Proton Wires via One-Dimensional Water Chains Adsorbed on Metallic Steps

R. Scipioni, D. Donadio, L. M. Ghiringhelli,*,[†] and L. Delle Site*

Max Planck Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany

ABSTRACT: The process of proton transfer is here analyzed for one-dimensional water chains adsorbed on metallic steps. When the water chain contains a hydronium and a hydroxyl ion, two different mechanisms are possible, depending on the metal substrate. On coinage metals (Ag, Au), recombination is observed through a spontaneous Grotthuss mechanism. On more reactive surfaces (Pd and Pt), the hydronium ion is unstable and releases a proton that adsorbs onto the metal, leaving the negatively charged OH^- unbalanced. In this case, the negative charge can be transferred along the wire with very low activation barriers.

1. INTRODUCTION

Metallic surfaces, due to their hydrophilicity, present fascinating possibilities to induce ordered two- and one-dimensional water networks stabilized by the adsorption interaction of water molecules onto the surface. Such networks may provide channels through which protons can move along paths of hydrogen bonds. Indeed, metal surfaces represent technologically relevant interfaces for water[1] and influence the proton transfer capabilities of adsorbed water.[2,3] However, on flat highly symmetric surfaces (e. g., the 111 cut of a fcc lattice), water builds 2D (or even 3D) networks, and the direction of proton transfer is not uniquely defined. This makes the experimental as well as the theoretical study more ambiguous, and the system remains of unclear technological utility.[4] It would be different instead to have 1D chains, where protons move along well-defined and controlled paths. (Quasi-)monodimensional chains of water molecules adsorbed on the step edge of Pt(111) terraces have been experimentally observed:[5] this initial finding obtained with STM was later confirmed with X-ray diffraction[6] and thermal desorption.[7] The edge of a step on a terraced metal surface represents an ideal model of a 1D system. In fact, the step consists of an aligned row of atoms, which are more reactive than the surface atoms laying in the terraces due to their lower coordination.[8-10] It follows that water molecules bind more strongly to the atoms along the step edge than to the atoms in the terraces, so that the formation of water wires is promoted: one-dimensional chains are only observed on steps and are stable up to 150 K.[5] This peculiar structural arrangement is such that the interaction of a hydrogen with the oxygen of the next molecule represents the only relevant degree of freedom for the proton transfer mechanism. Therefore, it is of major interest to explore the possibility of having proton transfer in water chains on stepped surfaces.

In this work, we report on a computational *ab initio* study about the proton transfer along water wires adsorbed on several different stepped metallic surfaces (namely, the 221 surfaces of Pt, Pd, Au, and Ag). We consider H_2O wires containing one hydronium and one hydroxyl ion, in order to trigger the proton transfer mechanism, yet enforcing charge neutrality. The main issue that we want to address is the ability of each metal species to promote different proton transfer mechanisms in the wire at low temperatures. To this aim, we perform a combination of density functional (DFT) *ab initio* static (geometry optimization) and molecular dynamics (MD) calculations and find two different mechanisms each occurring on specific metals. The results show the occurrence of spontaneous recombination of OH^- and H_3O^+ via a Grotthuss mechanism[11] on less reactive metals (Au, Ag), whereas on more reactive metals (Pt and Pd), the surface captures one excess proton from the H_3O^+, and the remaining negative charge is transferred along the wire by proton hopping. We interpret these qualitatively different behaviors as a consequence of the subtle balance between water/metal bonding and hydrogen bonding, which varies from one metal to another, and to the tendency of the metal to adsorb protons.

2. TECHNICAL DETAILS

We used the FEMD approach of Alavi et al.[12] within density functional theory (DFT). This is a state of the art method for treating metals and molecular adsorption on metal surfaces.[13,14] The method is implemented within the CPMD code.[15] In this method, the electron density and the Hellmann—Feynmann forces are calculated via a subspace diagonalization of a finite electronic temperature density matrix. We used the PBE functional.[16] All of the pseudopotentials are generated through the Troullier—Martins scheme,[17] and the plane-wave cutoff is set to 60 Ry. This setup has been extensively tested by some of us in previous work on the adsorption of molecules on metal surfaces.[14,18] We considered systems consisting of (221) metallic steps for Pt, Pd, Ag, and Au; the lattice constants of each metal are those obtained in previous studies.[14] The metal slabs consisted of four layers, where the bottom two were fixed. We have also checked that increasing the number of layers in the metal slab does not influence significantly the adsorption energy of a molecule. In fact, the difference in adsorption energy for a water molecule on a four- and five-layer slab is about 0.01 eV, which is within the accuracy of the method. The size of the lateral supercell was 6×1 (84 metal atoms) with a variable number of water molecules, from two to six, prearranged in a chain oriented along the step edge. The chains counting from two to

