

Proton transfer and H/D isotopic exchange of water molecules mediated by hydroxide ions on ice film surfaces

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J. Chem. Phys. **2009**, *131*, 044705

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31-10-09

❖ Introduction

- The high mobility of H^+ (aq) and OH^- (aq) in liquid water is very high. The mechanism proposed is “structural diffusion” or “Grotthuss” mechanism.
- But the corresponding picture for OH^- (aq) is less clear. The earlier proposed “proton hole” mechanism lost its ground to a recent investigation.
- It has been suggested that the hydrogen-bonded water structures involved in the structural diffusion of OH^- (aq).
- An interesting environment for the study of hydroxide ion transport through water molecules can be found in an ice surface.
- Solvation of hydroxide ions may be quite different from that in liquid water or even in the interior of ice also.
- Experimentally, the studies of proton transfer at the surface or at bulk of ice have been performed most widely by preparing ice samples doped with excess protons, and then proton migration and the resulting H/D isotopic exchange in water molecules are monitored by using various spectroscopic tools.

- Park *et al.* reported that the H/D exchange process occurs very efficiently at the surface of an ice film upon the adsorption of HCl, while the H/D exchange process hardly propagates into the ice film interior.
 - The present investigation talks about a study of the H/D exchange reaction between H_2O and D_2O molecules at the surface of ice films in the presence of excess hydroxide ions.
 - At 120 K, the hydroxide ion tends to reside at the ice film surface, whereas counter cation, Na^+ , migrates toward the film interior.
 - Therefore a hydroxide ion with an affinity to the ice surface can effectively participate in the H/D exchange reaction occurring at the surface.
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❖ Experimental

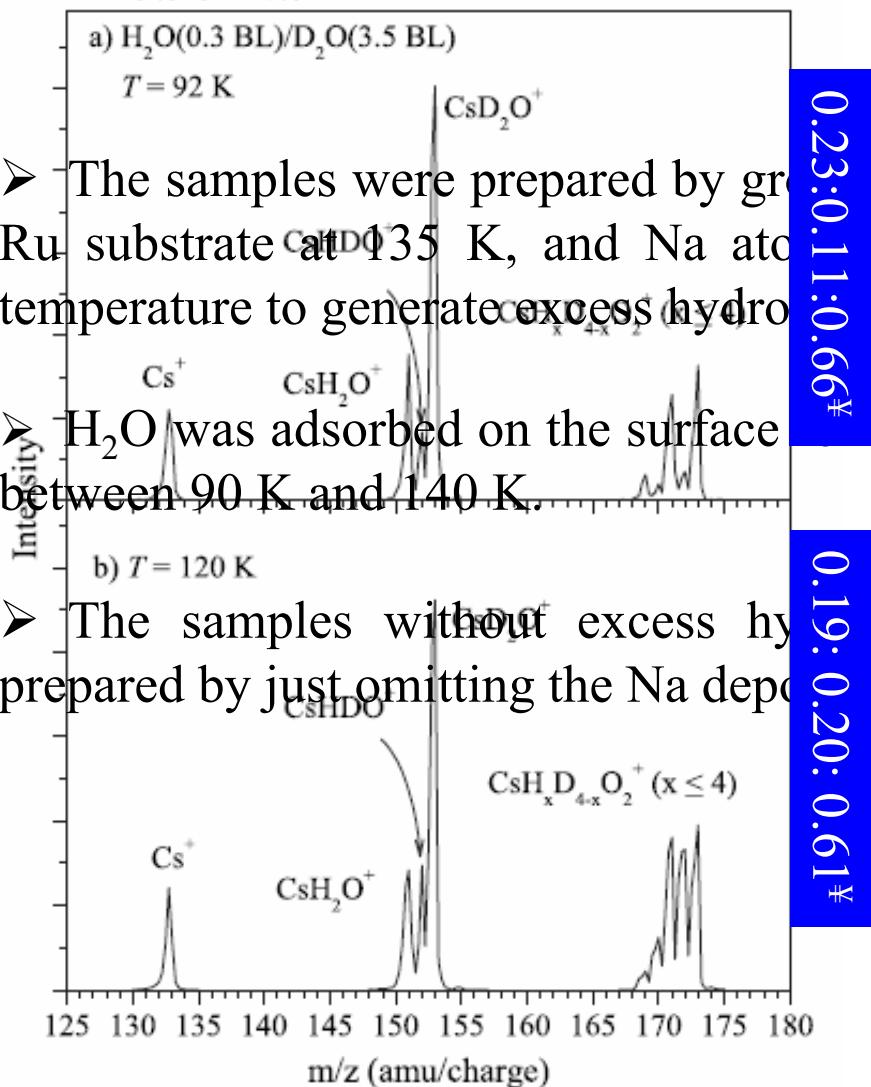
- D₂O-ice films were grown onto a Ru (0001) surface at 135 K by backfilling the UHV chamber with D₂O vapor at a partial pressure of 1.0×10^{-8} torr i.e., 2 BL/min. (1 BL = 1.1×10^{15} water molecules cm⁻²).
- Na atoms were deposited onto the D₂O film at 135 K by employing a commercial alkali metal dispenser @ 0.02 MLE/min. {Na coverage is expressed in units of monolayer equivalents (MLEs), where 1 MLE corresponds to the full monolayer coverage of Na on a bare Ru (0001) surface 1 MLE = 0.53 ML of Ru surface atomic density = 8.5×10^{14} atoms cm⁻²}
- Neutral and ionic species present at the ice film surface were analyzed by RIS and LES, respectively.

