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First-principles study of the role of solvent in the dissociation of water over a Pt-Ru alloy

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Self-consistent gradient-corrected periodic density functional theoretical calculations are used to examine the effects of an aqueous environment on the dissociation of water over a Pt-Ru alloy. This reaction is thought to be one of the rate-limiting steps in oxidative removal of CO from the anode surface of both the direct methanol and reformate fuel cells. The reaction leads to the formation of surface hydroxyl (OH) intermediates that can subsequently oxidize adsorbed CO into CO_2. We examine the energetics and mechanism for the dissociation of water over $Pt_{66}Ru_{33}(111)$ in the presence of 23 water molecules (per 615 $Å^3$ unit cell volume) that act as a solution phase and in the absence of solution (vapor phase). The reaction is endothermic by $+53$ kJ/mol and has an activation barrier of $+105$ kJ/mol when carried out in the vapor phase, but was found to be much less endothermic ($+26$ kJ/mol) and has a significantly lower activation barrier ($+27$ kJ/mol) when carried out in solution. In the vapor phase, the reaction occurs homolytically whereby the dissociation is activated by insertion of a Ru atom into the O-H bond of water. The products formed are adsorbed hydroxyl and hydrogen intermediates. In contrast, in solution, the dissociation occurs via a heterolytic path whereby the solvent molecules are directly involved in activating the O-H bond. The reaction leads to the formation of a hydroxyl intermediate that is bound to the alloy surface and a proton that is released into the solution phase. *Ab initio* molecular dynamics simulations were performed at 300 K to establish the sequence of elementary steps that can occur. The simulations show that water dissociates over Ru and that the hydroxyl intermediate that first forms over Ru rapidly diffuses along the metal surface, migrating over Pt as well as Ru sites. We believe that this evidence shows that diffusion occurs as the result of the proton transfer between the coadsorbed water and hydroxyl intermediates in an aqueous environment. This could have important consequences for CO oxidation in PEM fuel cells whereby the diffusion of CO and/or OH intermediates is important for the reaction at the edge of the Pt/Ru boundaries. The work reported herein applies at open-circuit potentials, but may also be appropriate at other potentials as well.

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I. INTRODUCTION

Carbon monoxide is known to poison anode surfaces (usually supported platinum) of both the direct methanol and reformate fuel cells and thus limits the cell performance. It is now well established that alloying Pt with Ru helps to alleviate this problem by weakening the metal-CO bonding[1,2] and by accelerating the oxidation of CO. The latter is commonly accepted to involve the activation of water to form hydroxyl intermediates and the subsequent reaction of CO with the surface hydroxyl groups:[3,4]

$$H_2O \rightarrow OH + H^+ + e^-, \tag{1}$$

$$CO + OH \rightarrow CO_2 + H^+ + e^-. \tag{2}$$

The properties of CO oxidation indicate that either water activation or the disproportionation of CO with the OH intermediates may be the rate-determining steps.[5,6] The generation and migration of surface hydroxyl are critical in both steps. In this paper, we present *ab initio* molecular dynamics (MD) simulations along with more traditional density functional theory (DFT) calculations to elucidate the activation of water over Pt/Ru alloys. We examine the energetics and mechanism for this reaction over Pt/Ru in the vapor phase as well as in solution. The results indicate that water activation in solution is heterolytic and results in the generation of protons along with surface hydroxyl intermediates. It has been argued that both CO and OH surface intermediates can form islands, thus limiting their mobility and oxidation kinetics. We propose the evidence that suggests that OH mobility can proceed via proton-transfer processes across a network of water in the local vicinity of the surface.

II. THEORETICAL DETAILS

All calculations were performed using periodic density functional theory as implemented in the code VASP (Vienna *ab initio* simulation package).[7] The Kohn-Sham equations were solved using a plane-wave basis set with a cutoff energy of 330 eV. The PW91 functional was used to describe the exchange correlation term.[8] The core electrons and nuclei of the atoms were described by the Vanderbilt ultrasoft pseudopotential.[9] Electronic energies were calculated using a $3\times3\times1$ k-point grid mesh. We have verified that the energetics are converged at the chosen cutoff energy and k-point grid density. Increasing the k-point grid density to $5\times5\times1$ was found to affect the reaction energies by less than 3 kJ/mol.

