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<th>A density-functional theory study of the interaction of N2O with Rh(110)</th>
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<td>Author(s)</td>
<td>Kokalj, Anton; Matsushima, Tatsuo</td>
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<td>Citation</td>
<td>The Journal of Chemical Physics, 122: 034708</td>
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<td>Issue Date</td>
<td>2005-01-15</td>
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A density-functional theory study of the interaction of \( \text{N}_2\text{O} \) with \( \text{Rh}(110) \)

Anton Kokalj

Jožef Stefan Institute, 1000 Ljubljana, Slovenia

Tatsuo Matsushima

Catalysis Research Center, Hokkaido University, Sapporo 060-0811, Japan

(Received 29 June 2004; accepted 18 October 2004; published online 3 January 2005)

The adsorption of nitrous oxide, \( \text{N}_2\text{O} \), on a \( \text{Rh}(110) \) surface has been characterized by using density-functional theory. \( \text{N}_2\text{O} \) 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 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, \( \Theta \leq 1/4 \) ML (ML—monolayer), the adsorption of a few horizontal \( \text{N}_2\text{O} \) configurations is dissociative, i.e., \( \text{N}_2\text{O} \rightarrow \text{N}_2(a) + \text{O}(a) \). The \( \text{N}_2\text{O} \)-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, \( \text{N}_2\text{O} \), is an intermediate in the removal of \( \text{NO}_x \) on automobile three-way catalysts. Furthermore, \( \text{N}_2\text{O} \) 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 \( \text{N}_2\text{O} \) is the main byproduct in this process.\(^1\) In particular, much attention have been given to the decomposition of \( \text{N}_2\text{O} \) on rhodium surfaces, because rhodium is one among the best catalysts for removing nitrogen oxides.\(^2\) Despite the importance of this system, the interaction of \( \text{N}_2\text{O} \) with rhodium surfaces is not yet well understood. Peculiar inclined \( \text{N}_2\text{O} \) desorption observed recently on some fcc\( (110) \) surfaces\(^3\)–\(^12\) is expected to provide further insight. On a \( \text{Rh}(110) \) surface, the nitrogen molecules produced during the thermal dissociation of \( \text{N}_2\text{O} \) were detected to desorb in inclined bidirectional lobes in a plane along the \( [001] \) direction.\(^10,12\) The collimation angle was about \( 70^\circ \), which is larger than \( 43^\circ–50^\circ \) found on \( \text{Pd}(110) \).\(^7\) Recent report of \( \text{N}_2\text{O} \) adsorption on a clean \( \text{Rh}(110) \) showed significant dissociation to \( \text{N}_2(a) \) and \( \text{O}(a) \) at temperatures around 60 K [where \( X(a) \) refer to adsorbed \( X \) species, this notation will be used hereafter] at small \( \text{N}_2\text{O} \) exposures,\(^13\) indicating that the dissociation barrier is rather small.

Computational studies of \( \text{N}_2\text{O} \) adsorption on transition metal surfaces are very scarce.\(^14\)–\(^17\) Instead, several authors have reported on the interaction and decomposition of \( \text{N}_2\text{O} \) with transition metal atoms\(^18\)–\(^20\) or small clusters.\(^21\) Burch et al.\(^22\) studied the formation of \( \text{N}_2\text{O} \) via the \( \text{NO} + \text{N} \) reaction on \( \text{Pt}(111) \) surface using density-functional theory (DFT), but the adsorption of \( \text{N}_2\text{O} \) was not discussed. Bogicevic and Hass\(^23\) performed DFT study of NO pairing and transformation to \( \text{N}_2\text{O} \) on \( \text{Cu}(111) \) and \( \text{Pd}(111) \). They briefly mentioned that \( \text{N}_2\text{O} \) is preferentially adsorbed on the on-top site, but geometry of the adsorbed \( \text{N}_2\text{O} \) was not discussed. To the best of our knowledge, the interaction of \( \text{N}_2\text{O} \) with \( \text{Rh} \) surfaces (or atoms) has not yet been studied by computational first-principle methods. For this reason we have undertaken a DFT study of \( \text{N}_2\text{O} \) adsorption on \( \text{Rh}(110) \) surface. Since very little is known about the nature of the \( \text{N}_2\text{O} \) 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 \( \text{N}_2\text{O} \) is an important ingredient to provide an explanation of the mechanism of the above-mentioned peculiar \( \text{N}_2 \) desorption. Moreover, the structure of \( \text{N}_2\text{O}(a) \) immediately before dissociation can be studied only by means of theoretical calculations. In our previous contributions\(^14,15\) we studied the adsorption structures of \( \text{N}_2\text{O} \) on \( \text{Pd}(110) \). In this paper we report on a detailed first-principle density-functional study of the geometry and orientation of \( \text{N}_2\text{O}(a) \) on \( \text{Rh}(110) \) 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).\(^24\) Nuclei and core electrons were described by ultrasoft pseudopotentials.\(^25,26\) 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\(^27,28\) with a smearing parameter of 0.03 Ry. Calculations have been done using the PWSCF package,\(^29\) while molecular graphics were generated by the XCRYSDEN (Refs. 30 and 31) graphical package.

