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Towards gold shells shaped by carbon cores: From a gold cage to a core–shell aurocarbon

Fedor Y. Naumkin *

Faculty of Science, UOIT, Oshawa, Canada ON L1H 7K4

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ABSTRACT

A new aurocarbon species, $C_{10}Au_{18}$, is investigated in terms of its geometry, stability, charge distribution and properties involving changes of the electronic and charge state. The system consists of a carbon-radical core inside a gold shell. The property variations upon adding the carbon molecular 'dopant' to the gold cage cluster of equivalent geometry are analyzed via isolating the effects of the shell shape change and core influence. The charge distribution in the system exhibits interesting, sometimes counterintuitive features. An approximate splitting of the total binding energy into the in-shell and core–shell components is attempted, indicating comparable values for both.

1. Introduction

Properties of polyatomic systems of a given atomic composition are well known to be dependent on their geometries. Variations in the characteristics of isomers of molecules (organic and inorganic) are one common example. Atomic clusters can serve as another rich illustration of the importance of structure-property relationships. Electronic structure is the origin of polyatomic system properties, varying significantly with the system shape.

Metal clusters can form stable cages, with shells of atoms around empty spaces. A core of different composition, inserted into such a cage, can affect its characteristics directly, by chemically bonding with the metal shell atoms, or indirectly, via significantly modifying its shape, or in both ways. Properties of such a core–shell system can then differ from those of an equivalent uniform all-metal (filled-cage) counterpart as well. A core–shell structure can also be exhibited by systems whose shell is unstable by itself and supported by the core. Recent examples of (neutral) such species include non-metal atom doped XAl_{12} [1] and $SiAu_{16}$ [2], another-metal atom doped MAl_{12} [3] and MAu_{12} [4,5], molecular-radical doped C_5Au_{12} [6], gold-encapsulated fullerenes [7] and systems with more layers [8]. There are also ionic counterparts detected in photoelectron spectroscopy experiments, such as XAu_{16}^- [9], MAu_{12}^- [10] and XAu_{16}^- [11]. Since $SiAu_{16}$ has another, lower-energy isomer with the silicon atom at the gold cluster surface [12], stability of the core–shell species is determined by the energy barrier to isomerisation and by temperature (an isomer can be long-living at sufficiently low temperatures).

In the present work, the above-mentioned in/direct core-doping effects are investigated for a $C_{10}Au_{18}$ cluster composed of a gold cage and a matching molecular carbon radical inside it and forming bonds with its atoms, the influence of the cage-shape change alone being isolated. The affected parameters of interest include geometry and stability of the system, its excitation and ionization energies, electron affinity, and electron-detachment energy of the corresponding anion. Another, lower-energy $C_{10}Au_{18}$ isomer has also been found, with a very different bond pattern (including C–C bonds) implying a high barrier between the two isomers. Among many possible isomers, the present study focuses on the core–shell species.

Such mixed carbon–gold species may have practical applications as catalysts (gold clusters/nanoparticles are known as versatile ones [13,14]) with tunable properties, elements of molecular electronics (with direct carbon–gold junctions), units of new materials (with the strength and elasticity of carbon-based matter incorporated into mechanically-soft and inelastic gold), etc. A related issue is the possible dis- or similarity of Au to H atoms in their ability to form aurocarbon compounds structurally analogous to hydrocarbons, the two studied isomers illustrating either outcome.

2. Computational procedure

Calculations have been carried out at a DFT/B3LYP level of theory using the 6-31G* basis set for C and the LANL2dz effective core potential and basis set for Au atoms. Limited additional calculations have used a larger, Stuttgart's RSC ECP and basis set for gold. Predicted at this level and experimental parameters of constituent atoms and diatoms were shown to be in a good agreement [6].

Full optimization with no symmetry constraints (for the C_1 group) has been performed, together with vibrational frequency calculations to confirm minima of energy. Different spin states are investigated for neutral and ionic species, in particular to

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* Fax: +1 905 7213304.
E-mail address: fedor.naumkin@uoit.ca

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establish their ground states. Charge distributions are characterized by natural charges.

The NWChem ab initio package [15] has been employed for electronic structure computations, and the Viewmol3d software [16] for visualization and measurement of obtained structures.

