

Structures of neutral and anionic Au₁₆ clusters revisitedGang Chen,^{1,2,a)} Qian Wang,¹ Qiang Sun,^{1,3} Yoshiyuki Kawazoe,² and Puru Jena¹¹Department of Physics, Virginia Commonwealth University, Richmond, Virginia 23284, USA²Institute for Materials Research, Tohoku University, Aoba-ku, Sendai 980-8577, Japan³Department of Advanced Materials and Nanotechnology, Peking University, Beijing 100871, China

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Using the density functional theory and generalized gradient approximation for exchange and correlation potential, we have performed an extensive search to obtain the ground state geometries of both neutral and anionic Au₁₆ cluster by considering over 200 low lying isomers. For the neutral Au₁₆ cluster we found a new T_d compact structure to be the lowest energy configuration, which is nearly degenerate in total energy with the previously reported C_s and C_{2v} noncage structures. While the Au₁₆⁻ cluster, in agreement with previous calculations, is found to have a T_d hollow cage structure, an isomer with a planar structure is found to be lower in energy. The photoelectron spectra from all the nine lowest energy isomers are calculated and compared with experiment to determine the possibility of their existence. Molecular dynamics simulations on both neutral and anionic Au₁₆ clusters are carried out to provide further insight into the origin and stability of these structures. Our comprehensive study allows us to answer the following questions: (1) Why are the adiabatic and vertical detachment energies of Au₁₆ cluster nearly identical when the lowest energy structures of the anion and the neutral are so very different? (2) How is Au₁₆⁻ formed? Is it born neutral and the extra electron attaches afterwards or is it born anionic and the structure evolves during the electron attachment process? © 2010 American Institute of Physics. [doi:10.1063/1.3427293]

I. INTRODUCTION

One of the most important features of clusters is that their structures are unlike their bulk and can change abruptly even with the addition of a single atom. Since the structure of a cluster is intimately linked to its properties, an understanding of the cluster geometry is of fundamental interest. Unfortunately, there are no experimental techniques that can currently determine the structure of a cluster in the gas phase directly and unambiguously. While this can be achieved using theoretical methods, the limitations in current theoretical approach do not make it easy to predict the ground state geometry with absolute certainty not only because there is no exact theory that can treat large systems, but because clusters can have numerous low lying isomers often protected by energy barriers. As cluster size increases, the number of local minima in the potential energy surface increases exponentially and search for the ground state geometry becomes a very difficult task.

The current geometry optimization process is usually carried out by starting with a large number of initial configurations and using a scheme that allows it to hop over energy barriers to sample as much of the phase space as possible. Any isomer lying within a very small energy range of the lowest energy structure is considered a potential candidate for the ground state geometry. The correct ground state structure is then identified by finding out which of the isomers in this narrow energy range accurately predicts properties in agreement with experiments. Currently there are three experimental techniques, namely, ion mobility,^{1,2} photoelectron

spectroscopy (PES),³⁻⁶ and trapped ion electron diffraction (TIED),^{7,8} which are used to shed light on the geometries of size-selected *charged* clusters. While ion mobility and TIED experiments can be carried out on both anion and cation clusters, PES experiments are confined only to anions due to low photon energies of the lasers used. In the PES experiment one measures the adiabatic electron affinity (AEA) (which provides the energy difference between the anion and neutral ground states), vertical detachment energy (VDE) (which provides the energy difference between the anion ground state and the neutral state at the anion geometry) as well as the photodetachment spectra. In the TIED approach, on the other hand, one compares the simulated diffraction pattern of theoretically generated candidate geometries with experiment. The advantage of the later approach is that one compares the entire simulated and experimental diffraction pattern. Note that in the PES experiment, it is difficult to calculate, within DFT, the entire photoelectron spectra^{5,9} and hence one is limited to comparing a few selected data such as AEA, VDE, and the first several peaks in the PES. In addition, experimental determination of the AEA becomes difficult if the geometries of the ground states of the anion and neutral clusters are very different and are protected by significant energy barrier. Nevertheless, the above experimental techniques complement each other and the theoretical structure that explains all available experiments is considered to be the preferred structure of the charged cluster. A fourth experimental technique that provides information on the structure of *neutral* clusters is the infrared absorption spectroscopy¹⁰ that measures the vibrational spectra of clusters and directly reflects the symmetry of the particle. However, all the above experiments rely on theoretical calcula-

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tions of geometries of possible low lying isomers. We have used Au₁₆ cluster as a test case to provide a comprehensive analysis of the ability of current methods to determine the geometry of the ground state of clusters.

