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A study of the attack to one water molecule by either aluminum or cadmium atoms

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A study of the attack to a water molecule by either aluminum or cadmium atoms is accomplished for determining their interaction geometry. The existence of certain number of geometrical zones for repulsion and attraction of Al and Cd atoms when these interact with the water molecule is obtained using Density Functional Theory. Our results clearly show the existence of defined geometries where the interaction is the strongest for chemical bonds formation.

Keywords: Atomic bonding; potential energy curves; density functional theory; metal-molecule interaction.

Un estudio del ataque de una molécula de agua por átomos de aluminio o cadmio se lleva a cabo para determinar su geometría de interacción. La existencia de cierto número de zonas geométricas de repulsión y atracción de los átomos de Al y Cd cuando éstos interactúan con la molécula de agua se obtiene usando la Teoría de Funcional de la Densidad. Nuestros resultados muestran claramente la existencia de geometrías definidas en las que la interacción es más fuerte para la formación de enlaces químicos.

Descriptores: Enlaces atómicos; curvas de energía potencial; teoría de funcional de la densidad; interacción metal-molécula.

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1. Introduction

Potential energy curves of the attack on one water molecule by either aluminum or cadmium metal atoms in order to determine their interaction geometry and a possible insertion of the metal atom in a water molecule. Geometrical zones for repulsion and attraction of Al and Cd atoms when these interact with the water molecule are expected. Water contamination by metals is a problem requiring systematic studies. The water molecule by itself has been theoretical an experimentally widely studied since very long time ago for many researchers [1-4].

Recent studies have shown the importance of observing the different answers of the preferential adsorption in connection with the positions and geometric directions of the reactants, with important applications to electrochemistry [5]. It is important to know the nature of the metal-water interaction, binding energies, geometric forms and frequency of the reaction, in order to eliminate a greater amount of metallic components polluting the residual waters of industrial processes [6].

Sun *et al*. [7] studied reaction mechanisms of aluminum water systems by using B3LYP method [8] with 6-311+G(d,p) basis set [9,10] to achieve geometry optimization, and QCISD(T)/6-311++G(d,p) in calculating the stationary points corresponding with the reactants, products, intermediates and transition states. They were focused on enriching data concerning the vapor phase reaction of Al–H_2O system, and of calculating the enthalpy and the free energy changes of the reaction at 298 and 2000 K. They accomplished all this through 15 specific geometry orientations of optimized reactants. In our case, we are taking into account all possible orientations in order to get the zones and sites of reaction in general.

Price [11] achieved nearly *ab initio* calculations of the molecular and electronic distributions at the interface of hcp cadmium and liquid water. The first peak in their oxygen and hydrogen densities as a function of the distance from the center of the metal slab is around 7.93 A.

Álvarez-Ramírez *et al*. [12] accomplished (random) molecule–molecule interactions at different orientations obtaining much dispersed points. Instead of potential energy surfaces, they obtained a curve among the dispersed points as a linear regression fit in one of their cases analyzed. Such random interaction hides many interaction trajectories, and then their linear fitting hides something else.

In a previous work we considered a water molecule interacting with ionized copper and we found conical zones where the interaction is the strongest in the region of the symmetry plane [13]. We show now, that this is not only a case for ionized copper/water [13] but also for metal/water (metal = Al, Cd). We study here the case of the interaction of aluminum and cadmium with the water molecule, two metals in consecutive different groups of the periodical table, in order to determine: potential energy surfaces (PES) and using them to obtain the most favorable places of the interaction.

We achieved DFT calculations to study the interaction among one metal atom in ground state and one water molecule by approaching them since a certain distance, and repeating this closing at several angles. In addition our conical zones suggest accomplishing experimental studies using appropriate external electrical fields and polar properties of the water for orientation in one direction of a very big system of metals in water. This might help in some way to add, eliminate or transport metals by water molecules

We determine interaction zones among water molecule and aluminum or cadmium atoms through a geometrical dependence. The localized existence of certain number of geometrical zones of repulsion and attraction of Al or Cd atoms with the water molecule in the ground state is studied in DFT approximation. Our results exhibit geometrical zones where the interaction is more prominent. We emphasize those points which, in our opinion, require further development.

