

Theoretical Study on the Interaction of O₂ over the 110 Surface of Au and Its Effect on the Reaction of CN⁻

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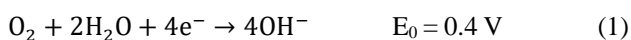
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ABSTRACT: Cyanidation of gold depends on the amount of oxygen in the reaction medium. In this study, the interaction of O₂ molecules with crystalline surfaces of gold (110_{surf0} and 110_{surf+1} surfaces) is investigated by using density functional theory (DFT). The results showed that the interaction of O₂ with Au₂ cluster was weak, which leads to overlapping orbitals of the 5d_{z²}-Au and the p_z-O₂. Oxygen reacts vertically with the surface was almost similar to its reaction with the Au₂ cluster. However, the parallel interaction of O₂ on the (110_{surf0}) and (110_{surf+1}) surfaces of Au is stronger than the vertical interaction state. Also, the interaction energy of CN⁻ with (110_{surf+1}) surface obtained about 13 kJ/mol more than (110_{surf0}) surface.

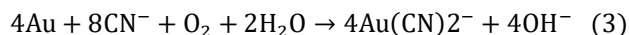
KEYWORDS: DFT; Cyanide, Gold extraction; Simulation; Au surface.

INTRODUCTION

The cyanidation process is one of the most effective methods of gold leaching in the Au processing industry and it is more than a hundred years old. Gold is one of the most stable elements known in nature and cannot be dissolved in water by oxygen alone, because the potential of the oxygen electrode is less than the oxidation of gold [1-4], according to Equations (1,2):



In addition, gold remains insoluble in acidic media (oxygen electrode potential 1.23V). However, in the presence of a strong complexing agent such as cyanide and reducing its half-reaction potential of anodic to -0.57 V, this reaction is performed, according to Equation (3) [5,6]:



Cyanide salts, whether potassium, sodium, or calcium, decompose by CN⁻ release. The cyanide anions are good ligands for many intermediate elements. The strong interaction between metals and CN⁻ ion can be attributed to the negative charge, the small size of the ligand and the possibility of participation in the bonds. In addition to the effect of cyanide, the amount of oxygen in the environment affects the dissolution of gold, which per mole of the O₂ can be dissolved 4 moles of the Au [7,8]. Due to the presence of minerals in the solution medium, the amount of O₂ required to dissolve Au increases and these compounds disrupt the leaching of gold. The formation of passive layers of Au-CN or Au-CN-OH and AuS_x and presence of organic materials as oxygen and cyanide consumer, disrupts the leaching process [3,9,10].

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Gold is the 79th element in the periodic table and has an electron configuration of [Xe] 4f¹⁴ 5d¹⁰ 6s¹. The 5d orbitals of the Au⁺ ion have been introduced as the main reason for the reaction [11, 12]. The d orbitals of the gold atom and elements of the d-category of the periodic table have an effective role in the reactions by moving towards higher energy levels. Molecular systems or atomic structures with heavy atoms often have significant properties such as relativistic effects that the rapid movement of electrons leads to significant orbitals contraction of s, p [12-15]. Au dimer (Au₂) is the simplest molecular form of gold which activity is due to the interaction and dispersion of electrons in the d¹⁰ shell of gold atoms [11, 16]. Previous studies have shown that the interaction of O₂ depends on the number of Au atoms and its charge in the cluster or lattice that Au⁺ ion was the most probable and the most active state of the Au [16,17].

Due to the atomic properties and low reactivity of gold as well as the effect of oxygen on the oxidation process of gold in cyanide medium, in this paper, the interaction of the O₂ molecule with Au₂ molecule and (110_{surf0}) and (110_{surf+1}) surfaces of gold crystal is first studied by using molecular simulation and DFT method. Then, in the presence of oxygen, the reaction of cyanide with the surfaces is investigated to gain a better understanding of the effect of O₂ on the oxidation of Au.