Gold, the noblest of all metals has been of interest to scientists and society for ages. Its chemical inertness and permanent luster in the bulk phase make gold a precious metal. However, its properties change dramatically when the length scale is reduced to nanometers. Here, gold becomes highly reactive and is considered to be a good candidate for heterogeneous and homogeneous catalysis. Potential of gold nanostructures for applications in electronics and medicine has further fueled interest in the study of this noble metal.^{11–18} Recently Au clusters have attracted considerable attention as experiments and theoretical calculations revealed some unexpected properties.^{1–10,19,20} Unlike monovalent alkali metals, small gold clusters containing less than a dozen atoms favor planar structures.^{1,2,6–8} Au₂₀ cluster forms a pyramidal structure with tetrahedral symmetry and can be thought of as an embryonic form of the bulk face-centered cubic crystal. With a large energy gap of about 1.8 eV between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), Au₂₀ is also a very stable cluster.⁴ By removing the four vertex atoms of the Au₂₀ cluster and allowing an outward relaxation of the face-centered atoms, one would arrive at a hollow cage structure with tetrahedral symmetry for the Au₁₆ cluster.

In a recent study Bulusu *et al.*,⁵ by comparing the experimental photoelectron spectra with those calculated from theory, identified the ground state geometry of the Au₁₆[−] anion cluster to be a hollow cage. A later experiment by Xing *et al.*⁷ using electron diffraction also identified this structural assignment for the anion Au₁₆[−]. In addition, this experiment identified cage structures for Au_n[−] with n=14–17. Experimental discovery of these hollow cage structures has created a great deal of excitement^{5,7,21–29} not only because it mimics the fullerene structure well known for C clusters but also because the diameter of the cage is about 5 Å. This would make it possible to dope other atoms such as transition metal or radioactive atoms as endohedral species. Such clusters could have applications in magnetism and drug delivery as gold atoms are biocompatible and easy to functionalize. Studies of endohedral doping of Mg, Ca, Sr, Cu, and Si atoms in Au₁₆ clusters have already been reported.^{21–29}

The discovery of the cage structure of Au₁₆[−] has also raised some interesting questions. For example, does neutral Au₁₆ also possess a hollow cage structure? As pointed out earlier, both PES and TIED experiments are carried out on charged clusters and hence cannot directly provide any information on the structure of the neutral cluster. The properties that are frequently used in PES studies for the structural information of the neutral cluster are the AEA and VDE. The difference between these two energies reflects the degree of relaxation the ground state geometry of the anion cluster undergoes when the extra electron is photodetached. If these two energies are nearly the same, it indicates that the geometry of the anion does not relax as the extra electron is removed. Bulusu *et al.*⁵ measured the AEA and VDE to be, respectively, 3.99 ± 0.03 eV and 4.03 ± 0.03 eV. Within ex-

perimental error, these values are identical and, therefore, suggest that the ground state of the neutral Au₁₆ most likely has a hollow cage structure. However, this conclusion is at odds with the calculations by Wang *et al.*³⁰ and Bulusu *et al.*³¹ who predicted different noncage structures for the neutral Au₁₆ cluster.

