The interaction of oxygen with small gold clusters

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Presented in this work are the results of a quantum chemical study of oxygen adsorption on small Au_n and Au_n^- $(n=2,3)$ clusters. Density functional theory (DFT), second order perturbation theory (MP2), and singles and doubles coupled cluster theory with perturbative triples [CCSD(T)] methods have been used to determine the geometry and the binding energy of oxygen to Au_n. The multireference character of the wave functions has been studied using the complete active space self-consistent field method. There is considerable disagreement between the oxygen binding energies provided by CCSD(T) calculations and those obtained with DFT. The disagreement is often qualitative, with DFT predicting strong bonds where CCSD(T) predicts no bonds or structures that are bonded but have energies that exceed those of the separated components. The CCSD(T) results are consistent with experimental measurements, while DFT calculations show, at best, a qualitative agreement. Finally, the lack of a regular pattern in the size and the sign of the errors [as compared to CCSD(T)] is a disappointing feature of the DFT results for the present system: it is not possible to give a simple rule for correcting the DFT predictions (e.g., a useful rule would be that DFT predicts stronger binding of O_2 by about 0.3 eV). It is likely that the errors in DFT appear not because of gold, but because oxygen binding to a metal cluster is a particularly difficult problem.
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I. INTRODUCTION

Recent experiments have shown that small gold clusters deposited on a metal oxide surface are good oxidation catalysts.[1] This has stimulated theoretical work on oxygen adsorption in the gas-phase,[2] on oxide-supported Au clusters,[3] and on the mechanism of CO oxidation catalyzed by gold.[4] These papers used density functional theory (DFT) to calculate the binding energies and the activation energies needed for clarifying the reaction mechanism. Most catalytic systems have many electrons, making it challenging, but not impossible given new linear scaling methods,[5] to employ more reliable and more accurate methods.

When using DFT it is implicitly assumed that the calculated energies are sufficiently accurate for the task at hand. In most cases it is difficult to assess the accuracy of DFT methods, since the experimental data needed for such tests are not available. Moreover, the theory is particularly valuable when it provides information about aspects of a reaction that cannot be obtained by experiments (e.g., the transition state, transient reaction intermediates). In such cases, the reliability of the results given by the DFT calculations must be determined without appeal to experiments.

One approach to testing the accuracy of DFT methods is to compare the results to those provided by better methods. To accomplish this one must study ''model systems'' that are small enough to allow the use of accurate methods, and large enough to contain all the significant aspects of the system of interest.

This article presents calculations of the binding energies of one or two oxygen molecules to Au_2 and Au_3 neutral and negatively charged clusters. To test the accuracy of the DFT calculations, energy differences based on the B3LYP[6] and PW91[7] functionals are compared with those obtained using second-order perturbation theory (MP2)[8] and singles and doubles coupled cluster theory with perturbative triples [CCSD(T)],[9] as well as with multireference methods. The multireference approaches ensure that a correct zeroth-order wave function is used, while the perturbation and (especially) coupled cluster methods provide a correct accounting of dynamic correlation.

In assessing the practical importance of the findings obtained in the present work, it is important to recognize that the key issue in catalysis studies is to understand the reaction mechanisms that lead to products via pathways that have the smallest activation energy. For example, in the case of CO oxidation one can envision two mechanisms: in one O_2 dissociates and an O atom reacts with CO producing CO_2; in the other O_2 reacts with CO to form a carbonate and this reacts with CO to produce two CO_2 molecules. One can decide between the two possibilities by finding which one has the lowest activation energy. A theoretical prediction is useful if it is sufficiently accurate to tell which of the two activation energies is smaller. The same can be said about finding the most likely reaction intermediate from a set of candidates. DFT calculations could be very useful, if they are accurate enough for the tasks described earlier.

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TABLE I. Bond distances R(Å), dissociation energies D_e(eV), and vibrational frequencies ω_e(1/cm) of Au_2 at different levels of theory.

