

# Dynamical properties and the proton transfer mechanism in the wetting water layer on Pt(1 1 1)

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## Abstract

We have investigated the structural properties and the dynamics in the  $(\sqrt{39} \times \sqrt{39})R16.1^\circ$  (RT39) wetting layer on Pt(1 1 1) found in recent experiments, by ab initio molecular dynamics simulations. The RT39 bilayer is found to consist of 20% water molecules in the first flat layer, and 66% in the second layer, and a small fraction extending further away. Two-dimensional pair correlation functions are obtained, and calculated vibration spectra are in agreement with experiment. A small fraction of water in this RT39 bilayer dissociates due to both the lateral compression and the substrate effect. Most interestingly, surface mediated proton transfer mechanism in water layers at surface, which differs from the counterparts in bulk water, is discovered.

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Water covers most real surfaces in nature. One of the most interesting and technological important water/surface systems is water–metal contact, which is important, for instance, in catalysis, electrochemistry, and biological implants [1,2]. In particular, as a prototype system, water on the

simplest Pt(1 1 1) surface receives most interests and was intensively studied in laboratories in the last three decades. Concerning the first water layer on Pt(1 1 1), bilayer in a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  (RT3) phase was first proposed by earlier experiments [3], in which water molecules form a puckered hexagonal network as in bulk ice Ih [4]. However, recent experiments [5,6] have observed at 130–140 K the bilayer structures in  $(\sqrt{39} \times \sqrt{39})R16.1^\circ$  (RT39) and  $(\sqrt{37} \times \sqrt{37})R25.3^\circ$  (RT37) phases. Among the three observed adstructures, only the

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RT39 bilayer was found to form the complete first-bilayer [5,6]. It wets the surface, and transforms into RT3 at a coverage of  $\approx 5$  bilayers [6]. The RT39 bilayer phase is most interesting because it marks the initial formation of the H-bonded water networks on the surface. However, detailed characterization of the structure and dynamics of this new phase is still lack in literature.

In this paper, we present a theoretical investigation on the wetting layer RT39 on Pt(111). We have studied the structure and dynamics of the RT39 water layer by ab initio molecular dynamics (MD) simulations based on density functional theory (DFT). As it includes the electronic structure and the electron dynamics into consideration, this method is parameter-free and counts the Pt–water and water–water interactions more properly and precisely than classical MD simulations employing empirical potentials [7,8]. We found that the RT39 bilayer on Pt(111) is composed by the flat first layer with an O–H separation along the surface normal as small as 0.1 Å, and a broader top layer with OH groups pointing either parallel or perpendicular to the surface. This characteristic is similar to the standard RT3 bilayer structure, but has a different partition in the two layers. Pair correlation functions (PCF) in a two-dimensional (2D) geometry and the vibration spectrum are calculated, and generally they are in agreement with experiment whenever available. In particular, we found a small fraction of water molecules are dissociated in the RT39 layer, similar to Feibelman's calculations [9]. The reason for water dissociation are discussed. And most interestingly, the surface mediated proton transfer mechanism in the water layer at surface, which is different from that in bulk [10,11], has been discovered and discussed.

The calculation was performed with the Vienna ab initio simulation program, VASP [12,13]. The supercell consists of three layer of Pt(111) surface atoms in a  $(\sqrt{39} \times \sqrt{39})R16.1^\circ$  period, and an adsorbed water layer with 32 molecules. Therefore totally 213 atoms are presented in the supercell. A vacuum region of 13.4 Å is placed between the Pt slabs to eliminate the interactions between the unitcells. A planewave energy cutoff of 300 eV and a single  $k$ -point sampling at  $(0.5, 0.5, 0)$  in the surface Brillouin Zone was used. During the

molecular dynamics simulation, all atoms in water and the first Pt layers are allowed to move according to the calculated forces. Full relaxation of the first several surface layers would not change the dynamics, given the very small amount ( $<1\%$ ) of the relaxation effect of Pt(111). A constant energy simulation with a timestep of 0.5 fs, has been run for 3.3 ps at temperature  $\sim 130$  K, after equilibrating the system for 0.2 ps. The total energy is conserved at the level of  $<2 \times 10^{-4}$  eV/step. The Vanderbilt ultrasoft pseudo-potentials [14] and the gradient-correction exchange-correlation energy by Perdew and Wang (PW91) [15] were used. After extensive comparison, the PW91 (and its derivatives PBE) are shown to be promising for describing the hydrogen bonding [16] and bulk water [17]. In particular, it has been shown to be most successful for surface systems [18].

