# Dynamical and geometrical aspects of NO chemisorption on transition metals: Rh, Pd, and Pt

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The technical relevance of Rh, Pd, and Pt as catalysts used to reduce $NO_x$ pollutants has stimulated great interest in a detailed understanding of the chemisorption process of these systems. While experiment indicates Rh to be a better catalyst than the other transition metals, theory still does not give a satisfying explanation for this behavior. We have examined the $c(2\times2)$ atop chemisorption of NO on Rh, Pd, and Pt substrates with our full-potential linearized augmented-plane-wave method for thin films. Simultaneous relaxation of the NO bond length and the distance between the metal and N, as well as surface relaxation of the metal, was performed. Various vibration frequencies were determined from the dynamical matrix of the system. The analysis of the dynamical matrix shows stronger bonding of NO to Pd and Pt compared to the Rh surface. We find the metal surface to be strongly affected by NO chemisorption, including a buckling that is about 50% larger on Pd and Pt than on the Rh surface. While the calculated electronic properties, such as density of states, give very similar results for the three systems the geometric and dynamical properties may explain the observed higher efficiency of Rh as a catalyst. [S0163-1829(97)02920-2]

## I. INTRODUCTION

Understanding the catalytic reduction of nitrogen oxides ($NO_x$) is of great technological importance. In the automotive industry, three-way catalysts, notably Rh, Pd, and Pt, are used to reduce the emission of noxious nitrogen oxides. While Rh is more efficient in the reduction of $NO_x$ compared to Pd and Pt, and many experimental investigations of these systems have provided new and interesting information, the key reason for the efficiency of Rh is still not known. With ever more stringent air quality regulations being imposed on automobile manufactures, a detailed understanding of the catalytic reduction of NO becomes even more urgent.

The adsorption and chemical reaction of NO molecules on Rh, Pd, and Pt show a complicated and complex nature. Depending on the crystal surface of the substrate, dissociative adsorption may be promoted or hindered.[1–4] Also, a strong dependence of the adsorption site on temperature and coverage has been reported,[5] and experimental results are sometimes considered controversial.[5,6].

So far, on the theoretical side these systems have been investigated only very little. Most of the calculations invoke semiempirical methods, which lack the ability to describe the complexity of these systems.[7] Another approach uses cluster methods.[8,9] While appealing, one of the major drawbacks of the cluster approach is its difficulty in accounting for the metallic nature of the substrate. Recently, Tsai and Hass have provided a first-principles study of these systems using a pseudofunction method.[10–12] While the bare metal results obtained are in good agreement with experiment, the treatment of the free NO molecule showed some difficulties.

In this paper, we present detailed calculations for NO chemisorption on Rh, Pd, and Pt with our full-potential linearized augmented-plane-wave method (FLAPW) for thin films.[13] This method can treat both molecules and metal systems on the same footing and is therefore very well suited to deal with chemisorbed NO on transition metals. The precision of this approach has been demonstrated previously.[15].

The dissociative adsorption of NO is generally considered to occur in two steps. In a first step, the NO molecule is adsorbed on different possible sites of the surface, with the N atom towards the metal surface. It is a widely accepted picture that in a second step the actual dissociation takes place with the molecule bent down into the surface.[4] Therefore, not only are the electronic properties of the NO chemisorption important, but so are the dynamical and geometrical aspects of the chemisorption process. Clearly, a tightly bonded molecule is less likely to be bent down into the surface. Also, while possible surface reconstruction and relaxation can have a strong influence on the dissociative chemisorption of the NO molecule, they have been neglected in previous investigations. Further, vibrational frequencies are usually calculated by freezing the degree of freedom of the surface atoms.[10].

In our calculations, all atoms are allowed to relax, which includes possible surface relaxation. The stretching frequency of the bonded NO molecule and the vibration mode of the molecule against the substrate are calculated from the dynamical matrix. Thus, geometrical and dynamical aspects, including the dynamics of the substrate, can be determined. Because of the above-mentioned complexity of NO chemisorption, we focused in these first investigations on the (100) surface and a $c(2\times2)$ atop coverage for all three substrates. This allows a systematic analysis of the chemisorption properties of NO on these transition metals and a clearer revelation of any differences the three substrates may exhibit upon chemisorption.

