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# Spring College on Computational Nanoscience

*17 - 28 May 2010*

## Chemically stabilized gold nanoclusters - building blocks of nano-matter?

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# Chemically stabilized gold nanoclusters – building blocks of nano-matter?

Hannu Häkkinen

Lecture 2

Trieste 5/2010

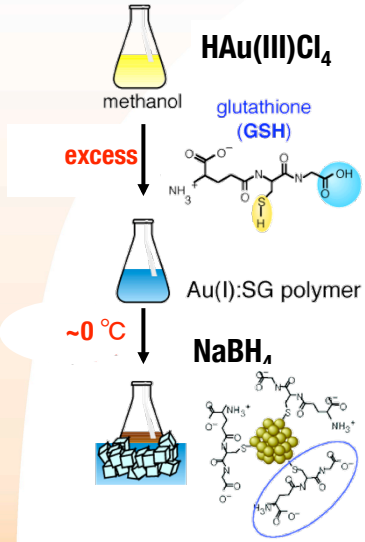


## Suggested reading

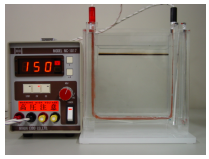

- P.D. Jadzinsky et al, Science 318, 430 (2007)
- R. Price and R.L. Whetten, Science 318, 407 (2007)
- M. Walter et al, Proc. Natl. Acad. Sci USA 105, 9157 (2008)
- H. Häkkinen, Chem. Soc. Rev. 37, 1847 (2008)
- J. Akola et al, J. Phys. Chem. C ASAP article 4/2010 (DOI: 10.1021/jp1015438)

## Size-selective synthesis of Au:SG clusters

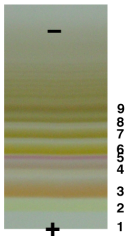
[ originally: Brust-Schiffrin method, Chem. Comm. (1994) 801 ]




*Tsukuda group*
*JACS* 2004, *126*, 6518.
*JACS* 2005, *127*, 5261.



Polyacrylamide gel electrophoresis(PAGE)

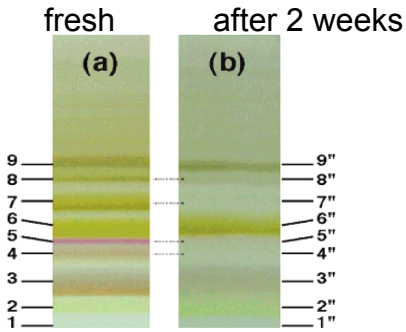




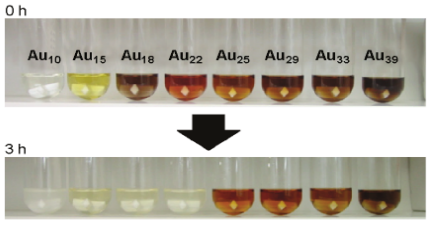

Several metastable sizes & compositions

Smallest thermodynamically stable composition:
$Au_{25}(SR)_{18}^{q}$ (q=+1,0,1)
Anion most abundant in gasphase (ESI, Murray & Kappes 2007)

Mass spectrometry:
LDI / MALDI, ESI

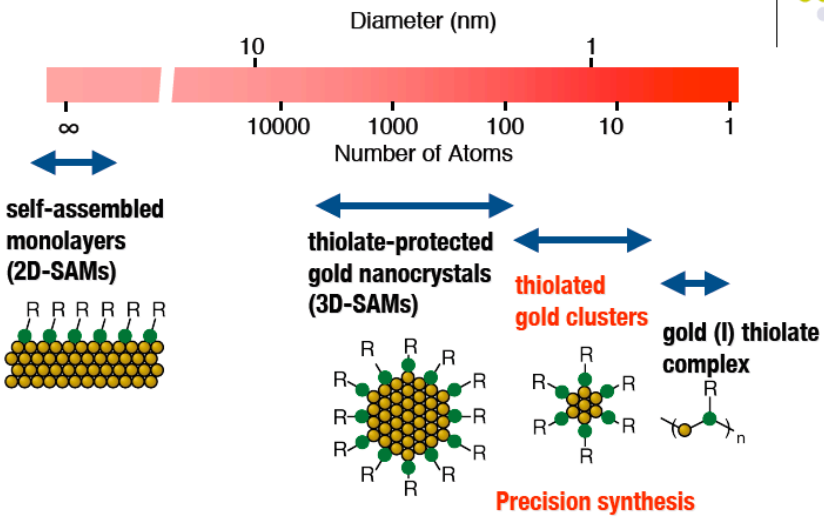



Negishi et al, *JACS* 127, 5261 (2005)




