Consistent picture for the wetting structure of water/Ru(0001)

Sheng Meng [a,b], E.G. Wang [b], Ch. Frischkorn [c], M. Wolf [c], Shiwu Gao [a,b,*]

[a] Department of Applied Physics, Chalmers University of Technology and Göteborg University, Soliden 3037, SE-412 96 Göteborg, Sweden
[b] Institute of Physics, Chinese Academy of Sciences, P.O. Box 603, Beijing, 100080, China
[c] Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin, Germany

Received 27 October 2004; in final form 16 December 2004
Available online 5 January 2005

Abstract

The wetting layer of D_2O on Ru(0001) has been reanalyzed with ab initio molecular dynamics and full-potential calculation. The work function change induced by D_2O overlayers clearly favors the picture of molecular wetting rather than partial dissociation and suggests a mixed structure consisting of both hydrogen-up and hydrogen-down bilayers. This is further supported by the vibrational spectra, where agreement is only found for the intact overlayers but not for a half-dissociated overlayer. The larger barrier for dissociation in comparison with that for desorption suggests that dissociation is kinetically forbidden at low temperatures. These findings resolve the current controversy between previous calculations and experiments.
© 2004 Elsevier B.V. All rights reserved.

The water–metal interface [1,2] has been under intensive studies during the past decade, due to the fundamental interest in the hard-soft interfaces and the broad applications in many interdisciplinary areas such as catalysis, electrochemistry, fuel cells, and biomaterials. Much understanding has been gained on the detailed structures and properties of water on single-crystalline metal surfaces, where theory and experiment seem to converge in most cases with few exceptions. One current controversy concerns the wetting structure of water on Ru(0001) [3–11]. To explain the nearly flat geometry of oxygen atoms in the water overlayer observed by low-energy-electron-diffraction (LEED) experiments [3,4], Feibelman proposed, based on a density-functional-theory (DFT) calculation, a half-dissociated over-layer for D_2O/Ru(0001) [5]. However, for adsorption at low temperatures, such a wetting structure, with partial dissociation in the overlayer, has so far not been verified by experiments. In contrast, various experiments [4,6,9] seem to indicate that D_2O on Ru(0001) remains intact. This discrepancy between theory and experiment has very recently culminated in a back-to-back publication of two contradictory X-ray photoelectron spectroscopy (XPS) studies [10,11], claiming water dissociation on Ru(0001) is an activated and hence artificially induced process versus a generally valid experimental verification of a partially dissociated water bilayer. Apparently, despite numerous publications, the wetting structure of the D_2O on Ru(001) still persists as one of the puzzling and unresolved issues for water–metal interfaces.

Already in his original publication [5], Feibelman was aware of the large discrepancy (~1 eV) in the work function between the half-dissociated overlayer and the measured data, but could not resolve this problem. In this context and in light of those latest inconsistent experiments, we have carried out a detailed work function, energetic, and vibrational analysis of D_2O/Ru(0001) using both pseudopotential and full-potential DFT methods. Our results show that the work function change of only a mixed molecular bilayer consisting of D-up and D-down (structural details below) can reproduce the experimental value [3,8]. Comparing the vibra-

* Corresponding author. Fax: +46 31 772 8426.
  E-mail address: tfysg@fy.chalmers.se (S. Gao).

tional resonances of the free and hydrogen-bonded OD modes with experiments [6,8] further supports the picture of molecular wetting rather than half dissociation. Finally, we find a high barrier between the molecular bilayers and the dissociated one. This strongly suggests that dissociation is kinetically forbidden at low temperatures, although the half-dissociated overlayer is globally more stable. Activation with excessive energy may overcome this barrier, leading to an artificially induced overlayer exhibiting partial dissociation [9,10]. This picture now explains all experimental observations consistently.

The calculations have been performed with the Vienna ab initio simulation program, VASP [12], while the energetics of the optimized structures are checked against the full-potential linearized augmented plane-wave method (FLAPW) [13]. The Ru(0001) surface is modeled by a supercell that contains a 5-layer slab (with the calculated in-plane lattice constant 2.72 Å) and a vacuum layer exceeding 13 Å. Water molecules are put on one side of the slab in a two-dimensional $(\sqrt{3} \times \sqrt{3})R30°$ unitcell. The Monkhorst–Pack sampling scheme [14] with $5 \times 5 \times 1$ k-points in the Brillouin zone is used. Energy cutoff is 300 eV in the VASP and 340 eV in the FLAPW. The dissociation path and barrier were calculated by the nudged elastic band (NEB) method [15]. Other details of the calculations can be found in recent studies [16,17].

