20-nanogold Au$_{20}(T_d)$ cluster and its hollow cage isomers: structural and energetic properties

E S Kryachko$^{1,2}$ and F Remacle$^2$

$^1$Bogolyubov Institute for Theoretical Physics, Kiev-143, 03680 Ukraine
$^2$Department of Chemistry, Bat. B6c, University of Liège, B-4000 Liège, Belgium

E-mail: $^1$eugene.kryachko@ulg.ac.be; $^2$fremacle@ulg.ac.be

Abstract. The present work discusses the capability of 20-nanogold low-energy clusters to encage atomic and molecular species and investigates hollow cages of Au$_{20}$, their structures and stability, and their void reactivity. We begin with performing a systematic computational search of hollow cages on the potential energy surface of doubly anionic Au$_{20}$ which, according to the experimental abundance spectra of Au$_{20}^{2-}$, has an approximately degenerate ground state. Since the computed second electron affinity of the neutral tetrahedral ground-state cluster Au$_{20}(T_d)$ agrees well with the experimental value EA$_{2}^{\text{exp}}$(Au$_{20}$), this ground state is thus partly occupied by [Au$_{20}(T_d)$]$^{2-}$ whose original neutral T$_d$-symmetry is broken. Determining the other, yet unknown isomer and applying ‘reverse’ charge state mappings Z = -2 ⇒ Z = 0, ±1, we identify stable and low-energy Au$_{20}$ hollow cages which are further studied from different angles and compared with Au$_{20}(T_d)$. The void reactivity of these 20-nanogold hollow cages is the key theme - it is suggested that, together with the global characteristics, such as the ionization potential and electron affinity, the molecular electrostatic potential and HOMO-LUMO patterns are actually tools that may shed a light on the general features of voids of these golden fullerenes and their capability to encage H and Li. The confinement character of the studied golden fullerenes is compared with the classical examples, C$_{60}$ in particular.

1. Introduction

The discovery in the 1980s of the buckyball C$_{60}$ and larger fullerenes [1] enables to form, by trapping guest atoms, ions, and molecules into their nanosized voids (nanovoids), so called ‘endohedral’ or @-fullerenes which voids a variety of remarkable features. This discovery raised the question of existence of similar fullene-like structures or hollow cages for other chemical elements. Among the latter, gold is a particular element – definitely ‘noblesse oblige’ – because of its rather unique properties which are mostly dictated by the strong relativistic effects [2].

The first fullerene-type cluster of gold – a ‘golden fulleren’ [3] - is the smallest hollow icosahedral cage Au$_{12}(I_6)$ that was predicted in 2002 [4] and, as demonstrated computationally [5-7], is only stable endohedrally, i. e. as M@Au$_{12}$ with a metal atom M = W, V, Nb, and Ta. The cage Au$_{14}$ is similar: it is bound as the endohedral golden fullerene M@Au$_{14}$ and unbound in the gas phase [8]. Larger hollow cages Au$_{N=16-18}$ in the anionic charge state have recently been observed in photoelectron spectroscopy experiments [9]. Their voids are characterized by a diameter that determines a spatial confinement of ca. 5.5 Å [9], i. e., these voids are large enough to accommodate some guest atoms. The concept of golden fullerenes has recently been extended to N > 18 and already reached 55 [10] and 72 [11]. Among them is, for instance, the ground-state and highly stable icosahedral golden fullerene Au$_{12}(I_6)$
[3] whose HOMO-LUMO gap $\Delta := \epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}$, defined as the difference of the energy eigenvalues of the HOMO (highest occupied molecular orbital) and of the LUMO (lowest unoccupied molecular orbital), falls into the interval of 1.5 – 2.5 eV, being thus close to $\Delta \in (1.57,1.80 \text{ eV})$ of C$_{60}$ [12].

Generally speaking, an arbitrary 3D molecular structure is either space-filled, compact, without any void or possesses some voids (emptiness) that result in a hollow cage shape [9]. The space-filled structures, such as for example, the magic gold cluster Au$_{20}$(Td) [13]' (see also the current work [14] and references therein) are expected to be more energetically stable, at least in the neutral charge state (see particularly [8,13,15-20]).

