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Published in:
Journal of Chemical Physics

DOI:
10.1063/1.480146

Published: 01/01/1999

Document Version
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

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Adsorption of ammonia on the rhodium (111), (100), and stepped (100) surfaces: An ab initio and experimental study

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(Received 3 May 1999; accepted 28 July 1999)

The adsorption of ammonia on the two low index (111) and (100) surfaces of rhodium has been studied by periodic calculations with density functional theory and compared to experimental results. The geometries of the adsorbates and the surfaces are completely optimized. For both surfaces the top site is found to be the most stable while the adsorption energy of ammonia is 8–10 kJ·mol⁻¹ larger on the (100) surface. The presence of steps on the (100) surface has a minor effect on the heat of adsorption. The theoretical predictions of the adsorption energies and the changes in work function by NH₃ are in good agreement with experimental data. Moreover the prediction of the ontop adsorption as well as the weak interactions between the adsorbates is confirmed. The broadening of the temperature programmed desorption spectra and the two desorption peaks for the first adlayer are mainly due to an entropy effect which affects the preexponential factor of the desorption rate constant. © 1999 American Institute of Physics.

I. INTRODUCTION

The interaction of ammonia with rhodium is an important step for different catalytic processes. It is essential for HCN synthesis and for the formation of NO by oxidation of NH₃. It is also of interest in the automotive exhaust catalysis where NH₃ could be a possible product from the reduction of NO by H₂. Information on the chemisorption of NH₃ on Rh is sparse when compared to other transition metals like Ni, Cu, Ag, Pt, or Ru.

As a consequence, theoretical studies on the adsorption of NH₃ concern mainly the same metals. Ab initio calculations for the adsorption of NH₃ have been done mainly with clusters as models of the metal surfaces: Hermann et al. for Al(111), Chattopadhyay et al. for Ni(111), Biemolt et al., Bagus et al., and Bauschlicher for Cu(111) and Cu(100), Burns et al. and Mijoule et al. for Pd, Fierro, Fahmi, and van Santen, and Jennison et al. for Pt(111). It should be noticed that Jennison et al. did some periodic calculations which are used as a reference for their large P₉₂₃ cluster, in which they focused on the adsorption of the second layer of NH₃ on a quarter of monolayer directly bound to the metal.

These calculations show that the ammonia is essentially located on top of a metal atom, perpendicular to the surface, and bound via the nitrogen atom. The adsorption energies (E_ads) range from −30 kJ·mol⁻¹ (Cu) up to −180 kJ·mol⁻¹ (Pd). The difference between the different sites can be small as for Ni(111) (Ref. 3) where E_ads amount for −79, −75, and −71 kJ·mol⁻¹ for the top, fcc, and bridge sites, respectively. In general the sites other than top interact much more weakly or are even repulsive. E_ads is larger on the (100) surface than on the (111) one for Cu. Moreover the energies are dependent strongly on the size of the clusters. In the case of Cu clusters modeling the (100) surface, energies of adsorption range from −29 to −52 kJ·mol⁻¹ for clusters containing 10 to 18 Cu atoms.

Periodic calculations with extended slabs avoid the artifacts introduced by the small sizes (terminations) of the clusters employed as surface models. The main limitation is the difficulty to represent a low coverage. However, nowadays it is possible to study a large range of coverages and an 11% coverage (θ=0.11) can be considered as a good approximation of the zero coverage limit for small adsorbates.

