THE JOURNAL OF PHYSICAL CHEMISTRY A LETTERS

2006, *110,* 1689−1693

Published on Web 01/14/2006

Gold Apes Hydrogen. The Structure and Bonding in the Planar $B_7Au_2^-$ and B_7Au_2 Clusters

Hua-Jin Zhai and Lai-Sheng Wang*

Department of Physics, Washington State University, 2710 University Drive, Richland, Washington 99354 and W. R. Wiley Environmental Molecular Sciences Laboratory and Chemical Sciences Division, Pacific Northwest National Laboratory, MS K8-88, P.O. Box 999, Richland, Washington 99352

Dmitry Yu. Zubarev and Alexander I. Boldyrev*

Department of Chemistry and Biochemistry, Utah State University, Logan, Utah 84322-0300

Received: October 15, 2005; In Final Form: November 18, 2005

We produced the $B_7Au_2^-$ mixed cluster and studied its electronic structure and chemical bonding using photoelectron spectroscopy and ab initio calculations. The photoelectron spectra of $B_7Au_2^-$ were observed to be relatively simple with vibrational resolution, in contrast to the complicated spectra observed for pure B_7^-, which had contributions from three isomers (Alexandrova et al. *J. Phys. Chem. A* **2004**, *108*, 3509). Theoretical calculations show that $B_7Au_2^-$ possesses an extremely stable planar structure, identical to that of $B_7H_2^-$, demonstrating that Au mimics H in its bonding to boron, analogous to the Au−Si bonding. The ground-state structure of $B_7Au_2^-$ ($B_7H_2^-$) can be viewed as adding two Au (H) atoms to the terminal B atoms of a higher-lying planar isomer of B_7^-. The bonding and stability in the planar $B_7Au_2^-$ ($B_7H_2^-$) clusters are elucidated on the basis of the strong covalent B−Au (H) bonding and the concepts of aromaticity/antiaromaticity in these systems.

Pure boron clusters have received limited experimental attention in the literature over the past couple of decades (see refs 1−7 and references therein). A major breakthrough has resulted from a series of recent joint experimental and theoretical studies that have established that all the small boron clusters are planar or quasi-planar.[8−15] These studies have shown that photoelectron spectroscopy in conjunction with accurate ab initio calculations is a powerful approach to elucidate the complex structures of atomic clusters. Furthermore, the theoretical analysis has yielded detailed information about the chemical bonding in the clusters and allowed the planarity of the boron clusters to be understood on the basis of π and σ aromaticity/antiaromaticity.

Among the small boron clusters, the B_7^- cluster is a particularly interesting and complex system, because we observed the presence of three quite different isomers in its photoelectron spectra:[12] (1) a wheel-type quasi-planar doubly (σ and π) aromatic triplet C_{6v} ($^3A_1$) global minimum (structure **I** in Figure 1), (2) a σ-aromatic and π-antiaromatic singlet C_{2v} ($^1A_1$) isomer (structure **II** in Figure 1) with a quasi-planar shape (only 0.7 kcal/mol above the global minimum), and (3) an elongated planar doubly (σ and π) antiaromatic C_{2v} ($^1A_1$) isomer (structure **III** in Figure 1) (7.8 kcal/mol above the global minimum). Upon addition of two hydrogen atoms to the B_7^- cluster, it is found very recently using ab initio calculations that an inversion in stability occurs.[16] The planar $B_7H_2^-$ (C_{2v}, $^1A_1$) isomer (structure **IV** in Figure 1), formed by the addition of two hydrogen atoms to the doubly antiaromatic C_{2v} ($^1A_1$) B_7^- isomer **III**, is overwhelmingly favored as the global minimum structure. It is 27 kcal/mol more stable than the lowest high-energy isomer **V** of $B_7H_2^-$, originated from the addition of two hydrogen atoms to the global minimum of B_7^-.

Wang and co-workers have recently discovered that gold atoms exhibit chemistry similar to that of hydrogen in Au−Si clusters, forming $SiAu_x$ and Si_2Au_x clusters similar to the corresponding silicon hydrides, SiH_x and Si_2H_x, respectively.[17,18] Because of the similar electronegativity between B and Si, we conjecture that Au may also form Au−B clusters similar to the corresponding valence isoelectronic H−B clusters. If that is true, we hypothesized that the $B_7Au_2^-$ cluster would behave similarly to the $B_7H_2^-$ system, thus yielding a predominantly stable cluster similar to the global minimum of $B_7H_2^-$ (**IV** in Figure 1). In this case, we would expect to obtain a somewhat simpler photoelectron spectrum for $B_7Au_2^-$, because only the global minimum structure is expected to be present in the experiment due to its overwhelming stability.

