Simulations of metastable states near the apex of a force microscope tip interacting with an ionic crystalline surface

B. Ittermann\textsuperscript{1}, R. Hoffmann-Vogel\textsuperscript{1*} and A. Baratoff\textsuperscript{2}

\textsuperscript{1} Physikalisches Institut and DFG-Center for Functional Nanostructures (CFN), Karlsruhe Institute of Technology Campus South, D-76128 Karlsruhe, Germany

\textsuperscript{2} National Center of Competence in Research (NCCR) on Nanoscale Science, Institute of Physics, University of Basel, Klingelbergstrasse 82, CH-4056 Basel, Switzerland

\textsuperscript{*}email: r.hoffmann@kit.edu

(Dated: August 24, 2012)

Atoms or pairs of ions picked up by probe tips in dynamic force microscopy (DFM) can be strongly displaced and even hop discontinuously upon approach to the sample surface. The energy barriers for some of those hops are of the right order of magnitude to explain the rise in energy dissipation commonly observed in DFM measurements at room temperature. The systematic computations reported here can explain the infrequent jumps and very low average energy dissipation observed low temperature in a previous DFM study on a KBr(001) sample. Close to the surface we indeed find new states separated by small energy barriers which account for those phenomena. These energy barriers strongly depend on details of the atomic arrangement in the vicinity of the tip apex.

I. INTRODUCTION

Dynamic force microscopy (DFM) has developed into a valuable tool not only for surface characterization of non-conducting samples, but also for controlled modification at the atomic level. This has become possible mainly thanks to sensitive measurement modes where the tip is oscillated with a constant amplitude in the nm range at a resonance frequency of the force sensor \textsuperscript{[1]}. Atomic-scale precision is then achieved if the tip apex stays or periodically comes to distances at which short-range site-selective forces act, thereby causing a measurable frequency shift. Atom manipulation experiments in that mode have inspired computations of changes in the potential landscape induced by the tip apex and of resulting fingerprints in measurable quantities on semiconductor surfaces \textsuperscript{[2,3]}, as well as on ionic crystal surfaces \textsuperscript{[4,5]}. The average dissipation of energy stored in the cantilever oscillation also exhibits atomic-scale contrast, even on defect-free surfaces, and its magnitude indicates that it mainly originates from hysteretic hopping of atoms between two or more stable positions \textsuperscript{[6,8]}. Sudden but infrequent contrast changes, typically more pronounced in dissipation images, have been attributed to long-lived rearrangements of the tip apex \textsuperscript{[10]}. Three different causes of dissipation induced by hysteretic tip-sample interactions must be considered: hopping on the sample, hopping between tip and surface, and hopping on the tip. Hopping on the sample is usually not expected because diffusion or other rearrangements on clean flat terraces of low-index surfaces usually involve rather high energy barriers, except for some reconstructed surfaces which exhibit bistable configurations \textsuperscript{[11]}. The presence of long-lived localized defects can be excluded by taking high-resolution images. However, in scanning tunneling microscopy studies \textsuperscript{[12]}, as well as for DFM on insulating surfaces, mobile adatoms can merely lead to blurry or streaky images and to additional noise in a certain temperature range thus causing blurred or streaky images when the scan and hopping rates roughly match \textsuperscript{[13]}. Hopping between tip and sample \textsuperscript{[8,9]}, that can in the extreme case even lead to atomic chain formation and breaking in some oscillation cycles \textsuperscript{[14]}, manifests itself indirectly via the average energy dissipation. However, in order to unambiguously interpret measured results, the third scenario, hopping on the tip, must be excluded or else taken into account \textsuperscript{[15,16]}. This is in general difficult because the structure and chemical composition of the tip are unknown. For many commonly studied crystals (Si, KBr, NaCl), there are indications that sample material is picked up by the tip owing to intentional or accidental contact prior to or during DFM measurements. Using large-scale simulations several groups have characterized force microscope tips and derived construction principles for realistic model tips from comparisons with experiments \textsuperscript{[4,7,11]}.\n
II. MODEL TIP

