

Molecular Alligator Clips for Single Molecule Electronics. Studies of Group 16 and Isonitriles Interfaced with Au Contacts

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Abstract: A density-functional-theory treatment has been carried out on chalcogenide- and isonitrile-containing molecular systems (alligator clips) involved at the interface of molecule/Au-electrode contacts. The B3PW91 functional was used with effective core potentials provided within the LANL2DZ potentials and basis set. An extended basis set, LANL-E, was implemented by combining the valence, diffuse, and polarization basis from the 6-311++G** for H, C, N, S, and Se and by adding polarization and diffuse functions for Te and Au atoms. Results, including bond lengths and angles, ionization potentials, electron affinities, and binding energies for small systems containing Au atoms, were obtained with acceptable precision for those systems with available experimental information. Predicted quantities are reported for other systems that, as yet, have no experimental information available. This study indicates that, of the alligator clips studied, S would provide the best embodiment followed closely by Se- and Te-terminated molecules. This study also indicates that the precision obtained with calculations of first- and second-row atom-containing molecules can also be achieved with systems possessing heavier elements such as Au.

Introduction

Molecular scale electronics promises to utilize single molecules as the basic operational elements of future computational architectures. The transition from semiconducting bulk arrays to single molecule-based systems may increase the performance of present electronic devices by several orders of magnitude. To set the stage for molecular electronics research, it is important to perform precise experiments and computations on single molecules to determine their electrical and electronic properties. At the heart of the initial experiments are conductance measurements on single molecules. Several experiments^{1–6} dealing with current/voltage characteristics as well as calculations^{7,8} with a wide variety of methods and levels of theory have been reported. One of the problems in these conductivity measurements is the characterization of effects produced by the “alligator clips” on the metal surfaces or tips. By “alligator clip” we imply a moiety that allows the connection of a single molecular system to a macroscopic interface, usually a metallic tip or a nanoscale cluster, thereby providing a covalent bond between the molecule and the macroscopic world. The precise characterization of the

tip/molecule interface is of fundamental importance for the design of molecular circuits and for numerous other research areas incorporating self-assembled monolayers. Presented here is a study of small Au clusters, the most widely used experimental metallic component, interfaced with the alligator clips. Our interest centers on the use of chalcogenide- and isonitrile-based alligator clips. These systems are studied with the goal of obtaining properties predicted within chemical precision (presently approaching 1 kcal/mol) assessed by comparison with experimental information.

Methodologies and Computational Details

Density functional theory (DFT) is the main technique used in this work.^{9–15} The central functionals used are the Perdew-Wang 91 for correlation and Becke-3 for exchange (B3PW91).^{16–19} The basis set used was the triply split valence with polarization functions, 6-311G**.^{20–22} When the Au clusters are included in the calculations,

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we combined the above methods with effective core potentials.²³ Presently, this seems to be the most powerful combination of tools to deal with relatively large numbers of very heavy atoms. The use of the pseudopotentials with relativistic corrections has been widely demonstrated to be a good compromise with the alternative use of full-electron procedures. This reduces the required computational effort without loss of accuracy.²⁴ The basis set used for the Au atom is the Los Alamos National Laboratory (LANL) set for effective core potentials (ECP) of the double- ζ type.^{25–27} This basis set is usually sufficient for the geometric and one-electron properties of systems containing Au atoms. However, for more precise energetic results, it is necessary to increase the basis set of Au atoms adding extra s, p, d, and three sets of f-polarization functions. This increase of the basis set for the Au atom allows us to pursue the same good accuracy that is already obtained with the first row atoms. Accordingly, the double- ζ basis set implicit in the LANL2DZ basis has been extended for all the other atoms to be used when accurate energetics is needed. We added the triply split valence portion of the 6-311G basis set and the corresponding polarization function (i.e., the polarization function from the 6-311G** basis set) as indicated below. The original LANL2DZ and its extended version (LANL-E) introduced in the present work for H, C, N, O, S, Se, Te, and Au are shown in the supplementary information.

The use of DFT is fully justified due to the fact that it is a first principles tool able to deal with a broad variety of systems. Several successful applications of DFT have been reported with use of the hybrid functionals, where a portion of the exchange functional is calculated as a fully nonlocal functional of the wave function of an auxiliary noninteracting system of electrons. Since this resembles the exchange in the Hartree–Fock (HF) procedure (actually in any wave function procedure), it is common to refer to this functional or procedure as a DFT–HF hybrid. However, it should be considered that the so-called exchange is being calculated by using a noninteracting wave function whose density, but not its wave function, corresponds to the real system. A detailed analysis and their theoretical rigor was recently reviewed.²⁸ All calculations were performed with use of the Gaussian-94 program.²⁹ All geometry optimizations were performed via the Bery algorithm in redundant internal coordinates.³⁰ The threshold for convergence was 0.00045 atomic units (au) and 0.0003 au for the maximum force and root-mean-square force, respectively. The self-consistency of the noninteracting wave function was performed with a requested convergence on the density matrix of 10^{-8} , and 10^{-6} for the root mean square and maximum density matrix error between iterations. These settings provide correct energies of at least five decimal figures and geometries of an accuracy of around three decimal figures within the level of theory.

