Energy Barrier of Proton Transfer at Ice Surfaces

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J. Chem. Phys. **2010**, *133*, 044709

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CY08D021
28-08-10

Introduction

- Proton transfer on ice surface was under investigation.
- It is known that proton tries stay on surface rather than interior.
- Proton activity was greatly enhanced on the surface ice nanocrystal relative to the ice interior.
- Proton was deposited using HCl vapor.
- The vertical proton transfer from surface to the film interior is inefficient at 95 K.
- At 130 K, sandwiched proton moves surface and triggers H/D exchange.
- It appears from the observation that proton transfer occurs very easily on ice surface with negligible energy barrier.
- But it is true that if proton is stabilized on ice surface then it has to overcome certain amount energy barrier for the release of proton.
- Determination of this activation energy is the purpose of this study.

Experimental

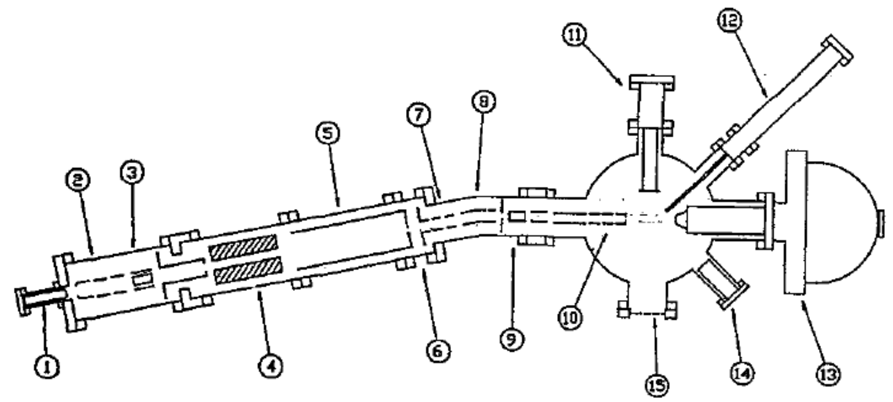
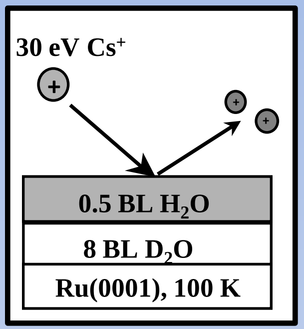
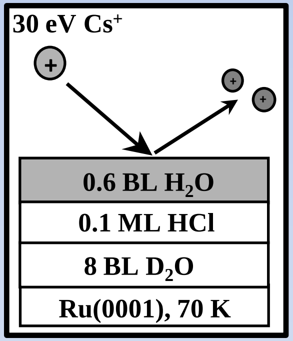


