Segregation of hydroxide ions to an ice surface

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Introduction:

- An excess of protons or hydroxide ions present at an ice surface can have important consequences for the physical and chemical properties of the surface.

- Recent studies have shown that protons tend to reside at the surface of ice films rather than in the interior which have been investigated by using different spectroscopic technique.

- In the case of hydroxide ions, there have been relatively few investigations compared with the studies of protons on ice surfaces.

- Surface hydroxyl species were formed on the surface by the adsorption of Na atoms onto ice films which have been investigated by using different spectroscopy and spectrometry.

- The hydroxide ions produced remained on the ice film surface at all temperatures investigated, whereas sodium ions migrated to the ice interior at temperatures above \( \sim 110 \) K.
Density functional theory (DFT) calculations showed that the energy of hydroxide ion species at an ice surface, on average, was significantly lower than that in the ice lattice, similar to the case of hydronium ions.

It remains unclear, however, whether this behaviour is due to the thermodynamic affinity of hydroxide ions for the ice surface or to a lack of mobility for surface hydroxide ions to move to the ice interior.

This question was the main purpose of the exploration in the present study.

For that, they prepared an ice film that contained hydroxide ions at the interface between H₂O and D₂O layers and examined if the buried hydroxide ions migrated to the film surface. In addition, they examined the transport mechanism of hydroxide ions in ice by monitoring the H/D exchange kinetics of hydroxide ions and water molecules on the ice films.
Experimental Section:

- The experiments were conducted in an ultrahigh vacuum surface analysis chamber equipped with instrumentation for RIS, LES, and temperature programmed desorption (TPD).

- Na atoms (deposition rate was estimated to be approximately 0.033 MLE min\(^{-1}\)) were deposited onto ice films using a commercial alkali metal dispenser (SAES Getters).

- Neutral and ionic species present at the ice film surface were analyzed by RIS and LES, respectively.

- Cs\(^+\) (incident Cs\(^+\) flux of \(1 \times 10^{11}\) ions cm\(^{-2}\) s\(^{-1}\)) beam from a low-energy ion gun was scattered at a sample surface.

- Both positive and negative ions emitted from the surface were detected with a quadrupole mass spectrometer.

Result and Discussion: A. Transport of buried hydroxide ions to the ice surface.
FIG. 2. OH$^-$ and OD$^-$ signal intensities measured by LES from a hydroxide-sandwich ice film at 135 K as a function of time. The ice sample was prepared to have the same structure as the samples used for Figs. 1(c)–1(e) [D$_2$O (3 BL)/Na (0.2 MLE)/H$_2$O (70 BL)/Pt(111)]. The temperature profile of the experiment is displayed in the upper panel.
FIG. 3. (a) LES signal intensity of hydroxide ions measured as a function of time on a hydroxide-sandwich ice film [D$_2$O (3 BL)/Na (0.2 MLE)/H$_2$O (70 BL)/Pt(111)]. (b) After the kinetic measurement shown in (a), the sample was again cooled to 90 K, a second D$_2$O overlayer (3 BL) was deposited onto the sample, and the kinetic measurement was resumed along the same temperature profile as for the first experiment.
B. H/D-substituted water isotopomers

(a) $\text{D}_2\text{O}/\text{H}_2\text{O}/\text{Pt}(111)$, $T = 90\text{K}, 30\text{min}$

- $\text{Cs}^+$
- $\text{Cs(}\text{D}_2\text{O})^+$
- $\text{Cs(HDO)}^+$
- $\text{Cs(H}_2\text{O})^+$

Intensity ($10^2 \text{cps}$)

(b) $\text{D}_2\text{O}/\text{H}_2\text{O}/\text{Pt}(111)$, $T = 135\text{K}, 30\text{min}$

- $\text{Cs}^+$
- $\text{Cs(}\text{HDO})^+$
- $\text{Cs(}\text{D}_2\text{O})^+$
- $\text{Cs(H}_2\text{O})^+$

- $0.08 : 0.07 : 0.85$
- $0.20 : 0.49 : 0.31$

(c) $\text{D}_2\text{O}/\text{Na}/\text{H}_2\text{O}/\text{Pt}(111)$, $T = 135\text{K}, 30\text{min}$

- $\text{Cs}^+$
- $\text{Cs(HDO)}^+$
- $\text{Cs(H}_2\text{O})^+$
- $\text{Cs(D}_2\text{O})^+$

- $0.26 : 0.46 : 0.28$

$\text{m/z (amu/charge)}$

FIG. 4. RIS spectra obtained for three different water-ice films.
FIG. 5. Relative surface populations of H$_2$O, HDO, and D$_2$O measured as a function of time on a pure ice sample (a) and a hydroxide-sandwich ice sample (b), both at 135 K.
The observations (Fig. 1 & 2) made for the hydroxide-sandwich ice films described above indicate that buried hydroxide ions transported through the film and became segregated at the surface at 135 K.

The continued growth of hydroxide ions at the ice film surface through the multiple D₂O overlayers clearly demonstrates (Fig. 3) that the hydroxide ion transport to the surface is due to its thermodynamic tendency to reside at the ice surface rather than in the interior.

The increased selfdiffusion in the presence of buried hydroxide ions may be, in its fundamental origin, analogous to the lowering of ice melting temperature in the presence of foreign impurity species.

The H₂O : HDO : D₂O ratio at t = 10 min was approximately 0.12 : 0.44 : 0.44 for the pure ice film and approximately 0.23 : 0.45 : 0.32 for the hydroxide-sandwich film, which indicated that H/D exchange reactions occurred, with yields of ~100% and ~80%, respectively. Therefore, the H/D exchange of surface water molecules must have been very active at 135 K for both samples, such that it occurred faster than the diffusional mixing of water molecules in the vertical direction.
Conclusion:

- The results of the present study show that hydroxide ions initially buried within an ice film segregate to the ice surface at high temperature.

- Hydroxide ions have a thermodynamic preference for residing at the ice surface rather than in its interior.

- Accumulation of hydroxide ions on an ice surface may have an important influence on the acid–base chemistry of the surface and its other physical and chemical properties.

- Two types of transport mechanisms were identified for hydroxide ions in ice. At 90 K, a small portion of hydroxide ions are transported from the ice film interior to the surface by a proton hopping mechanism. As water self-diffusion is activated near the ice surface at 135 K, the migration of hydroxide molecular ions to the surface becomes the major transport channel.
What further can be done:

- Instead of ionic species, neutral molecule (such as: CO, NO, H₂, etc) can be kept in the interface between H₂O and D₂O layers.

- It is difficult to use negative as a projectile but negative ion can be generated on the surface and that may trigger some chemical reaction on the surface and which can be analyzed using mass spectrometer.

- Several reaction can be done on the surface of ice using hydronium or hydroxide ion as a catalyst