



First-principle study of Au_nFe ($n = 1-7$) clusters

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ABSTRACT

The geometrical structures, relative stabilities, and magnetic moments of iron-doped gold clusters, Au_nFe ($n = 1-7$), have been investigated using density functional method B3LYP and LanL2DZ basis set. Many low-lying isomers of the Au_nFe clusters are obtained along with their electronic states. The results show that the ground-state Au_nFe isomers possess a linear structure for $n = 1-2$ and a planar structure for $n = 3-7$. The relative stabilities of Au_nFe clusters for the ground-state structures are analyzed based on the averaged binding energies, fragmentation energies, second-order difference of energies, and HOMO–LUMO energy gaps. It is found that the Au_2Fe and Au_4Fe clusters are magic clusters with high chemical stability. The magnetic moment calculations for the ground-state Au_nFe clusters, which are magnetic, indicate that the total magnetic moment of the clusters is mainly localized on the Fe atom and two magic clusters are larger in total magnetic moments than others.

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1. Introduction

A transition metal atom doped in small cluster of other metals can strongly change the properties of the host cluster. Gold clusters doped with transition metal atoms, such as Ti, V, Cr, etc., have been actively pursued to tailor the desired structural, electronic, magnetic, and optical properties for potential applications in materials science, solid state chemistry, microelectronics, biology, and nanotechnology [1–8]. For example, the isolated vanadium-doped Au_{12} cluster, which shows an enhanced electron density on gold atoms, is an improved novel catalyst for CO oxidation [4]. Recently, the pure gold materials doped with iron element have been extensively studied because of their unique physical and chemical properties [9–16]. It was shown that the Fe in fcc disordered Au–Fe alloys is in high-spin state [9]. The magnetic moments of the Au and Fe interface in Au–Fe multilayers do not depend on the spacer thickness [12]. The fusion of the Au and Fe elements into one nanostructure entity retains the optical and magnetic properties of the individual components [10]. Moreover, these studies primarily focus on the Au–Fe alloys and multilayers. It is well known that small clusters and nanoparticles usually have special properties, which should be very different from those of the atom or the bulk, in virtue of the so-called size and surface effects. In particular, the small clusters can provide an ideal medium to gain a fundamental understanding

on the geometry, electronic structure and the nature of bonding. To the best of our knowledge, however, there is no theoretical work on small neutral Fe-doped gold clusters so far. Therefore, in this paper, the geometric structures, relative stabilities, and magnetic moments of the small Au_nFe ($n = 1-7$) clusters will be investigated systematically by density functional theory (DFT). It is hoped that this work would be useful to understand the influence of material structure on its properties and could offer relevant information for further experimental and theoretical studies.

2. Computational method

Geometry optimizations and vibrational frequency analyses were carried using DFT with the unrestricted B3LYP exchange–correlation functional and an effective core potential LanL2DZ basis set [17–19], as implemented in GAUSSIAN03 program package [20]. To search the lowest energy structures of Au_nFe ($n = 1-7$) clusters, lots of possible initial configurations, which have different bond length, bond angle, or point group, were used in geometry optimizations. Furthermore, the previous studies on gold clusters are also employed as a guide [7,21–24]. Due to the spin polarization, every initial configuration was optimized at various possible spin multiplicities. Each geometry optimization was followed by a calculation of harmonic vibrational frequencies to confirm that the optimized geometry corresponds to a local minimum. In all calculation, the convergence thresholds were set to 0.000015 Hartree/Bohr for the forces, 0.000060 Å for the displacement, and 10^{-6} Hartree for the energy change.

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The accuracy of the computational method has been checked by calculations on gold dimer and iron dimer. The results show that the ground-states are $^1\Sigma_g$ for Au_2 and $^9\Sigma_g$ for Fe_2 . The calculated bond lengths (2.57 Å for Au_2 and 2.15 Å for Fe_2) and dissociation energies (1.87 eV for Au_2 and 1.28 eV for Fe_2) are in good agreement with experimental bond lengths (2.47 Å for Au_2 and 2.02 Å for Fe_2) and dissociation energies (1.88 eV for Au_2 and 1.30 eV for Fe_2) [25–27]. These indicate the suitability of current computational method to describe small Au_nFe ($n = 1–7$) clusters.

3. Results and discussion

3.1. Geometrical structures

The calculated results for AuFe show that the quartet spin state is lower in energy than the doublet and sextet spin states by 1.77 and 0.22 eV, respectively. Accordingly, the quartet AuFe dimer with electronic state of $^4\Sigma_g$ is the ground-state structure, and the bond length of ground-state AuFe dimer is 2.47 Å.

For the Au_nFe ($n = 2–7$) clusters, many isomers have been obtained. The lowest energy structure and four low-lying isomers for each Au_nFe cluster are plotted in Fig. 1. According to the energies from low to high, these isomers are designated by na , nb , nc , nd , and ne , where n represents the number of Au atoms in the Au_nFe clusters. Meanwhile, their symmetry, spin multiplicity and energy difference compared to each of ground-state structures are also indicated in the figure.

The linear 2a isomer with quintet spin state, which is energetically lower than the same structure with other spin states, is found to be the ground-state structure of Au_2Fe cluster. The corresponding electronic state is $^5\Sigma_g$ and the Au–Fe bond length is 2.45 Å. The triplet 2b isomer with C_{2v} symmetry, which is similar to the ground-state structure of Au_3 cluster [21,22], is 0.96 eV higher in energy than the 2a isomer. The 2c isomer with an apex angle of 68.8° is another metastable isomer and has the same spin multiplicity and symmetry as the 2b isomer. The 2d and 2e isomers with $C_{\infty v}$ and C_s symmetry are above the ground-state by 1.20 and 1.57 eV, respectively.

