

This article was downloaded by:

On: 14 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Simulation

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713644482>

Simulation of Adsorbate-Induced Surface Reconstruction

P. A. D. M. A. Dale^a; D. W. Bullett^a

^a School of Physics, University of Bath, Bath, England

To cite this Article Dale, P. A. D. M. A. and Bullett, D. W. (1989) 'Simulation of Adsorbate-Induced Surface Reconstruction', *Molecular Simulation*, 4: 1, 187 — 192

To link to this Article: DOI: 10.1080/08927028908021974

URL: <http://dx.doi.org/10.1080/08927028908021974>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SIMULATION OF ADSORBATE-INDUCED SURFACE RECONSTRUCTION

P.A.D.M.A. DALE and D.W. BULLETT

School of Physics, University of Bath, Claverton Down, Bath BA2 7AY, England

(Received January 1989, accepted February 1989)

Adsorbed atomic monolayers of atoms such as carbon and nitrogen can cause substantial reconstructions of a nickel {001} surface. In this simulation we combine an atomic-orbital-based calculation of electronic structure with an empirical pair-wise repulsive potential to model the covalent part of the total energy. For 0.5 monolayer coverage by the adsorbate, the surface metal layer relaxes into a $p(2 \times 2)$ structure, with transverse displacements of about 0.4 Å. At the same time these displaced surface nickel atoms ride up above second layer nickels, with a vertical displacement of about 0.4 Å. The covalent contribution to the relaxation energy comes out at about 2.0 eV per carbon atom and 1.4 eV per nitrogen atom, of which the reconstruction contributes about 0.3 eV.

KEY WORDS: Surface reconstruction, atomic overlayer, nickel, atomic orbital

INTRODUCTION

Adsorption of an atomic overlayer on a transition-metal surface can cause substantial rearrangements of the local atomic geometry. The properties of carbon monolayers have been particularly well studied because of the key role which adsorbed carbon atoms appear to play as the active intermediate in the Fischer-Tropsch synthesis of hydrocarbons from mixtures of carbon monoxide and hydrogen [1-4]. In this process, the surface carbide species results from the dissociative adsorption of CO on active catalysts such as iron, cobalt, ruthenium or nickel.

The present contribution concentrates on the reconstruction induced in the Ni{001} surface by adsorption of carbon (or nitrogen) overlayers. At a coverage of 0.5 monolayers, one might have expected to find a $c(2 \times 2)$ surface mesh, with adsorbate atoms occupying half of the four-fold hollow sites in the surface. In fact the true mesh observed is $p(2 \times 2)$, and beam absences in LEED reveal glide lines characteristic of the $p4g$ space group [5]. It appears that the four surface nickel atoms around each adsorbed atom are each displaced in different directions in order to accommodate the adsorbate. One possible surface geometry is depicted in Figure 1, where the four-fold hollow adsorption sites are enlarged by rotation and translation of the surrounding metal atoms around each adsorbed atom. At 0.5 monolayer coverage, these rotations must of necessity be in opposite senses at neighbouring sites, thus automatically removing the centering condition from the $c(2 \times 2)$ lattice of carbon atoms and forcing the surface into a $p(2 \times 2)$ arrangement. In addition to LEED studies, this C and N induced reconstruction has been investigated using surface phonon [6, 7] and photoemission probes [8-10].

The object of the present simulation was to see to what extent a simple electronic structure calculation could reproduce the driving force for the reconstruction. It is assumed that the energy can be written in the form