COMPUTATIONAL DETAILS

All the calculations were performed with the Perdew–Burke–Ernzerhof (PBE) functional and b3lyp code by implemented in the Dmol³ module [18, 19]. The geometry optimization for the bulk Au was performed with 5×5×1 K-points. The cell of gold crystal is shown in Fig. 1. The DFT method which has proven to be one of the most accurate methods for the computation of the electronic structure of solids [18-21]. After building the (110) surfaces, calculations of these surfaces were performed on supercell surface 2×2, with 4×4×1 k-points, using the COSMO method (water solvent) [22]. A double numerical with polarization (DNP) basis set was employed in the DFT calculations, while the all-electron relativistic method was used for the relativistic effects.

To evaluate the stability of O₂ molecule and or CN⁻ ion adsorbed on the (110) surface of Au, the adsorption energy (E_{ads}) was calculated according to Equation (4):

$$E_{\text{ads}} = E_{\text{total}} - (E_{\text{surf}} + E_{\text{react on surf}}) \quad (4)$$

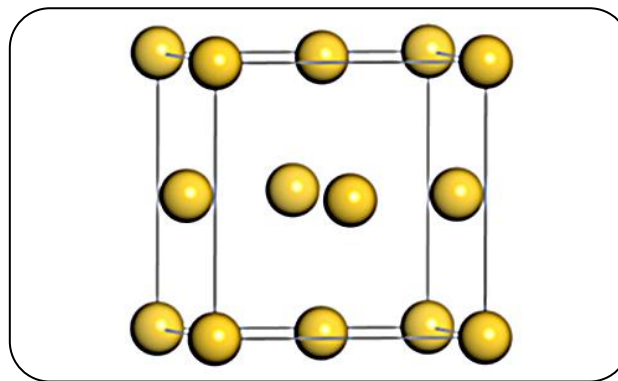


Fig. 1: Conventional unit cell of gold.

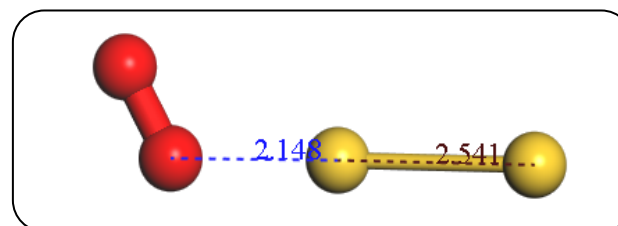


Fig. 2: Image of the interaction of molecular O₂ and Au₂ cluster.

Where E_{total} is the total energy of the surface and the reactors on surface, E_{surf} corresponds to the total energy of the surface, and E_{React on surf} is the energy of the O₂ molecule and or CN⁻ ion.

RESULTS AND DISCUSSION

Interaction of oxygen (O₂) and Au₂

The reaction of oxygen and gold depends on the number of Au atoms in the gold cluster, the dimer of which is the simplest molecular form of gold [16]. The calculations in this section were performed using the b3lyp function. The interaction of oxygen with Au₂ was weak resulting the overlap of the 5d_{z²} orbital of Au with the p_z orbital of oxygen atom. Also, the bond distance between the oxygen atom and the adjacent gold is 2.14 Å, as the Fig. 2, which corresponded to values of previous studies [16]. The Fig. 3 shows the HOMO orbital image of the interaction of O₂ and Au. The 5d_{z²} orbital participation of Au is seen in the interaction, which is due to the properties of the relative effects of the intermediate elements [14].

In the following of calculations, first interaction of the O₂ on neutral surface of 110 (110_{surf0}) was investigated, then the central Au atom at 110 surface as Au⁺ is defined and the interaction of O₂ on the (110_{surf+1}) surface was studied.

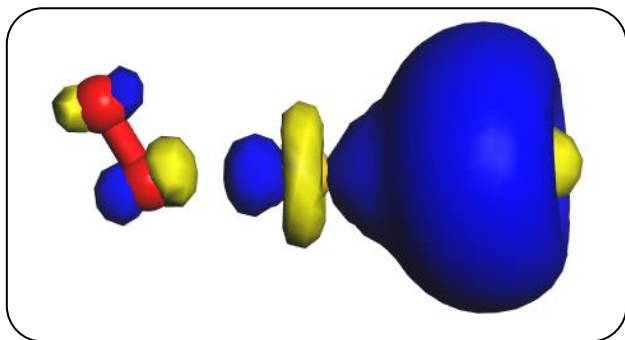


Fig. 3: Image of the HOMO orbital, interaction of molecular O₂ and Au₂ cluster.