Since the hydrocarbon analogue, $C_{10}H_{18}$, has more than 170 known isomers [17], investigation of a comparable variety of possible equivalent structures of $C_{10}Au_{18}$ is beyond the scope of the present work. A rational design is therefore preferred here, based on the relative bond strengths of constituent diatoms as $C_2 > CAu > Au_2$. Hence, a non-fragmented carbon core is to be bound to as many gold atoms as possible. Efficient C–Au bonding can be provided in systems similar to saturated hydrocarbons. Out of various possibilities, those leading to core–shell structures of interest are considered here.

3. Results and discussion

In the previous work [6], the neopentane molecule C_5H_{12} was used as a prototype of the gold-substituted counterpart, $C_5Au_{12} = C(CAu_3)_4$, shown in Fig. 1. By cutting off one CAu_3 group (rightmost in Fig. 1b) and making a dimer of the resulting C_4Au_9 radical, we initially arrive at $C_8Au_{18} = (CAu_3)_3CC(CAu_3)_3$, a counterpart of hexamethylethane C_8H_{18} with hydrogens replaced by gold atoms. Optimization, however, leads to dissociation of the axial (single) C–C bond and disfigurement of the cluster. Previously [6], the CAu_3 groups in $C(CAu_3)_4$ were found to repel. Assuming too strong such a repulsion between these groups on closely spaced axial C atoms in C_8Au_{18}, another pair of axial carbons has been added in-between. The corresponding aurocarbon system $(CAu_3)_3CC_2C(CAu_3)_3$, a counterpart of di-*t*-butyl-acetylene $C_{10}H_{18}$, has been found to have a stable structure of a near-C_3 symmetry (Fig. 2). The gold shell of $C_{10}Au_{18}$ is composed of two imperfectly-staggered Au_6 (slightly chair-bent) rings formally capped by two (somewhat remote) Au_3 equilateral-triangles. For the geometry separating two equivalent such equilibria, with one $CC(CAu_3)_3$ half-system rotated around the axis so that the gold atoms of the Au_6 rings are aligned with the axis, the energy is ≈0.3 eV higher.

For this $C_{10}Au_{18}$ isomer the ground electronic state is closed-shell, with the triplet state only marginally higher in energy, by ≈0.01 eV. This tiny gap slightly widens (to 0.04 eV) for the Stuttgart's RSC basis set for Au atoms. The very narrow singlet–triplet splitting is similar to that for C_5Au_{12} predicted, however, to have triplet ground state [6]. The quintet state of $C_{10}Au_{18}$ is ≈1 eV above the ground state.

Another, quite different trial geometry has been based on decahydro-naphthalene having a flatter carbon core with two fused six-atom (chair-bent) rings. Gold shell in such a structure would (initially) have an oblate shape consisting of two planar Au_5 units above and under the C_{10} core and eight atoms framing it. Upon optimization, however, the carbon core flattens completely and the gold pentamers turn around their sides and lift, exposing the core (Fig. 3). This isomer, even though lower in energy than the first one (mainly due to phenol rings), thus does not represent an endohedral species of interest. Besides, its triplet state is appreciably lower in energy (by ≈0.8 eV), making it more reactive than the previous isomer, hence likely less stable kinetically.

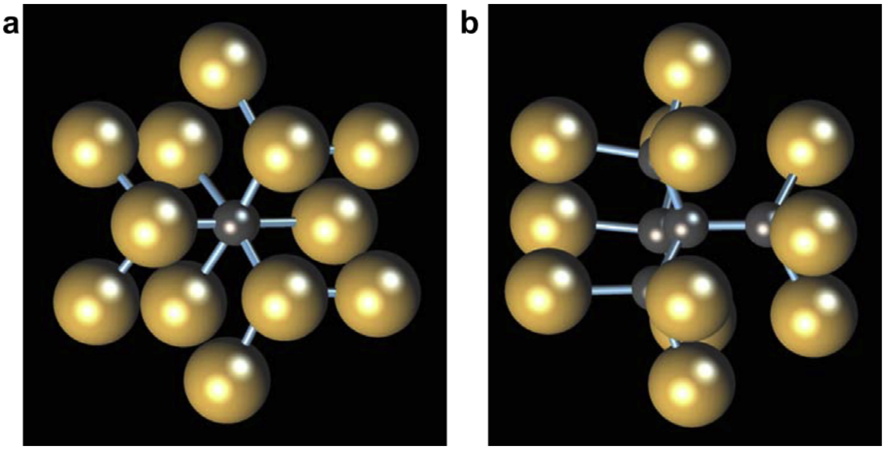

Fig. 1. C_5Au_{12} core–shell cluster [5]: front (a) and side (b) views.

