

Metastability of a gold nanoring: Density-functional calculations

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First-principles calculations based on gradient corrected density functional theory show that a cluster of as few as 90 gold atoms can be stabilized in a ring structure having fcc (111) motif with the binding energy/atom and interatomic distance approaching 91% and 96% of the bulk values, respectively. Although the ring structure lies 0.139 eV/atom higher in energy than a polyicosahedral structure, the calculated frequencies are real. Thus under appropriate experimental conditions it may still be possible to synthesize a metastable form of gold nanoring, as found in the recent experiment.

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Gold is the preeminent noble metal, prized throughout history for its beauty, permanence, rarity, and resistance to corrosion and chemical reaction.¹ Thus the discovery² that gold nanoparticles are reactive has caused a great deal of interest in exploring the synthesis of gold at the nanoscale such as clusters,³⁻⁸ nano-wires,^{9,10} and nanoshells.¹¹⁻¹⁴ Because of their unique electronic, optical and catalytic properties, it is believed that gold nanostructures can have important applications in catalysis, molecular electronics, sensors, bioconjugate probes, gene mapping, and in the treatment of cancer and tumours.

Recently, gold in the form of nanoring with a diameter of about 100 nm has been synthesized.¹⁵ Compared to other forms of nanostructures, the nanoring acquires special properties.¹⁵ When light is directed at the ring, the electrons in the ring get excited and create a wave which in turn can resonate with the incoming light. Nanorings exhibit a redshift with respect to solid gold particles of similar size. Furthermore, the ring cavity provides a special space where molecules, drugs, and proteins can be stored. A fundamental understanding of the structure and stability of the gold nanoring is essential before the promise of a gold nanoring for technological applications can be realized. However, compared to the other extensively studied gold nanostructures such as clusters and wires, the study of a gold nanoring is in its primitive stage. One of the main unknowns is the atomic arrangements in the ring. It is well established that gold clusters prefer to form icosahedral and fcc-like stacking, while gold wire can have helical structure and bulk gold is fcc. Nothing is known about the atomic structure for a gold nanoring.

It is interesting to note the geometry of an Au₂₀ cluster, which was studied experimentally and theoretically.³ The lowest energy structure was found to have a compact tetrahedral geometry with four of its surfaces having fcc (111) packing. By comparing the calculated adiabatic electron affinities and vertical detachment energies with experiment it was shown that this indeed is the ground state of an Au₂₀ cluster. We recall that in the jellium model for nearly free electrons, a cluster with 20 electrons is unusually stable and hence is referred to a magic number. In fact it was found to

have a (HOMO-LUMO) gap of 1.77 eV which is even larger than that of C₆₀. This magic Au₂₀ cluster shows the trace of fcc packing in nanoscale. To explore the possible geometric packing of a gold nanoring, we have considered an Au₉₀ cluster. This choice was based on following factor. Since gold clusters prefer both icosahedral and fcc (111) packing, initial structures with these motifs can be constructed out of 90 gold atoms.

We have used^{16,17} density functional theory and generalized gradient approximation for exchange and correlation.¹⁸ In order to optimize the geometry, a plane-wave basis set is adopted with the projector-augmented wave (PAW) method developed by Blöchl¹⁹ and recently adapted by Kresse and Joubert.²⁰ The particular advantage of the PAW method over the ultra soft pseudo-potentials is that the pseudoaugmentation charge can be avoided. The structure optimization is symmetry unrestricted with conjugate-gradient algorithm. We have used super-cells with 14 Å vacuum spaces along the *x*, *y*, and *z* directions for all the calculated structures. The Γ point is used to represent the Brillouin zone due to the large supercell. The cutoff energy is taken as 300 eV, and the convergence criteria for energy and force are 10⁻⁴ eV and 0.01 eV/Å, respectively. The accuracy of the method was tested by computing the structure and properties of the well-known magic clusters of Au₁₂W and Au₂₀. For Au₁₂W, the bond lengths of W-Au and Au-Au are 2.74 and 2.88 Å, respectively, in agreement with the values of 2.75 and 2.89 Å in previous studies.^{4,21} The HOMO-LUMO gap is 1.78 eV, in good agreement with the experimental finding of 1.68 eV.⁴ The lowest energy structure of Au₂₀ was found to have *T_d* symmetry and the HOMO-LUMO gap is 1.70 eV, which is in agreement with experiment (1.77 eV) and previous calculations.³ For the simplest case of dimer Au₂, the calculated bond length is 2.48 Å, in agreement with the experimental value of 2.50 Å.²²

