Dynamics and metastable surface structure of double atomic layer of water molecules and ions at the interface between KBr(c) and water*

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Abstract: The metastable surface structure and dynamics of water molecules, cations, and anions at the interface between KBr(001) and water have been in situ observed in atomic resolution using atomic force microscopy. The vertical motion of potassium ions, which means their own transfer from the equilibrium sites to the upper height right on the underlying bromide ions, has been observed at the interface. They are used to be located in some steady state stabilized by their interaction with water molecules in the double atomic layer at the interface. The observed water molecules bridge two bromide ions by hydrogen bond; the water molecules are sandwiched by the potassium ions and vice versa.

INTRODUCTION

Since 1992, the observation of mineral growth and dissolution processes in aqueous solution has been achieved in real time [1–3]. Atomic force microscopy (AFM) allowed the tool for imaging the crystal growth process and for observing the step density and its formation velocity on the cleavage plane of the minerals. The in situ observed images revealed that layer-by-layer growth occurred through the forward motion of steps. In advanced research, the ionic crystal growth and dissolution processes may also be interpreted in terms of nonequilibrium array of ions and water molecules at the interface between their crystal and water. An AFM study on the interface of the cleavage plane immersed into water is certainly of considerable interest.

The AFM technique has a chance to give almost a step-function impetus in visibly understanding the microscopic mechanisms of the crystal growth and dissolution processes at the interface covered with water, and in eventually inducing or enhancing crystal growth on the subnanometer scale [4,5]. The AFM observation of water on NaC1(001) has been done through the spontaneous motion of monatomic steps that depend upon relative humidity [6]. Surprisingly little is, however, known about the two-dimensional array and motion of water molecules and ions at the interface between ionic crystal and water. The water film on mica surface immersed in water was imaged by AFM, and the water layers were demonstrated by topographic observation [7].

The metastable array and dynamics of water molecules and ions in double atomic layer at the interfaces of ionic crystal covered with water will lead to a build-up of the more explicit mechanism related to the crystal growth and dissolution in aqueous solution. The ions may undertake many restrictions on their translational freedom to move on terrace. The energy necessary for the transfer of the equilibrium surface structure of NaCl(001) to a metastably ordered array should be supplied by the molecular interaction between ions and water molecules at the interface; the intermolecular force against

the attractive force between unlike ions may originate from the so-called hydrogen bond of water molecules with anions [8].

Water is a common substance as well as an unusual substance; it is accorded a special place in the annals of phenomena dealing with intermolecular forces [9]. An empirical parameter for the donor–acceptor properties of solvents was proposed as acceptor number AN, determined by the NMR chemical shifts for each pure solvent [10]. The AN of water 54.8 is the largest value among the typical polar and nonpolar solvents. Thus, two hydrogen atoms in water molecule are likely to favor the lone pair provided by some dipolar molecules as well as anions; the hydrogen bond between water molecules and anions should be established by a strongly attractive force along a direction [8].

This work presents the atomic resolution observation of the AFM images for metastable surface structure at the interface between KBr(001) and water. The in situ observed AFM images in atomic resolution will visualize a change from one stationary state to another state. It may be revealed for ions in the double atomic layer at the interface how the water molecules give rise to the vertical and horizontal motion, and how the surface structure creates its metastable arrays.

EXPERIMENTAL

All the AFM images were measured in the constant force mode. The sample surface was imaged by mechanically tracing its topography using a microfabricated cantilever with an integrated pyramidal Si_3N_4 tip [11]. Here, the cantilever's force constant is $k = 0.58$ nm^{-1}. The z-axis displacement is read as the height of the surface feature, but maintaining the height sensitivity of a fraction of monatomic layer. In our experiments, the scanning force over the surfaces of samples was $F = 1{\sim}2$ nN in water, the image acquisition time was less than 10 s [11,12]. The overall force is attractive and corresponding to be negative values in the observed force curve plots, where the zero force point is measured for tip-sample separations.

