Supplementary Information for

Hydroxide trapped in the interior of ice – a computational study

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Hydroxide in medium sized ice-like clusters

We calculated the energy difference between optimized in-the-lattice and off-the-lattice structures in two medium sized clusters, containing, each, 38 water molecules and one hydroxide in the middle, with different proton arrangements of water molecules and different locations of the hydroxide O-H bond with respect to the c-axis of the ice crystal (see Figs. S1 and S2). Clusters were cut from ice slabs and they included two surfaces and one interior bilayer. In order to preserve the ice structure of clusters during minimizations the positions of 27 oxygen atoms in water molecules at the periphery of the clusters were fixed whereas the positions of all the hydrogen atoms, the hydroxide and 11 water molecules in the middle of the cluster were fully allowed to relax. Energies of both cluster configurations were minimized using non-periodic DFT with the BLYP functional and 6-31+G* basis set. Then single point energies were calculated employing B3LYP functional with the same basis. For these calculations we employed Gaussian03 software.[1] For the cluster presented in Fig. S1 stabilization energy of off-the-lattice configuration was 5.1 and 7.7 kcal/mol calculated with BLYP and B3LYP functional respectively. Corresponding stabilization energies for the second cluster were, respectively, equal to 9.8 and 10.4 kcal/mol. The difference in stabilization energies between the two clusters is caused by different proton arrangements and hydroxide orientations.

Energy barrier of in-the-lattice to off-the-lattice transition

Energy barrier was estimated for the in-the-lattice to off-the-lattice transition in ice-like water cluster of 7 water molecules and hydroxide ion. We performed relaxed potential energy surface scan starting from in-the-lattice structure shown in Fig. S3 A. Positions of all atoms of water molecules were fixed with the exception of two hydrogen atoms marked in green. Positions of the atoms forming the hydroxide were also allowed to relax. The H_w-O_w-O_{OH^-} angle defined in Fig. S3 was chosen as a reaction coordinate. In each step of the scan, i.e, for a given value of the angle, we allowed for relaxation of all unfixed coordinates. BLYP functional was employed with the 6-31+G* basis set using the Gaussian03 software. The scan was started from the structure near the in-the-lattice minimum (Fig. S3 A) with the H_w-O_w-O_{OH^-} angle equal to 110 degrees. The resulting energy profile along the reaction coordinate is presented in Fig. 3 A. The maximum of the energy was obtained for the angle equal to 83 degrees and

the transition structure corresponding to this point is depicted in Fig. S3 B. At this point the H-bond between the rotating water molecule and its neighbor is broken whereas this molecule is still accepting an H-bond from the hydroxide; thus a new, fourth, H-bond is not yet accepted by OH^-. Continuing the scan for the values of H_w-O_w-O_{OH^-} angle below 83 degrees we observed creation of the off-the-lattice minimum (see Fig. 2 E) where the value of angle was equal to 5 degrees (not shown in Fig. 3 A).

Molecular dynamics simulations

For two slabs, one with in-the-lattice and the second with off-the-lattice configuration of hydroxide in the same site in the structure (similar to these presented in Fig. 1B and 1D) we calculated *ab initio* molecular dynamics trajectory at T=130 K using the NVE/CP2K/Quickstep code. The selected temperature corresponds to that of the experimental studies on isotopic exchange in base-doped ice.[2] The starting points were the optimized structures, and the distance of the oxygen atom of hydroxide with respect to its initial position was calculated (Fig. 3 B). For off-the-lattice configuration a 2 ps trajectory was calculated (only initial 1 ps is shown in the plot); the position of OH^- oxygen was changed by less than 1 A due to small movement of OH^- in the structure, however, no migration of hydroxide between lattice sites was observed. For in-the-lattice structure a 1 ps trajectory was calculated; and migration of OH^- via a proton jump was observed on the time scale of tens of femtoseconds, as reflected by a rapid change of OH^- position in the slab in Fig. 2 G.

References

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(2) Devlin, J. P.; Buch, V. *J. Chem. Phys.* **2007**, *127*, 091101.