Results and Discussion

Tables 1a and 1b show the results for the calculations of all atoms in this work with use of the B3PW91/LANL2DZ and

B3PW91/LANL-E levels of theory for Au, H, N, C, O, S, Se, and Te. In some cases, the lowest excited state of different symmetry to the ground state was also calculated to check that the method employed finds the correct configuration for the ground state, and this was always the case. We have tabulated the HOMO, LUMO, and HOMO–LUMO gap for all atoms. The total energy for the H atom is underestimated by only 0.63 and 2.40 kcal/mol for the LANL2DZ and LANL-E levels, respectively. These are very good estimations for a total energy of -313.75 kcal/mol. Notice that for hydrogen the Hamiltonian does not contain the term $1/r_{ij}$, which is part of the Hamiltonian from which the functionals have been developed. For the one-electron case, DFT simply reduces to the one-electron Schrödinger equation that yields the exact value of $0.5 E_h$ (313.8 kcal/mol). Evidently, the HOMO and LUMO energies have no meaning for the H case. The LUMO overestimates the exact value for H of $-0.02775 E_h$ (17.4 kcal/mol), and the HOMO should be exactly $-0.5 E_h$. The fact that the values of -0.31638 and $-0.32636 E_h$ are obtained is because the functional considers the classical self-interaction in this one-electron system. These values of 198.5 and 204.8 kcal/mol (or 8.61 and 8.88 eV) are important quantities for each particular functional and basis set. We can notice large differences in the total energies using the two different basis sets. However, the changes in the HOMO, LUMO, and gap energies are not as large as in the total energies. This is in accord with the fact that one-electron properties do not have a strong dependence with the basis set. As indicated before, ignoring the case of H, the largest gap corresponds to N followed by O. The following atoms and their respective HOMO–LUMO gaps are of interest to us as molecular alligator clip bonding units: O, 99.1 kcal/mol (4.30 eV), S 56.9 kcal/mol (2.47 eV), Se 50.0 kcal/mol (2.17 eV), and Te 43.9 kcal/mol (1.90 eV). Au has a gap of 51 kcal/mol (2.21 eV) that is very close to the gap of Se, and differs by less than 0.5 eV from the S and Te gaps. As shown in Tables 1a and 1b, the results obtained with the original LANL basis set are of less accuracy than those obtained with the extended basis set; however, their qualitative performance is still acceptable. This is of primary importance because it will allow us to extend the calculations with the original basis set to much larger clusters, reserving the large LANL-E only for cases where a large discrepancy could exist, and for bench mark calculations. A clear demonstration of the great quality of energetics calculations with the extended basis set is illustrated in Tables 2a and 2b where we report the results for the atomic cations and anions, respectively. In all cases, the total errors are about 2% of the total ionization potential, which was calculated as the energy difference of the cation minus the neutral. The largest errors are obtained for C, O and N. The results for the heavier elements, Se, Te, and Au, are of acceptable precision. In the case of the electron affinities, which were calculated as the energy difference of the neutral minus the anion (Table 2b), with the exception of C, all the other errors are smaller than 2 kcal/mol. We can also observe that the negative of the HOMO, in all cases, underestimates the ionization potential, thus making a strong point against the proposition that the negative of the HOMO should correspond to the ionization potential.¹² It is evident that when an interacting electron leaves the atom, the reorganization energy for the noninteracting HOMO would have to be larger due to a net decrease in the electron–electron interactions of the leaving electron. Recent arguments regarding whether the negative of the K–S HOMO should be the ionization potential have been given.^{31–33} Something similar

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Table 1. Total, HOMO, LUMO, and HOMO–LUMO Gap (Δ_{H-L}) Atomic Energies (kcal/mol) Using the B3PW91/LANL2DZ and B3PW91/LANL-E Levels of Theory

