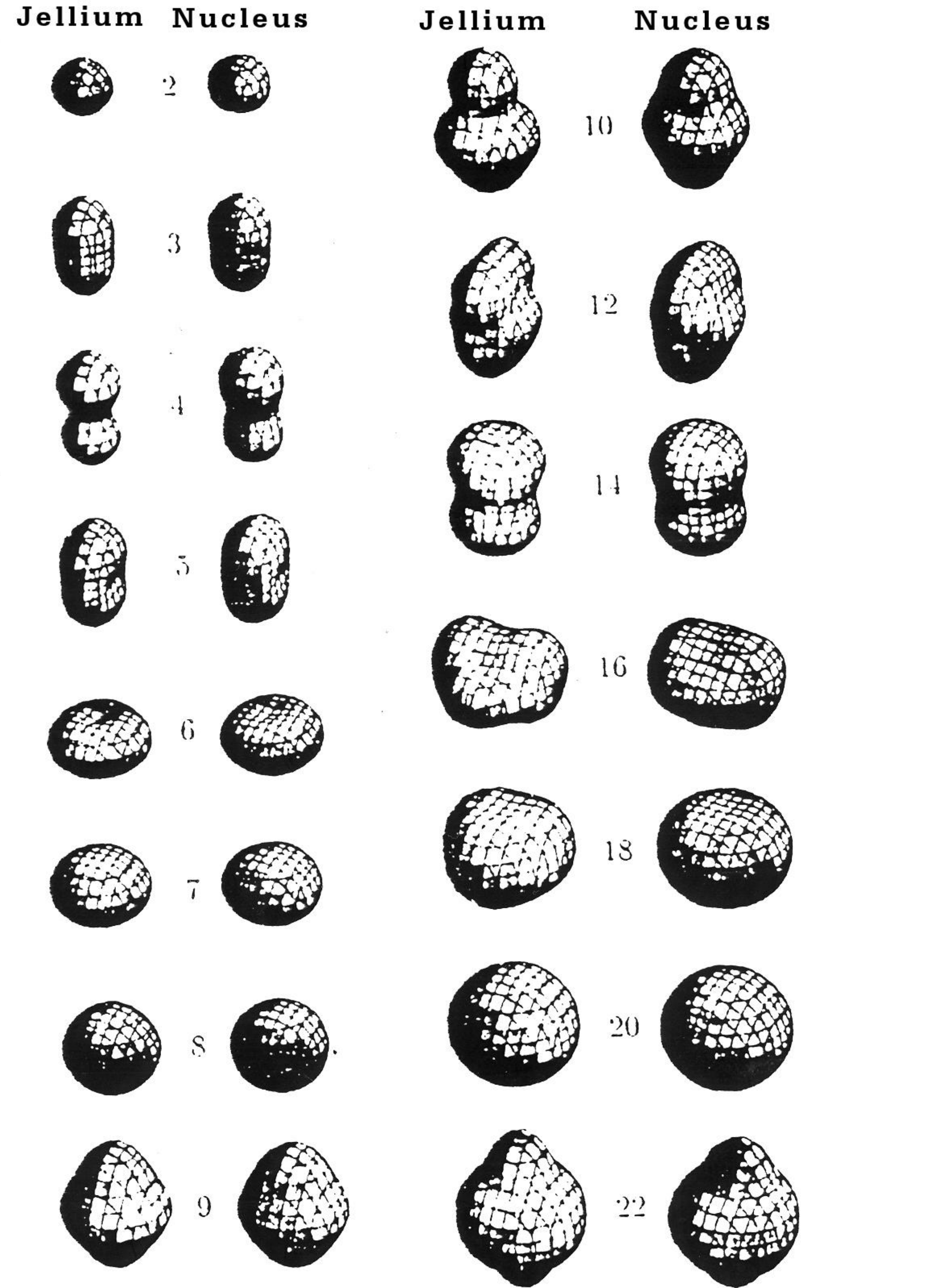
The absorption cross section probes the shape of the particle



Chem. Phys. Lett. **189**, 28 (1992); **190**, 42 (1992)

constant-density surfaces

for electron clusters and nuclei. The density of the surface is 0.00125 atomic units (or scaled units for nuclei), which corresponds to 38% of the bulk density



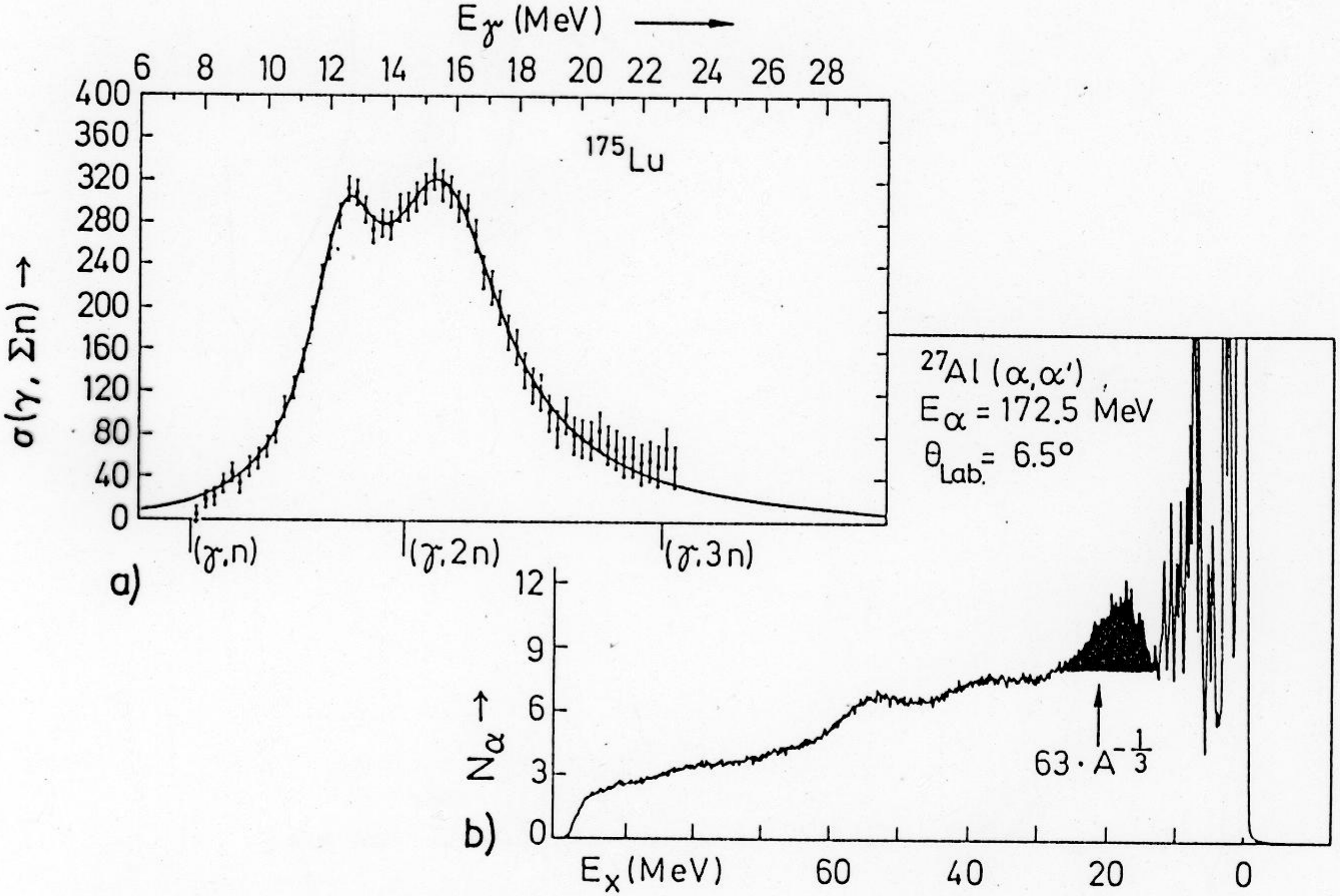
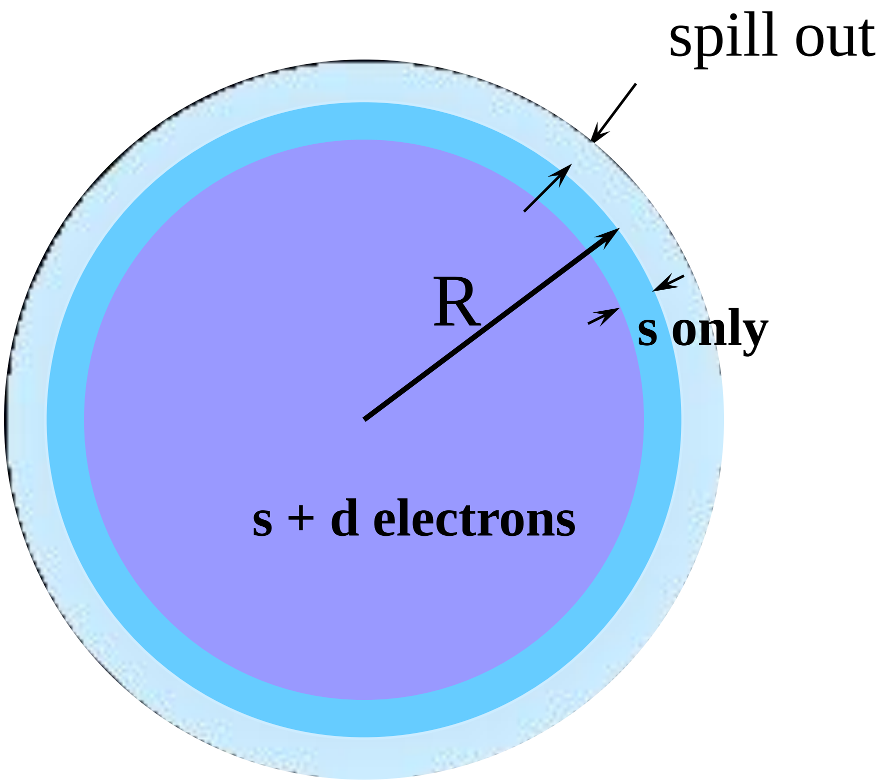