The above discrepancy prompted us to examine in depth the role of charge on the ground state energy structure of Au₁₆ and why the measured AEA and VDE values are so close even though the ground state geometries of the neutral and anion are different. Since the properties of clusters obtained from experiments mostly correspond to charged species and bulk properties are associated with neutral systems, it is important to understand the role of charge on cluster structure and properties, especially when clusters are small. Our conclusion regarding the structure of neutral Au₁₆ is different from that drawn from the nearly identical values of VDE and AEA. We find that the neutral Au₁₆ cluster does *not* form a hollow cage structure with tetrahedral symmetry as was found to be the case with the anionic cluster.^{5,7} A new compact structure with *T_d* symmetry has been identified to have the lowest total energy, although it is energetically nearly degenerate with the previously reported *C_s* and *C_{2v}* structures.³¹ Using molecular dynamics simulation we provide an explanation regarding the origin of this unexpected result.

II. COMPUTATIONAL DETAILS

Our calculations were carried out by using the density functional theory^{32,33} with generalized gradient approximation (GGA) as implemented in the Vienna ab initio simulation package (VASP).^{34,35} The Perdew, Burke, and Ernzerhof (PBE) (Ref. 36) parameterizations for the GGA functional was applied. The relativistic effects were included using the scalar relativistic approach and the total energies were converged within 1 meV. All configurations were fully relaxed until the forces acting on each atom fell below 0.01 eV/Å. The basis sets are given in terms of plane waves. The projector augmented-wave potential^{37,38} and a supercell with edge length of 24 Å were used in the calculations. Due to the large size of the supercell, the interaction between a cluster and its periodic images in neutral state could be neglected. For the calculation of the anionic state, a background charge was applied to maintain charge neutrality. The dipole and quadrupole moment corrections were taken into account³⁴ to efficiently handle the electrostatic interaction within the images that result from periodic repetition.^{39,40} The wave functions were expanded in a plane wave basis with an energy cutoff of 230 eV. The grid size for numerical integration was chosen to be 90 × 90 × 90. Only the Γ point was used in the summation of the Brillouin zone. To test the accuracy of our results with regard to choice of energy cutoff and numerical grid we calculated the binding energy of the Au₂ dimer by doubling both the grid size and the energy cutoff. The results differed by only 4 meV. The calculated interatomic distance of Au₂ dimer is 2.53 Å which is 2% larger than the experimental value of 2.4719 Å.⁴¹ We have repeated the calculations presented here using molecular orbital approach ADF

(Refs. 42–44) and DMOL3 (Ref. 45) codes. We have also studied the sensitivity of our results to different exchange-correlation functionals such as Tao–Perdew–Staroverov–Scuseria (TPSS) meta-GGA^{46,47} included in the ADF code. Since the main conclusions presented here are not altered, we only present results based on the VASP code. However, these are available to the reader upon request.

Search for the ground state geometry of the anionic and neutral clusters was carried out by starting with more than 200 different geometrical configurations. We used two different methods for generating these configurations. First, we started from a single atom ($n=1$) and determined the structures of larger clusters by adding one atom at a time. The structure of the $(n+1)$ -atom cluster was optimized by starting with the low-lying isomers of the n -atom cluster. Second, we also considered published structures in the literatures and those with high symmetry configurations. The vertical detachment energies for the low lying isomers were calculated by taking the difference between the energy of the neutral cluster at the geometry of the anion and that of the anionic cluster. Among the structures of neutral and anionic Au₁₆ clusters, we selected the first nine low-lying isomers for detailed discussion for each cluster which lie within ~ 0.2 eV compared to the reference geometry. The low-lying isomers within 0.2 eV could be considered as structure candidate for the cluster used in experiment. Their structural and electronic properties would be then used to compare with the experimental observation to choose the ground structure of the cluster source of experiment study.^{5,7} Also, among the previously published theoretical results obtained with first principles method within the framework of density functional theory,^{5,7,31,48,49} an error of about 0.2 eV in total energy calculated by using different numerical methods can be seen. As to the Au₁₆ cluster, for both the neutral structures and the anionic structures, we first optimized the structures using VASP code, and then reoptimized the low-lying isomers using ADF and DMOL3 codes with different basis sets and exchange-correlation functionals. In these results, an inaccuracy of about 0.2 eV can be concluded also.

