WATER IN THE ACCRETION DISK: EFFECT OF COMPOSITION AND SURFACE STRUCTURE ON THE ENERGY OF ADSORPTION ONTO OLIVINE GRAINS

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Introduction: The origin of water in the inner solar system is not yet well understood. Because of the coexistence of water and small solid particulates in the accretion disk from which our planetary system formed, we propose that adsorption of water onto the surfaces/pores of olivine could play an important role in the delivery of water to the rocky planets. To this end, our group has been involved in studying the interaction between water gas and olivine surfaces by means of atomistic simulation, investigating the effect of orientation of the surfaces [1], chemical composition [2], mode of adsorption (this work), and surface defects (this work) on the heat of adsorption (E_{ads}). We concentrated on olivine, because this mineral is well studied computationally and is the major silicate phase in protoplanetary disks [1, 3].

Different types of adsorption: There are two main modes of adsorption: physisorption or molecular adsorption, and chemisorption or dissociative adsorption. The E_{ads} for physisorption can span a wide range from 50 to 200 kJ/mole [1, 4] as is a function of how the water molecule binds to the surface, i.e., hydrogen interacting with lattice oxygens or oxygen from the water molecule interacting with surface cations, respectively. Chemisorption, generally preceded by physisorption, occurs when the water molecule dissociates into an –OH group and a proton which become covalently bonded to surface atoms, usually releasing an E_{ads} in excess of 200kJ/mole [4].

Surface Structure: Another important variable that controls the energetics of adsorption is surface structure. Atoms at the surface are underbonded. The more unsatisfied the surface bonds, the more unstable is the free surface, and the stronger is the bond with the adsorbed molecule, as evidenced by the binding energies, which are higher for stepped surfaces than for planar/defect-free surfaces. The stronger the substrate/water bond, the higher the temperature at which water is retained at the surface.

Because the accretion disk had low p_{H2O} and repetitive high temperature processes, the fraction of surface sites at which water can be adsorbed and retained strongly is important, as these could also be the sites where physisorption is followed by chemisorption. In the accretion disk there is probably not enough water to create multilayer adsorption, thus it is important to know where the first water molecule would adsorb and the energetics of these interactions. Thus, we set out to understand the detailed effects of surface structure for three selected olivine planes [1]. We investigated the effect of both composition (forsterite vs. fayalite) and defects (steps) on the energetics of adsorption for both chemisorption and physisorption.

Methods: We studied the interaction between water and selected olivine surfaces using atomistic simulation techniques. Bulk olivine was modelled using periodic boundary conditions, formal charges for the Coulombic interactions, and well tested parameterized potentials for the short-range interaction between ions [4]. The virtual crystal was then cleaved by introducing a vacuum normal to the {010}, {100} and {110} directions, thus creating free surfaces.

Physisorption: After energy minimization of the free surface, we divided the surface into a grid with a spacing of 0.25Å. On top of each grid point we generated a water molecule and minimized the energy for the water/olivine system. Two schemes were used: 1) the water molecule was allowed only to vary its height with respect to the surface and to rotate, but not to move parallel to it; 2) the water molecule could minimize all of its coordinates, thus migrating on the surface toward a local minimum energy position. The two approaches provide different information: method (1) gives the surface structure of the potential energy, which is the energetic environment as perceived by a water molecule; method (2) allows the identification of preferred adsorption sites.

Chemisorption on planar/defect-free surfaces: Because our code cannot model breaking and formation of bonds, we applied a well-tested method to obtain information for the energetics of chemisorption using classical atomistic simulation techniques [4-6]. Having first located the position of strong physisorption sites on the surface (which correspond to the position of the Mg atoms), we placed the –OH group and the proton close to surface Mg and undersaturated surface oxygen, respectively, and then allowed minimization of the system in the same way as in method (1). Because there are several underbonded oxygen and Mg atoms on each surface, we repeated the method recursively, until all the possible combinations were studied. This procedure allowed us to obtain the dissociation energy related to the chemisorption of water at the preferred sites.

