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Trends in the Adsorption and Dissociation of Water Clusters on Flat and Stepped Metallic Surfaces

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Abstract

Understanding the structure and the chemical reactivity of water adsorbed at metallic surfaces is of central importance in a variety of processes such as catalysis, corrosion, and electrochemistry. Using density functional theory calculations, we investigate the adsorption and dissociation of water clusters on flat and stepped surfaces of several transition metals: Rh, Ir, Pd, and Pt. We find that water binds preferentially to the step edges than to terrace sites, so that linear clusters or one-dimensional water wires can be isolated by differential desorption. The clusters formed at the step are stabilized by the cooperative effect of chemical bonds with the metal and hydrogen bonding. The enhanced reactivity of the step edges and the cooperative effect of hydrogen bonding **improve** the chances of partial dissociation of water clusters. We also assess the correlations between adsorption and dissociation energies, observing that they

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are **enhance** on stepped surfaces, and we present a detailed interpretation of water dissociation by analyzing changes in the electronic structure of both water and metals. The identification of trends in the energetics of water dissociation at transition metals is expected to aid the design of **better** materials for catalysis and fuel cells, in which the density of steps at surfaces would be a relevant additional parameter.

Keywords: Water/metal interface; Density functional theory calculations; Scaling relation; d-band model; Zero-point energy correction

1. INTRODUCTION

The interaction of water with transition metal surfaces plays a fundamental role in several chemical processes, such as catalytic surface reactions, corrosion, fuel cells and hydrogen production.^{1,2} These processes often include the formation and/or dissociation of water on metallic substrates. The adsorption of water on metal surfaces, often considered as a prototype system to understand more complicated water-solid interfaces, has been extensively investigated both experimentally and theoretically.³⁻⁶ With the help of scanning probe microscopy and theoretical calculations, mostly at the level of density functional theory (DFT), it has been possible to get local images and to characterize the adsorption of water on metals.⁷⁻⁹ These scanning probe techniques are mostly viable for well-defined low-index surfaces of single crystals, at low temperature, low coverage and ultra-high vacuum conditions. Changes in coverage and thermodynamic conditions result in water structures with different dimensionality, ranging from isolated monomers to one-dimensional (1D) chains, 2D layers and 3D structures.⁹⁻¹⁴ In addition, it is difficult to assess the protonation state of interfacial water by scanning probe microscopy, so that understanding the water-metal interfaces at the atomistic level remains a challenging open problem.

The effect of surface structure on catalytic reactions plays an important role to design efficient catalysts.¹⁵⁻¹⁷ Although the adsorption of water on flat and defect-free surfaces has been extensively studied, the chemistry of water at high index vicinal surfaces, occurring in realistic situations, is largely unexplored. Only recently, under the motivation of experimental findings,^{7,10,18-20}

theoretical studies have started to examine defect sites, such as steps and kinks, on the adsorption of water.^{21–28} The contribution of surface defects to adsorption and dissociation energies is significant since these sites are usually more reactive than closed-packed surfaces. For example, the presence of steps and kinks is known to reduce the reaction barriers for water dissociation and hydrogen recombination on Cu surfaces.¹⁵

Considering the large number of potentially interesting systems for different applications and that both experiments and theoretical calculations are feasible for a limited number of systems, it is crucial to identify trends that may aid the search for materials with targeted functionalities.²⁹ So-called "scaling relations",³⁰ which correlate different adsorption energies, have been used to demonstrate trends in catalytic systems. For example, using the adsorption energies of C, N, O, and S on stepped and close-packed metal surfaces,^{30,31} and OH on oxide surfaces³² the potential energy diagram for a surface catalyzed reaction was estimated. Other studies showed that the binding energy of methyl^{33,34} on metal surfaces can be used as a descriptor for a DFT-based catalyst design.