Determination of the geometry of a cluster containing as many as 90 atoms is a formidable task as there can be an enormous number of local minima in the potential energy surface. The optimized geometry may often depend upon the starting geometry particularly if the local minimum in the potential energy surface is protected by large energy barriers.

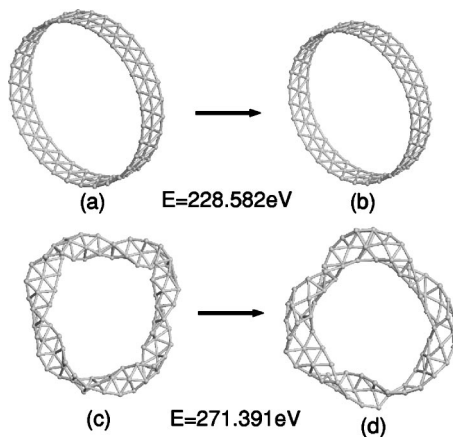


FIG. 1. Geometries of an Au_{90} ring based on FCC (111) strand. The numbers give the total binding energy E of the optimized structure.

With this realization in our mind, we have used some of the characteristics of bulk and smaller clusters of gold in constructing the initial geometries. Note that bulk Au has the fcc structure. An octahedron can be thought of as the building block of fcc structures. In addition, the (111) surface of a fcc crystal is very stable. Since clusters are characterized by large surface areas, a stable gold cluster can exhibit octahedral and/or (111) motif. The ground state of an Au_{20} cluster has been found to possess fcc (111) packing.³ Small clusters of gold also exhibit pentagonal structures and an Au_{13} cluster is an icosahedron. Thus we have used fcc (111) packing, octahedral, and pentagonal arrangement of atoms or combinations of these in formulating the starting geometries. The optimizations were then carried out without symmetry constraint.

We have used eight different starting geometries as discussed following. The first structural motif we chose is a strand from an Au (111) face. By cutting the strand and folding it, we get Fig. 1(a). Upon optimization the structure remains [Fig. 1(b)]. However when the ring is twisted to a helical form [Fig. 1(c)], the binding energy, defined as the energy difference between the cluster and the separated atoms, of the resulting optimized structure [Fig. 1(d)] increases considerably, suggesting that a single strand ring is not stable energetically. In the third starting configuration we used a torus structure [Fig. 2(a)] that consists of 18 pentagons which are important building blocks for gold nanostructures.^{6,9} In addition, the torus surface is fcc-(111)-like. However when fully optimized the structure [see Fig. 2(b)], is seriously distorted and consists of several fragments with fcc (111) motif. The binding energy is increased by 25 eV as compared to the helixlike single strand structure in Fig. 1(d). In an attempt to further stabilize the torus structure, we constructed a stuffed torus by adding a central strand consisting of 15 Au atoms, which links 15 pentagons [Fig. 2(c)], similar to the stuffed gold wire.⁸ However, in the final structure [Fig. 2(d)], the 15 Au atoms in the central strand moved to the surface, and the total binding energy is reduced by 2 eV compared to the optimized structure from Fig. 2(b). In Fig. 3(a) we show a different starting geometry in which the Au_{90} cluster is constructed from Au_6 octahedrons by sharing a triangular face.

