Proton transfer in adsorbed water dimers

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Density functional theory simulations of water on MgO(001) reveal rapid proton transfer within clusters of just two water molecules. Facile dissociation and recombination of the molecules within the dimers along with a concerted surface-mediated exchange of protons between water and hydroxyl molecules makes this possible. We suggest that surface-mediated proton transfer is in general likely to lead to proton transfer in interfacial water systems whenever the relative energies of intact and dissociated states of water are similar.

Proton transfer between water molecules is a fundamental process in chemistry, biology, and physics. For example it is central to all acid/base reactions in aqueous media, to water wires inside proteins and to the electrical conductivity of ice.1 The Grotthuss mechanism2,3 has for more than 100 years provided the basic picture for how protons or protonic defects diffuse through extended three dimensional (3D) hydrogen bonded networks. However, less is known about proton transport where extended 3D networks do not persist. A prominent example is water at interfaces, where understanding of proton transport is in its infancy despite compelling environmental and economic incentives to better understand the molecular-level details of e.g. nanofluidics, corrosion, and electrochemistry. Nonetheless, water at interfaces, particularly at well-defined oxide, semiconductor, and metal surfaces, provides an excellent opportunity to probe the most intimate details of proton transport, as demonstrated by recent experimental and theoretical studies.4-8

Here we report density functional theory (DFT) simulations of water on MgO(001). This is one of the most widely studied interfacial water systems9 and we show that despite having been intensively interrogated for the last twenty years it still has interesting secrets of general importance to reveal. Specifically we show that adsorbed water clusters of just two molecules (i.e. dimers) are sufficient to facilitate proton transfer between oxygen atoms. Facile dissociation and recombination of the molecules within the dimers along with a concerted surface-mediated exchange of protons between water and hydroxyl molecules makes this possible. We suggest that surface-mediated proton transfer is in general likely to lead to proton transfer in interfacial water systems whenever the relative energies of intact and dissociated states are similar.

DFT calculations were performed with the periodic plane-wave codes CASTEP10 and VASP.11 Most results have been obtained with the PBE exchange-correlation functional,12 although results of test calculations with the hybrid PBE013 functional are also reported. The Born–Oppenheimer molecular dynamics (MD) simulations reported here were within the canonical ensemble, had deuterium masses for the hydrogens, and a 1 fs timestep. All MD simulations ran for either 25 or 50 ps and were performed on a thin two layer MgO slab along with a (2×2)\(a_0\) surface cell (\(a_0 = 4.25\) Å for PBE and 4.21 Å for PBE0), \(\Gamma\) point sampling of the Brillouin zone, and a 400 eV plane-wave cutoff. An extensive set of geometry optimizations, some of which are reported in Table 1, revealed that this setup yielded adsorption energies of each of the key adsorption structures shown in Fig. 1 that come within 0.02 eV/H\(_2\)O of those obtained with more expensive settings (four or eight layer MgO slabs in a (2×2)\(\sqrt{2}a_0\) surface cell with 2×2×1 Monkhorst–Pack\(1\)\(k\) point sampling). In addition, it can be seen from Table 1 that the results obtained from CASTEP (with ultra-soft pseudopotentials15) and VASP (with PAW potentials16) agree to within 0.02 eV/H\(_2\)O.

Before discussing the water dimer, water monomer adsorption is briefly considered. The most stable monomer adsorption structure, with an adsorption energy of −0.5 eV (Table 1), has the oxygen of the water molecule located 2.2 Å above an Mg site with one of the OH bonds directed at a neighboring O site and the other OH bond directed toward the vacuum.17-19 An extensive series of calculations were performed in an attempt to identify stable dissociated monomer structures. However, consistent with previous DFT studies,19,20 the dissociated structures were considerably less stable (by at least 1 eV) than the intact molecular adsorption structure.

Moving to the water dimer, the situation is more complex and interesting. Several dimer structures with similar stabilities

![Fig. 1 Top views of water dimer structures on MgO(001). Diss1 and Diss2 are the partially dissociated H\(_2\)O–OH–H dimers and Int1 and Int2 are the intact water dimers. The white, red, and green spheres are hydrogen, oxygen, and magnesium atoms, respectively.](image-url)
have been identified. Four particular structures are shown in Fig. 1. In stark contrast to the adsorbed water monomer, some low energy structures include dissociated water molecules. Indeed, consistent with previous studies,21,22 the most stable dimers are “partially dissociated” $H_2O-OH-H$ complexes such as those shown in Fig. 1(a) and (c). In these partially dissociated structures the water molecule that is accepting the hydrogen bond has dissociated into an OH and a chemisorbed H. The chemisorbed H has a variety of surface sites at which to adsorb, but those closest to the OH of the dimer are most stable. In particular the chemisorbed H bonds preferentially to either the surface O site between the oxygen of the two adsorbates (Diss2 in Fig. 1) or to an O site adjacent to the OH and far from the water (Diss1 in Fig. 1). This chemisorbed H forms a bond 1 Å long to its surface O and a hydrogen bond 1.6 Å long to the oxygen of the OH. The O–O distance within the dissociated dimer is 2.5 to 2.6 Å, which is 0.2 to 0.4 Å shorter than the O–O distance in the intact water dimers (for example, Int1 and Int2 in Fig. 1). Although the dissociated dimers are marginally more stable than the intact ones, the four dimers have similar stabilities with adsorption energies ranging from ~0.5 to ~0.6 eV/H$_2$O (Table 1). They are, therefore, only slightly more stable than two isolated monomers. A series of hybrid functional calculations with PBE0 supports the conclusions to come from PBE and demonstrates that the dissociated $H_2O-OH-H$ complexes are not sensitive to large self-interaction errors as OH–H radical complexes in the gas phase are.23 Specifically, from Table 1 it can be seen that the PBE and the PBE0 adsorption energies of the intact and dissociated dimer structures are all within 0.1 eV/H$_2$O. Likewise, the PBE and PBE0 structures are similar with all bond lengths in the various adsorption systems differing by 0.04 Å or less.

