

## Adsorption of Water Molecules on Flat and Stepped Nickel Surfaces from First Principles

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**Abstract:** We present an ab initio density functional study of the adsorption of a series of water oligomers (molecule, dimer and trimer) on nickel surfaces with and without step defects. We investigate the preferred adsorption geometries and adsorption energies and analyze the binding mechanisms by means of electronic density difference maps. Special attention is devoted to the incremental adsorption process, i.e., the way additional molecules attaches to an already adsorbed water. In agreement with recent findings, we show that the first water molecule is bound to the surface with an energy of about 0.2–0.4 eV, i.e., with up to twice the strength of a hydrogen bond. In contrast to this, subsequent water molecules increase the total adsorption energy by typically 0.5 eV. However, electron density difference considerations indicate that this additional attraction is *not* due to the interaction of the new molecule with the surface but mediated by the first water molecule. The interaction of the additional molecule with the surface appears even to be repulsive. We discuss the implications of these findings for the wetting properties of transition metal surfaces.

### 1. Introduction

The interaction of water with metal surfaces is of tremendous importance for industrial applications and of very high relevance in surface chemistry. The fundamental mechanisms of the initial phases of this adsorption process has been the subject of a variety of recent experimental and theoretical investigations<sup>1–6</sup> and is still a matter of intense controversy.<sup>7–9</sup>

There is evidence that the water molecules can approach the surfaces in both hydrogen-up and hydrogen-down orientations. Depending on the metal species, a water monolayer can be formed through simultaneous binding of all water molecules to the surface, e.g. in the case of Pt(111), or alternatively as a partially dissociated layer, which is the case for Ru(0001).<sup>2,4</sup>

The deposition of isolated water molecules has already been studied on several flat metallic surfaces, such as Ru(0001), Rh(111), Pd(111), Pt(111), Cu(111), and Ag(111).<sup>10–12</sup> An interesting mechanism for dimer diffusion

through a combined proton tunneling and molecular rotation scheme has been proposed recently.<sup>13</sup>

Most of these studies deal with the interaction of either a single water molecule on a metallic slab or the adsorption of a highly symmetric water monolayer. A high degree of order facilitates the computational modeling within periodic boundary conditions, because the unit cell can be kept small.

In this work, we study more extended systems, which allow for significantly more geometrical relaxation. Our aim is to focus on a realistic description of the initial steps of wetting, going beyond a single adsorbed molecule but without imposing a complete coverage of the surface. For this purpose, we look at the adsorption of a sequence of water oligomers on nickel. Starting from an isolated molecule, we investigate a water dimer as well as a trimer, paying particular attention to the influence of hydrogen bonding on the adsorption energy and the structure of the adsorbate. In particular, we compare the incremental adsorption energy due to the addition of a second and third molecule.

Inspired by previous studies,<sup>14–17</sup> we look not only at a perfect surface but also at the simplest possible defect, a one-dimensional step. This is realized by using a surface in the

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**Table 1.** Energetical and Structural Data for the Various Water Oligomers and Surfaces<sup>a</sup>