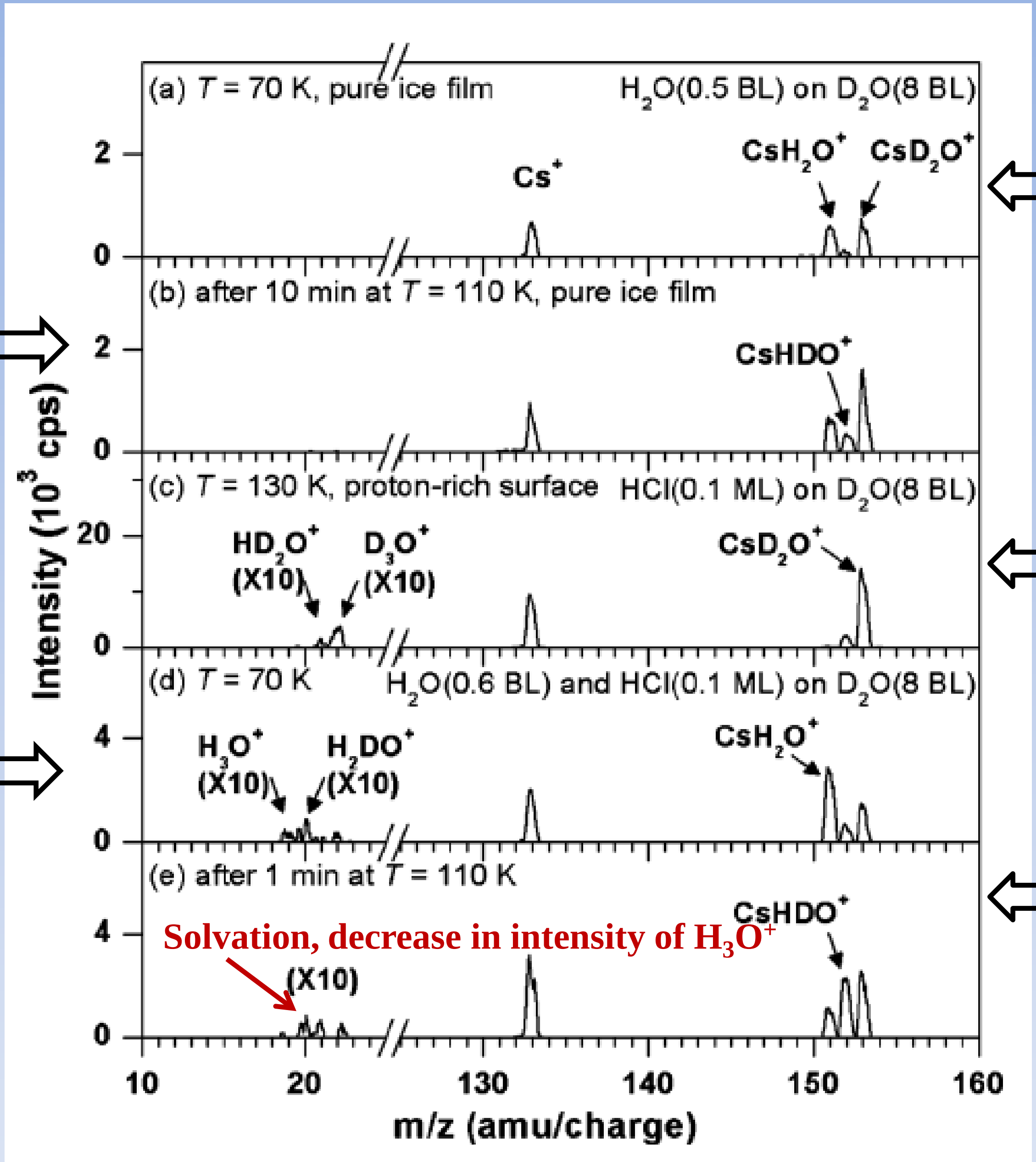
FIG. 1. Schematic diagram of ion beamline and UHV analysis chamber. The components labeled are (1) ion source; (2) extraction and acceleration lenses; (3) *x,y*-deflector; (4) Wien velocity filter; (5) flight tube; (6) gate valve; (7) Einzel lens; (8) 12° deflector for neutrals elimination; (9) *x,y*-deflector; (10) deceleration and focusing lenses; (11) quadrupole mass spectrometer; (12) UV source; (13) 180° hemispherical energy analyzer; (14) Auger electron gun; and (15) viewport.

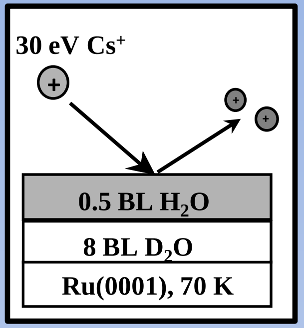
1. Experiments were performed in the above instrument.
2. Ice film (D_2O) was grown on the Ru(0001) surface.
3. Temperature was maintained at 135 K (this will create polycrystalline ice with mixed domains of amorphous and crystalline structure).
4. The ice film was typically 8 BL (BL= bi-layer).
5. Ice film surface was analysed using RIS (reactive ion scattering) and LES (low-energy sputtering).