*Ab initio* MD simulations were performed on the monomer and dimers at temperatures ranging from 100 to 273 K, the approximate temperature range used to study water films on MgO(001) experimentally.9,24 Simulations of the water monomer showed that it readily varies its orientation and adsorption site, but otherwise does not do anything unexpected.18,19 The water dimers on the other hand exhibit a range of interesting behavior, including several distinct types of proton transfer events. We now describe the key observations of these MD simulations.

During the MD simulations water dimers fluctuate between dissociated and intact states. As an example we show in Fig. 2(a) results from a simulation at 200 K in which the dimer rapidly flips from a dissociated state (Diss1) to an intact state (Int1). This can be seen by looking at the O–H bond lengths: when both the $O^B-H^1$ (green) and $O^B-H^2$ (orange) bonds are short (1.0 Å) the dimer is intact and when one of the bonds is long (1.6 ± 0.1 Å) the dimer is dissociated. Therefore, during the 25 ps shown the dimer flips between dissociated and intact states about fourteen times. Either one of the two covalent O–H bonds in the acceptor water molecule can break, due to the easy rotation of this molecule in the intact state. The key to whether the covalent bond dissociates is the O–O separation (or equivalently the hydrogen bond length) between the two molecules. Specifically, when the O–O bond is short (~2.7 Å) the dimer is dissociated and either $H^1$ or $H^2$ is on the surface. When the O–O separation increases to ~3 Å or more both water molecules in the dimer are intact. Therefore, the system resembles a molecular switch that is in a dissociated state if the hydrogen bond between the water molecules is short and in an intact state if it is long or broken. The switching between states is, of course, dependant on temperature and at lower temperatures no longer happens rapidly enough to be observed in the MD simulations. For example at 100 K the water dimer simply remains trapped in the more stable dissociated state. Similar transitions between the dissociated and intact states are observed for the Diss2 dissociated dimer. As an example in Fig. 2(b) we show 10 ps from a 273 K MD simulation. Again, exchange between the dissociated and intact structures and a coupling of this to the O–O separation are observed. Analogous switching between an intact and partially dissociated state has also been suggested for water on ZnO.25

So far we have seen from MD that through water dissociation and recombination there can be rapid proton transfer between the dimer and the MgO substrate. However of more interest is a surface-mediated proton transfer mechanism that enables the concerted exchange of protons between the two molecules of the dimer. This exchange is illustrated in Fig. 2(c), which reports the evolution of certain bond lengths during a 200 K MD simulation that started from Diss2. At the outset $H^2$ is on the surface forming a hydrogen bond with $O^B$. After ~4 ps $H^2$ moves away from $O^B$ toward $O^A$, forming a new hydrogen bond with $O^A$ in the process. This change in allegiance of the adsorbed hydrogen can be seen in the $O^A-H^2$ distance which changes from 2.6(±0.1) to 1.6(±0.1) Å, where the error bars refer to one standard deviation. Simultaneously $H^1$ transfers from $O^A$ to $O^B$, as indicated by the changes in the $O^B-H^1$ (green) and $O^A-H^1$ (orange) distances. The effect of this

| Table 1 | Adsorption energies (eV/H$_2$O) on MgO(001) for the structures shown in Fig. 1 and the water monomer. Values have been obtained from geometry optimizations with VASP except those in parentheses, which are from CASTEP. Adsorption energies are defined relative to isolated gas phase water molecules and clean surfaces through: $E_{ads} = (E_{water/MgO} - E_{MgO} - N.E_{water})/N$, where $E_{water/MgO}$, $E_{MgO}$, and $E_{water}$ are the total energies of the intact or partially dissociated water clusters adsorbed on the surface, the clean surface, and the isolated water molecule, respectively. N is the number of adsorbed intact or partially dissociated water molecules in each structure |
|----------|----------|----------|----------|----------|----------|
| Diss1    | Int1     | Diss2    | Int2     | Monomer  |
| PBE$^a$  | −0.57    | −0.51    | −0.61    | −0.50    | −0.48    |
| PBE$^b$  | −0.57    | −0.52    | −0.61    | −0.50    | −0.48    |
| PBE$^c$  | −0.55 (−0.57) | −0.51 (−0.52) | −0.59 (−0.60) | −0.50 (−0.50) | −0.48 (−0.49) |
| PBE0$^d$ | −0.56    | −0.53    | −0.59    | −0.49    | −0.48    |

