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Observable Structures of Small Neutral and Anionic Gold Clusters

Han Myoung Lee* and Kwang S. Kim*[a]

Abstract: Since gold clusters have mostly been studied theoretically by using DFT calculations, more accurate studies are of importance. Thus, small neutral and anionic gold clusters (Au_n and Au_n^- , $n=4-7$) were investigated by means of coupled cluster with singles, doubles, and perturbative triple excitations [CCSD(T)] calculations with large basis sets, and some differences between DFT and CCSD(T) results are

discussed. Interesting isomeric structures that have dangling atoms were obtained. Structures having dangling atoms appear to be stable up to $n=4$ for neutral gold clusters and up to $n=7$ for anionic clusters. The relative stabi-

Keywords: ab initio calculations • cluster compounds • gold • isomers • photoelectron spectroscopy

ties and electronic properties of some isomers and major structures are discussed on the basis of the CCSD(T) calculations. This accurate structure prediction of small gold clusters corresponding to experimental photoelectron spectral peaks is valuable in the field of atom-scale materials science including nanocatalysts.

Introduction

Atomic-scale metal clusters are important subject for their possible use as highly effective catalysts and in atom-scale electronic devices.^[1-5] These clusters show intriguing structural arrangements and interesting features for a certain specific cluster size depending on the charge state. In particular, gold clusters are known to be special in showing high ductility, which is quite different from other coinage metals such as silver and copper. The Au atom shows effective sd hybridization with more stabilized 6s orbitals and less stabilized 5d orbitals due to the large relativistic effect.^[6] This relativistic effect is known to play a crucial role in the formation 2D planar structures for small gold clusters in contrast to the 3D structures of silver and copper clusters.

There have been numerous studies on small gold clusters Au_n . Experimental electron affinity (EA) and ionization potential (IP)^[7] of Au_n and the experimental photoelectron spectra (PES)^[8] of Au_n^- have been reported. In general, odd-numbered gold cluster anions tend to have larger vertical-electron detachment energies (VDEs) than their neighboring even-numbered counterparts.

On the basis of quantum theoretical calculations alone and/or calculations based on the above experimental data, diverse structures of Au_n and Au_n^- , such as linear,^[9] planar,^[9-13] cage (fullerene like),^[14-16] pyramid,^[17] tubular,^[18]

and core-shell types^[19] have been reported.^[20] Many structural competitions of medium-sized gold clusters were reported.^[21] Recently, the 2D–3D structural transition in Au_{12}^- was investigated.^[22] Anionic gold clusters are suggested to have planar structures for $n \leq 12$, 2D–3D competing structures for $n=12-15$, cage structures for $n=15-19$, pyramid structures for $n=20$, and tube, core-shell, and fullerene-like structures for $n=21-34$. Some of the low-energy structures have interesting conformations which have comparable stabilities to the major structures.

Known structures may not perfectly match the experimental PES because of the possible existence of other energetically low lying structures which match the experimental PES. Thus, to obtain more reliable and conclusive results it is important to investigate the structures of small gold clusters more intensively. Since the energies, spectra, and electronic properties of the clusters depend on their structures, we investigated those of the neutral and anionic gold clusters (Au_n and Au_n^- , $n=4-7$) using DFT, MP2, and high-level CCSD(T) calculations. Neutral and anionic gold monomers to trimers,^[23] octamers,^[11] and neutral and anionic decamers^[9] were studied at the CCSD(T) level of theory. However, for Au_{4-7} and Au_{4-7}^- reliable CCSD(T) calculations with large basis sets have not yet been performed, in spite of many DFT studies. Thus, accurate prediction of small gold clusters would be of importance for atom-scale materials research.

Computational Details

We investigated not only the structures of neutral and anionic gold clusters (Au_{4-7} and Au_{4-7}^-) reported in many previous DFT studies,^[9-12] but also many other new structures through the screening test. Then, various structures were studied by using DFT with Becke's three-parameter ex-