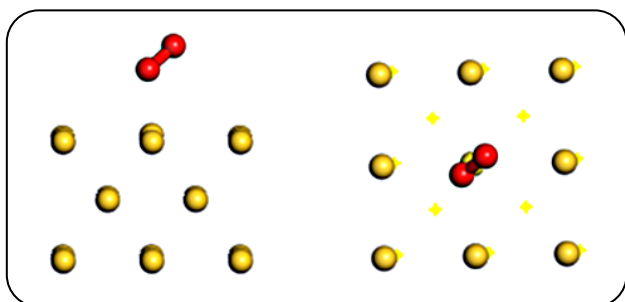


Fig. 4: Image of how O₂ is placed vertically near the (110_{surf0}) surface; a. vertical view, b. side view.

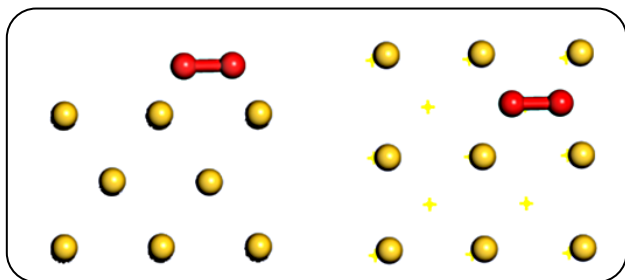


Fig. 5: Image of how O₂ is placed parallel near the (110_{surf0}) surface; a. vertical view, b. side view.

Interaction of oxygen (O₂) on (110_{surf0}) surface of Au

To investigate the interaction of O₂ with the (110_{surf0}) surface, O₂ was placed vertically and parallel over the surface. The way O₂ reacted vertically was almost similar to react with an Au₂ cluster and was located at a distance of 2.17 Å from the surface Au atom, as shown in Fig. 4. The low adsorption energy also indicates a weak interaction between the O₂ and the (110_{surf0}) surface. However, according to Fig. 5, oxygen has a stronger interaction in the state parallel to the surface and more adsorption energy was obtained than before the state.

By comparing the PDOS diagrams in Fig. 6, the density changes for oxygen that was absorbed in parallel were

greater. The presence of four Au atoms of (110) surface around O₂ causes the d orbitals of Au to interact more strongly with the p orbitals of O₂. In this case, the overlap of the Au-d_{xy} and O₂-p_y orbitals provides the conditions for electron transfer. In addition, in the Fig. 7, the d-orbital density change of the four Au atoms is confirmed electron transfer from the surface atoms to the O₂-adsorbed.

The performance of cyanide in the Au leaching depends on the presence or amount of oxygen in the environment [25, 26], as a result, it is important to study its reaction with the surfaces. Our calculations showed that cyanide interacts better than oxygen at the (110_{surf0}) surface. Its adsorption energy was 54 kJ and about 37 kJ was more than O₂ interaction. Cyanide tends to approach the surface vertically and reacts with the central Au atom of the surface. The DOS diagram shows a comparison of total density changes for both O₂ and CN⁻ with the (110_{surf0}) surface, according to the Fig. 8. The interaction of CN⁻ ion causes more charge to be drawn towards the Fermi level and fewer anti-bonding orbitals are created, which results in better adsorption and stronger interaction of the CN⁻ than the O₂.

Interaction of oxygen (O₂) on (110_{surf+1}) surface of Au

As shown above, O₂ reacts better in parallel with (110_{surf0}) surface and has a stronger interaction with the surface, so further studies have focused on this state (parallel oxygen interaction). To create the desired surface, it was optimized with the central Au¹⁺ atom and then the interaction of the oxygen molecule with the resulting surface was investigated. In this case, the O₂ had a stronger interaction with the (110_{surf+1}) surface, and its adsorption energy was greater than the (110_{surf0}) surface, adsorption energy was equal to 23 kJ.