The only theoretical study for NH₃ on Rh is the empirical approach of Cholah et al. which did not find any stable form of adsorbed NH₃ on Rh(111) or Rh(100). Such results disagree with the experiments and calculations presented below and with the conclusions of van Hardeveld et al. who have recently described the adsorption/desorption of NH₃ on Rh(111). Using temperature programmed desorption (TPD), they determined the adsorption energy of NH₃ on Rh(111) in the limit of zero coverage to be −81.5±3 kJ·mol⁻¹ at a presumed preexponential factor of 10¹³ s⁻¹. At increasing coverages, the desorption peak shifts to considerably lower temperatures, which the authors assigned to an increase of the preexponential factor with increasing coverage, rather than to repulsive adsorbates interactions. In addition, the work function (Φ) was seen to decrease steadily with adsorbate coverage to a maximum decrease of 2.5 eV, reached at 0.25 ML, where the ammonia orders in a (2×2) structure. Thermal desorption data of the NH₃ on Rh(100) surface, however, are not available.

Closely related to these experiments, the ab initio calcu-
lations presented here corroborate the conclusions for the Rh(111) surface and also give an explanation for the difference of the adsorption energies between the (100) and (111) surfaces in terms of molecular orbital interactions. Combination of the experimental and theoretical data will allow further insight into ammonia adsorption. Additional calculations for a stepped (100) surface will show that the adsorption of ammonia is not sensitive to the presence of steps.

II. METHODOLOGY

A. Experiments

Thermal desorption data were measured in a stainless steel ultra high vacuum chamber, equipped with a Leybold SSM 200 mass spectrometer, as described in Ref. 14.

B. Theory

A detailed description of the VASP program (Vienna ab initio simulation package) has been published, only the main features of the code will be briefly outlined with the related parameters used for this study. The VASP code performs periodic density functional theory (DFT) calculations by solving the Kohn–Sham equations (KS) with a plane wave basis set and the ultrasoft pseudopotentials introduced by Vanderbilt and generated by Kresse and Hafner. The functional from the generalized gradient approximation (GGA) of Perdew and Wang has been chosen because of its good description of chemical bond energies. The main advantage of ultrasoft pseudopotentials (UP) is to reduce significantly the number of plane waves by relaxing the norm conservation constraint on the pseudowavefunction. More complexity is introduced for solving the KS equations but the overall result is a significant decrease of the computational cost for hard elements as the first row atoms or the transition metals. The KS equations are solved self-consistently with an iterative matrix diagonalization. Only the occupied and some of the lowest unoccupied KS electronic levels are determined. The efficient Broyden mixing method for the charge density enables to speed up the convergence to the electronic ground state, especially for the metallic systems. The nonlocal projection operators of the UP are evaluated and optimized in real space with the procedure of King-Smith et al., providing a better scaling with the size of the system.

The Rh and H pseudopotentials are converged with an energy cutoff for the planewave basis set \( E_c \) of 200 eV while for the N pseudopotential it is 350 eV. A Gaussian smearing with \( \alpha = 0.2 \) eV was applied during the geometry optimization. A single point calculation on the optimized geometry with the linear tetrahedron method did not show any significant changes (below 1 kJ·mol\(^{-1}\)) for the adsorption energies.

The size of the grids for the fast Fourier transforms where chosen as roundoff errors were avoided. A conjugate-gradient algorithm or a quasiNewton algorithm is used to relax the atoms to the equilibrium geometry until the \( \Delta E_{\text{Total}} < 0.1 \) kJ·mol\(^{-1}\).

The surface model consists of a supercell which includes a slab of five metal layers separated by a vacuum of 13.4 Å before relaxation, a value enough to prevent the interactions between the surface and the adsorbates on those surfaces (calculations with 15.4 Å of vacuum give identical results). The supercells have a \((2 \times 2)\) or \((3 \times 3)\) structure in the \(x\) and \(y\) directions (corresponding to a 25% or 11% coverage with one adsorbate on each side of the slab). The \(k\)-point sampling was done following the Monkhorst–Pack procedure, with \(5 \times 5 \times 1\) and \(7 \times 7 \times 1\) grids for the \((2 \times 2)\) cells and a \(3 \times 3 \times 1\) grid for the \((3 \times 3)\) cells. The \(7 \times 7 \times 1\) grid was used for checking the convergence of the adsorption energies and also for producing the densities of states. Calculations for a \((2 \times 2)\) cell and six metal layers gives almost the same adsorption energies and geometries. The value of 350 eV for \( E_c \) was used for all the surface calculations, an increase up to 440 eV did not show any clear improvement.