The lowest energy structure of Au_3Fe cluster is the planar 3a isomer with C_{2v} symmetry. Interestingly, the 3a isomer with Au–Fe–Au bond angle of 137.8° can almost be viewed as the overlap of two 2c isomers. The electronic state for the 3a isomer is 4A_1 . The rhombus 3b and 3d isomers, which resemble the lowest energy structure of Au_4 [21,22], are less stable than 3a isomer by 0.12 and 0.94 eV. The y-like 3c isomer with the Fe atom occupying the apex position can be seen as intermediate between 3b and 3d isomers. The doublet 3e isomer with C_s symmetry, which is a very slight distortion of C_{3v} configuration, is the first three-dimensional (3D) structure, and its energy is 1.37 eV higher than that of the 3a isomer. In addition, the 3e isomer with other spin states is not found in geometry optimizations.

The most stable structure of Au_4Fe cluster is the 4a isomer with C_{2v} symmetry. The Au–Fe–Au bond angle is 166.3°. The electronic state is 5A_1 . The 4b isomer in a 5B_2 electronic state is energetically higher than the 4a isomer by 0.36 eV. Both 4a and 4b isomers exhibit a configuration similar to the ground-state structure of Au_5 [21,22]. The triplet 4c isomer, which is more stable than the same configuration with other spin multiplicities, is obtained by distorting the geometry stating from D_{4h} to D_{2h} symmetry. The 4d isomer is a 3D structure with C_{4v} symmetry and its energy is close to the 4c isomer. The 4e isomer, which is 0.18 eV higher in energy than the 3D 4d isomer, possesses a planar trapezoidal structure.

In the case of Au_5Fe clusters, the low-lying isomers evidently favor planar structures, which are similar to the ground-state structure of Au_6 cluster [20,21]. The 5a with electronic state of 4B_2 and

C_{2v} symmetry is the lowest energy structure. The 5b isomer, whose Fe atom is shifted much more towards the center of the structure, is only 0.01 eV less stable than 5a isomer. The 5c and 5d isomers are slightly higher in energy than 5a, i.e. by 0.12 and 0.19 eV, respectively. The 5e isomer with the Fe atom occupying the apex position has a big energy difference relative to the foregoing four isomers. As for the 3D configurations of Au_5Fe clusters, the tetragonal bipyramid and pentagonal pyramid, etc., were found to be unstable.

With regard to the Au_6Fe cluster, two triplet planar Au_6 rings with the Fe atom at the center, namely 6a and 6b isomers, are more stable than other planar and 3D structures. The former with the electronic state of $^3B_{3g}$ is energetically lower than the latter by 0.09 eV and the ground-state structure. Due to the Jahn–Teller effect, each of the Au_6 rings with D_{2h} symmetry has a different slight deviation from D_{6h} symmetry, as shown by 6a and 6b in Fig. 1. The 6c and 6d isomers in quintet spin state, which correspond to the ground-state structure of Au_7 cluster [21,22], are, respectively, 0.18 and 0.47 eV less stable. The 6e isomer with C_{5v} symmetry, which is the most stable 3D configuration, is still higher in energy than the planar 6a isomer.

The quartet planar 7a configuration with electronic state of 4A_2 is the lowest energy structure of the Au_7Fe cluster, but this configuration corresponds to the second most stable Au_8 isomer [24]. The 7b and 7d isomers, which relate to the ground-state structure of the Au_8 cluster [24], are energetically higher than the 7a isomer by 0.18 and 0.86 eV, respectively. The 7c isomer with C_{2v} symmetry, whose energy is the lowest in 3D isomer, is 0.22 eV less stable than the 7b isomer. The 7e isomer shows a similar structure to that of the ninth isomer of the Au_8 cluster and is a planar structure [24]. Other planar and 3D isomers for the Au_7Fe cluster, which are not displayed in Fig. 1, are significantly higher in energy.

From the above discussions, it is obvious that the ground-state structures of Au_nFe ($n = 1–7$) clusters favor the linear structures for $n = 1–2$ and planar structures for $n = 3–7$. On the other hand, the planar structures have a large 4p populations on the Fe atom, as shown in Table 1. For $n = 2, 6$, and 7, the ground-state geometries of Au_nFe clusters are very different from those of pure Au_{n+1} clusters.

3.2. Relative stabilities

In this part, the relative stabilities of the Au_nFe ($n = 1–7$) clusters for ground-state structures are analyzed in terms of the atomic averaged binding energies, second-order difference of energies, fragmentation energies, and energy gaps between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).

The atomic averaged binding energies (E_b) of the Au_nFe clusters are defined as [28]

$$E_b[\text{Au}_n\text{Fe}] = (nE[\text{Au}] + E[\text{Fe}] - E[\text{Au}_n\text{Fe}]) / (n + 1), \quad (1)$$

where $E[\text{Au}]$, $E[\text{Fe}]$, and $E[\text{Au}_n\text{Fe}]$ are the energies of a Au atom, a Fe atom, and the Au_nFe cluster. The calculated binding energies per atom for the ground-state Au_nFe clusters are shown in Fig. 2. As seen from Fig. 2, the averaged binding energy of the AuFe dimer is much smaller than those of other Au_nFe ($n = 2–7$) clusters. For $n > 3$, the E_b of Au_nFe clusters stay nearly constant. A visible peak occurs at $n = 2$. This hints that the Au_2Fe cluster is more stable than its neighboring clusters. Simultaneously, it was found from Mulliken population in Table 1 that the Au_2Fe cluster has a large charge transfer from the Fe atom to Au atoms.

In cluster physics, the second-order difference of energies (Δ^2E) is an extremely sensitive quantity that reflects the relative stability of the clusters [29]. For the ground-state Au_nFe clusters, it can be calculated as

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