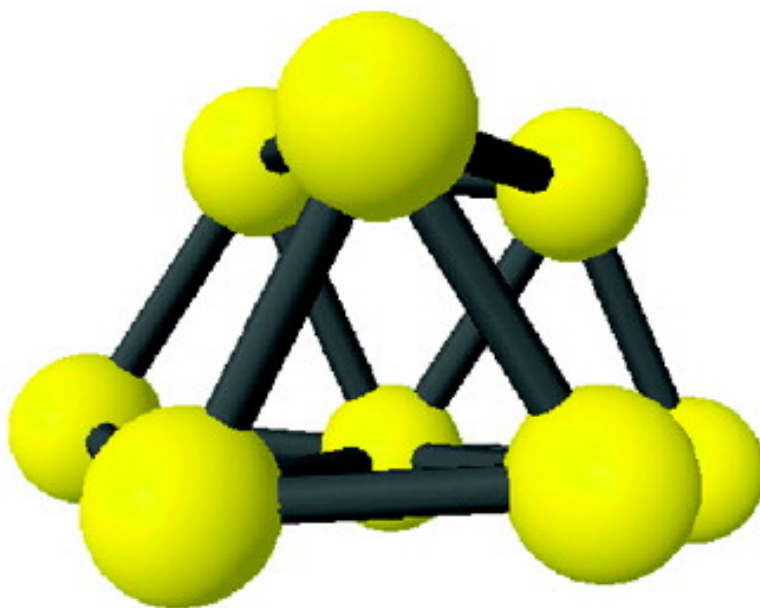Article

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Where Does the Planar-to-Nonplanar Turnover Occur in Small Gold Clusters?

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Abstract: Several levels of theory, including both Gaussian-based and plane wave density functional theory
(DFT), second-order perturbation theory (MP2), and coupled cluster methods (CCSD(T)), are employed to
study Au_6 and Au_8 clusters. All methods predict that the lowest energy isomer of Au_6 is planar. For Au_8,
both DFT methods predict that the two lowest isomers are planar. In contrast, both MP2 and CCSD(T)
predict the lowest Au_8 isomers to be nonplanar.

I. Introduction

Since the discovery that small (2 nm ≤ diameter ≤ 4 nm)
gold clusters Au_n can selectively catalyze reactions, such as the
epoxidation of propene,[1] there has been a flurry of interest from
both experimentalists and theorists in developing an understand-
ing of the origin of this catalytic activity. It appears that several
factors play a role in this activity, including the presence of a
metal oxide (e.g., TiO_2) support[2] and the presence of molecular
hydrogen.[2] We have previously explored both bare Au_n clusters[3]
and the interactions of these clusters with both molecular
oxygen[4,5] and molecular hydrogen[6] to explore these first two
factors. It has also been proposed[7] that surface roughening plays
an important role in the catalytic activity, since nonplanarity
(e.g., corners) in Au_n clusters localizes the electron density and
promotes reactivity.

Given the apparent important role of surface roughening in
determining the catalytic activity of gold clusters, it is important
to determine the value of *n* at which nonplanar structures begin
to dominate as the lowest energy isomers. There have been a
number of papers dedicated to the structure of both neutral and
ionic gold clusters over the past decade or so,[8−28] but there
appears to be little consensus regarding the "turnover point"
from clusters in which planar isomers are lowest in energy to
those in which nonplanar isomers dominate. There now does
seem to be agreement that the lowest energy structure of Au_6
is planar. In early papers, Balasubramanian and Liao proposed,
based on "restricted" multireference CI calculations, that the
Au_6 global minimum is a nonplanar pentagonal bipyramid.[8,9]
Michaelian, Rendon, and Garzòn,[12] based on an *n*-body Gupta
potential predicted that the lowest energy Au_6 isomer is a

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nonplanar square bipyramid. On the other hand, Bravo-Perez, Garzòn, and Novarro[13,14] used second-order perturbation theory (MP2)[29] with a relativistic effective core potential (RECP) and concluded that the lowest energy isomer of Au_6 has a planar D_{3h} geometry, with the lowest energy nonplanar isomer (C_{3v} pentagonal pyramid) 0.47 eV higher in energy. These authors also speculated that the transition from planar to nonplanar occurs between $n = 6$ and $n = 7$ and that nonadditive effects play an important role in favoring planarity. On the other hand, Wilson and Johnston, using a Murrell−Mottram model potential including 2- and 3-body terms, predict the Au_6 global minimum to be octahedral.[15]