2. Methodology

We investigate both the aluminum-water and cadmium-water interactions in an appropriate group of symmetry (C_1 or C_{2v} or C_s) depending on the orientation among metal and oxygen atoms, through the DFT electronic structure program proposed by Delley [14]. The density functional proposed by Becke [15] for an exchange gradient corrected exchange potential is used in a self-consistent field (SCF) calculation. We use a gradient corrected Hamiltonian, named BOP in the generalized gradient approximation (GGA) [16] for exchange correlation potential. This Hamiltonian consists of two parts: exchange functional of Becke [17] and correlation functional of Tsuneda and Hirao [18]. The correlation part is a much improved Colle-Salvetti-type correlation functional for both opposite and parallel spin correlations and it obeys all the necessary conditions of the exact correlation functional.

The calculations are in all-electron and spin-unrestricted (different orbitals for different spins) accomplished, where the molecule is set into a center of mass coordinate system, unable to construct rotation matrix. For spin-polarized systems, the parameters proposed by Janak, Moruzzi, and Williams (JMW) from their original work on metals [19] were used. Open-shell systems, with unrestricted wave functions are run. For these molecules, we use a double numerical basis with polarization functions, *i.e.*, functions whose angular momentum is one higher than that of the highest occupied molecular orbital in the free atom. The size of the DNP basis sets are comparable to 6-31G** sets.

A weakness of the DFT-BOP-GGA approach is its tendency to overestimate the energies [20]. The errors in the DFT-BOP/DNP energies tend to increase as the number of electrons increases and the number of nuclei decreases [21].

3. Aluminum-water Interaction

In the study of aluminum-water interaction, we always consider the water molecule in the XY plane with the oxygen atom in the origin and the two hydrogen atoms placed symmetrically with respect to the positive part of Y axis (Fig. 1). The appropriate symmetry group of the metal atom toward the oxygen atom of H_2O is investigated by considering the aluminum attack to the water molecule from several angles with respect to the main axes according to Fig. 1. For H_2O we use the geometry HOH bond angle 104.52° and OH bond length r_{OH}= 0.9572 Å, which is an experimental result [22] and also corresponds to the TIP4P model, presented by Jorgensen *et al.*, [3].

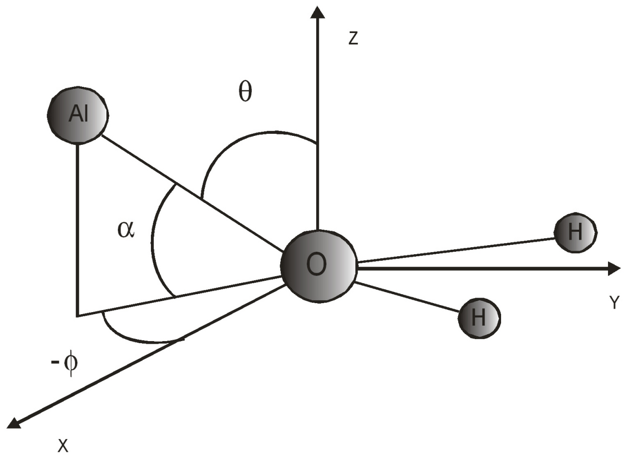


FIGURE 1. Geometry of the aluminum-water interaction.

