

Theoretical studies of energy photoemission spectra (XPS) of S and SO₂ adsorbed on Ni clusters by Hartree-Fock method.

E. Martínez, A. Rodríguez*

*Lab. de Física de Superficies. Dpto. de Física, Facultad de Ciencias.
Universidad de Los Andes, Mérida, Venezuela.*

*e-mail: alfonso@ciens.ula.ve

L. Rincón

*Grupo de Química Teórica. Dpto. de Química, Facultad de Ciencias,
Universidad de Los Andes, Mérida, Venezuela.*

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Theoretical results of photoemission energy spectral of the atomic sulfur and of the SO₂ molecule, adsorbed over surfaces of Ni(110) and Ni(111) clusters, are reported in this work. Clusters with 11, 13, 15 and 17 atoms of Ni were used for the model. The calculations were done by Hartree-Fock method, and basis sets of type STO-NG and p-q1G (p=3,6; q=2,3; N=3,6) were used. The ionization potentials (IP) were interpreted within the Koopmans Theorem. The results obtained for the IP of 1s, 2s and 2p orbitals are 2472.03 eV, 238.14 eV and 173.55 eV, respectively; while for the same orbitals of the sulfur in SO₂ these values are 2481.30 eV, 246.61 eV and 182.17 eV. The theoretical results were compared with experimental results reported in the references, and the error ranges are between 5 eV and 30 eV, in agreement with the standard for the Hartree-Fock method.

Keywords: Adsorption; XPS; Hartree-Fock; sulfur; sulfur dioxide.

En este trabajo se reportan resultados teóricos de espectros de energía de fotoemisión (XPS), del azufre en estado atómico y en la molécula de SO₂ adsorbidos sobre conglomerados de Ni(110) y Ni(111). Conglomerados con 11, 13, 15 y 17 átomos de Ni fueron usados en cada modelo. El potencial de ionización (PI), fue interpretado usando el teorema de Koopmans. Los resultados obtenidos para el PI de los orbitales 1s, 2s y 2p del azufre atómico son de 2472.03 eV, 238.14 eV y 173.55 eV, respectivamente; mientras que el valor para los mismos orbitales del azufre en la molécula SO₂ fueron 2481.30 eV, 246.61 eV y 182.17 eV. Los resultados fueron comparados con datos experimentales reportados en la literatura y el error entre 5 eV y 30 eV es estándar en este método.

Descriptores: Adsorción; XPS; Hartree-Fock; azufre; oxígeno.

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1. Introduction

Adsorption of gas molecular on crystal surfaces is the topic of numerous works [1,2], and the reactivity of SO₂, with well-characterized single-crystal surface of transition-metal oxides has received a great deal of attention in recent years. These studies have been motivated by the nature of sulfur as a catalyst poison and because SO₂ is a main air pollutant.

Research related with the adsorption of sulfur and sulfur dioxide on nickel had been doing by ultraviolet photoelectron spectroscopy (UPS), S K-edge near-edge X-ray absorption fine structure (NEXAFS) spectroscopy techniques[3], and it has become clear that the SO₂ molecule is lying nearly completely flat and the sulfur atom locates at the bridge sites on both the Ni(111) and Ni(100).

S. Rassias *et al.* [4] studied the adsorption of SO₂ over clean surface of Ni(210), by XPS technique and they obtain 162.6 eV for the 2p orbital of S and 530.1 eV for the 1s orbital of the oxygen. L. Wilde *et al.*[3], did a similar experiment on Ni(110) surface, at low temperature (160 to 210 K), and they obtained (161.1 ± 0.5) eV for 2p orbital of atomic sulfur, (163.4± 0.5) eV. and (164.1 ±0.5)eV for the orbital of the sulfur of SO₂ molecule.

S. Terada *et al.* [5] adsorbed SO₂ on nickel surfaces (111), (110) and (100). They obtained, by XPS, for the 1s orbital

of atom of S and sulfur of SO₂, over Ni(110), the values 2469.5 eV and 2476.6 eV respectively. For the Ni(111) and Ni(100) surfaces the ionization potential for the 1s orbital was 2472.8 eV.

