

A theoretical study of the interaction of water molecules with the Cu(100), Ag(100) and Au(100) surfaces

Anna Ignaczak¹, J.A.N.F. Gomes^{*}

CEQUP / Faculdade de Ciências, Universidade do Porto, Rua do Campo Alegre 687, P-4150 Porto, Portugal

Received 28 March 1996; accepted 20 May 1996

Abstract

The interaction of a water molecule with copper, silver and gold surfaces has been studied using a cluster model approximation. The B3LYP method has been used to introduce a correlation effect into this type of calculation. Since this is a relatively new technique, its performance in conjunction with different basis sets has been tested using the Cu–H₂O system as a test case. These tests were performed to select the basis sets for water and metal atoms to be used in studies on the water–metal cluster interaction. Additionally, a set of B3LYP calculations for the Cu_n–H₂O ($n = 2, 4, 5, 9, 12$) systems has been performed to investigate the influence of the metal cluster size on the results. Significant variations in the quantities computed have been found for the smaller clusters, while for the larger ones, a degree of convergence seems to be achieved. Thus, the Cu₁₂, Ag₁₂ and Au₁₂ clusters have been used to mimic the (100) crystallographic plane of noble metals. The comparative results of the water–metal interaction for three different positions (on-top, bridge and hollow) are given; for each site the results for three different orientations of H₂O molecule are shown. Two preferred conformations, bridge-perpendicular and top-tilted, have been found to be effectively indistinguishable in terms of adsorption energy; in both, water adsorbs via its oxygen end. For the on-top site, the tilt angle between the H₂O molecular plane and the normal to the metal surface has been found to be in the range 50–65°, depending on the metal. The copper has been found to be the most hydrophilic metal ($\Delta E_{\text{ads}} = -31.8 \text{ kJ mol}^{-1}$) when compared with less attractive gold ($\Delta E_{\text{ads}} = -29.7 \text{ kJ mol}^{-1}$) and silver ($\Delta E_{\text{ads}} = -26.6 \text{ kJ mol}^{-1}$). The results obtained from our calculations are compared with some earlier theoretical results and with the experimental data available.

Keywords: Water adsorption; Noble metals surfaces; Cluster calculations; B3LYP

1. Introduction

The interaction of water with metal surfaces is a topic of interest in many areas of science. Extensive studies of the adsorption of water on metals have been performed using many different experimental techniques (see Refs. [1,2] for comprehensive reviews, and Refs. [3–8] for more recent results). However, the detailed description of the bonding of a water molecule onto the surface is still open to discussion. In the experimental conditions used to probe this problem, many other processes (e.g. the formation of water clusters near the surface, the dissociation of the water molecule, or redox phenomena) normally occur. The role that the water–metal interaction plays in these experimental results is not easy to ascertain. Additionally, the

likely occurrence of surface defects or surface reconstruction may perturb the structure and chemistry of the interface, thus making the interpretation of the results in terms of a pure crystallographic plane very risky. This type of difficulty has been considered in some recent work [9,10] that stresses the uncertainties of some earlier experimental studies where an ideal surface structure is simply assumed. However, from the wide variety of measurements that have been published, a general approximate picture emerges for the adsorption of water on metallic surfaces. Indirect spectroscopic evidence [11,12] seems to indicate that the water molecule is adsorbed on smooth (100,111) surfaces either on the on-top site or the two-fold bridge site but not on the four-fold hollow site [13]. A stronger preference for the on-top position is suggested by the EELS studies of Andersson et al. [12] for Cu(100) and Pd(100) at low temperatures. From the vibrational spectra, it was concluded that the molecular axis of water is tilted by ca. 60° relative to the normal to the surface. This was to be expected if it is

^{*} Corresponding author.

¹ On leave from the Department of Theoretical Chemistry, University of Łódź, Poland.

assumed that the bonding to the metal occurs through the lone-pair orbitals of the oxygen. This tilt could also be explained by hydrogen bonding between two water molecules adsorbed at neighbouring metal atoms; however, Andersson et al. [12] have argued that this is incompatible with the observed vibrational frequencies of adsorbed water. The chemical character of the water–metal bonding is confirmed by the decrease of the work function Φ of the electrode under water adsorption as a consequence of the sizable charge transfer from water to the metal [1]; this may also suggest that the water dipoles tend to orient perpendicular rather than parallel to the surface. Most experimental work reports only a slight perturbation of the structure of bulk water near the surface.

Another well established feature is the low barrier found by water migrating along the surface. This relative freedom of movement, even at low temperatures, explains the formation of water clusters at the surface, even at low coverage. The formation of these clusters, compounded by the other phenomena occurring at the surface as mentioned above, makes interpretation of the experimental results very difficult and often ambiguous.

A theoretical approach to this problem may be very useful in the interpretation and corroboration of experimental data. Accurate quantum chemical methods cannot presently be used to compute the interaction of a particle (ion or molecule) with an infinite metallic surface. The alternative commonly used consists of modelling the surface by an atomic cluster of a size as big as possible within the computational capabilities available. In this way, one tries to minimize the size dependence effect, which is difficult to predict, and hopes to approach the description of the actual metal with its conduction band electrons.

For this type of calculation, methods based on density functional theory (DFT) are becoming increasingly popular as they have some cost-effective advantages over standard ab initio methods. These DFT algorithms have a computational cost comparable with pure Hartree–Fock (HF) methods but include some electron correlation effect which is likely to be important for the interaction. In the past, most water–cluster calculations have been done at the simple HF [14–16] or, more frequently, at the semiempirical [17–22] levels. Other computational methods have also been applied to this problem [23–29], most of them not including electron correlation. The metal clusters are usually designed to reproduce a piece of metal near the surface, this being taken to be parallel to a well-defined crystallographic plane. In most cases, the results of these calculations do appear to show that the on-top position is preferred, i.e. the placement of the water molecule above one of the metal atoms of the surface, in accordance with the common interpretation of experimental data. Most of these calculations predict a tilt angle of about 60°. However, non-tilted conformations are also found in the literature, either as the result of calculation or as an initial assumption. Bauschlicher [14] showed for the Ni₁₄(100)–

H₂O cluster that the on-top position (untilted) is only slightly preferred to the two-fold bridge site, that is a few kilojoules per mole less stable, thus making the two positions essentially indistinguishable. The two-fold bridge site has been found to be energetically favoured for the Fe₅(100) cluster in Anderson's work [23]. The three-fold hollow site of Pt(111) [17] and the four-fold hollow site for Cu(100), Ag(100) and Au(100) [22] were found to be energetically favoured for water adsorption.

