

First-principle study of Au_nSc_m ($n = 1-7$, $m = 1, 2$) clusters

Gui-Xian Ge, Hong-Xia Yan*, Qun Jing, Hai-Bin Cao, and Jian-Jun Zhang

Key Laboratory of Ecophysics and Department of Physics, Normal College, Shihezi University, Xinjiang 832003, China

Received 10 September 2010; Accepted (in revised version) 15 October 2010

Published online 28 February 2011

Abstract. The geometries, stabilities, electronic, and magnetic properties of Au_nSc_m ($n = 1-7$, $m = 1, 2$) clusters have been systematically investigated by density functional theory. It is shown that the most stable structures of Au_nSc ($n = 1-7$) clusters favor planar structure and Sc atom is prone to occupy the center site of Au atoms ring. For Au_nSc_2 clusters, the $3d$ configurations become the lowest energy structure for $n \geq 3$; the growth is based on triangle bipyramid structure of Au_3Sc_2 cluster except Au_4Sc_2 . The second-order energy difference and the fragmentation energy show Au_3Sc , Au_5Sc , Au_3Sc_2 and Au_6Sc_2 clusters possess relatively higher stabilities than their neighbor size. The doping of Sc atom can greatly improve the stability of Au clusters. The doped one Sc atom changes the odd-even alternation trend of gaps in Au_n . The two doped-Sc atoms enhance chemical activity of Au_n in most cases. The total magnetic moments with even valence electrons are quenched on the whole due to electron pairing effects. The averaged coordination number for Sc should be major reason for reduce of local magnetic moments of Sc atom with cluster size increasing in cluster with odd valence electrons. The total magnetic moments in AuSc and Au_2Sc_2 are no quenched due to the smaller coordination number, the charge transfer and weak hybridization between the Sc and Au atoms.

PACS: 31.15.A-, 36.40.Cg

Key words: Au_nSc_m ($n = 1-7$, $m = 1, 2$) clusters, geometry structure, electronic properties

1 Introduction

Recent experiments have shown that the gold clusters have been aroused considerable interests by chemists and physicists due to their unique physical and chemical properties, particularly, their catalytic activities [1, 2]. Interestingly enough, the activity of gold clusters has

*Corresponding author. *Email address:* geguixian@126.com (G. X. Ge)

been found to depend critically on the size of the particle and the nature of the substrate. For example, when supported on the $\text{Mg}(\text{OH})_2$ surface, the best catalytic activity for oxidation of CO is observed for a system size of 13 atoms [3], while the optimal activity of gold clusters supported on TiO_2 surfaces occurs for sizes of 2–3 nm. Since the chemical and physical properties of gold clusters depend greatly on their physical structures, significant efforts have been made to determine the most stable configurations of gold clusters in this size range.

On the other hand, the structure and electronic properties of the doped clusters are usually different from the pure clusters. Many studies have been performed on impurity-doped or mixed gold clusters in order to enhance the stability of gold clusters and improve their chemical activities, or examine the electronic shell structures in mixed gold clusters [4–6]. For example, Bouwen *et al.* [7] and Heinebrodt *et al.* [8] investigated the bimetallic Au_nX_m^+ clusters ($\text{X}=\text{Cu}, \text{Al}, \text{Y}, \text{In}, \text{Cs}; n=1-65, m=1,2$). Especially, extreme size sensitivity of catalytic activity of supported Au clusters is worthy of particular attention [9]. Guo *et al.* investigated small Au_nNi^- [10], Au_nY_2 ($n=1-4$) [11], Au_nFe ($n=1-7$) [12], Au_nPd^- [13] and Au_nPd_2 [14] using the density functional method B3LYP with relativistic effective core potentials (RECP) and LANL2DZ basis set. Garzn *et al.* [15] investigated small Au_nS ($n=1-5$) and Au_nS_2 ($n=1-4$) clusters. Yuan *et al.* investigated geometric, electronic, and bonding properties of Au_NM ($N=1-7, \text{M}=\text{Ni}, \text{Pd}, \text{Pt}$) clusters [16], and found that the dopant atoms markedly change the geometric and electronic properties of gold clusters. Zhang *et al.* investigated the geometries, electronic, and magnetic properties of the 3d transition-metal-doped gold cluster: M@Au_6 clusters ($\text{M}=\text{Sc}, \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) [17]. Torres *et al.* [18] investigated the structural, electronic, and magnetic properties of Au_nM^+ clusters ($\text{M}=\text{Sc}, \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Au}; n \leq 9$) using first-principles density functional calculations in which the magnetic moment showed pronounced odd-even effects as a function of the cluster size and resulted in values very sensitive to the geometrical environment. Neukermans and co-workers [19, 20] have investigated the stability of cationic gold clusters doped with a 3d TM atom, Au_nTM^+ , with TM from Sc to Zn, and extended their investigations to multiply TM atoms doped gold clusters Au_NX_M clusters ($\text{X}=\text{Sc}, \text{Ti}, \text{Cr}, \text{Fe}; N=1-40, M=0-3$) by means of photofragmentation experiments [21].

Although there has been a substantial amount of research for doped gold clusters. No systematic studies on Sc-doped gold clusters have been reported to our knowledge. In this paper, we will provide an *ab initio* structural and electronic investigation for Au_nSc_m ($n=1-7, m=1,2$) clusters by using density functional theory. This information will be useful to understand the enhanced catalytic activity and selectivity gained by using Sc-doped gold catalyst. In order to examine the effect of Sc atom to gold clusters, geometry optimizations of pure gold clusters were also calculated using identical method. The rest of the paper is organized as follows: In Section 2, the calculation details are described. Section 3 presents the results and discussion. Finally, the summary and conclusions are given in Section 4.