

Adsorption of Water on NaCl (100) Surfaces: Role of Atomic Steps

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Received: August 20, 1996; In Final Form: January 13, 1997[®]

Using an atomic force microscope operated in contact and noncontact mode, we have studied the structures formed on the (100) cleavage surface of NaCl when exposed to water vapor. Above ~35% relative humidity (RH), a uniform layer of water is formed and the surface steps are observed to evolve slowly. At ~73% RH, the step structure becomes unstable and disappears abruptly because of dissolution (deliquescence) of the salt surface. Reversing the process by drying leads to the reappearance of new, more uniform monatomic steps. At humidity levels less than 30%, water adsorbs primarily at the step edges.

Introduction

Water is a ubiquitous atmospheric constituent and is involved in many chemical processes occurring on salt aerosols. In particular, its adsorption on alkali halides is an important process that affects their surface structure and chemical reactivity. Chemical reactions occurring on NaCl surfaces have been the subject of many investigations because of their significance in atmospheric chemistry.^{1,2} For instance, in the reaction of HNO₃ with NaCl surfaces, Finlayson-Pitts² et al. observed that the reaction does not stop at the top few surface layers. They showed that as the reaction proceeds, fresh NaCl is exposed, allowing further reaction to continue. They postulated that, even below the deliquescence point of NaCl, at 76% relative humidity (RH), the surface of the salt may already contain significant amounts of water.

Although these speculations are vital for understanding how NO₂ and other gases react with NaCl, few studies have been carried out to investigate the adsorption of water as a function of relative humidity.^{3–5} Fundamental questions such as the extent of water adsorption as a function of humidity, the nature of the adsorption sites, and the effect of water on the surface structure are still unresolved. Part of the problem is the lack of suitable techniques that can be applied in situ for real-time investigations under ambient conditions.

In a previous study of water adsorption and its effect on the cleavage faces of several alkali halides, Hucher et al.⁶ found that two different humidity points exist (40% and 75% for NaCl) that separate regions of different surface conductivity and step structure. They interpreted the first point as due to the completion of a water monolayer, with little or no modification in the step structure. Between the two points, a region of step modifications was observed. At humidity above 75%, dissolution of the crystal was observed to take place.

In this paper, we report our observations of water adsorption on NaCl surfaces investigated with a novel technique based on an atomic force microscope (AFM) operated in an electrostatic noncontact mode. Although the technique has been described previously, a short description of its operation is included at the end of the next section because of its importance in the present study. The great advantage offered by operation in

noncontact is that liquid structures can be imaged, including very thin films and layers, droplets, etc., that are impossible to see because of their strong perturbation by the tip in the standard contact operation of the AFM. Contact mode operation produces images of the solid part of the substrate that can be compared to the noncontact images for a more complete picture of the surface. Examples that illustrate this can be found in our recent publications.^{7,8} Some of our findings confirm the previous results,⁶ in particular, the step modification occurring at intermediate humidity levels.

Experimental Section

The experiments were carried out with a home-built AFM head and a commercial electronic control from RHK Technology (STM100). The microscope was enclosed in a humidity-controlled Plexiglass box. The cantilevers used in these experiments were purchased from Digital Instruments (0.58 N/m). They were made conductive by evaporating a layer of Pt (~500 Å thick). The AFM was operated both in the standard contact mode and in the noncontact electrostatic mode described below.

NaCl single crystals (Optovac, EM Industries) were cleaved along the (001) direction in the ambient laboratory environment and imaged within a few minutes. To understand the adsorption of water on these ionic surfaces and its effect on the surface structure, images were collected as a function of relative humidity. Humidity control was achieved by introduction into the AFM box of a beaker of water to increase the relative humidity or by blowing in dry nitrogen to decrease the relative humidity. Relative humidity was measured by an Omega hygrometer. The values quoted for the RH should be considered approximate, within ±5%.