2. Au$_{20}$ fullerenes

It is generally anticipated that golden fullerenes inherit many exceptional features of the classical fullerenes C$_{n}$ - the foremost one is the chemical reactivity which is broadly defined as a capability of a given molecular species to form chemical bonding patterns while interacting or contacting with other atoms, ions, or molecules. This is by large the reason why hollow cage gold nanoparticles (NPs) have recently attracted a great deal of attention in nanoscience. Since 20-nanogold fullerenes are definitely not the ground-state structures in the neutral charge state $Z = 0$ and since a tetrahedral space-filled shape $T_d$ is even preserved in the charge states $Z = \pm 1$ [13,14], the question arises whether and how they can be detected experimentally and also if they can be synthesized? In general, low-energy molecular isomers are hard to identify experimentally, though the experimental identification of low-energy gold isomers has recently been reported in the series of works [21-25], e. g.: (i) Ref. [22] where four isomers of Au$_{20}$ lying higher the ground-state within an energy interval of ~0.58 eV were observed; (ii) Ref. [21] that identifies four isomers of Au$_{7}$ placed by $\leq 0.74$ eV above the ground state. This experimental search has to be conducted in parallel with the theoretical research on golden cage isomers, by a direct analogy with a similar research of low-energy carbon fullerene’s isomers [26].

What are the experiments that have been performed for 20-nanogold? Only few such experiments have been conducted [13,22,27-36]. In 1992, using UV photoelectron spectroscopy, Taylor et al. [36] reported the (first) electron affinity of Au$_{20}$, $\text{EA}^\text{exp}(\text{Au}_{20}) = 2.732 \pm 0.050$ eV. In 2003, Li et al. [13] measured the experimental photoelectron spectroscopy spectrum of Au$_{20}$ and obtained $\text{EA}^\text{exp}(\text{Au}_{20}) = 2.745 \pm 0.015$ eV. They also provided a strong computational evidence of the existence of the ground-state neutral Au$_{20}$(Td) cluster that possesses a remarkably large HOMO-LUMO gap $\Delta(\text{Au}_{20}) = 1.77$ eV, thus exceeding $\Delta^\text{exp}(\text{C}_{60}) = 1.57$ eV by 0.2 eV. The collision induced dissociation experiments were also conducted in order to study the fragmentation channels of singly and multiply charged Au$_{20}^{\pm}$, Au$_{20}^{2\pm}$, and Au$_{20}^{3\pm}$ clusters [28-30].

In parallel, the experimental abundance spectra of Au$_{N}^{2\pm}$ for $12 \leq N \leq 30$, which were produced by laser vaporization of gold metal, storage of the anions Au$_{n}^{\pm}$ in a Penning trap, their mass selection, and a final electron attachment, definitely confirmed that the doubly charged negative cluster Au$_{20}^{2\pm}$ exists and is stable [31-35]. Hence, Au$_{20}$ has a positive second electron affinity $\text{EA}^\text{exp}_{2}(\text{Au}_{20})$ estimated, within the liquid drop model, as equal to $\approx 0.5$ eV. Moreover, as demonstrated in Figure 2 of [32], the ground state on the dianionic potential energy surface (PES) of 20-nanogold is quasi doubly degenerate, implying that there exist two isomers of Au$_{20}^{2\pm}$ which share it. Since the ZPE-corrected $\text{EA}^\text{exp}_{2}(\text{Au}_{20}(T_d))$ is computed equal to 0.525 eV for B3LYP and to 0.433 eV for PW91 [14] (see the next Section), it is quite close to the experimental value which suggests that the Au$_{20}^{2\pm}$(Td) lies at the very bottom of the PES. Besides, the Coulomb repulsion of the negative excess charges of Au$_{20}^{2\pm}$(Td) makes it, via breaking a $T_d$ symmetry, a hollow cage with an external diameter of $\approx 4$ Å. In contrast, the fullerene dianion C$_{60}^{2\pm}$ is metastable in the ground state with the lifetime of $\approx 20$ s (T = 0 K) with respect to autodetachment [37]. This feature therefore makes the chemical reactivities of the classical and golden fullerenes somewhat different.

