Adsorption of prototypical amino acids on silica: Influence of the pre-adsorbed water multilayer

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ABSTRACT

We explore the interaction between acetic acid, some typical α-amino acids (α-AAs), and a fully hydroxylated (0001) surface of α-quartz by means of theoretical calculations based on the density functional theory (DFT) under periodic boundary conditions. The influence of microsolvation, represented by a water multilayer, and dispersion forces is analyzed. All the considered molecules strongly adsorb on the hydroxylated surface and prefer to adsorb molecularly. The inclusion of dispersion forces increases the interaction energies by 15–30 kJ/mol, without significant changes in structure and mode of adsorption except for histidine where the interaction is improved through protonation of the α-amine group. When the water multilayer is included a decrease in the surface–adsorbate interaction energies is observed. Also, some α-AAs, glycine and alanine, change their adsorption mode and, now, the more stable structure is the zwitterion. Adsorption as zwitterions is always favored with respect to molecular interaction when dispersion forces are taken into account. Comparing the energies of adsorbed and solvated α-AA zwitterions, it turns out that inclusion of dispersion forces predicts that solvated zwitterions are the lower energy configurations.

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1. Introduction

Silicon oxide, also known as silica, is omnipresent in our world. Indeed, silicon and oxygen elements are the most abundant on the earth's crust, with percentages of 45.5% and 27.2%, respectively. Silica is not only the origin of the most abundant families of materials but also of the most complex, which manifests in a large variety of silica polymorphs and silicate minerals. Among polymorphs, some correspond to relatively simple structures, such as quartz, cristobalite, or tridymite, while others exhibit fascinating cage arrangements, as that of cubic faujasite. The most abundant polymorph is rhombohedral α-quartz that accounts for more than 10% by mass of the earth's crust, and transforms at 846 K to β-quartz, a closely related hexagonal structure.

The way that silica interacts with the wide diversity of materials, organic, inorganic or biologic, has been a major topic for more than a century. Mostly viewed from an adsorption point of view, there has been a myriad of research works devoted to unravel the nature and properties of the interactions between silica surfaces and adsorbates (a selected group of classical sources is given in references [1,2]).

In the analysis of the interaction between a solid and an adsorbate one necessarily needs to take into account that surfaces rarely are perfectly defined planes, but that they incorporate imperfections of distinct nature. This is not only the fact that they show defects as vacancies or

dopants, but because they are hydrated in more or less extension. From a chemical point of view the ubiquitous presence of water changes and determines the chemical properties of surfaces and, hitherto, the capability to physisorb or chemisorb an adsorbate. Chemisorbed water, also called structural water, is commonly considered in the theoretical modeling of adsorption processes. This is strongly bound water, normally as hydroxyls that persist even at relatively high temperatures (>700 °C). This is the case, for instance, of alumina and also, in less extension, silica. Besides this chemisorbed water, there is also physisorbed water forming a multilayer more or less thick [3]. Due to the presence of silanol groups at the surface, silica is mostly embedded with water in multilayer. The first layer of water has different characteristics than the subsequent layers, which is evident from thermogravimetric analysis. IR spectral data also reveal the differential status of water on silica surface [4].

From a computational point of view, the structure and bonding of water molecules around the silica surface have been simulated using different techniques. In particular, simulations using a modified Monte Carlo approach in a realistic Vycor-like silica mesoporous system at various temperatures have been reported [5]. Similarly, by using a combination of classical molecular dynamics (MD) and ab initio Car–Parrinello molecular dynamics (CPMD), the reaction of water with a free amorphous silica surface has been examined and described as an exothermic reaction of a water molecule with a two-membered ring, leading to the formation of two silanol groups on the SiO_2 surface [6].

In spite of the well established presence of surface water under normal temperature and humidity conditions, the theoretical studies

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that incorporate structural water in the modeling of surface reactions are scarce and, by and large, one can say that most of the models considered so far are of the anhydrous kind. Depending on the physical nature of the phenomena examined, this limitation might bias the answer and therefore becomes inappropriate. This is the case of processes or chemical reactions in which a significant change in the polarization of the intervening species takes place. Obviously, if the surface process is accompanied by a charge separation with the formation of ionic species, the presence of a multilayer solvent becomes unavoidable to obtain a meaningful energy profile [7].

The theoretical analysis of the interaction between a silica surface and a variety of organic molecules has been the subject of numerous works, and the reader is referred to the excellent review recently published by Rimola et al. [8]. This review describes the structure of the water layer in depth, and gathers experimental and theoretical data for the adsorption of biomolecules on silica.

However, despite the relevance that the understanding of the surface–water-biomolecule interaction has in different fields, the majority of studies that fully include the presence of multilayered water in the silica–biomolecule system were carried out with classical mechanics. Only in a few cases the interaction of some biomolecules with silica surfaces including the presence of a small number of water molecules to simulate a microsolvated state has been examined by means of some ab initio approximations [8]. In particular, we have restricted this study to model the interaction of some α-amino acids with the silica surface/multilayer water model, as they mediated the protein adhesion phenomena that are relevant to different biotechnology applications.

The research work presented follows an increasing line of complexity that starts by developing a model of hydroxylated silica. This first model incorporates the bound water and is used to analyze the binding properties for the selected adsorbates, namely acetic acid and several amino acids (α-AAs). After examination of this "anhydrous" model, the multilayered water is added, and the structure and energetics of the adsorbate–surface system are analyzed.