Shichibu et al, *Small* 3, 835 (2007)

# Thiolated gold clusters: missing link




Precision synthesis

Structure and physicochemical properties vs. compositions

*Tsukuda, 2006*
*ISSPIC Göteborg*



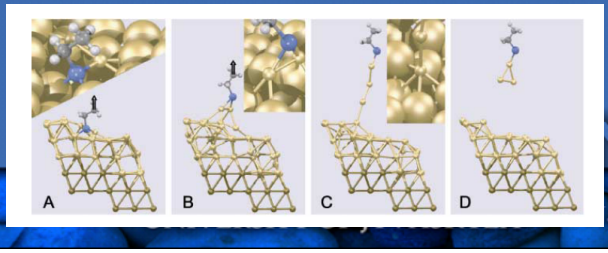
Hannu Häkkinen, Nanoscience Center, University of Jyväskylä

Bonding considerations (DFT/GGA):

Au-SR bond 2.5 eV (a single thiolate)
Au-Au bond 2.3 eV (Au dimer)

Au binding to surface : (c/12)*Ecoh (bulk)
(111): (9/12)*3.8 eV = 2.85 eV
(100): (8/12)*3.8 eV = 2.5 eV
(110): (7/12)*3.8 eV = 2.2 eV

Kruger, Fuchs, Rousseau, Marx, Parrinello, PRL 2002
pulling Au chain from Au surface by using S-Au bond as a c

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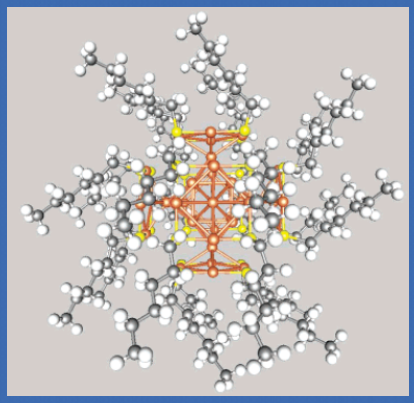
## "Divide & Protect" structure idea:

(a) (Au-SR)x rings protecting the central Au cluster
(b) Au in 2 different oxidation states: Au(0) in the core, Au(I) in the rings
(c) A significant % of Au atoms NOT in the core !



E.g: Au38(SR)24 = Au14 + 6 x (Au-SR)4
Häkkinen, Walter, Grönbeck, J Phys. Chem. B 110, 9927 (2006)

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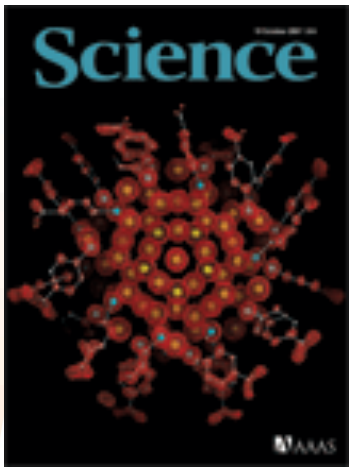
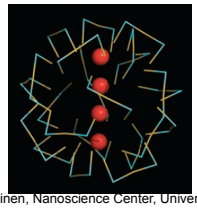


Science 19 Oct 2007

**Structure of a Thiol Monolayer-Protected Gold Nanoparticle at 1.1 Å Resolution**

X-ray crystallographic determination of $Au_{102}(p\text{-}MBA)_{44}$ cluster by R. Kornberg group (Stanford)

Pablo D. Jadzinsky,[1,2*] Guillermo Calero,[1*] Christopher J. Ackerson,[1†] David A. Bushnell,[1] Roger D. Kornberg[1‡]

CHEMISTRY

**Nano-Golden Order**

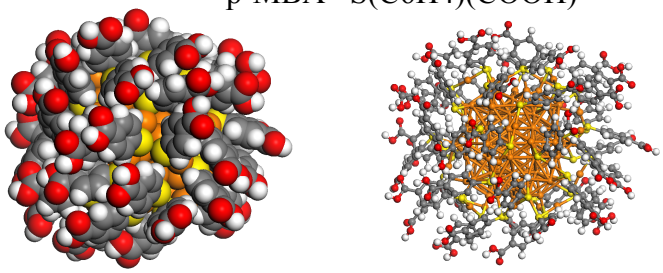
Robert L. Whetten and Ryan C. Price

An experimental tour de force reveals the crystal structure of a gold-thiolate nanocrystal compound and the surprising nature of the gold-sulfur bonding.