Here, we study possible low-energy configurations of an overall neutral KBr tip supporting two additional ions, and its interaction with a KBr (001) surface by means of extensive computations. The employed code, based on an atomistic shell model, was developed for simulations of DFM on ionic crystals \textsuperscript{[10,17]} and validated in previous studies \textsuperscript{[18,19]}. Such a model tip may represent the end of a nominal silicon tip typically used in force microscopy experiments decorated by sample material. More precisely, our model tip consists of a K\textsuperscript{+}-terminated cubic...
cluster of 64 K and Br ions exposing stable \{001\}-facets oriented such that the (111) direction is perpendicular to the sample surface. One K\(^+\) and one Br\(^-\) ion are added near one of the \langle100\rangle edges meeting at the tip apex, as illustrated in Fig. 1 right. The initial configuration of these two additional ions is chosen in accordance with simulations and a previous experimental study of diffusion on surfaces of rocksalt-type crystals \[20\]. This model is well-suited to studying rearrangements of the simplest moiety likely to be picked up by a stationary contact with the sample. Alternatively, the supported KBr dimer may be the remnant of a broken chain of ions formed during tip retraction \[14, 21\]. The assumed tip configuration is probably more likely than alternative ones involving other kinds of defects which produce appreciable force hysteresis and energy dissipation in the case of chemically similar NaCl model tips \[7\]. The sample was represented by a slab containing 6 layers of \(10 \times 10\) ions each. More details about the simulation procedure can be found in previous publications \[18, 19\].

First, the properties of the decorated tip alone were studied. One stable and four metastable configurations labelled A to E were found by constrained minimization while shifting the additional Br\(^-\) ion parallel to the edge (projected reaction coordinate \(q\)) and letting its two orthogonal coordinates and those of all ions in the bottom half of the cube relax. The corresponding profiles labelled \(z = \infty\) are shown in Fig. 2. In configurations A and E, the additional Br\(^-\) and K\(^+\) ions are essentially located along the cube edge, and the positions of the Br\(^-\) ion differ between both configurations by approximately one bulk lattice constant. The lowest total energy was found for the (Br\(^-\)-terminated) configuration A, because the electrostatic field outside the cube is enhanced in the vicinity of the low-coordinated edge especially around the apex. For the same reason the energy barrier to reach configuration A starting from E is much lower than for the opposite process. Configurations B and D arise when the additional Br\(^-\) ion is located above a bridge site on one facet adjacent to the cube edge. Between \(q = 2.1\) Å and \(q = 2.9\) Å the initial Br\(^-\) ion dips into the cubic cluster while a nearby bromine ion emerges from the cluster to form configuration C. Ion exchange processes analogous to that just described were also found in previous simulations of an MgO dimer diffusing on the MgO (001) surface \[22\]. Similar configurations were found when all Br\(^-\) ions were replaced by K\(^+\) ions and vice-versa.

To test the thermal stability of the different tip configurations, molecular dynamics simulations were performed at \(T = 200, 300\) and \(500\) K for the K\(^+\) and the Br\(^-\) terminated tip in configuration A. Below 500 K, no hopping was observed over the relatively short simulation time. At \(T = 500\) K the former tip showed a transition from the E to the A configuration nicely visualized in a movie \[23\]. In this transition the K\(^+\) ion did not, however, jump directly to the final position. Instead, it moved to the position of a nearby K\(^+\) ion in a configuration similar to that called C in the constrained minimizations mentioned earlier. This exchanged K\(^+\) ion then moved to the position of the K\(^+\) ion in the A configuration. Such exchange processes compete against pivoting around the dimer partner as in diffusion on (001) surfaces \[20, 22\] and may even be favored in the present lower coordination situation.