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change functional and the Lee–Yang–Parr correlation functional (B3LYP). As basis set we used the Hay–Wadt valence double-zeta ($n+1$) effective core potential (abbreviated as HW).^[24] The EA and IP of Au at the B3LYP/HW level are 2.17 and 9.42 eV, respectively, in good agreement with the experimental EA and IP (2.3 and 9.2 eV).^[7] On the basis of this method some available structures were selected (Figure 1). The term “-nd” in the nomenclature of the conformers denotes dangling gold atoms. The selected gold clusters (Figure 1) in neutral and anionic states were optimized at the B3LYP, Becke’s exchange and Perdew–Wang cor-

relation functionals (BPW91), and MP2 with MDF+2fg basis set levels.^[11b] For these MP2 geometries the scaling approach was performed at the CCSD(T)/MCDHF level.^[11b] In this approach the MP2 optimized coordinates were scaled by factors of 1.000, 1.025 and 1.050, and calculated at the CCSD(T)/MCDHF level. Using their energies, the minimally scaled structures were obtained through the polynomial fitting. Other CCSD(T) calculations with larger basis sets (cc-pVTZ-PP and cc-pVQZ-PP)^[25] were performed by using these CCSD(T)/MCDHF scaled structures. For Au₇[−], the CCSD(T) structural scaling approach was performed with the cc-pVTZ basis set. For Au₇ clusters, the CCSD(T) calculations were performed by using the relativistic 19-electron Stuttgart-Dresden-Bonn (SDB) pseudopotentials with the basis sets (8s7p6d2f/[6s5p3d2f]) developed by Martin.^[26] These large basis sets at the CCSD(T) level were successfully used previously.^[11b] The spin contaminations ($S^2 - S_z^2 - S_z$) of all the clusters in the singlet state were verified to be about zero in the calculations. The low-coordinate structures tend to be more stabilized even at the CCSD(T) level of theory and the basis set superposition error (BSSE) corrections tend to further stabilize low-coordinate structures with respect to high-coordinate structures. Thus, BSSE corrections were not performed here. The binding energies per atom for neutral clusters were calculated. The harmonic vibrational frequencies and the zero point energies (ZPEs) of the low-energy clusters were calculated at the BPW91/MDF+2fg level. All DFT and MP2 calculations were performed with the Gaussian 03 suite of programs,^[27] and the CCSD(T) calculations were carried out by using the Molpro2002.6 program package.^[28]

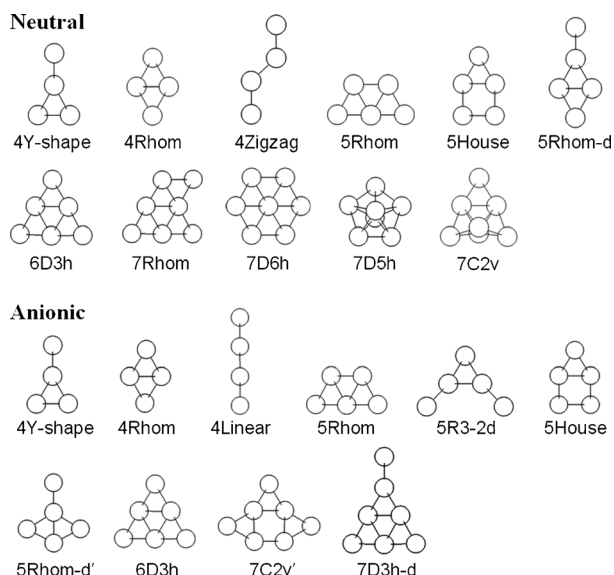


Figure 1. Structures of small neutral and anionic gold clusters Au_{4–7} and Au_{4–7}[−].

Results and Discussion

Table 1 shows the energetics of neutral and anionic gold clusters (Figure 1). For the neutral gold tetramer Au₄ at the DFT levels, 4Y-shape and rhombohedral 4Rhom are isoenergetic. However, at the CCSD(T)/cc-pVQZ level 4Rhom is more stable by 0.12 eV than 4Y-shape, which has a dan-

Table 1. Relative energies [eV], IPs [eV], and VDEs [eV] of neutral and anionic gold clusters (Au_n, $n = 4–7$).^[a]