The gross structure of the RT39 water layer was found to be similar to that of the RT3 bilayer on Pt(111). Water also forms puckered hexagonal networks in RT39. However, due to the compression by 3.3% in its two-dimensional surface unit-cell compared with the ideal ice Ih [5], RT39 bilayer shows a more disordered atomic distribution. To characterize the RT39 water structure, the atomic distribution along the surface normal is shown in Fig. 1. The atomic densities versus

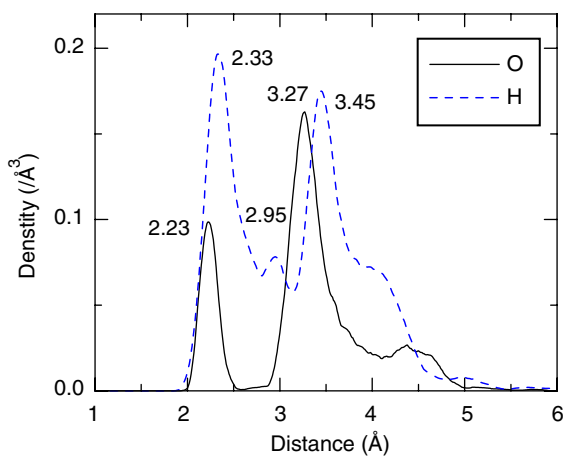


Fig. 1. The atomic distribution (O, solid line; H, dashed) along surface normal in the RT39 water bilayer. Atomic densities versus the atom–surface distance, averaged from 6000 configurations in the MD trajectory, are shown.

distance away from the Pt(111) surface for both O and H are shown. These densities are averaged from 6000 configurations recorded in the MD trajectory though they are not all independent. The averaged position of the surface Pt atoms in the MD simulation, which shows only a small outward relaxation of  $\sim 0.02$  Å, is used here to define the position of the surface plane.

Two major peaks centered at 2.23 and 3.27 Å for the O–surface separation ( $d_{OS}$ ) are presented in Fig. 1. It confirms the RT39 bilayer is mainly a bilayer structure, according to its O distribution. The first layer ( $d_{OS} = 1.92$ – $2.58$  Å) accommodates 6.50 molecules in the unitcell, i.e. 20.3% molecules. The second layer ( $d_{OS} = 2.59$ – $4.10$  Å) encloses the majority of water with a number of 21.12, that is, 66.0% of water molecules. Besides them, there is a low bump at  $d_{OS} = 4.50$  Å in Fig. 1, which could be considered as an extension of the second layer. As it is rather far away from surface, only a small fraction of water molecules (13.7%) have O–surface separations in this range. The features in the O-surface distribution for the RT39 bilayer are quite different from the traditional picture of the structure of a bilayer, especially the RT3 bilayer, where half molecules are in the first and the second layer, respectively. The distribution curve for the H–surface separations is a little more structured. The first peak at 2.33 Å demonstrates that the first water layer is rather flat, with a thickness as small as 0.1 Å. The other peaks sits either to the left or to the right of the corresponding peaks in the O-surface curve, showing that the H atoms are pointing to or away from the metal surface. These are consistent with the direct observation on the structures from MD trajectories.