The magnitudes of the calculated adsorption energies of water on the metal clusters do show very large variations: –210 kJ mol⁻¹ for the Fe(100) [23] and only –17.5 kJ mol⁻¹ for Ni(100) [14]. Experimentally, only a crude evaluation of this quantity is possible, the value most commonly quoted being between –40 and –50 kJ mol⁻¹ for non-dissociative adsorption of water on metal surfaces. It should be clear that in a theoretical approach the results of calculations depend markedly on the method, as well as on the basis sets used to describe the system. Additionally, a strong dependence exists on the shape and size of the atomic cluster used to model the metal surface.

A summary of the methods used is presented in Section 2. In Section 3.1 the results of tests of B3LYP calculations for the copper–water system with different basis sets are presented and compared with those of standard ab initio HF calculations without and with Møller–Plesset corrections. A selected combination of basis sets for Cu and H₂O have been used in Section 3.2, where the metal cluster size effect has been investigated. The results of comparative studies of the interaction of water with a set of different clusters intended to mimic the copper (100) crystallographic surface are presented. Clusters of up to 12 atoms are used and, in some cases, alternative shapes are considered. Finally, the calculations of the interaction of water with the three noble metals have been performed using the 12-atom cluster to model the (100) crystallographic plane of each metal; these results are discussed in Section 3.3. Finally, the major conclusions are summarized in Section 4.

2. Method of calculations

The intermolecular electron correlation effect for transition metal systems has been found [30–35] to play an important role. In this work, DFT has been used to approach this problem. It has been already shown [36] that the DFT method usually known as B3LYP gives good results for the interaction of copper with halide ions. This corroborates earlier results on the good performance of B3LYP for copper–carbonyl calculations [37,38]. B3LYP is the formalism proposed and parametrized by Becke [39]; it uses a mixture of the HF exchange with DFT exchange terms and includes the gradient-corrected correlation functional of Lee et al. [40].

In this work, the performance of B3LYP with different

basis sets was tested for the Cu–H₂O system and the results evaluated by comparison with those of standard ab initio calculations. A planar C_{2v} symmetry is used with the oxygen pointing towards the metal. The opposite orientation, i.e. with the water interacting with the metal via the hydrogens, has been found relatively repulsive and will not be considered. The following basis sets for the copper and the water molecule have been used:

For Cu: AKR&WAG — the (43321/4321/41) basis function of Rappe and Goddard [41]; LANL2DZ — the 10[Ne] inner electrons treated with an effective core potential (ECP) of Hay and Wadt; the 3s²3p⁶3d¹⁰4s¹ valence electrons described by the double-zeta quality Gaussian basis set [42]; LANL1MB — the 18[Ar] inner electrons treated as a core with ECPs of Hay and Wadt; the 3d¹⁰4s¹ valence electrons described by the (3s2p5d) Gaussian basis set [43].

For H₂O: D95 and D95V — the Dunning–Huzinaga full and valence (respectively) double-zeta basis sets [44]; 3-21G, 6-31G — split-valence Gaussian basis sets [45]; 6-31G** — the polarization functions added to the 6-31G basis set [46]; 6-31++G** — the diffuse (d, p) functions added to the 6-31G** basis set [47].

Two optimizations of the copper–oxygen distance have been done for each combination of basis sets. The first used the standard UHF procedure; for the equilibrium geometry, the fourth-order Møller–Plesset correction, that includes the single, double, triple and quadruple (SDTQ) substitution has been computed. The second used the hybrid B3LYP method. In all calculations, the H₂O molecule has been frozen at its experimental geometry with the H–O–H angle of 104.52° and the O–H distances of 0.9572 Å.

From the above tests the LANL1MB basis set for copper and the 6-31G Gaussian basis set for the water molecule (see description above) have been selected to be used in the studies of the effect of the size and shape of the metal cluster upon the computed quantities. The same type of basis sets was used later in the calculations with silver and gold. The seven copper clusters — Cu₂, Cu₄ planar, Cu₄ pyramidal, Cu₅ planar, Cu₅ pyramidal, Cu₉ and Cu₁₂ — used for tests, have been constructed as pieces of the f.c.c. crystallographic structure that is characteristic of the noble metals, with the nearest-neighbour Cu–Cu distances fixed at the experimental value of 2.55 Å [48].

The structures of the Cu₄, Cu₅, Cu₉ and Cu₁₂ are shown in Figs. 1–6. The Cu₂ cluster is just a dimer formed by two neighbouring Cu atoms belonging to the (100) plane. Three extremal positions at the metal surface — on-top, bridge and hollow — have been tested with these clusters (whenever possible) by means of the optimization of the oxygen to the surface distance and of the tilt angle between the molecular axis of the water and the surface normal. In all optimizations the oxygen atom of the water molecule is kept over the site studied; for hydrogen atoms an optimal position has then been found by their rotation

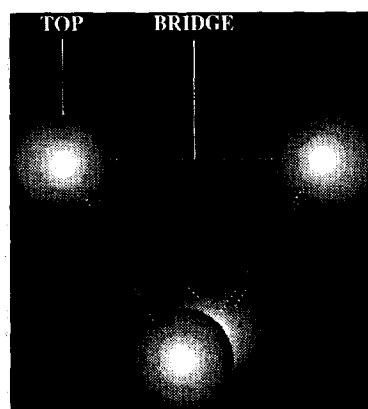


Fig. 1. The Cu₄ pyramidal cluster.

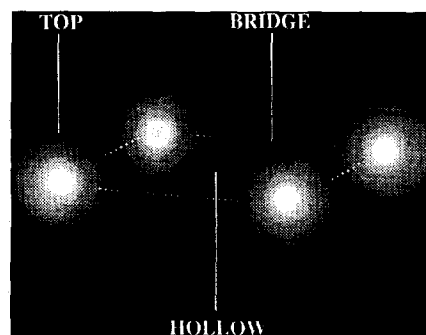


Fig. 2. The Cu₄ planar cluster.

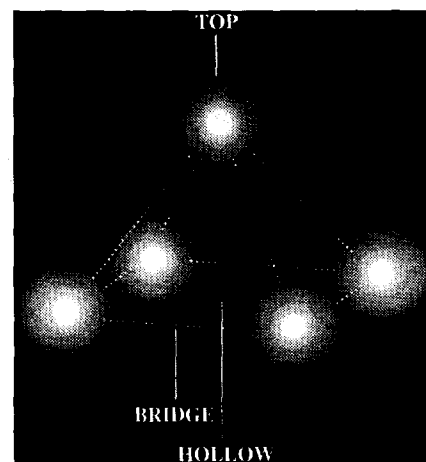


Fig. 3. The Cu₅ pyramidal cluster.

