Asymmetric transport efficiencies of positive and negative ion defects in amorphous ice

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Phys. Rev. Lett. 2012, *108*, 226103

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CY08D021
18-08-12

Introduction:

❖ Ice surface provides unique enviromnment for solid conductor like hydronium (H_3O^+) and hydroxide (OH^-) ions.

❖ These species exist as positive (H_3O^+) and negative (OH^-) ion defects in the ice lattice where they are in proton-transfer equilibrium with constituting water molecules.

❖The properties of ion defects in ice are an appealing subject of study in physics, environmental sciences, astrophysics, and chemistry owing to the ubiquity and importance of ice in natural environments.

❖ The mobility of H^+ on ice is ten times higher than that of OH^- ion.

❖ There exists plenty of reports on the mobility of the different charges on the ice surfaces.

❖ Based on these reports, the conduction mechanism of H_3O^+ is well understood.

❖ H_3O^+ moves via Grotthuss mechanism along the hydrogen bond chain of water.

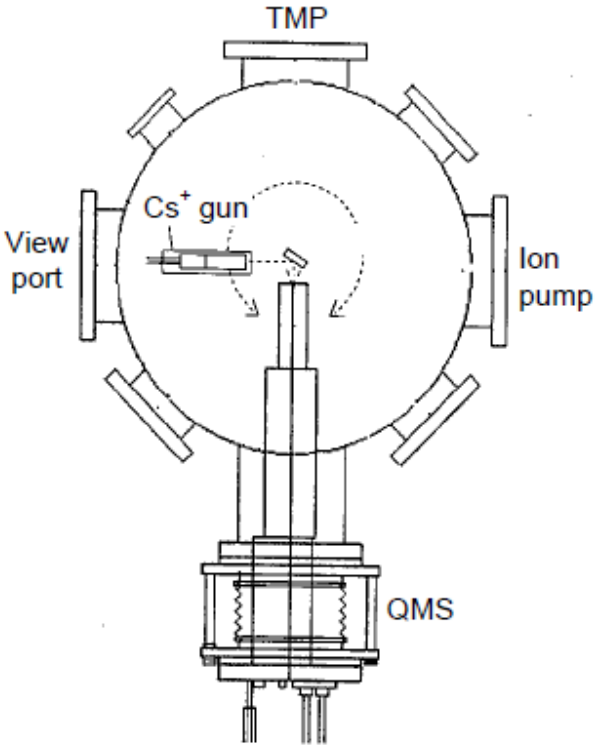
❖ However, the proper conduction mechanism of the positive and negative ion defects are not well understood so far.

❖ The question remains unanswered is, “What is the relative efficiency of charge transport by positive and negative ion defects?”

❖ In view of these, the present article reports the transport distance of hydronium and hydroxide ion by placing the hydroinum ion at the surface and the its counter base (and vice versa) at the bulk of ice film.

