Behaviour of ‘free-standing’ hollow Au nanocages at finite temperatures: a BOMD study

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(Received 14 May 2015; accepted 5 June 2015)

Finite-temperature behaviour of a hollow golden cage (HGC) plays a crucial role in its potential applications as a catalyst, drug delivery agent, contrasting agent and so on. This physico-chemical property of HGCs is not well understood so far. In that context, Born–Oppenheimer molecular dynamics (BOMD) simulations are performed on a well-known ‘free-standing’ HGC. The cluster considered in this study is the ground state \( \text{Au}_{18} \) cluster (a cage with a diameter of about \( >5.5 \, \text{Å} \)). The results thus obtained are compared with the BOMD simulation results reported earlier on \( \text{Au}_{13} \) icosahedron cage, a conformation with a diameter of nearly 5 Å. The sphericity of both the clusters is studied using a shape deformation parameter as a function of time and temperature. These results are supplemented by radial distribution function at various temperatures. The observations and analysis of results indicate that, both the clusters retain an HGC conformation from 300 to 400 K, admitting structural fluxionality by the \( \text{Au}_{18} \) cluster. Remarkably, the \( \text{Au}_{18} \) cluster is able to maintain its hollowness and sphericity up to a high temperature of 1000 K. Underlying structural and electronic properties influencing the individualistic behaviour of cages are highlighted. Composition of the frontier molecular orbitals and the charge distribution play a crucial role in the finite-temperature behaviour of the Au cages. The conclusions are supplemented by supporting calculations on another degenerate ground state \( \text{Au}_{18} \) hollow cage and a well-known pyramidal \( \text{Au}_{19} \) cage at 300 and 400 K.

Keywords: golden hollow cages; density functional theory; relativistic effects; Born–Oppenheimer molecular dynamics; finite-temperature behaviour

1. Introduction

Discovery of exceptionally stable fullerene molecules [1,2] has galvanised a pandemic interest among researchers to explore and synthesise similar ‘free-standing’ hollow-structured molecules. Owing to their unique hollow cage structures, fullerenes can enclose small molecules inside or be functionalised by various molecules on their surfaces for applications in drug delivery, as carriers of antibodies and as contrasting agents thereby offering far-reaching technological potential. Few ‘free-standing’ inorganic cages have been synthesised since then [3]. A combined experimental and theoretical report on a 20-atom gold cluster demonstrated for the first time that it is possible to have all the atoms on the surface with a hollow space of nearly 5 Å along the shortest diameter [4]. This and another exciting theoretical report on the possible existence of a pure gold fullerene cluster (with 32 atoms) [5] spurred several experimental [6] and theoretical [7–10] research investigations on neutral and charged gold nanoclusters with \( 10–100 \) atoms in the last decade. Conformations predicted varied from ‘hollow-spherical’, ‘tube-like’ hollow and ‘tetrahedral’ hollow conformations.

Despite several efforts, a conclusive evidence of pure gold cages was eluding till the first breakthrough confirmation of stable anionic ‘Hollow Golden Cages’ (HGCs) [11] (symmetrical structures for \( \text{Au}_{16} \), \( \text{Au}_{17} \) and \( \text{Au}_{18} \) nanoclusters) using combined experimental photo electron spectra (PES) and density functional theory (DFT) calculations. These results were pursued by another work reporting hollow ground state (GS) conformations for anionic \( \text{Au}_n \) clusters (\( n = 11–24 \)) using an electron diffraction method [12]. It is further established from the above as well as the ensuing research reports that as a consequence of strong relativistic effects anionic gold nanocages evolve from ‘Flat Gold Cages’ (\( \text{Au}_{13} \), \( \text{Au}_{14} \) and \( \text{Au}_{15} \)) to HGCs (\( \text{Au}_{16} \), \( \text{Au}_{17} \) and \( \text{Au}_{18} \)) and ‘Tetrahedral Gold Cages’ (\( \text{Au}_{19} \) and \( \text{Au}_{20} \)) [11–16]. Similar studies on neutral gold clusters followed later [17–21] demonstrating a flat-to-HGC transition at \( \text{Au}_{17} \) as compared to \( \text{Au}_{16} \) in anionic counterparts [17]. Studies on cationic \( \text{Au}_n \) (\( n > 10 \)) are relatively very few as compared to their neutral and anionic counterparts [16]. The HGC conformations in charged as well as neutral gold clusters have an interior space of nearly 5.5 Å and are thus capable of accommodating a foreign host atom, a radioactive atom, etc. This compounded with the fact that clusters with \( 10–100 \) atoms absorb light in the near-infrared region (thereby being biocompatible), which makes them attractive drug delivery or contrasting agents. In addition, a cage structure with all the atoms on the surface is likely to be more catalytically active with respect to compact conformations. Owing to the above implications, exploration

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and search for HGCs with more than 20 atoms continued during the last half decade [22–32].

