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Model studies of the chemisorption of hydrogen and oxygen on the Au (1 0 0) surface

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Abstract. The convergence of chemisorption energy for hydrogen and oxygen on gold clusters is studied. Two theoretical approaches have been employed; wavefunction methods at the self-consistent-field second–order Møller–Plesset level and density functional theory and the two methods are compared. Relativistic effective core potentials exploited in the former approach were developed in this work.

Key words: Gold clusters – Cluster preparation – Surface – Hydrogen – Oxygen – Chemisorption

1 Introduction

Au, which for a long time has been considered inert and not very useful in catalysis, has lately proved to be quite interesting [1]. For example, small Au particles deposited on metal oxides exhibit high catalytic activity at low temperatures and this can be exploited in a variety of reactions associated with environmental problems, for example, CO oxidation, NO reduction, complete oxidation of hydrocarbons and hydrogenation of CO and CO_2 [2].

The first step in a reaction on any metal surface is the interaction of the isolated reactants with the surface, and it is important to understand the chemisorption mechanism. One model which has been used extensively with considerable success since the early 1980s for theoretical studies of chemisorption and reactions on surfaces, is the finite-cluster model [3–12].

Although the general character of the surface chemical bond is well described by the cluster model, a central problem is the effect of the cluster size and structure on geometries, frequencies and, in particular, binding energies. Reasonably accurate information can be obtained using reasonably small clusters for geometries, frequencies and electronic spectra [5, 13], but binding energies are often more problematic.

There are different ways to compute chemisorption energies, and some methods yield stable results faster than others. Petterson and Faxen [7] showed that convergence of the hydrogen chemisorption enegy on Ni clusters required hundreds of atoms when the chemisorption energy was computed as the energy difference between the ground states of the chemisorbed and dissociated systems. Panas et al. [14] proposed an alternative, the cluster-preparation method, to estimate chemisorption energies on metal clusters. As reference states they used excited cluster states having the proper energy and symmetry to interact with the adsorbate. Stable chemisorption energies were obtained for clusters larger than Ni_{21} but even much smaller clusters provided reasonable results after bond preparation [15].

In the present work we investigated the stability of the chemisorption energy for H and O on a series of Au clusters (Au_5–Au_{50}) which all serve as models of the Au (1 0 0) surface. The cluster geometries were frozen, using geometrical parameters from metallic gold. O chemisorption was studied only at the fourfold hollow position, while for H both the fourfold hollow and the on-top adsorption were examined.

Conserning which quantum chemical method to use there are two choices, wavefunction-based and density-functional-based methods. Both approaches have their advantages and disadvantages.

A complete ab initio wavefunction-based quantum mechanical treatment of metal clusters with, let us say, more than 50 atoms is unrealistic; however, promising approximations do exist. In the work on Ni cited previously effective core potentials (ECPs), which only treat valence electrons explicitly, were used to describe the metal atoms. In the present study we have developed two different relativistic ECPs (RECPs), one with a small core, where the 5*d* orbitals are kept in the

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valence (19RECP), and a large-core RECP (9RECP), where the *d* orbitals are included in the core. Similar potentials were successfully used for clusters of the first-row transition-metal elements Ni and Cu [5, 14, 15]. The transition metals to the right in the first transition row (Co, Ni and Cu) are ideal metals to be described by ECPs where the *d* electrons are included in the core, since the nearly filled *d* shell is well separated from the valence for these metals. However, the *d* shell becomes more chemically active for the heavier metals partly because relativistic effects reduce the energy gap between the valence *s* and *d* shells. The ratio between the expectation value of r^2 for the 4*s* and 3*d* shells in Cu is 3.26, while for Ag it is 2.48 and for Au 1.94 [16]. Hence the inclusion of the *d* shell in the core might be a less satisfactory approximation for the heavier metals.

The flexibility of the *d* shell in Au made models using only large-core ECPs with the 5*d* shell in the core unreliable; however, such ECPs can be used to embed Au atoms described by more accurate ECPs, and in the most efficient model we used 9RECPs to embed a few Au atoms described by 19RECPs. Although this approximation substantially decreased the number of basis functions involved compared to models using only all-electron or full 19RECPs we reached an upper limit with respect to the size of the clusters that we were able to study for Au_{25}–Au_{30}.

An alternative which can handle larger clusters, is provided by density functional theory (DFT). Häberlen et al. [17] found DFT to be successful in a theoretical study of several properties on a series of increasingly large Au clusters, although chemisorption energies were not calculated.

Triguero et al. [18] studied chemisorption of H, O, C, N, CH, CH_2 and CH_3 on small Cu clusters [18] using both DFT and wavefunction-based methods. The results obtained with the PW86 functional were in reasonable agreement with correlated wavefunction results using MCPF, but for other functionals the agreement was less satisfactory. In a study of Pt_5H using the BP86 functional Swang et al. [19] found that the chemisorption energy was underestimated with respect to the experimental value, but attributed this to the small cluster size. Similar discrepancies had been found for other five-atom cluster models (Ni_5H and Cu_5H) but the error was reduced considerably when the clusters were enlarged. Swang et al. also reported results for Pt_9H which appear reasonable, but no comparison to wavefunction calculations was reported. Torras et al. [20] compared second-order Møller–Plesset (MP2) and DFT, using Vosko–Wilk–Nusair (VWN)/Perdew and Wang/Perdew functionals, for several properties of Cu_5O, Cu_5N, Ag_5O and Ag_5N. While the binding energy of Cu_5N was well described, DFT overestimated the binding energy compared to MP2 by 20–40 kcal/mol for the remaining systems. DFT results for Cu_5O agreed with experiment but this might be a coincidence owing to the small cluster size. The B3LYP hybrid exchange-correlation functional gave results close to the MP2 values with respect to chemisorption energies of ethylene in different positions on the Si_5^+ cluster [21].

