

# Simulating dynamic force microscopy imaging of a NaCl island using non-ideal tips

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## Abstract

We use atomistic simulation to study how the contrast pattern in dynamic force microscopy depends on the structure of the tip. Using a NaCl island on the NaCl(001) surface as a template, we consider several different NaCl tip configurations, with and without OH contamination. We find that the most significant changes in images are produced by very soft tips, which demonstrate large relaxations due to tip–surface interaction. Harder tips produce qualitatively similar images regardless of the atomic configuration presented to the surface. Contamination of the tip by hydroxyl groups reduces the strength of the interaction, and, in certain configurations, can produce asymmetries in the image even on the flat terrace of the island.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

In general the vast majority of atomically resolved dynamic force microscopy (DFM) [1] images are far from the perfectly symmetric patterns often predicted by simulations [2]. In most cases the published images are only the *best* selection from an experimental series, and may not be statistically representative. Images which deviate from ideal expectations are explained by the fact that surely real tips are usually far from the symmetric objects modelled in simulations, and relaxations and asymmetries in the tip have a significant effect on the contrast pattern. However, this prediction has not been systematically tested theoretically, and experimental evidence suffers from a lack of any real knowledge of the tip structure. Previous simulations [3] have shown how even the rotation of a symmetric tip demonstrates the significant convolution of tip and surface in images, so it is clear that these effects can be explored theoretically.

In this study we take a representative system, a sodium chloride island on the sodium chloride (001) surface, and simulate imaging with a wide variety of non-ideal tips and compare them to images with ideal, symmetric tips. This system has been imaged experimentally in atomic resolution [4–6], and simulated with a symmetric oxide tip (although only selective scanlines were presented in that work) [5]. The NaCl island offers both a very simple lattice structure on the terrace, where the effects of the tip structure

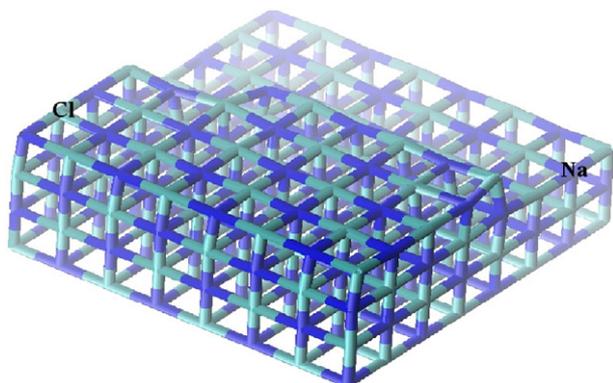
should be clear, and also step-edges and kink sites to explore more extreme displacements.

## 2. Methods

### 2.1. System setup

The specific tips used in the calculations will be discussed in detail later, but the general philosophy is that although the tips in experiments are originally silicon (which is then oxidized in air) and may be sputtered, contact with the surface can never be avoided and the apex is likely covered by NaCl. Also, most experimentalists imaging insulating surfaces find that the chances of obtaining atomic resolution are enhanced by contacting the surface directly before imaging in another location—as was done in [5, 7–10]. The exact shape of the tip apex at the nanoscale is unknown, but previous studies have shown that some form of nanoscale probe must be present to provide atomic contrast [5]. Hence, we use small NaCl clusters to represent the tip and orient them at different angles to provide different interactions with the surface. We also consider adsorption of OH groups onto the tip in order to simulate asymmetric tips. Unless otherwise mentioned, the top two layers of the tip are kept frozen and all other atoms are allowed to relax.

The NaCl island we use in the calculations is shown in figure 1. Although we refer to it as an island, it must be remembered that the calculations use a periodic cell, so this



**Figure 1.** NaCl island used in the calculations.

system actually represents an infinite kinked ‘strip’. The bottom layer of the island is kept frozen to represent bulk NaCl, but all remaining atoms are allowed to relax freely.

## 2.2. Tip–surface interactions

The calculation of the tip–surface interactions on the microscopic scale were performed using static atomistic simulations and the 2D-periodic MARVIN2 code [11]. This technique uses point charges and polarizable shells to represent atoms, and pair potentials to represent atomic interactions. The pair potential parameters for the systems discussed in this work have been taken from [12]. The tip–surface interaction is calculated on a grid of  $(29 \times 21 \times 60)$ , with a spacing of 0.07 nm in  $x$  and  $y$ , and 0.01 nm in  $z$ . The first point is labelled Cl in figure 1, and the last labelled Na, such that there is only a single island edge in images.