Also, due to the effect of the CN⁻ in accelerating the oxidation of gold, the interaction of CN⁻ on two surfaces of (110_{surf0}) and (110_{surf+1}) which contained oxygen was studied. The adsorption energy value was greater for the (110_{surf+1}) surface, and energy values were obtained for the (110_{surf0}) and (110_{surf+1}) surfaces, 58 and 58 kJ, respectively. As shown in Fig. 10, the CN⁻ ion was placed almost vertically on the Au¹⁺ atom, and simultaneously, the O₂ molecule was displaced as the cyanide ion approaches. While for surface of (110_{surf0}), according to the Fig. 9, cyanide ion is approached the surface and no displacement occurs for the oxygen molecule.

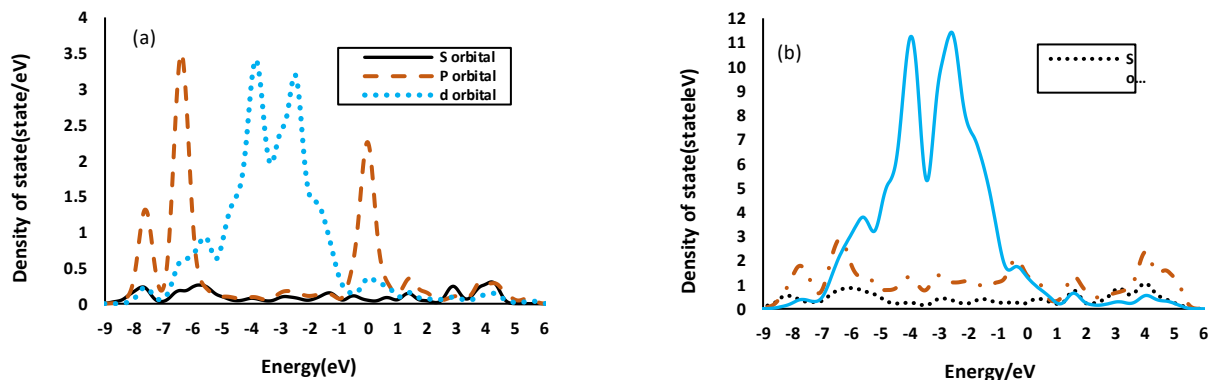


Fig. 6: PDOS diagram for two modes of O₂ interaction with (110_{surf0}) surface; a. vertically, b. in parallel.

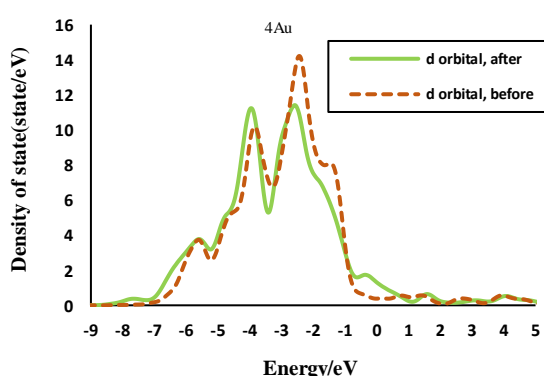


Fig. 7: PDOS diagram of d orbital Four Au atoms in (110_{surf0}) surface, before and after interactions with O₂.

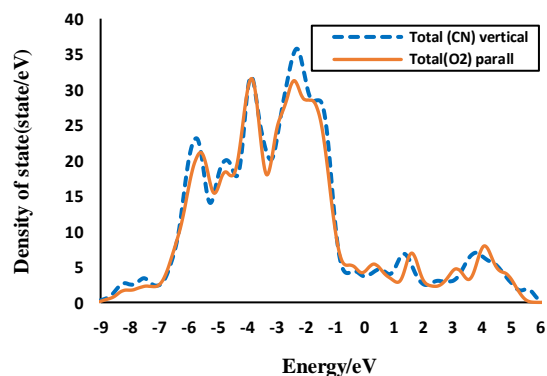


Fig. 8: DOS diagram of the interaction of oxygen and cyanide with (110_{surf0}) surface.