We produced the $B_7Au_2^-$ anions using a laser vaporization cluster source and obtained its photoelectron spectra using a magnetic bottle-type photoelectron spectrometer.[19−21] The photoelectron spectra of $B_7Au_2^-$ at 266 and 193 nm photon energies are shown in Figure 2, compared with that of B_7^-. Indeed, the photoelectron spectra of $B_7Au_2^-$ are substantially simpler and better resolved than those of B_7^-, despite its larger size. Most surprisingly, despite the addition of two heavy atoms, the ground-state transition (X) of $B_7Au_2^-$ is completely vibrationally resolved at 266 nm (Figure 2a) with the excitation of two vibrational modes, a low-frequency mode of 790 ± 40 cm^{-1} and a high-frequency mode of 1380 ± 40 cm^{-1}. The vibra-

---

* E-mail addresses: L.S.W., ls.wang@pnl.gov; A.I.B., boldyrev@cc.usu.edu.

10.1021/jp0559074 CCC: $33.50

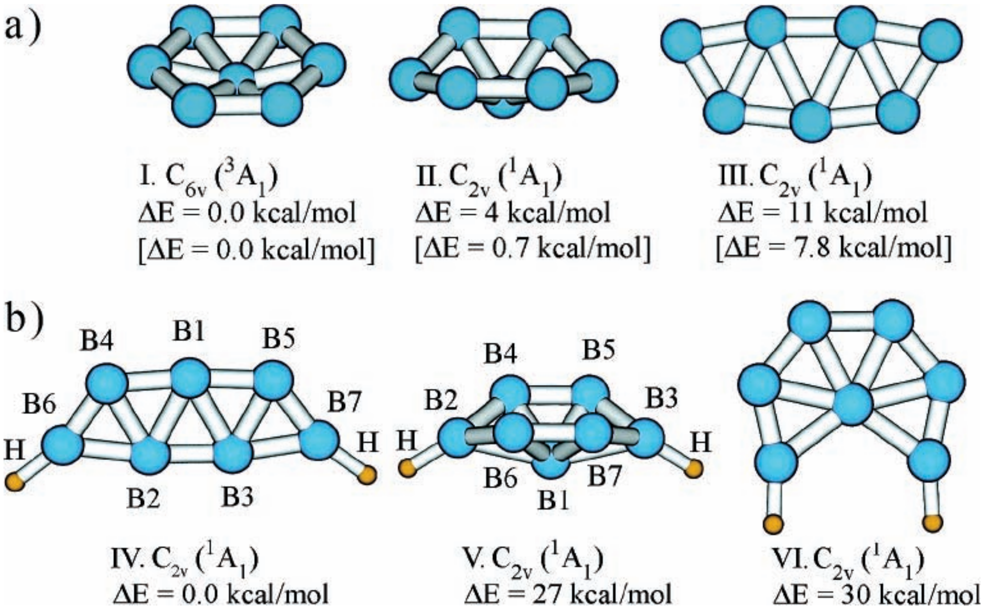

Figure 1. (a) Low-energy isomers of the B_7^- cluster at the B3LYP/6-311+G* level of theory (relative energies computed at the CCSD(T)/6-311+G(2df) level are shown in square brackets).[12] (b) The global minimum and two low-lying isomers of $B_7H_2^-$ at the B3LYP/6-311+G* level of theory.[16]

