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Interaction of water with a metal surface: Importance of van der Waals forces

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Choosing the water bilayer/Rh(111) interface as an example, we study the interaction of water with a metal surface, by taking into account the van der Waals (vdW) interactions using the vdW density functional (vdW-DF). There are two types of water in a water bilayer on the substrate, namely, chemisorbed and physisorbed ones. We show that for a chemisorbed water molecule, vdW-DF results agree well with those obtained using the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation. However, for a physisorbed water molecule, PBE severely underestimates the interaction energy. When we correctly include the vdW interaction, the relative strengths of the water-substrate and water-water interactions among different bilayer structures become comparable, and the water bilayer structures considered (H-up, buckled H-down, and H-flat water bilayers) become quasidegenerated, while PBE predicts one configuration more stable than the others. The structure of the water bilayer is determined by a delicate balance of Pauli repulsion and long-range vdW attractions in water-substrate and water-water interactions. Therefore, for the prediction of the water bilayer structure on the Rh(111) surface, it is important to describe Pauli repulsion and vdW interactions correctly.

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I. INTRODUCTION

Understanding the interaction of water with metal surfaces is essential in corrosion, catalysis, and electrochemistry, as water plays important roles in chemistry at the water/metal interface. *Ab initio* electronic structure methods with the generalized gradient approximation (GGA) to density-functional theory (DFT) (Refs. 1 and 2) have been routinely used to study water/metal interfaces.

While DFT-GGA has been successfully applied to a variety of systems, there is a well-known deficiency in describing the weak interaction, i.e., the van der Waals (vdW) forces. Though the vdW interaction is believed to be important in weakly interacting water/metal interfaces, there are no *ab initio* studies on this issue, except for a work by Feibelman,[3] who estimated the effect of the vdW interaction on a wetting water layer on Ru(0001) by using an Ar atom, based on the fact that the polarizability of Ar is similar to that of an H_2O molecule. In that work, he concluded that the Perdew-Wang (PW91) GGA underestimates the vdW contribution to the adsorption energy by 4.1 kJ/mol-H_2O. However, the importance of the vdW forces in water/metal systems is still to be clarified.

Herein, we have applied the van der Waals density functional (vdW-DF) (Ref. 4) to the H_2O bilayer[5] on Rh(111) as an example of a water/metal interface, to study the influence of the vdW forces on the interaction of water with a metal surface. This interface can be considered to be ideal to study the interaction of H_2O with the metal substrate because of the close match between the lattice constants of Rh(111) and ice Ih. The vdW-DF has been successfully applied to vdW complexes as well as the covalent solid and the adsorbed systems.[6] The functional is seamless by construction and can describe the nonlocal correlation at all length scale.

II. METHOD

All calculations were performed by using a plane-wave pseudopotential method as implemented in the STATE program package.[7] The electron-ion interaction was described by the ultrasoft pseudopotentials.[8] In our GGA calculations, Perdew-Burke-Ernzerhof (PBE) (Ref. 9) and a revised version of PBE (RPBE) (Ref. 10) functionals were used. Wave functions and the augmented charge density were expanded by a plane-wave basis set with cutoff energies of 36 Ry and 400 Ry, respectively.

The vdW attraction due to the nonlocal correlation was calculated with post-GGA vdW-DF (i.e., nonself-consistent). The vdW-DF total energy is expressed as

$$E^{\mathrm{vdW}} = E^{\mathrm{GGA}} - E_c^{\mathrm{GGA}} + E_c^{\mathrm{LDA}} + E_c^{\mathrm{nl}} = E^{\mathrm{vdW0}} + E_c^{\mathrm{nl}}, \qquad (1)$$

where E^{GGA} is the GGA total energy, E_c^{GGA} is the GGA correlation energy, and E_c^{LDA} is the correlation energy within the local-density approximation (LDA). In this approach, the exchange energy is described by GGA, while LDA is used to express the short-range correlation, and the nonlocal correlation energy is defined by

$$E_c^{\mathrm{nl}} = \frac{1}{2}\int\int d\mathbf{r}d\mathbf{r}'n(\mathbf{r})\phi(\mathbf{r},\mathbf{r}')n(\mathbf{r}'), \qquad (2)$$

with an interaction kernel $\phi(\mathbf{r},\mathbf{r}')$. All the terms are evaluated based on the charge-density self-consistently determined by RPBE and the same functional was used for the exchange energy to minimize the spurious exchange binding.[4,11–13] Such a post-GGA treatment of vdW-DF is justified by Thonhauser *et al.*[14] who showed that the differences between self-consistent and nonself-consistent vdW-DF binding energies are negligible. The vdW-DF total energy was calculated at the geometry optimized by using the RPBE functional because the vdW-DF equilibrium geometry is almost identi-