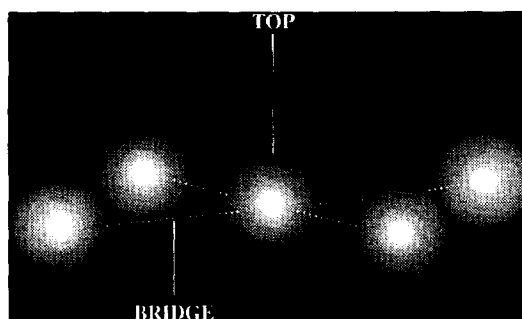
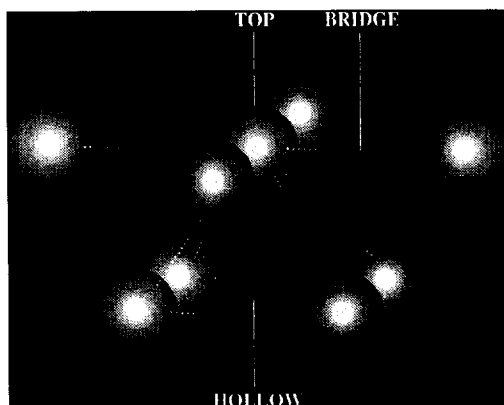
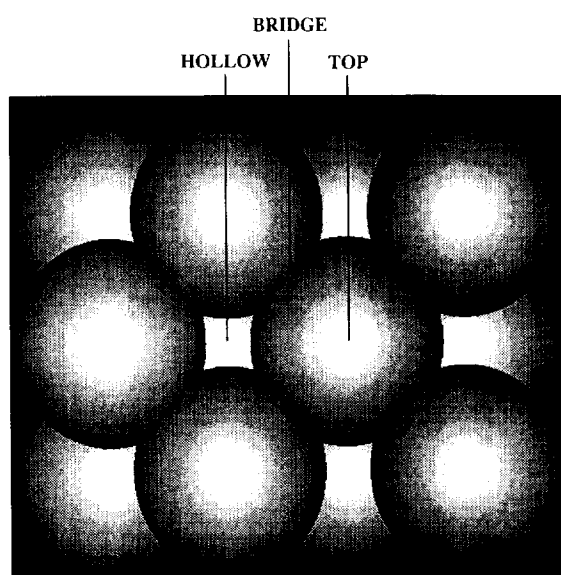


Fig. 4. The Cu₅ planar cluster.

Fig. 5. The Cu₉ cluster.Fig. 6. The Cu₁₂ cluster.

around the normal to the surface, with the oxygen fixed at the optimal distance to the surface.

All calculations have been performed using the GAUSS-1AN92 program [49].

3. Results

3.1. Cu–H₂O system

Results of B3LYP calculations of the interaction of copper with water using different basis sets are shown in Table 1. For comparison, the results of the calculation of the same energies using the UHF method without and with MP4 corrections are also shown. The basis sets tested for the copper atom and the water molecule have been chosen to be of widely different quality. For the copper atom the full-electron description as well as ECPs with different numbers of electrons included into the core have been

considered. For the water molecule the double-zeta quality basis sets have been preferred.

Several earlier works may be found in the literature where the Cu–H₂O system has been investigated by means of the standard HF method with [30–34] and without [50–52] an electron correlation correction, as well as, by the X- α method [26]. In general, these earlier published results show the great sensitivity of this system to the basis functions used. In the work of Itoh et al. [50] the calculations at the HF level with the smaller basis set for the water molecule produced the interaction energy of $-42.5 \text{ kJ mol}^{-1}$, while a little improvement on this basis set changed the results to $-1.93 \text{ kJ mol}^{-1}$. The investigations of Sauer et al. [30], where a different description of this system was used, gave estimates of -11 kJ mol^{-1} from the HF calculations and -34 kJ mol^{-1} at the CI level. From the standard HF calculations of Bauschlicher [51] a Cu–H₂O binding energy of $-19.3 \text{ kJ mol}^{-1}$ was reported; in this case a full electron basis set with diffuse functions on the Cu atom was used. An extremely weak interaction of water with the copper atom was found from some HF calculations [31,33,52] where the energies are in the range -2.9 to $-0.85 \text{ kJ mol}^{-1}$. Much larger values are always reported from computations made with inclusion of the electron correlation corrections. The result of -34 kJ mol^{-1} mentioned above [30,32] is the strongest copper–water interaction energy found at this level. Other proposed values, obtained with different methods and basis sets, deviate significantly from this latter value: $-17.4 \text{ kJ mol}^{-1}$ [31], $-11.6 \text{ kJ mol}^{-1}$ [33], $-5.42 \text{ kJ mol}^{-1}$ [34]. However, the largest value for this interaction was $-73.4 \text{ kJ mol}^{-1}$ as reported by Ribarsky et al. [26] using a full electron description of all atoms that includes the diffuse functions on the Cu as well as on the O and H atoms. A similar inconsistency in results for the reported equilibrium copper–oxygen distances is also observed. As one can see, the theoretical data for this system are very unclear and difficult to compare; unfortunately, to our knowledge, no experimental predictions about the Cu–H₂O interaction strength exist.

