

# Structure of Water Adsorbed on a Mica Surface

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## Abstract

Monte Carlo simulations of hydration water on the mica (001) surface under ambient conditions revealed water molecules bound closely to the ditrigonal cavities in the surface, with a lateral distribution of approximately one per cavity, and water molecules interposed between  $K^+$  counter ions in a layer situated about  $2.5 \text{ \AA}$  from a surface O along a direction normal to the (001) plane. The calculated water O density profile was in quantitative agreement with recent X-ray reflectivity measurements indicating strong lateral ordering of the hydration water but liquid-like disorder otherwise.

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The molecular structure of water adsorbed on micaceous minerals (2:1 layer type aluminosilicates [1]) has long been of widespread interest because of its crucial role in geochemical and biological processes [2, 3]. Early conceptualizations of this structure imputed to it an ice-like character because of its longer relaxation times when compared to bulk liquid water and its potential for epitaxy with the hexagonal array of oxygen atoms on the basal surfaces of mica and 2:1 clay minerals [3, 4]. These speculations have received support periodically from experimental and modeling studies [3–5], but recent spectroscopic data [6, 7] suggest that the hydration water on micaceous minerals is more disordered and more labile than ice  $I_h$ .

Cheng et al. [8] have provided remarkable new insight into this issue using high-resolution X-ray reflectivity to probe the structure of water adsorbed by muscovite mica under ambient conditions. Their data were fit well by an atomistic model which included a layer of adsorbed water molecules at  $1.3 \pm 0.2 \text{ \AA}$  above the mean position of a surface O and bound near the hexagonal (strictly, ditrigonal [1]) cavities in the mica surface. This was followed by a layer of water molecules at  $2.5 \pm 0.2 \text{ \AA}$  above the surface O that Cheng et al. [8] conjectured were immobilized through linear hydrogen bonds with the latter. The mean number density of this bipartite hydration structure was found to be about the same as that of bulk liquid water, as was the number density in succeeding, less well-organized hydration layers, indicating development of liquid-like structure.

In this Letter we present Monte Carlo (MC) simulations [9] of the structural properties of hydration water on a 2:1 layer type dioctahedral aluminosilicate with the muscovite formula  $\text{K}_2\text{Al}_4(\text{Al}_2, \text{Si}_6)\text{O}_{20}(\text{OH})_4$  [1]. Our results reveal the existence of an adsorbed layer of water molecules bound intimately to the ditrigonal cavities in the surface and surmounted by a network of hydration water molecules into which  $\text{K}^+$  counterions are interposed consistently with hydrogen bonding to the surface O. Thus our calculations not only confirm the liquid-like hydration structure proposed by Cheng et al. [8], but also provide additional molecular details not accessible to their experimental methodology.

The simulation cell comprised two opposing half-layers of the mineral structure with lateral dimensions sufficient to enclose eight unit cells having the chemical formula given above. Substitutions of Al for Si in the tetrahedral sheets were random and arranged to create equal negative charge in each half-layer. Sixteen  $\text{K}^+$  were placed between the two half-layers to balance this charge, and 256 water molecules were included to produce a hydration

phase nominally eight monolayers thick between the opposing basal surfaces. This cell was then replicated infinitely in three dimensions to mimic a macroscopic system.

The model potential functions used to represent water-water, couterion-water, counterion-counterion, counterion-mineral, and water-mineral interactions were MCY-type parameterizations described in detail in Ref. [10]. These potential functions have been tested extensively and successfully for 2:1 clay mineral hydrates [10–14]. (See Ref. [13] for a summary of previous MC simulations based on our model potential functions.) All molecular species thus are treated as rigid bodies, including the mineral structure. Relaxation of this structure in the presence of water was observed by Cheng et al. [8] to be limited to the outermost polyhedral sheet, which would not be expected to affect the overall qualitative character of the interfacial layer. Our simulations were performed in a constant ( $N\sigma T$ ) ensemble, in which absolute temperature ( $T$ ) and pressure applied normal to the mineral layers ( $\sigma$ ) are maintained at 300 K and 100 kPa, respectively.