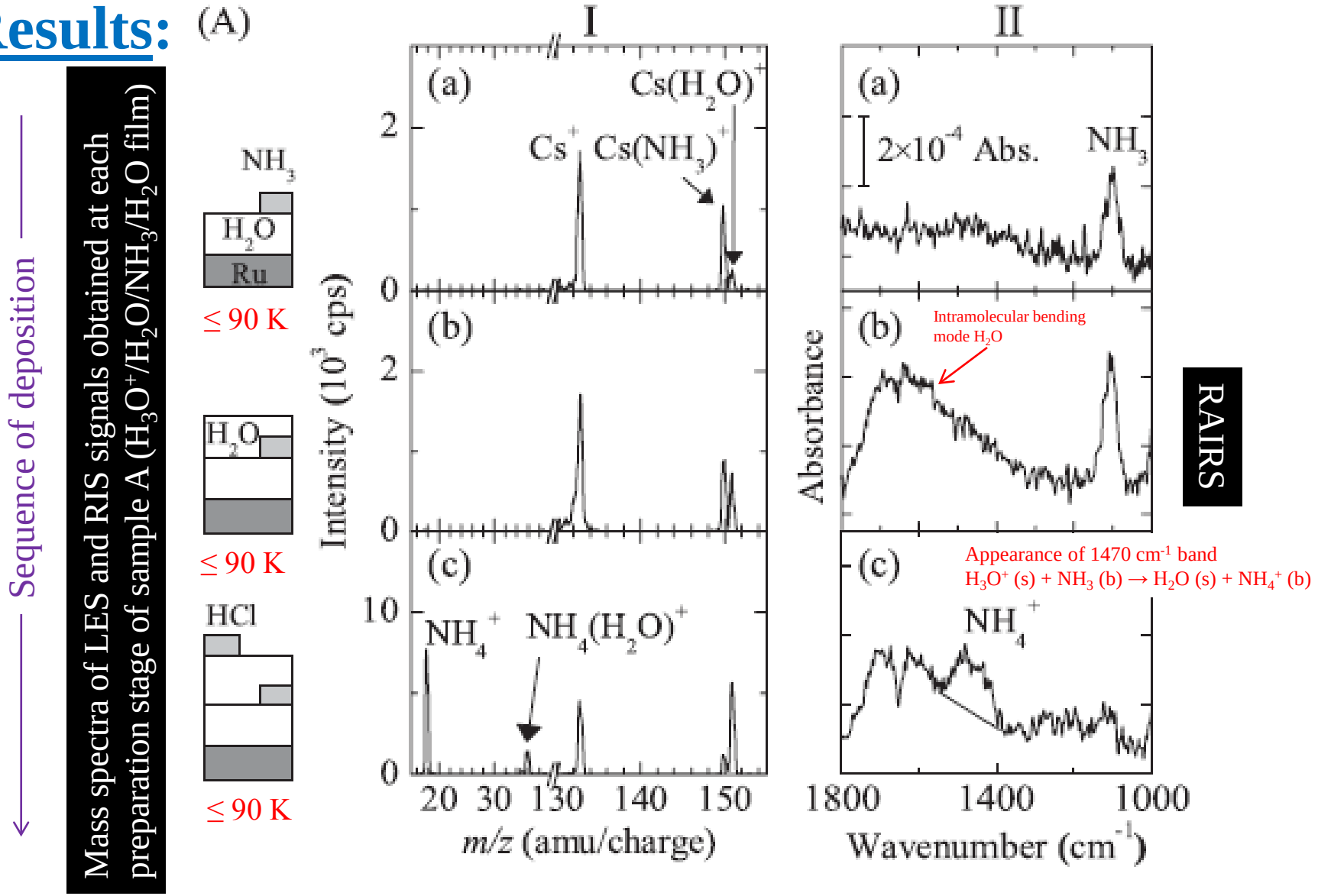
Experimental section:

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 RAIRS. The ice films were prepared on the (0001) face of a Ru single crystal. The thickness of the ice films was typically 50 bilayers (BLs, 1 BL = 1.1 × 10^{15} water molecules cm^{-2}) as deduced from TPD.
2. Neutral and ionic species present at the ice film surfaces were analyzed by the techniques of 30 eV Cs^+ RIS and LES, respectively.

