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Supporting Information: Initial stages of salt crystal dissolution determined with *ab initio* molecular dynamics

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Here we report further details of the simulations focusing specifically on (I) details of the simulation supercell used; (II) the molecular mechanics (MM) setup; (III) the *ab initio* (QM) setup; (IV) the metadynamics [1] setup and the tests preformed with various choices of collective variables; and (V) tests on the accuracy and reliability of the QM simulations.

I SIMULATION CELL

The same water/NaCl interface model has been used for both the QM and MM simulations and is shown in Fig. 1 of the main manuscript. It is comprised of a 3 layer thick NaCl slab in a (4×3) supercell. The (001) surface of NaCl is exposed and on top of the three layer slab is a partial fourth layer in a zig-zag arrangement designed to mimic a monoatomic step on the surface with geometrically equivalent Na and Cl corner ions. On top of this defective NaCl(001) surface is a film of 74 water molecules. In total there are 306 atoms in the system and the unit cell dimensions are 16.2×12.1×50 Å. Standard 3D periodic boundary conditions have been employed and there is at least 20 Å of vacuum along the surface normal direction between the top of the water film and the bottom layer of the periodically repeated NaCl slab. This model has been chosen in order to mimic as closely as possible the experimental conditions of Refs. [2–5], in which dissolution is initiated at kink sites from a NaCl surface covered with a film of water about 1 nanometer thick.

II MM SET-UP

Classical molecular dynamics simulations have been performed with the CP2K/FIST program [6]. The Born-Mayer-Huggins potential [7, 8] was used for NaCl, TIP3P [9] for water, and the ion-water interaction with the potential parameters taken from Smith and Dang [10]. This is a set-up previously used to simulate the water/salt interface [11, 12]. The initial water/NaCl structure was first run for an equilibration period of 1 ns at 300 K within the canonical (NVT) ensemble using a 1.0 fs time step. During this 1 ns we did not observe the dissolution of any ions, which is consistent with previous studies [12–15]. The MM metadynamics simulations and the QM molecular dynamics were subsequently initiated from structures taken from the latter stages of this simulation.

III QM SET-UP

Ab initio molecular dynamics simulations have been performed with the CP2K/Quickstep program [6], which employs a hybrid Gaussian and plane-wave basis set. The Perdew, Burke, and Ernzerhof (PBE) [16] exchange-correlation functional has been used for all total energy and molecular dynamics calculations. The accuracy of PBE in describing the salt dissolution process was further checked with calculations with the hybrid PBE0 [17] functional, as discussed below. Core electrons are described with norm-conserving Goedecker, Teter, and Hutter (GTH) pseudopotentials [18–20]. The wave functions of valence electrons are expanded in terms of Gaussian functions with a quadruple ζ doubly polarized basis set (QZV2P) for H, O, and Cl atoms, and a double ζ single polarized basis set (DZVP) for Na. For the auxiliary basis set of plane waves a 320 Ry cut-off is used. This basis set yields an adsorption energy for a water monomer within 1 meV of that obtained with a larger basis set of triple/quadruple-zeta quality (QZV2P for H, O, and Cl, TZV2P for Na). Further results on basis set tests can be found in ref. [11].

The initial water/NaCl structure was obtained from an equilibrated molecular dynamics simulation performed with MM. The *ab initio* molecular dynamics simulations reported here are of the Born-Oppenheimer (BO) type within the canonical (NVT) ensemble. Previous studies have shown that at room temperature DFT-PBE water is overstructured and has a diffusion coefficient much smaller than experiment [21–25]. To avoid this problem DFT-PBE simulations of liquid water are often performed at high temperatures (330-400 K) [21–24]. Here the QM simulations were performed at 360 K. The nuclear equations of motion have been integrated using a standard velocity Verlet algorithm with a 1.0 fs time step. Deuterium masses are used for the hydrogen atoms in order to allow a larger timestep. A regular *ab initio* molecular dynamics simulation was at first run for 20 ps and then followed by two individual metadynamics simulations.