Scanning Polarization Force Microscopy. To perform noncontact electrostatic AFM imaging, the metallized AFM tips are electrically biased. The resulting attractive electrostatic force when the tip is close to the surface is maintained constant by feedback control and used to obtain images of the surface. Tip–surface distances of a few hundred angstroms (100–500 Å) are typically used. This is important when imaging a liquid, since large distances are required to minimize perturbation of its mobile surface. We call this mode of operation scanning polarization force microscopy (SPFM)^{9,10} to emphasize the physical origin of the forces responsible for the contrast. These arise from various contributions to the local dielectric constant, including mobility of surface ions (as, for example, the solvated

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[®] Abstract published in *Advance ACS Abstracts*, February 15, 1997.

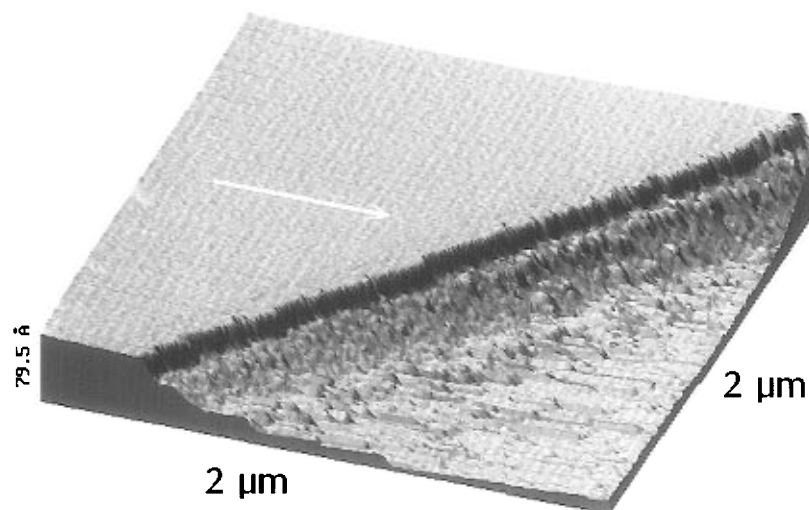


Figure 1. Contact $2\ \mu\text{m} \times 2\ \mu\text{m}$ AFM image of the NaCl surface after cleavage in air at 45% RH. Notice the rough step edge, with debris and dragged material producing streaks in the scanning direction (marked by the arrow). This indicates that the tip is causing wear of the salt surface.

Na^+ and Cl^- ions in the present case), molecular dipoles, lattice ionic polarizability, and electronic contributions. By changing the frequency of the applied bias, these contributions can be turned on or off, allowing polarization spectroscopy studies. At low frequency (in the kHz range) or when using dc bias, the contribution to the surface polarizability from mobile ions at surfaces is particularly important, as we will show in this study.

Results

Experiments at Ambient Laboratory Conditions (45% RH). The structure of the NaCl(100) surfaces produced by cleavage is characterized by the presence of numerous steps of mono- ($4\ \text{\AA}$ high) and multiple unit cell height, often crisscrossing the surface in [001] and equivalent directions, as revealed by both contact and noncontact AFM images. These steps are the result of the strain energy accumulated in the crystal due to the cleavage and correspond to a metastable surface configuration. Examples of these types of images taken both in air and in vacuum have been published by several authors (see, for example, the images in ref 8).

In the present ambient conditions, close examination of the contact mode AFM images shows abundant debris material near the step edges and trailing material in the scan direction (streaks), as shown in the example of Figure 1. Since this is observed only near steps, we conclude that it is not due to instrumental noise. Instead, we propose that the tip is mechanically dragging material from step edges as it scans across the surface. The process could be enhanced by the presence of water on the surface, since this weakens the binding of Na^+ and Cl^- to the lattice, particularly at the steps, thus facilitating wear by the tip. Indeed, no streaks are observed in images taken in vacuum-cleaved NaCl.^{11,12} This result agrees also with the studies carried out by Nakahara et al.¹³ when they investigated the wear of NaNO_3 surfaces by the AFM tip in humid environments. Wear was found when the relative humidity was $>45\%$, and the result was interpreted based on the hypothesis that the salt surface contains water. A recent study by Shindo et al.¹⁴ also demonstrates the mobility of surface structures and steps caused by humidity in contact AFM.