Table 1. Adsorption Energies E_{ads} for a Water Monomer and a Hydrogen Molecule onto the 221 Step of the Various Metals^a

step (221)	E_{ads} (H_2O) [eV]	E_{ads} (H_2) [eV]	d_{abs} (H_2O) [Å]	d_{abs} (H_2) [Å]	d_{OH} [Å]	d_{HH} [Å]
Pt	−0.42	−0.50	2.30	1.74	2.00	0.92
Pd	−0.40	−0.35	2.35	1.84	2.10	0.85
Au	−0.23	−0.05	2.60	2.20	2.20	0.77
Ag	−0.20	−0.03	2.65	2.30	2.20	0.70

^{a} The oxygen—metal and the H_2—metal distances are also reported, as well as the average hydrogen bond lengths O···H along the chain and H···H for the H_2.

five molecules had a (relatively) large interruption between periodic images and were prepared with the two charged defects at the chain ends. The chain with six molecules, even though there was no large interruption between the water molecules, had the hydrogen bond chain interrupted at one point. This is because there is no way to build a noninterrupted water chain (through boundary conditions) containing an OH defect. The six-membered chain was prepared with the defects according to the sequence: $H_2O-H_3O-3H_2O-OH$. The vacuum above the chain was at least 0.7−0.8 nm to make the interaction with the periodic images negligible, and a $1 \times 3 \times 1$ mesh of K points was used. For the geometry optimizations, first the OH distance of the hydronium is constrained while relaxing the rest of the system. Next, we further relax the system after the release of the OH constraint. As a criterion of convergence, we chose a threshold of 10^{-3} au on the force components. The MD runs were performed with chains of five water molecules on a 6×1 (221) surface in the NVE ensemble for a maximum time of 0.5−1.0 ps, after a thermalization period of 0.1 ps at 50 K. The time step was chosen to be 10 au, which is standard for a Born—Oppenheimer type of dynamics for a system containing light nuclei such as hydrogens.

3. PROTON TRANSFER, AU AND AG

For the four metals considered here, we have found that the adsorption energies of water molecules (monomers) onto (221) metal steps are (see Table 1) either around −0.2 eV (Au, Ag) or −0.4 eV (Pd, Pt), i.e., on the order of one and two hydrogen bonds, respectively.[23] The adsorption energy for the monomer on the step is systematically larger than that on flat (111) surfaces of the corresponding metals.[10,24] This stems from the lower coordination of the metal atoms at the edge of the step, as previously discussed for the case of nickel.[8] When a water wire is formed, one has to consider also the effect of hydrogen bonding on the metal/water interaction. In previous works,[8,18,22] it was observed that in the adsorption of water networks onto metal surfaces, the water molecules that directly bind to metal atoms (via their oxygen atoms) have the strength of their hydrogen bonds modified. If a water donates two hydrogen bonds (HBs) to other molecules, the bonding to the metal will be stronger, while if it accepts bonds, the water—metal bond will be weaker even to the point of detaching from the metal.[9] This competition/cooperation between the adsorption strength onto the metal and strength of hydrogen bonds along the chain determines the nature of proton transport and the stability of defective species. Our results show that H_3O^+ is unstable on all of the metallic substrates considered here (independently from the chain length).
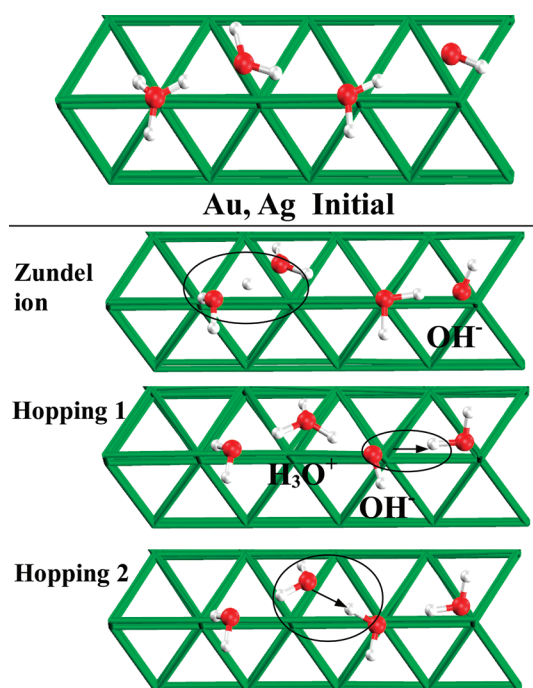