In this paper, we investigate the adsorption and dissociation energies and geometries of small water clusters - from monomers to trimers - on close-packed (111) and higher-index (211) surfaces of Rhodium, Iridium, Palladium and Platinum, by means of DFT calculations, **including zero-point energy (ZPE) corrections**. The trends among different adsorption energies, and adsorption and dissociation energies are analyzed to obtain a general understanding of water activity on flat (111) and stepped (211) transition metal surfaces. We examine the cooperative effect of hydrogen bonding (HB) between water molecules and surface bonding, which stabilizes the adsorption and dissociation states on both surfaces. This analysis reveals that the increased reactivity of atoms at the edge of steps enhances the adsorption energies of intact clusters. Moreover, the cooperative effect of hydrogen bonding increases the chance of partial dissociation of water clusters at steps. In addition to the scaling relations between different adsorption energies, we also show that the dissociation energies of water clusters on metallic surfaces correlate positively with the adsorption energies.

2. METHODS

First principles total energy calculations within the density functional theory were performed to investigate the adsorption and dissociation properties of water clusters (monomer to trimer) on (111) and (221) surfaces of Rh, Ir, Pt and Pd. Ultrasoft pseudopotentials (USPP)³⁵ were used to describe the interactions between ions and electrons. A plane wave basis set with a cutoff energy of 35 (for Rh and Pt), 40 (for Ir) and 45 (for Pd) Ry was employed. We employed the exchange and correlation functional by Perdew, Burke and Ernzerhof (PBE)³⁶ The integration over the first Brillouin zone was performed using Monkhorst-Pack³⁷ k -point meshes of $4 \times 3 \times 1$ for the (221) slabs with 4×1 periodicities and similar meshes of $4 \times 4 \times 1$ were used for (111) slabs and (221) slabs with 3×1 periodicities. The Methfessel-Paxton approach³⁸ with a Gaussian broadening of 0.27 eV was used to smear the electronic occupation at the Fermi level. The convergence threshold on forces for ionic relaxations was set to 10^{-3} atomic units (a.u.). Several tests have been performed to verify the convergence of results.³⁹ The calculations were carried out using the Quantum-ESPRESSO package.⁴⁰

The chosen PBE functional has proven good accuracy in describing H-bonding in ice⁴¹ as well as the structure and energetics of small water clusters.⁴²⁻⁴⁴ The adsorption energies of water monomers on flat Pd and Pt surfaces are instead systematically underestimated compared to experiments (0.25 vs 0.45 eV),^{45,46} and no experimental data is available for Rh and Ir. Considering explicitly van der Waals (vdW) interactions would substantially contribute to the adsorption energies of water on metals. However, it was recently shown that accounting for dispersion forces would not change either relative binding energies or adsorption geometries, and therefore would not affect the observed trends.⁴⁷

The calculated lattice constants of bulk Pd, Pt, Ir, and Rh are 3.98, 4.01, 3.89, and 3.86 Å, respectively: all within 1.5-2.3% of the experimental value of 3.89, 3.92, 3.84, and 3.80 Å.^{48,49} The supercells used for the (111) surfaces were $(4 \times 2\sqrt{3})$ for all calculations with a total of 48 metal atoms. The stepped (221) surfaces were cut from bulk metal supercells with the terraces having

a (111) orientation and the monatomic (110) steps are separated by four atomic rows. p(3x1) supercells (42 metal atoms) were used to study monomers and dimers on stepped surfaces, while larger supercells, p(4x1) (56 metal atoms) were used for trimers. The surfaces were modeled by four layers of metals and the vacuum space was set to 20 Å. The two bottom layers were fixed and the rest of the system was relaxed.

The ZPE of the vibrational modes induces significant shifts in both binding and dissociation energies:^{26,50,51} for example the inclusion of ZPE correction has been shown to decrease the adsorption energy of water clusters on flat and stepped Pt surfaces by ~ 0.1 eV.^{21,50} Thus, we computed the vibrational frequencies of the adsorbed and dissociated systems to take into account quantum effects in terms of ZPE. The vibrational analysis is carried out using the frozen phonon approach, in which the force constant matrix of the adsorbate is computed by finite differences of the forces. We use a finite displacement of the atoms of 0.01 Å. The ZPE corrections to the adsorption and dissociation energies are expressed as $\Delta E_{ZPE} = \sum_i \hbar \Delta \omega_i / 2$, where the sum runs over the vibrational modes of the molecules adsorbed on the surface. $\Delta \omega$ indicates the difference between the vibrational frequencies either of water in gas phase and adsorbed at the surface, or of intact and dissociated adsorbates. All reported **adsorption and** dissociation energies take into account the ZPE correction, unless otherwise noted.