Hannu Häkkinen, Nanoscience Center, University of Jyväskylä

## Au102(p-MBA)44, Two visualizations

p-MBA =S(C6H4)(COOH)



Initial coordinates: Jadzinsky et al Science Oct 19, 2007
- hydrogens added & structure relaxed

Full complex: 762 atoms and 3366 valence electrons

Large-scale scalar-relativistic DFT/PBE calculations with GPAW and CP2K
http://cp2k.berlios.de ; https://wiki.fysik.dtu.dk/gpaw

Walter, Akola, Lopez-Acevedo, Jadzinsky, Calero, Ackerson, Whetten, Grönbeck, Häkkinen, PNAS 105, 9157 (2008)

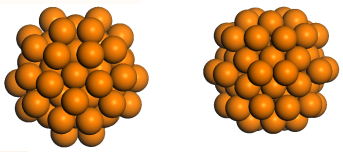
See also: Li, Galli, Gygi, ACS Nano 2, 1896 (2008); Gao, Shao, Zeng, ACS Nano 2, 1497 (2008)

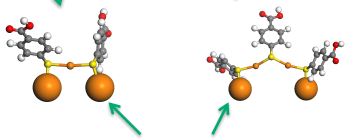


## Core – shell (OR: divide & protect) structure

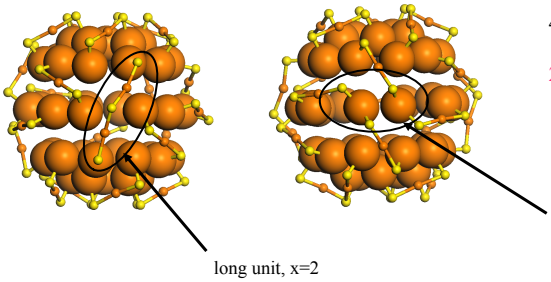
$Au_{102}(SR)_{44}$ = $Au_{79}$ + $(RS\text{-}Au\text{-}SR)_{19}$ + $(RS\text{-}Au\text{-}SR\text{-}Au\text{-}SR)_2$

Au79 core (D5h)





Core atoms



long unit, x=2

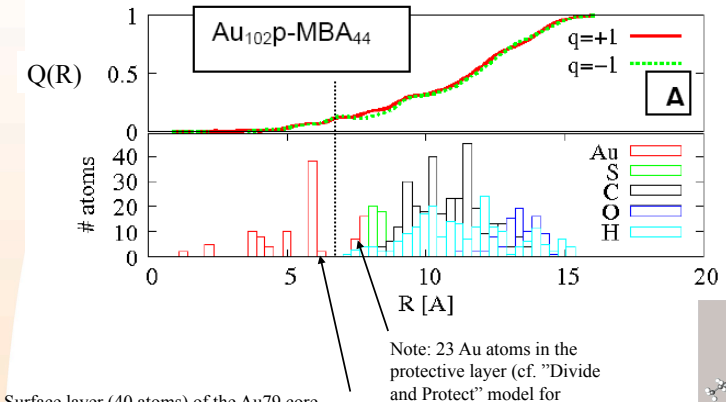
40-atom surface of the core
+
21 $(RSAu)_x$-SR units
(x=1 for 19 units and
x=2 for 2 units)

2 Au(core) atoms with 2 SAu bonds each

Walter et al, PNAS 2008

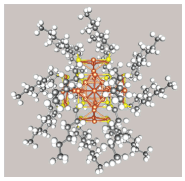
## $Au_{102}$ has a metallic $Au_{79}$ core !

Radial analysis of charge re-distribution upon ionizing:
virtually no changes inside 5Å radius, 10 % of the charge at the surface of $Au_{79}$,
90% charging inside the $Au_{23}(p\text{-}MBA)_{44}$ protective layer




Surface layer (40 atoms) of the Au79 core

Note: 23 Au atoms in the protective layer (cf. "Divide and Protect" model for Au38(SR)24 = Au14(Au4SR4)6 Häkkinen, Walter, Grönbeck, JPCB 110, 9927 2006))