$$E_{\text{tot}} = E_{\text{bs}} + U_{\text{rep}},$$

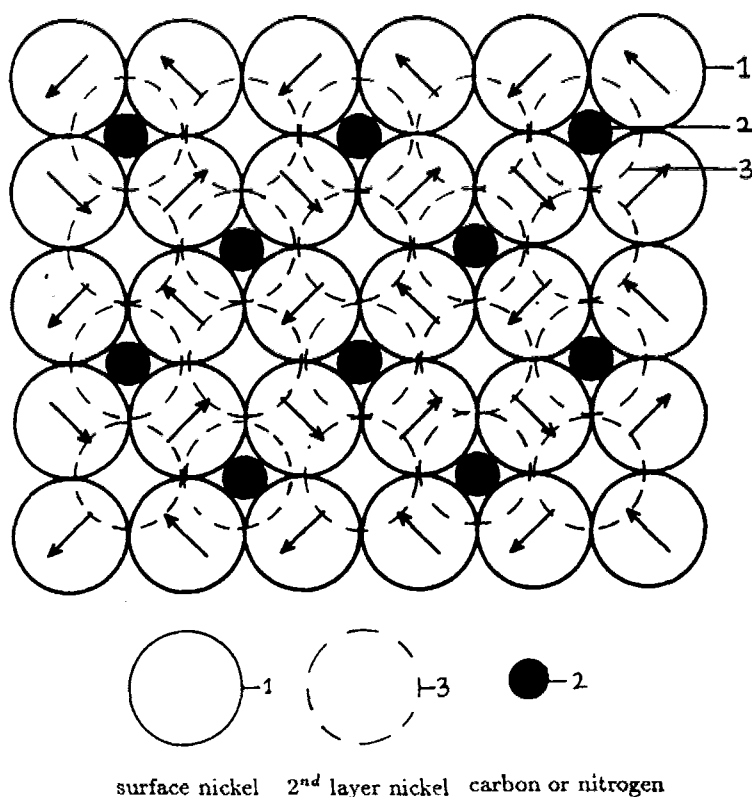


Figure 1 Symmetry for C/Ni(001) surface. Arrows indicate direction of surface displacement. Note the rotations for a central site are in the opposite sense compared to the four corners thereby removing the centering of the $c(2 \times 2)$ mesh.

where the total energy, E_{tot} , is made up of a covalent term E_{bs} , calculated from the one-electron eigenvalues of the system, and U_{rep} , an empirical short-range repulsive term. The covalent band-structure term was itself taken to be the difference of two terms,

$$E_{\text{bs}} = \sum_{i_{\text{occ}}} \varepsilon_i - \sum_{i_{\text{occ}}} n_i \varepsilon_i$$

where the first term is the sum of occupied one-electron energy eigenvalues ε_i , n is the occupation of the stated valence orbital and ε_i would be its corresponding energy in the isolated atom.

We modelled the system by a thin (3 atomic layer) slab of nickel with 0.5 monolayer coverage of adsorbed atoms in an infinite two-dimensional periodic lattice. The valence electron structure was calculated in the two-centre approximation, using numerical s, p and d functions on Ni, and s and p functions on the adsorbate atom, calculated within a local-density approximation to exchange-correlation. Within this approximation, matrix elements of the tight-binding Hamiltonian between orbitals on different sites are allowed to depend only on the separation (and direction) between

the sites, and are independent of the presence of any surrounding atoms [10–11]. The covalent contribution to the total electronic energy was estimated by sampling the energies of occupied crystal wave-functions at a representative set of \mathbf{k} -points in the irreducible Brillouin zone, and subtracting the diagonal energies for the equivalent isolated atoms with the same orbital occupations. Self-consistency was included only to the extent that the d-orbital energies of the nickel atoms were adjusted to be consistent with their calculated energies in isolated atoms of the same d-occupation.

The short-range repulsive contribution to the energy U_{rep} was included as a purely empirical pairwise term, in either of the forms

$$U_{\text{rep}} = \sum_a C_a \exp(-\alpha_a r_a) \text{ or } U_{\text{rep}} = \sum_a A_a r_a^{-12}$$

where the sums are over all near-neighbour atom pairs a at distances r_a . In the case of Ni-Ni interactions the former form of repulsive potential was used, with the exponential and pre-exponential coefficients chosen to fit the equilibrium bond length and bulk modulus of pure nickel; for the nickel-carbon and nickel-nitrogen repulsions we used the power-law type of potential with $A \approx 1.5 \times 10^6 \text{ eV } \text{\AA}^{12}$ in order to fit reasonable equilibrium interatomic distances in both nickel carbide and nickel nitride.