Figure 1 compares the water O density profile we obtained by MC simulation with that derived by Cheng et al. [8] from their reflectivity measurements. The match between their profile and ours within 4 Å from the surface O is excellent, encouraging a direct interpretation of the two principal features in terms of adsorbed water species predicted by our simulation. Figure 2 is a visualization of the water molecules that contribute solely to the first peak (denoted “ $a$ ” in Fig.1), showing clearly that they are indeed associated with the ditrigonal cavities in the mineral surface. The computed distribution of these water molecules is approximately one per cavity, in agreement with the estimate of  $1.0 \pm 0.2$  per cavity made by Cheng et al. [8]. On the basis of our previous simulations of near surface hydrate structure on K- and Cs-montmorillonite [10, 11, 14], we speculate that this configuration of adsorbed water molecules is facilitated by two factors: (1) the close proximity of the layer charge sites to the mineral surface and (2) the weak solvation characteristics of  $K^+$  [15], which permit a stronger influence of mineral surface charge on proximate water molecules than do strongly-solvating counterions like  $Li^+$  [12].

The second peak in the O density profile (denoted “ $b$ ” in Fig.1) corresponds to adsorbed water molecules distributed laterally at approximately 1.3 per surface cavity (the ratio of the height of the second peak to that of the first is 1.28), as also reported by Cheng et al. [8]. Visualization showed that most of these water molecules are oriented with one of their OH groups pointing toward the mineral surface O consistently with hydrogen bond formation.

However, the water molecules are interspersed among the  $K^+$  counterions, which reside in two distinct planes at 2.3 and 2.7 Å from the surface O (Fig.3). The corresponding adsorbed  $K^+$  species (Fig.4) are coordinated respectively to 7 surface O and 6 water O or to 3 surface O and 9 water O, with two of the water molecules being adsorbed near a ditrigonal cavity in the latter case (Fig.4). These strongly adsorbed water molecules prevent closer access of the counterion to the mineral surface.

Our simulation results are consistent with liquid-like disorder for the hydrate as a whole, as suggested by Cheng et al. [8] on the basis of their water O density profile tending to approach the bulk liquid limit after only a few oscillations (Fig.1). Our results show stronger oscillations, but are consistent with the same trend.

Liquid-like character of the hydration water also emerged from our calculation of the average O-O intermolecular coordination number with radial distribution functions simulated using the MC output (see Ref. [10] for the method of calculation). We find  $N_{OO} = 5.1$  for the coordination number of water O around a central water O, as opposed to  $N_{OO} = 5.2$  for the bulk liquid based on our simulation using the MCY potential [16]. (The experimental value is 5.4 [16].) Overall, therefore, the structure of water adsorbed by micaceous minerals appears to be significantly more disordered than that of ice  $I_h$ .

Our MC results may also help to clarify the molecular interpretation of recent surface-force balance experiments involving hydration water between mica surfaces [17]. These experiments indicate that  $K^+$  counterions are displaced into the hydration layers, in agreement with Fig.3; that a single layer of strongly-adsorbed water may exist at the mica surface, in agreement with Figs. 1 and 2; and that hydration water films thicker than about 4 Å are liquid-like. The “persistent fluidity” of hydration water [17] thus may be related intimately to the antagonistic effects of confined geometry on the hydrogen-bonded network in water that prevent freezing into the ice  $I_h$  structure.

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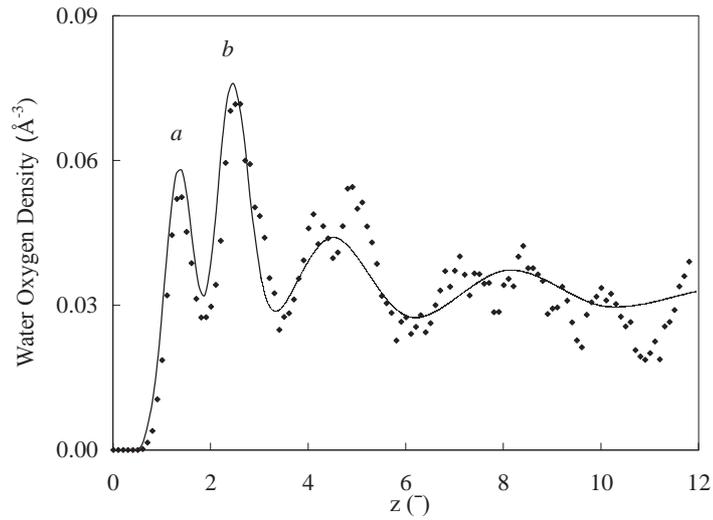


FIG. 1: Water O density distribution as a function of the distance  $z$  from the mean surface oxygen position. The solid curve is from Cheng et al.[8] while the data points are the results from our MC simulation; a:water molecules adsorbed near ditrigonal cavities; b:hydration water. To provide a common origin with the measured curve, the simulated data are offset by  $0.2 \text{ \AA}$  from their absolute position relative to the center of the mineral layer, which is within the precision of the measured peak locations.

