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### Permalink

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### Journal

The Journal of Physical Chemistry C, 121(31)

### ISSN

1932-7447

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### Publication Date

2017-08-10

### DOI

10.1021/acs.jpcc.7b03226

Peer reviewed

# Dissociative Adsorption of Water at (211) Stepped Metallic Surfaces by First Principles Simulations

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## Abstract

Steps at high-index metallic surfaces display higher chemical reactivity than close packed surfaces, and may give rise to selective adsorption and partial dissociation of water. Inspired by differential desorption experiments, we have studied the adsorption and dissociation of water clusters and one-dimensional wires on Pt(211) by density functional theory and molecular dynamics simulations. These calculations reveal that water at the step edges of Pt (211) adsorbs weaker than at Pt (221), but partial dissociation of adsorbed water clusters is energetically competitive. We observe that the one-dimensional structure proposed experimentally can be realized only by partially dissociated water wires. In addition, weaker adsorption allows the formation of structures, in which a number of water molecules detach from the step and form weak hydrogen-bonds with the terrace. This study is further extended to the energetics of small

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water clusters on (211) surfaces of Ir, Rh and Pd that evidence general trends in dissociative adsorption of water at transition metal surfaces.

## 1. INTRODUCTION

The early stages of solvation of transition metal surfaces are of utmost importance to understand electrochemical processes, such as catalysis and corrosion as well as water dissociation and recombination in fuel cells.<sup>1-6</sup> Although the interaction of water with flat and defect-free surfaces, especially Pt (111) surfaces, has been extensively investigated,<sup>7-10</sup> the chemistry of water at low-coordination and defect sites, which often occur in real materials, is still largely unexplored. Step edges are especially important, among the possible defect sites, as they easily occur in real surfaces and entail distinct electronic, chemical, and catalytic properties.<sup>11-13</sup> In particular, step edges control the selectivity of catalytic processes involving multiple reaction pathways:<sup>14</sup> for instance, the activation energy barriers calculated for water dissociation and hydrogen recombination is known to decrease on step surfaces of Cu(321) compared to terraces.<sup>15</sup>

Motivated by experimental studies about the interaction of water with stepped Pt surfaces,<sup>16-20</sup> few recent theoretical works have started to explore systematically the effect of kinks and steps on water adsorption.<sup>21-28</sup> The adsorption of water at Pt (100) and (110) steps (see Figure 1) has been studied by scanning tunneling microscopy (STM).<sup>16,20</sup> Experiments, however, suggest substantial differences regarding how water interacts with different types of step edges. Up to our knowledge, the only theoretical comparison of the adsorption of water at (110) and (100) steps suggested that the adsorption of a water monomer at (110) and (100) steps was almost iso-energetic.<sup>25</sup> Such small adsorption energy difference for water on (100) and (110) steps of Pt would not favor one type of step over the other. However, it is necessary to extend such study to water clusters, as hydrogen-bonding among water molecules may shift the energetics of adsorption.

The adsorption of water on single crystal stepped surfaces has been further explored in detail.<sup>16-18,29</sup> STM and surface X-ray scattering (SXS) experiments<sup>16,29</sup> showed that water molecules adsorbed as quasi-one-dimensional chains along the step edges of Pt(111) terraces. Since STM and

SXS can not detect hydrogen atoms, the protonation state of adsorbed water remains unsolved. Former theoretical calculations addressing the adsorption configuration of one-dimensional (1D) water chain on (100) step surfaces yielded contradictory results suggesting different stable configurations.<sup>17,29,30</sup> A recent DFT study on the adsorption of medium- to high-coverage of water on Pt(533) step edges revealed that water initially adsorbs as one-dimensional wires but eventually rearranges into two-dimensional hexagonal and pentagonal structures.<sup>31</sup>

The possibility of partial dissociation of water on stepped Pt surfaces is also a matter of debate: A recent DFT study calculated the dissociation energy (-0.20 eV) and activation energy (0.66 eV) of a water monomer on Pt(211), thus concluding that dissociation would not take place without a promoter, since the activation energy is larger than the absolute value of the adsorption energy (0.41 eV), but interacting water molecules were not considered.<sup>24</sup> In turn, experiments based on temperature programmed desorption (TPD) spectroscopy for repeated water doses suggested that the first water layer might partially dissociate into H and OH groups.<sup>32</sup>

In a previous study,<sup>26</sup> we investigated the adsorption and dissociation of small water clusters at flat (111) and stepped (221) surfaces of four different transition metals (Rh, Ir, Pt and Pd) using density functional theory (DFT) calculations. The (221) surface consists of three-atom wide terraces of (111) orientation and one-atom-high steps with (110) character. Even though it is difficult to observe the formation of small water clusters due to their high mobility and rapid formation of H-bonded larger clusters, monomer and small water clusters on different metallic flat and/or stepped surfaces have been studied both experimentally and theoretically, on which recent reviews and references within provide extensive information.<sup>33,34</sup>

In this paper, we focus on the adsorption and dissociation of small water clusters and one-dimensional chains at Pt(211) by means of first principles static and molecular dynamics (MD) methods based on DFT. The (211) surface is chosen as a model step-terrace system for (100) stepped surfaces, with a relatively small size and a well-defined geometry such that it can host water molecules on the step edge. This study is extended to the (211) surfaces of rhodium, iridium and palladium for small water clusters. We find that the partial dissociation of water clusters

and one-dimensional water chains is significantly facilitated on Pt(211) due to the increased reactivity of the surface as well as the cooperative effect of H-bonding. In addition, our results suggest that only partially dissociated water wires can assume a geometry similar to that observed in experiments.<sup>19,29</sup> MD simulations show that, due to low diffusion barriers and shallow energy minima, non-dissociated water clusters can assume several possible nearly iso-energetic configurations around the step edge.