All these tests (the results are presented in the next section) for the method and the surface model, give us confidence (within the DFT, GGA, and UP frameworks) in the values obtained for the adsorption energies and geometries.

III. RESULTS

A. Calculations for the bulk, (111), and (100) surfaces of rhodium

The lattice parameter \( a = 3.85 \) Å (Rh–Rh = 2.72 Å) for bulk Rh has been determined from a third-order polynomial fitting of the energy as a function of the lattice parameter for a four-atoms fcc cell. By increasing \( E_c \) from 200 eV up to 300 eV the total energy was slightly improved while the lattice parameter remains the same. All calculations were done with a \(11 \times 11 \times 11\) grid for Brillouin zone (35 irreducible \(k\)-points) which gives a well converged cohesive energy \(\Delta E_{\text{cohesion}} < 10^{-2} \) kJ·mol\(^{-1}\). The surfaces were modeled by a supercell containing a five or six layer slab separated by a vacuum. The \(x\) and \(y\) vectors are fixed to the lattice values obtained from the bulk and because of the symmetries the atoms relax only in the \(z\) direction. Reconstructions of the surface were not explored as there are no experimental nor theoretical indications for their occurrence.

The surface energies are 77 and 106 kJ·mol\(^{-1}\) of surface atoms, the relaxations are \(-1.7\%\) and \(-4.1\%\) relative to the ideal bulk termination for the (111) and (100) surfaces, respectively. These results are from the \(7 \times 7 \times 1\) grid with the \((2 \times 2)\) structure [8 (111) and 10 (100)] irreducible \(k\)-points, while it is 5 and 6 \(k\)-points for the \(5 \times 5 \times 1\) grid. Such values compare favorably to the results of Methfessel et al., Eichler et al., and Xie and Scheffler, and references therein.

The reference for the ammonia molecule in gas phase has been calculated with two molecules in the (100)-(3\(\times\)3) cell with an inversion center. The (3\(\times\)3) cell is large enough (rectangular parallelepiped of 8.17\(\times\)8.17\(\times\)20.98 Å\(^3\)) for the energy of an isolated molecule to be computed with an accuracy better than 1 kJ·mol\(^{-1}\). The related geometries are given in Table I.

B. Calculations for the adsorption of ammonia on the (111) and (100) surfaces of Rh

Adsorption of ammonia has been studied by locating it on both sides of the optimized surfaces and pointing the nitrogen atom toward the surface. The only symmetry con-
constraint is the presence of at least one inversion center. Dependent on the site and the surface more symmetries were used. The effect of these symmetry constraints has been extensively tested on the (2×2) surfaces, the top site has been optimized with the highest possible symmetry or with slightly displaced or tilted geometries (i.e., only inversion center). It results in identical final geometries and energies within numerical error after optimization. A top geometry with a tilt of 5º to 10º gives an adsorption energy ($E_{ads} = E_{slab+adsorbate} - E_{slab} - E_{adsorbate}$) only lower by few kJ·mol⁻¹ to the perpendicular one. Depending on the symmetries, from 5 to 13 k-points were used in the irreducible Brillouin zone for the $5\times5\times1$ division (9 or 16 for the $7\times7\times1$ grid).

The ammonia molecules have been placed on different sites for each surface [top, hollow fcc and hcp, or bridge for (111) and top, hollow, or bridge for (100)] with the x and y coordinates frozen for the nitrogen atoms. Except for the top site all the other sites lead to weakly adsorbed or almost unbound states with $E_{ads}$ in the $-4$ to $-36$ kJ·mol⁻¹ range (see Table II) and Rh–N bond lengths around 2.55–2.75 Å for the bridge sites and 2.93–3.05 Å for the hollow sites.