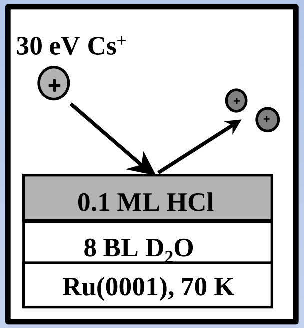
Results

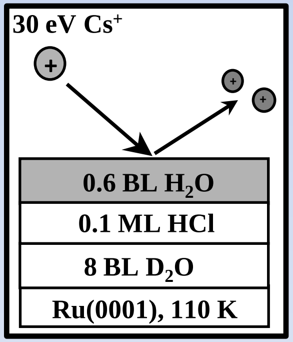






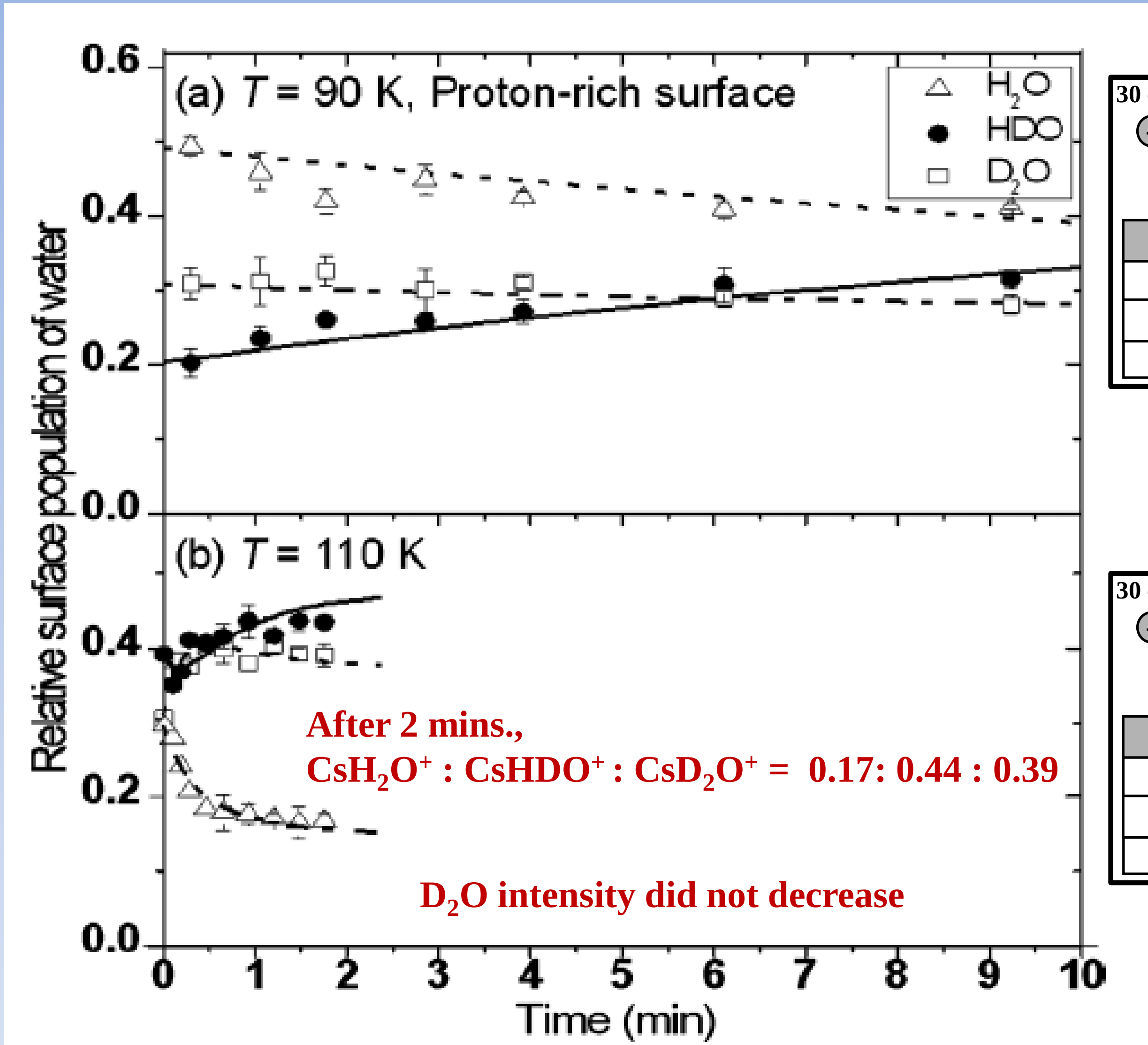