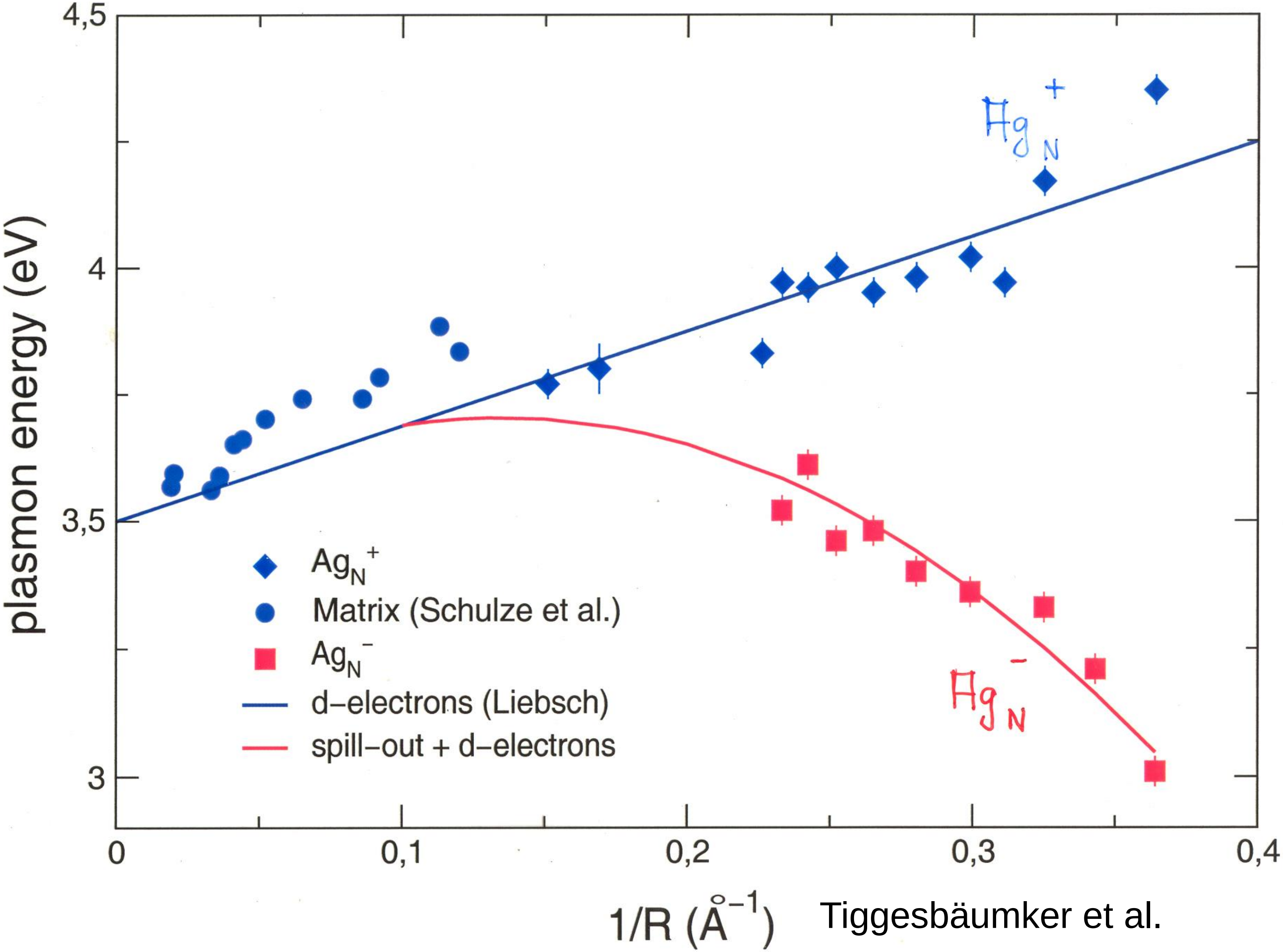
Fig. 99 Beispiele für Riesenresonanzen: a) In der Anregungsfunktion für (γ,n)-Prozesse an ^{175}Lu. Für deformierte Kerne ist der doppelte Höcker charakteristisch, da in der Deformationsachse eine andere Schwingungsfrequenz auftritt als senkrecht dazu [nach Ber 75a]; b) im Spektrum von unelastisch an Aluminium gestreuten α-Teilchen [Kis 76]

Mayer – Kuckuck p.237

Silver clusters: s- and d-electrons

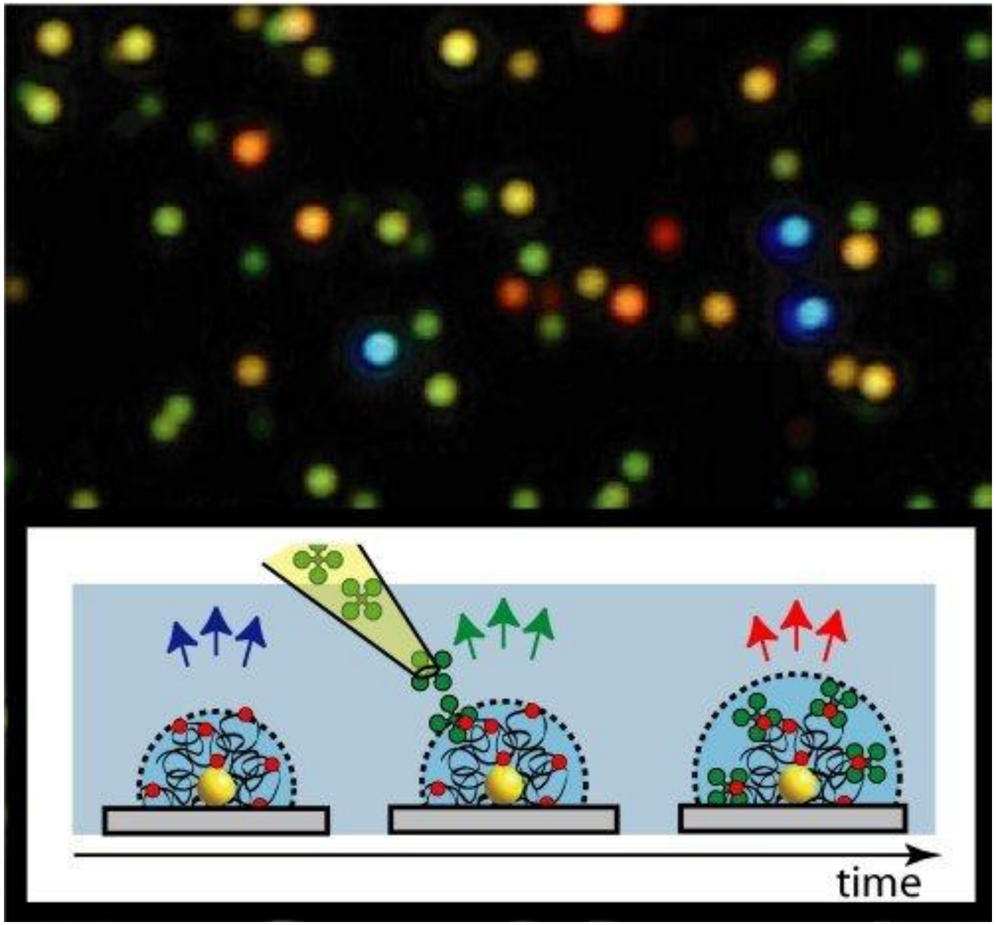


complex situation in Ag clusters



Tiggesbäumker et al.

