Nano-2

Nanoscience II: Properties of nanoclusters in vacuum

Hannu Häkkinen

12.11.2007

University of Jyväskylä

Nanoscience Center

Departments of Physics and Chemistry

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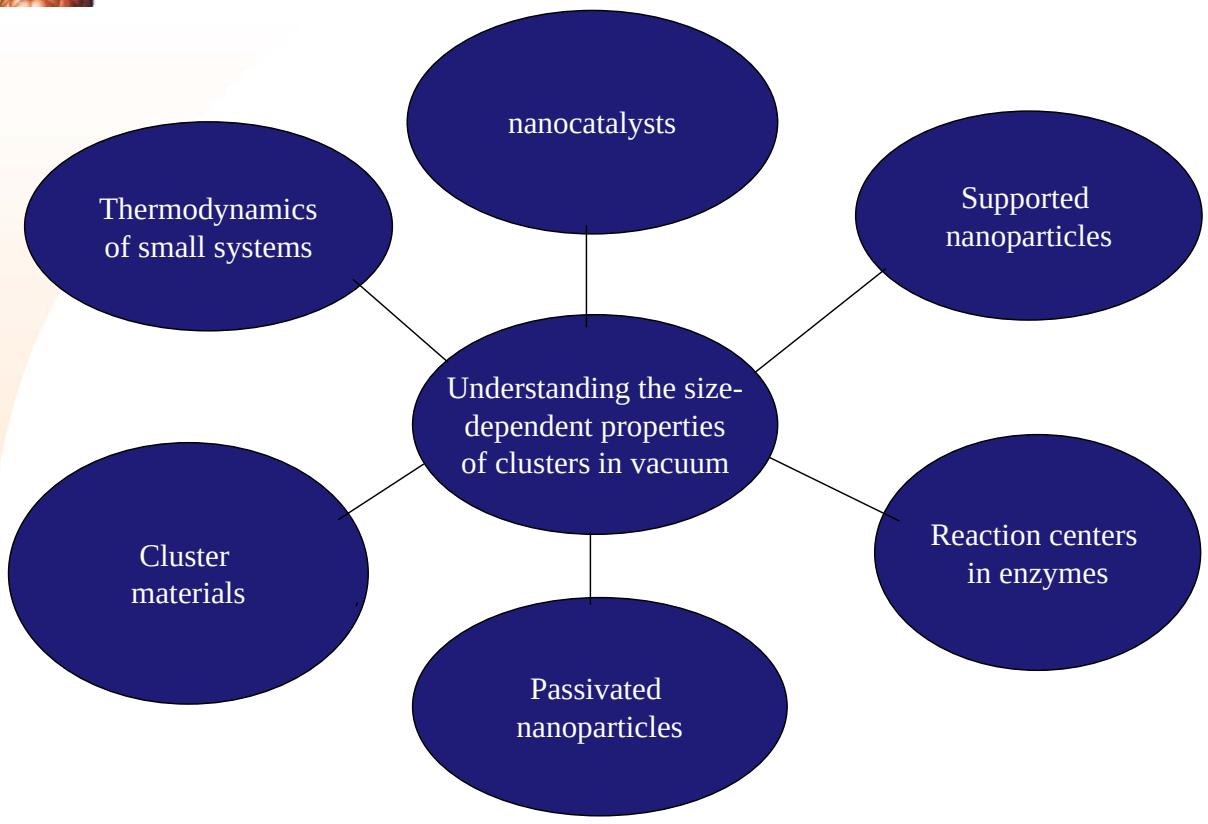
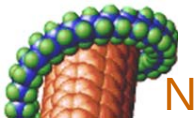
Cluster science – at the heart of ”Nano” !



Hannu Häkkinen, Nanoscience Center, University of Jyväskylä



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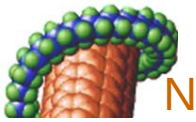
Contents

- Manufacturing of nanoclusters
- Cluster stability: atomic and electronic shells
- Experiment vs. theory: Na clusters from 4 to 350 atoms
- Thermodynamic properties
- Chemical and catalytic properties (example: gold)



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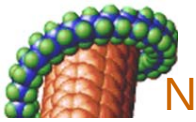
Some literature

- R. L. Johnston, Atomic and Molecular Clusters, Taylor & Francis (2002).
- W. A. de Heer, The physics of simple metal clusters: Experimental aspects and simple models, Rev. Mod. Phys **65**, 611 (1993).
- M. Brack, The physics of simple metal clusters: Self-consistent jellium model and semiclassical approaches, Rev. Mod. Phys. **65**, 677 (1993).
- F. Baletto, R. Ferrando, Structural properties of nanoclusters: Energetic, thermodynamic, and kinetic effects, Rev. Mod. Phys. **77**, 371 (2005).
- T. P. Martin, Shells of atoms, Phys. Rep. **273**, 199 (1996).



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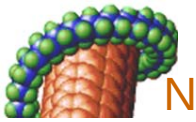
Manufacturing & analysis



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Cluster sources

- Seeded supersonic nozzle source
- Gas-aggregation source
- Laser vaporization source
- Sputtering source
- Liquid-metal ion source

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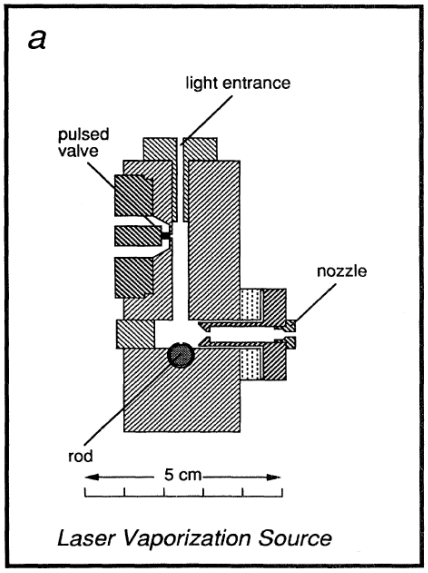
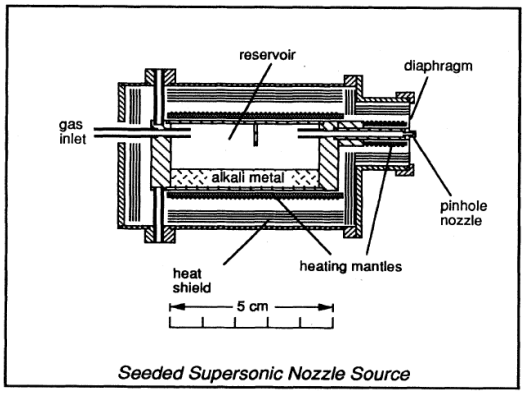
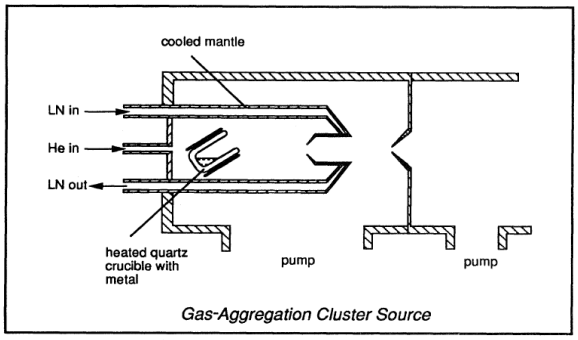
Cluster sources