The thermodynamic stability of the ground state structures of the anion and neutral clusters was also confirmed by using constant energy molecular dynamics simulations. Our molecular dynamics simulation lasted for 20 ps and the structures were monitored during this time. Each step in the molecular dynamics is 0.2 fs long. Due to the computer intensive nature of first principles molecular dynamics simulations, we used a smaller unit cell with the edge length of 16 Å which could still separate the cluster and its periodic images by ~ 10 Å.

III. RESULTS AND DISCUSSIONS

A. Anionic Au₁₆⁻

We begin our discussions with the geometries of the low lying isomers of the anionic Au₁₆⁻ cluster. A planar structure is found to be lower in total energy than the previously reported hollow cage structure. However, the PBE tends to lower the relative total energies of planar structures^{8,50} as compared to the TPSS^{46,47} exchanged correlation functional,

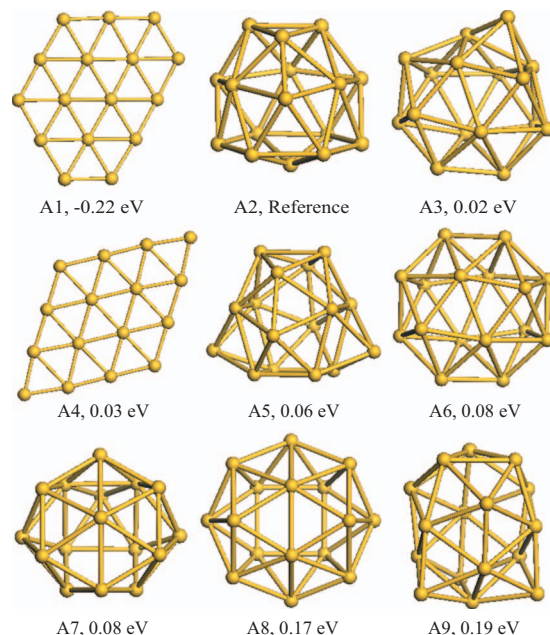


FIG. 1. Optimized geometries of anionic Au₁₆⁻ cluster for the first nine low-lying isomers. The relative energies are measured in eV with respect to the 3D hollow cage structure A2.

the PBE functional modified for solids (PBEsol),⁵¹ and the Zhao and Truhlar proposed M06-L functional.⁵² Also, the cage structure was previously predicted to be the geometrical structure detected in experiment.^{5,7} Therefore, we would like to select the cage structure as reference here and present all the low lying isomers being higher in total energy within 0.2 eV referred to the cage structure besides the planar structure which is lower in total energy, for these low lying isomers could be regarded as the potential structure candidate for the experimental detected cluster geometry. The selected low lying isomers are given in Fig. 1. The relative total energies of these isomers measured with respect to the A2 three-dimensional (3D) configuration are provided below each configuration. We note that the higher energy isomers lie within 0.2 eV above the A2 structure. The planar structure (A1) is 0.22 eV lower in energy than the T_d hollow cage structure (A2). To examine the effect of numerical grid size and energy cutoff on the relative stability of the isomers, we repeated the calculations for the A1 and A2 structures by doubling the grid size to $180 \times 180 \times 180$ and energy cutoff to 460 eV. The T_d cage structure (A2) is found to be 0.20 eV higher in energy than the planar structure (A1). Thus, the effect of a higher precision calculation only changes the relative stability by 0.02 eV, showing a good convergence in our calculated results. Our results agree with those calculated by Xing *et al.*⁷ using the density functional theory. However, these authors found the planar structure to be lower than the hollow cage structure by 0.08 eV. In order to make a direct comparison with the results of Bulusu *et al.*, we repeated the calculations with DMOL3 code by following the method used in their studies, i.e., using the PBE exchange-correlation functional, the double numeric basis sets with polarization functions (DNP), and the effective core potential. The planar structure A1 is found to be 0.2 eV lower in total energy than the A2 cage structure. We note that Bulusu *et al.*⁵ did not

