Cluster Science

with Electron Spectroscopy

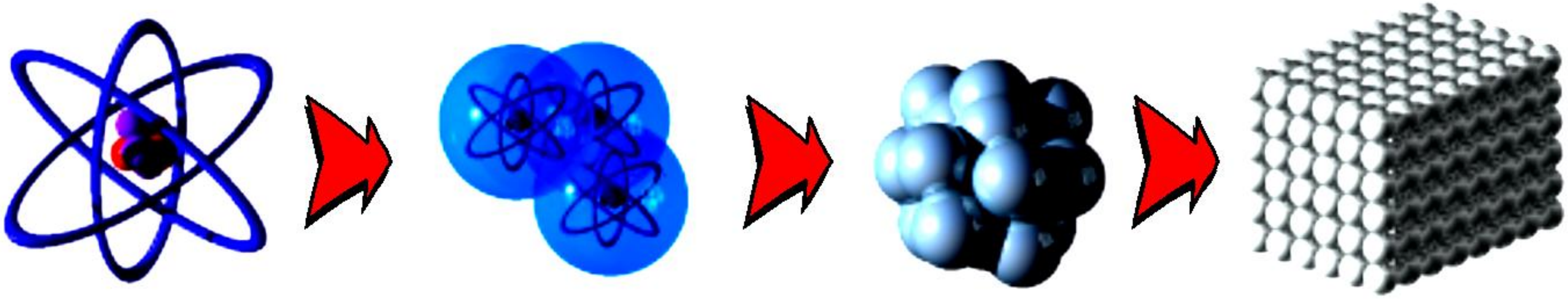
What are *clusters* ?

Aggregates consisting of a ”small” number of building blocks
(atoms or molecules)

Lecture Outline

1. What are Clusters ? Types of Clusters
2. Electron Spectroscopy
3. Synchrotron Radiation. What are the Advantages?
4. Production of Clusters out of Natural Gases
5. Examples of Electron Spectroscopy on Clusters
6. Metal-Cluster Sources and more Results

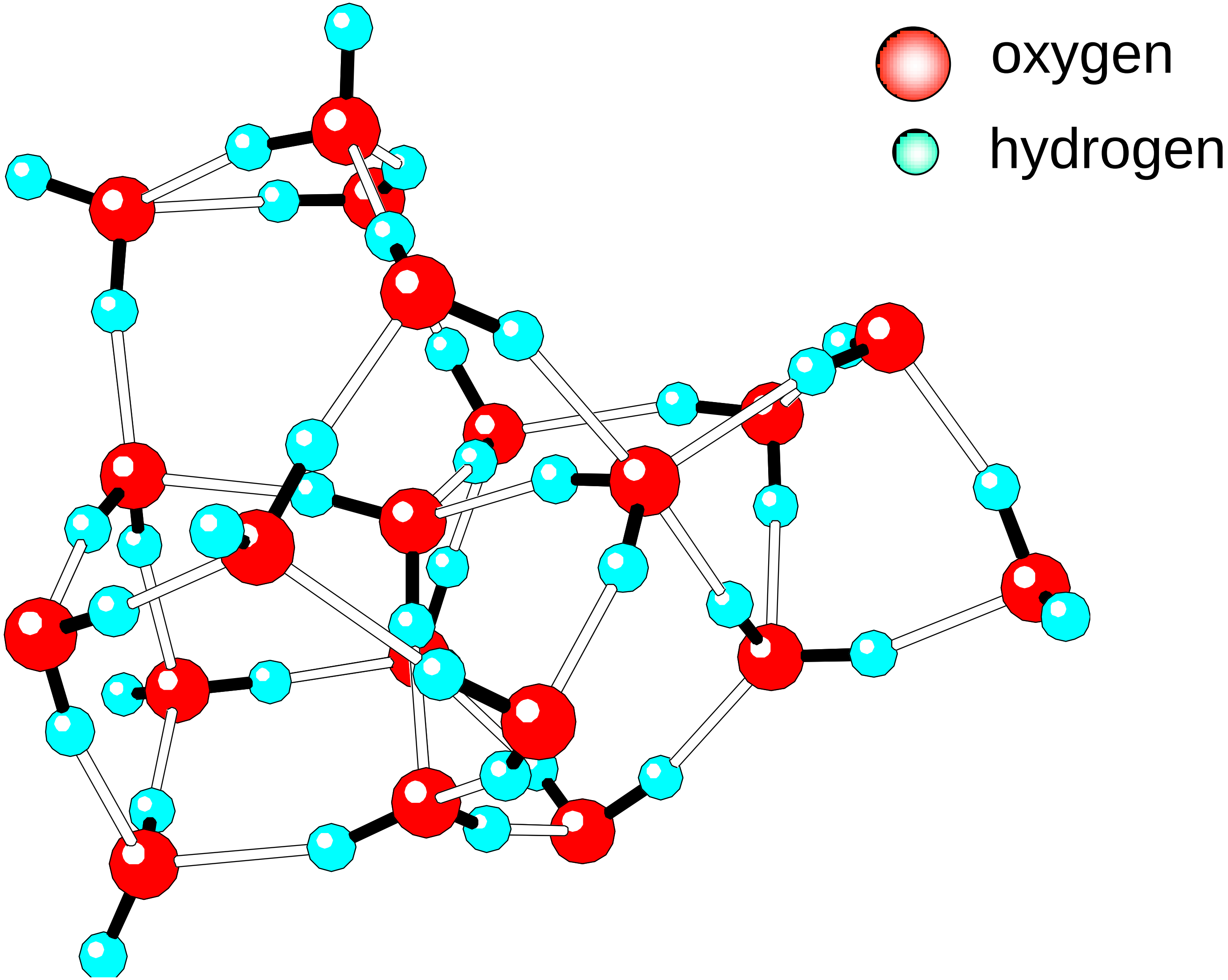
Transition from atoms to solids



Atom Molecule Cluster Solid

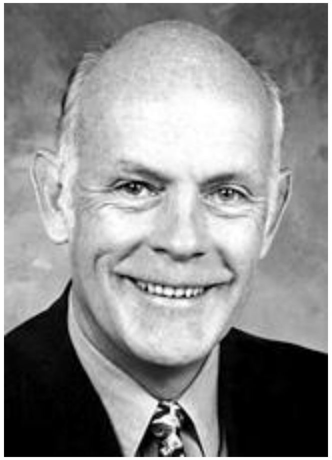
Clusters -
between separate molecules and solids-
an intermediate state of matter

Water Clusters – a Link to Everyday

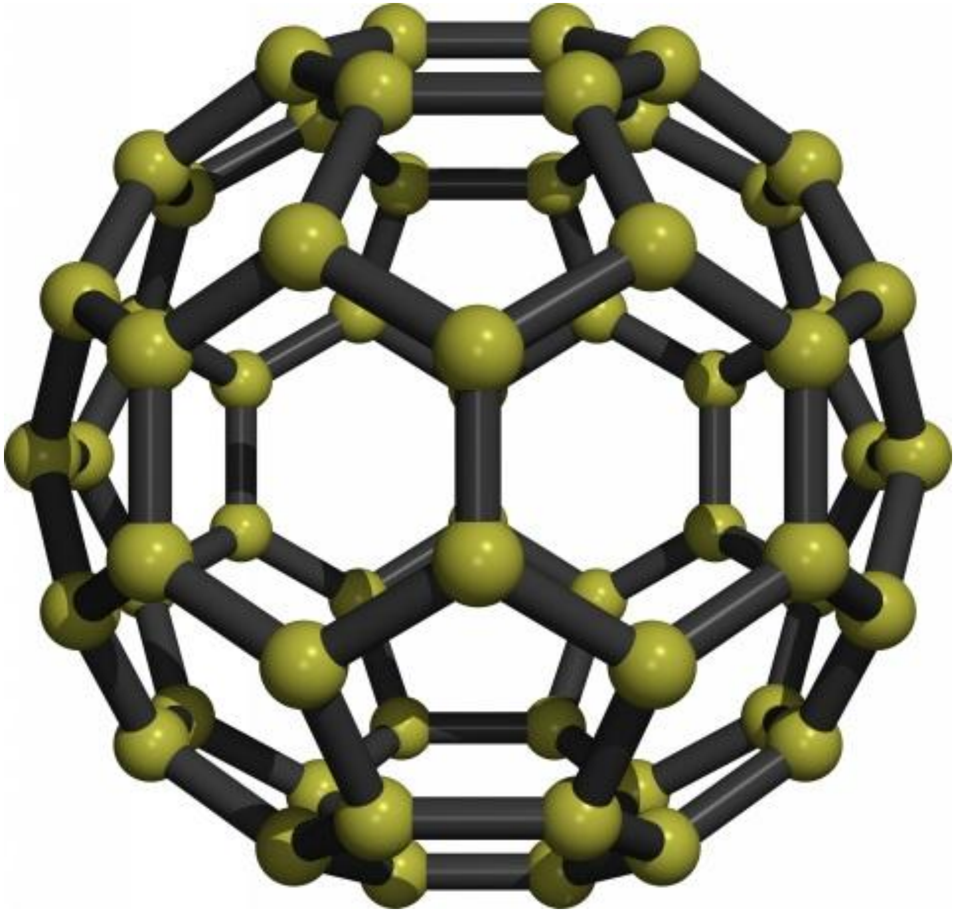


Two unused electrons of oxygen atoms are epmloyed in the bonding to the hydrogen atoms of the neighbours

Rigid Geometric Structure

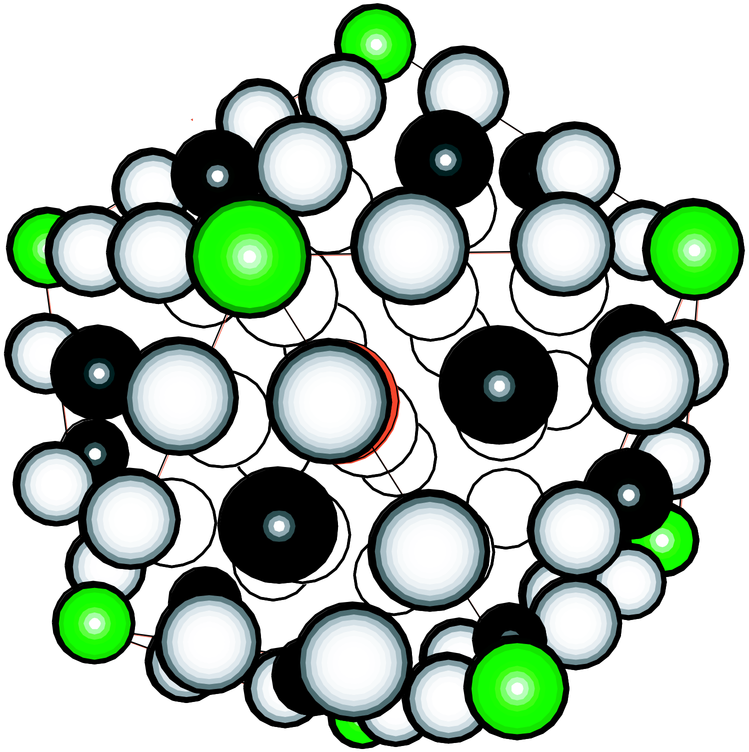


R. Smalley
Nobel prize
1996



Fullerene C_{60} with an atom inside

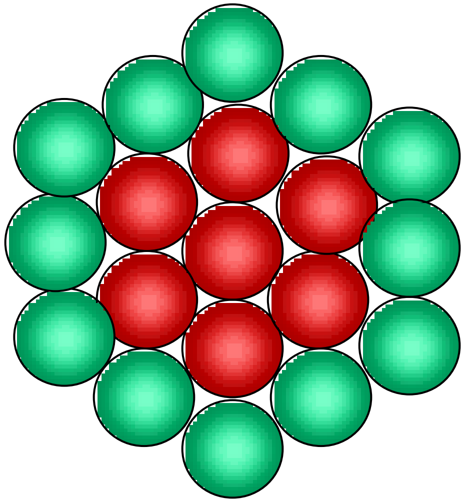
Rigid Geometric Structure



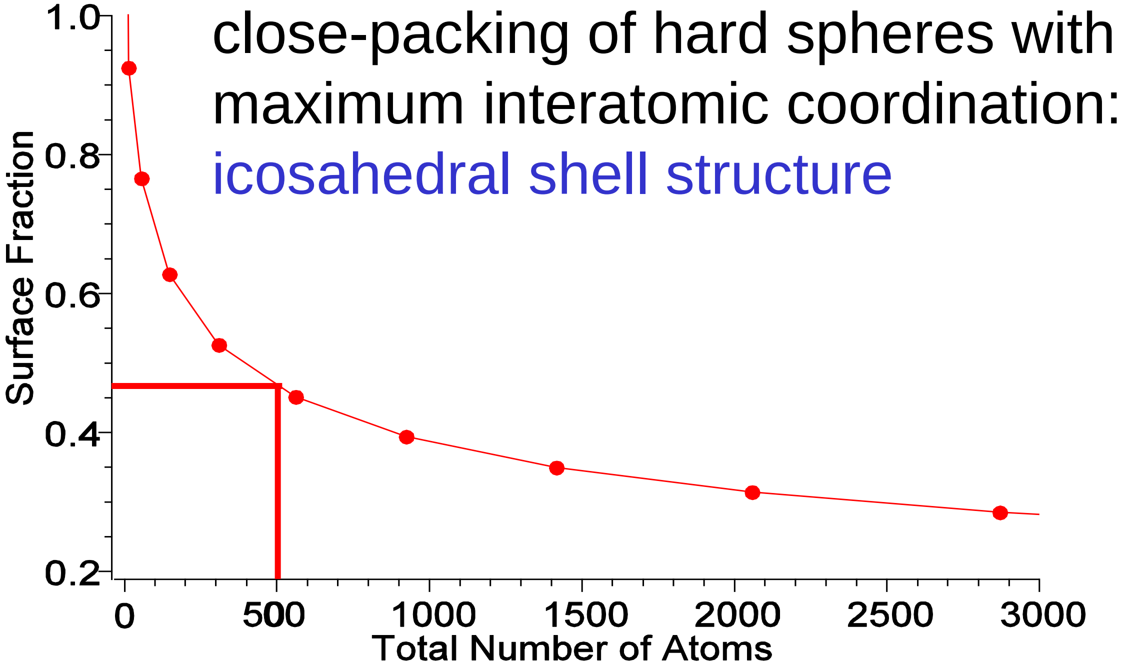
Enclosed shells - onion-like

Icosahedron - all vertices are on a spherical surface

Specificity of Clusters-
Size-dependent surface fraction



close-packing of hard spheres with
maximum interatomic coordination:
icosahedral shell structure

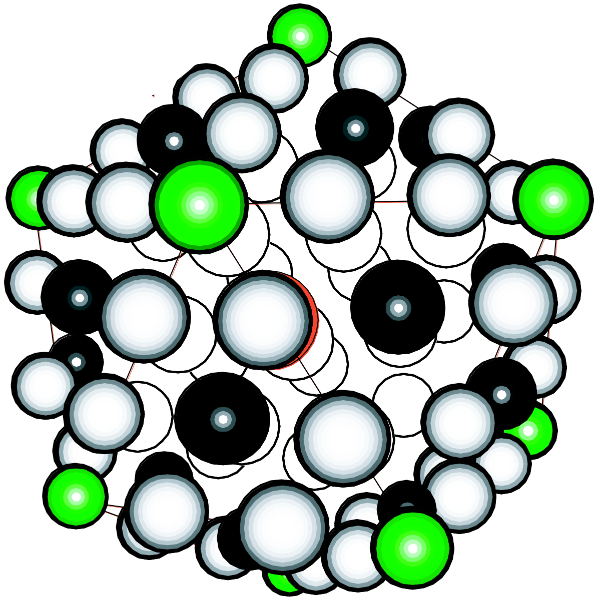


Good for:
systems with non-directional bonds (inert gases, metals)

Types of Clusters

Clusters held together by van-der-Waals forces

Convenient modell systems- rare-gas clusters- Ar, Kr, Xe



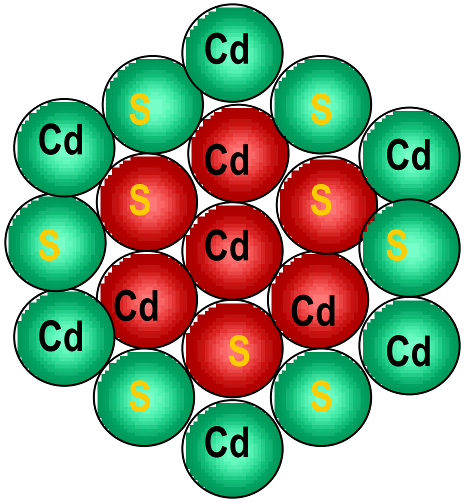
Energy minimum principle -

minimizing the number of surface atoms

Types of Clusters

Covalent bonding - Semiconductor Clusters

practical interest driven by modern electronics



Clusters out of two chemical elements Cd & S

CdS at macroscale - semiconductor

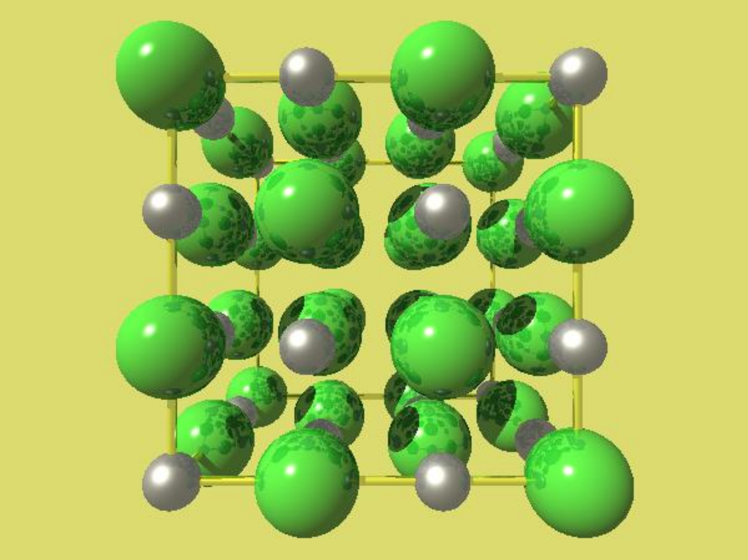
How do atoms of Cd & S arrange in CdS at nanoscale?

In a two-component substance – is there any segregation of elements?

Could one chemical be more on the surface than in the interior?