system	total energy	HOMO	LUMO	Δ_{H-L}
(a) B3PW91/LANL2DZ				
H ($^2S_{1/2}$)	-314.389	-198.5	-0.2	198.3
C (1D_2)	-23695.192	-132.9	-95.3	37.7
C (3P_0)	-23739.983	-168.8	-101.3	67.5
N ($^2D_{5/2}$)	-34175.140	-166.2	-139.6	26.5
N ($^4S_{3/2}$)	-34246.745	-225.3	-56.7	168.6
O (1D_2)	-47028.160	-229.2	-180.5	48.7
O (3P_2)	-47095.931	-202.4	-104.5	97.9
S (1D_2)	-6267.665	-174.6	-154.2	20.4
S (3P_2)	-6310.524	-160.9	-106.7	54.1
Se (1D_2)	-5729.833	-162.7	-145.9	16.8
Se (3P_2)	-5768.858	-150.4	-102.8	47.6
Te (1D_2)	-5008.429	-149.3	-136.1	13.2
Te (3P_2)	-5042.466	-138.7	-98.5	40.2
Au ($^2S_{1/2}$)	-85017.648	-156.1	-106.0	50.1
(b) B3PW91/LANL-E				
H ($^2S_{1/2}$)	-316.158	-204.8	-25.9	178.88
C (1D_2)	-23698.028	-136.9	-98.3	38.63
C (3P_0)	-23742.500	-170.3	-100.5	69.87
N ($^2D_{5/2}$)	-34180.110	-172.8	-143.7	29.10
N ($^4S_{3/2}$)	-34249.581	-228.1	-62.6	165.50
O (1D_2)	-47033.776	-237.0	-187.2	49.74
O (3P_2)	-47101.233	-209.9	-110.8	99.07
S (1D_2)	-6272.127	-177.4	-155.9	21.52
S (3P_2)	-6315.061	-163.8	-106.9	56.88
Se (1D_2)	-5735.682	-165.0	-147.3	17.64
Se (3P_2)	-5774.744	-152.8	-102.8	49.99
Te (1D_2)	-5010.218	-150.6	-134.9	15.67
Te (3P_2)	-5043.827	-141.1	-97.2	43.86
Au ($^2S_{1/2}$)	-85018.200	-155.7	-104.8	50.95

Table 2. Total, HOMO, and LUMO Energies (kcal/mol) for the Cations and Anions, Calculated and Experimental Ionization Potential (IP) or Electron Affinity (EA) (kcal/mol) of the Neutral, and Error (Calculated – Experimental) IP's or EA's Using the B3PW91/LANL-E Level of Theory

(a) Cations						
system	total energy	HOMO	LUMO	IP (calc)	IP (exp) ^a	error (calc – exp)
H ⁺	0.000			316.2	313.6	2.6
C ⁺ ($^2P_{1/2}$)	-23475.570	-450.0	-364.8	266.9	259.7	7.3
N ⁺ (3P_0)	-33908.863	-551.0	-455.1	340.7	335.2	5.6
O ⁺ ($^4S_{3/2}$)	-46780.237	-658.5	-123.3	321.0	314.0	7.0
S ⁺ ($^4S_{3/2}$)	-6075.578	-441.1	-114.1	239.5	238.9	0.6
Se ⁺ ($^4S_{3/2}$)	-5552.581	-404.0	-289.5	222.2	224.9	-2.7
Te ⁺ ($^4S_{3/2}$)	-4840.589	-363.3	-264.6	204.1	207.8	-3.6
Au ⁺ (1S_0)	-84802.487	-383.0	-275.0	215.7	212.7	3.0
(b) Anions						
system	total energy	HOMO	LUMO	EA (calc)	EA (exp) ^a	error (calc – exp)
H ⁻ (1S)	-332.919	26.9	125.8	16.8	17.4	-0.6
C ⁻ (4S)	-23776.203	26.3	116.7	33.7	29.1	4.6
N ⁻ (3P)	-34248.609	59.6	122.3	-1.0	<0	0
O ⁻ (2P)	-47135.169	37.3	118.1	33.9	33.7	0.2
S ⁻ ($^2P_{3/2}$)	-6363.693	7.9	56.7	48.6	47.9	0.7
Se ⁻ ($^2P_{3/2}$)	-5823.056	4.6	47.9	48.3	46.6	1.7
Te ⁻ ($^2P_{3/2}$)	-5090.269	5.3	46.1	45.5	45.4	0.1
Au ⁻ (1S_0)	-85069.536	-0.9	44.9	51.3	53.2	-1.9

^a Reference 41.

happens in the case of the negative of the LUMO. The negative of the LUMO overestimates the electron affinity; therefore, the

Table 3. Total Energies, Atomization Energies (D_0), and Error with Respect to Experiment (kcal/mol) and Bond Lengths (Å) (Experimental Values in Parentheses) for Dimer Systems Using the B3PW91/LANL2DZ and B3PW91/LANL-E Levels of Theory