The other(s) ground-state dianionic isomer of 20-nanogold has not yet been reported. Its identification partly initiated this work. In fact, the goal of this work is twofold: (a) to conduct a systematic search on the dianionic PES of 20-nanogold to determine the unknown bottom-energy
structure [say, cage I, since we define the neutral ground-state cluster 0 := \text{Au}_{20}(T_0) and correspondingly, 0^\circ)] and, in addition, one novel low-energy hollow \text{Au}_{20}^2 cage \text{II}^2; and (β) via sequentially mapping of the above PES to the PESs corresponding to Z = -1, 0, and +1, to show that in the neutral and cationic charge states cage II splits into two, \text{II}^0 and \text{III}^0 (Z = 0, +1), and to analyze different facets of the void reactivity of these new cages in different charge states. In particular, we investigate whether they are capable to encapsulate some atom or ion and show that some of the cages can indeed be doped, e.g. with a Li atom. Hence, these charge-state mappings suggest that cage I could be experimentally detected.

2.1. Computational methodology

All computations of gold clusters were carried out with the density functional (DF) potentials B3LYP, BP86, and PW91PW91 (PW91 for short) in conjunction with the energy-consistent 19-(5s^25p^65d^{10}6s) valence electron relativistic effective core potential of the Los Alamos double-zeta type LANL2DZ. The GAUSSIAN 03 package of quantum chemical programs [38] was used throughout the present work. All geometrical optimizations were carried out with the keywords “Tight” and “Int = UltraFine”. The harmonic vibrational frequencies and concomitant zero-point energies (ZPE) were calculated in order to locate the energy-minimum structures and to distinguish them from the saddles. The basis set comprised of the standard Pople’s basis set 6-311++G(d,p) is additionally used for the H and Li atoms.

2.2. Structure and stability of 20-nanogold cages

The structures of three novel cages I, II, and III of \text{Au}_{20} in the charge state Z = 0, characterized by external diameters of about 0.8-1.2 nm which are slightly larger that, 0.7 nm, of C_{60}, are shown in Figure 1. Regarding their voids, these cages are essentially hollow in the 0-charge state with cage or void diameters of ca. 4.5 – 6.0 Å. Structurally, cage I resembles a helix. Cage II exhibits a bilayer motif and is formed by two planar \text{Au}_{10}(D_{5h}) clusters which are twisted relative to each other by a dihedral angle of 33.1° and bonded to each other by means of 20 additional metallic bonds. Due to its quite specific bilayer shape, cage II could be synthesized.

All these cages are definitely energy minima on the 20-gold PESs for Z = 0, ±1, and -2 with real harmonic vibrational frequencies only, which are distributed, say for Z = 0, within 11 – 160, 12 – 118, and 15 – 154 cm\(^{-1}\), respectively. As neutral, they are closed-shell clusters which, as reported in Table, are highly stable with respect to the atomization channel \text{Au}_{20}^{1,II,III} \Rightarrow 20 \text{ Au}. This stability is corroborated by high absolute values, of ∼33 – 34 eV, of the corresponding energies, \(\Delta E_f\), and enthalpies, \(\Delta H_f\), of formation, despite a large entropy effect. The latter increases the Gibbs free energies, \(\Delta G_f^\text{298}\), of formation at T = 298 K and correspondingly lowers the cages’ stabilities by 6-7 eV, but they still remain strongly bound. Since II is formed by two bonded planar \text{Au}_{10}(D_{5h}) clusters, its corresponding energy of formation amounts to -2.34 eV with B3LYP DFT and to -4.34 eV with the PW91, and is hence strongly DF dependent. Cage II is less stable than I in the neutral charge state by approximately -43.15 – (-43.20) = 0.05 (- PW91; 0.11 – BP86, 0.37 – B3LYP) eV. On the other hand, in the same charge state, cage III is more stable compared to I by 0.11-0.16 eV. Nevertheless, within the numerical accuracy, they are located very close to each other.