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

\(^{4}\)Fax: +386-1-477-3811. Electronic mail: Tone.Kokalj@ijs.si; URL http://www-k3.ijs.si/kokalj/
TABLE I. Surface energies \( \sigma \), work functions \( \phi \), relaxations of the first layer \( \Delta d_{12} \), second layer \( \Delta d_{23} \) of a Rh(110) surface, and \( N_{\text{layers}} \) number of layers in the slab.

<table>
<thead>
<tr>
<th>( N_{\text{layers}} )</th>
<th>( \sigma ) (eV/atom)</th>
<th>( \phi ) (eV)</th>
<th>( \Delta d_{12} ) (%)</th>
<th>( \Delta d_{23} ) (%)</th>
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<tr>
<td>Present work</td>
<td>( 5 )</td>
<td>1.55</td>
<td>0.146</td>
<td>4.62</td>
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<tr>
<td></td>
<td>( 7 )</td>
<td>1.59</td>
<td>0.150</td>
<td>4.72</td>
</tr>
<tr>
<td></td>
<td>( 9 )</td>
<td>1.52</td>
<td>0.149</td>
<td>4.57</td>
</tr>
<tr>
<td></td>
<td>( 11 )</td>
<td></td>
<td></td>
<td>4.53</td>
</tr>
<tr>
<td></td>
<td>( 7,9,11 )</td>
<td>( 1.60 )</td>
<td></td>
<td>( 0.150 )</td>
</tr>
<tr>
<td>GGA FP-LAPW ( ^a )</td>
<td>( 7 )</td>
<td>( 1.43 )</td>
<td>( 0.138 )</td>
<td>( 4.59 )</td>
</tr>
<tr>
<td>Experiment</td>
<td>( 1.69 )</td>
<td></td>
<td>( 0.17 )</td>
<td>( 4.98 )</td>
</tr>
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</table>

\( ^a \)Surface energies estimated by equation \( \sigma = 1/2[E_{\text{slab}}(N) - N/2E_{\text{slab}}(11) - E_{\text{slab}}(9)] \).

\( ^b \)Surface energy calculated by fitting the equation \( E_{\text{slab}}(N) = 2\sigma + NE_{\text{bulk}} \).

\( ^c \)Reference 38.

\( ^d \)Data from Ref. 39, \( \sigma \) corresponds to an “average” high-index surface.

\( ^e \)Data from Ref. 34.

\( ^f \)Data from Ref. 35.

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 \( 8 \times 6 \) uniform shifted \( k \)-mesh. All the layers have been relaxed symmetrically for these calculations. The surface energy \( \sigma \) was estimated (i) by applying the Boettger-like equation, \( \sigma = 1/2[E_{\text{slab}}(N) - N/2E_{\text{slab}}(11) - E_{\text{slab}}(9)] \), and (ii) by fitting the slab potential energies \( E_{\text{slab}}(N) \) for \( N = 7, 9, 11 \), to the equation \( E_{\text{slab}}(N) = 2\sigma + NE_{\text{bulk}} \), where \( N \) and \( E_{\text{bulk}} \) 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 \( \sigma = 1.60 \text{ eV/atom} = 0.15 \text{ eV/Å}^2 \) and \( \phi = 4.6 \pm 0.1 \text{ eV} \). The relaxations of the first \( \Delta d_{12} \) and second \( \Delta d_{23} \) layers are \(-10\% \pm 1\% \) and \(+2\% \pm 1\% \), respectively, while experimental values are \( \Delta d_{12} = -6.9 \pm 1.0\% \) and \( \Delta d_{23} = +1.9 \pm 1.0\% \).