TABLE I. Equilibrium lattice parameter (c/a), volume per H_2O (V_0), and binding energy per H_2O (E_b) of ice Ih by using different flavors of the exchange-correlation functional.

	c/a	V_0 (nm^3)	E_b (kJ/mol)
PBE	1.643	0.03077	68.3
RPBE	1.638	0.03322	50.3
vdW-DF	(1.638)	(0.03322)	61.1
PBE[a]	1.636	0.03065	61.8
RPBE[a]	1.653	0.03448	45.4
MBPT2[b]	1.627	0.03211	55.1
CCSD(T)[b]	1.627	0.03212	55.7
Expt.	1.628[c]	0.03205[c]	56.0[d]

[a] Reference 19.
[b] Reference 20.
[c] Reference 21.
[d] Reference 22.

cal to the RPBE one when the RPBE exchange energy is used in Eq. (1). We verified that the vdW-DF total energy is minimum at the RPBE-optimized geometry by examining several structures near the equilibrium.[15] To evaluate E_c^{nl} in a periodic system, the interaction range for $\mathbf{r}'$ in Eq. (2) needs to be cutoff at a certain distance[16,17] while the integral over $\mathbf{r}$ is evaluated in a primitive unit cell. We chose cutoff radii of 2.12 nm for ice and 1.43 (0.85) nm in the direction parallel (normal) to the surface in the slab calculations. The adsorption energies of the H_2O bilayers on Rh(111) and binding energy of ice Ih converge within 0.1 kJ/mol-H_2O with respect to the interaction cutoff radius.

III. RESULTS AND DISCUSSION

A. Ice Ih

We start by calculating the binding energy of ice (E_b) to assess the accuracy of vdW-DF in describing the H_2O hydrogen bond. We optimized the structure of Hamann's[18] 12-H_2O ice Ih using a $2\times2\times2$ k-point set and calculated E_b. Optimized lattice parameters, equilibrium volumes, and E_b's are shown in Table I. Our GGA values are in good agreement with previous theoretical results. In particular, our PBE binding energy is in good agreement with that obtained by Feibelman[23] using the ultrasoft pseudopotentials. The results show that PBE overestimates E_b of ice Ih, while RPBE underestimates it, in agreement with the previous theoretical study.[19] We have found that the vdW-DF binding energy is very close to the results obtained using the second-order many-body perturbation theory (MBPT2) and the coupled-cluster theory with single, double, and perturbative triple excitations [CCSD(T)].[20] Note that our PBE and RPBE binding energies are larger than those obtained by Feibelman,[19] which were obtained by using the projector augmented wave (PAW) methodology and a large plane-wave cutoff (102.9 Ry). By considering the fact that the larger binding energy (E_b=64.6 kJ/mol) was obtained with PAW and smaller cutoff energy of 51.5 Ry,[23] we employed harder and more accurate pseudopotentials, and large cutoff energies of 49 Ry and 400 Ry for the wave functions and the augmentation charge, respectively, to obtain smaller binding energy of 64.2 kJ/mol with PBE. By increasing the cutoff energy, the discrepancy with the recent Feibelman's results may be further minimized. In the following, however, our standard soft pseudopotentials are used to keep the modest computational cost.

