

# Quantum calculations on the adsorption of halide ions on the noble metals

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## Abstract

The interaction of halide ions with the three noble metals has been investigated using the B3LYP density functional method and the cluster model approximation. The results of calculations for the  $M-X^-$  and  $M_{12}-X^-$  ( $M = Cu, Ag, Au$ ;  $X = F, Cl, Br, I$ ) systems are presented. At the (100) surface, modeled in the present work by the  $M_{12}$  cluster, all halide ions have been found to adsorb preferentially at the hollow site, followed by the bridge and by the top positions. The adsorption energy has been found to decrease when going from fluoride to iodide in both atom-ion and cluster-ion cases. The opposite trend is observed for the estimates of the charge transfer from the ions to the surface. When different metals are compared, the  $M_{12}-X^-$  interaction energies decrease in the order  $Au > Ag > Cu$ , but for the smaller ions some deviations from this line do appear. The relative values of the calculated harmonic vibrational frequencies do agree with those found experimentally, but their magnitude is much smaller as a result of the effect of the lower surface coverage.

**Keywords:** Ionic adsorption; Noble metals; Halide ions; Cluster calculations; B3LYP

## 1. Introduction

The specific adsorption of ions on metal electrodes is a phenomenon well known to electrochemists. There is evidence that, in aqueous solution, some ions (usually anions) are contact adsorbed on the metal surface whereas others are not; this was found by experimentalists many years ago, first for mercury and later for solid electrodes (see Refs. [1,2] for review). Much of the more recent work has been undertaken on the noble metal surfaces giving a comparative description of properties of the electrode/electrolyte interface. The results always show a clear tendency for the specific adsorption of halide ions on metals in aqueous solutions, that is the strongest for iodide and decreases when going to fluoride. The strongest adsorption of ions on the gold surface, when compared with silver and copper, was reported at the same time. However, a review published by Parsons [2], on the techniques applied to study this problem, clearly shows many of the limitations of such experimental measurements. The model assumed

to interpret the experimental results is found to greatly influence the conclusions. No explicit information about the strength of the pure ion-metal interaction is available from the experimental measurement; however, from those indirect results it was concluded that it is analogous to the adsorption trend in solution, i.e. very weak for fluoride, and much stronger for larger ions. This view was commonly accepted for many years and assumed in discussions on the specific adsorption phenomenon.

The theoretical studies of the metal-halides interaction undertaken at the semiempirical EHT [3–8] and CNDO levels [9–11] seemed to justify that conclusion. From these cluster model calculations the interaction energy values of the metal-halides systems have been found in the increasing order  $F^- < Cl^- < Br^- < I^-$ , the same as that proposed by electrochemists. When the ab initio methods were applied to study this problem, some doubts appeared. Hartree-Fock (HF) studies were performed on the  $Hg_7X^-$  systems ( $X = F, Cl, Br, I$ ) [12,13], where the adsorption of ions on the (111) crystallographic plane has been investigated. Unlike semiempirical calculations, the trend of adsorption energies estimated by the ab initio methods was found to be in the direction opposite to that suggested by electrochemists. It should be stressed, however, that these results showed a marked basis set dependence, and even

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the ordering of the interaction energies may be affected by the choice of basis set. This, as well as other limitations of the calculations are discussed by the authors.

Kuznetsov [14] in a recently reported work on  $\text{Cu}_7\text{X}^-$  appears to confirm the ordering of the adsorption energies predicted for mercury on the same (111) crystallographic plane, except for  $\text{Br}^-$  which deviated slightly from the general trend. In fact all HF calculations discussed above for the adsorption of halides on metal surfaces do have some difficulty with bromide, which frequently is off the general tendency.

In the calculations performed for the  $\text{Hg}_7\text{X}^-$  systems, the halide ion has always been located over the central Hg atom of the metal cluster, thus testing only one particular site on the surface, which happens to be not the most stable one as suggested by experiment. In fact, the in situ STM measurements [15–20] that have been undertaken in the last decade for the halide ions adsorbed on the noble metals give real-space images where the structural properties of the interface may be observed. They clearly show that the preferred position for the ion on the smooth (111, 100) surfaces is the multifold one characterized by the highest coordination number. On the (100) crystallographic plane this is a four-fold hollow site, followed in decreasing order of binding energy by bridge and top. Thus, in the theoretical calculations for the Hg(111) surface an ion should be situated over the three-fold hollow site rather than over the top position. In the above-mentioned studies of the copper–halides interaction [14], two positions, top and hollow, have been investigated, and the results also disagree with experimental findings: for iodide, bromide and chloride the top site was favored, fluoride being the only exception where the hollow site was preferred.