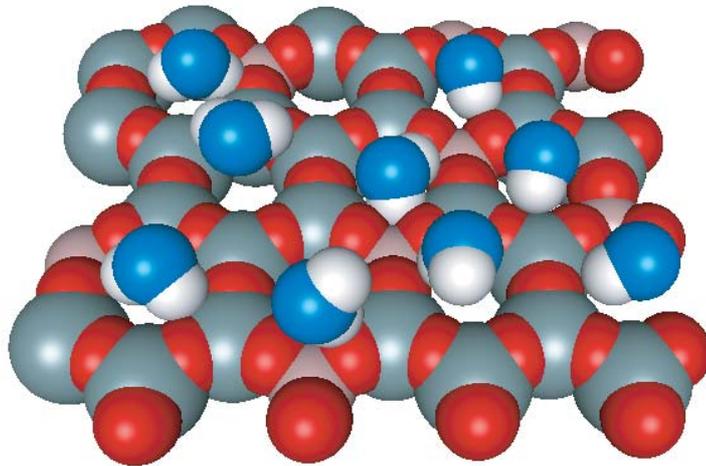


FIG. 2: Perspective visualization of the adsorbed water molecules represented by peak  $a$  in Fig.1 as predicted by MC simulation.

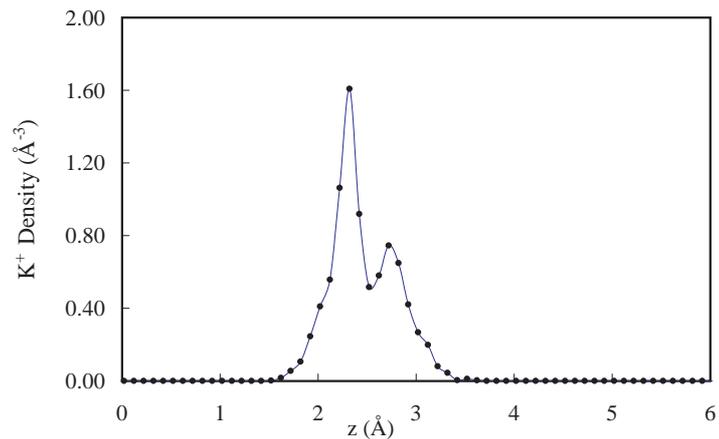


FIG. 3: Density profile for  $K^+$  counterions based on MC simulation, showing two populations near the mica surface.

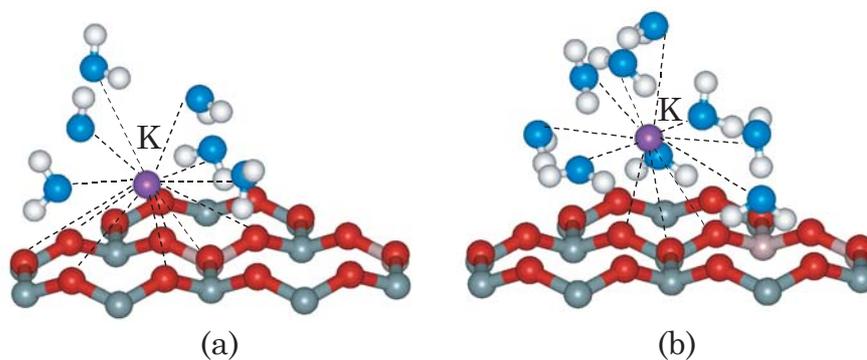


FIG. 4: Local coordination environment of the two  $K^+$  counterion species; a:  $K^+$  in layer 2.3 Å from the O surface; b:  $K^+$  in layer 2.7 Å from the O surface.