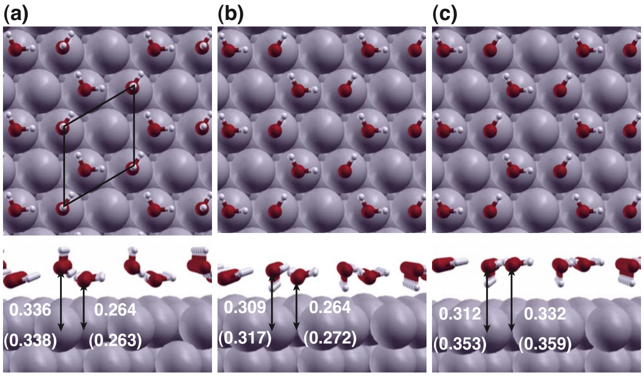

FIG. 1. (Color online) Structures of (a) H-up, (b) buckled H-down, and (c) flat H-down bilayers on the Rh(111) surface. Small, medium, and large balls denote H, O, and Rh atoms, respectively. A $(\sqrt{3}\times\sqrt{3})$ unit cell is shown by a rhombus in (a). Vertical distances (in nm) between O atom and Rh atom beneath, that are obtained by PBE (RPBE) are shown.

B. Water bilayer on Rh(111)

We calculated proton-ordered H-up and H-down H_2O bilayers on the Rh(111) surface in a $(\sqrt{3}\times\sqrt{3})$ periodicity,[24] which was modeled by a five-layer slab separated by a vacuum equivalent to an eight-layer spacing, using 6×6 k points and the first-order Hermite-Gaussian smearing[25] with the width of 0.05 eV. The lattice constant of 0.383 (0.386) nm for fcc Rh optimized by using the PBE (RPBE) functional was used to construct the slab. An H_2O bilayer was put on one side of the slab and spurious electrostatic interaction was eliminated by using the effective screening medium method.[26] In the standard GGA calculations, adsorption energy (E_{ads}) of H_2O was defined by the difference between the sum of the energies of isolated H_2O molecules and Rh substrate, and the total energy of the combined system. Geometry optimizations were performed with several initial configurations, to find stable H-up, buckled H-down, and flat H-down H_2O bilayer structures as shown in Fig. 1 with optimized geometries. Calculated adsorption energies are summarized in Table II.

Within PBE, we obtained the stable buckled H-down structure, in agreement with a previous study,[27] and the flat H-down structure[28,29] is found to be metastable. These structures are more stable than the traditional icelike H-up structure[30] by 3.4 kJ/mol and 1.3 kJ/mol for the buckled and flat H-down structures, respectively. Note that we also considered a half-dissociate H_2O layer[23] and found that it is unstable against the intact one, in agreement with previous studies.[27,30,31] On the other hand, the flat H-down structure is

TABLE II. vdW-DF adsorption energies per H_2O (E_{ads}) and its contributions [from the nonlocal correlation energy (ΔE_c^{nl}) and remaining part (ΔE^{vdW0})]. PBE and RPBE results are shown for comparison. The unit of energy is kJ/mol.

		PBE	RPBE	vdW-DF	ΔE^{vdW0}	ΔE_c^{nl}
$E_{int}(H_2O/Rh)$	H-up	6.5	−3.6	11.7	−19.0	30.6
	Buckled H-down	18.9	4.6	18.8	−14.4	33.2
	Flat H-down	7.4	−0.9	12.2	−6.7	18.9
$E_{int}(H_2O)$	H-up	48.0	35.4	40.9	26.1	14.8
	Buckled H-down	43.3	30.3	35.3	19.1	16.2
	Flat H-down	48.9	36.1	40.8	24.3	16.4
E_{rlx}	H-up	−4.1	−2.7	(−2.7)		
	Buckled H-down	−8.3	−5.4	(−5.4)		
	Flat H-down	−4.6	−2.9	(−2.9)		
E_{ads}	H-up	50.4	29.0	49.8		
	Buckled H-down	53.8	29.5	48.7		
	Flat H-down	51.7	32.3	50.0		

found to be the most stable with RPBE. E_{ads} obtained using RPBE is, however, much smaller than the experimental value[32,33] and the theoretical ice binding energy. We also employed the revPBE functional,[34] and obtained E_{ads}'s of 29.0 kJ/mol, 30.3 kJ/mol, and 31.6 kJ/mol for H-up, buckled H-down, and flat H-down structures, respectively, which are similar to the RPBE values. By comparing these results with the experimental E_{ads}, PBE seems to perform best among the GGA functionals employed in this study. However, this is attributed to the spurious binding of PBE caused by its underestimation of the Pauli repulsion; the underestimation is small in RPBE and revPBE.[4,11,12] Our results suggest that RPBE and revPBE need further binding such as the vdW force to describe the adsorption of the H_2O bilayer on Rh(111).