❖ Results

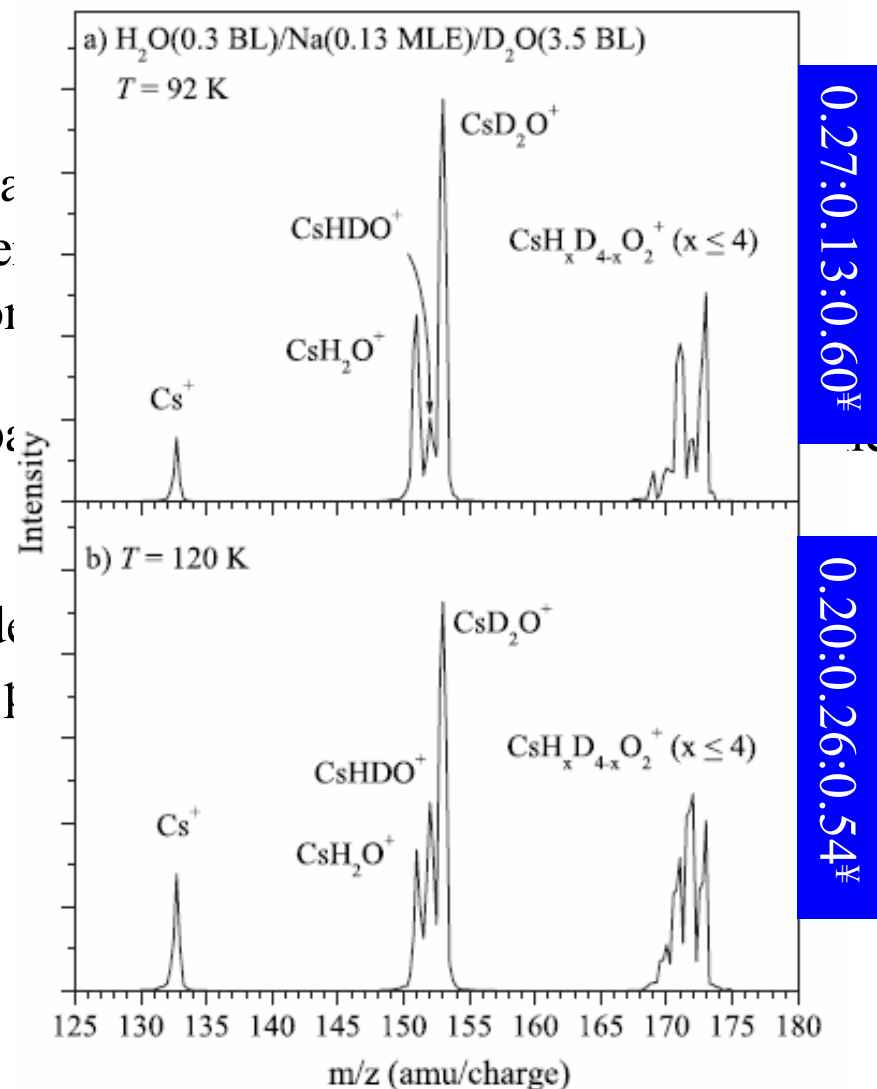
➤ The samples were prepared by growing a Ru substrate at 135 K, and Na atoms were deposited at 135 K, and then at a lower temperature to generate excess hydroxide ions.