The \( \text{N}_2\text{O} \) molecule is an anomalous member of \( \text{AB}_2 \) 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 \( N_t \) and \( N_c \) which stand for the terminal- and the central-nitrogen atoms, respectively. For the \( \text{N}_2\text{O} \) 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-Pargz) calculated distances (1.134 and 1.193 Å, respectively). The experimental values are 1.128 Å for \( d_{\text{NN}} \) and 1.184 Å for the \( d_{\text{NO}} \) distance.

The \( \text{N}_2\text{O} \) molecule in the adsorbed state was modeled by attaching the \( \text{N}_2\text{O} \) molecule onto the Rh(110) surface. In particular, we define the symbols \( N_t \) and \( N_c \) which stand for the terminal- and the central-nitrogen atoms, respectively. For the \( \text{N}_2\text{O} \) 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-Pargz) calculated distances (1.134 and 1.193 Å, respectively). The experimental values are 1.128 Å for \( d_{\text{NN}} \) and 1.184 Å for the \( d_{\text{NO}} \) distance.
nitriger and oxygen atoms are interacting with the substrate atoms (hereafter designated as horizontal form). The horizontal forms will be labeled as site \(_1(N)\)-site \(_2(O)\), meaning that the \(N\) atom is pointing toward the \(site_1\) site and \(O\) atom toward the \(site_2\). The \(N\) and \(O\) atoms can point either to the same type of site, i.e., on-top\((N)\)-on-top\((O)\) or bridge \((N)\)-bridge\((O)\), or to different type of site, i.e., on-top \((N)\)-bridge\((O)\) or bridge\((N)\)-on-top\((O)\). For brevity, the on-top\((N)\)-on-top\((O)\) or bridge\((N)\)-bridge\((O)\) forms will be referred shortly as on-top and bridge, respectively.

1. Molecular and dissociative adsorption of \(N_2O\)

Calculations indicate that the \(N_2O(a)\) 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 \(N_2O(a)\) 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 \(N_2O\) 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.\(^{15}\)

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, \(N_2O\) 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 \(\leq 1/4\) ML the adsorption of horizontal bridge form is dissociative, namely, the \(N_2O\) decomposes to \(N_2(a) + O(a)\) 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 \(N_2O(a)\) was modeled oriented either along the [001], [1\(\bar{1}\)0], 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 \(N_2O(a)\) oriented along [001] was predicted to be more stable than that oriented along the [1\(\bar{1}\)0] direction, the \(E_b\) being

<table>
<thead>
<tr>
<th>Site</th>
<th>Moiety</th>
<th>Super cell</th>
<th>Coverage (ML)</th>
<th>(E_b) (eV)</th>
<th>(d_{BN}) (Å)</th>
<th>(d_{NN}) (Å)</th>
<th>(d_{NO}) (Å)</th>
<th>(d_{BO}) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>On-top</td>
<td>Tilted</td>
<td>c(2(\times)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(\times)4)</td>
<td>1/2</td>
<td>0.53</td>
<td>2.04</td>
<td>1.15</td>
<td>1.22</td>
<td></td>
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<tr>
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<td></td>
<td>c(2(\times)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>
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<td></td>
<td>c(2(\times)4)</td>
<td>1/2</td>
<td>0.82</td>
<td>1.96</td>
<td>1.20</td>
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<td>2.08</td>
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<tr>
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<td>Tilted</td>
<td>c(2(\times)2)</td>
<td>1/2</td>
<td>0.25</td>
<td>2.23</td>
<td>1.16</td>
<td>1.22</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td>c(2(\times)4)</td>
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<td>0.24</td>
<td>2.22</td>
<td>1.16</td>
<td>1.22</td>
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<tr>
<td>Horizontal</td>
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<td>c(2(\times)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>
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<tr>
<td></td>
<td></td>
<td>c(2(\times)4)</td>
<td>1/4</td>
<td>Dissociates to (N_2(a) + O(a))</td>
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<td></td>
<td></td>
<td></td>
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</tbody>
</table>

