Electronic structure calculations of physisorption and chemisorption on oxide glass surfaces

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Abstract

A description of the physisorption and subsequent chemisorption of water on silica glass surfaces is presented that combines electronic structure calculations with classical molecular dynamics simulations. The method associates the strength of the physisorption sites with the gradient of the electrostatic potential, and the chemical reactivity with the chemical hardness of the surface. The physisorption results are compared with those of more classical physisorption energy mappings, and to ab initio calculations of water molecules physisorbing at specific sites. The chemisorption reactivity index is compared with calculated chemisorption energy barriers. The new techniques are applied to two types of silica glass surfaces: a fracture surface with high energy coordination defects and a low energy defect-free “melt surface”. The mappings show that the strongest sites for physisorption are network coordination defects, but that a high physisorption energy is not necessarily an indicator of a reactive site. The physisorption and chemisorption mappings were converted to energy distributions and reactivity distributions for a direct
comparison between the melt and fracture surfaces. Altogether, this approach combines the efficiency of classical molecular dynamics for structural determinations, with the chemical degrees of freedom provided by electronic structure calculations, to yield a semi-quantitative map of chemical reactivity across a surface.

PACS: 81.05.Kf

I. INTRODUCTION

Glass surfaces are subject to attack by water essentially from the instant they are created, and this attack can have a dramatic effect on the chemical state of the surface sites. Strong physisorption sites can rapidly attract water molecules to the surface, where they may break surface bonds and weaken the glass structure in the process of dissociative chemisorption. A detailed review of the interactions between water and solid surfaces is given in (Refs. 1 and 2).

The hydration and hydroxylation of glass surfaces is understood in general terms, but the mechanisms that control these processes at the atomic level are poorly understood. Because experimental techniques that can probe the structural effects of water adsorption reactions are limited for amorphous materials, it is necessary to employ computer modeling and simulation. Additionally, even in areas where experimental data is available, computer modeling can play an important part in interpreting and understanding the experimental results. Glasses were first investigated by computer modeling in 1979 when Woodcock et al. simulated the bulk structure of silica glass by molecular dynamics (MD). Since then, MD has come a long way and has provided many
useful results in the field of glass science (see review, Ref. 4). Garofalini laid the groundwork for the use of MD to simulate glass surfaces, and to introduce water to a simulated surface.

The biggest obstacle to simulating the adsorption of water on glass is the problem of scale. MD simulations are still very limited by the size of the surface and the time scale of simulation that can be investigated. The size limitation is not a problem in the case of the surfaces of crystalline materials, because the adsorption reactions of water can be modeled with a handful of representative surface sites in order to provide a global view of water adsorption over the surface. Conversely, because of the large number of site types on a glass surface, and the infinite number of possible structural arrangements surrounding each site, it is not feasible to study each site individually. In addition, the time limitations make it difficult to directly simulate the chemisorption process, which occurs much slower than physisorption.

Ideally, a method that maps out the distribution of physisorption energies and chemisorption probabilities over an entire region of a simulated surface would be the most effective means of modeling water adsorption on a heterogeneous surface. That process must then be repeated until enough area has been interrogated to obtain a statistical description of the water adsorption characteristics. Such a mapping should be able to predict the sites that would physisorb water most readily, and in turn predict whether that physisorption site could also chemisorb water. It would then be possible to examine in detail how water adsorption is affected by factors such as elemental composition, degree of surface hydration/hydroxylation, and surface preparation method. The goal of this paper is to present a new set of modeling techniques that use ab initio
quantum chemical calculations to obtain complete mappings of the physisorption and chemisorption properties of simulated oxide glass surfaces with respect to adsorption of water.

II. BACKGROUND

In our previous work, we reported a method for mapping out the water physisorption energy on a simulated surface by a conjugated gradient technique.\(^9\) For every \((x,y)\) point on a fine grid covering the surface, the energy of a water molecule was minimized with respect to its height above the surface and its orientation. This energy minimization provides a quantitative means of determining the strength of the interaction between a physisorbed water molecule and every point on the glass surface. This mapping procedure was repeated for other simulated surface models to provide a statistical sampling of the surface sites. The results showed that the strongest sites for physisorption are coordination defects such as 3 coordinated Si and non-bridging oxygen (NBO). While this technique does provide a quantitative, nanoscale description of water physisorption on glass, it cannot provide any direct information about chemisorption. Chemisorption involves chemical reactions, and so, it is best studied by ab initio quantum chemical calculations that take electronic structure into consideration.