## 2. COMPUTATIONAL DETAILS

The adsorption and dissociation energies of water clusters and 1D water chains are calculated using DFT, with the generalized gradient exchange-correlation functional by Perdew, Burke and Ernzerhof (PBE).<sup>35</sup> Ions and core electrons are described by ultrasoft pseudopotentials,<sup>36</sup> and Kohn-Sham orbitals are expanded on a plane-wave basis set with a cutoff energy of 35 Ry. For the smallest supercell size, which is a  $3 \times 1$  replica of the unit cell (Figure 2a) the integration over the first Brillouin zone is performed using Monkhorst-Pack<sup>37</sup> meshes of  $5 \times 4 \times 1$  k-points. Larger simulation cells are used to accommodate a given number of H<sub>2</sub>O molecules, and the size of the k-point meshes is scaled correspondingly. The electronic occupation at the Fermi level is smeared according to the Methfessel-Paxton scheme<sup>38</sup> with a Gaussian broadening of 0.27 eV. The convergence threshold on forces for ionic relaxations is set to  $5 \cdot 10^{-4}$  atomic units (au). Dissociation paths and reaction energies are calculated using the nudged elastic band (NEB) method with climbing images<sup>39</sup> and seven replicas of the system along the transition path. All the calculations were carried out using the Quantum-ESPRESSO package.<sup>40</sup> Convergence tests on plane-wave cutoff energy, k-point sampling, and the thickness of the metal slab, were previously performed for water adsorbed on Pt(221).<sup>23,26</sup> Here we also tested the lateral size of the supercell for monomer adsorption and dissociation energy, to exclude the interaction of water molecules on adjacent steps. In a supercell containing two steps, adsorption and dissociation energies changed by 0.02 eV/H<sub>2</sub>O and 0.02 eV, respectively.

The calculated lattice constant of bulk Pt is 4.01 Å, which is within 2.3% of the experimental value of 3.92 Å.<sup>41</sup> Pt(211) surfaces are modeled as four-layer-thick slabs, and the vacuum space between periodic replicas is set to 20 Å. The two bottom layers are fixed to mimic the bulk and the rest of the system is relaxed. With these settings, the bare surface relaxation reveals that the atoms in the first and the second layers shift by 0.24 and 0.04 Å, respectively, reducing lattice spacing normal to the surface, in good agreement with experimental observations.<sup>18</sup>

Since the PBE exchange and correlation functional does not account correctly for van der Waals (vdW) interactions, we have also tested the adsorption and dissociation energies of water monomer, dimer and trimer using the optB88 van der Waals functional.<sup>42</sup>

1D chain configurations, with four and six water molecules in a supercell (named chain-4 and chain-6, respectively), have been further investigated using Born-Oppenheimer Molecular Dynamics (BOMD), as implemented in the QBOX code.<sup>43</sup> Nonlocal norm-conserving pseudopotentials are used to represent ions and core electrons. PBE exchange and correlation functional is used and the cutoff of the plane waves is set to 60 Ry. The Brillouin zone is sampled at the  $\Gamma$ -point. Canonical (NVT) simulations using stochastic rescaling<sup>44</sup> (with the thermostat time constant  $\tau=24$  fs) at a temperature of  $T=110$  K were carried out. This temperature is within the range used in experiments to study the properties of water on metal surfaces.<sup>16,45</sup> MD simulations range from 10 to 30 ps run time (see details in the Supporting Information (SI), Figure S1). Deuterium is used in place of hydrogen to allow for longer MD integration time-step. The MD equations of motion are integrated using a time-step of 0.24 fs. The same slab settings are used for BOMD simulations as in the static electronic structure calculations.

### 3. RESULTS AND DISCUSSION

In this section, we first present the adsorption and dissociation energies and structural properties of small water clusters on Pt(211). In Section 3.2, this study is extended to 1D water chains on Pt(211) surface, and the energetics and configurations obtained by both static DFT and BOMD

simulations are discussed. The following section analyzes the adsorption and dissociation of small water clusters on (211) surfaces of Ir, Rh and Pd and addresses the effect of different substrates on the general properties of water adsorption and dissociation.

The adsorption energy ( $E_{\text{ads}}$ ) per water molecule is calculated as

$$E_{\text{ads}} = (E[(\text{H}_2\text{O})_n@M] - n \cdot E[\text{H}_2\text{O}] - E[M])/n \quad (1)$$

where  $n$  is the number of  $\text{H}_2\text{O}$  molecules in the simulation cell,  $E[(\text{H}_2\text{O})_n@M]$  is the total energy of the metal surface (M) with the adsorbed molecule,  $E[\text{H}_2\text{O}]$  is the energy of a single water molecule in gas phase, and  $E[M]$  is the energy of the bare metal surface. Thus, a negative adsorption energy corresponds to energetically favored adsorption. The partial dissociation energy,  $E_{\text{diss}}$ , is calculated as the total energy difference between the dissociated structure and the intact one, such as:

$$E_{\text{diss}} = E[(\text{H}_2\text{O})_{(n-1)} + \text{OH}^- + \text{H}^+]@M - E[(\text{H}_2\text{O})_n@M] \quad (2)$$

with negative  $E_{\text{diss}}$  indicating exothermic dissociation. We have studied the dissociation of one  $\text{H}_2\text{O}$  molecule for each  $n\text{H}_2\text{O}$  cluster.

Bader charge analysis<sup>46</sup> (in SI, Table S1) suggests that the dissociation products of a water monomer on Pt(211) are partially charged hydroxyl and a nearly neutral hydrogen atom. The net charge is compensated by the electron gas of the metal surface. Hence, we investigated the most favorable adsorption sites of a hydrogen atom and hydroxyl on Pt(211) surface. It is important here to mention that  $E_{\text{ads}}$  of hydrogen and hydroxyl should be considered as reference data. The adsorption sites and energies are presented in SI, Figure S2 and Table S2. The most favorable adsorption site of both H and OH on Pt(211) is the bridge site at the step edge, consistent with former DFT study.<sup>25</sup> The adsorption energy of H at the terrace is 0.27 eV less stable than that at the step edge. When OH sits on the step-edge bridge site, the configuration with H pointing to lower terrace is almost iso-energetic to that with H pointing in the opposite direction ( $\Delta E = 0.02$  eV).