One of the main objectives in the present work is to perform a systematic comparative study of self-consistent-field (SCF)/MP2 and DFT methods applied to O and H chemisorption on Au clusters.

2 Computational details

2.1 The wavefunction-based calculations

The calculations were done using both ECP-based and all-electron based models. The RECP method used is described in detail elsewhere [22, 23].

The all-electron Au basis consisted of 19s, 16p, 11d and 5f primitive functions which were optimized in nonrelativistic atomic calculations [24]. Relativistic effects were included in the all-electron calculations by the Douglas–Kroll transformation [25–27]. Atomic orbitals for the $(d^{10}\ s^1)^2S$ ground state were used to determine all contraction coefficients except for the 6*p* orbital, which was taken from a calculation on the $^2P(d^{10}\ p^1)$ excited state.

Two different RECPs, were developed a small-core RECP, with a valence consisting of the 5*s*, 5*p*, 5*d* and 6*s* orbitals, (19RECP), and a large-core RECP, where we also included the 5*d* orbitals in the core leaving the 5*s*, 5*p*, and 6*s* electrons in the valence (the 9RECP), were developed. The RECP parameters were optimized to reproduce relativistic all-electron results for the atomic valance orbital energies and shapes.

The primitive all-electron basis set was replaced by (9s, 9p, 8d) and (9s, 9p) primitive functions for the 19RECP and 9RECP valence bases. The outermost exponents were taken from the all-electron basis set and the inner exponents were optimized to fit the all-electron atomic orbitals. Both the 19RECP basis and the all-electron basis were augmented with one d function and three f functions to account for polarization. A general contraction scheme was used, and the final contracted basis set consisted of 3s, 3p, 3d and 2f. Electron correlation was treated on the MP2 level and only the 6*s* and the 5*d* electrons were correlated on the Au atoms. The 19RECP and 9RECP parameters are given in Ref. [28].

The MOLCAS4 program [29] and the direct SCF/MP2 program SUPERMOLECULE were used in the wavefunction-based calculations. In both programs relativity is included through the Douglas–Kroll procedure [25, 30].

The all-electron and RECP calculations were carried out on SGI Origin 2000 machines in Bergen and on a HP V2500 at the university of Tromsø. The MP2 calculations of the largest RECP clusters were done on the Cray C90 machines at the University of Minnesota, Supercomputer Institute.

2.2 The DFT calculations

The DFT calculations were done using the Amsterdam density functional (ADF) program [31–34]. A triple-zeta Slate-type orbital basis set (designated as basis set IV in the ADF library) was used throughout. The local part (local density approximation, LDA) of the exchange-correlation potential, $V_{xc}(r)$, was represented by the VWN functional [35] and the nonlocal part by the gradient corrections proposed by Becke [36] and Perdew [37]. Relativistic effects were treated within the quasirelativistic approximation using the first-order scalar relativistic Pauli Hamiltonian, diagonalized in the nonrelativistic basis set [38]. All atoms (except for H) in the ADF are normally treated using a frozen-core approximation. The K and L shells and the 5*s* and 5*p* were kept frozen on Au, and the 1*s* shell was frozen on O.

The ADF calculations were done on the HP V2500 at the Univertsity of Tromsø and on a Cray T3E at NTNU, Trondheim.

3 The accuracy of the models

Two different active sites on Au (1 0 0) were considered, the fourfold hollow site and the on-top site. We denote the different clusters by Au_n (n_1, n_2, n_3), which means that there are n_1 Au atoms in the first, n_2 in the second and n_3 in the third layer and where $n_1 + n_2 + n_3 = n$. Au_5 is the smallest cluster modeling the fourfold hollow site and all the larger clusters contain this Au_5 (4, 1, 0) cluster in the center. The geometries are fixed during the calculations, where the Au–Au bond distances are set equal to the experimental value of the bulk, 2.88 Å. All the clusters used have C_{4v} symmetry.

3.1 *Wavefunction-based models*

3.1.1 9RECP and 19RECP clusters

All-electron and 19RECP calculations were carried out at the SCF level for several states of the Au atom. The computed excitation energies are presented in Table 1. The quality of the 19RECP is quite satisfactory. The deviation from the all-electron results is on the average about 3 kcal/mol, which is of the same order as in other RECP calculations. In addition, the agreement with MRCI(SD) calculations on AuH is satisfactory [28].

The Au_5 system is the smallest cluster that can be used to model the fourfold hollow site on the (1 0 0) surface and it is essential that the RECPs are able to describe adsorption on this cluster correctly. We therefore carried out SCF and MP2 calculations on Au_5H and Au_5O both at the all-electron and the 19RECP levels. A satisfactory agreement for both the dissociation energy and the equilibrium was obtained (Table 2).

In previous studies on Ni and Cu clusters Siegbahn and coworkers [5, 39, 40] concluded that although the 3*d* orbitals were not invloved in the bonds to the adsorbate they were polarized away from the bonding area, and this polarization was energetically important. They successfully optimized an ECP for Ni and Cu, with the 3*d* orbitals included in the core, where the polarization of the 3*d* orbital was mimicked by an attractive projection operator of d type optimized to reproduce both bond distances and binding energies for H and O correctly on the five-atom clusters. However, the development of a 9RECP for Au turned out to be more demanding. In the same spirit as in Refs. [5, 39, 40] we tried to adjust the potential by adding an extra attractive diffuse d type projection operator which could mimic the polarization of the *d* shell; however, we did not succeed in reproducing the all-electron and 19RECP results for AuH, Au_5H and Au_5O simultaneously. The best compromise for Au_5H and Au_5O binding energies and distances gave the results presented in Table 2. From the numbers in Table 2 it is clear that the potential is too repulsive and cannot be used by itself to predict quantitative results for chemisorption energies and geomtries.