The KBr crystal can be cleaved easily along the (001) faces. No further surface treatment has been applied. The sample epoxidized into a stainless steel cup mount was sealed by an O-ring against a glass fluid cell filled with the aqueous solution by saturated KBr. Since the whole cantilever probe was immersed in water, the so-called capillary forces should be mostly eliminated [11,12].

RESULTS AND DISCUSSION

The atomic resolution image at the interface of KBr(001) covered with water is shown in Fig. 1. The AFM image shows the metastable array of the parallelogram reconstruction. Half of the protrusions show bromide ions, and half show potassium ions. The potassium ions are going up to the same height with the bromide ions, as shown by the cross-section profiles in Fig. 1; the AFM image of KBr was almost similar to the atomic resolution image for NaCl(001) except for magnitude of the interval between bright spots (Figs. 4 and 5 of NaCl in [12]). The intervals between like ions along the axis labeled by A became longer by ca. 0.3 nm relative to the lattice constant $a_0 = 0.6600$ nm of KBr [13] because of the surface diffusion of ions at terraces; along B axis the interval between like ions corresponds to the lattice constant within experimental error. If an alignment along C axis consists of potassium ions, the next consists of bromide ions.

The atomic resolution images at the terrace interface of KBr(001) covered with water are shown in Figs. 2 and 3. They show the metastable surface structure, which consists of the parallelogram or rectangle as unit cell. The potassium ions are located at the higher level right on the underlying bromide ions along the A and B axes in Figs. 2a and 2b, since the comparison between the AFM images of metastable array of Fig. 1 and equilibrium array (Fig. 1 in [13]) demonstrates the vertical motion of smaller and lighter potassium ions at the interface covered with water. An interval of ca. 0.25 nm between bright spots along C axis is very short relative to the nearest neighbor distance 0.330 nm between
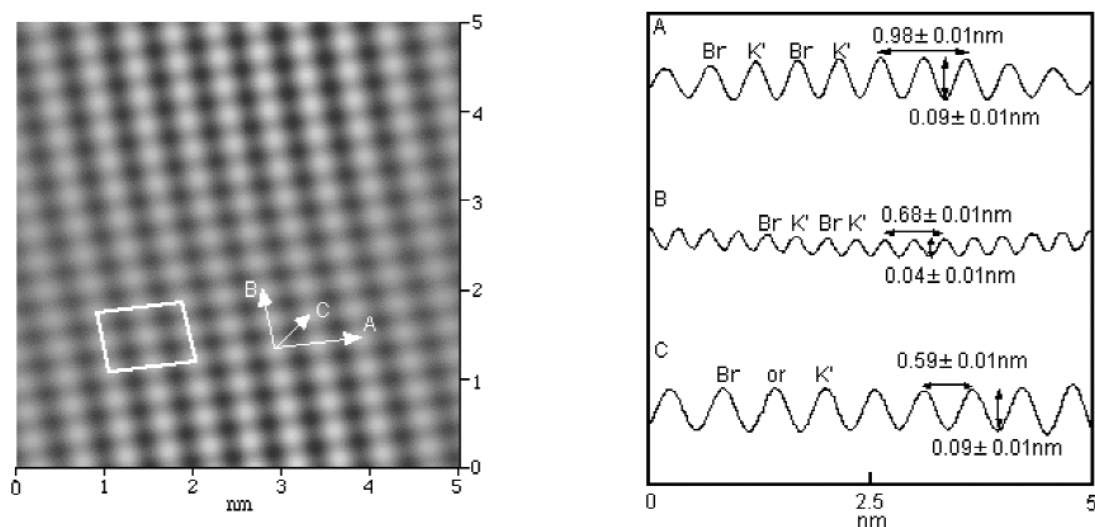
Fig. 1 Observed AFM images of KBr surface in water after KBr(001) had been covered with water for ca. 3 h; the parallelogram in the image indicates a unit cell. Cross-section profiles in the direction of the axes labeled by A and B show that potassium and bromide ions are alternately aligned and potassium ions are still located at the same height with bromide ions. Cross-section profile in the direction of C axes shows that if bromide ions are aligned along C axis, potassium ions are aligned along the next.

unlike ions and has been assigned to be the interval of water molecule and potassium ion (Fig. 2). The very short separation 0.20~0.25 nm between protrusions has never been observed near the step of KBr(001) as well as NaCl(001) (Figs. 5 and 7 of [12]). Each alignment along C axis in the AFM image of Fig. 2a may be of twist at the boundary noted by a dotted line along D axis, at which the metastable surface structures are slightly different to each other. It might have been, however, impossible to delete the effect of mechanical drift and/or thermal drift on the observed AFM images. If the potassium ions are aligned along D axis, the water molecules located at the same height are aligned along the next.

