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Bonding of water to copper atom at an almost random interaction

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The results of a density functional theory (DFT) study of the bonding between water and an ionized copper atom are presented through an all-electron calculation. The C_1, C_{2v} and C_s approaches of the metal atom toward the oxygen atom on H_2O are investigated. The analysis shows the geometric dependency of the copper-water bonding energy in the form of approaching this metal to the water molecule. Bonding exists only in the conical region perpendicular to the plane of the water molecule with vertex in the oxygen atom. Our results suggest experimental possibilities such as copper transport in water, or preventing the copper from attaching onto the water molecule by orienting it by means of external electric fields to the directions less favorable to the reaction.

Keywords: Atomic bonding; potential energy curves; density func- tional theory; metal-molecule geometric approach.

Los resultados de un estudio de teoría funcional de la densidad acerca del enlace entre una molécula de agua y un átomo de cobre ionizado se presentan por medio de un cálculo todo-electrón. Se investigan aproximaciones C_1, C_{2v}, y C_s del átomo de metal al átomo de oxígeno en H_2O. El análisis muestra la dependencia geométrica de la energía de enlace agua-cobre en la forma de aproximar este metal a la molécula de agua. El enlace existe solo en la región cónica perpendicular al plano de la molécula de agua con vértice en el átomo de oxígeno. Nuestros resultados sugieren posibilidades experimentales tales como transporte de cobre, o prevención del ataque del cobre a la molécula de agua orientándola por medio de campos eléctricos externos a la dirección menos favorable a la reacción.

Descriptores: Enlace atómico; curves de energía potencial; teoría funcional de la densidad; aproximación geométrica metal-molécula.

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1. Introduction

Many studies of water adsorption on copper surfaces have been carried out due to its technological importance and academic interest [1–7]; however, not too much has been said about the adsorption of water molecules on copper atoms [8–11] and even less about water molecules reacting with ionized copper [12]. We used density functional theory (DFT) in order to explore the adsorption of H_2O + Cu^{+2}, knowing it was designed to calculate ground state properties due to a set of nuclei in a given arrangement.

In recent theoretical studies, either copper or nickel atoms interacting with water molecules have been evaluated by a standard density functional approach, including gradient corrections. The computed geometries, harmonic wave numbers and dissociation energies show a good agreement with previously published post-Hartree-Fock data and with the few available experimental results [1, 8, 13].

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 [14]. In addition water contamination by metals is a problem requiring more and more a systematic study to know more about the nature of the reaction, 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. This is important because excessive copper intake might cause early childhood cirrhosis for example [15].

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.

In the present paper we report the results of the interaction of ionized copper (Cu^{+2}) with water molecule, using diverse geometric orientation attacks of the metal towards the water molecules, and we show that the capture of the copper atom is only possible in a semi-conical region with its center in the oxygen atom and perpendicular to the plane of the water molecule. In Sec. 2, we specify the method, the groups of symmetry considered, and the different space approaches between the water molecule and the ionized copper atom. In Sec. 3 we report the DFT results. Finally, in Sec. 4 we give a short summary of this work emphasizing those points which, in our opinion, require further development.

2. Methodology

We investigate the copper water reaction in an appropriate group of symmetry (C_1 or C_{2v} or C_s) depending on the orientation among copper and oxygen atoms in an almost random interaction, through the DFT electronic structure program proposed by Delley [19]. The density functional proposed by Becke [17] for an exchange gradient corrected exchange potential is used in a self-consistent field (SCF) calculations with a one-parameter BOP correlation gradient-corrected correlation potential. The functional specifies the local correlation and gradient-corrected functional for exchange and correlation. The calculations are all electron- and spin-unrestricted (different orbitals for different spins), 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 [20] were used. Open-shell systems, with unrestricted wave functions are run. For this molecule, 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-GGA approach is its tendency to overestimate binding energies [21]. The errors in the DFT-BOP/DNP energies tend to increase as the number of electrons increases and the number of nuclei decreases [22].

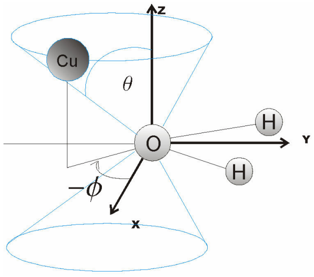

FIGURE 1. Geometry of a copper atom interacting with a molecule of water.

