

**Hydrolysis of Sodium Atoms on Water-Ice Films.
Characterization of Reaction Products and
Interfacial Distribution of Sodium and Hydroxide
Ions**

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Journal of Physical Chemistry C, 2009, 113, 321

Soumabha Bag
CY08D021
20-07-09

• Introduction

1. The reaction of sodium metal with liquid water is a well known exothermic reaction producing solvated sodium and hydroxide ions and molecular hydrogen.
2. Na atom interaction has been investigated not only in liquid water but also in various environments such as water-ice films and gas-phase water cluster.
3. Several pioneering work included interaction of K and H₂O co-adsorbed onto Ru(0001) using temperature-programmed desorption (TPD) and electron energy loss spectroscopy and observed that KOH is formed on the surface at a temperature of 80 K and exists up to 580 K.
4. Similar research using TPD and X-ray photoelectron spectroscopy (XPS) revealed that co-adsorbed potassium and water react very slowly at 100 K, and the reaction is complete at 300 K.
5. The interactions of alkali metals with water-ice films using metastable impact electron spectroscopy (MIES), ultraviolet photoelectron spectroscopy (UPS), and XPS suggested that Na atom donates a 3s electron to the ice film and then the solvated electron reacts with water molecule to form hydroxyl species. Upon the increase in alkali metal exposure, neutral Na clusters start to form at the film surface.

6. TOF-SIMS study suggested that unhydrated NaOH layer is formed (at 13 K) at the film surface, followed by the growth of a metallic Na layer at high Na exposure (and also at higher temperature 100 K).
7. Other experimental and theoretical studies revealed that Na hydrolysis reaction is initiated by the presence of a Na or Na₂ dimer in the water cluster leading to the formation of sodium hydroxide and the formed Na⁺ & OH⁻ may stay as contact pair or separated species.

What is the need of present study?

This study focuses on the understandings of nature of hydrolysis products using low energy sputtering (LES) and reactive ion scattering (RIS) techniques under various conditions for the temperature range of 95-135 K and Na coverage below the multilayer regime.