Our results in Table 1 seem to be more consistent, and several tendencies that were also found by other authors, can be observed. Comparing lines A and B, the small importance of the explicit inclusion of the ten inner electrons of the copper atom can be seen; almost no difference in computed quantities appears at both HF and MP4 levels. The HF interaction energy of $-22.9 \text{ kJ mol}^{-1}$ is close to the results of Bauschlicher [51]; the MP4 value predicts a stronger binding energy for this system than any of the earlier studies at this level. The good quality of the B3LYP method should be noted at the same time for this level of calculation, as it reproduces almost exactly the MP4 energy of $-42.26 \text{ kJ mol}^{-1}$, but a shorter equilibrium distance is found. It is worth stressing here that in all our calculations the inclusion of the electron correlation effect by means of MP corrections is found to increase the

Table 1

The equilibrium values of the Cu–O distances and binding energies for the Cu–H₂O system for different basis sets. Optimizations have been done using the UHF and B3LYP methods. The MP4 values of energy have been calculated for the minimum HF Cu–O distance

Basis sets			Quantum mechanics method				
Symbol	Cu	H ₂ O	UHF			B3LYP	
			$r_{\text{UHF}}/$ Å	$\Delta E_{\text{UHF}}/$ kJ mol ⁻¹	$\Delta E_{\text{MP4}}/$ kJ mol ⁻¹	$\Delta E_{\text{B3LYP}}/$ kJ mol ⁻¹	$r_{\text{B3LYP}}/$ Å
A	AKR&WAG	D95	2.22	-22.57	-42.26	-42.48	2.03
B	LANL2DZ	D95V	2.22	-20.75	-44.97	-45.60	2.01
C	LANL1MB	3-21G	2.19	-35.20	-46.48	-61.82	2.12
D	LANL1MB	6-31G	2.29	-17.77	-24.98	-37.47	2.19
E	LANL1MB	6-31G**	2.50	-7.44	-14.23	-24.69	2.30
F	LANL1MB	6-31++G**	2.52	-5.00	-12.57	-14.78	2.33
G	LANL1MB	D95	2.34	-13.32	-20.08	-30.24	2.23

Basis sets used for Cu: AKR&WAG — the (43321/4321/41) basis function of Rappe and Goddard [41]; LANL2DZ — the 10[Ne] inner electrons are treated with ECPs of Hay and Wadt, the 19 outer electrons described by the double-zeta Gaussian basis set [42]; LANL1MB — the 18[Ar] inner electrons are treated as a core with ECPs of Hay and Wadt, the 11 outer electrons described by the minimal Gaussian basis set [43]. For H₂O: D95 and D95V — the Dunning–Huzinaga full and valence (respectively) double-zeta basis sets [44]; 3-21G, 6-31G — split-valence Gaussian basis sets [45]; 6-31G** — the polarization basis set [46]; 6-31++G** — the diffuse (d,p) functions have been added to the 6-31G** basis set [47].

binding energy to about twice the HF values, a change in the same direction as found in the literature [30,31].

The substitution of the 18 inner electrons of the copper atom by pseudopotentials decreases the interaction energy significantly, as can be seen by comparing the cases A and G. However, the compensation of this effect, by using a poorer quality basis set for the water molecule like the 3-21G basis, can be detected at the same time from the combination C. This proves that LANL1MB is a good compromise basis set with rather good results for a relatively limited basis that may also be used in cluster calculations. The exact treatment of the 3d¹⁰4s¹ is, in our opinion, the lowest level of approximation that is acceptable for this atom. The loss of quality, when compared with the full-electron description of the Cu atom, may be compensated by the careful adjustment of the basis set used for the water molecule. Treating the first two combinations of basis sets (A, B) as the reference cases for tests, we may compare results obtained for several different basis sets of the water molecule, combined with the LANL1MB description of the copper atom (C–F cases in Table 1). It can be seen that an improvement on the H₂O basis sets weakens the copper–water interaction, increasing at the same time the Cu–O distance. The largest HF and MP4 energy values have been found for the most limited 3-21G description used for the water molecule, overestimating the Cu–H₂O interaction in relation to the A and B results. The 6-31G basis set gives an energy closer to the reference at the HF level, but much too small when the MP4 correlation correction is applied. When the polarization (E) and diffuse functions (F) are added to the 6-31G basis set, a significant decrease in the interaction energies is noticed, giving results that, at the MP4 level, are close to those reported in Ref. [31]. The quantities obtained in the last case tested — with the D95 basis set used for the H₂O molecule — are similar to those found for the 6-31G basis set.

The quality of the B3LYP technique has been tested in conjunction with all combinations of basis sets described above; these results are also shown in Table 1. As one can see, the B3LYP energy values always lie below those obtained by the HF method, thus exhibiting an electron correlation effect. As has already been mentioned, for the more extended description of the system (the A and B cases) an excellent agreement between MP4 and B3LYP values is observed. When the LANL1MB basis set for the copper atom is used, most of the basis sets tested give results which approximate much better the reference level than the MP4 values computed with the same combinations of basis sets. For most cases tested, the participation of the electron correlation into the interaction energy is found to be about 20 kJ mol⁻¹, when the B3LYP data is related to the HF values. Similar estimates have been reported by Sauer et al. [30].

From the considerations just presented, the 6-31G basis set has been selected for the water molecule in combination with the LANL1MB description of the copper atom to be used in the cluster model calculations by the B3LYP method. This combination gives the Cu–H₂O interaction energy and equilibrium copper–oxygen distance sufficiently close to those obtained with the full-electron description of this system. They coincide also with some earlier studies of the Cu–H₂O system at the HF and the electron correlation levels [30,32,51], as well as with an experimental prediction of -34 kJ mol⁻¹ for the copper–water interaction [53].

3.2. Cu_n-H₂O system

The metal cluster size effect has been tested by means of its influence on the computed properties of the Cu_n-H₂O system. The interaction energies and the optimal surface to oxygen distances for the on-top and bridge positions (defined as shown in Figs. 1–6) are presented in Table 2. In

Table 2

The binding energies ΔE_{min} , distances r and tilt angles α (on the on-top site) optimized with the DFT B3LYP procedure for the different $\text{Cu}_n\text{-H}_2\text{O}$ clusters at the on-top and bridge positions of the water molecule

Cluster used	On-top			Bridge	
	$\Delta E_{\text{min}} / \text{kJ mol}^{-1}$	$r / \text{\AA}$	α / deg	$\Delta E_{\text{min}} / \text{kJ mol}^{-1}$	$r / \text{\AA}$
Cu_2	-38.68	2.22	46.0	-19.94	2.03
Cu_4 -pyramid	-91.65	2.07	0	-95.02	1.85
Cu_4 -planar	-72.25	2.11	42.5	-58.09	1.91
Cu_5 -pyramid	-106.28	2.03	0	-62.70	1.94
Cu_5 -planar	-41.28	2.21	0	-58.97	1.90
Cu_9	-25.81	2.19	22.7	-39.52	1.94
Cu_{12}	-30.80	2.23	55.0	-31.8	1.96

all cases the water has been approaching the surface through the oxygen end. Since the hollow site has been found to be relatively repulsive, those results are not shown and will only briefly be commented on. For the on-top site, the tilt angle between the water molecular plane and the normal to the surface has been measured. All distances are computed in relation to the (100) plane of the first atomic layer. The binding energies are calculated according to the formula $\Delta E = E_{\text{tot}}(\text{Cu}_n\text{-H}_2\text{O}) - E_{\text{tot}}(\text{Cu}_n) - E_{\text{tot}}(\text{H}_2\text{O})$. For complete comparison, the B3LYP results for the $\text{Cu-H}_2\text{O}$ system obtained with the same LANL1MB and 6-31G basis sets should also be taken into account (Table 1, case D).

