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DFT–LDA study of NO adsorption on Rh(110) surface

D. Liao [a,*], K.M. Glassford [b], R. Ramprasad [c], J.B. Adams [d]

[a] *Department of Materials Science and Engineering, University of Illinois, Urbana, IL 61801, USA*
[b] *Molecular Simulations Incorporation, San Diego, CA 92121, USA*
[c] *Department of Physics and Astronomy, Albuquerque, NM 87131, USA*
[d] *Department of Chemical, Bio and Materials Engineering, Arizona State University, Tempe, AZ 85287, USA*

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Abstract

We examine the interaction between NO and the Rh(110) surface using ab initio DFT–LDA pseudo-potential plane-wave total energy calculations. Four different adsorption sites for perpendicular NO are considered. The short-bridge site with linear NO is found to be the optimal adsorption configuration. It is also possible for NO to bond parallel to the surface, and this may be the precursor to NO dissociation. © 1998 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

Rhodium is one of the active ingredients of three-way catalysts (TWCs) used in automotive catalytic converters. Its primary role is in catalyzing NO_x reduction [1,2]. However, the mechanism of NO_x reduction is unclear. In this paper, we examine part of the reaction path, namely NO adsorption.

Depending on the temperature, NO can adsorb either molecularly or dissociatively on Rh surfaces. At room temperature, NO adsorption is dissociative at low coverages on all low index planes. Experimental studies [3–8] have shown that only at quite low temperatures does NO adsorb molecularly on Rh. The onset of dissociation at higher temperatures depends on the NO coverage and crystallographic plane. NO adsorption and dissociation on Rh single-crystal surfaces has been the focus of several groups [3–18]. Although there are several different mechanisms for NO reduction on the single crystal surface, the dissociation of NO to form atomic nitrogen and oxygen is considered to be an important step of such reactions [19]. Understanding the nature of the NO–Rh bonding is the first step to determining the mechanism of the reactions and is important for the further search for other effective substitutes for expensive Rh.

The bonding configuration of molecular NO has been studied on all of the major surfaces, i.e. (111) [3,5], (100) [6], and (110) [13,14]. Most of the structural information for NO chemisorption comes from high-resolution electron energy loss spectroscopy (HREELS). The vibrational mode obtained from HREELS is usually compared with the infrared reflection absorption spectra (IRAS)

* Corresponding author. Fax: (+1) 217 244 6917; e-mail: d-liao@uiuc.edu

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of metal–nitrosyl cluster compounds and assigned the corresponding site and configuration by analogue [20,21]. Dynamical LEED analysis has also been employed to resolve the bonding geometry [5]. The various configurations of NO bonding found for the major low index planes are reviewed briefly below.

For NO adsorption on Rh(111), disagreement exists about the adsorption site. The HREELS study by Root et al. [3] has shown a single bridge-bonded state with NO perpendicular to the surface at all coverages. No LEED pattern other than the (1×1) was observed at 95 K. Kao et al. [5] reported that the adsorption sites of NO depend strongly on surface coverage and adsorption temperature. Their HREELS shows that NO adsorbed at 120 K only occupies bridge sites, whereas new energy loss peaks were found after much larger exposures at 250 K which they attributed to the appearance of on-top linear species. They also observed a $c(4\times2)$ LEED pattern (0.5 coverage) at 120 K and a (2×2) (0.75 coverage) pattern at 250 K. Their dynamical LEED analysis of the latter favored a model with two NO molecules in near-top-sites and one in a bridge site, all perpendicular to the surface. Kim et al. [15] also studied the geometry of the (2×2)-3NO structure by X-ray photoelectron diffraction. Their structural model consists of NO molecules bound to atop, threefold hollow fcc, and threefold hollow hcp sites with the molecule axis normal to the surface.

In the case of NO/Rh(100), Ho and White [10] found that, at 100 K and all coverage, the adsorption is predominately molecular, with a small dissociative contribution at low coverage. They suggest that there are two major chemisorption states involved: one is a normal molecular adsorption and the other has highly inclined NO molecules whose N and O atoms are both bound to the surface with a weakened N–O bond. Upon heating, the latter decomposed before desorption. Later, Villarrubia and Ho [6] reported two adsorption states from their HREELS experiment. The low vibrational frequency of 920 cm^{-1} observed at low NO coverage and at temperatures lower than 140 K is assigned to the N–O stretching mode of a highly inclined species. This species dissociates readily at temperatures above 140 K. Another mode with frequency of 1580–1678 cm^{-1} is observed at higher coverages, which they assigned to a vertically bonded species at twofold bridge sites.