The metal surface was modeled as the (111) surface of $Pt_{66}Ru_{33}$ bulk alloy (66% Pt, 33% atomically mixed Ru). The alloy favors a face-centered-cubic structure in the bulk with an optimal lattice constant of 2.78 Å. Three parallel layers, each with a Pt:Ru ratio of 2:1, were chosen to describe the thickness of the metal slab. The top two layers were allowed to relax during geometry optimization. The metal atoms in the bottom layer are not directly involved in the reaction and were therefore held fixed at their bulk positions. In order to verify that energetics are converged at the chosen slab thickness, we examined chemisorption of hydrogen over three-, four-, and five-layer metal slabs. The binding energies of the H atom over these slabs were found to be less than 5 kJ/mol apart. This is within the present-day accuracy of the density functional theory methodology. Hence a three-layer slab is sufficiently accurate to model energetics over Pt-Ru.

All calculations were performed within a 3×3 unit cell. A spacing of 10 Å was used to separate the metal slab and its periodic images in the direction normal to the surface plane. In order to model the solvent phase, the unit cell was packed with 23 water molecules. This number was chosen so that the density of water within the unit cell is about 1 g/cm^3. The intermolecular and intramolecular geometries of all water molecules were relaxed during the calculation to allow for the formation of hydrogen bonds. A validation of the solvent model is available in our earlier paper.[10]

Reaction energies (E_{rxn}) were calculated as a difference in the electronic energies of the products ($E_{products}$) and reactants ($E_{reactants}$):

$$E_{rxn}=E_{products}-E_{reactants}. \tag{3}$$

As per our conventions, a positive value of E_{rxn} indicates that the reaction is endothermic, while a negative value indicates that the reaction is exothermic and hence thermodynamically favorable.

Transition states were isolated using the nudged elastic band approach.[11] The electronic energy of the transition state relative to that of the reactant state is the activation barrier (ΔE_{act}).

The environment at the anode of an actual fuel cell is quite complex. In addition to incorporating a second metal such as Ru and the solvent, the chemistry is complicated by electric field effects. This effect is not considered in the present model, but will certainly play an important role. We are progressively building the complexity of our model and will report the effect of electric field in a future communication. In this paper, we wish to isolate and investigate the role of solution in the reaction chemistry. The current model would be that which is equivalent to the open circuit electrochemical cell.

III. RESULTS AND DISCUSSION

A. Vapor-phase dissociation of water

We have examined the dissociation of water over Pt-Ru in the vapor phase in detail in a separate study.[12] Herein, we present only the key results of that work to compare with the reaction chemistry that occurs in solution. The dissociation of water in the vapor phase occurs homolytically and leads to the formation of hydrogen and hydroxyl intermediates that are both bound to the metal. Hydrogen adsorbs at the threefold fcc hollow site, while the hydroxyl intermediate adsorbs at the atop Ru sites. In the vapor phase, the dissociation of water involves insertion of a Ru atom into its O-H bond. The Ru atom weakens the bond, thereby initiating the reaction, and in addition offers stabilization to the hydrogen atom as it breaks from the adsorbed water. The reaction occurs via a three-center transition-state complex that involves an insertion of the Ru atom into the O-H bond. The transition state is quite late along the reaction channel whereby there is a considerable stretch of the O-H bond (Fig. 1). The activation barrier for the reaction over $Pt_{66}Ru_{33}(111)$ was found to be +105 kJ/mol. The overall reaction is endothermic by +53 kJ/mol. The energetics and mechanism of the reaction, however, are both affected by the presence of a solvent environment.