None of those ab initio studies includes the electron correlation effect, while this has been already shown to play an important role for structures containing the transition metal atoms [21–27]. The standard methods to incorporate such correction to large systems are obviously too expensive in terms of computational time to approach this problem. At present, the methods based on the density functional theory (DFT), that make such calculations feasible, may be applied to the cluster model calculations at the correlation level. In this work the computations have been performed using the hybrid HF/DFT B3LYP method, which contains the non-local electron correlation term. The results of the interaction of halide ions with the three noble metals, namely copper, silver and gold, are presented. The  $\text{M-X}^-$  and  $\text{M}_{12}\text{-X}^-$  systems ( $\text{M} = \text{Cu}, \text{Ag}, \text{Au}$ ;  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ ) have been studied, where M and  $\text{M}_{12}$  are respectively a metal atom and a 12-atom cluster modeling the (100) surface. Since a relatively large basis set superposition error (BSSE) has been found in earlier tests [27], all values of the ion–metal interaction energy have been corrected by this factor. The quantities obtained are compared with theoretical and experimental data available.

## 2. Method of calculation

All calculations were done using the B3LYP method. This relatively new technique is a mixture of the HF exchange with the DFT exchange terms (Becke three-parameter functional) [28] and includes the gradient-corrected correlation functional of Lee et al. [29]. The B3LYP method has already been tested in several studies of transition metal small systems [30–32] and shown to give better description of geometries and energetics even when compared with the MP2 level of calculations. Additionally, it has been tested for the  $\text{Cu-X}^-$  and  $\text{Cu}_5\text{-I}^-$  systems [27], where the B3LYP results have been compared with those from the standard calculations. The basis sets used are those selected from the comparison done in this latter work. For all metal atoms, and for the three larger halide ions, the inner shells have been treated with the effective-core potentials of Hay and Wadt [33,34]. The  $(n-1)dns$  valence electrons of the noble metal atoms have been described by the Gaussian-type of basis sets proposed by the same authors: the (3s2p5d) basis set for copper, the (3s3p4d) basis set for silver, the (3s3p3d) basis set for gold. For the three above-mentioned halides the double-zeta quality basis sets have been applied to  $nsnp$  valence electrons. The fluoride ion has been treated with the all electron double-zeta quality basis set of Dunning–Huzinaga [35]. The studies of the interaction of halide ions with the noble metals have been first performed for the  $\text{M-X}^-$  systems, where  $\text{M} = \text{Cu}, \text{Ag}, \text{Au}$  and  $\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$ . The interaction energies, optimal distances, charge transfer between ion and metal, and harmonic vibrational frequencies have been computed. Next, using the cluster model approximation, the chemisorption of halides on the (100) surface of three metals has been investigated. The 12-atom cluster  $\text{M}_{12}$ , presented in Fig. 1, has been used. It has a

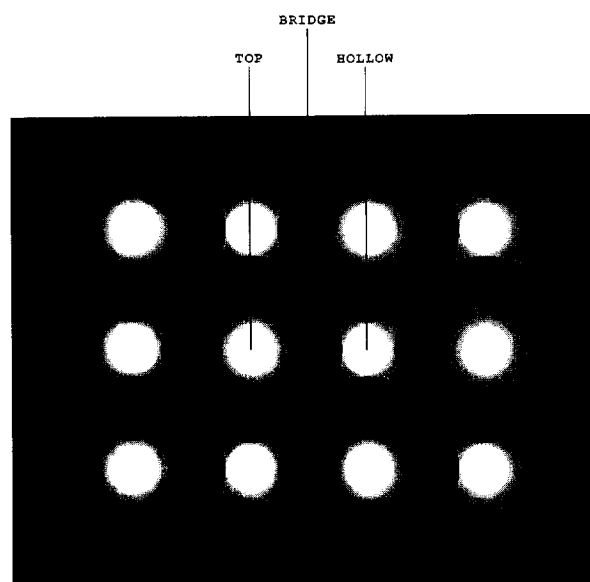


Fig. 1. The  $\text{Cu}_{12}$  cluster used in quantum calculations.

face-centered cubic crystallographic structure typical for the noble metals, with the nearest-neighbor M–M distances fixed at experimental values [36] of 2.55 Å for Cu–Cu, 2.89 Å for Ag–Ag and 2.88 Å for Au–Au. The cluster contains two layers, each consisting of six atoms modeling the (100) crystallographic plane. This structure allows the continuous search of the different positions over the surface without reaching the borders. To test the quality of the cluster used, the energies of the highest occupied molecular orbitals (HOMOs) have been computed for Cu<sub>12</sub>, Ag<sub>12</sub> and Au<sub>12</sub> clusters and compared with the experimental estimates of the work function of the three noble metals. All calculations have been performed using the GAUSSIAN92 program [37].