	$\Delta E$	$d_{\text{Ni-O}}$	$\Delta_{xy}(\text{O})$	$\Delta_z(\text{Ni})$	$\alpha$	$d_{\text{O...O}}$
(H <sub>2</sub> O) <sub>2</sub>	0.22					
Ni <sub>flat</sub> *(H <sub>2</sub> O) <sub>1,atop</sub>	0.242	2.26	0.14	0.17	5	
Ni <sub>flat</sub> *(H <sub>2</sub> O) <sub>1,bridge</sub>	0.10	3.02	0.02	0.16	-10	
Ni <sub>step</sub> *(H <sub>2</sub> O) <sub>1,atop,trans</sub>	0.403	2.12	0.04	0.10	4	
Ni <sub>step</sub> *(H <sub>2</sub> O) <sub>1,bridge,trans</sub>	0.249	2.46	0.03	0.08	8	
Ni <sub>step</sub> *(H <sub>2</sub> O) <sub>1,atop,cis</sub>	0.397	2.10	0.07	0.05	2	
Ni <sub>step</sub> *(H <sub>2</sub> O) <sub>1,bridge,cis</sub>	0.137	2.51	0.05	0.03	0	
Ni <sub>flat</sub> *(H <sub>2</sub> O) <sub>2,atop</sub>	0.675	2.12	0.16	0.19	22	2.71
Ni <sub>step</sub> *(H <sub>2</sub> O) <sub>2,atop</sub>	0.900	2.09	0.13	0.08	28	2.69
Ni <sub>flat</sub> *(H <sub>2</sub> O) <sub>3,atop</sub>	1.26	2.08	0.2	0.25	34	2.72/2.81
Ni <sub>flat</sub> *(H <sub>2</sub> O) <sub>3,bridge</sub>	1.09	2.24	0.2	0.11	72	2.69/2.7

<sup>a</sup> Adsorption energies ( $\Delta E$ ) are in eV and are always computed relative to isolated water molecules according to eq 1, such as to include also the hydrogen bonding energy. The Ni–O bond lengths ( $d_{\text{Ni-O}}$ ), the vertical displacements of the binding nickel atom ( $\Delta_z(\text{Ni})$ ), and the lateral displacements of the binding oxygen atom from its optimal position ( $\Delta_{xy}(\text{O})$ ) are given in Å, and the angle between the molecular plane of the adsorbing water molecule and the surface ( $\alpha$ ) is in degrees. A negative angle means that the hydrogens are pointing toward the surface. For oligomers, the distance between the oxygen atoms ( $d_{\text{O...O}}$ ) is also shown in Å.

(221) direction. The adsorption-enhancing effect of such steps has also been shown very recently by experimental studies of germanium deposition on silicon surfaces.<sup>18</sup>

## 2. Computational Details

We have modeled the flat and stepped surfaces within density functional theory (DFT) as two-dimensional slabs under periodic boundary conditions. We have chosen hexagonal supercells containing 3 (111)-layers for the (221) step and 4 layers for the flat surface, with nickel supercells of  $2 \times 2$  atoms for the water monomer on the flat surface,  $3 \times 3$  for the water dimer and trimer on the flat, and  $1 \times 2$  for the monomer and dimer on the step surface. In all cases, the slabs were separated in the third dimension by about 10 Å of vacuum. Throughout this work, a plane-wave cutoff of 60Ry has been used,<sup>19</sup> together with Troullier-Martins pseudopotentials<sup>20</sup> in the Kleinman-Bylander scheme for hydrogen and oxygen as well as a special pseudopotential by Lee<sup>21</sup> for nickel. All calculations have been done with the PBE exchange-correlation functional.<sup>22</sup> The electronic structure has been computed using the implementation of the free energy functional of Alavi.<sup>23,24</sup> In this approach, a finite-temperature propagator is diagonalized iteratively for the electronic degrees of freedom, ensuring a Fermi distribution function for the occupation levels of the Kohn–Sham orbitals. We have used a  $4 \times 4 \times 1$  and a  $3 \times 3 \times 1$   $k$ -point mesh within the Monkhorst-Pack scheme<sup>25</sup> to sample the Brillouin zone for the step and flat surfaces, respectively. Using this computational setup, we could reproduce the recently published results of Michaelides et al.<sup>26</sup> for the adsorption of a highly structured water monolayer with a numerical error of less than 50 meV.

Geometry optimizations were done until the atomic forces dropped below a threshold of  $2 \cdot 10^{-3}$  atomic units. This level is sufficiently strict for the considered systems; further optimization changes the total energy by negligible amounts only.<sup>27</sup> We have also computed an estimator for the artificial energy lowering due to the periodicity of our simulation cell. An isolated water molecule in our standard box has a total energy which is about 0.01 eV lower than that in a box of twice the lattice constant.

