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Isomers of Au₈

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Isomers of Au₈

Abstract

Using newly developed correlation consistent basis sets for gold, the relative energies for the neutral Au₈geometric isomers have been re-evaluated and the vertical ionization potentials calculated. The results using the correlation consistent basis sets show that second-order Moller-Plesset perturbation theory calculations strongly favor nonplanar Au₈structures for all basis sets that were employed. However, the general trend at the coupled cluster singles and doubles with perturbative triples level of theory is to increasingly favor planar structures as the basis set is improved. The effects of basis set and the effects of core-valence correlation are discussed.

Keywords

Gold, Basis sets, Ionization potentials, Density functional theory, Electron correlation calculations

Disciplines

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Comments

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Isomers of Au 8

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Isomers of Au₈

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Using newly developed correlation consistent basis sets for gold, the relative energies for the neutral Au₈ geometric isomers have been re-evaluated and the vertical ionization potentials calculated. The results using the correlation consistent basis sets show that second-order Moller-Plesset perturbation theory calculations strongly favor nonplanar Au₈ structures for all basis sets that were employed. However, the general trend at the coupled cluster singles and doubles with perturbative triples level of theory is to increasingly favor planar structures as the basis set is improved. The effects of basis set and the effects of core-valence correlation are discussed. © 2007 American Institute of Physics. [DOI: 10.1063/1.2743005]

INTRODUCTION

There has been a booming interest in gold and gold clusters since the discovery of Haruta and *et al.*¹ that metal oxide supported gold nanoparticles are active catalysts for a variety of oxidation reactions. One important feature of small gold clusters is the structures of these species. One reason that the structural details are of interest is that it has been proposed² that surface roughening can serve to localize the electron density and therefore increase the reactivity of the gold system. In terms of small to moderate size clusters, “roughening” can be interpreted as nonplanarity. Therefore, the cluster size, i.e., n in Au _{n} , at which the clusters first begin to be predominantly nonplanar is important.

There have therefore been numerous structural studies^{3–24} using a variety of theoretical methods to examine the relative stability of Au _{n} isomers, with particular attention given to the “crossover point” in which nonplanar isomers become the energetically preferred geometry. One of the most intriguing and perhaps unexpected results of these structural studies of Au _{n} isomers is the prediction by most calculations that planar structures are lower in energy than nonplanar structures for clusters with n much larger than 6. This is found mainly for the neutral^{11–18,20,24} and anionic^{14,22,23} Au _{n} species.

In a study of neutral Au _{n} for $n=3–6$, Bravo-Perez *et al.*^{3,4} used second-order Moller-Plesset perturbation theory (MP2) and a valence-only 11-electron ($5d^{10}6s^1$) Hay-Wadt basis set and relativistic effective core potential²⁵ (RECP) to predict that the global minima for clusters up to Au₆ are planar. Based on nonadditive effects, these authors concluded⁴ that the planar to nonplanar turnover point for the MP2 method occurs between $n=6$ and $n=7$. This conclusion is consistent with the study by Olson *et al.*⁵ who employed MP2 calculations using the 19-electron ($5s^25p^65d^{10}6s^1$) SBKJC RECP and associated basis set,²⁶ augmented with one set of f functions (exponent=0.89),²⁷ to predict that whereas the Au₆ global minimum is planar, the nonplanar D_{2d} dodecahedron Au₈ structure is favored over the D_{4h} and C_{2v} planar structures by more than 20 kcal/mol. Other nonplanar structures, including one with T_d symmetry, are also