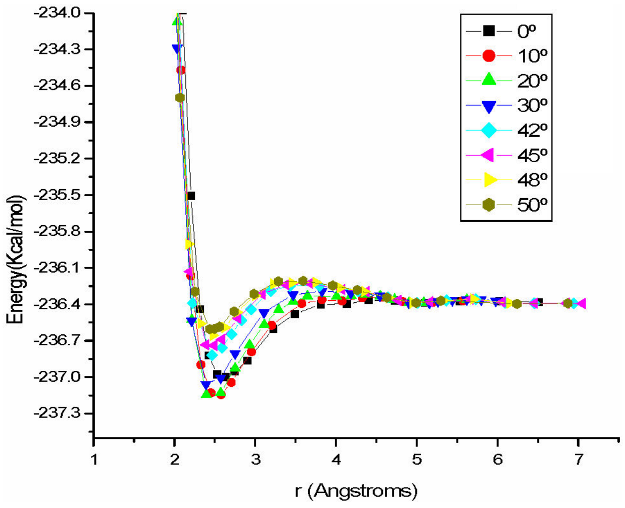

FIGURE 2. X = 0 plane, approach along the negative part of the Y-axis.

3. Results and discussion

The appropriate symmetry approach of the metal atom toward the oxygen atom of H_2O is investigated by considering that copper attack the water molecule from several angles with respect to the main axes according to Fig. 1. For H_2O the experimental geometry HOH bond angle $104.52°$ and OH bond length 0.9572 angstroms is adopted.

The dependency of the reaction on the geometry of the copper attack on the water molecule is established more clearly if we separate the study of the reaction in different zones.

We always fix the water molecule to the plane XY, with oxygen at the origin of the coordinates and with hydrogen atoms in symmetry with respect to the positive part of the Y-axis, and we use spherical coordinates to establish the position of the copper atom.

We consider different attacks of copper on the oxygen of the water molecule along the coordinate planes $y = 0$, $z = 0, x = 0$ both positive and negative parts. In addition we consider approaching planes at an angle of 45° to construct a three-dimensional image of the behavior of the reaction.

In Fig. 1, we display the resulting qualitative behavior for attractive zones (inner region of the cone), and we show the asymmetry of the bonding zone (with respect to the Z-axis).

3.1. YZ-Plane

For approaching along the X=0 plane, we obtain the most active zones along the negative part of the Y-axis: Fig. 2 displays the DFT interaction energies for some selected sites and orientations as a function of the distance for different angles with respect to the Z-axis.

$$\theta \in \{0°, 10°, 20°, 30°, 42°, 45°, 48°, 50°\},\ \phi = -\frac{\pi}{2}.$$

We can see an almost random effect in this graph despite the well-organized curves obtained, where the depth of the well decreases as the angle increases while the minimum distances remain almost stable.

Figure 3 displays the DFT interaction energies for the selected angles

$$\theta \in \{10°, 20°, 30°, 45°\},\ \phi = \frac{\pi}{2}.$$

with respect to Z-axis, for approaches by the positive part of the Y-axis.

We summarize the results of energy minima along YZ-plane approaches, where the numerical values for energy and distances are given in Table I. The angles with minus signs are used to indicate the approaches along the negative part of the Y-axis. We consider important to mention that for each point of the $H_2O + Cu^{+2}$ reaction, the symmetry of the intermediary $HCu^{+2}OH$ product is C_s, and that the minimum in potential wells corresponds to the adsorption points where the intermediary product is formed. From the graph in Fig. 4

we notice the evident asymmetry, which clearly is more favorable to the reaction of attacking along the negative part that corresponds to the zone of reactants, whereas for the approaches along the positive part of the Y-axis correspond to the breaking of the intermediary product, that is to say to the possible formation of new products.

We emphasize that the formation of the intermediary product starts at the maximum of the curve in Fig. 4, and it has its most stable point at the minimum of the curve that corresponds to attacks along the positive part of Y-axis. In addition since copper is an acid (acceptor) [23], 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 to the orbitals 39-HOMO and 40-LUMO, both in the A' state. Details of the Fukui function are extensive and this function provides a different approach and results from those obtained by us here.