Clean Rh(110) usually forms an unreconstructed surface. A clean, metastable (1×2) reconstructed surface with missing-row-type structure can also be prepared [22,23], which is reported to be less active towards NO dissociation [17]. Most structural information available about NO adsorbates on Rh(110) is for the more stable (1×1) surface.

For the adsorption of NO on the (1×1) surface of Rh(110), a poorly ordered $c(2\times8)$ structure has been reported for saturation coverage at around 120 K [14,17,18], and the saturation coverage is evaluated to be 0.9 ML by X-ray photoemission spectroscopy (XPS) [18] and 0.82 by temperature programmed desorption (TPD) [17]. Baraldi et al. [17] speculated that NO molecules were absorbed on the ridges in a zigzag way and tilted. This structure converts to a (2×1)pg after being heated to $\sim$200 K. Although they did not observe any LEED pattern, Cautero et al. [13] reported there was only one adsorption state in their HREELS study for NO adsorption for the whole coverage range. The measured N–O stretching mode shifts from 1560 to 1710 cm^{-1} with increasing NO coverage, which falls into the range of on-top bent NO. However, their off-specular measurement did not support the existence of off-normally bound NO molecules. They proposed a linear bridge-bonding configuration instead and argued that the N–O vibrational band was close to that of linear bridge-bonded NO on Rh(100). The linear geometry model is also supported by a synchrotron radiation study by Morgante et al. [14] whose near edge X-ray adsorption spectra (NEXAFS) indicate that the molecule axis is close to normal to the surface at all coverages. Their result shows the molecule is either dynamically or statically tilted by $11\pm5^{\circ}$.

Thus, some ambiguity still exists regarding the structure of NO adsorbates. Assignment of vibrational modes to certain configurations on surfaces by comparison with nitrosyl compounds is questionable because of the intrinsic differences between the extended surface and the compounds

[24]. Besides that, owing to the lack of dynamic LEED analysis or other structure-determining method, the details of the structure are not known.

There are not many relevant theoretical calculations of NO chemisorption on metal surfaces. Most of the calculations are based on small cluster models [25] which do not reliably describe NO bonding to metallic surfaces. Among the few theoretical studies of NO adsorption on single-crystal Rh surfaces, Hoffmann and co-workers studied NO/Rh(100) using the extended Hückel theory (EHT) [26,27], a very approximate quantum method. They found that, for several coverages ranging from 0.25 to 1, the binding energies of geometries with NO bound to bridges are significantly higher (0.74 eV for $c(2\times2)$) than those of atop geometries. They then studied the bending of NO and found that the NO tend to stay linear at the atop site. As to NO at the bridge site, one configuration with NO lying parallel to the surface is found to be energetically preferred to the others. These studies yielded many important insights into the problem, but the results are only semi-quantitative owing to the simplicity of their method. Tsai and Hass [28] used an ab initio pseudo-function method and studied the $p(2\times1)$ structure of NO on Rh(100) with the molecule axis fixed normal to the surface. They found the bridge site was favored over the on-top site by 1.84 eV per NO molecule.

There have not been any prior theoretical calculations of NO on Rh(110). Starting from a simplified (2×1)-NO model, this first-principles study concentrates on the adsorption configuration of NO molecules on the Rh(110) surface. The adsorption energies at four different sites are compared and the bridge-site is found to be the energetically favored site. We also calculated the energy of the bending geometry and the preferred geometry is determined to be linear at this coverage.

2. Methods of calculation

The calculations presented here are based on the local-density approximation (LDA) to density functional theory (DFT) [29,30]. The Ceperley–Alder exchange-correlation potential [31] as parameterized by Perdew and Zunger [32] was used, and the Kohn–Sham equations [29,30] were solved self-consistently using a plane-wave basis set.