Next, we calculated E_{ads} of the H_2O bilayer using vdW-DF. The calculation of adsorption energy within vdW-DF must be done with great care because of the slow numerical convergence of the vdW-DF total energy due to the sensitivity of E_c^{nl} to the choice of the fast Fourier-transform (FFT) grid.[16,17] We followed the prescription given in Ref. 35 to minimize the error in the calculation of E_{ads} as follows: First, the energy to isolate the H_2O bilayer and the Rh substrate [$E_{int}(H_2O/Rh)$] and then, the energy to isolate H_2O molecules in the bilayer [$E_{int}(H_2O)$] were calculated. To minimize the FFT grid related error, calculations of isolated fragments were performed at exactly the same positions as in the adsorbed states, and the FFT grid spacing was kept constant in all calculations. Finally, the energy necessary to relax isolated H_2O molecules and Rh substrate to their RPBE-optimized geometries (E_{rlx}) was evaluated. Adsorption energies thus obtained are summarized in Table II with the contributions from the nonlocal correlation E_c^{nl} (ΔE_c^{nl}) and the remaining E^{vdW0} part (ΔE^{vdW0}). The former accounts for the long-range vdW attraction, and the latter, for the attractive hybridization and the Pauli repulsion. $E_{int}(H_2O/Rh)$ and $E_{int}(H_2O)$ with PBE and RPBE are also shown and compared.

For the H_2O-Rh interaction, ΔE^{vdW0}'s are negative in all configurations, suggesting that the Pauli repulsion predominates over the attractive hybridization. (See below for further analysis on interaction energy curves and the bonding characters.) However, by adding ΔE_c^{nl}, we found that $E_{int}(H_2O/Rh)$ becomes attractive. Thus, the binding of the H_2O bilayer is solely due to the nonlocal correlation, i.e., vdW interactions.[36] Note that although PBE does not contain the nonlocal correlation, it also gives the binding (see Table II). However, the PBE binding is caused by the underestimation of the Pauli repulsion, as discussed above, or the error cancellation of the exchange and correlation. Indeed, RPBE gives almost no binding of an H_2O bilayer. To understand the H_2O-Rh interaction clearly, we calculated the interaction energy of H_2O *monomer* as a function of distance. We extract H_2O monomer/Rh(111) structures from H-up and buckled H-down bilayers on Rh(111) and calculated the H_2O-Rh interaction energies as a function of O-Rh distance. Figure 2 displays interaction energies for H_2O lying approximately parallel to the surface (H_2O_p) [(a) H-up and (c) H-down] and for H_2O lying a plane vertical to the surface (H_2O_v) [(b) H-up and (d) H-down]. ΔE^{vdW0} and ΔE_c^{nl} are also shown for H_2O_p of the H-up structure [Fig. 2(a)]. Those for other structures show very similar feature and omitted for clarity. The plot clearly demonstrates that the nonlocal correlation is responsible for the binding of H_2O. For chemically bonded H_2O_p close to the surface, interaction energy obtained using PBE is in good agreement with that using vdW-DF. However, for weakly bonded or nonbonded H_2O_v far from the surface, PBE underestimates the interaction energy because of the lack of long-range vdW interactions.