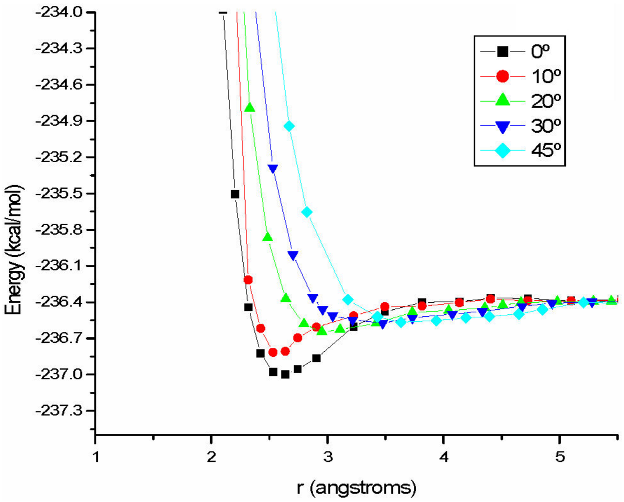

FIGURE 3. X = 0 plane, approach along the positive part of the Y-axis.

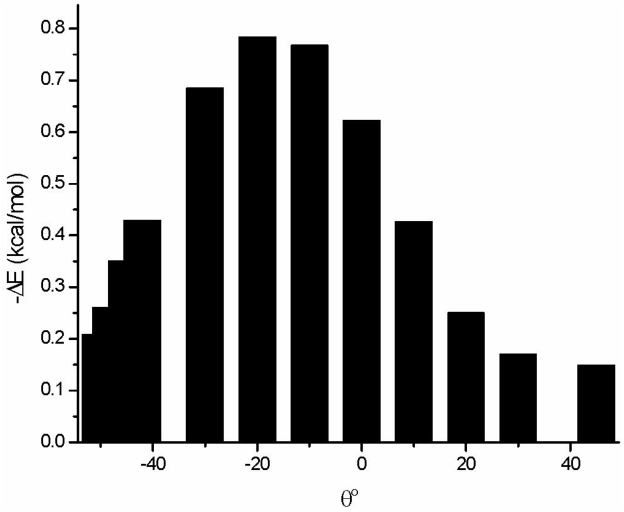

FIGURE 4. Angular dependency of bonding energy.

TABLE I.

θ	r_o	-Δ E	Symmetry Group	Homo-Lumo
-50	2.438	0.208	C_s	39-40
-48	2.475	0.26	C_s	39-40
-45	2.491	0.35	C_s	39-40
-42	2.467	0.429	C_s	39-40
-30	2.394	0.684	C_s	39-40
-20	2.396	0.783	C_s	39-40
-10	2.58	0.767	C_s	39-40
0	2.639	0.622	C_s	39-40
10	2.709	0.426	C_s	39-40
20	2.954	0.25	C_s	39-40
30	3.128	0.17	C_s	39-40
45	3.634	0.149	C_s	39-40

In order to show the existence of asymmetric preferences for the reaction, we graph the function $-\Delta E\ vs.\ \theta$ in Fig. 4 (where $\Delta E = E_\infty - E_{\min}$).

By approaching by the YZ-plane the results indicate that the water molecule presents the strongest binding energy ΔE=-0.783 kcal/mol, at $\theta = 20°$, when the radial distance is $r = 2.396\ \mathring{A}$.

3.2. XZ-Plane

In this case we consider only the attack along the positive part of the X-axis, because the results are the same when approaching along the negative part of the X-axis

3.2.1. X positive approach

In this case we consider copper toward water molecule approaches for different angles in the $Y = 0$ plane: the geometric dependency of the reaction in this case is still more evident and it becomes more quickly repulsive. The zones of greatest activity are for small angles with the Z-axis; we show the behavior of the reaction for angles

$$\theta \in \{10°, 20°, 30°, 50°, 60°, 70°\}, \phi = 0°$$

with the Z-axis, in Fig. 5. Again, we observe repulsive and attractive curves, where the deep potential energy well corresponds to the 10° angle, which in this case is very similar to the 20° angle.

3.3. $X = -Y$ Plane

Finally we annexed the graphs of approximations of the copper atom along the plane at 45° in Figs. 6 and 7. In this case the deep potential energy well corresponds again to both 10 and 20° angles, and the rest corresponds to repulsive curves.

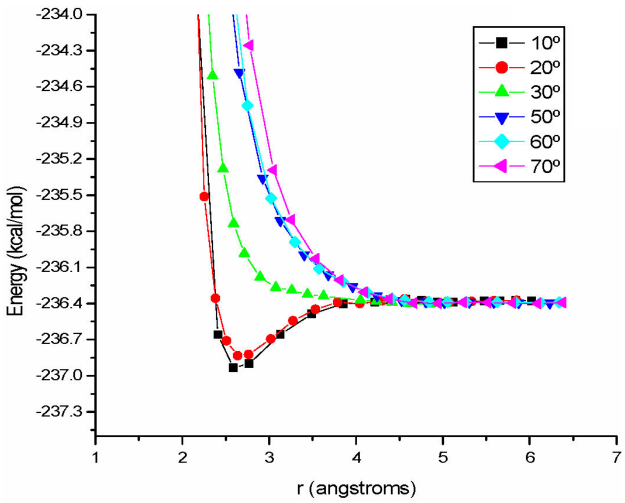

FIGURE 5. Y = 0 plane, X positive approach.