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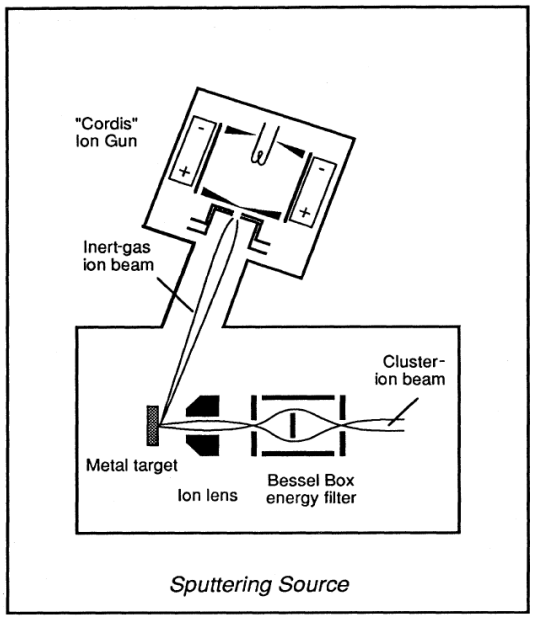
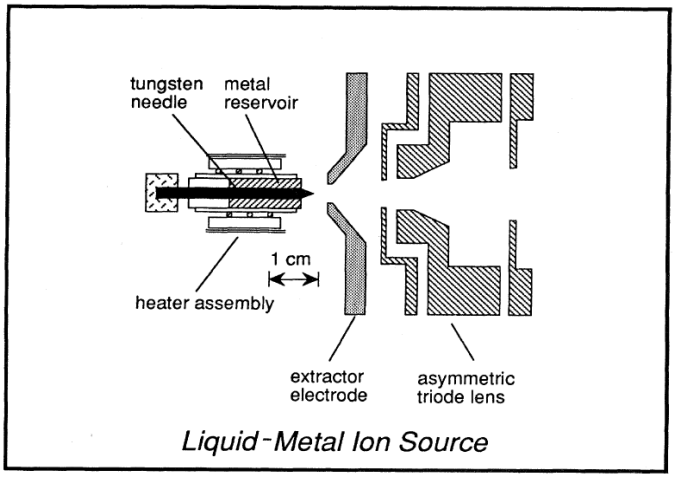
Cluster sources





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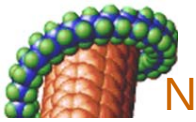

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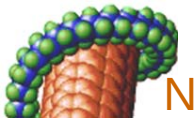
Cluster sources – overview

- Seeded supersonic nozzle source: intense continuous beams, low-boiling-point materials, evaporative cooling -> structured mass spectra (magic stabilities visible), temperature not well controlled
- Gas-aggregation cluster source: efficient for production of large clusters (up to 20 000+), low intensity, low-to-medium boiling point materials (< 2000 K), low cluster temperature (< 100 K)
- Laser vaporization source: pulsed beams from any material, cluster temperature near the source temperature
- Sputtering source: energetic heavy inert-gas ion sputtering beam (Kr+, Xe+, 10 – 20 keV) -> continuous beam of singly ionized (hot) clusters, cooling by evaporation
- Liquid-metal ion source: singly and multiply ionized (hot) clusters of low-melting metals



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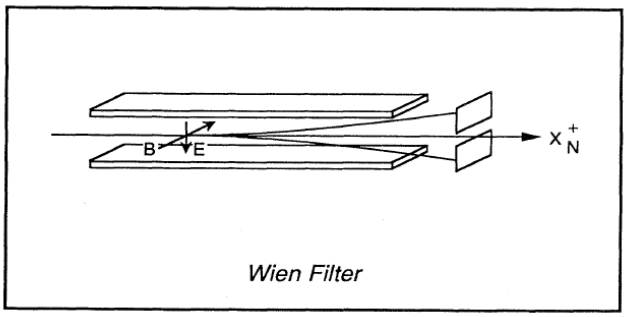
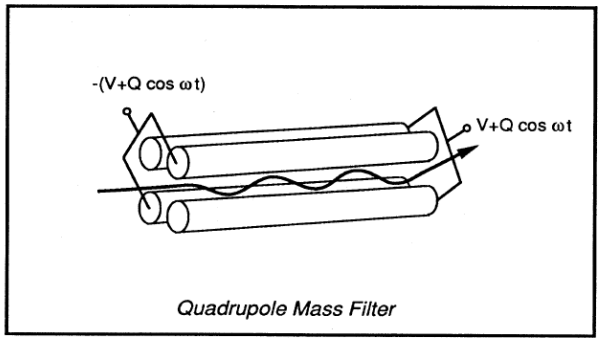
Analysis techniques

- Wien filter
- Quadrupole mass filter
- Time-of-flight mass spectrometry
- Ion cyclotron resonance mass spectrometry in ion trap
- Molecular-beam mobility analysis
- Electron diffraction in ion trap (structure factor)
- Photoelectron spectroscopy