Häkkinen and Landman[16] used the generalized gradient approximation (GGA) density functional theory (DFT) approximation with the PBE functional and molecular dynamics simulations to probe the potential energy surfaces of small gold clusters. These authors predicted a planar capped W structure for Au_6. Au_7 was predicted to be planar as well. Furche et al.[18] studied small Au_n^- anions using the BP86 functional and molecular dynamics and predicted a planar structure for both $n = 6$ and $n = 8$. These same authors examined the corresponding cations and found Au_6^+ to be planar and Au_8^+ to be nonplanar.[22] Wang, Wang, and Zhao[23] used DFT/LDA with an RECP basis (with 11 explicit valence electrons on each Au atom) to predict that Au_6^- and Au_8^- have planar D_{3h} and D_{4h} structures.

There have been only a few theoretical studies of neutral Au_8. Wilson and Johnston[15] used the Murrell−Mottram model potential to predict that the lowest energy isomer is a D_{2d} dodecahedron, while Hakkinen and Landman[16] used the GGA DFT method with an RECP to predict a T_d capped tetrahedron. Wang, Wang, and Zhao[23] used a different functional with the LDA/DFT/RECP approach to predict Au_8 to be a distorted bicapped octahedron. Most recently, Xiao and Wang used a plane wave DFT basis set and the PW91 functional for Au_{14} and Au_{20} to predict by interpolation that the crossover from planar to nonplanar gold clusters occurs between 14 and 15 gold atoms.[30]

One can conclude, based on the foregoing brief historical summary, that there appears to be a consensus that the Au_6 global minimum is planar, although most of the previous calculations were performed at a fairly low level of theory and the actual structure has not obviously been resolved. The nature of the Au_8 global minimum structure remains unresolved.

The present work examines the global and local minimum structures for closed shell singlet states of Au_6 and Au_8 using several levels of theory that include DFT, MP2, and the coupled cluster method[31] with singles, doubles, and noniterative perturbative triples (CCSD(T)).[32] The latter is generally considered to be the state of the art in electronic structure theory calculations. The following section summarizes the methods used for the calculations. This is followed in section III by a presentation of the results and discussion of them. Conclusions are drawn in section IV.

II. Computational Approach

Two sets of calculations were carried out, one using Gaussian basis sets and the other using plane waves. In the former, the SBKJC effective core potential (ECP),[33] augmented in the valence basis set by a set of

f functions (exponent $= 0.89$) was used for geometry optimizations and single-point coupled cluster calculations. To probe basis set effects on the predicted relative energies, a much larger basis set, consisting of the completely uncontracted SBKJC ECP valence basis, augmented by three sets of f functions (exponents $= 2.0, 0.84, 0.31$) and two sets of g functions (exponents $= 1.90, 0.69$), was used. Using the smaller basis set, geometries were fully optimized, employing analytic gradients, with both DFT methods using the B3LYP functional[34] and MP2.[29] The initial structures correspond to some of the structures optimized with the plane wave PW91 method (see below). For Au_8, only those structures located within a 10 kcal/mol window relative to the lowest energy structure have been considered. In each case, the nature of the stationary point was determined by calculating and diagonalizing the matrix of energy second derivatives (Hessian): A minimum (first-order saddle point) is characterized by zero (one) imaginary frequencies. Single-point calculations at the MP2 geometries were performed using the standard CCSD(T) approach.[32] In addition to the foregoing calculations with the smaller basis set, single-point MP2 calculations were also performed using the larger basis set. CCSD(T) calculations for Au_8 with the larger basis sets are currently beyond the available computational resources. All of the reported MP2 and CCSD(T) calculations were performed using the GAMESS (general atomic and molecular electronic structure system)[35] suite of programs, enhanced by the recently implemented coupled-cluster options.[36,37]

Periodic Kohn−Sham density functional theory calculations have been performed with the Vienna ab initio simulation package (VASP) program (version 4.4.5).[38] The potential energy surfaces of the closed shell singlet states of Au_6 and Au_8 were initially sampled with the combination of the Perdew and Wang 1991 (PW91)[39] functional and an ultrasoft pseudopotential of 11 "valence" electrons.[40] Relativistic effects were partially taken into account through the use of a relativistic scalar pseudopotential. The Brillouin zone has been sampled at the Γ-point only. The energy cutoff for the plane-waves expansion was 180 eV, the default for the VASP Au soft pseudopotential. This value is usually set to obtain an error that is less than 10 meV for the bulk cohesive energy. Tests performed with the PAW (projector augmented wave) pseudopotential, for which a larger cutoff (230 eV) is used, produce no major differences in the predictions presented here. Dipole and quadrupole corrections to the energy were taken into account (to avoid interaction between the cluster and its periodic replicas) by using a modified version of the method proposed by Makov and Payne.[41] A

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Table 1. Relative Energies in kcal/mol for Au_6 Isomers[a]

	S1	S2	S3
UCSB PW91	0.0	18.6	10.5
B3LYP	0.0	19.8	*a*
MP2	0.0	10.1	10.3
CCSD(T)	0.0	15.0	12.4

a Optimizes to S1.