➤ H₂O was adsorbed on the surface at a pressure between 90 K and 140 K.

➤ The samples without excess hydroxide were prepared by just omitting the Na deposition step.

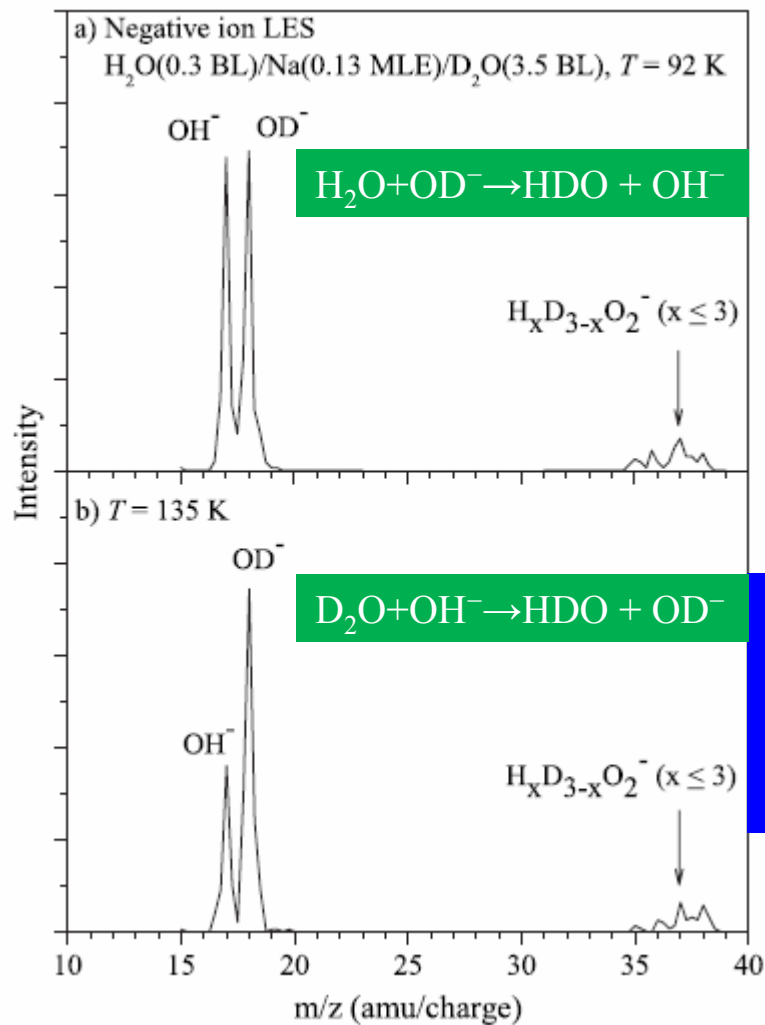


RIS of H₂O 0.3 (BL)/D₂O (3.5 BL)