To calibrate the internal water structure, two-dimensional pair correlation functions for OO, OH, and HH pairs are plotted in Fig. 2. All atoms are projected onto the surface plane, and then counted. The gross features are similar to both the theoretical [19] and experimental [20] PCFs for bulk ice [three dimensional (3D) PCF]. The first and second peaks in OO PCF ( $g_{OO}$ ) are located at 2.55 and 4.45 Å, respectively. They are much shorter than those in bulk water (2.7–2.8 Å, and 4.5–4.6 Å), because of the compression effect in the RT39 water layer. In contrast to the

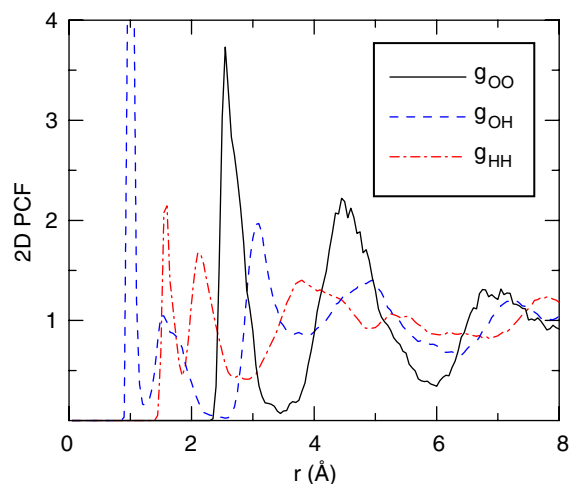


Fig. 2. The two dimensional pair correlation functions for OO (solid line), OH (dashed line), and HH (dot-dashed line), respectively.

coordination number of four in the bulk ice, integrating  $g_{OO}$  to the first minimum at 3.45 Å gives the coordination number of 2.9, which corresponds to a 2D structure at surface. In a perfect 2D hexagonal ice lattice, the coordination is three for each water molecule. PCFs for OH and HH are also qualitatively comparable to that for the bulk ice at 100 K from MD simulations employing model potentials [19].

Detailed comparison with experiment can be made by calculating the vibration spectrum for the RT39 layer. Fig. 3 shows the calculated vibrational spectrum, obtained from Fourier transform of the velocity–velocity autocorrelation function as in earlier studies [21]. Good agreement with the experimental reflection absorption infrared (RAIR) spectra (Fig. 4, in Ref. [6]) are found, for both the positions and the shape of vibration peaks. In details, OH stretch modes at 409 and 430 meV is similar to the main peak/shoulder at 410 and 426 meV in experiment, after multiplying an isotope factor of 1.35 ( $D_2O$  layers, instead of  $H_2O$ , are used in experiments). A small peak at 460 meV for free OH also looks similar to that in experiment at 456 meV. The HOH scissor mode is calculated to be at 200 meV, agrees with experimental value (201 meV) again. Experiments did not show vibration energies below 150 meV, where

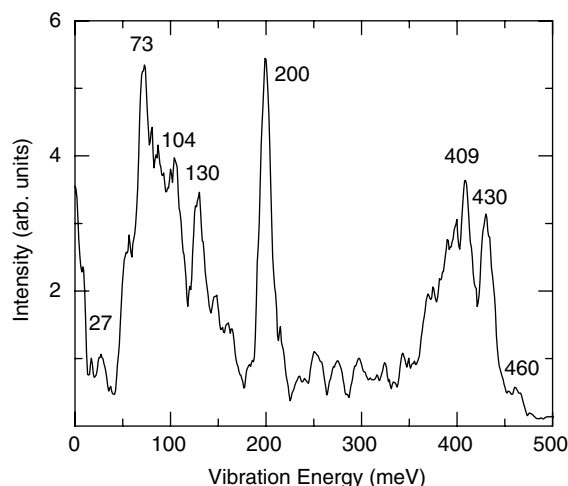


Fig. 3. Calculated vibration spectrum for the first RT39 bilayer from MD trajectories.

we calculated several peaks at 130, 104, 73 and 27 meV for the librational and translational modes, which are also characteristic for a hydrogen-bonded water network. In detail, they correspond to water wagging/twisting/rocking modes, and the lowest mode at 27 meV is the  $\text{H}_2\text{O}-\text{OH}_2$  and/or  $\text{Pt}-\text{OH}_2$  translational modes. Although they are hard to assign precisely, these modes frequently appear in a lot of experiments [22]. The close match between calculated and experimental vibration spectra provides us confidence that we have simulated the real structure for the RT39 bilayer that exists in experiments.

