Water Adsorption and Diffusion on NaCl(100)

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At low coverage and temperature the water−surface interaction determines the adsorption geometry of the water molecule on the NaCl(100) surface. However, at room temperature the molecules are also able to move on the surface and form islands where the water molecules are held together by hydrogen bonds. As a step toward the description of such complex phenomenology, in this work we have used density functional theory calculations to study the most favorable adsorption geometry of an isolated water molecule and the energy barriers associated with different hopping mechanisms between equivalent adsorption configurations on this surface. We propose different hopping processes that can be classified as translations, if the molecule moves from one adsorption site to the adjacent one, or reorientations, if the molecule only changes its orientation on the surface and remains in the same adsorption site. The straightforward parallel translation of the water molecule along the surface exhibits the highest barrier. All other processes, either translations or reorientations, involve the rotation of the water molecule around certain axes and present much smaller barriers (at least 50% smaller). To obtain a net movement of the molecule along the surface it is always necessary to combine one of these translational and reorientational processes. Such combinations provide favorable and plausible pathways for the diffusion of the water molecule on the NaCl(100) substrate.

I. Introduction

The role of humidity in the heterogeneous chemistry of aerosol surfaces has, for nearly forty years, inspired experimental and theoretical research revealing the importance of the water coverage.[1−8] In recent years, electronic structure calculations have been used to gain a better understanding of the configuration of water adsorbed on NaCl surfaces.[9−13] In particular, much attention has been paid to the dependence of the adsorption geometry on the competition between the water−surface and water−water interactions. Much research has concentrated on coverages close to one monolayer (ML) and low temperatures. In fact, there is an unsolved controversy concerning the adsorption geometry of water at 1 ML coverage on NaCl(100). Whereas some experimental techniques, such as He atomic scattering, show a 1×1 periodicity[14] in which water−surface interactions seem to play a predominant role, low-energy electron diffraction indicates a c(4×2) structure[15,16] which would point toward the importance of intermolecular interactions. Thus, the low-temperature structure of a water monolayer on NaCl(100) and the driving force behind its particular conformation remain unknown. In the limit of very low coverage, it has been claimed that even at room temperature the water−surface bonds are favored over water−water hydrogen bonds.[17] However, both molecular dynamics simulations[18,19] using model potentials and experimental results using infrared spectroscopy[20] indicate the formation of islands of water molecules at room temperature for coverages below 0.5 ML. The relative importance of dipole−dipole interactions versus

hydrogen bonding in such molecular clustering is also a matter of debate.[18,19] According to the results by Foster et al.,[20] 0.5 ML could be a critical coverage above which the water tends to form multilayer structures at room temperature. In summary, water on NaCl(100) shows a complex behavior that needs more investigation both experimentally and theoretically.

It is evident that the knowledge of the energetics of water diffusion on this surface is instrumental in understanding and predicting the kinetics of island formation as a function of temperature and water coverage. Despite this, there has been very few theoretical studies of the diffusion of water on NaCl-(100). Most of them have been limited to the calculation of the energy landscape for a limited set of molecular orientations as a function of the position of the molecule on the surface and for relatively large coverage, like the work by Meyer et al.[8] More relevant for the low-coverage limit is the work by Engkvist et al.[21] These authors performed calculations, using model potentials based on intermolecular perturbation theory, of three possible transition states of the water molecule in its movement along the surface. They only considered two reorientational processes and the parallel translation of the molecule from one adsorption site to the next. Their approach also presents some shortcomings, besides the possible problems of the accuracy of the utilized interaction potentials, since the molecules were treated as rigid rotors and no surface relaxation was permitted. The impact of such approximations in the results is unclear and therefore has to be investigated.