The discussion of those works have motivated us to study, by theoretical Hartree-Fock method, the energy photoemission spectrum of sulfur and sulfur dioxide adsorbed on a Ni surface.

2. Computational details

2.1. Hartree-Fock calculations

Ab-initio UHF calculations [6] were performed using molecular orbital theory. In order to include the core electrons, the basis sets used in all cases were the full electron STO-3G and split valence p-q1G (p = 3, 6 and q = 2, 3). Similar theoretical level and basis sets were used by other authors [7], to study the electronic structure of nickel clusters.

The calculations were done with spin multiplicity 1 and 3. In all case the triple spin multiplicity were found the most stable and this result are shown in all tables of the next section. Similarity, the surfaces were modeled by different clusters, varying the basis set, geometric and dimension of the clusters.

Gaussian-98 programs [8] calculation with the default parameter were performed in IBM-SP2 and SGI-Origin 2000 computers [9], and the ionization potentials were calculated using the Koopmans theorem. The SCF convergency in transition metals clusters calculation is problematic, in many cases the initial GUESS is build from the core density matrix and over 200 SCF cycles are used. Typically about 2 to 3 days of Gaussian computation per SCF cycle is needed in one processor of IBM-SP2. Due to this expensive CPU time the geometry optimization in large clusters are prohibitive.

2.2. Cluster model

The nature of the interaction adsorbate-surface and other related properties have been studied by means of a cluster model [10]. For ours cases of sulfur and sulfur dioxide chemi-adsorbed on nickel surface, we used the model proposed for L. Ackermann *et al* [11], shows in Fig. 1, where geometric configuration of atoms with sequences ABCA.. and cubic center face type were used for Ni(110), and ABAB.. with and hexagonal compact were used for Ni(111).

In the employed cluster model Ni_n(110)-S and Ni₇(111)-SO₂ the dimension were varied between 11,13,15 and 17 atoms for Ni(110), and 7 atoms for Ni(111). Nearest-neighbor nickel-nickel distance were fixed to bulk value of 2.49 Å.

3. Results and discussion

Figure 2 shows the geometry and the position of the sulfur atom for the simulation of the chemical-adsorption of S on the Ni_n(110)-S cluster, using STO-3G basis sets. The first simulation was performed following the Ackermann schema [11], using his values for the perpendicular distance (d_{\perp}) fixed and the numbers of atoms of Ni has been varied. The results are shown in the Table I. The theoretical energy value for each orbital (1s, 2s, and 2p), change very little, already at 2474 eV, 240.5 eV and 176 eV, respectively.

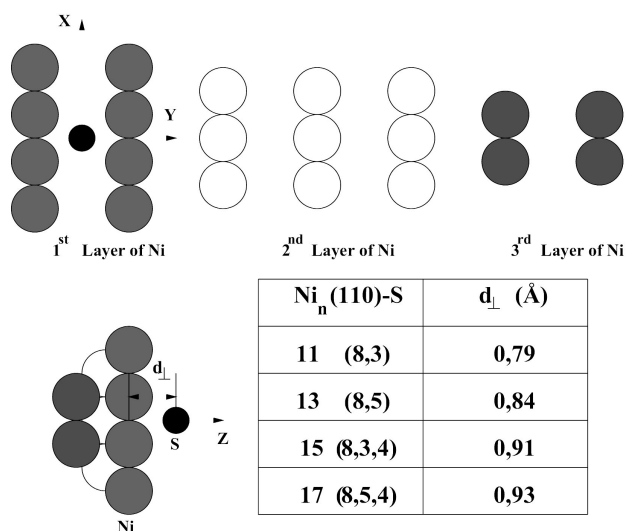


FIGURE 1. After Ackermann *et al*[11].