\(N_2O(a)\)
0.82 and 0.65 eV, respectively, while the adsorption of [11\text{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\text{1\text{0}}] direction and one of the terminal atoms (N$_t$ or O) of the molecule was pointing toward the on-top site, while the other toward the bridge site, i.e., on-top($N_t$)–bridge(O) and bridge($N_t$)–on-top(O) structures. The calculated $E_b$ of bridge($N_t$)–on-top(O) structure is 0.67 eV. This structure is therefore less stable than the horizontal on-top structure oriented in the [0\text{0\text{1}}] direction. Note that the bend of bridge($N_t$)–on-top(O) structure is somewhat peculiar as the molecule is not bent only toward the surface, but also laterally (see Fig. 2). The adsorption of the other “asymmetric” structure, on-top($N_t$)–bridge(O), is predicted to be dissociative—a prediction similar to that for the [1\text{1\text{2}}]-oriented molecule.

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
The interaction of N₂O with Rh(110)

3. Less stable and unstable N₂O(a) forms

Calculations indicate that the N₂O 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 N₂O 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 N₂O(a) adsorbed via the N₁ atom, the N₁-surface distance is only 2.03 Å]. Such a weakly oxygen bonded and highly tilted N₂O form is also predicted on Pd(110).33 The Eₜ for the highly tilted O-bonded molecule adsorbed on the bridge site is similar, 0.12 eV. Results for the O-bonded N₂O(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,16 we calculated the interaction between N₂O and a single Pd atom—the N₂O 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 Möller-Plesset perturbation theory44 was virtually zero.

IV. DISCUSSION

A. Stable adsorption and dissociation of N₂O

Calculations predict the attractive adsorbate-substrate interaction when the molecule is adsorbed in a tilted configuration bonded to the surface with the N₁ atom, or lying horizontally on the surface. At lower adsorbate coverage Θ≤1/4 ML the adsorption of some horizontal N₂O configurations is predicted to be dissociative, i.e., N₂O→N₂(a)+O(a).

The geometry of the tilted N₂O(a) is linear and intramolecular distances are almost unchanged on adsorption. In the case of horizontal N₂O(a), the geometry is not linear but bent, with the N₁ and O atoms pointing toward the surface. The dₙN and dₙO distances are greater than in the tilted structures—an indication of larger charge backdonation into the antibonding 3τ molecular orbital. This charge backdonation is evidenced in the projected density of states45 (PDOS) plots shown in Fig. 6, and by integrated local density of states46 (ILDOS) plots of Fig. 8. This issue will be described in more detail below (see Sec. IV B).

The geometry of adsorbed N₂O on transition metal surfaces has not been widely studied experimentally (see recent review of Zeigarnik47 or Matsushima48). It has been proposed that N₂O adsorbs via the terminal nitrogen atom in an inclined49–52 or upright49,53,54 form. The inclined form was proposed on the basis of vibrational spectroscopy work on Ru(001) (Ref. 49) and Pt(111),50 NEXAFS (near edge x-ray absorption fine structure spectroscopy) analysis on Ni(111) (Ref. 51) and Cu(100),52 and also use of the kinetic isotope effects approach to polycrystalline Cu.53 However, the angle of tilt is still unclear from experimental work, because there

![FIG. 4. Side view of the optimized highly tilted N₂O(a) structure adsorbed with O atom to the on-top surface site.](image)