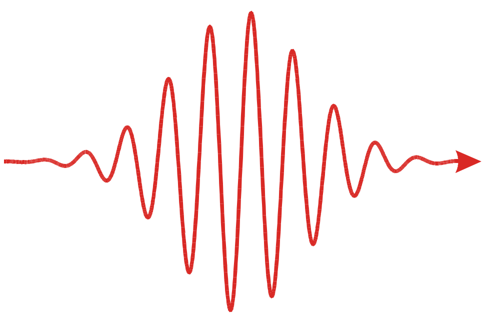
technical application as fluorescent labels

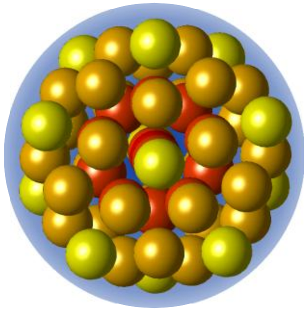


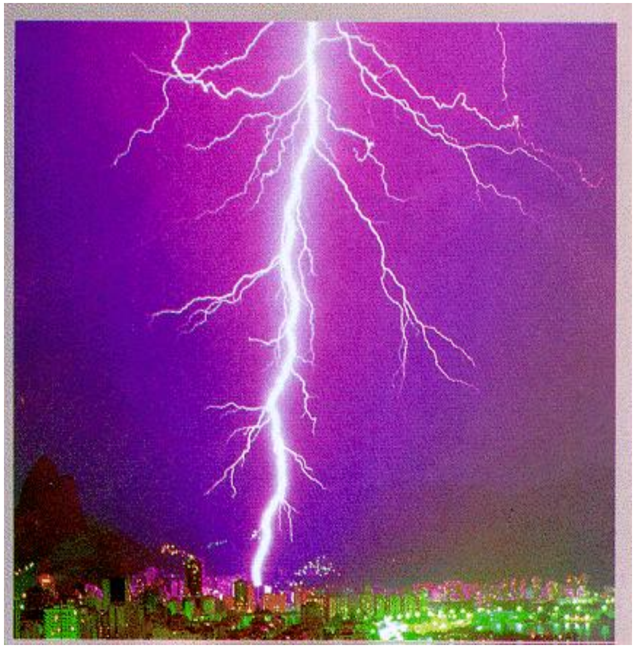
the following slides on clusters in strong laser fields have not been presented in the lecture.
This subject is an important topic in the Sonderforschungsbereich SFB 652.

in strong laser pulses:
clusters act as strong nano antennas

Gigawatt laser pulse







Pulse length: 100 femto seconds
power densities up to 10.000 Gigawatts per cm^2

SFB 652

→ minuature plasmas

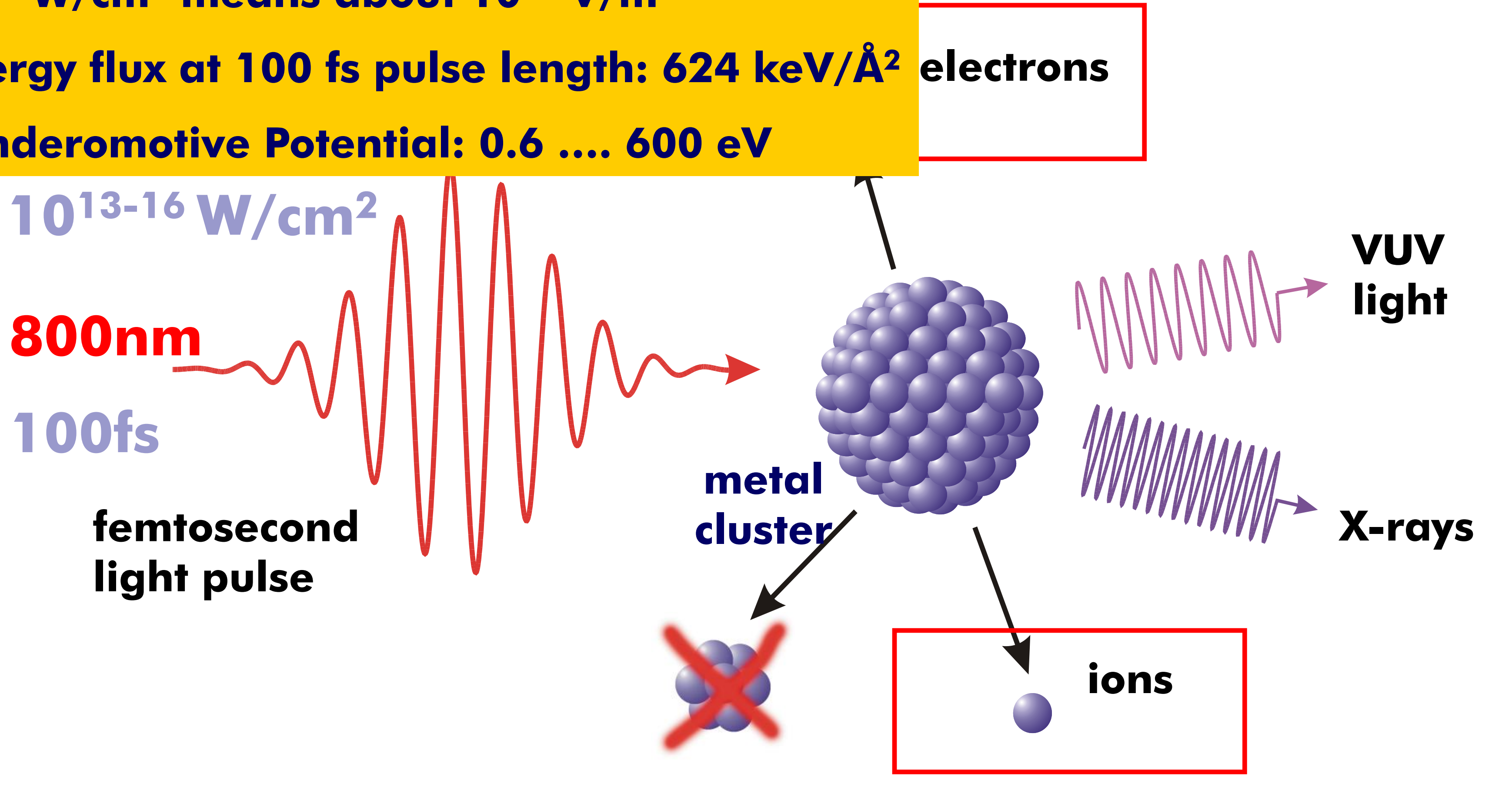
clusters in intense laser fields: nanometer-sized plasmas far from equilibrium