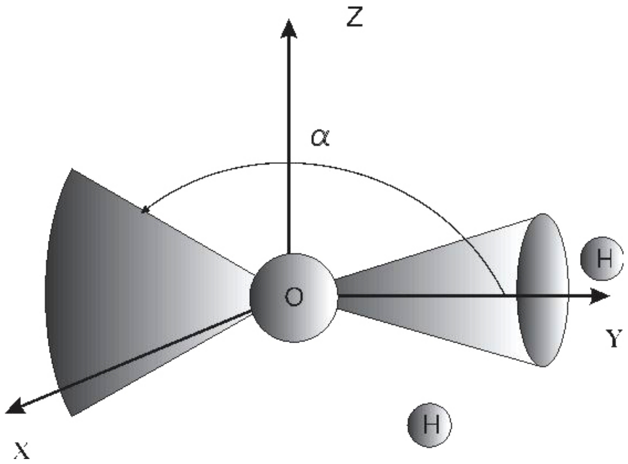
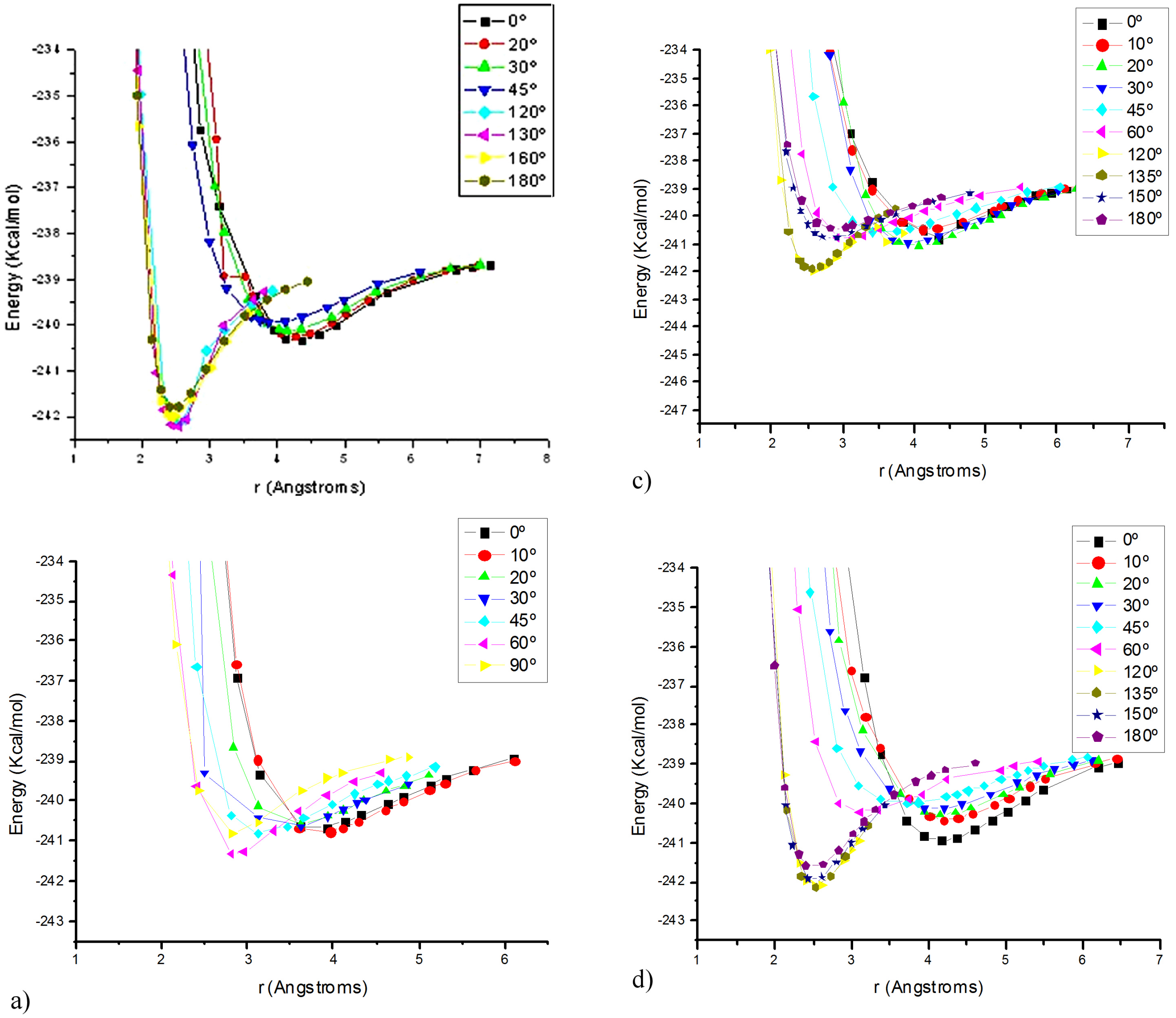


FIGURE 2. Geometric zones for Aluminum/Water reaction.