Recently, computing power has increased and schemes for approximating wave functions have become more efficient; thus, ab initio calculations are now common modeling tools for simulating structures and reactions of various systems at the atomic level. Also, because experimental data is not available as a means of validation for more classical MD simulations, ab initio has become an alternative validation method. Ab
initio calculations are limited to a much smaller system of atoms than for MD, and typically involve small clusters of atoms that are intended to represent the continuous material; such clusters have been used to model the bulk structure of silicate glasses.\textsuperscript{10,11} Ab initio modeling of clusters has been utilized, for example, to model water adsorption on MgO crystal surface sites.\textsuperscript{12,13} One modification that has been employed to render the cluster more representative of a surface is to embed it in an array of point charges; in this way, the array becomes representative of the extended surface and bulk of the material, for example, see (Refs. 14-17). In the case of crystalline materials at least, it is possible to perform ab initio calculations by representing every type of surface site in a small simulation cell containing only a few atoms. Such periodic ab initio modeling has had widespread use in the modeling of water adsorption on crystal surfaces of TiO\textsubscript{2} and MgO\textsuperscript{18-25} and others.\textsuperscript{26,27} Unfortunately, the application of these ab initio techniques to modeling water adsorption on heterogeneous glass surfaces is not as straightforward as in the case of homogeneous crystal surfaces.

In silica glasses, the process of hydroxylation occurs predominately at Si-O-Si linkages; these linkages form the structural network of silica and silicate based glasses. During hydroxylation, the linkage is broken and replaced with two Si-OH (silanol) groups as shown in Fig. 1. The hydroxylation of Si-O-Si linkages has been studied using ab initio calculations on small clusters of atoms that represent a linkage and the local environment around it.\textsuperscript{28-31} Such calculations are very useful for determining the activation energy barriers for chemisorption reactions at specific sites, but are limited in their relation to a continuous surface because of the small cluster size. Site reactivity is dependent on the electronic local density of states of the surface at energies close to the
The important difference between a finite cluster and an infinite surface is that the former will present a discrete number of states, whereas the latter will have a continuum density of states. One approach for relating cluster models to surfaces has been proposed by Walsh et al. First, a continuous periodic surface with a large repeat cell size is simulated by MD. Next, clusters of atoms, each representing a specific type of adsorption site, are removed from the surface model. Ab initio calculations are then performed on the clusters to determine chemisorption activation energy barriers of several different site types. Another more recently developed method, which allows for ab initio molecular dynamics simulation of the bulk and surface of glasses, is based on the Car-Parrinello (CP) scheme. Although still limited to a small cell size, the CP method utilizes a continuous surface instead of a discontinuous cluster. Using this method, hydroxylation of Si-O-Si linkages has been investigated for a select group of 2 membered ring (edge shared tetrahedra) sites.

In contrast, the goal of the calculations reported here is to map/predict the physisorption energy and the chemisorption probability of water over the surface as a function of composition. The physisorption mapping would provide the physisorption energies across a surface based solely on the charge density and electrostatic field of the surface (without having to repeatedly calculate the interaction energies between water and the surface). Similarly, the chemisorption mapping would determine the chemisorption probabilities across a surface based on the properties of the charge density of the surface (without having to repeatedly simulate chemical reactions). Whereas our previous work used classical MD and energy minimization techniques to map out the physisorption energy, this work is focused on ab initio calculations. The ab initio work
can be broken down into two components. First, we use ab initio modeling to map out the physisorption energy over a surface, and then we establish a framework for chemisorption mapping of glass surfaces. The latter is not possible with classical simulations. Because all of the chemisorption studies of water mentioned previously have only considered reactions at a select group of sites, rather than a mapping of an entire surface, we have introduced a local reactivity index that can be evaluated from the electronic structure of the entire surface. This index is obtained using one self-consistent calculation, and provides a snapshot of the location and intensity of the reactive sites. This is in contrast to cluster calculations of chemisorption where only selected sites are considered. This method yields a map of the electronic “softness” across a surface, and equates softness to chemical reactivity.

Because of the distinction between the two different methods for probing and mapping adsorption, it was necessary to break the process down into molecular adsorption and dissociative adsorption. For the remainder of the paper, the terms physisorption and chemisorption will be referring to molecular adsorption and dissociative adsorption, respectively.

III. MODELING PROCEDURE

A. Theory

The theoretical basis for our simulations of water adsorption is that water approaches the glass surface through electrostatic interactions, and then dissociates if the physisorption site is sufficiently strong and/or reactive. Our method extracts from electronic structure calculations the regions of the surface that are strong sites for
physisorption, and also provides a measure of the associated physisorption energy. Most importantly, it creates a map of the chemical reactivity of the surface for water dissociation.