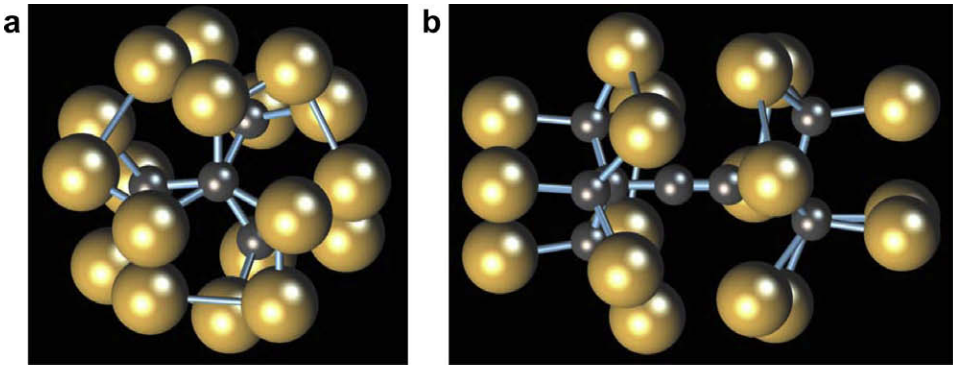

Fig. 2. Optimized geometry of the $C_{10}Au_{18}$ core–shell cluster: front (a) and side (b) views.

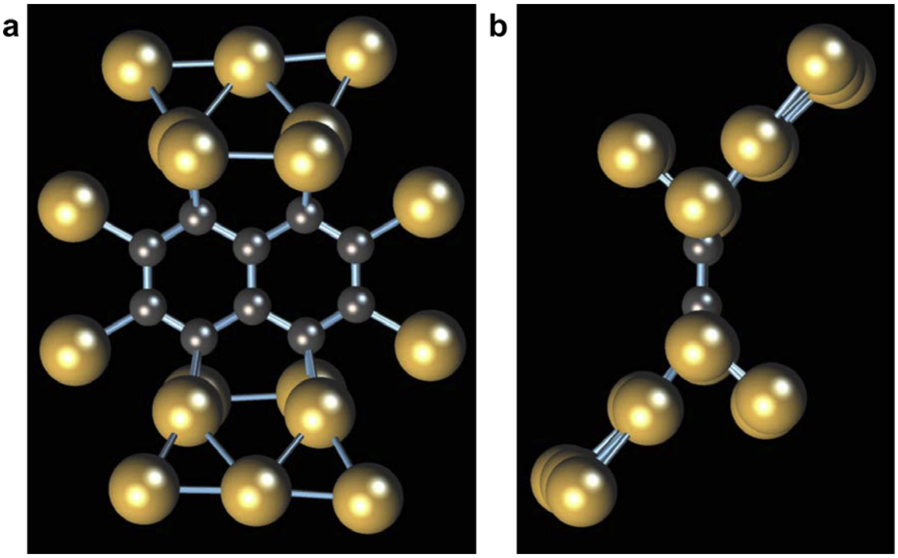

Fig. 3. Optimized geometry of the $C_{10}Au_{18}$ flat-core cluster: front (a) and side (b) views.

The two isomers have very different C–C bond patterns, which suggests a high energy barrier between the two structures, preventing such an isomerisation, similar to the hydrocarbon counterparts. Many other $C_{10}H_{18}$ analogues do not even initially make desired core–shell structures when H's are replaced by Au's. Hence in the following, the focus is on the first isomer of $C_{10}Au_{18}$.

The C–C distances increase from the centre to the periphery of the carbon core, from inner to outer axial to non-axial atom pairs (Table 1). Along each Au_6 ring, the Au–Au distances alternate in value within 0.25 Å, the larger value being the side of the Au_3 triangle-caps as well. The gold–gold separation between the rings slightly varies around the same average as along the rings and is ≈0.5 Å shorter than between the rings and caps. The C–Au distances are slightly shorter for the cap as compared to the ring gold atoms. The C–C–C bond angles are 105° in the plane containing the axis and 114° otherwise. The C–C–Au bond angles are 108.5 ± 1° (almost tetrahedral) for the ring and 113° for the cap Au atoms. Finally, the Au–C–Au bond angles are 94° for two ring atoms and 112 and 117° for the ring-cap gold pairs.