As suggested above, on the diatomic PES, \text{Au}_{20}^{2}(T_0) shares the very bottom of the diatomic PES with \(\text{I}^2\), though actually, in a strict computational sense, the latter lies slightly below \text{Au}_{20}^{2}(T_0) by \(-0.05\) eV. Relative to the asymptote comprising of 18 \text{Au} + 2 \text{ Au}, \text{I}^2 is essentially stable that is manifested by \(\Delta E_f = -34.32\) eV and a Gibbs free energy \(\Delta G_f^{298} = -27.56\) eV at the B3LYP computational level. Notice that in the diatomic charge state, II and III merge to one another and are less stable than I by 0.39 eV. Via the mapping Z = -2 \Rightarrow Z = -1, I approaches \text{Au}_{20}^{-1}(T_0) from above by 0.59 – 0.77 eV, which only differ by 0.01 – 0.19 eV from the energy range reported in recent diffraction experiments [22], and by construction, \(\text{I}^1\) and \(\text{II}^1\) are identical. The neutral cages I, II, and III are placed energetically within 1.40-1.85 eV relative to the ground-state cluster \text{Au}_{20}^{-2}(T_0). On
the other hand, on the cationic sheet of the 20-gold PES, III becomes closer to $\text{Au}_{20}^{+} (T_d)$ by 0.66 eV. Both energy gaps can likely be achievable in experiments.

Both energy gaps can likely be achievable in experiments.

**Figure 1.** The golden hollow cage clusters I, II and III in the neutral charge state $Z = 0$. Cage I resembles a helix with the void diameter of ~5.9 Å. Its external diameter is ~1.2 nm. The void diameter of the cage II is approximately equal to 0.84 nm, i.e. it slightly exceeds that of $\text{Au}_{20}(T_d)$. As readily seen in this Figure 1, II is composed of the two planar $\text{Au}_{10}(D_{2h})$ clusters colored correspondingly in yellow (light in b/w) and brown (correspondingly dark). The angle between the longest diagonals $\text{Au}_5-\text{Au}_9$ and $\text{Au}_3-\text{Au}_{12}$, each of which connects the two vertex gold atoms mostly separated from each other, amounts to 33.1°. Cage III is characterized by a void diameter, $R(\text{Au}_9-\text{Au}_{16})$, of 5.5 Å. Its external diameter associated with $R(\text{Au}_{11}-\text{Au}_{12})$ amounts to 0.98 nm. Selected bond lengths are given in Å (reading from top to bottom: B3LYP, BP86, and PW91 DF potentials). The B3LYP Mulliken charges of some gold atoms are indicated by superscripts.
The HOMO and LUMO eigenvalues and the corresponding HOMO-LUMO gap

\[
\Delta \varepsilon = \varepsilon_{\text{HOMO}} - \varepsilon_{\text{LUMO}}
\]

**Table 1.** Selected properties (in eV) of the cages I, II, and III in the neutral charge state. $\Delta E_f$ is defined as the ZPE-corrected energy of formation of the cage, taken with respect to twenty non-interacting gold atoms. $\Delta H_f$ determines the corresponding heat of atomization and $\Delta F_f^{298}$ is the corresponding free Gibbs energy at $T = 298$ K. $\Delta E$ is the relative ZPE-corrected energy of the cage with respect to the ground-state cluster $\text{Au}_{20}(T_d)$. IE$_i$ is the first ionization energy and EA$_i$ the adiabatic electron affinity.