In these previous studies, contact with the tip was an important factor in the evolution of the surface through capillary condensation and humidity-enhanced wear. Even in the absence of mechanical interaction with the tip, we find that a slow evolution of the step structure takes place over a period of a few hours under the laboratory conditions of 45% RH. This is

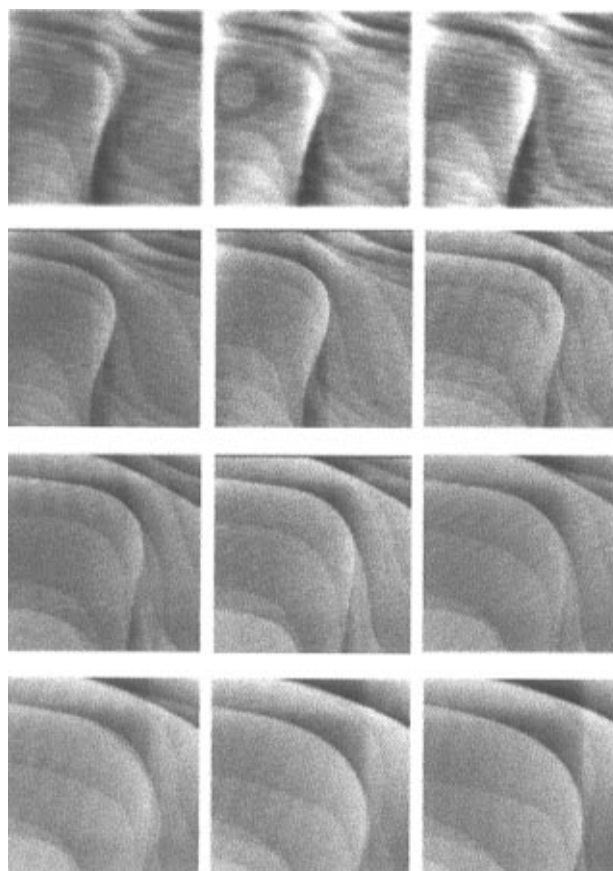


Figure 2. Noncontact SPFM images obtained at ambient 45% RH, showing the evolution of the step structure over a period of 5 h. A round island $4\ \text{\AA}$ high above the terrace can be seen to disappear in the top three images. A general flow of the smaller steps is observed from the bottom left to the top right. The time intervals starting from the top left image are (in minutes): $t = 0, 1, 3, 8, 8.5, 25, 39, 62, 103, 157, 196,$ and 262 .

demonstrated by imaging in the noncontact SPFM mode, as shown in the images in Figure 2 taken over a period of 5 h. These images reveal the slow evolution of the steps over time under the effect of humidity. The smaller steps change faster than the tall ones (the dark band in the images is a multiple atom height step). In the first three images, a small circular terrace can be seen to shrink and disappear. The mobility of the steps is most likely due to the diffusion of hydrated Na^+