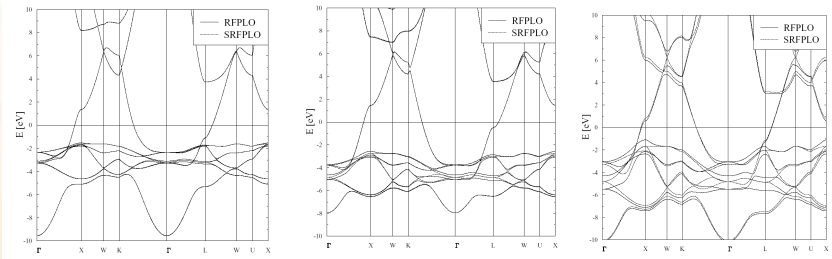


Walter et al, PNAS 2008



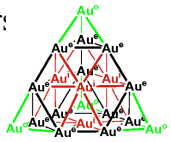
## Band structure of noble metals

Cu Ag Au

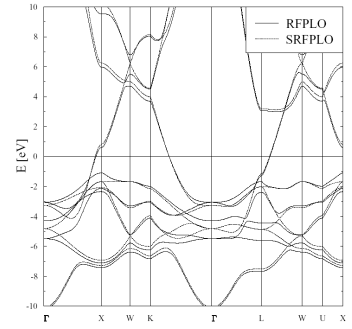


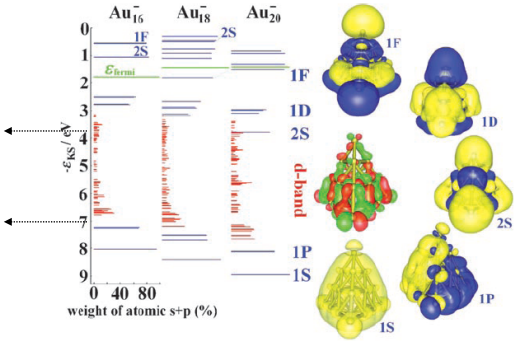

Ingo Opahle, PhD thesis Dresden 2001
Also: for Au: N.E. Christensen 1970's

## Electronic structure of free Au clusters
## Comparison to bulk band structure



$Au_{20}$, $T_d$ structure




"Band picture" of gold clusters:
The Au(5d) derived band
"embedded" in the Au(6s6p) derived
conduction electron shells, which
can be found at $E \approx E_{bottom}$ and $E \approx E_{fermi}$

Yoon, Koskinen, Huber, Kostko,
von Issendorff, Häkkinen, Moseler,
Landman, ChemPhysChem 8, 157 (2007)



## (Global) angular momentum analysis of
## Au(6s)-derived "conduction electron" states in the gold core

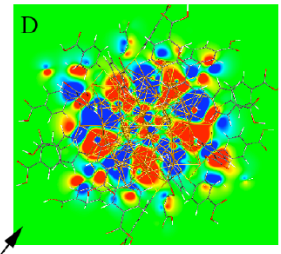
$$c_{i,l}(R_0) = \sum_m \int_0^{R_0} r^2 dr \, | \varphi_{i,lm}(r) |^2$$

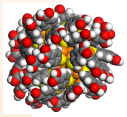
$$\varphi_{i,lm}(r) = \int d\hat{r} Y^*_{lm}(\hat{r}) \psi_i(\vec{r})$$

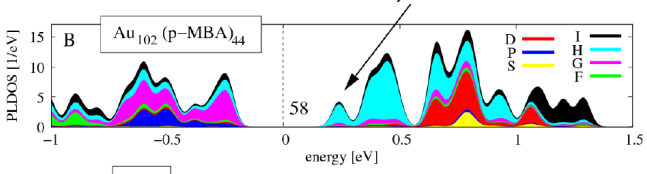
Evaluate the coefficients c(R) for each
Kohn-Sham state i (done up to $l = 6$: I-symmetry)

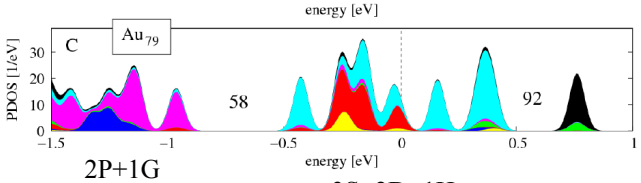
# Electronic structure: Angular momentum projected DOS around Fermi level (at E=0)

- Au79 core supports the (expected) shell structure (58, 92 e gaps , proper symmetries)
- Upon dressing the core with 21 ((RSAu)x-SR) units, 21 shell electrons depleted from the 3S+2D+1H manifold (→ surface-covalent S-Au(core) bonds), thereby revealing the 58 e gap, which becomes the HOMO-LUMO gap of the protected cluster!! Sterical protection, electronic closed shell → "A NOBLE-GAS SUPERATOM"





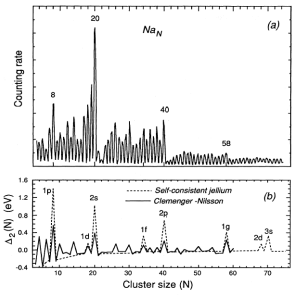




2P+1G

3S+2D+1H

Walter et al, PNAS 2008





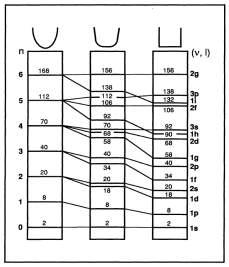




FIG. 2. Energy-level occupations for spherical three-dimensional, harmonic, intermediate, and square-well potentials. After Mayer and Jensen, 1955.

