Transport and Surface Accumulation of Hydroniums and Chlorides in an Ice Film. A High Temperature (140−180 K) Study

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Introduction:

Information about the mobility of small molecules in ice and their partition behavior between the ice surface and interior is very important to understand the heterogeneous atmospheric chemistry of ice particles.

The transport of hydronium ions in ice.

The partition behavior of hydroniums between the surface and interior of ice was investigated for ice samples prepared in the form of thin films or nanoparticles at low temperature (≤140 K).

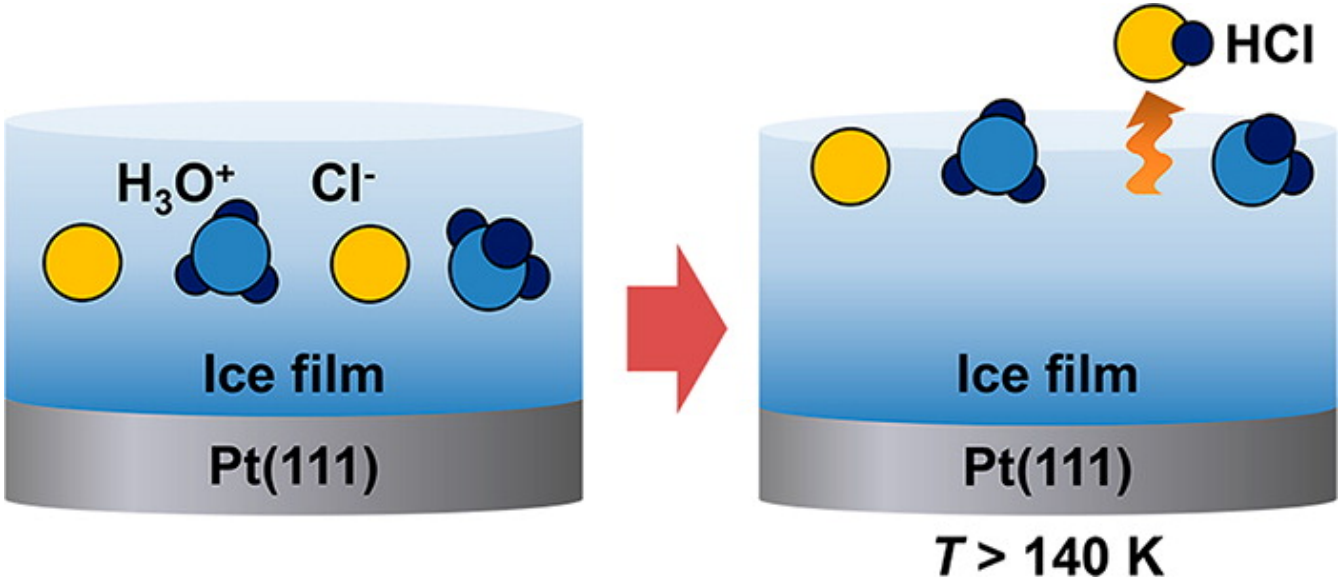
Segregation properties of other ions --determined largely by ion specificity.

An experimental approach widely used in the study of ice surface properties is to grow thin films of ice on metal substrates at low temperature in an ultrahigh vacuum (UHV) and to investigate the film surface with surface spectroscopic techniques.

It was demonstrated that thermal desorption spectrometry employing a rapid heating ($\sim 10^5$ deg s^{-1}) method can be used to examine the H/D exchange kinetics in an ice film near the melting temperature of ice.

In the present work they studied the transport properties of hydronium, chloride, and water in an ice film for temperatures in the range 140−180 K in UHV.