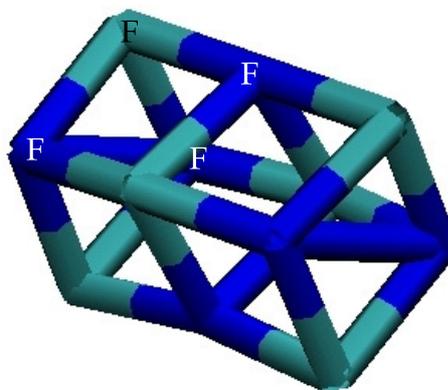
In order to generate images which can be compared to experiment, it is also important to include the long-range macroscopic van der Waals interaction between the tip and surface [2]. This force is effectively controlled by the radius of the tip and Hamaker constant of the system. Since the tip is likely originally oxidized silicon, we fix the Hamaker constant at the value for  $\text{SiO}_2\text{--NaCl}$  [13] and fit the radius to produce the experimentally measured contrast [5] at experimental constant frequency change ( $\Delta f$ ). A tip radius of 20 nm provides a good match.

Finally, the microscopic and macroscopic forces are combined to provide a total map of the force across the surface. This is then used in a simple model [14] of the cantilever oscillations (using experimental parameters [5]—amplitude 1.8 nm, equilibrium frequency 158 kHz and spring constant  $26 \text{ N m}^{-1}$ ) to provide a simulated image for a given constant frequency change. The simulation method described briefly here is in itself not novel, and greater detail can be found in [2].

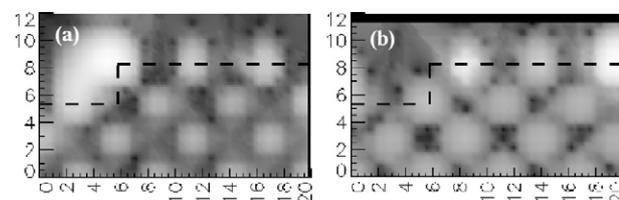
## 3. Simulated images

### 3.1. Ideal tip

For the first example, we consider an ‘ideal’ tip, in that the apex presents a single atom to the surface in a locally symmetric configuration. To provide this we use a cuboid of NaCl (shown in figure 2), which can be oriented to have a single  $\text{Na}^+$  or



**Figure 2.** Cuboid NaCl tip. Frozen atoms in the tip are labelled F.

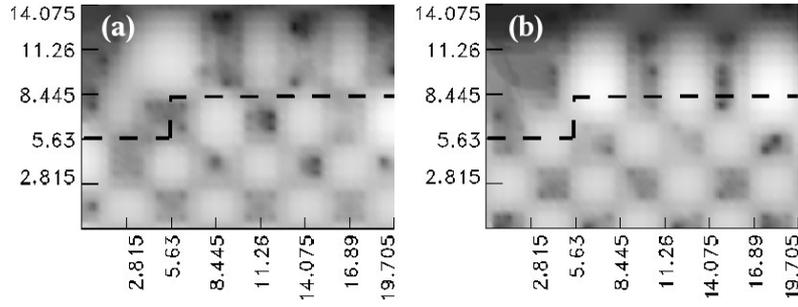


**Figure 3.** Simulated images of the NaCl island top layer at  $\Delta f = 140 \text{ Hz}$  (average tip–surface distance 0.4 nm) with (a) a  $\text{Cl}^-$  and (b) a  $\text{Na}^+$  terminated tip. The dashed line shows the location of the island edge. Axes scales are in Å.

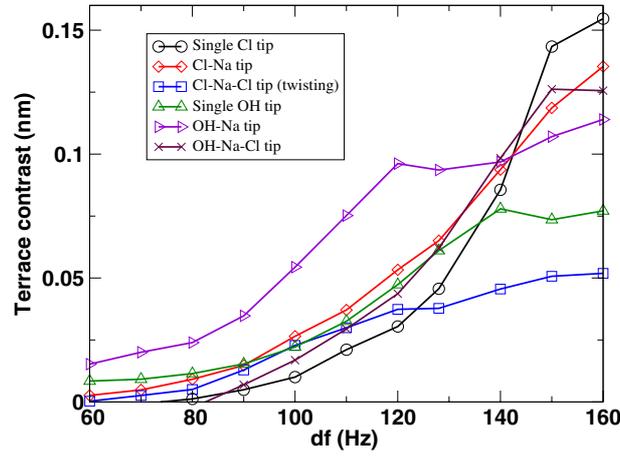
$\text{Cl}^-$  ion at the apex towards the surface. In the symmetric orientation this model is very similar to that in simulations with an  $\text{MgO}$  tip [5], and although the formal charges of ions are now halved, and the tip is softer, we would expect similar behaviour. For example, the simulated scanlines in [5] show an increase in contrast at step-edges and kink sites due to the low coordination of the ions, and this agrees with the increased contrast at similar sites seen in experimental images.