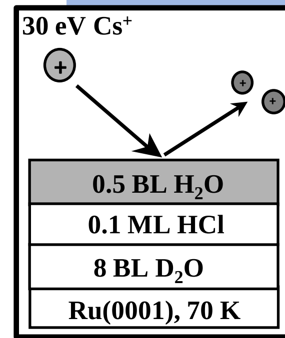


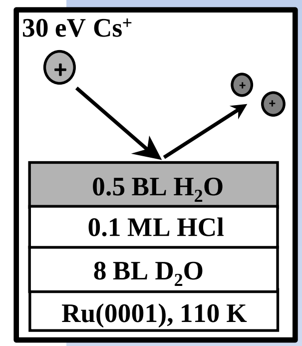


For 1 (C), $D_3O^+ + H_2O = D_2O + H_2DO^+$

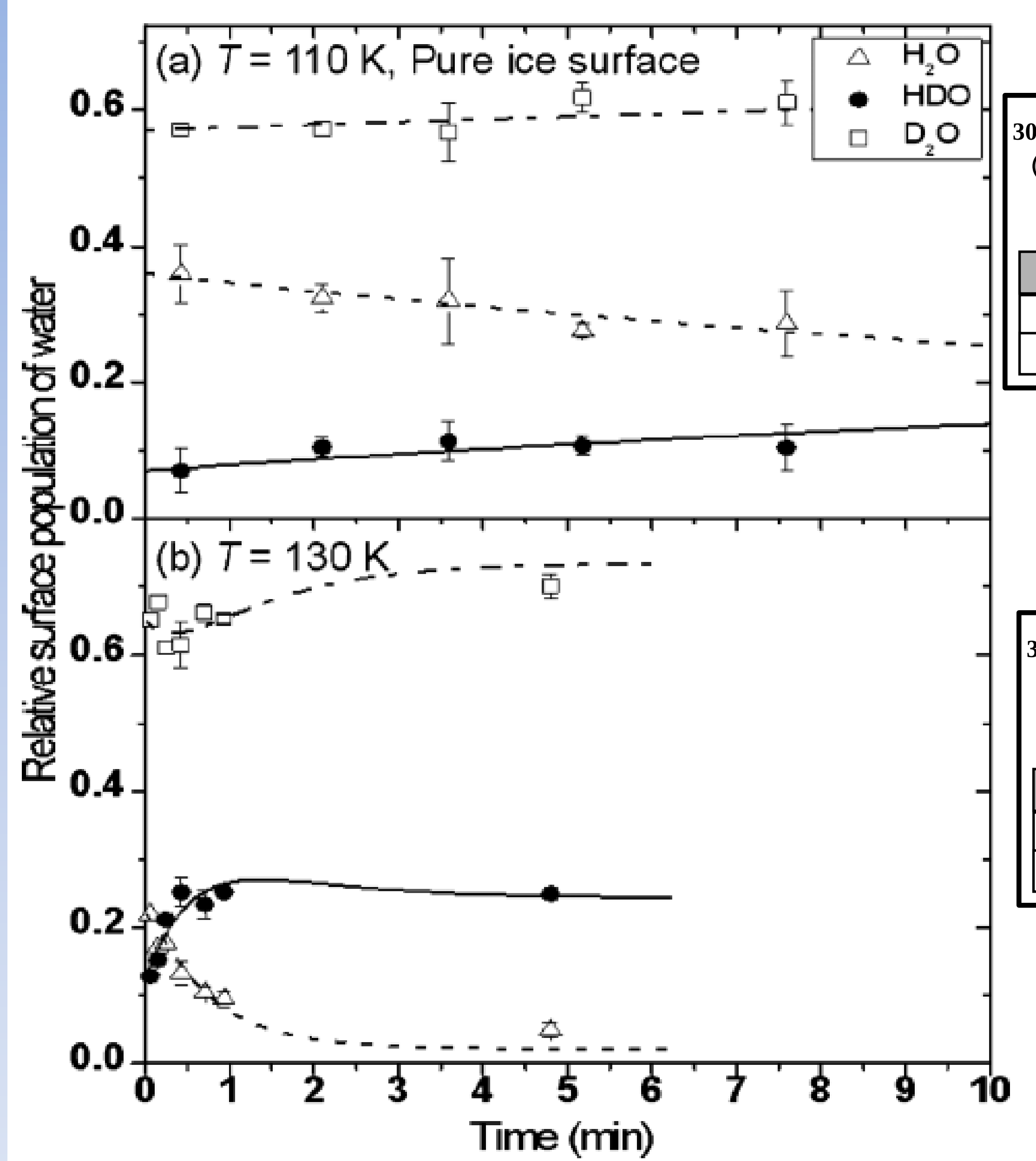
At 1 (e), $CsH_2O^+ : CsHDO^+ : CsD_2O^+ = 0.19 : 0.41 : 0.4$