In the present work we reexamine the problem of the energetics of the adsorption and diffusion of water on the NaCl-(100) substrate. First, we have investigated the adsorption of a single water molecule on the NaCl(100) surface using density functional calculations and including the effects of the relaxations of the substrate. Then, we have investigated several possible processes for the molecular hopping between equivalent adsorption configurations. The studied processes included those

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previously proposed by Meyer et al.[8] and Engkvist et al.,[21] as well as other reorientations and translations. Combining different translations and reorientations of the individual water molecule on the NaCl(100) surface, we arrive at a plausible diffusion mechanism with an activation energy ~50% lower than previous proposals.

II. Computational Method

All calculations were performed with the Vienna ab initio simulation package (VASP),[22−24] implementing the density functional theory (DFT) within the Perdew-Wang 1991 (PW91) version of the general gradient approximation (GGA).[25] The projector augmented wave (PAW) potentials[26,27] were used to describe the Na, Cl, O, and H atoms. A plane wave basis set is used in our calculations.

We used a supercell/slab geometry to represent the surface, with periodic boundary conditions along the three spatial directions. Previous DFT calculations used a slab consisting of only two atomic layers, which were not allowed to relax.[10] This approximation seems justified by the fact that ionic crystals are very inert and show no tendency toward surface reconstruction. However, in our investigations we have observed that, even with relatively low water coverage, the NaCl(100) surface can be strongly modified showing signs of deliquescence.[28] Consequently we have decided to include the effects of the relaxations of the substrate in the present calculations. We have used slabs consisting of four NaCl layers with a 2 × 2 lateral periodicity. We have verified that this thickness is enough to produce consistent adsorption properties. The adsorption energy increases ~30 meV when the number of layers in the slab is increased to six, which is less than 9% change. The in-plane lattice constant (5.68 Å) has been determined from bulk calculations by using the same parameters as in the rest of the computations (fineness of the k-point sampling, plane-wave cutoff, PAW, etc.). The vacuum gap along the normal to the surface was 10.6 Å. This has proven to be sufficient to prevent any significant overlap of the electronic densities corresponding to different periodic images of the slab. In most of our calculations we only considered the adsorption of water molecules on one surface of the slab. For a few cases we have checked that very similar results are obtained using a symmetric configuration, with molecules adsorbed on both sides of the slab. During geometry optimization the bottom two NaCl layers were fixed. All other degrees of freedom were allowed to relax until all the components of the forces were smaller than 0.01 eV/Å. For the estimation of the energy barriers for different diffusion processes certain constraints had to be imposed on the position and orientation of the water molecules. They will be described in detail in the next section. We used a plane-wave cutoff of 400 eV and a 2 × 2 × 1 Monkhorst-Pack k-point sampling. With these parameters our total energies are converged to within 5 meV, and a better convergence can be expected for total energy differences such as adsorption energies or energy barriers. More explicitly, we have checked that increasing the cutoff energy to 500 eV typically yields changes of the adsorption energy of ~5 meV, whereas using the finer 4 × 4 × 1 k-point mesh translates into a variation smaller than 3 meV.

The adsorption energy E_{ads} is defined as the energy difference between the optimized system and those of the relaxed NaCl-(100) surface and the isolated water molecule.

$$E_{ads} = E_{H_2O}/NaCl - E_{NaCl} - E_{H_2O}^{isol}$$

For $E_{H_2O}^{isol}$ we take here the energy of a water molecule in a large unit cell with the same height as the supercell used for
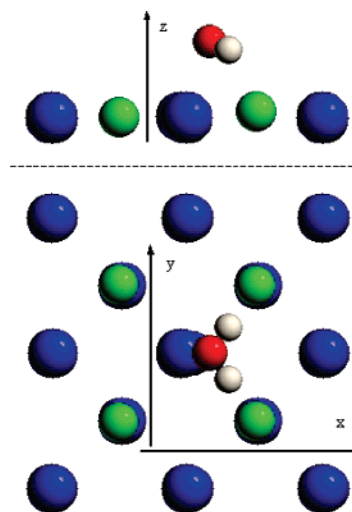