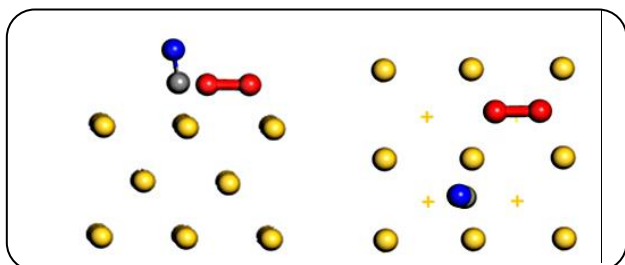


Fig. 9: Image of cyanide interaction in the presence of O₂ on (110_{surf0}) surface.

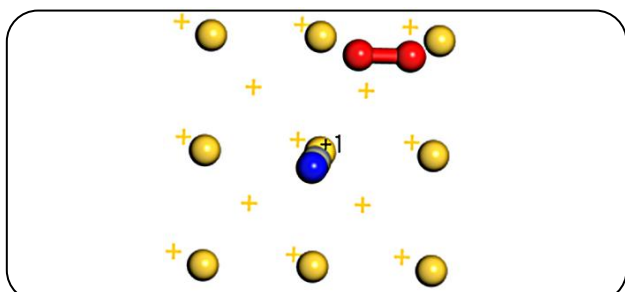


Fig. 10: Image of cyanide interaction in the presence of O₂ on (110_{surf+1}) surface.

The tendency of Au surface to absorb the CN⁻ was greater than O₂. In addition, oxygen and carbon (C in CN⁻ ion) distance was approximately 3 Å, which could be an optimal distance for the effect of O₂ on the CN⁻ reaction. The PDOS diagram in Fig. 11, showed electrons in the d orbital of Au atom move towards the Fermi level, and the accumulation of charge was greater for the (110_{surf+1}) surface than (110_{surf0}) surface. In addition, more anti-bonding orbitals were formed for the (110_{surf0}) surface which had a negative effect on the interaction, which had a negative effect on the interaction.

The DOS diagram of Fig. 12, and the electron density map image of Figs. 13, 14., confirmed the above, and the total density changes for the (110_{surf+1}) surface were more than the (110_{surf0}) surface.

The electronic properties of the systems were investigated by Molecular Orbital (MO) analysis, according to equation:

$$E_g = E_{\text{Lumo}} - E_{\text{Homo}} \quad (5)$$

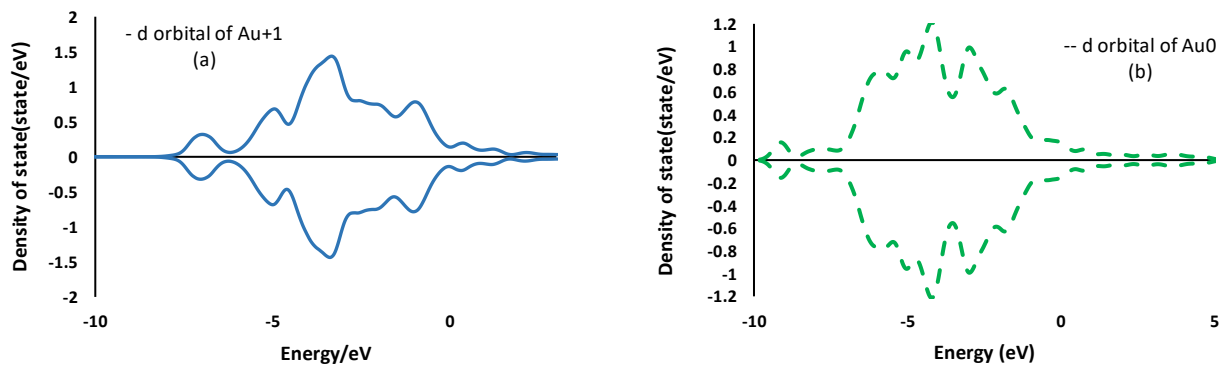


Fig. 11: PDOS diagram of d Orbital of central Au: a. (110_{surf+1}) surface, b. (110_{surf0}) surface.

