

# Covalent origin of adsorbate-induced demagnetization at ferromagnetic surfaces

S. J. Jenkins,<sup>1</sup> Q. Ge,<sup>1,2</sup> and D. A. King<sup>1</sup>

<sup>1</sup>*Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom*

<sup>2</sup>*Department of Chemical Engineering, University of Virginia, Charlottesville, Virginia 22903*

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First-principles density-functional theory calculations are presented for the chemisorption of NO on Ni{110}. These demonstrate a strong localization of the adsorbate-induced demagnetization at ferromagnetic surfaces, suggestive of a covalent origin for this intriguing phenomenon. Comparisons with previous work for CO adsorption on the same substrate reveal a number of similarities, but additionally suggest that the initially unpaired electron of the NO molecule results in a more pronounced demagnetization effect.

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## I. INTRODUCTION

Density-functional theory has lately become established as the primary theoretical tool for elucidating the properties of molecules at transition metal surfaces. Adsorption of CO and NO at the fcc {110} surface alone has been the subject of a sizeable body of published work.<sup>1,2</sup> Structural, energetic, and electronic properties of such systems are regularly reproduced with great accuracy, but studies of the spin structure of molecules at surfaces are more rare and largely limited to the case of paramagnetic molecules at nonferromagnetic surfaces. The interaction of adsorbates with ferromagnetic surfaces has comparatively been almost entirely neglected from a first-principles theoretical standpoint.

It has long been understood that narrowing of the  $d$  band leads to an enhancement of magnetic moment in the uppermost surface layers of  $3d$  ferromagnets.<sup>3–11</sup> Equally, it is well established that adsorption of certain molecules can reduce, or even entirely quench, the magnetic moment of that surface layer.<sup>12–14</sup> The consequences of this latter phenomenon are likely to be profound in determining possible detrimental effects of adsorbed impurities on all manner of magnetic devices reliant on small atomic clusters, thin films, or surfaces. On a more positive note, control of the patterning of molecules on a surface may be a potential route towards atomic scale spin-electronic devices.

Although semiempirical modeling<sup>13,14</sup> had previously suggested that adsorbate-induced demagnetization is not only heavily influenced by the local adsorption geometry, but also strongly localized to the uppermost surface layer, it has only recently been noted that the phenomenon is subject to strong lateral localization *within* the metallic surface layer itself.<sup>15</sup> The aim of the present paper is to add depth to our previous study of CO adsorption on Ni{110}<sup>15</sup> by providing detailed comparison with new calculations for NO adsorption on the same surface.

## II. THEORETICAL METHOD

The density-functional calculations reported in this paper were performed using the CASTEP computer code.<sup>16</sup> The surface was represented by a slab consisting of 5 Ni layers, within a periodically repeated supercell of length equivalent

to 16 layers and cross section corresponding to a  $(2 \times 1)$  surface unit cell (Fig. 1). Adsorbates were placed, N atom down, on one side of the slab only, and all atoms apart from the back two layers were allowed to relax according to the calculated forces. Sampling of the Brillouin zone was achieved through summation over a  $4 \times 6 \times 1$  mesh of Monkhorst-Pack  $\mathbf{k}$  points.<sup>17</sup>

Electron-ion interactions were accounted for through the use of ultrasoft pseudopotentials<sup>18</sup> and exchange correlation energies were calculated with the Perdew-Wang form of the generalized gradient approximation.<sup>19</sup> In the case of spin-polarized calculations, a form of pseudopotential including nonlinear core corrections<sup>20</sup> was used, as these have previously been found to be essential in properly describing the magnetic properties of  $3d$  transition metals. Electronic wave functions were expanded in a basis set of plane waves up to a kinetic-energy cutoff of 320 eV. Convergence tests, including large slabs up to nine layers, show that these parameters lead to a good description of bulk, surface, and molecular properties.

Although an ideal basis set for calculations on a periodic surface, plane waves nevertheless have one major drawback regarding the analysis of the results; they are inherently delocalized across the entire system, and localized properties are difficult to obtain. In order to quantify our calculated charge and spin density at an atom-resolved level, we employ the topological method suggested by Bader.<sup>21</sup>

## III. RESULTS

As reported in our earlier letter,<sup>15</sup> the clean Ni{110} surface displays a striking 23% enhancement of the magnetic moments of its top layer atoms over the calculated bulk value of  $0.62 \mu_B$  (experimental value,  $0.61 \mu_B$ ). This effect, due to  $d$ -band narrowing at the surface, appears to be a general feature of ferromagnetic surfaces, and has previously been calculated<sup>11</sup> as 25%. We have also described previously<sup>15</sup> how the adsorption of CO at this surface leads to a marked *demagnetization* (up to 78% of the clean surface value) of just those substrate atoms directly involved in bonding with the molecule. The adsorbed molecule itself gains a small amount of minority spin. Inclusion of spin polarization was found to be crucial in bringing calculated