Since the above-mentioned configurations of ions in double atomic layer at the interface do not correspond to equilibrium surface structure, they should depend on real time as well as the surface spots. The interatomic force, which transfers the ions from the equilibrium state to a metastable state and from a metastable state to another metastable state, originates from the hydrogen bond of bromide ion with water molecule as an optimized dipole vector and from the electrostatic bond between potassium ion and water molecules.

The vertical motion of the smaller and lighter cations takes place in double atomic layer at the interface. The equilibrium configuration is transferred to their metastable states; the cations are located at (α) the same height with the anions (Fig. 1 in this work; Figs. 4 and 5 of NaCl in [12]) or (β) the upper height right on the underlying anions (Figs. 2 and 3), and to the other metastable surface structure which consists of (γ) the larger and heavier anions and no cations at the interface (Fig. 6 of NaCl in [12]). No observation for (γ) metastable state has been done for KBr(001).

The schematic diagrams of Figs. 4 and 5 reproduce the top and side views of the observed AFM images of the double atomic layer at the interface. The separation 0.20~0.25 nm between bright spots in the observed AFM images (Figs. 2 and 3) provides the ordered array of water molecules sandwiched by potassium ions in the upper layer of double atomic layer in (β) metastable state, as shown in Figs. 4 and 5. The observed separation between water molecules may depend on time and space spots; a water molecule bridges two bromide ions by hydrogen bond $Br^-\cdots H\text{–}O\text{–}H\cdots Br^-$ in (β) metastable state. These bromide ions in the lower double atomic layer come to close for a moment to the contact pair (i.e., ca. 0.4 nm of Fig. 5b) and separate for a moment nearly to the lattice constant (i.e., ca. 0.6 nm of
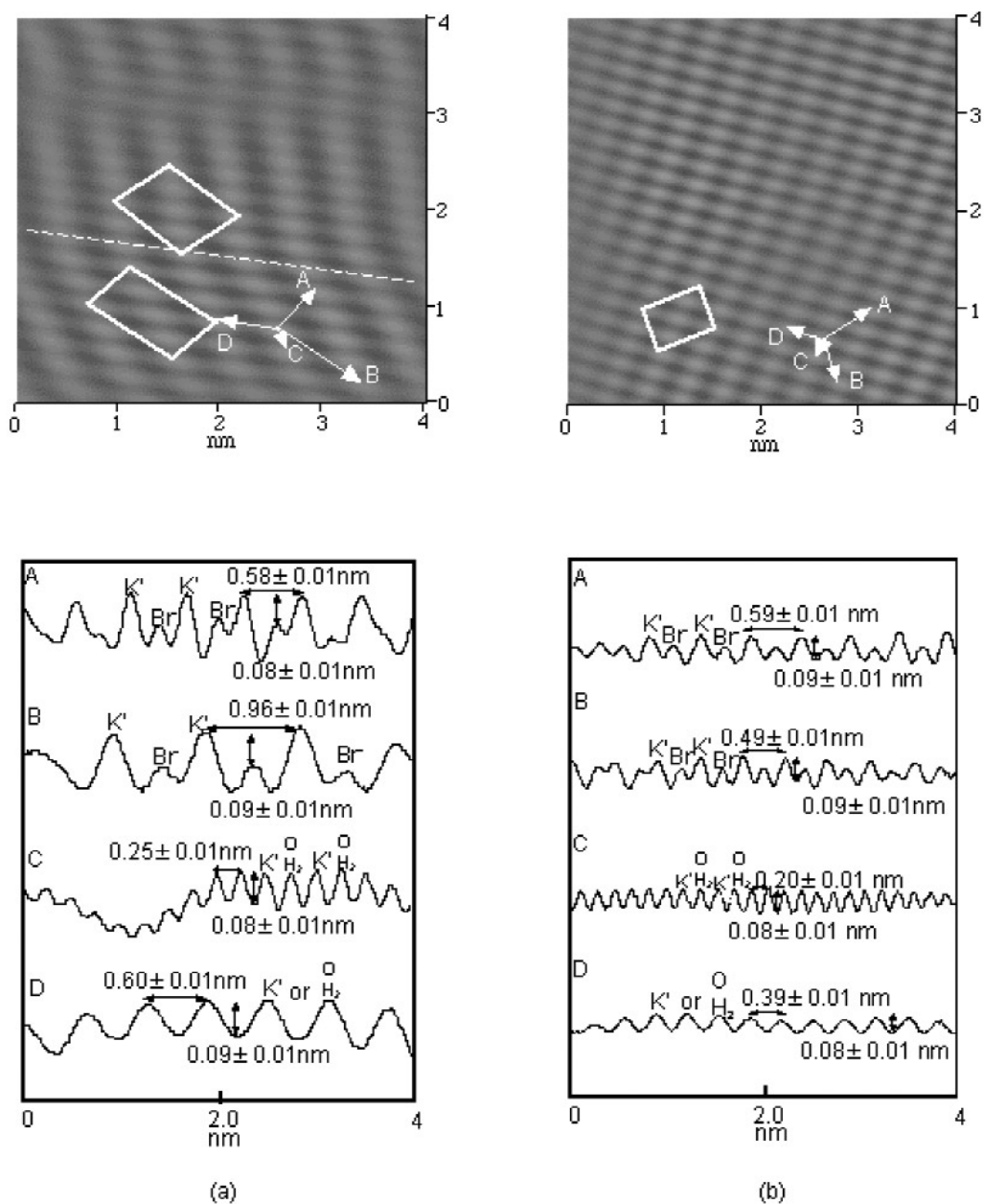
Fig. 2 The AFM images at the terrace of KBr surface in water; the (a) parallelogram and (b) rectangle indicate each unit cell. Cross-section profiles in the direction of the A and B axes show that the potassium ions are transferred from their own equilibrium sites to the higher level right on the underlying bromide ions. In the direction of C axis, the above-mentioned potassium ions and the water molecules are aligned alternately. If potassium ions are aligned along D axis, the water molecules are aligned along the next.
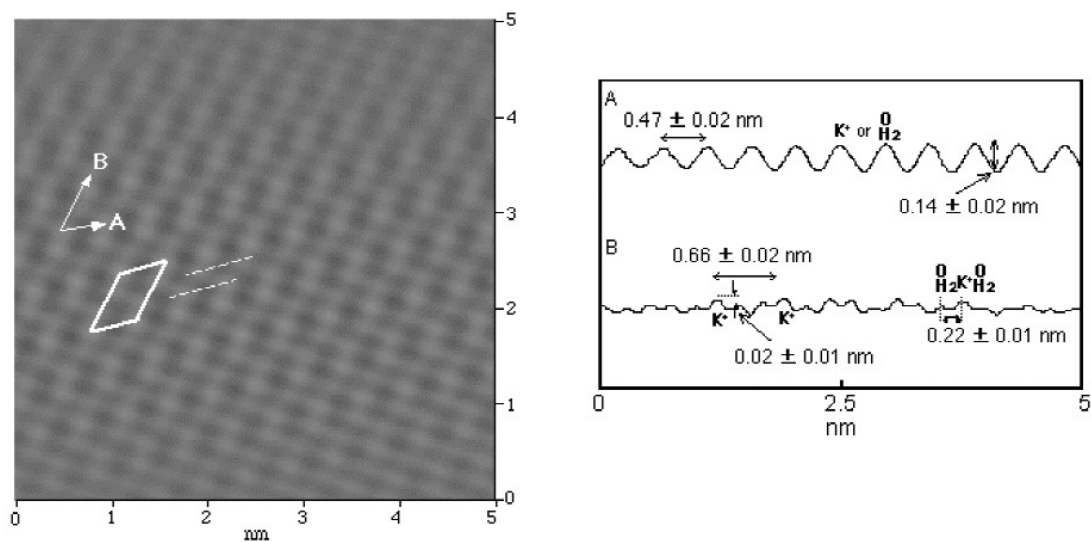
Fig. 3 The AFM image at the terrace of KBr surface in water shows a parallelogram as a unit cell. If potassium ions are aligned along A axis, water molecules are aligned along the next. In the direction of B axis each potassium ion is sandwiched by two water molecules located at the higher level right on the underlying bromide ions.
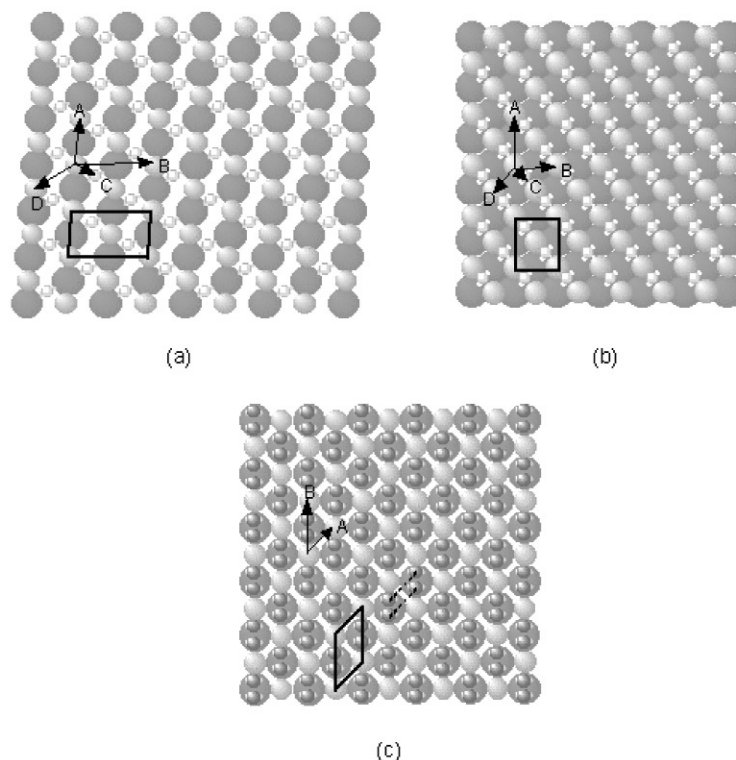