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

$$E_{\text{ads}} = (E[(H_2O)_n@M] - n \cdot E[H_2O] - E[M]) / n \quad (1)$$

where n is the number of water molecules in the simulation cell, $E[(H_2O)_n@M]$ is the total energy of the metal surface (M) with the adsorbed molecule, $E[H_2O]$ is the energy of a single water molecule in gas phase, and $E[M]$ is the energy of the bare metal surface. **Consequently, a negative adsorption energy means energetically favored adsorption.**

The dissociation energy, E_{diss} , is calculated as the total energy difference between the dissoci-

ated structure and the intact one, such as:

$$E_{\text{diss}} = E[(H_2O)_{(n-1)} + OH^- + H^+]@M - E[(H_2O)_n@M] \quad (2)$$

where negative E_{diss} indicates exothermic dissociation.

We tested the dissociation energy of water monomer on Ir surfaces with different exchange-correlation functionals (PBE, PBEsol^{52,53} and PW91⁵⁴) and pseudopotentials (USPP, Troullier-Martins (TM)⁵⁵ and Projector Augmented Wave (PAW)^{56,57}). The E_{diss} calculated with different density functionals ranges from 0.23 to 0.47 eV for Ir(111) and -0.09 to -0.19 eV for Ir(221). For more details see the Table S1 in Supporting Information(SI).

3. RESULTS

In this section we first present the adsorption and dissociation energetics and structure of water clusters, including monomers, dimers and trimers, on (111) metal surfaces. The following part of this study is extended to (221) metal surfaces and the adsorption and dissociation of clusters are explored. Then, the trends in the adsorption and dissociation energies of water clusters on different metals and surface types are discussed. The electronic structure calculations are discussed in Section 3.5.

3.1 Adsorption of Water Clusters on (111) Surfaces

We have first investigated the adsorption of a water monomer on flat Rh, Ir, Pt, and Pd surfaces. We have found that the most favorable adsorption site with the PBE functional is atop (Figure 1(a)), consistent with previous studies.^{5,21,58–61} The plane containing the dipoles of monomers adsorbed on (111) surfaces is tilted with respect to the surface because of the directional interaction of $1b_1$ molecular orbital of water with the metal. The adsorption energies of water monomers on flat surfaces are summarized in Table 1. The interaction of water monomers with Rh and Ir is

Table 1: Calculated adsorption energy per water molecule with ($E_{\text{ads}}^{\text{ZPE}}$) and without (E_{ads}), and dissociation energies with ($E_{\text{diss}}^{\text{ZPE}}$) and without (E_{diss}) zero-point energy corrections for water clusters on (111) surfaces. The adsorption energies of ring-like configurations are presented in parenthesis for trimers.

Surface	Cluster	E_{ads} [eV/H ₂ O]	$E_{\text{ads}}^{\text{ZPE}}$ [eV/H ₂ O]	E_{diss} [eV]	$E_{\text{diss}}^{\text{ZPE}}$ [eV]
Rh(111)	1H ₂ O	-0.36	-0.30	0.05	-0.11
	2H ₂ O	-0.46	-0.38	-0.03	-0.22
	3H ₂ O	-0.49(-0.46)	-0.41	-0.29	-0.43
Ir(111)	1H ₂ O	-0.32	-0.25	0.47	0.30
	2H ₂ O	-0.45	-0.37	0.20	0.01
	3H ₂ O	-0.47(-0.43)	-0.40	0.01	-0.12
Pt(111)	1H ₂ O	-0.25	-0.20	0.70	0.53
	2H ₂ O	-0.39	-0.31	0.47	0.27
	3H ₂ O	-0.43(-0.28)	-0.37	0.37	0.24
Pd(111)	1H ₂ O	-0.25	-0.20	0.46	0.31
	2H ₂ O	-0.38	-0.31	0.44	0.28
	3H ₂ O	-0.41(-0.40)	-0.36	0.20	0.02

stronger than that with Pt and Pd, yielding a stability order Rh > Ir > Pt > Pd. Even though the present computational framework is different the results are in good agreement with those of several previous studies^{21,47,50,59–64} (Table S2). The details of the optimized structural parameters are collected in Table S3.

