A density-functional theory study of the interaction of N$_2$O with Rh(110)

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The adsorption of nitrous oxide, N$_2$O, on a Rh(110) surface has been characterized by using density-functional theory. N$_2$O was found to bind to the surface in two alternative forms. The first, less stable form is tilted with the terminal N atom attached to the surface, while the second, more stable form lies horizontally on the surface. Adsorption on the on-top site is more stable than that on the bridge site. The tilted form remains linear on adsorption, while the horizontal form is bent, with the terminal-nitrogen and oxygen atoms pointing towards the surface. At lower adsorbate coverage, O$_{\leq 1/4}$ ML (ML—monolayer), the adsorption of a few horizontal N$_2$O configurations is dissociative, i.e., N$_2$O$\rightarrow$N$_2$(a) + O(a). The N$_2$O-surface interaction is discussed in terms of the electronic structure analysis. © 2005 American Institute of Physics. [DOI: 10.1063/1.1829652]

I. INTRODUCTION

Nitrous oxide, N$_2$O, is an intermediate in the removal of NO$_x$ on automobile three-way catalysts. Furthermore, N$_2$O itself is harmful and yields a remarkable greenhouse effect. Therefore its decomposition on noble metals has attracted much attention, because these metals are good catalysts and N$_2$O is the main byproduct in this process. In particular, much attention have been given to the decomposition of N$_2$O on rhodium surfaces, because rhodium is one among the best catalysts for removing nitrogen oxides. Despite the importance of this system, the interaction of N$_2$O with rhodium surfaces is not yet well understood. Peculiar inclined N$_2$O desorption observed recently on some fcc(110) surfaces is expected to provide further insight. On a Rh(110) surface, the nitrogen molecules produced during the thermal dissociation of N$_2$O were detected to be adsorbed in inclined bidirectional lobes in a plane along the [001] direction. The collimation angle was about $70^\circ$, which is larger than $43^\circ$–$50^\circ$ found on Pd(110). Recent report of N$_2$O adsorption on a clean Rh(110) surface showed significant dissociation to N$_2$(a) and O(a) at temperatures around $60$ K [where X(a) refer to adsorbed X species, this notation will be used hereafter] at small N$_2$O exposures, indicating that the dissociation barrier is rather small.

Computational studies of N$_2$O adsorption on transition metal surfaces are very scarce. Instead, several authors have reported on the interaction and decomposition of N$_2$O with transition metal atoms or small clusters. Burch et al. studied the formation of N$_2$O via the NO$+\text{N}$ reaction on Pt(111) surface using density-functional theory (DFT), but the adsorption of N$_2$O was not discussed. Bogicevic and Hass performed DFT study of NO pairing and transformation to N$_2$O on Cu(111) and Pd(111). They briefly mentioned that N$_2$O is preferentially adsorbed on the on-top site, but geometry of the adsorbed N$_2$O was not discussed. To the best of our knowledge, the interaction of N$_2$O with Rh surfaces (or atoms) has not yet been studied by computational first-principle methods. For this reason we have undertaken a DFT study of N$_2$O adsorption on Rh(110) surface. Since very little is known about the nature of the N$_2$O chemical bonding with transition metal surfaces, we discuss in this work to some depth the electronic factors that govern the adsorption phenomenon.

The structure of the adsorbed N$_2$O is an important ingredient to provide an explanation of the mechanism of the above-mentioned peculiar N$_2$ desorption. Moreover, the structure of N$_2$O(a) immediately before dissociation can be studied only by means of theoretical calculations. In our previous contributions we studied the adsorption structures of N$_2$O on Pd(110). In this paper we report on a detailed first-principle density-functional study of the geometry and orientation of N$_2$O(a) on Rh(110) at coverages ranging from 1/6 to 1 monolayer (ML).

II. COMPUTATIONAL METHOD

All calculations were performed with the DFT using the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE). Nuclei and core electrons were described by ultrasoft pseudopotentials. The Kohn–Sham orbitals were expanded in a plane-wave basis set with a kinetic energy cutoff of 27.5 Ry (220 Ry for the charge-density cutoff). Brillouin zone (BZ) integrations have been performed with the Gaussian-spreading special-point technique with a smearing parameter of 0.03 Ry. Calculations have been done using the PWSCF package, while molecular graphics were generated by the XCRYSDEN graphical package.