(a)

(b)

(c)

Fig. 4 The possible models for the atomic-resolution AFM images of Figs. 2 and 3; the two-dimensional ordered-array models (a), (b), and (c) for double atomic layer at the terrace interface can simulate the atomic-resolution AFM images of Figs. 2a, 2b, and 3, respectively. The bromide ions (the largest and dark spheres) are partially covered by water molecules and/or potassium ions (the smaller sphere) at the interface. The potassium ions located at the higher level right on the inderlying bromide ions were sandwiched by two water molecules.
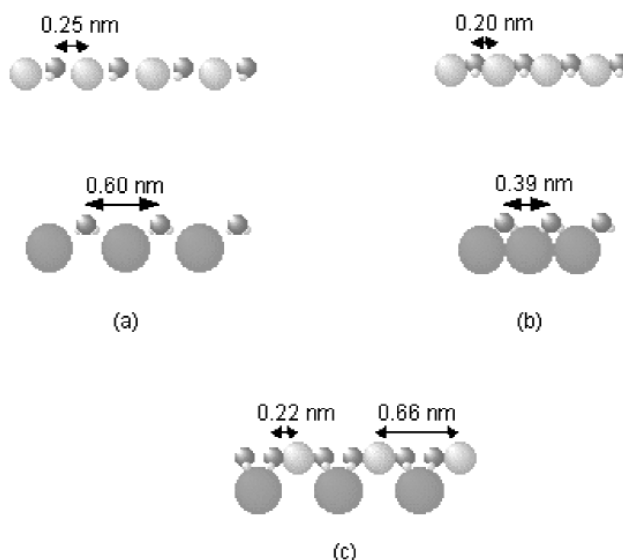
Fig. 5 Cross-section profiles for the models shown in Fig. 4; (a), (b), and (c) were obtained from the models Figs. 4a, 4b, and 4c. The observed water molecules bridge two bromide ions and are sandwiched by potassium ions, and vice versa.