The water dimer on metal surfaces is the simplest H-bonded water system on surfaces. Since H-bonding between water molecules and water-metal interaction take place at the same time, water dimers on metallic substrates reveal important information on the cooperative effect of these two interactions. As shown in Figure 1(b) both proton donor (D) and acceptor (A)* prefer atop sites on all the surfaces considered. On the other hand, the O-metal distance is very different for the H-bond donor (2.22-2.30 Å) with respect to the acceptor (3.01-3.20 Å), indicating much weaker surface-water interaction for the latter. Compared to their gas-phase counterparts the distance between the oxygen atoms of the adsorbed dimer significantly decreases by 0.18 Å and the O-H bond length of donor increases slightly by 0.02 Å pointing out that the H-bonding in adsorbed dimer is enhanced. The reason is that the dipole moment of the donor is increased by polarization effects

*The molecule donating its hydrogen atom in the H-bond is called "donor" and the other one accepting the hydrogen atom in the H-bond is called "acceptor".

induced by the metal surface.¹⁴

The presence of a second water molecule, resulting in the formation of a H-bond between adsorbed molecules, increases the adsorption energy per molecule by about 0.13 eV compared to the monomer (see Table 1). The stability order is the same as for the monomer case with the adsorption energies ranging from -0.38 (for Rh) to -0.31 eV (for Pd), respectively. The cooperative effect between the H-bonding and O-metal bonding can be better understood by separating the adsorption energy into hydrogen bonding (E^{ww}) and O-metal interactions (see [section 4 in SI and Table S4](#)). The contribution of hydrogen bonding to the adsorption energy per water molecule goes from 53 to 78 meV, and as the clusters increase in size E^{ww} increases.

Further increasing the number of water molecules results in different possible configurations with competing binding energies. For example, Meng et al.⁵⁹ claimed that trimers adsorbed on Pt(111) surface would retain a ring-like geometries with one OH contributing to the H-bonding and the other free for each water molecules so each of them behave as donor-acceptor. Thus, we have investigated two different adsorption configurations, ring- and chain-like, on the metal surfaces (see Figure S1). We have found that the chain-like structure is slightly more favorable, as the system prefers to form linear hydrogen bonds than very distorted ones, as in the case of rings. In addition, the chain-like structure favors stronger water-metal interactions, especially for the H-bond donor (see Table S5).

The adsorption energy of trimers increases by 0.03 eV/H₂O compared to dimers. This small energy gain can be explained by the increased number of H-bonds formed between water molecules, which is partly compensated by the weaker H-bond formed between the acceptor/surface and central/surface. The O-metal and H-bond contributions to the adsorption energy of each system is summarized in Table S3. The wetting order is the same as for the monomer and dimer cases, with the adsorption energy ranging from -0.41 (for Rh) to -0.36 eV (for Pd).

3.2 Adsorption of Water Clusters on (221) Surfaces

The adsorption energies of monomers on stepped surfaces are significantly larger than on flat

surfaces - by 0.17-0.30 eV - in good agreement with the previous calculations,^{21,65} due to the increased reactivity of step edges (see Table 2). Water monomers prefer to sit at atop sites at the step edge rather than at kinks or on terraces (see Figure 2(a)). The distance between the O atom and the closest metal atom ranges from 2.27 (for Rh) to 2.35 Å (for Pd), and H atoms are tilted towards the lower terrace. The O-metal distances are shorter than those of flat surfaces by 0.06 Å, indicating stronger chemical bonding.

While a good matching of hydrogen bonding distance to the nearest neighbor distance of the metal atoms of the step edge (2.8 Å) may facilitate adsorption, in the case of dimers only the HB donor binds strongly to the metal. The HB acceptor sits farther from the step edge and forms a weak H-bond with the lower terrace of the metals (see Figure 2(b)). H-bonding makes the binding of dimers only slightly stronger than that of monomers. These small energies gained for dimers, 0.01 eV for Rh and Ir, and 0.06 eV for Pt and Pd compared to monomers, can be explained by analyzing their relaxed geometries in detail. The oxygen atom of the H-bond donor is bonded to the step atoms of Rh and Ir (Pt and Pd) with O-metal distances of 2.19(2.23) Å, whereas the acceptor is farther from the step with O-metal distances of 3.62(3.38) Å (Table S6). The interaction between H-bond acceptor and the step atoms of group IX elements significantly weakens compared to that for group X elements, thus the energy gained by the formation of a H-bond between molecules is compensated by the weaker O-metal interaction.