All adsorption energies have been computed with respect to single isolated water molecules in the same simulation box (thus eliminating the dipole interaction error):

$$\Delta E = E[\text{Ni}(\text{H}_2\text{O})_n] - E[\text{Ni}] - nE[\text{H}_2\text{O}] \quad (1)$$

This definition also allows to obtain directly the incremental adsorption energies for an additional water molecule, which would be more involved when considering the adsorption energy of the water cluster as an entity (i.e. when taking  $E[(\text{H}_2\text{O})_n]$  instead of  $nE[\text{H}_2\text{O}]$ ).

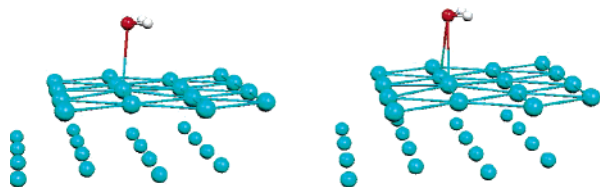
We have further computed electron density difference maps for selected energetically favorable configurations, showing the rearrangement of the density between the surface-adsorbed  $\text{Ni}(\text{H}_2\text{O})_n$  complex and the fragments. For visualizing these maps, we plot color-coded slices with the projected electron density differences  $\delta\rho$  defined as

$$\delta\rho(x, z) = \int dy (\rho^{\text{Ni}(\text{H}_2\text{O})_n}(\mathbf{r}) - \rho^{\text{Ni}}(\mathbf{r}) - \rho^{(\text{H}_2\text{O})_n}(\mathbf{r})) \quad (2)$$

Here, in contrast to the definition of the energy difference, the density plots compare the adsorbed system with the water oligomer cluster and the isolated surface. In this way, the density displacements due to the formation of hydrogen bonds between the water molecules are not plotted, while the modifications of these densities due to the adsorption become visible. The density difference maps were computed in orthorhombic cells obtained by doubling the original hexagonal unit cells and by cutting out a suitable orthorhombic subpart of at least the size of the original setup. This was necessary for a proper visualization of the densities with the program MOLEKEL.<sup>28</sup>

## 3. Results

**3.1. Monomer.** The geometry for three typical adhesion sites (“top”, “bridge”, and “hollow”) of a single water molecule on a flat nickel surface was optimized as well as “top” and “bridge” sites on a 221-surface which represents a step defect. Pictograms illustrating the top and bridge geometries on the flat and stepped surfaces are shown in Figures 1 and 2. The corresponding adsorption energies for these configurations which exhibit a (local) minimum of the potential energy



**Figure 1.** Pictogram of the two adsorption sites for the flat nickel surface which constitute local minima of the potential energy surface: top (left) and bridge (right). The hollow structure turns out to converge toward the top configuration. Only two layers of nickel atoms are shown: the first surface layer is drawn with bonds, the second layer as spheres only.

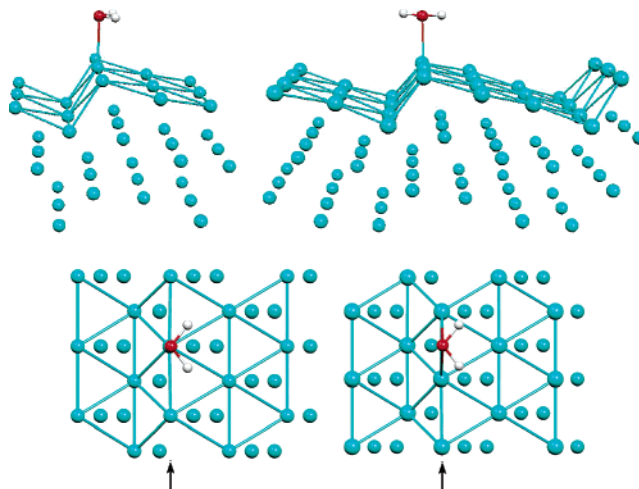
surface are shown in Table 1. The energies of the top site differ from those of the bridge position by typically a factor of 2 in favor of the top configuration. Since the hollow system relaxed to the top site, it was not considered further. Despite the tetrahedral location of the lone pairs of the oxygen atom, the geometry optimization yields a flat arrangement of the molecule, so that the protons are found at the same distance from the surface as the oxygen (for both flat and step cases).