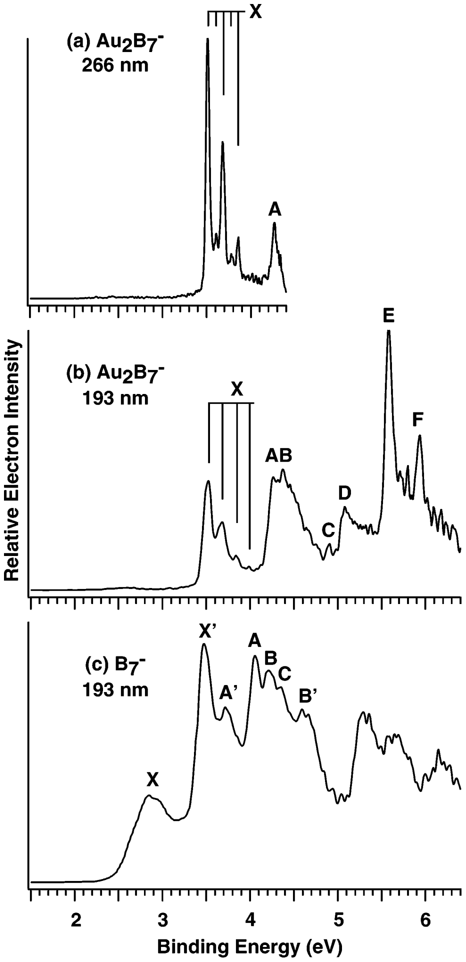

Figure 2. Photoelectron spectra of $Au_2B_7^-$ at (a) 266 nm (4.661 eV) and (b) 193 nm (6.424 eV). The 193 nm spectrum of B_7^- (c) is also included for comparison.[12]

TABLE 1: Experimental Vertical Detachment Energies (VDEs) of $B_7Au_2^-$ from the Photoelectron Spectra, Compared with Theoretical Calculations

feature	VDE (expt)[a] eV	MO	VDE (theor)[b] eV
X[c,d]	3.52 (2)	$3a_2$	3.46
A	4.27 (2)	$9a_1$	4.21
B	4.38 (3)	$8a_1$	4.36
C	4.90 (2)	$7b_2$	4.92
D	5.08 (3)	$6b_2$	5.19
E	5.58 (2)	$7a_1$	5.31
F	5.93 (2)	$3b_1$	5.75

[a] Numbers in parentheses represent experimental uncertainties in the last digit. [b] At TD-B3LYP/B/aug-cc-pvTZ/Au/ Stuttgart_rsc_1997_ecp+2f1 g on Au level of theory. [c] Electron affinity of B_7Au_2 is 3.52 ± 0.02 eV. [d] Ground-state vibrational frequencies for the B_7Au_2 neutral are measured to be 790 ± 40 and 1380 ± 40 cm^{-1}.

tionally resolved ground-state transition yielded an accurate electron affinity (EA) of 3.52 ± 0.02 eV for B_7Au_2. Interestingly, the EA of B_7Au_2 is very close to that of isomer **III** for B_7 (3.44 ± 0.02) corresponding to feature X′ in the spectrum of B_7^- (Figure 2c).[12] Clearly, only one dominant isomer was present in the spectra of $B_7Au_2^-$. The observed detachment energies for the various detachment channels are summarized in Table 1. The observed $B_7Au_2^-$ cluster is likely to correspond to the isomer **III** of B_7^- by adding two Au atoms to its two terminal B atoms similar to the ground-state structure of $B_7H_2^-$, as we expected.

To prove our hypothesis and confirm the observed $B_7Au_2^-$ structure, we performed quantum chemical calculations[22] for a variety of $B_7Au_2^-$ structures (**VII**−**XII**, Figure 3), which were derived from the low-lying structures of $B_7H_2^-$.[16] We initially optimized geometries at the B3LYP/B/cc-pvDZ/Au/LANL2DZ level of theory and found that the structure **VII** of $B_7Au_2^-$ (C_{2v}, $^1A_1$) (Figure 3), nearly identical to the ground state of $B_7H_2^-$, is indeed substantially more stable than the other structures. We then reoptimized the geometry of the $B_7Au_2^-$ global minimum structure **VII** at the B3LYP/B/aug-cc-pvTZ/Au/ Stuttgart_rsc_1997_ecp + 2f1g ($\alpha(f) = 0.448$, $\alpha(f) = 1.464$, $\alpha(g) = 1.218$) additional functions on Au level of theory and found that the two levels of theory gave nearly identical structures (see Table S1 in the Supporting Information). We also optimized the geometry for the neutral B_7Au_2 cluster and obtained its ground-state structure similar to that of the anion as summarized in Table S1. The vertical detachment energies