The perfect Rh(110) surface was modeled by periodically repeated slabs consisting of five (110) layers and vacuum region of 12.5 Å. N$_2$O molecules were adsorbed on one side of the slab (by using the stated vacuum thickness.

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The N$_2$O molecules are more than 8 Å away from the adjacent slab. N$_2$O adsorption was modeled at 1, 1/2, 1/3, 1/4, and 1/6 ML coverages and (2×1), (3×1), (4×1), (2×2), (3×2), c(2×2), and c(2×4) supercells were used. The BZ integrations were performed with a 5×5, and 3×3 uniform shifted k mesh for the c(2×2), and c(2×4) primitive supercells, respectively, while for (2×1), (3×1), (4×1), (2×2), and (3×2) supercells the 4×6, 3×6, 2×6, 4×3, and 3×3 uniform shifted k meshes were used, respectively. The calculated bulk lattice parameter was used as the in-plane lattice spacing. The spacing of the bottom three layers of the slab was fixed at the bulk interplane spacing, whereas the geometries of the top two layers and N$_2$O molecule were fully optimized using the Broyned-Fletcher-Goldfarb-Shanno algorithm with analytically calculated forces according to the Hellmann-Feynmann theorem. In all the optimized systems the forces acting on the atoms, which were allowed to relax were below 10$^{-3}$ Ry/Å.

The binding energy $E_b$ of adsorbed N$_2$O was calculated as $E_b=(E_{\text{Rh(110)}}+E_{\text{N}_2\text{O}})-E_{\text{N}_2\text{O/Rh(110)}}$, where $E_{\text{Rh(110)}}$, $E_{\text{N}_2\text{O}}$, and $E_{\text{N}_2\text{O/Rh(110)}}$ are the potential energies of the pure substrate, the isolated N$_2$O molecule, and the N$_2$O/substrate adsorption system, respectively. With this definition, positive binding energies indicate stable adsorption.

III. RESULTS
A. Isolated constituents: Bulk Rh, Rh(110) surface, and the N$_2$O(g)

The experimental lattice parameter of bulk rhodium is 3.80 Å, whereas our GGA calculations yield 3.87 Å—an overestimation of 2%. This agrees with the results obtained by the other GGA pseudopotential calculations, 3.85 Å (Ref. 36) and 3.87 Å. The lattice parameter predicted by GGA full-potential linearized augmented-plane-wave (FP-LAPW) method is 3.83 Å. Our GGA calculated bulk modulus is 250 GPa, while experimental value is 269 GPa. This agrees with the results obtained by the FP-LAPW method, 259 GPa and other pseudopotential calculations, 244 GPa (Ref. 36) and 251 GPa.

The properties of the clean Rh(110) surface have been calculated using 5-, 7-, 9- and 11-layer slabs with a 1×1 surface geometry and the BZ integrations were performed by 8×6 uniform shifted k-mesh. All the layers have been relaxed symmetrically for these calculations. The surface energy $\sigma$ was estimated (i) by applying the Boettgerlike equation, $\sigma=1/2[E_{\text{slab}}(N)-N/2[E_{\text{slab}}(11)-E_{\text{slab}}(9)]]$, and (ii) by fitting the slab potential energies $E_{\text{slab}}(N)$ for N = 7, 9, 11 to the equation $E_{\text{slab}}(N)=2\sigma+N\varepsilon_{\text{bulk}}$, where N and $\varepsilon_{\text{bulk}}$ stand for number of layers in the slab and bulk energy, respectively. The work function $\phi$ was calculated as the difference between the average electrostatic potential in the vacuum and the Fermi level. The calculated properties of the clean Rh(110) surface are reported in Table I. Our GGA calculations yield $\sigma=1.60$ eV/atom and $\varepsilon_{\text{bulk}}=0.15$ eV/Å$^2$ and $\phi=0.1$ eV. The relaxations of the first $\Delta d_{12}$ and second $\Delta d_{23}$ layers are $-10\pm1\%$ and $+2\pm1\%$, respectively, while experimental values are $\Delta d_{12}=-6.9\pm1.0\%$ and $\Delta d_{23}=+1.9\pm1.0\%$.

