

Theoretical Study of H Chemisorption on NiO Surface

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Self-consistent Hartree-Fock and generalized valence-bond calculations for H chemisorption on a cluster model of a NiO(001) surface have been performed. In the cases where the H approaches over a surface Ni or O site, bond strengths of less than 0.65 eV are found. This is in contrast to those found at a surface Ni vacancy site where the bond strengths are 4.5–7.7 eV. The strong bonds are due to the formation of a singly occupied orbital in the surface complex.

Experimental studies¹ on highly divided nickel oxide indicate that only a fraction of the total surface is reactive in the chemisorption of molecules such as O₂, CO, and CO₂. Furthermore, there appear to be several different active sites taking part in the chemisorption. In the case of O₂ chemisorption at 200°C, calorimetric studies indicate that the initial adsorption takes place at sites giving very high (≥ 114 kcal/mole) heats of adsorption. Furthermore, these differential heats decrease rapidly to ~ 60 kcal/mole where they remain constant until about $\frac{3}{4}$ maximum coverage. They then drop to zero for a maximum surface coverage of 26% ($\theta = 0.26$). Behavior such as this clearly indicates that simple chemisorption to the clean, nondefective (i.e., perfect) surface is not the dominant mechanism. In this work we undertake the study of the interaction of a simple adsorbate with the perfect NiO surface, as well as with the cation vacancy defect on a surface, employing a molecular-cluster method. This is, to our knowledge, the first detailed atomistic calculation of a transition-metal oxide surface and of any surface defect.

In the case of the transition-metal oxides, the d electrons of the transition metal have been thought to be the primary factor in the chemisorption process.² This is derived, in part, from a similar viewpoint for the transition metals. However, recent theoretical³ and experimental⁴ work has indicated that the s -like electrons of the transition metal are responsible for chemisorptive bonds in first-transition-series metals. Thus we will employ the premise that s -like electrons are necessary on the transition-metal ions for strong chemisorptive bonds.

Using this premise, an *a priori* understanding of the NiO surface can be obtained. NiO is an ionic solid consisting of Ni⁺² and O⁻² ions. The geometry and charge density at a (001) surface will not be significantly different from the bulk.

O⁻² is isoelectronic with neon and thus should be inert. Ni⁺² is a $(3d)^8$ ground-state configuration. The lowest excited state with a $(3d)^7(4s)^1$ configuration is about 7 eV above the ground state and thus is chemically inaccessible. Hence little bonding to the Ni⁺² ions should be expected either. However, a cation or anion vacancy on the surface might give rise to other species (Ni⁺¹ or O⁻¹, respectively) which would be reactive. A cation vacancy giving rise to an O⁻ would be an active site since O⁻ is isoelectronic to F. Similarly, an anion-vacancy-derived Ni⁺¹ ion might be reactive since the $(3d)^8(4s)^1$ excited state is ~ 1 eV above the $(3d)^9$ ground state. Thus we would expect the perfect-surface calculations to give little or no binding while the binding to surface defects should be relatively strong.

In this study we have employed a cluster model for the NiO surface and have used a single H atom as the adsorbate. All of the calculations are done using *ab initio* self-consistent techniques. Previous calculations on a cluster model of NiO using these techniques have been quite successful.⁵ In the second section we will outline the details of the calculation. The following sections will give the results, a discussion of them, and our conclusions.

As stated previously, NiO is an ionic solid of Ni⁺² and O⁻² ions having the rocksalt structure with an Ni-O distance of 2.09 Å.⁶ In these calculations a small cluster of Ni and O ions is used to model various (001) surface sites. The clusters are embedded in a $5 \times 5 \times 4$ point ion array (charge ± 2) which provides (i) charge neutrality for the system and (ii) the appropriate Madelung potential for the cluster. For the center of the (001) face (the center of a 5×5) the Madelung potential is accurate to within 0.5%.