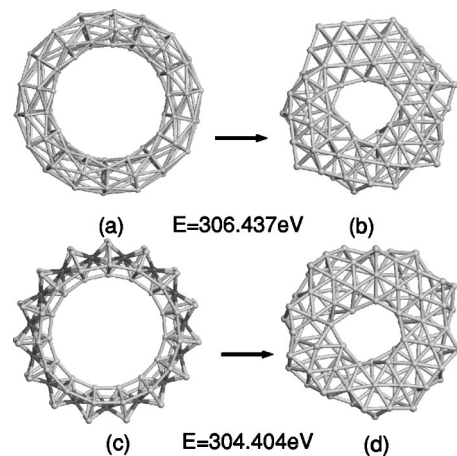


FIG. 2. Geometries of an Au_{90} ring based on pentagons assembled torus. The numbers give the total binding energy of the optimized structure.

After relaxation, the structure is distorted, and the stacking feature of fcc-(111) appears [Fig. 3(b)]. The binding energy is about 15 eV less than the structure in Fig. 2(b), indicating the Au_6 octahedron cluster assembled ring is not stable energetically. We also assembled a ring structure with the icosahedra Au_{13} as the building block [Fig. 3(c)]. However the cluster identity could not be kept upon relaxation, and there is no trace of the fcc (111) feature in the optimized geometry [Fig. 3(d)]. Although the binding energy is considerably improved as compared to Fig. 3(b), it is still 0.4 eV less than that in Fig. 2(b).

Thus far the structure in Fig. 2(b) is more stable than the others, and this structure was obtained from the stacking of pentagons with fcc-(111)-like motif. This suggests that fcc (111) packing is a preferred arrangement. Following this clue, we constructed a crownlike structure shown in Fig. 4. We began with nine centered pentagons to make a ring by sharing a common bond [Fig. 4(a)]. Then an Au-9-atom ring was added as an inner strand. This constitutes a 45-atom cluster [Fig. 4(b)]. Finally we combined these two structures to get Au_{90} , where the outer shell consists of centered pentagons and hexagons. Figs. 4(c) and 4(d) show the top and side

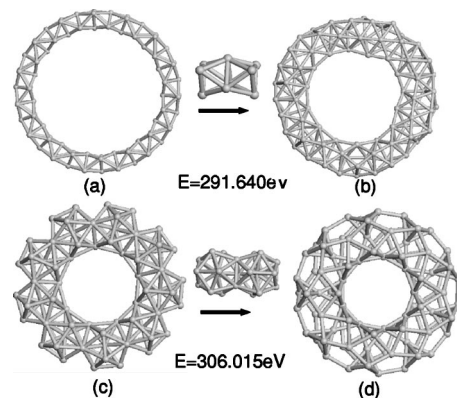


FIG. 3. Geometries of an Au_{90} ring based on cluster assembled ring with octahedron Au_6 (a) and icosahedron Au_{13} (b). The building blocks are also shown with triangle face sharing.

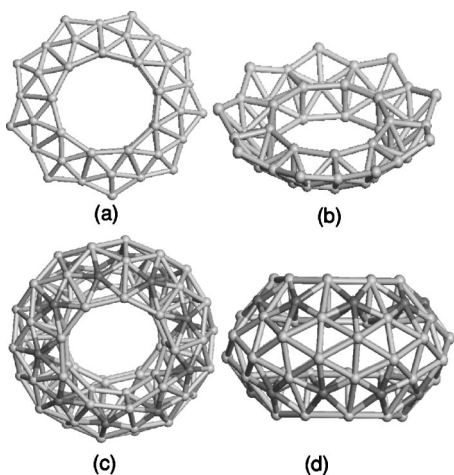


FIG. 4. Construction of the initial geometry of an Au₉₀ ring by using centred pentagons and hexagons.

view for this initial geometry. After optimization, the ring finally acquires D_{3d} symmetry, the two inner nine-atom rings in the initial structure bind together forming a compound inner strand [Fig. 5(a)]. In the outer shell the pentagons are broken, but the centred hexagons as well as the fcc-(111)-like features remain [Fig. 5(b)]. The 18 Au atoms in the inner strand are capped on the 18 squares on the outer shell. The top view and side view for the optimized geometry are shown in Figs. 5(c) and 5(d).