| Selected properties | Cage I | Cage II | Cage III |
|---------------------|--------|---------|----------|
| $-\Delta E_f$       | B3LYP  | BP86    | PW91     |
|                     | 33.94  | 41.73   | 43.20    |
|                     | 33.95  | 41.76   | 43.24    |
|                     | 27.15  | 34.82   | 36.28    |
| $\Delta H_f$        | B3LYP  | BP86    | PW91     |
|                     | 1.48   | 1.56    | 1.60     |
|                     | 1.85   | 1.67    | 1.65     |
|                     | 1.42   | 1.40    | 1.43     |
| $-\Delta F_f^{298}$ | B3LYP  | BP86    | PW91     |
|                     | 5.71   | 5.48    | 5.36     |
|                     | 5.50   | 5.32    | 5.20     |
|                     | 4.52   | 5.08    | 4.97     |
|                     | 4.37   | 4.93    | 4.79     |
|                     | 1.19   | 0.40    | 0.39     |
| $\Delta$            | B3LYP  | BP86    | PW91     |
|                     | 6.692  | 6.852   | 6.730    |
|                     | 6.539  | 6.722   | 6.602    |
|                     | 6.647  | 6.862   | 6.744    |
| $\varepsilon_{\text{HOMO}}$ | B3LYP  | BP86    | PW91     |
|                     | 3.543  | 3.748   | 3.630    |
|                     | 3.776  | 3.628   | 3.502    |
|                     | 3.340  | 3.359   | 3.280    |

2.3. One-electron properties

The HOMO and LUMO eigenvalues and the corresponding HOMO-LUMO gap $\Delta$, the first adiabatic electron affinities (EA$_i$) and ionization potentials (IE$_i$) are the key features that determine chemical reactivity. All these features of cages I, II, and III are summarized in Table 1. The HOMOs and LUMOs are placed ca. 0.4-0.9 eV higher the HOMO of $\text{Au}_{20}(T_d)$. Cages I and II feature rather narrow gaps $\Delta \approx 0.4$ eV (BP86 and PW91), compared to $\text{Au}_{20}(T_d)$. The EA$_i$ of the studied cages are significantly large, falling within 3.3 - 3.8 eV, thus exceeding the EA$_1^{\text{B3LYP}}(\text{Au}_{20}(T_d)) = 2.606$ eV (notice that EA$_1^{\text{B3LYP}}(\text{C}_{60}) = 2.57$ eV) by ca. 0.5-1.2 eV. The IE$_1$ of I, II, and III are lower - within 6.6-6.7 eV - compared to IE$_1^{\text{PW91}}$ of $\text{Au}_{20}(T_d) = 7.34$ eV and IE$_1^{\text{B3LYP}}(\text{Au}_{20}(T_d)) = 7.398$ eV. Altogether, the above distinctions between the studied hollow cages I, II, and III and the space-filled cluster $\text{Au}_{20}(T_d)$ allow us to conclude that the reactivity of these cages is drastically different from that of $\text{Au}_{20}(T_d)$. Yet another indicator of the reactivity of a given molecule or cluster is the chemical hardness $\eta$ that is approximately defined as a half of the difference between the IE$_1$ and EA$_1$, viz., $\eta = (\text{IE}_1 - \text{EA}_1)/2$. Within this reactivity scale, II with lowest hardness, $\eta_{\text{B3LYP}}(\text{II}) = 1.38$ eV, is more reactive than both I and III, with I being more reactive than cage III : $\eta_{\text{B3LYP}}(\text{II}) < \eta_{\text{B3LYP}}(\text{I}) = 1.57$ eV $< \eta_{\text{B3LYP}}(\text{III}) = 1.65$ eV. All cages are more reactive than $\text{Au}_{20}(T_d)$ which is characterized by $\eta_{\text{B3LYP}}(\text{Au}_{20}(T_d)) = 2.40$ eV.

2.4. Quantifying void reactivity of $\text{Au}_{20}$ cages

When molecules interact with one another, chemical bonding patterns arise between their atoms. Typically, these patterns are spread over the outer space of each interacting partner. In this sense, cages are different – by definition, they possess atoms which are assumed to be capable to form chemical bonds with molecules from the outer space as well as from the inner one (inside the cage, in voids), i.e. with those which are encapsulated or confined within the cage. This hence implies a bifunctionality of the chemical reactivity - the outer or exo-reactivity and the inner, void, or endo-reactivity - of some atoms which compose cages and thus suggests potential routes to control both
kinds of chemical reactivities. The features, such as the ionization energies and electron affinities that indicate how a given cage overall reorganizes either upon removal or upon addition of an electron, which are examined in the previous Subsection are those which are usually invoked to characterize chemical reactivity. They are, however, the global characteristics of a cage that cannot be partitioned into those which may be solely ascribed either to the outer or to the inner void.