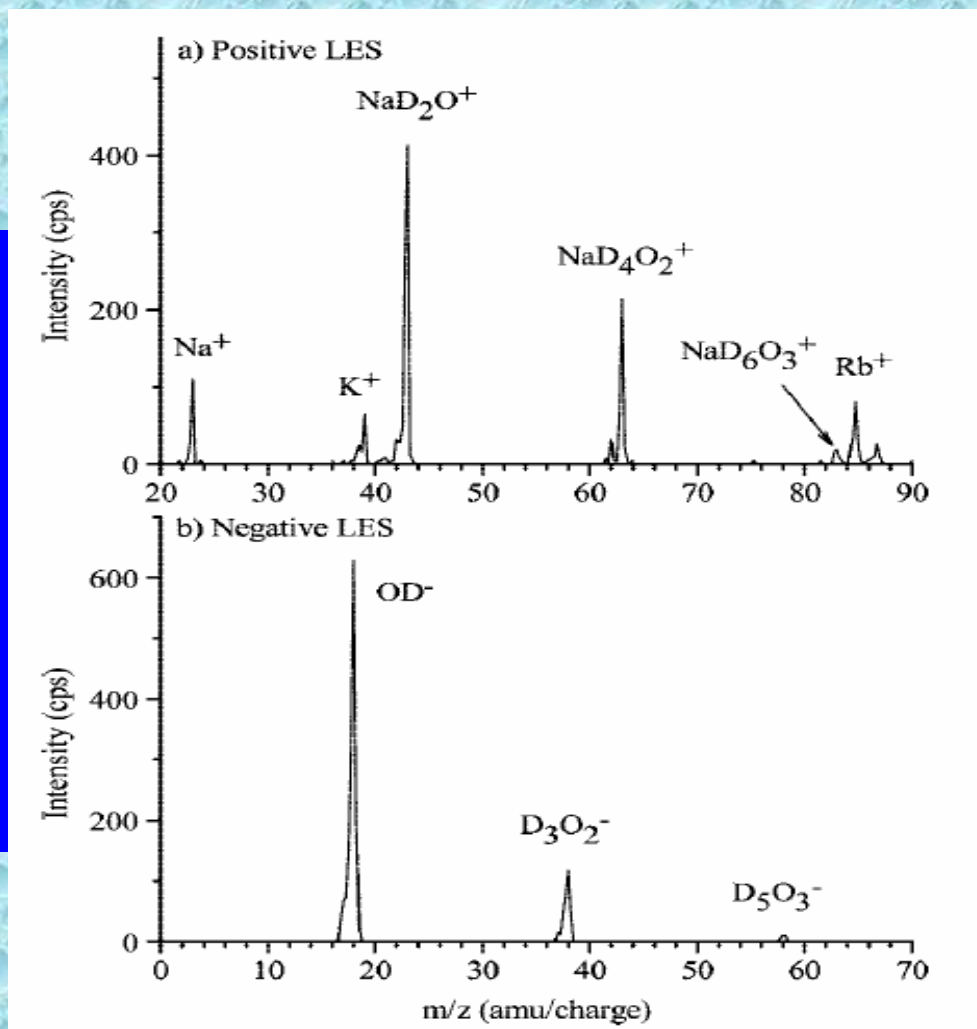
• Experimental Section

1. The experiment was carried out in an ultrahigh vacuum (UHV) surface analysis chamber equipped with instrumentations for LES (low energy sputtering), RIS (reactive ion scattering), TPD, and Auger spectroscopy. The ice films were prepared on the (0001) face of a Ru single crystal. The thickness of the ice films was typically 4 bilayers (BLs, $1 \text{ BL} = 1.1 \times 10^{15} \text{ water molecules cm}^{-2}$) as deduced from TPD.
2. Na atoms were deposited onto the ice film by employing a commercial alkali-metal dispenser and the surface coverage of Na atoms & deposition rate were determined using TPD.
3. Neutral and ionic species present at the ice film surfaces were analyzed by the techniques of Cs^+ RIS and LES, respectively. The incident energy has been kept 20 to 65 eV. The beam incidence and detector angles were fixed at 65 and 55°, respectively with respect to surface normal.