A water molecule is attracted to the surface by the interaction of its dipole moment with the gradient of the electric field produced by the adsorbate. Charge transfer, which is a characteristic of the ionic bonding between silicon and oxygen, generates strong gradients of electric field that can be calculated by ab-initio methods. The dipolar water molecules are attracted by these electrostatic interactions until the Pauli repulsion between electrons prevents further approach. This electrostatic interaction is the basis of our method for extracting information about physisorption using ab-initio calculations.

The dissociation of a water molecule on the glass surface occurs through redistribution of the charge density at the surface. The active chemisorption sites will be those that can facilitate this charge rearrangement. In this sense, the reactivity of the surface can be associated with the concept of chemical hardness or softness.\textsuperscript{40} We define a water dissociation index based on the local isoelectronic reactivity.\textsuperscript{39} The isoelectronic reactivity is a map of the change in charge density when the electrons are thermally excited from the ground state. To define our water dissociation index we combine this local isoelectronic reactivity,\textsuperscript{39} which is a property of the surface, with a windowed average that preferentially weights the regions with acidic and basic sites that are in close proximity on the surface. Thus, the index reveals those regions where water is most likely to be chemisorbed. The full procedure, described in detail below, provides a map of the physisorption and chemisorption sites on a glass surface based solely on properties of the material, accessible via electronic structure calculations, without the need to model
individual interactions or chemical reactions per se. It should be noted that both the physisorption and chemisorption mappings only apply to neutral molecular water. We are interested in water attack that comes from the vapor phase, and in the vapor phase, ionization is negligible so it is not necessary to take species such as H\(^+\), H\(_3\)O\(^+\), or OH\(^-\) into consideration. The techniques described below for studying physisorption and chemisorption could certainly be adapted to accommodate these other species in order to study water-surface interactions in aqueous environments.

### B. Surface Simulation

The atomic scale glass surface structure models were created by a classical MD procedure.\(^9\) First, the bulk was simulated with a cubic base cell and periodic boundary conditions (PBC) in all directions. Because the goal was to perform ab initio calculations on the model, a small cell size of 240 atoms was chosen. After the bulk was simulated, the PBC were removed in the positive z direction to create a surface that was periodic in the (x,y) plane on top of a periodic bulk in the negative z direction. To create a model fracture surface, the surface was relaxed using a MD simulation at 300K (a side view of the relaxed fracture surface is shown in Fig. 2(a)).

The silica melt surface studied in this work was created using a hybrid molecular dynamics / Monte Carlo (MD/MC) method that is described in (Ref. 41). To create a defect free surface, the fracture surface was heated to an elevated temperature (~8000K) and a MD simulation was carried out to relax the surface atomic structure. At the end of each MD time step, the number of dangling bonds on the surface was evaluated. As long as this dangling bond concentration did not increase, the MD simulation was allowed to
continue. If the number of dangling bonds increased, the velocities of all the atoms were replaced with velocities picked at random from a Maxwell distribution that was based on the temperature. The simulation was carried out in this manner until there were no coordination defects remaining on the surface. The surface was then slowly cooled to 300K, resulting in a defect free melt surface.

The surfaces were prepared for the subsequent ab initio calculations by removing all but the top few atomic layers of the surface. This removal of the atoms below the surface layer resulted in a thin (6-10 Å) slab of the ‘surface model’ with PBC in the plane of the surface (x,y) only. The dangling bonds on the bottom of the slab were terminated with silanol groups, as shown in the side view in Fig. 2(b). All density functional theory (DFT) calculations were performed using the Vienna Ab-initio Simulation Package (VASP).42-45 The simulation cells ranged in size from 15-18 Å in the plane of the surface (x and y directions), and 30 Å in the z direction. The cells contained 110-170 atoms, and the vacuum space between layers was a minimum of 20 Å. All calculations utilized ultra-soft pseudopotentials from the generalized gradient approximation (GGA). Because of the large cell size, a single gamma point was used. The value of the smearing width was 0.2 eV, except in the chemisorption mappings where the 0.2 eV smearing was compared to a 0.3 eV smearing. The default convergence criteria of 0.0001 eV for the electronic self-consistency loop and 0.001 eV for the ionic relaxation loop were implemented for all calculations.
C. Physisorption