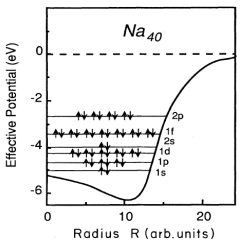
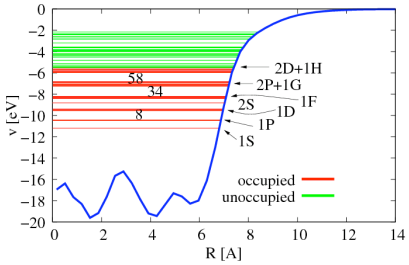


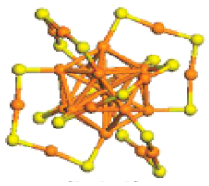

FIG. 3. Self-consistent effective potential of jellium sphere corresponding to $Na_{40}$ with the electron occupation of the energy levels. After Chou *et al.*, 1984.



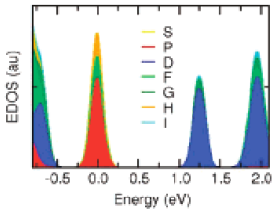

Au79 KS levels and effective radial potential
6s-only calculation (M. Walter)
H. Häkkinen, Chem. Soc. Rev 2008

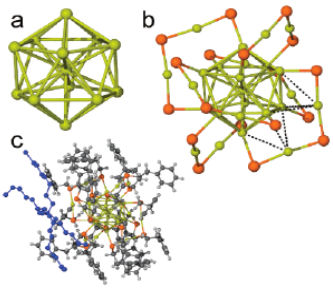
## Success of the superatom model: The case of $Au_{25}(SR)_{18}^{-1}$

Predicted: $Au_{25}(SR)_{18} = Au_{13} + 6\,[Au_2(SR)_3]$ Observed !



Akola et al *JACS* 130, 3756 (2008)



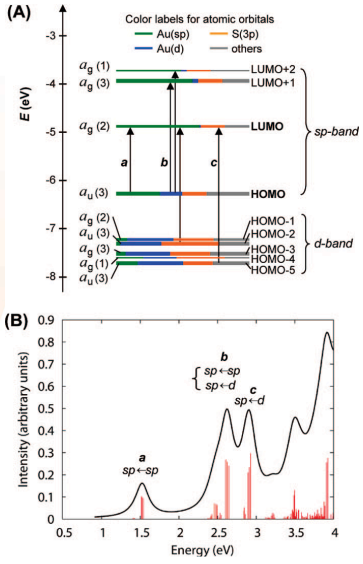




Heaven et al *JACS* 130, 3754 (2008)
Zhu et al *JACS* 130, 5883 (2008)
TOA+ w/ Au25(SR)18- R=(CH2)2Ph

$Au_{25}(SR)_{18}^-$ is a 8e superatom:
25 – 18 + 1 = 8 !
13 – 6 + 1 = 8 !

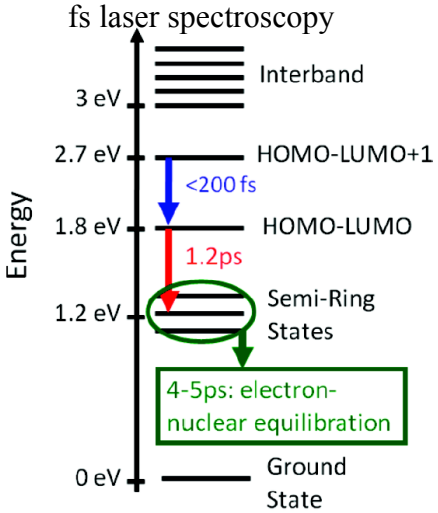
Hannu Häkkinen, Nanoscience Center, University of Jyväskylä

## Analysis of transitions




Zhu, Aikens, Hollander, Schatz, Jin
*JACS* **130**, 5883 (2008)

## Superatom picture confirmed by fs laser spectroscopy




Miller, Womick, Parker, Murray, Moran, JPC-C 113, 9440 (2009)

Decay of electronic excitations into vibrations important (Akola et al in preparation)

Hannu Häkkinen, Nanoscience Center, University of Jyväskylä

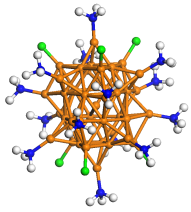
Phosphine-chemistry of Au clusters

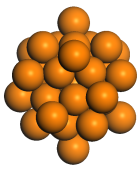
- various low-nuclearity Phosphine / halide stabilized gold compounds known & structure-resolved since late 1970's ! (review: Mingos in Schmidbaur: Gold book)
- Au39 compound crystallized & characterized by Teo et al 1992 (JACS):

Any similarites to thiolate-chemistry? Traditional answer : NO!