Results

1. LES mass spectra of the species emitted from the Na-adsorbed D₂O-ice film

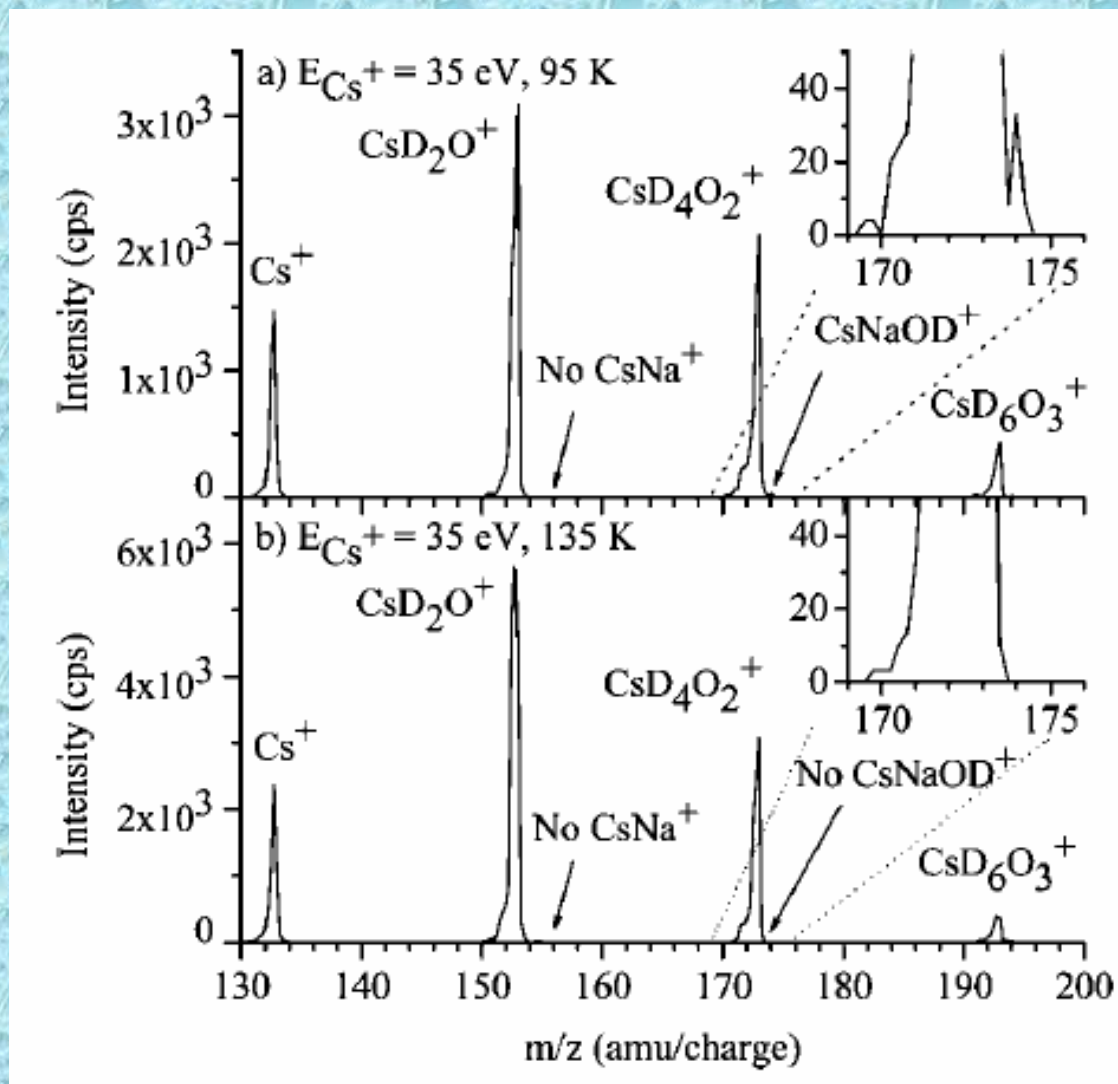
Cs⁺ beam energy = 35 eV



Na⁺ ($m/z = 23$) & other products at $m/z = 23 + 20n$, ($n = 1-3$)

The D₂O-ice film was grown at 130 K to a thickness of 4 BL, and Na atoms were deposited onto the film surface at 95 K for coverage of 0.13 MLE

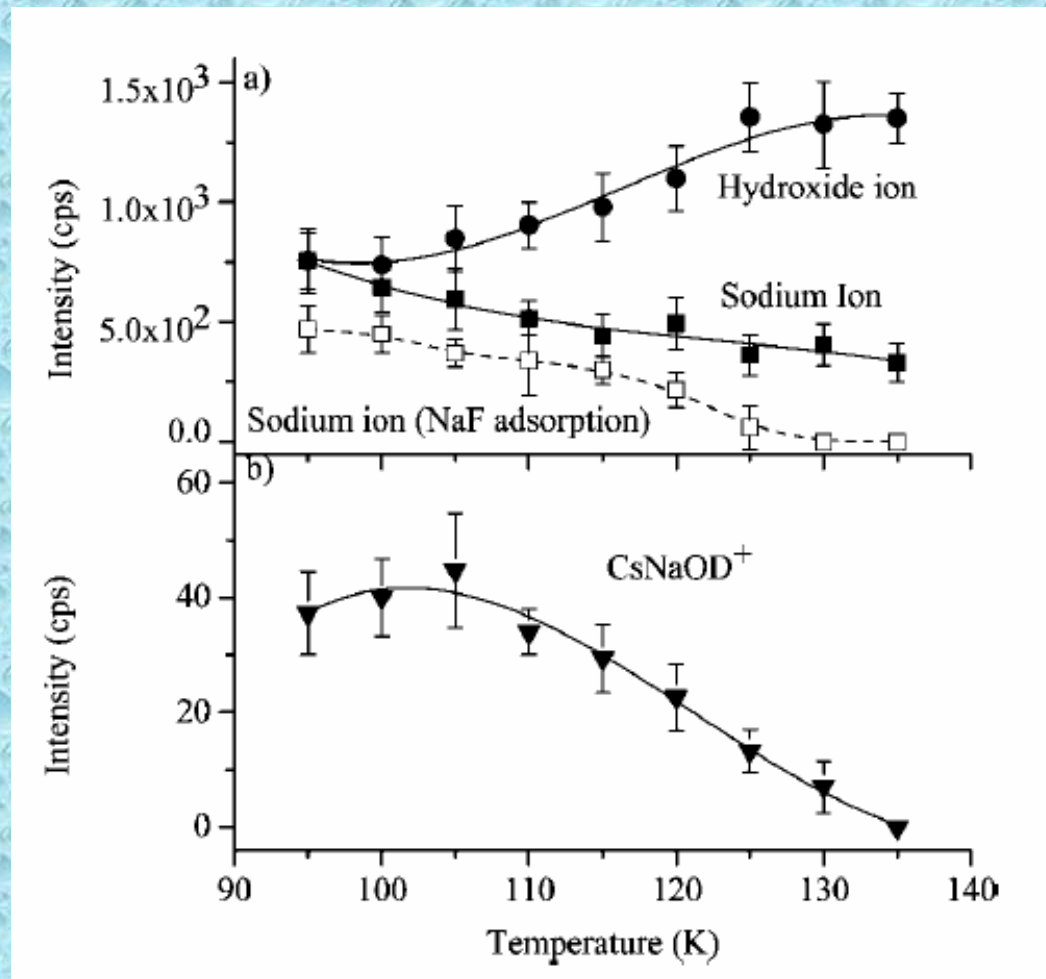
2. RIS mass spectra of the species emitted from the Na-adsorbed D₂O-ice film