Neutral <i>n</i>	D ^[b]	Conf.	B3LYP		BPW91		MP2		CCSDT/MCDHF			CCSDT/cc-pVTZ		CCSDT/cc-pVQZ	
			ΔE	IP	ΔE	IP	ΔE	IP	SF ^[c]	ΔE	IP	ΔE	IP	ΔE	IP
4	2D	4Y-shape	0.00	8.06	0.00	8.18	0.29	8.33	1.0177	0.14	8.16	0.13	8.02	0.12	8.11
	2D	4Rhom	0.08	7.80	0.03	7.90	0.00	8.07	1.0203	0.00	7.96	0.00	7.84	0.00	7.95
	1D	4Zigzag	0.32	8.40	0.36	8.48	–	–	–	–	–	–	–	–	–
5	2D	5Rhom	0.00	7.41	0.00	7.48	0.00	7.42	1.0217	0.00	7.43	0.00	7.32	0.00	7.39
	2D	5House	0.15	7.56	–	–	0.46	7.55	1.0292	1.82	6.01	1.83	5.89	1.84	5.97
	2D	5Rhom-d	0.69	7.15	–	–	1.26	7.05	–	–	–	–	–	–	–
6	2D	6D3h	0.00	8.37	0.00	8.45	0.00	9.01	1.0218	0.00	8.64	0.00	8.53	0.00	8.61
7	2D	7Rhom	0.00	7.12	0.00	7.14	0.00	7.03	<i>1.0450</i>	<i>0.00</i>	<i>6.83</i>	–	–	–	–
	2D	7D6h	0.38	6.50	0.35	6.62	0.01	6.27	–	–	–	–	–	–	–
	3D	7D5h	0.77	7.00	0.63	7.04	−1.41	7.29	<i>1.0176</i>	<i>1.21</i>	<i>5.53</i>	–	–	–	–
	3D	7C2v	0.46	6.80	0.39	6.83	−0.81	6.96	–	–	–	–	–	–	–
Anion <i>n</i>	D ^[b]	Conf.	B3LYP		BPW91		MP2		CCSDT/MCDHF			CCSDT/cc-pVTZ		CCSDT/cc-pVQZ	
			ΔE	VDE	ΔE	VDE	ΔE	VDE	SF ^[c]	ΔE	VDE	ΔE	VDE	ΔE	VDE
4	2D	4Y-shape	0.15	2.75	0.10	2.75	0.21	2.52	1.0246	1.14	1.42	1.18	1.30	1.18	1.37
	2D	4Rhom	0.40	2.60	0.31	2.60	0.00	2.45	1.0319	1.08	1.36	1.13	1.25	1.14	1.31
	1D	4 Linear	0.00	3.39	0.00	3.34	0.62	3.23	1.0212	0.00	3.57	0.00	3.44	0.00	3.52
5	2D	5Rhom	0.00	3.12	0.00	3.11	0.00	3.33	1.0246	0.00	3.10	0.00	2.99	0.00	3.06
	2D	5R3-2d	−0.30	4.05	−0.19	4.01	0.46	4.57	1.0209	0.01	4.50	−0.01	4.38	−0.01	4.45
	2D	5House	0.37	3.28	–	–	0.31	3.53	1.0246	0.19	4.47	0.19	4.36	0.19	4.43
6	2D	5Rhom-d'	0.32	3.71	0.28	3.62	0.41	3.90	1.0238	0.21	3.74	0.19	3.62	0.19	3.70
	2D	6D3h	0.00	2.15	0.00	2.19	0.00	1.73	1.0247	0.00	2.06	0.00	1.94	0.00	2.01
7	2D	7C2v'	0.00	3.36	0.00	3.40	0.00	3.69	1.0258	–	–	0.00	3.35	–	–
	2D	7D3h-d	−0.10	3.72	−0.06	3.70	0.09	4.03	1.0252	–	–	−0.02	3.81	–	–

[a] The MDF2f1g basis set was used at the B3LYP, BPW91, and MP2 levels. The italicized data are from the CCSD(T)/SDB calculations. [b] D: dimensionality. [c] SF: scaling factor used for geometry optimization.

gling gold atom. Thus, 4Rhom is the minimum-energy structure and 4Y-shape is an isomer. The IP of 4Y-shape is 8.06/8.18, 8.33, and 8.11 eV at the B3LYP/BPW91, MP2, and CCSD(T)/cc-pVQZ levels, respectively. The IP of 4Rhom is 7.80/7.90, 8.07, and 7.95 eV at the B3LYP/BPW91, MP2, and CCSD(T)/cc-pVQZ levels, respectively. These calculated IPs of 4Y-shape and 4Rhom are underestimated relative to the experimental IP (8.6 eV).^[7] The 4Zigzag structure is higher in energy than 4Y-shape at the DFT level, while this structure optimized into the 4Rhom structure at the MP2 level.