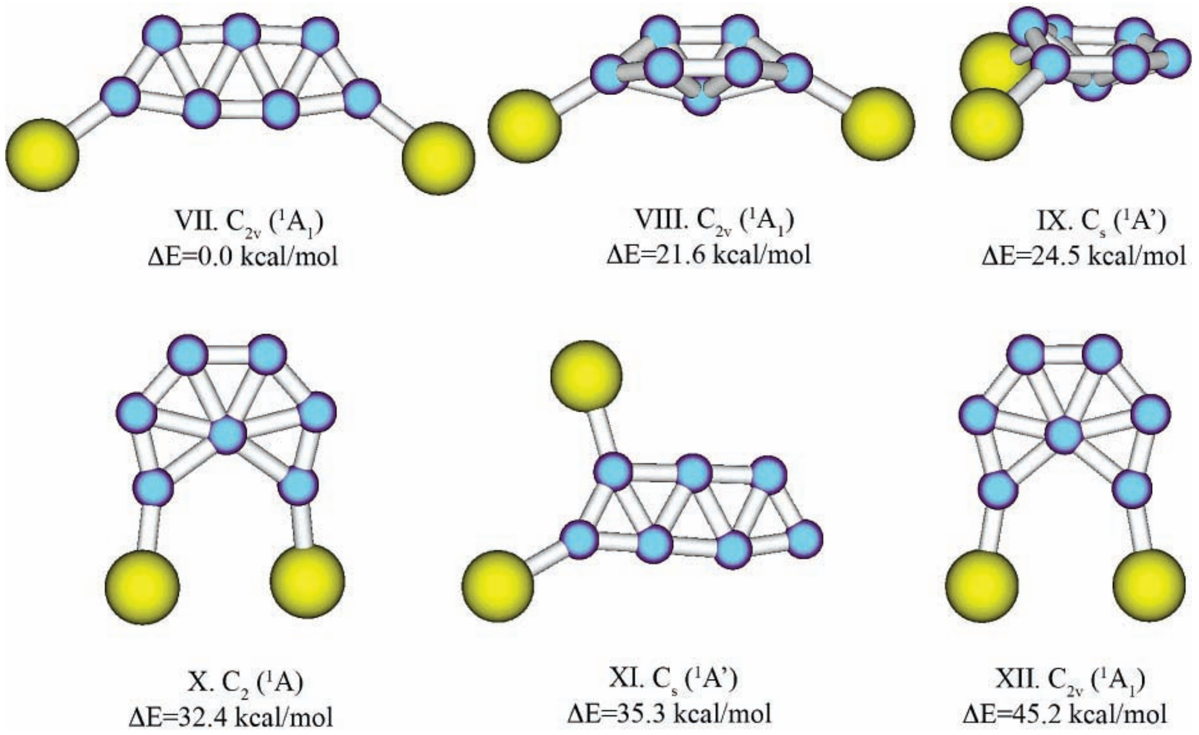
VII. C_{2v} ($^1A_1$) ΔE=0.0 kcal/mol
VIII. C_{2v} ($^1A_1$) ΔE=21.6 kcal/mol
IX. C_s ($^1A'$) ΔE=24.5 kcal/mol
X. C_2 (^1A) ΔE=32.4 kcal/mol
XI. C_s ($^1A'$) ΔE=35.3 kcal/mol
XII. C_{2v} ($^1A_1$) ΔE=45.2 kcal/mol

Figure 3. The global minimum and low-lying isomers of $B_7Au_2^-$ at B3LYP/B/cc-pvdz/Au/LANL2DZ level of theory.

(VDEs) of the $B_7Au_2^-$ global minimum structure were computed using the TD-B3LYP/aug-cc-pvTZ/Au/Stuttgart_rsc_1997_ecp+2f1g on Au level of theory, and they are compared with the experimental data in Table 1. All valence molecular orbitals of the global minimum structure of $B_7Au_2^-$ are depicted in Figure 4.