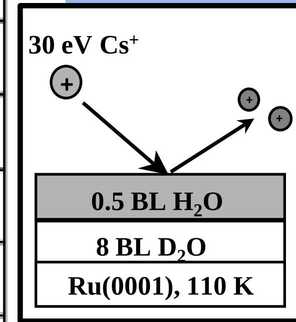


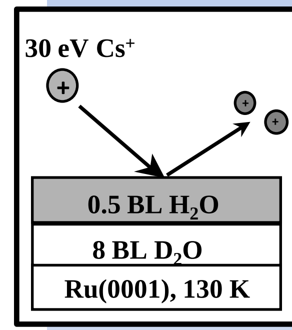




The kinetic measurement on doped ice films

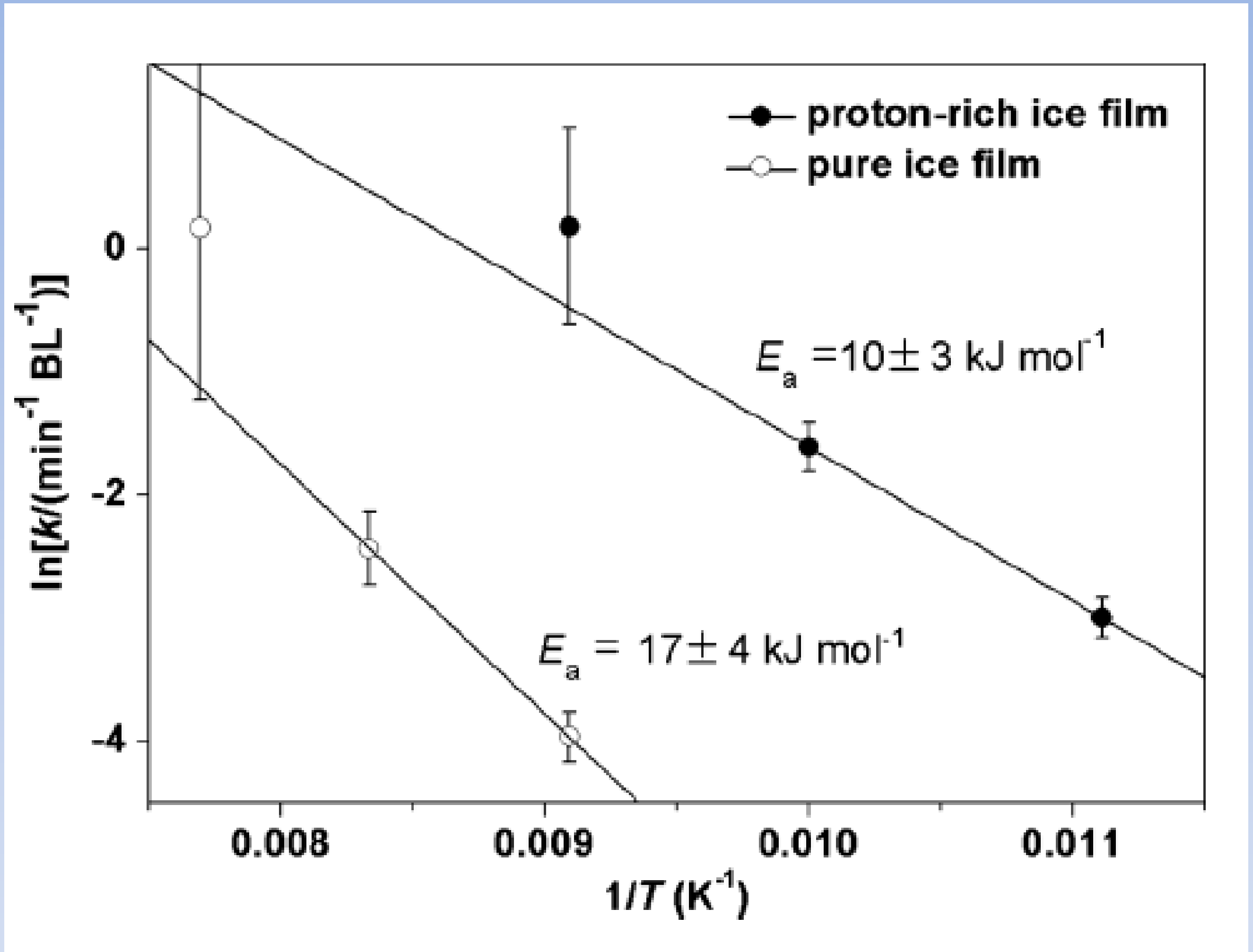






The kinetic measurement on pure ice films

$$H_2O + D_2O \underset{k_b}{\overset{k_f}{\rightleftarrows}} 2HDO$$



Arrhenius plot of the H/D exchange rate coefficients *k* on ice film surfaces.

H/D exchange on pure ice surface takes place first by ion pair formation $2H_2O \leftrightarrow H_3O^+ + OH^-$ followed by $D_3O^+ + H_2O = D_2O + H_2DO^+$

Discussion

$$H_2O\ (s) + D_2O\ (s) \underset{\frac{1}{4}k}{\overset{k}{\leftrightarrow}} 2HDO\ (s) \text{ ------- } (1)$$