Figure 1. Top and side views for the adsorbed monomer. Large blue circles correspond to Na$^+$ ions, while green, red, and white circles correspond respectively to Cl$^-$ ions, O atoms, and H atoms. The z axis runs perpendicular to the surface and x and y axes are as shown. Figures 2, 3, and 5 use the same definition of the Cartesian axes. The water molecule adsorbs at ~2.24 Å above the NaCl(100) surface, with an adsorption energy of 329 meV. The spacing between the first and second NaCl layer varies between 2.78 and 2.88 Å.

the surface calculations, and twice as large along the basal plane (corresponding to a (4 × 4)-NaCl(100) supercell). When describing the different mechanisms for diffusion (see Figure 4 below), the activation energies will always be referred to the minimum energy of the water adsorbed on the NaCl(100) substrate.

In both situations, adsorption and motion of the molecule, we aim to describe an isolated water molecule on the surface. However, the (2 × 2) supercell used still corresponds to a relatively large coverage of 0.25 ML. The importance of the interaction with the water molecules in the neighboring cells can be estimated from the energy difference of a single water molecule calculated by using unit cells of different sizes. We have compared the results obtained for the large (4 × 4) cell described above and a (2 × 2) cell equivalent to that used for the slab calculations. This difference turns out to be rather small (~4 meV).

Along the different diffusion paths considered below the orientation of the water molecule with respect to the surface changes. To study the influence of water orientation on the periodic water−water interactions, for each process we compared the initial configuration, corresponding to a water molecule almost parallel to the substrate (xy-plane of our supercell), with the most distorted configuration, in which the molecule has one or two of the OH bonds pointing upward or downward from the surface. We performed calculations of the isolated water molecule in our (2 × 2)-supercell with these extreme orientations. The energy difference between such differently oriented water molecules varies from 3 to 10 meV, depending on the process considered. Therefore, considering the k-point sampling, cutoff energy, and periodic water interaction, we expect our results to be converged within a range of 10 meV.

III. Results and Discussion

Single Water Adsorption. We first determine the adsorption geometry of a water monomer on the NaCl(100) surface using a 2 × 2 unit cell. Figure 1 shows the relaxed configuration,

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TABLE 1: Adsorption Energies E_{ads} (meV) and Structure Parameters for a Single Water Molecule on Top of a NaCl(100) Surface[a]

	E_{ads} (meV)	d_{OH} (Å)	Φ_{HOH} (deg)	Z_O (Å)	d_{O-Na} (Å)	d_{H-Cl} (Å)
a	329	0.981	103.7	2.24	2.38	2.38
b	330			2.27	2.41	2.53
c	520	0.960	104.7		2.38	
d	360			2.38		
e	362			2.20		
f	413					
g	601					
h	680					

[a] d_{OH} and Φ_{HOH} are respectively the bond length and bond angle of the adsorbed water molecule; Z_O is the height of the oxygen atom on the surface; d_{O-Na} is the distance from the oxygen to the sodium ion underneath; and d_{H-Cl} is the average distance from the hydrogen atoms to the closest Cl ions. [b] This work. [c] Park, J. M.; et al.: DFT-GGA results.[12] [d] Ahlsewede, B.; et al.: Quantum chemical results using a semiempirical molecular orbital method (MSINDO).[13] [e] Jug, K.; et al.: Quantum chemical results using a semiempirical method (SINDO1).[9] [f] Stöckelmann, E.; et al.: Molecular dynamics simulation, using a simple point charge/extended model (SPC/E).[19] [g] Engkvist, O.; et al.: Results using model potentials derived from the intermolecular perturbation theory (IMPT).[21] [h] Bruch, L. W.; et al.: Experimental isosteric heat; the surface was analyzed later on with helium atom scattering (HAS).[14] [i] Fölsh, S.; et al.: Experimental isosteric heat; the surface was analyzed later on with low-energy electron diffraction.[15]