In contrast to the H_2O-Rh interaction, both ΔE^{vdW0} and ΔE_c^{nl} are attractive in the interaction between H_2O molecules in the bilayer. $E_{int}(H_2O)$'s calculated with vdW-DF are smaller than those with PBE, because vdW-DF improves a description of the H_2O hydrogen bond energy which is overestimated by PBE,[37–39] as in the case of ice Ih. We obtained slightly smaller $E_{int}(H_2O)$ for the buckled H-down configuration by ~5 kJ/mol than the others. This is because the buckled H-down bilayer is distorted as a result of the chemical interaction between the Rh substrate and H_2O_p, and the

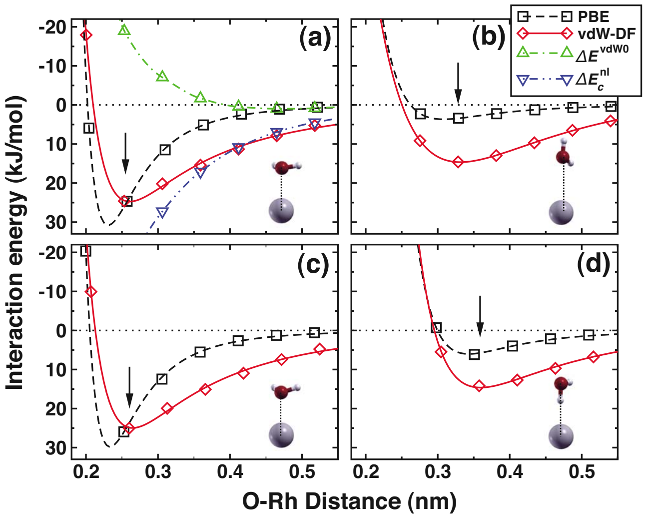

FIG. 2. (Color online) Interaction energy of H_2O monomer with the Rh(111) surface as a function of vertical O-Rh distance for (a) H_2O_p and (b) H_2O_v of the H-up bilayer and for (c) H_2O_p and (d) H_2O_v of the buckled H-down bilayer. The lines are obtained by fitting to a function $f(r)=a\exp(br)+c/r^n$. Insets show the geometries (only the Rh atoms beneath the H_2O monomers are shown). Arrows indicate the O-Rh distances in their bilayer structures.

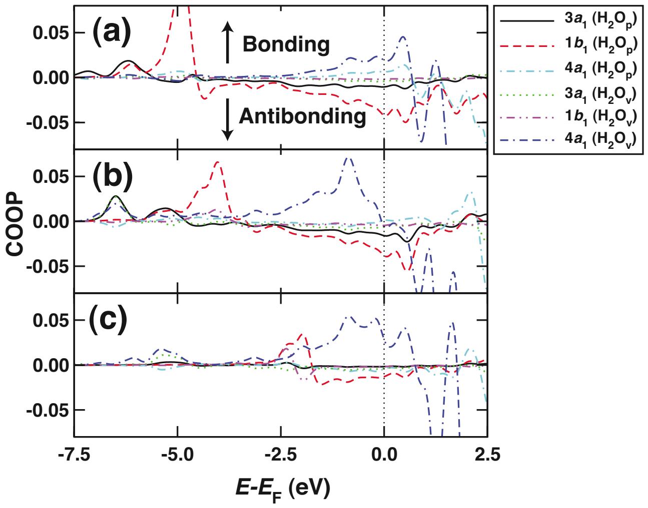

FIG. 3. (Color online) COOP between H_2O_p and the substrate, and COOP between H_2O_v and the substrate for (a) H-up, (b) buckled H-down, and (c) flat H-down H_2O bilayer, calculated by using the RPBE functional. Energy zero is set to the Fermi level (E_F).

bilayer structure deviates from an ideal tetrahedral configuration, whereas in the other structures, favorable tetrahedral networks are formed, resulting in similarly larger values. The relative strengths of hydrogen bonds are not sensitive to the choice of exchange-correlation functional, as can be seen from the differences in $E_{\mathrm{int}}(H_2O)$'s.

E_{rlx} is also influenced by the H_2O-Rh interaction, because the chemical interaction between H_2O and Rh induces a displacement of the underlying Rh atom, hence the large magnitude of E_{rlx}. In particular, the chemical interaction between H_2O_p and Rh in the buckled H-down configuration induces the largest distortion of the Rh substrate, which results in the largest E_{rlx}: substrate contribution to E_{rlx} in the buckled H-down configuration is −2.5 kJ/mol, whereas for the H-up and flat H-down configurations, the values are only −0.7 kJ/mol and −0.2 kJ/mol, respectively.