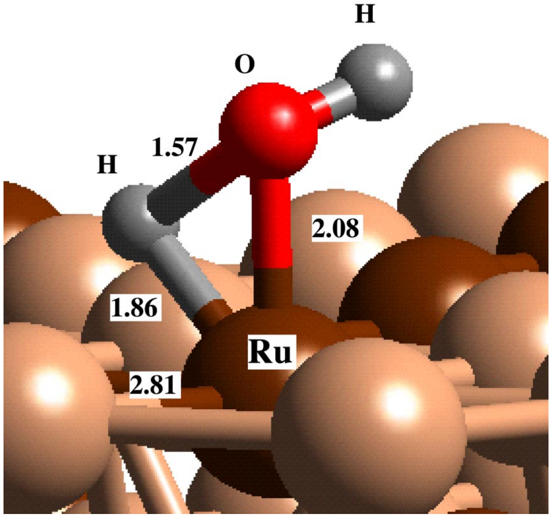

FIG. 1. (Color online) Transition-state structure for the dissociation of water over $Pt_{66}Ru_{33}$. A Ru atom inserts into the O-H bond of water, forming a three-center complex.

B. Solvent-phase dissociation of water

Water adsorbs on the surface through donation of electron density from one of the lone pair of electrons on its oxygen into vacant states at ruthenium sites. The ad-layer forms a $\sqrt{3}\times\sqrt{3}$ arrangement in conjunction with the surface distribution of Ru atoms. In the solution phase, adsorbed water forms a series of hydrogen bonds with an overlayer of solvent molecules; the overlayer in turn forms hydrogen bonds with additional water molecules (Fig. 2). The structural arrangement of water close to the surface is similar to that proposed by Doering and Madey for multilayer adsorption of water over Ru(0001).[13] In our model, the network of hydrogen bonds between water molecules extends within the unit cell as well as across adjacent unit cells, thereby simulating the effect of an aqueous environment.

Our focus here is to examine the effect of solution on the dissociation of adsorbed water. In solution, the adsorbed water can dissociate in two ways: homolytically [Eq. (4a)], forming surface hydroxyl intermediates along with hydrogen adatoms, or heterolytically [Eq. (4b)], forming OH^- intermediates and protons in solution:

$$H_2O^*\rightarrow OH^*+H^*, \tag{4a}$$

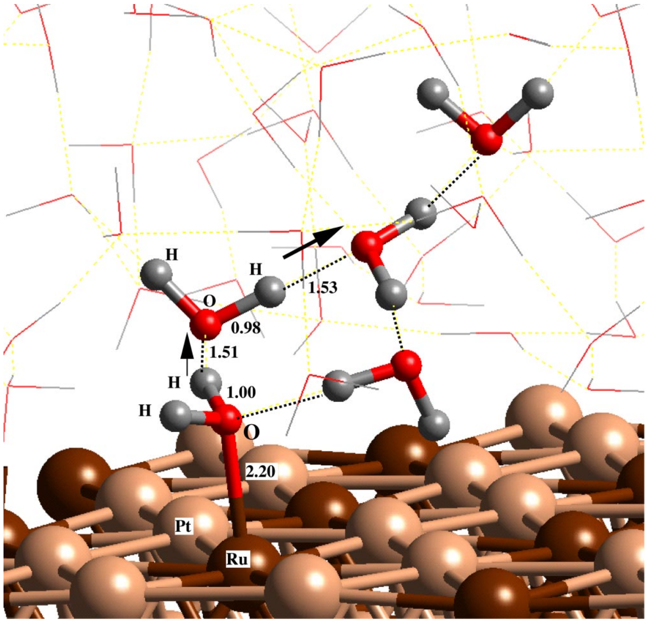

FIG. 2. (Color online) Optimized structure of water adsorbed over the Pt-Ru surface in the presence of an aqueous environment. The arrows represent the path along which the adsorbed water prefers to dissociate. For the sake of clarity, only water molecules involved in the chemistry are highlighted. Hydrogen bonds are shown by dotted yellow lines.