Experimental Section:



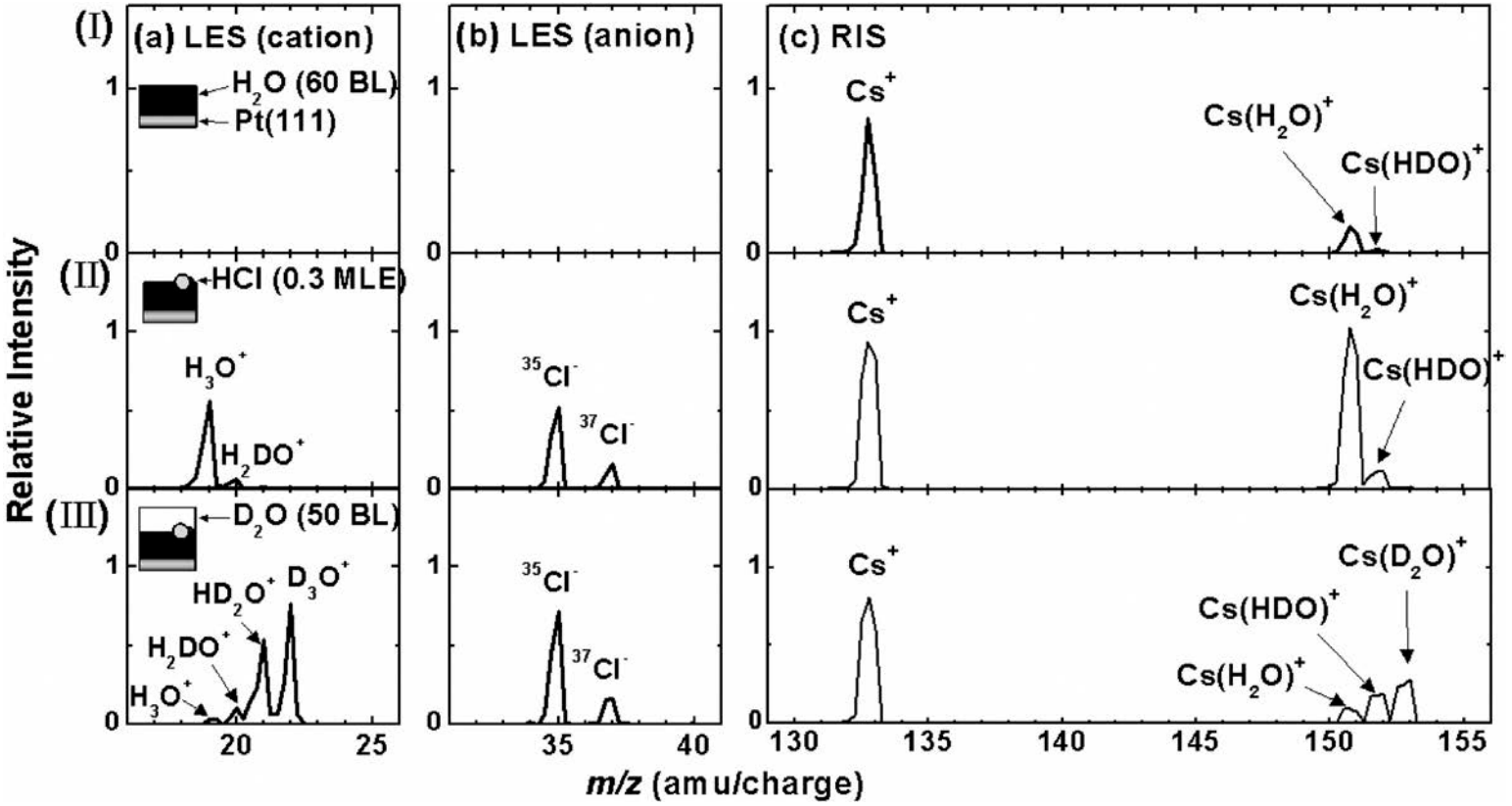
Techniques used for the investigation…….