predicted to be lower in energy than the planar isomers. Olson *et al.* also found⁵ that single point energies at the MP2 geometries, calculated using the coupled cluster singles and doubles with perturbative triples [CCSD(T)] method and the same basis set, favor the nonplanar T_d and D_{2d} structures. However, the range of relative energies among the planar and nonplanar structures is significantly smaller at the CCSD(T) than at the MP2 level of theory. Several other studies^{6–10} have predicted nonplanar structures as the lowest energy isomer for $n \leq 8$. Using a cubic three-body Murrell-Mottram potential parameterized by Cox *et al.*²⁸ to fit experimental properties such as lattice and vacancy formation energies, lattice spacing, elastic constants, and phonon frequencies, Wilson and Johnson⁶ predicted nonplanar gold clusters starting at $n=4$ based on molecular dynamics/simulated annealing techniques. Michaelian *et al.*⁷ used a genetic algorithm for global optimizations and the n -body Gupta potential to predict nonplanar structures as the lowest energy minima for Au₆ and Au₇. Balasubramanian and Liao⁸ proposed, based on “restricted” multireference configuration interaction calculations, that the Au₆ global minimum is a nonplanar pentagonal bipyramid; however, no planar structures were examined in that study. More recently, density functional theory (DFT),^{15,18} MP2,^{3–5,19} and CCSD(T) (Refs. 5 and 19) studies have generally concluded that neutral Au _{n} up to $n=6$ are planar; however, depending on the methods used, there remains a wide range of predicted crossover points.

Wang *et al.*⁹ have reported a DFT study using the local density approximation (LDA) and an exchange-correlation potential parameterized by Perdew and Wang²⁹ with a RECP and a double numerical basis set including polarization functions only as large as d functions. This study predicted the first nonplanar (pentagonal bipyramidal) structure to occur at $n=7$. Hakkinen and Landman¹⁰ used a DFT based molecular dynamics approach using the Perdew-Burke-Ernzerhof form³⁰ of the generalized gradient approximation (GGA) for the exchange-correlation potential to predict planar structures up to $n=7$, and non-planar structures for $n \geq 8$.

However, other DFT studies,^{11–19,24} all using RECPs, have shown the opposite trend in which a planar minimum is

predicted for Au₈. Remacle and Kryachko¹¹ have used DFT with the B3LYP hybrid exchange-correlation functional³¹ to predict a planar global minimum for Au₈. These authors also suggest that the planar to nonplanar crossover begins at $n=9$, where two-dimensional (2D) and three-dimensional (3D) structures are very similar in energy. Bonacic-Koutecky *et al.*¹⁵ predicted planar lowest energy minima for Au_{*n*} clusters with $n \leq 10$. These researchers used both a 1-electron RECP basis set with the BLYP functional³² and a 19-electron RECP basis set with the BP86 functional.³³ Clusters larger than $n=10$ were not examined by Bonacic-Koutecky *et al.* Walker¹² used a series of basis sets including the Stuttgart 1997,³⁴ LANL2DZ,^{25,35} and CRENBL (Ref. 36) basis sets with a variety of exchange-correlation functionals [PW91PW91-GGA,³⁷ B3LYP-hybrid,³¹ and SVWN5-LDA (Ref. 38)] to predict the crossover point for neutral Au_{*n*} to occur at $n=11$. Fernandez *et al.*^{13,14} also predict the crossover point to occur between $n=10$ and $n=11$ using GGA DFT methods. Plane wave DFT studies by Xiao and Wang¹⁷ using PW91 (Ref. 39) have predicted the crossover point in Au_{*n*} clusters to occur between $n=14$ and $n=15$. This study was later updated by Xiao *et al.*¹⁶ to predict the crossover to occur between $n=13$ and $n=14$, with Au₁₃ predicted to be the last cluster for which the global minimum is planar. Most recently, an all-electron DFT/GGA study by Wei and Dong²⁴ concluded that there is a wide coexistence range for gold clusters between $n=8$ and $n=15$, with energy differences between planar and nonplanar structures predicted to be less than 0.15 eV. These authors also found that the vibrationally active radial breathing mode is very sensitive to the planar to nonplanar transition. Wei and Dong²⁴ predicted Au₁₃ to be the first cluster that has a nonplanar global minimum structure.

In a recent study comparing Au₈ and Cu₈, Gronbeck and Broqvist¹⁸ have shown that the explicit treatment of semicore electrons ($5s^25p^6$) can have a significant impact on the relative energies of geometric isomers. They determined Au₈ to be planar, noting strong relativistic effects.⁴⁰ Han¹⁹ recently recalculated the MP2 and CCSD(T) energies from the work of Olson *et al.*⁵ to include the effects of core-valence correlation, i.e., the semicore electrons were correlated. The results of the latter two studies were very similar, in that:

- (1) the single point energies calculated using MP2 and CCSD(T) with the augmented SBKJC basis sets all predict 3D minimum energy structures;
- (2) increasing the size of the basis set used for MP2 stabilizes the 2D isomers with respect to the lowest energy 3D isomer, both with and without core-valence contributions;
- (3) there are significant differences in the relative energies of 2D structures relative to 3D structures for MP2 vs CCSD(T).