IV METADYNAMICS SIMULATIONS

To explore the salt dissolution process, we used metadynamics which employs an extended Lagrangian of the form [26]:

$$\mathrm{L} = \mathrm{L}_{\mathrm{BOMD}} + \sum_{\alpha} \frac{1}{2} \mu_{\alpha} \dot{\mathrm{s}}_{\alpha}{}^{2} - \sum_{\alpha} \frac{1}{2} \mathrm{K}_{\alpha} \left(\mathrm{S}\left(\mathbf{r}\right) - \dot{\mathrm{s}}_{\alpha} \right)^{2} - \mathrm{V}\left(\mathrm{t}, \mathrm{s}\right) \ . \tag{S1}$$

The first term on the right hand side is the standard Born-Oppenheimer MD Lagrangian describing the ion motion. The second term on the right hand side is the total kinetic energy of the fictitious particles. Each fictitious particle is connected to its actual collective variable, S($\mathbf{r}$), by a harmonic spring. The third term is the total potential energy of a harmonic spring. The last term, V(t,s), is the history-dependent repulsive potential acting on the fictitious particles, which is a sum of Gaussians,

$$\mathrm{V\,(t,s)} = \mathrm{H} \sum_{\mathrm{t}_i=\mathrm{T,2T,3T...t}_i<\mathrm{t}} \exp\frac{(s - s(t_i))^{\,2}}{2\,(\delta\mathrm{S})^{\,2}}\,, \tag{S2}$$

where H and δS are the height and width of the Gaussians, and T is the time interval after which a new Gaussian is added. The spring constant, K_α, is chosen as 0.2 a.u. and the mass of the collective variable (CV), μ_α, is chosen as 60 amu. The width and height of the Gaussian-shaped potential hills were set to 0.15 au and 0.0002 au (0.0054 eV), respectively. Two criteria were used to control the frequency with which Gaussians were added. The first is that there must be at least 100 MD steps between consecutive Gaussians. The second is that a new Gaussian is not added until the CV has diffused 1.5 times δS (except when 250 MD steps have passed).

In order to identify suitable CVs to explore the dissolution process an extensive set of test calculations were performed at the MM level. For the various combinations of CV multiple independent metadynamics simulations were performed, typically 10, in order to assess the numerical accuracy of the simulations. Three different groups of CVs are used: G1 - the height of the Cl (Na) ion above the surface ($\mathrm{CV^{I}}$) and the coordination number (CN) of the departing Cl (Na) with the Cl (Na) ions in the topmost complete layer of the substrate ($\mathrm{CV^{II}}$). G1 is the CV choice used in the DFT simulations; (ii) G2 - $\mathrm{CV^{I}}$ and the CN of the departing Cl (Na) with the hydrogens (oxygens) of the water molecules ($\mathrm{CV^{III}}$); (iii) G3 - $\mathrm{CV^{I}}$ and the distance of the departing Cl (Na) with the Na (Cl) ion that originally was directly underneath it ($\mathrm{CV^{IV}}$). CN is defined as,

$$\mathrm{n} = \sum_{\mathrm{j=1}}^{\mathrm{M}} \frac{1}{\mathrm{N}} \sum_{\mathrm{j=1}}^{\mathrm{N}} \left[\frac{1-(\mathrm{r/r_0})^{\,6}}{1-(\mathrm{r/r_0})^{12}}\right], \tag{S3}$$

where N is the number of Na (Cl) atoms, r is the interatomic distance between the ith and jth atoms. For the Cl-Cl and Na-Na bonds $\mathrm{r_0}$ was taken as 4.76 Å and for the bond between the corner Cl (Na) with the H (O) atoms of the water molecules, $\mathrm{r_0}$ was taken as 2.60 (2.80) Å.

With the three different combinations of CVs we then examined the mechanism and free energy barriers for both the Cl and Na dissolution processes. Ten simulations were performed for each combination of CVs for both Cl and Na dissolution events, resulting in a total of 60 independent metadynamics simulations. Each simulation started from a slightly different initial configuration randomly selected from the latter stage of the regular equilibrated molecular dynamics simulation. The metadynamics simulations were ended when the Cl (Na) arrived at the intermediate state (IM). The free energy barriers for the corner Cl and Na to go from the initial state to the IM state and the corresponding position of the transition state (TS^{I}) for the three groups of CVs are listed in Tables SI and SII, respectively. For the 10 different simulations in the same group, there are only differences in the height of the energy barriers and the locations of the transition states. Specifically, the standard deviation on the ten energy barriers within each set are of the order of 10 %. In addition, the energy barriers obtained from the different sets of CVs are also quite close for either Cl or Na. This shows that the reaction barrier and mechanism are not strongly affected by the choices of the CVs. In particular, we note that although for G1 the the Cl-H (Na-O) CN is not used as a CV, its value at the transition state is quite close to the value obtained when it is used as a CV (*cf.* $\mathrm{CV}^{\mathrm{III}}$ from set G1 and G2 in Tables SI and SII).