The addition of another water molecule causes further increase in the adsorption energies with respect to dimers. These small energies gained in trimers are the result of increasing the number of H-bonds in clusters, which are partly compensated by a weaker attraction between the molecules and the metal. The adsorbed configurations of trimers on metal stepped surfaces display two of the water molecules (donor and central) bonded atop on the step edges and a H-bond acceptor detached from the step (Figure 2(c)). The hydrogen atoms of the attached molecules are in alternating directions and one of the hydrogen atoms of the acceptor points towards the lower terrace. The calculated equilibrium O-metal distances and other geometrical details are presented in Table S6. Other possible trimer configurations on Pt(221) were suggested,^{21,26} however these

row-like configurations are less stable by 0.08 eV than the one proposed here (see Table S5 and Figure S1(e)).

3.3 Dissociation of water clusters on (111) surfaces

We have investigated the dissociation of one water molecule for each $n\text{H}_2\text{O}$ clusters with the resulting intermediates being $\text{H}^+ + \text{OH}^- + (n-1)\text{H}_2\text{O}$, on metal surfaces. The calculated adsorption sites for the dissociation of water monomers are in agreement with those suggested for OH adsorption in former theoretical studies.^{50,62,63} The hydroxyl radical is adsorbed on a bridge site for all metals (see Figure 1(d) for a monomer dissociation on a metal surface), while the dissociated proton sits on an fcc-hollow site.⁶⁴ Further details on the structural parameters of the dissociation are reported in Table S7.

The dissociation energies with ($E_{\text{diss}}^{\text{ZPE}}$) and without (E_{diss}) ZPE correction are collected in Table 1 and shown in Figure 3. The E_{diss} on flat Pt, Ir, and Rh surfaces are in good agreement with the previously reported dissociation energies.^{50,61} Small differences with respect to former studies arise (about 0.07 eV) due to the different simulation setup chosen, among which are coverage, exchange correlation functional, and pseudopotentials. ZPE correction stabilizes E_{diss} by 0.15–0.17 eV and leads to exothermic dissociation on Rh surface.

Due to the adsorption configurations of water dimers and trimers, discussed in the previous section, the hydrogen of the HB acceptor pointing towards the metal surface offers the easiest path for partial dissociation. The dissociated dimer and trimer configurations are presented in Figure 1(e) and (f), respectively. Due to the structural rearrangements between O-O and O-metal, breaking an O-H bond costs less energy than splitting monomers. For example, $E_{\text{diss}}^{\text{ZPE}}$ of the dimer decreases by 0.29 eV for Ir(111) with respect to the monomer and is nearly iso-energetic ($E_{\text{diss}}^{\text{ZPE}}=0.01$ eV) (see Table 1). Upon splitting of a water molecule, the $\text{OH}^- - \text{H}_2\text{O}$ interaction gets stronger with O-O bond length decreasing by 0.22 Å for dimers compared to the intact dimer cases.

In the case of trimer, breaking the O-H bond of the HB acceptor results in a proton transfer mechanism, which leads to a stable configuration (Figure 1(f)). The remaining OH^- is the central molecule of the cluster which accepts hydrogen bonds from both neighboring water molecules. The

water-metal interaction and hydrogen bonding between water molecules are stronger in the dissociated geometries. These tighter interactions cooperate to compensate the energy loss from splitting the O-H covalent bond, thus making dissociation possible. Moreover, ZPE correction stabilizes further dissociated species on surfaces. For instance, the partial dissociation of trimer turns from iso-energetic to exothermic on Ir surface and from endothermic to almost iso-energetic on Pd surface.

Table 2: Calculated adsorption energy per water molecule with ($E_{\text{ads}}^{\text{ZPE}}$) and without (E_{ads}), and dissociation energies with ($E_{\text{diss}}^{\text{ZPE}}$) and without (E_{diss}) zero-point energy corrections for water clusters on (221) surfaces.