Contrary to the smaller Au_n (n = 10–20) clusters, GS structural identification in bigger Au_n (n > 20) clusters presented major challenges due to the structural diversity in later [22–29]. GS structure in some of the above reports is deduced experimentally using techniques, such as photoelectron spectroscopy (PES), trapped ion electron diffraction (TIED), ion mobility (IM) and infrared absorption spectroscopy in conjunction with DFT. While IM and TIED experiments are carried out on both anion and cation clusters, PES experiments are confined only to anions due to low photon energies of the lasers used. Infrared absorption spectroscopy is commonly used to determine the structure of neutral clusters. Therefore, it is likely that a number of isomers can be found to coexist experimentally and many clusters with more than 20 atoms may have fluxional property contributing significantly to discrepancies in structural predictions. As a consequence, even for a small cluster, such as Au_{16}, few reports disagree with the fact that anionic and neutral Au_{16} clusters are HGCs [33]. Thus, despite significant experimental and theoretical efforts, structures of large bare gold clusters remain less resolved. The largest bare Au cluster that has been well characterised experimentally is Au_{34} with a 4-atom core and 30-atom shell [26]. The search further continued and the neutral Au_{32} cluster has been reported to be a GS conformation by a later report [29]. Double shell structures (with one shell enclosing a Au_{n}, n > 12, HGC) have been proposed for the Au_{58} cluster [34]. Nevertheless, a definitive proof on the existence of an HGC conformation with more than 20 atoms remained elusive, particularly, among charged gold clusters. Among the neutral clusters, two HGC conformations, viz., Au_{18} and Au_{32} are widely studied for their potential electronic and catalytic properties [35–40]. These studies validate that both the HGCs are excellent red-ox agents and can be even an eminent choice for the selective oxidation of styrene to benzaldehyde [37].

Effective application of HGCs in various applications ranging from catalytic activity to drug delivery requires an insight on their finite-temperature behaviour. While most of the catalytic reactions are carried out at room temperatures, some of them are carried out between 400 and 1000 K [41–44]. On the other hand, biological applications require the cage to be stable between 300 and 400 K. For example, once an HGC is stabilised, it is usually used for a controlled release with near-infrared light between 300 and 400 K [45]. In order to stable the cage at working temperatures, there have been attempts to dope or functionalise gold cages so as to increase the energy gap between occupied and unoccupied molecular orbitals. This is done by endohedral doping [46–50] or by functionalising them on the surface [51]. Although, this increases the possibility of a higher thermal stability at working temperatures, it does not always ensure it. In addition, many issues remain, such as synthesising and trapping HGC structures experimentally. One of the bottlenecks in the synthesis and application of HGCs is the lack of an in-depth understanding on the finite-temperature behaviour of ‘free-standing’ HGCs in spite of their wide importance and potentiality. In fact, the finite-temperature studies on gold clusters are few and scattered [52–56]. In one of the rare and consolidated study on a gold cage, Manninen et al. [55] clearly show that the surface of the doped cage is retained only up to 366 K. In another study, we show that the 32-atom icosahedron gold cluster is stable only up to 300 K [56]. However, the underlying electronic factors stabilising a golden cage are still not well understood.