![Figure 2. The MEPs of cage I, II, and III mapped from -0.016 (red) to +0.016 (blue) \(|e|/(4\pi\varepsilon_0 a_0)\) onto 0.001 \(|e|\cdot \text{Å}^{-3}\) isosurface of the one-electron density \(\rho(r)\) and from -0.01 to +0.01 \(|e|/(4\pi\varepsilon_0 a_0)\) onto 0.004 (the right column, correspondingly, for cages I, II, and III respectively) \(|e|\cdot \text{Å}^{-3}\) isosurface of the one-electron density \(\rho(r)\). \(\rho(r)\) is computed at the B3LYP computational level.](image)

The void regions of cages I, II, and III are in fact spatially confined areas which can accommodate some heteroatom M or heteroatoms (dopant). A remarkable feature of these cages is that they all have only one-atom-layer that separates the void from the outer surface which may thus facilitate the direct control of the outer reactivity from the inner one. A typical point of view that often prevails is that the void reactivity of a cage is a direct consequence of the spatial confinement, i.e., the dopant feels the cage’s boundary, and therefore, the size of dopant plays a decisive role for a stable encapsulation. Put in other words, if the size of the void is of the same order of magnitude or comparable with that of the dopant, one may anticipate that doping is stable. Obviously, doping influences the outer reactivity. It is well known that the patterns of the molecular orbitals, particularly of the HOMO and LUMO, and the concept of the molecular electrostatic potential (MEP) [39] are crucial for understanding of both facets of chemical reactivity. For example, the buckyball fullerene \(C_{60}\) exhibits two different behaviors of the MEP [40]. It is positive in the entire void region, where \(C_{60}\) is capable to encage atoms, ions, and some molecules, and reaches the outer central regions of the pentagon rings. On the contrary, it is negative in the outer region and the most negative at the midpoints of the bonds linked two hexagonal rings.

The MEP patterns of the studied golden fullerenes I, II, and III are plotted in Figure 2. These MEPs look quite different from that of \(C_{60}\). First: the outer MEP is nonnegative, as demonstrated by blue converging to green regions. The void MEP of cage I can be both, either negative - as shown in red, particularly in the neighborhood of the gold atoms \(\text{Au}_1\) and \(\text{Au}_5\) - or positive, that is in blue, as in a small and rather deep (due to its color) ‘pocket’ around \(\text{Au}_{17}\). By analogy with \(C_{60}\), the neighborhood of the latter atom is therefore attractive to accommodate an atom. The MEP patterns of cage II are positive in its outer region and admit both signs in the void. Two symmetric MEP regions in the neighborhood of the gold atoms \(\text{Au}_{12}, \text{Au}_{14}, \text{Au}_{20}, \text{Au}_{13}, \text{Au}_7, \text{and Au}_{19}\) are negative, whereas the
other two, around Au\textsubscript{13}, Au\textsubscript{17}, and Au\textsubscript{10}, Au\textsubscript{18}, are positive, implying thus two different sites for encaging. In addition, there exists a ‘pocket’ with a slightly negative charge in the center of the MEP of cage III and the surface mapped on the \(\rho(r) = 0.004\) isocontour is essentially positive. To summarize: the MEPs of the studied cages I, II and III imply that their voids are capable, in general, to confine neutral, as well as both, positively and negatively, charged atomic and molecular guests.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure3.png}
\caption{The endohedral golden fullerenes Li@cage I and Li@cage II in the neutral charge state. The geometry of Li@cage I is determined by the following B3LYP distances \(R(\text{Au}_4\text{-Au}_6) = 9.789\), \(R(\text{Au}_4\text{-Au}_{12}) = 7.282\), and \(R(\text{Au}_8\text{-Au}_{17}) = 8.055\) Å. The Li atom forms bonds with Au\textsubscript{6} and Au\textsubscript{12} of the cage I with the equal bond lengths \(R(\text{Li}\text{-Au}_6) = R(\text{Li}\text{-Au}_{12}) = 2.745\) Å. The latter are comparable with those of Li@cage II which amount to \(R(\text{Li}\text{-Au}_{15}) = 2.811\) and \(R(\text{Li}\text{-Au}_{9}) = 2.832\) Å.}
\end{figure}