Table 1. Excitation energies (kcal/mol) calculated at the self-consistent-field (*SCF*) level for the gold atom

State	Electronic configuration	All-electron	RECP
^2S	$d^{10}s^1$	0.00	0.00
^2D	d^9s^2	41.34	38.22
^2P	$d^{10}p^1$	95.91	95.93
^4F	$d^9s^1p^1$	114.58	111.52

An important prerequisite for the large-core approximation is that role of the 5*d* orbitals in the chemisorption process is cluster-specific, such as relaxation or hybridization with the *sp* band, and that they do not contribute significantly to the covalent bonds. In contrast to Ni and Cu this is apparently not the situation in Au clusters; however, the population analysis does not show any important *d*-orbital participation in the chemisorption bond. In fact, in Table 3 the population analysis of Au_5, Au_5H and Au_5O shows that the *d* occupation of 9.9 electrons in Au_5 does not change significantly upon chemisorption of H and O. The difference between Au and the lighter elements is rather a very strong mixing between the 5*d* orbitals and the 6*s* – 6*p* band, including that the *d* orbitals participate actively in the covalent bonding in the cluster. A contributing factor to the strong *d*–*sp* mixing is probably the rela-

Table 2. 19RECP results compared to all-electron results for Au_5H and Au_5O. The $^4A_1$ state of Au_5 is used as a reference for the binding energies (kcal/mol). For Au_5H we used the $^3A_2$ state and for Au_5O the ^2E. Bond lengths are given in Ångstroms

	All-electron		19RECP		9RECP	
	R_e	D_e	R_e	D_e	R_e	D_e
Au_5H/Au_5, $^3A_2/^4A_2$						
SCF[a]	1.33	−1.91	1.31	−1.87	1.6	−11.64
MP2[a]	1.03	21.84	1.05	22.29		
SCF[b]	1.30	−1.32	1.30	−1.49		
MP2[b]	0.92	21.83	0.92	22.26		
Au_5O/Au_5, $^2E/^4A_2$						
SCF[a]	1.10	−41.52	1.06	−39.76	1.62	−33.61
MP2[a]	1.16	53.99	1.14	55.89		
SCF[b]	1.07	−37.59	1.01	−36.33		
MP2[b]	1.07	53.71	1.09	51.83		

[a] Without f functions
[b] With f functions

Table 3. Mulliken population of Au_5H and Au_5O from 19RECP SCF calculations without f functions

	Au			Total
	s	*p*	*d*	
Au_5 $^4A_2$				
Au 1 layer	2.95	6.31	9.91	19.11
Au 2 layer	2.82	6.25	9.91	18.97
Au_5H $^3A_2$				
Au 1 layer	2.97	6.13	9.98	19.03
Au 2 layer	2.71	6.35	9.91	18.97
H				1.09
Au_5O ^2E				
Au 1 layer	2.88	6.29	9.90	19.07
Au 2 layer	2.75	6.25	9.89	18.88
O				8.40

tivistic contraction of the 6*s* orbital and the simultaneous expansion of the 5*d* orbitals, which increases the overlap between the valence 5*d* band and the 6*s*–*p* band.

3.1.2 Mixed RECP clusters

The repulsive character of the 9RECP is only a problem at rather short distances, whereas at larger distances it behaves very similarly to the 19RECP. Although the 9RECP failed to describe the chemisorption properly the electron distribution is fairly well described.

It thus appeared reasonable to try to use the 9RECP to describe cluster atoms at long distance from the chemisorption site. We did this by keeping a 19RECP representation of the four or five atoms close to the active site, and using the 9RECP for the remaining atoms in the cluster (MIXRECP). This concept, where the adsorbate and a cluster comprising the active-site atoms are described with higher-accuracy methods while coupling this system to a less accurately described lattice, is often referred to as cluster embedding. Whitten and Yang have given a review of embedding schemes in Ref. [13].

We used the MIXRECP approach for clusters larger than nine atoms. In MIXRECP(I) five Au atoms are used to describe the active fourfold hollow site (four Au atoms in the first layer and one in the second layer). However, for large clusters linear dependencies in the basis sets became a problem owing to an important overlap between the 6*p* orbital of the second layer central Au atom with orbitals on the first layer atoms. For the larger cluster we therefore replaced the 19RECP on the second layer atom by a 9RECP and discarded the 6p function for all the 9RECP atoms. This combination, which we labeled MIXRECP(II), was reasonably accurate. For Au_9 the D_e increased by 2.75 kcal/mol, whereas the bond distance remained unchanged. Minot and Markowitz [41] also found that in bulk metal calculations the *p* valence orbital occupation is, in general, low and they could be withdrawn from a basis set without a significant loss of accuracy.

In order to assess the accuracy of the MIXRECP schemes we compared them with 19RECP calculations of Au_9H, $Au_{13}H$ and $Au_{17}H$. Table 4 shows a satisfying agreement. The deviation in D_e is less than 1 kcal/mol and the R_e differ by no more than 0.04 Å.

3.2 DFT-based models

One of the main objectives of this work was to compare DFT- and wavefunction-based methods for Au clusters. In Table 4 we show computed distances and chemisorption energies obtained with both wavefunction-based methods and with DFT, using the ADF program. The correspondence between DFT (Becke Perdew, BP) and SCF/MP2 is rather good with regard to D_e and R_e, whereas the LDA gives much higher binding energies. This was somewhat expected since the LDA tends to overestimate bond strengths, owing to an overestimate of the correlation energy. This was pointed out by Jensen in Ref. [42].

The correlation energy contributes significantly to the chemisorption energies. Dynamical correlation effects account for 30–50% of the chemisorption energy, regardless of the cluster size.