Figure 1. Au_6 isomers.

correction to the forces similar to the Harris–Foulkes correction were included. The convergence criterion was 10^{-4} eV for the self-consistent electronic minimization and for the change of the total energy between two consecutive ionic steps. Fractional occupancies of the bands were allowed at the beginning of a geometry optimization, using a window of 0.05 eV and the Methfessel–Paxton (first-order) method,[42] but all the equilibrium structures were converged to integer occupation numbers.

It is very important to systematically sample the configuration space, especially as the number of atoms in the cluster increases. More than 50 starting structures have been fully optimized for Au_6 and Au_8 without symmetry constraints to gain a good sampling of the potential energy surfaces. All the starting structures were optimized in a 15 and 16 Å^3 supercell for Au_6 and Au_8, respectively. The clusters were aligned along the diagonal of the box in order to maximize the separation between the clusters and their replica. This ensures a separation larger than 9.5 Å between the cluster and its replicas in all the starting structures studied.

The main focus of the present work is on the lowest energy singlet states of Au_6 and Au_8. It is important to make certain the singlets are indeed the ground states. This was accomplished by performing spin restricted open shell second-order perturbation theory energy calculations at each of the MP2 singlet geometries. In each case, the triplet state is at least 1 eV (23 kcal/mol) higher in energy than the corresponding singlet. Further, for both Au_6 and Au_8 the lowest energy triplet isomer is higher in energy than the highest energy singlet isomer. These observations justify the focus on singlet states. Spot checks on the lowest energy Au_8 isomers with MCSCF wave functions also suggest that these states are essentially closed shell with little configurational mixing.

III. Results and Discussion

The key geometric parameters for the three isomers (local minima) found for Au_6 are summarized in Table 1, and the structures and their relative energies are given in Figure 1. All of the methods agree that the lowest energy isomer for Au_6 is the planar S1 structure. All methods except B3LYP and MP2 predict the second lowest isomer to be S3, which is also planar. B3LYP optimization of S3 results in a rearrangement to S1. The only nonplanar isomer found at the MP2 level of theory is the pentagonal pyramid, S2. This structure is predicted by the two density functional theory methods and by CCSD(T) to be the highest of the three isomers, by ∼15−20 kcal/mol. According to MP2, S2 and S3 are essentially isoenergetic. Two other structures were identified by the plane wave PW91 geometry

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Table 2. Relative Energies in kcal/mol for Au_8 Isomers

	S1	S2	S3	S4	S5	S6	S7	S8	S9
UCSB PW91	0.0	5.5	7.0	7.4	7.4	9.6	9.6	9.9	10.4
B3LYP	0.0	10.1	15.3	15.4	12.2	18.9	12.4	16.4	14.6
MP2	30.8	32.4	5.7	7.4	25.4	0.0	21.8	24.4	41.7
MP2 (large)	26.0	26.6	5.9	5.7	22.9	0.0	20.1	20.9	36.3
CCSD (T)	4.7	11.7	0.0	2.2	8.5	1.5	9.4	10.3	19.8
TRIPLES	0.0	−4.0	−8.0	−8.6	−4.5	−10.7	−6.3	−5.5	−3.4

optimizations, for which Hessian calculations cannot be performed. Both B3LYP and MP2 find these structures to be saddle points (first or second order), so they are not considered here.

The salient geometric parameters for the isomers found for Au_8 are summarized in Table 2, and the structures and their relative energies are illustrated in Figure 2. All of the methods employed here predict similar structures. However, in contrast to Au_6, the four methods used in this work display marked differences for the relative energies of the Au_8 isomers. Even though the two DFT methods differ in the type of basis set, type of core potential, and type of functional, they both predict that the two lowest energy species are the planar S1 and S2 isomers. The two DFT methods differ quantitatively, since PW-PW91 and B3LYP find S1 to be 5 and 10 kcal/mol, respectively, higher than S2. Similarly, PW-PW91 finds several nonplanar isomers that are only 2−5 kcal/mol higher in energy than S2, whereas the energy spread predicted by B3LYP is much larger. Nonetheless, the two methods agree that the lowest energy isomers are planar.

