Energetic and molecular structural properties of small gold clusters

N. Sierralta
Departamento de Física, Universidad de Los Andes, Mérida-5101, Venezuela

L. Rincón and R. Almeida
Departamento de Química, Universidad de los Andes, Mérida-5101, Venezuela

Recibido el 20 de febrero de 2002; aceptado el 15 de julio de 2002

A systematic study of the structural and energetic properties of gold clusters, ranging from monomer to hexamer, is performed. For the calculations, density functional theory is employed, using the B3LYP functional, and the basis set used for the gold atoms is the effective core potential of Stevens, Basch and Krauss (ECP-121G). After exploring the potential energy surface, optimized geometric parameters and energies have been calculated for several stable configurations. With the exception of the hexamer cluster, the results obtained are qualitatively similar to those reported for alkali metal clusters.

Keywords: Gold clusters; density functional theory; electron Core potential; structural properties.

Se ha realizado un estudio sistemático de las propiedades energéticas y estructurales de los agregados de oro desde el monómero hasta el hexámero. En los cálculos se usó la teoría del funcional de la densidad con el funcional B3LYP, y como base el potencial efectivo del core de Stevens, Basch y Krauss (CEP-121G). Luego de explorar la superficie de energía potencial, los parámetros energéticos y estructurales se obtuvieron para diferentes configuraciones estables. Con la excepción del hexámero, los resultados obtenidos son muy similares a los reportados para agregados de los metales alcalinos.

Descriptores: Agregados de oro; teoría del funcional de la densidad; potencial efectivo del Core; propiedades estructurales.

PACS: 36.40.M; 31.15.E

1. Introduction

The experimental and theoretical study of gold clusters is a subject of current interest [1-9]. Part of this interest arises from their use as a tip, or contact, in molecular circuits. Thus, it is well known [10, 11] that small gold clusters play a crucial role in experiments of molecular conductance. In these experiments, is assumed that the final contact is formed by only a small number of gold atoms [8, 9]. Besides this, there is also a more basic interest in the study of gold clusters. This is so, because, in most of the cases, the electronic properties and structures of small metallic clusters reveal little resemblance with their corresponding bulk properties and, at the same time, they show important difference with respect to those of isolated atomic or molecular systems [12-15]. Thus, the study of metallic clusters opens some issues which are not met neither in molecular or solid state physics.

In this work, we present a systematic study of the structural and energetic properties of small gold clusters, Au_n (n from 1 to 6), using density functional theory (DFT) calculations in conjunction with a effective core potential (ECP) basis set. Let us point out that there have been a number of previous theoretical studies on “naked” gold clusters, most of them involving extensive basis sets and relativistic methodologies employing ab-initio or DFT technics [3-8], and evidencing the important role of electron correlation in all these systems. However, as far as we know, only few a systematic studies of the variation of geometric and energetic properties of these clusters with the number of atoms, have been performed, Seminario and Tour [5] considered using DFT calculations, conglomerates up to the tetramer; while, Bravo-Peréz, Garzón and Novaro [7] studied clusters from dimer to hexamer at the MP2/MP4 level, and Hääkinen and Landman by a Born-Oppenheimer local-spin-density molecular dynamics methods [8] (BO-LSD-MD). In the present work, we study gold clusters up to the hexamer exploring the geometric configurations of several of the low lying energetic isomers, some of them not considered by those authors. Finally, taking into account the fact that, due to their simpler electronic structure, alkali metal clusters have been the most widely studied systems [13], and that the atomic configuration of gold atoms (s^1d^{10}) resembles the s^1 valence configuration of alkali metal, we have also performed some comparisons between the properties of these two kind of clusters.