$$H_2O^* \rightarrow OH^{\delta -} + H^{\delta +}(aq) + e^{-}(?). \qquad (4b)$$

The former is analogous to what was found to occur in the vapor phase. The latter, on the other hand, is novel to the solvent phase and is possible due to stabilization of protons by water. Both reactions (4a) and (4b) were found to be thermodynamically more favorable and had lower activation barriers than dissociation in the vapor phase. The reaction leading to the formation of adsorbed hydroxyl and hydrogen intermediates was found to be endothermic by +43 kJ/mol, while that leading to the formation of hydroxyl intermediates and protons was significantly less endothermic at +26 kJ/mol. Transition-state calculations indicate that the activation barrier for the formation of chemisorbed hydroxyl and hydrogen intermediates [Eq. (4a)] is 80 kJ/mol. The barrier for the formation of hydroxyl intermediates and solvated protons [Eq. (4b)] is, however, only +27 kJ/mol. In solution, water is therefore more likely to dissociate into hydroxyl intermediates and protons rather than hydrogen adatoms. This, we note, holds for "open-circuit potentials" (no electric field effects) at which the current simulations are performed. At potentials negative to the "open-circuit potential," it is possible that the hydrogen may adsorb more favorably on the metal.

The hydroxyl intermediates that form adsorb atop Ru sites. They are partly stabilized by the solution and partly by the metal surface. The proton resides in water, close to the metal, as an $H_5O_2^+$ species where it is directly solvated by two water molecules that are in turn hydrogen bonded within the water network (Fig. 3). Only one water molecule separates the proton from the surface hydroxyl group. Together, the hydroxyl intermediates and protons form the well-known *double layer* from electrochemistry—a layer of anion intermediates directly adsorbed on the surface followed by a cationic solvation layer.[14]

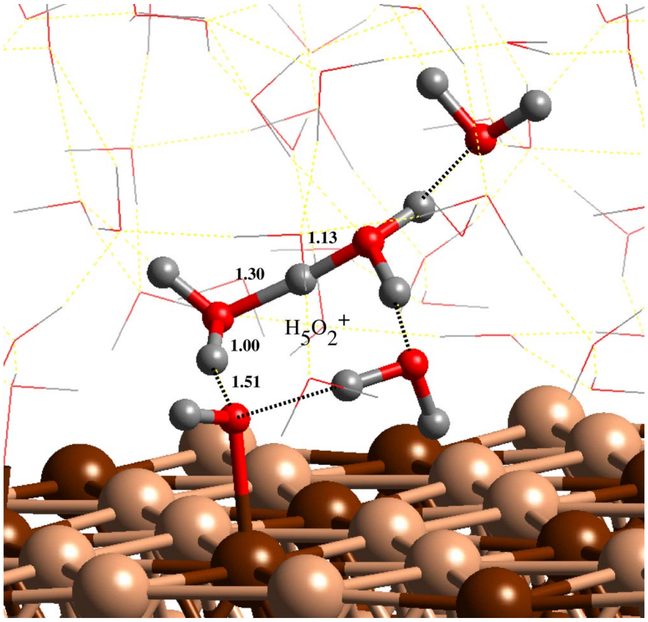

FIG. 3. (Color online) DFT-optimized structure of the reaction products: hydroxyl intermediate bound atop Ru and proton solvated in water.

The transition-state structure for the dissociation of water in the presence of solvent is shown in Fig. 4. In the reactant state, adsorbed water forms hydrogen bonds with its neighboring water molecules. At the transition state, one of its covalently bonded hydrogen atoms begins to split off into