### III. APPROACH TO THE SURFACE - NEW CONFIGURATIONS

In a second step, the interaction of the tip with the sample surface and possible hysteretic processes were studied as a function of the nominal tip-sample distance defined as the separation of the foremost ions when ignoring relaxation. Ions in the top half of the tip cluster and in two boundary layers of the sample slab were frozen, while the rest were allowed to relax. The rigid part of the tip was incrementally approached perpendicular to the surface such that the protruding Br\(^-\) in configuration A was facing a particular surface ion. The results were compared to configuration E at the same positions of the rigid tip body (Fig. 1). If the tip is approached above an ion of the same charge, the energy difference between configurations A and E becomes smaller, but never vanishes. In contrast, if the tip is approached above an oppositely charged ion, the energy first drops faster then the energy difference decreases and vanishes for the K\(^+\)-terminated tip, and even becomes negative for the Br\(^-\)-terminated tip below a critical tip-sample distance of about 1 Å. One therefore expects the Br\(^-\)-terminated
tip to change from configuration A to configuration E below that distance if the energy barrier between the two states can be overcome by thermal fluctuations.

In order to investigate changes in the energy landscape induced by the tip approach, we performed constrained minimizations like those discussed in Section II at a few tip-sample distances. Figure 2 shows that the number and character of the metastable configurations changes significantly. While at relatively large distances five configurations analogous to A, B, C, D, and E are observed, only three remain at close tip-sample distances above the Br$^-$ surface ion. Lateral hysteresis is also observed, e.g., for $z = 1$ Å, indicating the presence of inequivalent energy barriers along paths starting from configurations A and E. A new configuration (A*), even lower in energy than configuration A, appears above the oppositely charged K$^+$ surface ion for $z = 1$ Å. In configuration A* the additional K$^+$ and Br$^-$ ions of the molecule are bound to both tip and surface. This configuration arises when the body of the cubic tip pushes the added dimer aside, until the dimer ions approximately bind to ions of opposite charge on the surface as well as on a tip facet, as illustrated in another set of movies.

**IV. ENERGY BARRIERS FOR CONFIGURATIONAL CHANGES**

Our study originally focused on hopping between A and E configurations, because simulations of diffusion on rocksalt type (001) surfaces identified this process as the most probable [24]. The presence of intermediate metastable configurations implies that direct hopping between A and E is less probable than hopping via the intermediate states B, C, and D, due to the reduced intervening energy barriers which are the relevant ones for thermal activation. The highest energy barrier between any of those configurations represents the bottleneck of the process and therefore determines the effective hopping rate. The bottleneck barrier for the transition from E to A ranges from 80 to 175 meV while the bottleneck barrier for the opposite transition from A to E ranges from 260 to 660 meV for all of the constrained energy profiles studied [25]. These values should be compared to the thermal energy at room temperature (25 meV) or at low temperatures (8 - 40 K, i.e., 0.7 - 3.4 meV) depending on the experiment to be considered. Two limiting cases are of particular interest [15, 16]: if the hopping rate is low enough (one jump every $0.1 - 10$ s), individual atomic jumps can be experimentally observed. If, in contrast, the hopping rate exceeds the cantilever oscillation frequency ($\sim 100 - 200$ kHz) the individual states involved are averaged over in a dynamic force measurement, but the energy dissipation due to hops into lower energy configurations becomes appreciable. Our results imply that, for most potential energy landscapes so far considered, the tip configuration would be rapidly flipping at room temperature on time scales faster than the cantilever oscillation, but that tip changes due to hops would be frozen out at low temperatures. The main reason is that in configuration A, the protruding Br$^-$ ion is subjected to the positive electrostatic potential localized around the apex of the cubic [24]. This lowers its binding energy and thus raises the bottleneck energy barrier between A and E. Therefore, hopping between A and E can only account for infrequent jumps at room temperature, but not for the single jumps observed at low temperatures [15].

As an alternative model tip one may consider a KBr cubic cluster with the additional K$^+$ and Br$^-$ ions placed in positions of higher coordination such as a facet. However, with this premise it is more difficult to realize an atomically sharp tip, as required for lattice-resolved images without appreciable distortions [27] observed experimentally.

**V. LOW ENERGY BARRIERS**

The jumps observed at low temperatures might be explained by the occurrence of new states similar to A*. Indeed, the energy barrier between A and A* being only 64 meV at a tip-sample distance of 1 Å, individual jumps could be observed at temperatures between 25 and 30 K.