Figure 3 shows that these features can be clearly seen in simulated images of the top of the NaCl island. For the negatively terminated tip in figure 3(a) bright contrast is over  $\text{Na}^+$  ions in the island, with brighter contrast at the step-edge and very strong contrast over the Na kink site in the top-left. At long range ( $>0.5 \text{ nm}$ ) the only significant contrast is over the kink site, and there is no atomic resolution on the terrace sites, but in general we will focus on those images which demonstrate resolution across the whole island.

Conversely, figure 3(b) shows that the positively terminated tip shows the  $\text{Cl}^-$  ions as bright, with large contrast over the Cl kink in the top right of the image. Note the delocalization of the bright contrast around the Na kink site in figure 3(a) and the increased contrast on the  $\text{Cl}^-$  ion next to the Na kink in figure 3(b). This is a result of the increased displacement of ions at and near the kink sites resulting in increased tip–surface interaction [5]. At a tip–surface distance of 0.4 nm, terrace ions displace towards the tip by 0.049 nm, compared to 0.090 nm at the step-edge and 0.103 nm at the kink site. Note that the displacements represent an average for all sites of that type, including both tip terminations, e.g. the total kink displacement is the average of the Na kink displacement due to the Cl tip and the Cl kink displacement due to the Na tip.



**Figure 4.** Simulated images of the NaCl island top layer at  $\Delta f = 140$  Hz (average tip–surface distance 0.39 nm) with a two atom terminated tip with the edge (a) perpendicular and (b) parallel to the step-edge. The dashed line shows the location of the island edge. Axes scales are in Å.



**Figure 5.** Contrast as a function of  $\Delta f$  on the terrace of the NaCl island for the different tip models.

### 3.2. Two atom edge tip

If we orient the cuboid so that one of the short edges faces the surface, we image the surface with both an  $\text{Na}^+$  and  $\text{Cl}^-$  ion at the same height. We can further consider two possible orientations of the cuboid edge—perpendicular and parallel to the step edge. Since the apex remains identical despite the orientation, we would expect the general contrast pattern should be the same in both cases—figure 4 shows that this is true. However, in both images the bright contrast is shifted from the atomic sites, due to a convolution of the tip we see contrast maximums in between the atomic sites. To aid in seeing this, the axes tick marks have been re-scaled to the positions of atoms in the island. In figure 4(a) we see that the image is shifted in the direction perpendicular to the edge, matching the orientation of the tip. Similarly, in figure 4(b) the image is shifted along the direction parallel to the edge.

The interaction of two oppositely charged ions at the apex both reduces overall attraction and repulsion from the island, and the resulting contrast remains quite similar to that for the ideal tip (see figure 5). Displacements are also quite similar, and at a tip–surface distance of 0.4 nm, terrace ions displace towards the tip by 0.019 nm, compared to 0.025 nm at the step-edge and 0.040 nm at the kink site.

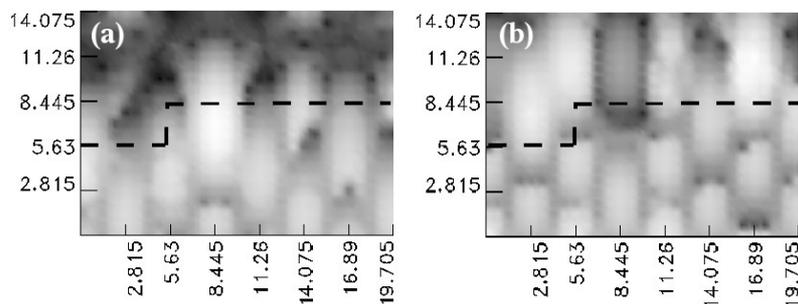
### 3.3. Three atom edge tip

The long edge of the cuboid provides a tip with three atoms presented to the surface, and an asymmetry in the number of