We have explicitly checked a possible vertical adsorption geometry for the flat surface on the hollow site and a tilted one (with one OH-bond parallel to the surface and the other OH normal to it) on the atop site. For both initial geometries, the optimization yields a flat orientation, and in the case of the hollow site, the oxygen atom also moves over to the atop site. Intermediate adsorption energy values from the optimization process are in the area of 0.1 eV during the turning process. This indicates that when the water molecule approaches the surface vertically, the adsorption strength is roughly half as large as in the parallel orientation. These results are in full agreement with the orientations found by Ranea, Michaelides, and others<sup>10,11,13</sup> for water configurations on various other metallic surfaces.

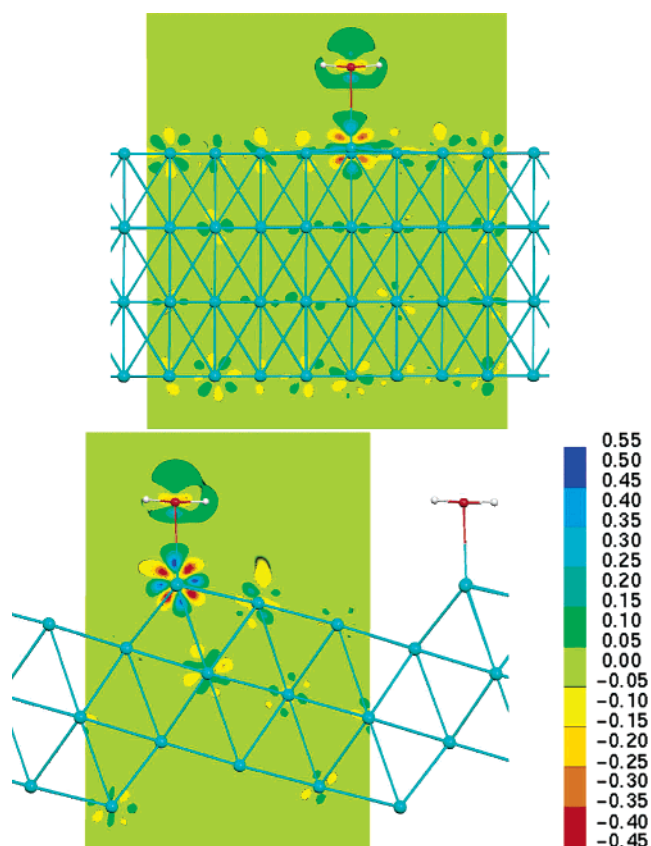
Similar to the recently studied case of an adsorbed benzene molecule,<sup>14</sup> the adsorption of a water molecule is significantly stronger on the surface with the step defect than on the flat one. The adsorption energy for the latter is roughly one hydrogen bond (cf. the (H<sub>2</sub>O)<sub>2</sub> value in Table 1), while the step provides about twice that attraction. There exists a cis and a trans orientation (both shown in Figure 2) for the step defect, but their adsorption energy is almost the same. Thus, the top position on the step surface reaches the highest energy value, which is also approximately equal to the typical hydrogen bond energy of a 4-fold-coordinated liquid water molecule.

The electron density difference according to eq 2 for both the flat and step surfaces is shown in Figure 3. The plot represents the density of the aggregate minus the sum of the densities of the isolated surface and the water molecule at the top site (trans configuration for the step).

The formation of a weak bond between the surface nickel atom and the oxygen is clearly visible through the displacement in electronic density (dark green and blue regions). To some extent, we also find additional density on top of the water molecule, while relatively little is removed from the central area around the oxygen. Most of the electronic density



**Figure 2.** Pictogram of the two adsorption sites for the stepped nickel surface: top/cis (upper left), top/trans (upper right). A comparison with the bridge site is given below, from a top view: top/cis (lower left), and bridge/cis (lower right). As in Figure 1, the atoms of the top layer are drawn with bonds, those of the deeper layers as spheres only.

