Physics Letters A 375 (2011) 1877–1882

Contents lists available at ScienceDirect

Physics Letters A

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Geometries, stabilities, and electronic properties of gold–magnesium (Au_nMg) bimetallic clusters

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ARTICLE INFO

Article history:
Received 26 December 2010
Received in revised form 10 March 2011
Accepted 20 March 2011
Available online 30 March 2011
Communicated by R. Wu

Keywords:
Au_nMg cluster
Density functional theory
Relative stability
Natural population analysis

ABSTRACT

The geometrical structures, relative stabilities, and electronic properties of bimetallic Au_nMg ($n = 1$–8) clusters have been systematically investigated by means of first-principle density functional theory. The results show that the ground-state isomers have planar structures for $n = 1$–7. Here, the calculated fragmentation energies, the second-order difference of energies, the highest occupied–lowest unoccupied molecular orbital energy gaps, and the hardness exhibit a pronounced odd–even alternation, manifesting that the clusters, especially Au_2Mg, with even-number gold atoms have a higher relative stability. On the basis of natural population analysis, the charge transfer and magnetic moment are also discussed.

1. Introduction

During the last decade, noble-metal Au has been a considerable topic in experimental and theoretical studies due to its special technical applications in the fields of optics, materials science, and solid-state chemistry [1–7]. Especially, gold-based catalysts have attracted more attention for their fascinating catalytic activity exhibited by Au particles supported on metal oxide surfaces [8–12]. As for simple small-sized clusters, the gold clusters are formed by a few up to tens of thousands of atoms occurring closely together, which represent a bridge between atomic state and bulk material.

Gold is known to be particularly convenient for spectroscopic studies due to the closed d-shell electronic configuration $5d^{10}6s^1$. The alkali atoms have the same s^1 unpaired electron. They all can be viewed as "simple" s-only metals, which are easily characterized experimentally and investigated with less computational effort. It is well known that an electronic shell model (jellium model), in which valence electrons move freely in an averaged electronic potential, successfully explains size-dependent features of both coinage and alkali metal clusters. Solving the Schrödinger equation for the potential results in an electronic shell structure $1s^2$, $1p^6$, $1d^{10}$, $2s^2$, $2p^6$, $1f^{14}$, ... So when the number of valence electrons in the clusters is just enough to complete one of the electronic shells, the corresponding clusters exhibit enhanced stability. Meanwhile, because an especially large electronegativity exists between alkali metal and gold atom, the alkali–gold series are found to be particularly stable. Therefore, alloys of gold with various alkali metals have roused interest of both chemists and physicists [13–18]. For example, the complete alkali auride series (LiAu, NaAu, KAu, RbAu, CsAu) have been studied by Belpassi et al. [17] using the G-spinor basis set in the program BERTHA. The intermetallic bond that occurs in these series is characterized by a large charge transfer from the alkali metals to gold atom. Besides, because the electronegativity difference is larger in sodium–gold cluster than that of sodium–silver cluster, Heiz et al. [14] have found that this leads to a higher polarization and more directionalities of the metal–metal bonds for sodium–gold system. In recent years, the intermetallic bond in gold–alkaline earth molecules is also found to be particularly stable [19–22]. Among them, it is obtained that the bond energy of AuBe and AuCa is 5%–10% higher than that of the gold dimer Au_2 while 30%–40% higher compared with the species AuMg, and the doping Mg atom hardly deforms the electronic structure of Au_n^- clusters for $n = 2$–4 [20,22]. Since the chemical and physical properties of clusters depend strongly upon the microscopic structure around the dopant, we have made significant efforts to understand the structural and electronic properties of Au_nMg^- clusters recently [23]. A good agreement between

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0375-9601/$ – see front matter
doi:10.1016/j.physleta.2011.03.036