Spin polarization is not considered in our calculations because it usually makes only a minor contribution to the total energy of most molecules and the effect on molecular geometries is negligible. Previous local-spin-density approximation (LSDA) calculations [33] for diatomic molecules showed that average difference was about 1% in bond lengths, and 5% in the vibrational frequencies. Earlier LDA calculations [34,35] also showed good agreement with experiments in these two aspects.

The pseudopotentials used in our work were constructed self-consistently within the LDA by the method of Troullier and Martins [36,37] and were transformed using the separation techniques of Kleinman and Bylander [38]. The above method is reported to be able to produce "soft core" pseudopotentials which are computationally favorable. The Rh pseudopotential was generated from the atomic ground-state configuration ($4d^8 5s^1 5p^0$) with radial cutoffs of 2.16 a.u., 2.57 a.u. and 2.16 a.u. for the s, p and d components respectively. The 5s potential was chosen as the local component. The N pseudopotential was generated from the ground-state configuration ($2s^2 2p^1$) with radial cutoffs of 1.36 a.u. for both s and p components. The O pseudopotential was from ($2s^2 2p^4$) with radial cutoffs of 1.35 a.u. for both s and p components. The 2p potentials were chosen as the local components of both the N and O potentials. No ghost state was introduced [39] from our choice of local components and core radii.

The criteria for self-consistency was that the Fourier components of the potential differed by less than 0.01 mRy from the previous iteration. At self-consistency, the total energy was stable to within 10^{-5} eV/atom.

Choosing an adequate number of plane-waves in the basis and k points in sampling of the Brillouin zone (BZ) is important for total energy convergence in the structural calculations. In our test, the total energies of bulk Rh, and the mole-

cules N_2 and O_2, were calculated using varying number of plane waves and k points.

The results show that a plane-wave cutoff energy of 49 Ry yields well-converged total energies for bulk Rh. Increasing it to 81 Ry decreased the total energy by only 0.01 eV/atom. E_{cut} of 64 Ry was chosen for N_2 and O_2. The energies per atom are 0.04 eV and 0.07 eV lower when an E_{cut} of 121 Ry is used. Therefore, we chose a plane-wave cutoff energy of 64 Ry in all the structural studies. 18 special k points (per irreducible wedge of BZ) were used for calculation of the bulk Rh structure. Increasing the number of special k points to 28 only changed the total energy by 0.01 eV/atom. For larger supercells, we used six special k points for the clean Rh(110) surface, and two special k points for the NO-covered Rh(110) surface (see below). They were all found to yield well-converged results.

The supercell method is used in the molecule and surface calculations. A supercell of size $(10 \times 10 \times 10)$ a.u.^{3} was used for the molecular calculation. This size was reported to be large enough that the calculated structural parameters are insensitive to the spacing, except for molecules with large bond length or large dipole moments [34,35]. Two larger cells, $(15 \times 15 \times 15)$ a.u.^{3} and $(20 \times 20 \times 20)$ a.u.^{3}, were also used for NO to evaluate the effect of dipole interaction. We found that with the increase of the cell size, both the bond length and the vibrational frequency of the NO molecule converge towards the experimental value. We finally chose the $(20 \times 20 \times 20)$ a.u.^{3} cell for the NO molecule calculation, which is the largest allowed by our computational resources. We used a three-layer slab to model the Rh surface. Supercell sizes of $(a_0/\sqrt{2}) \times a_0 \times (4a_0/\sqrt{2})$ were chosen for the clean Rh(110) surface and $(2a_0/\sqrt{2}) \times a_0 \times (4a_0/\sqrt{2})$ for the NO-covered surface, where a_0 is the calculated bulk lattice constant. The large space (six bulk (110) interplanar spacings) inserted between the slabs ensured a well-converged total energy. For the chemisorbed systems, the NO molecule was put on only one side of the Rh surface to obtain enough vacuum space and avoid interaction between the strong NO dipoles from adjacent surfaces. Geometry optimizations were performed using a conjugate gradient minimization method. In most cases, all atoms were allowed to move in an unconstrained manner until the magnitude of the forces was less than 0.008 Ry a.u.$^{-1}$. The only exception is NO adsorption on the Rh surface, where the bottom layer of the Rh slab was fixed in the bulk position to simulate the effect of a thicker substrate on the top layers.