Chemisorption on stepped surfaces: Chemisorption was also studied on stepped surfaces, using the code METADISE that allows creation of free surfaces with

steps and terraces [4, 5]. We proceeded as described above, but in this case we placed the proton only on undersaturated oxygens in proximity of the chosen surface cation, because this configuration is the more stable.
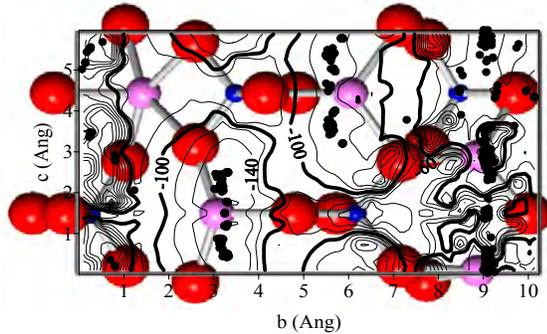

Figure 1: surface energy potential contours map overlaid on the unit cell for the {100} plane of forsterite. Valleys represent strong adsorption sites. Black dots, final position for H_2O according to scheme (1); pink: Mg, red: oxygen; blue: Silica; Intervals at 20kJ/mole.

Results: Fig. 1 shows the surface potential contour lines overlaid over the unit cell of {100} for forsterite. The energy field shown in Fig. 1 represents the energetic environment as perceived by the first water molecule approaching this plane. For all three surfaces we found that there exist a variety of bonding environments for the adsorbed molecular water, with binding energies ranging from less than 44kJ/mole to in excess of 200kJ/mole (on {100}). Adsorption sites with E_{ads} greater than 100kJ/mole for molecular water coincide with the locus of surface cations, and can range in energy as a function of the cation underbonding. The strongest sorption sites for each of the three surfaces studied have energies of 120kJ/mole, 230kJ/mole and 170 kJ/mole for the {010}, {100} and {110} planes, respectively. Similar calculations for fayalite demonstrated a small compositional effect on the adsorption energy, i.e., less than 20kJ/mole for {010} [this work]. Chemisorption on {100} releases energies in excess of 300kJ/mole (compare with 230kJ/mole for the strongest site for physisorbed water), while on {010} the energies for chemisorbed and physisorbed water are comparable, consistent with the results of [7]. Dissociative adsorption on stepped surfaces is under investigation at this time, but initial results show that the E_{ads} on the {111} are greater than 200kJ/mole.

Discussion: The binding energies associated with water on these surfaces are strong enough to retain physisorbed water up to 700K and chemisorbed water up

to 1000K on selected planes [8].

Equilibrium calculations show that the ratio H_2/H_2O in the accretion disk was about 5×10^{-4}, and it was constant throughout the inner solar system [9]. Note that the equilibrium partial pressure is probably a lower limit [10-12]. A surface exposed to gas is constantly bombarded by molecules, and thus it becomes quickly covered. The kinetic theory of gas allows one to compute just how quickly the coverage can occur. For example, at p_{H2O} of 10^{-8} bars and at 700K there is one hit/second/$Å^2$ on any given surface. The {100} surface of forsterite (Fig 1), with a total surface area of ~ 60 $Å^2$, can host up to 6 molecules of water at full monolayer coverage. We see that this surface has 4 strong adsorption sites with energies in excess of 130kJ/mole and, in particular, one (to the left of the figure) has E_{ads} up to 230kJ/mole. Also note that about 60% of the surface is represented by the energy wells of the local strong sorption site [1]. Because so much of this surface is involved in strong interactions with water, it is conceivable that within a few seconds of exposure the strong sorption sites could be saturated by water. Once the water molecule has sorbed at the surface, how likely is it to be retained? The residence time of a molecule of gas on a substrate is related to the vibrational frequency of the molecule at the surface and to the desorption energy, which is comparable to the E_{ads}. Although this work is still in progress, we can make a few simple predictions. For a molecule on the {100} surface, the half-residence time on the strongest physisorption site, assuming a vibrational frequency 10^{12}Hz, is of the order of a few milliseconds. In comparison, a chemisorbed particle will remain on the same surface for $\sim10^8$ seconds. This latter value is high and one can conclude that water, once adsorbed, is not going to be lost quickly. ***Thus it seems inevitable that some water in the terrestrial planets was originally adsorbed onto grains in the accretion disk.***

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