In contrast, the two ab initio methods, MP2 and CCSD(T), predict the lowest energy isomers to be the nonplanar species S3 and S6. These two methods also differ quantitatively, as the predicted MP2 energy spread is much larger than that predicted by CCSD(T). This spread in relative MP2 energies contracts somewhat when the larger basis set is used, but the changes are all small. CCSD(T) predicts S6 to be slightly higher in energy than S3, while the order of these two isomers is reversed by MP2, with S3 being higher by ∼6 kcal/mol. MP2 finds all six nonplanar isomers to be lower in energy than any of the planar ones (S1, S2, S9), while CCSD(T) predicts the planar S1 structure to be the fourth isomer in energy order and the other two planar structures, S2 and S9, to be higher in energy than all of the nonplanar species. Still, these two methods predict that the lowest energy Au_8 isomers are nonplanar. One can describe S3 as a capped tetrahedron and S6 as a bicapped octahedron, similar to the two nonplanar species predicted by two earlier DFT studies.

Although all structures in Figure 2 are predicted to be local minima by B3LYP, MP2 finds one very small imaginary frequency for each of the S1, S5, S7, and S8 structures of 3, 11, 12, and 20 cm^{-1}, respectively. These imaginary frequencies are so small that either they could result from numerical noise or the structures could be first-order saddle points. In the latter case, the imaginary mode in S1 corresponds to an out of plane motion that would clearly lead to one of the nonplanar structures. So, this would not alter any conclusions drawn here. The other three structures are much higher in energy and therefore not central to the main issue addressed here.

To understand the origin of the relative stability of the nonplanar isomers, Table 2 also presents the contribution of the connected triples excitations for each isomer, relative to the planar isomer S1, as estimated by the CCSD(T) approach.
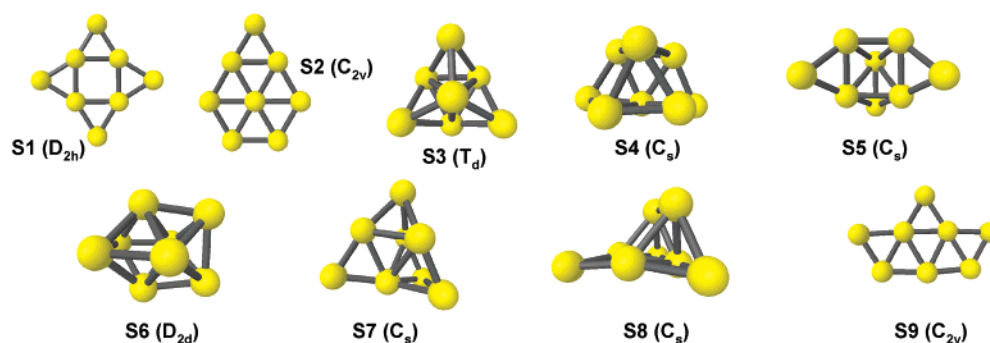
Figure 2. Au$_8$ isomers.

Clearly, the triples make an essential contribution of this stabilization, since their most favored isomers are S6, S4, and S3 in that order.

IV. Conclusions

The primary conclusion to be drawn from the present work is that although both density functional methods, one based on Gaussian basis sets and one based on plane waves, predict that the crossover from planarity to nonplanarity occurs at clusters larger than Au$_8$, both correlated ab initio methods predict that this crossover occurs between Au$_6$ and Au$_8$. It is likely that the fundamental difference between the DFT and correlated ab initio results is that the DFT calculations cannot account for long-range interactions such as dispersion. It is also clear that the inclusion of triple excitations is critical for the CCSD(T) predictions of nonplanarity.

Because this issue of crossover from planar to nonplanar structures may be important in the determination of catalytic activity, it is necessary to consider the remaining limitations in the ab initio calculations. The most reliable method employed here is certainly CCSD(T). Due to the high computational demands of this method (the N^7 scaling with the system size), it is not currently possible to optimize the geometries of the Au$_8$ species at this level of theory. So, the impact such CCSD-(T) geometry optimizations may have on the predicted relative energies is unknown. Additionally, basis set effects (always a potential factor) cannot be assessed for similar reasons. Finally, the catalytic activity of small gold clusters is observed when such clusters sit on metal oxide surfaces, and the impact of the surface on the structure of the clusters is not yet known.

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