The total binding energy of this structure is 5.1 eV lower than the one from Fig. 2(b), and thus is the most stable one among the isomers studied thus far. The average binding energy per atom is 3.462 eV, while the corresponding value in bulk gold is 3.810 eV,²³ so the binding energy in this nanoring is 91% of the bulk value. The average bond length is 2.75 Å which is 96% of the bulk value. To check the dynamic stability of this structure, we calculated the frequency spectrum and found all the frequencies are real, suggesting that this nanoring is stable energetically as well as dynamically. Figure 6(a) shows the vibrational density of states. The pair correlation function, given in Fig. 6(b), shows that most of the atoms have a narrow distribution in

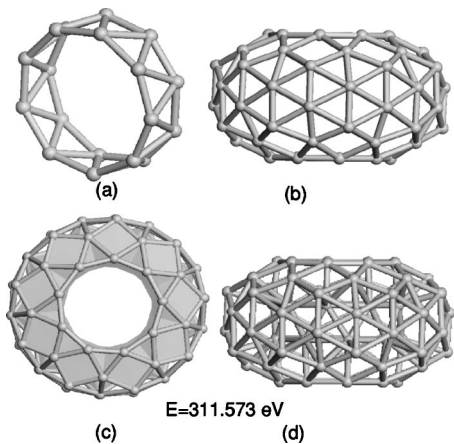


FIG. 5. The optimized Au₉₀ ring from the structure in Fig. 4. Inner shell (a), outer shell (b), top view (c) and side view (d).

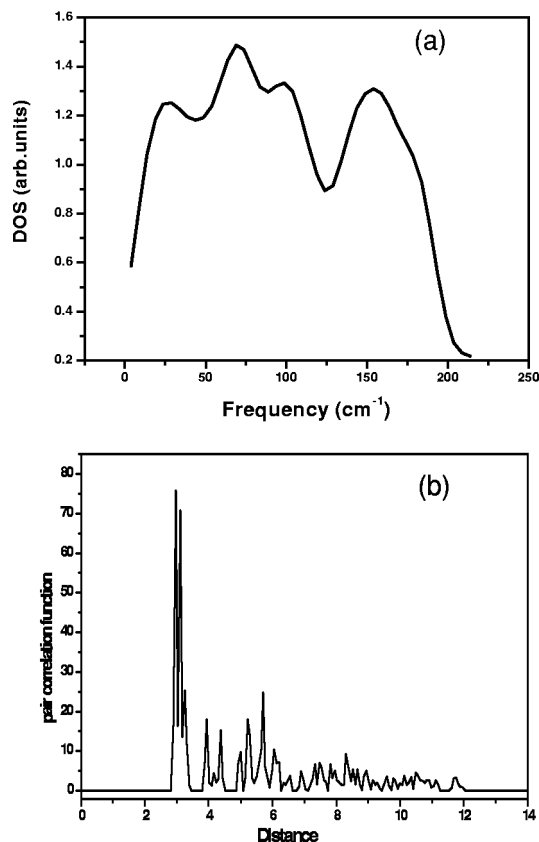


FIG. 6. The vibrational density of states (a) and pair correlation distribution function (b) for the Au₉₀ ring in Fig. 5.

the nearest neighbor bonds. Although we cannot guarantee that the geometry in Fig. 5 is the ground state structure of the Au₉₀ ring it is stable energetically and dynamically. We will show in the following that this ring constitutes a metastable state of Au₉₀ as compared to the compact one.