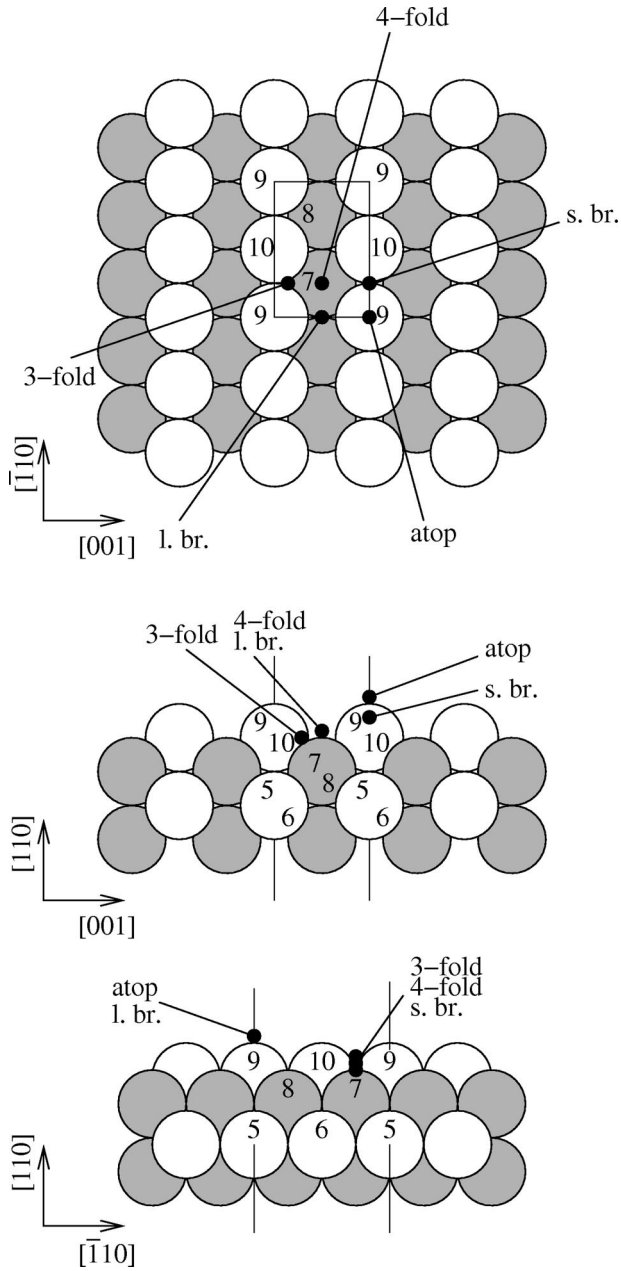


FIG. 1. Schematic diagram for CO/NO adsorption on Ni{110}, showing the unit cell used in the calculations and the various high-symmetry sites considered.

adsorption energies closer to the calorimetrically measured integral heat of adsorption,<sup>22</sup> reducing the spin-unpolarized figure by approximately 0.2 eV per molecule for all adsorption sites. Adsorption was found to occur at the short bridge site at both 0.5 and 1.0 ML coverages, with binding energies of 1.98 and 1.88 eV per molecule, respectively (see Table I).

The adsorption of NO on Ni{110} at 0.5 ML coverage is superficially rather similar to that of CO on the same substrate. Once again, the short bridge site is found to be most stable (see Table I), with minimal molecular tilt away from the surface normal. The main difference is that the pseudo-fourfold hollow site is found not to be a local minimum for NO—a molecule placed here spontaneously shifts laterally

TABLE I. Adsorption energies (in eV per molecule) for CO and NO on Ni{110}. Adsorption sites are as labeled in Fig. 1.

	0.5 ML					1.0 ML	
	s. br.	Atop	l. br.	fourfold	threefold	s. br.	Atop
CO	1.98	1.80	1.49	1.42	...	1.88	1.13
NO	2.66	2.04	1.73	...	2.31	2.35	1.83

into a threefold hollow site adjacent to the short bridge. The tilt in the threefold site amounts to  $34.1^\circ$  away from the surface normal, and considering both its spatial *and* energetic proximity to the short bridge ground state (it is only 0.35 eV per molecule higher in energy) we suggest that it may be a possible intermediate for the activated dissociation of NO.