In an attempt to address the above issue, in this work, we carry out Born–Oppenheimer molecular dynamics (BOMD) simulations on a well-known ‘free-standing’ HGC viz., the neutral GS Au_{18}(Au_{18}-GS) cluster, at various working temperatures. BOMD simulations are carried out between 300 and 1000 K (working temperatures for catalytic applications) on Au_{18}-GS cluster. The results obtained on Au_{18}-GS are compared with the earlier simulation results on Au_{32} icosahedron cage. In addition, we dwell in particular on the behaviour of both the clusters at 300–400 K. As mentioned earlier, behaviour of a hollow conformation in this temperature range is important for its potential application in drug delivery or as contrasting agent. To support our understanding on the behaviour of Au_{18}-GS hollow conformation at 300–400 K, we also perform BOMD simulations on two other non-GS conformations viz., Au_{18} spherical conformation (one of the low-lying hollow conformation of Au_{18}) and Au_{18} pyramidal conformation, at these two temperatures. These two conformations are low-lying conformations with a high possibility of coexisting along with their GS counterpart.

2. Computational details

All the calculations in the study are performed under the framework of auxiliary DFT [57], using a linear combination of Gaussian orbitals as implemented in deMon 2.2.6 code [58]. Several conformations are generated for the Au_{18} cluster. All the generated conformations are optimised using the Perdew–Burke–Ernzerhof exchange and correlation functional [59] with 1997 Stuttgart–Dresden relativistic effective core potentials (RECPs) [60] as the basis set for the valence electrons of gold. It is well established that, relativistic effects play an important role in describing the structure–property correlation within gold clusters [20,61–64]. 5s, 5p, 5d and 6s electrons are considered to constitute the valence electrons. No additional polarisation functions are added. The GEN-A2 auxiliary functions are used to fit the charge density [65]. The convergence of the geometries is based on gradient and displacement criteria with a threshold value of 10^{-5} a.u and the criteria for convergence of an SCF cycle was set to 10^{-9} a.u.
GS conformations of Au\textsubscript{18} is chosen as the initial geometries to perform \textit{ab initio} molecular dynamics simulations. The finite-temperature behaviour for each cluster is studied using BOMD with the same exchange correlation and RECPs stated above. The simulations are carried out between 300 and 1000 K with an interval of 100 K. As already mentioned earlier, the behaviour of a cage at a lower temperature range (300–400 K) is of potential interest for bio-medical applications. Its behaviour at a higher temperature range (400–1000 K) is important for potential catalytic applications. At each temperature, the cluster is equilibrated for a time period of 10 ps followed by simulation time of 30 ps. The temperature of the cluster is maintained using Berendeson’s thermostat (τ = 0.5 ps) in an NVT ensemble. It is well known that the Noose–Hoover thermostat is superior than Berendeson’s thermostat. However, we have verified the molecular dynamics results obtained by the two thermostats at lower temperatures and found them to be consistent with each other. The nuclear positions are updated using a velocity Verlet algorithm with a time step of 1 fs. We hold the total angular momentum of the cluster to zero, thereby suppressing the cluster rotation. The atomic positions are analysed using a traditional parameter, viz., mean-squared ionic displacements (MSDs).

The MSD of an individual atom is defined as

\[ \langle R_i^2 \rangle = \frac{1}{M} \sum_{m=1}^{M} [R_i(t_{0m} + t) - R_i(t_{0m})]^2, \]

where, \( R_i(t_{0m}) \) is the instantaneous position of atom \( i \) at \( t_0 \) and \( R_i(t_{0m} + t) \) is the corresponding position of atom \( i \) after a time interval \( t \).

In addition, we also calculate the deformation parameter or sphericity parameter, viz., \( \epsilon_{\text{pro}} \) to analyse the shape of the geometry as a function of temperature and time. The deformation parameter \( \epsilon_{\text{pro}} \) is defined as

\[ \epsilon_{\text{pro}} = \frac{2Q_1}{(Q_2 + Q_3)}. \]

where \( Q_1 \geq Q_2 \geq Q_3 \) are eigenvalues of the quadrupole tensor \( Q_{ij} = \sum R_{Li}R_{Lj} \) with \( R_{Li} \) being the \( i \)th coordinate of the ion \( I \) relative to the centre of mass of the cluster. A spherical system (\( Q_1 = Q_2 = Q_3 \)) has an \( \epsilon_{\text{pro}} = 1 \), while \( \epsilon_{\text{pro}} > 1 \) indicates a deformation from the spherical system of some kind. The presence of a hollow space in the centre as a function of temperature is demonstrated by plotting the radial distribution function (RDF) for the cluster from the centre of mass.