### 3. Results

#### 3.1. Energetics

In Table 1 the BSSE-corrected results for the halide–metal atom interaction energies are presented together with the optimal distance and charge transfer. It should be stressed that the BSSEs are relatively large, the major part arising from the X<sup>−</sup> ion in the presence of the Cu ghost basis functions. This correction may be as big as 30%, a situation known in the literature [30].

When going up from I<sup>−</sup> to F<sup>−</sup>, the interaction energies increase while the optimal atom–ion distances decrease, a tendency clearly observed for any of the three metals. Comparing the metals, silver is seen to interact the weakest. Thus, for these atom–ion systems a clear order in interaction energies appears, this being for ions F<sup>−</sup> > Cl<sup>−</sup> > Br<sup>−</sup> > I<sup>−</sup> and for metals Au > Cu > Ag. The one exception is fluoride, in which case gold and copper exchange positions.

From the electrochemical point of view another very important property is the charge donation of the ions to the metal. For the atom–ion systems, the Mulliken population analysis predicts a charge transfer of about 1/3e, the smallest being for fluoride owing to its larger electronegativity. It should also be noted that the charge transfer to copper and to silver is very similar, while that to gold is larger, again for electronegativity reasons. For the three larger ions the calculated values of the charge transfer are

Table 2

EAs for halide ions computed using the UHF, MP4 and B3LYP methods. For comparison, experimental values and those reported by Blanco et al. [12] in their HF studies on the adsorption of halides on mercury are included

Ion	EA/eV				
	UHF	MP4	B3LYP	Ref. [12]	Experiment
F <sup>−</sup>	0.516	1.781	2.107	0.24	3.40
Cl <sup>−</sup>	1.879	2.143	2.791	2.29	3.62
Br <sup>−</sup>	1.974	2.172	2.903	2.34	3.36
I <sup>−</sup>	2.106	2.256	2.979	—	3.06

very close in magnitude. This may be associated with the errors of the calculated electron affinities (EAs) that are shown in Table 2. Values are calculated as  $EA = E_{\text{tot}}(\text{X}) - E_{\text{tot}}(\text{X}^-)$  and B3LYP results are compared with experimental data. For evaluation of this, UHF and UHF-MP4 results obtained with the same basis set are also shown and compared with those calculated at the HF level by Blanco et al. [12] in their study of the adsorption of the halides on mercury. It is noted that results at the HF level are always poor and B3LYP does give better estimates than UHF. Compared with the estimates of Blanco et al. or even with our results at the UHF-MP4 level, it may be seen that B3LYP gives a very good gain in quality. This improvement is particularly striking for fluoride. However, it may be noted that, when compared with the experimental data available, the B3LYP estimates still do have an error that grows in arithmetic progression from 0.1 to 1.3 eV as we go from iodide to fluoride. This growing error is likely to show up in the estimates of the charge transfer. This being the case, the value of  $q(\text{X}^-)$  for iodide would be essentially correct, but the calculation for the other ions would produce growing underestimates.

As a test on the quality of the M<sub>12</sub> cluster model used to represent the (100) surface of copper, silver and gold, the energies of the HOMOs have been calculated. In Table 3 these results are compared with experimental values of the electronic work function  $\Phi$  of the metallic monocrystals. A wide range of experimental results have been reported in the literature for these metals, which makes the comparison rather difficult. However, when we consider the most recent experimental data, agreement with our

Table 1

The B3LYP optimized distances  $r_{\text{min}}$ , interaction energies and charge on the ions for the Cu–X<sup>−</sup>, Ag–X<sup>−</sup> and Au–X<sup>−</sup> systems. All energies are corrected by the BSSE

Metal	Cu			Ag			Au		
	$r_{\text{min}}/\text{Å}$	$\Delta E/\text{kJ mol}^{-1}$	$q(\text{X}^-)$	$r_{\text{min}}/\text{Å}$	$\Delta E/\text{kJ mol}^{-1}$	$q(\text{X}^-)$	$r_{\text{min}}/\text{Å}$	$\Delta E/\text{kJ mol}^{-1}$	$q(\text{X}^-)$
F <sup>−</sup>	2.025	−142.7	−0.71	2.219	−127.2	−0.71	2.323	−134.9	−0.63
Cl <sup>−</sup>	2.512	−95.2	−0.66	2.725	−89.5	−0.67	2.777	−98.1	−0.61
Br <sup>−</sup>	2.738	−78.7	−0.68	2.923	−76.1	−0.69	2.953	−86.3	−0.62
I <sup>−</sup>	3.013	−62.3	−0.69	3.196	−61.9	−0.70	3.194	−73.5	−0.63

Table 3

Selected experimental values of the electronic work function  $\Phi$  of the Cu(100), Ag(100) and Au(100) monocrystals and the calculated energy of the HOMOs for the  $\text{Cu}_{12}$ ,  $\text{Ag}_{12}$  and  $\text{Au}_{12}$  clusters used in our studies