The ground-state transition in the spectra of $B_7Au_2^-$ (X, Figure 2) involves electron detachment from the $3a_2$-HOMO, which is a π bonding/antibonding orbital over the B_7 moiety with some small contributions from the Au 5d orbitals (Figure 4). The calculated VDE of 3.46 eV agrees well with the experimental VDE (3.52 eV) of the X band (Table 1). Because both $B_7Au_2^-$ and B_7Au_2 have the same symmetry in their ground states, only the totally symmetric modes (a_1) can be active in the detachment transition. The C_{2v} B_7Au_2 possesses eight symmetric modes (Table S1), among which the ω_1 (B−B in-plane stretching) and ω_3 (B−Au stretching) modes with frequencies of 1358 and 828 cm^{-1} are in good agreement with the two observed vibrational modes (1380 ± 40 cm^{-1} and 790 ± 40 cm^{-1}). The geometry changes between the anion and neutral ground states are very small (Table S1), consistent with the short vibrational progressions observed. Calculated adiabatic electron detachment energy is 3.35 eV (B3LYP/aug-cc-pvTZ/Au/Stuttgart_rsc_1997_ecp+2f1g on Au), and it agrees well with the experimental value of 3.52 ± 0.02 eV. The next six detachment channels are due to electron removal from HOMO − 1 to HOMO − 6 (Figure 4), respectively, and the computed VDEs for these detachment channels are in good agreement with the experimental data (Table 1).

The good agreement between the experimental and theoretical VDEs confirmed the theoretical prediction of the global minimum structure **VII** for $B_7Au_2^-$, which is the same as that of $B_7H_2^-$. Why the structure **IV** is the most stable for $B_7H_2^-$ has been discussed in the details of ref 16. The same applies to $B_7Au_2^-$ and can be understood from the MO pictures depicted in Figure 4. Among the 22 occupied valence MOs, 10 can be approximately assigned due the Au 5d orbitals (HOMO − 8 to HOMO − 16 plus HOMO − 18 (although a few of the lower-lying orbitals have significant mixing with the B_7 backbone); 7 are primarily responsible for the formation of 7 2c-2e peripheral B−B bonds (HOMO − 2, HOMO − 4, HOMO − 7; HOMO −17, and HOMO − 19 to HOMO − 21; see ref 16 for more details); 2 are primarily responsible for the B−Au bonding (HOMO − 3 and HOMO − 5); and 2 are π orbitals (HOMO and HOMO − 6). This leaves the HOMO − 1 ($9a_1$), which is a σ delocalized orbital responsible for the global bonding over the 5 boron atoms that are not bonded to Au. Thus, $B_7Au_2^-$ is π-antiaromatic (4π delocalized electrons) and σ-aromatic (2 delocalized σ electrons) with all other MOs representing the 2 2c-2e B−Au bonds and the 7 2c-2e B−B peripheral bonds. The planar $B_7Au_2^-$ structure can then be viewed as originating from the mixing of the Au hybrid 6s−5d orbitals with one of the delocalized σ orbitals in the B_7^- isomer **III**, thus transforming the doubly antiaromatic B_7^- into a σ-aromatic but still π-antiaromitc $B_7Au_2^-$. Essentially, a delocalized σ orbital, forming the original σ-antiaromatic pair of orbitals in B_7^-, is transformed to 2 B−Au localized bonds, gaining major stabilization to the structure **VII** for $B_7Au_2^-$. The second most stable isomer for $B_7Au_2^-$, originating from the quasi-planar doubly aromatic isomer **I** of B_7^-, becomes doubly (σ- and π-) antiaromatic and thus significantly less stable. The stability of the planar structure **VII** of $B_7Au_2^-$ is also reinforced by the 2 strong B−Au bonds formed. The calculated dissociation energy for the $Au_2B_7^-$ (C_{2v}, $^1A_1$, structure **VII**) → Au_2 ($^1\Sigma_g^+$) + B_7^- (C_{2v}, $^1A_1$, structure **III**) reaction is +119 kcal/mol at B3LYP/B/aug-cc-pvTZ/Au/Stuttgart_rsc_1997_ecp+2f1g on Au.

The similarity in stability, structure, and bonding in the global minima of $B_7Au_2^-$ and $B_7H_2^-$ is analogous to the previous discovery of the Au/H analogy in Si−Au clusters.[17,18] Similar to the Si−Au bond, which is highly covalent, we found that the B−Au bonds in $B_7Au_2^-$ are also highly covalent with very little charge transfer from Au to B (NBO charges at B3LYP/B/cc-pvDZ/Au/LANL2DZ are Q(Au) = −0.007 e and Q(B) = −0.251 e). This is again due to the close electronegativity