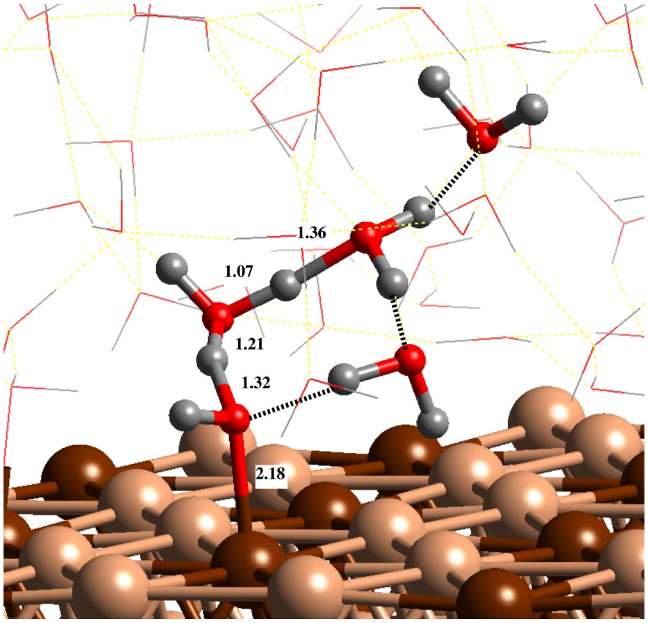

FIG. 4. (Color online) Transition-state structure for the dissociation of water into adsorbed hydroxyl intermediates and protons ($\Delta E_{act} \sim 27$ kJ/mol).

solution and starts to form a covalent bond with a neighboring water molecule from the solvent to which it was initially hydrogen bonded. The solvent molecule in turn begins to transfer one of its internal hydrogen atoms to the next adjacent water molecule. The dissociation of water into hydroxyl intermediates and protons thus involves a concerted migration of hydrogen atoms from the adsorbed molecule into solution along the hydrogen-bonded water network. The water molecules provide a direct route for proton conduction away from the adsorbed water. This mechanism is very different from that in the vapor phase.

In the vapor phase, the dissociation was found to be mediated by the Ru surface, whereby ruthenium activates the O-H bond and subsequently inserts into it. Both the hydroxyl and hydrogen intermediates that form are stabilized by the surface. In the presence of the solvent, the analogous *metal-mediated* route, which leads to the formation of surface bound hydroxyl and hydrogen species [Eq. (4a)], was found to be enhanced by the presence of water. Solvent molecules interact with each other only via hydrogen bonds. The solvent structure can readily rearrange during the course of the reaction to help stabilize the hydrogen as it dissociates from adsorbed water to the Ru surface. The solvent plays an *indirect* role in that it helps to stabilize the partial charges on the transition-state complex. This effect of the solvent, however, is weak as the barrier is lowered by only 15 kJ/mol from that in the vapor phase. The preferred route in solution is the heterolytic path, which involves the *direct* participation of the solvent and leads to the formation of surface hydroxyl groups and protons [Eq. (4b)]. The metal is involved in the initial activation (weakening) of the O-H group. Our calculations results indicate that the dissociation of water over Pt(111) ($E_{rxn} = +73$ kJ/mol, $\Delta E_{act} = +75$ kJ/mol) has a significantly higher activation barrier and is more endothermic than the reaction over the Pt-Ru alloy ($E_{rxn} = +26$ kJ/mol, $\Delta E_{act} = +26$ kJ/mol). Subsequent *ab initio* molecular dynamics showed that water remains intact at 300 K. Ru in the surface helps to catalyze water dissociation. Water preferentially adsorbs on Ru which inserts into the O-H bond. Water mediates the reaction in that it helps to stabilize the formation of the $O^{\delta-}$-$H^{\delta+}$ in the transition state and the $H^+(aq) + OH^* + 1e^-$ reaction products. Dissociation thus involves the cooperative coordination of the metal and water solution—an electron is transferred to the metal along with the -OH group, while a proton stabilizes into water solution.