While the trends and the calculated values from the studies by Han and Olson *et al.* are very similar, the conclusions drawn based on their calculated results are quite different. Olson *et al.*⁵ acknowledged deficiencies in the basis set; however, computational limitations at that time prevented CCSD(T) calculations with larger basis sets. Han increased

the number of electrons correlated in the MP2 and CCSD(T) calculations by including core-valence correlation; however, no improvements to the one-electron basis sets were made. The additive formula,

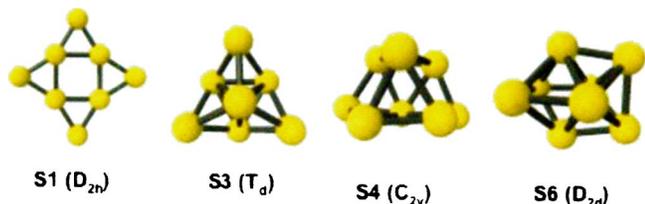
$$\text{CCSD(T)/large} = \text{CCSD(T)/small} + [\text{MP2/large} - \text{MP2/small}], \quad (1)$$

was used to estimate the large basis set CCSD(T) energy from the difference in MP2 correlation energy between large [SBKJC(3*f*,2*g*)] and small [SBKJC(1*f*)] basis sets. Using Eq. (1), Han concluded that the lowest energy isomer of neutral Au₈ is the planar D_{4h} structure. However, although schemes like that embodied in Eq. (1) are commonly used in methods such as G3 (Ref. 41) and ONIOM,⁴² they rely on modest changes in relative energies, whereas for the Au₈ system, the basis set correction in Eq. (1) stabilizes the planar structures by as much as 14 kcal/mol relative to the nonplanar structures. In view of the large magnitude of this correction, it is unclear how reliable corrections due to the improvements in the basis set measured for MP2 will be for estimating the corresponding improvement for CCSD(T). In the three years since the paper by Olson *et al.*⁵ appeared, improvements in CCSD(T) algorithms have enabled the use of larger basis sets for CCSD(T) calculations applied to this problem. Therefore, the present work will examine the impact of systematically improving the basis set on the predictions of structures and relative energies for Au_{*n*} clusters. This will in turn facilitate an analysis of the validity of additive schemes such as that embodied in Eq. (1).

The goal of this work is to systematically study the effects of the basis set on MP2 and CCSD(T) calculations for Au₈ geometric isomers using the correlation consistent basis sets recently developed by Peterson and Puzzarini (PP),⁴³ combined with the RECP developed by Figgen *et al.*⁴⁴ Core-valence effects as a function of structure and as a function of basis set are also studied. In addition, the vertical ionization potential for Au₈ isomers are calculated and examined with regard to basis set and core-valence effects.

COMPUTATIONAL DETAILS

Ab initio calculations on Au₈ and Au₈⁺ isomers were performed using several Gaussian basis sets to calculate the relative stabilities and vertical ionization potentials of Au₈ isomers. The one-electron Gaussian-type basis sets for Au used small-core RECPs to describe the 60 core electrons, the remaining 19 electrons, 8 semicore ($5s^25p^6$), and 11 valence ($5d^{10}6s^1$) electrons were explicitly treated in the variational space of the reference Hartree-Fock wave function.⁴⁵ First, the standard SBKJC basis set and ECP (Ref. 26) for gold augmented with one set of *f* functions (exponent=0.89) [SBKJC(1*f*)] (Ref. 27) were used. Second, a fully uncontracted version of the SBKJC valence and semicore functions augmented with three sets of *f* (exponents=2.0,0.84,0.31) and two sets of *g* functions (exponents=1.90,0.69) [uSBKJC(3*f*,2*g*)] (Ref. 27) were used. Next, in order to systematically improve the basis set, the recently published correlation consistent basis sets, cc-pVDZ-PP and cc-pVTZ-PP,⁴³ developed by Peterson and Puzzarini were

FIG. 1. Au₈ structures and symmetries.