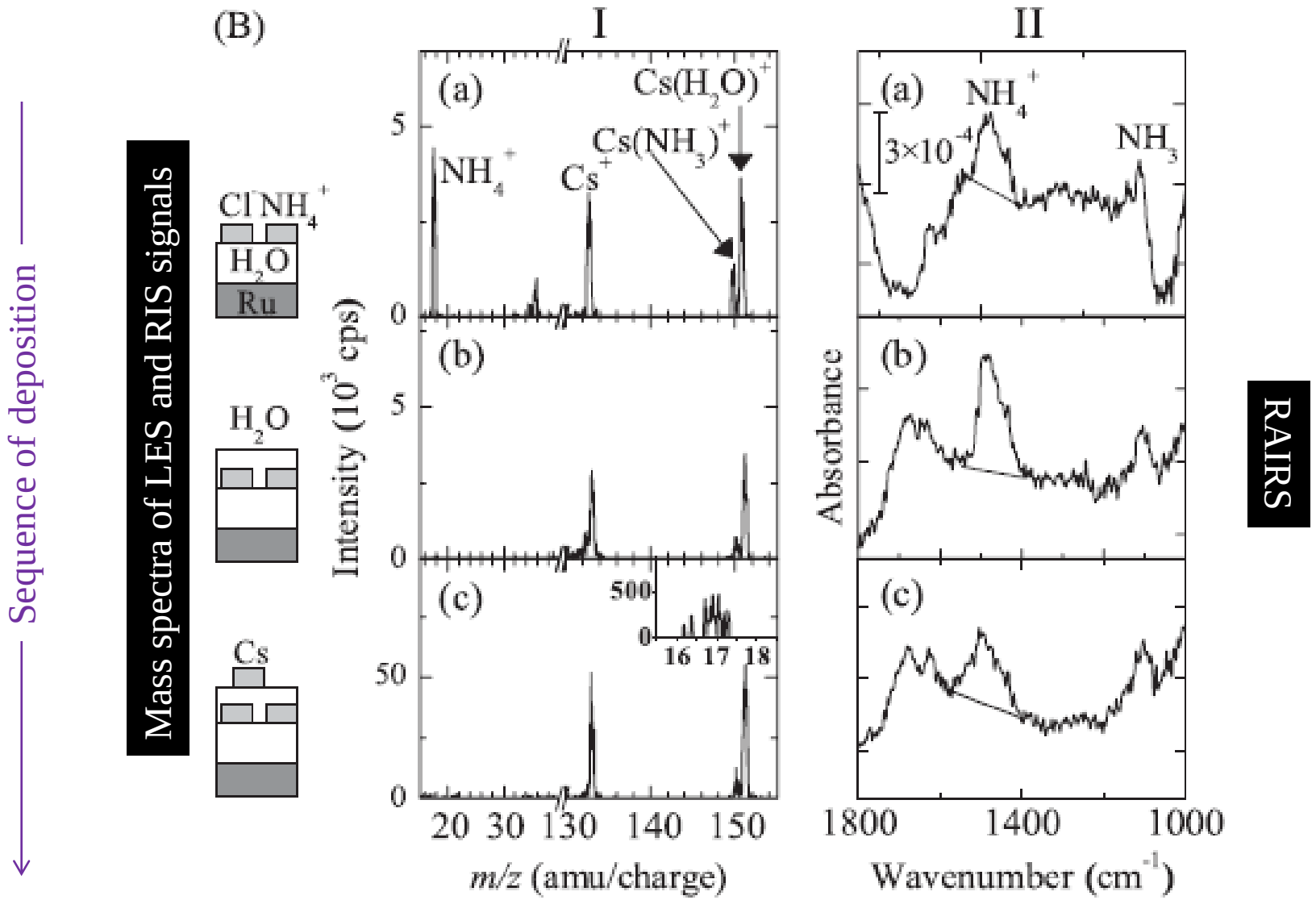


3. HCl and NH_3 vapors were introduced into the chamber through separate leak valves and guided close to the sample