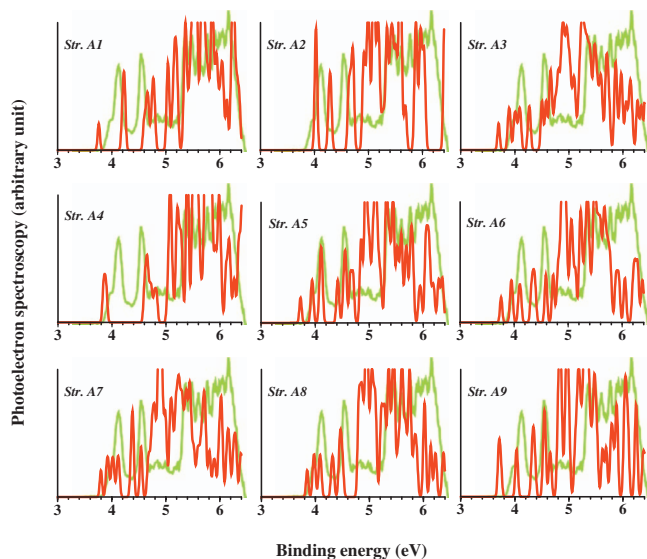


FIG. 2. The simulated photoelectron spectra for the optimized structures shown in Fig. 1 for the anionic Au_{16}^- cluster. The calculated vertical detachment energies are provided in Table I. The gray (green) and black (red) curves are for the experimental and simulated PESs, respectively. The experimental PES spectra are cited from Ref. 5.

identify a planar structure among the low lying isomers. This is probably due to the procedure adopted by these authors to search for the ground state geometry. The procedure in selecting low lying isomers by these authors was that the possible candidate geometries were first generated by a basin-hopping technique and then used as the starting configurations for the optimizations with the DMOL3 code. The planar structure was probably excluded in the first step by the basin-hopping technique, and hence accounts for the discrepancy between their results and ours obtained using the DMOL3 code.

To determine which of the low lying isomers is the preferred structure seen in experiment we have to rely on comparison of calculated properties with experiment. One such experiment is PES. Here one measures the VDE, the AEA as well as the photoelectron spectra. The VDE is obtained from the lowest energy peak of the PES data. To simulate the PES, we broadened the molecular energy levels using a Gaussian function with 0.05 eV full width at half-maximum. The simulated spectra were then shifted to coincide the energy of HOMO electron with the calculated VDE value, following the procedure of the so-called “generalized Koopman’s theorem.”^{53–55} The results are given in Fig. 2. Note that in Table I, the positions of the first peak, namely, VDE for all the isomers are given. In Ref. 5, Bulusu *et al.* identified the hollow cage to be the preferred geometry of Au_{16}^- since their calculated PES spectra resembled that of the experiment more closely than those due to any other isomer, especially when focusing on the first two peaks as the fingerprint for

such comparison. In Fig. 2, our calculated spectrum for the cage structure A2 agrees with Bulusu’s spectrum and bears resemblance with experiment. However, the energy gaps between the first two peaks in the simulated PESs of A1 and A9 isomer are 0.44 and 0.32 eV, respectively, and agree much better with the experimental value of 0.4 eV than that obtained from the A2 isomer. On the other hand, the VDE value for the hollow cage isomer A2, namely, 4.02 eV in Table I agrees with the experimental value of 4.03 ± 0.03 eV much better than VDEs calculated from the A1 and A9 isomers. We should point out that Bulusu *et al.* reported a VDE value of 4.18 eV (Refs. 5 and 56) for the A2 isomer which they calculated using GAUSSIAN03 code and the PBE functional. Our calculations yield a value of 4.02 and 3.78 eV when VASP and DMOL3 codes are used at the PBE level, respectively. This shows the uncertainty in the VDE calculated within DFT to be within 0.2 eV. In addition, density functional theory is known to be insufficient in giving accurate description of the spin configuration compared to multireference configuration interaction method, since limitation in the basis sets may introduce spin contamination.^{48,57–59} This is especially the case for the anionic Au_{16}^- cluster which, due to the unpaired electron, may have a larger error in the calculated VDE. The error in calculated VDE would affect the shift of the simulated PES and in turn introduce error in comparison with experimental spectra. So, accurate multireference configuration interaction method would be required for comparison between the calculated and the experimental VDEs. Unfortunately, it is currently not computationally feasible to study Au_{16} cluster using the above quantum chemical technique. In addition, we note that the shoulder in the low energy peak of the PES is not reproduced in the cage isomer. It is possible that this may arise due to the coexistence of some low-lying isomers. It should be pointed out that difficulties associated with Kohn–Sham HOMO energy levels in interpreting PES spectra can be avoided by using time-dependent density functional method as discussed by Water and Häkkinen.⁹