As with the tight-binding matrix elements, portability of the repulsive term for atom-pair types from bulk to surface is assumed. The nickel potential coefficients were first used on a clean nickel surface to see if E_{tot} would predict an observable surface relaxation. The results for calculations on a three-layer slab predicted a contraction of about 2% (0.03 Å) in the separation of the outer two layers; LEED analysis [12] in fact suggest that there may be a very slight expansion by $0.02 \pm 0.02 \text{ Å}$ at the {001} surface of Ni, in contrast to the small contractions of 0.025 ± 0.025 and $0.06 \pm 0.02 \text{ Å}$ at the {111} and {110} surfaces respectively.

RESULTS

The system used in the main simulations was a three-layer slab of Ni with adatoms placed in half of the four-fold hollow sites on one face of the slab, in an initially $c(2 \times 2)$ arrangement above second layer nickels. The two-dimensional unit cell thus contained 12 Ni atoms and 2 C or N atoms, i.e. 116 basis functions in the \mathbf{k} -dependent secular determinant. Results from other thin slab calculations [13] would suggest the three-layer slab used here is adequate for this type of calculation. E_{tot} was obtained for the system as it underwent a series of reconstructions and relaxations in the search for the minimum energy geometry. The variable parameters were:

- (i) the surface Ni perpendicular displacement z_{Ni}
- (ii) the transverse displacement of surface nickel atoms x_{Ni} (along the [001] and [010] crystallographic directions of fcc Ni)
- (iii) the adatom z displacement, z_{C} or z_{N} ,

the positions of second and third layer nickel atoms being held fixed.

The results are presented in Figures 2 and 3 as contour plots of the energy at the optimum value of z_{Ni} as a function of the two other parameters x_{Ni} and z_{C} or z_{N} . The contour plots therefore indicate the most favourable position for the adatom in terms of E_{tot} . Tables 1 and 2 show the bond-lengths at these equilibrium positions.

For both adsorbates the simulation does indeed predict substantial adsorbate-

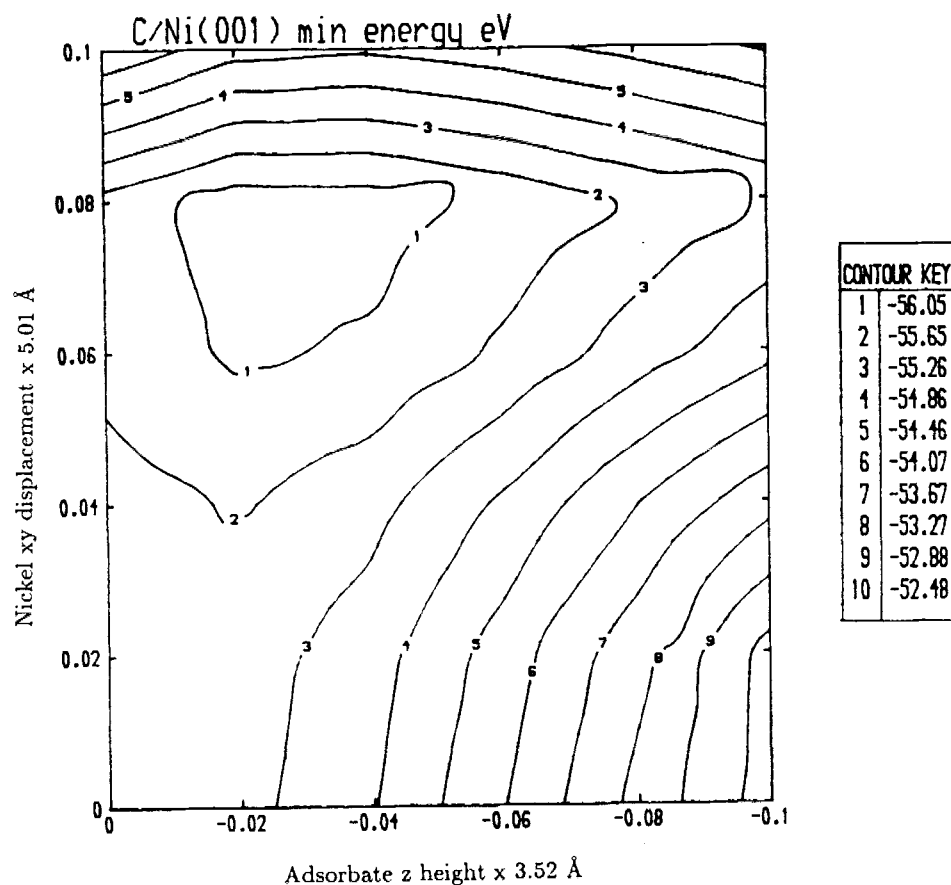


Figure 2 A contour plot of minimum energies for nickel z heights as a function of nickel transverse displacement and carbon z height.