The charge density of the surface slab was computed by DFT using VASP. In the VASP calculations, PBC were applied in all directions, which means the slab was repeated above and below in addition to being repeated in the (x,y) plane. Because of this periodicity, the height (z) of the repeat cell was chosen to be large enough so that the surface of one slab was not affected by the slabs above or below it. Figure 3 shows a side view slice of the charge density ($\rho$) through the surface slab. (Figure 6(a) shows the top view of the structure model represented in Figure 3, and the dashed line in Figure 6(a) indicates the location and orientation of the slice.) According to our model, a water molecule will move toward the surface until the Pauli repulsive forces prevent further approach. For this reason, a surface profile, $Z(x,y)$ was defined by “rolling” a sphere with a 1Å radius across the $\rho_0 = 0.053e/Å^3$ isosurface (see Fig. 4). This value of $\rho_0$ was adjusted to match the calculated surface-to-water distance for water physisorption. The results are not very sensitive to the choice of this value, as long as they are close to the van der Waals surface. The $Z(x,y)$ was determined for each (x,y) position by lowering a 1Å sphere from above the surface until the sphere’s surface first came into contact with the isosurface. At the point of contact with the isosurface, the center of the sphere was recorded as the $Z(x,y)$ value. Figure 5 shows the top view of the surface profile, which approximates the closest possible approach of a water molecule to the surface during physisorption. (This procedure also prevents voids from being included.) Because of the high degree of heterogeneity of glass surfaces, the distance from points on the surface profile to the closest atom varied widely, with most values in the range 1.7-2.4Å.
The local electric potential $V(x,y,z)$ over the entire slab was also computed using VASP. Then, for every point on the surface profile $Z(x,y)$, the electric field ($\mathbf{E}$) was calculated by taking the gradient of the electric potential:

$$\mathbf{E}(x,y,Z(x,y)) = -\nabla V(x,y,Z(x,y))$$

The magnitude of the electric field at every point on the surface was then multiplied by the dipole moment of water ($p_{\text{water}}$) to give the electrostatic interaction energy between the surface and a water molecule at position $(x,y,z)$:

$$U(x,y) = -p_{\text{water}} \| \mathbf{E}(x,y,Z(x,y)) \|$$

The interaction energy was then plotted as a top view “mapping” of the surface as shown in Fig. 6(b). The surface profile created from the charge density isosurface assured that the electrostatic interaction was not over estimated due to the unrealistically close approach of a water molecule. Multiplying the dipole moment of water by the electric field gives the maximum interaction energy for a point dipole aligned with the electric field. To account for the fact that the water molecule occupies a finite amount of volume, the gradient of the potential was averaged over an area of the surface representing the size of a water molecule. For each point $(x,y)$ on the surface profile, the potential gradient as a vector was averaged over all points on the surface within 1Å of $(x,y)$. Averaging as a vector took into account the possibility of the field changing direction across the volume occupied by the water molecule.

The “dipole approximation” of a water molecule was checked against a three point charge model of water in the same position, orientation, and electric field as the dipole above a surface, and the agreement was very good; i.e. when the two interaction energy mappings were compared, they both showed the same sites, with similar site
geometry and site strengths. As a check of the thin slab model for a surface, the thickness of the surface layer used in the ab initio calculations was doubled, and the resulting physisorption mapping did not change. Also, in a separate check, the height of the vacuum region in the periodic cell was doubled and it was determined that the original cell height was big enough to eliminate any significant interaction between repeated layers.

To provide an extra check for the interaction energy approximations described above, the interaction energies between a water molecule and select group of surface sites were calculated directly using VASP. Instead of calculating the electric field and multiplying by the dipole moment of a water molecule, the energy of a water molecule located at a surface site was computed by taking into account the electronic structure of both the surface and the water molecule. First, a water molecule was placed above the surface at a distance large enough to ensure that the water-surface interaction was negligible, and the total energy of the system was calculated. Next, the water molecule was placed at an (x,y) point on the surface profile with its dipole oriented along the electric field vector. The position of the water molecule was then relaxed using VASP, and the final energy of the system with the relaxed water molecule was calculated. (It should be noted that during the relaxation of the water molecule at specific sites, the water molecule did not dissociate.) The difference in the initial and final energies (desorbed water versus adsorbed water) was then computed to give the physisorption energy for that point on the surface. The results of the physisorption energy calculations are shown in Table I.
For further comparison/validation, a second technique for obtaining physisorption energy mappings was employed. This mapping used classical pair-wise potentials and a conjugated gradient algorithm to minimize the energy of interaction between a water molecule and the surface for each (x,y) point at the surface. The minimization was done with respect to the water molecule’s orientation and height above the surface, and resulted in a physisorption energy mapping similar to the one described above. (The details of the conjugated gradient physisorption energy mapping method can be found in Ref. 41.) The physisorption energy values in the first column of Table I were computed using this conjugated gradient method. (It should be noted that for all energy values in Table I and those discussed in the text, the minus sign has been dropped. Hence, sites whose physisorption energies are the most negative are referred to strong, high-energy sites.)