employed. The ECP for the correlation consistent basis sets was developed by Figgen *et al.*⁴⁴ Post-Hartree-Fock methods, including MP2 (Ref. 46) and CCSD(T) (Refs. 47 and 48) were used to recover electron correlation energy from the valence molecular orbitals and, in some cases, the $5s^25p^6$ semicore orbitals. The partially spin-restricted⁴⁹ [RCCSD(T)] open-shell variant of the closed shell CCSD(T) method was used to calculate single point energies for open-shell Au₈⁺ isomers. Electron correlation energy from the excitations of the semicore orbitals ($5s^25p^6$ orbitals) will be referred to as core-valence (CV) contributions. The calculations were performed using the GAMESS (Ref. 50) and MOLPRO (Ref. 51) electronic structure packages. The focus here is on the four lowest energy Au₈ isomers (shown in Fig. 1) predicted in the previous study⁵ by CCSD(T) calculations with the smaller basis set. The geometries were optimized at the MP2 level of theory with the SBKJC(1f) basis set, without CV correlation contributions. All coupled cluster energies in this study were calculated at these MP2 optimized geometries. Since the optimized structure S4 has nearly C_{2v} symmetry, the geometry used in the CCSD(T) calculations on this isomer was symmetrized from C_s to C_{2v} . It was confirmed that this symmetrization resulted in no significant change in energy for the smallest basis set. Valence-only electron correlation energies and CV correlation contributions were calculated for MP2, CCSD, and CCSD(T) using SBKJC(1f), cc-pVDZ-PP, and cc-pVTZ-PP. CV contributions to the open-shell RCCSD(T)/cc-pVTZ-PP energy for the cations could not be calculated due to computational limitations; however, CV contributions to the RCCSD(T)/cc-pVDZ-PP energies were calculated.

DISCUSSION

The important low energy neutral Au₈ structures (S1, S3, S4, and S6) reported by Olson *et al.*⁵ were reevaluated using the correlation consistent basis sets. The relative energies of the four isomers in Fig. 1, with respect to the lowest energy minimum structure for the MP2, CCSD and CCSD(T) methods, along with the relative contributions from the perturbative triples correction and the relative CV correlation effects for neutral Au₈ are given in Table I. The results for the three levels of theory are discussed in turn in the following paragraphs.

MP2. The S6 structure is the lowest energy MP2 neutral isomer, regardless of basis set or contributions from core-valence correlation (Table I). MP2 strongly favors the nonplanar S6 structure over the planar S1 structure by more than 20 kcal/mol for all cases. The relative energy of the planar S1 structure with respect to the S6 structure decreases by

TABLE I. Relative energies (kcal/mol) for neutral Au₈ isomers. The relative triples contributions to the CCSD(T) method is listed as (T).

Method	S1	S3	S4	S6
MP2/SBKJC(1f)	30.8	5.7	7.4	0.0
MP2/SBKJC(1f)+CV	36.9	6.1	7.7	0.0
MP2/SBKJC(3f, 2g)	26.0	5.9	5.7	0.0
MP2/SBKJC(3f, 2g)+CV	24.3	5.9	5.1	0.0
MP2/cc-pVDZ-PP	22.3	5.4	6.5	0.0
MP2/cc-pVDZ-PP+CV	25.5	5.6	6.3	0.0
MP2/cc-pVTZ-PP	21.8	6.4	5.5	0.0
MP2/cc-pVTZ-PP+CV	23.3	6.8	5.5	0.0
CCSD/SBKJC(1f)	0.0	3.3	6.1	7.5
CCSD/SBKJC(1f)+CV	1.1	0.0	2.6	4.0
CCSD/cc-pVDZ-PP	0.0	11.6	13.8	16.4
CCSD/cc-pVDZ-PP+CV	0.0	9.1	10.9	13.7
CCSD/cc-pVTZ-PP	0.0	15.6	16.4	20.3
CCSD/cc-pVTZ-PP+CV	0.0	14.9	15.3	19.2
CCSD(T)/SBKJC(1f)	4.7	0.0	2.2	1.5
CCSD(T)/SBKJC(1f)+CV	10.0	0.0	2.1	1.1
CCSD(T)cc-pVDZ-PP	0.0	3.6	5.2	5.6
CCSD(T)/cc-pVDZ-PP+CV	0.0	0.1	1.3	1.8
CCSD(T)/cc-pVTZ-PP	0.0	7.5	7.5	9.1
CCSD(T)/cc-pVTZ-PP+CV	0.0	6.0	5.7	7.2
(T)/SBKJC(1f)	0.0	-8.0	-8.5	-10.8
(T)/SBKJC(1f)+CV	0.0	-11.1	-11.6	-14.0
(T)cc-pVDZ-PP	0.0	-8.0	-8.6	-10.8
(T)/cc-pVDZ-PP+CV	0.0	-9.0	-9.5	-11.9
(T)cc-pVTZ-PP	0.0	-8.1	-8.9	-11.2
(T)/cc-pVTZ-PP+CV	0.0	-8.8	-9.6	-11.9