TIED technique has emerged as a very effective experimental tool to identify the ground state structure of a cluster. Here, one starts with a number of low lying isomers generated from state-of-the-art theoretical techniques, calculates the diffraction pattern of each of these isomers, and compares these with the experimental data. The advantage of this approach is that one compares the entire diffraction pattern. This approach was followed by Xing *et al.*⁷ who found that the cage structure reproduced the experimental electron diffraction data for $n=14–17$. Note that both Xing *et al.* as well as our present calculations provide planar structure to be the ground state which, depending upon the calculational procedure, lies between 0.08 and 0.22 eV lower in energy than the hollow cage structure.

TABLE I. The calculated first vertical detachment energies in eV for the low lying isomers shown in Fig. 1 of the anionic Au_{16}^- cluster. The experimental value of VDE is of 4.03 ± 0.03 eV.

A1	A2	A3	A4	A5	A6	A7	A8	A9
3.76	4.02	3.70	3.87	3.73	3.76	3.80	3.85	3.70

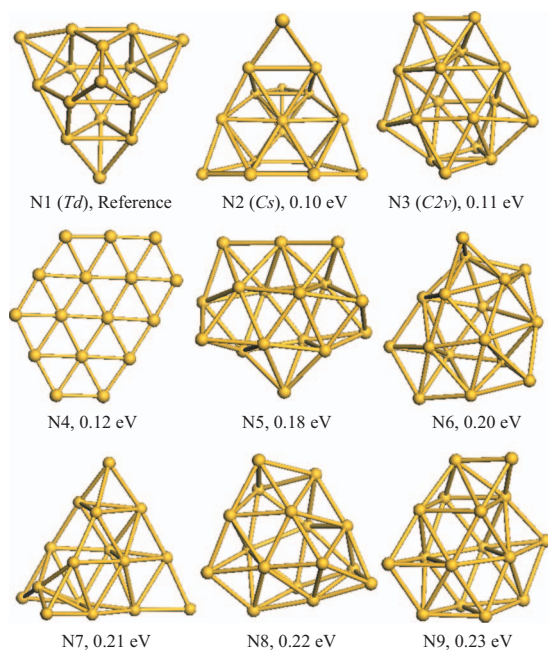


FIG. 3. Optimized geometries of neutral Au₁₆ cluster for the first nine low-lying isomers. The relative energies are measured in eV with respect to the lowest energy structure N1. The symmetries of the structures N1, N2, and N3 were given in the parentheses.

B. Neutral Au₁₆

As pointed out before, most of the experiments discussed above cannot provide direct information on the geometry of the neutral clusters as experiments are carried out on charged clusters. However, one can draw conclusions on the neutral cluster geometry by comparing the VDE and AEA and by studying the sharpness of the PES peaks. Bulusu *et al.*⁵ found the first two peaks in the PES not only to be sharp, but the VDE of 4.03 ± 0.03 eV is identical to that of the AEA of 3.99 ± 0.03 eV within experimental error. This would suggest that the neutral cluster retains the *T_d* symmetry hollow cage structure of the anionic cluster after the electron is removed.