system	total energy	D_0 (exp) ^a	error	bond length (exp) ^a
(a) B3PW91/LANL2DZ				
OH($^2\Pi$)	-47504.686	94.4 (105.5)	11.1	0.998 (0.970)
CN($^2\Sigma$)	-58137.055	150.3 (179.0)	28.7	1.196 (1.172)
SH($^2\Pi$)	-6699.781	74.9 (84.5, 90.5) ^b	9.6, 15.6	1.389 (1.341)
SeH($^2\Pi$)	-6152.643	69.4 (72.9)	3.5	1.512 (1.475)
H ₂ ($^1\Sigma_g$)	-736.701	107.9 (108.6)	0.7	0.744 (0.741)
O ₂ ($^3\Sigma_g$)	-94286.277	94.4 (119.6)	25.2	1.260 (1.207)
S ₂ ($^3\Sigma_g$)	-12685.820	64.8 (100.8)	36.0	2.078 (1.889)
Au ₂ ($^1\Sigma_g$)	-170079.202	43.9 (52.1)	8.2	2.547 (2.472) ^d
AuH($^1\Sigma$)	-85398.904	66.9 (70.0)	3.1	1.553 (1.524)
AuS	-91371.075	42.9 (58.8, 96.9) ^c	15.9, 54.0	2.331
AuO	-132149.579	36.0 (52.1)	16.1	1.946
(b) B3PW91/LANL-E				
OH($^2\Pi$)	-47522.499	105.1 (105.5)	0.4	0.975 (0.970)
CN($^2\Sigma$)	-58167.577	175.5 (179.0)	3.5	1.165 (1.172)
SH($^2\Pi$)	-6716.435	85.2 (84.5, 90.5) ^b	-0.7, 5.3	1.356 (1.341)
SeH($^2\Pi$)	-6167.829	76.9 (72.9)	-4.0	1.479 (1.475)
H ₂ ($^1\Sigma_g$)	-739.137	106.8 (108.6)	1.8	0.747 (0.741)
O ₂ ($^3\Sigma_g$)	-94323.921	121.5 (119.6)	-1.9	1.200 (1.208)
S ₂ ($^3\Sigma_g$)	-12726.181	96.1 (100.8)	4.7	1.921 (1.889)
Au ₂ ($^1\Sigma_g$)	-170085.666	49.3 (52.1)	2.8	2.547 (2.472) ^d
AuH($^1\Sigma$)	-85405.361	71.0 (70.0)	-1.0	1.532 (1.524)
AuS	-91389.411	56.2 (58.8, 96.9) ^c	2.6, 40.7	2.240
AuO	-132163.710	44.3 (52.1)	7.8	1.925

^a Reference 41. ^b References 34–36. ^c References 37 and 38. ^d Reference 34.

filling of a noninteracting LUMO would have to be accompanied by an increase in energy due to the electron–electron interaction of the new electron. Again it can be seen also in Table 2b that the electron affinity predictions for the heavier atoms are of chemical accuracy and, in general, for the atomization potential of all atoms.

Tables 3a and 3b show the results for the diatomic systems. The bond lengths are predicted fairly well with the original LANL2DZ basis set. Except for the case of S₂, all the errors are smaller than 0.075 Å and the average error is 0.054 Å. With the extended basis set, the situation is far superior. With the exception of Au₂, which does not have good experimental accuracy, the errors are smaller than 0.03 Å with an average error of 0.018 Å. The existing experimental values are indicated in parentheses. Interestingly, the bond length for Au₂ is the same with both basis sets. We have to keep in mind that, in most cases, the reported experimental bond lengths are not of high certainty. The errors in the bond energies with the LANL2DZ basis set are relatively higher and care must be taken when incorporating them into our final conclusions. The error in the atomization energy of CN (isonitrile) is 28.7 kcal/mol and the error for S₂ is 36.0 kcal/mol. Although the original idea was to use the LANL basis set with heavier elements, it is important to keep in mind how results would compare to exact experimental values such as those that already exist for lighter elements. Fortunately, the bond energy predictions show a tremendous improvement by extending the LANL2DZ basis set by additional s, p, d, and 3f functions, forming the LANL-E basis set. The errors for this small set of molecules are comparable to those obtained with the best uncorrected high level ab initio calculations. The largest error of 4.7 kcal/mol is obtained for the S₂ dimer, which represents a dramatic improvement over an error of 36 kcal/mol obtained with the original LANL basis set. There are two reported experimental values for SH and for AuS. For the case of SH, our theoretical result

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Table 4. Bond Length (Å), Total, HOMO, and LUMO Energies (kcal/mol) for the Two-Atom Cations and Anions, Ionization Potential or Electron Affinity (Calculated and Experimental, kcal/mol), and Error (Calculated – Experimental) for the Two-Atom Neutral Systems Using the B3PW91/LANL-E Level of Theory