The computational details are described in Sec. II, results for the free NO molecule as well as the bare metal substrates are presented in Sec. III, the chemisorbed system is discussed in Sec. IV, and a summary is given in Sec. V.

## II. METHOD AND COMPUTATIONAL DETAILS

The FLAPW method for a thin film geometry is an all-electron *ab initio* method with no shape approximations for

the potential and charge density.[13] The exchange correlation effects are treated within the local density approximation using a Hedin-Lundqvist[14] parametrization of the exchange-correlation potential. The method is very well suited for surface-related problems, since no artificial periodicity along the $z$ direction is imposed. This is particularly important for systems like a free NO molecule, which have an electrostatic dipole, since then the potential at plus infinity differs from that at minus infinity. The substrate system was simulated by a three-layer slab, which appears to be thick enough to provide sufficient screening. A sensitive quantity with respect to the slab thickness is the work function. A five-layer slab calculation for Rh gave a work function that differed by less than 0.1 eV from that for the three-layer slab. We used the following muffin-tin (MT) radii (in a.u.): 1.0 for both O and N, 2.4 for the center layer, and 2.3 for the surface layer, in order to allow the system to relax. A cutoff of 4.7 and 12.6 a.u. for the plane-wave basis and potential representation were necessary to achieve convergence. To obtain self-consistency, six special $k$ points in the irreducible Brillouin zone were used, and after that 21 $k$ points were used for quantities like the density of states.

The implementation of the FLAPW method for thin films includes total energy[16] and atomic-force calculations,[17] which allow structure optimization. For each self-consistent structure, the forces on all atoms were determined. A stable configuration is found, when the $3n$-dimensional force vector of the system (with $n$ atoms) is zero. A Broyden[18] scheme was used to find the multidimensional zero. We considered a relaxed structure, when the force on each atom was smaller than 2 mRy/a.u., and the position did not change more than $3 \times 10^{-3}$ a.u. The present investigations are within the framework of the local density approximation; no parameter-dependent gradient corrections such as the generalized gradient approximation (GGA) were employed, although it is known that GGA can improve quantities such as bond distances, etc. In addition, the dynamical matrix of an optimized structure is calculated, from which the eigenmodes of the system are determined. The dynamical matrix is defined as

$$D_{i,j} = \frac{1}{\sqrt{m_i m_j}} \frac{\partial^2 E}{\partial x_i \partial x_j}, \qquad (1)$$

where $m_i$ and $x_i$ are the mass and the position of the $i$th particle and $E$ is the total energy of the system. Since the forces are calculated from an analytical expression derived for the FLAPW method,[17] one can rewrite Eq. (1) in terms of forces. The resulting expression,

$$D_{i,j} = -\frac{1}{\sqrt{m_i m_j}} \frac{\partial F_i}{\partial x_j} \approx -\frac{1}{\sqrt{m_i m_j}} \frac{\Delta F_i}{\Delta x_j} \qquad (2)$$