While the (dynamical) structure for the RT39 bilayer is well-characterized through our atomic density plot, pair correlation functionals, and also the vibration spectrum, the intrinsic and mysterious dynamical processes have not been explored yet. The most interesting issue in the RT39 bilayer on Pt(111) is the water dissociation and proton transportation mechanism therein. As previous theoretical studies revealed [9,23,24], there are a few  $\text{H}_2\text{O}$  molecules dissociated in the RT39 water layer, forming  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  like molecules. We find that only a small fraction of water molecules, 3 out of 32 (9%), dissociate in the first RT39 bilayer, and all  $\text{H}_3\text{O}^+$  lie in the upper layer. The dissociated OH residues approach the Pt surface,

stabilized at a height of 2.1 Å above the surface. The  $\text{H}_3\text{O}^+$ -like molecule is found to have a longer OH bond length, about 1.05 Å averaged from MD simulations, and hence have a lower OH stretch energy of 250 meV.

The possible reason for the partial dissociation in the RT39 bilayer on Pt(111) lies in both lateral compression of the water film and its interaction with the substrate. This is evidenced by the fact that if we remove the Pt substrate while keep the water configuration as before, still one and only one  $\text{H}_2\text{O}$  molecule is found dissociated by geometry optimization, compared to three in the adsorbed bilayer on Pt(111) among 32 molecules in the unitcell. In the RT39 ice layer, the averaged distance between two neighboring water hexagons is estimated to be 4.33 Å, compressed by 3.3% compared to that of 4.48 Å in bulk ice Ih. The deviation of water separation from its optimized value implies a stress exists in the RT39 layer, which modifies to some extent the pure H bonding interaction between water molecules in the 2D film, and consequently affects the water structure and dynamics. As a result, it not only results in the diffuse distribution of water molecules (Fig. 1) and the shortage in O–O separations (Fig. 2), but also leads to one water molecule dissociation in the free-standing RT39 bilayer here. The other two dissociated water are retained by the substrate. Further evidence for the collective effect on dissociation is shown by the potential energy surface for an H atom along two adjacent O atoms ( $\text{O}_A$  and  $\text{O}_B$ ) in Fig. 4. In the case of the water dimer/Pt(111), whose configuration is obtained by removing all irrelevant  $\text{H}_2\text{O}$  from the RT39 bilayer, the minimum of potential energy is close to  $\text{O}_B$  forming two intact  $\text{H}_2\text{O}$  molecules on the surface. While in RT39 bilayer, the minimum bounces back to  $\text{O}_A$  end, forming an  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  pair. Therefore the  $\text{H}_2\text{O}_B$  molecule is dissociated due to the change in the potential field, which in turn comes from the interaction with the neighboring  $\text{H}_2\text{O}$  around molecule A and B.

Evidence for the surface induced dissociation comes from the fact that only bottom  $\text{H}_2\text{O}$  donates proton to neighboring molecules. On the contrary, none of the upper  $\text{H}_2\text{O}$  molecules is found to donate a proton to other molecules. Bottom  $\text{H}_2\text{O}$

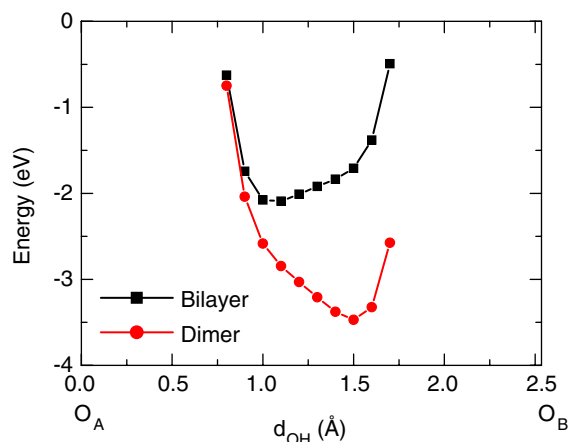


Fig. 4. The relative energy versus the O–H separation in the adsorbed dimer (dots) and the bilayer that contains this dimer (squares). Water  $H_2O_B$  is dissociated in the latter case, showing the collective effect in RT39.

