Energy Barrier of Proton Transfer at Ice Surfaces

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Proton transfer on ice surface was under investigation.

It is known that proton tends to stay on the surface rather than the 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 a certain amount of energy barrier for the release of proton.

Determination of this activation energy is the purpose of this study.
Experimental

1. Experiments were performed in the above instrument.
2. Ice film (D₂O) 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).

**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.
Results

For 1 (C), $\text{D}_3\text{O}^+ + \text{H}_2\text{O} = \text{D}_2\text{O} + \text{H}_2\text{DO}^+$

At 1 (e), $\text{CsH}_2\text{O}^+ : \text{CsHDO}^+ : \text{CsD}_2\text{O}^+ = 0.19 : 0.41 : 0.4$

Solvation, decrease in intensity of $\text{H}_3\text{O}^+$
After 2 mins.,
\[ \text{CsH}_2\text{O}^+ : \text{CsHDO}^+ : \text{CsD}_2\text{O}^+ = 0.17 : 0.44 : 0.39 \]

\( \text{D}_2\text{O} \) intensity did not decrease

The kinetic measurement on doped ice films
The kinetic measurement on pure ice films

\[ \text{H}_2\text{O} + \text{D}_2\text{O} \xrightleftharpoons[k_f]{k_b} 2\text{HDO} \]
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 $2\text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^-$ followed by $\text{D}_3\text{O}^+ + \text{H}_2\text{O} = \text{D}_2\text{O} + \text{H}_2\text{DO}^+$
Discussion

\[ \text{H}_2\text{O} (s) + \text{D}_2\text{O} (s) \xrightarrow{k/k_2} 2\text{HDO} (s) \quad \text{------- (1)} \]

According to law of mass conservation at the outermost surface,

\[ [\text{HDO}] - [\text{HDO}]_0 = -2([\text{H}_2\text{O}] - [\text{H}_2\text{O}]_0) = -2([\text{D}_2\text{O}] - [\text{D}_2\text{O}]_0) \]

The rate expression is,

\[
\frac{1}{2} \frac{d[\text{HDO}]}{dt} = k[\text{H}_2\text{O}][\text{D}_2\text{O}] - \frac{1}{4} k[\text{HDO}]^2
\]

The solution of this rate expression is,

\[
[\text{HDO}]_t = 2[\text{H}_2\text{O}]_0[\text{D}_2\text{O}]_0 + [\text{HDO}]_0 - \frac{1}{2} [\text{HDO}]_0^2
\]
\[
- \left(2[\text{H}_2\text{O}]_0[\text{D}_2\text{O}]_0 + \frac{1}{2} [\text{HDO}]_0^2\right) \exp(-kt)
\]
\[
= 2f_D f_D - (2f_H f_D - [\text{HDO}]_0) \exp(-kt)
\]
\[
= c_2 - c_1 \exp(-kt).
\]

here \( f_D = [\text{HDO}]/2 + \text{D}_2\text{O} \)
Theoretical plot based reaction 1

From this model, $E_a = 7.5 \pm 1.5 \text{ kJ/mol}$ for the proton-rich ice surface and $E_a = 20 \pm 4 \text{ kJ/mol}$ for pure ice film.
$\text{H}_2\text{O}_i$ denotes a $\text{H}_2\text{O}$ molecule located in the $i$th layer, $\text{H}_2\text{O}_{\text{adj}}$ denotes a molecule in the adjacent layer [$(i+1)\text{th}$ or $(i-1)\text{th}$ 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 $k = 6k_v$
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 $\sim 0.16$ eV which is consistent with our observation.