The surface clusters employed were for a surface Ni (O₄Ni), a surface O (NiO), and a Ni vacancy on the surface (O₅). These configurations

are shown in Fig. 1. For the O_5 case, the H was brought up to the surface over three sites: atop a surface O, bridged between two surface O's, and into the center, which is atop a second-layer O.

Various calculations were done using restricted Hartree-Fock (RHF), unrestricted Hartree-Fock (UHF), and generalized-valence-bond (GVB)⁷ wave functions. Specifically, by RHF we mean that the wave function is of the form

$$A[\varphi_1\alpha\varphi_1\alpha\beta\varphi_2\alpha\beta\cdots\varphi_m\alpha\varphi_m\alpha\beta\varphi_{m+1}\alpha\cdots\varphi_n\alpha], \quad (1)$$

where A is the antisymmetrizer or determined operator and the φ_i may be required to be symmetry functions. The UHF wave functions, then, are of the form

$$A[\varphi_1\alpha\varphi_2\alpha\cdots\varphi_n\alpha\varphi_{n+1}\beta\cdots\varphi_{n+m}\beta]. \quad (2)$$

The perfect-pairing form of GVB wave function is obtained from (1) by replacing one or more doubly occupied orbital pairs, $\varphi_i\varphi_i\alpha\beta$, with the singlet-coupled pair function $(\varphi_{ia}\varphi_{ib} + \varphi_{ib}\varphi_{ia})(\alpha\beta - \beta\alpha)$ where

$$\langle \varphi_{ia} | \varphi_{ib} \rangle \neq 0. \quad (3)$$

The orbitals of *different* pairs are still taken to be orthogonal. In all cases the orbitals φ_i are solved for variationally and self-consistently. The φ_i are expanded in terms of the same basis of contracted Cartesian Gaussian functions as used for NiO_6 (Ref. 5) and the same set of programs was used for the calculations.

The potential energy curves for H approaching atop a surface O (Ni-O-H) and a surface Ni (O_4 -Ni-H) are shown in Fig. 2. Note that for the systems containing one Ni atom and one H atom, at large separation there will be three singly oc-

cupied orbitals, the Ni $3d_{z^2}$ and $3d_{x^2-y^2}$ and the H $1s$. The various states for these systems are obtained by using different spin-couplings of these orbitals. We find that in each case the preferred state is the quartet and that the Ni $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals remain singly occupied. In each case requiring the Ni $3d_{z^2}$ and the H $1s$ to be GVB paired (and hence bonding) served only to raise the energy. In the O_4 -Ni-H case, the UHF wave function remains a pure quartet spin state, indicating no cross or interaction with low-lying excited state. The UHF wave function for $S_z = \frac{1}{2}$ is 0.30 eV above that for $S_z = \frac{3}{2}$ near the equilibrium distance (4 a.u.) indicating that the quartet is the lowest state. In the Ni-O-H case, bending the Ni-O-H bond produces a minimum at 180° , that is, directly atop the O. In Table I the well depths and minimum-energy bond lengths are listed. Note that the largest bond energy is 0.64 eV = 14.7 kcal.

For the surface defect cluster, we wished to investigate the possibility of nearby states with different numbers of electrons. We did this for the centered configuration of the O_5 -H cluster with a hydrogen surface distance of 15 a.u. (thus the H is noninteracting). These results are given in Table II. Starting with five O^{-2} ions on the surface (10^-) we find that the configuration $4O^{-2}1O^{-1}$ (9^-) is 0.11 eV lower while the configuration $3O^{-2}2O^{-1}$ is 3.75 eV higher. For the (10^-) surface the addition of the H leads only to doublet states while for the (9^-) surface both singlet and

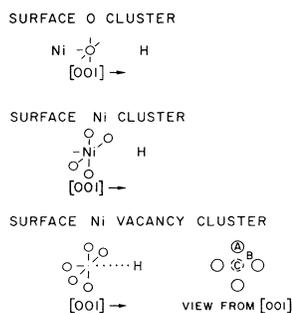


FIG. 1. Molecular clusters used to model various surface species. For the surface Ni vacancy, A indicates the atop site, B the bridged and C the centered.