According to law of mass conservation at the outermost surface,

$$[HDO] - [HDO]_0 = -2([H_2O] - [H_2O]_0) = -2([D_2O] - [D_2O]_0)$$

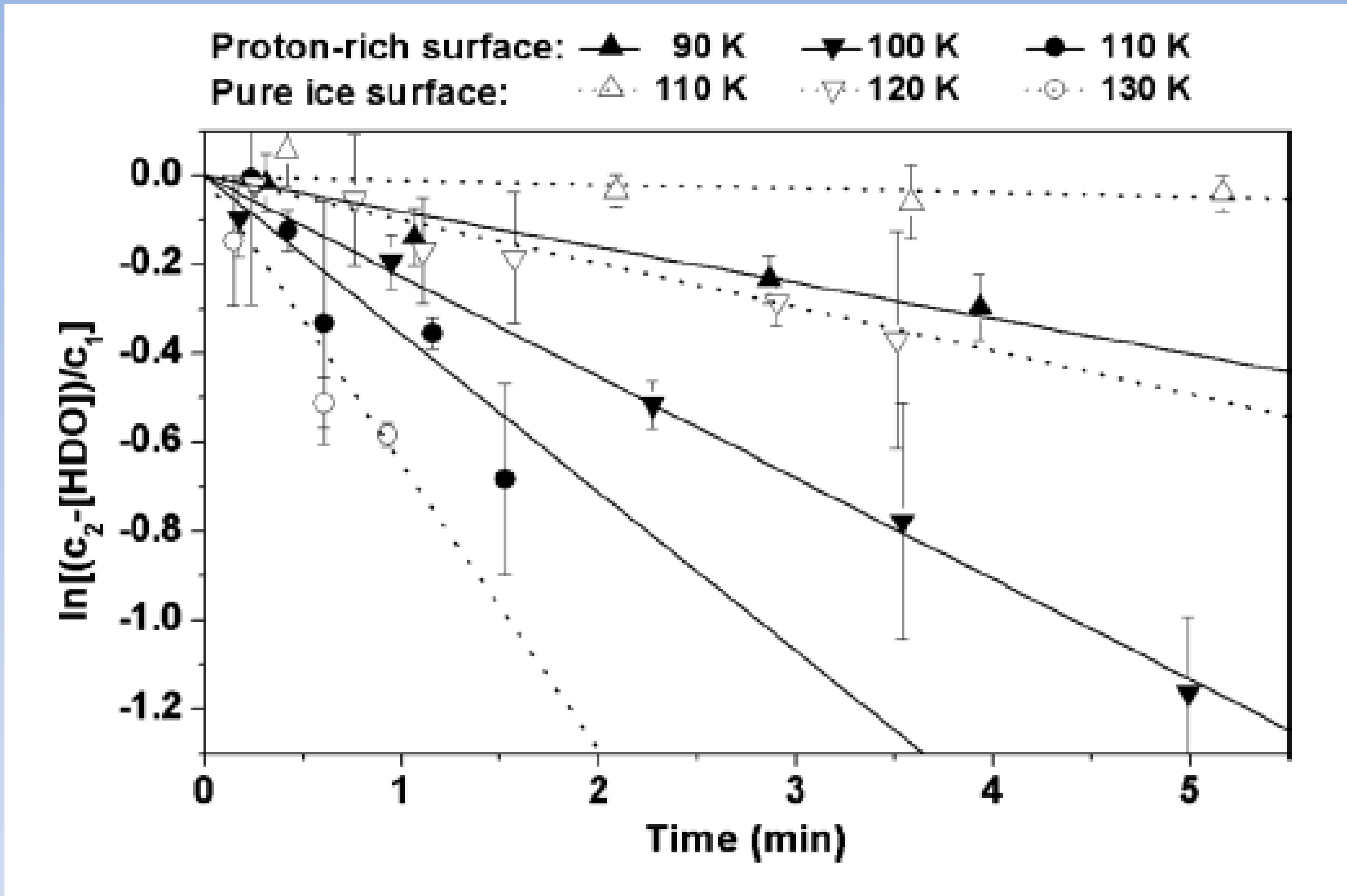
The rate expression is,

$$\frac{1}{2}\frac{d[HDO]}{dt} = k[H_2O][D_2O] - \frac{1}{4}k[HDO]^2$$

The solution of this rate expression is,

$$\begin{aligned}[HDO]_t &= 2[H_2O]_0[D_2O]_0 + [HDO]_0 - \tfrac{1}{2}[HDO]_0^2 \\ &\quad - \left(2[H_2O]_0[D_2O]_0 + \tfrac{1}{2}[HDO]_0^2\right)\exp(-kt) \\ &= 2f_H f_D - (2f_H f_D - [HDO]_0)\exp(-kt) \\ &= c_2 - c_1 \exp(-kt).\end{aligned}$$