	SBKJC(f)+sp			uSBKJC(f)+sp			uSBKJC($3f$)+sp			uSBKJC($3f2g$)+sp		
	R(Å)	D_e(eV)	ω_e(1/cm)	R(Å)	D_e(eV)	ω_e(1/cm)	R(Å)	D_e(eV)	ω_e(1/cm)	R(Å)	D_e(eV)	ω_e(1/cm)
HF	2.615	0.80	156	2.612	0.83	156	2.605	0.86	156	2.598	0.88	156
MP2	2.494	2.24	190	2.472	2.28	194	2.469	2.35	196	2.448	2.47	200
CCSD	2.539	1.89	[e]	2.521	1.89	[e]	2.527	1.87	[e]	2.509	1.94	[e]
CCSD(T)	2.535	2.04	175	2.517	2.07	[e]	2.523	2.06	[e]	2.504	2.14	[e]
CASSCF(2,2)	2.654	1.12	136	[e]	[e]	[e]	[e]	[e]	[e]	[e]	[e]	[e]
MRMP2(2,2)	2.506	2.17	184	2.483	2.22	[e]	2.488	2.23	[e]	2.465	2.35	[e]
B3LYP	2.562	1.98	167	2.560	1.97	167	2.547	2.01	167	2.539	2.03	168
PW-PBE[a]	2.54	2.22										
PW-PW91[b]	2.528	2.27										
cp-CCSD(T)[c]	2.488	2.19	187									
Experiment[d]	2.472	2.31	191									

[a]DFT with plane-wave basis set and PBE functional [Ref. 4(a)].
[b]DFT with plane-wave basis set and PW91 functional (Ref. 2).
[c]Counterpose-corrected CCSD(T) with all electron PJHN-$4f2g1h1i$ basis set (Ref. 28).
[d]Experimental values (Ref. 29).
[e]Values are not available yet.

II. COMPUTATIONAL METHODS

For all systems studied here, the geometries were first determined using Hartree–Fock (HF) calculations. To ensure that the optimized geometries correspond to minima on their respective potential energy surfaces, the Hessian (matrix of energy second derivatives) was calculated and diagonalized. Hessians that are positive definite (no negative eigenvalues) correspond to local minima. Those with n negative eigenvalues correspond to nth order saddle points. The optimized HF geometries were used as the initial structures for DFT and MP2 geometry optimizations. The optimized MP2 geometries were then used for single point CCSD(T) calculations. The energy gradients for geometry optimizations were evaluated analytically for all HF, DFT, and closed shell MP2 calculations. For open-shell MP2 geometry optimizations, the gradients were calculated numerically.

To avoid spin contamination in the wave function, restricted open-shell methods were used for all open shell calculations. For open-shell second-order perturbation theory, the Z-averaged perturbation theory (ZAPT[10]) version of restricted MP2 was used. The ZAPT and the restricted RCCSD(T)[11] method are based on a restricted open-shell HF wave function that is free of spin contamination. In the MP2 and CCSD(T) calculations the $1s$ orbitals of oxygen and $5s$ and $5p$ core orbitals of gold atoms were not included in the correlation part of the calculation.

To study the importance of nondynamic electron correlation, and to assess whether the single determinant-based methods provide an acceptable zeroth-order wave function in the small gold clusters, complete active space self-consistent field (CASSCF)[12] and multireference second-order perturbation theory (MRMP2)[13] calculations were carried out on Au_2 and Au_3 clusters.

The restricted DFT method with the B3LYP functional was used to compare with the results of previous plane wave-based DFT calculations[2] using the PW91 functional and with the MP2, MRMP2, and CCSD(T) calculations described earlier. The B3LYP functional consists of five functionals, namely Becke+Slater+HF exchange and LYP+VWN5 correlation.

In all calculations the effective core potential (ECP) with scalar relativistic corrections developed by Stevens *et al.* (SBKJC)[14] was used for the gold atoms. This ECP retains 19 explicit electrons. The Gaussian contracted SBKJC basis set[13] was augmented with one f polarization (exponent $=0.89$) and one s and one p diffuse function (both exponents$=0.01$) centered on the gold atoms. The standard contracted 6-31+G* basis set was centered on each oxygen atom. In all calculations, spherical harmonic basis functions were used with five d orbitals and seven f orbitals. In order to study the effect of the contraction of the basis set on the computational results, calculations on Au_2 were also carried out with uncontracted basis sets.