Table 4. Hydrogen and oxygen chemisorption on different clusters. Several methods are compared. D_e denotes the dissociation energy (kcal/mol) of the absorbate from the cluster and R_e is equilibrium distance (Å). For each system, the same electronic state is considered when different methods are compared

System	All-electron		19RECP only		Mix-RECP(I)		Mix-RECP(II)		ADF BP	ADF LDA	9RECP SCF
	SCF	MP2	SCF	MP2	SCF	MP2	SCF	MP2			
$Au_5H(4, 1)$											
R_e	1.33	1.03	1.31	1.05				1.19	1.03	0.87	1.6
D_e	−1.91	21.84	−1.87	22.29				28.17	21.90	35.50	−11.64
$Au_9H(4, 5)$											
R_e			0.93	0.67	0.91	0.71	0.91	0.71	0.70	0.57	
D_e			30.10	46.48	31.26	46.05	33.71	48.80	47.48	61.78	
$Au_{13}H(12, 1)$											
R_e			1.14	0.93	1.18	0.91			0.93	1.16	1.46
D_e			16.53	31.03	16.70	32.85			31.6	43.7	14.33
$Au_{17}H(12, 5)$											
R_e			0.79		0.79	0.51			0.59	0.48	
D_e			28.45		29.05	52.66			51.4	56.4	
$Au_{21}H(12, 9)$											
R_e					0.63	0.46			0.55		
D_e					43.48	57.21			56.3		
$Au_{21}H(12, 5, 4)$											
R_e								1.01	0.97		
D_e								32.98	32.14		
$Au_5O(4, 1)$											
R_e			1.06	1.14					1.22		1.62
D_e			−40.9	44.34					44.91		−33.61

Since DFT/BP provided the same accuracy as SCF/MP2 the cluster convergence was studied at the DFT/BP level.

4 Cluster convergence

When Siegbahn and Wahlgren [5] and Panas et al. [14] used the ground states at long and short distances for H and O chemisorption on Ni and Cu they found strong oscillations in the calculated chemisorption energy for a series of cluster from M_5 to M_{50} (M is Ni or Cu). However, when they "prepared" the clusters for bonding, as suggested in Ref. [14], the oscillation were damped significantly and the binding energy stabilized to values close to experiment [5, 14, 43, 44].

One important difference between Au clusters and Ni and Cu clusters in that the *d* orbitals are more active in Au than in Ni and Cu. It is therefore not clear if the same bond preparation principle as was used for Ni and Cu can also be applied for Au. Häberlen et al. [17] studied convergence of some bulk properties of Au by the DFT approach. Their results demonstrated an important contribution of 5*d* in the HOMO of Au_{147}. They also observed a marked dependence of the cluster size on the density of states, from Au_{13} having a sparse and discrete spectrum to Au_{147} with a continuous bandlike structure and with Au_{55} lying in some sense in between.

All calculations reported in this section were done using the gradient-corrected LDA.

4.1 O chemisorption at the fourfold hollow site

O chemisorption energies were calculated at the fourfold hollow site for 11 Au clusters ranging from Au_5 to Au_{50}. The results for O chemisorption are shown in Table 5.

Let us first consider the chemisorption energies obtained using the actual ground states at long and short distances, the first entry in Table 5. In this case the O cluster binding energy increases with cluster size but seems to stabilize above Au_{25} to values in the range 60–64 kcal/mol. Only Au_{25} (12, 9, 4) deviates somewhat, with a binding energy of 69 kcal/mol. The calculated chemisorption energy for the two smallest clusters, Au_5 and Au_9, is only 45 kcal/mol. The ground state of Au_5 is $^2\mathrm{E}(a_1^2e^3)$, which also is the ground state at the correlated level for Cu_5. The mean value for all the clusters is 56.95 kcal/mol and the standard deviation is 7.41 kcal/mol. If the two smallest clusters are ignored, the mean value of D_e increases to 59.56 kcal/mol and the standard deviation is reduced to 5.44 kcal/mol.

The reaction mechanism was analyzed by considering the orbital occupations of the bare clusters and of the chemisorbed systems. In Table 5 we also show the configurations before and after chemisorption in separated columns which are divided into an O configuration column and a cluster configuration column. We show only orbitals where the occupation is changed during the chemisorption.

O by itself has a triplet ground state, which in C_{4v} notation can be described by the valence occupation $a_1(2)e(2)$, with a doubly occupied $2p_z$ orbitals in A_1 symmetry and a doubly occupied but doubly degenerate orbital in E ($2p_x$ and $2p_y$). In the chemisorbed state O has the formal electron configuration $a_1(2)e(4)$, corresponding to O^{2-}. In order to attain this "oxo-oxygen" state two electrons have to be transferred to the E symmetry during the chemisorption process [the process can also be viewed as the formation of covalent bonds in the A_1 (σ) and the E (π) symmetries]. The most common O chemisorption mechanism found by Siegbahn and coworkers on a Ni surface was where the two electrons were transferred from an initially doubly occupied a_1

Table 5. Oxygen adsorption on different gold clusters. $\langle D_e \rangle$ denotes the average value and σ is the standard deviation. From temperature-programmed desorption experiments the value of D_e is estimated to be 56–64 kcal/mol. The change in occupation that occurs during the reaction in the outermost orbitals of the clusters and of oxygen is also shown

