

Computational Chemistry Investigation of Solid-Aqueous Interface: Hydration of Surfaces

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1. Introduction

The chemistry of solid and aqueous interface is of fundamental importance in surface and material science as well as in many industrial and environmental processes. Atoms, molecules and ions exert forces upon each other at the interface; hence, adsorption reactions at the interface are affected directly in terms of intermolecular interactions between the aqueous and the solid phase. Dealing with interaction phenomena at solid–aqueous interfaces, the presence of structured water layers must be taken into account as under those conditions, the adsorbent is always covered by water molecules, so-called *hydrated surface*. Oxides, especially those of Si, Al, Mg and Fe, which are important materials in catalytic processes, are also covered with surface hydroxyl groups in the presence of water.

In this study, the hydration of α -Al₂O₃(001) surface is investigated by means of computational chemistry methods. The structure and dynamics of single water molecule on the α -Al₂O₃(001) surface has been studied.

2. Method

The periodic density functional calculations have been performed using DMol³ program. The geometries of the systems are optimized to get stable structures at local density approximation (LDA) level. The energies are evaluated at generalized gradient approximation (GGA) level with Perdew-Wang exchange and correlation functional. The adsorption energy (E_{ads}) has been calculated according to the expression;

$$E_{\text{ads}} = E_{(\text{adsorbate} + \text{substrate})} - (E_{\text{adsorbate}} + E_{\text{substrate}})$$

Also an accelerated quantum chemical molecular dynamics program “Colors”, which is developed in our laboratory, will be used in order to simulate the interaction of H₂O at the interface, comparing with the DFT calculations.

3. Results

After optimization of the surface, the surface layers undergo significant rearrangement with the Al ions sinking down into the space between the upper oxygens, making the Al-O distances as short as 1.69 Å in the upper layer. Single water molecule was added on top of the α -Al₂O₃(001) surface as hydrogens were facing to the surface oxygens (Figure 1). The water molecule went away from the surface, however one of the H interacts with the surface O (Figure 2). The interatomic distances are shown in Table 1. Adsorption energy of the system is calculated as -57.533 kcal/mol. The results indicate that there is a physical interaction between the surface aluminum and water oxygens, as well as the surface oxygens and water hydrogens. Hence, physical adsorption takes place in the hydration mechanism of α -Al₂O₃(001) surface. These results will be supported with the study of water adsorption to extended surface of α -Al₂O₃ to investigate the structure and dynamics of water layers.

Table 1. Interatomic distances of the structures.
(numbers 1 to 6 indicates that the atomic orders vertically)

Ion pairs	Atomic distances (Å)		Ion pairs	Atomic distances (Å)	
	initial	final		initial	final
H ₁ – O ₃	2.087	3.214	H ₂ – O ₄	2.413	2.927
H ₁ – O ₄	1.178	1.572	O _w – H ₁	0.962	1.060
H ₂ – O ₅	1.160	2.535	O _w – H ₂	0.962	0.980

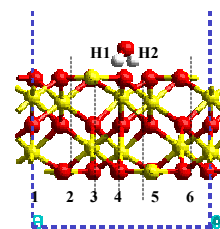


Figure 1. Initial structure of water molecule.

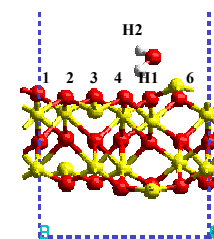


Figure 2. Final structure of water molecule and the surface.