D. Chemisorption

Our procedure to simulate physisorption, described above, involves mapping the closest approach of water molecules to the glass surface and the strength of the physisorption at each site. We now turn our attention to the dissociation of water on the surface.

To compute the chemisorption probability over the entire surface profile Z(x,y), the charge density was recomputed using a larger smearing value. (The smearing value determines how far above and below the Fermi level the partial occupancies of the wave functions are spread.) The difference in charge density (Δρ) for the smaller versus larger smearing values was then calculated for each point on the surface profile. Because the
dissociative chemisorption of a water molecule requires a site that will accept charge and a site that will donate charge to be adjacent, a method was developed to analyze the spatial distribution of positive and negative Δρ values. Regions with positive values of Δρ correspond to sites that readily accept charge, and regions with negative values of Δρ represent charge donors. For each point (x,y) on the surface profile, Δρ was examined for all other points on the profile that were within 1Å of (x,y). The highest positive value (Δρ_{max}+) and the lowest negative value (Δρ_{min}−) were determined. (If there were no positive values for Δρ then Δρ_{max}+ was set to zero, and if there were no negative values for Δρ then Δρ_{min}− was set to zero.) If Δρ_{max}+ was less than the absolute value of Δρ_{min}−, then Δρ_{max}+ was assigned as the index of reactivity for that (x,y) point on the surface. Conversely, if the absolute value of Δρ_{min}− was less than Δρ_{max}+, then the absolute value of Δρ_{min}− was assigned as the index of reactivity for (x,y). This method assured that reactivity indexes were assigned according to sites possessing both donor and acceptor properties. It should be noted that the reactivity index is a qualitative parameter, and can only be used for comparison between different surface models if all other parameters for calculating the charge density are not varied. (The index was scaled to put the majority of sites in the 0.0-0.5 range, with only the very highly reactive sites in the 0.5-1.0 range.) The reactivity was then plotted as a two-dimensional mapping of the surface chemisorption probability, such as the one shown in Fig. 6(c) for the silica fracture surface.

In a few test cases, ab initio MD was used to validate whether a water molecule would dissociate rapidly (less than 100fs) at specific sites that were identified as very reactive by the reactivity index (index values >0.4). A water molecule was placed above a
selected site, and ab initio MD was employed (using VASP) at a temperature of 300K. The atoms in the water molecule, along with those in and around the site were allowed to move, while the rest of the surface remained frozen in place. Because of the very short time scale of the ab initio MD (~300 time steps of 0.3fs), if a water molecule chemisorbed, the site was considered very reactive. If the water molecule did not chemisorb, it was not possible to determine whether a reaction would take place given a longer time frame. Sites with reactivity indices above 0.4 were shown by the ab initio MD to chemisorb water molecules within ~100fs. Sites that had reactivity indices less than 0.4 did not chemisorb water molecules in the very short time scale of the ab initio MD simulations.

IV. RESULTS AND DISCUSSION

A. Physisorption

The physisorption energy mapping provides a convenient method for obtaining detailed information on the strength of adsorption sites without actually having to simulate the adsorbate (in our case a water molecule). The method fuses the surface charge density distribution and electric field to predict physisorption, rather than focusing on the water molecule. Figure 6(a) shows the structure of the surface that corresponds to the adsorption energy mapping in Fig. 6(b). The surface contains four coordination defect sites: two NBO sites, a 3-coord Si site, and a site consisting of both a NBO and a 3-coord Si. The two NBO sites are represented in the energy mapping as large, poorly defined regions of moderate interaction energy (in the 40-60 kJ/mol range). The 3-coord Si sites, on the other hand, are smaller in size and very well defined, with higher interaction
energies in the 100-150 kJ/mol range. Other adsorption sites can also be seen in the physisorption map (Fig. 6(b)). All of these other sites correspond to the faces of (SiO₄) tetrahedra.

The tetrahedral sites on the silica fracture surface are very narrow, well defined, and triangular in shape. The shape and orientation of the adsorption sites in the energy mapping are directly related to the position of the tetrahedral face as shown in Fig. 7. In addition to dictating the size and shape of the adsorption site, the local geometry also influences the strength of the adsorption site; specifically, the orientation and geometry of the tetrahedral face affects the distance of closest approach. The DFT validated physisorption energy values for [SiO₄] tetrahedral faces are in the 30-100 kJ/mol range, which is slightly higher than previously reported. The high energy of these sites is a result of their distortion due to the fact that they are located on the surface instead of in the bulk. If the tetrahedra are examined more closely, it is found that those with O-Si-O bond angles close to the equilibrium value of 109.5° have low interaction energies (30-40 kJ/mol), while the more distorted tetrahedra with much higher interaction energies have O-Si-O bond angles up to 15 degrees from equilibrium. The strained tetrahedra have high adsorption energy because they are distorted in a manner that would expose the charge and electrostatic field of the Si atom, and therefore, enhance the gradient that attracts the water molecule to the surface. Essentially, the tetrahedra with higher physisorption energy values had an exposed face that was larger in area than those tetrahedra with lower energy values. The most distorted tetrahedra were found in two membered rings on the surface, and they corresponded to the tetrahedra with the highest physisorption energy (in the 60-100kJ/mol range). Three membered rings also contributed to the tetrahedral
distortion, but the distortion and physisorption energies were not as high as the tetrahedra located in two membered rings.