Types of Clusters

Ionic Clusters- of salt molecules



practical interest driven by environmental issues

Two-component ionic substance -

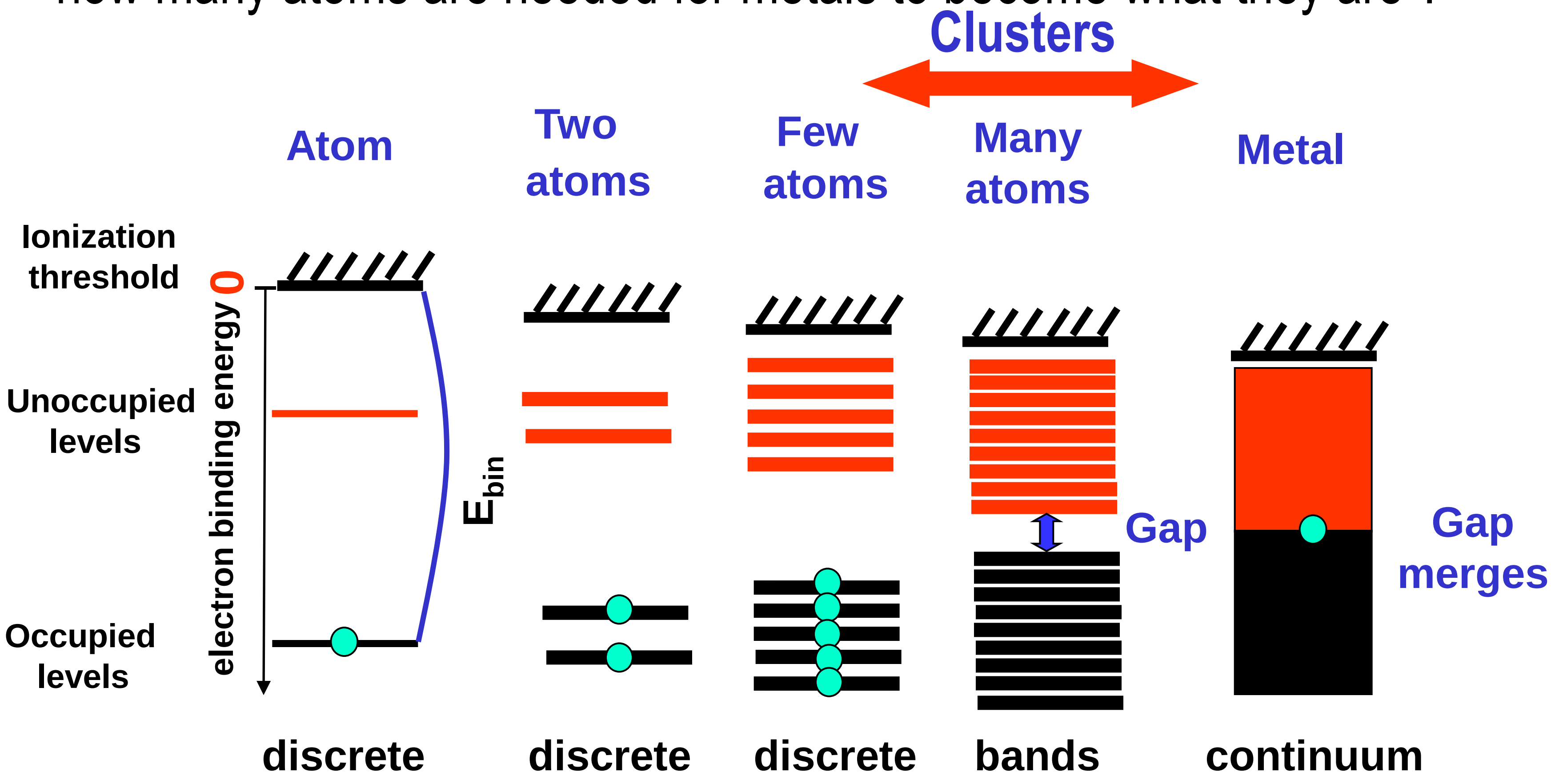
At macroscale it is an alternating M^+ - X^- lattice

How do the salt molecules arrange themselves at nanoscale?

Types of Clusters

Metal Clusters

how many atoms are needed for metals to become what they are ?



At what cluster size the gap merges?

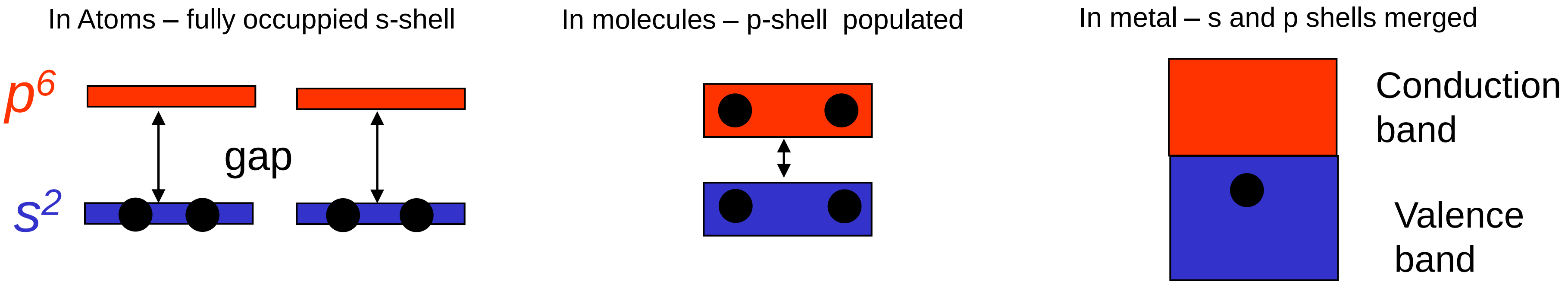
Types of Clusters

Metal Clusters

Example:

Bivalent metals of IIA, IIB groups (mercury)

- *s* orbital in atoms fully occupied, *p* orbital vacant
- *s*-*p* hybridization - increases with the size
- *s*-*p* gap decreases with the size



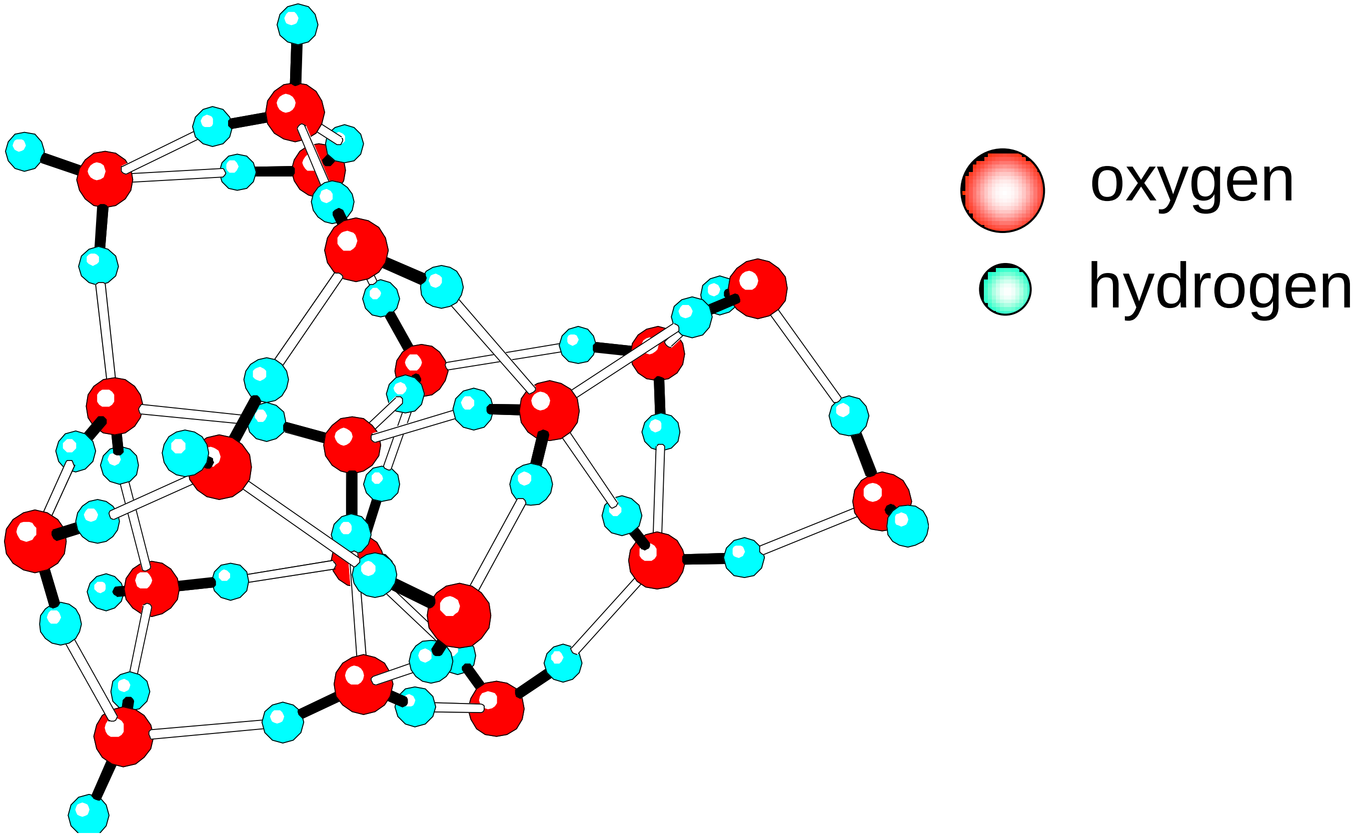
In Atoms – fully occuppied s-shell

In molecules – p-shell populated

In metal – s and p shells merged

Types of Clusters

Clusters with hydrogen bonds



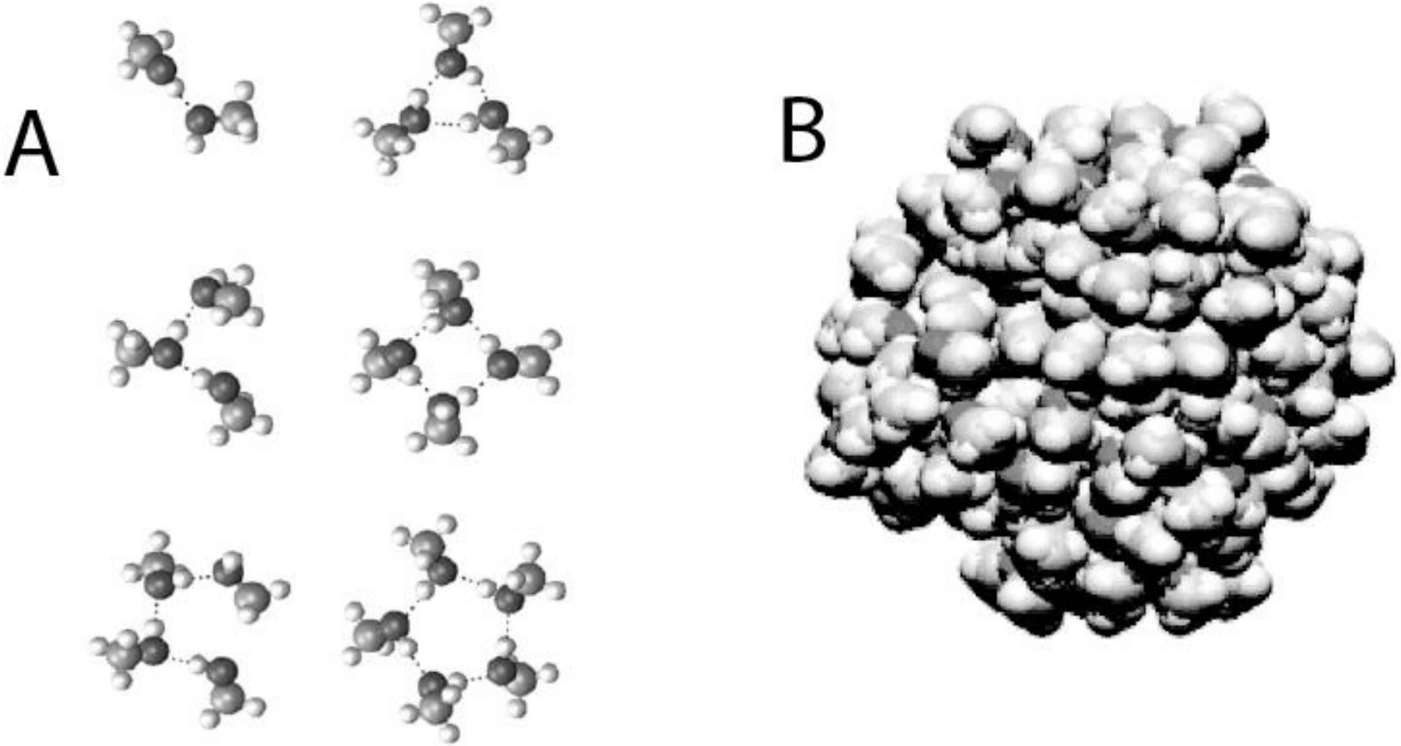
practical interest driven by environmental issues

unused electrons of oxygen atoms
bind to the hydrogen atoms of other molecules

Types of Clusters

Clusters with hydrogen bonds

simple organic molecules - methanol CH_3OH

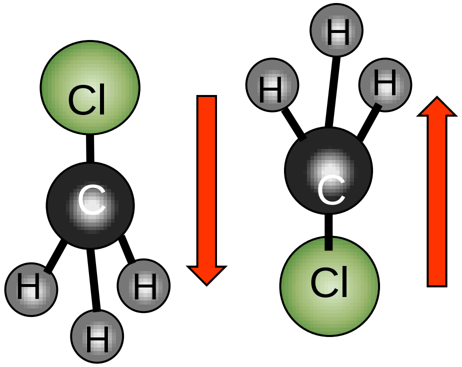


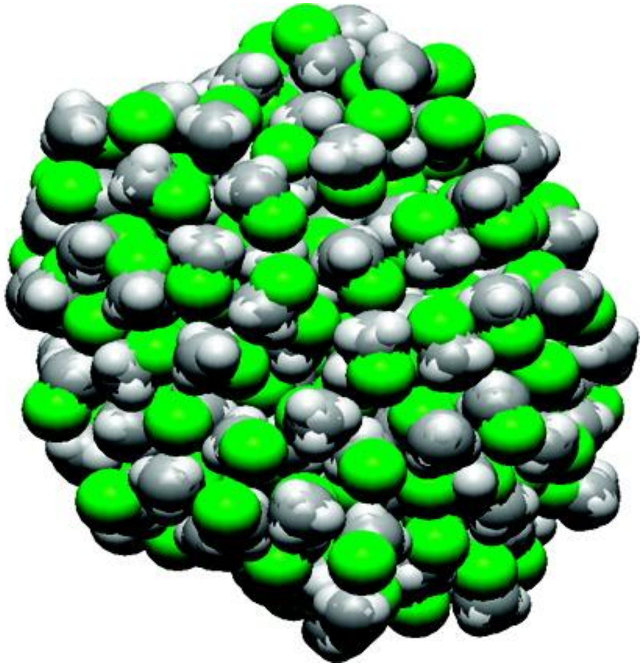
unused electrons of oxygen atoms
bind to the hydrogen atoms of other molecules

Types of Clusters

Clusters out of dipole molecules

simple organic molecules - chloromethane CH_3Cl

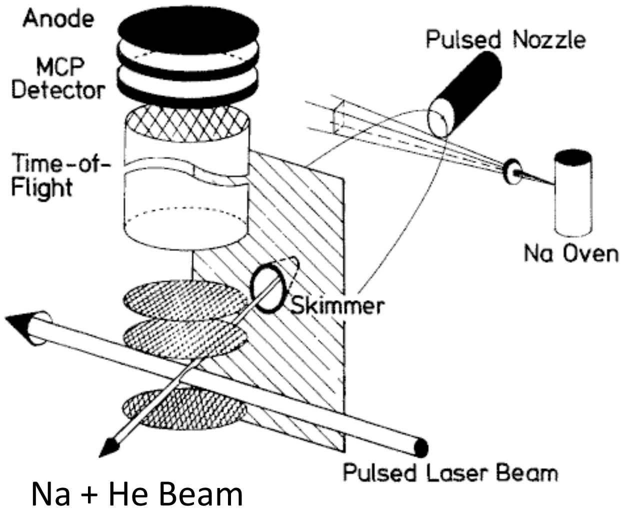




Inherent dipoles of molecules arrange anti-parallelly

Historical Perspective

- How did people discover clusters the first time?
- Mass-spectroscopy studies of atomic ionization energies
- Ionization by an electron beam, discharge lamp, laser…
- Metal vapour picked-up by helium- condensation in a beam



setup: schematic of the pickup source and the time of flight mass spectrometer

A.Hoareau. Surface Science 106 (1981)

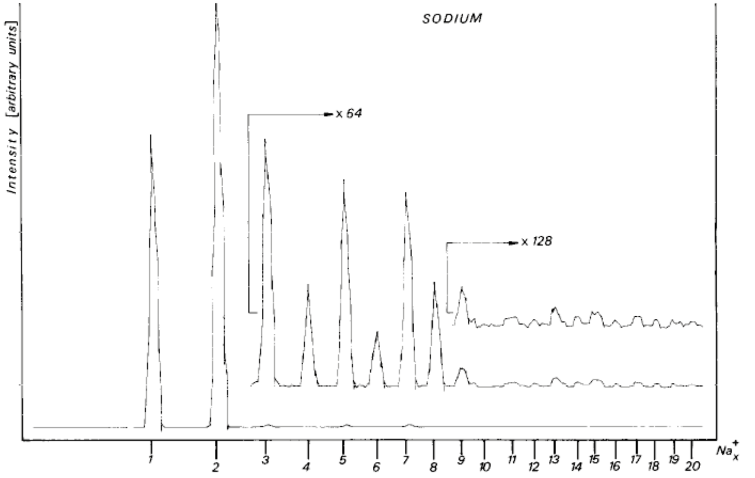
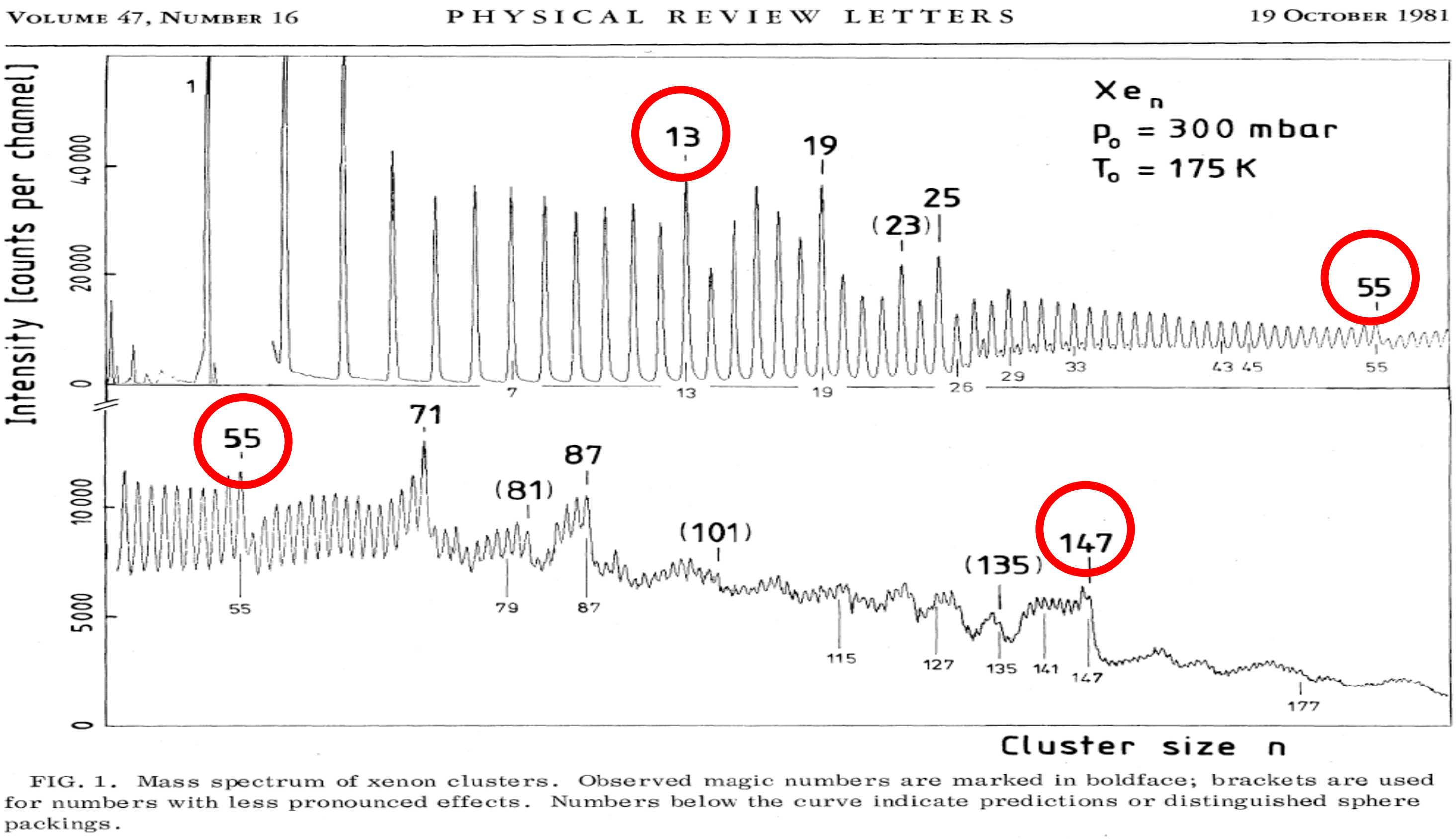


Fig. 1. Typical time-of-flight spectrum of sodium aggregates recorded with ionising electrons at 9 eV and for a temperature $T_0 = 1200$ K. The intensities have been multiplied by 64 for $3 \leq x \leq 8$ and by 128 for $x > 8$.

