

THEORETICAL STUDIES OF CHEMISORPTION AND SURFACE REACTIONS  
ON NICKEL AND SILICON

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J. L. Whitten

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State University of New York

DE91 004171

at Stony Brook

Stony Brook, N.Y. 11794

and

North Carolina State University

Raleigh, N.C. 27695

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# Theoretical Studies of Chemisorption and Surface Reactions

## on Nickel and Silicon

Grant DE-FG02-84ER45100.A008

Jerry L. Whitten

State University of New York at Stony Brook

and

North Carolina State University

### Abstract

The research is part of a theoretical program on the structure of molecules adsorbed on solid surfaces and dissociative chemisorption with emphasis on transition metal substrates and electronic materials. An embedding theory for treating chemisorption on metals is further developed and applied to the reaction of hydrocarbon fragments and hydrogen coadsorbed on nickel, the dissociation of water on nickel, and the systems H/Ni, NH<sub>3</sub>/Ni, and C<sub>6</sub>H<sub>6</sub>/Ni. The main emphasis of the work is on the energetics of adsorption as a function of surface site, the potential energy for adsorbate motion between surface sites and the energetics of surface reactions. Equilibrium geometries, vibrational frequencies and ionization potentials are also calculated. Preliminary work on the description of Si(100) surfaces has been completed in preparation of H/Si and N/Si adsorption studies. Studies of  $\pi$  bonding on Si(111) were also completed and work was begun on the Auger ionization of F/Si. The original form of the embedding theory has been extended to make use of an effective potential representation of the bulk electrons interacting with the embedded surface region. Effective core potentials for Fe have been developed.

## Final Report

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The original form of the embedding theory has been extended to make use of an effective potential representation of the bulk electrons interacting with the embedded surface region. Surface sites are described by an improved basis (radial, polarization and correlation functions), and in the case of transition metals by variable d occupancy. Electronic wavefunctions are constructed by configuration interaction and the coupling of the local subspace and adsorbate to the bulk lattice electrons,  $\{\varphi\}$ , defined by a localization transformation, is represented by a pseudopotential (1,9,16).

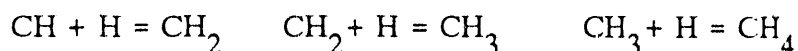
$$\Psi = \sum_{\mathbf{k}} \lambda_{\mathbf{k}} A(x_1^{\mathbf{k}} x_2^{\mathbf{k}} \cdots x_n^{\mathbf{k}} \varphi'_m \cdots \varphi'_N)$$

local region pseudopotential

The nickel surface calculations are carried out by modelling the lattice as a 26-atom, three layer cluster which is extracted from a larger cluster by the orbital localization transformation. Hydrogen atoms are found to bind strongly to the Ni(111) surface at three-fold and bridge sites (13). Calculated H binding energies are in the range 2.50-2.66 eV, for optimized Ni-H bond lengths ranging from 1.81 to 1.87 Å. Vibrational frequencies are in the range 1043-1183 cm.<sup>-1</sup> These quantities are in excellent agreement

with experiment. Work on the recombination reaction of hydrogen on nickel was also started during this period. Studies of H-H interactions show a repulsive interaction for hydrogens adsorbed in adjacent three-fold sites that share two nickel atoms compared to separated three-fold sites sharing only one nickel atom. Similar behavior was found in earlier studies of hydrogen adsorbed on Ti(0001).

The following reactions have been studied in detail on Ni(111) (9,10):



Energetics and structural information are obtained for the CH, CH<sub>2</sub>, CH<sub>3</sub> and H species at the most stable sites on Ni(111) and for intermediate steps along the reaction pathway. Both CH and CH<sub>2</sub> species are found to bind strongly to the surface at three-fold and bridge sites. A three-fold site is the most stable for CH<sub>3</sub> with indistinguishable adsorption energies for filled or hollow sites. Adsorption energies are between 2.9 and 3.1 eV for CH adsorption, 2.5 and 2.9 eV for CH<sub>2</sub> adsorption and 1.7 eV for CH<sub>3</sub>. Atop Ni adsorption sites are more than 1 eV higher in energy. The Ni-C bond lengths range from 2.00 to 2.04 Å for CH and CH<sub>2</sub> on the surface. Vibrational frequencies for HC-surface and H<sub>2</sub>C-surface vibrations are between 400 and 600 cm<sup>-1</sup> and CH stretching frequencies are around 3050 cm<sup>-1</sup> in both CH and CH<sub>2</sub>. The reaction of CH + H = CH<sub>2</sub> on the nickel surface is 1.45 eV exothermic; however a barrier exists to moving H to a three-fold site adjacent to one occupied by CH. Energy barriers exist for the approach of H toward the adsorbed fragments until distances become short enough to begin to establish C-H bonds. Experimental values for the adsorption energies of hydrocarbon fragments on nickel are inferred only indirectly; however, the reaction CH<sub>3</sub> + H = CH<sub>4</sub> is known to be nearly energetically neutral as is found by the calculations. Calculations on the dissociation of CH<sub>4</sub> on Ni(111) show that an atop Ni dissociation site is most favorable energetically, but the calculated barrier to dissociation is quite high, 23 kcal/mol (11).