Table I summarizes the energies of specific sites found on silica fracture and melt surfaces from the conjugated gradient method mapping, and from the DFT gradient of electric potential mapping reported here. Both are compared with the DFT water-surface interaction energy calculations for verification. Good agreement is observed, except in the case of the conjugated gradient underestimating the energies of SiO₄ tetrahedra sites. The potential gradient physisorption mapping is in good agreement for all site types with the ab initio water-surface interaction energy calculations of both the surface and the water molecule together (column 3 in Table I). This agreement with the full DFT calculations of the water/surface indicates that the physisorption mapping based on energy minimization was underestimating the physisorption energies of the tetrahedral sites. This underestimation could be due to the fact that the tetrahedral sites are spatially very narrow, and so, the interaction energy will be exceedingly sensitive to the position and orientation of the water molecule. The conjugated gradient method may not be able to find such specific positions and orientations for the water molecule (for practical grid resolution), and would always result in an underestimation of the energy. It should be noted that if many different starting configurations were sampled when using the conjugated gradient approach, the method was more likely to find a lower minimum. However, this approach makes the technique highly inefficient, especially when compared to the efficiency of the DFT physisorption mapping method.

Figure 8(a) shows a top view of the simulated coordination-defect-free silica melt surface. The figure shows a surface of interconnected, randomly oriented SiO₄ tetrahedra
that are distorted to varying degrees. The physisorption energy mapping in Fig. 8(b) shows that the defect-free melt surface does not contain the high energy adsorption sites found at coordination defects on silica fracture surfaces. The only sites present on the melt surface are those of SiO$_4$ tetrahedra faces, and these sites have energies in the 25-70 kJ/mol range. Again, it is found that each of the triangular shaped regions of higher interaction energy (adsorption sites) correspond directly to a tetrahedral face on the surface. The amount that each of these tetrahedral faces was distorted, or “opened” to expose the central Si atom, was determined by averaging the three tetrahedral angles opposing the face. Figure 9 shows the correlation between tetrahedral face distortion and the water physisorption energy for the adsorption sites on the silica melt surface. The distortion is measured as the average of the three O-Si-O angles that include the O atom opposite the face of interest. It should be noted that the physisorption energy is a very localized phenomenon in that it depends almost entirely on the local structure of the site without regard for neighboring sites. Figure 9 supports this conclusion by showing that the physisorption energy at a specific tetrahedron face can be estimated to a first approximation by looking at the tetrahedral distortion. (The same correlation between physisorption energy and tetrahedron distortion was observed for sites on the fracture surfaces, but the melt surfaces were used to illustrate the connection because didn’t have the added complexity of coordination defects.)

The heat of liquefaction of water, at 44 kJ/mol, is a value that has been used in the literature as a measure of the hydrophilicity/hydrophobicity of a surface site. Physisorption sites that are stronger than 44 kJ/mol are considered hydrophilic, while
those weaker than 44 kJ/mol are considered hydrophobic.\textsuperscript{41,46} By this definition, on the fracture surface, the coordination defect sites (NBO and 3 coord Si) and the strained tetrahedron sites are hydrophilic, while the tetrahedra with little or no distortion are hydrophobic. Because silica glass melt surfaces are believed to be fully connected, the distortion and strain in the tetrahedral network dictates whether the melt surface physisorbs water or not. As shown in Fig. 8(b), the simulated silica melt surface contains [SiO\textsubscript{4}] tetrahedra with low and high strain. While much of the surface area shows an interaction energy less than 44 kJ/mol, there are a number of hydrophilic sites due to strain in the network at the surface.