surface through tube dosers. Cs atoms were deposited onto the sample by using an alkali metal dispenser.

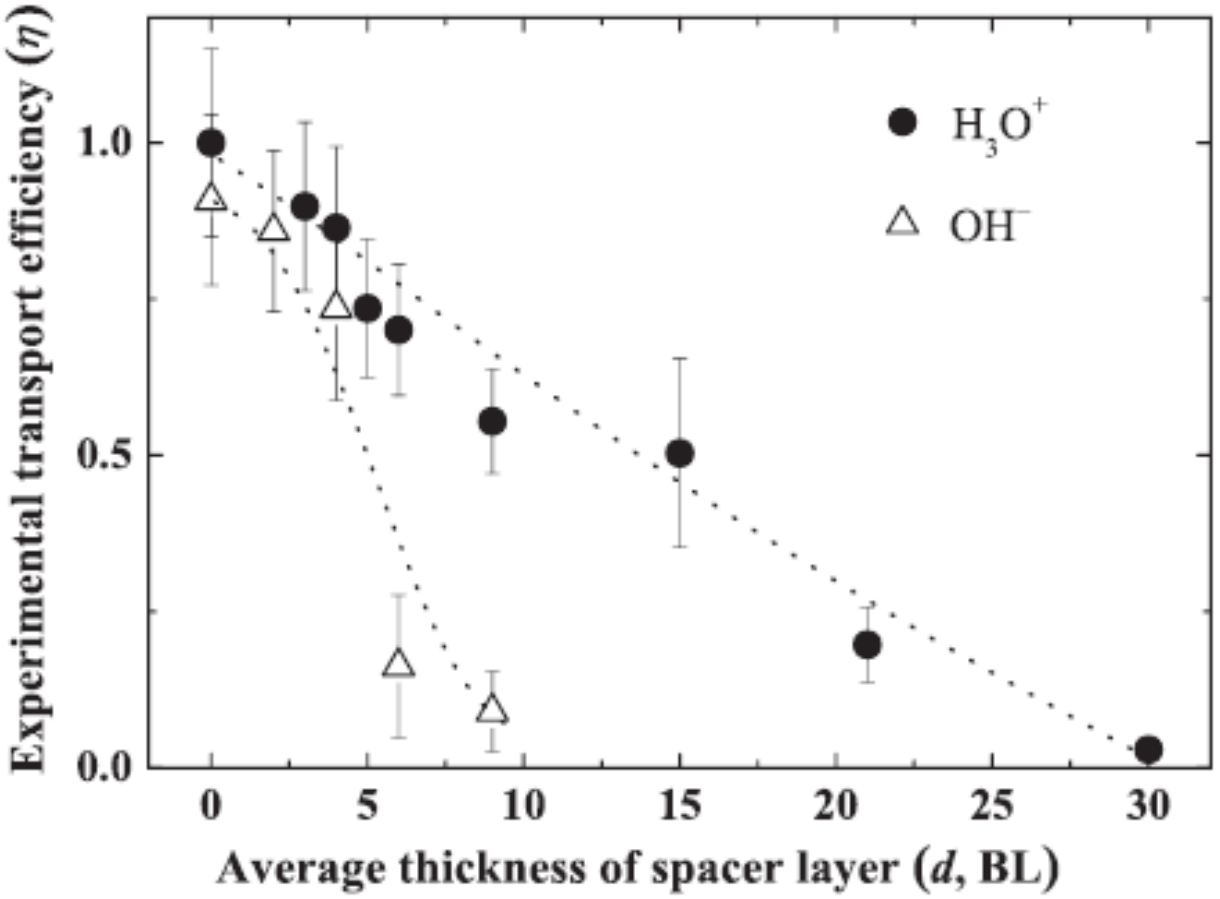
Results:



(a) An H_2O-ice film (50 BL thickness) was grown on Ru(0001), and NH_3 was adsorbed on the surface for a coverage of 0:3 ML. (b) An H_2O film (3 BL) was overlaid onto the surface. (c) HCl was adsorbed for 0:2 ML at 90 K to generate H_3O^+ on the surface. The Ru substrate temperature was kept at 90 K or below during the construction of the sample.



(a) NH_3 (0.30 ML) and HCl (0.25 ML) were coadsorbed on an amorphous H_2O-ice film (50 BL thickness) to generate NH_4^+. (b) An H_2O overlayer (3–4 BL) was added to make an NH_4^+-sandwich ice film. (c) OH species (0.15 ML) were provided by the hydrolysis of Cs atoms on the surface.



Experimental measurement for the transport efficiencies of H_3O^+ (•) and OH^- (Δ) as a function of H_2O spacer thicknesses (d). The temperature was ~80 K during the experiment.

$$\eta(H_3O^+) = \frac{\Delta\theta_s(H_3O^+)}{\theta_s^{\text{initial}}(H_3O^+)} = \frac{\Delta\theta_b(NH_3)}{\theta_s^{\text{initial}}(HCl)}$$

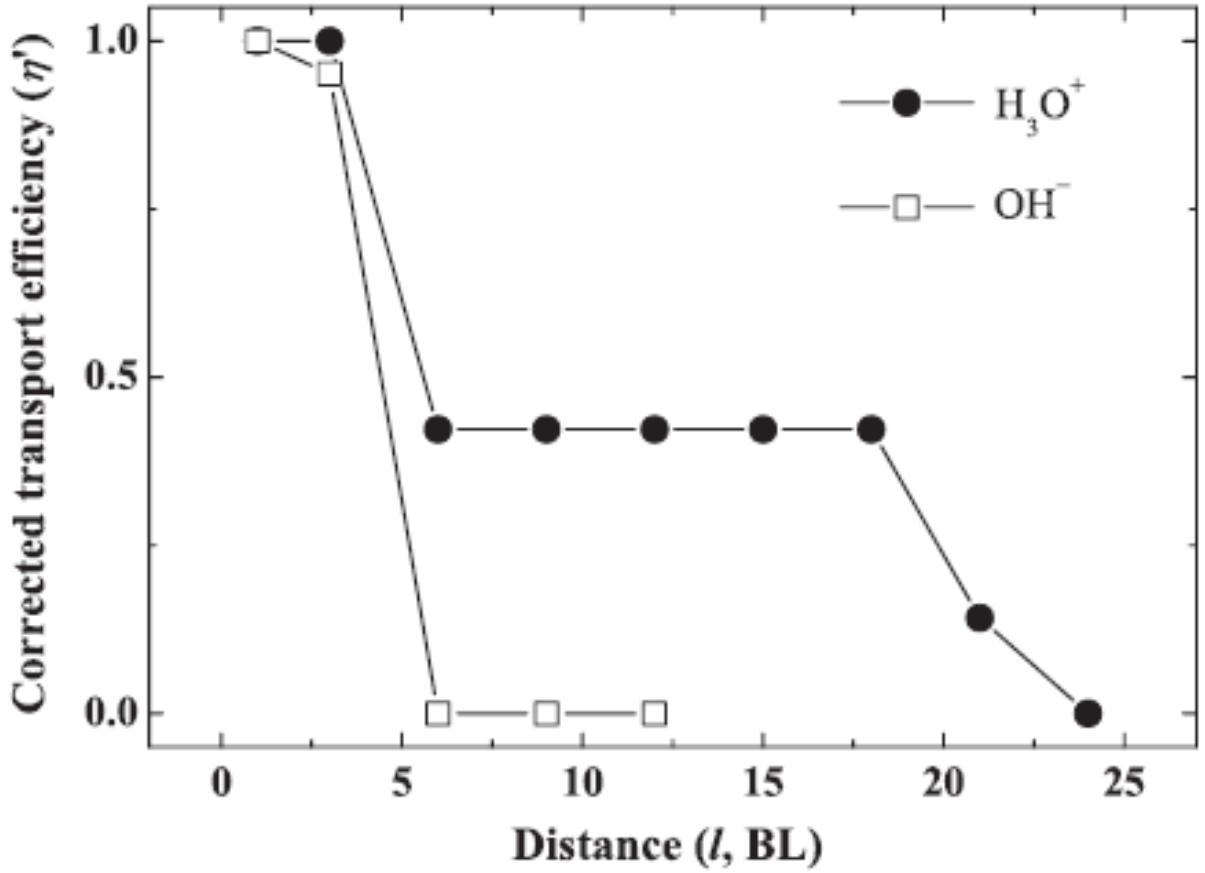
$$\eta(OH^-) = \frac{\Delta\theta_s(OH^-)}{\theta_s^{\text{initial}}(OH^-)} = \frac{\Delta\theta_b(NH_4^+)}{\theta_s^{\text{initial}}(Cs)}$$

η: Transport efficiency

η of H_3O^+ is equivalent to the NH_3 population as measured by RAIRS

Caution: (a) Deposition of water molecules in a random way.

(b) Difference of sticking probability of water on H_2O (~1), NH_3 (~0.14), NH_4+(~1).



The corrected transport efficiency (η') of H_3O^+ (•) and OH^- (□) *as a function of the separation distance (l) of acid* and base.

$$\eta(d) = \sum_{l} P_{\text{spacer}}(l;d)\eta'(l)$$

P_{spacer} *(l;d)* is the thickness distribution function of a spacer film after making the correction for surface NH_4^+ species.

Discussion:

1. It is well known that H_3O^+ moves via a proton hopping relay from H_3O^+ to the neighboring water molecules along the hydrogen bond chain, and that the associated energy barrier is very small.
2. For OH^- transport an analogous mechanism of proton relay does not operate, and as per the present observation that proton transfer does not occur between the separated NH_4^+ and OH^- species.
3. These measurement were performed in the amorphous ice (ASW) where defects are high. In case of crystalline ice (CW), the transport distance of hydronium ion will increase due to periodic nature of the surface. The OH^- transport will be even more difficult in CW than in ASW due to restricted molecular diffusion.
4. Hydronium and the hydroxide ion preferentially stay on the ice surface than bulk due to the thermodynamic stability.
5. In the experiment, the hydronium and hydroxide ions were produced by the hydrolysis of HCl and Cs which are exothermic. This energy may trigger local heating which in turn assist the ion transport in the short distance.
6. Since the energy release is higher for OH^- for than hydronium ion, this energy may push the hydroxide ion more than hydronium ion. But the observation is just the opposite. This implies that the energy release does not promote the transport of the ions.

Summary and conclusion:

1. In amorphous ice at low temperature H_3O^+ migrates across a much longer distance than OH^- due to an efficient proton relay involving H_3O^+.

2. The acid-base reactions involving H_3O^+ may be important for the chemistry of ice in terrestrial and space environments at low temperature whereas the activity of OH^- is less important except for its role as a proton-transfer inhibitor.

3. The asymmetric mobility of H_3O^+ and OH^- may be able to provide a better understanding for the charge imbalance phenomena of ice, including its thermoelectric effect and the charging of ice surfaces.

Thank you

- ✓ Plan for the experiment is very important.
- ✓ There are several possibility exists. However, without proper instrument functioning none of these will be feasible.