Reactive ion scattering (RIS)

Low energy sputtering (LES)

Temperature programmed desorption (TPD)

Results and Discussion:



(a) Positive-ion LES spectrum, (b) negative-ion LES spectrum, and (c) RIS spectrum measured at each preparation step of an HCl-sandwich ice sample. The sample was prepared in the following sequence: (I) a crystalline H_2O film (~60 BL thick) was grown on Pt(111). (II) HCl was adsorbed onto the film for a coverage of 0.3 MLE. (III) Addition of an amorphous D_2O overlayer (~60 BL thick) at 95 K completed an HCl-sandwich sample. The spectra III(a)–(c) were taken after brief heating of the HCl-sandwich sample at ~160 K. All the spectra were measured at 95 K with a Cs^+ beam energy of 35 eV.

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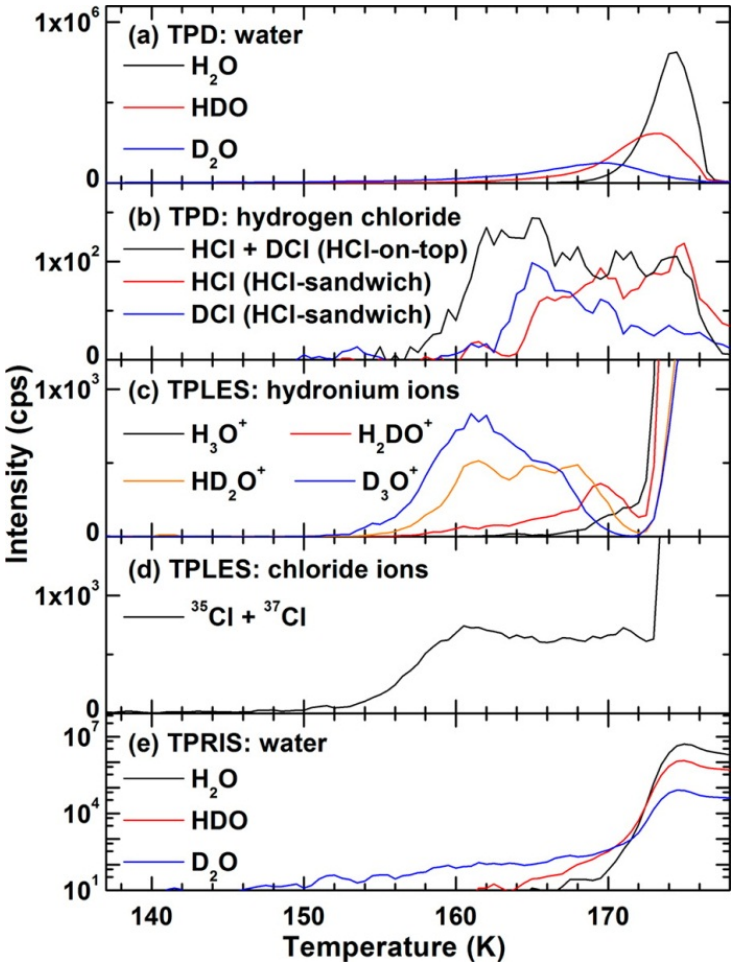

TPD, TPLES, and TPRIS results obtained for an HCl-sandwich ice film having a structure of amorphous D_2O (~70 BL)/HCl (0.3 MLE)/crystalline H_2O (~120 BL)/Pt(111). (a) TPD curves of water isotopomers (D_2O, HDO, and H_2O). (b) TPD curves of hydrogen chlorides ($H^{37}Cl$ and $D^{37}Cl$). For comparison, a TPD spectrum of hydrogen chloride measured from an "HCl-on-top" sample [HCl (0.3 MLE)/amorphous D_2O (~70 BL)/crystalline H_2O (~120 BL)/Pt(111)] is also shown in the black curve. (c) TPLES measurements of various hydronium isotopomers on the surface. (d) TPLES measurements of chlorides (sum of $^{35}Cl^-$ and $^{37}Cl^-$ intensities). (e) TPRIS measurements of water isotopomers on the surface.