Cs^+ ($m/z = 133$) & other products at $m/z = 133 + 20n$, ($n = 1-3$)

No $CsNa^+$ signal is detected

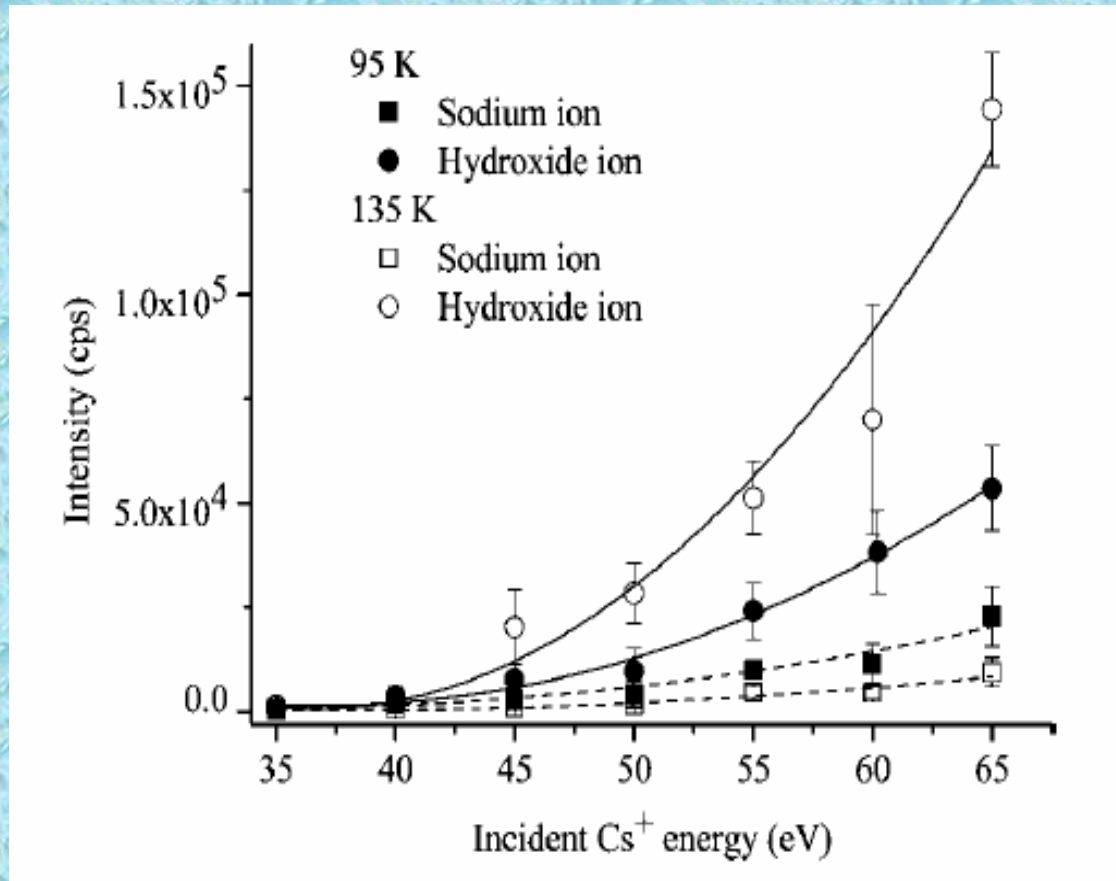
3. Temperature-dependent variation in LES intensities for Na^+ , OD^- and CsNaOD^+ ions



Surface pH increases!!