Additionally, ammonia has been studied in between the three-fold (four-fold), bridge and top sites on the Rh(111) [Rh(100)] surface and allowed to freely relax. As the molecule has no velocity, it moves to the nearest local minimum which is the bridge or top site.

For the (3×3) structure the $C_{2h}$ symmetry has been used, with a $3\times3\times1$ division of the Brillouin zone leading to 4 k-points in the irreducible Brillouin zone (3 k-points for the bare surface).

The adsorption energies for the different sites for both surfaces and the top site for the lower coverages are listed in Table II. The results of the different tests for validating our surface models are listed in Table III. The geometries of the adsorbates for the top site are depicted on Table IV and are close to the values of the gas phase. This is not a surprise as the NH₃–Rh bond involves mainly the (almost) nonbonding lone pair of NH₃. The NH₃ molecule in the (2×2) and (3×3) structures is free to rotate around the N–Rh axis. The potential for this rotation is very flat, below the accuracy of our calculations, therefore no preferential orientation could be found. The surface relaxation is small and concerns essentially the Rh atoms bound to NH₃ with upward relaxations of 0.11 Å for (111) (2×2)-NH₃, 0.09 Å for (111) (3×3)-NH₃, 0.07 Å for (100) (2×2)-NH₃, and 0.10 Å for (100) (3×3)-NH₃. The remaining surface Rh atoms move perpendicular to the surface in the ranges of 0.0 to $-0.01$ Å for (111) and $+0.01$ to $-0.02$ Å for (100).

An important phenomenon which occurs during the adsorption of NH₃ on Rh is the drastic decrease of the work function. This is due to the surface dipoles and charge transfers induced by the adsorbate. It can be extracted from our calculations by shifting the Fermi level by the mean value of the electrostatic potential in the middle of the vacuum between two surfaces. The agreement is fairly good with the experimental data for Rh(111) [no data available for Rh(100)] as the calculated values are $\Delta \Phi = -1.55$ eV ($-1.50$ eV exp²⁴) and $-2.60$ eV ($-2.50$ eV exp²⁴) for $\theta = 0.11$ and 0.25, respectively. For the Rh(100) surface the variations are only slightly smaller with $\Delta \Phi = -1.30$ eV for $\theta = 0.11$ and $\Delta \Phi = -2.30$ eV for $\theta = 0.25$. The work functions for the bare surfaces are 5.07 eV for Rh(100) and 5.20 eV for Rh(111). These values compare well with other calculations²²,²⁴ and the expected larger work function for the (111) surface is reproduced. The absolute values for the bare surface should be taken with some caution as no extensive testing of the dependence of the work function values on our model has been done (see the recent work of Fall et al.²⁵ for a discussion on the determination of work functions from calculations).

Projected density of states (PDOS) are displayed in Figs. 1 and 2; only the PDOS which show noticeable differences after adsorption are included (the PDOS are made by projecting the wave function to spherical harmonics within a sphere centered on the ions). For the surface Rh atoms (Fig. 1), the main changes occur for the $d_{3z^2-r^2}$ and $p_z$ orbitals of the Rh atom are involved but to a less extent and without too many differences between both sur-

### Table I. Geometries for the gas phase NH₃.

<table>
<thead>
<tr>
<th></th>
<th>$E_c = 350$ eV</th>
<th>$E_c = 450$ eV</th>
<th>Exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>N–H(Å)</td>
<td>1.021</td>
<td>1.020</td>
<td>1.021</td>
</tr>
<tr>
<td>$\angle$ H-N-H</td>
<td>107.8°</td>
<td>107.8°</td>
<td>106.7°</td>
</tr>
</tbody>
</table>