The GAMESS[15] suite of programs was used for all calculations except for CCSD(T), which was done in MOLPRO.[16]

III. RESULTS AND DISCUSSION

A. Results for Au_2

In Table I, we show the bond length, the binding energy, and the vibrational frequency of Au_2, calculated with a variety of methods and basis sets, as well as the experimental results. The starting basis set is the standard SBKJC ECP, augmented by a set of f functions and a set of diffuse s and p functions. Several observations about Table I are pertinent. (a) As one might expect, compared with the experimental values, the bond distances predicted by HF are much too large, the dissociation energies much too small, and the vibrational frequency too small. These observations are essentially independent of basis set. (b) The B3LYP results are considerably better than those obtained using HF, they are essentially independent of basis set (suggesting that these results are converged with basis set), the dissociation energy is still about 0.3 eV too small, and the vibrational frequency

TABLE II. Au_2 vertical and adiabatic electron affinities (eV) calculated with different levels of theory. Experimental values for the adiabatic electron affinity are 1.94 eV (Ref. 17) and 2.02 eV (Ref. 18). PW-PW91 (Ref. 2) and PW-PBE [Ref. 4(a)] values for adiabatic electron affinity are 2.02 and 2.08 eV. Relativistic CCSD(T) with all electron $(10s7p5d3f)/[10s6p5d3f]$ basis set value is 1.83 eV (Ref. 21).

		HF	MP2	CCSD(T)	CASSCF(2,2)	MRMP2	B3LYP
Contracted basis set	Vertical	0.58	1.43	1.46	0.33	1.49	1.66
	Adiabatic	0.64	1.47	1.51	0.36	1.52	1.71
Uncontracted basis set	Vertical	0.59	1.48	1.51	0.34	1.54	1.68
	Adiabatic	0.65	1.53	1.56	0.37	1.58	1.74

is only marginally better than the HF value. (c) The MP2 results are in surprisingly good agreement with experiment, but this is clearly an artifact of the cancellation of basis set errors and level-of-theory errors since the agreement deteriorates as the basis set is improved. (d) The CCSD(T) results, with the smallest basis set, are already better than DFT and, unlike MP2, steadily improve as the basis set is improved. (e) Uncontracting the ECP valence basis set has little effect, and the same may be said of the multireference methods, CASSCF and MRMP2. Previous plane wave DFT calculations[2] also predict reasonable dissociation energies, but these calculations are not expected to be as accurate as CCSD(T) in general.

Table II contains the values of vertical (anion has the neutral geometry) and adiabatic (optimal geometries for both neutral and anion) electron affinities (EA) of Au_2 dimer, calculated with different methods using contracted and completely uncontracted basis sets. The experimental adiabatic EA has been estimated to be 1.94 eV.[17] Taylor *et al.* estimate the EA to be 2.02 eV.[18] Mills, Gordon, and Metiu[2] calculate an adiabatic EA of 2.02 eV using plane waves and the PW91 functional, and Hakkinen and Landman,[4(a)] using the PBE functional,[19] predict 2.08 eV. Turning to Table II, it is clear that, as was noted for the results in Table I, uncontracting the basis set does not significantly improve the results. Of course, this only expands the underlying *s,p* basis. The HF and CASSCF results are again unsatisfactory. All other methods are in much better agreement with experiment, although they all underestimate the experimental value of 1.94 eV by 0.2–0.4 eV. However, based on the results in Table I, it is expected that an analogous basis set improvement, by adding more and higher l polarization functions, will bring the CCSD(T) results into much better agreement with experiment, while having little effect on the DFT predictions. We also note that both PW91 and PBE calculations are in excellent agreement with the experiments.

B. Results for Au_3

The D_{3h} geometry of the Au_3 cluster has one electron in the doubly degenerate highest occupied molecular orbital, so it is subject to Jahn–Teller distortion. The distorted Au_3 cluster has C_{2v} symmetry and two possible electronic states, $^2A_1$ and $^2B_2$ (Fig. 1). The energy relative to the $^2B_2$ state and the geometry of the Au_3 cluster are shown in Table III. According to experiment,[20] the ground state of Au_3 is $^2B_2$, and the energy splitting between the $^2A_1$ and the $^2B_2$ states is very small. Wesendrup *et al.*[21] showed that even relativistic CCSD(T) calculations with large basis sets predict the $^2A_1$ state to be the ground state with the energy splitting between it and the $^2B_2$ state of 4.4 kcal/mol. The same authors showed that relativistic MP2 calculations predict the $^2B_2$ state to be 0.9 kcal/mol more stable than $^2A_1$. The last result is consistent with the order of the states predicted by the multireference singles and doubles configuration interaction (MRSDCI[22]) method.[23]

The HF and MRMP2 methods predict, respectively, that the $^2A_1$ state is 1.1 and 0.1 kcal/mol lower in energy than the $^2B_2$ state. However, the CASSCF and MP2 methods predict that the $^2B_2$ state is lower than $^2A_1$ by 1.9 and 1.0 kcal/mol, respectively. Interestingly, the B3LYP method and the plane-wave PW91 calculations predict no Jahn–Teller distortion: the linear $^2\Sigma_u^+$ is the lowest energy state. These results indicate that larger basis sets and consideration of the spin–orbit interaction among the states is required for an accurate prediction of the order of the Au_3 electronic states. Since the energy difference between the $^2B_2$ and $^2A_1$ states is very small, in the following calculations of the binding energy of oxygen molecules to the Au_3 cluster, it is assumed that $^2B_2$ is the ground state.