molecules are usually thought to be much modified by the substrate due to the strong water–metal binding. Consequently, all the  $H_3O^+$  lies in the upper layer of the first RT39 bilayer, while  $OH^-$  binds to the Pt surface with a Pt–O bond length of 2.1 Å.

Water dissociation into  $H_3O^+$  and  $OH^-$  like groups in the RT39 bilayer, results in abundant proton transfer processes at the surface. Proton transfer mechanism at surfaces is found to be different from that in bulk water [10,11], because of the low coordination in the 2D surface water and the presence of substrates. Each molecule forms only 3 hydrogen bonds at most to its neighbors at surface, compared to 4 when proton transfer occurs in bulk water. Our molecular dynamics simulation reveals four types of proton transfer processes at surface: (i)  $H_3O^+$  migration, (ii)  $OH^-$  group migration, (iii)  $OH^-$ ,  $H_3O^+$  recombination, and (iv) H dancing (i.e. an H atom hopping between two neighboring O atoms now and then). All processes involve the motion of a proton jumping from one O to the adjacent O along the hydrogen bond.

The general scheme for proton transfer at the Pt(111) surface is illustrated in Fig. 5. Structures from the MD simulation for the process that, an  $H_2O$  molecule dissociates and the separated pro-

ton then transfer to neighboring molecules, are shown. Initially,  $H_2O_A$ ,  $H_2O_B$ , and  $H_2O_C$  are three adjacent molecules in the RT39 bilayer (Fig. 5(a)). One of the H-bonded proton ( $H_A$ ) of molecule A, jumps from  $O_A$  to  $O_B$  at a time  $t$  of 115 fs (Fig. 5(b)). Thus there form  $H_3O_B^+$  and  $O_AH$  (Fig. 5(c)). However, the newly formed  $H_3O_B^+$  is metastable. It then donates its own hydrogen ( $H_B$ ) to adjacent  $O_C$  in the molecule C at time  $t = 208$  fs (Fig. 5(d)). Therefore the hydrated proton ( $H_3O^+$ ) migrate from site B to site C. Along with the H dancing process between two adjacent O atoms (not shown), where water dissociates into  $H_3O^+$  and  $OH^-$  and then gets recombined from them in turn, we found that: (i) The O–O separation is around 2.5 Å when a proton transfer process occurs. This is in good agreement with other calculations [10,11] and experiments [25]. (ii) Proton transfer is a prompt process, which is usually completed in 0.2–0.5 ps. This is verified by the low barrier for H transfer,  $\approx 40$  meV, estimated from our MD simulation. The barrier should be further smoothed when the quantum motion of H atoms is taken into consideration [11].

The substrate plays key roles in proton transport processes in a surface water layer. Fig. 6 shows an  $OH^-$  transportation process, where the substrate is found to be greatly involved. In this process, the proton from the interfacial  $H_2O$  transfers to the neighboring  $OH^-$ , forming a new  $OH^-$  and  $H_2O$ . The variations of Pt–O and O–H bond lengths for the two adjacent molecules  $H_2O_A$  and  $O_BH^-$  are plotted. Initially  $H_2O_A$  lies high (3.5 Å) on the surface, while the  $O_BH^-$  binds to the Pt surface at 2.1 Å as aforementioned. Then by rotating the molecule (corresponding to the reduction of  $O_BH^-$  distance from 3.6 Å to 1.7 Å in the first 500 fs), the H atom in A turns to form an  $O_AH \cdots O_B$  hydrogen bond, and then jumps from  $O_A$  to  $O_B$  forming an  $O_B-H$  covalent bond at  $\approx 1.1$  ps. Simultaneously, the surface Pt atom come to bind  $O_A$  (now in  $O_AH^-$ ) strongly, indicated by the equilibrium Pt–O distance around 2.1 Å they form. After the proton transfer process is completed,  $O_B$  (now  $H_2O_B$ ) gradually departs from the Pt surface and move higher. In the meanwhile the beneath atom  $Pt_A$  (which binds  $O_A$ ) is lifted up about 0.1 Å, while  $Pt_B$  (which binds  $O_B$ )