Metal	Experimental values of $\Phi$ /eV	$E_{\text{HOMO}}$ /eV
Cu(100)	4.59 [38,39], 5.10 [40], 4.65 [41], 4.77 [42], 4.83 [43], 4.70 [44]	4.87
Ag(100)	4.64 [45], 4.62 [46], 4.22 $\pm$ 0.04 [47–49] 4.25 [44]	4.58
Au(100)	5.47 [46], 5.00 [44]	5.41

Table 4

The interaction energies (corrected by BSSE)  $\Delta E$  together with the equilibrium distances  $z_{\text{min}}$  (in parentheses) of halides to the metal surface for the  $\text{Cu}_{12}-\text{X}^-$  system. Results for three different positions of an ion on the (100) surface (hollow, bridge and top) are shown. The charge on the halide ion at the minimum energy position (at the hollow site) is also included

Ion	$\Delta E_{\text{hollow}}/$ $\text{kJ mol}^{-1}$ ( $z/\text{\AA}$ )	$\Delta E_{\text{bridge}}/$ $\text{kJ mol}^{-1}$ ( $z/\text{\AA}$ )	$\Delta E_{\text{top}}/$ $\text{kJ mol}^{-1}$ ( $z/\text{\AA}$ )	$q(\text{X}^-)_{\text{hollow}}$
$\text{F}^-$	-240.7 (1.3)	-217.3 (1.6)	-192.6 (2.0)	-0.55
$\text{Cl}^-$	-141.0 (2.0)	-126.2 (2.2)	-116.5 (2.4)	-0.37
$\text{Br}^-$	-117.5 (2.3)	-102.7 (2.5)	-94.3 (2.6)	-0.36
$\text{I}^-$	-92.5 (2.6)	-82.3 (2.7)	-80.1 (2.9)	-0.35

Table 5

The interaction energies (corrected by BSSE)  $\Delta E$  together with the equilibrium distances  $z_{\text{min}}$  (in parentheses) of halides to the metal surface for the  $\text{Ag}_{12}-\text{X}^-$  system. Results for three different positions of an ion on the (100) surface (hollow, bridge and top) are shown. The charge on the halide ion at the minimum energy position (at the hollow site) is also included

Ion	$\Delta E_{\text{hollow}}/$ $\text{kJ mol}^{-1}$ ( $z/\text{\AA}$ )	$\Delta E_{\text{bridge}}/$ $\text{kJ mol}^{-1}$ ( $z/\text{\AA}$ )	$\Delta E_{\text{top}}/$ $\text{kJ mol}^{-1}$ ( $z/\text{\AA}$ )	$q(\text{X}^-)_{\text{hollow}}$
$\text{F}^-$	-221.3 (1.4)	-198.9 (1.8)	-173.7 (2.2)	-0.56
$\text{Cl}^-$	-138.6 (2.1)	-125.7 (2.4)	-114.0 (2.6)	-0.43
$\text{Br}^-$	-117.6 (2.4)	-106.4 (2.6)	-98.1 (2.8)	-0.41
$\text{I}^-$	-96.3 (2.7)	-86.8 (2.8)	-83.0 (3.0)	-0.41

Table 6

The interaction energies (corrected by BSSE)  $\Delta E$  together with the equilibrium distances  $z_{\text{min}}$  (in parentheses) of halides to the metal surface for the  $\text{Au}_{12}-\text{X}^-$  system. Results for three different positions of an ion on the (100) surface (hollow, bridge and top) are shown. The charge on the halide ion at the minimum energy position (at the hollow site) is also included

Ion	$\Delta E_{\text{hollow}}/$ $\text{kJ mol}^{-1}$ ( $z/\text{\AA}$ )	$\Delta E_{\text{bridge}}/$ $\text{kJ mol}^{-1}$ ( $z/\text{\AA}$ )	$\Delta E_{\text{top}}/$ $\text{kJ mol}^{-1}$ ( $z/\text{\AA}$ )	$q(\text{X}^-)_{\text{hollow}}$
$\text{F}^-$	-229.5 (1.5)	-205.8 (1.9)	-178.3 (2.2)	-0.51
$\text{Cl}^-$	-156.5 (2.2)	-145.2 (2.4)	-130.5 (2.6)	-0.39
$\text{Br}^-$	-139.0 (2.4)	-130.4 (2.6)	-119.5 (2.8)	-0.36
$\text{I}^-$	-121.3 (2.7)	-115.9 (2.8)	-109.3 (3.0)	-0.35

results in a semiquantitative way stands out. The ordering found  $\text{Ag} < \text{Cu} < \text{Au}$  is very likely to be correct. It should be noted that there is good agreement between the results presented in Table 3 and the predictions made by Romanowski et al. (fig. 1 of [59]).