### 3.1. Water clusters on Pt(211)

**Monomer.** First we have explored the adsorption of a water monomer on Pt(211) by considering various possible adsorption sites (see Figure S3 in SI). The most favorable adsorption site is atop at the step edge with the hydrogen atoms pointing to the upper terrace, Figure 2(a). The adsorption energy is -0.40 eV and the distance between the O atom and the closest Pt at the step edge is 2.32 Å. The corresponding geometry found for Pt(221),<sup>26</sup> with H atoms pointing to the lower terrace, is marginally less stable by only 0.03 eV.

The dissociated monomer is presented in Figure 2(b). The calculated  $E_{\text{diss}}$  is nearly iso-energetic (0.014 eV). Not only the increased reactivity of metal atoms at (211) step edge significantly lowers the partial dissociation energy of the monomer by 0.69 eV with respect to the (111) terrace, but also by 0.50 eV with respect to the (221) step. The optimal configurations for  $\text{H}^+$  and  $\text{OH}^-$  are on step-edge bridge site. The geometrical details of adsorbed and dissociated monomer are reported in SI, Table S3. The computed dissociation barrier of monomer by NEB is 0.80 eV, which is similar to that computed for the monomer dissociation on Pt(221).<sup>23</sup>

**Dimer.** Among all the different configurations probed (see SI, Figure S4), the most stable one for the dimer is shown in Figure 2(c) with adsorption energy equal to -0.53 eV/ $\text{H}_2\text{O}$ . The H-bond between adsorbed water molecules stabilizes the adsorption energy by 0.13 eV compared to the monomer. Whereas H-bond donor takes an atop site on the step edge coupling to the step Pt atom more strongly, the H-bond acceptor sits farther from the step edge and forms a weaker bond with the lower terrace. This dimer configuration is similar to the one found for Pt(221) surface.<sup>23</sup> The O-Pt distance of donor and acceptor is 2.21 and 3.50 Å, respectively, and the O-O distance is 2.60 Å, which is shorter by 0.26 Å than that of a free calculated dimer indicating that the interaction with Pt enhances hydrogen bonding. A former theoretical study suggested a different configuration for a dimer on Pt(322), with both O atoms sitting on the step Pt atoms and the free H atom of donor pointing to lower terrace, namely chain-like configuration.<sup>21</sup> We calculated this proposed chain-



like configuration to be only 0.06 eV less stable than the zigzag one, thus suggesting that also this configuration may be accessible at finite temperature.

The partial dissociation of the dimer is shown in Figure 2(d). The splitting of one water does not lower the dissociation energy significantly compared to the monomer and it is again almost iso-energetic ( $E_{\text{diss}} = 0.007$  eV). In turn, the dissociation energy is lowered by 0.46 and 0.19 eV compared to (111) and (221) surfaces, respectively. The dissociated proton belonging to the detached H-bond acceptor and initially pointing to the lower terrace of the surface was chosen to dissociate, as discussed in previous studies.<sup>23,26</sup> The optimized configuration shows that both O atoms are on atop sites at the step edge, with the Pt-O distances are 2.13 and 2.09 Å for water and OH<sup>-</sup>, respectively, and O-O distance is 2.42 Å, revealing a strong H-bond between them.

**Trimer.** We considered five different initial geometries for the adsorbed water trimer on Pt(211) (see SI, Figure S5), and the most stable configuration is displayed in Figure 2(e) with the geometrical details summarized in SI, Table S3. In this optimal structure, two water molecules sit atop of the step atoms and the H-bond acceptor sits farther from the step edge with both H atoms pointing towards the lower terrace. This configuration is more stable by 0.03 eV than the optimal trimer configuration found for Pt(221) surface, for which the central water was on atop site on the step atom, and donor and acceptor molecules detached from the step edge.<sup>26</sup> The counterpart of the most stable configuration (the detached acceptor is on the upper terrace and the other two molecules sit atop of the step, see SI, Figure S5(b)) is just 0.02 eV less stable. Furthermore, the adsorption energies of the other possible configurations, i.e., chain-like, ring-like and zigzag, are less stable by 0.06–0.10 eV/H<sub>2</sub>O.

The dissociation of one water is similar to the dimer case, i.e., the detached acceptor releases the H atom initially pointing to the lower terrace. As it was previously observed on transition metal (221) surfaces,<sup>23,26</sup> proton transfer occurs within the trimer and it leads to a stable configuration. The optimal geometry, presented in Figure 2(f), displays O atoms sitting at the step Pt atoms with the remaining OH<sup>-</sup> being the central molecule, which accepts H-bonds from the other neighboring

molecules. The geometrical details of the dissociated trimer, given in SI Table S3, show that O–O distances between neighboring molecules are smaller than those of the intact cluster. The cost of breaking an O–H bond is compensated by stronger water–water and water–metal interactions, which results in an exothermic dissociation for trimers ( $E_{\text{diss}} = -0.15$  eV).

A summary of adsorption and dissociation energies with their corresponding configurations is provided in Table Table 1. As for the monomer and dimer cases, the partial dissociation energy of water is significantly lowered on (211) surface by 0.52 and 0.16 eV compared to (111) and (221) surfaces of Pt, respectively. Comparison of the stepped Pt surfaces shows that (211) surface is more reactive towards water dissociation than (221) surface. Table Table 1 also reports adsorption and dissociation energies computed using van der Waals functionals. In agreement with former studies,<sup>47</sup> taking into account dispersion forces systematically enhances adsorption energies by about 0.1 eV/mol, leaving however adsorption geometries and dissociation energies unchanged.