The results obtained for the Au\textsubscript{18} cluster are compared with simulations results carried out earlier on Au\textsubscript{32} [56]. Spherical deformation parameter is extracted from the simulations carried out in the earlier reported work [56] and the results are presented in this work. Apart from the BOMD simulations on the GS conformations of Au\textsubscript{18} and Au\textsubscript{32}, simulations are also carried out on one of the low-lying hollow cage conformation of Au\textsubscript{18} and the pyramidal conformation of Au\textsubscript{18} at 300–400 K.

3. Results and discussions

3.1. Structure, electronic properties and finite-temperature behaviour of HGCs

We begin with a note on GS geometries and representative high-energy isomers of Au\textsubscript{18} and Au\textsubscript{32} clusters as obtained from our calculations (see Figures 1 and 2). The GS geometry of the Au\textsubscript{18} cluster (Figure 1(a)) is an HGC with three distinct layers. The bottom layer is composed of seven atoms, a central atom surrounded by hexagonal ring. The middle atomic layer is also a hexagonal ring but without a central atom. The top layer is a four-membered ring with a cap. The stacking of these three layers gives a hollow but a prolate cage structure to the Au\textsubscript{18}-GS conformation. Interestingly, Au\textsubscript{18} has several nearly degenerate GS conformations (all of which are hollow) lying within 5 kcal/mol above the GS conformation. Noticeably, the lower four conformations have a hexagonal bottom layer. The presence of this layer has implications on the finite-temperature behaviour of Au\textsubscript{18} HGCs as will be discussed later. In fact up to 10 kcal/mol above the GS geometry, we have not been able to note any core–shell conformation (conformations with one or two atoms surrounded by a cage) for the 18-atom cluster. On the other hand, Au\textsubscript{32}-GS conformation is a highly symmetric icosahedral cage (see Figure 2(a)). Different high-energy conformers of the Au\textsubscript{32} cluster are shown in Figure 2(b)–2(l). In contrast to the Au\textsubscript{18} cluster, the first low-lying isomer of Au\textsubscript{32} is 4.42 kcal/mol higher in energy with respect to the GS. Distorted and compact isomers (core–shell conformations, where an atom is seen in the centre of the cage) lie about 10 kcal/mol above the GS conformation. The above-discussed isomer distribution for both the clusters matches with the trends mentioned in earlier reports with some disparity in relative energy values [17,29].

Turning to the electronic properties of Au\textsubscript{18} and Au\textsubscript{32}-GS HGCs, some noticeable differences are highlighted in a table given in Figure 3. For the sake of better understanding of the structure, and further elucidation of the ionic motion in Au\textsubscript{18}-GS and Au\textsubscript{32} clusters at finite temperatures, we classify the distribution of atoms in both the clusters in terms of number of inter-atomic layers (\( N_{\text{at}} \)). Au\textsubscript{18} and Au\textsubscript{32} have three and five inter-atomic layers, respectively, as shown in Figure 3(a) and 3(b). The shortest inter-atomic bond distance found in Au\textsubscript{18} cage is 2.72 Å, which is between the top and middle layer (highlighted as blue in Figure 3(c)). The next shortest inter-atomic distances in Au\textsubscript{18} are 2.79 Å, spreading between the inter-atomic layers as represented by black lines in Figure 3(c). On the other hand, in case of Au\textsubscript{32} cage the shortest inter-atomic bond distances of 2.79 Å are evenly distributed throughout the icosahedron cage.
(see Figure 3(d)). Au_{32}-GS being icosahedral has an $\epsilon_{\text{pro}}$ value of exactly 1.00, while that for Au$_{18}$ is 1.41 indicating it to be cylindrical/tubular (dimension along one axis is nearly 1.4 times the dimension along the other two axis).