Cluster	D_e (kcal/mol)	R_e (Å)	q_o	Cluster configuration	Oxygen configuration	Chemisorbed oxygen	Configuration cluster	Mechanism
Au_5(4, 1)	44.9	1.22	−0.70	$a1(2)e(3)$	$a1(2)e(2)$	$a1(2)e(4)$	$\mathrm{a}1(2)e(1)$	D^1
Au_5(4, 1)	55			$a1(2)a1(1)e(2)$	$a1(2)e(2)$	$a1(2)e(4)$	$a1(1)e(2)$	B
Au_5(4 ,1)	89.7			$a1(2)a1(2)e(1)$	$a1(2)e(2)$	$a1(2)e(4)$	$a1(2)e(1)$	A
Au_9(4, 5)	45.53	1.44	−0.66	$a1(2)b1(1)$	$a1(2)e(2)$	$a1(2)e(4)$	$b1(1)$	A^1
Au_{17}(12, 5)	53.08	1.25	−0.73	$a1(2)e(3)$	$a1(2)e(2)$	$a1(2)e(4)$	$e(3)$	A^1
Au_{21}(12, 9)	57.94	1.21	−0.76	$a1(2)e(3)$	$a1(2)e(2)$	$a1(2)e(4)$	$a1(1)e(2)$	B^1
	56.84	1.18	−0.73	$a1(2)e(3)$	$a1(2)e(2)$	$a1(2)e(4)$	$e(3)$	A
Au_{21}(16, 5)	51.50	1.30	−0.71	$a1(2)e(1)$	$a1(2)e(2)$	$a1(2)e(4)$	$e(1)$	A^1
Au_{21}(12, 5, 4)	54.80	1.23	−0.68	$a1(2)e(3)$	$a1(2)e(2)$	$a1(2)e(4)$	$a1(1)e(2)$	B^1
	62.60	1.23		$a1(2)a1(1)e(2)$	$a1(2)e(2)$	$a1(2)e(4)$	$a1(1)e(2)$	A
Au_{25}(16, 9)	60.41	1.20	−0.80	$a1(2)b2(1)$	$a1(2)e(2)$	$a1(2)e(4)$	$b2(1)$	A^1
Au_{25}(12, 9, 4)	69.34	1.21	−0.77	$a1(2)b2(1)$	$a1(2)e(2)$	$a1(2)e(4)$	$a1(1)$	C^1
	69.07	1.14		$a1(2)b2(1)$	$a1(2)e(2)$	$a1(2)e(4)$	$b2(1)$	A
Au_{29}(16, 9, 4)	61.9	1.23	−0.72	$a1(2)e(1)$	$a1(2)e(2)$	$a1(2)e(4)$	$e(1)$	A^1
Au_{41}(16, 9, 16)	63.2	1.27	−0.74	$a1(2)b2(1)$	$a1(2)e(2)$	$a1(2)e(4)$	$b2(1)$	A^1
Au_{50}(16, 9, 16, 9)	63.9	1.21	0.76	$a1(2)$	$a1(2)e(2)$	$a1(2)e(4)$	$a1(0)$	A^1
$\langle D_e \rangle^{\mathrm{all}}_{(\mathrm{g.st-g.st})}$	56.95	$\sigma^{\mathrm{all}}_{(\mathrm{g.st-g.st})} = 7.41$						
$\langle D_e \rangle^{\mathrm{above}}_{\mathrm{Au_9(g.st-g.st)}}$	59.56	$\sigma^{\mathrm{above}}_{(\mathrm{g.st-g.st})} = 5.44$						

orbital on the cluster to the *e* orbital predominantly on O. The transfer was interpreted by Siegbahn and Wahlgren [5] as being caused by a strong Pauli repulsion in symmetry A_1 owing to the interaction between a doubly occupied cluster orbital and the doubly occupied O($2p_z$) orbital. Formally, this mechanism can also be seen as the addition of a singlet O with the electron configuration e^4 (corresponding to two *p* electrons in p_x and two in p_y). This mechanism is also the most frequent among our results and is labeled A in Table 5.

However Au appears to be much less sensitive than Cu, to which cluster orbitals the two electrons are transferred. In mechanism B, which occurs for Au_{21} (12, 9), the two electrons come from a_1 and *e*. In Au_{25} (12, 9, 4) the electrons come from a_1 and b_2 (mechanism C), and for the smallest cluster, Au_5 (4, 1), both electrons come from a cluster *e* orbital (mechanism D). Except for Au_5 (4, 1), the excitation energy needed to invoke mechanism A is small.

Mechanism A gives a somewhat better convergence than the ground-state to ground-state principle, but the difference is rather small. The mean value for mechanism A is 58.8 kcal/mol and the standard deviation is 6.66 kcal/mol, which is 0.75 kcal/mol less than the standard deviation obtained by the ground-state to ground-state principle. The standard deviation is also somewhat reduced when some of the small clusters are excluded from the series. If only clusters larger than Au_9 are considered, thus ignoring the rather poor results from the two smallest clusters, the standard deviation is 5.44 kcal/mol and the mean value is 59.56 kcal/mol for ground state to ground state. For mechanism A the mean value is 60.27 kcal/mol and the standard deviation 5.25 kcal/mol. If we only consider clusters above Au_{21} (12, 5, 4) we find the smallest standard deviation, 3.04 kcal/mol, and the largest mean value, 63.75 kcal/mol. In general, the largest clusters give rise to the strongest O bonds presumably because they have larger electron reservoirs, which reduce the energy cost needed for the cluster–O electron transfer. Our results are thus compatible to the findings in Ref. [17], where the computed ionization potential decreased from Au_6 to Au_{55}.

In Au_5 no electron transfer occurs across the symmetries during the chemisorption process. The occupied a_1 orbital is a strongly bonding cluster orbital and it is expensive to move electrons from this orbital; however, the next A_1 cluster orbital is available and is well suited for interaction with the $2p_z$ orbital, giving rise to a bond in A_1. Indeed, if we use the $^4A_1(a_1^2a_1^1e^2)$ state of the cluster, which is the ground state for Cu_5 and Ni_5, we are back to mechanism B and the chemisorption energy becomes 55 kcal/mol. Moving to mechanism A we need the second a_1 orbital to be doubly occupied, i.e. we need the cluster state $^4E(a_1^2a_1^2e^1)$. Using this state for the bare cluster we arrive at a chemisorption energy which is unreasonably large, 90 kcal/mol, owing to a very high cluster excitation energy.

Both Au_5 and Au_9 differ from the remaining clusters in that they give much lower values for the chemisorption energies in spite of the fact that Au_9 follows mechanism A. An explanation of the weak O bonds may be that these two clusters are electron deficient. The energy gain from O chemisorption can not compensate for the cost involved in the electron donation from the cluster to the O as efficiently as in the larger clusters. We will show later that electron deficiency also makes the small Au clusters poor models for H chemisorption.