3. Results and discussion

We first did calculations to determine the structures of bulk Rh, a Rh slab and the molecules N_2, O_2, and NO. They served as tests for the pseudopotentials and helped to determine the number of plane-waves and k points required for convergence. Finally, we were able to explore the configuration of NO adsorbed on the Rh(110) surface.

3.1. Bulk Rh

Crystalline Rh has an fcc structure. The ground-state was obtained by minimizing the total energy with respect to the lattice constant. The ground-state structural and elastic properties were determined by fitting the values of energy and volume to the integrated equation of state by Birch–Murnaghan [40]. In Table 1 we compare our result with calculations by linearized augmented place wave (LAPW) [41], LSDA [42], another similar LDA calculation with different pseudopotentials [43], and with experiment. The lattice constant is in excellent agreement with the experimental value. The cohesive energy is about 27% higher than the experimental value; this is slightly higher than expected, since LDA generally overestimates the cohesive energy by 10–20% [47]. The bulk modulus is about 13% higher than the experimental value measured at ambient conditions [46]. Although the 0 K value is not known, the bulk moduli of two similar metals, Pd and Pt, are increased by 1.2% and 2.0%, upon cooling from room temperature to 0 K [48]. Thus, the 0 K value for Rh is estimated to be 2.75×10^{11} Pa. Our error is about 10% higher, which is reasonable.

Table 1
Present calculations of the lattice constant, cohesive energy, and bulk modulus of Rh compared with values from other calculations and with experiment

	LAPW [41]	LSDA [42]	LDA [43]	Present work	Experiment
a_0 (a.u.)	7.091	7.131	7.173	7.200	7.186 [44]
E_0 (eV/atom)	—	5.972	10.82	7.319	5.75 [45]
B_0 (10^{11} Pa)	3.31	3.014	3.15	3.046	2.75[a]

[a] Estimated from the room temperature value [46].

3.2. N_2, O_2 and NO

The equilibrium bond lengths R_e of N_2, O_2 and NO molecules were determined by minimizing the total energy of the molecules with respect to their bond lengths. The harmonic vibrational frequencies ω_e were obtained by fitting the energy and bond length values around $\pm 1\%$ of the equilibrium bond length. In Table 2 we compare our equilibrium bond length R_e and vibrational frequencies ω_e with the experimental values for each molecule. Overall agreement of the calculations with experiment is generally very good. Bond lengths are all within 2%. Vibrational frequencies are excellent for N_2 and O_2, but there is a -8% error for NO, most likely due to the dipole interaction between NO across the supercells. Generally, results are typical for LDA calculations.

3.3. Clean (1×1) Rh(110)

A three-layer slab and a five-layer slab were used to model the clean (1×1) Rh(110) surface.

Table 2
Bond lengths R_e and vibrational frequencies ω_e for N_2, O_2 and NO[a]

Molecule	R_e (a.u.)	ω_e (cm^{-1})
N_2	2.067 (2.074)	2350 (2358)
O_2	2.320 (2.282)	1571 (1580)
NO	2.195 (2.175)	1757 (1904)

[a] Numbers in parentheses are experimental values [49].

For the three-layer model, geometry optimization yields a -7.5% inward relaxation of the first layer. The surface energy for this relaxed structure is 1.83 eV/atom. Our five-layer slab model gives -9.5% relaxation of the first layer and a surface energy of 1.89 eV/atom.

In Table 3 our calculations are compared with previous calculations and experiments. Our results agree well with other calculations. Methfessel et al. [50] performed a full-potential linear-muffin-tin-orbital (LMTO) calculation with a seven-layer model and only considered the top-layer relaxation. Both the situation and the results are very close to those of our three-layer model. Eichler et al. [43] used a pseudopotential method similar to ours and their result also agrees very well with our five-layer calculation. However, comparison with experiment is difficult because the measured values disagree with one another. One possible explanation for this disagreement is that the experiments may have had some passivation of the surface by hydrogen and/or other contaminants, which tends to reduce the amounts of relaxation. This hypothesis is supported both by LEED work on hydrogen-covered Rh(110) surface by Nichtl et al. [53], and by theoretical calculation of $H(1\times1)$ Rh(100) by Feibelman and Hamann [41]. Direct experimental measurement of the surface energies of rhodium are not available. Approximate values of $2.65\ J\,m^{-2}$ and $2.85\ J\,m^{-2}$ have been estimated from the liquid surface energies and heats of sublimation respectively (for a detailed review, see Methfessel et al. [50]). Methfessel et al. took the average of the calculated values of the (111), (100) and (110) planes as an estimate of the surface energy and got $2.74\ J\,m^{-2}$. Our results are similar to the other