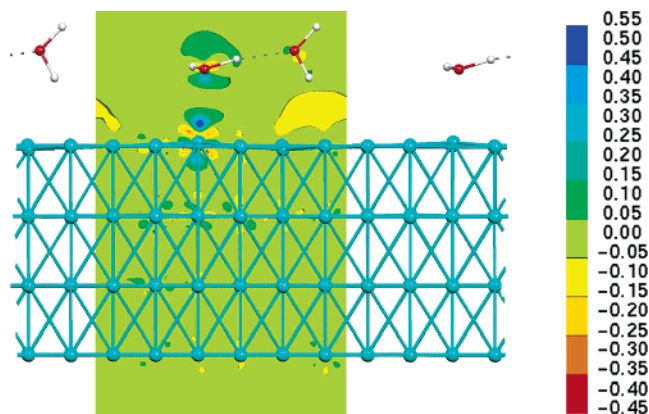


**Figure 3.** Density difference plots for the adsorption of a water molecule on the flat (top plot, atop configuration) and the step surfaces (bottom plot, atop trans configuration). The scale is given in units of  $e/\text{\AA}^2$ .

is taken from the bonding nickel atom, which is strongly polarized, and its first neighbors.

Similar to the case of an adsorbed benzene molecule,<sup>14</sup> the polarization of the nickel atom which is bonded to the water molecule is significantly stronger on the step surface





**Figure 4.** Electron density difference plot for the adsorption of a water dimer on the flat surface.

than on the flat one. This effect also translates into the higher adsorption energy for the latter.

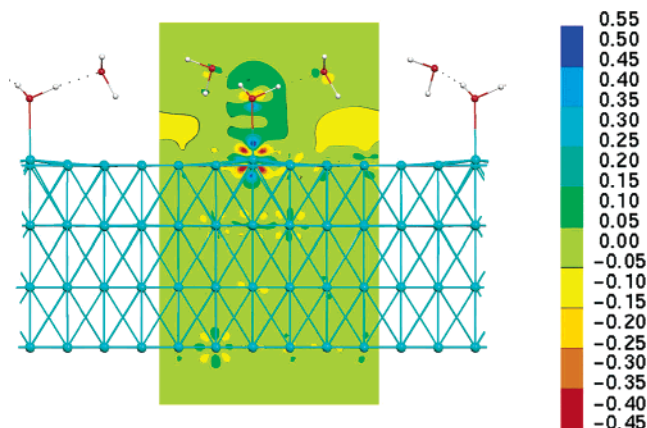
**3.2. Dimer.** The second step in water adsorption on the surface is the attachment of a second water molecule to the first one. For this purpose, the geometries of a water dimer on the nickel surfaces (flat and with the step defect) have been optimized. Since the monomer adsorption is energetically significantly more favorable on the top site than in the bridge position, only the atop configuration has been considered.

The computed Ni–O bond distances and adsorption energies are shown in Table 1. They are taken relative to isolated water molecules in order to have a common reference for all systems. On both the flat and the step surfaces, the attachment of an additional water molecule to the first one through a hydrogen bond yields an additional 0.43 eV and 0.5 eV, respectively. These energies are about twice as large as it would be expected for a standard hydrogen bond (cf. the water dimer in Table 1), leading again to an adsorption strength that is comparable to that of a water molecule in liquid water. Especially on the step defect, two water molecules attach with an energy that is equivalent to four hydrogen bonds, while still possessing two hydrogen bond acceptor sites (one on each oxygen) and two dangling donor protons.

Thus, the dimer adsorption on the metal surface can energetically compete with the solvation of the second molecule in liquid water, even though the optimized cluster on the surface is not directly comparable to the situation in liquid water due to the high dynamics of the hydrogen bond network at finite temperature.