properties of the radiation field

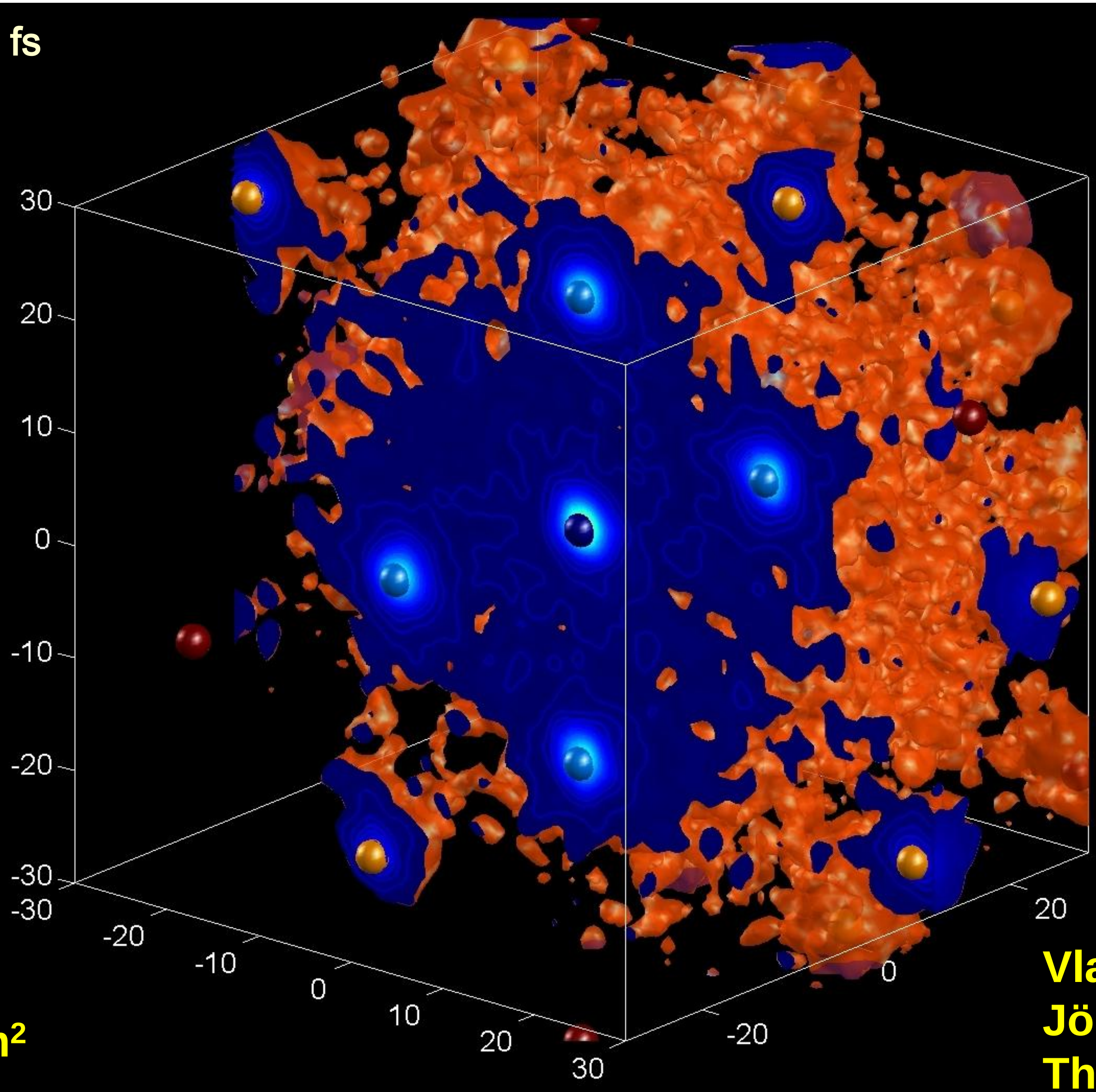
10^{16} W/cm^2 means about 10^{11} V/m

Energy flux at 100 fs pulse length: 624 keV/Å^2

Ponderomotive Potential: 0.6 .... 600 eV



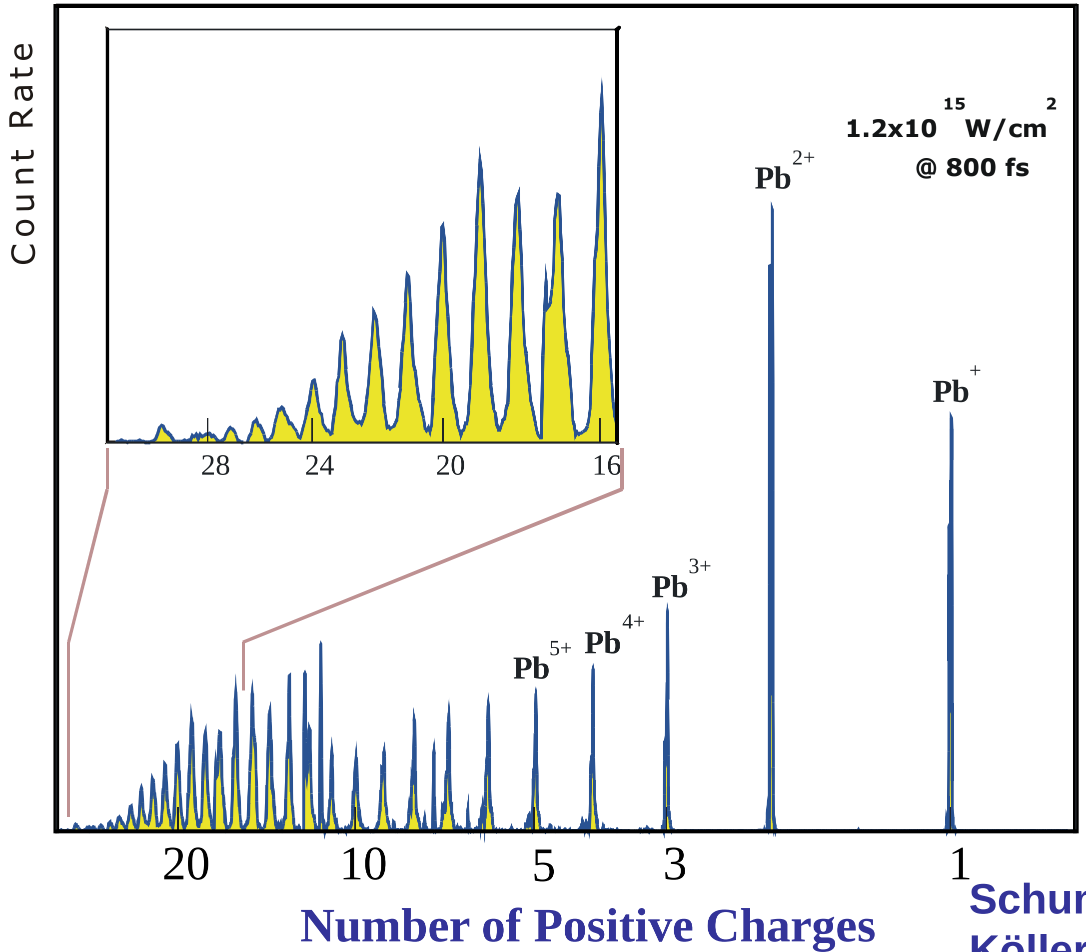
simulated Coulomb explosion Na_{55}



$E_{Photon} = 2.7$ eV
$t = 50$ fs
$I = 4 \times 10^{12}$ W/cm^2

Vlasov-VUU
Jörg Köhn
Thomas Fennel

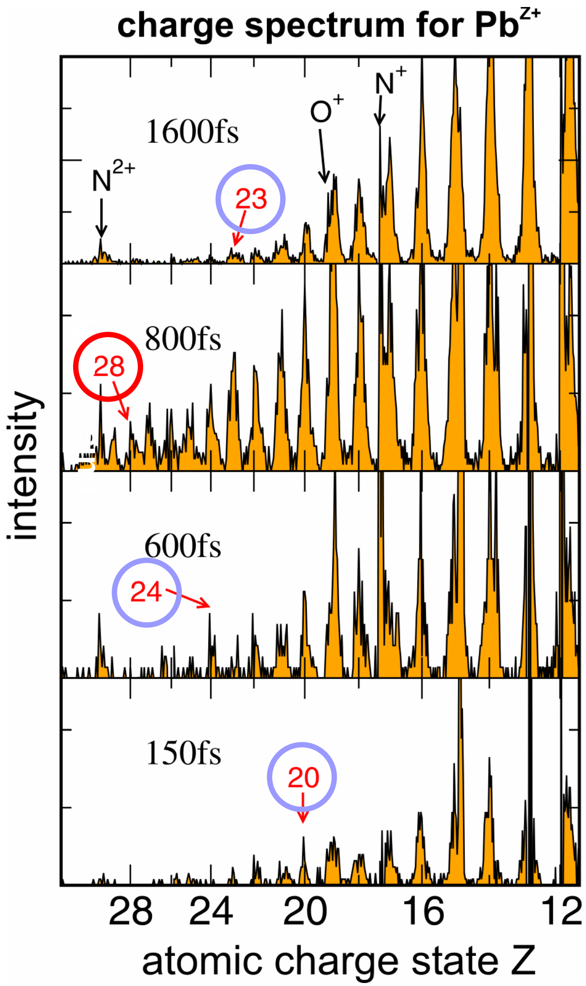
Charge distribution of Pb ions from Coulomb explosion