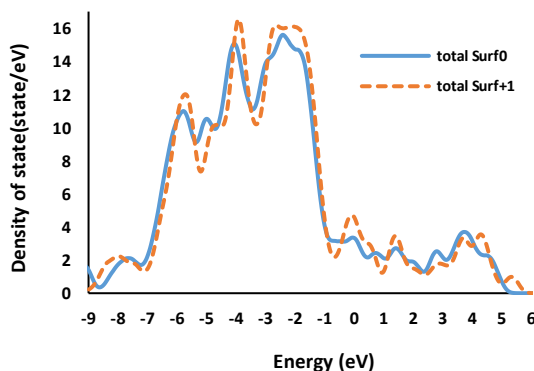


Fig. 12: DOS diagram of (110_{surf+1}) and (110_{surf0}) surfaces.

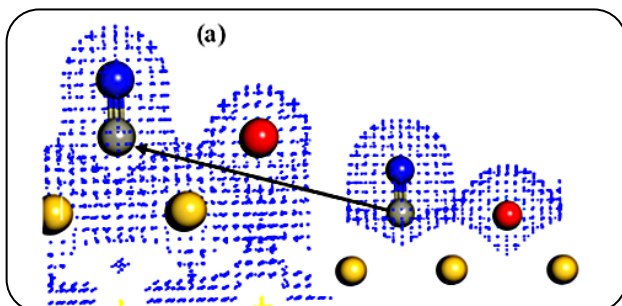


Fig. 13: Total electron density map of the CN⁻ adsorbed over the (110 surface. The image: isosurface map.

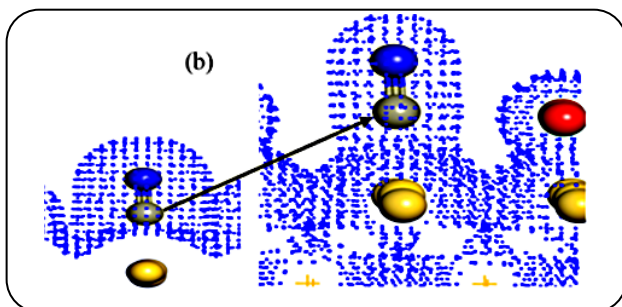


Fig. 14: Total electron density map of the CN⁻ adsorbed over the (110 surface. he image: isosurface map.

Where E_{HOMO} is the value of the Highest Occupied Molecular Orbital (HOMO), E_{LUMO} is the value of the Lowest Unoccupied Molecular Orbital (LUMO) and E_g is the energy gap difference between HOMO and LUMO [27, 28]. By calculating the value of gap energy or the difference between HOMO and LUMO orbitals for the two structures, according to Equation 6, its value was less in the state of the (110_{surf+1}) surface, which electron excitation of surface requires less energy (as a soft structure) [29,30].

Also, the electron density analysis confirmed accumulation of electron charge between the surface and the CN⁻ ion at the (110_{surf+1}) surface. Fig. 14, shows that the attraction of surface electrons by the cyanide ion was further at the (110_{surf+1}) surface. Due to the greater excitability of the surface electrons and confirmation of the electron properties of the structure [31], electron exchange between the surface and the CN⁻ is higher in this state [31].

CONCLUSIONS

The present study related to the interaction of oxygen with gold, in the form of clusters (Au₂) and crystal surface, showed that if the lower level of the d-orbital is involved with the p-orbital of oxygen, the interaction will be stronger and the effect of O₂ will be more effective. Cyanide also interacts better with surfaces in the presence of oxygen and reacts more strongly with (110_{surf+1}) surface due to greater action freedom of (110_{surf+1}) surface electrons.

The presence of oxygen changed the electronic structure of the surface and increased the electrical charge on the surface. Then, as the cyanide ion approaches the desired surface, the charge density at the surface will change and electron transfer around the Fermi surface will be provided. The CN⁻ ion reacts to a certain distance from the O₂ at the gold surfaces, where the effective

distance between the molecular oxygen and the cyanide ion was about 3 Å.

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