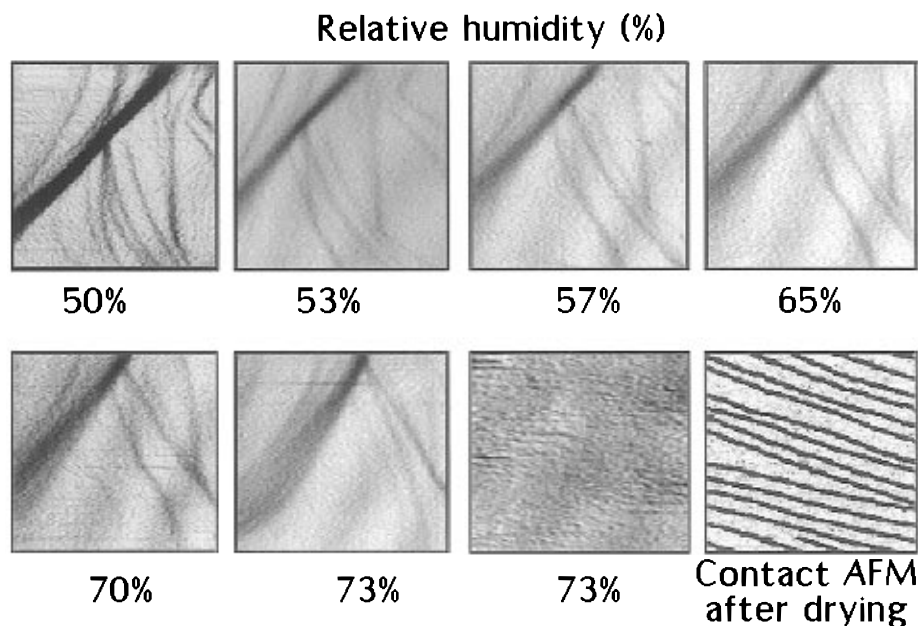


Figure 3. Samples of $4\ \mu\text{m} \times 4\ \mu\text{m}$ SPFM images collected as the humidity in the environment is increased from 50 to 73%. The images are displayed with artificial shading to enhance contrast. A large multiatomic step (darkest shade) of $\sim 50\ \text{\AA}$ height is seen running approximately along one diagonal. Many smaller steps join this large step. The smaller steps evolve faster, many of them disappearing as the humidity increases. At the highest humidity (73%), the features become unstable and the image changes abruptly to one without any features. A contact AFM image ($2\ \mu\text{m} \times 2\ \mu\text{m}$) taken in the same area after the humidity in the chamber was lowered to $<20\%$ is shown at the bottom right. Only monatomic steps were observed on the surface.

and Cl^- ions, as suggested by Moffat and McIntosh.¹⁵ Hydration of surface ions weakens ionic bond strength to the point where they become mobile. This mobility facilitates diffusion to regions of lower energy, relieving stress energy accumulated in the cleavage steps. In the following sections we report these humidity effects. The results are presented in two separate groups, corresponding to high ($>45\%$) and low ($<45\%$) RH conditions. As we shall see, the surface structure and the properties due to adsorbed water are strikingly different in these two ranges.

High Humidity (45–80% RH). After cleavage at 45% RH, the NaCl crystal was introduced into the environmental chamber and noncontact SPFM images were collected while the RH was increased slowly. An example of the evolution of the surface is shown in the $4\ \mu\text{m} \times 4\ \mu\text{m}$ images in Figure 3 for a few values of RH from 50% (top left) to 73%. Modifications of the step structure occur as the humidity rises, similar to those observed at 45% RH. Some small steps disappeared, while large ones underwent changes in shape. These changes are small, however, compared to the abrupt disappearance of all steps when the RH reaches values near the deliquescence point of the salt. This is shown by the two images taken at 73% RH just before and after the change. The abruptness of the change is presumably caused by some uncontrolled perturbation.

We believe that, at this high humidity level, the surface is supersaturated with water, and as a result, even a slight perturbation of the surface results in the rapid step flow and loss of all surface structures (dissolution). The process is similar to the melting of a superheated solid.

Following the wetting cycle, we decreased the RH in the chamber in order to investigate the reverse process of recrystallization. The $2\ \mu\text{m} \times 2\ \mu\text{m}$ image at the bottom right of Figure 3 was taken in the contact mode in the same area after the RH in the chamber had decreased from 76% to 20%. In this image, the surface is covered with $4\ \text{\AA}$ high steps with almost uniform terrace width. In some places, some screw dislocations can be observed as well. Thus, after “dissolution” of the surface, the drying process produced a completely

restructured surface. This surface is much closer to the equilibrium structure of the salt crystal, since the strain energy stored in the cleavage steps is “annealed off” in the dissolution process. It should be noted that the terrace width of the new steps depends on the rate of drying, an observation we did not pursue in further detail.