Figure 1. Proton transfer mechanism on Ag and Au (221). The top view of the initial configuration is shown in the top panel; the step edge is along the central sequence of metal atoms along the water chain. Below is illustrated the sequence of the different steps of the proton transfer. First, an intermediate Zundel ion (i.e., an excess proton shared by two water molecules) is formed, and then the proton is captured by the second water molecule, which in turn becomes a H_3O^+ ion. Next, the water molecule close to the OH^- ion releases its proton, becoming in turn an OH^-. This brings close the H_3O^+ and OH^-, which recombine in two neutral water molecules. The final configuration is that of a neutral chain of water molecules.

On Au and Ag, we found that H_3O^+ and OH^- recombine spontaneously. Recombination proceeds via a Grotthuss mechanism initiated from the hydronium H_3O^+, which acts as the starting point of a proton hopping along the chain (see Figure 1), toward the OH^- defect. This entails breaking and reforming of HBs, which in turn results in the proton being topologically transferred along the chain. However, MD runs performed on the coinage metals show that also the desorption barrier for the overall chain is very low (indeed, the chain typically desorbed, after the proton transfer completed). This observation seems to suggest that this Grotthuss mechanism on coinage metals may never be experimentally observed.

4. PROTON TRANSFER, PT AND PD

A different mechanism holds for Pt and Pd; in this case, one proton of the hydronium is captured by the surface. This dissociation is barrierless (see Figure 2) for all of the chains consisting of at least three molecules; when the system counts only one H_3O^+ and one OH^-, we observed a barrierless transfer of the excess proton between the two ions. The MD run shows that the water molecule remaining from the dissociation of hydronium is lifted from the surfaces but does not break the HBs with the neighboring water molecules. The readsorption of this water molecule is not seen within the time-span of our MD simulation, but we found that the readsorption of this water molecule needs to overcome a small barrier of 0.1−0.2 eV.
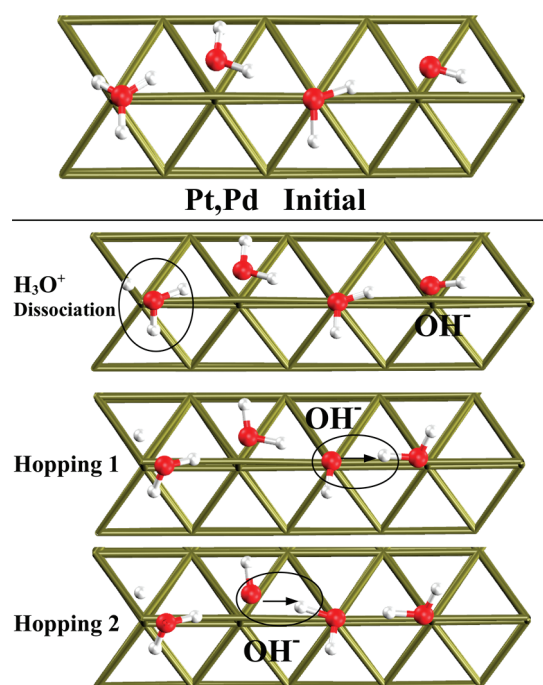
Figure 2. As in the previous figure, but for Pt and Pd. The first step is the dissociation of the H_3O^+, which donates a proton to the surface. The remaining chain is no more neutral and is characterized by the presence of a negative (OH^-) defect. The mechanism of traveling of this latter example happens in the following way: the molecule close to the OH^- releases a proton, and the proton is captured by the OH^-, which then becomes a water molecule. As a consequence, the donating molecule becomes in turn an OH^- ion. This mechanism is repeated along the chain. The hopping of the proton is characterized by low activation barriers, which can be overcome by thermal fluctuations.