C. Results for Au_3^-

All methods find that the Au_3^- cluster is linear, although local minima are also found in C_{2v} and D_{3h} symmetry. The energies of the C_{2v} $^1A_1$ and the D_{3h} $^3A_1$ states relative to linear $^1\Sigma_g^+$ are shown in Table IV. All methods predict that the $^3A_1$ and $^1A_1$ states are approximately 20 and 40 kcal/mol, respectively, higher than $^1\Sigma_g^+$. However, the methods that include dynamic correlation [MP2, CCSD(T) and MRMP2] all predict significantly shorter distances for all isomers than the other methods (Fig. 2).

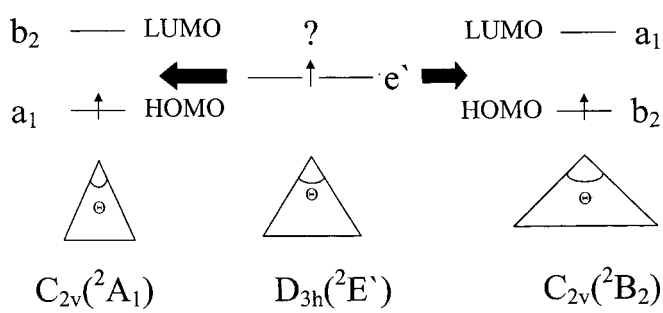

FIG. 1. Jahn–Teller distortion in Au_3 cluster. Highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals of Au_3 are shown.

TABLE III. Bond distances R(Å), angles Θ(deg) and energies ΔE(kcal/mol) relative to $^2B_2$ state of Au_3 at different levels of theory.

	$^2B_2$		$^2A_1$			$^2\Sigma_u^+$	
	R	Θ	ΔE	R	Θ	ΔE	R
HF	2.711	71.8	−1.1	2.983	52.6	1.4	2.701
MP2	2.580	64.3	1.0	2.688	56.3	6.5	2.558
CCSD(T)	MP2[d]	MP2	0.3	MP2	MP2	5.0	MP2
CASSCF(3,3)	2.749	143.5	1.9	3.031	52.2TS[c]	0.0	2.755
MRMP2	2.591	64.9	−0.1	2.681	56.8	34.8	2.629
RB3LYP	2.649	68.6	0.7	2.945	52.2	−0.5	2.628
UB3LYP	2.650	68.5	0.7	2.793	55.7	−0.5	2.630
R-CCSD(T)[a]	2.607	65.4	−4.4	2.723	56.2	58.4	2.573
R-MP2[a]	2.552	65.1	0.9	2.665	56.1	3.2	2.517
MRSDCI[b]	2.60	65.7	0.6	2.72	56.4	⋯	⋯

[a]Relativistic CCSD(T) and MP2 with all electron $(10s7p5d3f)/[10s6p5d3f]$ basis set (Ref. 21).
[b]Multireference single and double configuration interaction with Davidson correction [Ref. 23(a)].
[c]This is a transition state on the potential energy surface.
[d]MP2 geometries.

D. Results for Au_2O_2 and $Au_2(O_2)_2$

The binding energies of the first and second oxygen molecules to the neutral gold clusters were determined from

$$E_{b1}=E[\mathrm{Au}_n]+E[\mathrm{O}_2]-E[\mathrm{Au}_n\mathrm{O}_2],$$

$$E_{b2}=E[\mathrm{Au}_n\mathrm{O}_2]+E[\mathrm{O}_2]-E[\mathrm{Au}_n(\mathrm{O}_2)_2].$$

Here n is the number of atoms in the gold cluster and $E[X]$ is the energy of the ground electronic state of the molecule X. The binding energies of the oxygen molecules to the negatively charged gold clusters were determined in the same way. Positive values for E_{b1} and E_{b2} indicate that adding the oxygen molecule lowers the energy. A negative value indicates that the energy of the oxygenated cluster (although a minimum on the PES) is *higher* than that of the separated reactants.

