

## THEORETICAL STUDIES OF THE GEOMETRIES OF O AND S OVERLAYERS ON THE (100) SURFACE OF NICKEL\*

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Geometries for O and S overlayers on the (100) surface of Ni have been calculated using *ab initio* wavefunctions for O and S bonded to small clusters of Ni atoms (1 to 5 Ni atoms). The calculated distance of the adatom from the surface is 0.96 Å and 1.33 Å for O and S, respectively, in excellent agreement with the results of dynamic LEED intensity calculations,  $0.9 \pm 0.1$  Å and  $1.3 \pm 0.1$  Å, respectively. This indicates that accurate geometries of chemisorbed atoms may be obtained from calculations using clusters.

A first step in understanding the mechanisms of heterogeneous catalysis at transition metal surfaces is to investigate the nature of the bonding of atoms and molecules to the surface.

Experimentally, geometric information is obtained by detailed analysis of low energy electron diffraction (LEED) intensities (1). Because the theoretical analysis involves some severe approximations, these geometries cannot be described as purely experimental; however, with high quality LEED intensities, it appears that the determination of geometric spacings of atomic overlayers to within  $\sim 0.1$  Å is possible (in the direction perpendicular to the surface).

We are in the process of developing theoretical techniques for solving directly for the geometries of chemisorbed species. Such theoretical procedures, if reliable, would be extremely valuable, since one could consider special surface defects (e.g., steps) and reaction intermediates, both of which are relevant for studying catalysis. In our theoretical model we solve for the states of finite clusters representing the semi-infinite solid, using the *ab initio* generalized valence bond (GVB) method (2); this differs from the usual Hartree-Fock (HF) method in that we include the dominant electron correlation (many-body) effects. We feel that the chemisorptive bond is sufficiently localized that our description of the chemisorbed species is valid for the real metal; however, detailed comparison with experiment would be valuable.

As a test of our theoretical methods, we have examined the geometries of O and S overlayers on the Ni(100) surface, a case that has been thoroughly studied with LEED and dynamic intensity calculations (1). The results of these calculations also provide some information for the (110) surface. The calculations will be described in detail elsewhere (2e); the approach used is the same as described in Ref. 2c.

Table I summarizes the results for S. For the (100) surface we denote the four surface atoms

at the corners of the surface unit cell as Ni1, Ni2, Ni3, and Ni4, and we denote as Ni5 the atom in the second layer below the center of this cell. Including the four Ni atoms (Ni1, Ni2, Ni3, and Ni4) to which the S bonds, we calculate an optimum position of the S, 1.33 Å above the surface. This is in excellent agreement with the results from dynamic LEED intensity calculations [ $1.30 \pm 0.10$  Å (1)].

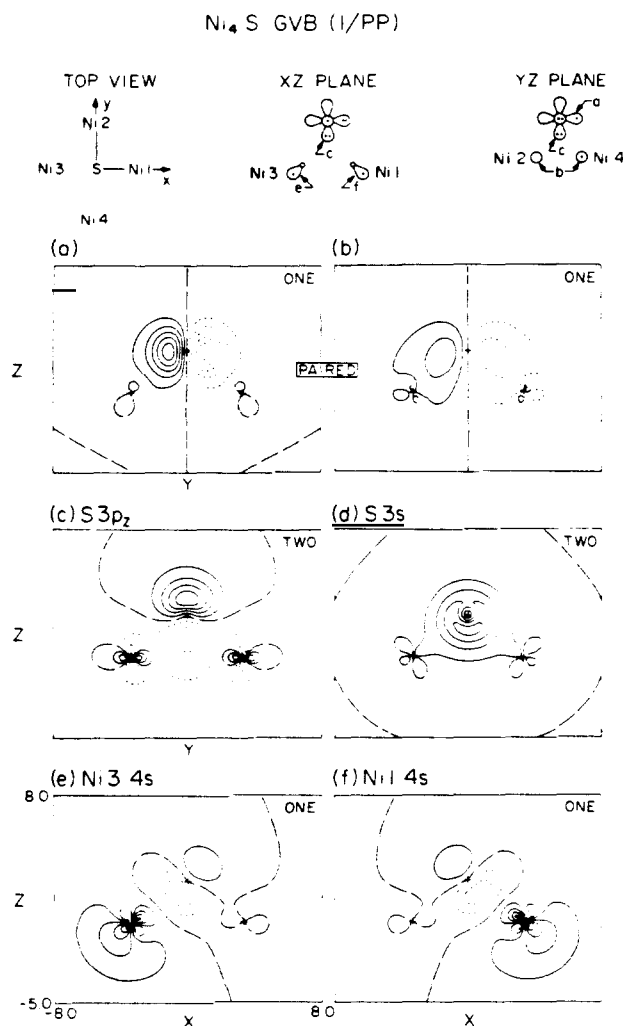
We find that the bonding in this cluster is across one diagonal (say, Ni2-Ni4), somewhat analogous to the bonding in H<sub>2</sub>S (3). There is a repulsive interaction between the S (3p<sub>π</sub>) lone pair and the other diagonal atoms (Ni1-Ni3). The extent of this repulsive interaction was tested by removing Ni1 and Ni3 and recalculating the optimum S position; the S moved to a position 1.04 Å above the surface. We tested the effect of Ni5 using the Ni2, Ni4, Ni5 complex, finding the optimum S position at 1.07 Å above the surface. The conclusion here was that the Ni5 does not affect the S position.