Surface	Cluster	E_{ads} [eV/H ₂ O]	$E_{\text{ads}}^{\text{ZPE}}$ [eV/H ₂ O]	E_{diss} [eV]	$E_{\text{diss}}^{\text{ZPE}}$ [eV]
Rh(221)	1H ₂ O	-0.57	-0.51	-0.14	-0.30
	2H ₂ O	-0.58	-0.52	-0.19	-0.35
	3H ₂ O	-0.63	-0.56	-0.45	-0.57
Ir(221)	1H ₂ O	-0.62	-0.55	-0.09	-0.24
	2H ₂ O	-0.63	-0.56	-0.18	-0.36
	3H ₂ O	-0.65	-0.58	-0.48	-0.60
Pt(221)	1H ₂ O	-0.48	-0.43	0.51	0.33
	2H ₂ O	-0.55	-0.49	0.20	0.00
	3H ₂ O	-0.57	-0.53	0.01	-0.12
Pd(221)	1H ₂ O	-0.43	-0.37	0.34	0.19
	2H ₂ O	-0.49	-0.43	0.29	0.15
	3H ₂ O	-0.53	-0.47	0.03	-0.08

3.4 Dissociation of Water Clusters on (221) Surfaces

The products of the dissociation of a water monomer, OH⁻ and H⁺, adsorb on bridge position at the step edge and on hollow terrace site, respectively. When a water monomer is dissociated on a (221) surface the OH⁻ adsorbs on bridge position at the step edge, and the H⁺ adsorbs on the terrace. The distance between the hydroxyl and the closest step atom is about 2.1 Å. The structural parameters are given in Table S8. The most favorable adsorption site for the dissociated proton was previously investigated for Pt(221) and it was reported that the fcc-hollow site adjacent to the step edge was energetically the most favorable.²⁶ We explored the adsorption energy of an atomic hydrogen on Rh(221) surface taking into account different adsorption sites and we found that the preferred adsorption site is again the fcc-hollow. Thus, we assume the same proton adsorption site

also for Pd and Ir.

The increased reactivity of the metal atoms at the step edge facilitates the dissociation of water monomer compared to flat surfaces by 0.19 for Rh, 0.54 for Ir, 0.20 for Pt, and 0.12 eV for Pd (see Table 2). Similar to the case of flat surfaces, the dissociation of a monomer is endothermic on Pt and Pd stepped surfaces, while it turns from endothermic to exothermic on Ir and is exothermic on both flat and stepped Rh surfaces. The energy required to break a covalent O-H bond is partially compensated by the formation of a stronger O-metal bond: the balance between these two energetics decides on the character of dissociation.

In the dimer, the H-down molecule, already detached from the step edge, facilitates its partial dissociation. The optimal configurations with oxygen atoms bonded to atoms at the step edge and the geometry of dissociated dimer on (221) surface is presented in Figure 2(e). The distances between the oxygen atoms are reduced by ~ 0.2 Å compared to the intact dimers, showing that stronger chemical bonds are formed not only between the hydroxyl and step edge atoms but also between the hydroxyl and the neighboring water molecules. The energy required to break an O-H bond is compensated by the formation of new OH-metal bond, the adsorption of proton, and by a stronger H-bond between water and hydroxyl. The dissociation of water dimers is exothermic on Rh(221) and Ir(221), iso-energetic on Pt(221), and endothermic on Pd(221) yet with a reduced energy cost.

The dissociation of one water molecule in trimers takes place in a similar way to dimers, i.e., the detached H-bond acceptor releases the H atom initially pointing towards the lower terrace and adsorbed on the lower terrace. The interesting part in the dissociation process is the proton transfer occurring within the clusters. The relaxed geometry, displayed in Figure 2(f), shows that the central water molecule is responsible for the proton transfer mechanism by giving its H atom to the dissociated one and accepting hydrogen bonds from the neighboring molecules. The distances among neighboring water molecules and with the step edge atoms are smaller than the intact trimer. This leads to the conclusion that water-water and water-metal interactions are stronger than those for intact trimers. The partially dissociated configurations of water on group IX and group X stepped

surfaces are energetically more favorable than their intact geometries by about 0.58 and 0.10 eV, respectively.

3.5 Projected Density of States

To shed light on the bonding between water clusters and metal surfaces, we have calculated the density of states (DOS) of the molecules and surfaces. The surfaces of Rh and Ir show a much higher DOS distribution near the Fermi level than those of Pt and Pd, which makes them more reactive. The empty/filled electronic states near the Fermi level can accept/donate more electrons to enhance the reduction/oxidation reactions.