Table 3
Comparison of our calculated top-layer relaxation Δd_{12} and surface energy σ_{110} of the Rh(110) surface with previous calculations and experiment

	This work (3-layer)	LMTO [50]	This work (5-layer)	LDA [43]	Experiment
Δd_{12} (%)	-7.5	-7.5	-9.5	-9.8 ± 0.6	$-0.5+0.7$ [51] -2.7 ± 2.0 [52] -6.9 ± 1.0 [53]
Δd_{23} (%)	—	—	1.6	2.6 ± 0.7	—
σ_{110} (eV/atom)	1.83	1.84	1.89	2.054	—
σ_{110} (J m^{-2})	2.86	2.88	2.95	3.23	—

calculations (see Table 3) and in reasonable agreement with experiment.

The three-layer slab model was chosen to represent the (1×1) Rh(110) surface for the study of NO adsorption. We can see from the above results that although five or more layers is generally required to describe surface relaxation in detail, three layers is enough to give a good approximation of the true surface, i.e. the inner layer approaches the electronic properties of the bulk, the outer layer those of the surface.

3.4. NO/Rh(110)

The only patterns observed for NO-covered (1×1) Rh(110) surface are weak c(2×8) and (2×1)pg, with a saturated coverage of about 0.9, depending on the temperature. At elevated temperatures, NO dissociation begins spontaneously. We used a (2×1) model with 50% coverage to study the adsorption, because this coverage is physically realizable and reasonably low for the study of the highly inclined species, but high enough that it requires a minimal unit cell size.

We first set out to find where the NO molecule can absorb perpendicular to the Rh surface. Four adsorption sites were tried: the atop site, short-bridge site, long-bridge site and fourfold site, as shown schematically in Fig. 1. The NO molecule was initially aligned perpendicular to the surface (N-down) and was placed on one of these sites and allowed to relax until the total energy was minimized. Table 4 lists the optimal geometries and the corresponding chemisorption energies, where R_{N-O} are the N–O bond lengths and R_{Rh-N} represents the distances between the N atom and the nearest Rh. All the Rh(110) surfaces reconstruct to a certain extent and show a significant reduction of inward relaxation of the top layer, Δd_{12}, further supporting the "contamination" hypothesis in Section 3.3. Within the assumption of linear geometry, the present work finds the short-bridge site to be preferred over other sites considered. Fig. 2 shows the structure of this model. Note that this is consistent with calculations for the (100) surface that also find the bridge

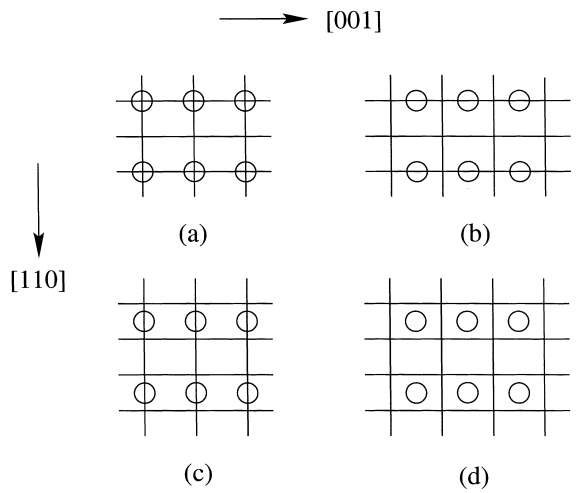

Fig. 1. Adsorption sites (○) for a half-monolayer of NO on a (110) surface, as viewed from above: (a) atop; (b) long-bridge; (c) short-bridge; (d) fourfold. Surface atoms lie at line intersections.