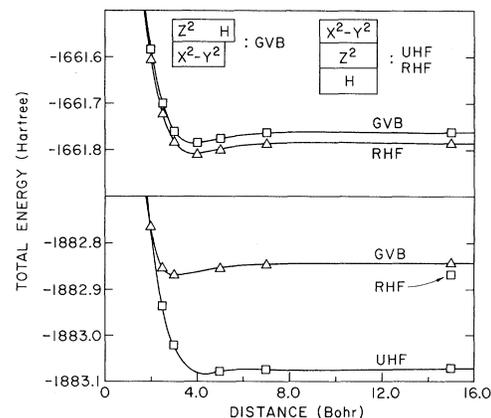


FIG. 2. The potential energy curves for a H atom approaching a surface O (NiOH) (top) and a surface Ni (O_4 NiH) (bottom). The tableaux indicate that the Ni $3d_{z^2}$ and H $1s$ are singlet coupled in the GVB case with the Ni $3d_{x^2-y^2}$ singly occupied to form a doublet state, while the three orbitals are coupled to form a quarter state for the RHF and UHF curves.

TABLE I. Binding energies and equilibrium distances for H approaching various surface sites on NiO.

Cluster	Electronic state	Wave function used	Binding energy (eV)	Equilibrium distance (a.u.)
NiOH	Quartet	RHF	0.606	3.82
	Doublet	GVB	0.579	3.85
O ₄ NiH	Quartet	UHF	0.245	4.36
	Doublet	GVB	0.645	2.97
O ₅ H (atop)	Singlet	GVB	5.30	1.72
	Singlet	GVB	4.47	0.24 ^a
	Singlet	GVB	7.72	-2.23 ^a

^aAs measured from surface plane. In these cases there is no atom along the specific [001] direction of the H atom in the surface plane.

triplet states are possible. In Fig. 3 we present the calculations for the H approaching atop a surface O. In this case the doublet and triplet curves are RHF while the singlet state is treated as a GVB pair involving the H orbital and the unpaired surface orbital. Note that the doublet and triplet are essentially nonbonding, yielding potential curves similar to the O and Ni cases, while the singlet produces a typical bound-state curve. The distance at equilibrium is 1.72 a.u. and the binding energy is 4.70 eV. For the bridged and center geometries, the curves are qualitatively the same, the doublet and triplet having a shallow potential-energy wells while the singlet produces strongly bound state. The singlet curves for the three different approach geometries are shown in Fig. 4. Here we find that the bridged site produces a fairly broad potential-energy curve while the centered site produces a steep curve with a fairly flat bottom. The binding energy for the centered site is 7.62 eV.

The potential energy curves for the surface Ni and O (Fig. 2) are clearly nonbonding as was predicted. A typical O-H bond length is 1.8-1.9 a.u. while the "bonds" to the surface are ~3.8 a.u. By comparison, the O-H bond to the Ni vacancy in

the atop position is slightly shorter (1.72 a.u.). The bonding at the atop site in the Ni vacancy is a typical covalent bond. At the bridged site, one finds that the bonding is ionic. The H loses a part of its electron to the two neighbors in the bridge. The equilibrium position is in the plane where approximately 50% of the orbital density has shifted from the H to the two nearest O's. For the case of the centered site, one finds that there is an ionic bond of the same type as the H moves into the surface. However, as the H goes below the surface it begins to form a covalent bond with the O⁻² in the second layer. When the H reaches its equilibrium position it has formed a covalent bond to the second-layer O⁻² and given up its electron to the four surface O's. Thus the configuration is 4O⁻² on the surface with an OH⁻ in the vacancy.

For the case of an H atom bonding to a NiO surface, some mechanism which produces active surface species is necessary for chemisorption since the perfect surface is essentially inert. We have found that a Ni vacancy on the surface will produce such an active site. The role of the anion vacancy is currently being studied but is expected to be reactive as well.