Au_2O_2 and $Au_2(O_2)_2$ are unstable at both the MP2 and HF levels of theory. In contrast, the previous DFT/PW91 calculation[2] predicts a binding energy of 0.49 eV for the first oxygen molecule and 0.29 eV for the second. There is thus a substantial difference between the DFT and MP2 results.

E. Results for $Au_2O_2^-$ and $Au_2(O_2)_2^-$

As shown in Table V, CCSD(T) theory gives 1.07 eV for the binding energy of O_2 to Au_2^-. This is slightly lower than the value predicted by the B3LYP calculations performed in the present work (1.22 eV), the plane wave PW91 DFT calculations (1.40 eV),[2] and the plane wave PBE DFT calculations (1.39 eV).[4(a)] The experiments of Lee and Ervin[24] give 1.01 ± 0.14 eV. Again, the binding energy predicted by density functional theory is too high. This is not entirely surprising, since it has been noted frequently that DFT tends to "overbind."[25] If this error were systematic, one could "correct" for it and bring the results closer to reality. Unfortunately, as discussed in the following, the errors do not appear to be systematic overbinding.

The CCSD(T) binding energy of the second O_2 to form $Au_2(O_2)_2^-$ is −0.56 eV. The negative value indicates that this local minimum on the potential energy surface is higher in energy than the sum of the energies of the separated $O_2+Au_2O_2^-$. This implies the presence of an intervening barrier for the removal of the second O_2 molecule from the Au_2 cluster. MP2 predicts a negative E_{2b} that is even larger in

TABLE IV. Bond distances R(Å), angles Θ (deg), and energies ΔE(kcal/mol) relative to Au_3^- $^1\Sigma_g^+$ state at different levels of theory.

	$^1\Sigma_g^+$	$C_{2v}(^1A_1)$			$D_{3h}(^3A_1)$	
	R	ΔE	R	Θ	ΔE	R
HF	2.711	37.1	3.326	46.2	18.8	2.880
MP2	2.550	37.8	2.785	53.6	23.4	2.664
CCSD(T)	MP2[b]	36.0	MP2	MP2	24.4	MP2
CASSCF(3,4)	2.718	40.5	MP2	MP2	24.2	2.880
MRMP2	2.559	38.8	MP2	MP2	18.4	MP2
B3LYP	2.631	38.9	2.945	52.2	28.4	2.78
R-CCSD(T)[a]	2.573	41.3	2.844	53.4	29.1	2.717
R-MP2[a]	2.511	45.4	2.792	52.7	30.0	2.647

[a]Relativistic CCSD(T) and MP2 with all electron $(10s7p5d3f)/[10s6p5d3f]$ basis set (Ref. 21).
[b]MP2 geometries.