Fig. 1 shows the structures for the D-up, D-down, and half-dissociated overlayer proposed by Feibelman. Their geometries and adsorption energies are specified in Table 1. These structures are similar to what was obtained in earlier calculations [5,18,19]. In the molecular bilayers, the two water molecules in the unit cell are connected by three hydrogen bonds (H bonds), forming a puckered hexagonal network as in the bulk ice I_h [20]. The other D atom is free (or unhydrogen-bonded), and points either upward (D-up case, panel a, d) or down to the surface (D-down case, panel b, e). These two bilayers are degenerate in adsorption energy, 531 (D-up) and 533 meV (D-down, see Table 1), respectively, and have a small barrier (∼55 meV) in between.
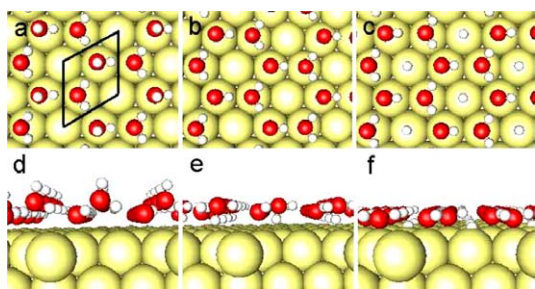

Fig. 1. Atomic structures for the (a) D-up, (b) D-down, and (c) half-dissociated water bilayer on Ru (0001). They are also shown in side views (d–f). The 2D $(\sqrt{3} \times \sqrt{3})R30°$ unitcell is marked in (a).

Table 1
Geometry and energetics for the D-up, D-down, and half-dissociated water overlayer on Ru(0001)

	z_{OO} (Å)	z_{Oru1} (Å)	z_{Oru2} (Å)	E_{ads} (meV)
D-up	0.86	2.46	3.42	531
D-down	0.42	2.69	3.22	533
Half-dis.	0.05	2.09	2.16	766

Here z_{OO}, z_{Oru1} and z_{Oru2} are the vertical distances between the upper and lower O atoms, the bottom O and the underneath Ru, and the upper O and underlying Ru, respectively. The adsorption energy is defined as the energy difference per molecule between the adsorbed system and the sum of the Ru slab and the free molecules.

This barrier is much smaller than that calculated by Michaelides and coauthors (300 meV) using constrained optimization techniques [19]. The NEB method yields the globally optimal path rather than the locally restricted one, and is thus more reliable than the constrained optimization method [19]. Such a small barrier indicates that coexistence of the two structures is possible. The half-dissociated layer is formed by breaking the free OD bond in the molecular bilayer and transferring the D atom to the center of the hexagonal ring. The dissociation leads to a flat water layer with a vertical OO distance reduced to 0.05 Å. This half-dissociated layer is energetically most stable, $E_{ads} = 766$ meV. The small OO distance also seems to be consistent with the LEED experiments [3,4]. The flat structure and the larger adsorption energy are the two reasons, on which the proposal for the half-dissociated layer was based [5].

To look for a possible resolution of the discrepancy in the work function change, we have carried out detailed calculations of $\Delta\Phi$ including dipole corrections in the asymmetric slab geometry (see Table 2). For the half-dissociated overlayer, the work function change is only 0.34 eV, as also found by Feibelman [5], which represents a dramatic deviation from the experimental value ($\Delta\Phi \sim 1.3$ eV [3,8]) as already pointed out. In addition, neither the pure D-up bilayer ($\Delta\Phi = 3.01$ eV) nor the pure D-down ($\Delta\Phi = 0.40$ eV) bilayer yields a work function change close to experiment. This seems to suggest the coexistence of the two molecular bilayers, which is already highly probable due to the degenerate adsorption energies. Calculation for the mixed D-up and D-down bilayers, with larger supercells [$(2\sqrt{3} \times 2\sqrt{3})R30°$ and (3×3)] result in work function changes of 1.70 eV (with ratio of D-up/D-down = 1:1), 1.54 eV

Table 2
The calculated change in work function upon adsorption ($\Delta\Phi$) for pure and mixed water bilayers with ratio between D-up:D-down

Structure	D-up	1:1	1:2	1:3	D-down	Half-dis.	Expt.
$\Delta\Phi$ (eV)	3.01	1.70	1.54	0.82	0.40	0.34	1.26

The experimental value is also listed [3].