We consider different attacks of the aluminum atom to the water molecule (in spherical coordinates (r,θ,ϕ)), each one belong to a specific plane determined by the angle ϕ=cte. We always use the complementary angle $\alpha=90^\circ-\theta$, varying from $0^\circ \rightarrow 180^\circ$, and r∈[1.5 Å,6 Å] to determine the DFT interaction energies for the selected sites and orientations as functions of the distance r.

For approaching along ϕ=90° plane (*i.e.*, the YZ plane), here we are considering the cases $\alpha \in \{0^\circ, 20^\circ, 30^\circ, 45^\circ, 120^\circ, 130^\circ, 160^\circ, 180^\circ\}$. From the Fig. 3 we may predict that the strongest interaction should be at α=130° and another weaker at α=0°. These two lines define the axis of symmetry of two approximately conical areas, with $\alpha \in [120^\circ,180^\circ]$, where the bond strength is greater, and $\alpha \in [0^\circ,30^\circ]$ for a weaker bond in front of the hydrogen atoms.



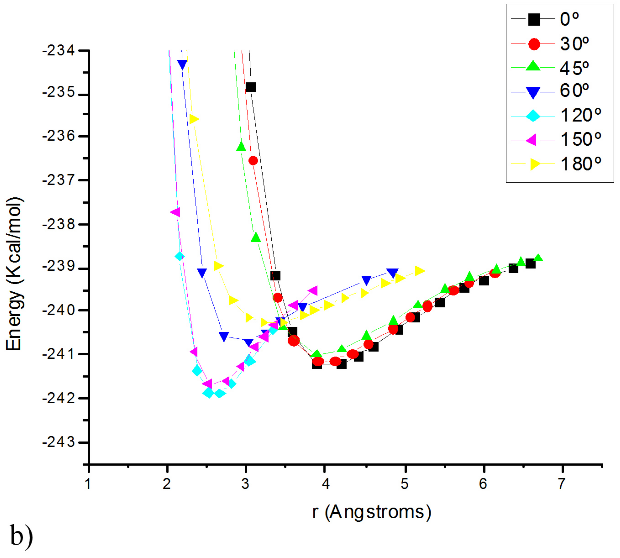


FIGURE 3. Plane ϕ=90°, a) Plane ϕ=0°, b) Plane ϕ=30°, c) Plane ϕ=45°, d) Plane ϕ=60°.

For approximating the aluminum atom to the water along other four planes $\phi \in \{0°, 30°, 45°, 60°\}$ [Figs. 3a, 3b, 3c and 3d, with the corresponding cases $\alpha \in \{0°, 10°, 20°, 30°, 60°, 90°\}$, $\alpha \in \{0°, 30°, 45°, 60°, 120°, 150°, 180°\}$, $\alpha \in \{0°, 10°, 20°, 30°, 45°, 60°, 120°, 135°, 150°, 180°\}$, and $\alpha \in \{0°, 10°, 20°, 30°, 45°, 60°, 120°, 135°, 150°, 180°\}$, respectively] we always confirm that there are only two active zones more suitable for the interaction. We summarize the results of minimum energy along YZ plane approaches in Table I, where the numerical values for energy and distance are given.

We consider important to mention that for each point of the H_2O + Al interaction, the symmetry of the intermediary HAlOH product is C_{2v} for α=0° and C_s for α=130°; and that the minimum in potential wells of E vs r corresponds with the adsorption points where the intermediary product is formed. From the graph in Fig. 4 the formation of the intermediary product starts at the maximums of this curve, and it has its

TABLE I. Distance in angstroms and energy in kcal/mol at the minimum of each curve in the Plane ϕ=90° of the Al-H_2O reaction at the α angle in degrees; where: ΔE=E_{∞}-E_{min}; SG $\equiv$ Symmetry Group and H-L $\leftrightarrow$ Homo-Lumo.