C. *Ab initio* molecular dynamics

In the previous section we presented results from static density functional theory calculations. These calculations allow us to examine changes in electronic energies resulting from the dissociation of water. The potential energy surface for the water solution, however, consists of a large number of minima of nearly the same energy. By performing static calculations, we have possibly optimized the solvent structure into one such minimum and have not fully captured the influence of the fluctuating nature of the solution on the reaction chemistry. In order to be able to account for this effect and to incorporate the accompanying entropic effects, we further examined the dissociation of water using *ab initio* molecular dynamics simulations.[15] The dynamics was performed within the canonical N-V-T ensemble for $\sim$2 ps with a time step of 1 fs. The temperature was maintained constant at 300 K using a Nose-Hoover thermostat.[16,17] The other computational parameters were the same as those used for geometry optimization.

The dynamic simulations were started using the optimized structures found from the static water/metal interface calculations reported above. Snapshots of the system at various time intervals are shown in Fig. 5. Water favorably adsorbs over Ru. At about 0.8 ps of the dynamics run, one of the adsorbed water molecules begins to heterolytically dissociate, transferring one of its hydrogen atoms directly into solution. The dissociation leads to the formation of a solvated proton and a hydroxyl intermediate that is adsorbed over Ru. The negative charge is found to be delocalized over the top layer of the metal surface, particularly over Ru, and the adsorbed hydroxyl intermediate. The reaction products formed and the reaction pathway are both in agreement with the predictions from our static calculations.

The dissociation of water at the Ru site acts to induce coadsorption of water at a neighboring Pt site. The dissociation over Ru leads to the formation of $OH^{\delta-}$ and a proton. This promotes activation of the newly adsorbed water molecule. Water adsorbed to Pt subsequently dissociates, transferring a proton to the neighboring hydroxyl group on Ru. As a result, the Ru-hydroxyl intermediate is converted into Ru water, whereas the Pt-water molecule is converted into Pt hydroxyl. The hydroxyl species thus diffuses from Ru to Pt. The hydroxyl intermediate subsequently diffuses to another neighboring site during the course of the dynamics via a similar proton-transfer path. The diffusion of hydroxyl, however, is not due its physical movement on the surface, but instead is the result of proton transfer between adsorbed water molecules and the hydroxyl intermediates as is shown schematically in Fig. 6. This observation is of direct relevance to fuel cell chemistry. It is believed that CO oxidation occurs at the Pt-Ru boundaries;[5,18] CO forms islands on Pt, whereas the hydroxyl intermediates are adsorbed at Ru sites.[19] The reaction between CO and OH is thought to occur along the periphery of CO islands. As CO at the periphery is oxidized to CO_2, more CO begins to diffuse from the interior to the Pt-Ru boundaries. Recent evidence by Davies *et al.*,[20] however, suggests that in addition to the reaction at the Pt-Ru boundary, there may be a spillover of the oxidant onto Pt. This is consistent with the results reported herein. The dynamics run indicates a very high mobility of hydroxyl intermediates including over Pt once they are formed. We believe that the path for diffusion involves (a) stable adsorption of water on Pt once hydroxyl and protons form in solution and (b) proton shuttling between water and hydroxyl intermediates. While the mobility of surface hydroxyl groups may be limited on Pt due to islands of CO that form, they can readily diffuse on both Ru and Pt, provided that vacant sites are available. The diffusion of the hydroxyl intermediate is therefore not likely to limit the oxidation of CO.