The dissociation energy of $C_{10}Au_{18}$ is defined with respect to (the lowest-energy) C_{10} + 18 Au. For consistency, the carbon skeleton has been relaxed from its geometry in $C_{10}Au_{18}$, for spin states from $S = 0$ to 9. The energy is minimal for the triplet state, the singlet being ≈0.7 eV higher. For triplet C_{10}, D_e ($C_{10}Au_{18}$) = 26.6 eV, or on average ≈1.5 eV per gold atom, same as for C_5Au_{12} at the same level of theory [6]. Detachment of an Au atom from the ring requires ≈1.8 eV, and the remaining system preserves its shape. A gold atom removed from the cap is replaced by the nearest ring atom upon relaxation. The $C_{10}Au_{18}$ moiety remains essentially unchanged upon attachment of another Au atom to the cap (axially) or to the rings (sideways), the binding energy being 2.17 and 2.42 eV, respectively.

Calculated charge distribution in $C_{10}Au_{18}$ indicates negative carbons and positive gold atoms, as expected (Table 2). The C atoms

Table 1
Equilibrium interatomic distances (in Å) of $C_{10}Au_{18}$ and Au_{18} C_3-cage, and their ions.

System	r(C–C)	r(Au–Au)	r(C–Au)
$C_{10}Au^{18}$	1.20, 1.44, 1.57	2.89–3.14[a], 3.14[b] 2.98–3.06[c], 3.42–3.58[d]	2.10–2.16[e], 2.03[f]
$C_{10}Au_{18}^-$	1.20, 1.44–1.45, 1.58–1.59	2.90–3.20[a], 3.12–3.17[b] 2.94–3.12[c], 3.35–3.63[d]	2.09–2.16[e], 2.04–2.05[f]
$C_{10}Au_{18}^+$	1.20, 1.45–1.46, 1.55–1.57	2.83–3.11[a], 3.12–3.17[b] 3.01–3.20[c], 3.41–3.58[d]	2.09–2.16[e], 2.02–2.03[f]
Au_{18} cage		2.91–2.98/2.88–4.66[g], 2.86–2.91[h] 2.80–2.84[i], 2.79–2.93[j]	
Au_{18}^- cage		2.90–2.95/2.87–4.64[g], 2.87[h] 2.82–2.93[i], 2.81–2.91[j]	
Au_{18}^+ cage		2.87–2.99/2.90–4.79[g], 2.81–3.09[h] 2.77–3.00[i], 2.77–2.98[j]	

[a] Rings.
[b] Caps.
[c] Between rings.
[d] Between rings and caps.
[e] Ring gold atoms.
[f] Cap gold atoms.
[g] Smaller/larger hexagon.
[h] Caps.
[i] Between hexagons.
[j] Between hexagons and caps.

Table 2
Natural atomic charges (in e) in $C_{10}Au_{18}$ and its ions.

System	q(C–C_2–C axis)	q(non-axial C_3)	q(Au_6 ring)	q(Au_3 cap)
$C_{10}Au_{18}$	2 × −0.01, 2 × −0.29	−0.57	3 × 0.19, 3 × 0.24	0.24
$C_{10}Au_{18}^-$	±0.02, −0.27, −0.28	−0.57 ± 0.02	0.20 ± 0.05	0.16 ± 0.01
$C_{10}Au_{18}^+$	0.02 ± 0.01, −0.28 ± 0.01	−0.59 ± 0.04	0.27 ± 0.06	0.31 ± 0.02

become more negative in the direction from the centre of the system towards its periphery, the central diatom being nearly neutral and the outer axial atoms charged by half the charge on the non-axial atoms. The gold atoms carry more uniform charges which slightly vary in value and alternate along the rings, the larger value being close to that for the cap atoms. Hence the caps are about half as positive as the rings. The total charge in the gold shell is calculated as +4.0e, neutralized by the anionic carbon core. By comparison, the (natural) charge in the gold shell of C_5Au_{12} is +2.9 ± 0.2e, i.e., lower than in $C_{10}Au_{18}$, in accord with smaller number of gold atoms donating the electron density to the carbon core.