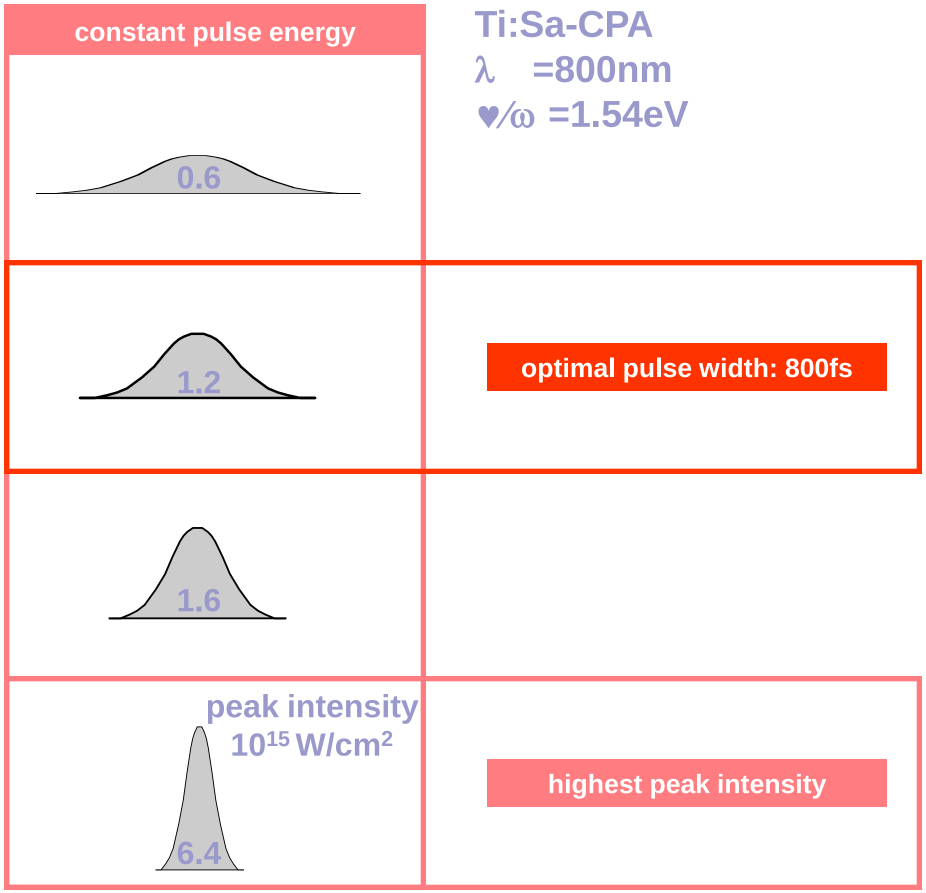


- Max. charge state z=30!
- Highest charging at 800 fs
- Max recoil energy E_{max} = 180 keV

Schumacher et al., EPJD 9, 411-414 (1999)
Köller et al., PRL 82, 3783-3786 (1999)

Coulomb explosion Pulse width dependence



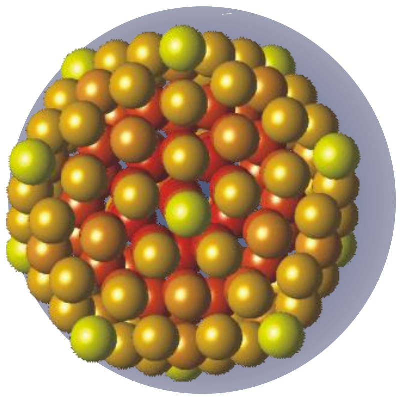


Ti:Sa-CPA
λ =800nm
♥/ω =1.54eV

Döppner et al., Appl. Phys. B **71**, 357 (2000)
Köller et al., Phys.Rev. Lett. **82**, 3783 (1999)

mechanism for the high absorption

plasmon-enhanced ionization

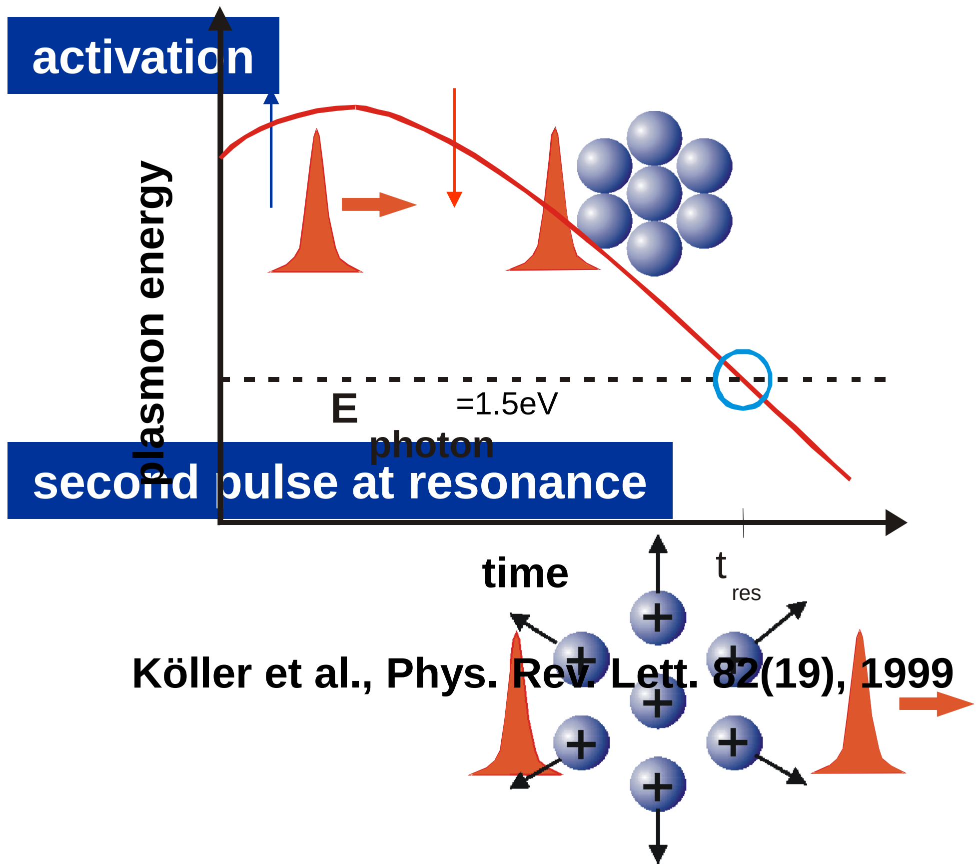


$$\omega_{Mie} = \sqrt{\frac{n_{bg}e^2}{3m\varepsilon_o}} = \frac{\omega_p}{\sqrt{3}}$$