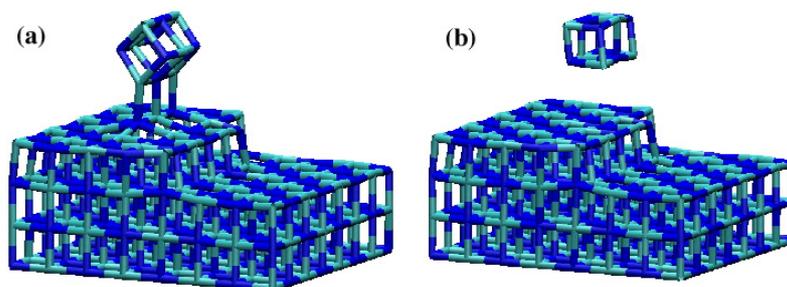
ions—two like and one opposite charge ion. Here we consider two orientations both parallel to the island edge, but containing a different ion balance. For the Cl–Na–Cl edge, figure 6(a) shows an image with some similarities to the Na-terminated tip shown in figure 3(a), but with contrast smeared out. The smearing is actually caused by the distortions of the tip. In the simulations only the opposite three atom long edge is frozen, and hence the whole tip is free to move around this axis (see figure 7(b)). At a close approach the tip twists to find a lower energy minimum, smearing out the contrast. Figure 6(b) shows similar smearing, but now the contrast maximums are based on the Na sublattice. Although one might expect that the contrast maximum for a tip with two  $\text{Na}^+$  and a single  $\text{Cl}^-$  at the apex to be over  $\text{Cl}^-$  in the surface (and vice versa for the Cl–Na–Cl tip), you must remember that the tip is over three ions in the surface. Hence when the central Cl is over Na, each of the tip apex ions is over its opposite, providing maximum interaction.

The combination of three imaging ions and the twisting of the tip results in the smallest contrast on the terrace of all the tips (see figure 5), and smaller atomic displacements. At a tip–surface distance of 0.4 nm, terrace ions displace towards the tip by 0.012 nm, compared to 0.021 nm at the step-edge. However, displacements at or near the kink site ranged from 0.03 to 0.10 nm—the large displacements occurred when the all the tip apex ions were over ions at the step edge and kink, producing a very strong interaction.

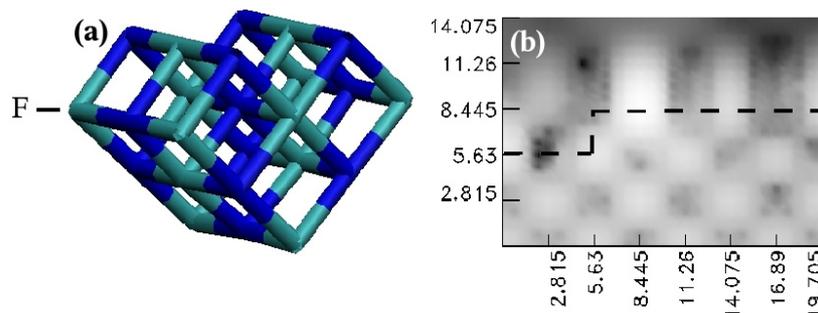
A more rigid tip, where twisting is much reduced, can be simulated by increasing the size of the tip and hence



**Figure 6.** Simulated images of the NaCl island top layer at  $\Delta f = 140$  Hz (average tip–surface distance 0.44 nm) with a three atom terminated tip with the edge containing (a) Cl–Na–Cl and (b) Na–Cl–Na. The dashed line shows the location of the island edge. Axes scales are in Å.



**Figure 7.** Snapshots from simulations with the three atom tip, showing how the tip twists from its standard orientation in (a) by almost 45° in (b).



**Figure 8.** (a) Large cluster tip with three atom edge. (b) Simulated image of the NaCl island top layer at  $\Delta f = 140$  Hz (average tip–surface distance 0.42 nm) with a large three atom terminated tip. The dashed line shows the location of the island edge. All atoms above the line F are frozen. Axes scales are in Å.