here $f_D = [HDO]/2 + D_2O$



Theoretical plot based reaction 1

From this model, E_a = 7.5   1.5 kJ/mol for the proton-rich ice surface

&

E_a = 20   4 kJ/mol for pure ice film

$$H_2O_i + D_2O_{adj} \underset{1/4k_v}{\overset{k_v}{\leftrightarrow}} HDO_i + HDO_{adj},$$

$$D_2O_i + H_2O_{adj} \underset{1/4k_v}{\overset{k_v}{\leftrightarrow}} HDO_i + HDO_{adj},$$

$$HDO_i + H_2O_{adj} \underset{1/2k_v}{\overset{1/2k_v}{\leftrightarrow}} H_2O_i + HDO_{adj},$$

$$HDO_i + D_2O_{adj} \underset{1/2k_v}{\overset{1/2k_v}{\leftrightarrow}} D_2O_i + HDO_{adj}.$$

H_2O_i denotes a H_2O molecule located in the *i*th layer, H_2O_{adj} denotes a molecule in the adjacent layer [(*i*+1)th or (*i*−1)th layer]

The number of the proton transfer events occurring along the surface plane and in the vertical direction has the ratio of 6:1, and a relationship $k = 6k_v$

$$H_2O_i \underset{k_d}{\overset{k_d}{\leftrightarrow}} H_2O_{adj},$$

$$HDO_i \underset{k_d}{\overset{k_d}{\leftrightarrow}} HDO_{adj},$$

$$D_2O_i \underset{k_d}{\overset{k_d}{\leftrightarrow}} D_2O_{adj}.$$

Self diffusion

$$\begin{aligned}\frac{d}{dt}[H_2O]_i = &-k[H_2O]_i\Big([D_2O]_i + \tfrac{1}{6}[D_2O]_{i+1} + \tfrac{1}{6}[D_2O]_{i-1}\\ &+ \tfrac{1}{12}([HDO]_{i+1} + [HDO]_{i-1})\Big)\\ &+ \tfrac{1}{12}k[HDO]_i\Big(3[HDO]_i + [H_2O]_{i-1}\\ &+ [H_2O]_{i+1} + \tfrac{1}{2}([HDO]_{i-1} + [HDO]_{i+1})\Big)\\ &+ k_d([H_2O]_{i-1} + [H_2O]_{i+1} - [H_2O]_i), \qquad (A6)\end{aligned}$$

$$\begin{aligned}\frac{d}{dt}[D_2O]_i = &-k[D_2O]_i\Big([H_2O]_i + \tfrac{1}{6}[H_2O]_{i+1} + \tfrac{1}{6}[H_2O]_{i-1}\\ &+ \tfrac{1}{12}([HDO]_{i+1} + [HDO]_{i-1})\Big)\\ &+ \tfrac{1}{12}k[HDO]_i\Big(3[HDO]_i + [D_2O]_{i-1}\\ &+ [D_2O]_{i+1} + \tfrac{1}{2}([HDO]_{i-1} + [HDO]_{i+1})\Big)\\ &+ k_d([D_2O]_{i-1} + [D_2O]_{i+1} - [D_2O]_i), \qquad (A7)\end{aligned}$$

$$d[HDO]_i = -d[H_2O]_i - d[D_2O]_i. \qquad (A8)$$

Can’t be solved, so found numerical solution using MATHEMATICA

Discussion

- This work examined the energy barrier of proton transfers at the outermost surface of an ice film through the measurement of the H/D exchange reaction on the surface with excess protons.

- The energy barrier was estimated to be 10 3 kJ.mol^{-1} on a polycrystalline ice film that was grown at 135 K, although this energy varied with the ice surface morphology.

- At a temperature of 70 K, proton transfer occurred from hydronium ions mostly to adjacent water molecules, and the proton transfer rate and distance increased with temperatures above 90 K.

Thank you

- First report on kinetic determination of E_a value of H/D exchange on ice surfaces.
- It can be extended to alcohol (for long chain alcohols also) and amines.
- For pure ice films the E_a of H/D exchange is ~ 0.16 eV which is consistent with our observation.