(a) Cations						
system	R_e Å	total energy	HOMO	LUMO	IP (exp) ^a	error (calc – exp)
H ₂ ⁺ (² Σ _g)	1.104	–383.986	–569.1	–359.4	355.1 (355.7)	–0.6
O ₂ ⁺ (² Π _g)	1.104	–94035.141	–460.0	–381.9	288.8 (278.4)	10.4
S ₂ ⁺ (² Π _g)	1.839	–12502.964	–328.4	–286.7	223.2 (215.8)	7.5
CN ⁺	1.232	–57844.817	–474.0	–399.1	322.8 (324.9)	–2.2
OH ⁺ (³ Σ)	1.036	–47220.912	–578.0	–396.0	301.6 (299.8)	1.8
SH ⁺ (³ Σ)	1.378	–6478.427	–426.3	–307.9	238.0 (239.1)	–1.1
SeH ⁺ (³ Σ)	1.497	–5945.100	–393.2	–287.8	222.7	
TeH ⁺ (³ Σ)	1.669	–5224.807	–353.8	–263.2	202.9	
AuH ⁺ (² Σ)	1.532	–85167.742	–369.7	–305.5	237.6	
AuO ⁺ (³ Σ)	1.981	–131932.624	–361.5	–288.9	226.5	
AuS ⁺ (³ Σ)	2.228	–91183.826	–334.6	–260.8	205.6	
AuSe ⁺ (³ Σ)	2.342	–90649.690	–324.5	–250.3	197.4	
AuTe ⁺ (³ Σ)	2.516	–89931.756	–309.9	–234.3	181.8	
Au ₂ ⁺ (² Σ _g)	2.671	–169870.813	–310.4	–264.0	214.9	
(b) Anions						
system	R_e	total energy	HOMO	LUMO	EA (exp) ^a	error (calc – exp)
H ₂ [–] (² Σ _u)	0.772	–708.032	–152.8	82.4	–31.1	
O ₂ [–] (² Π _g)	1.335	–94333.258	53.1	117.8	9.3 (10.4)	–1.1
S ₂ [–] (² Π _g)	2.039	–12765.840	10.1	47.0	39.7 (38.5)	1.2
CN [–] (¹ Σ)	1.176	–58258.666	–27.4	118.6	91.1 (88.1)	3.0
OH [–] (¹ Σ)	0.966	–47561.235	28.1	106.3	38.7 (42.1)	–3.4
SH [–] (¹ Σ)	1.357	–6768.951	3.5	92.0	52.5 (53.4)	–0.9
SeH [–] (¹ Σ)	1.483	–6220.113	0.6	95.3	52.3 (51.0)	1.3
TeH [–] (¹ Σ)	1.673	–5479.062	1.4	96.3	51.4 (48.5)	2.9
AuH [–] (² Σ)	1.626	–85422.184	19.7	37.8	16.8	
AuO [–] (¹ Σ)	1.910	–132213.635	–6.7	44.7	54.5	
AuS [–] (¹ Σ)	2.260	–91444.500	–9.9	38.7	55.1	
AuSe [–] (¹ Σ)	2.379	–90901.867	–10.6	35.9	54.8	
AuTe [–] (¹ Σ)	2.556	–90170.743	–11.6	33.6	57.2	
Au ₂ [–] (² Σ _u)	2.697	–170129.152	–5.3	34.6	43.5 (44.7)	–1.2

^a Reference 41.

of 85.2 kcal/mol is closer to the experimental value of 84.5 kcal/mol³⁴ than to the alternate experimental value of 90.5 kcal/mol.^{35,36} For the case of the AuS system, our theoretical result of 56.2 kcal/mol is closer to the experimental 58.8 kcal/mol³⁷ value than to the other reported experimental value of 96.9 kcal/mol.³⁸ The corroboration with specific experimental results confirms the validity of our calculations and aids in solving the disagreement between experiments. These results provide confidence with calculations with use of the LANL extended basis set. The results for molecules containing heavier elements are excellent. The B3PW91/LANL-E level of theory provides a superb approach for the analysis of Au–chalcogenide systems.

Table 4 shows the results for the cations and anions of the diatomics. Table 4a shows an excellent agreement with the experimental results which are within chemical accuracy, with the exception of O₂ and S₂ which are reasonably accurate. Notice that the largest error (10.4 kcal/mol) for the diatomics corresponds to the ionization potential of O₂, which is slightly better than the MP4SDTQ/6-311G** error of 11.3 kcal/mol. We are reporting acceptable estimated values of ionization potentials for the AuH, AuO, AuS, AuSe, AuTe, and Au₂ sitmaps. Table 4b shows the atomization energies, all of which are in excellent agreement with existing experimental data. The electron affinity

(34) Huber, K. P.; Herzberg, G. *Molecular Spectra and Molecular Structure*; Van Nostrand Reinhold Company: New York, 1979; Vol. IV. Constants of diatomic molecules.(35) Dibeler, Liston J. *Chem. Phys.* **1968**, *49*, 482.(36) Meyer, Rosmus J. *Chem. Phys.* **1975**, *63*, 2356.(37) Smoes; Mandy; Auwera-Mahieu, V.; Drowart *Bull. Soc. Chim. Belges* **1972**, *81*, 45.(38) Gingerich *Chem. Commun.* **1970**, 580.**Table 5.** Total Energy, Structural Parameters, Atomization Energies (ΣD₀, kcal/mol), and Au Bond Energy (kcal/mol) for the Trimer Systems Using the B3PW91/LANL2DZ and B3PW91/LANL-E Level of Theory