Both anion and cation are found to essentially preserve the shape of neutral $C_{10}Au_{18}$, with minor variations in geometry (Table 1), including a slight expansion and contraction, respectively, of the gold rings. This is reflected in the close values of vertical and adiabatic electron affinities (VEA and EA) as well as ionization energies (VIE and IE) of $C_{10}Au_{18}$ (Table 3). The vertical electron-detachment energy of the anion is also close to the VEA value. The values of (V)EA is slightly higher and (V)IE slightly lower than the corresponding C_5Au_{12} values [6], VDE being same. For both ions of $C_{10}Au_{18}$, the ground states are doublets, with quartets higher in energy by ≈0.2 and ≈0.8 eV for the anion and cation, respectively. By comparison, for C_5Au_{12} the anion has a lower-energy doublet state, while the cation shows a slight energy preference to quartet.

Both electron attachment and ionization lead to the extra-charge localization predominantly in the gold shell which thus becomes less and more positive, respectively (Table 2). This is similar to what was found for the C_5Au_{12} counterpart [6]. Most of the added negative charge in $C_{10}Au_{18}^-$ is on the caps, even though rings are more positive in the neutral system. In $C_{10}Au_{18}^+$, the extra positive charge distributes mainly over the rings, the carbon core even becoming a bit more negative (mainly on non-axial atoms).

In order to compare the above properties with those of the equivalent empty gold cage, the carbon core has been removed and the gold shell relaxed from its geometry in $C_{10}Au_{18}$. The Au_{18} cage cluster is known from earlier work to have several cage isomers [18] (also as anion [19]) but for consistency a structure of C_3 symmetry has been considered here as most appropriate (closest in geometry – for isolating the core influence), while not being among those previously found. The new C_3-symmetric isomer is shown in Fig. 4 and represents the lowest-energy structure out of a few obtained in this work, with a closed-shell ground state. It geometrically resembles the original shell and still has the overall design of two near-staggered distorted hexagons between two triangular caps, though with the overall structure about twice shorter along the axis and one hexagon larger than the other one. The axial distances between the hexagons and triangles are thus shorter, and the Au–Au distances along the hexagons show larger variations than in $C_{10}Au_{18}$ (Table 1).

Table 3
Excitation and ionization energies and electron affinities (in eV) of $C_{10}Au_{18}$, its frozen Au_{18} shell and Au_{18} C_3-cage, and electron-detachment energies of their anions (prefix V denotes vertical values).

System	$E^*(S = 0 \rightarrow 1)$	IE	EA	$VE^*(S = 0 \rightarrow 1)$	VIE	VEA	VDE[a]
$C_{10}Au_{18}$	0.01	5.68	2.94	0.05	5.82	2.88	2.98
Au_{18} shell				0.18	7.02	4.08	4.08[b]
Au_{18} cage	0.99	7.17	3.22	1.22	7.33	3.16	3.29

[a] For cation → neutral.

[b] For the Au_{18}^- shell frozen at the equilibrium geometry of $C_{10}Au_{18}^-$.

The long C_{10} radical, when inserted, considerably stretches the Au_{18} cage (from ≈5 to ≈9 Å between the caps). It therefore appears interesting to attempt separating the effects of the cage geometry-change alone and of the carbon–gold bond formation, i.e., in essence, non-covalent and covalent core–shell interactions. The overall property alterations upon 'doping' the cage with the molecular core are considered first.

The calculated energy of the $Au_{18} \rightarrow 18Au$ dissociation is 30.8 eV or 1.7 eV per atom, i.e., somewhat higher than in the core–shell system. This could be related to a partial loss of the aurophilic interaction in the stretched cage. The triplet state of the empty gold cage is ≈1 eV above its closed-shell ground state (Table 3), which is an appreciable gap completely diminishing in $C_{10}Au_{18}$. This could be due to the longer Au–Au distances in $C_{10}Au_{18}$ as well as the largely ionic character of the C–Au interactions.

Similar to the $C_{10}Au_{18}$ case, both Au_{18}^+ and Au_{18}^- C_3-cages show rather small geometry variations relative to the neutral species (Table 1), consistent with the close values of the vertical and adiabatic ionization energy or electron affinity of Au_{18}, as well as of VEA and VDE (Table 3). The (V)EA and VDE values of the $Au_{18}^{(-)}$ cluster reduce by only 10% for the core–shell system, which weak variation could be associated with the extra-charge concentration in the gold shell. The (V)IE value of the gold cage decreases by ≈1.5 eV upon inserting the carbon core, consistent with a polarization of the core by the charged shell. The next question is which contribution out of the in-shell and core–shell is mainly responsible or both are important for each of the above property variations.