2. Computational details

Here, all DFT calculations, using the Becke hybrid exchange functional [14], and the Lee-Yang-Par correlation functional [15], B3LYP, have been performed with the Gaussian-98 suite of programs [16]. The basis set used for gold atoms is the Stevens, Basch and Krauss effective core potential of triple-ζ quality (CEP-121G) [17]. This ECP includes relativistic corrections in the core potential, which allows to apply standard non-relativistic techniques, rendering substantial computational savings in systems of large numbers of electrons, as metallic clusters. The ECP used in this study, has been shown to be similar in quality to that of Los Alamos National Laboratory ECP (LANL2DZ), used in the work of Seminario and Tours [5] and Bravo-Peréz, Garzón and Novaro [7]. Let us mention that the performance of DFT in conjunction with ECP in molecules containing metals has re-
3. Results and discussion

The typical check of the suitability of DFT with ECP basis set for metallic systems is the calculation of the atomic ionization potential (IP), and the equilibrium bond length (r_e) and dissociation energy (D_a) for the dimer. Table I shows the results of our calculations for these parameters. There, it is also shown the experimental (Exp) values and the results corresponding to other DFT/ECP and to some more expensive post-Hartree-Fock calculations, as configuration interaction (CI) and quadratic configuration interaction including single doubles excitations (QCISD). For the IP, all DFT calculations are in excellent agreement with the experimental observation, in most cases within 1% or 2%, rendering slightly better results than some of the expensive relativistic post-Hartree-Fock methods. For all calculations, the predicted bond distances are larger and the dissociation energies smaller than their experimental counterparts. These comparisons show errors between 2% and 4% for the bond lengths, including the extensive post-Hartree-Fock methods; while larger errors are observed for the dissociation energies for this property, the calculations performed here give an error of 17%, while those with the B3P86 functional and similar basis sets have errors of 11% to 12%. The best D_e value (8% error) is found for the expensive QCISD(T) calculation. Our predicted ground state harmonic frequency, 165 cm⁻¹, is within 14% of the experimental value of 191 cm⁻¹. These results lead us to conclude that the methodology and the ECP employed here are capable to describe gold clusters.

In Fig. 1-A the optimized geometries obtained for the trimer clusters are displayed. Three stable minima were found: the one with the smallest energy (structure I) corresponds to a zig-zag chain, with C_{2v} symmetry, an Au-Au-Au bond angle α of 137.5°, a near neighbor Au-Au distance a of 2.628 Å and a dissociation energy of -276 kJ/mol. The second most stable structure (II) is 9 kJ/mol higher in energy and has a triangular geometry with C_{2v} symmetry characterized by two Au-Au distance (a = 2.660 Å and b = 3.013 Å) and a Au-Au-Au bond angle α of 78.3°. This structure is similar to that reported in Refs. 5, 7 and 8. Finally, 100 kJ/mol above the zig-zag chain, a symmetric linear structure (D_{inh}) was found (structure III). This structure has the smallest near neighbor distance (2.548 Å), and in agreement with Ref. 7, is the only stable linear chain found for the gold clusters studied in this work.

Figure 1-B displays the results for the tetramer gold clusters. Here, three stable planar structures are obtained: the most stable one (IV) has a rhombus geometry, with side distance, a, of 2.747 Å, acute angle, α, of 60.9°, D_{zh} symmetry and dissociation energy of -471 kJ/mol. Let us point out here, that similar geometric structures are reported for the cases of the most stable Li and Na tetramer clusters [13]. Again, other DFT/ECP, ab-initio, and BO-LSD-MD studies [5-8] have also found this structure as the most stable one for the tetramer. Only 1 kJ/mol above the energy of the rhombus, we have found a triangular arrangement connected to a fourth gold atom by one of the vertex and located at a distance of 2.582 Å and an angle of 56.6° (V) having symmetry C_{2v}. The triangular arrangement has internuclear distances of 2.773 Å and 2.629 Å, and an angle of 56.6°. This kind of structure, that resembles a tip, was reported by Seminario and Tours after performing an optimization that began from a tetrahedron [5], and by Bravo-Pérez et al too. Finally, with 30 kJ/mol more than the rhombus structure energy, a zig-zag chain (VI), with internuclear distances of 2.583 Å and 2.679 Å, and an angle α of 126.1° was obtained. In this case no stable linear chain was found.