system	total energy	bond length, angle(Å, deg)	ΣD ₀	D _e ^a
(a) B3PW91/LANL2DZ				
AuCN(¹ Σ) C _{∞v}	–143242.416	1.921, 1.186	238.0	87.7
AuCN(¹ A') C _s	–143242.416	1.921, 1.186, 180.0	238.0	87.7
AuOH(¹ Σ) C _{∞v}	–132543.153	1.916, 0.959	115.2	20.8
AuOH(¹ A') C _s	–132566.640	1.994, 0.985, 107.8	138.7	44.3
AuSH(¹ Σ _g) C _{∞v}	–91716.958	2.303, 1.356	74.4	–0.5
AuSH(¹ A') C _s	–91764.598	2.359, 1.384, 95.1	122.0	47.2
AuSeH(¹ Σ) C _{∞v}	–91161.562	2.410, 1.473	60.7	–8.7
AuSeH(¹ A') C _s	–91218.119	2.453, 1.502, 93.1	117.2	47.8
AuTeH(¹ Σ) C _{∞v}	–90422.519	2.554, 1.647	48.0	–15.5
AuTeH(¹ A') C _s	–90486.117	2.591, 1.681, 91.2	111.6	48.1
(b) B3PW91/LANL-E				
AuCN(¹ Σ) C _{∞v}	–143277.092	1.922, 1.159	266.8	91.9
AuOH(¹ A') C _s	–132589.821	1.990, 0.966, 104.3	154.2	49.1
AuSH(¹ Σ _g) C _{∞v}	–91738.419	2.261, 1.338	89.0	3.8
AuSH(¹ A') C _s	–91791.544	2.280, 1.356, 94.7	142.1	56.9
AuTeH(¹ A') C _s	–90503.606	2.549, 1.665, 92.2	124.5	57.7

^a Dissociation energies for the Au–L bond, L = CN, OH, SH, and TeH.

(EA) for the Au₂ system is reproduced with acceptable success; an error of only 1.2 kcal/mol is obtained. We report here precise estimations for the electron affinities of AuH, AuO, AuS, AuSe, and AuTe systems. All of them are of major importance in the development of alligator clips.

With the success of the B3PW91/LANL-E level of theory and the relative success of the B3PW91/LANL2DZ level of

Table 6. Structural Parameters and Total, HOMO, and LUMO Energies (kcal/mol) for the Cation and Anion Triatomic as well as Ionization Potential (IP) and Electron Affinity (EA) (kcal/mol) for the Neutral Systems Using the B3PW91/LANL-E Level of Theory

(a) Cation					
system	R_e , angle (\AA , deg)	total energy	HOMO	LUMO	IP
AuOH ⁺ (² A') C_s	2.052, 0.984, 116.0	-132350.583	-343.9	-295.7	239.2
AuSH ⁺ (² A'') C_s	2.272, 1.368, 96.8	-91583.543	-328.2	-262.5	154.9
AuTeH ⁺ (² A'') C_s	2.536, 1.670, 93.0	-90314.625	-307.4	-237.4	189.0
(b) Anion					
system	R_e , angle (\AA , deg)	total energy	HOMO	LUMO	EA
AuOH ⁻ (² A') C_s	2.194, 0.965, 99.0	-132630.151	2.0	43.2	40.3
AuSH ⁻ (² A') C_s	2.493, 1.355, 93.6	-91829.288	1.2	42.3	37.7
AuTeH ⁻ (² A') C_s	2.761, 1.668, 92.6	-90539.342	-0.2	42.1	35.7

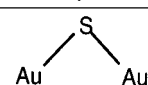
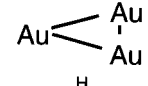
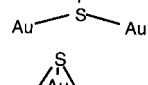
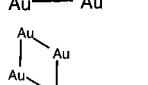
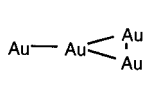
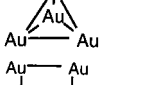
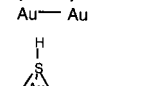
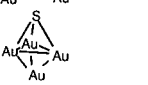
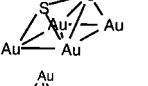
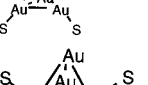
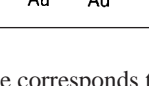
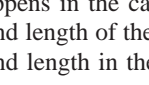
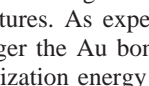
Table 7. Total, HOMO, LUMO, and Atomization Energies (ΣD_o) (kcal/mol) for Gold-Sulfur-Hydrogen Clusters Using the B3PW91/LANL2DZ Level of Theory