### Table II. Adsorption energies (kJ·mol⁻¹) for NH₃ on the Rh(111) and Rh(100) surfaces for different sites and coverages.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Coverage</th>
<th>$\theta = 0.25$</th>
<th>$\theta = 0.11$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sites</td>
<td>Top</td>
<td>Bridge</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>θ = 0.25</td>
<td>−70</td>
<td>−13</td>
</tr>
<tr>
<td></td>
<td>θ = 0.11</td>
<td>−82</td>
<td>/</td>
</tr>
</tbody>
</table>

### Table III. Adsorption energies (kJ·mol⁻¹) for the top site and $\theta = 0.25$ as a function of different parameters (nkpt: division of the Brillouin zone, nl: number of layers for the metallic slab, vac: width of the vacuum between surfaces, $E_s$: the cutoff for the plane wave basis set).

<table>
<thead>
<tr>
<th>Parameters</th>
<th>(111)</th>
<th>(100)</th>
</tr>
</thead>
<tbody>
<tr>
<td>nkpt = 5</td>
<td>2 × 2</td>
<td>5</td>
</tr>
<tr>
<td>vac = 13.4 Å</td>
<td>350 eV</td>
<td>70</td>
</tr>
<tr>
<td>vac = 15.4 Å</td>
<td>52</td>
<td>70</td>
</tr>
<tr>
<td>nl = 6</td>
<td>100</td>
<td>72</td>
</tr>
<tr>
<td>$E_s = 450$ eV</td>
<td>68</td>
<td>−80</td>
</tr>
</tbody>
</table>

### Table IV. Geometries for NH₃ adsorbed on the top site.

<table>
<thead>
<tr>
<th>Coverage</th>
<th>$\theta = 0.25$</th>
<th>$\theta = 0.11$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface</td>
<td>(111)</td>
<td>(100)</td>
</tr>
<tr>
<td>Rh–N(Å)</td>
<td>2.174</td>
<td>2.149</td>
</tr>
<tr>
<td>N–H(Å)</td>
<td>1.023</td>
<td>1.023</td>
</tr>
<tr>
<td>$\angle$ H-N-H</td>
<td>111.4°</td>
<td>111.4°</td>
</tr>
<tr>
<td>$\angle$ H-N-Rh-H</td>
<td>120.±</td>
<td>120.±</td>
</tr>
</tbody>
</table>
surfaces and coverages. The \( d^3 z^2 - r^2 \) orbital for a surface Rh atom at the (111) surface is much broader than for the (100) surface because of the higher coordination number of the (111) surface (nine neighbors against eight). The position of the \( 4d \) orbitals for a free Rh atom would lie around \(-5\) eV for \( \theta = 0.25 \) or \(-6\) eV for \( \theta = 0.11 \), corresponding to the nonbonding peaks in the middle of the PDOS. The main peak for the \( d^3 z^2 - r^2 \) orbital from the (100) surface can be assigned to antibonding levels.

The PDOS for the unbound Rh atoms derive from surfaces with adsorbed \( \text{NH}_3 \). Because of the large shift of the work function induced by the overlayer dipole moment of \( \text{NH}_3 \), a comparison with the Rh atom bound to \( \text{NH}_3 \) would be difficult if the PDOS was from a Rh atom from the bare surface. Once a Rh atom is bound to \( \text{NH}_3 \), a sharp peak appears at the bottom of the \( d \)-band. This peak is directly related to the lone pair of \( \text{NH}_3 \) (3a1 level) which is shown on Fig. 2 with the other molecular levels. The lone pair is mainly composed of the \( p_z \)-orbital (\( z \) being the main axis of the molecule) of the N atom (normal line on Fig. 2) with some hybridization with the \( Ns \) orbital. The three bonds between the N and H atoms are the 2a1 (\( Ns + Np_z \) and \( Hs \)) and the degenerate 1e levels (\( Npx,py + Hs \)) which have negligible interactions with the surface. These levels are almost unchanged: the separation for \( \text{NH}_3 \) gas is 9.8 eV while after adsorption the separation is 9.6–9.7 eV. The lone pair is stabilized by 1.8–2.0 eV if the 2a1 level is used as the reference for comparing \( \text{NH}_3 \) gas to \( \text{NH}_3 \) adsorbed (arrows on Fig. 2).