	Plane ϕ=90°		Al-H_2O	
α	r	ΔE	SG	H-L
0°	4.361	1.437	C_{2v}	23-24
10°	4.265	1.424	C	24-25
20°	4.271	1.357	C_s	24-25
30°	4.139	1.222	C_s	24-25
45°	3.864	1.034	C_s	24-25
60°	3.247	0.994	C_s	23-24
80°	3.156	1.564	C_s	23-24
90°	2.760	1.901	C_s	23-24
120°	2.535	3.247	C_s	23-24
130°	2.543	3.299	C_s	23-24
145°	2.484	3.243	C_s	23-24
160°	2.448	3.1	C	23-24
180°	2.458	3	C_{2v}	23-24

most stable point at the minimums of the curve that corresponds with attacks along the Y-axis.

In addition since aluminum is an acid (acceptor) [15], it can receive an electron pair in its lowest unoccupied molecular orbital (LUMO) from the highest occupied molecular orbital (HOMO) of a base (donor). That is, the HOMO from the base and the LUMO from the acid combine with a bonding molecular orbital, which in our case corresponds with the orbital 23-HOMO and 24-LUMO, in the A' and A'' irreducible representations of the C_s symmetry, respectively.

Details of the Fukui function are extensive and this function provides a different approach and results from those obtained by us here. Those Fukui surfaces at Al-H_2O interaction, some of them approximately conical, are not the initial part of our conical zones as we expected, because they have a different orientation. They are produced with a really different theory in which the local reactivity describes better the charge sensitivity, while our interaction orientations describes better the potential energy surfaces.

As a comment, our calculations are hardly useful at collisions at slow velocities; because it is required to obtain the probability transition first [23]. Probability transitions can be theoretically calculated only when avoided crossings among excited states exist. The level of theory used in the present work is not enough to reach excited states, TDDFT or *ab initio* calculations have to be accomplished for comparison among calculated and experimental cross section in a simple case.

To show the existence of asymmetric preferences for the interaction, we graph the function ΔE vs α in Fig. 4 (where ΔE = E_{∞}-E_{min}). Attacking water with aluminum along the YZ-plane the results shows that the water molecule presents three binding energies from which the strongest are located at $\alpha = \pm 130°$ with their corresponding energies at ΔE=3.299 Kcal/mol, when the radial distance is r=2.543 A.

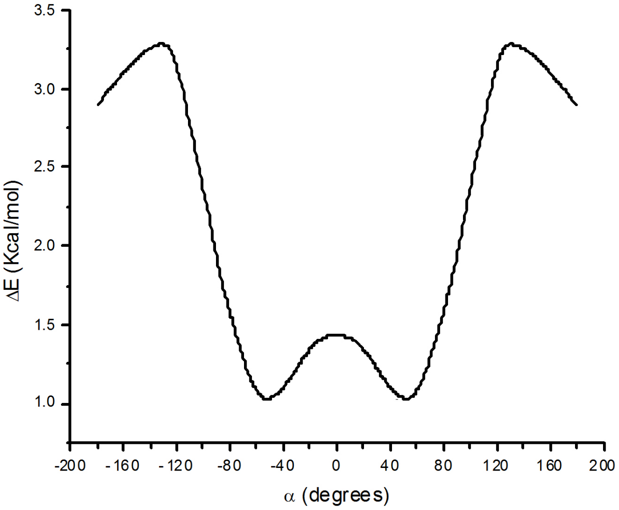


FIGURE 4. Angular dependence of bonding Al-H_2O.

In Fig. 4 we show the binding energies for different values of α, and clearly shows the existence of three well defined maxima, one around α=0° and the other around ±130°.

4. Cadmium-water Interaction

In the case of cadmium-water interaction, as before we always consider the water molecule in the XY plane with the oxygen atom in the origin and the two hydrogen atoms placed symmetrically with respect to the positive part of Y axis (Fig. 1). By attacking the water with the metal from angles with respect to the main axes according to Fig. 1 (where the aluminum is substituted with Cd), the symmetry group of cadmium toward the oxygen in H_2O is obtained. Again, for H_2O we use HOH=104.52° bond angle and r_{OH}=0.9572 A bond length

Here we consider only approaches by $\phi = 90°$ plane. As before, we use spherical coordinates (r,θ, ϕ) and we always use the complementary angle $\alpha = 90° - \theta$, varying from $0 \rightarrow 180°$, and r $\in$ [1.5 A,6 A] to determine the DFT interaction energies for the selected sites and orientations as functions of the distance r.