V TESTS ON THE ACCURACY AND RELIABILITY OF THE QM BARRIERS

In the main text, it mentioned that in the QM simulations both the free energy and potential energy barriers to remove the corner Cl are smaller than the equivalent barriers obtained from Na. To verify the accuracy of the PBE functional in describing such potential energy differences and in particular to establish if the potential barriers determined here are sensitive to self-interaction errors, calculations with the hybrid PBE0 functional were also performed, using the same simulation cell and basis sets [27]. The PBE0 potential energy changes relative to the initial state as a function of height for the corner Na (Cl) are shown in Fig. S1 along with those calculated with PBE. Although the absolute potential energy barriers obtained with the PBE0 functional are somewhat larger (by about 0.1 eV) than those obtained with PBE the main conclusion that the barrier for Cl removal from the lattice is smaller than that for Na removal remains unaltered. Specifically the potential difference at the the TS^{I} location (4.3 Å) between the Cl and Na barriers is 0.08 eV with

PBE and 0.09 eV with PBE0. We conclude that compared to PBE0, PBE is good enough to describe the potential energy change as a function of Na (Cl) height.

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TABLE SI: Free energy barriers (ΔG) obtained from 30 independent MM metadynamics simulations for the corner Cl to go from the initial state (IS) to the location of the first transition state (TS^{I}). Ten separate simulations for each of the three choices of CVs considered are reported. The three combinations of CVs reported are: (1) G1 - the height of the Cl ion above the surface (CV^{I}) and the CN of the departing Cl with the Cl ions in the topmost complete layer of the substrate ($\mathrm{CV}^{\mathrm{II}}$). G1 is the CV choice used in the DFT simulations; (ii) G2 - CV^{I} and the CN of the departing Cl with the hydrogens of the water molecules ($\mathrm{CV}^{\mathrm{III}}$); (iii) G3 - CV^{I} and the distance of the departing Cl with the Na ion that originally was directly underneath it ($\mathrm{CV}^{\mathrm{IV}}$). All heights and distances are given in Å and energy in eV. The error bar on the averages is one standard deviation.

	G1				G2			G3		
	ΔG	CV^{I}	$\mathrm{CV}^{\mathrm{II}}$	$\mathrm{CV}^{\mathrm{III}}$	ΔG	CV^{I}	$\mathrm{CV}^{\mathrm{III}}$	ΔG	CV^{I}	$\mathrm{CV}^{\mathrm{IV}}$
1	0.30	4.2	2.1	4.1	0.26	4.3	4.1	0.38	4.6	5.0
2	0.38	4.3	1.9	4.5	0.31	4.4	4.8	0.42	4.4	4.7
3	0.32	4.3	1.8	4.4	0.34	3.9	3.8	0.32	4.3	4.6
4	0.34	4.1	2.1	4.4	0.27	4.3	3.9	0.34	4.2	4.5
5	0.32	4.5	1.7	4.2	0.32	4.6	4.2	0.37	4.2	4.4
6	0.31	4.1	2.1	4.4	0.28	4.1	4.0	0.30	3.7	3.8
7	0.29	4.2	1.9	4.3	0.26	4.7	4.0	0.38	4.6	5.0
8	0.32	4.4	1.8	4.3	0.27	4.3	4.0	0.35	4.6	4.9
9	0.33	4.6	1.6	4.4	0.27	4.3	4.0	0.32	4.3	4.7
10	0.29	4.6	1.9	4.4	0.27	4.4	3.5	0.24	4.0	4.4
Average	0.32±0.03	4.3±0.2	1.9±0.2	4.3±0.1	0.29± 0.03	4.3±0.2	4.0±0.3	0.34±0.05	4.3±0.3	4.6±0.4

TABLE SII: Free energy barriers (ΔG) obtained from 30 independent MM metadynamics simulations for the corner Na to go from the initial state (IS) to the first transition state ($\mathrm{TS^I}$). Ten separate simulations for each of the three choices of CVs considered are reported. The three combinations of CVs reported are: (1) G1 - the height of the Na ion above the surface ($\mathrm{CV^I}$) and the CN of the departing Na with the Na ions in the topmost complete layer of the substrate ($\mathrm{CV^{II}}$). G1 is the CV choice used in the DFT simulations; (ii) G2 - $\mathrm{CV^I}$ and the CN of the departing Na with the oxygens of the water molecules ($\mathrm{CV^{III}}$); (iii) G3 - $\mathrm{CV^I}$ and the distance of the departing Na with the Cl ion that originally was directly underneath it ($\mathrm{CV^{IV}}$). All heights and distances are given in Å and energy in eV. The error bar on the averages is one standard deviation.