Compounds studied here:

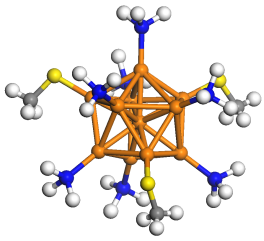


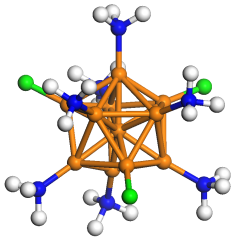


$D_3$

Au39(PH3)14Cl6-

Au39 core



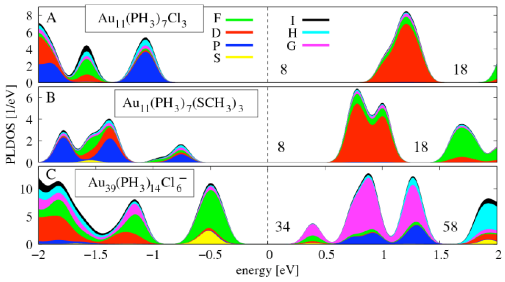


$C_{3v}$

Au11(PH3)7(SCH3)3

Au11(PH3)7Cl3

## Au11 and Au39 superatoms



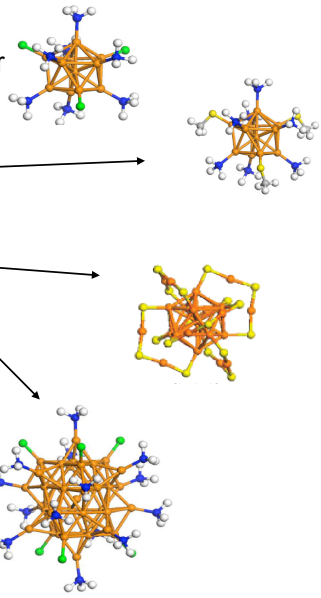

Surviving gaps: 8, 18, 34, 58 electrons
8 e HL gap in Au11
34e shell closing in Au39 compound:
below HL gap : 2S/1F character (as expected)
above HL gap: 1G/2P character (as expected)



## X-ray structures & orbital analysis establish a simple rule:

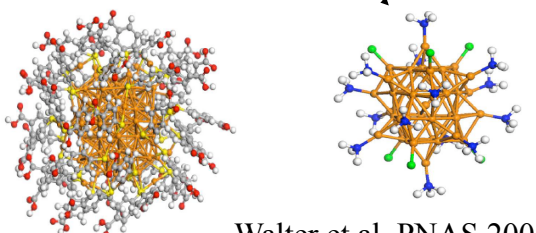
$( L_S \bullet Au_N X_M )^Z$ is stable IF:
N (Au,6s) – M – z = n*, n* = shell closing number

| | |
|---|---|
| $Au_{11}(PH_3)_7Cl_3$ | n* = 8 ($1S^21P^6$) |
| $Au_{11}(PH_3)_7(SCH_3)_3$ | 8 |
| $Au_{13}(PH_3)_{10}Cl_2^{3+}$ | 8 |
| $Au_{25}(SR)_{18}^-$ | 8 |
| $Au_{39}(PH_3)_{14}Cl_6^-$ | 34 (8e- $1D^{10}2S^21F^{14}$) |
| $Au_{102}(SR)_{44}$ | 58 (34e- $2P^61G^{18}$) |



Here L = $PR_3$
and X = Cl, SR

L "weak ligand"
X electron
withdrawing
(localizing) ligand



Walter et al, PNAS 2008

# HOMO-LUMO GAPS (DFT/PBE)

| Shell closing | Experiment | | Theory (this work) | |
|---|---|---|---|---|
| | Cluster | Gap | Cluster compound | Gap |
| 8e ($1S^21P^6$) | | | $Au_{11}(PH_3)_7(SMe)_3$ | 1.5 eV |
| 8e | | | $Au_{11}(PH_3)_7Cl_3$ | 2.1 eV |
| 8e | | | $Au_{13}(PH_3)_{10}Cl_2^{3+}$ | 1.8 eV |
| 8e | | | $Au_{25}(SMe)_{18}^-$ | 1.2 eV |
| 34e (8e + $1D^{10}2S^21F^{14}$) | $Au34^-$ (a) | 1.0 eV | $Au_{39}Cl_6(PH_3)_{14}^-$ | 0.8 eV |
| 58e (34e + $2P^61G^{18}$) | $Au58^-$ (b) | 0.6 eV | $Au_{102}(p\text{-}MBA)_{44}$ | 0.5 eV |
| 58e | | | $Au_{102}(SMe)_{44}$ | 0.5 eV |