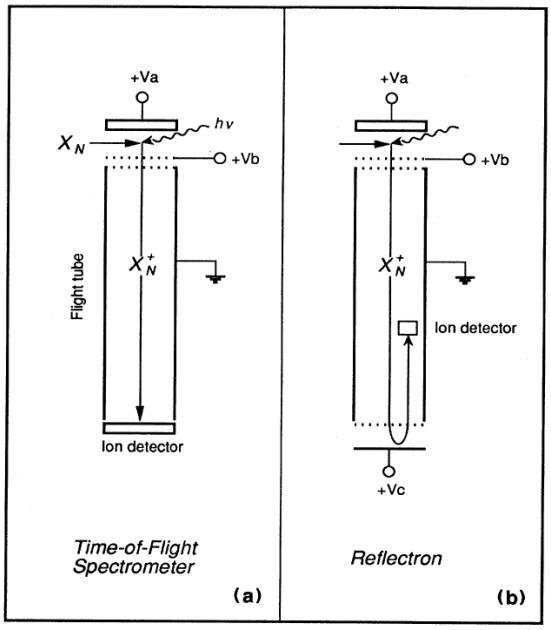
Cluster mass analysis



Wien Filter



Quadrupole Mass Filter

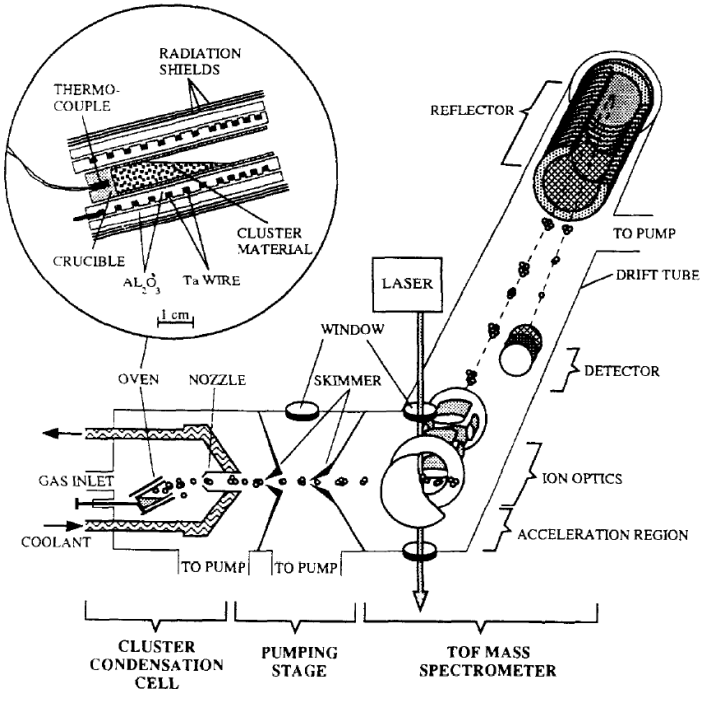


Example of a full setup

Gas-aggregation source

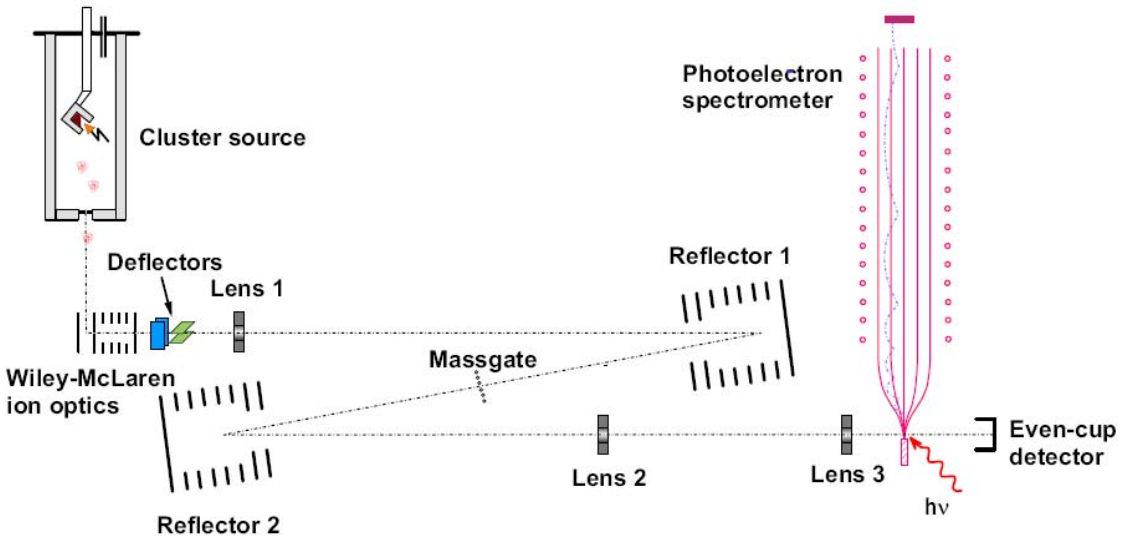
Photoionization by laser

Time-of-flight mass analysis



Martin, Phys. Rep. 273, 199 (1996)

Photoelectron spectroscopy



O. Kostko, PhD Thesis Freiburg 2007

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Cluster stability: atomic and electronic shells

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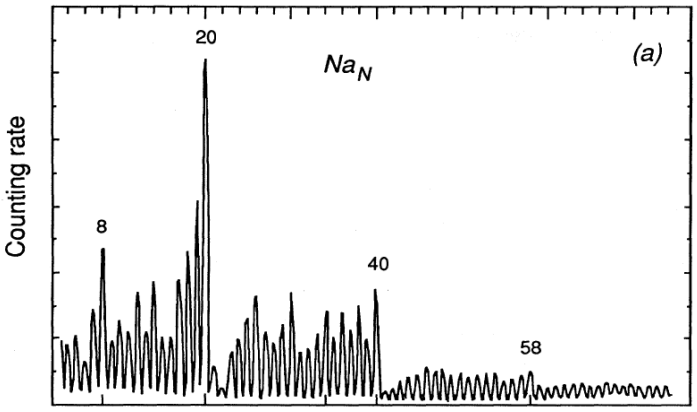
Cluster stability – ”magic numbers”

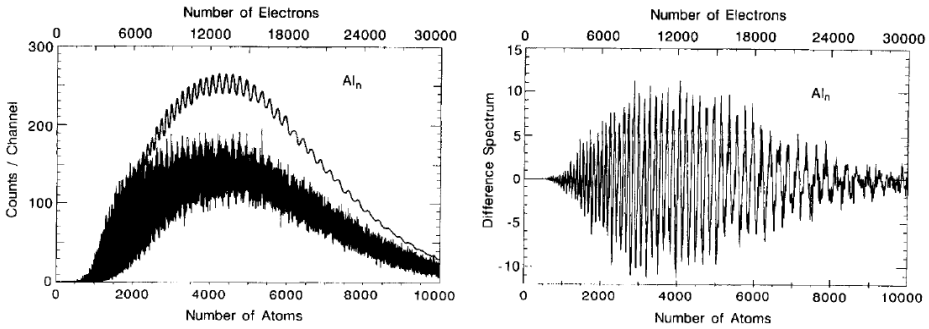
Sodium

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



Aluminium

Martin, Phys. Rep. 273, 199 (1996)



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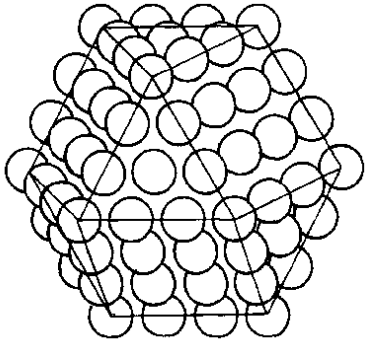
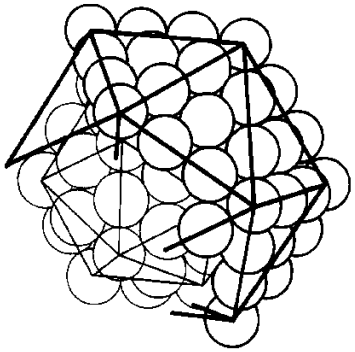
Cluster stability – atomic shells