The effect of the coverage and of the nature of the surface on the adsorption can be seen separately.

At the top of the \( d \)-band appears the antibonding contribution of the Rh–N bond which is essentially located on the Rh atom while the bonding contribution is principally composed of the lone pair. The splitting between the bonding and antibonding levels for the Rh–N bond is similar for the four cases (around 6.5 eV). The main difference between the two coverages is an up shift of 1 eV for the 25% coverage, directly related to the variations of the work function. Except for this shift, the PDOS for each surface are very similar and therefore the bonds are also equivalent. Consequently, the repulsions can be mainly assigned to the dipole–dipole interactions. By comparing the free \( \text{NH}_3 \) molecules in (2 \( \times 2 \)) and (3 \( \times 3 \)) cells, the repulsions between the \( \text{NH}_3 \) can be guessed around 2–3 kJ·mol\(^{-1}\). Once adsorbed the dipole moment of \( \text{NH}_3 \) is enhanced from 1.47 to around 1.9 debye, and also a dipole image appears on the surface, explaining the increase in the repulsions.

The (100) surface is less stable with the Rh \( d^3 z^2 - r^2 \) orbital essentially involved in antibonding surface states (above the nonbonding peaks but below the Fermi level). After adsorption this peak is split and the PDOS for the \( d^3 z^2 - r^2 \) orbitals are analogous for both surfaces. The energy gain must be more important for the (100) surface (recall that the difference before adsorption is 29 kJ·mol\(^{-1}\) per surface atom).

The bond between \( \text{NH}_3 \) and the Rh surfaces is a mixing of electrostatic and covalent contributions: the electrostatic component controls the variations of \( E_{\text{ad}} \) with the coverage while the chemical bond is influenced by the electronic structure of the surface.

**C. Experiments for the adsorption of \( \text{NH}_3 \) on Rh(100)**

Figure 3 compares the thermal desorption spectra of \( \text{NH}_3 \) from Rh(111) and Rh(100), respectively. Close inspection of the data reveals that the desorption peak temperatures in the limit of low coverage are 360 K on the Rh(100) and 320 K on the Rh(111) surface. The thermal desorption spectra of \( \text{NH}_3 \) from both surfaces exhibit a considerable shift to lower temperatures when the coverage increases. On Rh(111) the peak shifts from 320 K at zero coverage to around 150 K for a coverage of 0.25 ML. Unfortunately, in the absence of a suitable calibration point, the absolute coverages of \( \text{NH}_3 \) on Rh(100) are unknown. The trends in the spectra with increasing coverage, however, are quite similar.

The TPD spectra of \( \text{NH}_3 \) from Rh(111) show a small shoulder towards higher temperatures, which increase somewhat with total coverage. This shoulder which accounts for
about 1% of a monolayer at most, may be caused by defects, or by readsorption of desorbed NH$_3$ due to insufficient pumping speed, or by a combination of both effects. We have chosen to ignore this contribution. The activation energies of desorption have been calculated in the limit of zero coverage by means of the approximate Redhead equation:

$$E_{\text{des}} = k_B T_{\text{max}} \left[ \ln \left( \frac{\nu T_{\text{max}}}{\alpha_{\text{max}}} \right) - 3.46 \right]$$

by assuming a preexponential factor $\nu$ of $10^{13}$ s$^{-1}$. The use of this value is justified in the discussion section. $T_{\text{max}}$ and $\beta$ correspond to the temperature at the maximum of the TPD peak and the heating rate.