The physisorption mappings can be converted to physisorption energy distributions by mapping many surfaces and obtaining information on over a hundred different sites.\textsuperscript{9} Figure 10 shows the cumulative physisorption energy distributions for fracture and melt surfaces obtained by both the new DFT mapping technique and the CG technique.\textsuperscript{9} The two mapping techniques agree qualitatively and quantitatively except for a few small deviations. The biggest difference between the DFT and CG energy distributions is a result of the CG mappings underestimating the physisorption energy of tetrahedral sites. This underestimation can be seen in the gap between the DFT and CG energy distributions in the 25-70 kJ/mol range; the CG curves are shifted to lower energies. As noted earlier, this difference is due to the fact that the CG method was not finding some of the lowest energy configurations for water molecule physisorption at certain sites. There is also a slight difference between the two techniques in the case of high energy 3 coordinated Si sites (>100 kJ/mol). The dashed line at 44 kJ/mol in Fig. 10 represents the dividing line between hydrophilic and hydrophobic sites. The DFT energy
distributions show that more than 90% of the sites on the silica fracture surface are hydrophilic, while the melt surface contains only ~15% hydrophilic sites.

**B. Chemisorption**

The most interesting observation about the chemisorption mappings is the fact that they do not always match the physisorption mappings. That is, the sites with the strongest physisorption energy do not necessarily correspond to the sites with the highest chemisorption probability. Figure 6(c) shows the chemisorption probability map calculated for the silica surface model that is shown in Fig. 6(a). The strongest chemisorption site found on the silica surface is a NBO / 3 coord Si pair, which is logical because of the donor/acceptor abilities of the two site pair. Chemisorption at the defect pair site was verified by an ab initio MD simulation in which dissociation of the water molecule occurred. In the simulation, a proton from the water molecule was transferred to the NBO site and the remaining OH from the water molecule chemically bonded to the 3 coord Si resulting in the formation of two hydrogen bonded silanol groups. This ab initio MD simulation was repeated in the vicinity of the lone defect sites on the surface, and no chemical reaction occurred during the short time scale of the simulation. In order for chemisorption to occur at defect sites, they must exist as a donor/acceptor pair that is close enough for both sites to chemically interact with the water molecule simultaneously, but not so close that the sites can interact more strongly with each other than with the adsorbate.

Other sites on this silica surface show considerably lower chemisorption probability, except for a 2 membered ring site with a moderate chemisorption probability.
The 2 membered ring on the silica surface shows up as a possible chemisorption site, but much less so than the defect pair. The ab initio MD simulations were extended to longer time scales (300fs) at elevated temperatures (600K) to show that reaction is possible at such highly strained sites. Two-membered rings have also been shown to be reactive by other simulation methods.\textsuperscript{32,37,38} The chemisorption mappings show that the 2 membered rings are the most reactive sites on the silica network, excluding those associated with coordination defects.

To relate the reactivity index used in the mappings with a more quantifiable chemisorption parameter, the index was compared with chemisorption energy barriers reported in the literature. Using ab initio cluster calculations, energy barriers were obtained for the hydrolysis of Si-O-Si bonds where none, one or both of the Si atoms had some form of coordination defect.\textsuperscript{32} Five of these Si-O-Si types are present on the simulated silica fracture surface in Fig. 6(a). The five types are: no defects (two fully connected Si tetrahedra and no edge sharing), one NBO site, one 3 coordinated Si site, two fully connected edge shared tetrahedra (a two membered ring), and a NBO / 3 coordinated Si pair. The graph in Fig. 11 shows a comparison between the reactivity index from the chemisorption probability mapping, and the calculated energy barriers for chemisorption.\textsuperscript{32} The highest reactivity indices found on the silica fracture surface (>0.4) correspond to sites with chemisorption energy barriers less than 25kJ/mol, and were shown by ab initio MD to chemisorb water in less than 100fs. Sites with reactivity indices less than 0.1 have chemisorption energy barriers greater than 100kJ/mol, and can be considered highly unreactive in the short time scale of MD simulation.
The chemisorption reactivity of fully connected Si-O-Si linkages was also investigated by performing the chemisorption mapping on the silica melt surface shown in Fig. 8(a). As can be seen in the mapping in Fig. 8(c), a silica melt surface containing no coordination defects would have a very low reactivity with respect to chemisorption of water molecules. Based on the correlation in Fig. 11, reactivity indices less than 0.1, which includes all of the silica melt surface, correspond to chemisorption energy barriers greater than 100 kJ/mol.

Figure 12 illustrates the chemical reactivity for our two extreme models of the silica surface. The reactivity mappings are plotted as cumulative distributions of chemical reactivity for melt and fracture surfaces. The coordination-defect-free melt surface represents the lowest reactivity of any of the surfaces examined by the mapping technique, while coordination defects on the fracture surface result in reactivity indices that correspond to chemisorption activation energy barriers that are close to zero in some cases. However, it should be noted that the highly reactive sites consisted of coordination defect pairs, and that the isolated dangling bonds are much less reactive.