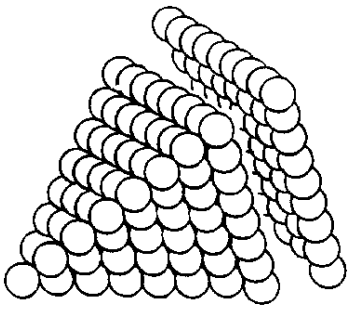


Cuboctahedron (fcc)



Icosahedron

T.P. Martin
Physics Reports
273, 199 (1996)



Tetrahedron (fcc)

Delocalized-electron shell model
Spherical clusters

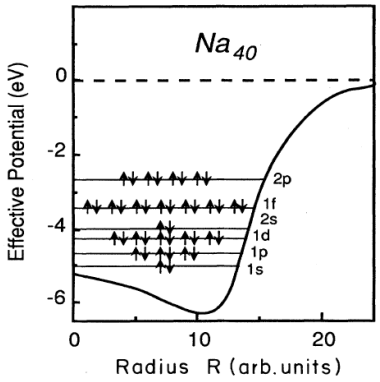


FIG. 3. Self-consistent effective potential of jellium sphere corresponding to Na_{40} with the electron occupation of the energy levels. After Chou *et al.*, 1984.

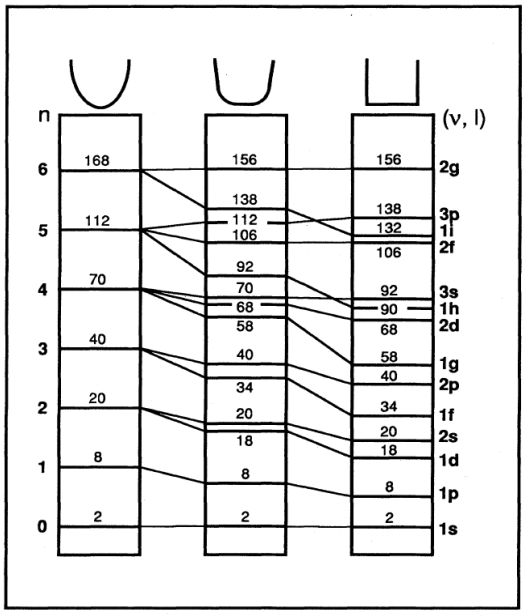


FIG. 2. Energy-level occupations for spherical three-dimensional, harmonic, intermediate, and square-well potentials. After Mayer and Jensen, 1955.

3D isotropic anharmonic oscillator

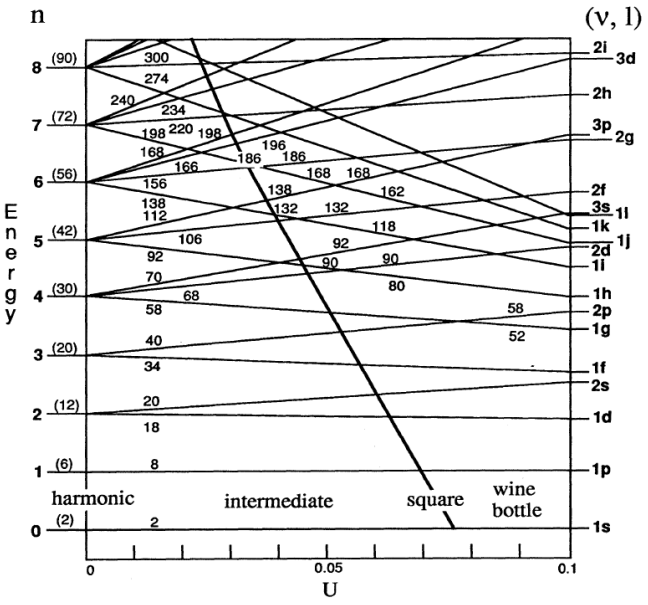
- Single-particle Hamiltonian

$$H = \frac{\mathbf{p}^2}{2m} + \frac{m\omega_0^2\mathbf{q}^2}{2} - Uh\omega_0[l^2 - n(n+3)/6]$$

$$R_0 = r_s N^{1/3} \qquad \hbar\omega_0 = E_F / N^{1/3}$$

- Eigenvalue spectrum

$$E_n = h\omega_0\{(n+\tfrac{3}{2}) - U[l^2 - n(n+3)/6]$$



Electron shells - Effect of deformations

- Clemenger (1985) <- Nilsson (nuclear physics, 1955 !) model: for a fixed volume, the cluster shape adjusts to minimize the total energy
- Deformation → cluster radii Rx, Ry, Rz → tri-axial oscillator

$$E(n_x,n_y,n_z)=\hbar\omega_0\left[(n_x+\tfrac{1}{2})\frac{R_0}{R_x}+(n_y+\tfrac{1}{2})\frac{R_0}{R_y}+(n_z+\tfrac{1}{2})\frac{R_0}{R_z}\right]$$

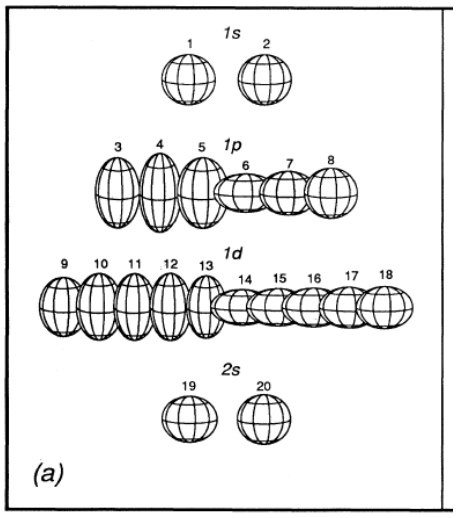
- Spheroid (Rx = Ry), distortion parameter