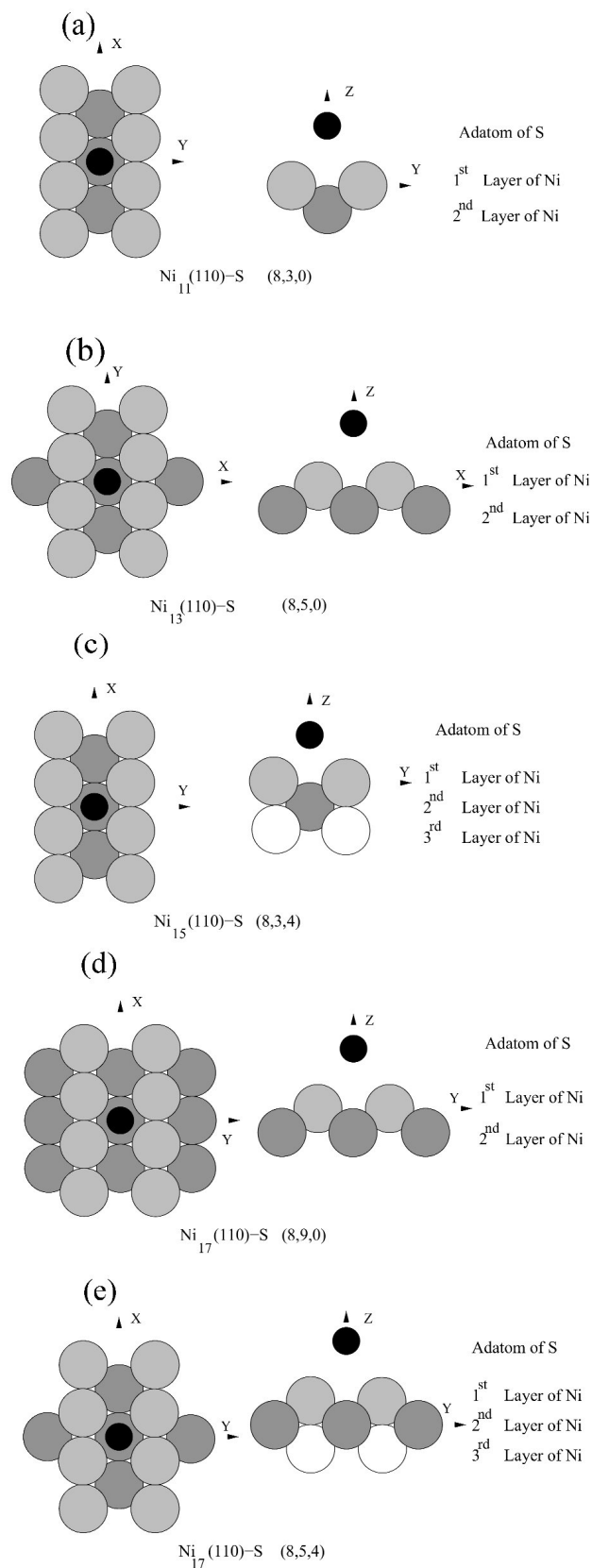


FIGURE 2. S on top of central Ni_n(110) cluster.

TABLE I. Results for Ni_n(110)-S, using STO-3G basis sets.

Cluster	1s IP(eV)	2s IP(eV)	2p IP(eV)	d _⊥ (Å)	Mulliken Charge for S ¹⁶	Mulliken Charge for Ni ¹⁶
Ni ₁₁ (110)-S (8,3)	2474.99	241.07	176.55	0.79	0.014089	-0.340968
Ni ₁₃ (110)-S (8,5)	2475.12	241.01	176.48	0.84	0.140498	-0.295091
Ni ₁₅ (110)-S (8,3,4)	2475.08	240.87	176.37	0.91	0.163294	-0.865726
Ni ₁₇ (110)-S (8,5,4)	2474.55	240.29	175.77	0.93	0.204096	-0.717079
Experimentals	2469.5 ⁵	229.0 ¹⁷	161.0 ³			
Values (eV)	2472.8 ⁵	230.9 ¹⁸	163.6 ¹⁹			

For the second simulation, where the perpendicular distance d_{\perp} , to the cluster was varied and the parameter n is fixed (Ni₁₁(110)-S), the output data (Table II) give three minimal values of energy for 1s, 2s, 2p orbitals, correspond to 2472.03 eV, 238.14 eV and 173.63 eV respectively, for Ni₁₁(110) at 0.93 Å. This value for perpendicular distance is in agreement with the reference results obtained by LEED and ICISS techniques [12-14]. Due to the prohibitive computational time, this study was not performed for large number of atoms (n).