induced reconstructive displacements of the surface layer nickel atoms. In each case the adatoms seem to be able to "dig in" to the surface by forcing surface metal atoms aside. The calculated transverse displacement of surface Ni's is about 0.4 Å for carbon adsorption and 0.35 Å for nitrogen adsorption. In the process, the surface nickels are forced to ride up over the second layer nickel atoms resulting in vertical displacements z_{Ni} of also about 0.4 and 0.35 Å respectively. In both cases the adsorbate atoms end up further in to the metal than the plane of the displaced surface layer of nickel; at equilibrium the adatoms lie about 0.09 Å outside the original Ni layer position. Although the relaxed and reconstructed geometries for the two adsorbate systems are very similar, the driving force for the reconstruction appears to be stronger for carbon than for the case of nitrogen adsorption. The binding energy per chemisorbed atom was calculated to be about 6.7 eV for C and 2.6 eV for N, and the calculated energy gain associated with the relaxation is quite different in the two cases: 2.0 eV per carbon atom but only 1.4 eV for each nitrogen atom. Clearly, these estimates must be treated with considerable caution as they do not include any long-range coulomb contri-

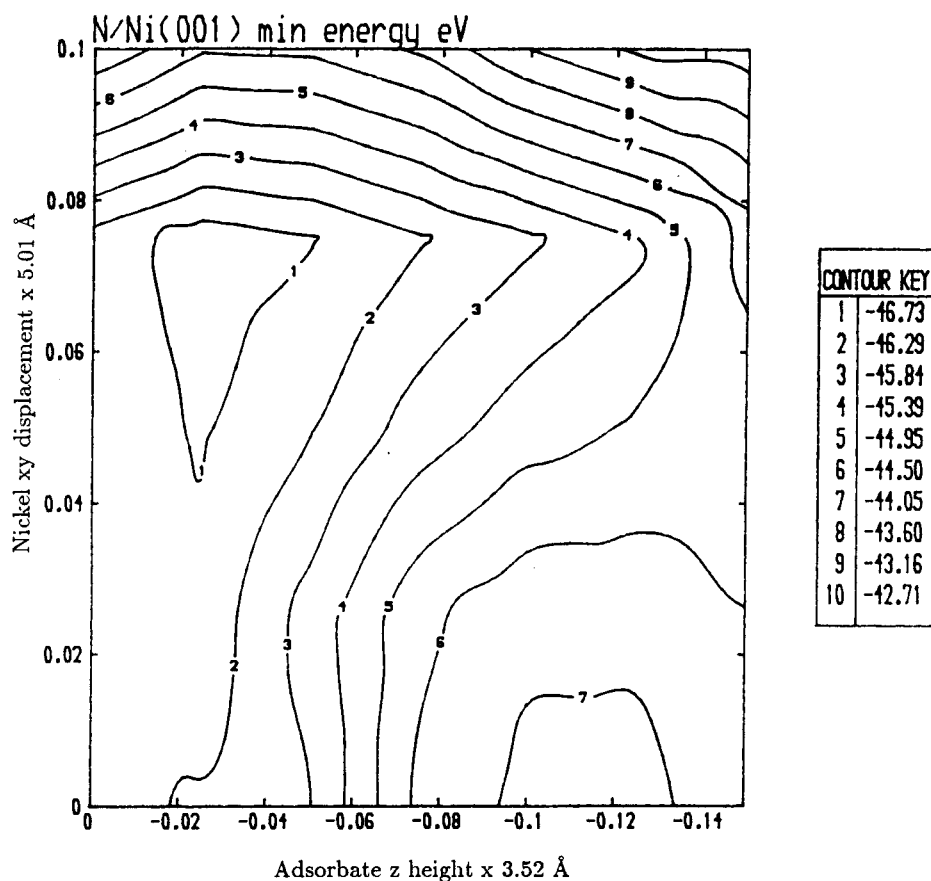


Figure 3 A contour plot of minimum energies for nickel z heights as a function of nickel transverse displacement and nitrogen z height.

