



Geometric evolution, stability trend and electronic properties of rhenium-doped gold clusters



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ABSTRACT

Based on the density functional theory with using relativistic all electron methods, this work systematically studies the geometrical structures, relative stabilities, electronic properties, and chemical hardness of Au_nRe ($n = 1-12$) clusters. Low-lying energy structures include two-dimensional and three-dimensional geometries. Especially, for the lowest energy structures of Au_nRe ($n = 1-12$) clusters, the planar to three dimensional transformation is found to occur at cluster size $n = 10$ and the dopant Re atom prefers being located at highly coordinated site. After doping a Re atom, the relatively stable odd-numbered Au _{$n+1$} cluster becomes the relatively unstable odd-numbered Au _{n} Re cluster, while the relatively unstable even-numbered Au _{$n+1$} cluster becomes the relatively stable even-numbered Au _{n} Re cluster. Moreover, the presence of dopant Re atom leads to the chemical reactivity of even-numbered gold clusters becomes weaker, but the chemical reactivity of odd-numbered gold clusters turns stronger. Additionally, the *spd* hybridization in the Re atom of Au_nRe clusters is stronger than that in the corresponding Au atom of Au _{$n+1$} . Au–Re bonds of Au_nRe clusters have stronger covalent characteristics than corresponding Au–Au bonds of Au _{$n+1$} , meaning the stronger interaction between the Re and Au atoms than that between the corresponding Au and Au atoms in pure clusters.

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1. Introduction

In the recent years, a number of explorations [1–3] exhibited that the bimetallic clusters has the distinctive catalytic, structural, electronic, magnetic and optical properties. Especially, transition metal-doped gold clusters have been becoming a growing interest because transition metal elements possess intricate *d*-orbital bonding, strong electron correlation, and spin–orbit coupling [4,5], which strongly influence the chemical and physical properties of host gold clusters [6–10]. For instance, the ground geometric structures, the stability and electronic properties of the small Au _{n} M ($n = 1-7$, M = Ni, Pd, Pt) clusters were researched [11], and it was found that the stability of Pd- and Pt-doped gold clusters is evidently changed due to the relative strong bonding interaction contributed by *d*-electrons, and the *d*–*d* and *s*–*d* interaction between impurities and gold atoms can markedly modify the electronic properties of doped gold clusters. The theoretical study [12] of Au _{n} M⁺ clusters (M = Sc, Ti, V, Cr, Mn, Fe, Au; $n \leq 9$) discovered that the positive charge of the cationic Au _{n} M⁺ clusters which is localized mainly in the impurity, and the magnetic and geometrical configurations

are strongly correlated with cluster sizes. The geometric and electronic properties of neutral and anionic bimetallic vanadium–gold clusters Au _{n} V ($n = 1-14$) were theoretically studied [8], which found the smaller ground state clusters of Au _{n} V prefer 2D geometries up to Au₈V involving a weak charge transfer, but the larger systems bear 3D conformations with a more effective electron transfer from Au to V. Au _{n} Pd[−] ($n = 1-4$) and Au _{n} M ($n = 1-7$; M = Pd, Ni, Zn, Cu and Mg) were investigated by anion photoelectron spectroscopy [13,14], which displayed that the remarkable electronic and geometric similarity between Au _{n} [−] and Au _{$n-1$} Pd[−] indicates that one of 4*d* electrons of Pd is promoted to the 5*s* orbital from the ground state of [Kr](4*d*)¹⁰(5*s*)⁰, and the 5*s* electron of the promoted electronic configuration of [Kr](4*d*)⁹(5*s*)¹ contributes to the bonding with Au atom(s). Neukermans et al. [15] studied Element-dependent 3*d* electron delocalization of 3*d*-shell atoms (Sc, Ti, V, Cr, Mn, Fe, Co, Ni), which revealed that the lightest 3*d* elements (Sc, Ti) delocalize their 4*s* and 3*d* electrons, while for the heavier 3*d* elements (Cr, Mn, Fe, Co, Ni), only 4*s* electrons are delocalized. Moreover, a number of researches about the adsorption of doped Au clusters were reported [16–19], showing the difference of catalysis from the adsorption of pure gold clusters. These examples sufficiently illustrate that the doping metal atom of gold-based mixed cluster has a notable act to change the geometries, chemical activities and stabilities of the corresponding gold cluster.

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Hence, the transition metal-doped gold clusters are expected to design the desired structural, magnetic, and chemical properties for potential applications [20–22].