The calculated D<sub>e</sub> for Ni<sub>4</sub>S is 5.37 eV as compared to 3.32 eV<sup>e</sup> for NiS, indicating that bridging is much more favorable than bonding directly above a surface Ni atom (as is generally presumed).

Qualitatively the electronic configuration of the Ni<sub>4</sub>S cluster is as shown in the diagram at the top of Fig. 1. The important orbitals of the Ni<sub>4</sub>S cluster are shown in Fig. 1a-f. One bonding pair (Fig. 1ab) involves one component (Fig. 1a) which is essentially an S(3p<sub>y</sub>) orbital, while the other component (Fig. 1b) corresponds approximately to Ni2(4s)-Ni4(4s). The other bonding orbital (Fig. 1c) is essentially S(3p<sub>x</sub>)-like, but has built in a bonding combination<sup>z</sup> of Ni(4s) character on all four Ni atoms.

The 4s orbitals of the remaining two Ni atoms (Fig. 1ef) are triplet-paired and have significant nonbonded repulsions with the doubly-occupied S(3p<sub>x</sub>) orbital. These orbitals are involved in bonds to adjacent S atoms for the full

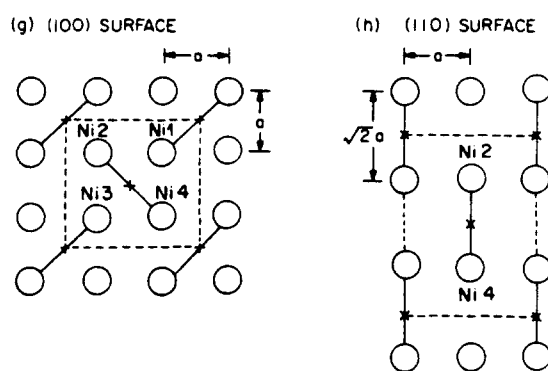
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(a)-(f): Selected orbital of the GVB(1) wavefunction for the Ni<sub>4</sub>S cluster. These plots have uniformly spaced contours with a separation of 0.05 a.u. Positive contours are indicated by solid lines, negative contours are indicated by dashed lines, and nodal surfaces are indicated by long dashes.

overlayer, as illustrated in Fig. 1g. The localized bonds shown in Fig. 1g suggest a  $p(2 \times 2)$  structure, with the center and corner atoms connected by a glide plane. However, there is a degenerate structure with all the bond directions rotated by  $90^\circ$  and these two structures are expected to have a strong interaction (resonance), leading to all the S atoms being equivalent. This results in  $c(2 \times 2)$ , as observed.

The wavefunctions for the (100) cluster suggest that on the (110) surface the S is along the long side of the rectangle as indicated in Fig. 1h. Thus, the simplest model for the (110) surface is the Ni<sub>4</sub> cluster with the Ni atoms separated by  $\sqrt{2}$  times the nearest neighbor separation. The calculations lead to an optimum S position 1.04 Å away from the Ni surface, in fair agreement with the results of dynamic LEED intensity analysis which leads to  $0.93 \pm 0.10$  Å (1). The



(g)-(h): Bonding patterns for  $c(2 \times 2)$  overlayers on the (100) surface (g) and on the (110) surface (h). The circles represent surface Ni atoms, while the S and O atoms are indicated by crosses. The solid lines represent the bonding orbitals, while the unit cell is outlined by dashed lines.

LEED calculations assumed the S to be centered in alternative rectangular cells; however, these calculations are not sensitive to lateral displacement of the overlayer (4).

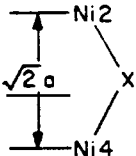
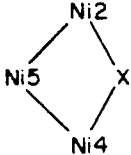

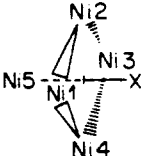
The geometries for bonding of an O atom to the various Ni clusters are also summarized in Table I. The principal differences between the S and O results have to do with (i) the smaller size of the oxygen atom and (ii) the larger electronegativity for O (5). We found here that the presence of Ni5 has a significant effect on the O position due to the much greater charge transfer. Consequently, Ni5 was included in subsequent calculations.

The calculated  $D_e$  for Ni<sub>2</sub>O is 4.37 eV as compared with 3.95 eV for NiO, indicating that bridging is more favorable than bonding directly above a surface Ni atom. The smaller energy difference here as compared with the S case results mainly from loss of  $\pi$  bonding effects (which are more important for NiO than for NiS) upon forming Ni<sub>2</sub>O.