For approaching along the ϕ=90° plane, (the YZ plane), here we consider the cases $\alpha \in \{0°, 30°, 45°, 90°, 120°, 130°, 145°, 180°\}$. From Fig. 5 we predict that the strongest interaction is at α=0° thus defining the symmetry axis of one approximately conical area, with $\alpha \in [0°,45°]$ which has the highest bond strength in front of the hydrogen atoms. In Fig. 6 we can see that there is only one maximum at zero degrees and the behavior tends to be repulsive when we move away from the axis.

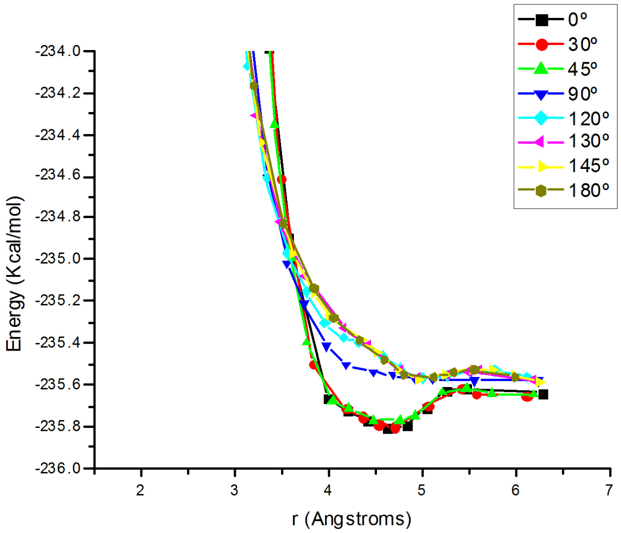


FIGURE 5. Plane ϕ=90° Cadmium/water.

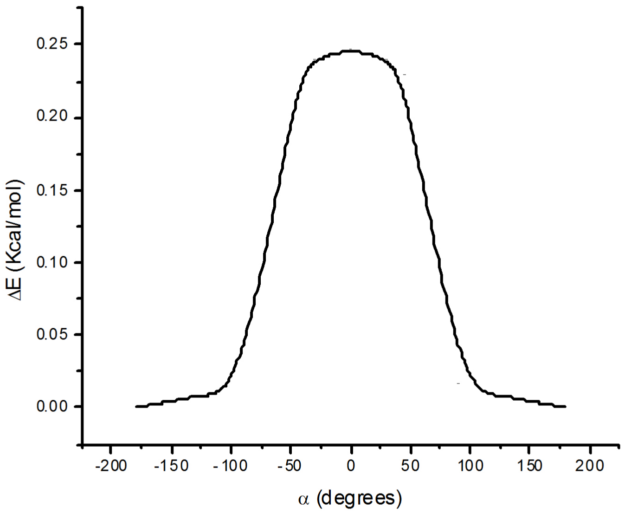


FIGURE 6. Angular dependence of bonding energy Cd/H_2O.

TABLE II. Distance in angstroms and energy in kcal/mol at the minimum of each curve in the Plane ϕ=90° of the Cd-H_2O reaction at the α angle in degrees; where: ΔE=E_{∞}-E_{min}; SG $\equiv$ Symmetry Group and H-L$\leftrightarrow$Homo-Lumo.

	Plane ϕ=90°		Cd-H_2O	
A	r	ΔE	S-G	H-L
0°	4.618	0.248	C_{2v}	58-59
30°	4.706	0.24	C_s	58-59
45°	4.752	0.229	C_s	58-59
90°	5.56	0.017	C_s	58-59
120°	5.005	0.008	C_s	58-59
130°	4.946	0.008	C_s	58-59
145°	6.246	0.024	C_s	58-59
180°	5.977	0	C_{2v}	58-59