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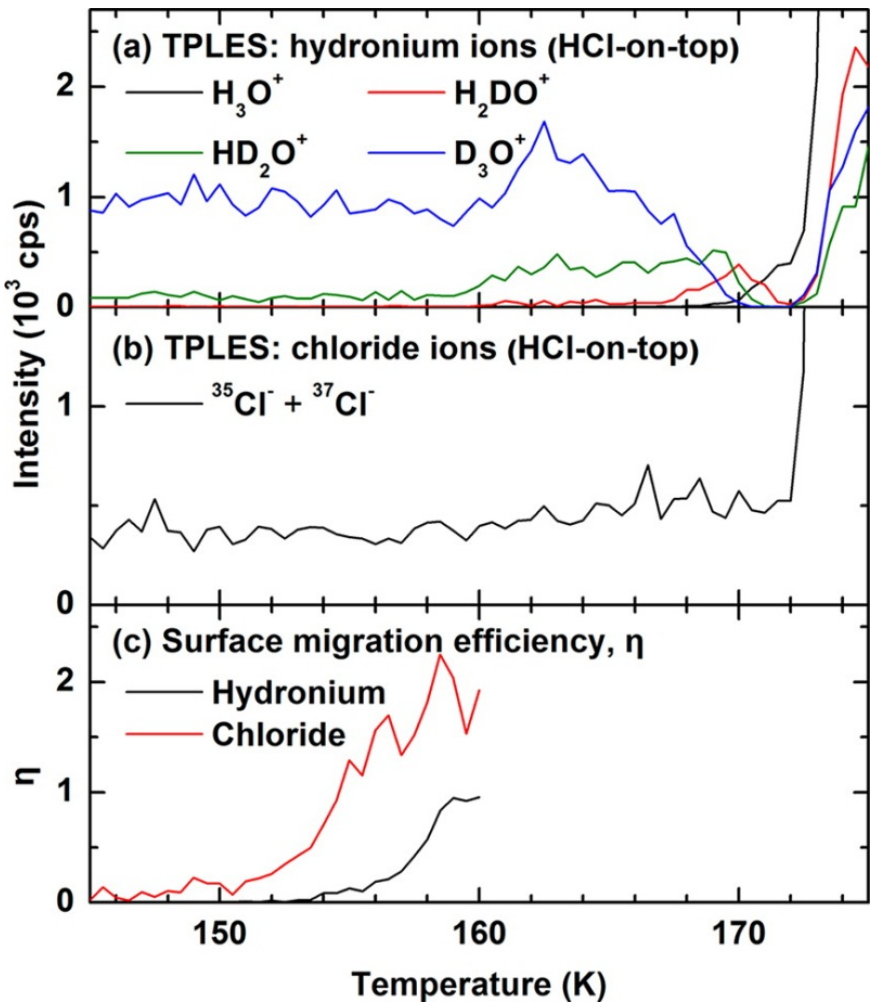

(a) TPLES intensity of hydronium isotopomers measured on an HCl-on-top sample [HCl (0.3 MLE)/amorphous H_2O (~70 BL)/crystalline H_2O (~120 BL)/Pt(111)]. (b) TPLES intensity of chlorides on the same sample. (c) Surface migration efficiency (η) of hydroniums and chlorides in an HCl-sandwich sample [D_2O (~70 BL)/HCl (0.3 MLE)/H_2O (~120 BL)/Pt(111)].