**V. CONCLUSIONS**

We have demonstrated a new method for mapping the physisorption energy over a continuous glass surface model, and the energies have been validated with full DFT calculations of water-surface interaction energies. The strained tetrahedra sites on silica surfaces have been shown to have higher physisorption energies than previously reported. More than 90% of the fracture surface sites are found to be stronger than 44 kJ/mol, which classifies them as hydrophilic.
We have mapped out the physisorption and chemisorption properties of a fully connected, coordination-defect-free silica melt surface. The physisorption sites on the melt surface are much weaker than those of previously simulated fracture surfaces. Nevertheless, a small percentage of the melt surface sites (~15%) may be considered hydrophilic based on their physisorption sites being stronger than the heat of liquefaction of water. The strength of the physisorption sites, which are located at the faces of \([\text{SiO}_4]\) tetrahedra, is defined by the structural distribution of the tetrahedron.

A method for mapping the chemisorption probability has also been demonstrated and applied to glass surfaces to identify sites that are the most reactive. One of the key findings of the chemisorption mapping is that the most chemically reactive sites cannot be predicted based on the strength of physisorption energy only. Coordination defect sites, which have high physisorption energies, are not very reactive unless they exist in just the right geometry as charge donor/acceptor pairs. The chemisorption mappings showed that the coordination-defect-free melt surface was not very reactive, especially when compared to energy mappings of silica fracture surfaces.

In looking to the future application of these techniques, many possibilities exist. The ability to fully map the adsorptivity of a glass surface allows for a more comprehensive investigation of the adsorption process, and its dependence on composition and thermal history. The next step is to use these tools to examine, for example, how the hydrolysis of one Si-O-Si bridge affects subsequent water adsorption events, or to study how the addition of modifier ions such as Na\(^+\) affect reactivity of the surface. The surface of a glass is composed of individual sites, but each one is linked to many others through the network, and its tendency to redistribute charge via polarization
and inductive effects; changes in one site will influence the other sites. This effect of composition on the network defect sites may be even more apparent in the case of Al additions to silicates.
REFERENCES


ACKNOWLEDGEMENTS

The authors would like to gratefully acknowledge the financial support of the NSF Center for Glass Surfaces, Interfaces, and Coatings Research (EEC-9908423)
FIG. 1. Schematic of the process of water attack on an Si-O-Si bridge, resulting in the formation of two silanol groups.
FIG. 2. Side view of a simulated silica fracture surface (a) before and (b) after being made ready for importing into DFT calculations.
FIG. 3. Side view of the charge density through the surface layer shown in fig. 2(b).
FIG. 4. Schematic of the process for creating a surface profile from a charge density isosurface.
FIG. 5. Top view of the surface profile, \( Z(x,y) \), of a silica fracture surface.
FIG. 6(a). Top view of the sample silica fracture surface with the adsorption sites of interest indicated. (Dashed line represents the position of the charge density slice shown in figures 3 and 4.)
FIG. 6(b). DFT Physisorption energy mapping of the silica fracture surface shown in (a).
FIG. 6(c). Chemisorption reactivity mapping of the fracture surface shown in (a).
FIG. 7. Diagram of the physisorption of molecular water onto the faces of [SiO4] tetrahedra, and the corresponding physisorption mapping signature.
FIG. 8(a). Top view of a simulated coordination-defect-free silica melt surface.
FIG. 8(b). Physisorption energy mapping of the melt surface shown in (a).
FIG. 8(c). Chemisorption reactivity mapping of the melt surface shown in (a).
FIG. 9. Correlation between [SiO4] tetrahedron distortion and physisorption energy. (Dashed line indicates the heat of liquefaction of water at -44kJ/mol.)
FIG. 10. Conjugated gradient and DFT cumulative physisorption energy distributions for silica fracture and melt surfaces. (Vertical dashed line represents the heat of liquefaction of water.)
FIG. 11 Relationship between chemisorption reactivity index and chemisorption energy barriers.
FIG. 12. Cumulative chemisorption reactivity index distributions for silica fracture and melt surfaces.
Table I. A comparison of water/surface site interaction energies for the conjugated gradient, gradient of potential (DFT), and full DFT calculation methods. (All values are in kJ/mol.)

<table>
<thead>
<tr>
<th>Site Type</th>
<th>Conjugated Gradient</th>
<th>Gradient of Potential Energy</th>
<th>DFT water-surface interaction energy</th>
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<tr>
<td>NBO</td>
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<td>65</td>
<td>58</td>
</tr>
<tr>
<td></td>
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<td>63</td>
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<td>127</td>
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<td></td>
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