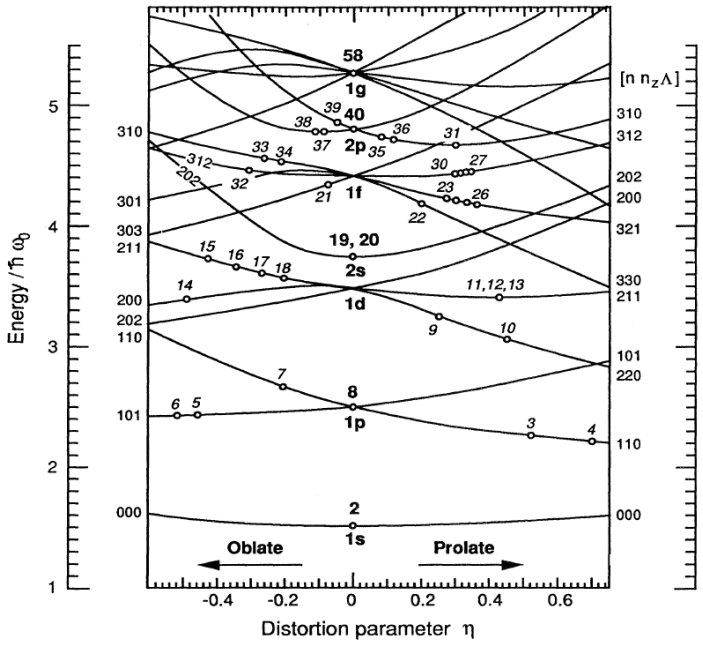
$$\eta=2\frac{R_z-R_x}{R_z+R_x}$$

- Total energy for spheroids

$$E_{\mathrm{tot}}(\eta,N)=\tfrac{3}{4}\sum E(\eta,n_x,n_y,n_z)$$

Clemenger – Nilsson diagram





Cluster stability – electron shells

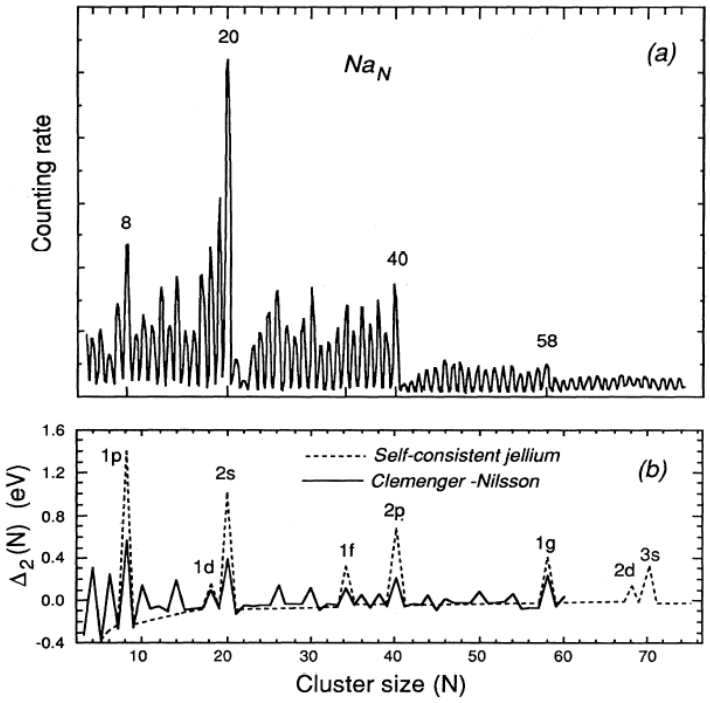


FIG. 1. Sodium cluster abundance spectrum: (a) experimental (after Knight *et al.*, 1984); (b) dashed line, using Woods-Saxon potential (after Knight *et al.*, 1984); solid line, using the ellipsoidal shell (Clemenger-Nilsson) model (after de Heer, Knight, Chou, and Cohen, 1987).

W.A. deHeer
Rev. Mod. Phys
65, 611 (1993)

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Experiment vs. theory: Na clusters from 4 to 350 atoms

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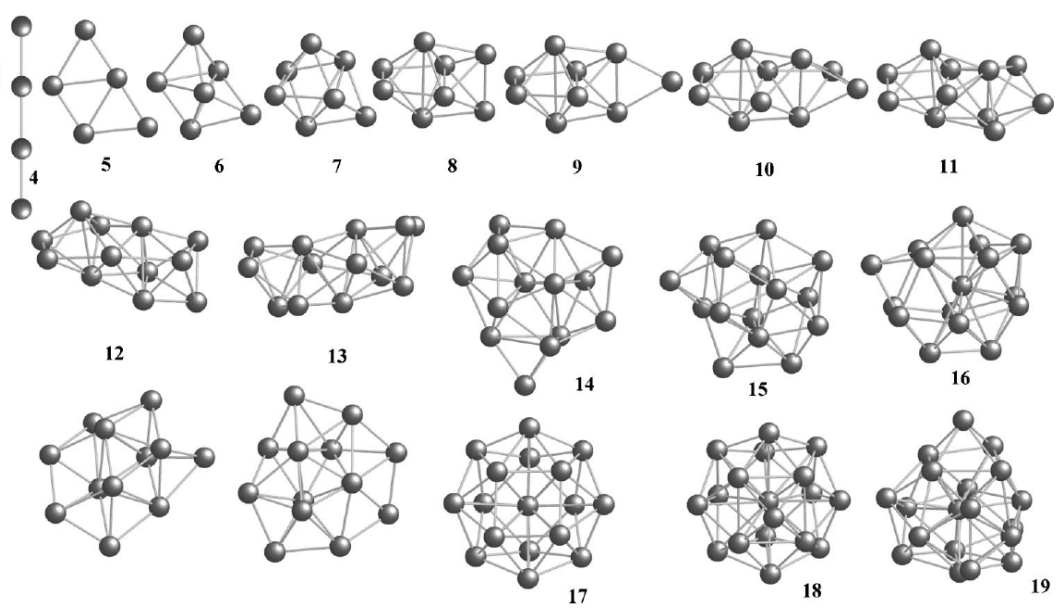
Na cluster anions I : optimised structures at T=0 from density functional theory (DFT)



Moseler, Huber, Häkkinen, Landman, Wrigge, Hoffman, von Issendorff, PRB **68**, 165413 (2003)

