Structural and vibrational properties of gold-doped titanium clusters: A first-principles study

R. Britto Hurtado [a], M. Cortez-Valadez [b,*], R. Gámez-Corrales [c], M. Flores-Acosta [a]

[a] Departamento de Investigación en Física, Universidad de Sonora, Apdo. Postal 5-88, 83190 Hermosillo, Sonora, Mexico
[b] CONACYT-Departamento de Investigación en Física, Universidad de Sonora, Apdo. Postal 5-88, 83190 Hermosillo, Sonora, Mexico
[c] Departamento de Física, Universidad de Sonora, Apdo. Postal # 130, Hermosillo, Sonora 83000, Mexico

ARTICLE INFO

ABSTRACT

This article presents the fabrication of Metallic structures made of ultra-small clusters. The study of metallic clusters is essential in the understanding of the physical properties of this type of systems. In this sense, first-principles calculations of the structural and vibrational properties of the clusters Ti_nAu (n = 2–15) and $(TiAu)_m$ (m = 1–10) were studied by density functional theory (DFT) with the functional B3LYP and the LANL2DZ basis set. The results indicate that cases Ti_7 and Ti_{13} are magic number clusters that correspond to those reported in literature. Similarly, case Ti_2Au is a magic number cluster, as it shows a maximum value in the second difference of energy. The study found that the symmetrical modes which show a radial expansion-contraction movement are the most intense vibrational modes in all the structures.

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1. Introduction

Currently the synthesis of metallic nanoparticles and nanoalloys are essential for nanotechnological development. Recent studies report the fabrication of metallic nanoparticles [1–3] and bimetallic nanoalloys (core-shell, janus, random, order alloys) [4–7] with sizes <10 nm. Such nanoalloys are commonly used in applications such as catalysis [8], biomedicine [9], antibacterial products [10], solar cells [11], etc. On the other hand, the fabrication of new metallic structures made of few tens of atoms is facilitated by the development of more potent electronic microscopes and upgraded handling techniques of the experimental conditions. This type of structures are called "clusters". For instance, Wang et al., obtained clusters of Pd encapsulated in zeolite with sizes between 1.5 and 1.8 nm [12], rhenium clusters between 2 and 13 atoms [13] and germanium clusters between 6 and 45 atoms [14]; these clusters were studied with high annular dark field - scanning transmission electron microscopy (HAADF-STEM). Currently, the theoretical study of the structural, optical and vibrational properties of metallic and bimetallic clusters using ab initio methods is popular among the scientific community in order to predict physicochemical behaviors that can be handled in diverse technological applications.

Titanium is one of the most used metals in the development of aeroespacial, aeronautical and medical technologies [15,16], due to characteristics such as high resistance to extreme temperature conditions, corrosion, and its compatibility with the human tissue. Both gold and titanium show biocompatibility [17,18]. Few experimental studies report the extraction and application of bimetallic nanoalloys Ti-Au; the studies only report nanometric alloys of Ti-Ni with ~4 nm [19,20], which are noteworthy due to the Shape Memory Alloy effect SMA. SMA consists in the reversible change of the alloy's crystallographic structure under thermal and mechanical conditions [21]. Studies also report nanoparticles of Ti-Cr with sizes between 10 and 40 nm [22]. On the other hand, there are no theoretical/experimental studies in the literature about clusters of Ti doped with Au atoms. Until now, it is only possible to find studies about pure Ti_n clusters and titanium-doped gold clusters of Au_nTi using the density functional theory (DFT). For instance, Salazar-Villanueva et al. report a structural analysis of clusters Ti_n (n = 2–15) [23]; Dong et al. studied the geometry, stability and the magnetic properties of clusters Au_nTi (n = 1–9) [24]. Ming-Xing and Yan study the structure and stability of clusters Au_nTi (n = 2–16) [25]. They report the study of the structural and vibrational properties of gold-doped titanium clusters of Ti_n-Au = 2–15 and $(TiAu)_m$ with n = 2–15 and m = 1–10 respectively, using DFT with the functional B3LYP and the basis set LANL2DZ.

2. Computational details

The geometry and the calculations of the vibrational properties were optimized with the Becke's hybrid exchange-correlation functional, three parameter, Lee-Yang-Parr (B3LYP) [26,27] in combination with the basis set Los Alamos National Laboratory 2 double ζ (LANL2DZ) [28] using the density functional theory DFT with the computational package Gaussian 09 [29]. First we considered the clusters made only of Ti with one geometrical configuration of local minimum energy with the reports published for Ti_n. These were our initial structures [30–32]. Subsequently, these clusters were 'doped' (Ti_nAu $n = 2$–15) with a gold atom and optimized to their low energy configuration. Similarly, for the clusters $(TiAu)_m$; we initially took the pure Ti clusters and added m gold atoms for each m titanium atom ($m = 1$–10). Ochterski describes in a general way the steps used by Gaussian for the vibrational analysis of the polyatomic systems [33], with which it is possible to calculate the Raman intensities following expression 1 [34,35].

$$R_i = \frac{2^4 \pi^4 (v_0 - v_i)^4}{45} \left[\frac{h}{8\pi^2 c v_i (1 - \exp\left(-\frac{hv_i c}{kT}\right))} \right] (S_i) \tag{1}$$

$$h = 6.626 \times 10^{-34} \, J\,s; \quad c = 2.997 \times 10^{10} \, \frac{cm}{s};$$

$$k = 1.380 \times 10^{-23} \, \frac{J}{K}; \; Si: \; are\ the\ raman\ activities;$$

$v_0 : \; frequency\ of\ the\ incident\ light,$
$v_i : \; frequency\ of\ the\ vibrational\ mode$