Nucleus-independent chemical shift (NICS) is calculated for both the clusters. Both the clusters are seen to have negative NICS values with that of Au$_{32}$ twice high as compared to Au$_{18}$ indicating a more spherically de-localised electron.
Table 1. The table gives number of inter-atomic layers, shortest Au–Au bond distances, $\epsilon_{\text{pro}}$ (deformation parameter), NICS value and HOMO–LUMO energy gap for Au$_{18}$ and Au$_{32}$ clusters.

| Structure | $N_{\text{str}}$ | (Au-Au)$_{\text{str}}$ | $\epsilon_{\text{pro}}$ | NICS | $E_g$ |
|-----------|------------------|------------------------|------------------------|-------|-------|
| Au$_{18}$ (GS) | 3 | 2.72 | 1.41 | $-47.60$ | 1.08 |
| Au$_{32}$ (GS) | 5 | 2.79 | 1.00 | $-81.10$ | 1.61 |

Figure 3. The table gives number of inter-atomic layers, shortest Au–Au bond distances, $\epsilon_{\text{pro}}$ (deformation parameter), NICS value and HOMO–LUMO energy gap for Au$_{18}$ and Au$_{32}$ clusters. (a) and (b) project various atomic layers in ground state conformations. (c) and (d) highlight the distribution of short Au–Au bond distances (less than or equal to 2.80 Å).

Now, we will begin the discussion on the finite-temperature behaviour with a note on atomic displacements (obtained by visualising the trajectories) as a function of temperature. An analysis of the trajectories reveals that the Au$_{18}$-GS cluster vibrates around its starting conformation at 300 K (room temperature). Between 400 and 600 K, the cluster undergoes structural rearrangements leading to the presence of other high-energy conformations. At these two temperatures, Au$_{18}$-GS conformation translates into 18$_1$, 18$_2$ and 18$_3$ (see Figure 1(b)–1(d)) conformations, which are 0.25, 0.27 and 0.87 kcal/mol higher in energy, respectively, and back. The structural rearrangements take place through the constant displacement between atoms of the top and middle layers. On the other hand, the atoms in the bottom hexagonal layer undergo structural rearrangements and inter-layer displacements only occasionally (for about 10% of simulation time). For the rest of the simulation time (90%), atoms in the lower hexagonal layer undergo only an up-and-down motion and as a consequence the orientation of the layer changes slightly from one isomer to another (see Figure 4). Thus, though Au$_{18}$-GS is not able to maintain its GS geometry above room temperature, it undergoes structural fluxionality between the four low-lying hollow conformations. Between 700 and 900 K, the cluster transits through several isomers all of which are hollow in nature. Importantly, we note only isomerisation where the cluster visits all the conformations shown in Figure 1 from 700 K with the exception of 18$_1$. There is no diffusion of atoms around this temperature range. Around 1000 K, the atoms visit other higher energy conformations, which are hollow in nature. In short, we do not note any core–shell conformation even at 1000 K.

In case of Au$_{32}$, the GS structure is retained with slight structural modifications at 300 K [56]. The atoms in the top and bottom two layers show inter-layer diffusion at 400 K, while maintaining the central eight-membered ring (see Figure 3). The atomic motion increases at 500 K and the starting conformation gets distorted with the cluster transiting through hollow and non-hollow but spherical isomers. Between 600 and 800 K, core–shell conformations begin to dominate the trajectories of the Au$_{32}$ cluster. In this temperature range, cluster occasionally visits hollow conformations for about 20% of simulation time. Above 900 K, the spherical shape is lost and the cluster begins to visit some prolate shape conformations. Thus, in contrast to the Au$_{18}$ cluster, Au$_{32}$ retains an HGC conformation only up to 400 K as reported in an earlier work [56].

The observations on ionic motion are further converged by the calculation of $\epsilon_{\text{pro}}$ as a function of time and temperature. Figure 5 shows an $\langle \epsilon_{\text{pro}} \rangle$ at various temperatures. The plot for Au$_{18}$ clearly shows that the average value around 300 K is same as that of the GS geometry. From 400 to 600 K, the value undergoes a dip due to frequent structural transitions between the GS and other three high-energy conformations mentioned earlier (18$_1$, 18$_2$ and 18$_3$). Out of the three high-energy conformations, the cluster visits 18$_3$, a more spherical conformation with an $\epsilon_{\text{pro}}$ of 1.27 and the
cluster resides in the conformation for nearly 30% of simulation time. This is demonstrated through the absolute $\epsilon_{\text{pro}}$ values plotted as a function of time at 300, 400 and 600 K in the same figure. The value returns to the nearly GS $\epsilon_{\text{pro}}$ value (1.41) around 700 K (1.47) and 800 K (1.49) owing to transition through several isomers. Around 1000 K, the value rises to 1.55. Thus, the Au$_{18}$ cluster at 1000 K undergoes a structural deformation of only about 10% with respect to its starting $\epsilon_{\text{pro}}$ value. On the other hand, the $\epsilon_{\text{pro}}$ value for Au$_{32}$ begins to deviate from a value of 1.0 at 300 K itself. It sees a steady raise as the cluster begins to deviate from its starting conformation as a function of temperature. The cluster begins to visit more prolate conformations with the value increasing by nearly 70% at 1000 K with respect to its starting value at 300 K. In addition to it, it is also observed from Figure 5 that the $\epsilon_{\text{pro}}$ value for the Au$_{32}$ cluster increases drastically around 800 K. Therefore, this temperature can be taken as an onset for melting of the Au$_{32}$ cluster.