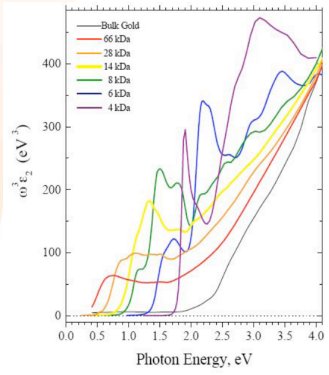
(a) Lechtken et al, ACIE 2007
(b) Häkkinen et al, PRL 2004

Walter et al, PNAS 2008



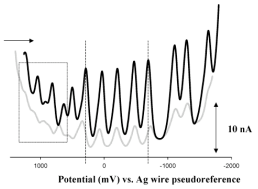
The 29 kDa cluster, known since late 1990's

- most recent compositions, Tsukuda group JACS June 2008: Au144(SR)59 and Jin group Au144(SR)60 (Nano Letters 2009)
- no apparent "HOMO-LUMO gap" from electrochemistry (Murray, Quinn)
- absorption edge well into IR: < 0.5 eV
- structural hints from early work (Schaaff et al 2001, XRD factor from powders)
- what stabilizes this particle ?

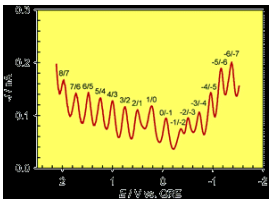



Wyrwas et al EPJD 2007

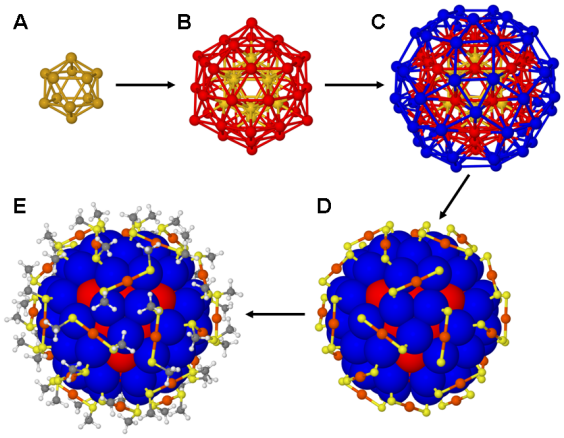
Hicks et al
JACS 124, 13322 (2002)




Quinn et al
JACS 125, 6644 (2003)



Our suggestion: 29 kDa = $Au_{144}(SR)_{60}$ = $Au_{114}(RSAuSR)_{30}$

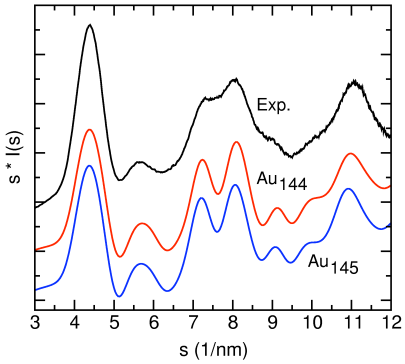



- 12-atom hollow shell, 30+12 shell = 54 atom Mackay Icosahedron
- 60 – atom rhombicosi-dodecahedron → 114-atom core, I-symmetry
- Arrangement of RS-Au-SR units chiral ( like $Au_{102}(SR)_{44}$ but unlike $Au_{25}(SR)_{18}$ )

Lopez-Acevedo et al, JPC-C 113, 5035 (2009)



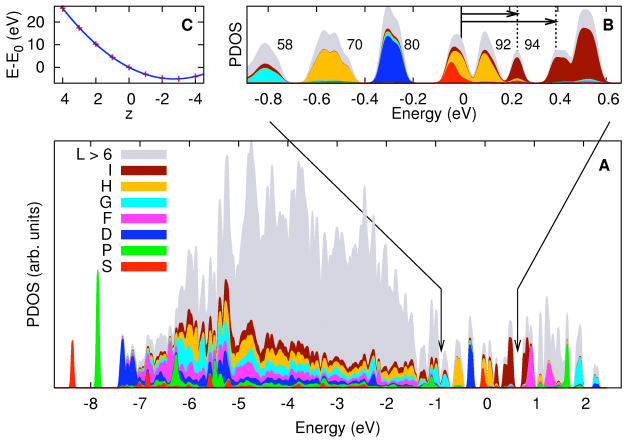
Theoretical vs. experimental X-ray structure factor




experiment: Schaaff, Shafigullin, Khoury, Vezmar, Whetten JPCB 105, 8785 (2001)

