

Ligand-protected gold cluster superatoms

Hannu Häkkinen^{a,b}

*Departments of Physics and Chemistry, Nanoscience Center
University of Jyväskylä, Finland*

hannu.hakkinen@phys.jyu.fi

Synthesis, characterization, and functionalization of self-assembled, ligand-stabilized gold nanoparticles are long-standing issues in the chemistry of nanomaterials. Factors driving the thermodynamic stability of well-documented, discrete sizes and compositions have been largely unknown. The recent breakthrough in total-structure-determination of an all-thiolate-protected Au₁₀₂ cluster [1] triggered renewed interest in this field.

Herein, we provide a unified view of principles that underlie the stability of particles protected by thiolate (SR) or a combination of phosphine and halide (PR₃, X) ligands [2,3]. The picture has emerged from analysis of large-scale density functional theory calculations of structurally characterized compounds, namely Au₁₀₂(SR)₄₄, Au₂₅(SR)₁₈⁽⁻⁾, Au₃₉(PR₃)₁₄X₆⁽⁻⁾, Au₁₁(PR₃)₇X₃, and Au₁₃(PR₃)₁₀X₂⁽⁺³⁾, where X is either a halogen or a thiolate. Attributable to a compact, symmetric core and complete sterical protection, each compound has a filled spherical electronic shell and a major energy gap to unoccupied states. Consequently, the exceptional stability is best described by a “noble-gas superatom” analogy. The success of our superatom model was highlighted during this work via simultaneous and independent theoretical prediction [3] and experimental confirmation [4] of the same ground-state structure for the Au₂₅(SR)₁₈⁽⁻⁾ cluster.

Traditionally, the “phosphine chemistry” and the “thiolate chemistry” have been regarded as separate branches to prepare ligand-protected gold nanoparticles; no general, unifying theoretical concepts have been available to understand and classify the wealth of experimental information that points to well-defined, discrete compounds. Our work thus provides guiding principles for molecular-precision-synthesis and functionalization of these exciting building blocks of nano-materials that are finding applications in diverse fields of biolabeling, photonics, sensing and nanocatalysis.

^a Theory team: J. Akola, O. Lopez-Acevedo, M. Walter (Jyväskylä); H. Grönbeck (Chalmers, Gothenburg)

^b Collaboration: C. J. Ackerson, G. Calero, P.D. Jadzinsky, R. Kornberg (Stanford University); R.L. Whetten (Georgia Tech, Atlanta)

[1] P.D. Jadzinsky, G. Calero, C.J. Ackerson, D.A. Bushnell, R.D. Kornberg, *Science* **318**, 430 (2007).

[2] M. Walter, J. Akola, O. Lopez-Acevedo, P.D. Jadzinsky, G. Calero, C. J. Ackerson, R. L. Whetten, H. Grönbeck, H. Häkkinen, *Proc. Natl. Acad. Sci USA* in press (2008).

[3] J. Akola, M. Walter, R.L. Whetten, H. Häkkinen, H. Grönbeck, *J Am. Chem. Soc* **130**, 3756 (2008).

[4] M.W. Heaven, A. Dass, P.S. White, K. M. Holt, R.W. Murray, *J Am. Chem. Soc.* **130**, 3754 (2008).