The DOS projected on the atomic orbitals of the oxygen p -states and metal d -states are computed for both intact and dissociated clusters on flat and stepped surfaces. Since the general behavior is similar among the different metals considered here, only the projected DOS (pDOS) for Ir(111) and Ir(221) surfaces are shown in Figure 4 and the pDOS of the other systems are displayed in Figures S3-S6. The deep $2a_1$ and $1b_2$ molecular orbitals of water lie far below the Fermi level (about 22 and 10 eV, respectively), and thus they interact very weakly with the metal states and are not shown in the pDOS. The $1b_1$ and $3a_1$ states are shifted down in energy with respect to their free molecular states and the $1b_1$ state hybridizes with the d -states of the substrates showing covalent bond behavior.

The oxygen-related p -states of all the intact clusters are well localized. For the donor molecule, which is closer to the surface than the acceptor and the central molecule, the O p -states are broadened. On the stepped surfaces, since the adsorption is stronger, the O p -states of the donor molecules are more broadened than those on flat surfaces. There is no significant difference between the p -state of the acceptor molecule of dimer on flat and stepped surfaces since their adsorption geometrical are similar on both surfaces. On the other hand, the O p -states of the central molecule in trimer differ significantly between flat and stepped surfaces. On the flat surface the bonding between the central molecule and the surface is as weak as it is for the acceptor molecule, while on the step edge the central molecule is closer to the surface and has a stronger interaction

with the step edge atoms leading to more broadening. Dissociation leads to significant distortions of the O p -states, and a strong hybridization between the molecular and surface states takes place. All of the p -states are broadened and hybridize with the d -states of the metal.

4. DISCUSSION

From the collection of data presented above, we can now identify trends that may contribute to the general understanding of the chemistry of water at transition metal surfaces. Both the adsorption and the dissociation of water clusters are related to the reactivity of the metallic surfaces. We then argue that there can be a relation between adsorption and partial dissociation energies of water clusters on flat and stepped surfaces (Figure 5). Atoms at steps have different coordination, which leads to different electronic properties. The electron density at low coordinated step edges is smoothed, i.e., electrons move from step edge toward the lower terrace so that their kinetic energy is lowered.⁶⁶ This smoothing induces a charge dipole that interacts with the local charges of adsorbed molecules, thus increasing the reactivity of the steps. The higher reactivity at step sites not only enhances the adsorption energy of water clusters but it also facilitates their partial dissociation. The stepped surfaces augment the adsorption energy of water clusters by 0.11-0.23 eV and favor dissociation by 0.10-0.54 eV. While flat surfaces show a single trend on the adsorption versus dissociation energies, the elements of period V and VI for stepped surfaces display different trends due to the enhanced atomic character of the low-coordinated step atoms (see Figure 5).

The scaling relations, also known as "corollary d-band model", relate the adsorption energy of any hydrogen containing molecule, AH_x , with the adsorption energy of its heavy atom, A .³⁰ Since the adsorption energies of O and OH are strongly correlated,⁶⁷ the scaling relation holds between the adsorption energy of OH^{65,68-72} and adsorption and dissociation of water clusters. Here we probe the scaling relations for the adsorption of water clusters and we extend them showing that also the dissociation energies correlate linearly with the adsorption energy of hydroxyl.⁷³

Figure 6 illustrates the scaling relations of the adsorption and dissociation energies of nH_2O

with the adsorption energy of OH. In general, the scaling behavior of each data set (from monomer to trimer) has very similar linear relations for adsorption and dissociation energies. The scatter around the linear relations can be attributed to the differences in surface geometries and thus leading to different adsorption energies. For instance, the adsorption energy of hydroxyl on different metals varies by 0.5 eV from flat to stepped surfaces. Figure 6(a) shows that increasing the number of water molecules does not have a significant effect on the scaling relations, with slopes very close to each other, for different surface geometries (see Figure S2). The adsorption energy of hydroxyl, which is an indicator of the energetics of the dissociation of water, enhances the differences in reactivity of stepped surfaces between group IX and X elements. This analysis shows that the propensity of water clusters to dissociate is mostly determined by the adsorption energy of the single hydroxyl, and that hydrogen bonding contributes to stabilize the dissociated phase with a nearly rigid shift towards lower energies of the $E_{\text{diss}}^{\text{ZPE}}$ vs. E_{ads} linear fit.