system	total energy	HOMO	LUMO	ΣD_o
AuSH(¹ Σ_g) $C_{\infty v}$	-91716.958	-137.6	-110.6	74.4
Au ₂ S(¹ A ₁) C_{2v}	-176436.871	-148.3	-84.8	91.1
Au ₃ (² Σ_u) $D_{\infty h}$ ^a	-255117.395	-160.0	-125.8	64.5
Au ₃ (² B ₂) C_v ^a	-255117.257	-124.5	-87.9	64.3
Au ₂ SH(² A ₁) C_{2v}	-176794.451	-136.2	-102.4	134.2
Au ₃ S(² A ₁) C_{3v}	-261474.662	-123.8	-87.7	111.2
Au ₄ (¹ A _g) D_{2d} ^a	-340184.452	-142.1	-94.5	113.9
Au ₄ (¹ A ₁) C_{2v} ^a	-340184.910	-146.0	-98.5	114.3
Au ₄ (³ B ₁) D_{2d} ^a	-340112.119	-13.2	-152.9	41.5
Au ₄ (³ A _{1g}) D_{4h} ^a	-340166.110	-140.2	-105.1	95.5
Au ₃ SH(¹ A ₁) C_{3v}	-261844.114	-152.7	-84.9	166.3
Au ₄ S(¹ A ₁) C_{3v}	-346539.461	-137.0	-85.7	158.3
Au ₄ S ₂ (¹ A ₁) C_{2v}	-352903.411	-140.9	-106.8	211.8
Au ₄ S ₂ (¹ A ₁) C_{2v}	-352897.155	-129.4	-111.8	205.5
Au ₄ S ₂ (³ B ₂) C_{2v}	-352901.472	-138.6	-110.6	209.8
HAu ₄ SH C_{3v}	-347269.104	-149.4	-93.7	259.2

^a Reference 42.

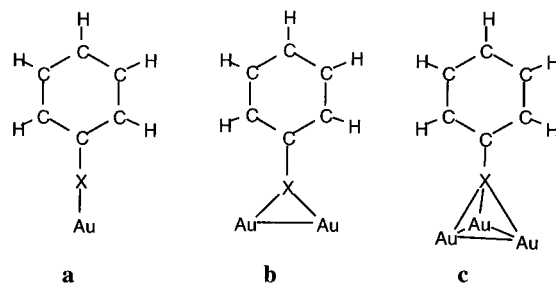
theory, we proceeded to perform calculations for larger systems containing Au atoms. Results for triatomic systems containing one Au atom are shown in Tables 5a and 5b. Unfortunately, no experimental information was found for triatomic systems containing Au; however, the previous results for diatomics provided confidence on the validity of the present results. We have tabulated in Tables 5a and 5b the bond energies involving one Au atom. Interestingly, the strongest connection is to a C atom. The next strongest bond corresponds to Au connected to a S or Te atom, and the lowest to an O atom. The AuSH lowest ground state corresponds to the bent configuration with an angle of 95.0°. The linear configuration apparently does not exist. Forcing the geometry optimization toward the corresponding symmetry, the calculation yields a structure with a bond energy of only 3.8 kcal/mol. This latter structure is 53.1 kcal/mol above the triangular case. DFT calculations yield the common feature that, as the system size increases, the accuracy in the energetics of the whole molecule improves due to the fact that the electron density becomes more uniform. The effect of the extended basis set on the Au bond energies goes from 4 to 13 kcal/mol as can be observed from Tables 3 and 5, suggesting an additive correction of about 9 kcal/mol for bond energies when the smaller basis set is used. Tables 6a and 6b show the results for cations and anions of AuOH, AuSH, and AuTeH systems with use of the B3PW91/LANL-E level of theory. Using the information in Tables 5b, 6a and 6b, we conclude that the effect of the electron on the structure of AuCN is to decrease the bond angle from 116.0° to 104.3° to 99.0° when the molecule bears a total charge of +1, 0, or -1, respectively. However, the Au bond length is minimum when the molecule is neutral, and increases when the molecule is positive or negative; the negative

Table 8. Binding Energies of Interest for Au-S-H Systems Using the B3PW91/LANL2DZ Level of Theory

Geometry	System	Reaction	D_e (kcal/mol)
	Au ₂ S(¹ A ₁) C_{2v}	Au ₂ +S	-47.1
	Au ₃ (² B ₂) C_v	Au ₂ +Au	-20.4
	Au ₂ SH(² A ₁) C_{2v}	Au ₂ +SH	-15.5
	Au ₃ S(² A ₁) C_{3v}	Au ₃ +S	-46.9
	Au ₄ (¹ A _g) D_{2h}	Au ₂ +Au ₂	-26.0
	Au ₄ (¹ A ₁) C_{2v}	Au ₂ +Au ₂	-26.5
	Au ₄ (⁵ B ₁) D_{2d}	Au ₂ +Au ₂	46.3
	Au ₄ (³ A _{1g}) D_{4h}	Au ₂ +Au ₂	-7.9
	Au ₃ SH(¹ A ₁) C_{3v}	Au ₃ +SH	-27.1
	Au ₄ S(¹ A ₁) C_{3v}	Au ₄ +S	-116.8
	Au ₄ S ₂ (¹ A ₁) C_{2v}	Au ₄ +S ₂	-33.1
	Au ₄ S ₂ (¹ A ₁) C_{2v}	Au ₄ +S ₂	-99.2
	Au ₄ S ₂ (³ B ₂) C_{2v}	Au ₄ +S ₂	-103.5

case corresponds to the longest bond length. A similar situation happens in the case of AuSH and AuTeH except that the Au bond length of the neutral becomes slightly longer than the Au bond length in the positive ion.