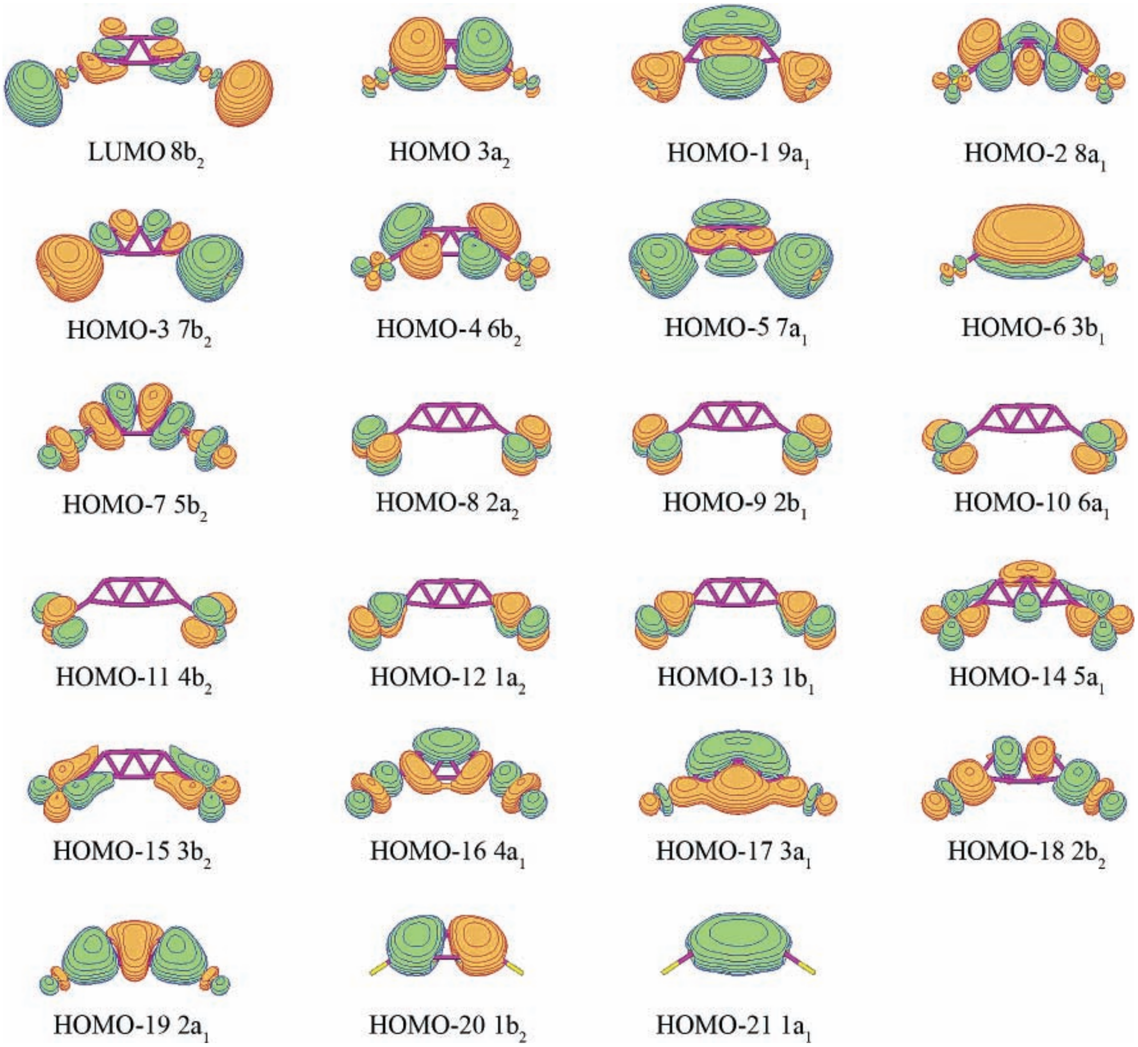

Figure 4. Molecular orbitals (B3LYP/B/cc-pvDZ/Au/LANL2DZ) of $B_7Au_2^-$ C_{2v} ($^1A_1$). MOs are ordered according to the TD-B3LYP/B/aug-cc-pvTZ/Au/ Stuttgart_rsc_1997_ecp+2f1g on Au level of theory.

of B and Au, as a result of the strong relativistic effects in Au.[25] This study demonstrates that the Au/H analogy may be a more general phenomenon and may exist in many species involving Au. The Au/H analogy will not only extend our understanding of the chemistry of Au, but will also be highly valuable in predicting the structures and bonding of many Au alloy clusters.