Historical Perspective

- Dedicated cluster sources
- Mass-spectroscopy study goes on
- Magic size numbers – stable geometries



VOLUME 47, NUMBER 16 PHYSICAL REVIEW LETTERS 19 OCTOBER 1981

FIG. 1. Mass spectrum of xenon clusters. Observed magic numbers are marked in boldface; brackets are used for numbers with less pronounced effects. Numbers below the curve indicate predictions or distinguished sphere packings.

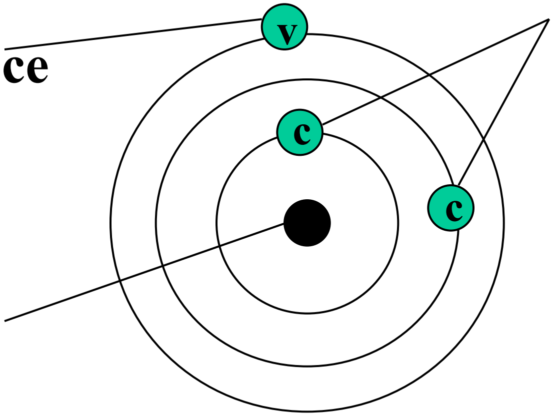
Electron Spectroscopy with Photons: electronic structure of the sample is probed

- Einstein's photoeffect law: $h\nu = E_{binding} + E_{kinetic}$
- Electrons of various $E_{binding}$ give a *spectrum* of $E_{kinetic}$
- A device determining $E_{kinetic}$ – electron spectrometer
- Spectroscopy of valence, delocalized electrons - UV, VUV
- Spectroscopy of core-level, localized electrons – X-rays
- Electron spectroscopy with photons – photoelectron spectroscopy

PES

What does one see in a PES experiment?

Scheme of electron energy levels in an atom



Outer / valence electrons

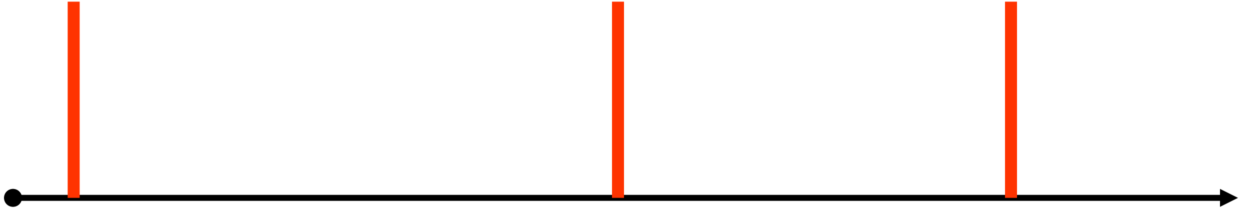
Inner /core electrons

nucleus

Electron Spectroscopy

K.Siegbahn
1981

Binding energy *spectrum* of electrons in an atom



Valence el.

Core el. 1

Core el. 2

0

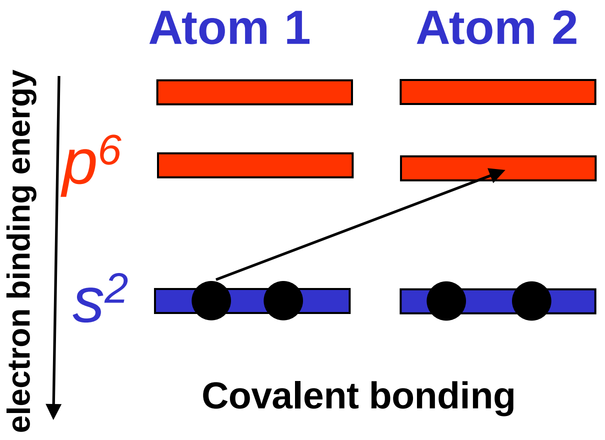
Electron binding energy

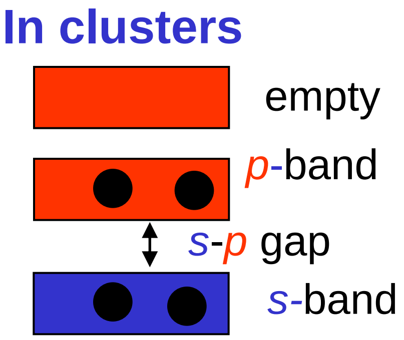
Core-electrons are bound much stronger than the valence ones

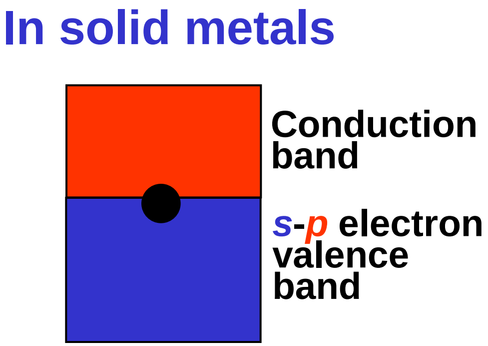
Electronic structure reveals a change in conductivity

Bivalent metals of the IIB group

- **In separate atoms *s* levels are fully occupied, *p* levels are empty**
- **In solid metals valence bands are built by both *s* and *p* electrons**
- **In clusters:**
    - ***p* levels of neigbhour atoms get populated by *s*-electrons**
    - ***s-p* hybridization appears – covalent bonding**
- **With the cluster size increase:**
    - **the discrete energy levels develop into bands**
    - ***s-p* and other inter-band gaps decrease**
- **Metallic bonding appears when the gap merges**







Ionization with Different Photon Sources

- **Lasers**

Typical ionization energies are ≈10 eV

Visual range photons –up to 3 eV.

Fluorine laser -7.9 eV

- **Discharge lamps**

Helium lamps 21 eV photons, ≈ 40 eV photons

Nitrogen lamp ≈ 10 eV

- **Rotating metal discs bombarded by fast electrons**

Discs of aluminium – ≈1500 eV photons

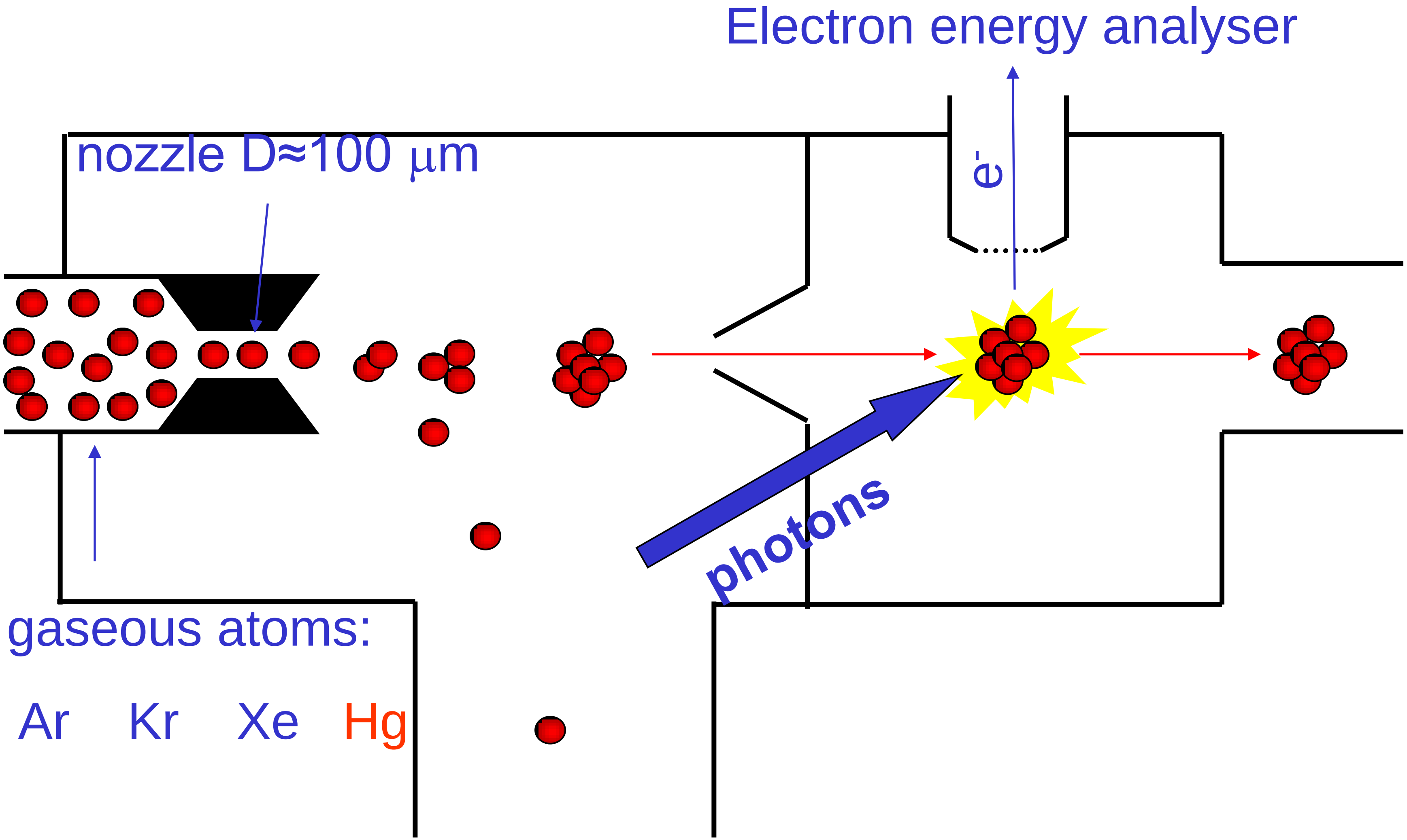
- **Synchrotron rings**

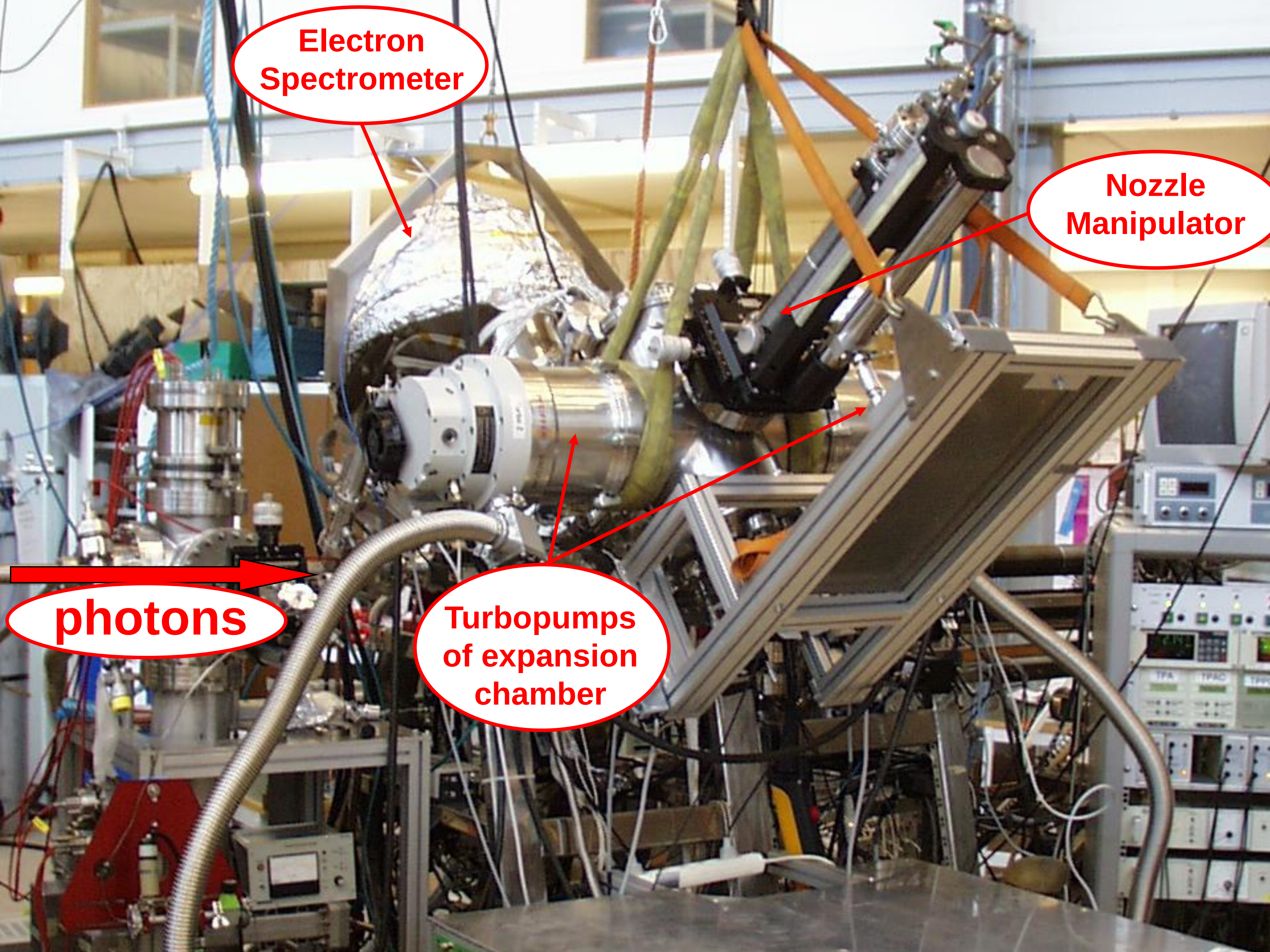
accelerated electrons emit from IR to hard x-rays

Why synchrotron radiation (SR) ?

- The change of the properties manifests itself in the electronic structure – or the electron binding energies - demands ionizing radiation
- Those energy levels are possible to probe which are not reachable by other light sources
- Selectivity and tunability – for an enhancement of interaction between matter and radiation
- Core-levels –elemental sensitivity- each element has distinctly different response
- Core-levels - separate responses from the inner atoms (bulk) and surface

How clusters are produced ?