For the flat surface, a part of this increased energy probably stems from the decreased Ni–O bond distance compared to the water monomer, whereas the step surface does not show this effect.

The analysis of the electronic density difference for the dimer adsorption on the flat surface is shown in Figure 4. According to eq 2, the isolated water dimer is taken as reference system, to suppress the charge difference due to the water–water hydrogen bond and to show rather how much this hydrogen bond is changed due to the adsorption on the surface. The plot reveals that the bonding mechanism of the first water molecule is essentially the same as for the



**Figure 5.** Electron density difference plot for the adsorption of a water trimer on the flat surface.

monomer, except that the charge displacement around the first water is now less symmetric than before. There is a region of strongly increased electron density leading to a Ni–O bond and an additional charge increase on top of the first water molecule. Furthermore, the amount of electronic charge density which is found on top of the bonding Ni atom is significantly stronger than for the water monomer (deep blue color in Figure 4 compared to light blue in Figure 3).

It is interesting to note that the second water molecule does not bind directly to the surface, it is even repelled from it. The second oxygen is not accumulating any electronic density toward the metal surface, and there is a distinguishable region of decreased electron density (yellow color coding) below the hydrogen which points toward the surface. In contrast to this, the hydrogen bond between the two water molecules becomes slightly stronger than in the isolated dimer, as seen by the polarization of the H-bond accepting oxygen.

**3.3. Water Trimer on the Flat Surface.** The last point in our investigation focuses on the adsorption of a third water molecule onto H<sub>2</sub>O dimer on the flat nickel surface. As before, the energy and the bonding distance of the first water are shown in Table 1 for both the bridge and the top sites. The energy difference between bridge and top geometries is conserved upon adsorption of further molecules, implying that the secondary water molecules do not feel any significant influence from the adsorption site of the first one.

It is surprising that the third water increases the total adsorption energy by almost 0.6 eV, thus practically doubling the value of the dimer. This can be explained only in parts by the decreased Ni–O bond length directly. The density difference map of the trimer, which is shown in Figure 5 for the top site, reveals a highly increased electronic charge density in the Ni–O bond region, at the expense of the areas below the dangling protons of the secondary water molecules. Together with a very high polarization of the binding nickel atom as well as slightly stronger hydrogen bonds between the waters, this indicates a much stronger binding of the first oxygen atom.

It is interesting to note that this increased binding of the first water is practically not related to any of its geometric properties but is rather due to the mere presence of secondary water molecules, which constitute a kind of a first solvation

shell. These additional water molecules perturb and repel the electron density at the metal surface in the neighborhood of the initial molecule in such a way that the polarization of the bonding nickel is significantly increased. This phenomenon is already visible for the adsorbed dimer but even stronger in the presence of a third water molecule.

#### 4. Conclusion

We have presented an investigation of the energetic details and the electronic mechanism of the adsorption of water oligomers on nickel surfaces with and without a step defect. The data shown indicates an increased binding strength on the step and in “top” geometries. The findings are in good agreement with previous theoretical and experimental results for similar systems,<sup>6</sup> where an energetic enhancement of water adsorption was found along step defects on platinum surfaces.

Further, we could show by means of electronic density difference maps that additional water molecules tend to strengthen the nickel–oxygen bond. This effect leads to a significant stabilization of the binding of the first water molecule and to strongly increased binding energies of the dimer and trimer complexes. Not surprisingly, the adhesion of water to nickel surfaces is much weaker than of aromatic molecules such as benzene or phenol,<sup>14,29,30</sup> but the adsorption energies can definitively compete with those found in liquid water. The second and third water molecule increased the total binding energy by the equivalent of more than two hydrogen bonds each, which correspond to the average binding energy per molecule of standard 4-fold coordinated water.

By means of our study, the initial steps of aqueous wetting of transition metal surfaces can be understood on the basis of electronic effects that govern molecular adsorption.

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