The inspection of the on-top energy values in Table 2 shows that, in general, the small metal clusters produce a large overestimate of the binding of water to the metal surface. This effect is especially large for the Cu_4 and Cu_5 pyramidal structures. While the adsorption energy for the copper-water system is estimated experimentally to be of about -34 kJ mol^{-1} [53], the calculated interaction energies for the different non-pyramidal clusters (i.e. Cu_2 , Cu_3 planar, Cu_9 and Cu_{12}) are found within a 20% range of that experimental estimate. At the same time, the surface to oxygen distance is fairly insensitive to the cluster size, becoming markedly smaller only for the Cu_4 and Cu_5 pyramidal clusters.

For the larger clusters used, Cu_9 and Cu_{12} , some tilt angle is found in agreement with what is suggested experimentally. It should be stressed that this is found even when the water molecule is placed along the C_4 symmetry axis of Cu_9 or near the S_2 axis in Cu_{12} . For the smaller clusters the calculated tilt (or absence of it) may be an artifact of the calculation; this may be due to the large dipole moment associated with the calculated charge distribution on the cluster and, in both Cu_4 clusters, to the very unsymmetrical placement of the water molecule. The results in Table 2 for the bridge position show an overestimate of the interaction energy for the smaller clusters in a way similar to that observed for the on-top position. It should be noted

that, at the bridge site, the molecular plane of the water is perpendicular to the Cu-Cu axis. The high sensitivity of the interaction energy with respect to the cluster size should be related to the extreme dependence of the charge distribution on the cluster size and geometry; this effect is enhanced by the large value of the dipole moment of water as predicted by B3LYP. The charge transfer from the water to the metal cluster is always predicted to be slightly above $0.1 e^-$ and increasing as one moves from hollow, to on-top and to bridge positions. No significant variations of this property have been observed when the size of the copper cluster was changed. When the hollow position is approached by the oxygen end of the water molecule, the interaction energy is much smaller than that calculated for the on-top or bridge positions, and it even becomes repulsive for the Cu_9 cluster. The same relatively repulsive character of this site was reported in earlier work [14,25].

Our results for the copper-water system may be, at least in a qualitative way, compared with the work of te Velde and Baerends [54], where the cluster size effect has been tested for the $\text{Cu}_n\text{-CO}$ system using the local density functional method. Large variations in the adsorption energies were shown when the size of the copper cluster was changed. The difficulties of the cluster model were stressed to the point of showing that the energetically preferred adsorption site may be wrongly predicted. The importance of the polarization of the cluster by the approaching molecule has also been stressed.

Considering these difficulties, a reasonable convergence in our computed properties seems to be achieved for the relatively small clusters calculated. The 12-atom cluster, that allows a continuous search of the different positions over the surface without reaching the borders, gives adsorption energies close to the level experimentally estimated for the copper-water interaction. Therefore, this latter structure has been chosen for our further studies.

3.3. $M_{12}\text{-H}_2\text{O}$ interaction

A more detailed discussion of the metal-water interaction using the 12-atom cluster approximation for copper, silver and gold is now presented. These clusters (see Fig.

Table 3

The binding energies and the surface-oxygen distances obtained for the $\text{Cu}_{12}\text{-H}_2\text{O}$ system, for the on-top, bridge and hollow sites. The angle α is defined between the water molecular axis and the normal to the metal surface. The optimal energy for the on-top site for $\alpha = 55^\circ$ has been found to be $-30.8 \text{ kJ mol}^{-1}$ at a distance of 2.26\AA

Position	$\Delta E / \text{kJ mol}^{-1} (r / \text{\AA})$		
	$\alpha = 0^\circ$	$\alpha = 90^\circ$	$\alpha = 180^\circ$
On-top	-25.3 (2.2)	-24.6 (2.6)	-14.4 (3.4)
Bridge	-31.8 (1.9)	-19.5 (2.5)	-21.0 (3.5)
Hollow	-7.9 (2.5)	-15.7 (3.0)	-17.4 (3.2)

6) have been used to model Cu(100), Ag(100) and Au(100) surfaces; the nearest-neighbour distances have been fixed at their experimental values [48] of 2.55 Å for Cu–Cu, 2.89 Å for Ag–Ag and 2.88 Å for Au–Au. For all metals the metal–water interaction energy vs. the surface–oxygen distance has been scanned for the three above-mentioned sites at the surface. Additionally, for each position, three extremal orientations of the water molecule have been tested: (a) the H₂O molecular plane parallel to the metal surface; (b) the H₂O plane perpendicular to the surface and the oxygen end oriented towards the metal; (c) the same as (b) but with the hydrogens directed towards the metal. In all these configurations the H–H axis is kept parallel to the (100) crystallographic plane. In Table 3 (for copper), Table 4 (for silver) and Table 5 (for gold), the interaction energies and, in parentheses, the optimal distances are shown for each configuration. As already pointed out for copper, the water molecule is found to bind the strongest via oxygen for the bridge and on-top positions. At the bridge site, a rather rigid position is established, creating a tetrahedral-like bonding environment for oxygen. The on-top site is characterized by a quasi-indifference of the energy with respect to the tilt angle as the water molecule rotates from perpendicular to parallel to the surface. The optimal values of the tilt angles reported do not differ significantly for the three metals and lie close to the estimate of 60–70° reported by experimentalists. It was found that, when this tilted water molecule (at the on-top site) is rotated around the normal to the surface, the interaction energy changes only slightly: the most stable position is associated with a conformation of water having the projection of its dipole moment onto the surface pointing towards a neighbouring metal atom. In this way, each hydrogen atom is lying towards a hollow site. The relatively large decrease in interaction energy has always been noted at the two-fold bridge position, when the optimally oriented molecule is rotated by 90° around the normal to the surface, bringing the H–H axis parallel to the M–M axis. Earlier work [14,25] reported this weakening of the interaction as an effect of breaking the oxygen lone pair coupling to the metal atoms. The reorientation of the water monomer from its optimal orientation to that with hydro-