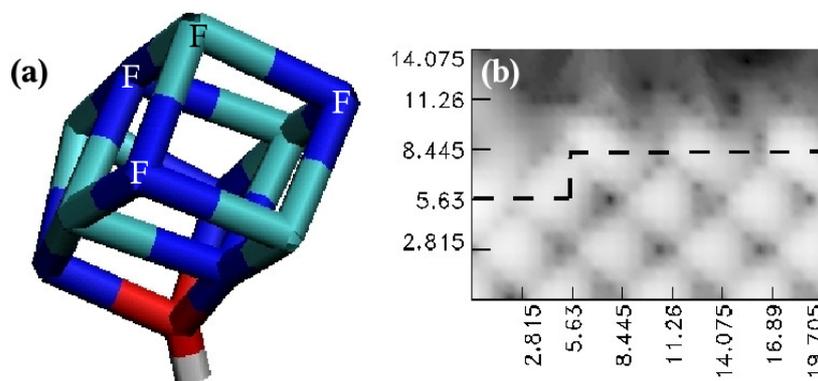
decrease the available degrees of freedom. Figure 8(a) shows the structure of this Cl–Na–Cl cluster, and figure 8(b) shows that with this tip the smearing is absent and we recover an image very similar to that for the Na-terminated tip, i.e. the Cl sublattice is bright.

### 3.4. OH contaminated tips

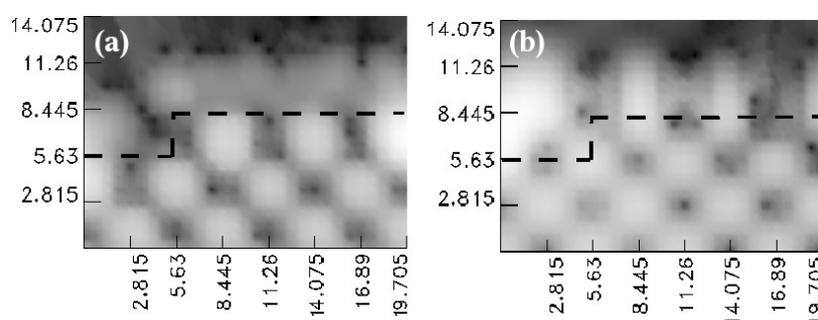
For the last series of tips, we consider the influence of an adsorbed OH group on the imaging properties of the previous tips. Due to the restriction of charge conservation, we can consider only an  $(\text{OH})^-$  group substituting for a  $\text{Cl}^-$  ion, but it is reasonably physical to consider adsorption at a vacancy in the tip. In the first case, we take an ideal Cl terminated tip and replace the apex Cl by OH (see figure 9(a)). Figure 9(b) shows that the positively charged H at the tip apex images the  $\text{Cl}^-$  sublattice as bright, but the reduced charge of the  $\text{H}^{0.44+}$  ion compared to  $\text{Na}^+$  reduces the contrast (see figure 5)

and displacements significantly—there is also no significant contrast increase at the step-edge and kink sites. At a tip–surface distance of 0.4 nm, none of the ions, even at the kink sites, displace towards the tip by a measurable amount. At distances of less than 0.35 nm, an asymmetry appears in the contrast pattern. This is due to the upper part of the tip, extending in the positive  $x$ -direction, affecting the image at very close distances, since there are no other asymmetries in the setup.

In the last two cases, we take the two atom edge tip and three atom edge tip (Cl–Na–Cl) and replace a Cl by an OH group. Figure 10 shows that even with the presence of the OH group, both tips behave very similarly to their clean versions. For the two atom edge OH tip, figure 10(a) shows that the contrast has been shifted off the atomic sites in the direction perpendicular to the edge, as in figure 4(a). However, the reduced interaction of the OH group reduces contrast at the step edge, and it appears as almost a strip, with only a slight increase at the kink site.



**Figure 9.** (a) Cuboid tip with OH at the apex. (b) Simulated image of the NaCl island top layer at  $\Delta f = 160$  Hz (average tip–surface distance 0.29 nm) with an OH tip. The dashed line shows the location of the island edge. Frozen atoms in the tip are labelled F. Axes scales are in Å.



**Figure 10.** Simulated images of the NaCl island top layer at (a)  $\Delta f = 140$  Hz (average tip–surface distance 0.39 nm) with a two atom edge OH tip and (b)  $\Delta f = 120$  Hz (average tip–surface distance 0.46 nm) with a large three atom edge OH tip. The dashed line shows the location of the island edge. Axes scales are in Å.