The energies amount to $-81.5 \pm 3$ kJ mol$^{-1}$ for NH$_3$ on Rh(111) and $-90.0 \pm 4$ kJ mol$^{-1}$ on Rh(100). The uncertainty is due to the difficulty to extrapolate precisely the maximum of the peaks to the zero coverage limit.

### D. Calculations for the adsorption of NH$_3$ on a stepped (100) surface

Beside the study of NH$_3$ on the (111) and (100) surfaces of Rh, the stepped (100) surface of Fig. 4 has been studied. The cell has a $(3 \times \sqrt{7})$ structure corresponding to three (100) rows for the terraces which are separated by a (111) step. It is a (511) plane for the Miller index notation or $(S)_5[3(100) \times (111)]$ with the stepped surface notation. The vacuum between the (511) surfaces is 13.4 Å and the slab has five layers of metal, the other parameters are the same as for the $(3 \times 3)$ cells (five irreducible $k$-points). The NH$_3$ molecules have been studied on the three different available top sites: on the step as displayed on Fig. 4, middle of the terrace, and the bottom of the step. The adsorption energy on the middle of the terrace is similar to that of the (100)-(3 $\times 3$) structure with $E_{\text{ads}} = -93$ kJ mol$^{-1}$. On the step, two minima have been found, one perpendicular to the terrace ($E_{\text{ads}} = -88$ kJ mol$^{-1}$) and another tilted by about 45° to the perpendicular position ($E_{\text{ads}} = -98$ kJ mol$^{-1}$). The adsorption on top of the Rh atom at the bottom of the step is not possible because of the proximity of the atoms constituting the step. The NH$_3$ molecule experiences significant repulsions from the step and migrates to the top sites in the middle of the terrace or on the tilted site on the step, depending on the starting geometry.

The presence of steps does not seem to really modify the adsorption of NH$_3$; energies and geometries are very close to the values found for the (100) surface, as can be seen in Table V. Hammer et al. have explored the adsorption of CO on stepped and reconstructed surfaces of Pt with DFT.
calculations. The results reveal a strong sensitivity of the adsorption energy to the structure of the surface. The general trend is an increase in bonding energy (up to 100 kJ·mol⁻¹) with decreasing coordination of the Pt atoms. In contrast, the energy of adsorption of NH₃ only slightly changes with the steps. For the sites on the middle of the terrace and perpendicular on the step, the PDOS for the orbitals of N and the d₃z²-r² orbital of Rh are very similar to the PDOS for (100)-(3×3)-NH₃ [Figs. 1(c) and 2(c)]. Some differences occur for the other d orbitals of Rh because of the missing neighbors but it is not relevant as these orbitals are not involved in the N-Rh bond. For the tilted geometry, the lone pair interacts with the dₓz and dᵧz orbitals in the same way as previously described with the d₃z²-r² orbital for the other top sites.

With CO, the key point is the backbonding interaction of the empty 2π* orbitals with the dₓz and dᵧz orbitals of the surface Rh atoms. For NH₃, the strength of the bond is controlled by the electrostatic surface interaction terms and a covalent bond with the lone pair. Contrary to CO the lowest unoccupied levels of NH₃ are not involved in the chemisorption. Therefore the adsorption of NH₃ is not too sensitive to the changes of the d-band induced by the lowering of the coordination of the surface metal atoms.

**IV. DISCUSSION AND CONCLUSION**

The calculations enable to assign the adsorption site of ammonia on the (111) and (100) surfaces of Rh to the top site. The energetic differences with the other sites is significant. The molecule is perpendicular to the surface, bound via the N atom and with the H atoms pointing outward. The agreement for the adsorption energies in the (3×3) structures are excellent with the experimental estimations for the zero coverage limit. Moreover the variations of the work function with the coverage are very well reproduced. The possibility for a second adsorbed species at θ=0.25 seems very unlikely. An important point is the low sensitivity of the adsorption energy to the presence of steps. The activation energy of desorption of NH₃ from two rhodium surfaces, equal to the adsorption energy because adsorption is nonactivated, has been calculated in the limit of zero coverage by means of the Redhead equation. In order to do so, the preexponential factor needs to be estimated. As we have argued before,¹⁴ we believe that the increase in rate of desorption when the surface becomes progressively more occupied by NH₃ is because adsorbed ammonia behaves like a two-dimensional gas, certainly at the temperatures towards the right of the spectra. As NH₃ is known to adsorb through a mobile precursor, desorption through a mobile precursor is expected as well. Hence, the rate of desorption is given by ²⁷