This leads to a stable adsorbed chain with only one OH^- defect. Since Pt and Pd steps gain energy by capturing protons, the conclusion is that, for Pt(221) and Pd(221), the hydronium would rather donate the proton to the surface than promote a Grotthuss mechanism along the water chains (for chains with at least three molecules). Regarding the process of proton transfer along the chain, we have found that, after the adsorption of the excess proton on the surface, a hopping mechanism is initiated at the OH^- ions. Namely, the water molecule sitting next to the OH defect donates a proton to the OH, becoming in turn an OH, and the process, which involves overcoming activation barriers on the order of 0.10 eV is repeated. These values have been evaluated by means of constrained geometry optimizations for the system with the longer chain. The exact values depend on the distance between the defects and the orientation of the water molecules, but they were found to be at most 0.15 eV, that is, at worst, on the order of a hydrogen bond, which in turn implies that the overcoming of the barrier is not unlikely upon local rearrangement of the chain. The height of the barriers is size-independent; i.e., it does not vary systematically with the length of the chains, and this is a further indication that the proton hopping is somewhat local, i.e., does not depend on the relative positions of the defects along the chain.

5. COMPARISON BETWEEN THE SURFACES

In Table 1 are reported several quantities which explain the trend in affinity of the different surfaces for the excess proton of

the hydronium. Pt and Pd show a clear trend, that is, strong interaction with the surface. In fact, adsorption energies for both the water and hydrogen molecules are rather large, bonding distances are short, and the ability of Pt and Pd in distorting the molecular structure is quite high. For Ag and Au, it is the opposite. In particular, for the coinage metals, the adsorption energy of molecular hydrogen is practically null, while for Pt and Pd, this energy is quite sizable. This explains the basic difference in the behavior of the excess proton of the H_3O^+ in the chains considered. Of course, further considerations need to be made because of the aspects neglected in this work. We have not adopted corrections to take into account dispersion forces, and these may play an important role regarding the stabilization of the chains on the surfaces.[20] However, given the energy differences in Table 1, it is unlikely that dispersions may convert the mechanism in Ag and Au to that for Pt and Pd. The interaction of the H_2 molecule with Ag and Au is by far too small compared to that of Pt and Pd, and it would be surprising if dispersion were on the order of 0.3−0.4 eV at short distances. Moreover, in ref 21, it was shown that dispersions do not play a significant role for water molecules in direct contact with the surface. In any case, even counting dispersion, the only difference would be an additional attractive force between the molecules and the metal and thus more stable chains on the surface. This actually would strengthen our conclusions about having stable one-dimensional systems along which the proton can diffuse. Another important phenomenon that would play a role in the mechanisms of transport is the delocalization of protons due to their quantum nature. In a very recent study of relatively small systems of H_2O on different metal surfaces,[3,19] it was observed that the delocalization of the proton is more relevant for metals with smaller lattice parameters. The effects of delocalization consist of a reduction in the free energy barrier for the transfer of the proton among water molecules compared to the case where this effect is not considered. We have not included quantum effects in our calculations because the computational costs would be prohibitive for large systems such as those considered in this work; however, on the basis of refs 3 and 19, what we may expect is simply that the barriers for the proton transfer are smaller. This would not change our conclusions about the mechanism of proton transport.

6. CONCLUSIONS

We have studied the dynamics of protons on water wires formed on the stepped surface of transition metals. We have identified two different mechanisms, one occurring on the more reactive metals (Pt and Pd) and one occurring on coinage metals (Au and Ag). Taken in perspective, there are potentially relevant implications for the mechanisms suggested above, at least for Pd and Pt step surfaces. A one-dimensional water wire represents, for example, a fascinating technological possibility that can be employed in disparate fields, for the process of protonation/deprotonation of molecules adsorbed on the surface, thus inducing a (at least partially) controlled functional change, fabrication of microcircuits, enhancing conductivity in ice, and several related technological realizations.[26−28] In this context, despite being at a basic theoretical level, these calculations propose a clear distinction between different metal species as possible candidates for building water wires and creating a proton current.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: luca@fhi-berlin.mpg.de; dellsite@mpip-mainz.mpg.de.

Present Addresses
†Fritz-Haber-Institut, Faradayweg 4—6, D-14195 Berlin-Dahlem, Germany

■ REFERENCES

(1) Michaelides, A. *Appl. Phys. A: Mater. Sci. Process.* **2006**, *84*, 415. Michelides, A.; Morgenstern, K. *Nat. Mater.* **2007**, *6*, 597. Carrasco, J.; Michaelides, A.; Forster, M.; Haq, S.; Raval, R; Hodgson, A. *Nat. Mater.* **2009**, *8*, 427.

(2) Hu, X. L.; Klimes, J.; Michaelides, A. *Phys. Chem. Chem. Phys.* **2010**, *12*, 3952.

