Insights into the structural, electronic and magnetic properties of Ni-doped gold clusters: Comparison with pure gold clusters

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ABSTRACT

The structural, electronic and magnetic properties of Au_{n+1} and Au_nNi (n = 1−9) clusters have been investigated using an unbiased CALYPSO structure searching method in conjunction with density functional theory. The structural searches show that Ni atom in the lowest energy Au_nNi cluster favors the most highly coordinated position. The ground state Au_{n+1} and Au_nNi clusters possess a planar structure, except for Au_6Ni and Au_8Ni. Vibrational spectra and photoelectron spectra are predicted to identify their structures in the future. The relative stability and chemical activity are analyzed based on the averaged binding energy, dissociation energy and energy gap for the most stable clusters. It is found that the dopant atom can enhance the thermal stability of the gold clusters. The magic number of stability is 5 for both Au_{n+1} and Au_nNi clusters. The substitution of a Ni atom for an Au atom significantly decreases energy gap of Au_n clusters with even n. The magnetism calculations show that the magnetic moments of Ni atom in Au_nNi clusters are reduced by 0.56−2 μ_B. This reduction may be attributed to the internal charge transfer from 4s to 3d orbital.

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1. Introduction

Gold clusters have attracted the attention of a wide range of researchers since the discovery of unexpected catalytic effects by supported gold nanoparticles [1−16]. In the meantime, theoretical and experimental studies have manifested that the nature of small clusters can be modified substantially by adding an impurity atom [17−30]. Gold clusters doped with a single atom have been expected to tailor the desired optical, catalytic, electronic, magnetic and properties for potential applications in solid state chemistry, nanotechnology, biology, microelectronics and materials science [31−42]. For example, Kaydashev et al. found that replacing an Au atom by a Pd atom in Au_n^+ ($13 \leq n \leq 20$) results in a significant decrease of the integrated absorption cross section as well as in shifts of the transition energies [31]. Mondal e*t al.* reported that Li atom doped in Au_{19} cluster can enhance the interaction of CO molecule with $Au_{19}Li$ cluster over that of pure Au_{20} cluster and the endohedrally doped cage-like $Au_{19}Li$ cluster may be better catalytic

agent than pure Au_{20} cluster for CO oxidation [32]. Kumar et al. performed *ab initio* calculations on Gd-doped gold clusters and obtained a magic magnetic cluster of gold, $Gd@Au_{15}$ with a large energy gap of 1.31 eV that can be useful for phototherapy of cancer cells. Furthermore there are large magnetic moments localized on Gd atom and this makes $Gd@Au_{15}$ also attractive for bioimaging [33]. Recently, several investigations have been devoted to binary Ni-doped gold clusters and Ni-Au alloy thin films due to their unique physical and chemical properties. It was shown that Ni atom in Au_{16}^- cage can dramatically change the geometric and electronic properties of the host cluster and the 4s electrons of Ni atom are observed to transfer to the Au_{16} cage [43]. The infrared spectra of the tubular Au_{24} cluster are greatly altered by Ni atom and the atom-like magnetism is retained for $Ni@Au_{24}$ [44]. The tunable surface composition and atomic assembly structure of the Ni-Au alloy surface have great potential in the improvement of catalyst design [45]. However, there are relatively few systematic works regarding the neutral Ni-doped gold clusters. On the other hand, some experiments which are used to shed light on the structures of clusters must depend on theoretical computations of geometries of possible low lying isomers. Consequently, in this paper, the structural, electronic and magnetic properties of Au_{n+1} and Au_nNi

(n = 1—9) clusters will be studied systematically on the basis of density functional theory (DFT). It is hoped that our work would be helpful to perceive the influence of material structure on its properties and could offer practical guidelines for coming experimental research.

2. Computational details

The structure prediction of Au_{n+1} and Au_nNi clusters is based on the CALYPSO method which has been successful in correctly predicting structures for various systems [46—48]. The important feature of this method is the capability of predicting the configuration with only the knowledge of the chemical composition. A local version of particle swarm optimization (PSO) algorithm is implemented to utilize a fine exploration of potential energy surface for a given non-periodic system. The bond characterization matrix technique is utilized to eliminate similar structures and define the desirable local search spaces. Each generation contain 20-30 structures, 80% of which are generated by PSO. The others are generated stochastically. We follow 20 generations to achieve the converged structure.

The accuracy of several exchange-correlation functionals [49—51] implemented in the Gaussian09 package [52] was firstly checked by computations on Au_2 and AuNi dimers. The computed results based on PW91PW91 functional with the basis sets (def2-TZVPP for Au and LanL2DZ for Ni) [53,54] are in good agreement with available experimental data, as listed in Table 1. Accordingly, this level of theory was used to describe Au_{n+1} and Au_nNi clusters. Due to the spin polarization, every configuration was optimized at possible spin states. Harmonic vibrational frequencies were computed at the same level of theory to confirm the stability of configuration. In all computation, the convergence thresholds were set to 6.0×10^{-5} Å for the displacement, 1.5×10^{-5} Hartree/Bohr for the forces and 10^{-6} Hartree for a total energy.