3. Results and discussions

3.1. Ti_n and $Ti_{n-1}Au$ clusters

Fig. 1 presents the optimization of clusters Ti_n y $Ti_{n-1}Au$ ($n = 2$–15) using DFT and the hybrid functional B3LYP combined with the LANL2DZ basis set, the structures correspond to the local minimum energy values. The extraction of a local minimum was confirmed when the negative frequency values were not detected in the vibrational spectrum. The structural configurations of the clusters Ti_n are similar to those obtained by other authors [30–32]. On the other hand, there are no reports of titanium clusters doped with one gold atom $Ti_{n-1}Au$. The optimization of the local minimum energy of these structures is an analysis of the first-principles. The metallic clusters can change their physical properties when one atom of another element is replaced in the structure; likewise, its structural configuration could be modified. We could observe that most of the structures did not show characteristic changes when one Ti atom was replaced by one gold atom, except for some cases, for instance, the structural transition of $Ti_7 \rightarrow Ti_6$-Au, this cluster changes from a decahedron to an irregular heptahedron.

On the other hand, we performed a relative stability study, that depends on the local minimum energy of each structure. In order to do so, we defined the structural stability parameters of Binding Energy (BE), and the second difference of energy ($\Delta_2 E$) [36–38]. The bond energy (BE) and the second difference of energy ($\Delta_2 E$) are predictive theoretical parameters widely used in the study of the stability of metallic clusters. The Binding Energy (BE) is defined as the average energy necessary to separate one atom from a cluster made of n atoms. The expression of BE is shown in Eq. (2).

$$BE_{X_n} = \frac{[nE(X) - E(X_n)]}{n} \tag{2}$$

where $E(X)$ and $E(X_n)$ correspond to the minimum energy of a single atom and the local minimum energy of the cluster made up of n atoms, respectively. For Ti clusters and clusters doped Ti_n-Au the BE can be described by Eqs. (3) and (4), respectively.

$$BE_{Ti_n} = \frac{[nE(Ti) - E(Ti_n)]}{n} \tag{3}$$

$$BE_{Ti_nAu} = \frac{[nE(Ti) + E(Au) - E(Ti_nAu)]}{n + 1} \tag{4}$$

With $E(Ti)$, $E(Au)$ and $E(Ti_nAu)$ the energy of an isolated Ti atom, the energy of one Au atom and the local minimum energy of the cluster Ti_nAu, respectively.

The second difference of energy ($\Delta_2 E$) allows to obtain the information between the energies and the neighboring clusters, generating a zig-zag graph that indicates the formation of magic number clusters. Clusters Ti_n and doped $Ti_{n-1}Au$ can be calculated using formulas (5) and (6).

$$\Delta_2 E_{Ti_n} = E(Ti_{n+1}) + E(Ti_{n-1}) - 2E(Ti_n) \tag{5}$$

$$\Delta_2 E_{Ti_nAu} = E(Ti_{n+1}Au) + E(Ti_{n-1}Au) - 2E(Ti_nAu) \tag{6}$$

Fig. 2a shows the bond energies calculated for the cases Ti_n and $Ti_{n-1}Au$. The bond energy shows a proportionality with the number of atoms, showing a tendency to a constant number. Furthermore, it is worth noting that in order to take one atom from the pure structures a higher energy is required than in those doped with one Au atom. This is an unexpected result considering that the studies in the literature for Ti structures doped with one metallic atom, such as TiNi and TiV show a higher bond energy that pure Ti clusters [39,40]. For $n > 7$ the values of this energy for clusters Ti_n and $Ti_{n-1}Au$ are every time closer, due to the superiority of Ti atoms, compared with one single gold atom.

Fig. 2b shows that clusters Ti_7 (pentagonal bipyramidal) and Ti_{13} (distorted icosahedron) show high stability, commonly denominated magic number clusters, this result agrees with those reported by other authors that use DFT, but with different functionals and basis sets [30,31]. In the case of the doped clusters, there is a new magic number cluster, Ti_2Au, which shows higher stability than the rest of the doped clusters. The results obtained show that the Ti dimer is more stable than a diatomic cluster made of one Ti atom and one Au atom (TiAu). On the other hand, when a Ti atom is replaced by an Au atom in the clusters Ti_7 and Ti_{13}, we observed that the pure structures are more stable (Note, we compared the clusters with the same number of atoms).

Fig. 3a and b show the theoretical Raman spectra of each one of the pure Ti clusters, as well as those from clusters doped with one gold atom. Symmetrical, asymmetrical, balance and torsion vibrations were observed; however, the symmetrical vibration modes showed generally the most intense vibration mode than the rest (higher Raman activity), when observing the vectorial shoft of each atom, these show a radial expansion-contraction tendency (marked with "$*$" in Fig. 3a in order to make reference to the RBM in each of the clusters). We compared the structures with the same size (see Fig. 3b). Given that bulk metals are not active in Raman, we observed that while the size of the cluster increases, the RBM shift to lower wave numbers. Even though the RBM are used for the analysis of vibrational and structural properties of carbon nanotubes [41,42], they are also used for predicting low frequency modes of clusters and small metallic nanoparticles [43–48]. The RBM for Ti_n clusters are located between 250 and 400 cm^{-1}; for $Ti_{n-1}Au$ we found that clusters $\leq Ti_6Au$ tend to be located between 190 and 310 cm^{-1} below the radial modes of the pure Ti clusters. Clusters $\geq Ti_7Au$ tend to show similar values to those from pure Ti structures with the same size between 250 and 350 cm^{-1}. With this the vibrational contribution that the Au atom presents in