In order to investigate the latter possibility in more detail, we calculated the total energy as a function of tip-sample distance for inequivalent rotations of the Br$^-$-terminated tip around the $z$-axis perpendicular to the
sample surface passing through a surface K\(^+\) site, starting from alignment of the added KBr dimer with one of the <100> axes of the sample at 0°. In this notation our previous calculations correspond to 30°. Due to the symmetries of the surface and the model tip, full information is contained for polar angles between 0° and 45°. At distances larger than about 2.0 Å, the data are qualitatively and quantitatively similar for all rotation angles (Fig. 3a and b). However, at smaller distances significant differences occur. Between 30° and 45°, a jump in the energy arises at an angle-dependent critical distance below maximum attraction. At smaller distances, the interaction energy decreases again upon approach. This behavior can be identified with the state A\(^*\) discussed above, as evident in movies of the approach [24]. In contrast, between 0° and 20°, the energy continuously increases further upon approach in the same distance regime. The foremost tip ion then remains in a deformed state A roughly under the tip apex, while for angles between 30° and 45°, the foremost tip atom jumps towards a next neighbor surface ion of opposite sign while the dimer becomes aligned with a surface <100> direction, as well as with a tip facet in configuration A\(^*\). For 20° the energy versus distance curve is deformed around the critical distance, an indication of the proximity to an additional state, but the tip remains in the deformed state A.

We finally studied the stability of configuration A\(^*\). When the tip is retracted starting from distances larger than critical, the initial values of the energy, force and atomic positions are smoothly recovered. Otherwise hysteresis is observed until eventually another jump restores the initial energy, force and atomic positions at a larger tip-sample critical distance. In Fig. 3c) an example for 30° is shown which is also further documented in a movie of the simulated retraction [28]. Since our calculations are done at zero temperature, the observed hysteresis implies that the energy barrier between A and A\(^*\) vanishes at the critical distance of approach and that energy is gained by jumping to A\(^*\) at closer tip-sample distances. Similarly, upon retraction energy is gained by jumping back to state A while the reverse energy barrier vanishes at the critical distance of retraction. Between the two critical points a finite energy barrier exists between the two states. This variation of the energy landscape as a function of tip-sample distance corresponds to the scenario proposed by Sasaki and Tsukada [8] with the modification that the atomic hops themselves need not occur in the z direction between the tip and the sample but must only be induced by the tip motion perpendicular to the sample surface. Results obtained for different relative orientations of the tip are summarized in table

| surface site | tip-sample distance [Å] | transition path | energy barrier [meV] | bottleneck |
|--------------|--------------------------|-----------------|---------------------|------------|
| Br           | 4.0                      | A→C            | 662                 | ×          |
|              |                          | C→D            | 94                  |            |
|              |                          | D→E            | 4                   |            |
|              | 1.4                      | A→C            | 461                 | ×          |
|              |                          | C→E            | 3                   |            |
| K            | 1.0                      | A→A\(^*\)      | 10                  | ×          |
|              |                          | A\(^*\)→D      | 264                 |            |
|              |                          | D→E            | 2                   |            |
| Br           | 4.0                      | E→D            | 88                  | ×          |
|              |                          | D→C            | 25                  |            |
|              |                          | C→B            | 103                 |            |
|              |                          | B→A            | 23                  |            |
|              | 1.4                      | E→C            | 107                 | ×          |
|              |                          | C→A            | 22                  |            |
| K            | 1.0                      | E→D            | 174                 | ×          |
|              |                          | D→A\(^*\)      | 51                  |            |
|              |                          | A\(^*\)→A      | 64                  |            |

TABLE I. Summary of all the energy barriers obtained in constrained minimizations above different surface sites.
The energy loss in approach-retraction cycle of the tip is equal to the area enclosed between the two distinct force-distance curves between both critical distances and amounts to up to 0.2 eV which is in the range of what is expected from low-temperature experiments [15].