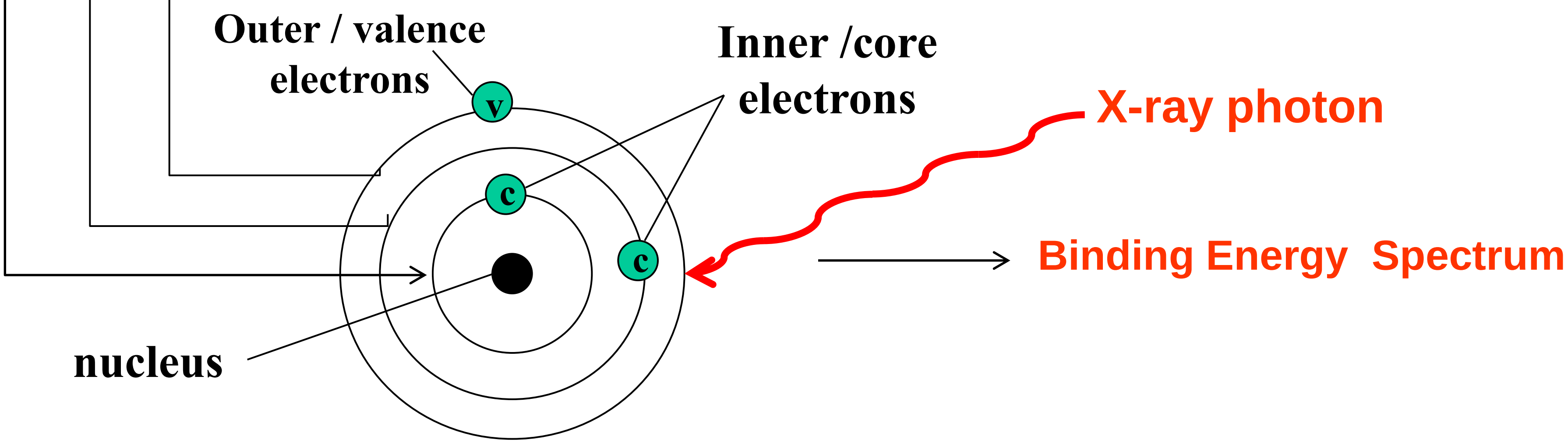

Electron Spectrometer
Nozzle Manipulator
photons
Turbopumps of expansion chamber

Photoelectron Spectrum of an atom- Ar atom

Electronic configuration of an argon atom:

- n=1 s^2 two s-electrons
  - n=2 $s^2 p^6$ two s-electrons and six p-electrons
    - n=3 $s^2 p^6$ two s-electrons and six p-electrons

Scheme of an atom



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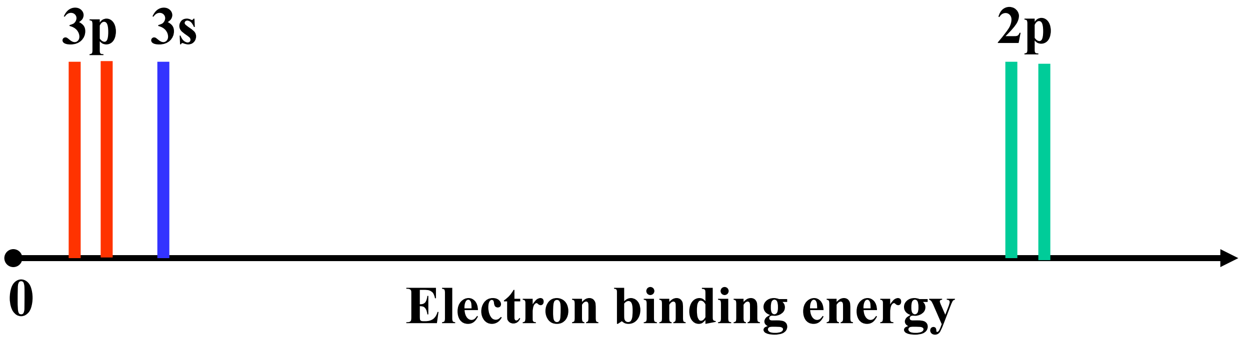
Binding Energy Spectrum

$h\nu=E_{binding}+E_{kinetic}$

Electrons of various $E_{binding}$ give a *spectrum*

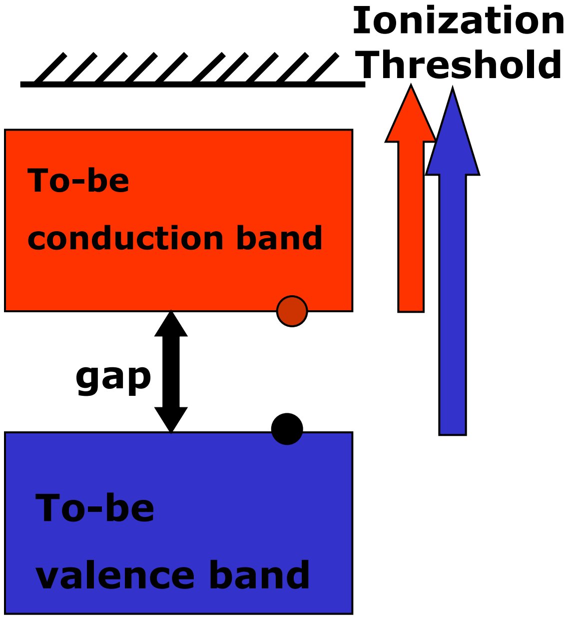


PES on negatively charged Hg clusters

- Pre-charged clusters– here with a crossing electron beam
- Mass-selected with a time-of-flight mass-spectrometer
- Ionized with a fluorine laser -7.9 eV
- Extra electron lands at the bottom of conduction band

PES on negatively charged Hg clusters

Busani, Folkers,
& Cheshnovsky
Phys. Rev. Letters 1998

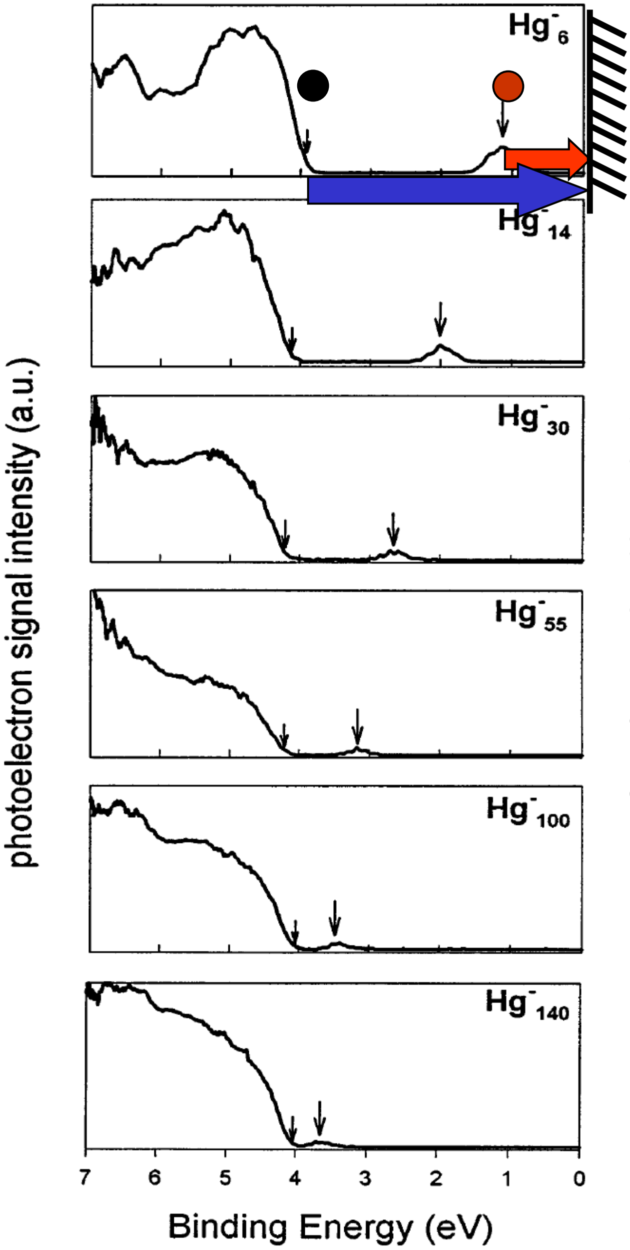


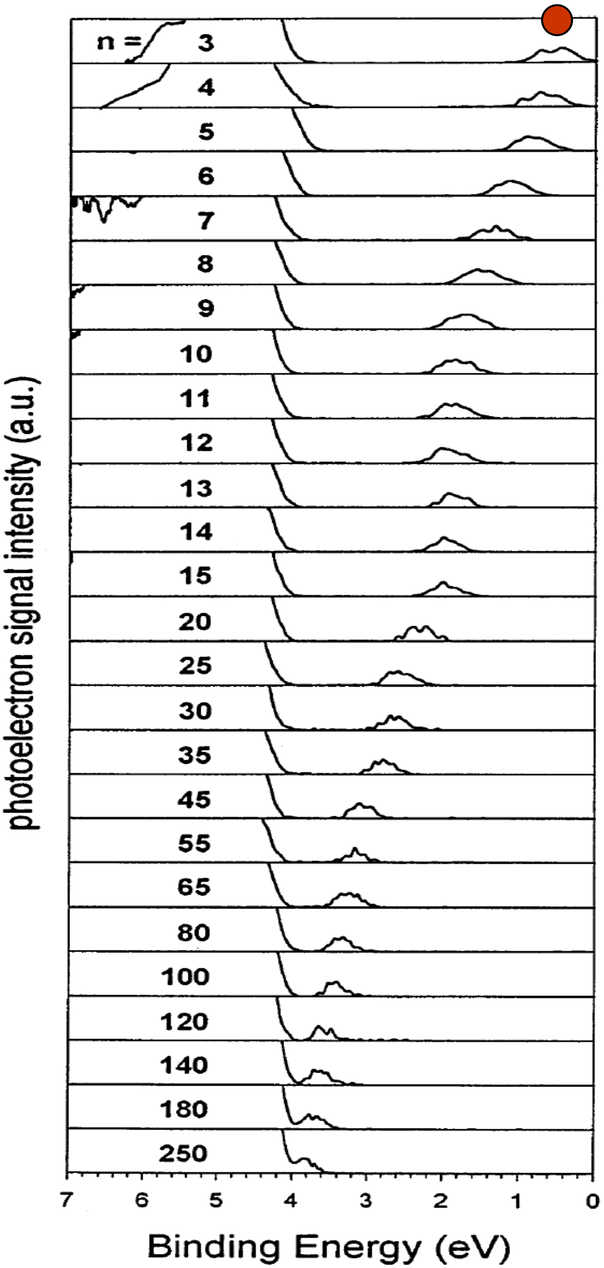
Ionization Threshold

To-be conduction band

gap

To-be valence band





The path of science is not always straight

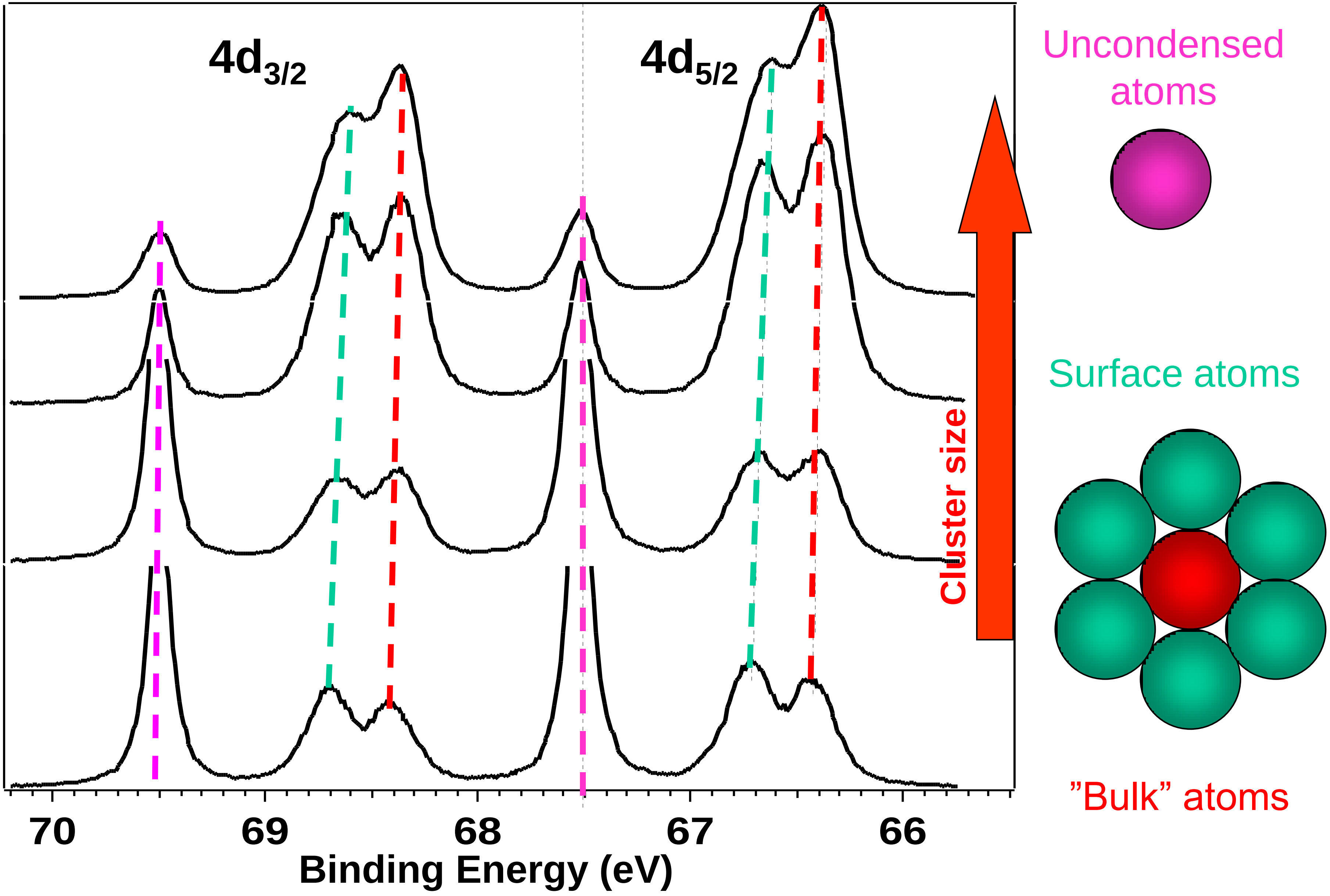
First clusters
studied with SR and PES
were mostly ”Model” systems:

Clusters of inert gas atoms:
Ne, Ar, Kr, Xe

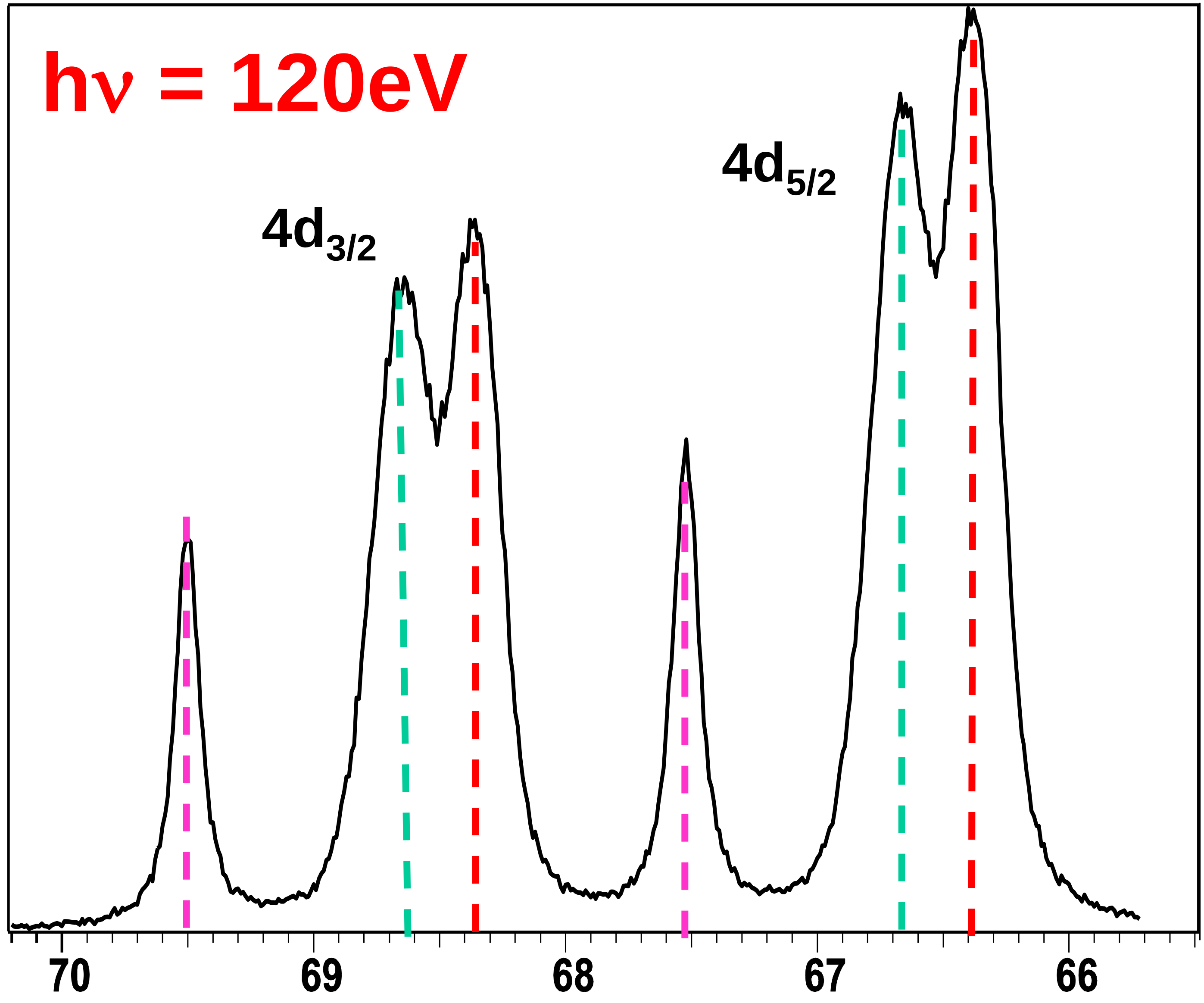
Clusters of simple molecules:
H_20, O_2 , CO, CO_2,
CH_3OH, C_2H_5OH, C_6H_6 , CH_3Cl/Br
some mixtures and solutions