Low Humidity (10–30% RH). In this set of experiments, the NaCl crystal was again cleaved at the ambient 45% RH and immediately inserted in the humidity-controlled box. It was imaged in the SPFM mode as the RH was decreased from 45% to 10% by blowing dry nitrogen into the system. Figure 4 shows a few images taken during this process. The image at 35% RH shows several single unit cell step heights on the order of $\sim 4\ \text{\AA}$. As the humidity decreased to $<35\%$ RH, the images began to exhibit striking contrast at the steps. The edges appear to bulge above the adjacent terraces with an apparent height of $\sim 20\text{--}25\ \text{\AA}$ at 30% RH. This height continued to increase with decreasing humidity, reaching a value of up to $65\ \text{\AA}$ at 25% RH. Beyond this point, the step edge bulges decreased in height and width with decreasing RH, as shown by the profiles at the bottom of Figure 4. A contact image of the same region obtained at 12% RH is shown also for comparison. No streaks at the step edges were observed in the contact images taken at low humidity, in contrast with the case of 45% RH mentioned above. Cross sections over similar locations in each image are displayed below that demonstrate this effect. Notice that, away from the step edge, the adjacent terraces are always separated by $\sim 4\ \text{\AA}$ (the gray area under the graphs is drawn with the same profile as the contact images and is shown as a reference).

Discussion

The observation of the disappearance of the steps in the noncontact SPFM images at high humidities of 73% illustrates the atomic scale origin of the start of crystal deliquescence. This humidity value is similar, within error, to the reported value found by the gold decoration technique by Hucher et al.⁶ Our study shows that the deliquescence phenomenon occurs abruptly

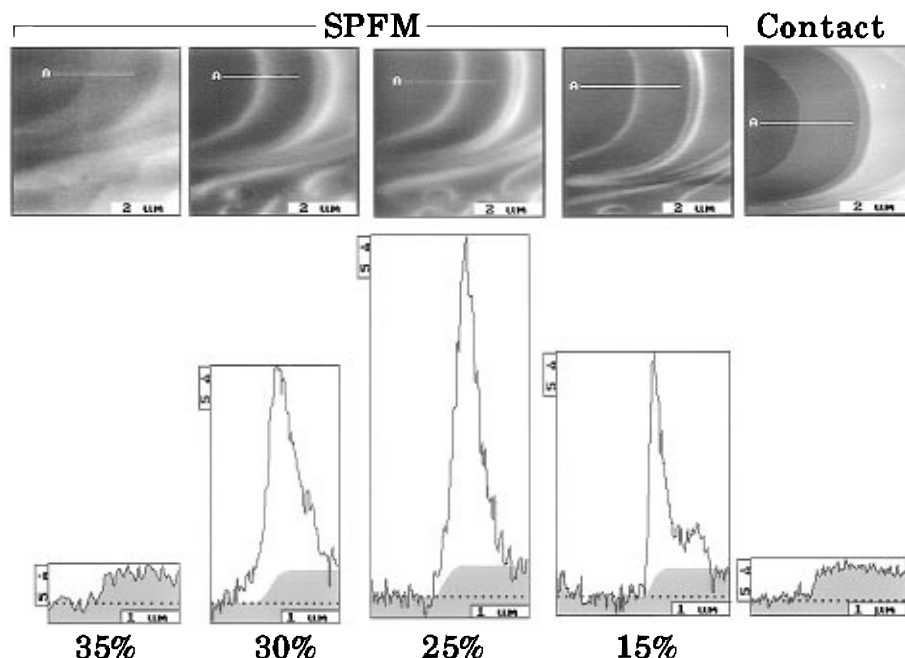


Figure 4. Samples of $4\ \mu\text{m} \times 4\ \mu\text{m}$ SPM and AFM images of the NaCl surface, acquired as the humidity decreased from 35 to 15%. The contrast at step edges increases at first, reaches a maximum at $\sim 25\%$ RH, and then decreases as the humidity continues to decrease. The high contrast at the step edges is associated with the presence of water at this location, which enhances ionic mobility and thus the local polarizability. No such step contrast enhancement is seen in contact AFM images taken at the same humidity values. In these images, the step height remains constant, as in the right image. The shade in the profiles shown at the bottom represents the profile obtained in contact mode (without the noise).

and is initiated at steps in a process akin to the melting and condensation of solid and liquid phases when they are overheated or supercooled. The surface is supersaturated with water, and a small perturbation triggers the deliquescence of the entire surface. The formation of nearly uniform and monatomic steps after drying the liquid surface indicates that the initial step structure produced by cleavage is metastable, since it stores large amounts of strain energy from the cleavage. Similar to an annealing process, the strain is released upon dissolution, and the newly formed surface is much closer to the equilibrium geometry.