3. Results and discussions

3.1. Geometrical structures and vibrational spectra

Firstly, geometry optimizations of Au_n (n = 3—10) clusters were carried out and the ground state structures of Au_n clusters are shown in Fig. 1. Our results are in line with the results of Wang et al. [5,39]. Besides, a structure with D_{2h} symmetry as the ground state of Au_4 cluster was also reported in previous reference [7] and will be discussed later. For Au_nNi (n = 2—9) clusters, large numbers of initial structures were optimized and many isomers were obtained. The lowest energy structure and three low-lying isomers for each Au_nNi cluster are shown in Fig. 2. According to the order of energy from low to high, these isomers are numbered in sequence na, nb, nc, and nd, where n represents the number of Au atoms in Au_nNi clusters. Their symmetry, spin multiplicity and energy difference compared to each of the lowest energy structures are also labelled in this figure.
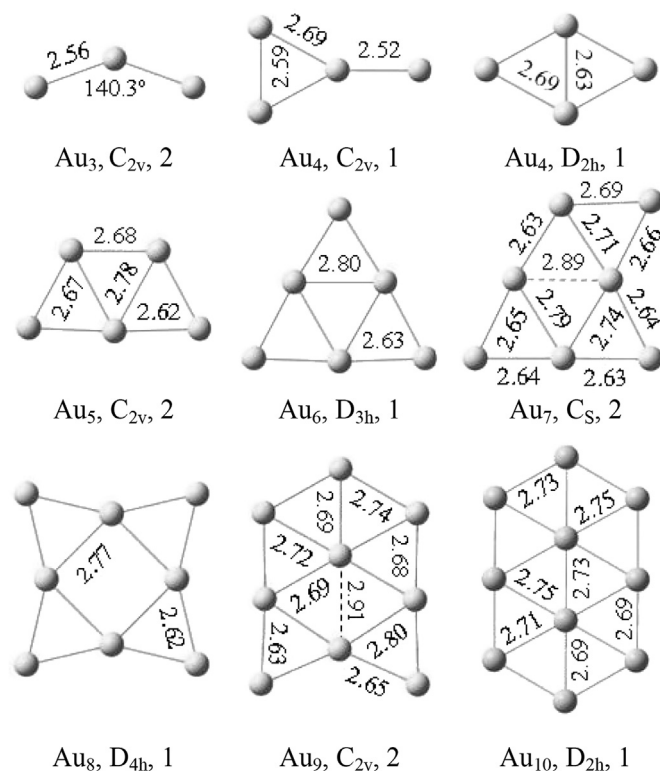

Fig. 1. The ground-state structures of Au_n (n = 3—10) clusters. Bond lengths are in Å. The point group and spin multiplicity are given below them.

The optimized results for AuNi dimer show the doublet spin state is 1.57 eV lower than the quartet spin state. Consequently, the doublet AuNi is the ground state. The bond length of AuNi is 2.38 Å and shorter than that of Au_2 (2.51 Å). This may be attributed to the fact that the radius of Ni atom (1.24 Å) is smaller than that of Au atom (1.44 Å). The most stable structures of Au_nNi (n = 2—5) clusters plainly prefer planar configurations. The lowest energy structures of Au_2Ni, Au_4Ni and Au_5Ni clusters are similar to those of Au_3, Au_5 and Au_6 clusters. The ground state structure of Au_3Ni cluster resembles the isomers with D_{2h}-symmetry of Au_4 cluster. These structures for Au_nNi (n = 1—5) are in accord with results reported by Yuan et al. [58]. The 2a isomer in singlet spin state turns into the 2b isomer. The 3d isomer, which can be regarded as a substitution of a Ni atom for an Au atom in the most stable Au_4 cluster, is less stable than 3a isomer by 0.302 eV. The 4c isomer is the first three-dimensional (3D) structure. The pentagonal pyramid and tetragonal bipyramid is not unstable for Au_5Ni cluster. Other isomers, which not displayed in Fig. 2, are higher in energy than the nd isomer.

Starting from n = 6, the stable 3D structures gradually increase in low energy isomers. To avoid leaving out the lowest energy

Table 1
The geometries and electronic properties of Au_2 and AuNi dimers.

Dimer	Functional/basis set	r(Å)		D_e (eV)		VIP(eV)		EA (eV)	
		Calc.	Expt.	Calc.	Expt.	Calc.	Expt.	Calc.	Expt.
Au_2	PW91PW91/TZVPP	2.51	2.47[a]	2.30	2.30[a]	9.51	9.50[a]	1.88	1.92 (1.94)[a]
	PW91P86/LanL2Dz	2.55		2.30		9.84		2.22	
	B3LYP/LanL2DZ	2.57		1.87		7.26		4.42	
AuNi	PW91PW91/Au-TZVPP, Ni-LanL2DZ	2.37	2.35 ± 0.01[b]	2.55	2.52 ± 0.17[b]	8.44	8.33 ± 0.38[b]	1.33	

[a] References [55,56].
[b] References [57].