The image for the three atom edge OH tip is even closer to the clean version (compare 8(b) and 10(b)). The presence of two unchanged ions reduces the influence of the OH<sup>−</sup>, and the tip does not show any strong differences at any distance range. Only at the left edge of the image can brightening be seen, caused by the H ion in the extreme left interacting with the Cl kink in the next image of the island, an effect that does not appear in 8(b).

Figure 5 shows that for both these tips the contrast on the terrace is a little less than the ideal tips. Displacements are also smaller—at a tip–surface distance of 0.4 nm, terrace ions displace towards the tip by 0.011 nm, compared to 0.016 nm at the step-edge and 0.020 nm at the kink site.

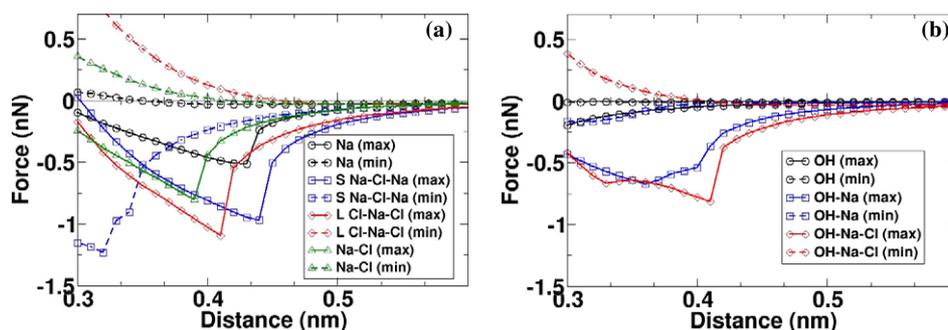
#### 4. Discussion

This study has demonstrated, as expected, the significant effect of the tip geometry, as well as chemistry, on the contrast pattern in DFM images. The strongest influence was seen for very distortive tips, which show very large relaxations on approach to the surface, smearing the contrast pattern. Although experimental images of this kind have been observed, such tips are likely to be quite unstable under the influence of significant tip–surface interaction and prone to rearrangement to a stabler configuration. The two- and three-atom edge tips demonstrate contrast patterns which are qualitatively similar to more ideal tips, and the shift of maxima from atomic sites would not be detectable in most experiments. This gives some

insight into the success of contacting the surface in producing tips which provide atomic resolution—it is not necessary to produce a perfect single probe, but rather any stable cluster with a sharp edge will serve.

When the dominant interaction is via a single OH group, the overall interaction is greatly reduced (see figure 11(b)) and displacements of the surface are almost zero. However, it is here that we see most clearly the effect of an asymmetric tip. The protrusion of the cuboid in one direction away from the OH at the apex produces a corresponding distortion in the contrast pattern, and atoms are seen as almost triangular. Images produced with OH-edge tips demonstrate that the asymmetry in the tip must be over a surface lattice constant away from the apex for any asymmetry to be produced in the image. Otherwise, the combined interaction merely produces a symmetric pattern, with quantitative changes in interaction, but little qualitative changes from an ideal tip.

Although we have not discussed ion transfer from the surface to the tip, it does occur in this system. Figure 11 shows a comparison of force curves for different tips over terrace sites, and in all of the maximum curves, apart from the weakly interacting ideal OH tip, force jumps can be seen, e.g. for the S Na–Cl–Na tip at about 0.45 nm in figure 11(a). At these points an atom jumps from the surface to the tip (no jumps of atoms from the tip to the surface were observed), producing a corresponding jump in the attractive force. Previous studies of systems with the same ionic material in the tip and surface have shown that if the tip is retracted, a cation and anion pair is likely to be removed [15]. Even in static simulations, this will



**Figure 11.** Tip-surface maximum and minimum force curves over the island terrace: (a) Na is the Na-terminated ideal tip (figure 3(b)), S Na-Cl-Na is the small three atom edge tip (figure 6(b)), L Cl-Na-Cl is the large three atom edge tip (figure 8(a)) and Na-Cl is the two atom edge tip (figure 4(a)); (b) OH is the ideal OH tip (figure 9(b)), OH-Na is the two atom edge tip (figure 10(a)) and OH-Na-Cl is the three atom edge OH tip (figure 10(b)).

result in a large hysteresis in the tip approach and retraction interactions.

In conclusion, we have shown some characteristic examples of tip-surface convolution in atomically resolved images of a NaCl island, which we think can be used as general references for experimental images which deviate from the ideal.

### Acknowledgments

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