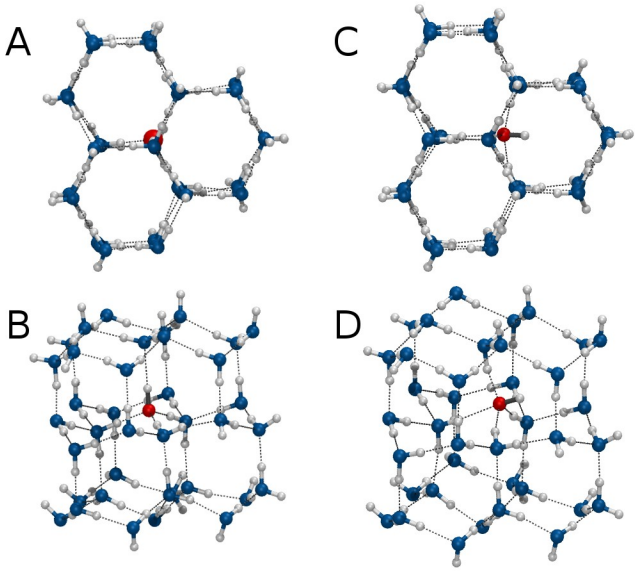

Figure S1. Optimized clusters of 38 water molecules with in-the-lattice (A, B) and off-the-lattice (C, D) configuration of hydroxide. Top view (A, C) and side view (B, D) of clusters is presented. Hydroxide in in-the-lattice configuration is located in parallel to c-axis of crystalline ice structure. Color coding: water oxygen – blue, hydroxide oxygen – red, hydrogen – gray, dashed lines - hydrogen bonds

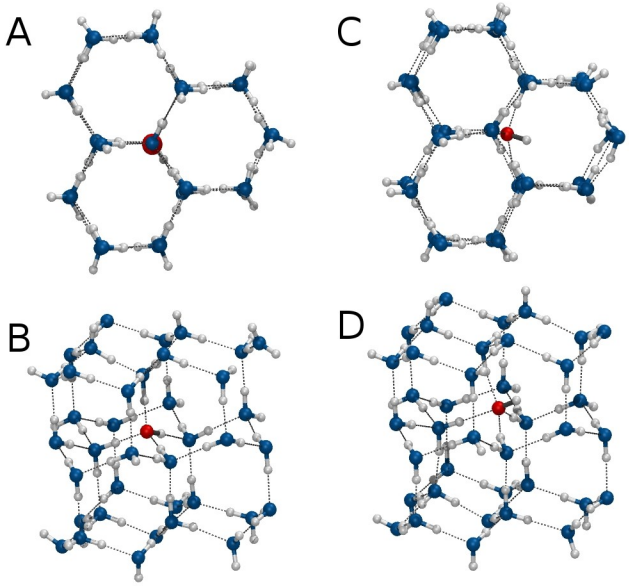

Figure S2. Optimized clusters of 38 water molecules with in-the-lattice (A, B) and off-the-lattice (C, D) configurations of the hydroxide. Top view (A, C) and side view (B, D) of the clusters is presented.

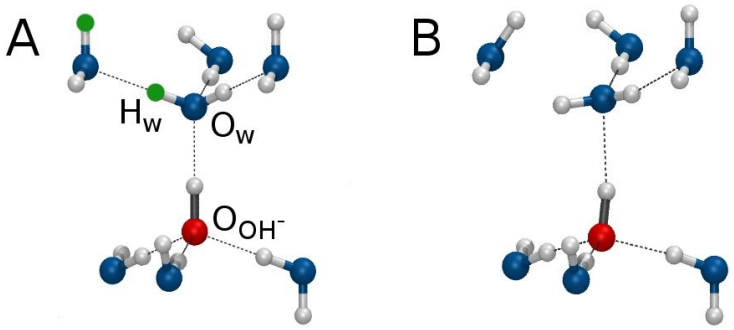

Figure S3. Cluster of 7 water molecules with hydroxide. Relaxed PES scan was performed starting from structure A. Positions of all atoms of water molecules with the exception of two hydrogen atoms marked in green were fixed. An H_w-O_w-O_{OH^-} angle was changed during the scan. Plot B depicts the structure with the highest energy along the scanned path. The structures correspond to the clusters depicted in Fig. 2C and 2E.