Table 4

The binding energies and the surface–oxygen distances obtained for the Ag₁₂–H₂O system, for the on-top, bridge and hollow sites. The angle α is defined between the water molecular axis and the normal to the metal surface. The optimal energy for the on-top site for $\alpha = 50^\circ$ has been found to be $-26.6 \text{ kJ mol}^{-1}$ at a distance of 2.5 Å

Position	$\Delta E / \text{kJ mol}^{-1}$ ($r / \text{\AA}$)		
	$\alpha = 0^\circ$	$\alpha = 90^\circ$	$\alpha = 180^\circ$
On-top	-22.3 (2.5)	-23.8 (2.7)	-13.5 (3.7)
Bridge	-25.9 (2.2)	-20.2 (2.7)	-18.8 (3.2)
Hollow	-8.1 (2.4)	-14.0 (3.0)	-15.9 (3.5)

Table 5

The binding energies and the surface–oxygen distances obtained for the Au₁₂–H₂O system, for the on-top, bridge and hollow sites. The angle α is defined between the water molecular axis and the normal to the metal surface. The optimal energy for the on-top site for $\alpha = 65^\circ$ has been found to be $-28.7 \text{ kJ mol}^{-1}$ at a distance of 2.6 Å

Position	$\Delta E / \text{kJ mol}^{-1}$ ($r / \text{\AA}$)		
	$\alpha = 0^\circ$	$\alpha = 90^\circ$	$\alpha = 180^\circ$
On-top	-25.3 (2.5)	-28.3 (2.7)	-16.0 (3.5)
Bridge	-29.7 (2.2)	-26.1 (2.5)	-21.7 (3.0)
Hollow	-16.7 (2.2)	-19.5 (2.5)	-17.5 (3.2)

gens pointing to the surface, at both on-top and bridge sites, always requires an extra energy of about 10 kJ mol^{-1} for all three metals.

At the hollow site the interaction via hydrogen atoms is found to be preferred, this being consistent with the view of this site as an electron-rich hole on the metal surface. The repulsion between this negative electronic charge and the lone pair of oxygen may explain the smaller interaction for the $\alpha = 0^\circ$ orientation. It should be stressed that the spatial scanning to find the optimal distance and tilt was done with a smaller step in regions preferred for adsorption. In other regions a rather crude scanning was done and thus these results may have a larger error.

The results of our calculations for the copper–water system may be compared with those reported by Ribarsky et al. [26], who used the X- α method to compute the interaction of the H₂O molecule with the single-copper atom and with the Cu₅ pyramidal cluster. Water has been found to adsorb at the on-top site with the molecular plane tilted by 70° from the normal to the surface. At this conformation, the optimal Cu–O distance of 2.2 Å and the interaction energy of -36 kJ mol^{-1} have been reported. These results are very close to those obtained from our B3LYP calculations, shown in Table 3 (see description above the table). Some small differences are probably due to the larger copper cluster used in the present calculations or to the non-optimized water monomer structure. An additional feature that is also in good agreement with the X- α results is the charge transfer from the water molecule to the copper cluster. The charge donation at the top-tilted position has been found to be ca. $0.12 e^-$ from our Cu₁₂–H₂O studies, this being very similar to that reported [26] for the Cu₅–H₂O system ca. $0.15 e^-$. It should be noted, that in the work now presented the on-top-tilted position is not the one preferred for the water adsorption on the Cu(100) surface. Nevertheless, the bridge site, that has been found to be slightly more stable than the on-top site, has not been tested in the X- α studies mentioned above.

The results shown in Tables 3–5 suggest that the water molecule adsorbs the strongest on copper, followed by gold and silver. Experimentally, there is no explicit data on the relative strength of the interaction; from measurements

of the potential of zero charge, the work function, the inner layer capacity and other hydrophilicity approaches, it has been inferred [55] that the order is $\text{Cu} > \text{Ag} > \text{Au}$. The same order for the water–metal interaction is sometimes assumed as a consequence of the metal–oxygen bonding energies [1]; however, the same authors show metal–hydroxide bonding energies that are in the order $\text{Cu} > \text{Au} > \text{Ag}$. Of course, the quantity that should be compared is the metal–water interaction energies, and these might be obtained from thermal adsorption spectra. For the noble metals, however, this technique does not give sufficient information as the desorption peak is indistinguishable from the sublimation peak. The only conclusion that can be drawn from this is that the interaction of water is very weak with any of the three metals, the interaction with copper probably being the strongest (-34 kJ mol^{-1}).

The charge transfer between the water molecule and the M_{12} clusters has also been collected for the three noble metals. Their relative magnitudes show the same tendency as found for the water–metal interaction: the smallest being to silver (ca. $0.1e^-$ at the on-top-tilted position, about $0.12e^-$ at the bridge site); the middle to gold (ca. $0.1e^-$ at the on-top-tilted position, about $0.14e^-$ at the bridge site); the largest to copper (about $0.12e^-$ for the on-top-tilted position, about $0.15e^-$ for the bridge site). For any of the less-preferred conformations the charge donation to the metal has been found to be markedly smaller.

To our knowledge, there is only one theoretical work that attempts to compare the hydrophilicity of all noble metals. Kuznetsov et al. [22] presented the results of CNDO calculations that, unexpectedly, predict a very strong metal–water interaction, that to gold being the strongest and to silver the weakest when the same crystallographic orientation of the surface is taken into account. Additionally, the hollow site is suggested to be the position energetically favoured for adsorption in contradiction with common experimental wisdom. Although chemisorption energies show a different tendency when the three metals are compared, the sequence in the charge transfer to the metal shown seems to agree with our results described above. However, while the magnitude of the charge donation for the top site is very close to our findings, for the hollow site the value reported is much larger. At both positions the charge transfer to the metal is shown to decrease in the order $\text{Cu} > \text{Au} > \text{Ag}$, in agreement with our results. It should be stressed that in their work the metal atoms were described using the one-electron ECPs, thus assuming a negligible role for the d orbitals; the relatively poor quality of these potentials has recently been shown for this type of system [56] and will be commented on below.

From the tabulated results it may be seen that, for copper and gold, the preferred adsorption position is the bridge ($\alpha = 0^\circ$), this being slightly lower in energy than

the on-top-tilted sites. For silver, the reverse situation is found, with a very small energy difference between the two sites. It should be stressed that small deviations, as those found here, may be the result of the assumptions made for the calculations, both in the method and in the model; the rigidity assumed for the structure of the water molecule may also play a role.