The N$_2$O molecule is an anomalous member of the AB$_2$ family of triatomic molecules, as it has asymmetric arrangement of its nuclei, i.e., $A-A-B$. For the ease of discussion we define the symbols $N_i$ and $N_e$ which stand for the terminal- and the central-nitrogen atoms, respectively. For the N$_2$O molecule in the gas phase our calculations predict a linear geometry with a nitrogen-nitrogen distance ($d_{\text{NN}}$) of 1.142 Å, and a nitrogen-oxygen distance ($d_{\text{NO}}$) of 1.210 Å, which agree with the B3LYP (Becke-3 Lee-Yang-Par) calculated distances (1.134 and 1.193 Å, respectively). Our GGA calculated bulk modulus is 250 GPa, while experimental value is 269 GPa. This agrees with the results obtained by the FP-LAPW method, 259 GPa and other pseudopotential calculations, 244 GPa (Ref. 36) and 251 GPa.

B. Adsorption structures and energies

Several possible configurations of molecular adsorption on the Rh(110) surface were examined in order to determine the orientation and site preference of the N$_2$O molecule. In particular, the adsorption was modeled by attaching the N$_2$O molecule either with the terminal nitrogen (hereafter labeled as $N_i$ bonded), the central nitrogen ($N_e$ bonded), or the terminal oxygen atom (O bonded) to the surface, and by placing the molecule horizontally on the surface so that its terminal...
nitorium and oxygen atoms are interacting with the substrate atoms (hereafter designated as horizontal form). The horizontal forms will be labeled as site$_1$(N$_t$)–site$_2$(O), meaning that the N$_t$ atom is pointing toward the site$_1$ site and O atom toward the site$_2$. The N$_t$ and O atoms can point either to the same type of site, i.e., on-top(N$_t$)–on-top(O) or bridge (N$_t$)–bridge(O), or to different type of site, i.e., on-top (N$_t$)–bridge(O) or bridge(N$_t$)–on-top(O). For brevity, the on-top(N$_t$)–on-top(O) or bridge(N$_t$)–bridge(O) forms will be referred shortly as on-top and bridge, respectively.

1. Molecular and dissociative adsorption of N$_2$O

Calculations indicate that the N$_2$O(a) binds to the surface in two forms. The first, less stable form is linear and tilted with the terminal N atom attached to the surface. The $d_{NN}$ and $d_{NO}$ distances are almost unchanged on adsorption. Precise estimation of the tilt angle is difficult due to the flatness of the potential energy surface. The second, more stable form lies horizontally on the surface and is bent, with the terminal nitrogen and oxygen atoms pointing toward the surface. The $d_{NN}$ and $d_{NO}$ distances are longer than in the tilted structures. The optimized tilted and horizontal N$_2$O(a) structures at 1/2 ML coverage are shown in Fig. 1. Here, the horizontal molecular structures are oriented along the [001] direction. The binding energies $E_b$ and structural parameters of N$_2$O adsorbed on the on-top and bridge sites for the two forms are listed in Table II. These adsorbed structures are analogous to those found previously on a Pd(110) surface. However, on Rh(110) the horizontal form is more stable by 0.2–0.3 eV than the tilted one, while their stabilities on Pd(110) are very similar, the $E_b$ being ~0.4 eV. Hence, N$_2$O binds more strongly to the Rh(110) surface, which is not surprising as Rh has less occupied d bands. Adsorption on the on-top sites is energetically favorable on both surfaces and the bridge configurations are less stable.

An interesting result is that at lower adsorbate coverage 0≤1/4 ML the adsorption of horizontal bridge form is dissociative, namely, the N$_2$O decomposes to N$_2$O(a)+O(a) during the geometry optimization calculation, presumably due to the absence of a dissociation barrier, leading to adsorbed nitrogen molecule and O(a).

The adsorption of horizontal N$_2$O(a) was modeled oriented either along the [001], [110], or [112] direction. Binding energies and structural parameters of various horizontal forms are reported in Table III, while top and side views of optimized structures are shown in Fig. 2. The N$_2$O(a) oriented along [001] was predicted to be more stable than that oriented along the [110] direction, the $E_b$ being

TABLE II. Calculated binding energies $E_b$ and structural parameters of the tilted and horizontal N$_2$O(a) moieties oriented in the [001] direction. The labels $d_{BNN}$, $d_{NN}$, $d_{NO}$, and $d_{BNO}$ stand for the distances between the corresponding atoms.