While $\epsilon_{\text{pro}}$ demonstrates the extent of sphericity of the cluster at various temperatures, RDF is indicative of the presence or absence of a shell structure within the cluster.
Figure 6 shows the RDF for the GS conformation and averaged RDF for 600 K for both the clusters. The RDF for the Au_{18}-GS conformation shows three prominent peaks in line with the three layers mentioned earlier. It is clearly seen that two prominent peaks are still retained in the RDF plot at 600 K. However, there is an inter-layer diffusion. Thus, combined results of RDF and \( \epsilon_{\text{pro}} \) modulations indicate Au_{18} to be fluxional between degenerate GS conformations highlighted in Figure 4 (as understood from \( \epsilon_{\text{pro}} \) values) thereby retaining the basic critical layers. Au_{18} also retains its hollowness at 600 K as understood from RDF plots. The RDF for Au_{32}-GS on the other hand shows two peaks corresponding to 20 atoms in the pentagon ring and 12 icosahedron vertices, respectively. At 600 K, RDF for Au_{32} is quite broad without any significant peaks. Thus, the starting conformation gets fully distorted by this temperature. Au_{18} cluster remains hollow until nearly 1000 K temperature with structural fluxionality up to 600 K and Au_{32} is an HGC only up to 400 K. Most importantly, at 300–400 K (temperature range for bio-medical based applications) [45], both the clusters retain their hollow structure with some structural fluxionality in case of Au_{18}.

Stability of Au_{18} and Au_{32} hollow conformations at 300–400 K has motivated us to explore the finite-temperature behaviour of some non-GS hollow conformations at these two temperatures. Hence, as a case study, BOMD simulations are carried out on Au_{18}-(SPH) (18,3, Figure 1(c)) conformation and Au_{18} pyramidal (Au_{18}-PYR) cluster ((18,10, Figure 1(c)) at 300–400 K. The impetus behind selecting Au_{18}-(SPH) is corroborated from the fact that, this spherical cage is dominantly visible between 400 and 600 K in the trajectory of Au_{18}-GS as discussed earlier. The motivation behind the selection of the Au_{18}-PYR cluster is the fact that this conformation is not visible in the trajectories of Au_{18}-GS at various temperatures that have been studied. The structure of Au_{18}-(SPH) (18,3) conformer, given in Figure 7 (a), is seen to be composed of three atomic layers. The bottom and middle layers are seven-membered rings (the lower ring is identical to the lower ring of Au_{18}-GS) and the top layer is a four-membered ring. The

| Structure   | N_{at} | (Au-Au)$_{sbd}$ | \( \epsilon_{\text{pro}} \) | E$_g$ | NICS  |
|-------------|--------|----------------|----------------|------|------|
| Au_{18}(SPH) | 3      | 2.75           | 1.21           | 1.18 | –55.01 |
| Au_{18}(PYR) | 3      | 2.70           | 1.41           | 0.52 | –28.68 |
structure of Au$_{18}$-PYR presented in the Figure 7(b) is seen to be composed of three atomic layers.

The shortest bond distances ($\leq 2.80$ Å) in Au$_{18}$-SPH are distributed throughout the cluster while in Au$_{18}$-PYR they are localised along the surface pyramidal atoms as seen in Figure 7(d). $\epsilon_{\text{pro}}$ of Au$_{18}$-SPH is 1.21 (as compared to 1.41 of Au$_{18}$-GS) while that of Au$_{18}$-PYR is 1.41 (indicative of the fact that dimension along z-axis is somewhat greater than that of along the x- and y-axis). The HOMO–LUMO gap is 1.18 eV for Au$_{18}$-SPH while that for Au$_{18}$-PYR is 0.52 eV.