The results of calculations on the chemisorption of halides on three noble metal clusters are presented in Tables 4–6. For each site of the (100) surface, hollow, bridge and top, the minimum of energy, together with the equilibrium distance, are reported. The adsorption energy has been calculated as follows:  $\Delta E = E(\text{M}_{12}\text{X}^-) - E(\text{M}_{12}) - E(\text{X}^-)$ ; the distance is always defined along the perpendicular to the plane containing the centers of the atoms forming the first metal layer. In all cases, the ions have been found to adsorb preferentially at the four-fold hollow site, followed by the two-fold bridge and the top site is the least attractive. The same ordering for the interaction energies of iodide ion on the three sites of the platinum (100) surface has been also reported by Seitz-Beywl et al. [50] based on HF calculations for the  $\text{Pt}_9\text{I}^-$  system. As mentioned above, an opposite tendency has been found by Kuznetsov [14] for the adsorption of halides on the Cu(111) surface. Although the magnitude of the adsorption energies found for the top site is similar to that of our results for this position of the same ion on the Cu(100) plane, the preference of this site for the chemisorption, as predicted in that work, remains in contradiction to the experimental data.

From our calculations a growing tendency in adsorption energies is clearly observed as we go from iodide to fluoride. To our knowledge there is no experimental data about the strength of these interactions in a vacuum to which these results could be directly compared. All predictions are based on the behavior of ions in the electrolyte|electrode interface region, where the larger ions are found to adsorb strongly, while fluoride is not contact-adsorbed or very weakly adsorbed on the metal surface. However, in the real system an ion is surrounded by solvent molecules as well as by other ions, and concurrent processes, like the desolvation of the ion and the metal, the coadsorption of other ions, or the formation of complexes on the surface, will markedly affect the ability of halides to be chemisorbed. Our calculations provide information about the pure metal–ion interaction, without any environment, and cannot be compared directly with experiment. The strength of interaction is predicted from our calculations to be in the order  $\text{I}^- < \text{Br}^- < \text{Cl}^- < \text{F}^-$  for any of the metals investigated, in contradiction to the electrochemical suggestions. A similar order, slightly perturbed for bromide, appears in ab initio results for the adsorption of halides on mercury and copper (111) surfaces that have been reported [12–14]. The differences between adsorption energies are rather smooth in these cases (except for fluoride), while from our calculations a clear growth in the values can be observed together with a decreasing distance of the ion from the surface. The magnitudes presented by

Kuznetsov for energy and distance values for Cu(111) are, in general, similar to ours, the main differences in the strength of interaction for  $\text{Br}^-$  and  $\text{Cl}^-$  being noticed. It should also be remarked that the average distance of the chloride, bromide and iodide from the hollow site, computed for the  $\text{Ag}_{12}$  and  $\text{Au}_{12}$  clusters, agrees very well with a value of  $2.4 \text{ \AA}$  proposed for this parameter from X-ray studies [51–53].

An additional piece of information about the systems studied may be obtained from the charge transfer between the adsorbate and the adsorbent. The experimental reports suggest almost total discharge of the halide ion when it is adsorbed on the metal [15,53]. As is shown in Tables 4–6, where the charge on the ion under adsorption at the most stable hollow position is included, for all ions significant charge donation to the metal cluster is observed. The extra negative charge on the metal is always located on the atoms situated farther from the ion, producing a local positive region on the metal surface. This suggests a very drastic limitation of our model; the charge delocalization inside the infinite metal layer will certainly differ from the well-defined charge distribution in the small cluster. This factor may modify our results quantitatively, especially for the larger ions where the greater charge transfer occurs. However, as we have found similar values of this property for iodide, bromide and chloride, the error originated thereafter is likely to be about the same, thus having no effect on our comparative study. Therefore, the qualitative picture presented here of interaction of halides with the (100) surface is likely to be correct. Nevertheless the results for the charge transfer from the ion to the surface should still be treated with caution, since, as was discussed above for the atom–ion systems, an additional error in this quantity may come from the underestimated EAs of halide ions.

The results obtained for silver may be compared with earlier semiempirical work on the chemisorption of halides on this metal. The adsorption of  $\text{F}^-$  and  $\text{Cl}^-$  on the (100) silver surface modeled by  $\text{Ag}_9$  and  $\text{Ag}_{37}$  clusters has been studied using the IEHT method [6]. They show charges of about  $-0.7$  and  $-0.46$  on the fluoride and chloride respectively, which are similar to our  $-0.56$  and  $-0.43$  values. The interaction energies have not been calculated by these authors. The IEHT results [7] cannot be compared with ours, as they are related to the mixed layer case. To our knowledge, no theoretical studies on the adsorption of halides on gold surfaces have been performed until now.