<table>
<thead>
<tr>
<th>Site</th>
<th>Moiety</th>
<th>Super cell</th>
<th>Coverage (ML)</th>
<th>$E_b$ (eV)</th>
<th>$d_{BNN}$ (Å)</th>
<th>$d_{NN}$ (Å)</th>
<th>$d_{NO}$ (Å)</th>
<th>$d_{BNO}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>On-top</td>
<td>Tilted</td>
<td>c(2×2)</td>
<td>1/2</td>
<td>0.53</td>
<td>2.03</td>
<td>1.15</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c(2×4)</td>
<td>1/4</td>
<td>0.53</td>
<td>2.04</td>
<td>1.15</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>Horizontal</td>
<td>Tilted</td>
<td>c(2×2)</td>
<td>1/2</td>
<td>0.71</td>
<td>1.98</td>
<td>1.19</td>
<td>1.30</td>
<td>2.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c(2×4)</td>
<td>1/4</td>
<td>0.82</td>
<td>1.96</td>
<td>1.20</td>
<td>1.33</td>
<td>2.08</td>
</tr>
<tr>
<td>Bridge</td>
<td>Tilted</td>
<td>c(2×2)</td>
<td>1/2</td>
<td>0.25</td>
<td>2.23</td>
<td>1.16</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>c(2×4)</td>
<td>1/4</td>
<td>0.24</td>
<td>2.22</td>
<td>1.16</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>Horizontal</td>
<td>Tilted</td>
<td>c(2×2)</td>
<td>1/2</td>
<td>0.42</td>
<td>2.13</td>
<td>1.22</td>
<td>1.39</td>
<td>2.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>c(2×4)</td>
<td>1/4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N$_2$O(g)</td>
<td>Dissociates to N$_2$(a)+O(a)</td>
<td>1.14</td>
<td>1.21</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

FIG. 1. Top and side views of optimized N$_2$O/Rh(110) structures for c(2×2) supercells representing 1/2 ML coverage. Larger balls are Rh atoms, while smaller gray (dark-gray) balls are N (O) atoms.
0.82 and 0.65 eV, respectively, while the adsorption of [1 \bar{1} 2]-oriented molecule is dissociative, namely, the geometry optimization calculation leads to dissociated \( N_2 O(a) \)—presumably due to the absence of a dissociation barrier or at least very small and narrow barrier—resulting to \( N_2 (a) \) and \( O(a) \). The molecule was also placed on the surface “horizontally-asymmetric,” i.e., it bridged atomic troughs of the substrate that are extending in the [1 \bar{1} 0] direction and one of the terminal atoms (\( N_t \) or \( O! \) of the molecule was pointing toward the on-top (bridge) and bridge (top) site, respectively. The “asymmetric” forms are labeled as bridge(\( N_t \))–on-top(\( O! \)) and on-top(\( O! \))—bridge(\( N_t \)). Other labels have the same meaning as in Table II.

### Table III. Calculated binding energies and structural parameters of the various horizontal \( N_2 O(a) \) forms, oriented in the [001], [1 1 0], and [1 \bar{1} 2] directions, or placed on the surface “asymmetrically”—the terminal \( N_t \) and \( O! \) atoms pointing toward the top (bridge) and bridge (top) site, respectively. The “asymmetric” forms are labeled as bridge(\( N_t \))–on-top(\( O! \)) and on-top(\( O! \))—bridge(\( N_t \)). Other labels have the same meaning as in Table II.

<table>
<thead>
<tr>
<th>Supercell Coverage (ML)</th>
<th>Moiety Orientation</th>
<th>( E_b ) (eV)</th>
<th>( d_{RN} ) (Å)</th>
<th>( d_{NN} ) (Å)</th>
<th>( d_{NO} ) (Å)</th>
<th>( d_{RhO} ) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>c(2\times4) 1/4</td>
<td>On-top horizontal [001]</td>
<td>0.82</td>
<td>1.96</td>
<td>1.20</td>
<td>1.33</td>
<td>2.08</td>
</tr>
<tr>
<td></td>
<td>On-top horizontal [1 \bar{1} 2]</td>
<td>Dissociates to ( N_2 (a) + O(a) )</td>
<td>0.67</td>
<td>2.03/2.15</td>
<td>1.24</td>
<td>1.32</td>
</tr>
<tr>
<td>(3\times1) 1/3</td>
<td>Bridge(( N_t ))–on-top(( O! )) Asymmetric</td>
<td>0.60</td>
<td>1.97</td>
<td>1.20</td>
<td>1.36</td>
<td>2.05</td>
</tr>
<tr>
<td>(3\times2) 1/6</td>
<td>On-top horizontal [1 \bar{1} 0]</td>
<td>0.65</td>
<td>1.97</td>
<td>1.21</td>
<td>1.37</td>
<td>2.05</td>
</tr>
</tbody>
</table>

**FIG. 2.** Top and side views of optimized horizontal \( N_2 O(a) \) structures oriented along the [001] and [1 \bar{1} 0] directions and asymmetric bridge (\( N_t \))–on-top(\( O! \)) form.