(ratio = 1:2) and 0.82 eV (ratio = 1:3), respectively, in the range of the experimental data [21]. The work function changes are relatively insensitive to the water–Ru distance. Forcing the O–Ru bond to a shorter distance by 0.3 Å (as found in FLAPW calculations) or even to the geometry of Held and Menzel's experiment [3] does not appreciably change the work function. The work function data listed in Table 2 suggest a mixed D-up/D-down structure with a ratio between 1:2 and 1:3. Such a mixed structure with D-down dominance is also favored by the more accurate energetics from the FLAPW, which give a larger energy difference (20 meV rather than 2 meV by VASP) between the two bilayers.

Next, we consider the vibrational spectra extracted from the velocity–velocity correlation functions [16]. The vibrational spectra are more reliable than those obtained in the dynamical matrix approach used by Feibelman [7,22]. Fig. 2 and Table 3 show the vibrational spectra obtained from our simulations. The low energy modes of the spectra (<120 meV) for all three structures look similar. They are featured by six modes at 20, 30, 48, 64, 87 and 117 meV for the D-up bilayer. These low frequency modes are comparable with the measured frequencies at 48, 68, 87 and 114 meV by electron energy loss spectroscopy [23] (see Table 3). They correspond to translation, frustrated rotations, and librational modes for the D_2O overlayer. Peaks at ~140 meV are the DOD scissoring/bending modes. By comparison with the experiment in the low-energy range, it is difficult to tell whether the overlayer is dissociated.

Table 3
Calculated and measured vibrational energies for the D_2O bilayer on Ru(0001) (in meV)

	Transl./libr.				δ(DOD)	v(O–D$_b$)	v(O–D)
D-up	48	64	87	117	141	273, 305	336
D-down	51	66	93	111	145	252, 306	336
Half-dis.	51	79	91	115	136	250,314	
Expt.[a]	48	68	87	114	140*	270*, 312*, 328*	338*
Expt.[b]						284, 316	339

See [6,23] for the assignment of these modes.
[a] Ref. [23]. Values with (*) are converted to D_2O from H_2O by counting for an isotope factor of 1.35.
[b] Ref. [6]

The high-energy OD stretch modes (>200 meV) are, however, qualitatively different for the molecular bilayers and the dissociated structure (Fig. 2), demonstrating the sensitivity of the OD stretch to the detailed structures at the surfaces [16]. The spectra for D-up and D-down bilayers are similar, as found in water/Pt(111) [16]. Both have a high-energy mode at 336 meV, which is absent in the dissociated overlayer. This high-frequency mode corresponds to the free OD in the molecular bilayers. It is very close to the measured vibrational mode, 338 meV, which starts to emerge at 1 bilayer D_2O coverage [6,8,24]. Other features in the spectrum of the half-dissociated bilayer are a sharp peak at 314 meV, corresponding to the dissociated OD groups, and peaks at around 250 meV, which belong to the OD stretch vibration within the undissociated D_2O molecule. The 250 meV resonance was not observed in the experiments. Comparison of the vibrational spectra clearly shows discrepancies between the half-dissociated structure and the experimental data, despite the recent attempts to tune the vibrational resonances by changing certain atomic configurations like the OO distance [8,22].