Table 1 Ni – Ni, Ni – C interatomic distances for unreconstructed relaxed (001) surface and for full reconstruction.

Atom Pair	Nearest Neighbour distance(s) Å/A.U.	
	Unrecon.	Recon.
1 – 1	4 × 2.49/4.70	2.39/4.52 4 × 2.61/4.94 2 × 3.70/6.98
1 – 2	4 × 1.88/3.55	4 × 1.88/3.54
1 – 3	4 × 2.44/4.61	2.46/4.65 2 × 2.83/5.35 3.16/5.98
2 – 3	2.34/4.42	1.83/3.46

Table 2 Ni – Ni, Ni – N interatomic distances for unreconstructed relaxed (001) surface and for full reconstruction.

Atom Pair	Nearest Neighbour distance(s) Å/A.U.	
	Unrecon.	Recon.
1 – 1	4 × 2.49/4.70	2.53/4.79 4 × 2.58/4.88 2 × 3.66/6.91
1 – 2	4 × 1.84/3.47	
1 – 3	4 × 2.44/4.61	2.46/4.65 2 × 2.79/5.28 3.09/5.83
2 – 3	2.34/4.42	1.85/3.49

bution to the binding energy, but it is encouraging to find that this type of simple simulation of covalent bonding does provide a reasonable account of the forces responsible for adsorbate-induced surface reconstruction.

References

- [1] DW Goodman, RD Kelley, TE Madey and JT Yates Jr, "Kinetics of the Hydrogenation of CO over a Single Crystal Nickel Catalyst." *J Catal* **63**,226(1980)
- [2] DW Goodman, "Model Catalytic Studies over Metal Single Crystals." *Acc Chem Res*, **17**,194(1984)
- [3] RW Joyner, "The role of surface science studies in elucidating the mechanism of the Fischer-Tropsch hydrocarbon synthesis." *Vacuum*, **38**,309(1988)
- [4] RW Joyner, GR Darling and JB Pendry, "Stability of bulk and surface carbide layers and their relation to the Fischer-Tropsch hydrocarbon synthesis." *Surf Sci*, **205**,513(1988)
- [5] JH Onuferko, DP Woodruff and BW Holland, "LEED structure analysis of the Ni{001} (2 × 2)C (p4g) structure; a case of adsorbate-induced substrate distortion." *Surf Sci*, **87**,357(1979)
- [6] TS Rahman and H Ibach, "Adsorbate-induced soft-phonon reconstruction of the Ni(100) surface." *Phys Rev Lett*, **54**,1933(1985)
- [7] W Daum, S Lehwald and H Ibach, "Surface phonon dispersion and adsorbate induced reconstruction of Ni(100)." *Surf Sci*, **178**,528(1986)
- [8] CF McConville, DP Woodruff, SD Kevan, M Weinert and JW Davenport, "Electronic structure of the (2 × 2)C p4g carbide phase on Ni{001}." *Phys. Rev.*, **B34**,2199(1986)
- [9] KC Prince, M Surman, Th Lindner and AM Bradshaw, "The symmetry-based constraints in angle-resolved photoemission from structures belonging to non-symmorphic space groups: p(2 × 2)-C/Ni(100)." *Sol St Comm*, **59**,71(1986)
- [10] DW Bullett and WG Dawson, "Electronic structure of carbidic and graphitic carbon adlayers on transition metals." *Vacuum*, **38**,385 (1988)
- [11] DW Bullett in *Solid State Physics: Advances in Research and Applications*, H Ehrenreich, F Seitz and D Turnbull eds., Academic Press, New York 1980, **35**, 129
- [12] JE Demuth, PM Marcus and DW Jepsen, "Analysis of low-energy-electron-diffraction intensity spectra for (001), (110) and (111) nickel." *Phys Rev*, **B11**,1460 (1975)
- [13] PC Stephenson and DW Bullett, "Electronic states and atomic positions at the {001}, {110} and {111} faces of W and Mo." *Surf. Sci*, **139**,1 (1984)