It is rather natural to consider the very small doping atoms H and Li. The atomic radii of H amounts to \(-0.25 \sim 0.53\) Å, thus implying its easiness to be accommodated within the voids of the studied Au\textsubscript{20} cages I, II, and III. It is however not the case because geometric arguments are in general insufficient for characterizing encaging that is close to a typical molecular process involving charge transfer: the computational scenarios of the initial endo-bondings of H within these cages end with the final exo-bondings to the Au-Au bonds and corresponding binding energies of \(-2.1 \sim -2.3\) eV. In contrast, we found that Au\textsubscript{20}(T\textsubscript{d}), while interacting with H, undergoes rather considerable extension of its void that becomes sufficiently large to encage the latter by the three planar 9-coordinated inner Au atoms and to form the centered triangle \(\text{Au}_{1,2,3} \sim 0.09\) -H \(\sim 0.33\), where H carries a negative Mulliken charge, with the binding energy equal to \(-0.53\) eV. Note that latter is slightly higher than the energy calculated in [41] by means of the PW91 DF and a plane-wave basis set. One may suggest that the emergence of the confinement propensity of the 3D space-filled and compact cluster Au\textsubscript{20}(T\textsubscript{d}) is the result of two main factors: the softness of its void Au-Au bonds whose stretching modes fall around \(~100\) cm\textsuperscript{-1}, compared to C\textsubscript{60}, and a lower value of its electron affinity compared to the above cages.

The MEP patterns of cages I and II and their differences with the MEP of C\textsubscript{60} are corroborated by encaging Li into the former and forming the endohedral golden fullerenes Li@cage I and Li@cage II which are demonstrated in Figure 3. In both endohedral systems, Li forms rather strong covalent Au-Li bonds with bond lengths of ca. 2.75 – 2.83 Å that are reflected in the large, by the absolute value, binding energies of 3.78 and 3.67 eV, respectively. The latter exceed by factor of \(~2.7\) the absolute value of the binding energy of the endohedral fullerene Li@C\textsubscript{60} and is simply explained by two facts: first, \(\text{IE}_1(\text{cages}) > \text{IE}_1(\text{Li}) = 5.62\) eV and second, \(\text{EA}_1(\text{cages}) > \text{EA}_1(\text{C}_{60}) > \text{EA}_1(\text{Li}) = 0.42\) eV, implying that the studied hollow golden cages have a stronger ionizing power on Li than the buckyball C\textsubscript{60}. It is also worth mentioning that the endo-binding energy of Li@Au\textsubscript{20}(T\textsubscript{d}) amounts to \(-2.49\) eV, and hence it is weaker compared to that of cages I and II, though the latter are less stable than Au\textsubscript{20}(T\textsubscript{d}).

**Acknowledgments**

This work was partially supported by the AIP ‘Clusters and Nanowires’ Project of the Belgian Federal Government, the EC FET proactive NanoICT Project ‘MOLOC’, and the F.N.R.S. (Belgium) FRFC Project 2.4565.06.
References