Table 4
Calculated optimal geometries and chemisorption energies of linear NO at four different sites on Rh(110), compared with those of highly inclined NO on the short-bridge site

Site	R_{N-O} (a.u.)	R_{Rh-N} (a.u.)	ΔE_{ad} (eV/molecule)	Δd_{12} (%)
Atop	2.215	3.376 (×1)	2.93	−5.8
Short-bridge	2.264	3.654 (×2)	3.37	0.7
Long-bridge	2.264	4.123 (×2)	2.54	−0.7
Fourfold	2.258	4.995 (×4)	1.66	−2.7
Short-bridge-level	2.321	3.486 (R_{Rh-O}=4.005)	3.18	−2.3

site to be preferred [26]. This also agrees with the site assignment of the HREEL experiment [13].

To determine if the NO may prefer to tilt, we calculated the total energies of NO/Rh(110) with the NO axis tilted 15°, 30°, and 45° in either the (100) or (110) directions. We found that the energies of tilting NO are always higher and the NO tends to return to the linear geometry if relaxation is allowed. This suggests that, for moderate coverage when interactions between the NO molecules is modest, the NO does not tilt. This agrees with the result of the NEXAFS experiment [14], which found that NO does not tilt or tilts very slightly. It is also consistent with the HREEL experiment [13] which found no evidence for the existence of off-normally bound NO molecules.

Since complete NO decomposition usually happens for coverages lower than 30%, we believe that NO dissociation to adatoms N_{ad} and O_{ad} is an intermediate step in the reduction process. Considering that for the (100) surface, experiments [6,10] and calculations [6,26] suggest that there is a highly inclined species involved in the dissociation, we speculate that there could be a similar species on the Rh(110) surface. We placed an NO molecule with its axis parallel to the surface over the bridge site and relaxed the structure. The result is shown in Fig. 3. The geometry and energy are collected in Table 4 for comparison. We can see that both the N and the O atoms are bonded to different substrate Rh atoms and the NO bond is longer (2.321 a.u.) than those in other geometries. The chemisorption energy of this structure is about 0.2 eV lower than the linear-on-short-bridge species, but higher than all the others considered. We consider this metastable species as one of the candidates of the precursor of NO dissociation, because upon thermal excitation and with empty sites available, this is one of the states that likely exist on the surface. Considering that the Rh(110)

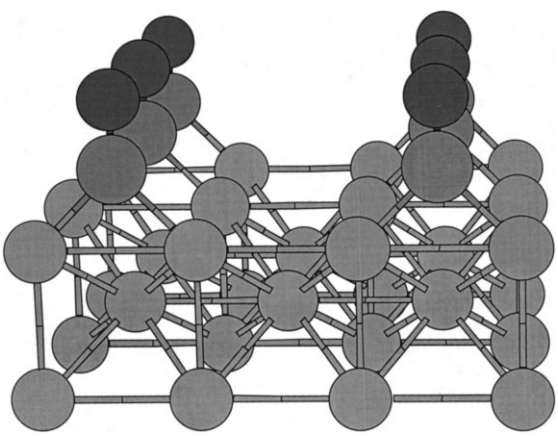

Fig. 2. Structure of the NO perpendicular to the surface on the short-bridge site.

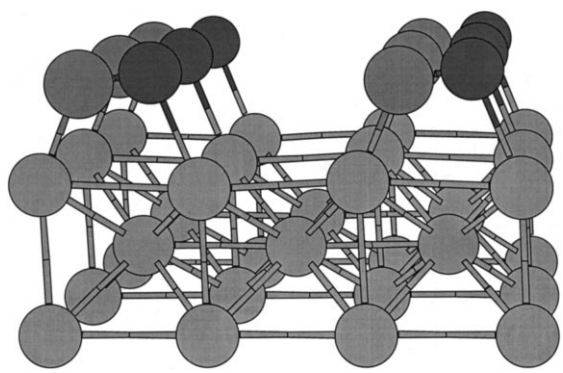

Fig. 3. Structure of the NO nearly parallel to the surface on the short-bridge site.

surface easily reconstructs upon the influence of adsorbents [18,54,55], it is possible that N and/or O atoms form stronger bonds with the surface and the N–O bond can be broken. Clearly, further investigation of this structure is needed.

4. Summary

We have performed ab initio total energy calculations for NO adsorption on Rh(110). The NO is found to prefer the short-bridge site with a linear orientation perpendicular to the surface at 50% coverage. This is consistent with other calculations for Rh(100). Also, we find that a highly inclined NO molecule binds strongly to the short-bridge site, and may be the precursor to NO dissociation.

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