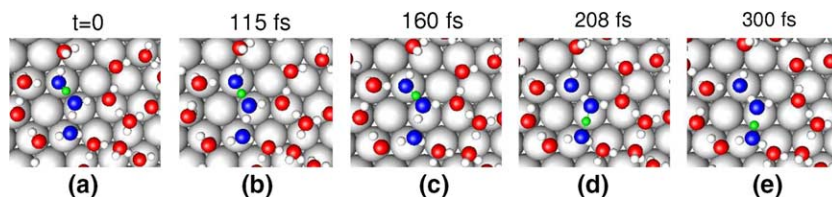


Fig. 5. Top views of water structures in a proton transfer process at the Pt(111) surface, recorded from the MD simulation. Big, middle, and small balls represent Pt, O, and H atoms, respectively. There forms an  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  like molecule after this process.

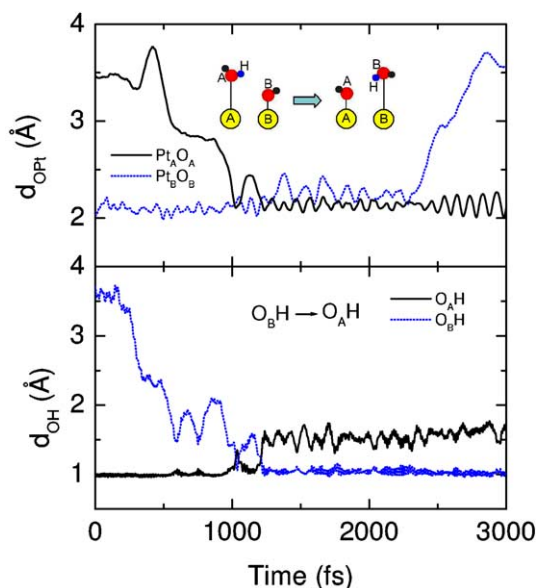


Fig. 6. The Pt–O separations (upper panel) and the corresponding OH bond lengths (lower panel) versus the simulation time, showing the surface mediated  $\text{OH}^-$  transport mechanism in the RT39 bilayer on Pt(111).

bounces back during  $\text{OH}^-$  transportation. Therefore we conclude that the metal substrate makes unique roles through binding and supporting the molecules, and leads to a “surface-mediated” proton transfer process. Similar proton transfer mechanism has been observed from MD simulations on polar surfaces, such as  $\alpha\text{-Al}_2\text{O}_3$  [26] and  $\text{SiC}(100)$  [27], which easily stabilize the separated protons and hydroxyl groups. But it is not the case on simple metal surfaces, where the proton transfer process is more difficult and tricky, and surfaces make a nontrivial contribution, because of the much weaker water–substrate interactions on the metal surfaces. The surface mediated proton trans-

fer processes on the inert noble metal surfaces, which differ much from the standard cases in bulk water, also have many implications in industries as well as the medical techniques.

In conclusion, we have characterized the RT39 water bilayer recently found on Pt(111) by experiments, using ab initio molecular dynamics simulations based on density functional theory. The RT39 bilayer consists of a flat first layer accommodating 20% water molecules and a broadened second layer. The dissociation of a small fraction of water (9%) are discussed, and the intriguing surface mediated proton transfer mechanism has been discovered. Our findings confirm the general belief that, water vicinal to (solid) surfaces usually exhibits anomalous behaviors which differ from bulk water.

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