The transition metal rhenium has considerable applications in catalysts, solar energy technologies and special alloys [23–27]. The experiment [28] displayed the Re_{10} cluster has remarkable catalytic performances for the direct phenol synthesis from benzene and O_2 . The theoretical investigation [29] also indicated the dopant Re can obviously improve the stability, lifetime and selectivity of catalyst Pt on the hydrogenation reaction. Notably, Re and Mn are group VIIB (7) elements, and namely, they possess same valence electron number and similar electronic configuration s^2d^5 . Mn-doped gold systems have valuable application prospects and have been comprehensively explored [30]. It is found that in Mn-doped systems, s , d -valence electrons of Mn atoms [31,32] are mostly transferred to host Au clusters as bonding and delocalized electrons, reflecting that impurity atoms consolidate the bonding and enhance the stability of Mn-doped gold systems. Previous experimental and theoretical researches [33,34] also have revealed a phenomenon that delocalized s , d -valence electrons from transition metal atoms may promote the stability of doped gold clusters. Seeing that Re and Mn possess same valence electrons and similar electronic configurations, it will be predicted that s , d -valence electrons of Re atom essentially have a pronounced contribution on geometric, electronic, and bonding properties of doped gold clusters. Meanwhile, we know that the dopant usually can modify the physical and chemical properties of gold clusters and improve the stability and catalytic activity of gold cluster, and that both Re and Au are excellent catalytic materials. Certainly, the Au–Re system is outstanding catalysts likewise. Such as, the study [35] indicated that the novel Au–Re catalyst are highly active for the water-gas shift reaction at high $\text{H}_2\text{O}/\text{CO}$ ratios. Especially, in the recent experiment [36], it was observed that the catalytic activity of the bimetallic ReAu nanoparticles on the Te particle reaction is obviously enhanced compared with that of pure gold nanoparticles, which means the distinctive property of Au–Re nano-system has the potential application in the field of catalysts. More importantly, AuRe nanoparticle is stable in liquid phase, while the pure Re nanoparticle is unstable although Re is a non-precious metal and has the strong catalytic activity. Additionally, in the latest biochemical analysis and clinical chemistry [37], AuRe nanoparticle was used as the nanoprobe to effectively detect the thrombin through its strong reactivity. Considering that Au–Re nano-systems have comprehensive application prospects, it is significant to explore the interesting properties of Au–Re nano-system which are determined by the special the electronic configuration and structure. However, given an overview of these previous investigations, the systematical and substantial studies on Re-doped Au nano-system are still relatively rare. Moreover, the small mixed metal clusters can clearly reflect the extraordinary size-dependent pattern and distinct electron-configuration of nano-system, which is a great favor for the overall realization of Re-doped Au nano-system. Hence, it is necessary to profoundly understand the construction and stability mechanism of Re-doped gold clusters. Especially, we should focus on: how the dopant Re atom influence the growth pattern of doped clusters? How greatly the geometries, electronic property and chemical reactivity of Au_nRe differ from the pure gold clusters?

In the present work, we systematically investigate the influence of impurity Re atom on the geometrical structures, relative stabilities, electronic properties, interaction between the dopant and host atoms and chemical hardness, coordinated mechanism of Au_nRe ($n = 1\text{--}12$) clusters, and the whole calculation is based on density functional theory with the generalized gradient approximation at PW91 level, and all-electron scalar relativistic effects. By the comparison with pure gold clusters, we hope to find the

evolutionary patterns and characteristics with the growth of the clusters size. We expect that our research would be constructive to understand the influence of material structure on its properties and guide further theoretical and experimental studies.

2. Computational details

The geometrical structures and electronic properties of Au_nRe ($n = 1\text{--}12$) clusters are calculated using the spin-polarized density functional theory (DFT) in the DMOL³ program package [38–40]. The generalized gradient approximation (GGA) in the Perdew–Wang 91 exchange–correlation functional (PW91) [41] is chosen in the calculations. A double-numerical basis set including d -polarization functions (DNP) are adopted for the description of the electronic wave functions. Due to heavy elements of gold and cadmium [38,42–50], the all-electron scalar relativistic (AER) method is used in our work for the higher accuracy of calculations. Meanwhile, the convergence criteria are set with 0.002 Ha/Å for the forces, 0.005 Å for the displacement, and 10^{-5} Ha for the energy change in our calculation. To ensure the reliability of initial structures, firstly, we re-optimized the structures of pure gold clusters in previous studies [49,51–53] with the same methods and same parameters. And then, based on these optimized equilibrium geometries of pure gold clusters, we can construct numerous possible initial structures of Au_nRe clusters by a Re atom replacing one gold atom at every possible nonequivalent site or adding a Re atom directly on each possible nonequivalent site in Au_{n+1} cluster or adding an Au atom directly on each possible nonequivalent site in Au_{n-1}Re . In the Meantime, we also refer to the structures available of doped gold cluster in previous literatures [11,12,53–56]. These possible initial structures of Au_nRe include one-, two-, and three-dimensional geometries. Moreover, all initial structures are optimized by relaxing fully the atomic positions without any symmetry constraints. Additionally, the harmonic vibrational frequencies of all configurations are computed in order to confirm all the optimized structures correspond to the local energy minima.

To examine the accuracy of our scheme, we calculate the bond-length, average binding energy and vertical ionization potential of Au_2 , Re_2 and AuRe dimers for comparison with the corresponding experimental data. In our calculations, the bond-length, dissociation energy and vibrational frequency is 2.487 Å, 1.214 eV and 183.1 cm^{-1} for Au_2 dimer, 2.067 Å, 3.292 eV and 385.7 cm^{-1} for Re_2 dimer, respectively. These calculated values are in good accordance with the corresponding experimental results [57–62] of 2.473 Å, 1.153 eV and 190.9 cm^{-1} for Au_2 , and 2.18 Å, $4 \pm 1\text{ eV}$ and $340 \pm 20\text{ cm}^{-1}$ for Re_2 , respectively. Additionally, for AuRe dimer, the bond-length of 2.518 Å and frequency of 174.4 cm^{-1} in our work are consistent greatly with previous DFT calculation results [63] of 2.525 Å and 174 cm^{-1} . Thus, we can confirm that our calculations are precise and valid enough to investigate the properties of Re-doped gold systems.

3. Results and discussions

3.1. Geometrical structure

As shown in Fig. 1, the typical and low-lying structures of Au_nRe ($n = 1\text{--}12$) are presented including the symmetry and relative energy of the geometries. Meanwhile, isomers are arranged according to the order of energies from low to high, and Au_nRe clusters is compared with corresponding pure gold clusters.

For Au_2Re , the lowest-energy state 2a is a linear $D_{\infty h}$ structure with the double coordination number of dopant Re. The isomer 2b is a triangle C_{2v} structure produced by a Re atom substituting an Au atom of Au_3 cluster, which is 0.649 eV less stable than the

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