8.5 kcal/mol (11.4 kcal/mol with CV effects) upon improving the basis set from SBKJC(1f) to cc-pVDZ-PP and an additional 0.6 kcal/mol (2.2 kcal/mol with CV effects) upon improving the basis set from cc-pVDZ-PP to cc-pVTZ-PP. The relative MP2 energies of the S3 and S4 nonplanar structures are 5.1–7.7 kcal/mol higher than S6 over the range of MP2 calculations. CV correlation effects are found to destabilize the planar S1 structure with respect to the nonplanar S6 structure by 6.1, 3.2, and 1.6 kcal/mol as the basis set is increased from SBKJC(1f), to cc-pVDZ-PP, to cc-pVTZ-PP, respectively. However, for the uSBKJC(3f, 2g) basis set, CV correlation has the opposite effect—it lowers the energy of S1 by 1.7 kcal/mol relative to S6.

CCSD. The planar isomer S1 is predicted to be the minimum energy CCSD structure for all calculations, except for CCSD/SBKJC(1f) with CV correlation effects. The CCSD/SBKJC(1f)+CV calculation predicts the S3 structure to be the lowest energy isomer, although the energy difference between the S1 and S3 structures is only 1.1 kcal/mol (Table I). Improving the basis set for the CCSD calculations has a similar effect to that described above for MP2: Upon improving the basis set from SBKJC(1f) to cc-pVDZ-PP, the planar S1 structure is stabilized with respect to the nonplanar structures by 7.7–8.9 kcal/mol (9.4–10.8 kcal/mol with CV correlation effects included). Likewise, the relative energy lowering of S1 is 2.6–4.0 kcal/mol (4.4–5.8 kcal/mol with CV correlation effects included) upon increasing the basis set from cc-pVDZ-PP to cc-pVTZ-PP. The core-valence correlation effects, on the other hand, destabilize S1 (increase its

TABLE II. Estimated large basis set CCSD(T) relative energies (kcal/mol) using Eq. (1). CCSD(T)/uSBKJC(3*f*,2*g*) was estimated using SBKJC(1*f*) as the small basis set and CCSD(T)/cc-pVTZ-PP was estimated using cc-pVDZ-PP as the small basis set.

	S1	S3	S4	S6
CCSD(T)/uSBKJC(3 <i>f</i> ,2 <i>g</i>) est	0.0	0.3	0.6	1.5
CCSD(T)/uSBKJC(3 <i>f</i> ,2 <i>g</i>) (CV) est	0.0	2.4	2.2	3.7
CCSD(T)/cc-pVTZ-PP est	0.0	5.2	4.8	6.1
CCSD(T)/cc-pVTZ-PP (CV) est	0.0	3.4	2.7	3.9
CCSD(T)/cc-pVTZ actual	0.0	7.5	7.5	9.1
CCSD(T)/cc-pVTZ (CV) actual	0.0	6.0	5.7	7.2

relative energy) with respect to the nonplanar isomers by 4.4–4.7 kcal/mol [SBKJC(1*f*)], 2.5–2.9 kcal/mol (cc-pVDZ-PP) and 0.8–1.2 kcal/mol (cc-pVTZ-PP).