(3) Li, X.-Z.; Probert, M. I. J.; Alavi, A.; Michaelidis, A. *Phys. Rev. Lett.* **2010**, *104*, 066102.

(4) Feibelman, P. J. *Phys. Rev. Lett.* **2003**, *90*, 186103.

(5) Morgenstern, M.; Michely, T.; Comsa, G. *Phys. Rev. Lett.* **1996**, *77*, 703.

(6) Nakamura, M.; Sato, N.; Hoshi, N.; Soon, J. M.; Sakata, O. *J. Phys. Chem. C* **2009**, *113*, 4538.

(7) Picolin, A.; Busse, C.; Redinger, A.; Morgenstern, M.; Michely, T. *J. Phys. Chem. C* **2009**, *113*, 691.

(8) Sebastiani, D.; Delle Site, L. *J. Chem. Theory Comput.* **2005**, *1*, 78. Murakhtina, T.; Delle Site, L.; Sebastiani, D. *ChemPhysChem* **2006**, *7*, 1215.

(9) Delle Site, L.; Sebastiani, D. *Phys. Rev. B* **2004**, *70*, 115401.

(10) Meng, S.; Wang, E. G.; Gao, S. *Phys. Rev. B* **2004**, *69*, 195404.

(11) de Grotthuss, C. J. T. *Ann. Chim.* **1806**, *LVIII*, 54.

(12) Alavi, A.; Kohanoff, J.; Parrinello, M.; Frenkel, D. *Phys. Rev. Lett.* **1994**, *73*, 2599.

(13) Lozovoi, A. Y.; Alavi, A.; Finnis, M. W. *Phys. Rev. Lett.* **2000**, *85*, 610. Benedek, R.; Alavi, A.; Seidman, D. N.; Yand, L. H.; Muller, D. A.; Woodward, C. *Phys. Rev. Lett.* **2000**, *84*, 3362. Michaelides, A.; Alavi, A.; King, D. A. *J. Am. Chem. Soc.* **2003**, *125*, 2746. Delle Site, L.; Alavi, A.; Abrams, C. F. *Phys. Rev. B* **2003**, *67*, 193406.

(14) Ghiringhelli, L. M.; Delle Site, L. *J. Am. Chem. Soc.* **2008**, *130*, 2634.

(15) *CPMD*, 3.13; IBM Corp.; MPI fur Festkorperforschung: Stuttgart, Germany, 1997—2004.

(16) Perdew, J. P.; Burke, K.; Erzerhorf, M. *Phys. Rev. Lett.* **1996**, *77*, 3865.

(17) Troullier, N.; Martins, J. L. *Phys. Rev. B* **1991**, *43*, 1993.

(18) Delle Site, L.; Ghiringhelli, L. M.; Andreussi, O.; Donadio, D.; Parrinello, M. *J. Phys.: Condens. Matter* **2007**, *19*, 242101.

(19) Davidson, E. R. M.; Alavi, A.; Michaelidis, A. *Phys. Rev. B* **2010**, *81*, 153410.

(20) Carrasco, J.; Santra, B.; Klimes, J.; Michaelides, A. *Phys. Rev. Lett.* **2011**, *106*, 026101.

(21) Hamada, I; Lee, K.; Morikawa, Y. *Phys. Rev. B* **2010**, *81*, 115452.

(22) Schiros, T.; Ogasawara, H.; Naslund, L. A.; Andersson, K. J.; Ren, J.; Meng, S.; Karlberg, G. S.; Odelius, M.; Nilsson, A.; Petersson, L. G. M. *J. Phys. Chem. C* **2010**, *114*, 10240.

(23) Suresh, S. J.; Naik, V. M. *J. Chem. Phys.* **2000**, *113*, 9727.

(24) Michaelides, A.; Ranea, V. A.; De Andres, P. L.; King, D. A. *Phys. Rev. Lett.* **2003**, *90*, 216102.

(25) Marzari, N.; Vanderbilt, D. *Phys. Rev. B* **1997**, *56*, 12847.

(26) Chen, Y.; Liu, S.; Lei, M. *J. Phys. Chem. C* **2008**, *112*, 13524.

(27) Kapetanakis, E.; Douvas, A. M.; Velessiotis, D.; Makarona, E.; Argitis, P.; Glezos, M. *Org. Electron.* **2009**, *10*, 711.

(28) Moon, E.-S.; Lee, C.-W.; Kang, K. *Phys. Chem. Chem. Phys.* **2008**, *10*, 4814.