### Table IV

<table>
<thead>
<tr>
<th>Site and moiety</th>
<th>Supercell</th>
<th>Coverage (ML)</th>
<th>Tilt</th>
<th>Eₜ (eV)</th>
<th>dₙN (Å)</th>
<th>dₙO (Å)</th>
<th>dₙN (Å)</th>
<th>dₙO (Å)</th>
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<tbody>
<tr>
<td>On-top tilted</td>
<td>(2x1)</td>
<td>1</td>
<td>In-phase</td>
<td>0.23</td>
<td>2.04</td>
<td>1.15</td>
<td>1.22</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Out-of-phase</td>
<td>0.39</td>
<td>2.03</td>
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<td>1.22</td>
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<tr>
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<td>(4x1)</td>
<td>1/2</td>
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<td>0.54</td>
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<td></td>
<td>Out-of-phase</td>
<td>0.54</td>
<td>2.04</td>
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### Table V

<table>
<thead>
<tr>
<th>Site and moiety</th>
<th>Supercell</th>
<th>Coverage (ML)</th>
<th>Eₜ (eV)</th>
<th>dₙN (Å)</th>
<th>dₙO (Å)</th>
<th>dₙN (Å)</th>
<th>dₙO (Å)</th>
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<tbody>
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<td>2.5</td>
<td>1.14</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td></td>
<td>c(2x4)</td>
<td>1/4</td>
<td>0.15</td>
<td>2.5</td>
<td>1.14</td>
<td>1.22</td>
<td></td>
</tr>
<tr>
<td>Bridge Tilted O-bonded</td>
<td>c(2x2)</td>
<td>1/2</td>
<td>0.12</td>
<td>3.15</td>
<td>1.14</td>
<td>1.21</td>
<td></td>
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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 N$_2$O on Pd(110) at around 60 K suggest that a majority of N$_2$O is in a horizontal form oriented along the [001] direction and a minor amount is standing,\(^*\) while no anisotropy was found in NEXAFS spectra on Rh(110), i.e., neither [001] oriented, nor [110] oriented N$_2$O nor the standing form was excluded.\(^*\) The N$_2$O(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 N$_2$O(O) 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 N$_2$O/Rh(110) we pass the discussion to the molecular versus dissociative adsorption of N$_2$O. In recent N$_2$O/Rh(110) experiments\(^*\)–N$_2$O/Rh(110) a significant amount of dissociated N$_2$O, i.e., N$_2$(a) + O(a), was observed already at a temperature below 100 K. The NEXAFS measurements\(^*\) indicate the dissociative N$_2$O adsorption takes place already at temperature around 60 K. These findings suggest that for some N$_2$O(a) configurations the dissociation barrier must be very low. The DFT-GGA calculations indicate that indeed some forms of horizontal N$_2$O(a) dissociate readily (i.e., during the geometry optimization the N$_2$O is decomposed to N$_2$(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 N$_2$O was also predicted by Orita and Itoh—using DFT-GGA calculations—on step edge sites of Ni(755) surface.\(^*\) Our preliminary constrained-optimization calculations, where the N–O distance was stepwise increased and all the other degrees of freedom were optimized, indicate that the dissociation barrier for the most stable [001]-oriented horizontal N$_2$O(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 N$_2$O(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 N$_2$O released O(a) on Rh(110).\(^*\) At present, it is not known how this O(a) affects the orientation of N$_2$O(a).

**B. Electronic structure of adsorbed N$_2$O**

Since very little is known about the nature of the N$_2$O 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 N$_2$O(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 $\Delta n(r) = n_{N_2O/Sur}(r) - [n_{Sub}(r) + n_{N_2O(O)}(r)]$ displayed in Fig. 5—and is further evidenced by the ILDOS plots in Fig. 8. The $n_{N_2O/Sur}(r)$, $n_{Sub}(r)$, and $n_{N_2O(O)}(r)$ are the electron charge density distributions of the N$_2$O-on-substrate, clean substrate, and N$_2$O, 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 $\Delta n(r)$ plots in Fig. 5 show that the redistribution of the charge on adsorption is larger for the horizontal form than for the N$_r$-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 N$_2$O molecule and to the surface Rh atoms that interact with the N$_2$O molecule for the tilted on-top and horizontal on-top c(2×4)–N$_2$O/Rh(110) structures. An analogous PDOS plot is also shown for the “noninteracting” system, where the N$_2$O 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 molecular 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 $4\sigma$ and $5\sigma$ states lie more than 10 eV below the $6\sigma$ 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$_2$O is reduced far less by adsorption than the PDOS of the horizontal form, we see that the PDOS of the tilted structure is affected significantly. The adsorption structures of N$_2$Oo nR h(110) predicted by DFT within the GGA approximation have been characterized in detail. As the main result two stable forms of N$_2$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 is not able to form a bond with the surface, while the O atom interacts readily with the surface in the horizontal form. The latter is demonstrated by the $\Delta n(r)$ plot of Fig. 5, the ILDOS plot of Fig. 8, and the PDOS plots shown in Fig. 9 where the molecular PDOS is decomposed into the PDOS projected to N and O atoms. There is significant contribution of O-projected density of states (DOS), starting near the bottom of the substrate $d$ bands and continuing to the Fermi level—an indication of “through oxygen” N$_2$O-surface interaction. In fact, the coupling of the molecular $\pi$ states with the metal $d$ states is more pronounced in the DOS projected to O than to N$_1$ atom. Despite that, the O-surface interaction is effective only for the horizontal form and not for the tilted O-bonded form.