Figs. 5a and 5c). For any NaCl(001) immersed into water there was, however, no observed AFM image in (β) state [12].

The metastable configuration of potassium and bromide ions in double atomic layers is inspired by water molecules at the upper double atomic layer; the surface structure of double atomic layer may depend on time as well as the local spaces of step and terrace. We have been observing for a moment a couple of atomic-resolution surface structures in (β) stationary state (Figs. 2 and 3). The horizontal or two-dimensional motion of larger and heavier anions is controlled by the hydrogen bond with water molecules and the electrostatic repulsion force between anions in (β) stationary state.

The observed water molecules and potassium ions are sandwiched by two potassium ions and two water molecules located at upper double atomic layer, respectively (Fig. 5). The water molecules are not freely rotating and may be regard as fixed dipole. Here, the hydrogen-bond angle $\angle$ Cl$^-$HO and the bond angle $\angle$ K$^+$OH, ϕ and θ defined in Fig. 6, are equal to ca. 0° and ca. 90°, respectively. Such configurations were observed for incompletely hydrated solution of ca. 20–35 mol % LiCl using the methods of time-of-flight neutron diffraction and stable isotopic substitution [14,15]. The most probable configuration around Li$^+$ means the local structure statistically averaged by time and coordination during the motion of chemical species in aqueous solution. It is much more interesting to be able to point out the coincidence of the local configurations of water molecule around ions obtained from the two different techniques, AFM for the observation of the interface of ionic crystal immersed into water and the neutron diffraction of the incompletely hydrated ionic solution.

The unusual anion–anion alignments in the metastable double atomic layer in (β) stationary state have been achieved by the ion–ion contact keeping the separation around 0.4 nm for Br$^-$–Br$^-$, as shown in Fig. 5. Each water molecule of the upper double atomic layer right on the underlying bromide ions bridges them by hydrogen bond. These bridging and orientated hydrogen bonds may win over the repulsion force between bromide ions located at the contact region; their contact alignment may be indeed stabilized at the lower double atomic layer. The nonlinear integral equation theory has insisted the clear minima at the anion-contact pair distance for the effective interaction between anions in water since 1986 [16–18]. This result is clearly at odds in dilute aqueous solution, but it is much more interesting. The molecular dynamics, Monte Carlo simulation, and integral equation theory cannot still con-
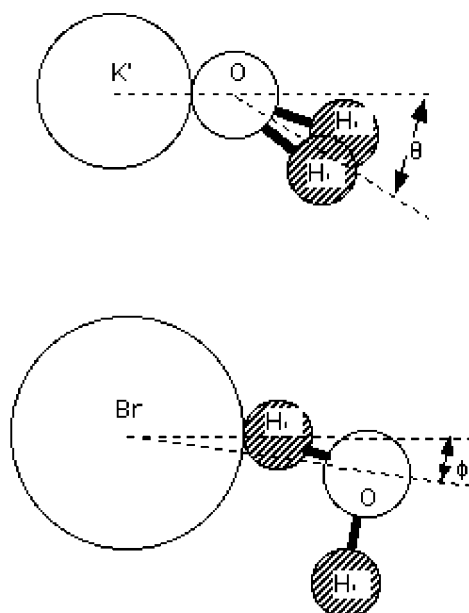
Fig. 6 Coordination of water molecule around potassium ion or bromide ion; θ and φ are defined as bond angle of $K^+\cdots OH_2$ and hydrogen-bond angle of $Br^-\cdots H\text{–}O\text{–}H$.

clude which the anion-contact $Cl^-\text{–}Cl^-$ pair makes its appearance or not in aqueous NaCl solution [19–22].

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