is solved in a finite-differences approach. The eigenvalues and eigenvectors of the matrix $D_{ij}$ give the phonon spectrum of the system. The step $\Delta x_j$, which is appropriate to obtain a reliable result for $D_{i,j}$, depends in general on the system under investigation. If the total energy curve deviates from a parabola in a certain direction, $\Delta x_j$ has to be chosen smaller to accurately determine $D_{i,j}$. In the present calculation, we used a value of $\Delta x_j = 0.03$ (a.u.) for the metal atoms and
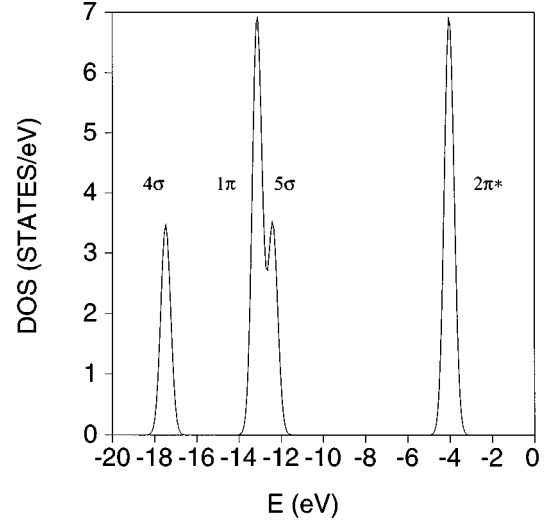


FIG. 1. Total density of states of the free NO molecule (in states/eV). The zero energy refers to the vacuum.

$\Delta x_j = 0.02$ (a.u.) for the N and O atoms. Small variations of these values did not change the results significantly.

### III. BARE METAL AND FREE NO

For understanding the chemisorbed system it is important to first investigate the properties of its constituents. This also provides a good test of the method, since a molecule and a metal have completely different physical properties, which have to be described at the same level of precision. Hence, we present here results for the free NO molecule and the bare metal substrate.

The free NO molecule was simulated by a monolayer of molecules arranged vertically in a two-dimensional square lattice. The lattice constant (or separation between molecules) was 7.18 a.u., which is more than three times the NO intra-atomic distance; this is sufficient to reveal the properties of a single molecule, even though the discrete eigenstates are slightly dispersed. The initial bond length of the NO molecule was set to 2.1 a.u., which is smaller than the experimental equilibrium distance in the gas phase. Then the NO molecule was allowed to relax according to the atomic-force and total-energy calculations. Also, the stretching frequency was determined from the dynamical matrix. The results for the equilibrium distance (2.16 a.u.) and the stretching frequency (1874 cm$^{-1}$) are found to be in excellent agreement with experiment, namely, an equilibrium distance of 2.17 a.u. and a stretching frequency of 1876 cm$^{-1}$ for NO in the gas phase. These results clearly demonstrate the accuracy of the FLAPW method in dealing with molecules; they also represent a successful test for the optimization procedure and the dynamical matrix approach developed here.

In Fig. 1, the density of states (DOS) of the free NO molecule is shown. Also here the calculated spectrum is in remarkably good agreement with photoemission data.[19]

The bare metal system was simulated by a three-layer slab and a (100) surface for Rh, Pd, and Pt. As an initial setup, we used the bulk value for the lattice constant. From atomic-force and total-energy calculations, we relaxed the surface

TABLE I. Distance between surface and subsurface layer.

|  | Rh | Pd | Pt |
|---|---|---|---|
| Bulk (a.u.) | 3.591 | 3.676 | 3.705 |
| Relaxed (a.u.) | 3.419 | 3.570 | 3.611 |

layer. The optimization procedure, which was mentioned and applied to the free NO molecule in Sec. II, was used to find the equilibrium structure. In all these metals, as shown in Table I, we find an inward relaxation of the top layer. The Rh surface layer relaxes by about 4.7%, while for Pd and Pt the relaxation is only 2.9% and 2.5%, respectively. The Rh result is in good agreement with another FLAPW calculation,[20] where a relaxation of 5% was found. For Pd and Pt a relaxation between 1 and 3% was reported.[21] Thus, the theoretical predictions of our calculations are consistent with previously found results. There are, however, experimental studies[22] that find an anomalous outward relaxation for Rh and also Pd. It was speculated that magnetism in the surface layer might be responsible for this behavior — although FLAPW calculations on these metals show them to be paramagnetic. We note, however, that contamination with H atoms at the surface can reduce an inward relaxation or even cause an outward relaxation[22]. Our calculated results are, of course, for a theoretically perfect surface, with no contamination or surface defects.