TABLE II. Restricted Hartree-Fock energies for various electron occupancies for the surface Ni vacancy cluster (O₅H).

Cluster configuration	Unpaired electrons on surface	Spin state	Total energy (hartree)
5O ⁻² (10 ⁻)	0	Doublet	-451,566 637
4O ⁻² 1O ⁻¹ (9 ⁻)	1	Triplet	-451,570 612
3O ⁻² 2O ⁻¹ (8 ⁻)	2	Quartet	-451,428 215

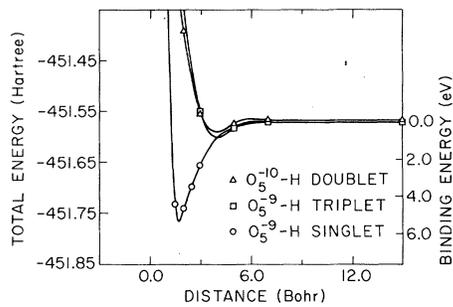


FIG. 3. The potential energy curves for H approaching a surface Ni vacancy atop a surface O atom. The doublet curve corresponds to a complex of $5O^{-2}$ while the singlet and triplet curves correspond to $4O^{-2}1O^{-1}$.

While H and molecules such as O_2 and CO are vastly different, the inference is that some active site, such as a vacancy, edge, corner, etc., is needed for chemisorption. Hopefully, these studies can be extended to include molecular adsorbates in the near future.

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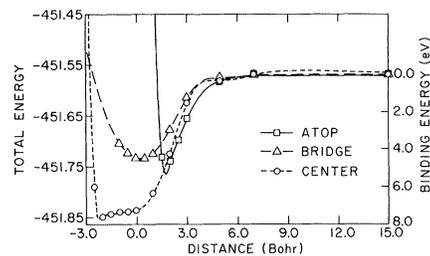


FIG. 4. The singlet (GVB) potential energy curves for H approaching a surface Ni vacancy in the three different configurations.

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ERRATA

SUPERFLUID-VORTEX THRESHOLDS AND THE VORTEX-CORE PARAMETER NEAR T_λ . I. H. Lynall, D. S. Shenk, R. J. Miller, and J. B. Mehl [*Phys. Rev. Lett.* **39**, 470 (1977)].

On page 471, second column, the equation near the center of the page should read " $A = A_0 [1 + (\sigma - \sigma_0)^2 \gamma^{-2}]^{-1/2}$." The words "at half-maximum" should be deleted from the following sentence and from the caption to Fig. 1.

OBSERVATION OF POLOIDAL ASYMMETRY IN IMPURITY-ION EMISSION DUE TO ∇B DRIFTS. J. L. Terry, E. S. Marmor, K. I. Chen, and H. W. Moos [*Phys. Rev. Lett.* **39**, 1615 (1977)].

In the second sentence of the second paragraph on page 1617 where the ∇B drift distance for a deuteron at an O VI radius is evaluated, " $d_{\nabla B}^{O11}$ " should be replaced by " $d_{\nabla B}^{D11}$."

MEASUREMENTS OF THE PARAMETRIC DECAY OF CO_2 -LASER RADIATION INTO PLASMA WAVES AT QUARTER-CRITICAL DENSITY USING RUBY-LASER THOMSON SCATTERING. J. J. Schuss, T. K. Chu, and L. C. Johnson [*Phys. Rev. Lett.* **40**, 27 (1978)].

The title should read as above; i.e., "CO" should be replaced by " CO_2 ."

ASYMPTOTICALLY SIMPLE DOES NOT IMPLY ASYMPTOTICALLY MINKOWSKIAN. Robert Geroch and Gary T. Horowitz [*Phys. Rev. Lett.* **40**, 203 (1978)].

Through a typographical error the second author's last name was printed incorrectly. The correct form is given above.