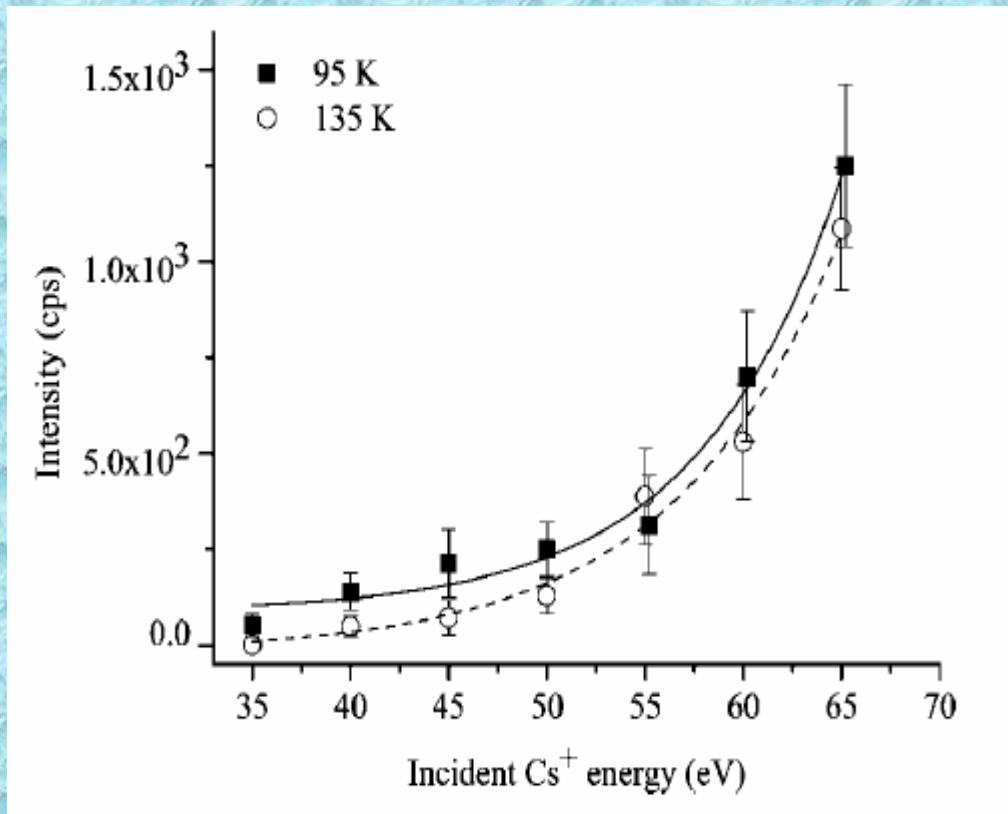
It is assumed that Na^+ & OD^- have the equal populations in the top surface layer at 95 K as ions are usually immobile in ice films at this temperature