The energetics of these three systems also shows interesting features. As expected, the larger the atomization energy, the larger the Au bond energy. But we also can observe that the ionization energy decreases as the bond energy increases. An analogous situation happens with the electron affinity; it

Table 9. HOMO, LUMO and Gap Energies for the Three Connections of the Alligator Clip with Gold Atoms Using the B3PW91/LANL2DZ Level of Theory


X	HOMO			LUMO			Δ_{H-L}		
	a	b	c	a	b	c	a	b	c
O	-122.8	nb ^a		-105.8			17.0		
S	-124.4	-147.9	-142.7	-108.4	-97.1	-84.4	16.0	50.8	58.3
Se	-121.3	-141.3	-143.7	-111.2	-94.4	-82.1	10.2	46.9	60.9
Te	-117.4	-140.6	-139.2	-113.4	-99.0	-80.1	4.0	41.6	59.1
NC	-97.8	nb ^a		-52.9			44.8		

^a No binding found.

decreases as the bond energy increases. Therefore, in these systems, when the addition of an electron becomes more difficult, the loss of an electron becomes easier. Thus there is an apparent dichotomy between molecular scale electronics and traditional bulk devices. In insulator materials, it is difficult to gain or to lose electrons whereas in conductors the gain or loss is a low-energy process. And, although in a conventional diode, both the p- and the n-semiconductors should be good carrier conductors, in molecular scale systems, a combination of electron donor and acceptor moieties might not be the ideal form for a diode.

The connection of Au to Te yields a small decrease in the electron affinity; therefore, in this case, there would be a minimal decrease in conductivity when connecting Au to Te. On the other hand, the ionization potential is strongly reduced when connecting Au to Te. Earlier studies seem to indicate that the electron affinity has a much stronger effect on conductivity than the ionization potential since the conductivity through single molecules is by injection of additional electrons through the molecules and not by the loss of electrons by the molecule.³⁹ Therefore, the use of Te as an alligator clip instead of S would likely lead to an increase in impedance. The LUMO of the anion is positive, which physically means that a second electron is not allowed in the molecule until this first one is ejected from the molecule. This latter effect is highly probable as indicated by the positive nature of the anion HOMO.

Table 7 shows several other combinations of Au clusters with S atoms. In several cases, H atoms have been used to cap the bonds. In general, we can observe that the electron affinity, by observing the trends in the negative of the LUMO, increases when S atoms are present on Au rather than when Au atoms are alone. In this case we have used the B3PW91/LANL2DZ level of theory. We observe that the negative of the LUMO energy strongly decreases with respect to the one in the bare

(39) Seminario, J. M.; Zacarias, A. G.; Tour, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 3970–3974.

clusters when S atoms are connected. Table 8 shows a few binding energies of interest for the set of clusters in Table 7. An S atom binds strongly to a tetrahedral cluster of Au atoms but it also binds strongly to a dimer of Au atoms. This fact is of major relevance if self-assembling fabrication of molecular circuits is to be utilized since the precise nature of a self-assembled monolayer's connection to a Au surface is not known with certainty.⁴⁰

Finally, Table 9 shows the HOMO, LUMO, and HOMO-LUMO gap (HLG) for several alligator clips connected to one, two, and three Au atoms, simulating a simple connection to a Au surface. The electron affinity, which maintains a direct relation to the negative of the LUMO energy, increases practically linearly as the atomic number of the alligator clip increases, thereby indicating a better electron affinity as the atomic number of the alligator clip approaches the atomic number of the Au atoms. On the other hand, the ionization potential, which is directly related to the negative of the HOMO energy, reaches a maximum for S, then decreases as the atomic number increases. However, the HLG gets smaller as the atomic number of the system increases. We can see that the use of the isonitrile as an alligator clip was only possible when the connection was made to one Au atom, and in this case the trend in the electron affinity, provided by the negative of the LUMO, dropped abruptly. Therefore, its use as an alligator clip may be limited.

Conclusion

Geometries, ionization potentials, electron affinities, and binding energies for small systems containing Au atoms were obtained with good precision. We compared our results with those systems having available experimental information to show the fine level of agreement. For those metal/molecule interfaces that are of special interest to the field of single-molecule electronics but have limited experimental information available, predicted quantities are reported. This study indicates that, among the alligator clips studied, S would provide the most efficient alligator clip connection to Au followed closely by Se- and Te-terminated molecules. This study also indicates that the precision obtained with calculations of first- and second-row atom-containing molecules can also be achieved with systems possessing heavier elements such as Au.

Acknowledgment. Support came from the Defense Advanced Research Projects Agency and the Office of Naval Research (N00014-97-1-0806). We thank NASA for the use of their supercomputing facilities and M. J. Frisch from Lorentzian Inc.

Supporting Information Available: LANL2DZ and LANL-E basis sets for H, C, N, O, S, Se, Te, and Au (11 pages). See any current masthead page for access instructions.

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