We looked into the Au₉₀ cluster having the structure of rings. As pointed out before, the magic Au₂₀ cluster has a compact tetrahedral structure. Can Au₉₀ have a similar structure and if so is it energetically more preferable? To construct a compact cluster we start with an Au₈₄ which has a complete shell of tetrahedral structure, we capped this cluster with atoms to get Au₉₀, as shown in Fig. 7(a). The structure was then optimized. The binding energy/atom of this cluster is 3.548 eV, which is about 0.086 eV/atom larger than the most stable ring structure in Fig. 5. As for the compact structure, polyicosahedron is another best choice. It has been

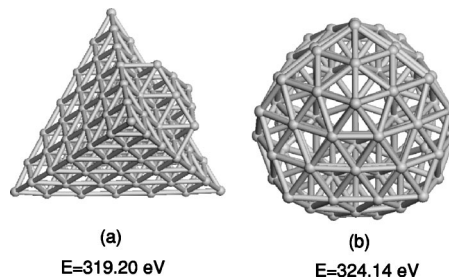


FIG. 7. Tetrahedral structure (a) and polyicosahedral structure (b) of Au₉₀.

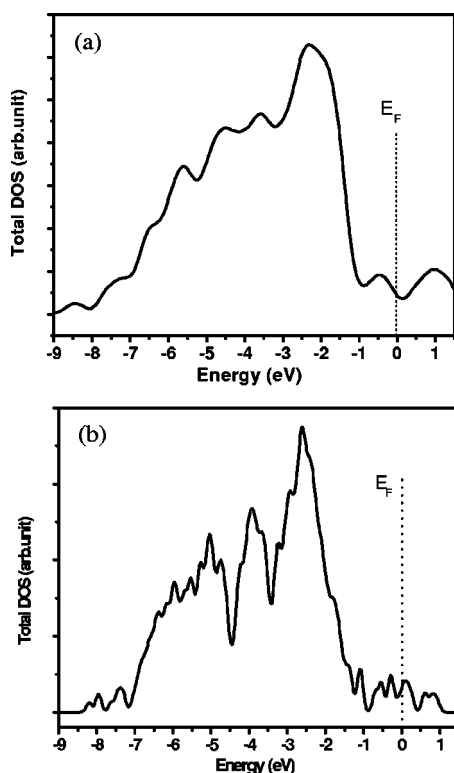


FIG. 8. DOS for polyicosahedral Au_{90} (a) and the stable ring Au_{90} (b).

found that rare-gas cluster²⁴ and some metal clusters with d -electron bonding.^{25–28} Gold atom has the electronic configuration of $5d^{10}6s^1$, d -electron is absolutely important in bonding and catalysis.²⁹ Therefore, the polyicosahedral structure can be expected to be preferable. In Fig. 7(b) we show the optimized polyicosahedral Au_{90} with incomplete shells. The total binding energy is about 5 eV lower than the tetrahedral structure in Fig. 7(a), suggesting the former is more stable. In fact we have systematically checked the rela-

tive stability of the polyicosahedral structure and tetrahedral one for the size of 20, 35, 56, 84, and 90. Except for Au_{20} , polyicosahedral structure is always more stable than tetrahedral one for the other sizes. Thus the Au_{90} in the form of a ring is metastable. The similar situation has also been found for a silica ring.³⁰ We should also note that the fcc (111) motif feature can be clearly seen on the surface of the polyicosahedral structure as shown in Fig. 7(b). For comparison we plot the density of states (DOS) of the polyicosahedral and the stable ring structure in Fig. 8. Although the details in DOS are different due to the different geometries, both share some common features in that the Fermi energy passes through a region of low density of states, similar to the bulk gold density of states.³¹

Although thermodynamically the ring structure is metastable, it does correspond to a local minimum in the potential energy surface. In experiment, the observed structures are sometimes highly dependent upon growth processes controlled by kinetic factors, rather than by energetics. Thus a system may easily get trapped in a local minimum on the potential energy surface by nonequilibrium processes.^{32–34} Therefore, even if the ring structure of Au_{90} is metastable, it can still be observed in experiment. This complements the experimental synthesis of large gold nanorings.¹⁵

In summary, using density functional theory we explored the structural feature of a gold nanoring. By searching several different possible isomers, we find that the nanoring with fcc (111) motif is more stable. The cluster and nanoring share similar structural features with gold bulk, namely, the (111) stacking motif becomes the unified bench mark for stability.

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