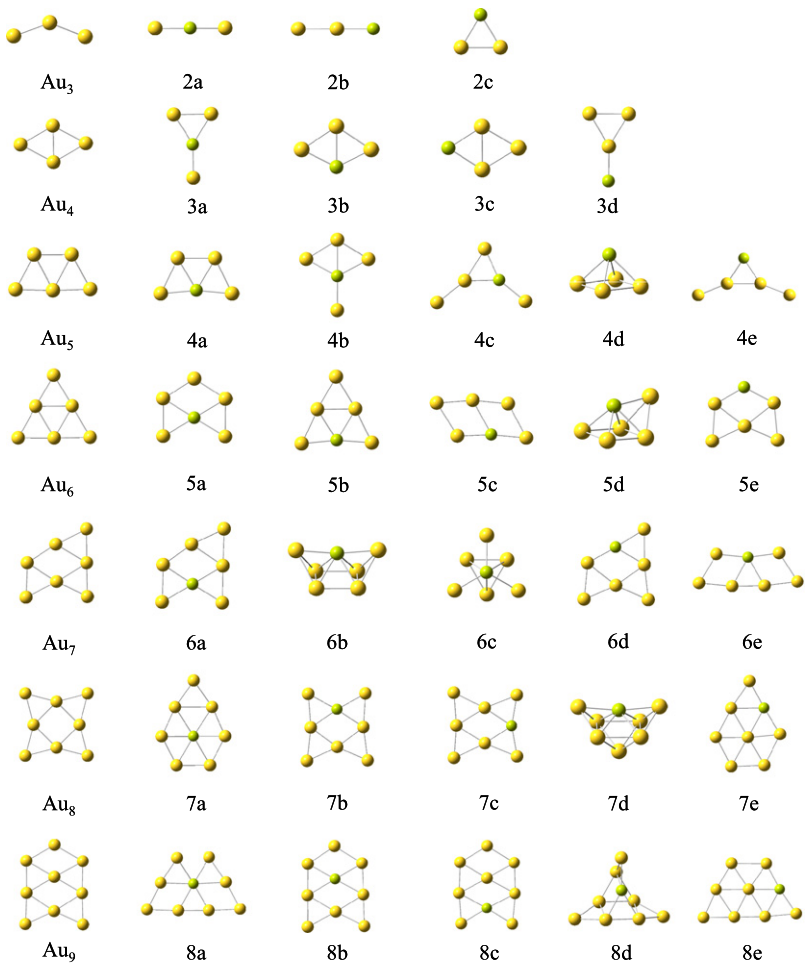

Fig. 1. The lowest energy structures and low-lying isomers for Au_nMg ($n = 2$–8) clusters, and the ground-state structures of pure gold clusters Au_{n+1} ($n = 2$–8) have been listed on the left. The yellow and green balls represent Au and Mg atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this Letter.)

theoretical and experimental results suggests good calculations of the physical structures. Although the intermetallic molecules AuMg and Au_5Mg have been studied by Balducci et al. [20] and Majumder et al. [21] by employing density functional theory (DFT), respectively, there is no systematically theoretical study on neutral gold–magnesium clusters until now. Are their structures and properties greatly distinct from the anionic ones? How does the dopant affect the bare gold clusters? These open questions are still unsolved, so it is urgent to understand the geometries, stabilities, and electronic properties of Au_nMg clusters.

In the current work, we systematically investigate the small neutral gold clusters doped by a single-impurity magnesium atom, Au_nMg ($n = 1$–8), using the first-principle method based on DFT. The Letter is organized as follows: Section 2 gives a brief description of the computational details. Then, the equilibrium geometry, relative stability, and natural population analysis (NPA) are given in Section 3. Lastly, the conclusions are summarized in Section 4.

2. Computational methods

In this work, all geometrical optimizations of Au_nMg ($n = 1$–8) clusters are performed by using a DFT-based *GAUSSIAN 03* package [24]. While calculations involving full electrons are rather time consuming due to the gold being a heavy atom, the effective core potentials including relativistic effects (RECP) are introduced to describe the inner core electrons. In this connection, the basis set labeled GEN (SDD for the Au atom and 6-311G* for the Mg atom) is adopted at the level of the PW91PW91 method [25,26]. In searching for the lowest energy structures, lots of possible initial structures have been extensively explored without any symmetry constraint, and different spin multiplicities are also taken into account. Here, the configurations are regarded as optimized when the convergence thresholds of the maximum force, root-mean-square (RMS) force, maximum displacement of atoms, and RMS displacement of atoms are set to 0.00045, 0.0003, 0.0018, and 0.0012 a.u., respectively. Furthermore, harmonic vibrational frequency calculations are performed to guarantee the optimized structures correspond to the potential energy minima. The highest occupied–lowest unoccupied molecular orbital (HOMO–LUMO) energy gaps, hardness (η), and NPA of the stable configurations are also obtained based on PW91PW91/GEN method.

3. Results and discussions

A large number of optimized isomers for Au_nMg ($n = 1$–8) clusters have been considered, but here we report only the few energetically low-lying ones in Fig. 1. According to the total energy from low to high, these isomers are designated by *n*a, *n*b, *n*c, *n*d, and *n*e (*n* is the number of Au atoms in Au_nMg clusters). Meanwhile, the corresponding electronic states, symmetries, relative energies, HOMO and LUMO energies are summarized in Table 1. In order to discuss the effects of doping impurity on gold clusters, we also performed optimizations for Au_{n+1} ($n = 1$–8) clusters by using PW91PW91/SDD method, and the lowest energy configura-