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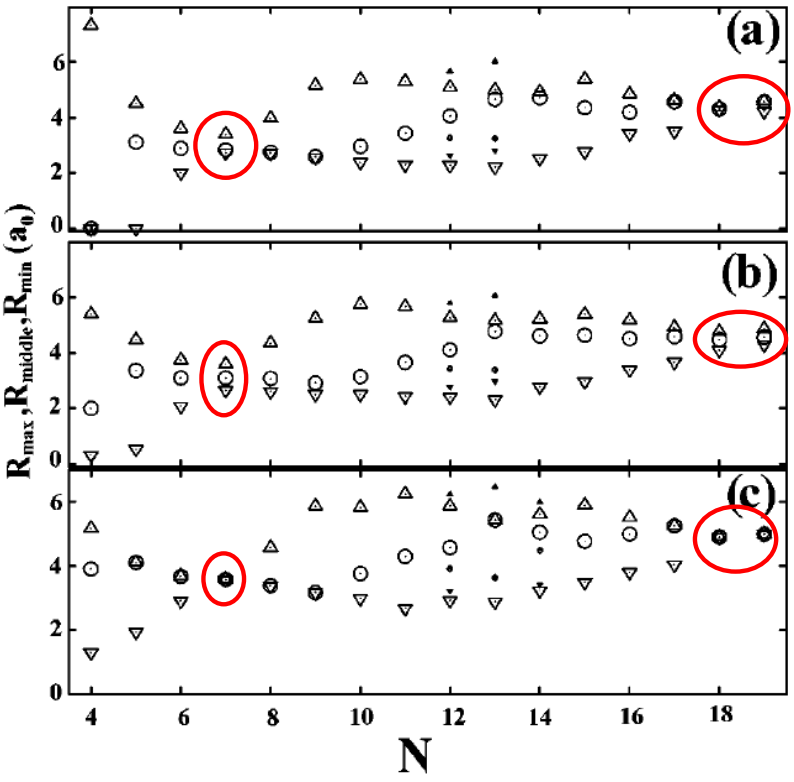
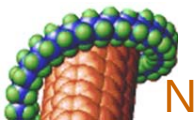
Na cluster anions II : Cluster shapes from DFT

Cluster radii from GS (T=0)

Radii from RT DFT-MD

Radii from jellium model
Koskinen, Lipas, Manninen
Z. Phys. D 35, 285 (1995)





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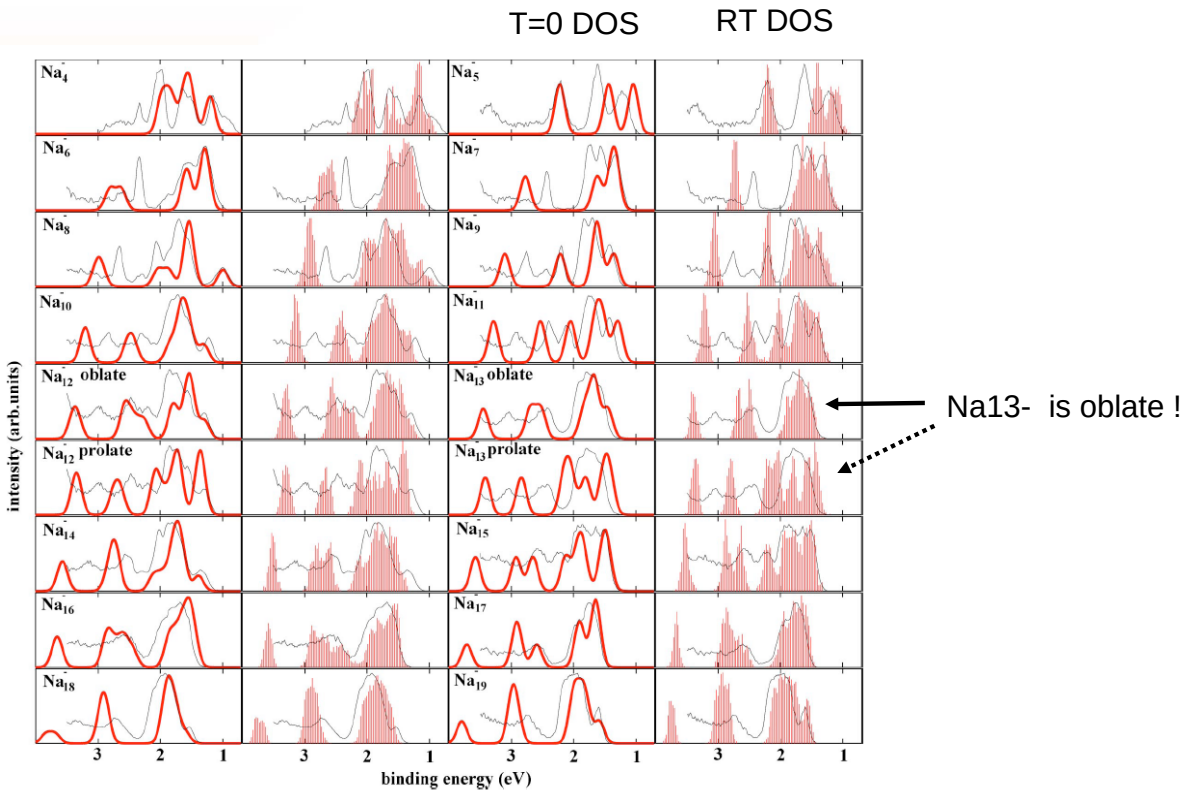
Na cluster anions III : Photoelectron spectroscopy vs. electron density of states



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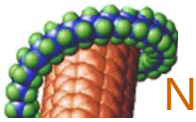

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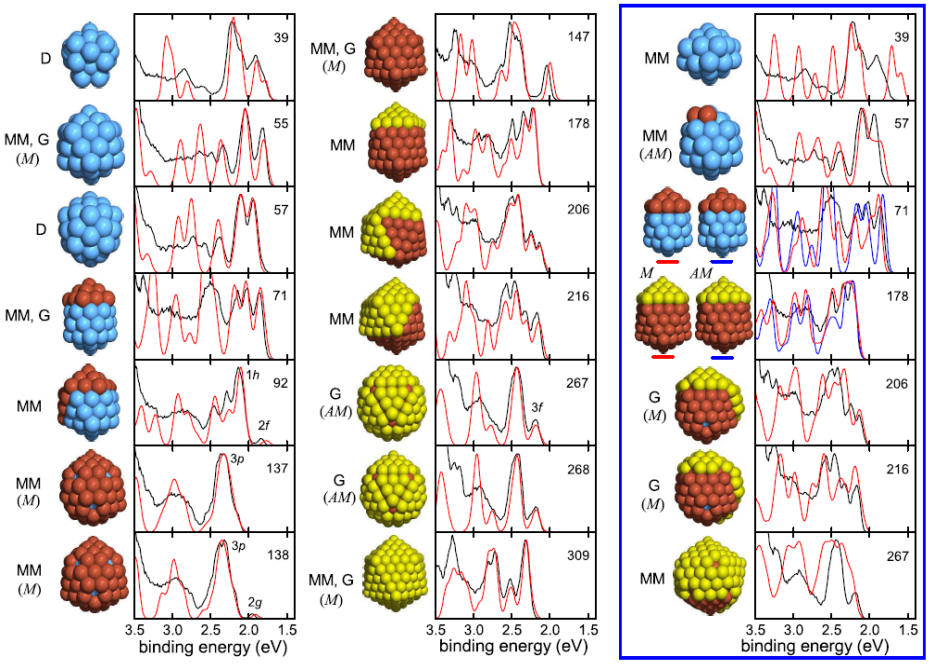
Na cluster anions IV : Photoelectron spectroscopy vs. electron density of states

55 –> 147 -> 309:

Icosahedral growth via overlayers



Kostko, Huber, Moseler, Issendorff, PRL **98**, 043401 (2007)

FIG. 2 (color online). Comparison of photoelectron spectra (black lines) to calculated electron densities of states (colored or shaded lines). The Kohn-Sham levels as obtained by DFT have been broadened by 70 meV width Gaussians and shifted as to reproduce the calculated electron affinity. The structures used in the calculations are indicated (left and center column: assigned ground state structures; right column: wrong structure candidates). The letters give the origin of the structures (MM: ground state structure for Murrell-Mottram potential [26], G: ground state for Gupta potential [26], D: ground state only within DFT) and indicate the structural motif of closed and open shell icosahedral structures (M/AM: Mackay/anti-Mackay overlayer [29]).