The qualitative picture about the strength of adsorption of water on the noble metals drawn from our calculations might additionally be compared with two recently published works, where the interaction of water with noble metals (excluding Au) atoms and dimers has been investigated at the ab initio level. In the paper of Neogrady et al. [34] the $\text{Cu-H}_2\text{O}$ and $\text{Ag-H}_2\text{O}$ systems have been widely studied. The method and the size of systems used in their calculations differ significantly from ours; nevertheless, some common features can be found. Perhaps the most relevant is the relation between the optimal interaction energies of water with metal atoms when the Cu and Ag are compared, the latter being clearly weaker. However, the magnitude of the $\text{Cu-H}_2\text{O}$ interaction energy is markedly smaller than the analogous value obtained from our atom–water calculations. The relatively repulsive character of the conformation, with the hydrogen atoms pointing towards the metal atom, is suggested in the work referred to above to be slightly weaker for the $\text{Ag-H}_2\text{O}$ than for $\text{Cu-H}_2\text{O}$. This last tendency does not appear in our results for the $\text{Cu}_{12}\text{-H}_2\text{O}$ and $\text{Ag}_{12}\text{-H}_2\text{O}$ systems (values for $\alpha = 180^\circ$ from Tables 3 and 4 should be compared): for both orientations of the water molecule, the interaction with copper is stronger. The same tendency, i.e. a stronger copper–water interaction, has been reported by Boussard et al. [56] for the $\text{Cu}_2\text{-H}_2\text{O}$ and $\text{Ag}_2\text{-H}_2\text{O}$ systems from the all-electron calculations at the SCF and CI levels. The dimer–water dissociation energies at the highest level of computation have been found in their work to be $-74.9 \text{ kJ mol}^{-1}$ for copper and $-44.4 \text{ kJ mol}^{-1}$ for silver; thus, the former value is almost twice as large as ours for the on-top configuration of the $\text{Cu}_2\text{-H}_2\text{O}$ system (Table 2). For comparison, the same authors reported analogous results for the same dimers, but obtained with the one-electron ECPs applied to the metal atoms. These give much weaker interaction energies both at the SCF and at the CI levels (the CI value of $-26.4 \text{ kJ mol}^{-1}$ for both metals is given), an effect that, though much weaker, was also observed in our $\text{Cu-H}_2\text{O}$ tests presented in an earlier section of this paper. The additional effect of exchanging positions of the copper and silver in the order of the water–metal interaction strength has been observed at the SCF level, this being caused by including the d orbitals into the pseudopotentials. As was mentioned above, the same one-electron ECP approximation has been applied in the CNDO studies of Kuznetsov et al. [22], and is probably responsible for the stronger preference of the hollow site for the water adsorption.

4. Conclusions

The results presented above confirm the good performance of B3LYP for systems containing noble metal atoms. The problem of the copper–water interaction was addressed and the results corroborate our earlier tests for the copper–halide ions interaction [36]. It was shown in Section 3.1 that B3LYP performs well with relatively inexpensive basis sets, this being crucial for the feasibility of calculations of the interaction of water with large metal clusters. This strategy, i.e. the conjunction of B3LYP with a relatively poor basis set, was found to lead to an acceptable convergence when the cluster size was increased. The copper–water interaction energies obtained for small clusters (Cu_4 , Cu_5) show significant deviations from the estimate of -34kJ mol^{-1} proposed by experimentalists, while for the larger structures they were found to approach this level. However, most of the smaller structures show a strong preference for the two-fold bridge site on the (100) surface, disfavoring the on-top-tilted position. This result for the smaller clusters is not compatible with the experimental findings, which suggest that the on-top-tilted position is preferred, without excluding the possibility of the bridge perpendicular position to be close by in energy. From these tests the 12-atom cluster has been shown to give good results for the copper–water system, and this structure has been used in the more extended studies on the water–noble metals interaction.

The calculations of the interaction of water with M_{12} ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$) clusters, presented in Section 3.3, clearly show that the hollow site in the (100) surface is never preferred for adsorption on either copper, or silver or gold. The on-top site with the water molecule tilted and the bridge site with the water molecule perpendicular to atom–atom axis do have very similar interaction energies. This confirms earlier results [13] suggesting that not only the on-top but also the bridge site should be considered for the preferential adsorption. The tilt angle for the top site is found from our calculations for the three metals to be in the range $50\text{--}65^\circ$, coinciding with values estimated from the experimental measurement of the H_2O monomeric adsorption on the $\text{Cu}(100)$ and $\text{Pd}(100)$ surfaces.

The results presented above point towards water being most strongly adsorbed on copper, when compared with silver and gold. This agrees with the commonly accepted view that copper is the most hydrophilic of the three metals [55]. The relative magnitude of the hydrophilicity of gold and silver is less clear. The calculations reported here point towards silver as the most hydrophobic of the noble metals, while some experimentalists have suggested otherwise [57]. However, it should be stressed that the experimental evidence is very indirect, as discussed in Section 3.3. Summing up, it may be said that the order of hydrophilicity found here, copper > gold > silver is the best estimate so far of the relative magnitude of this property.

This same order is found for the magnitude of the charge transfer between the adsorbed water and the metal.

Acknowledgements

Financial support from JNICT (Lisbon) is acknowledged. A.I. thanks INVOTAN (Lisbon) for a doctoral fellowship.