However, as mentioned before, both Wang *et al.*³⁰ and Bulusu *et al.*³¹ predicted different lowest total energy structures of neutral Au₁₆ cluster. Bulusu *et al.*, using the generalized gradient approximation, optimized the structures selected by the basin-hopping technique and proposed a *C_{2v}* and a *C_s* structures having almost degenerate total energies to be the best candidates for the equilibrium geometry of the neutral cluster. Using local density approximation Wang *et al.*, on the other hand, had proposed a compact near-spherical structure generated by capping the distorted icosahedron. We have used the same procedure as described for the Au₁₆⁻ anion to determine the geometries of low lying neutral isomers. We have performed an extensive search on the potential energy surface to identify the low lying isomers of neutral Au₁₆ cluster. The first nine low lying isomers are shown in Fig. 3 and the relative total energies with respect to the compact structure N1 with *T_d* symmetry are presented below each configuration. The structures N2 and N3 correspond to the previously reported *C_s* and *C_{2v}* geometries, respectively. Consistent with the results of Bulusu *et al.*,³¹ we found the

C_{2v} and *C_s* structures to be nearly degenerate in energy. However, we have found a new compact structure, N1 with *T_d* symmetry to be the lowest energy geometry which lies ~ 0.10 eV lower in energy than the *C_{2v}* and *C_s* structures. The compact capped distorted icosahedron structure identified by Wang *et al.*³⁰ is found to be more than 0.3 eV above the lowest total energy structure. Within the accuracy of DFT calculations, one cannot distinguish between N1, N2, and N3 structures as the preferred ground state of the neutral Au₁₆. However, one thing is certain—the structure of the neutral is *not* a cage. The question then remains: How does one reconcile with the PES experiment, which suggests that the neutral should have the same geometry as the anion?

To further probe the structure of neutral Au₁₆ we removed an electron from the cage structure A2 of anionic Au₁₆⁻ cluster, as shown in Fig. 1, and allowed the resulting neutral cluster to relax at 0 K. The relaxed geometry essentially remained unchanged from the cage structure. The calculated relative total energy of this neutral cage geometry is 0.53 eV with respect to the *T_d* compact N1 structure, which is beyond the uncertainty in our calculations. This reinforces our previous statement that the geometry of the neutral Au₁₆ cluster is *not* a cage. The discrepancy between the theoretically predicted ground state and the experimentally assumed one, therefore, can only be reconciled if an energy barrier between the *T_d* hollow cage and *T_d* compact structures of neutral Au₁₆ exists that prevents the Au₁₆⁻ to make a structural transition once the electron is removed. If the experiments were carried out at very low temperatures, one would not see a change in the neutral geometry and hence the AEA and VDE will be nearly identical. The temperature in the diffraction study was 120 K.⁷ Although the authors in the PES study did not measure the temperature of the gold cluster source, clusters' temperatures of 200 and 130 K were respectively used in an earlier combined theoretical and experimental study⁶⁰ of Al₁₄⁻ and Al₁₅⁻.

In order to see if these low temperatures can drive structural transition from the *T_d* hollow cage structure to the *T_d* compact structure after removing an electron from the Au₁₆⁻ anionic cluster, we performed a series of first principles constant energy molecular dynamics simulations up to 20 ps by heating the cluster from 200 K with an increment of 100 K. Similar studies have been carried out to examine thermal effects on the coexistence of two-dimensional and 3D structures of Au_n⁻ ($n=11-14$) clusters by Koskinen *et al.*¹⁹ The geometry resulting after each molecular dynamics simulation was reoptimized at 0 K. We then started with the *T_d* hollow cage structure of neutral Au₁₆ structure and performed molecular dynamics simulation starting at a temperature as high as 300 K for up to 20 ps. The structure remained a *T_d* hollow cage, although with minor distortion. We also studied the effect of temperature on the *T_d* hollow cage geometry of Au₁₆⁻ by carrying out molecular dynamics simulations. We started with the ground state *T_d* hollow cage structure. The resulting Au₁₆⁻ geometry, after 20 ps of simulations, remained as a slightly distorted *T_d* hollow cage structure at temperatures as high as 300 K. Note that this structure is nearly identical with that obtained after the 20 ps molecular dynamics simulation for the *T_d* hollow cage structure of neu-