From the location of the Fermi energy, one can determine the work function $\Phi$ to be 5.48, 5.68, and 6.19 eV for Rh, Pd, and Pt, respectively. A direct comparison of the theoretical predictions for the (100) surface and experiment is not straightforward; the experimental values for $\Phi$ differ for different crystal surfaces and measurements are often done on polycrystalline samples. Nevertheless, the calculated $\Phi$ is found to increase from Rh to Pt, which is consistent with experiment. Even though the absolute values differ, this trend was also found in other calculations by different methods.[10,26]

The calculated total density of states of the clean metal substrates is shown in Fig. 2. In all three cases, a dominant $d$ character is present, with a relatively high DOS at $E_F$. Even though the bandwidth is different for Rh, Pd, and Pt, there is no significant difference in the electronic properties of the bare metal that might indicate that Rh is a better catalyst. Since the chemisorption process takes place at the surface, we also calculated the surface projected DOS shown in Fig. 3. Also here, while differences are present, the results do not distinguish Rh as a more efficient catalyst.

## IV. CHEMISORBED SYSTEM

As mentioned above, we focused on the (100) phase of the metal substrate in all three cases. The calculations were performed for a vertically chemisorbed NO molecule on atop sites in a $c(2 \times 2)$ structure on both sides of the slab, which gives a coverage of $\Theta = 0.5$. This coverage is comparable to experimental studies,[5,6,23,25] and only doubles the two-dimensional unit cell, which makes the calculations still managable. In all three cases, we performed the following steps in the calculation: the NO molecule was placed near the surface with the calculated equilibrium distance. The metal
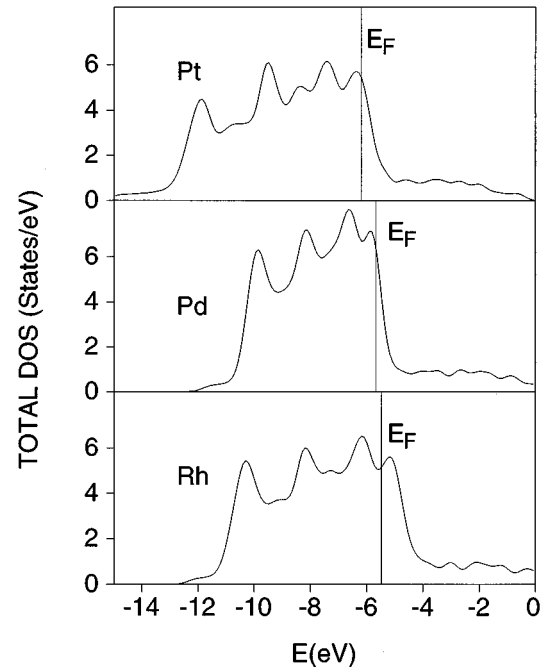


FIG. 2. Total density of states of the clean metal systems Rh, Pd, and Pt (in states/eV). The vertical lines indicate the Fermi energy, and the zero energy refers to the vacuum.

substrate was set up with its relaxed equilibrium distances. Then the total system was allowed to relax according to total-energy and atomic-force calculations. An automatic optimization procedure moved all the atoms simultaneously, and was terminated according to the criteria mentioned in Sec. II. From the optimized geometry the dynamical matrix was calculated, from which the vibrational eigenmodes of the system follow.
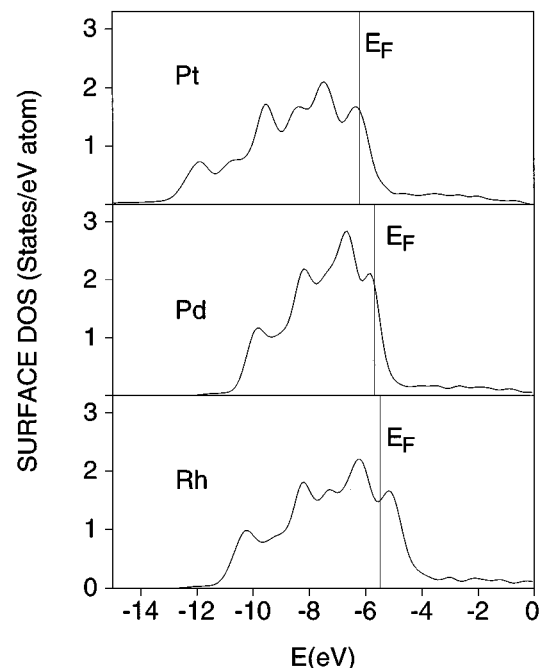