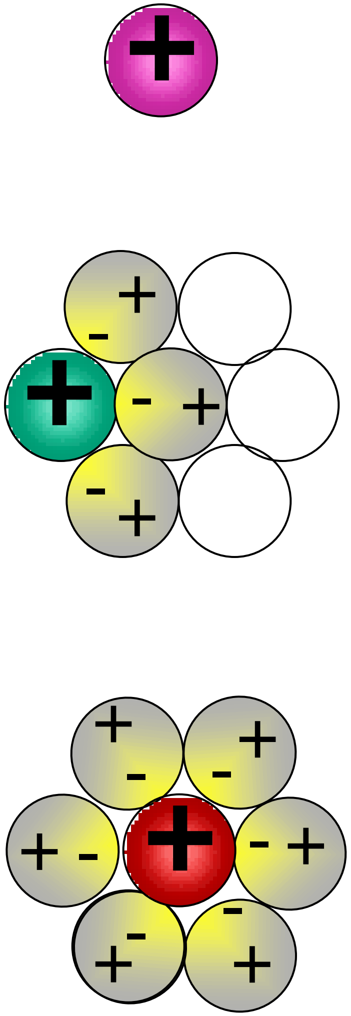
Xenon 4d photoelectrom emission

$h\nu = 120$ eV



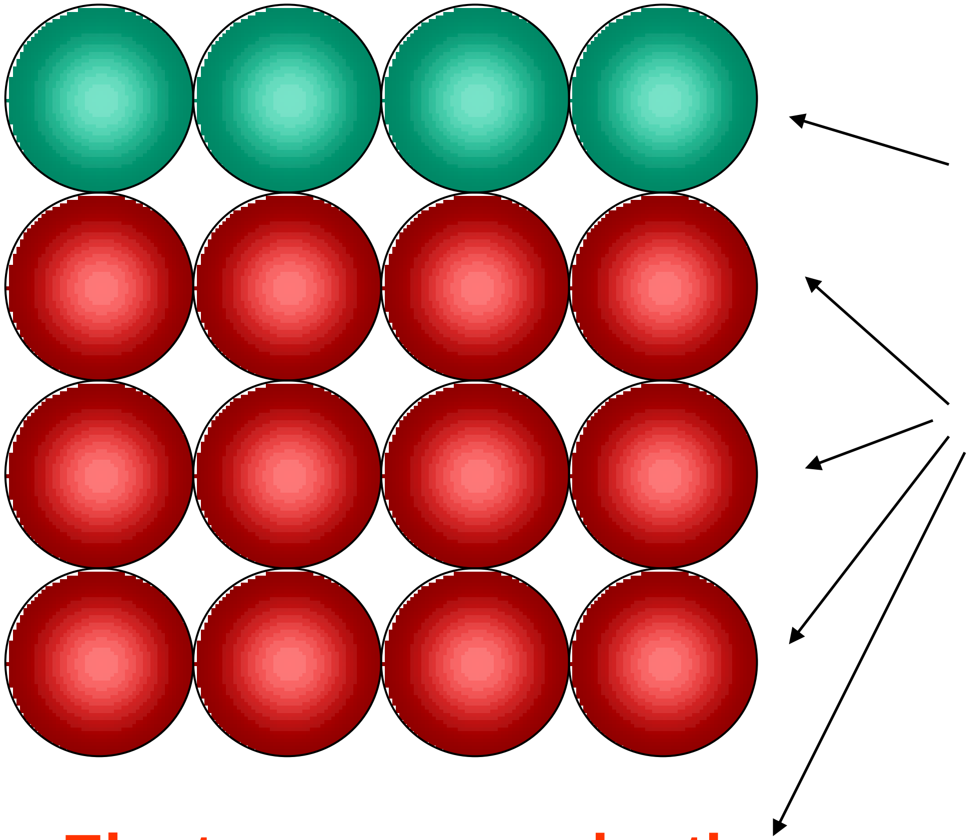
Polarization screening in Xe clusters





Photoelectrons from the inner part

flat layers

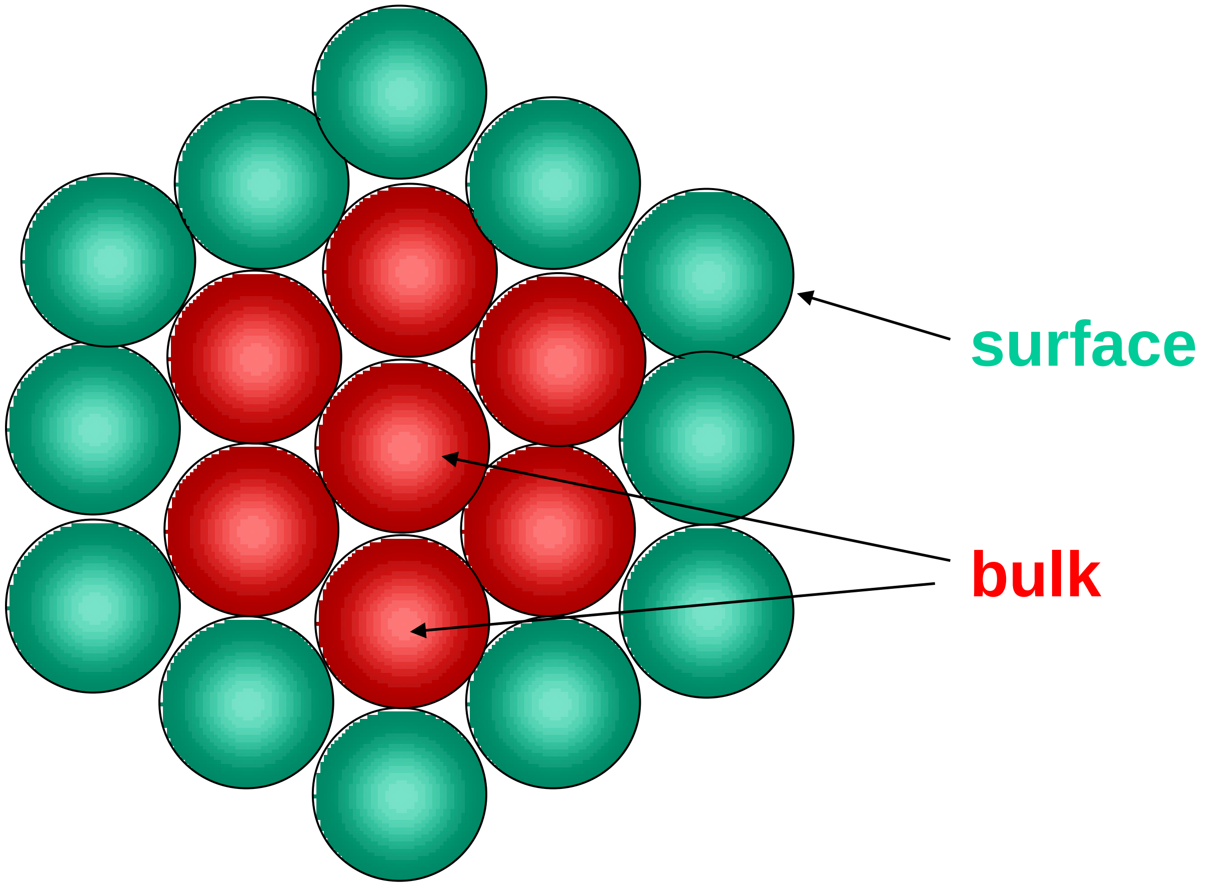


surface

bulk

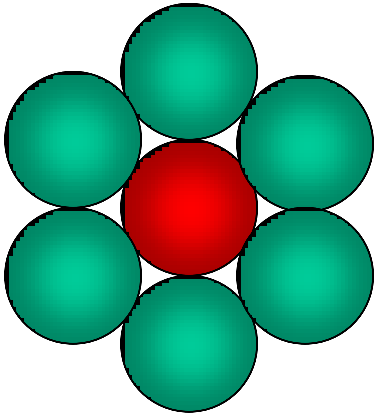
Electron escape depth

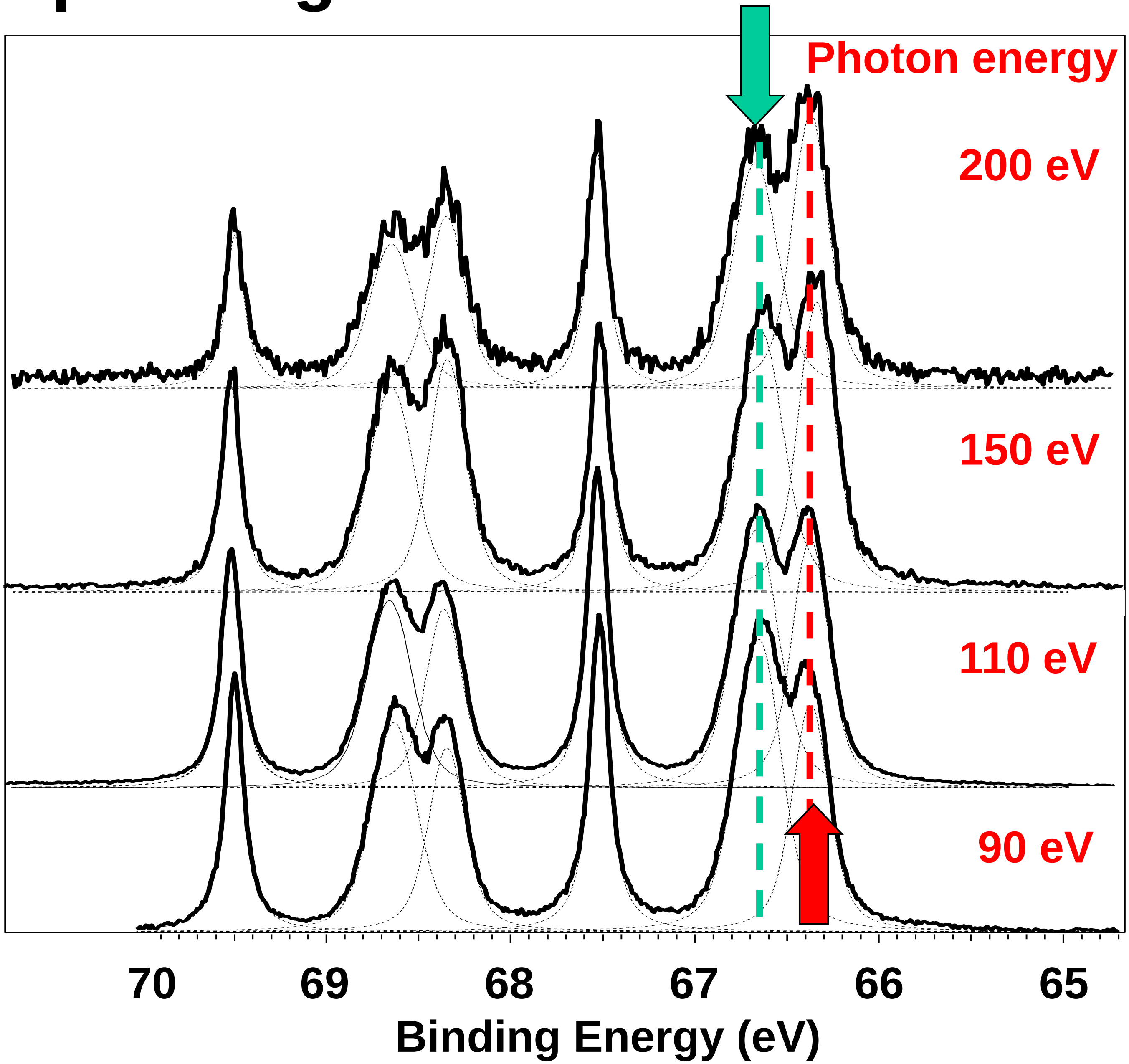
Photoelectrons from the inner part



Depth profiling in free Xe clusters

<N> = 1000





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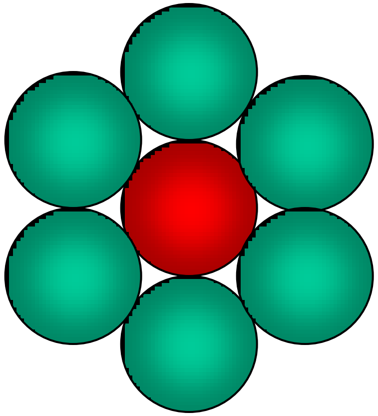

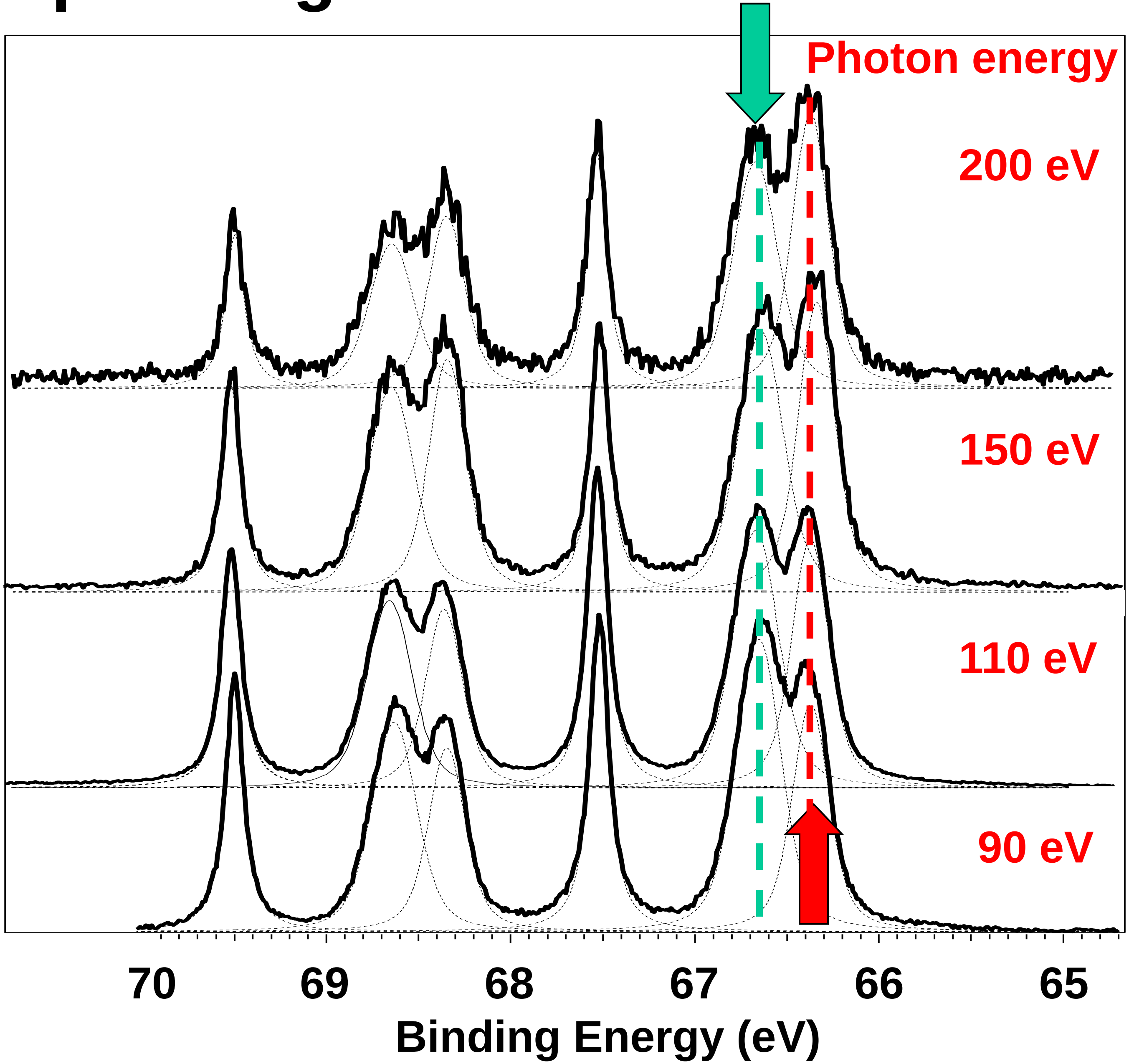

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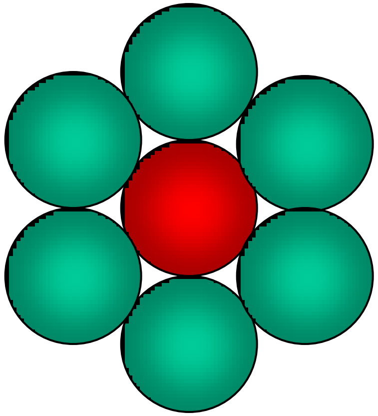
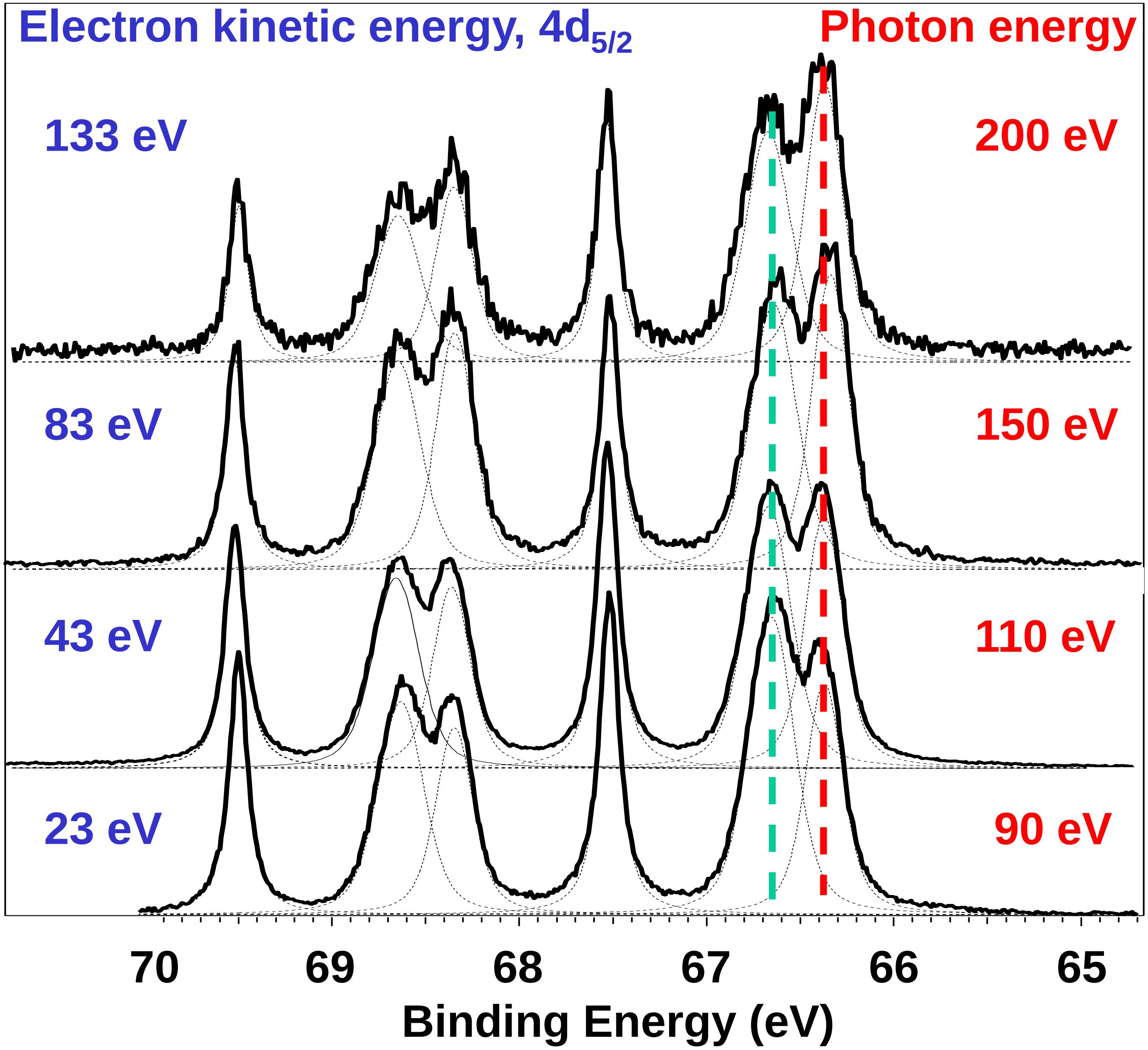




And so what ?

Is there any use of this knowledge except for our specific research area?

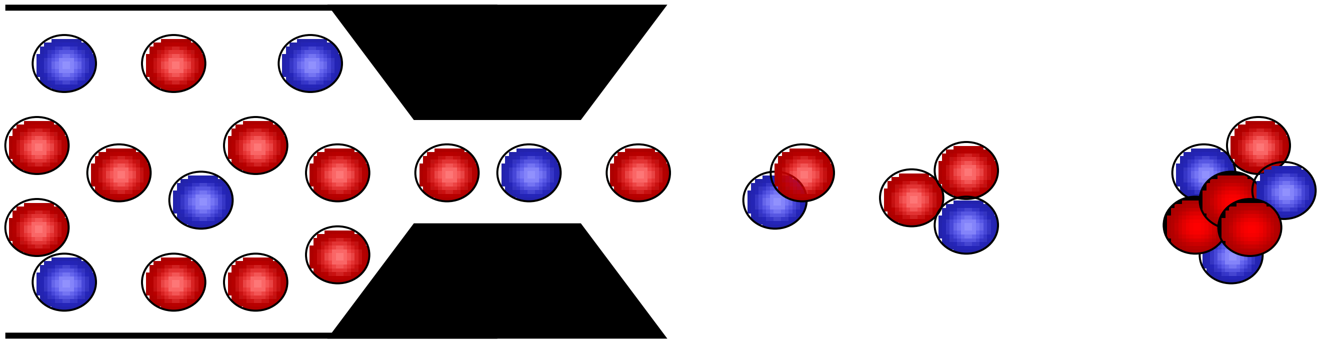
Fundamental questions to address:

When the matter is created out of separate different free atoms –

What kind of solid composition comes out ?