Coming to the finite-temperature behaviour of Au$_{18}$-SPH, analysis of ionic motions show that the cluster vibrates around its starting conformation at 300 K. Around 400 K, it undergoes an identical structural transition as seen in case of Au$_{18}$-GS trajectory at 400 K (viz., the structure undergoes structural fluxionality between the four lowest degenerate GS conformations). In contrast, surface atoms in Au$_{18}$-PYR diffuse leading to a hollow distorted structure with same spherical dimensions as that of starting pyramidal conformation. The atomic displacements in both the clusters reflect in the averaged relative $\epsilon_{\text{pro}}$ values given in Figure 8. The values given here are a difference between the values of the starting conformation and an averaged value at a given temperature. For the sake of completeness, relative values are also given for the conformations discussed in the earlier section. The $\epsilon_{\text{pro}}$ values for Au$_{18}$-SPH remain around its original value (a minor increase of 0.05 at 400 K). Incidentally, this value (1.21 + 0.05, which is 1.26) is same as the value obtained for Au$_{18}$-GS trajectory at 400 K. The $\epsilon_{\text{pro}}$ values for Au$_{18}$-PYR at 300–400 K do not show any significant change in line with its ionic motion owing to the diffusion of atoms along the surface of the cluster.

### 3.2. Structure-property and thermal stability correlation

Among the HGCs studied, Au$_{32}$ is the most symmetric conformation with an $\epsilon_{\text{pro}}$ value of exactly 1.00. The NICS value as well as the HOMO–LUMO gap varies in the following way for various clusters: Au$_{32}$ > Au$_{18}$-SPH > Au$_{18}$-GS > Au$_{18}$-PYR. The above trend indicate that the Au$_{32}$ cluster is most stable among the cluster studied in this work. The isomer energy distribution is non-degenerate with a reasonable high-energy gap of nearly 4 kcal/mol between the GS and first low-lying isomer. The structure also shows a uniform network of shortest bond distances. In spite of these structural advantages, Au$_{32}$ icosahedron conformation shows significant deviation from the spherically hollow orientation at 400 K and collapses by 500 K.

The finite-temperature behaviour of nanoclusters (clusters with atoms 10–100) in general has thrown many surprises [66–69]. Usually in clusters, the surface to volume ratio is higher as compared to that of bulk. This is traditionally expected to bring down the temperature up to which the cluster is stable (as compared to that of bulk). However this traditional expectation is seen to be inconsistent in case of some unique sized Na [66], Ga [67] and Al clusters [68]. In an earlier study on finite-temperature behaviour of Au clusters with 3–10 atoms [53], only Au$_4$, Au$_6$ and Au$_{10}$ clusters are seen to remain in their GS beyond 500 K. Au$_6$ is the most stable among the above three (stable up to 1200 K as compared to 800 K of Au$_4$ and Au$_{10}$). This stability is interestingly lost upon adding or removing an electron to Au$_6$ [54]. The above studies as well as further theoretical studies on other nanoclusters reveal that a confluence of structural and electronic properties of a cluster increases its thermal stability [54,69–73]. As a consequence, the whole cluster or part of a cluster retains its original orientation up to a much higher temperature as compared to its counterparts.

Progressing to the present HGCs, we have attempted to evaluate the charge distribution within the cluster and composition of frontier molecular orbitals to bring out, structure-electronic properties finite-temperature behaviour of the HGCs considered in this study. Loewdin population-based charges are calculated for all the four clusters and the distribution of positive and negative charges are given in Figure 9(a)–9(d). It is clearly seen from the figure that the bottom hexagonal rings present in Au$_{18}$-GS have a central

![Figure 8. Comparison of relative ($\epsilon_{\text{pro}}$) (deformation parameter) of Au$_{18}$-GS, Au$_{18}$-SPH, Au$_{18}$-PYR and Au$_{32}$ clusters.](image-url)
negatively charged atom surrounded by positively charged atoms. In case of Au$_{18}$-SPH, one of the atoms in the bottom ring has a negative charge on account of it being slightly out of plane (refer Supplementary Table 1). In addition, there is a homogeneous distribution (presence of an alternating positively and negatively charged centres) of charges over the Au$_{18}$-GS, Au$_{18}$-SPH clusters leading to greater electrostatic forces. Such a distribution is absent in case of Au$_{32}$ and Au$_{18}$-PYR clusters.