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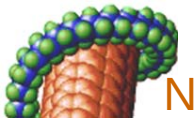

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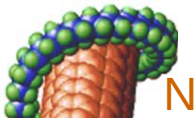
Thermodynamic properties



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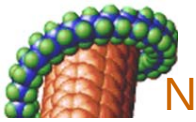
Thermodynamic properties - general

- Thermodynamics of small systems complicated and not always well defined !
- Experimental concerns: formation of clusters depends on source conditions, sometimes driven by thermodynamics, sometimes kinetics
- Nanoclusters exhibit a rich palette of thermodynamic phenomena: size-dependent melting, surface pre-melting, solid-solid structural transitions, freezing transitions, coalescence phenomena…
- Sometimes surprises in store: ”non-melting clusters” (melting point appears to be higher that in bulk, e.g. Sn ← bonding different in clusters)
- Bi-stability of ”phases”
- Experimentally the best studied cluster melting problem: Na clusters, work by Haberland group (original exp: Nature **393**, 238 (1998) + many later papers)
- Computational challenge: sampling of the phase-space
- Good review: Baletto, Ferrando, Rev. Mod. Phys. 77, 371 (2005)



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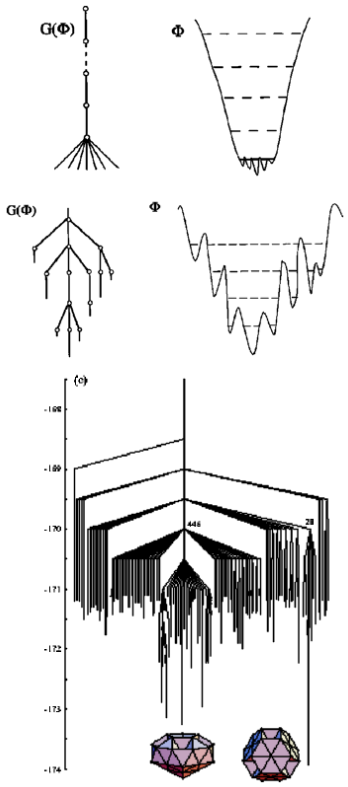
Global optimisation and potential energy surfaces



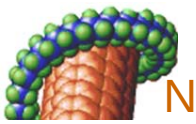
- Generally: finding **the** global optimal geometry for a given cluster size is a highly non-trivial problem

- A well-known example: 38-atom Lennard-Jones cluster has a narrow funnel for the global TO ground-state, but a wide funnel for icosahedral local minima

- A useful website for global minima: Cambridge Cluster Database www-wales.ch.cam.ac.uk./CCD.html

FIG. 11. (Color in online edition) Disconnectivity diagrams: Top panel, schematic of a single-minimum potential-energy surface (PES) with weak noise; center panel, a single-funnel PES. The disconnectivity diagrams of these two panels show at which energetic level the different local minima of a PES can be considered connected. Adapted from Becker and Karplus, 1997. The lowest panel gives the disconnectivity diagram for the complete double-funnel PES of the Lennard-Jones cluster of size 38. Figure courtesy of Jonathan Doye.

Rev Mod Phys. **77**, 371 (2005)



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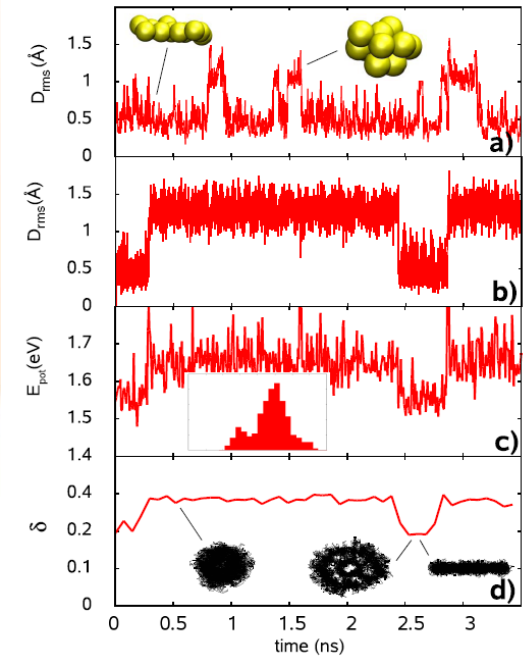
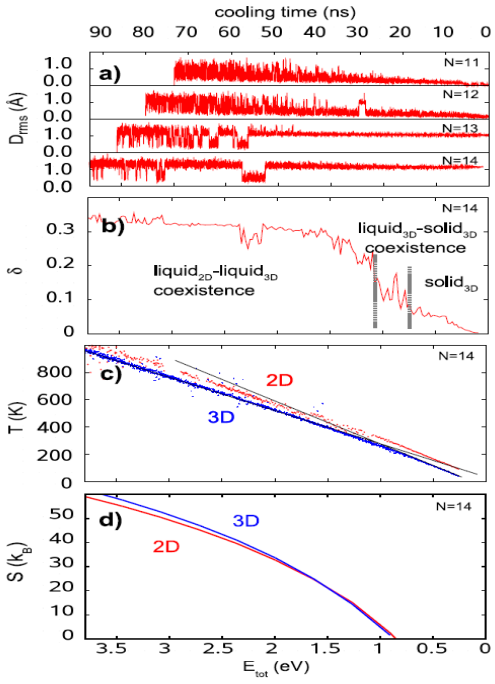
Dynamics of gold clusters from DFT-TB

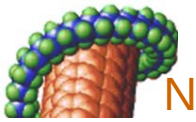
MD of Au11- at 750 K:
co-existence of 2D/3D liquid



Supercooling to ”wrong” dimensionality
(experimental time scale of cooling:
0.1 to 10 microseconds)



Koskinen et al, PRL 98, 015701 (2007)
Video in EPAPS



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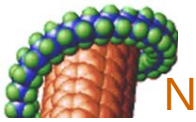
Chemical and catalytic properties of gold clusters