It should be recalled, that the ion–water interaction plays an important role in the adsorption of halides on metals, since its magnitude varies significantly when different ions are compared. The interaction of fluoride with a water molecule (about  $-97.5 \text{ kJ mol}^{-1}$ ) is twice as large as the analogous iodide–water quantity (about  $-42.7 \text{ kJ mol}^{-1}$ ). The existence of such a strong interaction, which has a competitive character with the metal–ion adsorption, cannot be neglected. This factor, however, will

become irrelevant when the comparison of the adsorption of each ion on different metals is performed. Assuming that the adsorption energies of water on copper, silver and gold do not differ very much, the experimentally found strongest adsorption of ions on the gold surface should be shown also by our calculations. Indeed, comparing energies from Tables 4–6, gold appears to be the most attractive metal for each of the ions considered. Copper and silver have been found to be weaker adsorbing metals, but their relative positions are not clear. For iodide the tendency is  $\text{Cu} < \text{Ag} < \text{Au}$ , as reported by electrochemists. For bromide, the adsorption energies at copper and silver become almost the same, while for chloride and fluoride the weakest adsorbing metal is silver.

As pointed out above, the error in the EAs is reflected in the charge transfer from the ion to the metallic atom or cluster. Using fluoride as a test, when the polarization and diffuse functions are added on the ion (this being achieved by the  $\text{D95V} + ^*$  basis set) the B3LYP calculated EA of  $3.48 \text{ eV}$  is obtained, very close to the experimental value of  $3.40 \text{ eV}$ . For the  $\text{Cu}-\text{F}^-$  system, the charge transfer to the metal atom is decreased by the use of the more extended basis set: a new charge on the ion of  $-0.81 e$  is obtained compared with the value of  $-0.71 e$  with the original basis set. At the same time, the interaction energy decreases by about 10%.

For the  $\text{Cu}_{12}-\text{F}^-$  system, however, the charge transfer to the metal cluster is very large, leaving a net charge of  $-0.20 e$  on the ion; the interaction energy increases by 18%. A similar effect of the extension of the basis set upon the charge transfer was reported by Blanco et al. [13] in their calculations for the  $\text{Hg}_7\text{X}^-$  system.

It should be noted that the energy values computed with the  $\text{D95V} + ^*$  basis set are not corrected for the BSSE, which would slightly decrease these quantities. This would make the improvement of the basis set still less relevant for energy calculations, giving higher credibility to the values in Table 4.

### 3.2. Vibrational frequencies

Another property that has been widely investigated for the halides adsorbed on the noble metals by experimentalists, and which might be compared with calculated quantities, is the vibrational frequency obtained from surface-enhanced Raman spectroscopy (SERS). The vibrational frequencies  $\nu$  calculated for the  $\text{M}-\text{X}^-$  systems are shown in Table 7. For the  $\text{M}_{12}-\text{X}^-$  systems the results for the top and hollow sites on the surface are presented in Tables 8 and 9, respectively.

When compared with the experimental data [54] appended in Table 9, the atom–halide vibrational frequencies in Table 7 reproduce the correct ordering along each column, i.e. the relative magnitudes of the frequencies of a given metal atom with different halide ions are well predicted. However, silver is predicted to give higher vibra-

Table 7

Harmonic vibration frequencies  $\nu$  for the Cu-X<sup>-</sup>, Ag-X<sup>-</sup> and Au-X<sup>-</sup> systems from the B3LYP calculations

Ion	$\nu/\text{cm}^{-1}$		
	Cu	Ag	Au
F <sup>-</sup>	452.6	363.7	345.1
Cl <sup>-</sup>	221.1	183.1	157.5
Br <sup>-</sup>	152.5	133.5	128.8
I <sup>-</sup>	111.1	89.9	82.4

tional frequencies than gold, which is contrary to experimental evidence. The modeling of the surface by an atomic cluster does correct this problem, as shown in Table 8. The differences between the values shown in Tables 7 and 8 may be explained by the different masses of the metallic side of the oscillator and the different strength of the bonding as measured by the interaction energies in Table 1 and in Tables 4–6. In fact, it may be shown that the square root of the force constant is proportional to the interaction energy to within a 15% error for the atom and top site cluster cases. This is not unexpected, considering that we have the same type of bonding between metal and ion.

Tendencies similar to those found in Table 8 also appear in Table 9, where the vibrational frequencies of the ions adsorbed at the hollow site of the M<sub>12</sub> cluster are presented. Since this position is preferred for the adsorption of halides on metals, these results should be directly comparable with those obtained from SERS measurement. Following the experimental suggestions, the tabulated data show the largest frequency value to be that for fluoride with all metals, and a decrease of this property for other ions as the ionic radius increases. However, these changes are slightly smoother when compared with the top site case. The comparison of different metals show that, for the most stable position of the ion on the surface, the frequencies for silver are correctly predicted by our model to be the smallest ones. The positions of copper and gold are less clear, as the results for copper are larger than for gold for the three smaller ions; for iodide the opposite situation occurs.