Finally by summing up all the contributions, we found that E_{ads}'s for H-up and flat H-down bilayers are comparable, while the buckled H-down bilayer is slightly less stable within vdW-DF. When we correctly include the vdW interactions, all three bilayer configurations become quasidegenerated, whereas PBE predicts one configuration more stable than the others. We estimated the zero-point energy (ZPE) contribution to E_b of ice Ih and E_{ads} of the water bilayer by calculating the harmonic vibrational frequency of H_2O using the finite difference method. Resulting E_b for ice Ih is 50.1 kJ/mol and E_{ads} for H-up, buckled H-down, and flat H-up configurations are 42.3 kJ/mol, 41.2 kJ/mol, and 42.1 kJ/mol, respectively. Relative stability is unchanged when ZPE is included. Therefore, for the prediction of H_2O bilayer structure on the Rh(111) surface, it is important to describe vdW interactions correctly. Note that contrary to an expectation that inclusion of the vdW forces increases the adsorption energy, E_{ads}'s obtained using vdW-DF is slightly smaller than the corresponding PBE values. This is mainly because $E_{\mathrm{int}}(H_2O)$'s obtained using vdW-DF are smaller than those with PBE, which is dominant in E_{ads}.

To gain insights into the bonding mechanism of the H_2O bilayer on the Rh(111) surface, we calculated the crystal orbital overlap population (COOP) (Refs. 40 and 41) between H_2O_p and the Rh substrate, and that between H_2O_v with the substrate. A positive peak in COOP indicates bonding interaction of a molecular orbital with the substrate, whereas a negative peak indicates an antibonding character of the interaction. In Fig. 3, COOPs for the lone pair ($3a_1$ and $1b_1$) and the $4a_1$ orbitals are shown. Bonding peaks originated from the $1b_1$ orbital of H_2O_p are found at −4.9 eV, −4.0 eV, and −2.0 eV for H-up, buckled H-down, and flat H-down bilayer, respectively [Figs. 3(a)–3(c)], suggesting the attractive hybridization of the orbital with the substrate. Small bonding peaks for $3a_1$ orbitals can be also found at −6.2 eV for the H-up and at −6.5 eV for the buckled H-down structures. Less pronounced peaks for the lone-pair orbitals of H_2O_p in the flat H-down structure [Fig. 3(c)] indicate their weak hybridization with the surface. In addition to the hybridization of lone-pair orbitals, noticeable hybridization of $4a_1$ orbitals of H_2O_v in the H-down structures can be found (at −0.9 eV for the buckled and at 0.20–0.85 eV below E_F for the flat ones), which results in the additional binding of the buckled and flat H-down bilayers. Here, it is important to note that the antibonding counterparts of the lone-pair orbitals (mainly of the $1b_1$ orbital of H_2O_p) are partially occupied, suggesting the Pauli repulsion between H_2O_p and the substrate.

With these electronic structures and the interaction energy curves of H_2O monomers in mind, we can understand the role of vdW interaction in the H_2O-Rh interaction. As is shown in the Fig. 2, the "comparable" performance of PBE with respect to vdW-DF in describing the H_2O-substrate interaction is not consistent. Even for a given bilayer structure it varies largely depending on the adsorption configuration and bonding character of water molecule. For the H_2O_p in the H-up and the buckled H-down configuration, difference is almost negligible. The H_2O_p's in these configurations are chemically bond to the surface, and for this type of bonding, PBE works quite well. On the other hand, for H_2O_v, the PBE binding is much weaker than the vdW-DF one by 11.0 kJ/mol and 8.6 kJ/mol in the H-up and the buckled H-down bilayer, respectively [see Figs. 2(b) and 2(d)].[42] The average of two water molecules in the bilayer is close to the Feibelman's[3] estimate on Ru(0001) of 4.1 kJ/mol-H_2O.

Within PBE, the H_2O-Rh interaction is a key factor which determines the stable bilayer structure. For example, $E_{\mathrm{int}}(H_2O/\mathrm{Rh})$ is the largest in the most stable buckled H-down configuration. However, it is not the case within vdW-DF. Differences in $E_{\mathrm{int}}(H_2O/\mathrm{Rh})$'s among the different bilayer structures become smaller than the PBE values and they become comparable with those in $E_{\mathrm{int}}(H_2O)$'s. As a consequence, the relative stability of the H_2O bilayer structure is determined by a delicate balance of the H_2O-Rh and H_2O-H_2O interactions, not only by the strength of the H_2O-substrate interaction.