Acknowledgment. The theoretical work, done partially at Utah State University, was supported by the donors of the Petroleum Research Fund (ACS-PRF# 43101-AC6 to A.I.B.), administered by the American Chemical Society and by the National Science Foundation (CHE-0404937 to A.I.B.). Part of the calculations was done at the W. R. Wiley Environmental Molecular Sciences Laboratory (EMSL), a national scientific user facility sponsored by DOE's Office of Biological and Environmental Research and located at Pacific Northwest National Laboratory (PNNL), which is operated for DOE by Battelle. The experimental work done at Washington was supported by the National Science Foundation (DMR-0503383 to L.S.W.) and performed at the EMSL of PNNL. D.Y.Z. wishes to thank Utah State University for a Presidential Fellowship, and A.I.B. is grateful to EMSL, the Chemical Sciences Division of PNNL, and Washington State University for their hospitality during this project.

Supporting Information Available: Optimized geometrical parameters, harmonic frequencies, and other calculated molecular properties are summarized in Table S1. Complete *Gaussian 03* and NWChem references are presented. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Hanley, L.; Anderson, S. L. *J. Phys. Chem.* **1987**, *91*, 5161. (b) Hanley, L.; Whitten, J. L.; Anderson, S. L. *J. Phys. Chem.* **1988**, *92*, 5803. (c) Ruatta, S. A.; Hintz, P. A.; Anderson, S. L. *J. Chem. Phys.* **1991**, *94*, 2833. (d) Sowa-Resat, M. B.; Smolanoff, J.; Lapicki, A.; Anderson, S. L. *J. Chem. Phys.* **1997**, *106*, 9511.

(2) (a) Wyss, M.; Riaplov, E.; Batalov, A.; Maier, J. P.; Weber, T.; Meyer, W.; Rosmus, P. *J. Chem. Phys.* **2003**, *119*, 9703. (b) Cias, P.; Araki, M.; Denisov, A.; Maier, J. P. *J. Chem. Phys*. **2004**, *121*, 6776. (c) Batalov, A.; Fulara, J.; Shnitko, I.; Maier, J. P. *Chem. Phys. Lett*. **2005**, *404*, 315.

(3) Bonačič-Koutecký, V.; Fantucci. P.; Koutecký, J. *Chem. Rev.* **1991**, *91*, 1035.

(4) (a) Kato, A. U.; Tanaka, E. *J. Comput. Chem.* **1991**, *12*, 1097. (b) Kato, H.; Yamashita, K.; Morokuma, K. *Chem. Phys. Lett.* **1992**, *190*, 361.

(5) (a) Ricca, A.; Bauschlicher, C. W. *Chem. Phys*. **1996**, *208*, 233. (b) Ricca, A.; Bauschlicher, C. W. *J. Chem. Phys.* **1997**, *106*, 2317.

(6) (a) Boustani, I. *Int. J. Quantum Chem.* **1994**, *52*, 1081. (b) Boustani, I. *Sur. Sci.* **1996**, *370*, 355. (c) Boustani, I. *Phys. Rev. B* **1997**, *55*, 16426.

(7) (a) Ma, J.; Li, Z. H.; Fan, K. N.; Zhou, M. F. *Chem. Phys. Lett.* **2003**, *372*, 708. (b) Jin, H. W.; Li, Q. S. *Phys. Chem. Chem. Phys*. **2003**, *5*, 1110. (c) Li, Q. S.; Jin, Q. *J. Phys. Chem. A* **2003**, *107*, 7869.

(8) Ritter, S. K. *Chem. Eng. News* **2004**, *82* (9), 28.

(9) Zhai, H. J.; Wang, L. S.; Alexandrova, A. N.; Boldyrev, A. I.; Zakrzewski, V. G. *J. Phys. Chem. A* **2003**, *107*, 9319.

(10) Zhai, H. J.; Wang, L. S.; Alexandrova, A. N.; Boldyrev, A. I. *J. Chem. Phys*. **2002**, *117*, 7917.

(11) Alexandrova, A. N.; Boldyrev, A. I.; Zhai, H. J.; Wang, L. S.; Steiner, E.; Fowler, P. W. *J. Phys. Chem. A* **2003**, *107*, 1359.