$^a$ Four layer MgO slab, 2 × 2 × 1 k point sampling, (2 × 2)/2×0 cell. $^b$ Eight layer MgO slab, 2 × 2 × 1 k point sampling, (2 × 2)/2×0 cell. $^c$ Two layer MgO slab, single (Γ) k point, (2 × 2)/0 cell.
concerted exchange of protons is that O^A is transformed from being part of the intact H_2O that donates the hydrogen bond to being part of the OH that accepts the hydrogen bond. In separate total energy calculations we established with the climbing image nudged elastic band (cNEB) method that the activation energy for this concerted surface-mediated transfer process is 0.11 eV. In the transition state both H^1 and H^2 are equidistant between O^A and O^B.

We have shown that when two adsorbed monomers make a dimer that one of them can readily switch between an intact and a dissociated state. We have also shown that through a surface-mediated proton transfer mechanism, the dissociated and non-dissociated molecules can be exchanged. These two types of proton transfer event allow the protons between the water molecules to be "scrambled" so that ultimately it is not appropriate to say that any given proton "belongs" to any particular oxygen. We illustrate schematically in Fig. 3 one sequence of events that would allow proton scrambling to happen with just two molecules. At first H^1 and H^2 are bonded to O^A and H^3 and H^4 to O^B. Should these two monomers combine to form a dissociated dimer, H^1 can, for example, be transferred to O^B and H^4 to O^A through the surface-mediated proton transfer mechanism. If the dimer breaks apart the result is that one water is now formed from O^A, H^2 and H^4 and the other from O^B, H^1 and H^3. As well as observing each of the individual elementary steps with MD we have confirmed that the total energy barrier for each step is low through cNEB calculations. As indicated in Fig. 3, all barriers are 0.2 eV or less. In addition, quantum effects such as tunneling and zero point energy which are not considered in our calculations, can be expected to further facilitate proton transfer at low temperatures (see e.g. refs. 27–29). Experimentally, it may be possible to verify the proton scrambling predicted here with measurements on combinations of heavy and light water, possibly even on the molecular-level with scanning tunneling microscopy (STM) and STM inelastic electron tunneling spectroscopy.

Let us now place the results of the present study in a somewhat broader context. A surface-mediated mechanism for proton transfer has been observed for water on MgO. It involves the concerted exchange of a surface bound proton and a covalently bonded proton between water and hydroxyl. The mechanism is distinct from the most widely studied proton transfer mechanism in solution, namely the Grotthuss mechanism, in that it does not involve an excess proton nor does it proceed through an H_3O^+ intermediate. Of the traditional proton transfer mechanisms in solution, our observations most resemble the predicted mechanism for hydroxide ion transport in liquid water. This process proceeds through an "OH–H–OH"-like complex similar to the transition structure predicted here but without the chemisorbed H. Proton transfer has been observed or predicted at a variety of water–solid interfaces before particularly when partially dissociated water–hydroxyl structures are involved. Indeed an analogous concerted exchange within a 2D water–hydroxyl overlayer on BaO has recently been predicted. Generally, however, the surface-mediated proton transfer mechanism observed here is distinct from other simpler proton transfer events in that it involves the concerted exchange of a surface bound proton and a covalently bonded proton. We have shown results for proton transfer in the smallest possible water cluster. Since dimers are also constituents of larger water clusters on MgO and the full monolayer structure, this suggests that the observations made here are likely to be of much broader relevance than just
Fig. 3 Schematic illustration and DFT PBE energy profile for proton scrambling within water dimers on MgO(001), made possible by facile water dissociation and recombination plus surface-mediated proton transfer. (a) represents two isolated monomers, that in (b) combine to form an intact dimer (Int2 structure, Fig. 1(d)). In (c) the dimer has dissociated to the Diss2 structure (Fig. 1(c)). Surface-mediated proton transfer leads to (d), an equivalent dissociated dimer to the one in (c), that then leads to an intact dimer (e) and to two monomers (f). The energy of each step and transition state is also given.

water dimers. Should this be the case then it may also be possible to detect signatures with infra-red spectroscopy and nuclear magnetic resonance. Indeed together with the recent report on BaO30 it is likely that surface-mediated proton transfer will provide a facile mechanism for proton transfer at many other interfacial water systems. Substrates upon which the energy of the intact and dissociated states are similar are the most likely candidates.

In conclusion, with the help of a series of static and MD simulations several aspects of proton transfer between adsorbed water molecules on MgO(001) have been elucidated. Due to the similar stabilities of isolated monomer, intact and dissociated dimer states, and to the small proton transfer barriers between them, proton transfer is predicted in clusters of just two water molecules. The key process that enables this is the concerted exchange of both a surface bound proton and a covalently bonded proton between water and hydroxyl. We expect that this surface-mediated proton transfer will facilitate the scrambling of protons in other interfacial water systems whenever the relative energies of intact and dissociated states are similar.

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