The results obtained at low humidities ($<35\%$) are particularly significant because they provide some information about the adsorption sites of water. To understand our observations, we need to make use of the fact mentioned earlier that the apparent height of surface features in the SPM images is determined by a mixture of the topography and local electric properties. The enhancement of the step edge height at low humidity is not due to topographic differences as revealed by the contact images. It is instead due to local differences in the contact potential and dielectric properties between step edges and terraces arising from differences in water concentration, ionic solvation, and mobility. When the humidity is $>30\text{--}35\%$ RH, the step heights in the SPM images are the same as the topographic heights. This can be seen in the images of the same area in Figure 4 in contact and noncontact modes. This result indicates that at $>35\%$ RH, both the density of hydrated ions and their mobility are uniform over the entire surface, including steps and terraces. This result is in line with the model of Hucher et al.⁶ where the water monolayer coverage saturates at 40% RH.

As the RH decreases below 35%, the number of mobile ions at the terraces decreases faster than at the step edges. This might be due to loss of water from the terraces relative to steps because of the higher surface energy at the step edges. Since the number and mobility of the ions depend on the availability of water for solvation, a higher concentration of water at the step edges would give rise to a higher local polarizability and, consequently,

to an increased apparent height. The dependence of the ionic mobility on the degree of solvation, which in turn depends on the humidity, was probed by measuring the strength of the polarization force when applying an ac bias voltage to the tip. The force decreased substantially at high frequencies (several kHz) and/or low humidity values. The results of these experiments, which are not reported here, will be published soon.¹⁶

The decrease of step edge contrast at humidity levels less than 25% RH indicates that, at such low humidities (and down to 13% RH, the lowest value attained in these experiments), the step edges are also losing water. This result agrees with the photoemission studies carried out by Henzler et al.,⁵ who found that water uptake was much higher on stepped KCl than on "defect-free" surfaces.

Conclusion

We have shown that SPM provides a simple and convenient method for studying the effects of water adsorption on hygroscopic crystal surfaces. By measuring the local electric properties of the surface, we can follow the differential adsorption of water at various sites. Water adsorbed on the ionic NaCl crystal surface solvates and detaches ions from the lattice, presumably starting at the steps. The presence of these mobile ions increases the local polarizability or dielectric constant. Areas of the surface containing solvated ions will give rise to high polarization forces.

We find that, at low relative humidities, water primarily adsorbs at step edges, a finding that is not surprising because step edges or surface defects have higher surface energy and are therefore more likely to be the adsorption sites. We also find that water adsorption induces structural changes in the NaCl surfaces. Exposure to medium humidities ($>35\%$) causes slow step flow due to diffusion of the solvated ions. If the humidity is increased to 73%, the deliquescence point, we find that the steps flow very easily and become invisible in the images. New and relatively well-ordered surface structures are obtained by decreasing the humidity in the environment.

Although in this paper we reported studies only on NaCl surfaces, we believe that with SPFM a whole new field involving liquid films that was difficult to study before can now be addressed. For instance, many scientists are interested in the deliquescence process of small salt particles such as (NH₄)-SO₄, NaCl, KCl, etc.¹⁷ Recent studies find that the uptake of water as a function of humidity resembles a step function.¹⁷ No uptake is observed below the deliquescence point, and complete solvation of the salt occurred once the humidity reached the deliquescence point. The drying process is similar, with a strong hysteresis. This finding may be misleading when applied to chemical reactions occurring on salt aerosols, since aerosol particles are usually very small and thus the surface contribution is significant. Our studies indicate that the salt surfaces are actually covered with water even though the humidity was far below the deliquescence point.

Acknowledgment. This work was supported by the Lawrence Berkeley Laboratory through the Director, Office of Energy Research, Basic Energy Science, Materials Science Division of the U.S. Department of Energy under Contract DE-AC03-76SF00098.

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