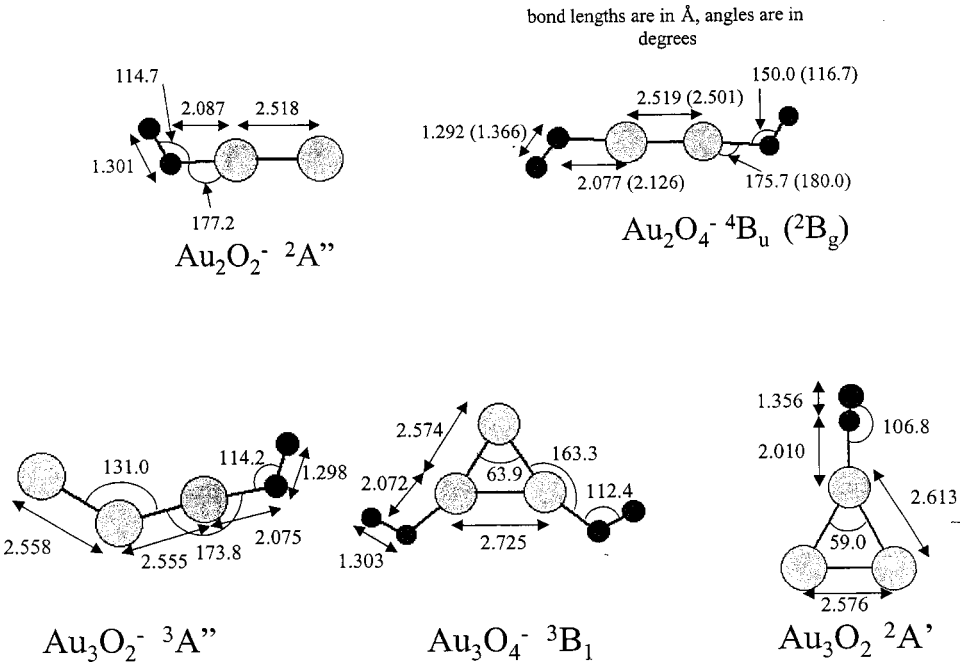

FIG. 2. MP2 optimized geometries of the lowest electronic states of $Au_2O_2^-$, $Au_2(O_2)_2^-$, $Au_3O_2^-$, and $Au_3(O_2)_2^-$, and Au_3O_2 complexes. For $Au_2(O_2)_2^-$, the geometries of the lowest quartet and doublet states are shown.

magnitude. Plane wave DFT/PW91 calculations give a binding energy, $E_{2b}=0.71$ eV, that is opposite in sign to the CCSD(T) and MP2 results. The discrepancy between the MP2 and CCSD(T), on the one hand, and the DFT calculation on the other, is substantial and again suggests that this level of theory tends to severely overbind oxygen to Au clusters.

Salisbury, Wallace, and Whetten[26] found that negatively charged Au clusters (a) will not adsorb O_2 if the cluster has an even number of electrons, and (b) will adsorb one O_2 molecule, but not a second one, if the cluster has an odd number of electrons. The MP2 and CCSD(T) results are in agreement with these experimental results, while the plane-wave DFT/PW91 results are not. The fast-flow reactor method used by Salisbury *et al.* has some limitations, as discussed recently by Wallace, Leavitt, and Whetten.[27] However, the experimental results taken together with the MP2 and CCSD(T) calculations provide reasonable evidence that DFT does not describe the $Au_2(O_2)_2^-$ complex correctly.

Figure 3 illustrates the manner in which the electronic states of Au_2^- and two O_2 molecules may correlate with the electronic states of $Au_2O_2^-$ and $Au_2(O_2)_2^-$. The ground state of $Au_2(O_2)_2^-$ is a quartet, whereas the ground states of Au_2^- and $Au_2O_2^-$ are doublets, and that of O_2 is a triplet. Therefore, Au_2^- and O_2 can spin couple to produce either a doublet or a quartet. The present calculations, as noted earlier, predict that the doublet is the ground state. So, there is no crossing of the doublet and quartet potential energy surfaces as the first oxygen molecule is added to the Au_2 cluster. Adding the second O_2 to the ground doublet state of $Au_2O_2^-$ can again produce either a doublet or a quartet. In this case, the calculations predict that the ground state of the product $Au_2(O_2)_2^-$ is the quartet. So, at some point between $Au_2O_2^-+O_2$ and $Au_2(O_2)_2^-$, the doublet and quartet potential energy surfaces cross. While an exhaustive study of these potential energy surfaces is beyond the scope of the present work, these results suggest that nonadiabatic interactions, such as spin–orbit coupling, could be important in this region of the potential energy surfaces.

The fact that the energy of $Au_2(O_2)_2^-$ is higher than that of $Au_2(O_2)_2^-+O_2$ indicates that at equilibrium the probability of observing this cluster with two oxygen molecules on it is small. This is consistent with the experiments of Salisbury *et al.*, assuming the clusters are in thermal equilibrium in their experiment. The results of the DFT/PW91 calculations, according to which the second oxygen binds strongly, are compatible with the experiments only if it is valid to assume that the rate of the reaction $Au_2O_2^-+O_2 \rightarrow Au_2(O_2)_2^-$ is so

TABLE V. Au_2^-. Binding energies (eV) for the first, E_{b1}, and the second, E_{b2}, O_2.

	HF	MP2	CCSD(T)	B3LYP	PW-PW91[a]
E_{b1}	0.69	0.51	1.07	1.22	1.40
E_{b2}	−0.52	−1.57	−0.56	[b]	0.71

[a]DFT with plane-wave basis set and PW91 functional (Ref. 2).
[b]The B3LYP calculation for E_{b2} did not converge.