CONCLUSION

In summary, the interaction of adsorbed and dissociated water clusters with flat and stepped metallic surfaces has been systematically investigated in detail by means of density functional theory calculations. Our results confirm that water molecules prefer to adsorb at the edge of steps rather than at terraces. The wetting order of the water clusters on flat and stepped surfaces is found as $\text{Rh} > \text{Ir} > \text{Pt} > \text{Pd}$ and $\text{Ir} > \text{Rh} > \text{Pt} > \text{Pd}$, respectively. Increasing the number of water clusters results in stronger adsorption due to H-bonding. The increased reactivity of low coordinated stepped surfaces and the cooperative effect of H-bonding facilitate the dissociation of water clusters on stepped surfaces. For instance, while only the water dimer and trimer could dissociate on Rh(111), the dissociation energy of all the clusters is exothermic on stepped Rh and Ir surfaces and dissociation of trimers on stepped Pt and Pd surfaces turns to almost iso-energetic. Quantum effects, accounted for as ZPE correction, favor dissociation and systematically shift E_{diss} by ~ 0.2 eV.

Scaling relations, among the adsorption energy of hydroxyl and the adsorption and dissociation energy of water clusters, suggest that the adsorption energy of OH^- is what mainly determines the energetics of water splitting, followed by the cooperative effect of hydrogen bonds in stabilizing partially dissociated clusters. This effect is magnified at steps which also enhances the differences in reactivity between group IX and group X transition metals.

The shift in the energetics of water dissociation at steps is expected to play a prominent role in catalysis and fuel cells reactions, as the density of steps at surfaces could be an additional parameter to design more efficient anode materials or catalytic substrates. We hope that the trends presented here will contribute to understand and develop specific types of catalysts and reactions.

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Supporting Information Available

Geometrical details of adsorbed and dissociated water clusters on (111) and (221) metal surfaces. Water-water and water-metal interaction energies. pDOS of the systems. This information is available free of charge via the Internet at <http://pubs.acs.org/>.

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- (73) The adsorption energies of OH on (221) surfaces are calculated using the same setup described in the methods section, while adsorption energies of OH and O on (111) surfaces are taken from the literature.^{68–72} We only considered the bridge site for OH adsorption which is predicted as the most stable site for Rh(221) surface⁶⁵.

Figure 1: Relaxed geometries of intact and dissociated water (a and d) monomer, (b and e) dimer and (c and f) trimer on Rh(111) surface. The periodically replicated cells used in the calculations are represented by white dashed lines. The fcc- and hcp-hollow sites are represented in (d) by the triangles pointing up and down, respectively.

Figure 2: Relaxed geometries of intact and dissociated water (a and d) monomer, (b and e) dimer and (c and f) trimer on Rh(221) surface. **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: Dissociation energies of water clusters with (full symbols) and without (open symbols) zero-point energy correction for (a) (111) and (b) (221) surfaces.

Figure 4: pDOS of O p -states and Ir d -states upon which OH^- and/or H_2O is adsorbed on the surface for the (a) monomer, (b) dimer and (c) trimer adsorbed on flat and stepped Ir surfaces. Left and right panels correspond to intact and dissociated configurations, respectively. The Fermi level is set to 0 eV. The dashed gray lines in (a) represent the $1b_1$ and $3a_1$ water orbitals in the gas phase, and the energy levels of water in vacuum have been shifted so that $2a_1$ levels of water in gas and on Ir coincide.

Figure 5: Adsorption vs. dissociation energies of water clusters on (a) (111) and (b) (221) surfaces. The right most and left most points represent monomers and trimers, respectively, for each metal.

Figure 6: The scaling relations for $n\text{H}_2\text{O}$ with $n = 1$ (square, red), $n = 2$ (circle, blue) and $n = 3$ (triangle, green) among the adsorption energy of OH^- and (a) adsorption energies of water clusters and (b) dissociation energies of water clusters on flat (full symbols) and stepped (open symbols) surfaces. Pearson's correlation (R) is indicated in the panels.

Graphical TOC Entry