In order to approximately isolate the influence of the cage expansion alone, the corresponding properties of the (neutral) gold shell frozen in its geometry within $C_{10}Au_{18}$ have been evaluated. The small vertical singlet–triplet excitation energy of the gold shell is much closer to the $C_{10}Au_{18}$ value than to that for the relaxed Au_{18} cage (Table 3). This parameter thus appears to be dominated by the shape of the shell rather than by the carbon core, and this excitation could be considered as localized mainly in the shell.

The vertical ionization energy of the Au_{18} shell is only slightly (4%) lower than VIE of the relaxed Au_{18} cage and significantly higher than VIE of $C_{10}Au_{18}$ (Table 3). This would suggest that the C_{10} core affects this property of the gold cage, with a little influence of the shape change. The VEA and VDE values of the shell are ≈1 eV higher than those of the relaxed Au_{18} cage and of the total system, both having close VEA as well as VDE values. This could be interpreted in terms of both the shape change and the carbon core counter-affecting this shell property and nearly compensating one another. Both VIE and VEA (VDE) thus significantly reduce upon inserting the carbon core into the (frozen) gold shell, consistent with the polarization of the (negative) core increasing upon ionization and decreasing upon adding electron to the positive shell of $C_{10}Au_{18}$.

Next, an approximate partitioning of the system energy has been attempted. The energy of the (neutral) frozen shell relative to 18 Au atoms is lowest for the singlet state, at −23.2 eV, or −1.3 eV per atom, which is ≈90% of the $\{C_{10}Au_{18} \rightarrow C_{10} + 18Au\}$

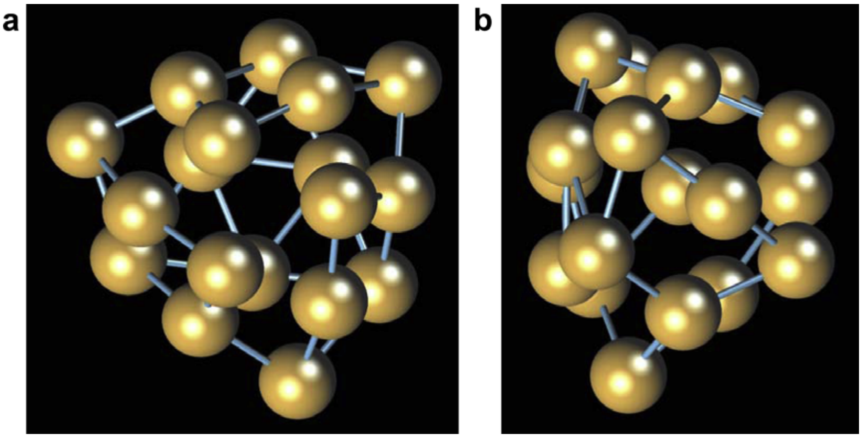

Fig. 4. Optimized geometry of the Au_{18} C_3-cage isomer: front (a) and side (b) views.

dissociation energy. The weak *net* influence of the core, in spite of its high charge and strong Coulomb interaction with the shell, results from the considerable core relaxation upon dissociation of the system. We should not, however, rush to conclude that the Au–Au interactions dominate the binding in the core–shell system, since there the gold atoms are attached to the core carbons and can therefore interact with one another quite differently. One apparent difference is the charge (+4e) leading to a Coulomb repulsion in the shell. In particular, the energy for the dissociation of Au_{18}^{4+} (frozen in the same geometry) into $14Au + 4Au^+$ is calculated as 15.8 eV for the lowest-energy singlet state, the triplet state being only ≈0.1 eV higher. This value may be further reduced due to the (unaccounted) repulsion of dipoles induced in the shell by the charged core, and due to that within the core–shell system the charge is concentrated in the middle of the shell, which corresponds rather to an excited state of isolated Au_{18}^{4+}.