V. CONCLUSIONS

The adsorption structures of N$_2$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$_2$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...
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 $\Theta\sim1$ 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 $\Theta\leq1/4$ ML the adsorption of some horizontal N$_2$O forms is dissociative, i.e., N$_2$O$\rightarrow$N$_2(a)+O(a)$. 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 [1 1 0] direction. However, calculations indicate that also this $N_2O(a)$ 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 $N_2O(a)$ forms, (ii) the effect of coadsorbed $O(a)$ that is released during the decomposition of $N_2O$, and (iii) to provide a mechanistic insight into the peculiar inclined $N_2$ desorption observed experimentally during the thermal dissociation of $N_2O$.

ACKNOWLEDGMENTS

The authors thank Professor Ivan Kobal, Hideyuki Horino, and Dr. Izabela Rzeźnicka for helpful discussions and careful reading of the manuscript. This work was supported financially by the Ministry of Education, Science and Sport of Slovenia, Grant Nos. P2-0148 and P0-0544-0106. A.K. is grateful to Japan Society for the Promotion of Science for financing his research visits to Catalysis Research Center in Sapporo, Japan.

26 Ultrafast pseudopotentials (US PPs) used in this work were obtained from the following references. US PPs for nitrogen and oxygen are from Ref. 58, while the US PP for rhodium is taken from http://www.pwscf.org/pseudo.htm download page (file: Rh.pbe-rkja.UPF).
43 This structure is a very narrow and shallow local minimum, namely, starting the optimization calculation with too tilted $N_2O(a)$ results in the horizontal on-top tilted $N_2O$, while starting the calculations with insufficiently tilted $N_2O(a)$ results in “desorbed” $N_2O$ located far away from the surface.
44 C. Møller and M. S. Plesset, Phys. Rev. 46, 618 (1934).
45 Projected densities of states (PDOS) are calculated using the orthonormalized atomic orbitals, say $|\phi(r)\rangle$, which are defined as: $\hat{\phi}(r) = \sum_{m=1}^{\infty} \sum_{n} \phi_{nm}(r) \phi_{nm}^*(r)$, where $S^{-1}e_i$ is the element of the square root inverse of the overlap matrix $S$ of the atomic orbitals $\phi_i(r)$, whose elements are $S_{mn} = \langle \phi_m | \phi_n \rangle$. The charge associated with the atomic orbital $m$ is then: $Q_m = \sum_{n} \langle \phi_m | S^{-1} e_i | \phi_n \rangle$. This is so called Löwdin population analysis.
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.

46 The integrated local density of states (ILDOS) in a given energy range \( [E_{\text{min}}, E_{\text{max}}] \) is defined as

\[
N(E_{\text{min}}, E_{\text{max}}, \mathbf{r}) = \int_{E_{\text{min}}}^{E_{\text{max}}} \sum_{\mathbf{k}} \sum_{\epsilon_v} |\psi_v(\mathbf{k}, r)|^2 \delta(\epsilon - \epsilon_v) \, d\epsilon
\]

where \( \psi_v(\mathbf{k}, r) \) is the \( v \)th Bloch orbital at wave-vector \( \mathbf{k} \), and \( \epsilon_v \) 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.