What governs the self-assembling mechanism of matter formation ?

Clustering from a binary gas mixture



Pure expansion:

$\langle N \rangle = \langle N \rangle(T, D, p, k_{A\text{-}A})$

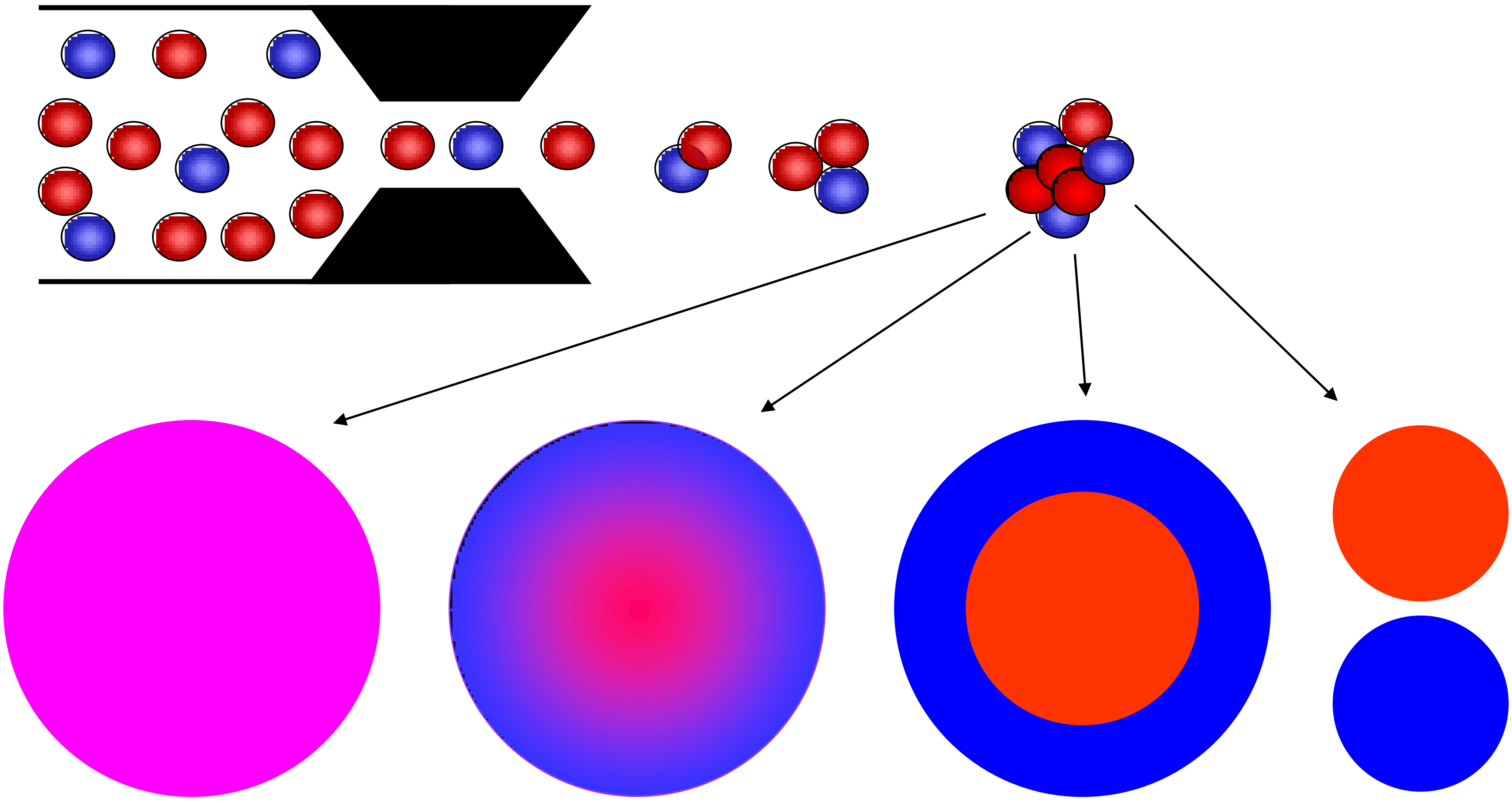
Mixed A B expansion:

$T, D, p, k_{A\text{-}A}, k_{B\text{-}B}, k_{A\text{-}B}, r_{A/B}$

Present experiment:

- T, D, p fixed
- $k_{A\text{-}A}, k_{B\text{-}B}, k_{A\text{-}B}, r_{A/B}$ varied

What one can expect ?

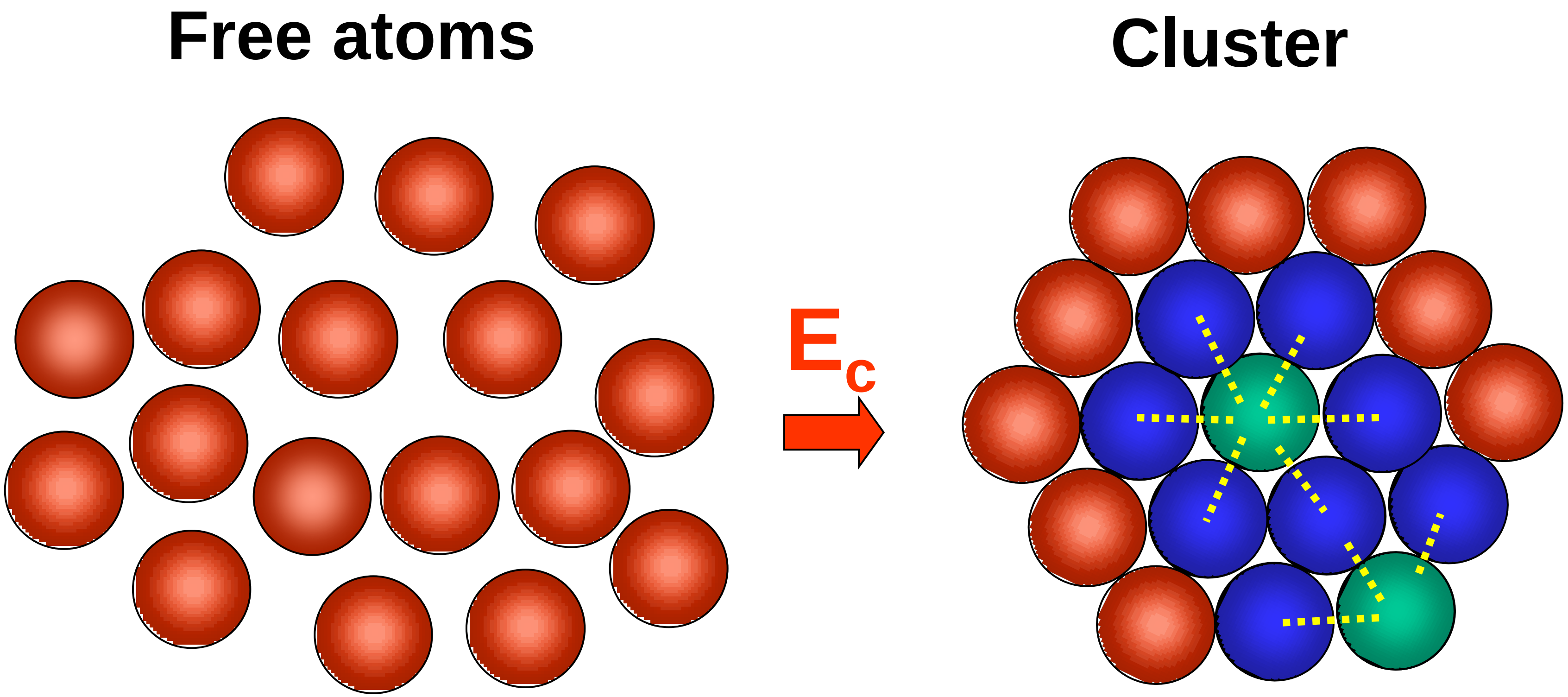


Homogenous mixing

Radial segregation

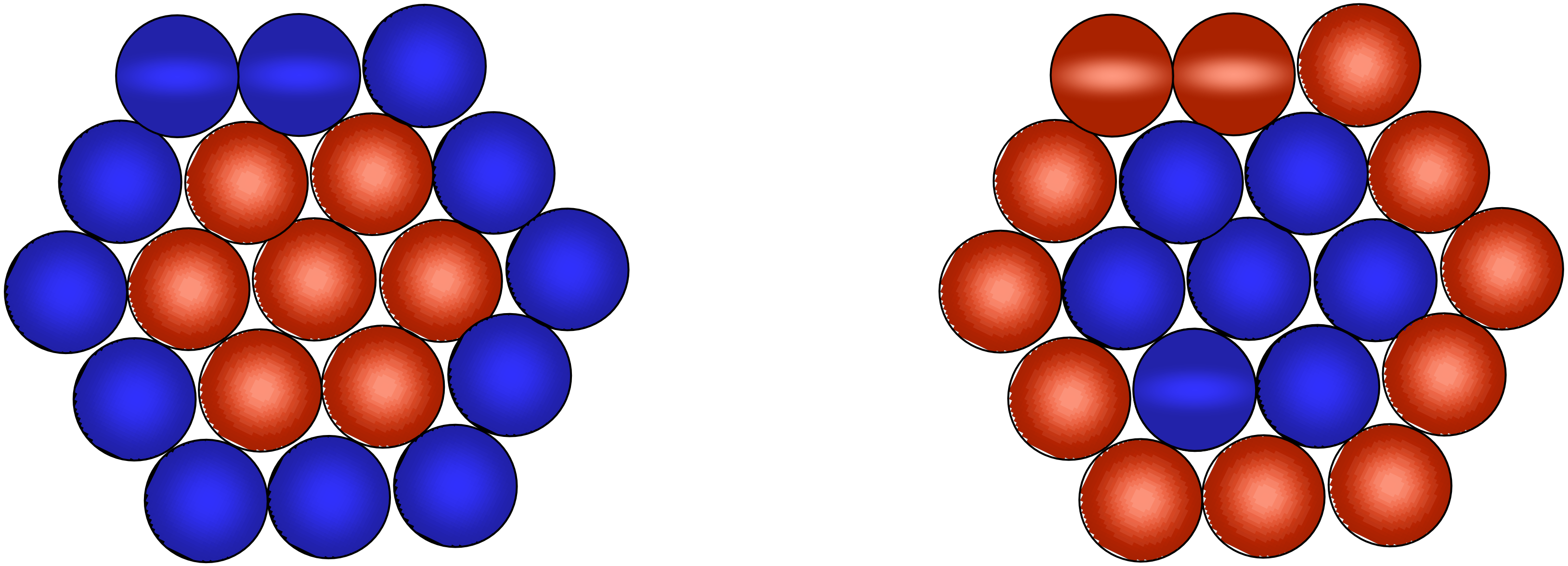
Radial layering

Non-mixing



Energy difference: cohesive energy, E_c

$E_c \alpha$ number of bonds



Fewer bonds at surface than in the bulk

Higher E_c value per atom in the bulk

→ high E_c component in the bulk

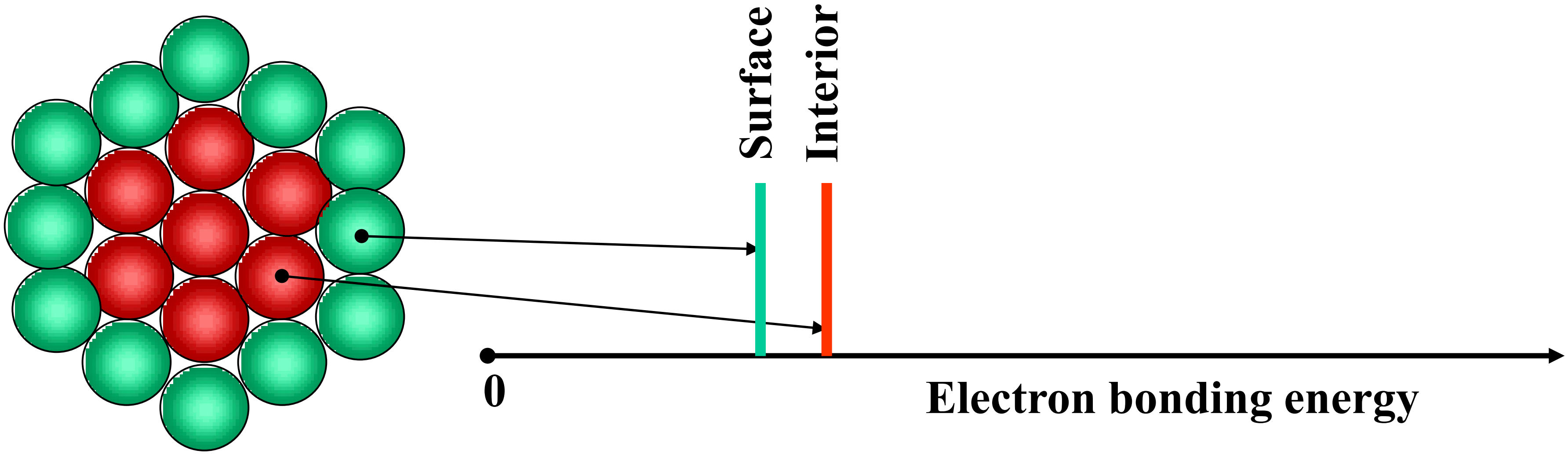
Relevant to practical nanoparticles?

- **Chemical element sensitivity:**

identifies different elements in compounds

- **Site-sensitivity:**

separate responses of inner and surface atoms



In a two-component substance -

what chemical is on the surface and what in the interior?

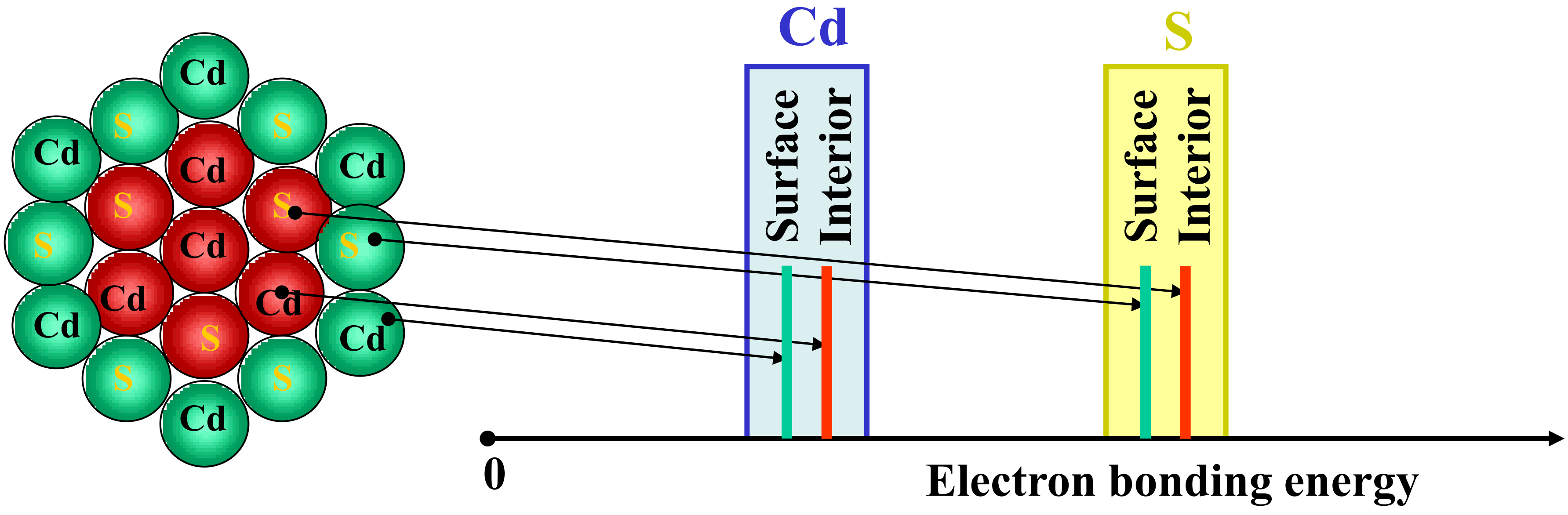
Relevant to practical nanoparticles?

In a two-component substance -

what chemical is on the surface and what in the interior?

An example linking to practice:

How do atoms of Cd & S arrange in CdS at nanoscale?