CCSD(T). The nonplanar S3 structure was previously reported to be the lowest energy Au₈ isomer at the CCSD(T)/SBKJC(1*f*) level of theory. In contrast, the planar S1 structure is the lowest energy CCSD(T) isomer when the correlation consistent basis sets are employed (Table I). For all basis sets, the perturbative triples correction in the CCSD(T) method preferentially lowers the energy of the nonplanar Au₈ structures, relative to the planar isomers. This may be seen most directly in the Table I entries labeled “(T)/(basis).” When the CV correlation effects are excluded, the triples correction for each isomer is essentially independent of basis set. The preferential energy lowering of the nonplanar structures due to the triples correction is 8.0–8.1 kcal/mol for S3, 8.5–8.9 for S4, and 10.8–11.2 kcal/mol for S6. This suggests that one might be able to reasonably estimate the triples corrections for the larger basis sets, for which the full calculations may be too computationally demanding.

Core-valence contributions to the triples are also found to have a stabilizing (relative energy lowering) effect on nonplanar structures. However, as may be seen in Table I, this effect decreases as the basis set is improved: The energy lowering due to the CV contributions to the triples correction for the nonplanar structures S3, S4, and S6 is 3.1–3.3 kcal/mol [SBKJC(1*f*)], 0.9–1.1 kcal/mol (cc-pVDZ-PP), and 0.7–0.8 kcal/mol (cc-pVTZ-PP).

Basis set+correlation additivity. As noted earlier [see Eq. (1)], one might assume that the effects of basis set improvement and correlation are additive, in order to estimate the CCSD(T)/large basis relative energies. The large basis set CCSD(T) relative energies estimated in this manner (with and without CV contributions) for uSBKJC(3*f*,2*g*) using SBKJC(1*f*) as the small basis set, and for cc-pVTZ-PP using cc-pVDZ-PP as the small basis set are presented in Table II, together with the explicitly computed CCSD(T)/cc-pVTZ-PP values. Although this was not mentioned by Han,¹⁹ the *estimated* CCSD(T)/uSBKJC(3*f*,2*g*) values without CV contributions suggest that S1, S3, and S4 are separated by as little as 0.6 kcal/mol, with the S1 structure only narrowly favored. These estimated values are in poor agreement (6.9–7.6 kcal/mol error) with the actual CCSD(T)/cc-pVTZ-PP values which are considered to be the most reliable calculations for Au₈ in the current study. Including

TABLE III. Relative energies (kcal/mol) and vertical ionization potential (vIP measured in eV) for Au₈⁺ calculations.

Method	S1	S3	S4	S6
Relative energies (kcal/mol)				
RCCSD/cc-pVDZ-PP	5.6	13.4	0.0	31.0
RCCSD/cc-pVDZ-PP+CV	10.3	13.4	0.0	30.3
RCCSD(T)/cc-pVDZ-PP	11.5	11.9	0.0	25.7
RCCSD(T)/cc-pVDZ-PP+CV	17.2	11.8	0.0	24.6
RCCSD/cc-pVTZ-PP	3.6	14.9	0.0	32.0
RCCSD(T)/cc-pVTZ-PP	9.7	13.5	0.0	26.6
Vertical ionization potential (eV)				
vIP(CCSD)/cc-pVDZ-PP	7.90	7.74	7.06	8.30
vIP(CCSD)/cc-pVDZ-PP+CV	8.03	7.77	7.11	8.31
vIP(CCSD(T))/cc-pVDZ-PP	7.96	7.82	7.23	8.33
vIP(CCSD(T))/cc-pVDZ-PP+CV	8.10	7.86	7.29	8.34
vIP(CCSD)/cc-pVTZ-PP	8.02	7.83	7.15	8.37
vIP(CCSD(T))/cc-pVTZ-PP	8.10	7.94	7.35	8.44

core-valence contributions, the estimated CCSD(T)/uSBKJC(3*f*,2*g*) (CV) relative energies differ from the explicitly calculated CCSD(T)/cc-pVTZ-PP (CV) relative energies by 3.5–3.6 kcal/mol. The estimated CCSD(T)/cc-pVTZ-PP relative energies differ from the explicitly calculated values by 2.3–3.0 kcal/mol (2.6–3.3 kcal/mol with CV effects). It is interesting to note, that the core-valence effects on the estimated CCSD(T)/uSBKJC(3*f*,2*g*) relative energies preferentially stabilize the planar structures. This is opposite to the trends observed for both the explicitly calculated correlation consistent basis set relative energies and the estimated cc-pVTZ results. On the other hand, the estimated CV correlation effects for the cc-pVTZ-PP basis set are in good agreement with the explicitly calculated values for this basis set, for example 1.8 vs 1.5 kcal/mol relative stabilization for S3, 2.1 vs 1.9 kcal/mol for S4, and 2.2 vs 1.9 kcal/mol for S6. Overall, the additivity assumption is not very reliable for the SBKJC basis sets. The approach is more reliable for the correlation consistent basis sets, but even here the errors are as large as 3 kcal/mol. The inability of MP2 to accurately estimate the basis set effects for CCSD(T) for Au₈ is likely due to the notably large differences between the two methods for predicting relative energies (as discussed earlier).