which consists of a quasiplanar water molecule located 2.24 Å above the surface. The oxygen atom is situated nearly on top of a sodium site, with a displacement of 0.83 Å from the Na site along the *x* direction. The water molecule is slightly tilted due to the electrostatic attraction between its H atoms and the Cl ions underneath; the H−Cl distance is 2.38 Å. This adsorption configuration is in good agreement with the results presented by Park et al.[12] The internal geometry of the adsorbed water (bond length = 0.981 Å; bond angle = 103.7°) does not change appreciably compared to an isolated water molecule calculated with the same unit cell (bond length: 0.973 Å and bond angle 103.9°). Theoretical and experimental adsorption energies, together with the structural data are listed in Table 1. The adsorption energy is found to be 329 meV, which is in good agreement with other theoretical results.[9,10,12,19,21] However, experimental values for the adsorption energy range from 600 to 680 meV.[14,15] The origin of this discrepancy is not completely clear. It could be due to the presence of surface defects, favoring the adsorption on defects and consequently showing a higher experimental energy. It could also arise from limitations in the density-functional treatment of relatively weak bonding.

During the adsorption of a single water molecule the NaCl-(100) substrate also suffers slight modifications. The water adsorption induces a translation of the sodium ion below the water oxygen atom by 0.23 Å toward the negative *x* direction in Figure 1. In addition, the two Cl ions nearest to the water molecule are pulled upward by ~0.17 Å, attracted by the water hydrogen atoms. As a consequence, the top layer undergoes a buckling of ~0.1 Å. This corrugation of the surface increases the adsorption energy by ~50 meV compared with the case in which all four NaCl layers are fixed. The adjustments of the geometry of the NaCl substrate are relatively small for this low water coverage. However, they are taken into account in our calculations since they can be important for the correct estimation of the energetics of surface processes. This is particularly important for the calculation of the energy barriers for diffusion due to the small energies involved. Therefore, in all the calculations below we allow for the relaxation of the two top layers of our NaCl slab, even if the structural changes are always quite small.
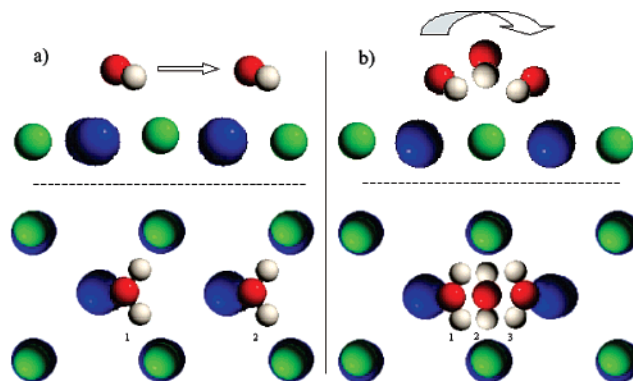

Figure 2. Top and side views for the water translation processes. The numbered water molecules correspond to the sequential positions of the molecule during each process. (a) Parallel translation: There is parallel translation from one Na site to the next. The molecule remains quasiplanar to the surface at all times, with little variation of its internal geometry. $E_{barrier}$ = 312 meV. (b) O-flip: The molecule pivots from one Na site to the next one keeping the H−Cl "bonds" at all times. At the midpoint the molecule is perpendicular to the surface with the hydrogen atoms pointing down with d_{H-Cl} = 2.16 Å and Z_O = 2.42 Å; the average O−H bond length is 0.986 Å, and the water bond angle = 104.8°. $E_{barrier}$ = 140 meV.

Energetics of the Water Diffusion. Clustering of water molecules at low coverage has been experimentally observed at 298 K[17] and molecular dynamics simulations have also demonstrated water clustering for coverages of 0.5 ML at room temperature.[18,19] To describe and understand this process in detail it is necessary to have information about the energy barriers that the molecule encounters during its diffusion along the surface. To date, there are very few studies of this problem with use of electronic structure calculations. For example, the energetics of the water displacement on the NaCl(100) surface has been discussed by Meyer et al.[10] However, those calculations only considered a large coverage of 1 ML and were performed by moving a rigid water layer in a particular orientation from one Na site to the next one.