Considering the full oxygen overlayer, Ni atoms 1 and 3 are involved in bonds to adjacent O atoms (see Fig. 1g). Here the ionic NiO bonds lead to a total charge (8) of 0.92 electrons on Ni atoms 1 and 3, as compared with the S case where the total charge was only 0.62. In order to include effects resulting from this charge distribution, we examined the positive ion state of the Ni<sub>2</sub>O cluster (involving removal of one of the 4s electrons from Ni1 and Ni3) (6). We find that the Ni<sub>2</sub><sup>+</sup> cluster has a higher effective electronegativity, resulting in more covalent bonding. The net effect is an increase in the bond energy along with a 0.31 Å vertical displacement away from the surface to 0.96 Å for the Ni<sub>2</sub><sup>+</sup>O cluster. This value is in good agreement with the distance from the LEED intensity analysis,  $0.90 \pm 0.10$  Å (1).

Using the Ni<sub>2</sub>O cluster to model the bonding of O along the long edge of the unit cell for the (110) surface leads to an optimum O position only 0.08 Å above the surface, indicating that at this location the O would penetrate the surface. LEED studies (7) for O on Ni (110) suggest that O bonds to the short edge of the 110 cell, a

Table I. Optimum geometries for the O and S overlayers.

Cluster	Geometry	Model for	Distance Above Plane (Å)	
			x=O	x=S
NiX	Ni—X		1.60	1.91
Ni <sub>2</sub> X			0.31	1.04
Ni <sub>3</sub> X		(110) surface X on long edge	0.08	1.07
Ni <sub>4</sub> X			(0.75) <sup>a</sup>	1.33
Ni <sub>5</sub> X		(100) surface X at center of cell	0.96 <sup>b</sup>	(1.36) <sup>c</sup>

<sup>a</sup> Estimated for the positive ion using Koopmans' theorem. For the neutral, 0.56 Å is obtained.

<sup>b</sup> Based on the positive ion calculation as described in the text. For the neutral, 0.65 Å is obtained.

<sup>c</sup> Obtained from Ni<sub>4</sub>S using the Ni<sub>2</sub>S and Ni<sub>3</sub>S correction.

geometry that we have not investigated.

We conclude that reliable geometric information for chemisorbed species on transition metal surfaces can be obtained using small clusters including only those atoms within bond-

ing distance. This encouraging result opens the way for theoretical studies of other chemisorbed species and reactive intermediates, systems that may well be impossible to study experimentally (due to lack of long-range order).

#### REFERENCES

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2. (a) GODDARD, W. A., III, DUNNING, T. H., Jr., HUNT, W. J. and HAY, P.J., Accts. Chem. Res. 6, 368 (1973); (b) The basis sets for the Ni<sup>c</sup>, O<sup>c</sup>, and S<sup>d</sup> are valence double zeta (allowing for contraction and delocalization effects) and should lead to good geometries. In order to obtain accurate bond energies for NiX and Ni<sub>2</sub>X, we also included d polarization functions on the O<sup>c</sup> and S<sup>d</sup>. Since the Ni configuration is 4s<sup>1</sup>3d<sup>9</sup> in all clusters, we simplified

- the calculations for  $Ni_3X$ ,  $Ni_4X$ , and  $Ni_5X$  by contracting the Ni basis to [2s, 1p, 1d] based on the  $(4s)^1(3d)^9$  state of the Ni atom; (c) See, for example, WALCH, S. P. and GODDARD, W. A., III, J. Am. Chem. Soc. 98, 7908 (1976); (d) BAIR, R. A. and GODDARD, W. A., III, *ibid.* 99, 3505 (1977); (e) See also WALCH, S. P., Ph.D. Thesis, California Institute of Technology (1977).
3. For the clusters considered here, the Ni atom has the character of the  $4s^1 3d^9$  configuration, leading to bonds between the singly-occupied S(3p) orbitals and the singly-occupied Ni(4s) orbitals.
  4. For example, for S on Ni(111) there are two possible three-fold coordinate sites. The LEED intensities are quite similar for these two sites, but they change significantly if the distance to the surface is changed (1a).
  5. The electronegativities involved are 3.5 for O, 2.5 for S, and 1.8 for Ni. PAULING, L., "The Nature of the Chemical Bond" (Cornell University Press, New York, 1973), Third Edition, p. 93.
  6. For O on Ni, the positively charged cluster is consistent with the overall charge distribution, while the neutral cluster is not. For S on Ni, the charge distribution is intermediate between a neutral cluster and the positively charged cluster, and we have used a neutral cluster as a model. We expect that charge transfer effects will be less important for the S case than for the O case, since the bonding of S to the surface is more covalent.
  7. DEMUTH, J. E., J. Colloid Interface. Sci. 58, 184 (1977).
  8. All charges used here are based on the standard Mulliken population analysis of the GVB wavefunction. That is, all overlap populations are associated equally with both atoms.