**FIG. 3.** Top-view of the “in-phase” and “out-of-phase” tilting \( N_2 O(a) \) configurations at 1 ML coverage.

2. “In-phase” versus “out-of-phase” tilt

The \( N_2 O(a) \) molecules can be considered tilted either in the same direction, i.e., in-phase tilt, or tilted such that adjacent molecules point in opposite direction, i.e., out-of-phase tilt. As the coverage of the admolecules increases the molecule-molecule lateral distances are becoming smaller, and the lateral molecule-molecule interactions more important. The out-of-phase tilt provide a packing where the adjacent molecules are avoiding each other better than the in-phase tilted molecules (see Fig. 3). The calculations indicate that at full monolayer coverage, the out-of-phase tilting configuration is more stable than the in-phase one, the \( E_b \) being
0.39 and 0.23 eV, respectively. However, already at 1/2 ML coverage the difference in $E_b$ between the two tilting configurations become insignificant. Table IV summarizes the binding energies and structural parameters of in-phase and out-of-phase tilted configurations at 1/2 and 1 ML coverage.

### 3. Less stable and unstable N$_2$O(a) forms

Calculations indicate that the N$_2$O cannot adsorb on the Rh(110) surface with the central-nitrogen atom—such an interaction is predicted to be repulsive.

The calculations also predicted a highly tilted N$_2$O form adsorbed to on-top site and attached to the surface via the oxygen atom (see Fig. 4), with very small binding energy of 0.15 eV and large oxygen-surface distance of 2.5 Å [note that for the on-top tilted N$_2$O(a) adsorbed via the N$_t$ atom, the N$_t$-surface distance is only 2.03 Å]. Such a weakly oxygen-bonded and highly tilted N$_2$O form is also predicted on Pd(110). The $E_b$ for the highly tilted O-bonded molecule adsorbed on the bridge site is similar, 0.12 eV. Results for the O-bonded N$_2$O(a) forms are summarized in Table V. These tiny binding energies for the O-bonded molecules are comparable with energies given by dispersion forces, moreover, the molecule-surface distances are quite large. At such large distances the dispersion forces are expected to be important, and hence the DFT predictions less reliable. Whether these GGA predicted energies are meaningful is questionable, because GGA is not able to describe the dispersion interactions. In our previous study, we calculated the interaction between N$_2$O and a single Pd atom—the N$_2$O was bonded with the oxygen atom to palladium. The current DFT implementation predicted the binding energy of 0.28 eV, while the binding energy predicted by the second-order Møller-Plesset perturbation theory was virtually zero.

### IV. DISCUSSION

#### A. Stable adsorption and dissociation of N$_2$O

Calculations predict the attractive adsorbate-substrate interaction when the molecule is adsorbed in a tilted configuration bonded to the surface with the N$_t$ atom, or lying horizontally on the surface. At lower adsorbate coverage the adsorption of some horizontal N$_2$O configurations is predicted to be dissociative, i.e., N$_2$O→N$_2$(a) + O(a).

The geometry of the tilted N$_2$O(a) is linear and intramolecular distances are almost unchanged on adsorption. In the case of horizontal N$_2$O(a), the geometry is not linear but bent, with the N$_t$ and O atoms pointing toward the surface. The $d_{NN}$ and $d_{NO}$ distances are greater than in the tilted structures—an indication of larger charge backdonation into the antibonding 3σ molecular orbital. This charge backdonation is evidenced in the projected density of states plots shown in Fig. 6, and by integrated local density of states (ILDOS) plots of Fig. 8. This issue will be described in more detail below (see Sec. IV B).