In this work, we suggest that the water diffusion process on the NaCl(100) surface is composed of several steps, classified as translational or reorientational, depending on whether the water molecule as a whole changes its adsorption site or just the hydrogen atoms vary their positions. Each of these processes involves the rotation of the water molecule around certain axes and presents a relatively low energy barrier, in the range 70−150 meV. Any combination of these mechanisms that includes a translation provides a diffusion path with the lowest activation energy reported to date for water on the NaCl(100) substrate. Therefore, the mobility of the water molecules on this substrate is much higher than could be inferred from previous calculations.

Initially, we study the "*parallel translation*" of the water molecule from its initial Na adsorption site to the adjacent Na site, in which the molecule remains almost planar to the surface at all positions (see Figure 2a). During calculations, the top two NaCl layers and the *z*-coordinate of the water molecule were allowed to relax, whereas the *x* and *y* coordinates of the atoms of the water molecule were fixed. The estimation of the energy barrier obtained with such a procedure can then be compared with previous results,[10] in which the energetics of the system was studied as a function of the adsorption site and the height of the molecule above the substrate. The energy barrier for this parallel translation is 312 meV, which is comparable to 280 meV, obtained by Engkvist et al.[21] using intermolecular potentials, based on IMPT, and a rigid molecule treatment of H_2O. In contrast, our energy barrier is about 25% lower than

the one proposed by Meyer et al.,[10] using the Local Density Approximation (LDA) of DFT. This difference is probably related to the different treatment of the exchange and correlation energy, for which we use the GGA-PW91 approximation. In addition, the lower water coverage and the relaxation of the substrate in our calculations influence the results, making our estimation more realistic.

We now introduce a new mechanism for the translation of the molecule. We call this process the "*O-flip*". Here the oxygen atom of the water molecule rotates 180° around the axis formed by its two hydrogen atoms. In this way, the molecule moves from one Na site to the next one keeping the hydrogen atoms pointing to the same Cl ions underneath (Figure 2b). Only the x coordinate of the oxygen and hydrogen atoms (which is determined by symmetry) is fixed in order to calculate the energy barrier; therefore, the distance to the surface, the substrate atoms, and the internal degrees of freedom of the molecule are permitted to relax. The geometry of the water molecule does not significantly vary during the process compared to the starting configuration (see Table 1 and caption of Figure 2b). At the barrier configuration the H−Cl distance is slightly reduced to 2.16 Å and the oxygen reaches its highest distance of 2.42 Å from the surface. The energy barrier in this case, 140 meV, is 55% lower than the barrier for *parallel translation*. This significant difference is due to the fact that the molecule avoids highly repulsive interactions during the O-flip process, whereas when the molecule moves parallel to the surface, the oxygen atom suffers a strong electrostatic repulsion from the underlying Cl ions at the barrier maximum. Since the barrier for O-flip is much lower than that for parallel translation, it will be a more relevant mechanism for diffusion at low temperatures. However, it needs to be accompanied by a reorientation of the water molecule, otherwise the water displacement would only occur from one Na site to the adjacent one and back.

We have considered three "*reorientation*" processes of the molecule. They are presented in Figure 3a−c. The name *reorientation* stems from the fact that the oxygen atom always remains adsorbed on the same Na site and only the hydrogen atoms move considerably from their initial positions. We now proceed to calculate the energy barriers associated with these movements. We have tried to introduce the minimum number of constraints in our calculations. Thus, the configuration of the two top layers of the slab, the height of the water molecule, and its internal degrees of freedom, at least as many as possible, are always optimized.