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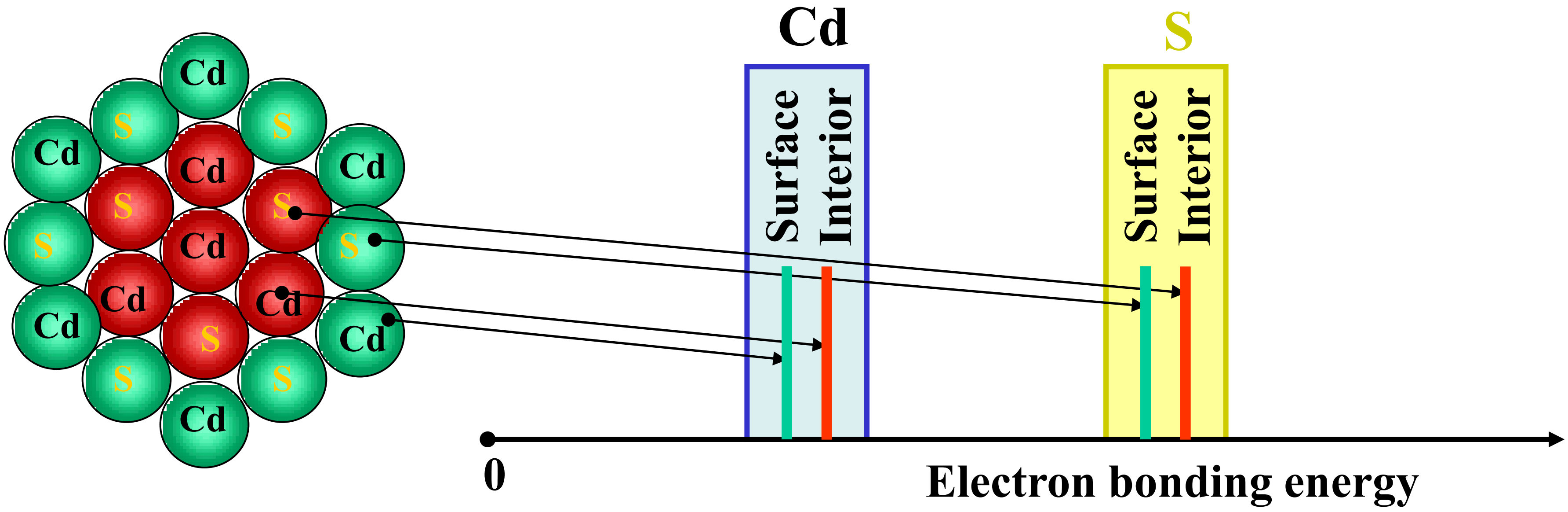


Conclusions: sulphur dominates the cluster surface

Consequences: properties of small light-emitting devices

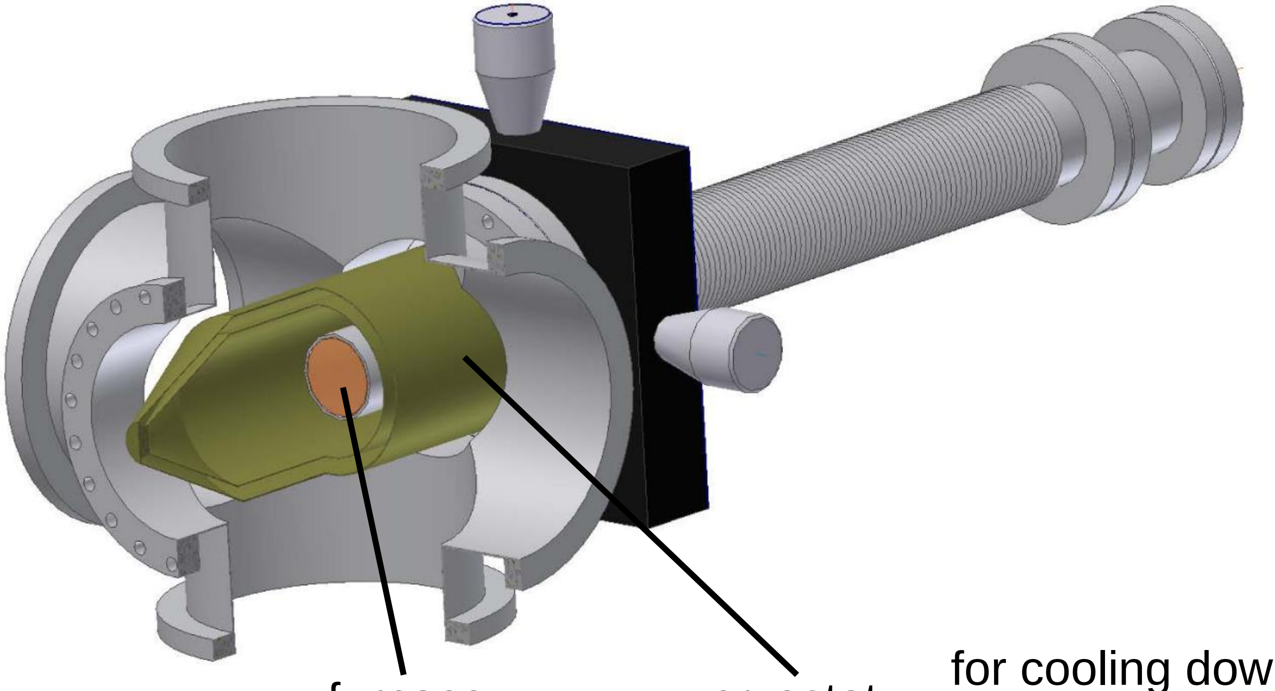
Metal or semiconductor clusters – how to produce them ?

vaporizing solids -

- heating solid in a furnace

or

by magnetron sputtering

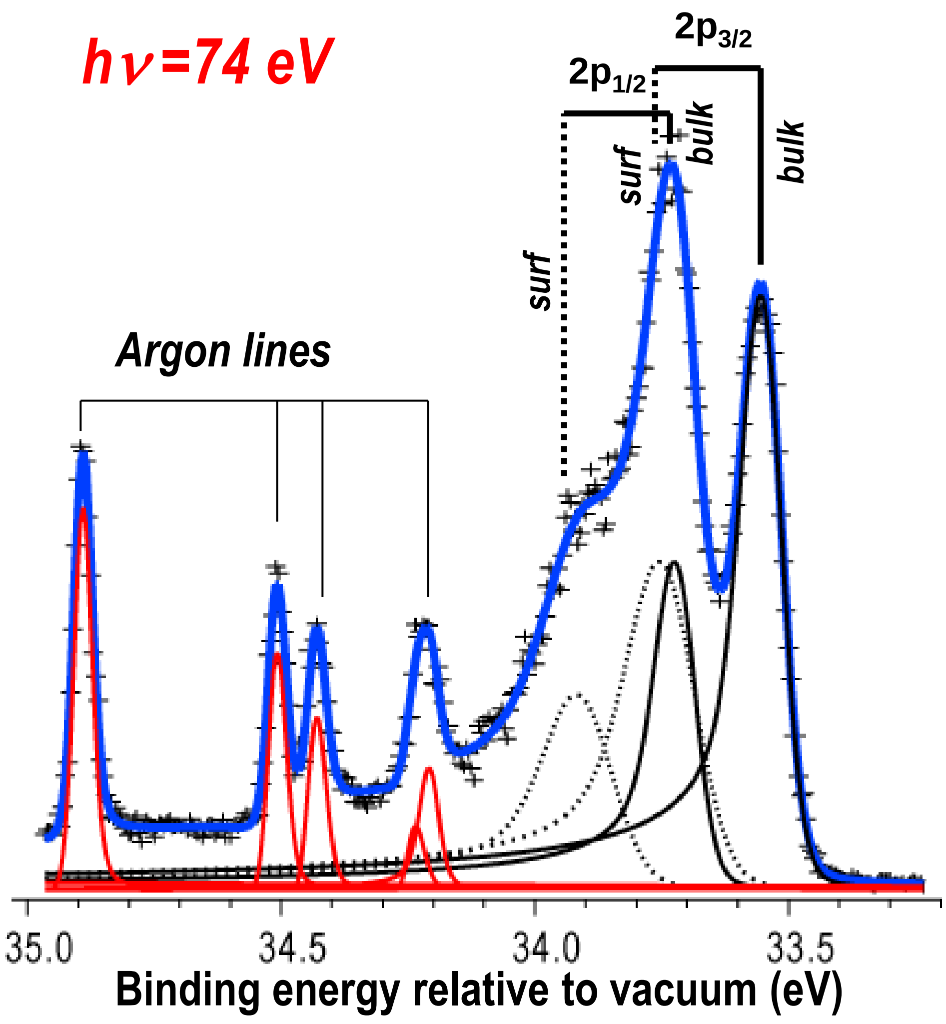


furnace
or magnetron

cryostat - for cooling down the vapour
in collisions with inert gas

Metal clusters – core-level photoelectron spectrum

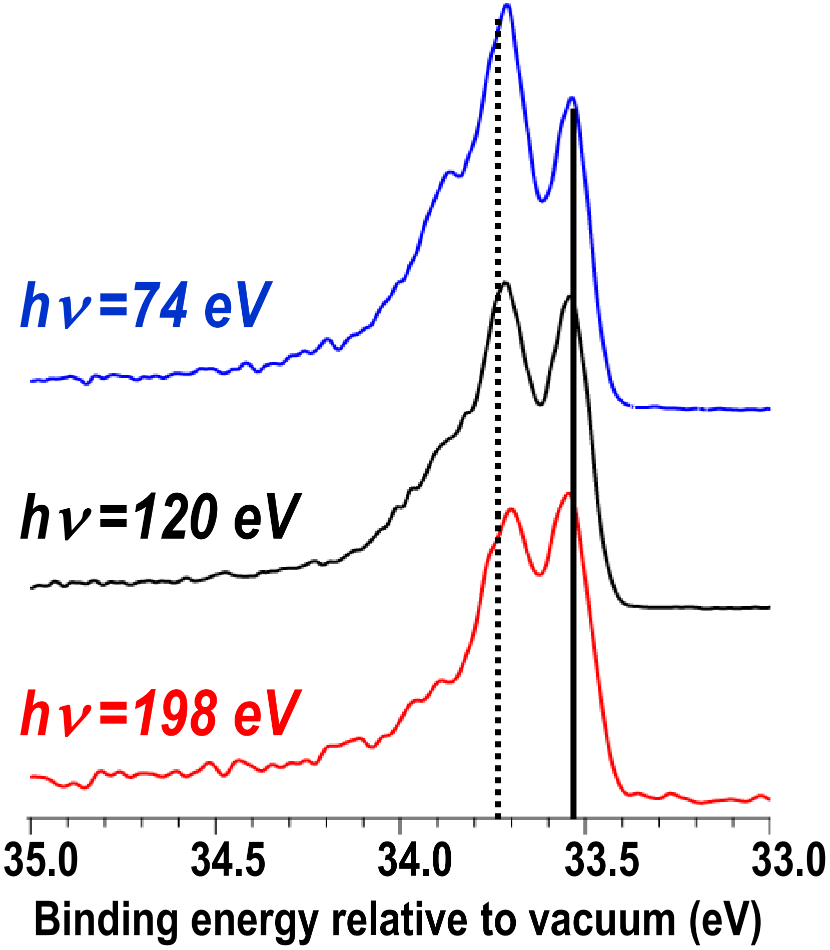
Sodium 2p core-level photoelectron spectrum



- *Measured relative to Vacuum*
- *BE shift from atoms – ≈ -4.5 eV*
- *Resembles solid Na XPS*
- *Coupling core-valence is absent*
- *Bulk is lower than surface*
- *Spectral profiles are asymmetric (valence involved in core-ionization)*

Metal clusters – core-level photoelectron spectra

Sodium 2p XPS - different photon energies



- *Used ideas from inert gases*
- *Bulk becomes stronger with $h\nu$*
- *Electron escape-depth probed*
- *$h\nu$= 74eV - surface-sensitive*

In clusters:

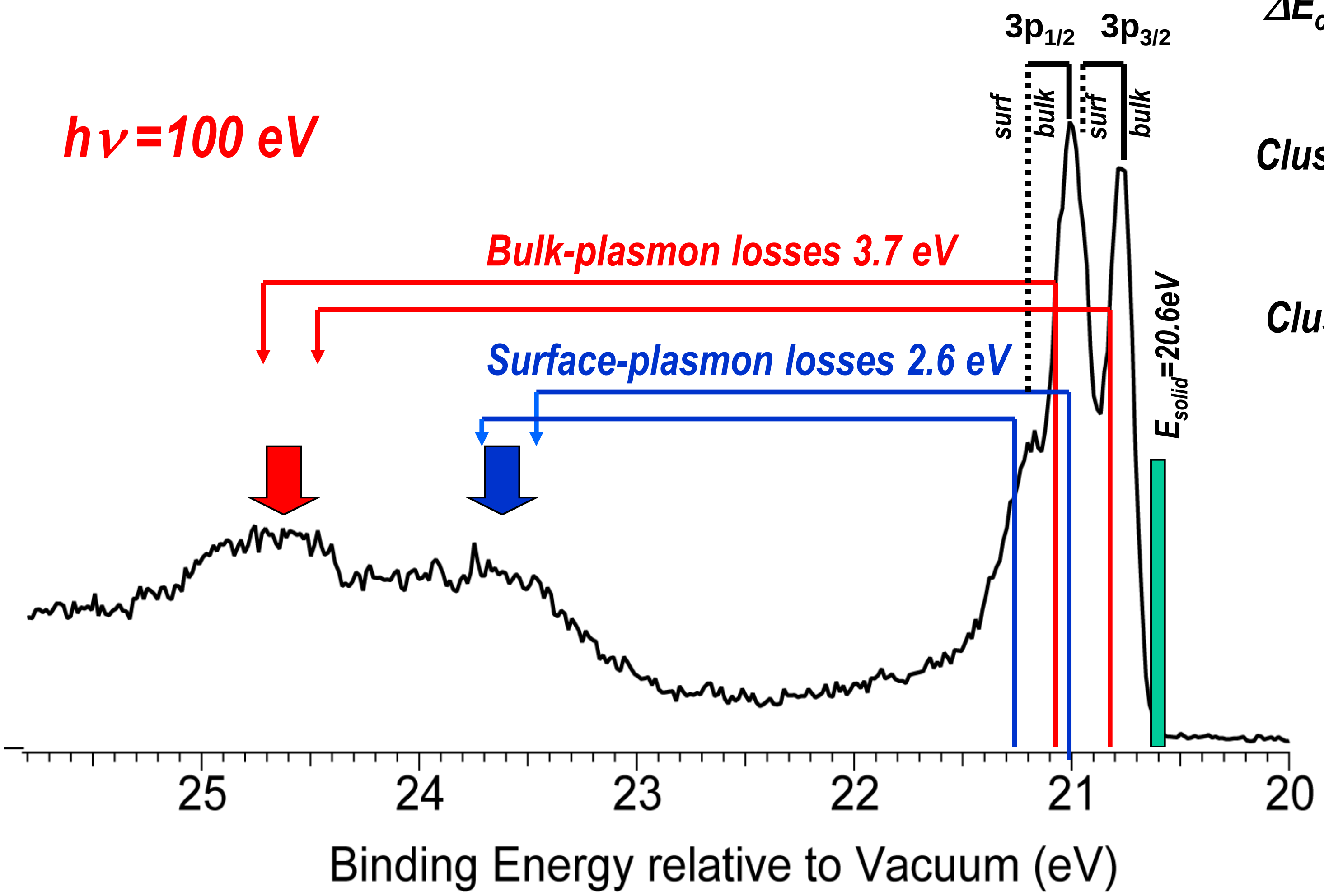
$$E_{cluster} = E_{vacuum}(solid) + \frac{1}{2}\frac{e^2}{R}$$

In solids the measured energy is :

$$E_{solid} = E_{vacuum}(solid) - W_{solid}$$

Metal clusters – core-level photoelectron spectra

Potassium 3p XPS



$\Delta E_{cluster}$ = 0.2 eV

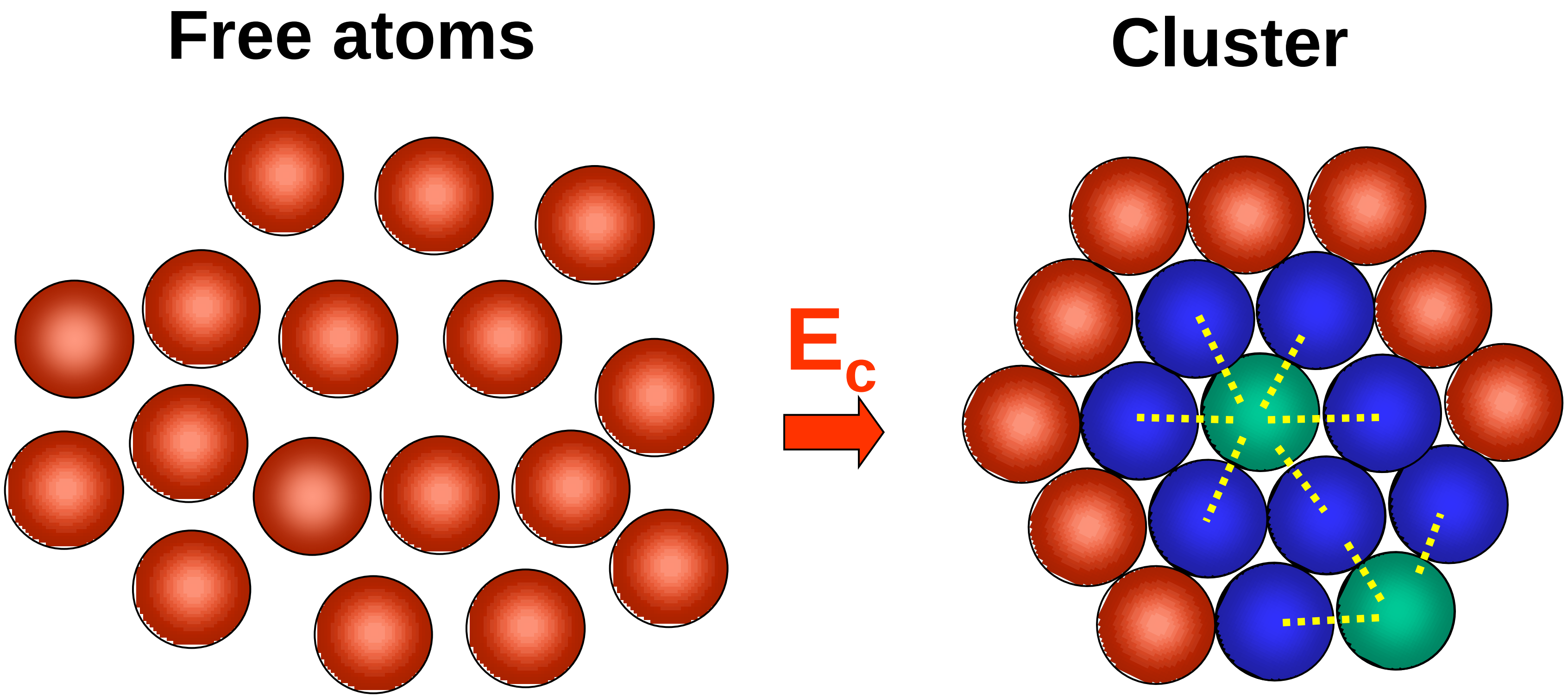
⬇

Cluster D ≈ 7 nm

⬇

Cluster N ≈ 2500

What governs the self-assembling mechanism of Matter formation ?