The geometry of adsorbed N$_2$O on transition metal surfaces has not been widely studied experimentally (see recent reviews of Zeigarnik or Matsushima). It has been proposed that N$_2$O adsors via the terminal nitrogen atom in an inclined or upright form. The inclined form was proposed on the basis of vibrational spectroscopy work on Ru(001) (Ref. 49) and Pt(111), NEXAFS (near edge x-ray absorption fine structure spectroscopy) analysis on Ni(111) (Ref. 51) and Cu(100), and also use of the kinetic isotope effects approach to polycrystalline Cu. However, the angle of tilt is still unclear from experimental work, because there

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**TABLE IV.** "Out-of-phase" vs "in-phase" on-top tilted N$_2$O(a): calculated binding energies and structural parameters. Full monolayer coverage Θ=1 ML has been modeled by placing two molecules in a (2×1) supercell, while for Θ=1/2 ML two molecules were placed inside the (4×1) supercell. The labels have the same meaning as in Table II.

<table>
<thead>
<tr>
<th>Site and moiety</th>
<th>Supercell</th>
<th>Coverage (ML)</th>
<th>Tilt</th>
<th>$E_b$ (eV)</th>
<th>$d_{NN}$ (Å)</th>
<th>$d_{NN}$ (Å)</th>
<th>$d_{NO}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>On-top tilted</td>
<td>(2×1)</td>
<td>1</td>
<td>In-phase</td>
<td>0.23</td>
<td>2.04</td>
<td>1.15</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>(4×1)</td>
<td>1/2</td>
<td>Out-of-phase</td>
<td>0.39</td>
<td>2.03</td>
<td>1.15</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>In-phase</td>
<td>0.54</td>
<td>2.04</td>
<td>1.15</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Out-of-phase</td>
<td>0.54</td>
<td>2.04</td>
<td>1.15</td>
<td>1.22</td>
</tr>
</tbody>
</table>

**TABLE V.** Highly tilted N$_2$O(a) forms adsorbed with the oxygen atoms to the surface, i.e., O-bonded forms: calculated binding energies and structural parameters. The labels have the same meaning as in Table II.

<table>
<thead>
<tr>
<th>Site</th>
<th>Moiety</th>
<th>Supercell</th>
<th>Coverage (ML)</th>
<th>$E_b$ (eV)</th>
<th>$d_{NO}$ (Å)</th>
<th>$d_{NN}$ (Å)</th>
<th>$d_{NO}$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>On-top</td>
<td>Tilted O-bonded</td>
<td>(2×2)</td>
<td>1/2</td>
<td>0.15</td>
<td>2.5</td>
<td>1.14</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(2×4)</td>
<td>1/4</td>
<td>0.15</td>
<td>2.5</td>
<td>1.14</td>
<td>1.22</td>
</tr>
<tr>
<td>Bridge</td>
<td>Tilted O-bonded</td>
<td>(2×2)</td>
<td>1/2</td>
<td>0.12</td>
<td>3.15</td>
<td>1.14</td>
<td>1.21</td>
</tr>
</tbody>
</table>

**FIG. 4.** Side view of the optimized highly tilted N$_2$O(a) structure adsorbed with O atom to the on-top surface site.
are difficulties in NEXAFS analysis which would provide the most reliable orientation (see discussion section in our previous study, Ref. 15).

Very recent NEXAFS measurements of N₂O on Pd(110) at around 60 K suggest that a majority of N₂O is in a horizontal form oriented along the [001] direction and a minor amount is standing,⁵⁶ while no anisotropy was found in NEXAFS spectra on Rh(110), i.e., neither [001] oriented, nor [110] oriented N₂O nor the standing form was excluded.¹³ The N₂O(a) forms as predicted by the DFT-GGA calculations for Pd(110) (Ref. 15) seem to be in agreement with these NEXAFS measurements, while the analogous N₂O(a) forms on Rh(110) predicted in this work are contradicting the NEXAFS results, namely, calculations indicate the [001] orientation of the horizontal form is more stable than the standing and [110]-oriented horizontal form.