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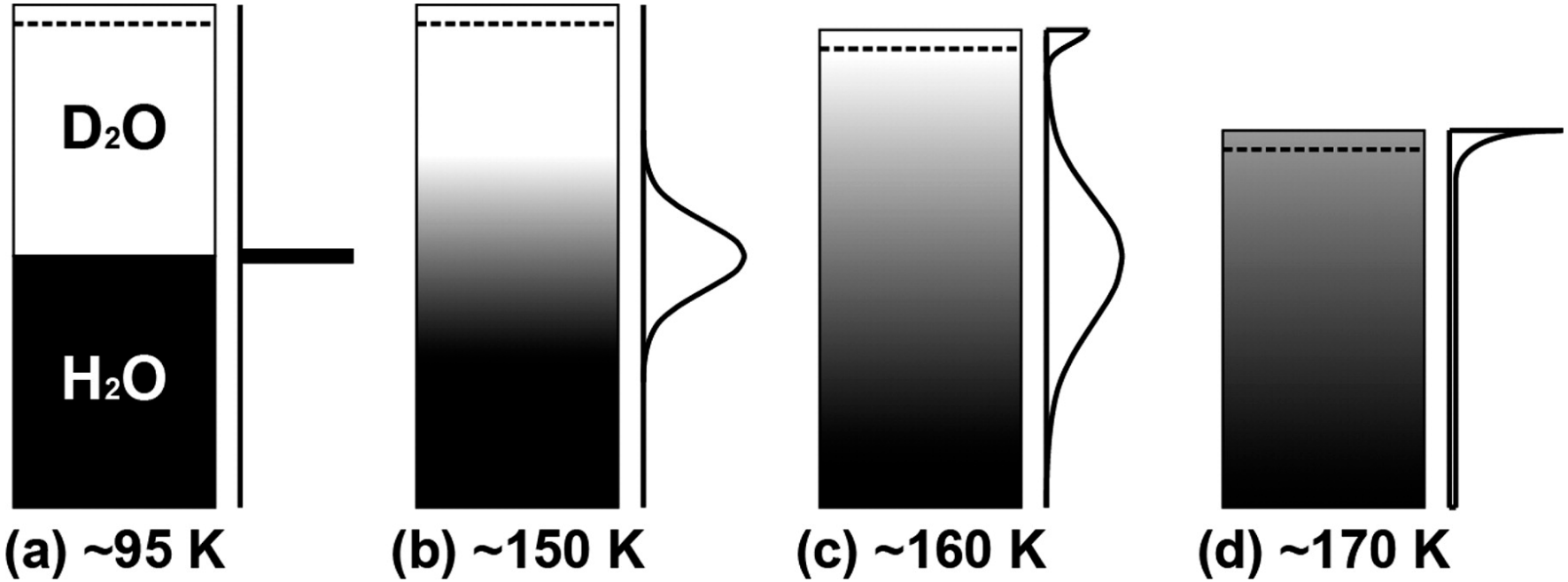

Schematic illustration for the transport of hydronium, chloride, and water in an HCl-sandwich ice film during an increase in temperature. The box depicts an ice film, where the upper D_2O region is shown in white and the lower H_2O region, in black. The profile drawn next to the box indicates the density distribution of hydroniums or chlorides. The dotted line in the upper part of the box symbolizes the boundary between the surface and interior regions of ice.

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Summary and Conclusion:

They investigated the transport and partition behaviors of hydroniums and chlorides in crystalline ice films at temperatures of 140−173 K, which is below a roughening transition temperature of the films on Pt(111).

The appearance and disappearance kinetics of hydroniums, chlorides, and water isotopomers at the ice surfaces were measured by using the TPLES and TPRIS methods. TPD experiments provided complementary information by monitoring gas desorption from the surface.

The study shows that hydroniums and chlorides spontaneously migrate from the interior of ice to the surface.

The present discovery expands upon the knowledge gained from previous studies performed at temperatures below 140 K and it shows that the surface segregative properties of hydroniums and chlorides appear for crystalline ice at higher temperatures as well.

The accumulation of hydroniums and chlorides at an ice surface may have important consequences for acid−base chemistry and heterogeneous atmospheric reactions at ice surfaces.

Future Possibilities:

Similar study can be carried out with ammonia at the interface of D_2O/H_2O. It is known that hydroxyl prefer to stay on the surface. What will be the fate of NH_4^+?

Heterogeneous reaction between HCl and ClONO2 can be looked at relatively higher temperature (~150-160 K) on ice surface which is of relevance to polar stratospheric chemistry.