We further characterized the stability of configuration $A^*$ by studying the energy barrier from state $A$ to state $A^*$ in constrained minimizations along the previously defined reaction coordinate $q$. The tip-sample distance was chosen to be 0.13 nm because this is the largest distance at which state $A^*$ is observed during approach and in a finite distance range upon retraction, and so we expected that the state could be observed for several tip angles. Indeed, between $30^\circ$ and $40^\circ$, where $A^*$ was observed in energy vs. distance data, state $A^*$ is also observed in constrained minimizations. For $20^\circ$, although state $A^*$ is not observed during approach, the system can be driven into a similar state under the constraint. The energy barriers range between 19 and 91 meV depending on the tip orientation. These energy barriers are of the right order of magnitude for explaining the infrequent jumps seen in low temperature experiments [15]. One should, however, consider that the chosen reaction coordinate $q$ was not modified to take into account the tip deformation. It is therefore possible that even lower energy barriers occur in other directions, in particular at close tip-sample distances. Obviously, the precise value of the energy barriers depend on the details of the atomic arrangement of the tip.

### VI. CONCLUSIONS

We conclude that ion pairs picked by force microscope tips decorated by sample material can be strongly displaced upon approach to the sample surface, in particular at close tip-sample distances where they become bound to both tip and sample. The resulting hops have components parallel to the sample surface. Some of those hops can account for rapid flipping of the tip configuration at room temperature. In addition, some metastable states which occur at close tip-sample distances can be separated by energy barriers that are low enough to explain infrequent individual jumps observed at low temperatures. The adsorbed dimers have a tendency to align with ions of opposite charge on the sample surface. Ion exchange processes previously identified in a study of surface diffusion are preferred for some of the investigated hops. Back and forth hops between metastable configurations result in a hysteretic force as a function of distance. The energy dissipated by such hops is in the range of what is expected from low-temperature experiments [15].

Financial support from the Landesstiftung Baden-Württemberg in the framework of its excellence program for postdoctoral researchers, from the European Research Council through the Starting Grant NANOCONTACTS (No. 239838) and from the NCCR Nanoscale Science of the Swiss National Science Foundation is gratefully acknowledged.

### TABLE II. Critical distances, hysteresis loop areas and energy barriers for different tip orientations.

| Rotation angle $q$ | Critical distance of approach $[\text{Å}]$ | Critical distance of retraction $[\text{Å}]$ | Hysteresis loop area $A^* \rightarrow A$ $[\text{meV}]$ | Energy barrier $A^* \rightarrow A$ $[\text{meV}]$ |
|--------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 20                 | -                               | -                               | 19                              | 91                              |
| 30                 | 1.3                             | 2.1                             | 200                             | 91                              |
| 35                 | 1.3                             | 2.1                             | 170                             | 93                              |
| 40                 | 1.1                             | 2.7                             | 190                             | 23                              |
| 45                 | 0.9                             | 1.9                             | 90                              | 40                              |

[1] Noncontact Atomic Force Microscopy, S. Morita, R. Wiesendanger and E. Meyer, eds. (Springer, Berlin, 2002)
[2] L. Pizzagalli and A. Baratoff, Phys. Rev. B 68, 115427 (2003)
[3] P. Dieska, I. Stich, and R. Perez, Phys. Rev. Lett. 95, 126103 (2005)
[4] N. Oyabu, P. Pou, Y. Sugimoto, P. Jelinek, M. Abe, S. Morita, R. Perez, and O. Custance, Phys. Rev. Lett. 96, 106101 (2006)
[5] O. Custance, R. Perez, S. Morita, Nature Nanotechnology 4, 803 (2009)
[6] T. Trevethan, M. Watkins, L. N. Kantorovich, A. L. Shluger, J. Polesel-Maris, and S. Gauthier, Nanotechnology 17, 5866 (2006)
[7] F. F. Canova and A. S. Foster, Nanotechnology 22, 045702 (2011)
[8] N. Sasaki and M. Tsukada, Jpn. J. Appl. Phys. 39, L1334 (2000)
[9] L. N. Kantorovich and T. Trevethan, Phys. Rev. Lett. 93, 236102 (2004)
[10] R. Bennewitz, A. S. Foster, L. N. Kantorovich, M. Bamberlin, C. Loppacher, S. Schär, M. Guggisberg, E. Meyer, and A. L. Shluger, Phys. Rev. B 62, 2074 (2000)
[11] L. N. Kantorovich and C. Hobbs, Phys. Rev. B 73, 245420 (2006)
[12] J. C. Dupuy, P. Sautet, D. F. Ogletree, O. Dabbousi, and M. B. Salmeron, Phys. Rev. B 47, 2320 (1993)
[13] M. Watkins, T. Trevethan, A. L. Shluger and L. N. Kantorovich, Phys. Rev. B 76, 245421 (2007)
[14] S. Kawai, F. F. Canova, T. Glatzel, A. S. Foster and E. Meyer, Phys. Rev. B 84, 115415 (2011)
[15] R. Hoffmann, A. Baratoff, H. J. Hug, H. R. Hilber, H.
v. Löhneysen and H.-J. Güntherodt, Nanotechnology 18, 395503 (2007)