tral Au₁₆ cluster. Thus, even heating up to 300 K no significant differences between AEA and VDE can be noticed. Thus, if the Au₁₆⁻ cluster was “born” as an anion, i.e., the geometry relaxed to its ground state during the attachment of the electron, it will remain as a hollow cage even after the electron is detached. This would happen if a potential barrier could not be overcome to reach the ground state geometry of the neutral. Thus, near equality between the AEA and VDE does *not* necessarily imply that the neutral cluster has the same ground state structure as the anion. These results clearly demonstrate that thermodynamics rules: Au₁₆⁻ cluster relaxes into ground state T_d hollow cage structure as it forms and is protected by an energy barrier to crossover to the neutral T_d compact structure once the electron is photodetached at low experimental temperatures. The computation of the magnitude of the energy barrier is difficult as one does not know the trajectory the cluster will take to relax.

We have also studied another possibility. What if Au₁₆ cluster was born neutral: Would it assume the cage structure once an electron is attached? To see this, we carried out first principles constant energy molecular dynamics simulations by adding an electron to the neutral ground state T_d compact structure. Starting with the initial T_d compact geometry, we relaxed the structure at 0 K after attaching an electron. The resulting geometry did not automatically assume the T_d hollow cage structure. We also carried out molecular dynamics simulations starting at a series of temperatures with T_d compact structure for both the neutral state and the anionic state. Both the neutral and the anion remain as the T_d compact structure after 20 ps molecular dynamics simulations up to a temperature of 600 K.

These studies clearly demonstrate that Au₁₆⁻ assumes a T_d hollow cage structure as it forms and does not make a transition to the T_d compact neutral geometry at low temperatures after an electron is removed. In this case, the experimentally measured AEA should correspond to the difference between the energy of the T_d hollow cage structure for Au₁₆⁻ anionic cluster and that of the T_d cage structure for Au₁₆ neutral cluster. The AEA calculated by using the PBE functional by assuming the T_d hollow cage structure for the neutral cluster is 3.89 eV which is very close to the experimental value of 3.99 ± 0.03 eV. However, if the experimental temperature is high enough to drive the structural transition from the T_d hollow cage structure to the T_d compact structure for neutral Au₁₆ cluster, the calculated AEA would be 3.36 eV. It will be very interesting if experiments can be repeated at higher temperatures to verify this prediction.

IV. CONCLUSIONS

An understanding of structure-property relationships of clusters and nanostructures is important in exploiting the novel properties of these systems. Unfortunately, obtaining information on cluster geometries based *solely* on current experimental techniques is difficult and theoretical modeling plays a crucial role in identifying possible structures. Comparison of calculated properties such as vertical detachment energies, adiabatic electron affinity, and the first several peaks of the photoelectron spectra with experiment may not

always be enough to identify the preferred structure of the anionic cluster, particularly when two nearly degenerate isomers exist. Electron diffraction experiments where one compares the entire diffraction pattern of a number of low lying isomers with experiment provides a complimentary and sometimes conclusive evidence for the observed structure of a charged cluster. Neither the PES nor the TIED experiment can provide direct evidence for the geometry of the neutral cluster. Inferring ground state geometry of a neutral cluster from the PES experiment may not be valid if the anion and neutral clusters have different ground state geometries and an energy barrier prohibits their transition from one geometry to another once the electron is removed. Thus, one cannot claim universally that the PES provides information on the neutral cluster. Similar conclusions were also made by Jellinek and co-workers.⁶¹ In addition, there are difficulties associated with using occupied energy levels calculated from DFT to compare with PES data.^{9,61,62} Experiments involving other techniques such as infrared absorption spectroscopy may be needed to identify the structure of neutral clusters. While the hollow cage is a possible structure for Au₁₆⁻ anionic cluster, the preferred structure of neutral Au₁₆ cluster is calculated to be a compact structure with T_d symmetry. Using molecular dynamics simulation we have shown that Au₁₆⁻, once formed in the hollow cage structure cannot return to the above compact structure when the electron is photodetached. Experiments performed at higher temperature may permit the structural transition from the cage anion geometry to compact neutral geometry. This can be established from the broadening of the PES as well as large difference between the VDE and adiabatic electron affinity.

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