A D_e^{vertical} ($C_{10}Au_{18}$) value can be defined relative to the neutral geometry-frozen carbon core and dissociated shell, and formally split as D_e(core–shell) + D_e(shell). Then the charge redistribution between the core and the shell is included into the first term representing the interaction between the geometry-frozen core and shell. The difference $D_e - D_e^{\text{vertical}}$ equals the energy of the carbon core relaxation upon detachment of the shell. The energy of C_{10} frozen in its $C_{10}Au_{18}$ geometry has been calculated for spin values $S = 0$–9, with a minimum at $S = 3$, the $S = 1$ state (correlating to the lowest-energy relaxed structure) being 1 eV higher in energy. For the carbon core in its triplet state (for a spin-preserving process), D_e^{vertical} is 44.2 eV, and then D_e(core–shell) = 44.2 − 23 = 21.2 eV, which nearly equals (within 10%) the shell dissociation energy. Here we have used the D_e(shell) value for the triplet state to preserve the zero spin of the total system. For a lower D_e(shell), the D_e(core–shell) value increases, for instance to 28.4 eV if to adopt the above D_e(shell) value for the quadruply charged shell.

4. Conclusions

A novel aurocarbon system, $C_{10}Au_{18}$ is investigated at a DFT level of theory and has a stable structure represented by a molecular carbon core encapsulated into a gold shell, with six CAu_3 groups attached at the ends of the linear C_4 unit. This species can be considered as a structural analogue of di-*t*-butyl-acetylene $C_{10}H_{18}$ as well as of the $Pd_2@Sn_{18}^{4-}$ cluster ion [20], and viewed as fused from two C_5Au_{12} units (with six interface Au atoms removed), with a low barrier to their relative rotation. If the C_5 half-cores of $C_{10}Au_{18}$ are replaced by two gold atoms, the resulting Au_{20} cluster collapses into an asymmetric isomer (with the original gold shell broken), indicating a significant directionality of the C–Au bonding in the aurocarbon.

The investigated structure is, strictly speaking, metastable, representing a local energy minimum, as shown by finding a lower-energy isomer (no hydrocarbon analogue). However, existence of lower-energy isomers does not necessarily imply instability if they are separated by sufficient energy barriers and temperature is not too high (cf. diamond versus graphite). The very different C–C bond pattern for the two $C_{10}Au_{18}$ isomers suggests a high barrier between them, hence potentially long-living core–shell species. Probability to produce a system isomer depends not only on its relative energy but also on experimental procedure. Analogous hydrocarbons are known to have a wealth of stable isomers (more than 150 for $C_{10}H_{18}$) – produced experimentally, long-living and having their own uses. A global minimum search for $C_{10}Au_{18}$ is beyond the scope of the present work.

The $C_{10}Au_{18}$ ground state is (marginally) closed-shell, being almost degenerate with the triplet state, unlike for the hydrocarbon structural analogue. The latter difference exhibits significance of the gold–gold (in-shell) interactions estimated to be comparable, in total, to the carbon–gold (core–shell) ones. This is consistent with the gold shell distortion (break) obtained at the Hartree–Fock level of theory which underestimates the aurophilic interactions. The low-energy open-shell state could be a consequence of the obtained mismatch in the lowest-energy spin states of the carbon core and the gold shell. The resulting chemical activity could be reduced via protection by appropriate ligands.

The charge distribution strongly varies along the axis, with a positive centre (due to the gold rings) between negative ends (due to the outer parts of the carbon core). In the corresponding ions, the added charge is localized in the shell and, rather unexpectedly, concentrates mainly in the regions of the same charge-sign (in the neutral system), i.e., in the middle for the cation and at the ends for the anion.

The effect of the carbon core and shape of the gold shell on its properties has been studied by comparing the stability, singlet–triplet excitation (E^*), ionization (IE), electron de- (DE) and attachment (EA) energies with those of the frozen gold shell and of the Au_{18} cage isomer of equivalent geometry. While the inserted carbon molecule stretches the cage considerably, its dissociation energy is affected rather weakly. The (vertical) VE^* value depends predominantly on the shell shape, VIE on the presence of the carbon core, and VEA and VDE is affected by both factors near-equally but in opposite directions. The C_{10} molecular ‘dopant’ can thus selectively modify the electron-donation of the relevant gold cluster while leaving its electron-acceptor efficiency unchanged. This is opposite to what was found for the C_5Au_{12} counterpart (relative to Au_{13}) [6], and indicates a potential for flexibly tuning catalytic characteristics of such clusters.

Finally, the observed property variations upon the molecular 'doping' may differ if to compare with another, in particular more stable isomer of the Au_{18} cluster [18], if its properties are significantly different. The switch between another and current isomer can, however, be considered as a separate factor not directly related to the carbon core influence which is best isolated when using the gold cage with a structure most closely resembling that of the shell in the total system.

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