Beside mechanism A Siegbahn and Wahlgren [5] found two more possibilities to prepare Ni clusters, and most of the clusters investigated (Ni_5 Ni_{41}) were prepared for bonding according to one of the principles for the ground state. However, the clusters which were not prepared in the ground state were significantly improved through bond preparation [5]. Again, mechanism A appeared to be much more favorable than the two other mechanisms.

However, in view of our results the best alternative to calculate the O chemisorption energy on Au clusters is to use the ground-state principle.

It seems reasonable to interpret the difference between Au on one hand and Cu and Ni on the other in terms of the active *d* orbitals in Au. The *d* participation in the cluster bonds increases the flexibility of the cluster as the number of cluster bonding orbitals increases and the states become closer in energy. After the electron-transfer process there are many possibilities for reorganization and relaxation of the cluster orbitals. The consequence is, on the one hand, that chemisorption energies computed by the ground-state to ground-state principle oscillate less for Au clusters than for Ni and Cu clusters, but, on the other hand, convergence cannot be accelerated through bond preparation. Therefore chemisorption on Au seems to be more dependent on cluster size than for Ni and Cu. In general, clusters smaller than Au_{21} give too small chemisorption energies, while for Ni and Cu the small clusters reproduced the converged number provided that the clusters were prepared for bonding. Ni and Cu clusters also bind O more strongly (about 110 kcal/mol) than Au.

The difference between Au and the lighter metals Ni and Cu can partly be ascribed to relativistic effects. The larger *d* contribution in the *s*/*p* band in Au occurs because relativistic effects stabilize the *s* orbitals relative to the *d* orbitals and reduce the energy gap between the valence *d* and *s* orbitals compared to Ni and Cu. Thus, the cluster orbitals which are responsible for electron donation to O are more stable for Au. The gain in energy from cluster–O bond formation is thus less for Au and this explains the smaller chemisorption energy and the need for larger and more electron-rich clusters in order to produce a reasonable chemisorption energy.

The "breakdown" of the bond preparation concept for Au is probably connected with to the mixed character of the conduction band. The 5*d* contribution to the bonding introduces a flexibility to the cluster bonds and the reduction in cluster bonding, caused by the electron donation, can be compensated for by new *sdp* hybridizations within the cluster. Hence, the nature of the donating orbital plays a less important role and cluster preparation becomes less important.

From a temperature-programmed desorption experiment of O adsorption on the Au (1 1 1) surface the Au–O bond strength is estimated to be about 56 kcal/mol with an upper limit of 64 kcal/mol [45]. We assume that the bond strength on the Au (1 0 0) surface is of the same order. All our computed mean values are within this range.

4.2 H chemisorption at fourfold hollow and on-top sites

H chemisorption at the fourfold hollow position on Au clusters was studied for Au clusters ranging from Au_5 to Au_{50} and at the on-top position for six clusters from Au_5 to Au_{25}. As for O, the binding energies were computed according to both the bond preparation [D_e (BP)] and the ground-state principles [D_e(GG)]. A cluster prepared for H adsorption must have one singly occupied cluster orbital of A_1 symmetry and moreover, this orbital must be localized at the active site where an overlap to the H(1*s*) orbital can arise when H approaches.

The results are shown in Tables 6 and 7. Both D_e(GG) and D_e(BP) show oscillating patterns as the clusters are enlarged.

Consider first the fourfold hollow site (Table 6). The oscillation in D_e(GG) is reasonably small with a standard deviation of 6.19 kcal/mol with a mean value of 36.46 kcal/mol. Surprisingly, the standard deviation from bond preparation is higher, 9.79 kcal/mol, and the mean value is higher, 40.05 kcal/mol D_e(BP) is, in particular, unstable below Au_{21} (12, 9).

In the ground state of $\mathrm{Au}_5\mathrm{H}$ H enters the surface. This occurs for none of the other clusters, where H is 0.5–1.0 Å above the surface plane. In the first excited state of $\mathrm{Au}_5\mathrm{H}$ the equilibrium distance is 1.03 Å but the binding energy for this state is only 21.09 kcal/mol relative to the Au_5 ground state. The peculiar behavior of Au_5 is due to the shape and the small size of the cluster. The large Au-Au distance, 2.88 Å compared to 2.56 Å in Cu, gives rise to a very open structure. The electrons become localized at the edges, which is reflected by the electronic states. The Au_5 ground state is ^2E; $(a_1^2e^3)$, with the $^3\mathrm{A}_2$; $(a_1^2e^2a_1^1)$ state 10.5 kcal/mol above, while the ground state of both Cu_5 and Ni_5 is $^3\mathrm{A}_2$, $(a_1^2e^2a^1)$. The *e* orbitals have nodes perpendicular to the surface plane, while the second a_1 orbital has a node between the first and the second layer. Since the electron density is low at the hollow site, the H will experience only a small electron repulsion when approaching the surface. The large hole also contributes to the small Pauli repulsion between the H and Au centers. The combined effect is that the repulsion cannot keep the H outside the surface. The electron coming from H enters bonding orbitals in the electron "band" in the electron-deficient cluster and the system becomes stabilized. Mulliken population analysis shows a negative charge of −1.63 on H whereas the first and second layer Au atoms have charges of 0.34 and 0.27, respectively. For comparison, in the larger clusters the charge of H ranges from −0.5 to −0.9.