FIG. 3. Surface layer projected density of states of the clean metal systems Rh, Pd, and Pt (in states/eV/atom). The vertical lines indicates the Fermi energy, and the zero refers to the vacuum.

TABLE II. Equilibrium distances for the chemisorbed molecule and buckling parameter (cf. Fig. 5).

|  | Rh | Pd | Pt |
|---|---|---|---|
| $d_{NO}$ (a.u.) | 2.203 | 2.187 | 2.186 |
| $d_{N\text{-}M}$ (a.u.) | 3.427 | 3.497 | 3.459 |
| $d$ (a.u.) | 0.183 | 0.281 | 0.264 |

First, we discuss the results obtained from the geometry optimization. We find that the surface layer is quite strongly affected by the NO chemisorption. Since the structure is a $c(2\times2)$ coverage, every second surface atom has a NO molecule on top. The metal atom with an NO molecule on top is pushed out of the (relaxed) surface, while the neighboring metal atom without NO is pulled further down with respect to the relaxed bare metal system, resulting in a surface buckling. As a measure of the degree of buckling, we denoted with $d$ the relative distance in the $z$ coordinate of the two neighboring atoms (see Fig. 5). The three systems show the same qualitative behavior, but differ quantitatively. For the ''buckling parameter'' $d$ we find 0.183 a.u. on the Rh surface, while Pd and Pt have approximately the same value, 0.281 and 0.264 a.u., respectively. Clearly, the Rh surface is less affected by the NO chemisorption than are Pd and Pt. This effect, which is about 50% larger in the case of Pd and Pt compared to the Rh surface, is expected to have a strong influence on the chemical reactivity of the NO molecules. For example, for a dissociative reaction, bending the NO molecule down onto the surface is certainly more difficult on Pd and Pt than on the Rh surface. The angle about which the NO molecule has to be bent in order to react with a surface atom is increased for the Pd and Pt surface. In Table II, we summarize the equilibrium distance $d_{NO}$ of the chemisorbed NO molecule and the distance $d_{N\text{-}M}$ between the N atom and the surface metal ($M$) atom. We find a bond length $d_{NO}$ on Rh of 2.203 a.u. and 2.187 and 2.186 a.u. on Pd and Pt, respectively. Thus, the chemisorption of NO on Rh increases the NO bond length by about 2% of the value of the free molecule, while the increase is only 1% in the case of Pd and Pt. This result suggests that the weakening of the bond between N and O is greater on the Rh surface.

To further investigate this effect, we looked at the dynamical aspects of the NO chemisorption. From the dynamical matrix of the system, we calculated the stretching frequency of the bonded NO molecule as well as the N-$M$ vibration frequency, including the full dynamics of the system. Table III summarizes the calculated vibrational modes. In all three cases, the NO stretching frequency is lowered. For Rh we find it to be 1634 cm$^{-1}$ and on Pd and Pt we find 1709 and 1699 cm$^{-1}$, respectively. This result is again consistent with the others in that a lower stretching frequency usually leads to a weaker bond. The results confirm the idea

TABLE III. Vibrational modes for the chemisorbed molecule.

|  | Rh | Pd | Pt |
|---|---|---|---|
| $\nu_{NO}$ (cm$^{-1}$) | 1634 | 1709 | 1699 |
| $\nu_{N\text{-}M}$ (cm$^{-1}$) | 337 | 523 | 632 |

that the NO bonding on Rh is weaker compared to Pd and Pt, even though the difference is not very large.

