



# A density-functional theory study of Au<sub>13</sub>, Pt<sub>13</sub>, Au<sub>12</sub>Pt and Pt<sub>12</sub>Au clusters



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## ABSTRACT

The geometrical and electronic properties of Pt<sub>13</sub>, Au<sub>13</sub>, Pt<sub>12</sub>Au and Au<sub>12</sub>Pt are investigated systematically by first-principle calculations combined with the genetic algorithm. A new candidate for the ground-state of Pt<sub>13</sub> is found, and there exists energetically closer isomers to the ground-state of the pure 13-atom clusters (especially for Au<sub>13</sub>), but the isomerization to the ground-state of the pure clusters can be suppressed by doping. The calculated vertical ionization potentials (VIPs) and vertical electron affinities (VEAs) of all configurations considered of Au<sub>13</sub> are close to the experimental data, and the three dimensional cage-like structure is the closest one. Doping has small effect on VIPs and VEAs of the pure Pt<sub>13</sub> and Au<sub>13</sub> clusters. However, doping has significant effects on the distributions of *d* electrons near the Fermi energy, which may strongly influence the catalytic activities of the mixed clusters.

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## 1. Introduction

Nano clusters have attracted much attention of scientists because of their unique electrical, optical, magnetic and chemical properties [1–7]. As the typical representations of 5*d* transition metal elements, the Pt and Au have important values in electronic devices, optical materials and catalysts. The structural, electronic and magnetic properties of the pure and mixed Au–Pt clusters have been investigated extensively in recent years. Much attention has been paid to the study of the structural properties of clusters in small sizes (typically less than 50 atoms [8–10]), among them the 13-atoms clusters are the most focusing objects [11–15]. It has been a long time to ascertain the lowest-energy geometry of the neutral Au<sub>13</sub> cluster, and the dimensionality (two- or three-dimensional?) of the neutral Au<sub>13</sub> is still unknown until now. In 2000, Häkkinen et al. [16] investigated the atomic and electronic structures of Au<sub>*n*</sub> (*n* = 2–10) by using the density-functional theory (DFT) with scalar-relativistic *ab initio* pseudopotentials and a generalized gradient correction, and the ground-state optimal geometries of Au<sub>*n*</sub> clusters are found to be planar up to *n* = 7. In 2002, Wang et al. [14] investigated the lowest-energy structures and electronic properties of the Au<sub>*n*</sub> (*n* = 2–20) clusters based on DFT with local density approximation, and they found that the small Au<sub>*n*</sub> clusters adopt planar structures up to *n* = 6. In earlier studies, many researchers have thought that Au<sub>13</sub> was unlikely to have a

planar configuration. In 2007, Idrobo et al. [15] investigated the ground state structures of Au<sub>*n*</sub> (*n* = 2–14 and 20) using first-principles all-electron relativistic calculations within DFT, and they found the shape transition from two-dimensional to three-dimensional occurs at *n* = 14. In 2009, Shafai et al. [11] carried out scalar relativistic DFT calculations within the projector augmented wave scheme and the pseudopotential approach and they found that the planar geometry of Au<sub>13</sub> has the lowest total energy while the icosahedral and cuboctahedral structures all undergo Jahn–Teller distortion. In 2010, Nijamudheen et al. [13] performed DFT calculations using the B3PW91 hybrid functional to study the structural and optical properties of Au<sub>*n*</sub> (*n* = 2–20) clusters and the lowest-energy geometry of Au<sub>13</sub> is found to be a planar structure. Also in 2010, Piotrowski et al. [12] performed a DFT study of the structural, energetic and magnetic properties of 13-atom 3*d*, 4*d* and 5*d* transition metal clusters. The initial geometries are considered by combining the high-temperature first-principles molecular-dynamics simulations, and a three-dimensional structure of Au<sub>13</sub> is found to be the lowest-energy one, which is about 0.10 eV lower in energy than the lowest energy known two-dimensional configuration. After that, although many works have been done to study the properties of doped and adsorbed Au<sub>13</sub> clusters [17–23] where both the two-dimensional [17–20] and the three-dimensional [21–23] geometries were chosen as the structural motifs, there is still a controversy that whether the Au<sub>13</sub> cluster prefers a planar structure or a three-dimensional structure [24].