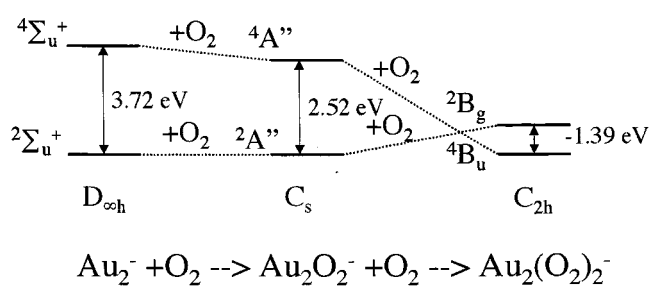

FIG. 3. Correlation of the electronic states of Au_2^- and two O_2 molecules with the electronic states of $Au_2O_2^-$ and $Au_2(O_2)_2^-$.

TABLE VI. Au_3/Au_3^-. Binding energies (eV) for the first, E_{b1}, and the second, E_{b2}, O_2. Unstable means that the molecule does not bind. Because of this CCSD(T) cannot be performed. B3LYP converged only for Au_3, E_{b1}.

	HF	MP2	CCSD(T)	B3LYP	PW-PW91[a]
Au_3^-, E_{b1}	−0.38	−1.10	−0.38		0.37
Au_3^-, E_{b2}	0.57	0.52	1.07		0.70
Au_3, E_{b1}	−0.14	−0.68	0.08	0.19	0.90
Au_3, E_{b2}	Unstable	Unstable			0.59

[a]DFT with plane-wave basis set and PW91 functional (Ref. 2).

low that $Au_2(O_2)_2^-$ is not formed during the experiments. However, the most plausible conclusion is that the DFT calculations are in error.

These results for $Au_2(O_2)_2^-$ are relevant to the mechanism for CO oxidation by a Au_2^- cluster proposed by Hakkinen and Landman.[4(a)] Based on DFT calculations, they proposed that catalysis takes place by adsorption of O_2 and CO to form a carbonate. These authors did not consider the possibility that a second oxygen molecule may adsorb on the cluster, blocking CO adsorption. The DFT/PW91 calculations,[2] which give (probably incorrectly) the binding energy for the second oxygen to be 0.71 eV, indicate that the rates of adsorption and desorption of the second oxygen ought to be included as one of the steps in the kinetic scheme. The present MP2 and CCSD(T) calculations show, however, that $Au_2(O_2)_2^-$ is an unstable local minimum, so its formation will not affect CO oxidation. Another rationale for ignoring the adsorption of a second oxygen molecule in the CO oxidation process is the large predicted adsorption energy of CO.[4(a)]

F. Oxygen binding to Au_3

The binding energies of one or two oxygen molecules to the Au_3 cluster are given in Table VI. CCSD(T) predicts the first oxygen molecule barely binds to Au_3 ($E_{b1}=0.08$ eV) while DFT/PW91 predicts a binding energy of 0.90 eV.[2] This degree of overbinding predicted by DFT is too large to be considered modest or systematically correctable. Both MP2 and HF predict a negative value for E_{b1}, while B3LYP predicts +0.19 eV. It is interesting that in this case the Gaussian-based hybrid functional is in considerably better agreement with the benchmark CCSD(T) calculations than is the plane wave-based PW91 approach. Mills, Gordon, and Metiu[2] extended, to neutral gold clusters, the rules proposed by Salisbury *et al.*[26] for adsorption of oxygen on negatively charged gold clusters. This extension, which was supported by the prior plane wave DFT/PW91 results,[2] postulates that oxygen binds weakly to neutral Au clusters having an even number of electrons, and more strongly to those having an odd number of electrons. The present CCSD(T) results are clearly incompatible with this conjecture.

The PW91 calculations predict that the binding energy of the second oxygen molecule to Au_3 is fairly strong (0.59 eV), whereas CCSD(T) predicts no binding. Clearly, the DFT/PW91 predictions for oxygen binding to Au_3 are in strong disagreement with those of CCSD(T).

G. Oxygen binding to Au_3^-

As shown in Table VI, for $Au_3O_2^-$, CCSD(T) predicts a bound state whose energy *exceeds* that of the separated Au_3^- and O_2, in their ground state, by 0.38 eV; that is, E_{b1} is negative. MP2 predicts the binding energy to be even more negative. In contrast, DFT/PW91 calculation finds that the energy of the bound state of $Au_3O_2^-$ is 0.37 eV below that of the fragments; that is, E_b is predicted to be positive. Therefore, the rule proposed by Salisbury *et al.*,[26] that oxygen does not bind to the cluster Au_3^-, because it has an even number of electrons, is in agreement with the CCSD(T) and MP2 results. The DFT calculation is in quantitative disagreement with this rule, since it indicates binding. However, DFT/PW91 does predict that the binding of one O_2 molecule to Au_3^- is much weaker than the binding to Au_2^-, in qualitative agreement with the rule of Salisbury *et al.*