### 3.2. One-dimensional water chains on Pt(211)

Experimental characterization of quasi-1D water chains on the step edges of Pt(111)<sup>16,18,19</sup> revealed that oxygen atoms of water molecules sit on step edge. X-ray diffraction experiment<sup>18</sup> reported two types of adsorbed water at the step site: while one was strongly adsorbed on the step Pt atom with  $d_{\text{Pt-O}} = 2.25$  Å, the other was weakly bound to the step atom with  $d_{\text{Pt-O}} = 2.64$  Å. The distance between two alternating oxygen atoms was 2.82 Å and the difference between the positions of the oxygen atoms along the step was 0.51 Å indicating a 1D chain configuration (see Figure 3 of Ref. 18). However, these techniques do not reveal the position of hydrogen atoms thus do not provide direct evidence about the partial dissociation of the molecules, which may be assigned by theoretical calculations.

Water molecules at step edges can form different configurations, ranging from either zigzag or linear chains to clusters, which depend on the strength of H–bonds between water molecules and water–metal interaction. Here we considered various initial configurations for chain-like geometries with four and six water molecules in a super cell (i.e., chain-4 and chain-6, respectively),

which include configurations suggested by former studies<sup>18,21</sup> as well as newly proposed ones (see Figure S6 and Figure S7, in SI). One of the initial configurations for chain-4 and chain-6 has led to the formation of a sequence of dimers with the H-bond acceptors detached and pointing to lower terrace with the chain of H-bonds broken as shown in Figure 3(a) for chain-4. The  $E_{ads}$  of this configuration for both chain types is -0.51 eV/H<sub>2</sub>O. Zigzag chain-like configurations with the weakly bonded water molecules on the upper or lower terrace are calculated to be iso-energetic. Having negligible  $E_{ads}$  difference shows that H-bonding between water molecules and interaction between water and step edge are more dominant than the interaction of acceptor and Pt atoms on the terrace sites. The structural details and  $E_{ads}$  of the configurations are summarized in SI, Table S4 and Table S5.

The dissociation of chain-4 and chain-6 leads to the reorganization of OH<sup>-</sup> and water molecules, and a proton transfer event occurs within the molecules. As a final configuration, a 1D chain and a periodic sequence of dissociated H-bonded hexamer have been formed with OH<sup>-</sup> bracketed by two intact water molecules for chain-4 and chain-6 as presented in Figure 3(b) and Figure 4(a), respectively. The structural parameters of the dissociated chain-4 configuration are presented in Table 2. We found that the distances between the step edge Pt atom and oxygen atom of the strongly bond water molecule, longitudinal and lateral distances between the alternating oxygen atoms along the step edge, and the angle between the oxygen atoms are in good agreement with experimentally suggested intact 1D water chain.<sup>18</sup> The dissociation energy is slightly endothermic ( $E_{diss} = 0.06$  eV) for chain-4 and clearly exothermic ( $E_{diss} = -0.12$  eV) for chain-6.

The calculated activation barrier for a water monomer diffusion on step and terrace of Pt(322) surface has been reported to be low ( $E_a=0.15$  eV).<sup>48</sup> Thus, in order to probe the varied landscape of possible configurations of water at steps we have performed first principles BOMD simulations using chain-4 and chain-6 configurations. We have observed that water molecules initially farther from the step are free to rotate and diffuse from step edge to upper terrace at 110 K. Thus, the experimentally suggested<sup>18</sup> initial zigzag chain-4 structure has evolved into a cluster configuration. After 14 ps of simulation time, the final configuration has been further geometrically optimized

using static DFT as shown in Figure 3(c). This new cluster-like structure has  $E_{ads} = -0.51$  eV, iso-energetic with the sequence of dimers. The dissociated cluster-like configuration is presented in Figure 3(d) and  $E_{diss} = 0.01$  eV is nearly iso-energetic. Furthermore, BOMD simulations performed for chain-6 has led to a sequence of zigzag dimer configurations, similar to chain-4 in Figure 3(a), at the end of 10 ps. The further relaxed configuration has  $E_{ads} = -0.50$  eV/H<sub>2</sub>O. The adsorbed and dissociated configurations for chain-6 on Pt(211) are presented in SI, Figure S7. Due to small terrace width of (211) surface, a cluster-like configuration formed for chain-4 could not have been obtained for six water molecules. Thus, it is important to mention that wider simulation cells, such as (533) or (755) surfaces, might result in different relaxed configurations for water chains with larger number of water molecules.

We have also computed the barrier for the partial dissociation of chain-6 configuration obtained by static DFT (see Figure S8 in SI). While the activation energy is 0.38 eV, the proton transfer and rearrangement of the chain are barrier free. Comparing to the activation energy calculated for the monomer dissociation on Pt(211) ( $E_{act} = 0.80$  eV), the lower barrier computed for the chain dissociation states that the non-dissociated water molecules serve as a catalyst for the proton dissociation. Former calculations showed that the increased number of water molecules decreases the activation energy for dissociation of water on Cu(110) surface.<sup>49</sup> Our work generalizes this finding to a set of other transition metal surfaces.