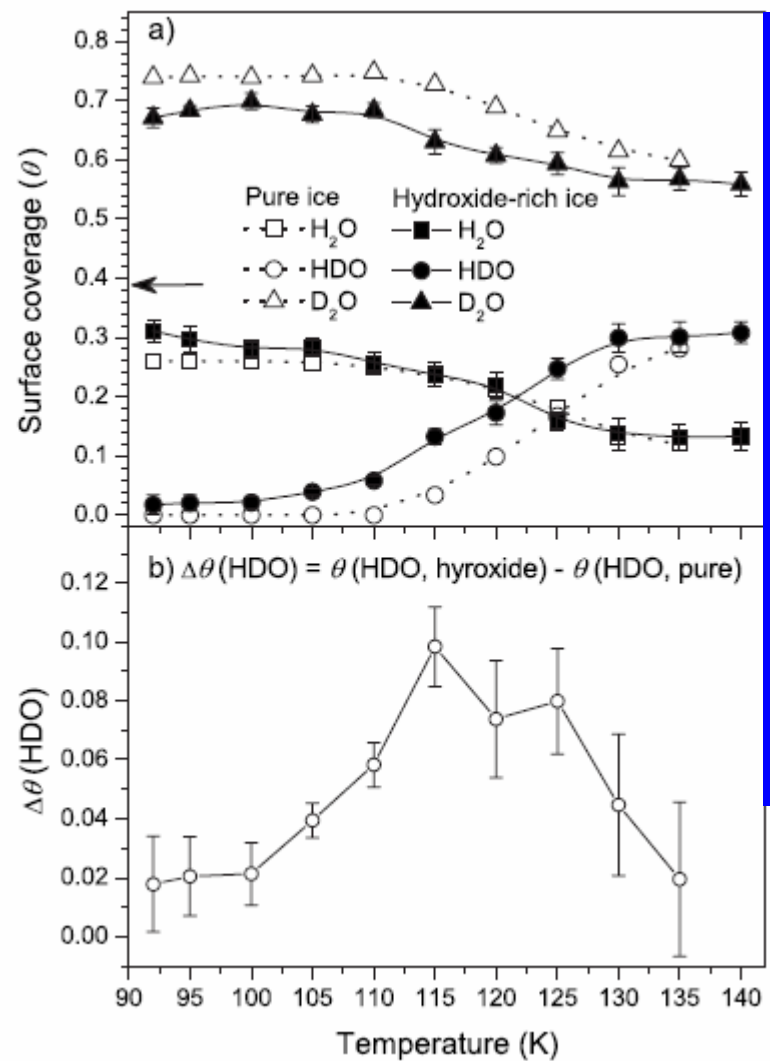
RIS of H₂O 0.3 (BL)/ Na (0.13 MLE)/
D₂O (3.5 BL)