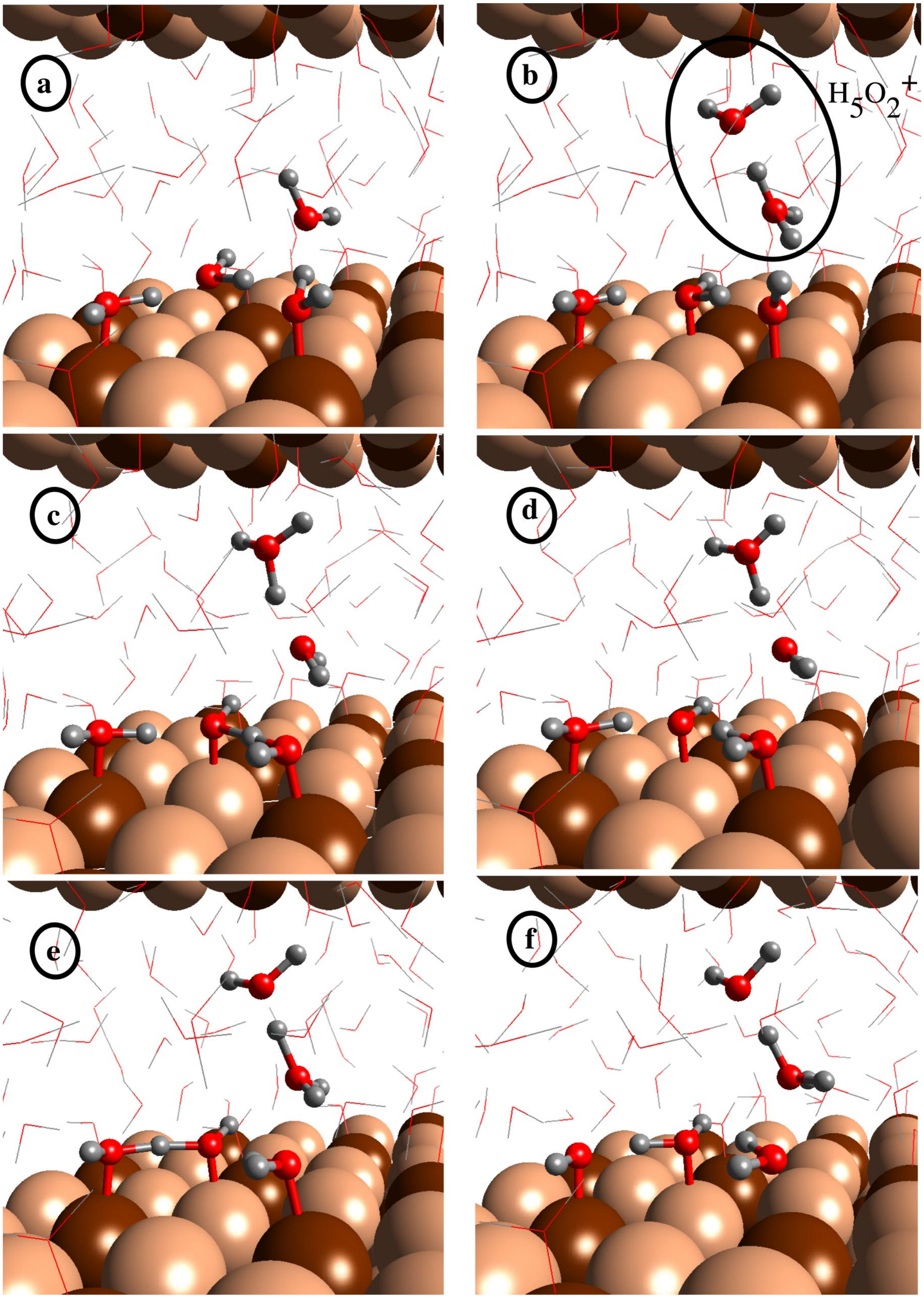

FIG. 5. (Color online) Snapshots from *ab initio* molecular dynamics simulations performed at 300 K. (a) shows the initial structure wherein water is adsorbed over the Ru sites on the surface. (b) shows the Ru-bound hydroxyl intermediate and the solvated proton that form on the dissociation of water (c)–(f) indicate the migration of the hydroxyl intermediates over the surface [from Ru (shown as darker atoms on the surface) to Pt (shown as the lighter atoms to Ru sites) via proton transfer].