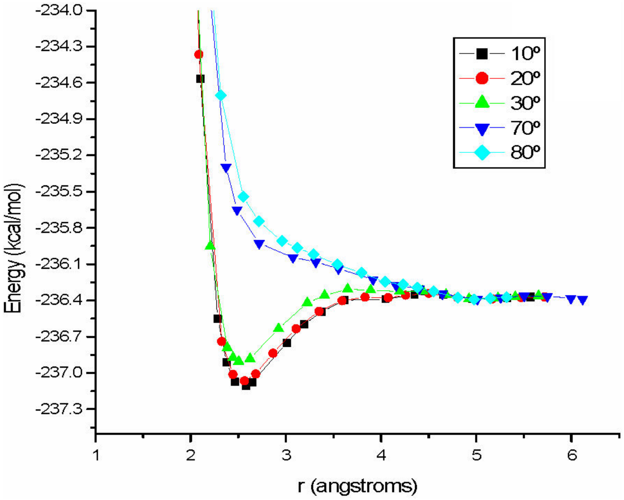

FIGURE 6. X=-Y plane, Y negative approach.

3.3.1. *Y negative approach*

The approach by points $\{(x,-y,z) \mid x,z \geq 0\}$ and for angles

$$\theta \in \{10^\circ, 20^\circ, 30^\circ, 70^\circ, 80^\circ\},\ \phi = -\frac{\pi}{4}.$$

are shown in Fig. 6.

3.3.2. *X negative approach*

The approaches by points $\{(-x,y,z) \mid y,z \geq 0\}$ and for angles

$$\theta \in \{10^\circ, 20^\circ, 30^\circ, 50^\circ, 60^\circ\},\ \phi = \frac{3\pi}{4},$$

are shown in Fig. 7.

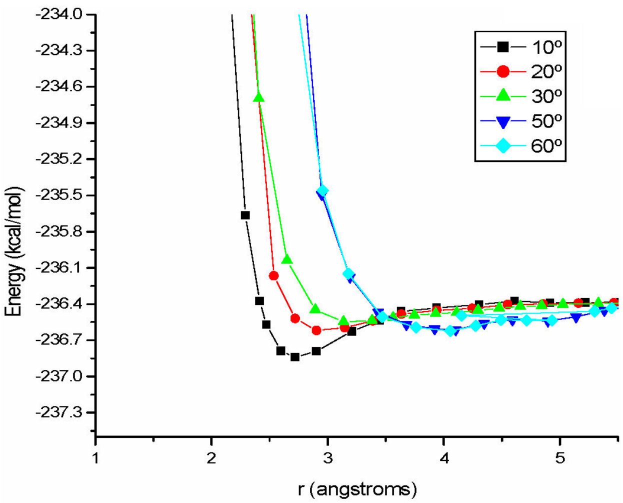

FIGURE 7. X=-Y plane, X negative approach.

4. Summary

We have carried out a DFT calculation of the bonding of water molecules to ionized cooper and we have analyzed different attacks from the copper atom on the water molecule, thus allowing us to establish the existence of repulsive zones clearly, as well as those geometric zones that are more favorable for the reaction.

While the energy is overestimated in all calculations of the water molecule with ionized copper as expected, the distances agree with those reported in most of our references.

The most propitious zone for the reaction is approximately conical and, as was to be expected (due to the symmetry), is more intense for the approaches along the negative part of the Y-axis.

This dependency suggests the possibility of experimentally exploring the adding or releasing to the water molecule of ionized copper atoms, using the direction of the water molecule in the presence of an external electric field.

In order to put our work in the right perspective and to suggest some possible lines of further research, we shall now make a few comments. The geometric dependency of the reactions has been little studied; the emphasis of the investigations normally is focused on determining the binding energies and the ranges within which these happen without taking into account the possibility from repulsive zones between molecules or atoms in interaction. We think that the determination of the more favorable geometric zones for bonding in each particular case would lead to the modification of the mechanisms or processes of the reactions. From our point of view, it is clear that these matters require further understanding.

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