For Au₅, 5Rhom is lower in energy than 5House at the DFT, MP2, and CCSD(T) levels. The 5Rhom-d structure is much higher in energy than 5Rhom at the DFT and MP2 levels. At the BPW91 level the 5House and 5Rhom-d structures optimized into the 5Rhom structure. That is, the neutral gold pentamer has the 5Rhom structure. The IP of 5Rhom is 7.41/7.48, 7.42, and 7.39 eV at the B3LYP/BPW91, MP2, and CCSD(T)/cc-pVQZ levels, respectively. The experimental IP of Au₅ is 8.0 eV.^[7]

For Au₆, only the well-known 6D3h structure was calculated. Its IP is 8.37/8.45, 9.01, and 8.61 eV at the B3LYP/BPW91, MP2, and CCSD(T)/cc-pVQZ levels, respectively. These values are larger than those of neutral gold tetramer clusters (4Y-shape and 4Rhom). The experimental IP of the neutral gold hexamer is 8.8 eV.^[7] The MP2 IP is slightly overestimated and the others underestimated in comparison with the experimental IP.

For Au₇, at the B3LYP and BPW91 levels the 2D 7Rhom structure is the most stable. However at the MP2 level the 3D structure 7D5h is the most stable. At the CCSD(T)/SDB level the 2D 7Rhom structure is more stable than the 3D 7D5h structure by 1.21 eV. The IP of the 2D 7Rhom structure is closer to the experimental value (7.8 eV)^[7] than that of the 3D 7D5h.

The ZPE-corrected binding energies per atom for 4Y-shape/4Rhom, 5Rhom, 6D3h, and 7Rhom are 1.36/1.35, 1.49, 1.72, and 1.67 eV at the BPW91 level and 1.47/1.50, 1.65, 1.92, and 1.91 eV at the CCSD(T)/cc-pVQZ level. Here, the ZPEs used are from the BPW91 frequency calculations. The neutral hexamer is the magic structure in that the successive binding energy per atom is larger than those for other neutral clusters. Structures having dangling gold atoms, such as 4Y-shape, are observed only up to tetramer as low-lying energy conformers.

The energetics and structures of anionic gold clusters are also listed in Table 1 and shown in Figure 1, respectively. For Au₄[−], the 4Linear structure is the most stable. The VDE of the 4Y-shape structure is 2.75 eV at both B3LYP and BPW91 levels, which corresponds to the first strong peak (at 2.75 eV) in the experimental PES for Au₄[−].^[8,9a] The VDEs of 4Rhom and 4Linear are 2.60 and 3.39 eV at the B3LYP level and 2.60 and 3.34 eV at the BPW91 level, which explains the small peaks (at 2.50 and 3.40 eV) in the experimental PES spectrum. The CCSD(T) VDEs of 4Y-shape and 4Rhom structures are underestimated. These main structure and isomers were studied in reference [9a]. The natural bond orbital (NBO) atomic charges of the dangling

atoms in 4Y-shape and 4Linear are all −0.33 a.u. at the BPW91/MDF+2fg level. The excess charge is strongly localized at the dangling sites. As a reference, the NBO atomic charge of the dangling atom in the neutral 4Y-shape structure is −0.17 a.u.

For Au₅[−], the 5R3-2d structure has two dangling gold atoms. At the B3LYP/BPW91 level, 5R3-2d is more stable than the 5Rhom structure by 0.30/0.19 eV, and at the MP2 level 5Rhom is more stable than 5R3-2d by 0.46 eV. However, at the CCSD(T) level 5R3-2d is isoenergetic within 0.01 eV to 5Rhom. The B3LYP/BPW91 VDE of 5Rhom is 3.12/3.11 eV, which identifies the first strong peak (at 3.09 eV) in the experimental PES spectrum of Au₅[−].^[8,9a] The energy difference between the HOMO and HOMO−1 of the 5Rhom structure is 0.99/0.74 eV at the B3LYP/BPW91 level, which corresponds to the energy difference (1.16 eV) between the first and second peaks (at 3.09 and 4.25 eV) in the experimental PES spectrum of Au₅[−]. The VDE of 5R3-2d is 4.05/4.01 eV at the B3LYP/BPW91 level, but 4.57 and 4.45 eV at the MP2 and CCSD(T)/cc-pVQZ levels, respectively. The DFT VDEs of the 5R3-2d are underestimated in comparison with the CCSD(T) ones because the neutral state of the low-coordinate 5R3-2d structure is overstabilized at the DFT level. This large VDE of 5R3-2d is expected to appear at a higher energy than the second peak (at 4.25 eV) of the experimental PES spectrum of Au₅[−]. 5R3-2d has the largest VDE among small anionic gold clusters ($n \leq 14$).^[9a] The NBO atomic charges of two dangling atoms in 5R3-2d are −0.38 a.u. at the BPW91 level. The 5House and 5Rhom-d' structures are relatively high in energy.