The dissociation of one, two and three water molecules have been investigated for the zigzag chain-6 configuration. The dissociation of one water molecule has been already discussed and the rearrangement has been presented in Figure 4(a). When two out of six water molecules dissociate, the dissociation energy decreases to -0.01 eV. The relaxed geometry rearranges into a periodic sequence of dissociated trimers as shown in Figure 4(b). When the ratio of the dissociated molecules is 1/2, the equilibrated structure is a periodic sequence of dissociated dimers as presented in Figure 4(c). This configuration is similar to the dissociated dimer discussed before. The dissociation energy becomes highly endothermic ( $E_{diss} = 0.43$  eV). We can conclude that the most favorable dissociation rate for the chain-6 is one molecule out of six. The structural parameters of the par-

tially dissociated chain-6 are collected in Table 2. As can be seen, two out of six water molecules dissociated configuration gives reasonably good O-Pt and O-O distances with the experimentally suggested 1D water chain configuration.<sup>18</sup>

At this point we can speculate whether the experimentally proposed 1D water chain is formed by intact water molecules or partially dissociated ones. The intact configurations have been shown to form by sequential zigzag dimers, thus intact water molecules do not satisfy the experimental configuration. As can be seen from Figure 3(b) and Figure 4(b), partial dissociation has resulted in reorganization of water molecules so that all the oxygen atoms sit on the step atoms. Therefore, we have further analyzed in detail the structural parameters between oxygen and Pt atoms of partially dissociated chain-4 and chain-6 configurations as summarized in Table 2. The structural details of the single proton dissociated chain-4 and two proton dissociated chain-6 configurations exhibit similar geometrical parameters as those measured experimentally,<sup>18</sup> especially concerning the alignment of water molecules ( $O\hat{O}O$  angle), compared to those of intact periodic water wires. In spite of remaining discrepancies, we argue that partially dissociated configurations are more likely to give rise to the experimental geometry.

Finally we considered vibrational quantum effects as zero point energy (ZPE) correction. ZPE is obtained by computing the vibrational frequency of the adsorbed species by finite differences. We found that the adsorption energy of water clusters and chains on Pt(211) surfaces decreases by  $\sim 0.1$  eV, whereas partial dissociated clusters are stabilized by up to  $\sim 0.2$  eV. These results are in agreement with other previous studies.<sup>21,23,24,26,50</sup>

### **3.3. Water clusters on other (211) surfaces**

We have also investigated the adsorption and dissociation of small water clusters (monomer to trimer) on (211) surfaces of Rh, Ir, and Pd. Our aim is to understand how the chemical reactivity of surfaces affects the water structures and their properties at surfaces.

We have first explored the most favorable adsorption geometry of a water monomer on these

transition metal surfaces. Three different initial geometries, i.e., water on step pointing to lower and upper terrace (step-LT and step-UT, respectively) and water on step edge (step-edge), have been relaxed. The most stable configuration is the step edge for all these three metals, different than the monomer adsorption site on Pt(211) (see Figure S9 in SI). The calculated adsorption energies are close to each other ( $\Delta E = 0.03\text{--}0.06$  eV) for each different configuration as tabulated in Table 3. The interaction of monomer with Ir and Rh is stronger than that of Pt and Pd, and the stability order is Ir > Rh > Pt > Pd, which is also supported by the trend found in the oxygen-metal distances. The same bonding order was also found for (221) surfaces.<sup>26</sup> A comparison of adsorption and dissociation energies between different surface types and metals is presented in Figure 5, Table 4 and Table S6. As can be noticed, the adsorption energy of monomer on (211) surfaces is smaller than those of (221) surfaces by 0.05-0.10 eV and larger by 0.08-0.24 eV for (111) surfaces. The details of the optimized structural parameters and energetics are given in Table S7 in SI.

The most stable dimer and trimer configurations obtained on Pt(211) surface have been used for the other metal surfaces, and the relaxed geometries are found to be similar to those on Pt(211). H-bond formation between adsorbed molecules increases the adsorption energy of dimer by about 0.14–0.60 eV compared to monomer on (211) surfaces. The calculated  $E_{ads}$  per water for dimers ranges from -0.47 eV for Pd to -0.62 eV for Ir. Further increasing the number of water molecules increases the adsorption energy of trimer by about 0.04 eV/H<sub>2</sub>O compared to dimers, and the  $E_{ads}$  ranges from -0.51 eV for Pd to -0.67 eV for Ir. The bonding order for dimers and trimers are the same as for the monomer case.

To understand in detail the cooperative effect of H-bonding and O-metal bonding, we have calculated the contribution of each type of bonding as summarized in SI, Table S8. As the cluster size increases, the contribution of H-bonding between adsorbed molecules ( $E^{ww}$ ) ranges from 41 to 72 meV/H<sub>2</sub>O for dimers and from 95 to 124 meV/H<sub>2</sub>O for trimers, similar to the (111) and (221) cases reported earlier.<sup>26</sup> Furthermore, the contribution of H-bonding between water molecules of chain configurations has significantly increased, while it is partially compensated by weaker O-

metal bonding.

The initial dissociated configurations of small water clusters on (211) surfaces of Ir, Rh and Pd have been taken from the most stable dissociated ones on Pt(211) surface. Since the adsorption site for H and OH have been investigated in details for Pt(211) surface, we have taken into account the same adsorption sites on (211) surfaces. The increased reactivity of (211) stepped surfaces facilitates the partial dissociation of water compared to flat (111) surfaces. The dissociation of a monomer on Pd(211) surface is endothermic, whereas the other metals exhibit exothermic dissociation energies. Thus, the energy required to break the O–H bond is compensated by the formation of stronger O–metal bonds for Ir, Rh and Pt surfaces. The dissociation energy order is Ir > Rh > Pt > Pd, which is the same with that of the adsorption energy.

The partial dissociation processes for dimer and trimer on metals are the same as Pt(211) surface, thus the optimized dissociated configurations are similar as presented in SI, Figure S10 and Figure S11. The distances between O–O are reduced by  $\sim 0.43$  and  $\sim 0.20$  Å compared to gas phase and intact dimer on surfaces, respectively. Furthermore, O–metal distances are significantly reduced as well. These clearly show that strong chemical bonds are formed not only between OH<sup>-</sup> and water molecule, but also between OH<sup>-</sup> and step edge atoms. Whereas, the dissociation of water dimer on Pd is still endothermic but decreased by 0.05 eV compared to monomer,  $E_{diss}$  on Pt is almost iso-energetic and the (211) surfaces of Ir and Rh present exothermic dissociation energies.