Analysis of HOMO orbital composition reveals that HOMO of Au$_{18}$-GS shows greater s–d hybridisation of atomic orbital (see Figure 9(e)). On the other hand, HOMO and LUMO of Au$_{32}$ are composed of d orbitals of vertex atoms each (see Figure 9(f) and 9(j), figures tilted by 45° with respect to the orientation shown in Figure 9(b)). Similar to the case of Au$_{18}$, frontier molecular orbitals of Au$_{18}$-SPH are s–d hybridised orbitals (see Figure 9(g), 9(h), 9(k) and 9(l)). These observations, ironically fall in line with the findings in a recent MD study on the Au$_6$ cluster, where s–d hybridised frontier orbitals along with symmetrically alternating negative and positive charges stabilise the D$_{3h}$ planar triangular structure up to nearly 1200 K [54].

4. Conclusions
In this work, we have attempted to understand the stability of hollow gold cages as a function of finite temperature. We have presented the results from BOMD simulations on hollow Au conformations (Au$_{18}$-GS, Au$_{18}$-SPH, Au$_{18}$-PYR, Au$_{32}$ [56]) at various finite temperatures. Our study precipitates out the different ways in which individual HGCs behave at finite temperatures. A confluence of structural and electronic factors contribute to the thermal behaviour of a given HGC conformation. The salient findings of the simulations are

(1) Au$_{18}$-GS, Au$_{18}$-SPH and Au$_{32}$ hollow cages are stable (retain their starting conformations) at a room temperature of 300 K. Atoms in the Au$_{18}$-PYR cluster diffuse along the surface at 300 K itself.
(2) The stability of a ‘free-standing’ cage at 400 K depends on the degeneracy of the GS geometry and its electronic structure. Au$_{18}$-GS and Au$_{18}$-SPH cages show structural functionality between the degenerate GS structures at 400 K. Au$_{32}$ icosahedron cage with high-lying isomers continue to reside in its starting conformation at 400 K, albeit with higher atomic displacements.
(3) At 500–600 K, Au$_{18}$-GS is seen to continue to fluctuate between four degenerate GS isomers and between 700 and 1000 K, the Au$_{18}$ cluster fluctuates between several hollow cage conformations. Thus, significantly, the Au$_{18}$-GS cluster retains an HGC
conformation (i.e. its sphericity and hollowness) up to 1000 K, albeit, with structural fluxionality. On the other hand, the icosahedron conformation of $\text{Au}_{32}$ is lost by 500 K. This trend is established by $\epsilon_{\text{pro}}$ values and RDF at finite temperatures. The reasons for the structural fluxionality of $\text{Au}_{18}$ hollow cage at lower finite-temperatures converge as (a) Better s–d hybridised frontier orbitals. (b) An ordered network of positive and negative charge centres particularly in the lower hexagonal layer. (c) Presence of couple of low-lying isomers with the same lower hexagonal layer, which gives the structure freedom to transit among various isomers until enough energy is acquired to overcome the forces binding the layers in the clusters.

Finally, it may be emphasised that structural fluxionality plays an important role in improving the catalytic properties of the clusters [74] and hence, $\text{Au}_{18}$ hollow cages have a greater potential as catalysts at even higher temperatures. The important conclusions from this work are also summarised in the graphical abstract (Figure 10).

Acknowledgements
The authors dedicate this work to Prof. Sourav Pal in honour of his 60th birthday. The authors acknowledge the Center of Excellence in Scientific Computing (CoESC) at CSIR-NCL, Pune and CSIR-Fourth Paradigm Institute, Bangalore for providing access to their high performance computing facilities. The authors also acknowledge a grant from MSM: CSC-0129 project.

Disclosure statement
No potential conflict of interest was reported by the authors.

Funding
The authors acknowledge a grant from MSM [CSC-0129] project.

Supplemental data
Supplemental data for this article can be accessed at http://dx.doi.org/10.1080/00268976.2015.1062151.

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