[16] S. A. Ghasemi, S. Goedecker, A. Baratoff, T. Lenosky, E. Meyer and H. J. Hug, Phys. Rev. Lett. 100, 236106 (2008)

[17] L. N. Kantorovich, A. S. Foster, A. L. Shluger, and A. M. Stoneham, Surf. Sci. 445, 283 (2000)

[18] R. Hoffmann, L. N. Kantorovich, A. Baratoff, H. J. Hug, and H.-J. Güntherodt, Phys. Rev. Lett. 92, 146103 (2004)

[19] K. Ruschmeier, A. Schirmeisen and R. Hoffmann, Phys. Rev. Lett. 101, 156102 (2008)

[20] A.L. Shluger, A. L. Rohl, and D. H. Gay, Phys. Rev. B 51, 13631 (1995)

[21] M. A. Lantz, R. Hoffmann, A. S. Foster, A. Baratoff, H. J. Hug, H. R. Hidber, and H.-J. Güntherodt, Phys. Rev. B 74, 245426 (2006)

[22] G. Henkelman, B. P. Uberuaga, D. J. Harris, J. H. Harding, and N. L. Allan, Phys. Rev. B 72, 115437 (2005)

[23] See Supplemental Material at (to be inserted by publisher) for movies illustrating the transition between states E and A for the $K^+$-terminated tip as observed in a molecular dynamics simulation performed at 500 K viewed from the front (supmovie1.avi) and from the right (supmovie2).

[24] See Supplemental Material at (to be inserted by publisher) for movies illustrating ion displacements which accompany the approach and subsequent retraction of a $<111>$-directed KBr cubic model tip supporting an additional KBr dimer such that the initially protruding Br$^-$ ion is above a $K^+$ ion in the top layer of a KBr(001) slab. The movies were generated from snapshots taken at increments of 0.02 nm over nominal tip-sample distances between 1.07 and 0.13 nm and back, using the relaxation procedure described in Ref. [18]. In the first movie (supmovie3.avi) the tip is approached up to a minimal distance of 1.3 Å to the surface. No jumps are observed. In the next movie (supmovie4.avi) the tip is approached up to a minimal distance of 1.1 Å to the surface where a jump is clearly observed and a different configuration can be observed during retraction. The last movie (supmovie5) is viewed from the y-direction whereas the other two movies (3 and 4) are viewed from the x-direction.

[25] The results shown in Fig. 2 were obtained in the direction from E to A with the exception of the path shown in grey above a surface Br$^-$ for $z = 4$ Å. For all other cases the barriers were assumed to be the same independent of the direction.

[26] P. V. Sushko, A. S. Foster, L. N. Kantorovich, and A. L. Shluger, Appl. Surf. Sci. 144-145, 608 (1999)

[27] R. Oja and A. S. Foster, Nanotechnology 16, S7 (2005)

[28] For a rotation angle of 20°, the dimer ions remain on the surface upon retraction if the tip is initially approached closer than 0.35 nm to the surface. The final state with the two additional ions transferred to the surface has an energy 310 meV lower than configuration E, because the dimer is now in a higher coordinated state on the surface compared to its location on a tip edge in configuration E.