[1] Kroto H W, Heath J R, O’Brien S C, Curl R F and Smalley R E 1985 Nature (London) 318 162
[2] Pyykö P 2008 Chem. Soc. Rev. 37 1967
[3] Johansson M P, Sundholm D and Vaara J 2004 Angew. Chem. Int. Ed. 43 2678
[4] Pyykö P and Runeberg N 2002 Angew. Chem. Int. Ed. 41 2174
[5] Li X, Kiran B, Li J, Zhai H J and Wang L S 2002 Angew. Chem. Int. Ed. 41 4786
[6] Yoon B, Koskinen P, Huber B, Kostko O, v Issendorff B, Häkkinen H, Moseler M and Landman U 2007 Chem. Phys. Chem. 8 157
[7] Sun Q, Wang Q, Jena P and Kawazoe Y 2008 ACS Nano 2 341
[8] Gao Y, Bulusu S and Zeng X C 2005 J. Am. Chem. Soc. 127 156801
[9] Bulusu S, Li X, Wang L-S and Zeng X C 2006 Proc. Natl. Acad. Sci. U.S.A. 103 8326
[10] Schmid G 2008 Chem. Soc. Rev. 37 1909
[11] Karttunen A J, Linnolahti M, Pakkanen T A and Pyykö P 2008 Chem. Commun. 465
[12] Taylor J, Guo H and Wang J 2001 Phys. Rev. B 63 121104(R)
[13] Apra E, Ferrando R and Fortunelli A 2006 Phys. Rev. B 73 205414
[14] Fernández E M, Soler J M, Garzón I L and Balbás L C 2004 Phys. Rev. B 70 165403
[15] de Bas B S, Ford M J and Cortie M B 2004 J. Mol. Struct. (Theochem) 686 193
[16] Fernández E M, Soler J M and Balbás L C 2006 Phys. Rev. B 73 235433
[17] Wang J, Bai J, Jellinek J and Zeng X C 2007 J. Am. Chem. Soc. 129 341
[18] Krishnamurty S, Shafai G S, Kanhere D G, de Bas B S and Ford M J 2007 J. Phys. Chem. A 111 10769
[19] Gruene P, Rayner D M, Redlich B, van der Meer A F G, Lyon J T, Meijer G and Fielicke A 2008 Science 321 674
[20] Xing X, Yoon B, Landman U and Parks J H 2006 Phys. Rev. B 74 165423
[21] Huang W, Bulusu S, Pal R, Zeng X C and Wang L-S 2009 ACS Nano 3 1225
[22] Häkkinen H, Moseler M, Kostko O, Morgner N, Hoffmann M A and von Issendorff B 2004 Phys. Rev. Lett. 93 093401
[23] Filsinger F, Erlekam U, v. Helden G, Küpper J and Meijer G 2008 Phys. Rev. Lett. 100 133003
[24] Killblane C, Gao Y, Shao N and Zeng X C 2009 J. Phys. Chem. A 113 8839
[25] The NIST, http://webbook.nist.gov, reports only two of them dealing with the first electron affinity
[26] Becker St, Dietrich G, Hasse H-U, Klisch N, Kluge H-J, Kreisle D, Krückeberg S, Lindinger M, Lützenkirchen K, Schweikhard L, Weidele H and Ziegler J 1994 Z. Phys. D 30 341
[27] Ziegler J, Dietrich G, Kruckeberg S, Lutzenkirchen K, Schweikhard L and Walther C 1998 Hyperfine Inter. 115 171
[28] Vogel M, Hansen K, Herlert A and Schweikhard L 2001 Eur. Phys. J. D 16 73
[29] Herlert A, Krückeberg S, Schweikhard L, Vogel M and Walther C 1999 Phys. Scr. T80 200
[30] Schweikhard L, Herlert A and Vogel M 1999 Phil. Mag. B 79 1343
[31] Yannouleas C and Landman U 2000 Phys. Rev. B 61 R10587
[32] Herlert A, Schweikhard L and Vogel M 2001 Eur. Phys. J. D 16 65
[33] Herlert A and Schweikhard L 2003 Int. J. Mass. Spectrometry 229 19
[34] Taylor K J, Pettiette-Hall C L, Cheshnovsky O and Smallay R E 1992 J. Chem. Phys. 96 3319
[35] Drew A and Cederbaum L S 2000 Phys. Rev. A 63 012501
[36] Frisch M J et al. 2004 GAUSSIAN 03 (Revision C.02) (Wallington, CT: Gaussian, Inc.)
[37] Politzer P and Truhlar D G (Eds) 1981 Chemical Applications of Atomic and Molecular Electrostatic Potentials (New York: Plenum)
[38] Mauser H, Hirsch A, van Eikema Hommes N J R and Clark T 1997 J. Mol. Model. 3 415
[39] Molina L M and Hammer B 2005 J. Catalysis 233 399