These theoretical predictions for the stretching frequency are also in good agreement with experiment,[23,5,25] although a direct comparison is not straightforward for reasons similar to the work function comparison of the bare metal; it is site and coverage dependent, and also varies with the crystal phase. Luckily, we found an experimental result for one of the systems calculated: For Pd(100) with a NO coverage of $\Theta=0.5$ in the atop position a stretching frequency of 1714 cm$^{-1}$ was reported,[25] which is in excellent agreement with our calculated value of 1699 cm$^{-1}$. Usually, a value of $1630-1750$ cm$^{-1}$ is assigned to the NO frequency on the atop position for these metals, which agrees nicely with the predictions of a perfect (100) surface with a purely atop overlayer of $\Theta=0.5$.

Another interesting result is the N-$M$ mode of the three systems, which increases from 337 cm$^{-1}$ for Rh to 523 and 632 cm$^{-1}$ for Pd and Pt, respectively — again indicating a stronger bonding of the NO molecule on Pd and Pt compared to the Rh surface. As stated above, the bonding of the NO molecule to the surface is certainly a further important factor in the dissociation of NO. A more tightly bonded NO decreases the chemical reactivity. It also results in a stiffer bond, and bending the molecule down into the surface, which is essential for the dissociative reduction of NO, becomes more difficult. Thus, compared to the Rh surface, the mobility and chemical reactivity of NO is reduced on a Pd or Pt surface.

Finally, we investigated the electronic properties of the NO chemisorption. In Fig. 4 we present the projected N-atom DOS and, for comparison, the N-atom DOS of the free NO molecule. The energy is on an absolute scale and the vertical line indicates the Fermi energy of the system. From Fig. 4, one can see that the NO states are strongly affected by the chemisorption. The $4\sigma$ state is shifted compared to the free molecule; also the $1\pi$ and $5\sigma$ are shifted and even a change in the relative order of these two states occurs. In addition, strong hybridization takes place; in particular, the $5\sigma$ state hybridizes with the $d$ states of the metal and forms new states. In contrast, the antibonding $2\pi^*$ state mainly keeps its position, and is broadened due to the interaction with the metal states. Also the $2\pi^*$ state hybridizes with the metal $d$ states, which produces new states lying just below $E_F$. This result is consistent with the frequently discussed picture of the ''$\sigma$ donation and $\pi$ back donation.''[24]

The relative occupancy of the hybridized $2\pi^*$ state has two effects. On the one hand, the filling of the antibonding state should elongate and weaken the NO bond. On the other hand, more charge is transferred into the bond region between the NO molecule and the metal, which strengthens the bonding between the molecule and the metal substrate. Therefore from Fig. 4, one would conclude that the bond length of the NO molecule should be larger on a Pd or Pt surface compared to Rh. Due to the smaller lattice constant of Rh (cf. Table I), however, there is a stronger interaction between the NO molecules on a Rh surface, which in addition to the NO-metal interaction reduces the bond length. Since electronic and geometric properties determine the NO bond length and strength of the bonding, Fig. 4 does not
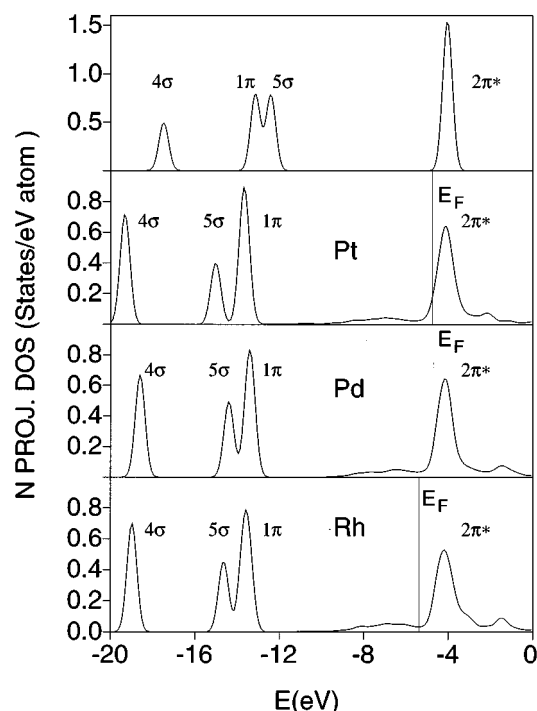
FIG. 4. N projected density of states of the three systems NO/Rh, NO/Pd, and NO/Pt (in states/eV/atom) and for comparison the N projected density of states of the free NO molecule. The vertical line indicates the Fermi energy and zero refers to the vacuum.