2. Models and computational details

DFT calculations were performed using the plane-wave-pseudopotential approach within the projector augmented wave method (PAW) [9] together with the Generalized Gradient Approximation (GGA) exchange correlation functional proposed by Perdew et al. [10] (PBE) as implemented in the VASP 5.3 code [11–13]. A plane-wave cutoff energy of 400 eV was used. We treated the Si $(3s, 3p)$, O $(2s, 2p)$, C $(2s, 2p)$ and N $(2s, 2p)$ electrons as valence states, while the remaining electrons were kept frozen as core states. To obtain faster convergence, thermal smearing of one-electron states $(k_B T = 0.01$ eV) was allowed using the Gaussian smearing method to define the partial occupancies.

The unit cell of α-quartz SiO_2 bulk was optimized using a $4 \times 4 \times 4$ k-point grid. The resulting cell parameters were 5.023, 5.511, 1.625, 1.628 Å and 146.8° for a, c, the two Si–O bond distances and Si–O–Si angle respectively, in good agreement with the experimental values (4.916, 5.4054, 1.605, 1.614 Å and 143.73°) [14] and with previous theoretical calculations (5.052, 5.547, 1.630, 1.633 Å and 147.9°) [15].

Based on the optimized bulk of silica we built our surface models. A previous work performed a deep theoretical study on modeling α-quartz (0001) surface [15]. According to that nomenclature we can model three surfaces for SiO_2 (0001): cleaved, reconstructed and hydroxylated. The first one is the slab of SiO_2 cut in the (0001) face and relaxed. The second one comes from the high surface energy of the cleaved one (2.22 J m^{-2}) that undergoes a geometrical reconstruction of the upper 6 atomic layers of the surface forming six-membered rings (6 Si–O units) parallel to the surface, lowering the surface energy to 0.36 J m^{-2}. Finally, given the hydrophilic character of silica, they built a model in which the surface layer adsorbs and dissociates water forming a network of hydrogen bonds (with lengths 1.80 and 2.38 Å)

on the surface which is then called hydroxylated, this surface being the most stable for the (0001) face of α-quartz SiO_2 (-0.19 J m^{-2}). In that study, the authors established a minimum number of full-relaxed 27 atomic layers (9 SiO_2 units) to get fully converged surface properties (surface energies, bond distances and angles) for the three surface models at the same time. Since in our work we plan to adsorb large organic molecules on the surface the supercell must be expanded increasing the number of atoms of the model and accordingly the computational cost. For this reason we need to build a smaller model that keeps however the same behavior than that of the 27-layer converged model.

Our model has 9 atomic layers (3 SiO_2 units) keeping the two bottom O and Si atomic layers fixed at their bulk positions and completing their lost coordination with H atoms fixed at previously relaxed positions. In that way, the 6 uppermost atomic layers affected by the reconstruction of the surface are allowed to relax including an extra layer (also relaxed) between them and the bulk-fixed H-saturated two bottom layers. The hydroxylated model also includes a water molecule dissociated on the surface, containing, thus, 14 atomic layers (2 H, 3 SiO_2 units, and dissociated H_2O) compared to the analogous 33 atomic layer model of the previous work [15].

In order to validate our model we calculated energies of some surface processes (reconstruction energy and hydroxylation energy) and representative bond lengths of the surfaces and we compared our results with the values reported for the converged model of 27 atomic layers (33 layers for the hydroxylated surface). The reconstruction energy is calculated as follows:

$$E_{\text{reconstruction}} = E_{\text{reconstructed}} - E_{\text{cleaved}}$$

where $E_{\text{reconstructed}}$ and E_{cleaved} are the energies of the optimized slabs corresponding to the reconstructed and cleaved surfaces respectively. While the hydroxylation energy is calculated as follows:

$$E_{\text{hydroxylation}} = E_{\text{hydroxylated}} - E_{\text{reconstructed}} - E_{\text{H}_2\text{O}}$$

where analogously $E_{\text{hydroxylated}}$ is the energy of the optimized slab corresponding to the hydroxylated surfaces and $E_{\text{H}_2\text{O}}$ is the energy of an isolated molecule of water. To compute the reconstruction and hydroxylation energies for the full model (27–33 atomic layers) it is necessary to divide it by 2 since it has 2 relaxed surfaces and, at the same time, to consider 2 water molecules for the hydroxylated model, one for each surface. The results are shown in Table 1.

Energy differences are under 0.05 eV and bond distance differences are below 0.07 Å. Therefore, we can conclude that our smaller model achieves also the converged surface properties of the previously proposed larger models. In Fig. 1(a) and (b) we show both models. While it may seem contradictory that we claim that our 14-layer model correctly reproduces the same surface properties that larger 27- or 33-layer models we have to remember that in our model we kept the four lower layers frozen, in an attempt to introduce the effect of having some bulk-like layers below the first surface layers. In the cited previous work, the authors show that at least the six top layers of the surface model are distorted in the reconstructed surface and, as the two sides of their slab model are allowed to relax the surface properties depending on the depth of the model. As we are not interested on the properties of the lower surface, we can keep some layers frozen damping the distortion of the surface layers and achieving the same top-surface properties with a model with a lower number of layers.

Finally, for modeling convenience we chose vectors a' and b' defining the surface periodicity which are orthogonal and not the hexagonal ones $a = b = 5.02$ Å of the unit cell (being $a' = a + b$, $b' = a - b$). Therefore we chose an orthorhombic supercell with $a' = 8.70$ Å, $b' = 5.02$ Å, and $c' = 30.32$ Å with a separation between slabs of 24.62 Å being the distance between the top of the adsorbed amino acid and the bottom of the lower surface on the image cell of at least 17.10 Å in