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Chemical and catalytic properties of gold clusters

- Bulk gold inert
- Finely dispersed gold (as nanoparticles) catalytically active, for review see eg. Haruta, Catal. Today **36**, 153 (1997)
- Oxide-supported size-selected clusters catalyze CO oxidation (Yoon, Häkkinen, Landman, Wörz, Antonietti, Abbet, Judai, Heiz, Science **307**, 403 (2005))
- Active site / charge state under debate
- Known for long: gold atom chemically active in many oxidation states (rich complex chemistry)
- Gas-phase reactivity with O2: anionic gold needed, highly size-dependent reactivity
- Reactivity associated with electron transfer to O2 π^* orbital

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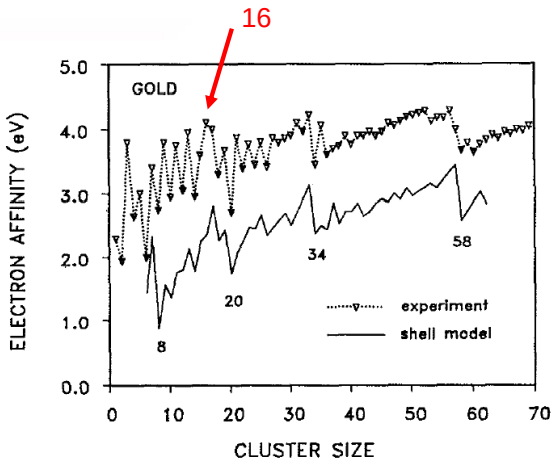
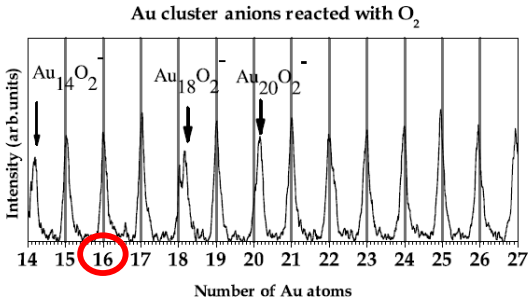
Gold: Electron affinity & reactivity with O2



Taylor et al JCP 96, 3319 (1992)

Anomalously inert Au16-



Gantefor group
CPL 377, 170 (2003)

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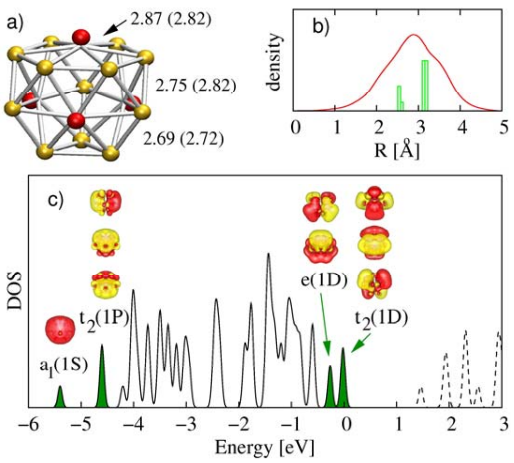
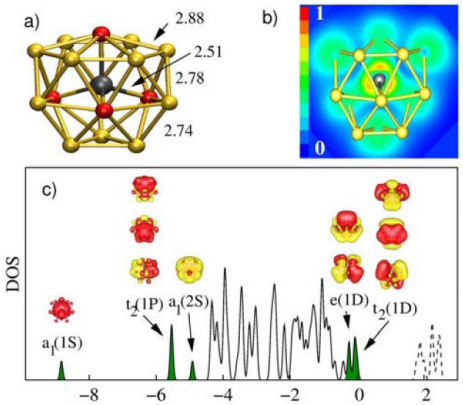
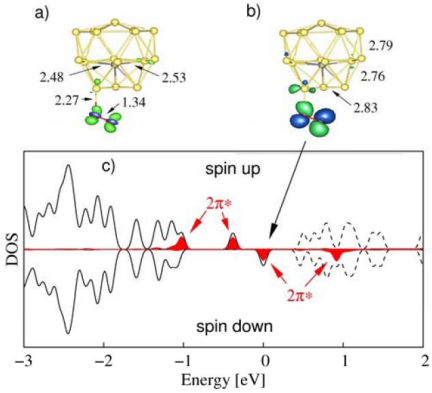
Au16 : electronic structure and reactivity





Si@Au16



Si@Au16-
+ O2

Au16 double-anion is a closed-electron-shell cluster with ”18e” shell closing (jellium-type 1S, 1P, 1D shells in a cage) → high EA → no electron transfer to O2 → no reactivity

Dope with Si → ”20e” shell closing (2S now in) → anion now reactive with O2

Catalytic oxidation of CO by gas-phase Au_2^-

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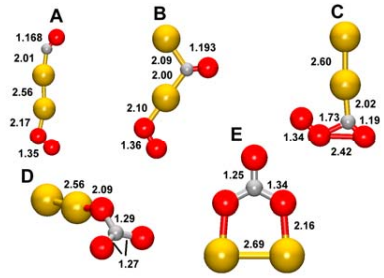
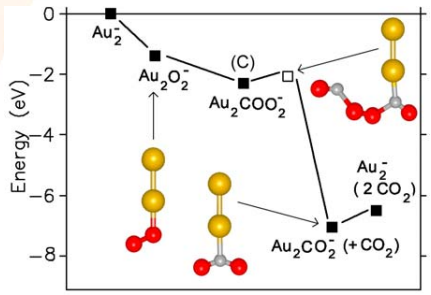
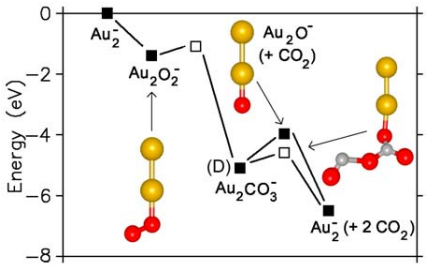
- Low-T activity (low barriers)
- Key intermediates: $AuCOO_2^-$ (C)
  or $AuCO_3^-$ (D)
- 2 scenarios I, II
- Eley-Rideal mechanism

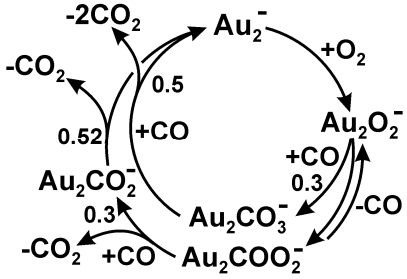


I



II





J. Am. Chem. Soc. 125, 10437 (2003)
Theory: Häkkinen, Landman
Experiment: Wöste group (Berlin)

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Summary: Cluster = a system with some ions and electrons !