The lowest barrier occurs for the reorientation named "*OH-flip*", in which the water molecule pivots 180° around the axis defined by the central Na ion and one of its Cl neighbors (alternatively one could visualize the molecule as pivoting around one of its OH bonds), shifting to an equivalent adsorption configuration (Figure 3a). For the calculation of an approximate energy profile for this movement the x and y coordinates of the oxygen and of the pivoting hydrogen atom were fixed at each transition step. At the top of the barrier, the bond angle of the water molecule increased to 110.4°. However, this deformation was compensated by the increase of the interaction with the surface atoms. The height of the oxygen atom over the surface decreased to 2.19 Å, and the H−Cl distance for the H remaining in-plane decreased to 2.33 Å. The energy barrier for this pivoting process is 72 meV, similar to the result of 70 meV obtained by Engkvist et al.[21] using model potentials. This barrier is low enough to expect the water molecule to be easily flipping in this fashion from one side to the other, even at low temperatures, as other authors have also suggested.[10,21]
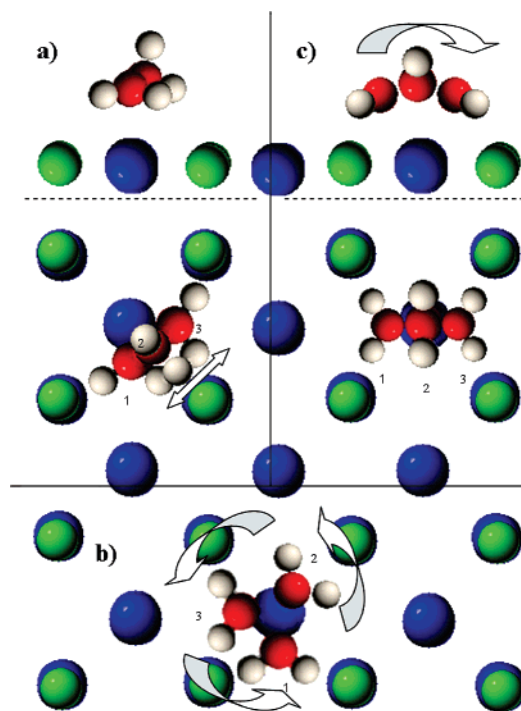

Figure 3. Top and side views for water reorientations. The numbered water molecules correspond to the sequential positions of the molecule during the process. (a) OH-flip: The molecule goes from the initial adsorbed configuration to an equivalent one, passing through an intermediate state perpendicular to the surface keeping one hydrogen pointing to the Cl ion underneath and the other hydrogen pointing away from the surface. The barrier occurs at position 2: $d_{H−Cl} = 2.33$ Å, $Z_O = 2.19$ Å, the OH bond lengths are 0.969 and 0.979 Å, and the water bond angle is 110.4°. $E_{barrier} = 72$ meV. (b) Parallel rotation: The molecule goes from its initial adsorbed configuration to an equivalent one, rotating 90° around the z axis that crosses its adsorption site. OH bonds remain quasiplanar during rotation. The barrier occurs at position 2: $Z_O = 2.20$ Å, the average OH bond length is 0.979 Å, and the water bond angle is 104.0°. $E_{barrier} = 91$ meV. (c) H-flip: The molecule turns simultaneously its OH bonds, crossing an intermediate configuration perpendicular to the surface with both hydrogen atoms pointing away from the surface. The barrier occurs at position 2: $Z_O = 2.29$ Å, the average OH bond length is 0.973 Å, and water bond angle is 107.5°. $E_{barrier} = 149$ meV.