While work function data and vibrational spectra clearly indicate that D_2O does not dissociate on Ru, this seems to contradict with the fact that the half-dissociated overlayer is energetically more stable. To check out possible errors in DFT/VASP calculations, a well-converged FLAPW calculation also confirms an energy difference of 0.198 eV between the D-down bilayer and the dissociated one, comparable to 0.233 eV given by VASP, though the binding energy is usually 0.1 eV larger than that given by VASP, and the bilayer is 0.2–0.3 Å closer to the surface. The resolution to this seeming discrepancy in the energetics may result from the kinetic constraint and the thermodynamics governing the adsorption and growth processes, though the energetics is physically correct. Water adsorbs as molecular water in monomers and clusters. The monomer adsorption energy (desorption barrier) is 0.41 eV, while the barrier for monomer dissociation is high, 0.85 eV on Ru(0001) [18]. Formation of clusters and overlayers is efficient,
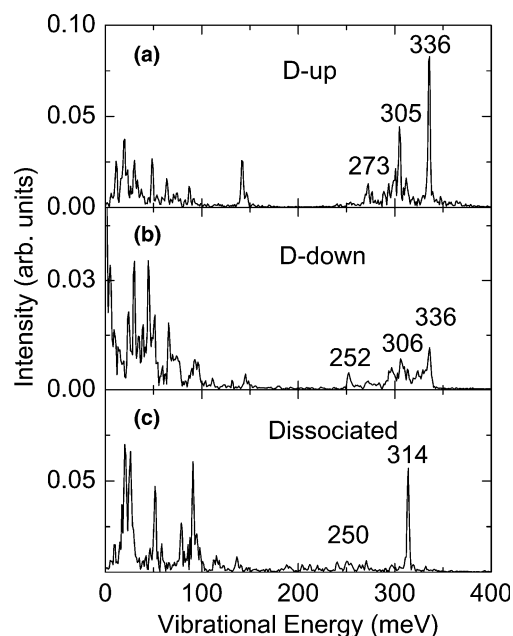

Fig. 2. Vibrational spectra for the (a) D-up, (b) D-down and (c) half-dissociated water bilayer calculated from ab initio molecular dynamics simulations at 80 K.

because water molecules are usually mobile on metal surfaces even at low temperatures. The calculated barrier for monomer diffusion on Ru(0001) is around 0.31 eV, suggesting that the formation of a molecular bilayer is favorable. However, whether the molecular bilayers can dissociate depends on the barrier between the molecular bilayers and the dissociated one.

We thus determined the barrier and the minimum energy path for bilayer dissociation using the NEB method (see Fig. 3). The barrier for dissociation from the D-down bilayer, 0.62 eV, is substantially lower than that in bulk ice and liquid water of ~0.9 eV [25]. The transition state corresponds to a configuration, where the dissociating OD bond is elongated to 1.43 Å. Note that Michaelides et al. [18] reported a smaller dissociation barrier of 0.5 eV in a larger, (3×3), supercell, however, a reduction of the barrier height does not appear in our NEB calculation when the size of the supercell is increased. The barrier obtained with NEB is larger than the mean adsorption energy of the water bilayers (0.53 eV) by ~0.1 eV. Moreover, it is also larger than the mean strength of H bonds within the water bilayer. The smaller binding energy in the bilayer, compared to the dissociation barrier, suggests that desorption of water from the bilayers would be more favorable than dissociation. The recent XPS results by Nilsson and coworkers [10] and reflection absorption infrared spectroscopy together with temperature programmed desorption (TPD) by the Hodgson group [9], all indicate that water dissociation indeed is an activated process.

Our results remove the controversy between theory and experiment regarding the partial dissociation of water on Ru(0001). D_2O bilayer remains intact as molecular bilayers at low temperatures, although the large OO buckling, 0.86 and 0.42 Å, for the D-up and D-down bilayers, seems to contradict with earlier LEED experiment [3], where a small OO distance of 0.1 Å was reported. However, recent XPS experiments by the Nilsson group [10] and TPD studies by Menzel and cowork-

ers [26] have provided new evidence that the water layers in the earlier LEED experiments may have been significantly dissociated by beam damage. In addition, coadsorption with impurity atoms such as oxygen could also induce partial water dissociation on a metal surface [1,2,9]. This might be also considered in the discussion of those controversial XPS results [10,11]. For all these reasons, the smal OO buckling probed by earlier LEED experiments is most likely the dissociated state, artificially created by the electron beam.

In summary, detailed calculation and analysis on the work function, energetics, and vibrational spectra have led us to the conclusion that D_2O on Ru(0001) remains molecularly intact at low temperatures. Under these conditions, water dissociation is suppressed at low temperatures, despite the fact that the half-dissociated structure is indeed the global minimum state. Wetting structures with mixed and intact D-up and D-down molecules, existing as metastable states, are found to comply with all experimental and theoretical findings available so far.
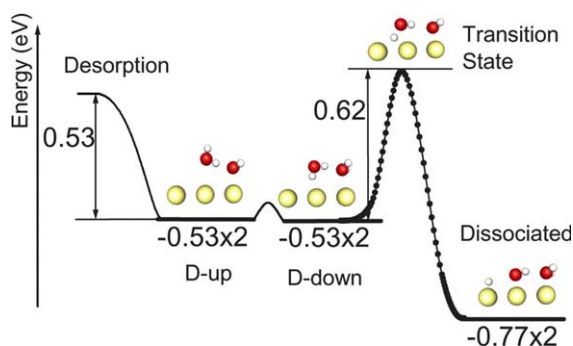
Acknowledgements

Fig. 3. Schematic energy diagram for the D-up, D-down, and half-dissociated water bilayer. A high dissociation barrier, of 0.62 eV, lies between the molecular bilayers (D-up and D-down) and dissociated state. This dissociation barrier is higher than the mean adsorption energy 0.53 eV of the molecular bilayer.