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For the Pt<sub>13</sub>, it is more difficult to maintain the planar structure than Au<sub>13</sub> [25]. Kumar et al. [26] investigated the evolution of atomic and electronic structure of Pt clusters by using ab initio ultrasoft pseudopotential and projected augmented wave methods, and they found that for the Pt<sub>n</sub> (n = 2–20) clusters the planar structures are preferred up to n = 9, while the layered and pyramidal structures are favored in the range of n = 10–20, and the lowest-energy geometry of Pt<sub>13</sub> is a double triangular (DTA) structure. Sun et al. [27] performed a global optimization of the 13-atom clusters for 26 elements by DFT calculations, and they found an oblate multiply capped trigonal prism (CTP) is the most favorable structure of Pt<sub>13</sub>, which is different from the results by Kumar et al. Aguilera-Granja et al. [28] investigated the structural and magnetic properties of the binary clusters X<sub>12</sub>Y (X, Y = Fe, Co, Ni, Ru, Rh, Pd, and Pt) by ab initio DFT calculations, where for both the DTA and the CTP were considered as the initial structures for Pt<sub>13</sub>. Later a non-compact low symmetric (NLS) geometry is found to be the lowest-energy structure of Pt<sub>13</sub> by Piotrowski et al. [12,29] through DFT calculations.

The mixed metal clusters have also been one of the hot research subjects in recent years. The mixed clusters can be obtained by doping impurity atoms into the pure clusters, and the properties of the pure clusters can be changed by doping. For example, the Au-Pt bimetallic clusters play important roles in many processes such as the adsorption and oxidation of CO [30–36], the adsorption and reduction of NO [37] and the oxidation of CH<sub>3</sub>OH [38,39], which indicates that some bimetallic clusters may have better catalytic properties than the pure metal clusters, and the in-depth and comprehensive studies of the structural properties and the interaction between different components of the mixed metal clusters can help us to better understand their catalytic activities.

Yuan et al. [40] investigated the geometric, electronic, and bonding properties of Au<sub>n</sub>M (M = 1–7, M = Ni, Pd, Pt) clusters by DFT calculations, and they found that the dopant atoms markedly change the geometric and electronic properties of gold clusters, and stronger bond energies are found in Pt-doped clusters. Within density functional theory with the general gradient approximation for the exchange and correlation, the structure and reactivity of the bimetallic AuPt and Au<sub>6</sub>Pt clusters are investigated by Tian et al. [41], and they found that the doping of Pt in Au cluster enhances the chemical regioselectivity of the Au cluster. The structural evolutions and electronic properties of bimetallic Au<sub>n-x</sub>Pt<sub>x</sub> (n = 2–14; x ≤ n) clusters are investigated by Yuan et al. [42] through DFT calculations, and they found that the planar configurations are favored for both Au<sub>n-1</sub>Pt and Au<sub>n</sub> clusters up to n = 13. The structural, electronic and magnetic properties of Au<sub>n</sub>Pt (n = 1–12) clusters and the chemical reactivity of Au<sub>12</sub>Pt are studied by Kuang and his co-workers [17,20] through all-electron scalar relativistic DFT calculations.

In this paper, the geometric structures and electronic properties of Au<sub>13</sub>, Pt<sub>13</sub>, Au<sub>12</sub>Pt and Pt<sub>12</sub>Au clusters are systematically investigated by density functional theory calculations combined with the genetic algorithm, and the influences on the structural and electronic properties of clusters by doping are emphasized.