Lastly, we mention that E_{ads} of the water bilayer calculated with a $(\sqrt{3}\times\sqrt{3})$ unit cell is smaller than the experimental value and also, they are too small to wet the surface because they are smaller than E_b of ice Ih.[43] To investigate a more stable H_2O bilayer structure on Rh(111), we performed calculations with a larger unit cell, inspired by the findings that the proton-disorder effect[27] and the mixture of H-up and H-down configurations[29,44,45] increase E_{ads} of the H_2O bilayer. We used a three-layer $(3\times 2\sqrt{3})$ supercell with 2×2 k points and performed a geometry optimization by using the RPBE functional and calculated E_{ads} with vdW-DF. We found that a mixed H-up and H-down H_2O layer with the ratio of 1:3 is the most stable structure as shown in Fig. 4. In this mixed H-up and H-down structure, heights of O atoms become random, and a proton disorder occurs spontaneously during the geometry optimization. E_{ads} for this structure is 56.9 kJ/mol, which is 14% larger than 49.9 kJ/mol for the proton-ordered flat H-down structure calculated with the same supercell. The calculated E_{ads} for this structure is still smaller than E_b of ice Ih and the experimental value [60 kJ/mol (Ref. 32)], however, the difference with ice E_b becomes smaller than that for the proton-ordered $(\sqrt{3}\times\sqrt{3})$ structure ($\sim$4 kJ/mol), implying that the further disorder effect may increase the adsorption energy. Thus, it is likely that the average structure was observed in the experiment[33] in which no buckling was found in the scanning tunneling microscopy images. The structure of a water layer may be much more complicated than we expect from DFT-GGA calculations.

IV. SUMMARY

In summary, we have studied the H_2O bilayer adsorbed on the Rh(111) surface with vdW-DF, to understand the influence of the vdW forces on the interaction between H_2O and a metal surface. We have found that the Pauli repulsion predominates over the attractive hybridization of the lone-pair orbitals of H_2O with metal d states. Although PBE agrees well with vdW-DF, PBE relies on the usual error cancellation rule in LDA and PBE, and it binds with a wrong reason. On the other hand, in vdW-DF, the nonlocal correlation is solely responsible for the adsorption of the H_2O on the surface. The relative strengths of H_2O-substrate and H_2O-H_2O interactions among the different bilayer structures become comparable when we correctly include vdW forces, and consequently, the stable structure of the H_2O bilayer is determined by a delicate balance of these interactions. This study demonstrates the importance of a correct account of vdW interactions for predicting an H_2O bilayer structure on a metal surface.

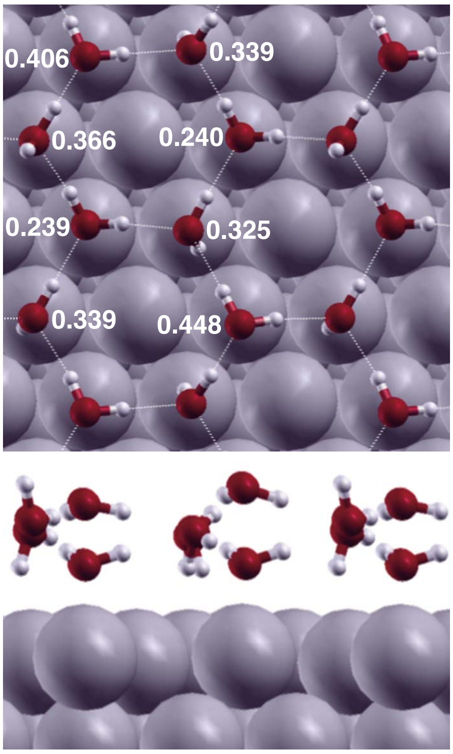

FIG. 4. (Color online) The most stable H_2O layer structure in a $(3\times 2\sqrt{3})$ unit cell. Numbers denote the vertical distance (in nm) between H_2O molecule and Rh atom underneath.

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