For Au₆[−], the VDE of the 6D3h structure is 2.15/2.19, 1.73, and 2.01 eV at the B3LYP/BPW91, MP2, and CCSD(T)/cc-pVQZ levels, respectively. These values correspond to the first strong peak (at 2.13 eV) of the experimental PES spectrum of Au₆[−].^[8,9a]

For Au₇[−], the 7D3h-d structure, which has one dangling gold atom, is more stable than the well-known 7C2v' structure at the B3LYP and BPW91 levels but less stable at the MP2 level. At the CCSD(T)/cc-pVTZ level the 7D6h-d structure is isoenergetic within 0.02 eV to 7C2v'. The VDE of 7C2v' is 3.36/3.40 eV at the B3LYP/BPW91 level and 3.35 eV at the CCSD(T)/cc-pVTZ level, which match the first strong peak (at 3.46 eV) in the experimental PES spectrum.^[8,9a] The VDE of the 7D6h-d structure is 3.72/3.70 and 3.81 eV at the B3LYP/BPW91 and CCSD(T)/cc-pVTZ levels, respectively. These values are in good agreement with the experimental second small peak (at 3.90 eV).^[8,9a] The NBO atomic charge of the dangling atom in 7D3h-d structure is −0.46 a.u. at the BPW91 level.

As the structural dimension increases, the number of bonds and bond lengths increase (see Table S1 of the Supporting Information). With increasing number of atoms, the bond lengths increase. An excess electron increases the bond lengths. Especially for the gold hexamer (6D3h) the three outer distances are shorter than the three inner distances in both neutral and anionic clusters. However, the excess electron increases the outer distances from 2.64 to 2.70 Å

and decreases the inner distances from 2.81 to 2.75 Å due to the characteristic frontier molecular orbitals.^[29]

The BPW91 vibrational frequencies of small neutral and anionic gold clusters are presented in Table S2 (see Supporting Information). The high-frequency modes including the breathing modes are redshifted due to the excess electron. It is interesting that the breathing mode (122 cm⁻¹) of the 6D3h structure of Au₆ splits into two breathing modes (136 and 101 cm⁻¹) in the presence of an excess electron, as shown in Figure S1 (see Supporting Information). In polyene systems the strong Raman active vibrational stretching modes (phonon modes) along the chain are related to the nonlinear optical (NLO) properties and electron-phonon interactions for the conducting properties.^[30] These phonon modes have high energies around 1600 cm⁻¹.^[31] However, the anionic 1D gold tetramer 4Linear as an atomic wire has a low-energy phonon mode of 172 cm⁻¹ at the BPW91 level (see Figure S2 of the Supporting Information).

Conclusion

We have carried out high-level CCSD(T) calculations with large basis sets for the energetically low lying DFT structures of small neutral and anionic gold clusters. The observable structures of small neutral and anionic gold clusters were verified at the CCSD(T) level. For neutral gold clusters Au_n, the lowest-energy structures are 4Rhom, 5Rhom, 6D3h, and 2D 7Rhom for $n=4-7$. For anionic gold clusters Au_n⁻, 4Y-shape is the main structure and 4Rhom and 4Linear are isomers for $n=4$, 5Rhom is the major structure and the 5R3-2d is the minor structure for $n=5$, 6D3h is the lowest-energy structure for $n=6$, and 7C2v' is the lowest-energy structure and 7D3h-d is a minor structure. The 4Y-shape structure having a dangling atom is the major structure of the gold tetramer anion. However, the 5R3-2d and 7D3h-d structures having dangling gold atoms are obtained as isomers for anionic gold pentamer and heptamer at the CCSD(T) level of theory, respectively. Interesting structures having dangling gold atoms are observed as low-energy structures up to $n=4$ for neutral gold clusters but up to $n=7$ for anionic clusters. The dangling atoms also seem to be stable in the small anionic clusters. For anionic gold clusters, the lower-coordinate structures were calculated to be stable more than for the neutral clusters. IR spectral analyses of small neutral and anionic gold clusters were performed. The 5R3-2d is an interesting structure that is slightly changed from the 1-D linear structure of Au₅⁻, while 5Rhom is folded from the 5R3-2d. The O₂-adsorbed structures of 5R3-2d and 7D3h-d structures with dangling gold atoms appeared in the experimental PES spectra, the theoretical results of which will be published elsewhere. Understanding of observable structures of small gold clusters at a high-level ab initio theory will be important in atom-size materials science.

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