Mie – Plasmon

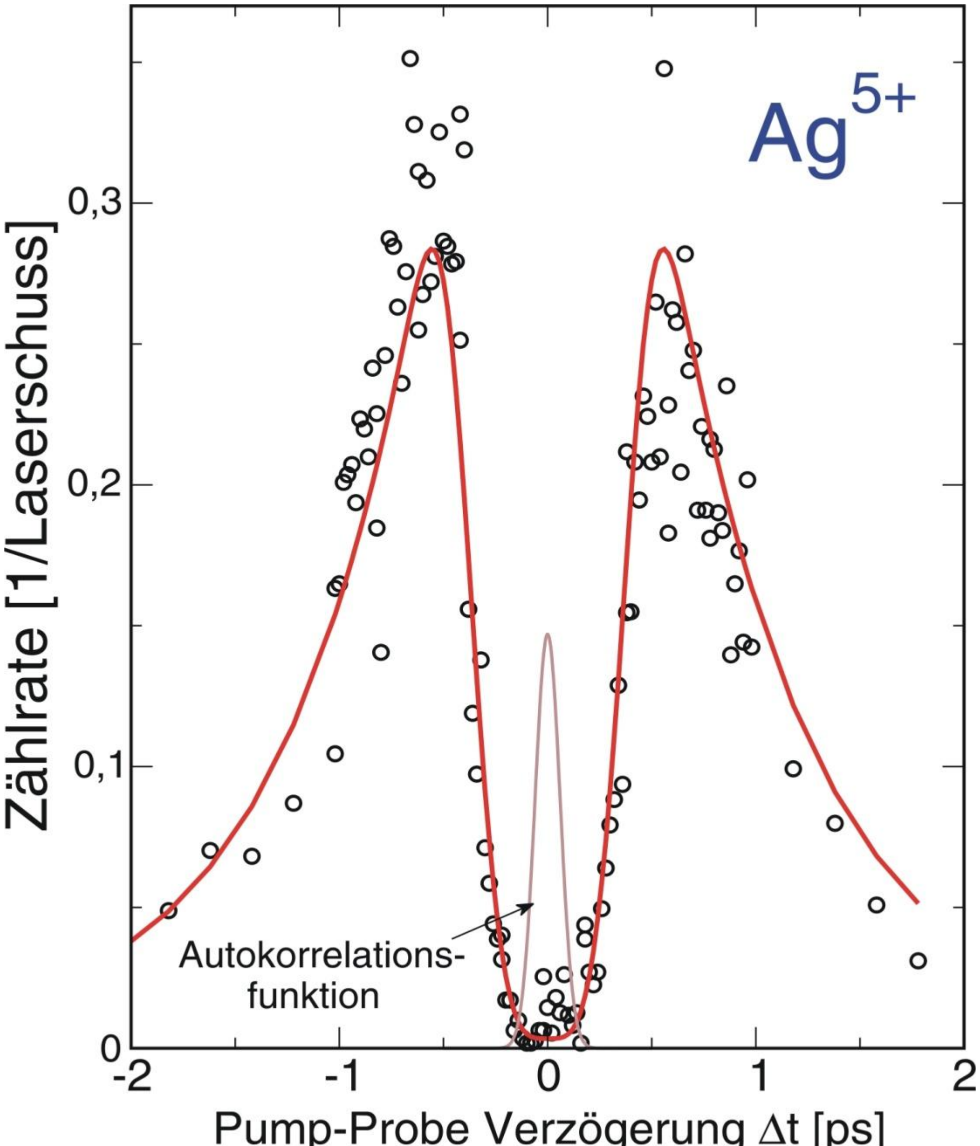
demonstration: dual-pulse technique

time dependent plasmon

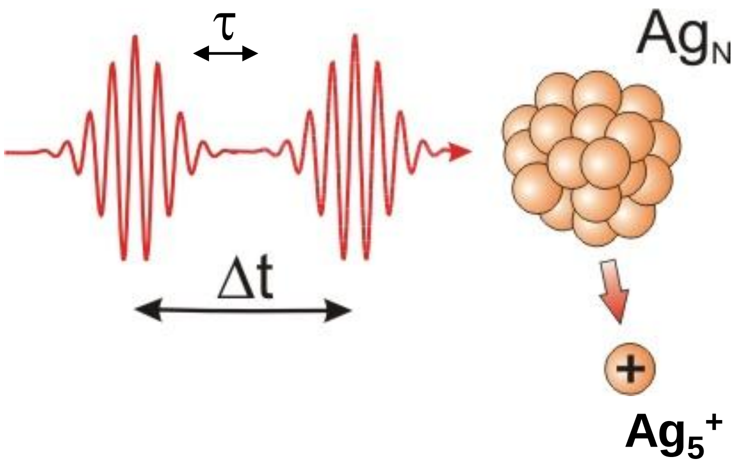


Köller et al., Phys. Rev. Lett. 82(19), 1999

dual-pulse excitation of Ag_N@He-droplet



delay

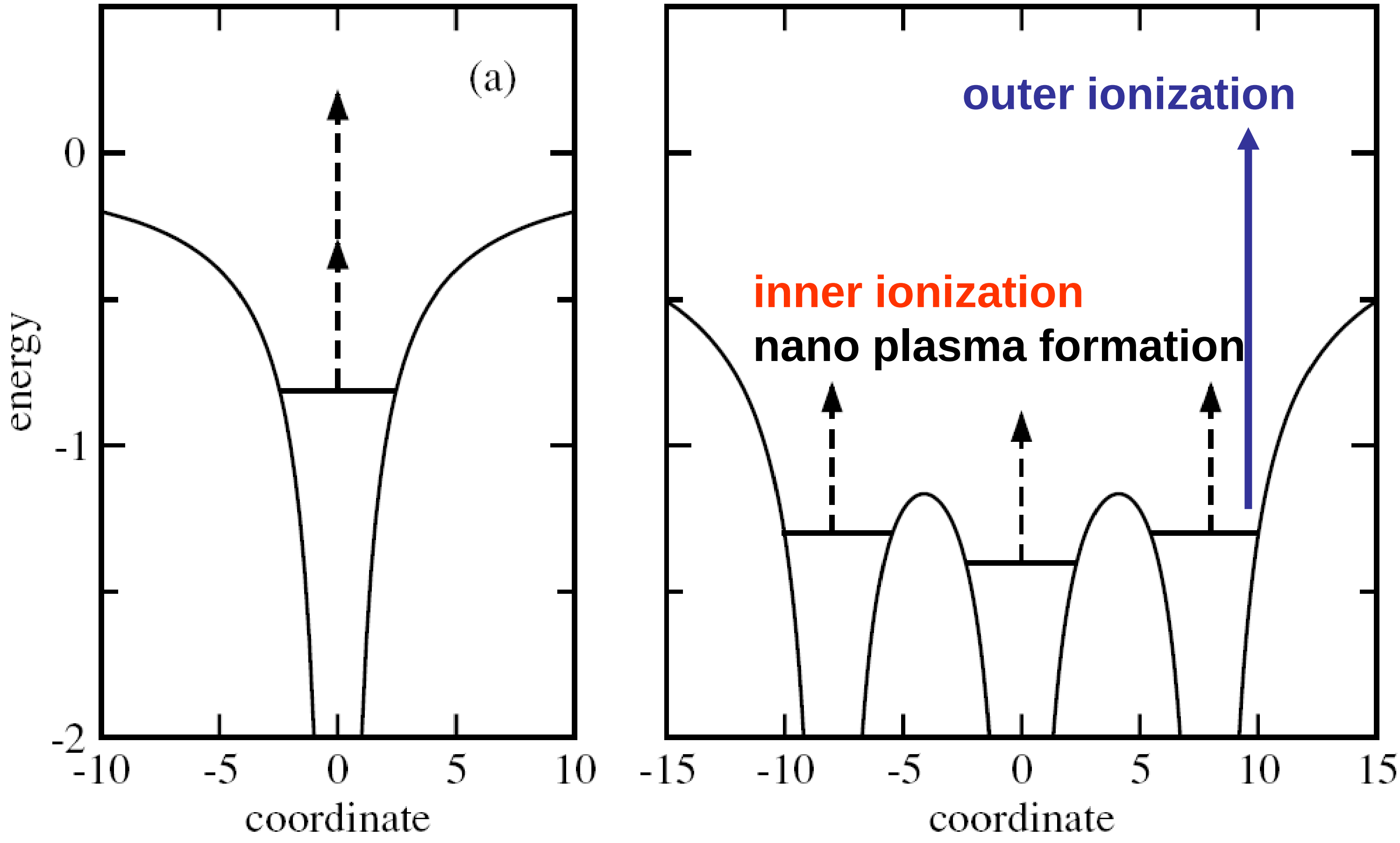


Laser parameters:

- **λ = 800 nm**
- **τ = 120 fs**
- **$I = 1.8 \times 10^{13}$ W/cm^2**

Döppner et al., Phys. Rev. Lett 94(13401), 2005

inner *vs.* outer ionization

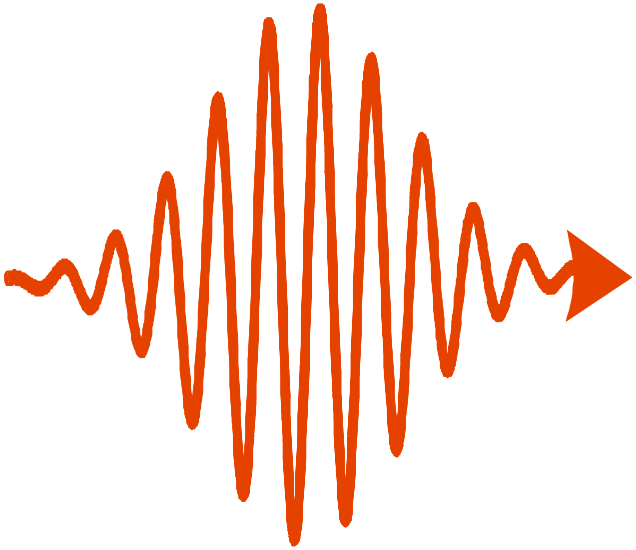


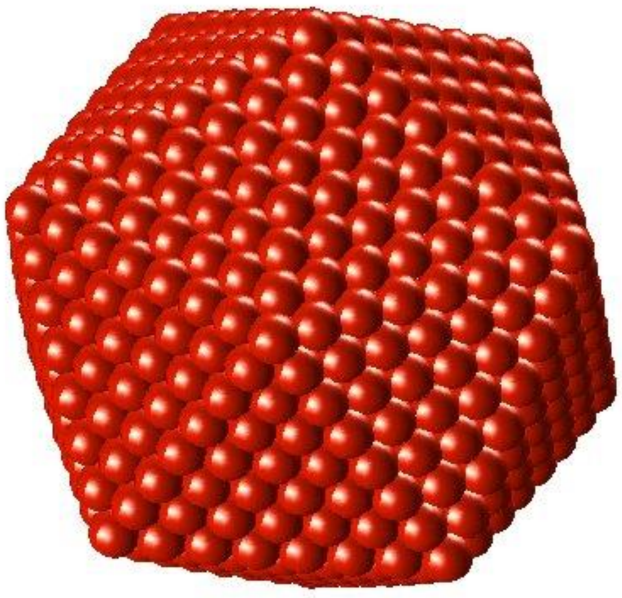
<u>several heating mechanisms</u>:
inverse bremsstrahlung
laser driven electron-ion collisions

after: Ch. Siedschlag and J M. Rost *PRL* **93** 043402 (2004)

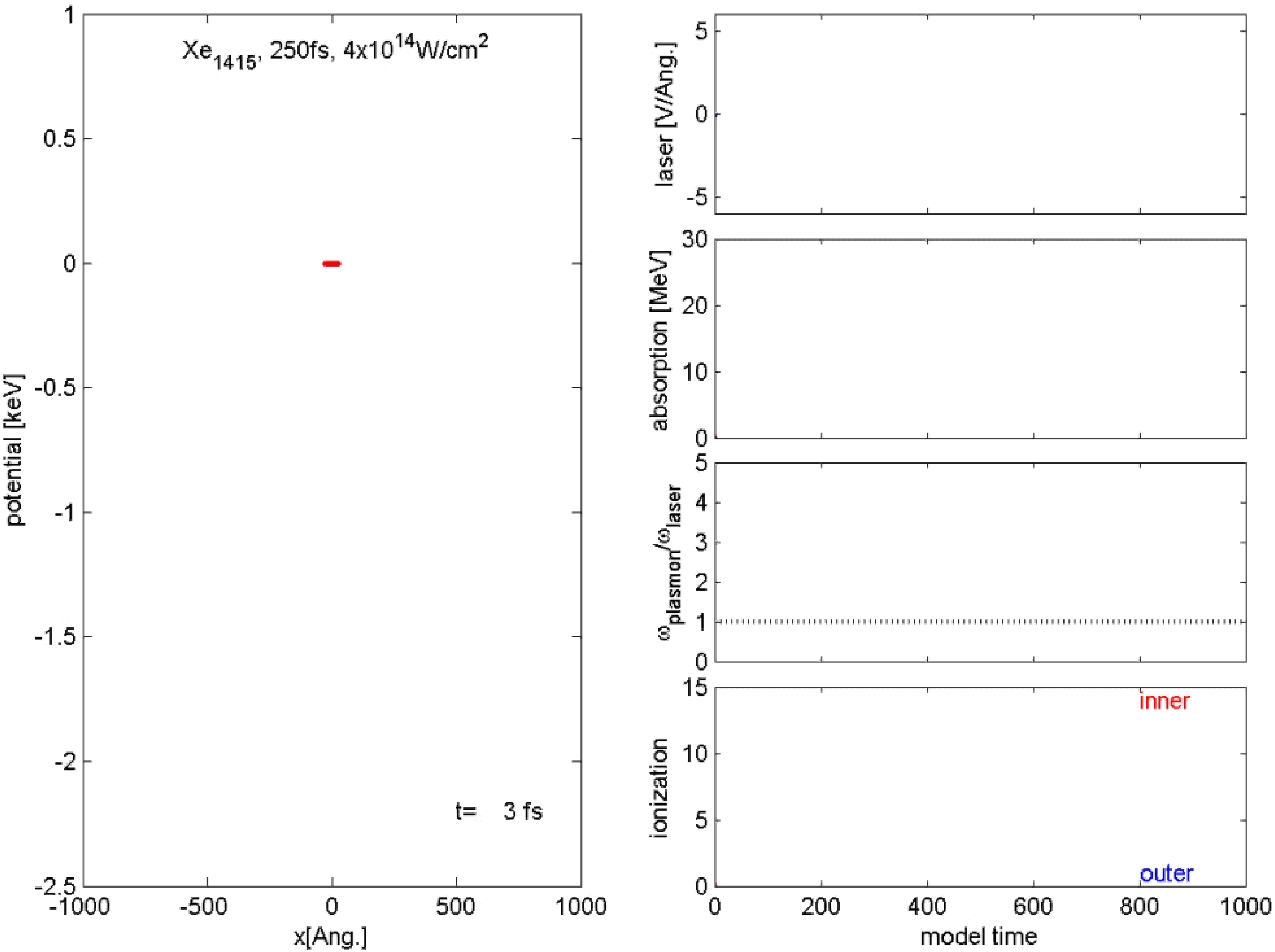
computer experiment: laser excitation of Xe clusters

250fs, 800nm,
4×10^{14} W/cm^2



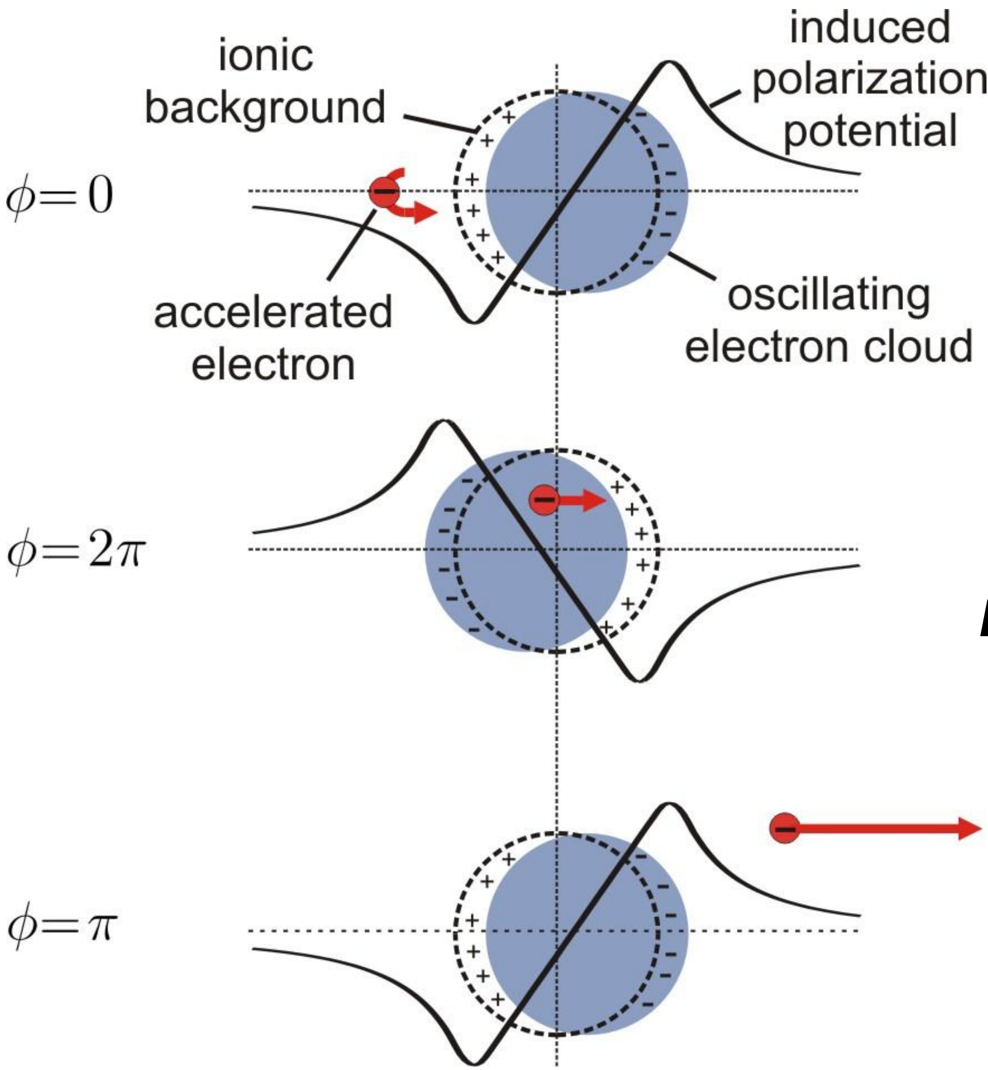


Xe_{1415}



Xe$_{1415}$, 250fs, 4x10^{14}W/cm^2
potential [keV]
x[Ang.]
t= 3 fs
laser [V/Ang.]
absorption [MeV]
$\omega_{plasmon}/\omega_{laser}$
ionization
inner
outer
model time

on plasmon resonance: dynamic electron acceleration



field strenght for N = 500:

140 GeV/m

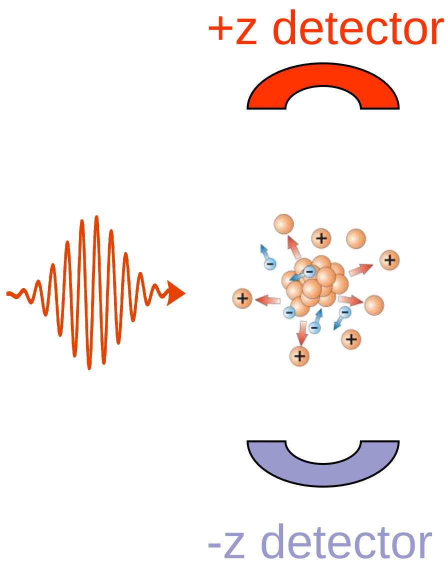
Surface-Plasmon Assisted Resonant electron acceleration in Clusters SPARC

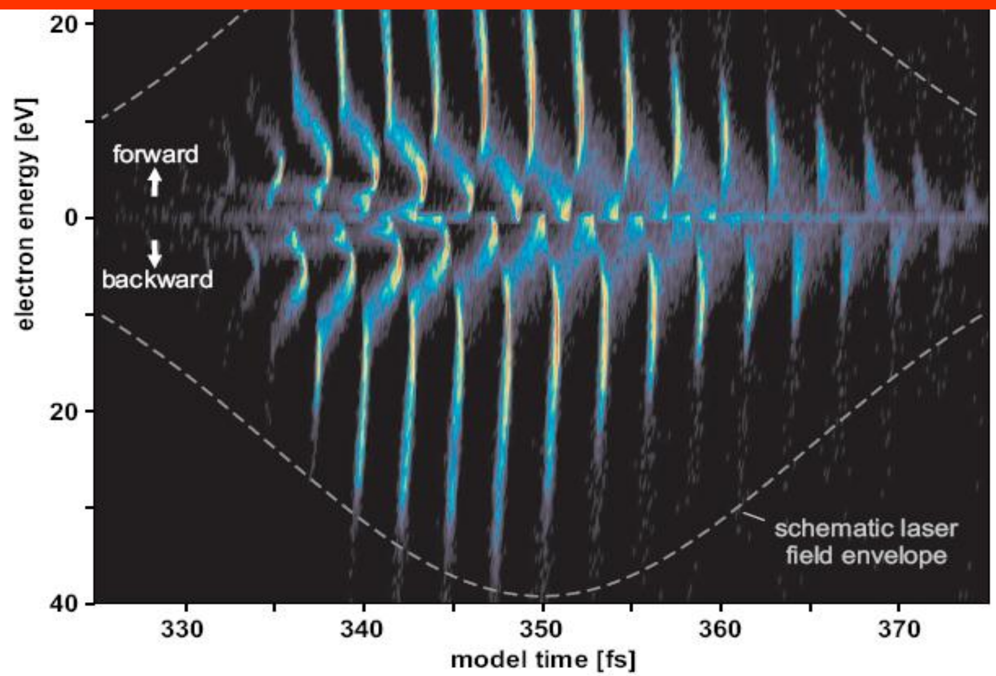
Nano electron accelerator

attosecond electron bursts

numerical experiment

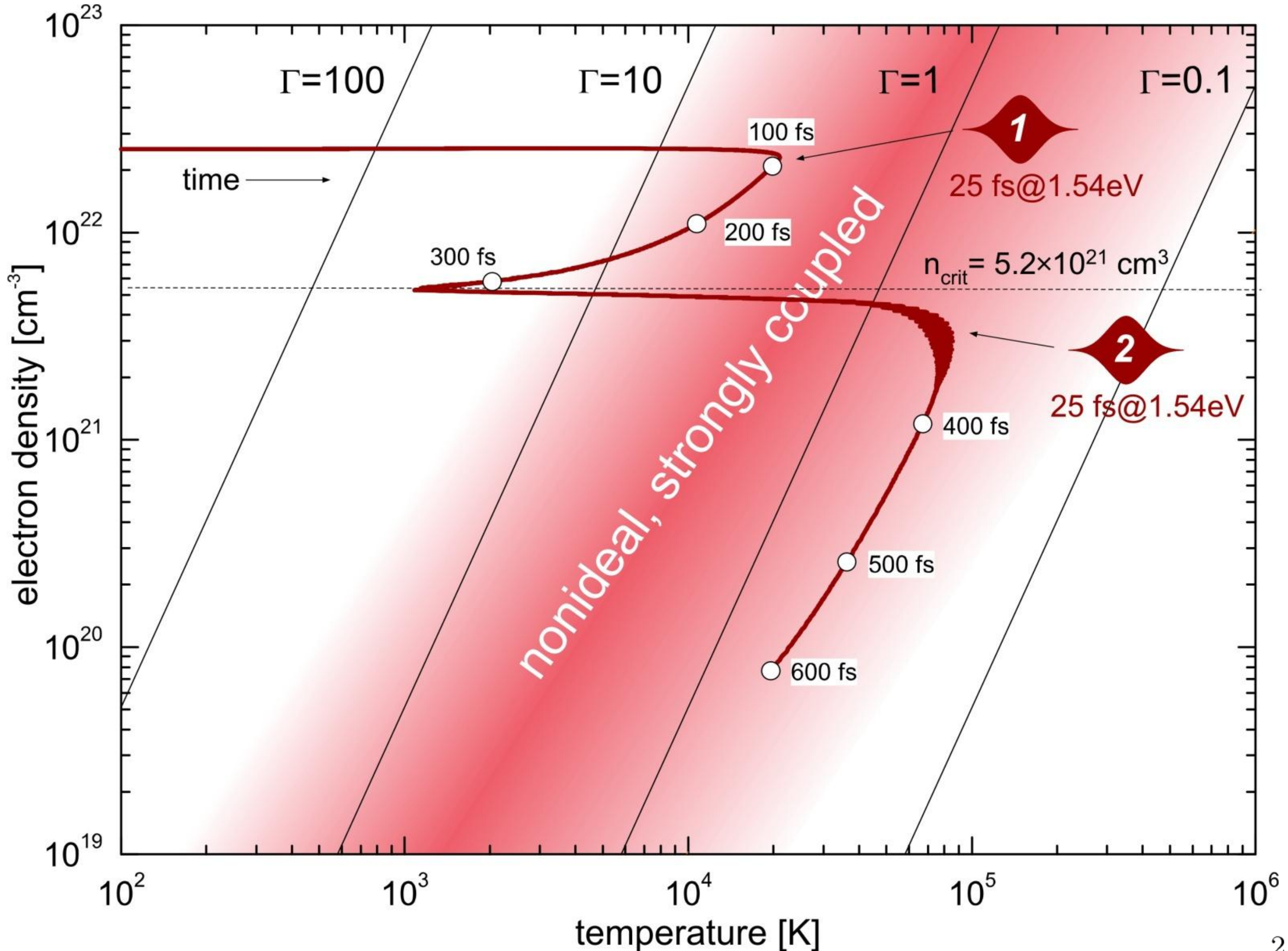
➢**interesting playground for future few-cycle and attosecond physics**





Fennel et al., PRL 98, 143401 (2007)

density-temperature plane



coupling parameter

$$\Gamma = \frac{e^2}{4\pi\varepsilon_0\, k_B T}(\frac{4}{3}\pi n_e)^{1/3}$$

plasma physics on the nm scale