Table 6. Results from a density functional theory (DFT) study of hydrogen chemisorption on 11 gold clusters. R_e is the equilibrium cluster–hydrogen distance (Å) and D_e (BP) and D_e(GG) are the (bond–prepared and ground-state to ground-state dissocition energies (kcal/mol), respectively). $\langle D_\mathrm{e}\rangle$ denotes the average values and σ is the standard deviation. The numbers in *italic* are explained explicitly in the text

Cluster	R_e	D_e (GG)	D_e (BP)
Au_5(4, 1)	0.0	44.13	
	1.03		*21.09*
Au_9(4, 5)	0.70	39.14	47.5
Au_{17}(12, 5)	0.59	43.25	51.40
Au_{21}(12, 9)	0.55	36.12	56.3
Au_{21}(16, 5)	0.61	42.96	46.42
Au_{21}(12, 5, 4)	0.61	27.51	*63.78*
	0.97		32.14
Au_{25}(16, 9)	0.55	33.79	41.43
Au_{25}(12, 9, 4)	0.55	27.03	33.80
Au_{29}(16, 9, 4)	0.49	34.51	37.38
Au_{41}(16, 9, 16)	0.74	42.50	42.5
Au_{50}(16, 9, 16, 9)	0.61	30.13	30.6
$\langle D_\mathrm{e}\rangle_{\mathrm{all}^\mathrm{a}}$		36.46	40.05
$\sigma_{\text{italic numbers}}$		6.19	9.79
$\langle D_\mathrm{e}\rangle_{\mathrm{selected}^\mathrm{b}}$		35.69	41.95
$\sigma_{\mathrm{selected}^\mathrm{a}}$		5.88	8.12
$\langle D_\mathrm{e}\rangle_{\mathrm{selected}^\mathrm{c}}$		32.57	37.75
$\sigma_{\mathrm{selected}^\mathrm{b}}$		5.26	4.63

[a] For Au_{21} (12, 5, 4) we used the number 32.14 for D_e (*BP*)

[b] The selected set comprises all clusters except Au_5

[c] The selected set comprises Au_{21} (12, 5, 4) and larger clusters

Table 7. On-top hydrogen chemisorption from DFT calculations. Energies in kilocalories per mole and distances in Ångstrom

Cluster	R_e	D_e (GG)	D_e (BP)
Au_5(1, 4)	3.36	55.17	65.62
Au_9(5, 4)	1.59	50.01	58.46
Au_{17}(13, 4)	1.59[a]	63.44	63.44
Au_{21}(9, 12)	1.59[a]	37.88	58.06
Au_{25}(13, 12)	1.59[a]	37.22	57.15
Au_{25}(9, 16)	1.59[a]	29.36	38.59

[a] Not optimized, but the potential surface is very flat and hence optimization would not incluence the dissociation energy remarkably

The ground state of $\mathrm{Au}_5\mathrm{H}$ is a closed-shell singlet state with the electron configuration $a_1(2)e(4)$, while the first excited state is a $^4\mathrm{E}$ state with the electron configuration $a_1(2)a_1(2)e(3)$, 23 kcal/mol above the ground state. In the excited state the Pauli repulsion is increased owing to the excitation of an electron into the a_1 orbital, and H becomes bound 1 Å above the surface plane. The ground-state to ground-state binding energy is 44 kcal/mol, compared to 21 kcal/mol for the $^4\mathrm{E}$ state. However, by comparing with the larger clusters it is clear that the closed-shell ground state of $\mathrm{Au}_5\mathrm{H}$ does not correspond to the situation at a real surface, since the cluster has been artificially stabilized by the electron coming from H. This is further illustrated by the Mulliken population analysis, where the charge on H is a reasonable −0.28 for the excited state compared to −1.6 in the closed-shell ground state.

For a real surface we do not expect large effects on the internal metal–metal bonds as a result of the chemisorption process. If this is the case for a finite cluster, it is likely that the state under consideraion is an artefact of the model. It is thus necessary to inspect the wavefunction for each cluster to ensure that the chemisorbed state is reasonable and not an artefact of the cluster size.

Au_{21} (12, 5, 4) suffers from a similar problem. If we use the ground state of the chemisorbed system and bond-prepare in the usual way, the excitation energy needed for the bare cluster is 36 kcal/mol, giving rise to a chemisorption energy of 64 kcal/mol. The large binding energy is again partly caused by an improved binding in the cluster, and bond preparation thus gives rise to an artificially high chemisorption energy. However, the first excited state of the chemisorbed system is only 2 kcal/mol above the ground state, and bond preparation relative to this state only requires an excitation energy of 7 kcal/mol, yielding a much more reasonable bond-prepared chemisorption energy of 32 kcal/mol.

In addition to the fourfold hollow position we also considered H chemisorption at the on-top site. The results are summarized in Table 7.

The on-top adsorption shows the same trend as the fourfold hollow adsorption with respect to D_e(BP). The values oscillate more than in the fourfold hollow case but seem to approach the fourfold hollow value as the cluster size increases. No stability is obtained even for the largest cluster, Au_{25}, neither for D_e(BP) nor for D_e(GG). Bond-prepared binding energies seem to converge slower than binding energies calculated using the ground states, and bond preparation is thus a less useful concept for Au than for lighter metals.

Consider the Au_{21} (12, 9) and the Au_{25} (16, 9) clusters. The larger surface is to used to model chemisorption at a fourfold hollow position, while the smaller surface can be used to model chemisorption at an on-top position. The fourfold hollow and on-top chemisorption energies for Au_{21} (12, 9), calculated from the ground states, are 36.1 and 37.9 kcal/mol and with bond preparation they are 56.3 kcal/mol and 58.1 kcal/mol. For Au_{25} (16, 9) we obtain 33.8 and 29.4 kcal/mol for the ground states and 41.4 and 38.6 kcal/mol with bond preparation (Table 6, 7) The average value obtained for the difference between chemisorption at the on-top and fourfold hollow positions is 2.7 kcal/mol. Our best estimate of the binding energies is 36 kcal/mol in the fourfold hollow position [the mean value for D_e(GG) in Table 6] and thus 39 kcal/mol for the on-top site (36 + ~3); however, the difference between the two sites is too small to allow any definite conclusion about the preferred chemisorption site.

As a general trend, addition of cluster layers reduces the chemisorption energy for H, but not for O. A speculation is that this is correlated to the increased degree of localization of the cluster orbitals as the clusters are enlarged. Siegbahn et al. [14] observed a similar but much less pronounced trend for Ni_n H.