Lopez-Acevedo et al, JPC-C 113, 5035 (2009)

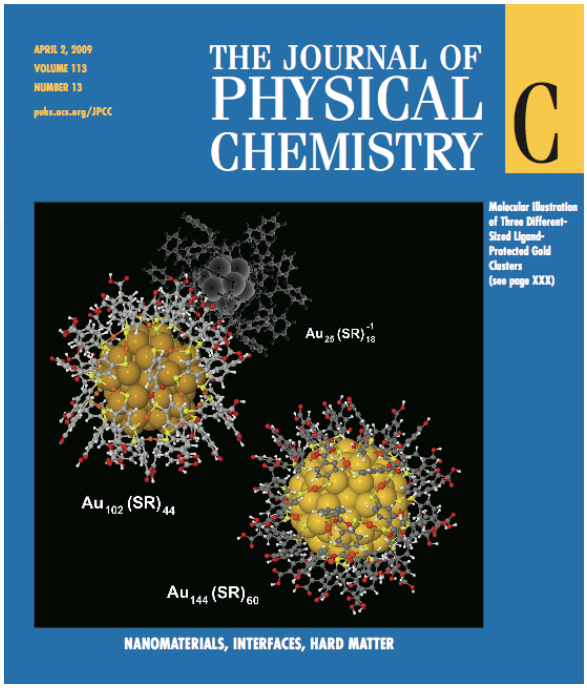
Lowest allowed transitions




- No HOMO-LUMO gap (z=0)
- lowest optically allowed excitations from H to I symmetry in the core
- classical Coulomb-staircase charging with voltage-steps e/C = 1.4 V, scales with realistic ε to about 0.2 – 0.3 V

Lopez-Acevedo et al, JPC-C 113, 5035 (2009)

Hannu Häkkinen, Nanoscience Center, University of Jyväskylä

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## The Periodic Table of Thiolate or Phosphine-Halide Gold Cluster Superatoms

$L_S \bullet Au_N X_M^z$
$n = N - M - z$

The table shows conduction electron numbers in the metal core and suggested compositions
Atomically resolved structures in RED

"Noble-atom group"

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | 2 |
| | | Semi-magic (core stabilized by strong prolate/oblate deformations) | | | | | | | 8 $Au_{11}(PR_3)X_3$ $Au_{25}(SR)_{18}^{-1}$ $Au_{13}(PR_3)_{10}Cl_2^{+3}$ |
| | 14 $Au_{38}(SR)_{24}$ | | | 16 $Au_{39}(SR)_{23}$ | | | | | 18 $Au_{44}(SR)_{28}^{-2}$ |
| | | | | | | | | | (20) $Au_{20}(PR_3)_8$ |
| | | | | | | | | | 34 $Au_{39}(PR_3)Cl_6^{-1}$ $Au_{68}(SR)_{34}$ |
| | | | | | | | | | (40) |
| | | | | | | | | | 58 $Au_{102}(SR)_{44}$ |
| | 84 $Au_{144}(SR)_{60}$ | Geometric shell closings dominate in these heavy superatoms ?? | | | | | | | 90/92 ?? $Au_{140\text{-}150}(SR)_{50\text{-}60}$ |

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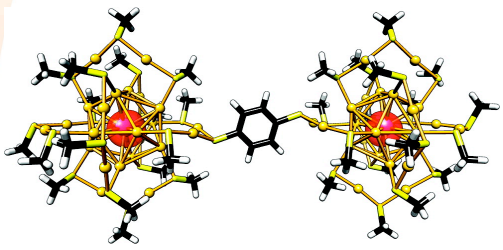
## How rigid / flexible is the superatom picture ?

- mixing/doping other metals (magnetic / non-magnetic) in the core
- Au core stabilized with other ligands (units) ?
- dimers, wires, networks, crystals of ligand-protected Au clusters?
- catalytic properties (lecture 3)



← A dimer of two Mn-doped Au25 clusters linked together by BDT, showing the spin-density of the system in a high ferromagnetic state (μ = 10 bohr magnetons)

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# Food for thought

- We start to (slowly) understand ”molecular metals”
- Superatom model provides a concept to account for ”itinerant / free” valence/conduction electrons in the metal core
- This concept is useful for understanding core shape, low-energy optical / NIR metal-metal transitions, (catalytic) reactivity of the metal core, magnetic properties of the core etc.
- $L_S \bullet Au_N X_M^z$, X = thiolate/halide  n = N – M – z  (1)
- Generalization of (1) seems possible

  recent example: $Au_N[Fe(CO)_x]_y^z$ clusters:

  n = N – 2y – z  for $Fe(CO)_4$

  n = N – 4y – z  for $Fe(CO)_3$