It is important to mention that for each point of H_2O + Cd interaction, the symmetry of the intermediary HCdOH product is C_{2v} for α=0°, and α=180°, and C_s for the other values of α; and the minimum of the potential wells of E vs r corresponds to the adsorption points where the intermediary product is formed. The formation of the intermediary products starts at the maximums of the curve in Fig. 6, and it has its most stable point at the minimums of the same, which corresponds to attacks along the Y axis. Since cadmium is an acid (acceptor), it can receive an electron pair in its lowest unoccupied molecular orbital (LUMO) from the highest occupied molecular orbital (HOMO) of a base (donor). That is to say, the HOMO from the base and the LUMO from the acid combine with a bonding molecular orbital, which in our case corresponds to the orbital 58-HOMO and 59-LUMO. Attacking water with cadmium along the YZ-plane, the results indicate that the water molecule presents one binding energy located at α=0°, with its corresponding energy ΔE=0.248 Kcal/mol, when the radial distance is r=4.618 A. This distance is proportionally in accordance with that one of 7.93 A obtained by Price [11], considering that he is calculating for an aggregated system of hcp cadmium (or an slab) and many water molecules as we said before, and in our case is just one cadmium atom and one water molecule.

5. Discussion

Here we report the results of the interaction of aluminum and cadmium with the water molecule (see Fig. 1), using diverse geometric orientation attacks of the metal towards the water molecule, particularly with the interaction Al+H_2O we show that the capture of the aluminum atom is only possible in two approximately semi-conical regions with its center in the oxygen atom with symmetry axis at α=0° and α =130°, measured relative to the axis of symmetry of the water molecule (Fig. 2).

In each atom the angles and the bonding energies are different as shown in the Table III. Until now we have not find reported any value for the bonding energies for cadmium and aluminum with water. Furthermore, we do not have any law allowing us to predict the magnitude of the angle and bonding energies for metal atoms in different groups. However we have shown that the angle and the boding energies are not constants.

These results suggest certain practical applications, as in polluted water with contents of cadmium, aluminum or cop-

TABLE III. Comparison of the bonding energies in kcal/mol and its corresponding angles in degrees and distances in angstroms for copper, cadmium and aluminum interacting with water.

	ΔE	θ	r
Cu[13]	0.783	110	2.395
Cd	0.248	0	4.618
Al	3.3	130	2.543

per; it is easier to liberate the water from contaminants as cadmium and copper than from aluminum.

In this case, where metal-water binding energies are lower than the water binding energy reported by Joergensen [3], the possible overestimation of the DFT-BOP-GGA approach will be reflected in the comparison among cadmium an aluminum interacting with water when either measurements or *ab initio* calculations were being achieved. Due to the small number of electrons however, we consider that the overestimation hardly will occur. At this time the binding energy of Cu(110) surface with one water molecule is 0.18 (4.15 kcal/mol) according to the experimental and theoretical work of Schiros [24], which we consider in agreement with the 0.783 kcal/mol for our previous result [13] of copper-water. We attribute the order of magnitude to the difference among a surface and an atom.

6. Conclusions

We carried out a DFT calculation of the bonding of water molecule to aluminum and cadmium, where we analyzed different attacks from the Al and Cd atoms toward the water molecule, thus allowing us to establish the existence of those geometric zones that are more favorable for the interaction.

The most propitious zones for the interaction are approximately conical and as expected (due to the symmetry), these are more intense for the approaches along the XY plane. Our DFT calculations allowed us to establish clearly, that there are several geometrical zones in which the interaction is more intense and more probable to occur. Then, as expected the symmetry plane give the most intense potential energy surfaces with localized adsorption points.

The confidence of our results on aluminum and cadmium is based on the fact that similar calculations for copper-water interaction were achieved, which agree in distance with the results in literature. The interactions for copper and for these two metals with water molecule show that the number of zones is not constant. For copper [13] and cadmium we have only one zone in the symmetry plane but there are two for aluminum. To establish the number of interaction zones is a question still open, and also the same for the variables determining its location.

The existence of these interaction zones and its particular location suggests the experimental possibility of exploring to add or release metallic atoms toward the water molecule using the direction of the water molecule in the presence of an external electric field. We think that the determination of the most favorable geometrical zones for bonding in each particular case would lead to the modification of the reaction mechanisms. From our point of view, it is clear that these matters require further understanding.

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