During this period, studies of the adsorption of H<sub>2</sub>O and NH<sub>3</sub> on Ni(111) were also completed (17,19). These lone pair electron species are found to adsorb preferentially at atop Ni sites, but energy differences between the 3-fold, bridge and atop

sites are calculated to be very small,  $< 0.2\text{eV}$ . These results are in sharp contrast to those for hydrocarbon and H atom fragments for which high symmetry sites were energetically preferred. Molecular  $\text{H}_2\text{O}$  adsorbed on the Ni(111) surface is found to prefer an atop atom site with an adsorption energy of 12 kcal/mol and a Ni-O equilibrium distance of 2.06 Å. The equilibrium geometry of  $\text{H}_2\text{O}$  is calculated to lie in a plane inclined by about  $25^\circ$  to the normal to the surface, but tilting the plane of the molecule from  $0^\circ$  to  $50^\circ$  or rotating the molecule about the Ni-O axis changes the energy only slightly. The OH radical binds strongly to the Ni(111) surface at both three-fold and bridge sites with adsorption energies of 87 kcal/mol and Ni-O bond lengths from 2.02 to 2.08 Å. The OH axis of adsorbed OH is inclined about  $10^\circ$  from the surface normal at a three-fold site. Dissociation of  $\text{H}_2\text{O}$  to OH and H adsorbed at nearby three-fold sites is exothermic, and for OH and H at a large distance of separation, the reaction  $\text{H}_2\text{O}(\text{ads}) = \text{OH}(\text{ads}) + \text{H}(\text{ads})$  is 52 kcal/mol exothermic. A high energy barrier is found at the initial stage of dissociation. The work function decreases by  $\approx 0.5\text{ eV}$  on  $\text{H}_2\text{O}$  adsorption and increases by  $\approx 0.2\text{ eV}$  on OH adsorption (17).

Molecular  $\text{NH}_3$  adsorbed on the Ni(111) surface at an atop atom site and a fcc three-fold site as well as a bridge site are of comparable stability, with adsorption energies of 19.4, 18.4 and 17.3 kcal/mol and with Ni-N equilibrium distances of 2.12, 2.78 and 2.74 Å, respectively; ammonia bonds to the substrate via the N atom with the H's pointing away from the surface. The equilibrium geometry of  $\text{NH}_3$  is calculated to have a pyramidal configuration with the molecular axis normal to the substrate, but tilting the molecular axis or rotating the molecule about the surface normal requires little energy. Calculated frequencies of the surface- $\text{NH}_3$  group vibration, perpendicular to the Ni(111) surface, are between  $460$  and  $500\text{ cm}^{-1}$  and the H-N stretching frequency in  $\text{NH}_3$  on the surface is  $3340\text{ cm}^{-1}$ . The work function decreases by  $\approx 0.6\text{ eV}$  on  $\text{NH}_3$  adsorption (19).

In studies of benzene adsorption on nickel,  $\text{C}_6\text{H}_6$  is found to be adsorbed molecularly, parallel to the surface, at a three fold site, bonding primarily through its  $\pi$  electron system. The equilibrium distance is 2.2 Å from the surface. The calculations show no distortion of the benzene ring other than a 2 percent expansion. C-H bonds tilt away from the surface  $8.5^\circ$ . The adsorption energy is calculated to be 1.2 eV. Adsorption

at the three fold hollow site gives a slightly higher energy than the hcp site, but the difference may be within the uncertainty of the calculation. The energy of the bridge adsorption site is higher than that of the hcp site by 0.5 eV. The photoemission spectrum of adsorbed benzene is explained in terms of final state relaxation effects analogous to image charge formation in the metal following ionization of benzene (18).

The role of  $\pi$  bonding in the (2 x 1) reconstruction of Si (111) was investigated (1). The difference in total energy ( $\Delta E$ ) between the planar and twisted Si-Si  $\pi$  systems in a single  $\pi$  bond ( $\text{Si}_2\text{H}_4$ ), a pair of  $\pi$  bonds ( $\text{Si}_4\text{H}_6$ ) and a  $\text{Si}_6$  chain with 3  $\pi$  bonds embedded in an  $\text{Si}_{12}$  cluster show a uniform decrease in  $\Delta E$  with the number of  $\pi$  bonds. For the largest system studied, a  $\text{Si}_{12}$  cluster model of the (111) surface,  $\Delta E$  is negligibly small. These results suggest that the partial breaking of Si-Si  $\pi$  bonds does not energetically inhibit surface reconstruction (5).

Effective core potentials for Fe ( $1s-3p^6$ ) and Fe ( $1s-3d^7$ ) cores have been developed and fully tested by comparison with all-electron SCF and CI calculations of Fe-H and Fe-Fe potential curves. Embedded cluster models for the Fe (110) surface have now been developed and calculations of H/Fe performed in preparation for the  $\text{H}_2/\text{Fe}$  surface studies.

### Future Research

Work planned for the near future includes the investigation of Si and  $\text{SiH}_x$  adsorption and decomposition on silicon surfaces and interactions with a Si(100) stepped surface in order to better understand surface diffusion and surface layer growth. Reaction of propene with Si(100) will also be studied in order to understand mechanisms for depositing C on silicon by vapor deposition techniques. A third project will involve surface reactions on Cd, Te semiconductor systems. New directions will be explored for the reaction of methane with nickel. Previous results strongly suggest an atop atom site for the  $\text{CH}_4 = \text{CH}_3 + \text{H}$  reaction, driven by the need to accommodate the products in separated sites on Ni(111). It is important to investigate the simultaneous involvement of two electronic configurations of Ni ( $d^9$ s and  $d^{10}$ ), states known to be important in single Ni

atom interactions with CO and CH<sub>4</sub>, to determine whether the interaction would lead to a lower calculated barrier for methane dissociation. Substitutional replacement of Ni by a more reactive transition metal atom will also be investigated to determine if there is sufficient retention of reactivity to induce dissociation of methane. The current theory which permits configuration interaction in the local subspace is ideally suited to address these questions. In collaborative work with P. Cremaschi, hydrogen interactions with Fe(110) will be calculated to determine vibrational excitations and dissociation probabilities on H<sub>2</sub> collision with a Fe wall.

*abstracts are @ hand,  
etc*

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