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DFT and QTAIM studies on structure and stability of beryllium doped gold clusters

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ABSTRACT

Impurity-doped clusters particularly the gold doped bimetallic clusters have received considerable attention in the last few years. The doped atoms can considerably alter the geometrical and electronic properties as well as the stability of gold clusters. Density functional theory (DFT) with B3LYP functional have been applied to study the geometrical structures and relative stabilities of small bimetallic neutral, cationic and anionic Au_nBe (n = 1–6) and Au_nBe_2 (n = 1–5) clusters. For Au_nBe_2 clusters, we obtained only planar structure whereas Au_nBe clusters show both planar and three dimensional structures. The relative stabilities of the clusters are compared on the basis of average binding energies, fragmentation energies and second order difference of energies. The fragmentation energies and second order difference of energies of all the three types of clusters shows the even–odd alternation phenomenon. The nature of bonding interaction is also investigated by using Bader's quantum theory of atoms in molecules (QTAIM). Based on QTAIM results, we can suggest that the beryllium doped clusters are more stable than the pure gold clusters due to strong covalent interaction between the gold and beryllium metal centres.

1. Introduction

In recent years, bimetallic nanoclusters have received much interest to scientific community due to their unique large surface to volume ratio and quantum size effects. They are composed of two different metal elements and are more promising than the monometallic nanoparticles because synergestic effect is expected [1]. They show novel catalytic behaviour based on the effect of second metal element added. This effect can often be explained in terms of an ensemble [2] or a ligand effect in catalysis [3]. Binary clusters basically that of gold(Au) found importance in catalysis, colloidal chemistry and medical science [4–7]. Now a days, lots of studies on Au clusters doped with different atoms have been conducted by many groups. Tafoughalt and Samah [8] observed structural and electronic properties of bimetallic Ag–Au cluster up to eight atoms by DFT using Wu and Cohen generalised gradient approximation functional. Au atoms inclusion in the cluster increases the binding energy and vertical ionisation potential, indicating higher stability as the number of Au atoms grows. Li et al. [9] investigated the electronic structures and magnetic properties of MAu_6^- (M = Ti, V, Cr) using combined photoelectron spectroscopy and DFT calculations. Ji-Xian et al. [10] carried out DFT calculations on Au_nRh (n = 1–8). Here they found the even number atoms clusters more stable than that of odd number atoms clusters. Wang et al. [11] studied theoretically the Al doped anionic Au clusters and reported that the doping of Al effect the ground state geometries of Au clusters and the stability order follows even odd alternation. Romero et al. [12] analysed the effect of boron atom on the properties of gold clusters and concluded that the boron atom enhanced the symmetry and shrinks the electron density of the gold clusters.

When we discuss about Beryllium (Be), it is a group II element having high melting and boiling point and high enthalpy of atomization [13]. Beryllium increases hardness and resistance to corrosion when alloyed to certain metals like Al, Co. Cu, Fe and Au etc. [14]. For Be–Au clusters, Balducci et al. [15] reported the dissociation energy, vibration frequency and bond energy of bimetallic AuBe dimer by using mass spectrometry and DFT. When one or two Be atoms are doped into neutral and cationic gold clusters, these corresponding isomers display an obvious even–odd alternation due to the closed opened-shell effects [16–18]. Consequently we think what will happen if we compared the structures and properties of bare neutral, cationic and anionic Au clusters on doping Be atoms? Therefore, by applying DFT we studied the structural and electronic properties of Au clusters doped with Be atom(s), Au_nBe (n = 1–6) and Au_nBe_2 (n = 1–5). During this study, we are taken into mind the previous reported structures and only

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Table 1
Comparison of calculated bond lengths of Au_2 and AuBe molecules with experimental at different levels of theory.

Methods	Au–Au	Au–Be
Experimental	2.49[a]	2.06[b]
B3LYP	2.54	2.07
BVP86	2.56	2.09
WB97XD	2.57	2.12
B3PW91	2.55	2.09

[a] Ref. [28].
[b] Ref. [29].

optimised a certain type of structures by doping Be in different positions of bare Au clusters. The importance of this work lies in the fact that nanosized Au clusters already shows tremendous catalytic activity for different types of reactions and the doping of a metal can further enhanced its catalytic property. The novelty of the work with reference to the previous works lies in the facts that for the first time we have studied the all neutral and charged clusters together and compared with the pure one. The comparison between charged and neutral Be doped Au clusters are also shown for the first time in this manuscript. Therefore, our present study can bring a new concept to consider the Be doped Au clusters in the field of catalysis and in this regard our work must be used as a platform.