The calculations for Ni_n(110)-S cluster, where the Ni atom number (n) was varied and the perpendicular distance sulfur Ni cluster was unchanged (fixed at 0.93 Å), are listed on Table III. The best results are obtained for the Ni₁₁(110)-S cluster; the energy value 2472.03 eV for the 1s orbital is very close to the one reported, which is 2472.8 eV. For the 2s and 2p orbitals the difference in energy value between experimental and theoretical results are less than 6%, in agreement with the standard results for Hartree-Fock method, using Koopmans theorem. In this calculation we not found convergency for the cluster with $n = 15$, after the 200 SCF cycles.

The chemical adsorption of SO₂ on Ni(111) cluster was studied in three cluster geometries as shown in Figs. 3a, 3b and 3c. The first cluster was built with one layer surface of seven Ni atoms, on which the SO₂ molecule was placed on top of the central nickel atom with O-S-O bond angle at 130°, and the distance Ni-Ni fixed at 2.49 Å. The second cluster geometry was structured in two layers, with 3 and 4 Ni atoms in the first and second layer respectively. The SO₂ molecule was placed perpendicular to the surface on the 3 fold-hollow axis, at a distance fixed at 2.05 Å¹⁵. In the third cluster model interchange the layer of the 4 atoms of Ni by the layer of 3 atoms.

Table IV shows the best results obtained for the ionization potentials (IP) for the 1s, 2s and 2p orbitals of the sulfur of the SO₂ molecule adsorbed on Ni₇(111) cluster. These calculations were done with the second cluster geometry (Fig. 3b).

TABLE II. Results for Ni₁₁(110)-S, where the perpendicular distance has been varied.

d _⊥ (Å)	IP(eV) 1s	IP(eV) 2s	IP(eV) 2p	ΔTotal Energy (a.u)
0.70	2475.61	241.76	177.23	-16786,8989099
0.78	2475.44	241.58	177.04	-16786,2544925
0.79	2474.99	241.07	176.22	-16785,7176082
0.83	2473.83	239.85	175.21	-16785,8329329
0.85	2473.53	239.60	175.06	-16785,8329326
0.87	2473.40	239.39	174.88	-16785,8329326
0.91	2473.22	239.24	174.73	-16786,6545515
0.93	2472.03	238.14	173.63	-16785,5881544
0.94	2472.43	238.46	173.93	-16785,8402217
0.95	2473.35	239.41	174.90	-16785,8482897
1.00	2473.59	239.42	174.91	-16785,7886436

In general, the IP are very similar for all basis sets used; the improvements in the values are only for the valence orbital. The best agreement with the experimental value is for the 1s orbital with an error less than 0.5 % (5 eV a 12 eV). In the cases of the 2s and 2p orbitals the error increases to less than 6 % (10 eV), these errors are typical for the Koopmans theorem.

4. Conclusions

The Hartree-Fock method and Koopmans theorem, using cluster model, has allowed to reproduce the ionization potentials for the 1s, 2s and 2p orbital of sulfur and sulfur on SO₂.

The results are in agreement with the typical errors reported in the references for this method.

The best results for the model of adsorption of S on Ni_n(110) were obtained with 3 spin multiplicity and 11

TABLE III. Results for Ni_n(110)-S, d_⊥ is fixed, using STO-3G basis sets.

Cluster	1s IP(eV)	2s IP(eV)	2p IP(eV)	d _⊥ (Å)	Mulliken Charge for S	Mulliken Charge for Ni
Ni ₁₁ (110)-S (8,3)	2472.03	238.14	173.63	0.93	-0.003386	0.367333
Ni ₁₃ (110)-S (8,5)	2473.75	239.77	175.26	0.93	0.031764	-0.081670
Ni ₁₇ (110)-S (8,9)	2474.23	240.10	175.58	0.93	0.132589	-0.159383
Experimentals Values (eV)	2469.5 ⁵ 2472.8 ⁵	229.0 ¹⁷ 230.9 ¹⁸	161.0 ^{3,20} 230.9 ¹⁹			

nickel atoms in the cluster, where the minimum energy values for 1s, 2s and 2p, correspond to the perpendicular distance values 0.93 Å reported in the literature.