¥Intensity of CsH₂O⁺ :CsHDO⁺ :CsD₂O⁺



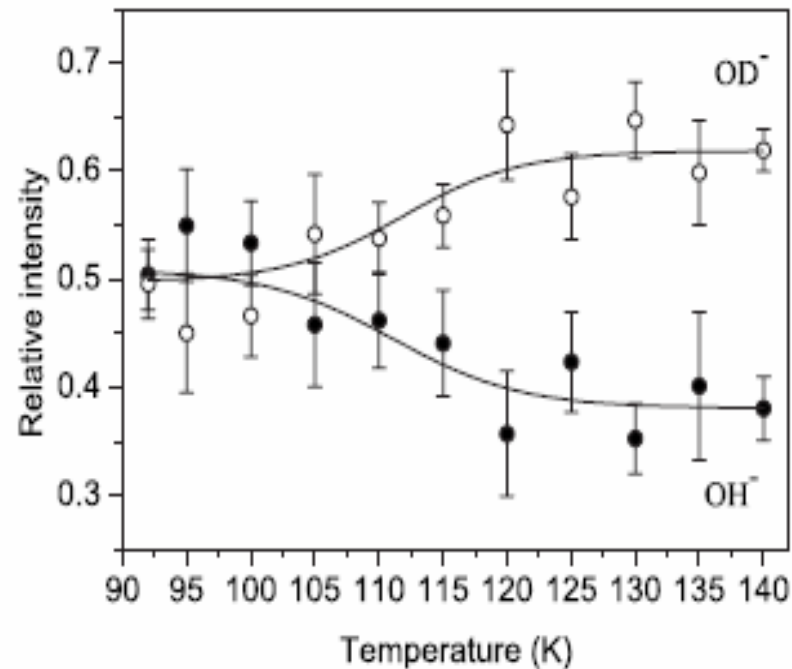
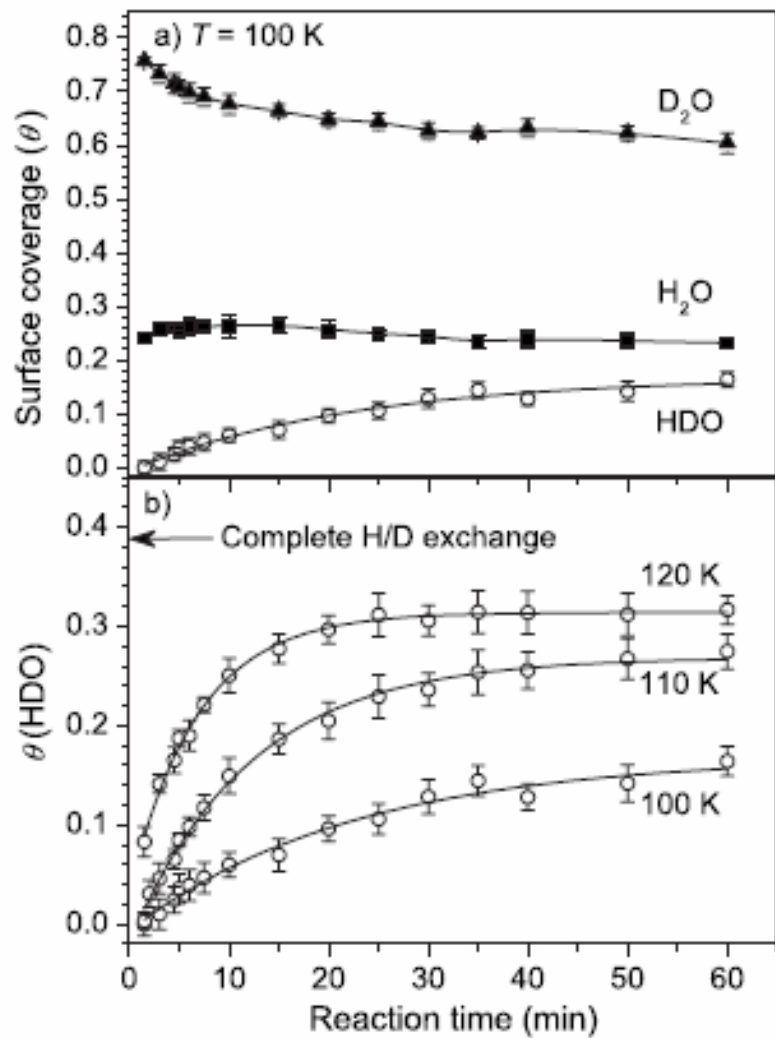
0.38:0.62 \ddagger

LES of H_2O 0.3 (BL)/ Na (0.13 MLE)/
 D_2O (3.5 BL)



$$\theta(\text{HDO}) = I(\text{HDO}) / (I(\text{H}_2\text{O}) + I(\text{HDO}) + I(\text{D}_2\text{O}))$$

\ddagger Intensity of OH^- : OD^-



LES measurement of the relative intensities of OH^- and OD^- signals as a function of temperature

H/D exchange rxn $E_a = \sim 9.6 \pm 2.0$ kJ/mol

❖ Summary & discussion

- The hydroxide ions can induce the H/D exchange reaction even at low temperatures.
 - The low-temperature proton transfer occurs mostly upon direct contact of a hydroxide ion.
 - At higher temperatures, the population of HDO molecules increases, and the population of OD^- also increases relative to OH^- . This indicates that proton transfer propagates over longer distances to involve more D_2O molecules.
 - For the H/D exchange reaction on a hydroxide-free ice where surface requires thermal creation of ionic defects as well as proton transfer, $E_a \geq 9.8 \text{ kJ/mol}$.
 - Hydroxide ions significantly enhance the rate of H/D exchange compared with that on pure ice films at temperatures below 135 K.
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