Figure 1-C shows the results for the pentamer. In this case, five stable planar structures were found: the less energetic (VII) shows a trapezoid geometry of C_{2v} symmetry, characterized by three internuclear distances of 2.843 Å (a), 2.731 Å (b), and 2.689 Å (c), two Au-Au-Au angles, 57.9° (α) and 63.2° (β), and a dissociation energy of -647 kJ/mol. For alkali metal clusters [15], and in some previous gold cluster studies [7,8] this kind of geometry has also been reported as the most stable one. Second (VIII), 67 kJ/mol above energy corresponding to the trapezoid geometry, there is a distorted rhombus (VIII) with an additional gold atom connected

<table>
<thead>
<tr>
<th>Base-DFT</th>
<th>E_{xc} (eV)</th>
<th>IP (eV)</th>
<th>r_e (Å)</th>
<th>D_a (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEP-121G</td>
<td>9.32</td>
<td>2.571</td>
<td>-184</td>
<td></td>
</tr>
</tbody>
</table>

Table I. Ionization Potential (IP) for the gold monomer, and bond length (r_e) and dissociation energy (D_a) for gold dimer obtained in this work (CEP-121G). The ext. row corresponds to the experimental values. The others rows are results reported in the literature (whose references are indicated in the brackets).
through one vertex at 2.611 Å from it and forming a bond angle $\gamma$ of 114.5°. The distances and angles defining the geometry are indicated in the structure VIII of Fig. 1-C ($b = 2.696$ Å, $c = 2.762$ Å, $d = 2.722$ Å, $e = 4.524$ Å, $\alpha = 113.5^\circ$, $\beta = 58.9^\circ$ and $\theta = 59.9^\circ$). A third planar stable structure (IX), 88 kJ/mol above the first one, which can be described as a scalene triangle of sides $a = 2.648$ Å, $b = 2.839$ Å and $c = 2.708$ Å, and angle $\gamma = 57.0^\circ$, connected, 2.630 Å distant, with a dimer gold of 2.634 Å Au-Au distance, through one triangle vertex forming an angle $\alpha$ of 122° and other $\beta$ of 146°. The fourth structure is a zig-zag shaped chain (X), characterized by the distances $a = 2.607$ Å, $b = 2.643$ Å and angles $\alpha = 130.5^\circ$, $\beta = 123.6^\circ$ whose energy is 100 kJ/mol above that of the trapezoid structure. Finally, we obtained an isosceles triangular structure (XI), with sides $a = 2.851$ Å and $c = 2.606$ Å, and angle $\alpha$ of 54.4°, bound to a dimer gold, with an internuclear distance $d$ of 2.572 Å, and separated from the triangle vertex by a distance $b$ of 2.565 Å, forming a three members linear tip geometry. This structure has an energy 224 kJ/mol above the corresponding to the most stable pentamer.

The results corresponding to the hexamer are displayed in Fig. 1-D. Three minima on the PES were found: the most stable one corresponds to a slightly distorted planar equilateral triangular structure (XII), with one gold atom at the center of each side ($D_{3h}$ symmetry), the internuclear distances between the atoms are 2.694 Å($a$) and 2.867 Å($b$); while the angles are 57.8° ($\alpha$) and 64.3° ($\beta$). This structure has a binding energy of -901 kJ/mol and has also reported as the most stable one through ab-initio [7] an BOLS- MD [8] calculations. The second most stable cluster is 81 kJ/mol above the previous one (XIII). It shows a pentagonal structure, side length of 2.859 Å, with one atom at the center and 1.034 Å above the plane of the pentagon (a pentagonal pyramid of symmetry $C_{5v}$) and an angle $\alpha = 63.1^\circ$. Again, it is interesting to notice that in the case of the alkali metal clusters these two structures are also reported; but, their stability order is inverted, that is, the pentagonal pyramid is the most stable form of the Li and Na hexamers. In addition, in the present calculations a larger energetic separation between those structures is found. The third stable hexamer structure corresponds to two perpendicular isosceles triangles (XIV), with sides $b = 2.812$ Å and $c = 2.619$ Å and an angle $\alpha = 55.5^\circ$, and whose vertexes are separated by a distance of 2.599 Å($\beta = 152.1^\circ$). The energy of XIV is 170 kJ/mol above that of the most stable geometry.

Acknowledgment

The authors gratefully acknowledge the financial support of the CDCHT-ULA. The computational calculation were partially performed at the center of Scientific calculation of the Universidad de Los Andes (CECALCULA).