Au₈⁺. The vertical ionization potentials for the Au₈ isomers were calculated by taking the energy difference between an Au₈⁺ cation and the corresponding neutral isomer at the optimized MP2 neutral geometry. The relative energies of the RCCSD(T)//MP2/SBKJC(1*f*) structures and the vertical ionization potentials are given in Table III. The Au₈⁺ calculations represent a limited snapshot of the Au₈⁺ potential energy surface on which the S4 structure is found to be the lowest energy cation structure studied. It should be noted that there are other potential lowest energy candidate structures²² for Au₈⁺ that were not studied. The calculations performed in this study were meant to examine the basis set effect on the ionization potential and not to unequivocally determine the minimum energy structure for Au₈⁺ cation. In general, the values of the vertical ionization potential were found to slightly increase (~0.1 eV) as the size of the basis set in-

creased. Similar trends were found when core-valence effects were included. It remains unclear what the effects on the ionization potential will be if the geometries of both the neutral and the cation structures were allowed to relax. As demonstrated above, there are significant differences between the MP2 and CCSD(T) potential energy surfaces. Therefore, to accurately measure the adiabatic ionization potential, the geometries of the structures should be optimized using CCSD or CCSD(T) and at minimum the cc-pVDZ-PP basis set.

CONCLUSIONS

This study illustrates a remarkable difference between the MP2 method and the coupled cluster methods, CCSD and CCSD(T), for predicting the lowest energy structure of Au₈. The tendency of MP2 to overbind strongly favors the nonplanar structures. Increasing the basis set stabilizes the planar structure at both the MP2 and CCSD levels of theory, while there is little basis set effect on the CCSD(T) triples correction. Core-valence effects are predicted to stabilize the nonplanar Au₈ structures relative to the planar structures for all correlation consistent basis sets; however, the effects of CV stabilization on nonplanar structures diminish as the basis set is increased. The CCSD(T)/SBKJ(1f) level of theory predicts S3 to be the minimum energy structure. However, as the basis set is increased to cc-pVDZ-PP and cc-pVTZ-PP, the triples and core-valence contributions that favor the nonplanar structures remain the same or diminish, while the CCSD contributions that favor the planar structure increase. As the basis set is increased, the CCSD(T) cross-over point at which the planar Au₈ structure becomes the global minimum occurs at the cc-pVDZ-PP basis set. Estimates of larger basis set CCSD(T) values based on MP2 basis set effects may be qualitatively correct, but these estimates are quantitatively highly inaccurate. If one wishes to estimate relative Au₈ CCSD(T) energies for larger basis sets (e.g., CCSD(T)/cc-pVTZ-PP), the smallest reliable reference basis set appears to be cc-pVDZ-PP. In any event, MP2 predictions of the relative energies using the correlation consistent basis sets are qualitatively incorrect. This is unfortunate, given the high computational demands of CCSD(T) calculations.

Using the correlation consistent basis sets, it was found that, in general, increasing the size of the basis set and including core-valence correlation both contribute to the stabilization of the neutral structure with respect to the cation; i.e., the value of the vertical ionization potential was found to be slightly (~0.1 eV or less) increased.

Finally, it should be noted that due to differences between the MP2 and the CCSD(T) methods for predicting relative energies of the neutral isomers, it is possible that the optimized MP2 geometries do not represent good candidate structures for single point calculations to describe the CCSD(T) potential energy surface. Relaxation of the neutral and cationic Au₈ cluster geometries by optimizations at the CCSD or the CCSD(T) levels of theory could still have a significant impact on the relative energies and ionization potentials of Au₈ isomers; however, those calculations are impractical at the present time.

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