References

- [1] P.A. Thiel and T.E. Madey, *Surf. Sci. Rep.*, 7 (1987) 211.
- [2] R. Parsons, *Chem. Rev.*, 90 (1990) 813.
- [3] B.W. Calleen, K. Griffiths and P.R. Norton, *Phys. Rev. Lett.*, 66 (1991) 1634.
- [4] J.D. Porter and A.S. Zinn, *J. Phys. Chem.*, 97 (1993) 1190.
- [5] C.A. Melendres, B. Beden, G. Bowmaker, C. Liu and V.A. Maroni, *Langmuir*, 9 (1993) 1980.
- [6] A.E. Russell, A.S. Lin and W.E. O'Grady, *J. Chem. Soc. Faraday Trans.*, 89 (1993) 195.
- [7] H. Ogasawara, J. Yoshinobu and M. Kawai, *Chem. Phys. Lett.*, 231 (1994) 188.
- [8] N. Pangher, A. Schmalz and J. Haase, *Chem. Phys. Lett.*, 221 (1994) 189.
- [9] B.J. Hinch and L.H. Dubois, *Chem. Phys. Lett.*, 181 (1991) 10.
- [10] R. Brosseau, M.R. Brustein and T.H. Ellis, *Surf. Sci.*, 294 (1993) 243.
- [11] D. Schmeisser, F.J. Himpsel, G. Hollinger, B. Reihl and K. Jacobi, *Phys. Rev. B*, 27 (1983) 3279.
- [12] S. Andersson, C. Nyberg and C.G. Tengstål, *Chem. Phys. Lett.*, 104 (1984) 305.
- [13] K.G. Lloyd, B.A. Banse and J.C. Hemminger, *Phys. Rev. B*, 33 (1986) 2858.
- [14] C.W. Bauschlicher, *J. Chem. Phys.*, 83 (1985) 3129.
- [15] R.R. Nazmutdinov, M. Probst and K. Heinzinger, *J. Electroanal. Chem.*, 369 (1994) 227.
- [16] I.I. Zakharov, V.I. Avdeev and G.M. Zhidomirov, *Surf. Sci.*, 277 (1992) 407.
- [17] M.A. Leban and A.T. Hubbard, *J. Electroanal. Chem.*, 74 (1976) 253.
- [18] S. Holloway and K.H. Bennemann, *Surf. Sci.*, 101 (1980) 327.
- [19] B.C. Khanra, *Chem. Phys. Lett.*, 84 (1981) 107.
- [20] G. Estiu, S.A. Maluendes, E.A. Castro and A.J. Arvia, *J. Phys. Chem.*, 92 (1988) 2512.
- [21] A. Kuznetsov, J. Reinhold and W. Lorenz, *J. Electroanal. Chem.*, 164 (1984) 167.
- [22] A.M. Kuznetsov, R.R. Nazmutdinov and M.S. Shapnik, *Electrochim. Acta*, 34 (1989) 1821.
- [23] A.B. Anderson, *Surf. Sci.*, 105 (1981) 159.
- [24] J. Paul and A. Rosen, *Int. J. Quantum Chem.*, 23 (1983) 1231.
- [25] J.E. Müller and J. Harris, *Phys. Rev. Lett.*, 26 (1984) 2493.
- [26] M.W. Ribarsky, W.D. Luedtke and U. Landman, *Phys. Rev. B*, 32 (1985) 1430.
- [27] S.K. Saha and N.C. Debnath, *Chem. Phys. Lett.*, 121 (1985) 490.
- [28] H. Yang and J.L. Whitten, *Surf. Sci.*, 223 (1989) 131.
- [29] H.P. Bonzel, G. Pirug and J.E. Müller, *Phys. Rev. Lett.*, 58 (1987) 2138.
- [30] J. Sauer, H. Haberland and G. Pacchioni, *J. Phys. Chem.*, 90 (1986) 3051.
- [31] L.A. Curtiss and E. Bierwagen, *Chem. Phys. Lett.*, 176 (1991) 417.
- [32] H. Haberland, J. Sauer and G. Pacchioni, *J. Mol. Struct.*, 149 (1987) 297.

- [33] J. Miralles-Sabater, I. Garcia-Cuesta, M. Merchan and I. Nebot-Gil, *J. Mol. Struct.*, 188 (1989) 1.
- [34] P. Neogrady, M. Urban and A.J. Sadlej, *J. Mol. Struct.*, 332 (1995) 197.
- [35] C.W. Bauschlicher, *Chem. Phys. Lett.*, 142 (1987) 71.
- [36] A. Ignaczak and J.A.N.F. Gomes, *Chem. Phys. Lett.*, 257 (1996) 609.
- [37] V. Barone, *Chem. Phys. Lett.*, 233 (1995) 129.
- [38] V. Barone, *J. Phys. Chem.*, 99 (1995) 11659.
- [39] A. Becke, *J. Chem. Phys.*, 98 (1993) 5648.
- [40] C. Lee, W. Yang and R.G. Parr, *Phys. Rev. B*, 37 (1988) 785.
- [41] A.K. Rappe and W.A. Goddard, supplied with the GAUSSIAN92 program, 1982.
- [42] P.J. Hay and W.R. Wadt, *J. Chem. Phys.*, 82 (1985) 299.
- [43] P.J. Hay and W.R. Wadt, *J. Chem. Phys.*, 82 (1985) 270.
- [44] T.H. Dunning and P.J. Hay, *Modern Theoretical Chemistry*, Plenum Press, New York, 1976, Chapter 1, pp. 1–28.
- [45] W.J. Hehre, R. Ditchfield and J.A. Pople, *J. Chem. Phys.*, 56 (1972) 2257.
- [46] M.J. Frisch, J.A. Pople and J.S. Binkley, *J. Chem. Phys.*, 80 (1984) 3265.
- [47] T. Clark, J. Chandrasekhar, G.W. Spitznagel and P.v.R. Schleyer, *J. Comput. Chem.*, 4 (1983) 294.
- [48] C.J. Smithells, *Metal Reference Book*, Butterworths, Washington, DC, 6th edn., 1983.
- [49] M.J. Frisch, G.W. Trucks, H.B. Schlegel, P.M.W. Gill, B.G. Johnson, M.W. Wong, J.B. Foresman, M.A. Robb, M. Head-Gordon, E.S. Reprogle, R. Gomperts, J.L. Andres, K. Ragchavachari, J.S. Binkley, C. Gonzales, R.L. Martin, D.J. Fox, D.J. DeFrees, J. Baker, J.P. Stewart and J.A. Pople, GAUSSIAN 92/DFT, Revision F.2, 1993 (Gaussian Inc. Pittsburgh, PA).
- [50] H. Itoh, G. Ertl and B. Kunz, *Z. Naturforsch. Teil A*, 36 (1981) 347.
- [51] C.W. Bauschlicher, *J. Chem. Phys.*, 84 (1986) 260.
- [52] M.R.A. Blomberg, U.B. Brandemark and P.E.M. Siegbahn, *Chem. Phys. Lett.*, 126 (1986) 317.
- [53] C. Au, J. Breza and M.W. Roberts, *Chem. Phys. Lett.*, 66 (1979) 340.
- [54] G. te Velde and E.J. Baerends, *Chem. Phys.*, 177 (1993) 399.
- [55] G. Valette, *J. Electroanal. Chem.*, 139 (1982) 285.
- [56] P.J.E. Bousard, P.E.M. Siegbahn and M. Svensson, *Chem. Phys. Lett.*, 231 (1994) 337.
- [57] S. Trasatti, *J. Electroanal. Chem.*, 33 (1971) 351.