Electron affinities (EA) have been computed for a series of Au clusters by Häberlen et al. [17]. They found that EA increased (almost linearly) as a function of cluster size. The increase is expected because the number of orbitals which can accommodate extra electrons increases, and the orbitals tend to delocalize over larger and larger clusters. This is consistent with a decreasing H chemisorption energy with cluster size for the larger clusters, since it becomes more and more difficult for the H to get electrons from the cluster. For the small clusters our results cannot be directly compared with the results of Haberlen et al. Since they used highly symmetrical clusters with optimized structures.

While bond preparation could be used for Ni and Cu even if excitations around 30 kcal/mol of the clusters were required, bond preparation cannot be used for H chemisorption on Au. The argument for bond preparation has been that excitations between electronic states on the surface are of negligible cost because of very close lying states in a very dense valence band. On the other hand, our study indicates that the metal bonds are local with a substantial contribution from the *d* orbitals, owing to the overlap of the *s* and *d* bands. This strong intermetal interaction gives rise to a broadening of the valence *d* band and apparently the metal bonds of the surface cannot be modeled by any small cluster. The bonding in the small clusters is strongly affected by the shape, symmetry and size of the clusters, and small clusters are poor models of the Au surface. In addition it is clear that bond preparation is not a useful concept for Au clusters.

On the basis of all our cluster calculations we estimate the atomic H chemisorption energy to be 35–40 kcal/mol. Our results are in fact in reasonable agreement with a recently published DFT study of H adsorption on Au (1 1 1) by means of an Au_{10} cluster [46]. Calculated adsorption energies in threefold hollow and on-top sites were 42 and 33 kcal/mol, respectively. Cluster preparation was not used in that study.

4.2.1 Experimental information

There are very few experimental predictions of the Au surface–H binding energy in the literature; however, there seems to be agreement that atomic H binds strongly to the Au surface although the H_2 molecule does not chemisorb at low temperatures [1, 47–52]. On the other hand, the reactivity of Au is strongly dependent on structure and H_2 is dissociatively chemisorbed on small particles in thin films or powders and on Au clusters [48, 51, 52].

In Ref. [53] D_e is reported to be less than 52 kcal/mol. Stobinski and coworkers [48, 51] studied thin sintered continuous Au film surfaces which consisted mainly of crystallites with dominant (1 1 1) surface planes. The heat of adsorption was 5.02 kcal/mol (6.46 on discontinuous films) and from that we can estimate the surface H bond to be 54 (and 55) kcal/mol if we take into account the H–H bond strength of 103 kcal/mol [54]. The reported numbers are thus very approximate and as the Au reactivity is claimed to be structure-dependent a straightforward comparison between our results of Au (1 0 0) and that of Stobinski and coworkers for the (1 1 1) surface cannot be performed.

Cox et al. [55] observed a strong dependence on the H–H activation with respect to cluster size and on the charge of clusters in an experimental study of small unsupported Au clusters. The reactivity decreased with cluster size and moreover decreased in the order cation clusters > neutral clusters ≫ anion clusters. Conversely, for O the reactivity order reported in Ref. [55] was anion clusters $\gg$ cation clusters. As O accepts electrons from the clusters, larger clusters are preferred because they represent the richest charge sources and the same trend is revealed in our cluster study. The reactivity is not only dependent on the chemisorption bond but also on the activation barriers. We will discuss activation of H_2 on Au else where.

5 Conclusion

In the present article we have studied 17 cluster models of the Au (1 0 0) surface (Au_5–Au_{50}) and we have undertaken a study of the H and O chemisorption energies as a function of cluster size.

The calculations were performed using two different quantum mechanical methods, the wavefunction-based method, at the SCF and MP2 level and using the gradient-corrected DFT method with the exchange–correlation potential, $V_{xc}(r)$, represented by the VWN functional [35] and the nonlocal part by the gradient corrections proposed by Becke [36] and Perdew [37]. The latter was applied to all the clusters, whereas the former only to the smallest where the two methods were compared. We have developed two different RECPs which we used instead of an all-electron description for the Au atoms in the SCF/MP2 calculations. The large-core potential (9RECP) had the 5*d* orbitals included in the core, whereas the small-core potential (19RECP) provided in explicit description of the 5*d* orbitals as they were a part of the valence space. Of course, it would have been desirable to use the 9RECP for all the Au atoms in the clusters, but this was not possible because the 5*d* orbitals are chemically active and contribute to the cluster–adsorbate bonds. We therefore had to resort to an embedding scheme, MIXRECP, where we used the 19RECP for the active-site Au atoms and the 9RECP for the surrounding atoms. This is in contrast to the first-row transition metals Ni and Cu, for which a large-core potential could be used for all the atoms in the clusters, even for the chemically active ones. The applicability of the MIXRECP models reached an upper limit with respect to cluster size at 25–30 Au atoms owing to computational demands. DFT, on the other hand, is a much less resource demanding method, and was applicable to all the clusters. An evaluation of the DFT method against wavefunction methods on those systems was, however, essential, and the agreement was satisfactory.

The chemisorption energy as a function of cluster size showed an oscillating pattern. For the lighter metals, Ni and Cu, a smoother convergence pattern was obtained using the cluster preparation principle suggested by Panas et al. [14]. However, the cluster preparation method could not be used for the Au clusters because of the active role played by the *d* orbitals in Au. In order to model the surface reactions on Au we therefore have to resort to larger clusters.

We only studied the fourfold hollow adsorption of O but for H we, in addition considered on-top chemisorption for clusters of up to 25 atoms. It was not possible to find a completely stable value for the chemisorption energy at the on-top site from these results only, but by comparing chemisorption at the on-top and fourfold hollow sites for similar clusters we can conclude that the chemisorption energies at these sites are comparable. Our best estimate of the chemisorption energy of H both at the fourfold hollow and the on-top sites is 35–40 kcal/mol. For O we estimate the chemisorption energy to be about 60 kcal/mol.

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