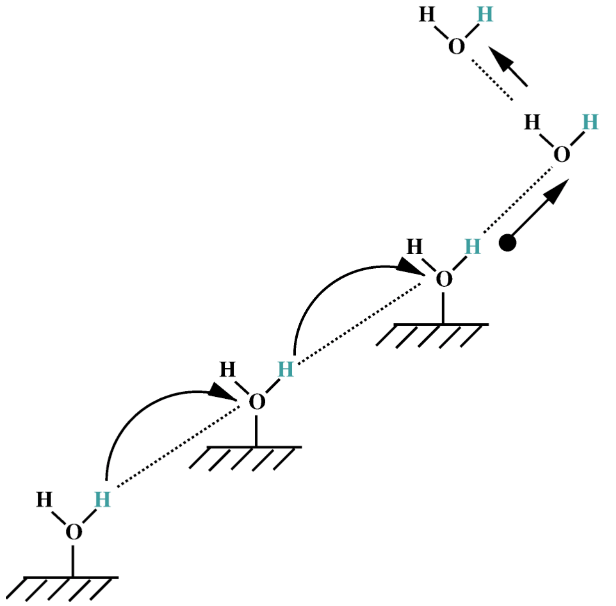

FIG. 6. (Color online) Schematic representation of pathways for the dissociation of water and the migration of hydroxyl intermediates over the surface. The arrows represent the paths for proton transfer.

The static activation barrier of +26 kJ/mol reported above can readily be overcome by the gain in activation entropy in going from the reactant to the transition state. This increase in the activation entropy could explain the relatively rapid dissociation (0.8 ps) seen in the *ab initio* molecular dynamics results. A surface-bound water intermediate reacts here to form a surface hydroxyl group and a proton in solution. The preexponential value will therefore be considerably greater than 10^{13} since we are moving from a single surface-bound intermediate to two much more mobile product states. The value should at least on the order of 10^{16}–10^{17}, which would indicate that the reaction can indeed occur by 0.8 ps. By using the simple gas-phase values reported in the literature the preexponential for the heterolytic splitting of water to form OH(−) and H(+) has a preexponential value greater than 5×10^{16}.

To better quantify the free energy (or entropy) of activation, we would need to perform constrained molecular dynamics simulations along the reaction trajectory that allow a map of the free energy of the system as a function of the reaction coordinate. In this paper we have performed unconstrained dynamics. Our focus has primarily been to identify the mechanism for the dissociation reaction in solution and to distinguish it from that in the vapor phase.

IV. CONCLUSIONS

We have examined the dissociation of water over a model Pt-Ru (111) surface in the vapor phase and in solution. In both cases, water preferentially dissociates over Ru sites. The energetics and mechanism for dissociation, however, are different for the two cases. In the vapor phase, the reaction was found to be endothermic by +53 kJ/mol and has an activation barrier of +105 kJ/mol. The presence of a solvent phase stabilizes the reaction products and transition-state complex. The reaction in solution is thermodynamically more favorable ($E_{rxn}=+26$ kJ/mol) and has lower activation energy ($\Delta E_{act}=+27$ kJ/mol) than in the vapor phase.

In the vapor phase, the dissociation is mediated by the metal surface (*metal mediated*). A Ru atom inserts into the O-H bond of water, activating the reaction, which then leads to the formation of surface bound hydroxyl and hydrogen intermediates. In the solution phase, the reaction is favorably mediated by water molecules rather than the metal. The dissociation occurs by a direct transfer of a proton from the adsorbed water into solution along the hydrogen-bonded network of water. The products formed are surface hydroxyl intermediates and solvated protons instead of hydrogen adatoms. The solvent also lowers the barrier for the *metal-mediated* route by an indirect effect whereby it stabilizes the partially charged transition state. The stabilization, however, is not large as the barrier is only reduced by 15 kJ/mol. This path may be favorable, however, in the presence of potential field effects.

Ab initio MD simulations performed at 300 K clearly elucidate the direct participation of water molecules in solution-phase chemistry. Water is activated via the concerted action of the metal surface and the solution phase which accommodate the heterolytic dissociation of water into $OH^{\delta-}$ and $H^{\delta+}$. Moreover, the simulations reveal that the hydroxyl intermediates nucleate over Ru, but can rapidly diffuse on the surface including over the Pt sites. The diffusion occurs due to the transfer of protons from adsorbed water molecules to the coadsorbed hydroxyl intermediates.

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