In order to reconcile the above mismatch between the NEXAFS results and DFT-GGA predictions of N₂O/Rh(110) we pass the discussion to the molecular versus dissociative adsorption of N₂O. In recent N₂O/Rh(110) experiments¹⁰–¹³,¹⁵,¹⁷ a significant amount of dissociated N₂O, i.e., N₂(a) + O(a), was observed already at a temperature below 100 K. The NEXAFS measurements¹³ indicate the dissociative N₂O adsorption takes place already at temperature around 60 K. These findings suggest that for some N₂O(a) configurations the dissociation barrier must be very low. The DFT-GGA calculations indicate that indeed some forms of horizontal N₂O(a) dissociate readily (i.e., during the geometry optimization the N₂O is decomposed to N₂(a) and O(a) presumably due to the absence of a dissociation barrier or at least very narrow and small dissociation barrier). A similar dissociative behavior of N₂O was also predicted by Orita and Itoh—using DFT-GGA calculations—on step edge sites of Ni(755) surface.¹⁷ Our preliminary constrained-optimization calculations, where the N–O distance was step-wise increased and all the other degrees of freedom were optimized, indicate that the dissociation barrier for the most stable [001]-oriented horizontal N₂O(a) form is very small. At 1/2 ML coverage it is ~0.15 eV, and is expected to be even smaller at lower coverage. This might indicate that the [001]-oriented horizontal N₂O(a) is prone to dissociate already at temperature at which the NEXAFS spectra were recorded. The most remarkable difference in NEXAFS measurements between Pd(110) and Rh(110) is in the amount of coadsorbed oxygen. At surface temperature of 60 K, no O(a) was detected on Pd(110), while about 20% of incident N₂O released O(a) on Rh(110).⁵⁷ At present, it is not known how this O(a) affects the orientation of N₂O(a).

B. Electronic structure of adsorbed N₂O

Since very little is known about the nature of the N₂O chemical bond with transition metal surfaces, the electronic factors that govern the adsorption phenomenon are discussed below.

We start the discussion of the electronic structure by observation that the oxygen-surface distance of the horizontal N₂O(a) form (2.1 Å for the on-top structure) is substantially shorter than 2.5 Å predicted for the O-bonded on-top tilted structure. Such short oxygen-surface distance is a clear indication that the horizontally adsorbed molecules also interact with the surface through the oxygen atom. This conclusion is supported by the accumulation of the charge in the Rh–O bonding region—as seen from the charge density difference Δn(r) = n_{N₂O/Sub}(r) − [n_{Sub}(r) + n_{O}/O(r)] displayed in Fig. 5—and is further evidenced by the ILDOS plots in Fig. 8. The n_{N₂O/Sub}(r), n_{Sub}(r), and n_{O}/O(r) are the electron charge density distributions of the N₂O-on-substrate, clean substrate, and N₂O, respectively. Compare, for example, charge accumulated between oxygen and surface for the horizontal and O-bonded tilted structures. Clearly, as seen from Fig. 5, such accumulation is substantial only for the former structure. The Δn(r) plots in Fig. 5 show that the redistribution of the charge on adsorption is larger for the horizontal form than for the N₁-bonded tilted form. The charge redistribution of the O-bonded tilted form is the smallest, thus being consistent with a very tiny predicted adsorption energy.

Now we describe in more detail the PDOS plots of Fig. 6, where PDOS is projected to N₂O molecule and to the surface Rh atoms that interact with the N₂O molecule for the tilted on-top and horizontal on-top c(2×4)–N₂O/Rh(110) structures. An analogous PDOS plot is also shown for the “noninteracting” system, where the N₂O is located ~6 Å above the surface. Fermi level is chosen as the zero energy level for these plots. The molecular-derived peaks are labeled by corresponding molecular-orbital symmetries. To help the interpretation of the figure, we plotted the molecular valence
and LUMO (lowest-unoccupied-molecular-orbital) states of the isolated molecule in Fig. 7, while the visualization of molecular states of the interacting molecule is utilized by the ILDOS plots shown in Fig. 8. The valence molecular 4σ and 5σ states lie more than 10 eV below the 6σ state and are not shown in Figs. 6, 7, and 8. By comparison of the two PDOS plots of interacting structures with that of the noninteracting one, we see that the PDOS of the tilted structure is affected far less by adsorption than the PDOS of the horizontal form. Although the symmetry of the horizontal N\textsubscript{2}O is reduced far less by adsorption than the PDOS of the horizontal form.

The only noticeable differences of the PDOS of the tilted structure compared to the noninteracting structure is a significant downshift of 1σ states are substantially broadened. There is a significant contribution of the molecular states in between the 2σ and 3σ states with the substrate d states (see ILDOS plot labeled as 2π+3π). The 3π state is only observable in the noninteracting system and is not present in the interacting system.