We call "*parallel rotation*" the process schematically described in Figure 3b. The water molecule moves from its initial adsorption configuration to an equivalent one by rotating 90° around an axis perpendicular to the surface plane located at the Na adsorption site. To get an approximate energetic profile for this movement we perform calculations with the constraint that the x and y coordinates of both hydrogen atoms remain fixed at each rotational step. Each step corresponds to a rotation of ∼15°. The barrier configuration corresponds to a rotation of 45°. The molecule remains adsorbed at ∼2.27 Å above the surface. The changes of the bond angle and bond lengths within the molecule are negligible during the rotation. The main difference can be found in the angle formed by the molecular and the surface planes. At the top of the barrier the molecule lies parallel to the surface. The barrier is slightly higher for the parallel rotation compared to the pivoting process, 91 meV. This can be easily understood from the electrostatic interactions at the transition state (Figure 3b, position 2). Here both hydrogen atoms increase their distance to the neighboring Cl ion and change their orientation from that of the optimum adsorption configuration, in other words both Cl−H hydrogen-like bonds are broken to allow for the parallel rotation of the molecule. In contrast, the
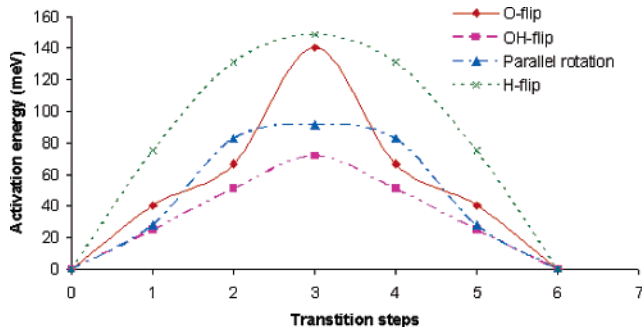
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Figure 4. Energy profiles for the different hopping mechanisms. Energy (meV) is plotted versus "transition step number" for each process. The transition step is an angle from 0° to 180° for "O-flip", "OH-flip", and "H-flip", with barriers occurring at 90°, of 140, 72, and 149 meV, respectively. For "parallel rotation" the angle ranges between 0° and 90°, with the barrier, 91 meV, occurring at 45°.

OH-flip described previously happens with the breaking of just one of the Cl−H "hydrogen bonds".

Our last reorientation mechanism, "*H-flip*", is illustrated in Figure 3c. Here the adsorbed water molecule moves to an equivalent configuration by simultaneous rotation of both OH bonds by 180°. In the transition state the molecule sites on a mirror plane of the substrate, with the dipole oriented upward. The energy curve was calculated by fixing the *x* coordinate for all the atoms of the water molecule. At the barrier configuration, the H−Cl "hydrogen bonds" are completely broken, and the height of the oxygen over the surface and the water bond angle increase, respectively, to 2.29 Å and 107.5°. As a consequence, the energy barrier increased to 149 meV corresponding to the highest reorientation barrier of this work.

The geometric restrictions imposed in these calculations yield only estimates of the transition states for the various diffusion paths. To refine these estimates, we have used the method of Ulitsky and Elber[29] (the Nudged Elastic Band Method, NEB, as implemented in VASP). The four processes *O-flip*, *OH-flip*, *parallel rotation*, and *H-flip* are proven to be real transition states of the molecule, with a deviation of the energy barriers within 4 meV of our estimates based on constrained geometries. In the case of the parallel translation, the NEB method does not find a converged transition state, reaffirming that this path is not a candidate for the diffusion pathway motion along the surface. Therefore, this value has just been assigned to compare with previous "rigid" calculations.[10,21]

Figure 4 illustrates the changes of energy for the different movements. "Transition step" here refers to the incremental change of the reaction coordinate that defines the movement of the molecule along a particular path. In most cases the reaction coordinate can be equated to an angle, defined by either the molecular and surface planes or the OH bonds and a given axis. The energy barriers for all the processes shown in Figure 4 are much lower than the 312 meV found for the parallel translation. Therefore, the combination of O-flip and molecular reorientations (OH-flip, parallel rotation, or H-flip) provides a plausible diffusion mechanism at moderate temperatures. OH-flip (Figure 3a) has a considerably lower energy barrier compared with the rest of the processes. Consequently, the pivoting of water molecules about an OH bond is expected to be very likely at room temperature. Parallel rotation (Figure 3b) is also expected to be a relevant process. We can visualize the diffusion pathway of the water molecule on NaCl(100) as a random sequence of the processes described above. We want to emphasize that only the combination of O-flip followed by one of the reorientation processes will allow the molecule to travel along the substrate.