\[
r_{\text{des}} = \frac{k_B T}{h} \frac{Q_{\text{trans}}^\#}{Q_{\text{trans}}} \exp\left(-\frac{E_{\text{ads}}}{k_B T}\right) \theta_{\text{NH}_3},
\]

in which \(Q_{\text{trans}}\) is the two-dimensional partition function for translation, and the superscript \(^\#\) refers to the mobile transition state.

Translational partition functions scale with the available surface area per adsorbed molecule. In the limit of zero coverage, the ratio of the partition functions becomes unity, and hence the preexponential factor equals \(e^kT/h\),²⁷ or about \(10^{13} \text{ s}^{-1}\). This justifies the use of this value in the application of the Redhead formula.

At higher coverages, the ground state partition function per molecule becomes much smaller than the partition function of the transition state, which is only occupied by a small fraction of the molecules. Hence the ratio of the partition functions and hence the preexponential factor becomes progressively larger when the surface coverage of ammonia increases. We propose that this is the main reason that the desorption spectra broaden and shift towards lower temperatures. In addition there may be some repulsions between the ammonia molecules, particularly at higher coverages. The present calculations indicate that this repulsion is of the order of 10 kJ·mol⁻¹ at 0.25 ML, or only 10%–15% of the adsorption energy at zero coverage. This interpretation disagrees with that of Benndorf and Madey, who assigned the entire shift of the spectra to lateral interactions.²⁸

Hence, the calculations support the notion that the large shift of the desorption peaks toward lower temperature is in fact caused by an increase in the preexponential factor, and only to a minor extent to lateral interactions.

One may wonder if the effects plays a role in other desorption systems as well. Indeed, well known first-order desorption systems such as, for example, CO from Rh(100) do exhibit a shift of the TPD peak to lower temperature at low coverage where repulsive interactions between the CO molecules are not yet expected.²⁹ These shifts, however, are much less pronounced than in the case of NH₃ desorption. Of course, a strong increase of the prefactor with increasing coverage can only be observed when the ground state of the adsorbed gas is mobile over a large part of the desorption regime. This makes NH₃ a somewhat special case.

**ACKNOWLEDGMENTS**

This work has been sponsored by the Stichting Nationale Computerfaciliteiten (National Computing Facilities Foundation, NCF) for the use of supercomputer facilities, with financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (Netherlands Organization for Scientific Research, NWO). We also acknowledge support from the Fundation of Environmental Research, Eindhoven (TDO) for partial funding of this project.

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TABLE V. Geometries for NH₃ adsorbed on the stepped (100) surface.

<table>
<thead>
<tr>
<th>Top sites</th>
<th>Step (tilted)</th>
<th>Step (⊥)</th>
<th>Terrace</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh–N(Å)</td>
<td>2.167</td>
<td>2.154</td>
<td>2.149</td>
</tr>
<tr>
<td>N–H(Å)</td>
<td>1.024±.003</td>
<td>1.022±.001</td>
<td>1.023±.001</td>
</tr>
<tr>
<td>∠ H-N-H</td>
<td>109.1±.8°</td>
<td>110.2±.5°</td>
<td>110.4±.6°</td>
</tr>
<tr>
<td>∠ H-N-Rh-H</td>
<td>120.±4.°</td>
<td>120.±2.°</td>
<td>120.±1.5°</td>
</tr>
</tbody>
</table>

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