During the dissociation of one water molecule in trimers, proton transfer event occurs within the clusters as observed for (111) and (221) surfaces. The proton transfer process on the other transition metals is similar to Pt(211) case. The partially dissociated trimers on (211) surfaces have exothermic energies, leading to the conclusion that the energy required to break the O–H of the hydrogen bond acceptor has been completely compensated by the formation of OH<sup>-</sup>–metal, H<sup>+</sup>–metal and H–bond between OH<sup>-</sup>–H<sub>2</sub>O. These newly formed stronger bonds are evident from analyzing the distances between O–O (decreased by  $\sim 0.3$  Å), OH<sup>-</sup> and neighboring H<sub>2</sub>O (decreased by  $\sim 1.04$  Å), and O–metal which decrease up to 0.23 and 1.45 Å for central and acceptor molecules, respectively. Further details of the geometries are presented in Table 2.

To sum up, comparing the adsorption and dissociation energies of small water clusters on (211) surfaces to those of (111) and (221) surfaces reveals interesting results. In general, while adsorption is more favorable on (221) surfaces compared to (211) and (111) surfaces, the increased reactivity of the (211) stepped surfaces facilitates the dissociation of water clusters compared to (111) and (221) surfaces (see Figure 5). While the dissociation energies of (221) surfaces of Rh and Ir (group 9) and Pd and Pt (group 10) are very close to each other,  $E_{diss}$  of (211) surfaces are spread. The adsorption energies of different surface types are found to be in the same order for (211) and (221) surfaces, while the dissociation energies show different orders for different surface types.

#### 4. CONCLUSIONS

We have investigated the adsorption and dissociation of small water clusters and one-dimensional water chains on Pt(211) surface by means of density functional theory. The dynamics of one-dimensional water chains and protons have been also studied. For a broader picture, small water clusters on (211) surfaces of Ir, Rh and Pd have been considered and the calculated results have been compared to the energetics obtained for (111) and (221) surfaces.

Consistent with the experimental findings, water molecules prefer to sit on step edges of (211) surfaces rather than on terraces. The adsorption energy increases for (211) surface in the order Ir > Rh > Pt > Pd, which is the same as (221) surfaces. On the other hand, this order is reversed for (111) surfaces of Ir and Rh. For each surface type, increasing the number of water molecules enhances the adsorption energy due to stronger H-bonding. The increased reactivity of (211) surfaces together with the cooperative effect of H-bonding significantly facilitate the partial dissociation of water clusters and 1D water chains. The  $E_{diss}$  is either iso-energetic or clearly exothermic except for the monomer and dimer on Pd(211). Whereas the adsorption energies of small water clusters on (221) surfaces are higher than (111) and (211) surfaces, dissociation is significantly facilitated on (211) surfaces.

Our calculations predict that experimentally proposed one-dimensional water wires can be



formed on the step of Pt(211) surface as long as partial dissociation takes place within the chain. Stronger hydrogen bonding interactions among partially dissociated species induce shorter oxygen–oxygen distances and favor alignment at the step edge.

Due to the very low diffusion barrier of water molecules around the step and terrace, *ab initio* molecular dynamics simulations revealed an alternative cluster-like configuration for one-dimensional water chain. This structure formed between the step edge and the upper terrace of Pt(211) suggests that, depending on growth conditions and temperature, chains may break into clusters.

These results provide useful fundamental insight into water–metal interfaces involved in catalysis and photo-electrochemical cells, where transition metal surfaces are significantly important for different applications such as co-catalysts or electrodes. The discussions based on the effect of surface types and metals on the adsorption and dissociation properties of water shed light on the main understanding and importance of these applications.

## **Supporting Information**

Geometrical details of adsorbed and dissociated water clusters and 1D water chain on (211) metal surfaces. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

## **Acknowledgment**

We are grateful to Mariana Rossi (FHI, Berlin) for useful suggestions. We acknowledge the provision of computational facilities and support by Rechenzentrum Garching of the Max Planck Society and access to the supercomputer JUQUEEN at the Jülich Supercomputing Center under project HMZ33. This project is funded by the MPRG program of the Max Planck Society.

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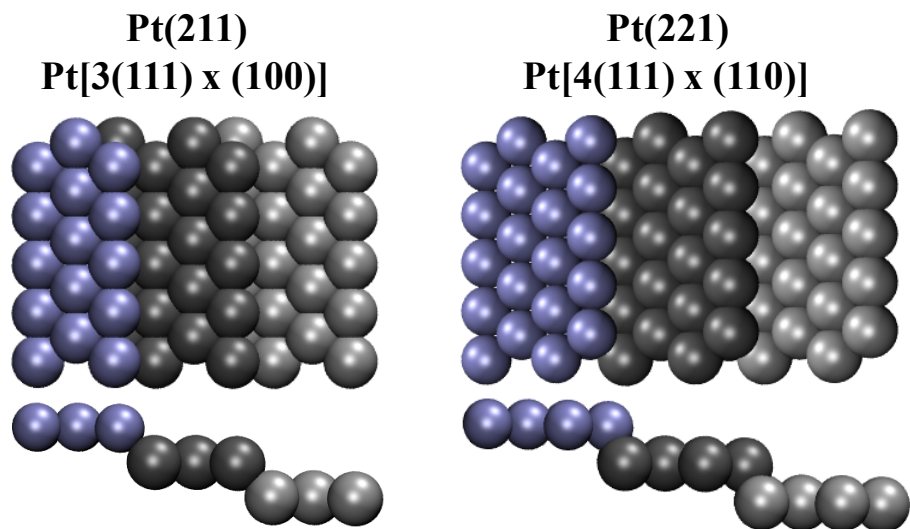


Figure 1: Schematic representations of the top and side views of clean Pt(211) and Pt(221) with (100) and (110) steps, respectively.