Of the compounds studied here, $Au_3(O_2)_2^-$ is the most surprising: the CCSD(T) binding energy of the second oxygen, E_{b2}, is 1.07 eV. This means that the energy

$$E_{b2}+E_{b1}=-E(Au_3(O_2)_2^-)+E(Au_3^-)+2E(O_2)$$

for forming $Au_3(O_2)_2^-$ from oxygen and Au_3^-, is $1.07+(-0.38)=0.69$; that is, the complex is stable with respect to separated 2 O_2 and Au_3^-.

This result seems to imply that the complex $Au_3(O_2)_2^-$ should be observed in the experiments, even though it is not seen. However, the absence of the complex in the experiments may be rationalized as follows. At the pressures used in the experiments, three-body collisions of Au_3^- with two oxygen molecules are very unlikely. Therefore, the complex must be formed by successive adsorption of oxygen molecules. However, the probability of forming $Au_3O_2^-$ is extremely low, since its energy exceeds that of separated Au_3^- and O_2. For this reason the rate of forming $Au_3(O_2)_2^-$ should be small. Of course, the fact that $Au_3(O_2)_2^-$ is bound relative to its separated constituents means that it must be present in an equilibrium mixture. However, the kinetics indicates that the time to reach equilibrium must be much longer than that used in the experiments of Salisbury *et al.*[26] Therefore, the absence of $Au_3(O_2)_2^-$ in the experiments is not in conflict with the CCSD(T) results. It does, however, disagree with the DFT/PW91 method, which predicts that clusters with one and two oxygen atoms on them should be observed. Although the experimental error is unknown, the CCSD(T) results are consistent with the available experimental evidence, and this is unlikely to change after a rigorous error analysis of the experiments is performed.

IV. SUMMARY

It is assumed that the CCSD(T) calculations performed here represent the current state of the art, against which the other levels of theory may be measured, especially when experimental data are lacking. Therefore, one concludes that density functional theory works well for the small neutral or negatively charged Au clusters considered here. In particular, DFT gives good results for the binding energy of Au_2, the electron affinity of Au_2, and the geometries of the larger clusters. However, DFT fails badly when it calculates the

binding energies of one or two oxygen molecules to Au_2, Au_2^-, Au_3, and Au_3^-. One may argue that it is more difficult to correctly describe the small clusters than the larger ones, and that the DFT results become better as the number of Au atoms is increased. However, the failure appears to be connected to the O_2 molecule, which is notoriously difficult to describe correctly by quantum chemical calculations. Binding of O_2 to Au_n involves a substantial charge transfer, and describing an O_2 molecule with an excess of electronic charge is even more difficult. There is a chance that binding of other molecules to Au is less demanding. Calculations on the binding of H_2 molecules to neutral and anionic Au clusters are now in progress.

The results presented here do not affect the mechanism proposed by Hakkinen and Landman for CO oxidation by Au_2^-. While the binding energy (1.07 eV) of O_2 to Au_2^- found by CCSD(T) differs from that found by Hakkinen and Landman (1.39 eV), this difference does not affect the qualitative conclusions drawn in their paper. Of course, only one step in their mechanism has been examined here.

It does not appear that the deviations of DFT from the CCSD(T) results are either systematic or predictable by some simple rule. Unfortunately, this means that no guidance can be provided regarding some reasonable corrections to be made when one uses DFT to study oxidation reactions.

The discrepancy between DFT and CCSD(T) is particularly dramatic because oxygen is involved. In a large number of cases, DFT calculations agree well with experiments.[25] We have also found that the results of PW91 DFT and those of B3LYP agree well with the CCSD(T) results for H adsorbed on Au clusters.[30] Moreover, B3LYP calculations in Michael Bowers's group[31] agree well with the binding energies of oxygen to small positive Ag clusters. In this case the binding energy of O_2 is small and the oxygen molecule is not changed much upon binding, resulting in cancellation of the errors made on oxygen molecules. Because the behavior of DFT is not predictable, it is nevertheless important that cases of failure are carefully cataloged and documented along with the successes, to serve as a target for new and more accurate versions of DFT and to warn the users that in certain systems the DFT results should be used with caution.

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