2. Computational methods

Geometrical structure optimisations and frequency analysis of Au_nBe and Au_nBe_2 clusters have been performed using the GAUSSIAN 09 suits of program [19]. In the frame work of DFT, we employ the hybrid B3LYP [20,21] functional to explore the stationary points on the potential energy surface. As we all know, the relativistic effects play a primary role in the structure and energetic of Au-containing clusters, we used the Los Alamos LANL2DZ [22,23] Effective Core Pseudopotentials (ECP) and valence double-ζ basis sets for Au. The Beryllium atoms are treated with 6–311+G(d) basis set. No symmetric constraints were imposed during geometry optimisation.

B3LYP functional is recently used successfully by various groups in the study of metal clusters [12,24–27]. In order to validate our results at B3LYP level, we have also performed some calculations on different DFT functionals and results are summarised in Table 1.

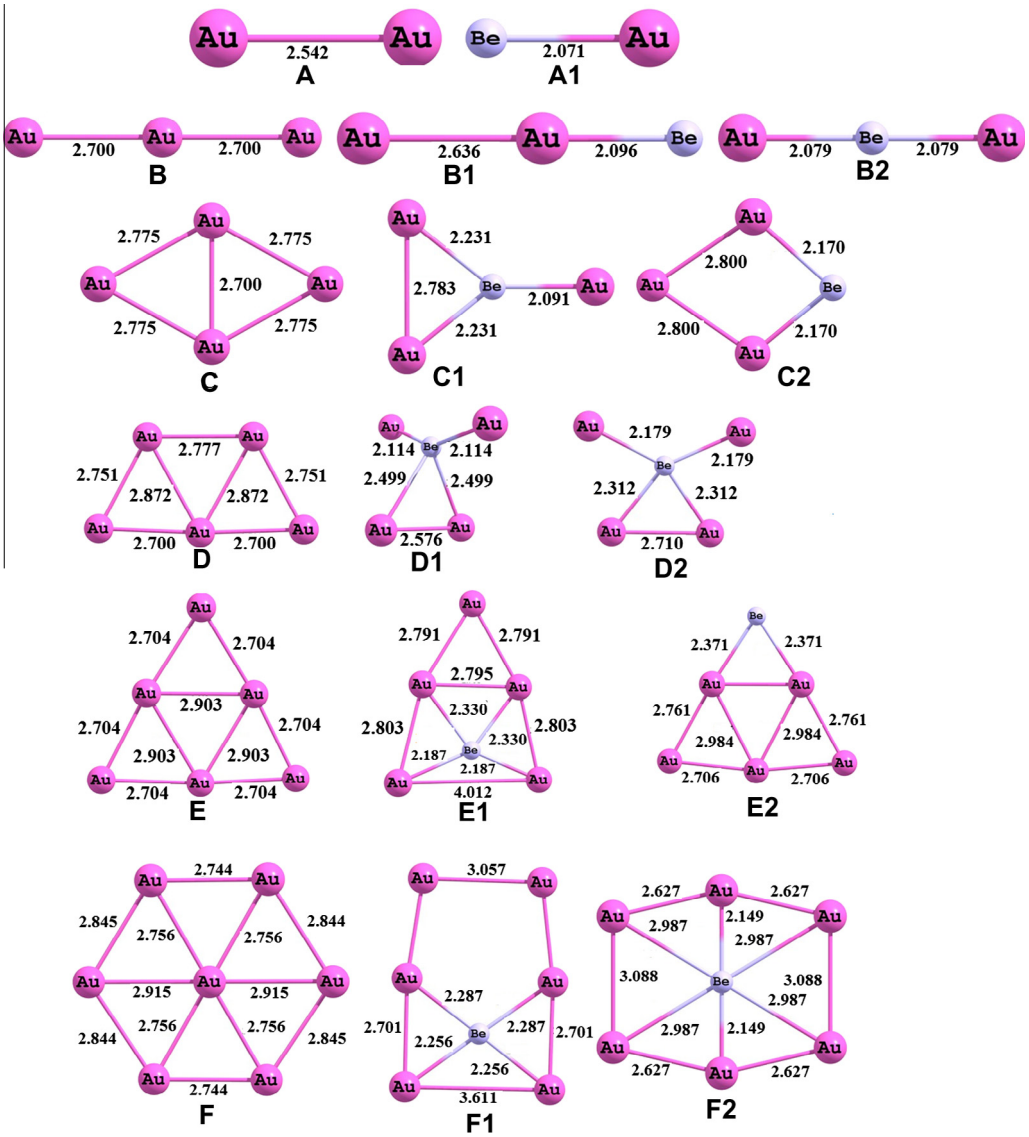

Fig. 1. Structures of neutral Au_{n+1} and Au_nBe (n = 1–6) clusters.