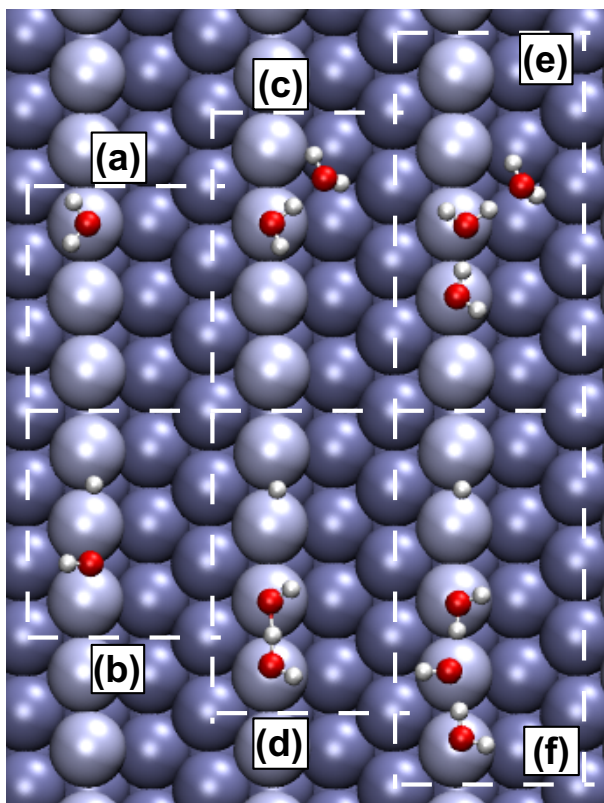


Figure 2: Relaxed geometries of intact (top panel) and dissociated (bottom panel) monomer (a and d), dimer (b and e) and trimer (c and f) on Pt(211) surfaces. The step edge atoms are shown with lighter color. The periodically replicated cells used in the calculations are represented by white dashed lines.



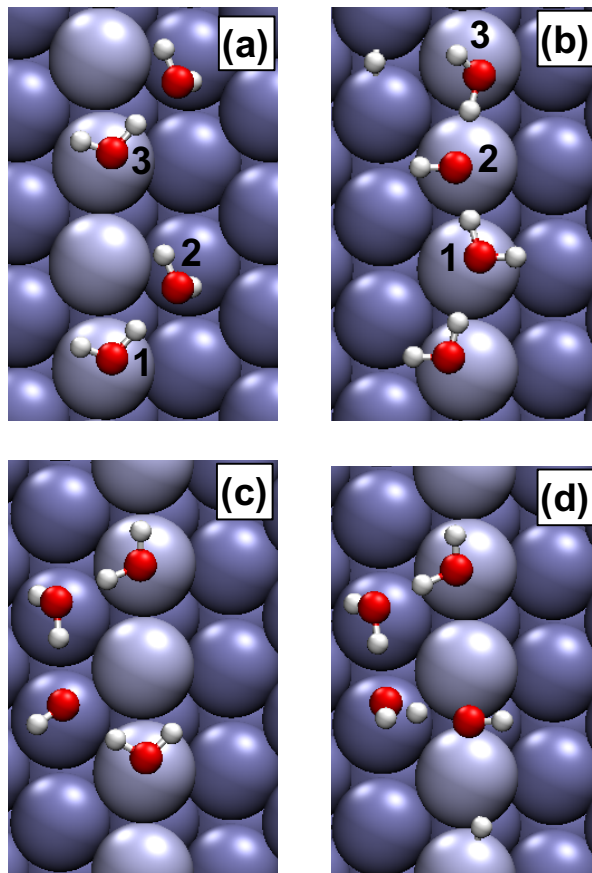


Figure 3: Relaxed geometries of intact (a and c) and dissociated (b and d) chain-4 calculated by static (upper panel) and BOMD (lower panel) methods on Pt(211) surface. The step edge atoms are shown with lighter color.

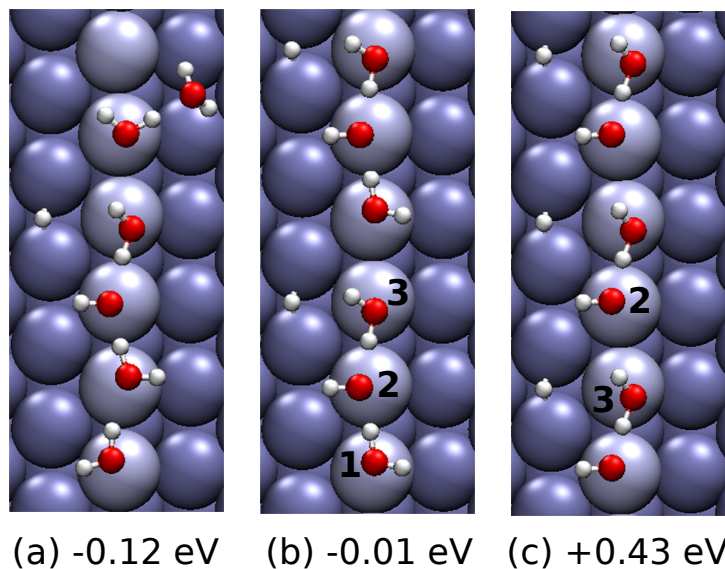


Figure 4: The configurations of chain-6 when one (a), two (b) and three (c) out of six molecules are dissociated. The dissociation energies are given.