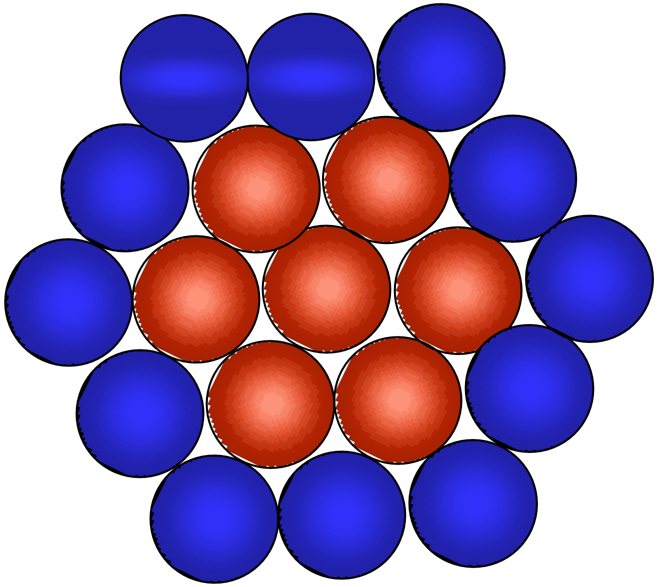


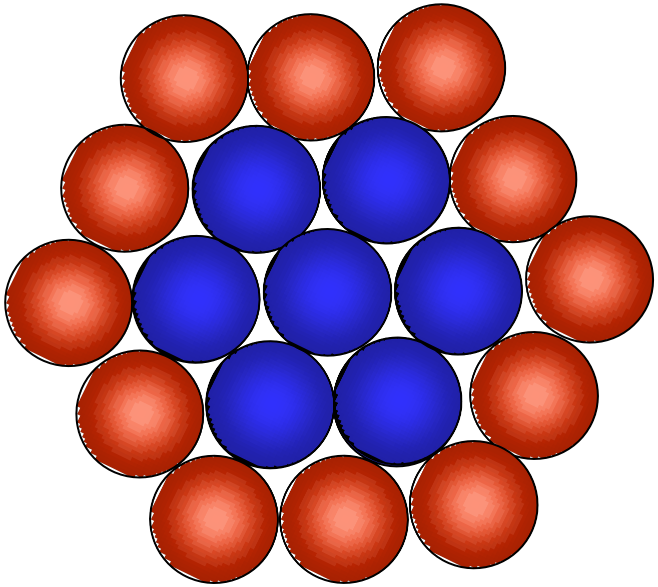
Energy difference: cohesive energy, E_c

E_c α number of bonds

What governs the self-assembling mechanism of Matter formation ?

A system tries to reach a state with the lowest energy





Fewer bonds at surface than in the bulk

↓

Higher E_c value per atom in the bulk

↓

high E_c component in the bulk

Binary metal clusters by self-assembling

Vaporizing NaK alloy

NaK – Na : K ≈ 1:2 by weight

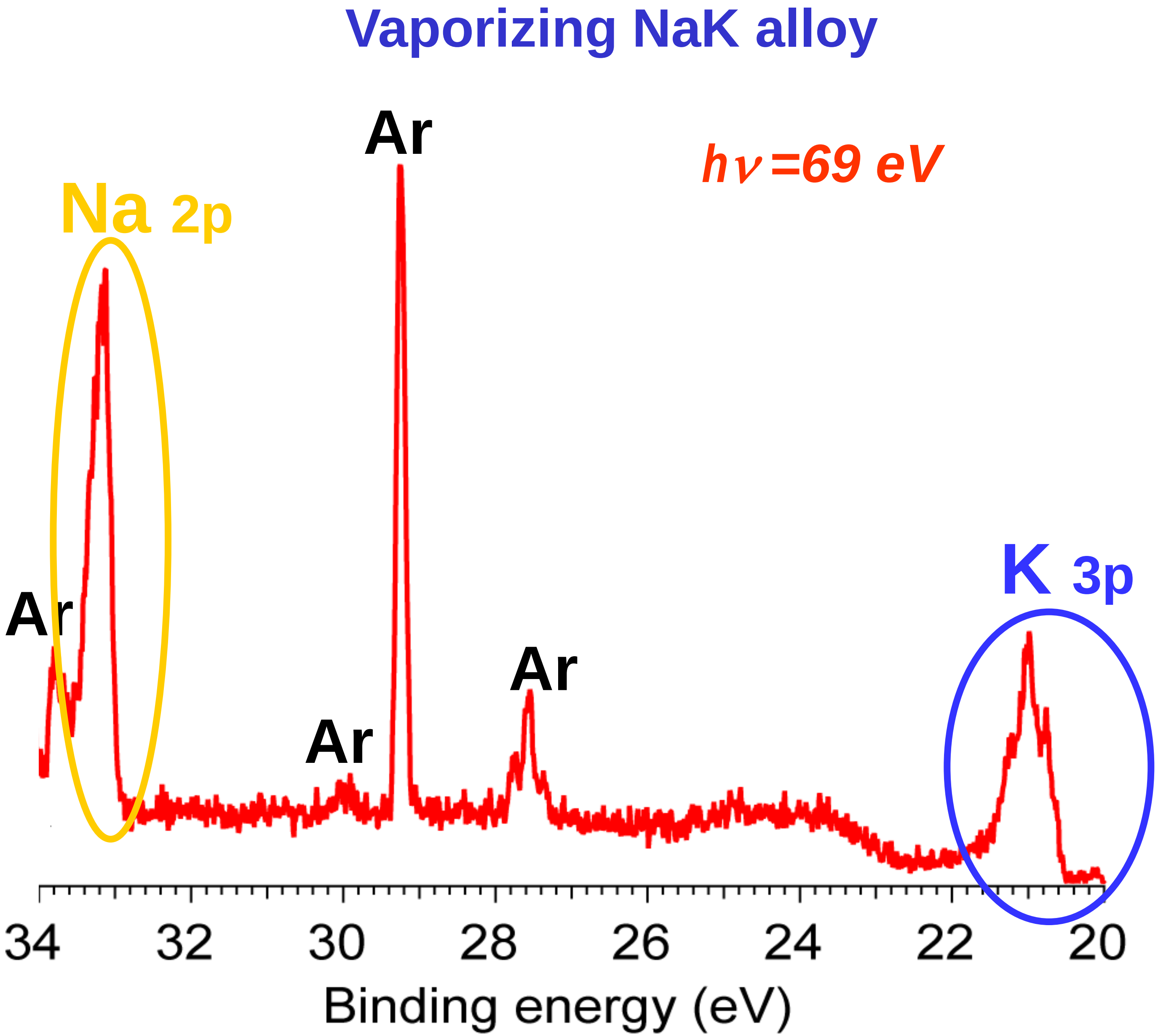
A composition liquid at room T and solid below -13^{o}C

On macroscopic scale:

In binary liquid alloys

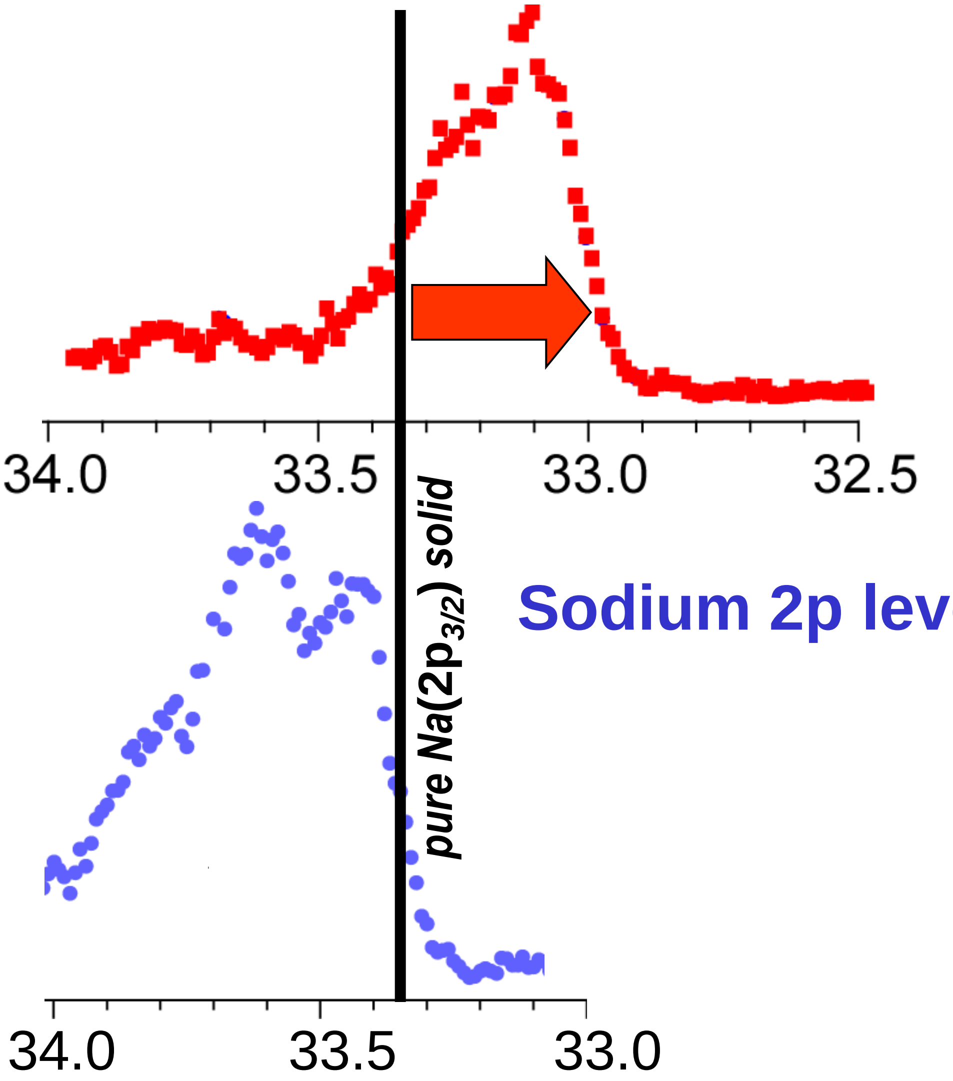
the surface is covered by the lower-surface-energy element

Binary metal clusters by self-assembling



Binary metal clusters by self-assembling

Sodium 2p level - NaK alloy



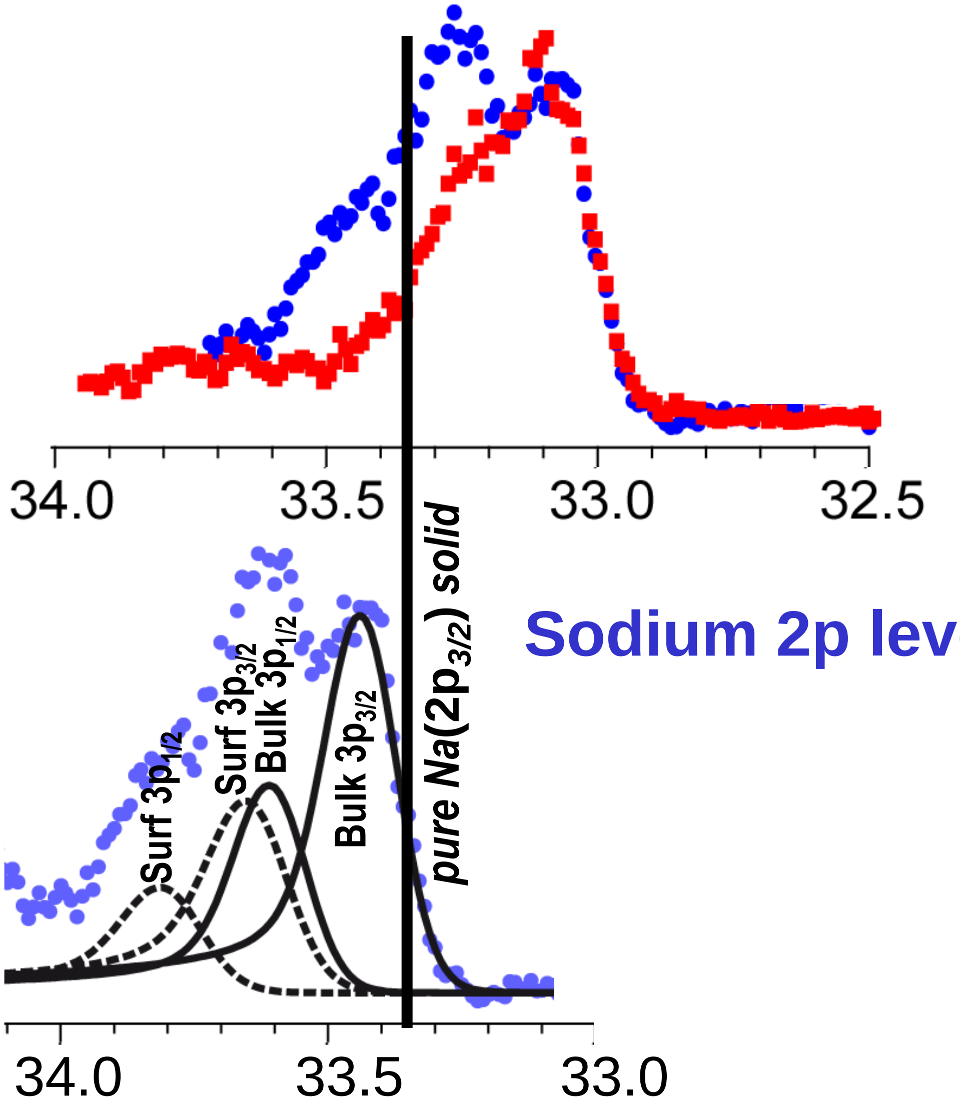
Sodium 2p level - pure

In free neutral clusters:

$$E_{cluster} = E_{vacuum}(solid) + \alpha \frac{e^2}{R}$$

$$E_{cluster} > E_{solid}$$

Binary metal clusters by self-assembling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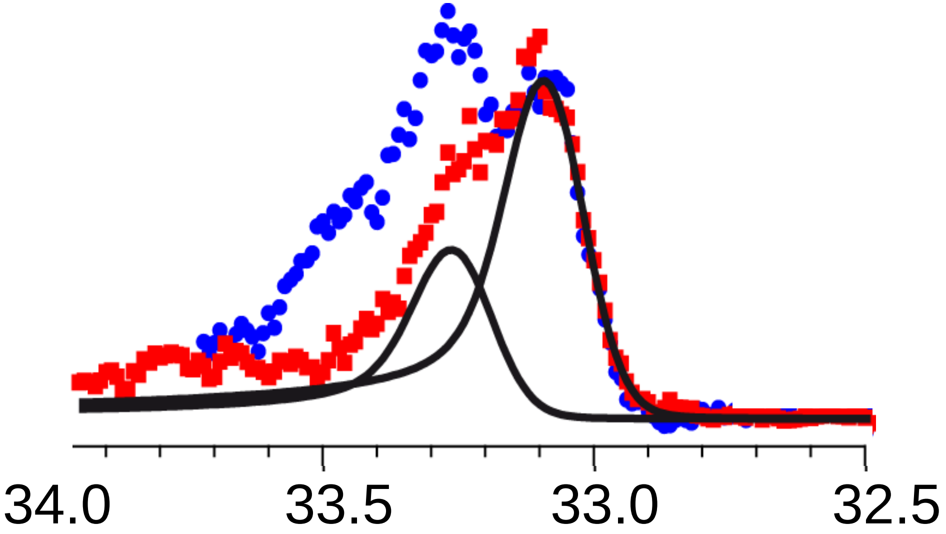

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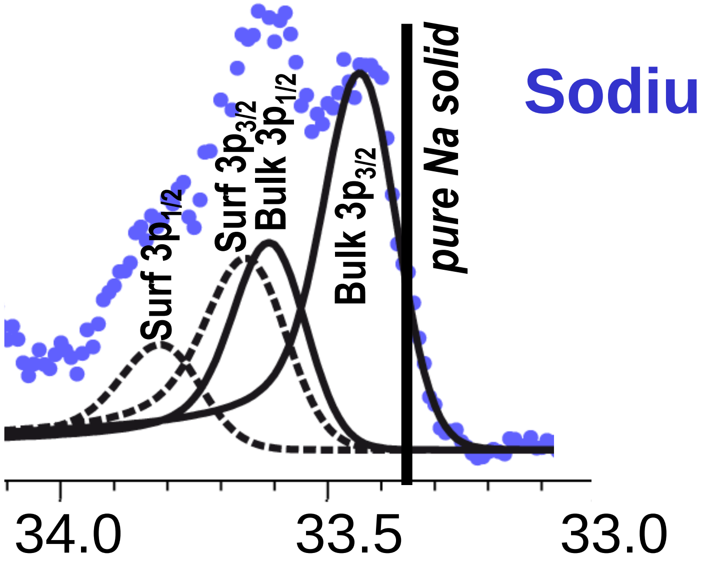
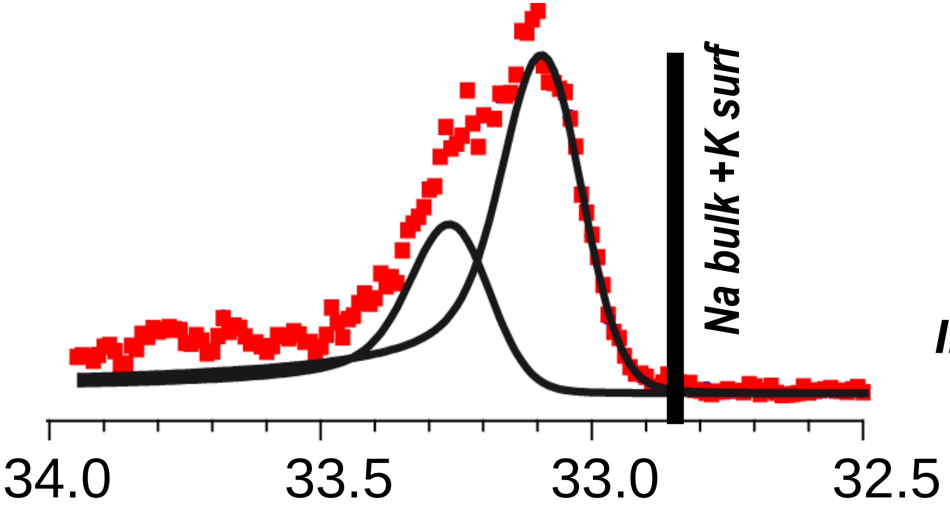
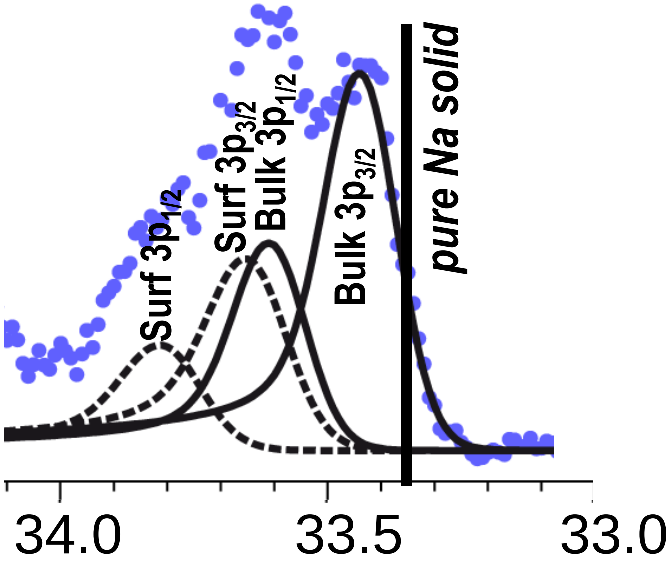


Binary metal clusters by self-assembling

Sodium 2p level - NaK alloy





In free neutral clusters:

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$$E_{cluster} > E_{solid}$$

In supported solids the energy is :

$$\boxed{E_{vacuum}\,(solid)} = E_{Fermi}(solid) + W_{solid}$$

In complex solids: W -?

W (Na) → *W* (K)

2.8 eV → *2.3 eV*

Potassium dominates the surface

No Na surface response in the alloy

Core-level PES discloses segregation