	G1				G2			G3		
	ΔG	$\mathrm{CV^I}$	$\mathrm{CV^{II}}$	$\mathrm{CV^{III}}$	ΔG	$\mathrm{CV^I}$	$\mathrm{CV^{III}}$	ΔG	$\mathrm{CV^I}$	$\mathrm{CV^{IV}}$
1	0.30	4.4	1.8	3.7	0.21	4.1	4.5	0.35	4.1	4.2
2	0.32	4.8	1.3	3.5	0.31	3.9	3.5	0.28	4.1	4.3
3	0.29	4.0	2.2	3.9	0.32	4.2	3.9	0.37	3.9	4.1
4	0.29	3.7	2.5	3.6	0.32	3.6	4.5	0.37	4.0	4.3
5	0.37	3.9	2.4	3.5	0.26	3.8	4.5	0.39	4.1	4.4
6	0.28	4.1	2.1	3.5	0.33	3.9	4.4	0.33	4.4	4.7
7	0.35	3.9	2.5	3.4	0.22	3.9	4.3	0.30	3.7	4.0
8	0.31	3.8	2.5	4.0	0.31	4.3	3.9	0.29	4.4	4.5
9	0.33	4.1	2.1	3.6	0.23	3.8	4.7	0.26	3.5	3.8
10	0.33	3.9	2.3	3.8	0.34	3.8	4.0	0.24	3.7	3.8
Average	0.32±0.03	4.1±0.3	2.2±0.4	3.9±0.2	0.29±0.05	3.9±0.2	4.2±0.4	0.32±0.05	4.0±0.3	4.2±0.3

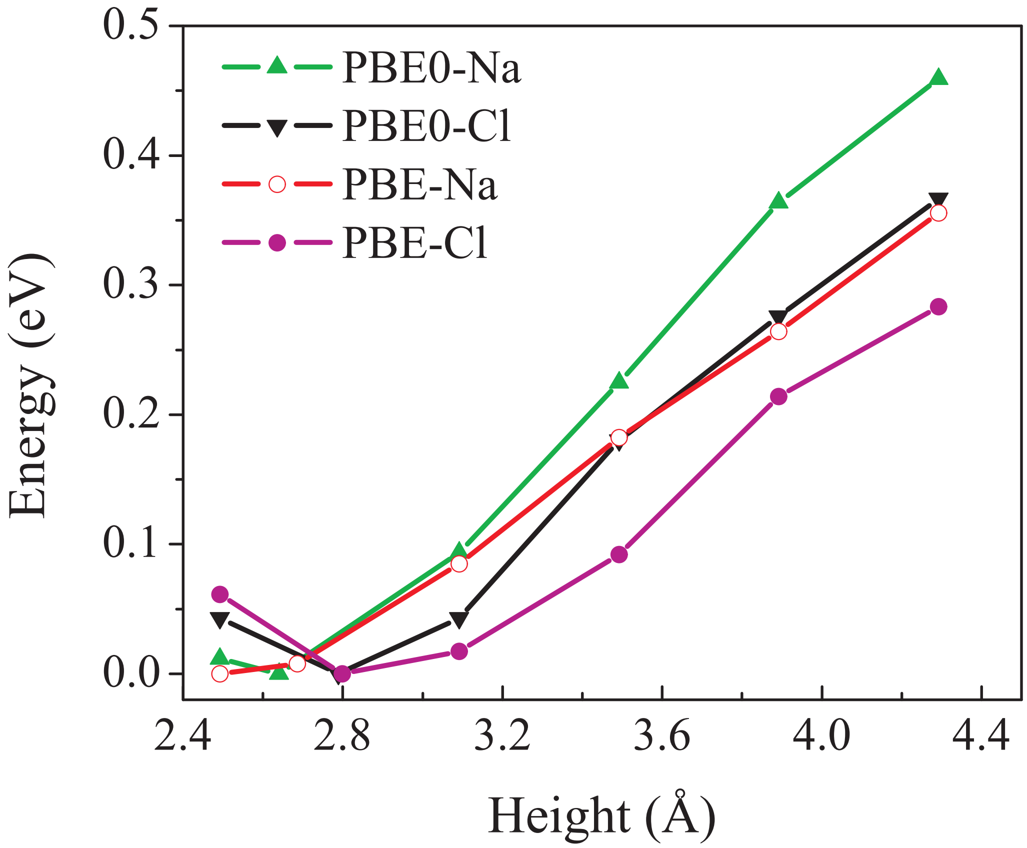

FIG. S1: The potential energy change relative to the initial state in the absence of water as a function of the height from the NaCl surface for both the corner Na and Cl, calculated using both the PBE and PBE0 functionals.