The experimental results of the vibrational frequencies for ions adsorbed on copper are very uncertain, especially for the larger ions. This is why they are not included in Table 9 for comparison. The chloride ion adsorbed on the

Table 8

Harmonic vibration frequencies  $\nu$  for the Cu<sub>12</sub>-X<sup>-</sup>, Ag<sub>12</sub>-X<sup>-</sup> and Au<sub>12</sub>-X<sup>-</sup> systems from the B3LYP calculations for the top site

Ion	$\nu/\text{cm}^{-1}$		
	Cu	Ag	Au
F <sup>-</sup>	467.1	314.2	338.2
Cl <sup>-</sup>	213.6	200.4	232.5
Br <sup>-</sup>	154.5	131.9	150.0
I <sup>-</sup>	86.5	79.6	83.9

Table 9

Harmonic vibration frequencies  $\nu$  for the Cu<sub>12</sub>-X<sup>-</sup>, Ag<sub>12</sub>-X<sup>-</sup> and Au<sub>12</sub>-X<sup>-</sup> systems from the B3LYP calculations for the hollow site. Additionally, the experimental  $\nu$  values for Cl<sup>-</sup>, Br<sup>-</sup> and I<sup>-</sup> on the silver and gold surfaces, measured in aqueous solution at the negative potentials of the electrodes [54] are given

Ion	$\nu/\text{cm}^{-1}$				
	Cu	Ag	Au	Exp. Ag	Exp. Au
F <sup>-</sup>	281.1	252.0	275.9	—	—
Cl <sup>-</sup>	177.9	157.8	170.2	238	245
Br <sup>-</sup>	104.2	97.1	104.1	158	181
I <sup>-</sup>	72.1	61.3	73.2	115	120, 158

Cu surface is the most widely investigated case, and always shows a well-defined band at about 290 cm<sup>-1</sup> in its SERS spectrum [55]. This was recently confirmed [56], suggesting that the vibrational frequencies for ions adsorbed on copper are significantly higher than those for silver and gold. As one can see in Table 9, the same conclusion can be drawn from our results for the hollow position of the M<sub>12</sub> cluster. As has already been mentioned, the  $\nu$  values for F<sup>-</sup>, Cl<sup>-</sup> and Br<sup>-</sup> are larger for copper than for the two other metals. The differences are not as great as those reported from experiment, since all calculated values of the vibrational frequencies are much lower than those measured in SERS. This latter disagreement, however, is to be expected when one considers the extremely different environment of an ion in the experimental and theoretical situations. Several phenomena occurring in the real system, that are not considered in the theoretical studies, may cause this discrepancy between the experimental and calculated estimates: the coadsorption of other ions, the solvation of an ion, the surface heterogeneity (the SERS measurement is usually performed on polycrystalline electrodes), as well as the potential-dependent reconstruction of the ionic adlayer on the surface can modify forces between an ion and the metal and thus may change the  $\nu$  values.

The most likely explanation for the much lower values always reported from quantum calculations is the dependence of the vibrational frequencies on the surface coverage by the adsorbed ions, which is associated with the concentration of them in solution. The SERS measurement is usually performed for a relatively high concentration of the electrolyte, and results obtained may be related to the full coverage of the surface by ions. If so, several questions should be considered in conjunction with these conditions. The first problem is the location of an adsorbed ion on the polycrystalline electrode. Assuming this surface to be a combination of several different crystallographic planes, one may expect that the preference of the hollow position should also be preserved in this complex case. If we agree with this assumption, another problem arises: whether, in high concentrations, the adlayer is perhaps compressed and the ions are thus relocated to the bridge or

even top site, as suggested by recently presented STM results [18]. Although such a compression effect has been observed for rather less negative electrode potentials, but at the same time the concentration of the solution used was much lower than that applied in SERS, there is a possibility that it might occur in the system investigated spectroscopically. One can see from Tables 8 and 9 that the vibrational frequencies for the top site are always higher than those for the hollow position, and the spectrum of the compressed adlayer is thus expected to be quite different from that for low coverages. On the contrary, in the work [56] mentioned above, the concentration of the solution used for the copper–chloride system was relatively small. The results of this study show that, when the more diluted solution is used, the position of the maximum of the band associated with the Cu–Cl vibrations is shifted to the region of lower frequencies; a decrease in its intensity is observed at the same time. Thus, the decrease of the  $\nu$  values that is observed should not be related to the migration of an ion from the less preferred sites to the more stable ones on the surface.