## 2. Computational details

The first-principles spin-polarized all electron relativistic calculations are performed using the DMol<sup>3</sup> package [43–45] based on the density functional theory (DFT) [43–49]. The widely used generalized gradient approximation (GGA) with an exchange correlation functional parameterized by Perdew and Wang (PW91) [50] and the double numerical polarized (DNP) basis sets are employed in the calculations. Self-consistent field electronic calculations are

done with a convergence criterion of 10<sup>-6</sup> a.u. of the total energy. In the process of geometry optimization the convergence criteria are set to be of 0.002 Hartree/Å for the forces, 0.005 Å for the displacement and 1 × 10<sup>-5</sup> Hartree for the total energy. The direct inversion in iterative subspace (DIIS) approach is used to speed up the SCF convergence.

In order to find the lowest-energy geometry of a cluster effectively, the initial configurations should be extensive enough to ensure sufficiently thorough exploration on the cluster potential energy surface. For the pure 13-atom clusters the initial configurations are constructed through the following three aspects: Firstly, a real-space genetic algorithm based on the semi-empirical Gupta potential is adopted, which can provide numerous initial configurations for the pure Au<sub>13</sub> and Pt<sub>13</sub> clusters; Secondly, it contains all representative structures reported so far in the literatures of the pure Au<sub>13</sub> and Pt<sub>13</sub> clusters (e.g., the DTA, CTP and NLS structures of Pt<sub>13</sub> mentioned in the introduction); Finally, the conventional four high-symmetric (I<sub>h</sub>, O<sub>h</sub>, D<sub>3h</sub>, D<sub>5h</sub>) close-packed geometries are also considered. All initial structures are re-optimized under DFT calculations using the DMol<sup>3</sup> package, and then the competitive structures (the ground-state and low-lying configurations) of the pure Au<sub>13</sub> and Pt<sub>13</sub> clusters can be obtained.

For the mixed Au<sub>12</sub>Pt and Pt<sub>12</sub>Au clusters, the initial configurations are constructed from the single-atom replacing on the inequivalent positions of the typical structures (the ground-state and low-lying configurations as well as the four high-symmetric configurations) of the corresponding pure Au<sub>13</sub> and Pt<sub>13</sub> clusters. And the lowest-energy geometries of the mixed Au<sub>12</sub>Pt and Pt<sub>12</sub>Au clusters can also be obtained through re-optimization of those initial structures.

For all stable geometries of the pure and mixed 13-atom Au-Pt clusters obtained from the re-optimization by DFT calculations, the calculations of frequencies are also performed to ensure the reliable stabilities of the optimized structures.

## 3. Results and discussion

### 3.1. Geometric structures

#### 3.1.1. Pt<sub>13</sub> clusters

The total binding energies and symmetries of the ground-state geometry, the low-lying isomers and the four high-symmetric configurations of Pt<sub>13</sub> are listed in Fig. 1. For comparison, all structures shown in Fig. 1 are sorted in increasing order of energy, and the energy of each structure is marked as the energy difference with respect to the ground-state structure (that is, the energy of the ground-state structure is labeled as zero). Structures A, D, E, F and G are all three-dimensional ones obtained from the genetic algorithm. Structures B, C and H are the same as those obtained previous by Piotrowski et al. [12,29], Sun et al. [27] and Kumar et al. [26], as stated above in the introduction as the NLS (non-compact low symmetric), CTP (oblate multiply capped trigonal prism) and DTA (double triangular) structures of Pt<sub>13</sub>. The Cartesian coordinates of the four typical structures (A, B, C and H) are given in Table 1 in the Supporting Information (SI).

The low energy structures (A, D, E and F) generated from the genetic algorithm show some similarities: All can be viewed as two or three-atom capped bi-layer geometries.

The optimized geometries of the initial four high-symmetric (I<sub>h</sub>, O<sub>h</sub>, D<sub>3h</sub>, D<sub>5h</sub>) structures are all much higher in energy than the ground-state, and they do not have any energetic competition to the ground-state geometry. In addition, different degrees of structural distortion can be found in the optimization of the four high-symmetric configurations: The I<sub>h</sub> and D<sub>5h</sub> can maintain their symmetry unchanged, while the O<sub>h</sub> takes place a little distortion with

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