contradict the above-mentioned results.

In accordance with the higher filling of the hybridized $2\pi^*$ state, there is a stronger polarization of the electrons towards the metal surface. This modifies the electrostatic potential in the surface region, and leads to a dipole layer that raises the electronic levels including $E_F$ and results in a reduction of the work function. The calculated work-function
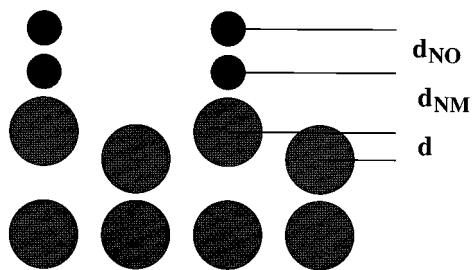


FIG. 5. Schematic side view showing the buckling ($d$) and bond distances ($d_{NO}$ and $d_{N\text{-}M}$). See Table II for their numerical values.

change $\Delta\Phi$ for the Pt and Pd surface is $-1.15$ and $-1.1$ eV, respectively; on the Rh surface $\Delta\Phi$ is much smaller, $-0.1$ eV. A negative $\Delta\Phi$ was also found in several experiments[4–6] on these metals, which show a strong dependence of $\Delta\Phi$ on the adsorption site and the crystal phase under investigation. Both negative and positive values are reported.[5,4] In Ref. 5, a correlation between site and sign was found in $\Delta\Phi$. The bridge site has a positive $\Delta\Phi$, while the atop has a negative $\Delta\Phi$; thus our calculated negative $\Delta\Phi$ values are in agreement with experiment. The calculated $\Delta\Phi$ values are quite large, which is due to the high coverage of a purely atop chemisorbed NO molecule. However, a coverage-dependent $\Delta\Phi$ is reported in Ref. 4 for the system NO on Rh(100). During exposure with NO $\Delta\Phi$ initially drops sharply to negative values. A maximum value for $\Delta\Phi$ of $-0.75$ eV was found.[4]

## V. SUMMARY AND CONCLUSIONS

We have presented results of *ab initio* local-density FLAPW calculations for (i) the free NO molecule, (ii) the clean metal surface, and (iii) chemisorbed NO molecules on the transition metals Rh, Pd, and Pt. The calculated properties of the free NO molecule are found to be in excellent agreement with experiment. For the clean metal surface, we find an inward relaxation of the surface layer. For the combined system, results for $c(2\times2)$ atop chemisorption on the (100) surface were presented, including a full geometry optimization. In addition, we calculated the dynamical matrix of the systems and presented the vibrational eigenmodes of the chemisorbed system. While the electronic properties of chemisorbed NO did not reveal the reason for the observed efficiency of Rh as a catalyst, our results suggest the importance of geometric and dynamical aspects of the chemisorption process: among the interesting results obtained, we found a surface buckling in all three systems upon chemisorption, which is more pronounced for the systems NO/Pd and NO/Pt. The dynamical properties of the NO chemisorption showed stronger bonding of the NO molecule on the Pd and Pt surface, compared to the Rh surface. The mobility and chemical reactivity of NO on a Pd and Pt surface is hindered due to the stronger bonding to the surface and a larger buckling of the surface layer. These two results may possibly distinguish Rh as a more efficient catalyst.

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