4. LES intensities of Na^+ and OD^- measured from Na-adsorbed ice films as a function of incident Cs^+ energy



There is difference in the increase in intensity of Na^+ and OD^-

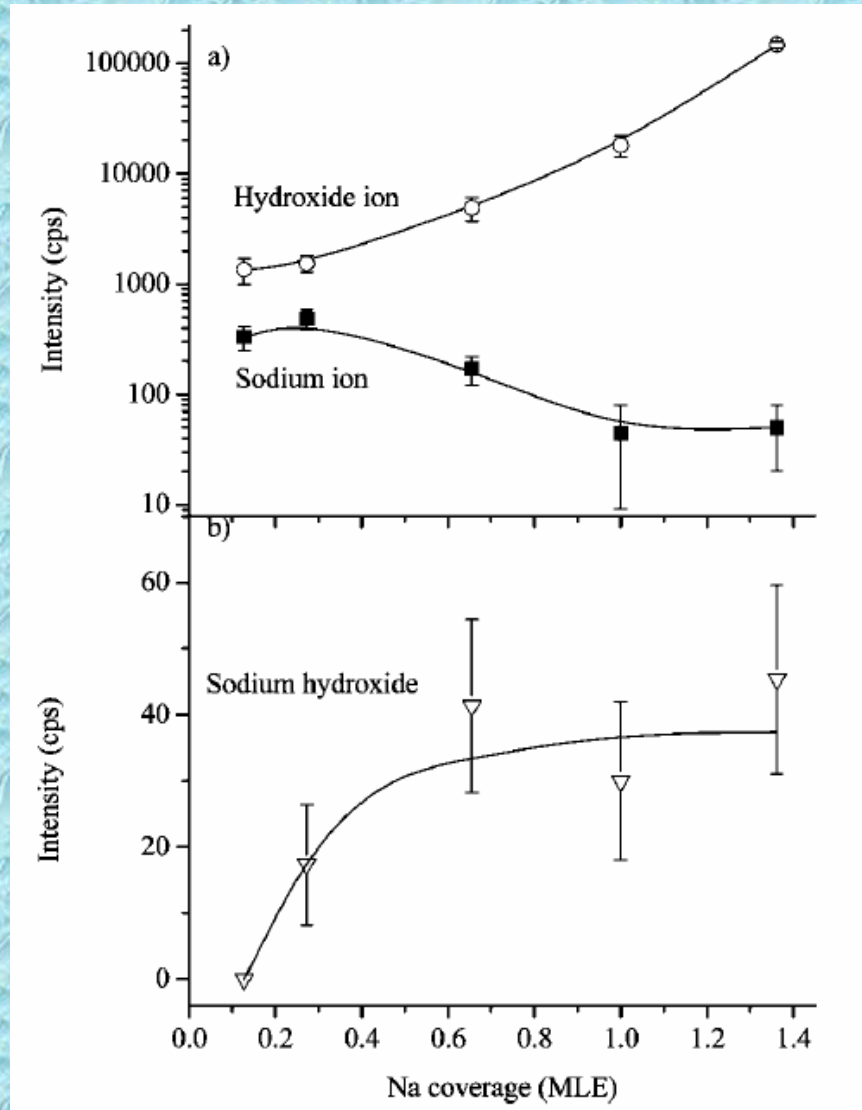
5. RIS signal intensity for NaOD as a function of incident Cs⁺ energy



Total intensity =
CsNaOD⁺ + Cs(NaOD)(D₂O)⁺

NaOD exists at 135 K at Cs⁺ energy > 35 eV !!!!

6. Variation in LES intensities of Na^+ and OD^- as a function of Na coverage on ice film at 135 K



CsNa^+ is not detected

CsNaOD^+ intensity approx. follow Langmuir adsorption kinetics

• Discussion

1. From the diagram at slide no. 5 it is clear the presence of isolated OD^- species at the ice surface.
2. At the higher temperature the diffusion of water molecules and hydration processes can be activated, the OD^- signals increase while the Na^+ signals decrease and that means OD^- & Na^+ move independently which supports that they are created as separated species (slide no. 7).
3. Though weak NaOD signal as CsNaOD^+ is detected in RIS but it disappears upon heating beyond 135 K. Its reappear again upon increase of Cs^+ energy indicates that instead of converting all NaOD to Na^+ & OD^- either they populate the subsurface region or covered by water molecule.
4. The CsNaOD^+ does not come from unhydrated sodium hydroxide layer according Prof. Souda's report that 'The "unhydrated NaOH" layer disappears when the film temperature is raised above 100 K'
5. Sodium ion intensity does not drop all the way to zero even at the highest temperature examined may be due to the fact that NaOD gives rise to extra Na^+ intensity by coalitional dissociation during LES process.
6. The LES intensity of hydroxide ion increases almost exponentially with increasing coverage of Na indicate a change in the electronic property (reduction of work function Φ) or structure of the film surface, which affects the efficiency of ion emission from the surface (slide no. 10).

• In summary

1. Na atoms adsorbed on a D₂O-ice film undergo a hydrolysis reaction to produce Na⁺ and OD⁻ ions as well as NaOD molecules on the surface.
2. The hydrolysis reaction can occur with single Na atoms and no neutral Na clusters on the surface.
3. Na⁺ and OD⁻ ions are efficiently solvated by water molecules to exist as isolated species.
4. NaOD molecules are also efficiently hydrated at high temperature to occupy subsurface positions.
5. OD⁻ ion tends to reside at the ice surface at elevated temperature, whereas Na⁺ ion migrates toward the film interior.

The background of the slide is a dense, repeating pattern of light blue water droplets of various sizes, creating a textured, refreshing appearance.

Thank you