This latter work seems rather to corroborate the other explanation of this phenomenon proposed in the theoretical work of Nichols and Hexter [57], where the image charge model was used to describe the reaction of the metal as a perfect electrical conductor to an increased concentration of ions in its neighborhood. On the basis of this approximation, the vibrational frequencies were then calculated as a function of the coverage of the surface by halogen atoms (which were assumed to have a charge of  $-1.0e$  under adsorption), positioned at the four-fold hollow sites of the Ag(100) surface. The results for the full coverage of the surface are very close to those reported for the halides adsorbed on polycrystalline silver. The so called ‘static field frequency’ reported in this work is thus equal to the  $\nu$  value that an adsorbed atom (ion) would have in an infinitely dilute solution. These have been found to be  $316.8\text{ cm}^{-1}$  for fluoride,  $159\text{ cm}^{-1}$  for chloride,  $100\text{ cm}^{-1}$  for bromide and  $82\text{ cm}^{-1}$  for iodide. If the influence of the solvent is negligible, these latter quantities should be similar to the results of the calculations for an ion situated at the hollow site of the  $\text{Ag}_{12}$  cluster. Indeed, an inspection of Table 9 shows that our results for silver are very close to those just quoted, especially in the  $\text{Cl}^-$  and  $\text{Br}^-$  cases. The greatest disagreement appears for the fluoride ion, since a much smaller  $\nu$  value is found in our calculations. As this ion adsorbs very weakly from an aqueous solution, there is no experimental data to compare with the results computed for full coverage obtained by Nichols and Hexter. Nevertheless, the value that is suggested for such a frequency from an extrapolation of the experimental  $\nu$  for the three other ions is significantly smaller ( $325\text{ cm}^{-1}$  [58]) when compared with the value of  $437\text{ cm}^{-1}$  reported. The result for zero-coverage is also expected to be overestimated for fluoride. If one assumes that the difference between the value of  $316.8\text{ cm}^{-1}$  quoted above and the

result of  $252\text{ cm}^{-1}$  in the present work comes from a systematic overestimation of the frequencies computed for fluoride in Ref. [57], then the full coverage result from that work should be reduced by about  $65\text{ cm}^{-1}$ . This would give a final ‘corrected’  $\nu$  value of about  $372\text{ cm}^{-1}$  that is much closer to that obtained from extrapolation. Following this line of argument, the results of the present work do appear to give a better description of the properties of this ion. Obviously, these considerations do have a relatively speculative character, since the models of calculation used in both works differ very much. One source of disagreement is probably an assumption in the work of Nichols and Hexter that a halogen atom adsorbed on the surface has a charge of  $-1.0e$  while in our calculations the halide ions are found to be partially discharged. The effect of such charge transfer to the metal and a smaller charge on the species adsorbed should thus be taken into account in the model proposed by the authors.

Both the results of the present studies and those of that theoretical work seem to confirm that the vibrational frequencies obtained from the cluster model calculations should not be compared quantitatively with those reported from SERS measurement. They may only reproduce the tendencies found in experimental data which the results reported here do very well.

#### 4. Conclusions

This work presents the results of a systematic study of the adsorption of halide ions on the (100) surface of the three noble metals. For each metal the adsorption of all ions at three different positions (hollow, bridge and top) has been tested using the B3LYP method. To our knowledge, this is the first time that the electron correlation has been included in theoretical investigations of such systems. A clear picture of the adsorption preferences has been obtained yielding the following general conclusions.

(1) In all cases the four-fold hollow site has been found correctly to be the preferred position for the ions on the (100) surface, as predicted experimentally.

(2) A significant charge transfer to the metal occurs under the adsorption process, the smallest one for the fluoride, the largest for iodide.

(3) For each ion (except  $\text{F}^-$ ) the charge donation to the metal increases in the direction:  $\text{Cu} \leq \text{Au} < \text{Ag}$ , but it should be stressed that the differences are very small.

(4) The adsorption energies of halides on each metal decrease remarkably as follows:  $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ . The sequence presented describes the interaction of ions with the metal in vacuum, and cannot be compared with the experimental results for a metal|solution interface.

(5) For any of the three larger halide ions, gold is the strongest adsorbent when compared with copper and silver, in agreement with the experimental data. Fluoride shows some small deviations from the general trends found for

the three other ions, which may arise from the larger error in EA for this ion.

(6) The vibrational frequencies calculated for halides adsorbed at the hollow site of the  $M_{12}$  clusters are found to describe correctly the tendencies reported from the SERS measurement. The  $\nu$  values increase in direction  $I^- < Br^- < Cl^- < F^-$ , when adsorption on the same metal is considered. For different metals the general trend  $Cu < Au < Ag$  for each of the three smaller ions was found.

(7) The apparent discrepancy in the magnitude of calculated and experimental  $\nu$  values, i.e. much smaller computed quantities, corroborates suggestions that this property depends strongly on the concentration of the ions on the surface.

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