We have shown a result for ionization potential of sulfur in the adsorber SO₂ molecule on Ni₇(111) cluster in reasonable agreement with the experimental value reported in the literature.

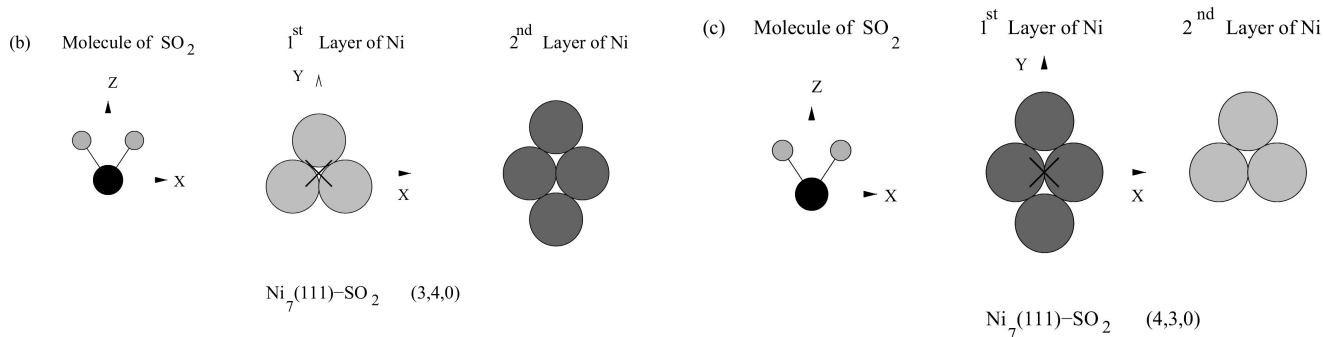
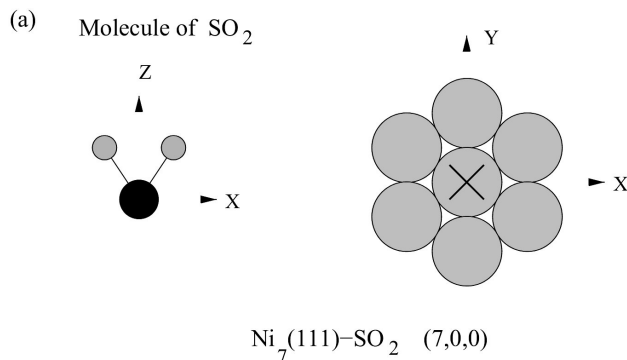


FIGURE 3. a) SO₂ on top of central Ni₇(111) cluster. b) SO₂ on 3 fold-hallow of Ni₇(111) cluster. c) SO₂ on 4 fold-hallow of Ni₇(111) cluster.

TABLE IV. Results for Ni₇(111)-SO₂ (Fig. 3b).

BASIS	STO-3G IP(eV)	STO-6G IP(eV)	3-21G IP(eV)	6-31G IP(eV)	Experimentals Value (eV)
Sulfur					
1s	2481.30	2510.19	2488.29	2503.89	2476.6 ⁵
2s	246.61	245.35	245.99	246.19	
2p	182.17	182.48	182.69	183.05	164.1 ³ -167 ²⁰
Mulliken Charge					
1 Ni	-0.024159	-0.273859	0.174265	0.002874	
2 Ni	0.168993	0.009332	0.116276	-0.003804	
3 Ni	-0.024159	-0.273859	0.174265	0.002874	
8 S	0.983494	1.133501	1.041242	0.925670	
9 O	-0.448022	-0.395301	-0.841013	-0.729778	
10 O	-0.448022	-0.395301	-0.841013	-0.729778	

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