Adsorption energies for NO on this substrate are significantly higher than those determined for CO. The favored short bridge site yields a value of 2.66 eV per molecule at 0.5 ML coverage, while even the least favored long bridge site yields 1.73 eV per molecule. Repulsive interactions between molecules lead to a reduction in adsorption energy at 1.0 ML coverage to 1.83 eV per molecule for the atop site and 2.35 eV per molecule for the short bridge site. The calculations, nevertheless, indicate a significant increase in adsorption energy for NO as compared to CO on this ferromagnetic substrate. In contrast, the few available calorimetric measurements of NO adsorption energies show no clear trend when compared to those of CO for a range of *nonmagnetic* substrates.<sup>1,2</sup> Further experimental work is required to determine whether the stronger binding of NO relative to CO is a general feature of adsorption on ferromagnetic substrates or is limited to the presently considered surface.

It is tempting to speculate that the higher adsorption energy for NO is mirrored by that molecule's enhanced quenching of the surface magnetic moments (Table II). This is particularly striking for short bridge adsorption at monolayer coverage, where the magnetic moment of top layer Ni atoms is reduced almost to zero. For all sites the quenching is more pronounced than for CO adsorption. Notably, this enhanced quenching effect is achieved without leading to any marked increase in the minority coupling of the mol-

TABLE II. The atom-resolved spin moments for NO on Ni{110} at 0.5 and 1.0 ML, in  $\mu_B$ . Adsorption sites and atom numbering are given in Fig. 1. The numbers in boldface show a decrease of more than 20% with respect to the corresponding clean surface slab.

	0.5 ML					1.0 ML	
	Clean	s. br.	Atop	l. br.	threefold	s. br.	Atop
5	0.65	0.54	<b>0.51</b>	0.67	0.58	0.52	0.53
6	0.65	0.54	0.61	0.58	0.58	0.52	0.53
7	0.58	0.56	0.54	<b>0.37</b>	<b>0.17</b>	0.49	0.54
8	0.58	<b>0.35</b>	0.54	<b>0.37</b>	<b>0.36</b>	0.49	0.54
9	0.76	<b>0.12</b>	<b>0.11</b>	<b>0.10</b>	<b>0.12</b>	<b>0.03</b>	<b>0.20</b>
10	0.76	<b>0.12</b>	0.68	0.70	<b>0.12</b>	<b>0.03</b>	<b>0.20</b>
NO		-0.10	-0.02	-0.03	-0.09	-0.03	-0.04

TABLE III. Acquired molecular charges, in units of the electronic charge, for CO and NO on Ni{110}. Adsorption sites are labeled in Fig. 1.

	0.5 ML				1.0 ML		
	s. br.	Atop	l. br.	fourfold	threefold	s. br.	Atop
CO	-0.24	-0.16	-0.48	-0.48		-0.21	-0.12
NO	-0.45	-0.26	-0.79		-0.72	-0.38	-0.26

ecule to the surface in comparison to CO. Charge transfer from surface to molecule is greater than for CO, but shows the same trends over different sites (Table III) and does not consistently confer any significantly greater minority magnetic moment on the molecule.

Subtracting the density of states (DOS) of the clean Ni{110} surface from that of the surface with 1.0 ML NO adsorbed in the short bridge site, we obtain an insight into the adsorbate-substrate bonding. In both majority and minority spin, we see an decrease in DOS at or just below the Fermi level, flanked on either side by a corresponding increase of similar weight (Fig. 2). The obvious implication is that substrate  $d$  states from close to the Fermi level are becoming involved in mixed orbital bonding and antibonding combinations with molecular  $2\pi^*$  states. The cumulative effect of these changes is that the number of majority spin states below the Fermi level remains more or less constant, while the number of minority spin states below the Fermi level rises considerably. The consequences of such behavior for the local spin structure of the surface are discussed in Sec. IV

#### IV. COVALENT MODEL FOR DEMAGNETIZATION

Ferromagnetism depends upon the existence of highly localized partially occupied  $d$  states that may be aligned through an itinerant exchange interaction mediated by the delocalized  $sp$  electrons. Since the exchange interaction is a subtle many-body effect, while partially occupied  $d$  states are a robust feature of the  $3d$  transition metals, it might reason-

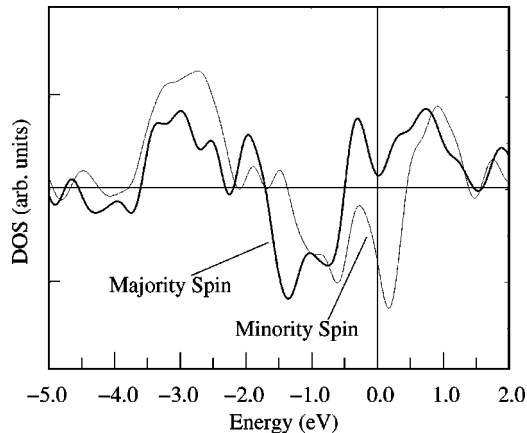


FIG. 2. Change in the DOS of Ni{110} upon adsorption of 1.0 ML of NO in the short bridge site. Energies are relative to the Fermi level.