TABLE 2: Energy Barrier E_a (meV), Preexponential Factor A (cm^{-1}), and Hopping Rate k (s^{-1}) at 298 K for Each of the Hopping Processes Studied Here^a

	OH-flip	parallel rot.	H-flip	O-flip	parallel transl.
E_a	72	91	149	140	312
A	19	88	62	22	46
k	3.5×10^{10}	7.7×10^{10}	5.7×10^9	2.9×10^9	4.6×10^7

^{a} The values of the activation energies are obtained from our first-principles calculations. The values of A and k are calculated following the harmonic approximation and Arrhenius's law (see the text).

The efficiency of the different processes will be proportional to the hopping rate k, which is assumed to be of the Arrhenius's form $k = Ae^{(-E_a/RT)}$. There is an exponential dependence on the activation energy of each process E_a. The preexponential factor A is given by the vibration frequency along the reaction coordinate for each hopping mechanism. We have followed the harmonic approximation to give a first estimation of A for each process. The harmonic equation below has been applied to the first (equilibrium), t_0, and the second configuration, t_1, of each energy curve illustrated in Figure 4. We have then

$$A = \frac{1}{2\pi}\sqrt{\frac{2\Delta E}{\sum_i m_i \cdot |x_i^{t_1} - x_i^{t_0}|^2}}$$

where ΔE corresponds to the energy difference between these two first configurations, and x_i and m_i denote, respectively, the coordinates and masses of every atom in the system.

Table 2 shows the values of E_a, A, and k for the different processes. The highest value of k is found for the parallel rotation, followed by OH-flip. The corresponding hopping rates at 298 K for the different reorientations clearly favor parallel rotation and OH-flip processes over H-flip. The O-flip process, which is the base of the proposed diffusion path, exhibits a lower hopping rate. However, this is still 2 orders of magnitude higher than the hopping rate for parallel translation. The mechanism of parallel translation is less efficient than the rest of the studied processes due to its much higher activation energy (312 meV), as expected from calculations of the diffusion barrier.

Certainly, the significance of the values of k is limited by the uncertainty in the determination of the activation energies; therefore, relative hopping rates k' have been calculated referred to k for O-flip ($k' = k/k_{O-flip}$) in order to give an estimate of the hopping variation within the postulated processes. Values of k' are 26.5 for parallel rotation, 12.0 for OH-flip, and 2.0 for H-flip, which make a more clear estimation of which are the favored processes at 298 K.

Thus, the succession of proposed processes provides a good candidate for the diffusion mechanism of a water molecule on top of a NaCl(100) surface. However, we acknowledge that to claim any diffusion path as valid it is necessary to perform molecular dynamics simulations. Furthermore, from the mean-square displacements one could then directly obtain the diffusivity rate as a function of temperature.[30] Unfortunately, performing such calculations with the same degree of accuracy as those reported here for a reasonable time and temperature interval is computationally very demanding and well beyond our capabilities at the present time.

IV. Conclusions

DFT-GGA calculations have been performed to study the adsorption and diffusion of water molecules on the NaCl(100) surface. We have studied the adsorption of a single water

molecule including the effects of the surface relaxation. Our results reveal a slight corrugation of the top layer of the NaCl substrate, which accounts for a ∼15% enhancement of the adsorption energy (329 meV).

The mobility of water on NaCl(100) also has been examined. We suggest a new diffusion mechanism composed of reorientation and pivoting processes. The most important process is O-flip, where the oxygen pivots from one adsorption site to the next one. This type of movement has to be accompanied by a reorientation of the water molecule to result in a net displacement of the molecule along the surface. Three different reorientations have been considered here: (i) OH-flip, (ii) parallel rotation, and (iii) H-flip. The activation energies for these processes lie in the range 70 to 150 meV. OH-flip presents the lowest barrier and, thus, can be assumed to be the most frequent event. As a first approximation one can visualize the diffusion path as composed of a random sequence of these individual processes. The barriers along such a sequence are significantly lower than previous estimates of the diffusion barrier from first-principles calculations. They are also consistent with the observation of the clustering of water molecules on NaCl(100) at room temperature. This leads us to suggest that a combination of the translation and reorientation processes described in this paper constitutes a very plausible candidate for the diffusion mechanism of water on NaCl(100).

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