(12) Alexandrova, A. N.; Boldyrev, A. I.; Zhai, H. J.; Wang, L. S. *J. Phys. Chem. A* **2004**, *108*, 3509.

(13) Zhai, H. J.; Alexandrova, A. N.; Birch, K. A.; Boldyrev, A. I.; Wang, L. S. *Angew. Chem., Int. Ed.* **2003**, *42*, 6004.

(14) Zhai, H. J.; Kiran, B.; Li, J.; Wang, L. S. *Nat. Mater.* **2003**, *2*, 827.

(15) Kiran, B.; Bulusu, S.; Zhai, H. J.; Yoo, S.; Zeng, X. C.; Wang, L. S. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 961.

(16) Alexandrova, A. N.; Koyle, E.; Boldyrev, A. I. *J. Mol. Model.* In press.

(17) Kiran, B.; Li, X.; Zhai, H. J.; Cui, L. F.; Wang, L. S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2125.

(18) Li, X.; Kiran, B.; Wang, L. S. *J. Phys. Chem. A* **2005**, *109*, 4366.

(19) Details of the photoelectron spectroscopy apparatus have been described elsewhere.[20,21] In brief, Au−B mixed cluster anions were generated by laser vaporization of an Au/B disk target in the presence of a helium carrier gas and analyzed by time-of-flight mass spectrometry. The $B_7Au_2^-$ anions were mass-selected and decelerated before being photodetached by a pulsed laser beam. Photoelectrons were collected at nearly 100% efficiency by a magnetic bottle and analyzed in a 3.5-m-long electron flight tube. The photoelectron spectra were calibrated using the known spectra of Au^- and Rh^-, and the energy resolution was $\Delta E_k/E_k \approx 2.5\%$, that is, approximately 25 meV for 1 eV electrons.

(20) Wang, L.S.; Cheng, H. S.; Fan, J. *J. Chem. Phys*. **1995**, *102*, 9480.

(21) Wang, L. S.; Wu, H. In *Advances in Metal and Semiconductor Clusters. IV. Cluster Materials*; Duncan, M. A., Ed.; JAI: Greenwich, CT, 1998; pp 299−343.

(22) The B3LYP/B/cc-pvDZ/Au/LANL2DZ calculations have been performed using *Gaussian 03* program[23] at Utah State University, and the B3LYP/B/aug-cc-pvTZ/Au/ Stuttgart_rsc_1997_ecp+2f1g on Au calculations have been performed using NWChem program[24] at the W. R. Wiley Environmental Molecular Sciences Laboratory (EMSL), Pacific Northwest National Laboratory (PNNL), Richland, Washington. Molecular orbital pictures were made using the MOLDEN 3.4 program.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.1; Gaussian, Inc.: Pittsburgh, PA, 1998.

(24) Aprà, E.; Windus, T. L.; Straatsma, T. P.; Bylaska, E. J.; de Jong, W.; Hirata, S.; Valiev, M.; Hackler, M.; Pollack, L.; Kowalski, K.; Harrison, R.; Dupuis, M.; Smith, D. M. A.; Nieplocha, J.; Tipparaju, V.; Krishnan, M.; Auer, A. A.; Brown, E.; Cisneros, G.; Fann, G.; Fruchtl, H.; Garza, J.; Hirao, K.; Kendall, R.; Nichols, J.; Tsemekhman, K.; Wolinski, K.; Anchell, J.; Bernholdt, D.; Borowski, P.; Clark, T.; Clerc, D.; Dachsel, H.; Deegan, M.; Dyall, K.; Elwood, D.; Glendening, E.; Gutowski, M.; Hess, A.; Jaffe, J.; Johnson, B.; Ju, J.; Kobayashi, R.; Kutteh, R.; Lin, Z.; Littlefield, R.; Long, X.; Meng, B.; Nakajima, T.; Niu, S.; Rosing, M.; Sandrone, G.; Stave, M.; Taylor, H.; Thomas, G.; van Lenthe, J.; Wong, A.; Zhang, Z. *NWChem, A Computational Chemistry Package for Parallel Computers*, version 4.7; Pacific Northwest National Laboratory, Richland, WA, 2005.

(25) Pyykkö, P. *Angew. Chem., Int. Ed.* **2004**, *43*, 4412.