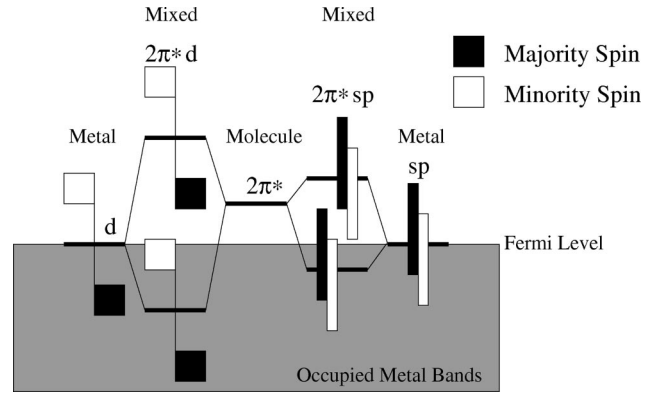


FIG. 3. Schematic illustration of bonding between CO/NO and Ni{110}.

ably have been assumed that surface demagnetization was due to disruption of the  $sp$  electrons. The result, however, would be a rather delocalized damping of magnetic moments at the surface, in contrast to the extreme localization revealed by the present calculations.

In contrast, this localization suggests that the origin of adsorbate-induced demagnetization is to be sought in the covalent bond between the adsorbate and individual substrate atoms. Indeed, the traditional model for the bonding of CO and NO on transition metals, dating back to Blyholder in the 1960's, stresses the interactions of the molecular  $5\sigma$  bonding orbital and the molecular  $2\pi^*$  antibonding orbital with the localized metal  $d$  states. Of these, the  $2\pi^*$  contributes most significantly to the bonding between metal and molecule, since the fully occupied  $5\sigma$  orbital lies well below the metal Fermi level, while the  $2\pi^*$  orbital lies much closer and is either initially empty (CO) or partially empty (NO). More modern theories emphasize the mixed  $5\sigma d$  and  $2\pi^* d$  nature of the metallomolecular orbitals, but retain much of the original flavor.<sup>23</sup>

The key point is that covalent bonding between adsorbate and substrate implies that the partially occupied  $d$  states of *certain* surface atoms are rehybridized into mixed orbitals with an energy well below the Fermi level, as shown highly schematically in Fig. 3. In this simple picture, the mixing of  $d$  and  $2\pi^*$  states leads to nearly complete occupation of the minority  $2\pi^* d$  states, with the consequent reduction in  $d$ -related residual majority spin. The formation of  $2\pi^* sp$  states does *not*, however, imply a corresponding decrease in  $sp$ -related residual minority spin, since the upper edge of both majority *and* minority channels may remain above the Fermi level. Nevertheless, the inclusion of  $2\pi^* sp$  states in the model is necessary to account for the observed molecular residual minority spin. Furthermore, the extra electron present in the case of NO implies a raised Fermi level relative to CO adsorption, which accounts for its greater ability to quench Ni magnetic moments.

In fact, the proposed model is consistent with several otherwise puzzling calculations for various adsorbates on magnetic and nonmagnetic surfaces. NO, for instance, loses its spin identity entirely when adsorbed on Pt{111},<sup>24</sup> whereas it retains it on Ag{111}.<sup>25</sup> This behavior becomes perfectly

understandable when one realizes that the partially occupied  $d$  states of Pt readily hybridize with the NO  $2\pi^*$  orbital, whereas the fully occupied  $d$  states of Ag do not. In one case the initially polarized orbital is subsumed into a new covalent bonding orbital, whereas in the other, it retains its original character. Furthermore, the adsorption of K on Co{10 $\bar{1}$ 0},<sup>26</sup> which occurs through ionic and metallic interaction between  $s$  and  $p$  electrons, but not through  $d$  states, is found not to induce any major demagnetization of the surface. An interesting opportunity to test the present calculations therefore exists in light of recent work showing phase segregation of NO and K adsorbates on the Co{10 $\bar{1}$ 0} surface.<sup>27</sup> Spin-polarized scanning tunnelling microscopy experiments should be able to distinguish the differing magnetic properties of the substrate underlying the segregated islands.

## V. SUMMARY AND CONCLUSIONS

We have demonstrated that NO causes a more pronounced local demagnetization at ferromagnetic surfaces than does CO. In addition, we propose a model for demagnetization based upon covalent mixing of molecular states with metal  $d$  states, and conclude that control of surface magnetism by means of appropriate adsorbates can potentially be used to create magnetic structures with atomic-scale patterning on single-crystal surfaces.

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