**V. CONCLUSIONS**

The adsorption structures of N\textsubscript{2}O on Rh(110) predicted by DFT within the GGA approximation have been characterized in detail. As the main result two stable forms of N\textsubscript{2}O(a) were found. The first, less stable form is tilted with the terminal N atom attached to the surface, while the second, more stable form lies horizontally on the surface. Adsorption on the on-top site is preferable for both forms. The tilted form remains linear on adsorption with the intramolecular distances almost unchanged. On the other hand, the horizontal form is bent, with the terminal-nitrogen and oxygen atoms

FIG. 6. Density of states projected (PDOS) to the N\textsubscript{2}O molecule and to the surface Rh atoms, labeled as Rh\textsubscript{surf} that interact with the N\textsubscript{2}O molecule. The top panel shows the PDOS for the “noninteracting” system (i.e., the N\textsubscript{2}O is located -6 Å above the surface), the middle panel shows the PDOS of the tilted-on-top structure, while the bottom panel shows the PDOS for the horizontal-on-top c(2\times4)-N\textsubscript{2}O/Rh(110) structure. The characters of the derived molecular peaks of N\textsubscript{2}O are also shown (labeling of the molecular states refer to the gas phase N\textsubscript{2}O). Fermi level is chosen as the zero energy level for these plots and is indicated by a vertical solid line. The PDOSs are Gaussian broadened with a broadening parameter of 0.15 eV.

FIG. 7. (Color) Plots of calculated square modulus of valence and LUMO molecular orbitals of the gas phase N\textsubscript{2}O molecule |ϕ(r)|\textsuperscript{2}. Contours are drawn in a logarithmic scale (five contours from 10\textsuperscript{-3}|ϕ(r)| to 10\textsuperscript{-1}|ϕ(r)|) and plots are colored rainbowlike (the magnitude of the plotted orbitals increases from red to violet).
pointing towards the surface. The intramolecular distances are greater than in the tilted form due to larger charge back-donation into the antibonding $3\pi$ molecular orbital as evidenced by the electronic structure analysis.

At high coverage $\Theta \sim 1$ ML the adjacent tilted molecules point in opposite direction, i.e., out-of-phase tilting configuration, while already at $1/2$ ML coverage the difference in binding energy between the out-of-phase and in-phase tilting configurations is insignificant.

An interesting result is that at lower adsorbate coverage $\Theta \leq 1/4$ ML the adsorption of some horizontal $\text{N}_2\text{O}$ forms is dissociative, i.e., $\text{N}_2\text{O} \rightarrow \text{N}_2(a) + \text{O}(a)$. This is presumably
due to the absence of dissociation barrier or at least very narrow and small dissociation barrier.

The undissociated horizontal form is preferentially oriented along the [001] direction and thus bridging atomic troughs of the surface extending in the [110] direction. However, calculations indicate that also this N$_2$O($a$) form is prone to dissociate, namely, the corresponding dissociation barrier is rather small $\sim$0.15 eV at 1/2 ML coverage and is expected to be even smaller at lower coverage. Therefore further calculations are required to address (i) the stability and dissociation of the horizontal N$_2$O($a$) forms, (ii) the effect of coadsorbed O($a$) that is released during the decomposition of N$_2$O, and (iii) to provide a mechanistic insight into the peculiar inclined N$_2$ desorption observed experimentally during the thermal dissociation of N$_2$O.$^ {58,59}$

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The PDOS projected onto a given atom or a group of atoms is then obtained by summing the PDOSs of all atomic orbitals located on these atoms. In the present case—due to the use of ultrasoft pseudopotentials—the PDOS equation contain also an augmentation term; see Ref. 59 for the corresponding full expression.

The integrated local density of states (ILDOS) in a given energy range \( [E_{\text{min}}, E_{\text{max}}] \) is defined as \[ N(E_{\text{min}}, E_{\text{max}}, \mathbf{r}) = \sum_{\mathbf{k}} \int_{E_{\text{min}}}^{E_{\text{max}}} \delta(\epsilon - \epsilon_{\nu, k}) d\epsilon \]
where \( \psi_{\nu, k}(\mathbf{r}) \) is the \( \nu \)th Bloch orbital at wave-vector \( \mathbf{k} \), and \( \epsilon_{\nu, k} \) is the corresponding energy eigenvalue. In the present case—due to the use of ultrasoft pseudopotentials—this equation contain also an augmentation term; see Ref. 59 for the corresponding full expression.