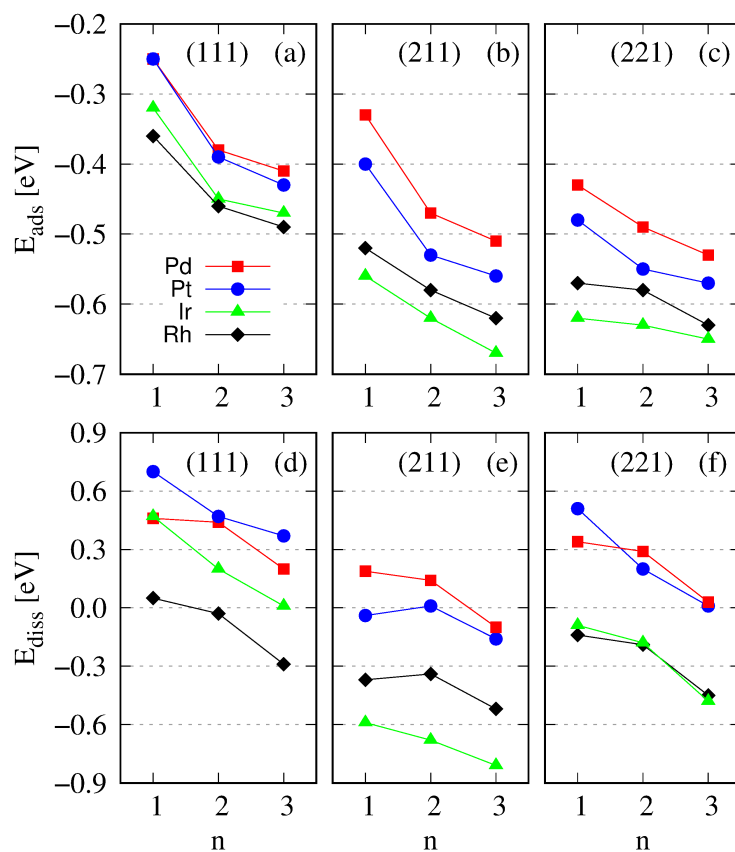


Figure 5: Adsorption (upper panel) and dissociation (lower panel) energies of water clusters for (a and d) (111), (b and e) (211), and (c and f) (221) surfaces of Pd, Pt, Ir and Rh as a function of number of water molecules ( $n$ ).

Table 1: Adsorption and dissociation energies of water clusters and periodic chains at Pt(211). Energies obtained with the optB88 vdW functional are given in parentheses.

Configuration	Figure	$E_{ads}$ [eV/H <sub>2</sub> O]	$E_{diss}$ [eV]
monomer	2(a,b)	-0.40 (-0.55)	+0.014 (+0.009)
dimer	2(c,d)	-0.53 (-0.66)	+0.007 (-0.013)
trimer	2(e,f)	-0.55 (-0.69)	-0.15 (-0.12)
chain-4	3(a,b)	-0.51	+0.064
chain-4	3(c,d)	-0.51	+0.011
chain-6	S7(b),4(a)	-0.50	-0.12

Table 2: Structural parameters of intact chain-4 and single and multiple proton dissociated chain-4 and chain-6 configurations. Indexes used for oxygen atoms are shown in Figure 3 and Figure 4.  $d[\text{O}_1\text{-O}_2]$  and  $d[\text{O}_2\text{-O}_3]$  are the distances between alternating oxygen atoms and  $\Delta[\text{O-O}]$  is the difference between the positions of the oxygen atoms along the step.  $\Theta[\text{O}_1\text{O}_2\text{O}_3]$  is the angle between the oxygen atoms. Distances are in Å.

System	Figure	$d[\text{Pt-O}_1]$	$d[\text{Pt-O}_2]$	$d[\text{Pt-O}_3]$	$d[\text{O}_1\text{-O}_2]/d[\text{O}_2\text{-O}_3]$	$\Delta[\text{O-O}]$	$\Theta[\text{O}_1\text{O}_2\text{O}_3]$
chain4	3(a)	2.26	3.28	2.26	2.66/4.13	1.81	111
H-chain4	3(b)	2.32	2.16	2.23	2.56/2.62	0.66	150
2H-chain6	4(b)	2.23	2.15	2.23	2.58/2.61	0.50	149
3H-chain6	4(c)	-	2.09	2.15	2.51/3.34	0.72	151
Expt. <sup>18</sup>	3(b) in Ref. [18]	2.25	-	2.64	2.82	0.51	159

Table 3: Calculated adsorption energies [in eV/H<sub>2</sub>O] of water monomers at (211) surfaces.

Configuration	Ir(211)	Rh(211)	Pt(211)	Pd(211)
step-LT	-0.52	-0.46	-0.37	-0.31
step-UT	-0.54	-0.46	<b>-0.40</b>	-0.33
step-edge	<b>-0.56</b>	<b>-0.52</b>	-0.34	<b>-0.34</b>

Table 4: Calculated adsorption energy per water molecule ( $E_{ads}$ ) and dissociation energies for water clusters on (211) surfaces.

surface	cluster	$E_{ads}$ [eV/H <sub>2</sub> O]	$E_{diss}$ [eV]
Ir(211)	1H <sub>2</sub> O	-0.56	-0.59
	2H <sub>2</sub> O	-0.62	-0.68
	3H <sub>2</sub> O	-0.67	-0.81
Rh(211)	1H <sub>2</sub> O	-0.52	-0.37
	2H <sub>2</sub> O	-0.58	-0.34
	3H <sub>2</sub> O	-0.62	-0.52
Pt(211)	1H <sub>2</sub> O	-0.40	-0.04
	2H <sub>2</sub> O	-0.53	0.01
	3H <sub>2</sub> O	-0.56	-0.15
Pd(211)	1H <sub>2</sub> O	-0.34	0.19
	2H <sub>2</sub> O	-0.47	0.14
	3H <sub>2</sub> O	-0.51	-0.10

# Graphical TOC Entry