References

[1] P.A. Thiel, T.E. Madey, Surf. Sci. Rep. 7 (1987) 211.
[2] M.A. Henderson, Surf. Sci. Rep. 46 (2002) 1.
[3] G. Held, D. Menzel, Surf. Sci. 316 (1994) 92;
    G. Held, D. Menzel, Surf. Sci. 327 (1995) 301.
[4] S.R. Puisto, T.J. Lerotholi, G. Held, D. Menzel, Surf. Rev. Lett. 10 (2003) 487.
[5] P.J. Feibelman, Science 295 (2002) 99.
[6] D.N. Denzler, Ch. Hess, R. Dudek, S. Wagner, Ch. Frischkorn, M. Wolf, G. Ertl, Chem. Phys. Lett. 376 (2003) 618.
[7] P.J. Feibelman, Phys. Rev. B 67 (2003) 035420.
[8] C. Frischkorn et al., to be published.
[9] C. Clay, S. Haq, A. Hodgson, Chem. Phys. Lett. 388 (2004) 89.
[10] K. Andersson, A. Nikitin, L.G.M. Pettersson, A. Nilsson, H. Ogasawara, Phys. Rev. Lett. 93 (2004) 196101.
[11] J. Weissenrieder, A. Mikkelsen, J.N. Andersen, P.J. Feibelman, G. Held, Phys. Rev. Lett. 93 (2004) 196102.
[12] G. Kresse, J. Hafner, Phys. Rev. B 47 (1993) 558;
    G. Kresse, J. Hafner, Phys. Rev. B 49 (1994) 14251;
    G. Kresse, J. Hafner, J. Phys.: Condens. Matt. 6 (1994) 8245.
[13] P. Blaha, K. Schwarz, J. Luitz, WIEN97: a Full Potential Linearized Augmented Plane Wave Package for Calculating Crystal Properties, Karlheinz Schwarz, Technische Universität Wien, Austria, 1999. ISBN 3-9501031-0-4.
[14] H.J. Monkhorst, J.D. Pack, Phys. Rev. B 13 (1976) 5188.
[15] H. Jonsson, G. Mills, K.W. Jacobsen, in: B.J. Berne, G. Ciccotti, D.F. Coker (Eds.), Classical and Quantum Dynamics in Condensed Phase Simulations, World Scientific, 1998.

[16] S. Meng, L.F. Xu, E.G. Wang, S.W. Gao, Phys. Rev. Lett. 89 (2002) 176104.
[17] S. Meng, E.G. Wang, S.W. Gao, Phys. Rev. B 69 (2004) 195404.
[18] A. Michaelides, A. Alavi, D.A. King, J. Am. Chem. Soc. 125 (2003) 2746.
[19] A. Michaelides, A. Alavi, D.A. King, Phys. Rev. B 69 (2004) 113404.
[20] D.L. Doering, T.E. Madey, Surf. Sci. 123 (1982) 305.
[21] Structural mixing between the two molecular bilayers is also favored by dipole interaction and entropy effects. The latter, however, was found to be of minor importance P.J. Feibelman, A. Alavi, J. Phys. Chem. B 108 (2004) 14362.
[22] P.J. Feibelman, Chem. Phys. Lett. 389 (2004) 92.
[23] P.A. Thiel, R.A. DePaola, F.M. Hoffmann, J. Chem. Phys. 80 (1984) 5326.
[24] The vanishing intensity of the free OD resonance below 1 bilayer observed in vibrational spectroscopy using sum frequency generation [6,8] might be caused by cancellation effects in the coherent signal within a mixed D-up/D-down overlayer due to the degenerate vibrational frequencies of both up and down structures (see Table 3).
[25] E. Schwegler, G. Galli, F. Gygi, R.Q. Hood, Phys. Rev. Lett. 87 (2001) 265501.
[26] D. Menzel, Private communication.