

Asymmetric Transport Mechanisms of Hydronium and Hydroxide Ions in Amorphous Solid Water: Hydroxide Goes Brownian while Hydronium Hops

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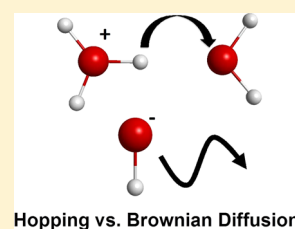
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ABSTRACT: The diffusion of hydronium (H_3O^+) and hydroxide (OH^-) ions is one of the most intriguing topics in aqueous chemistry. It is considered that these ions in aqueous solutions move via sequential proton transfer events, known as the Grotthuss mechanisms. Here, we present an experimental study of the diffusion and H/D exchange of hydronium and hydroxide ions in amorphous solid water (ASW) at 140–180 K by using low-energy sputtering (LES) and temperature-programmed desorption (TPD) measurements. The study shows that the two species transport in ASW via fundamentally different molecular mechanisms. Whereas hydronium ions migrate via efficient proton transfer, hydroxide ions move via Brownian molecular diffusion without proton transfer. The molecular hydroxide diffusion in ASW is in stark contrast to the current view of the hydroxide diffusion mechanism in aqueous solution, which involves proton transfer.

SECTION: Surfaces, Interfaces, Porous Materials, and Catalysis



Hopping vs. Brownian Diffusion

Diffusion of hydronium and hydroxide ions is of prime importance in many chemical and biological processes, ranging from simple acid–base reactions to complex enzymatic reactions. The anomalously high diffusion rates that these ions exhibit in water have been the subject of extensive research^{1–18} and have been attributed to proton transfer processes, known as the Grotthuss mechanisms.^{2–7} The proton transfer mechanism of the hydronium ion has been relatively well established; it is considered to occur via an intricate interplay between the Eigen cation, $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$, and the Zundel cation, $[\text{H}_2\text{O}\cdots\text{H}\cdots\text{OH}_2]^+$.^{2–4} The transport mechanism of the hydroxide ion has not been investigated as comprehensively as the hydronium ion,^{5–9} but it has been conceived that hydroxide ions also move via a proton transfer mechanism in aqueous solution.^{5–7} The critical solvation structures related to the proton transfers, however, are quite different for hydronium and hydroxide ions, according to theoretical studies.^{5–7} Experimental study for the diffusion dynamics of aqueous hydroxide ions has been relatively scarce,^{8,9} mainly because it is difficult to identify the transitory structures of hydroxide ion diffusion using spectroscopic methods.

Amorphous solid water (ASW) provides an interesting opportunity to study the diffusion of hydronium and hydroxide ions, and such a study may eventually be able to assist understanding of their behaviors in liquid water. Interesting similarities and variances can be found between ASW and liquid water for the structural, thermodynamic, and chemical aspects as reaction media.^{19,20} In its experimental aspect, an ASW sample has several advantages over a liquid sample. For

example, controlling the composition and structure of an ASW sample on the molecular scale is possible by means of thin-film-growing methods developed in ultrahigh vacuum (UHV). Also, the diffusion rate can be changed over a wide range in ASW by appropriate temperature control. As such, one can study the diffusion kinetics of hydronium and hydroxide ions in ASW in real time and real space even without the use of ultrafast spectroscopies.²⁰ The diffusion of hydronium ions in ASW has been extensively studied in previous works,^{13–15} which have shown that hydronium ions move via successive proton transfers along the hydrogen bond network of the lattice, as they do in crystalline ice.^{1,2,10–12} In ASW, however, the proton transfer relay is interrupted by numerous proton traps present in the disordered lattice. To release the trapped protons and resume the proton transfer, thermal activation is necessary.^{13–15} It has been observed that hydroxide ions are relatively immobile in ASW at low temperature, according to H/D exchange studies of ice nanocrystals doped with base adsorbates¹⁶ and measurements of the transport distances of hydronium and hydroxide ions in ASW at <100 K.¹⁷ The surface segregative behavior of hydroxide ions has also been reported,¹⁸ where hydroxide ions initially buried under a thin (3 ML) ASW film migrate to its surface through the film at 135 K. These studies have examined the transport of hydroxide ions through a thin film of ASW at low temperature, and questions still remain for

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the transport properties in the bulk phase. In the present work, we measure the diffusion rates and H/D exchange reactions of hydronium and hydroxide ions in bulk-like ASW samples and show that the two species move via totally different diffusion mechanisms.

We conducted the experiments in an UHV chamber equipped with instrumentation for various surface spectroscopic tools, including low-energy sputtering (LES), temperature-programmed desorption (TPD), and Cs^+ reactive ion scattering (RIS).^{21,22} ASW samples were prepared to have hydronium or hydroxide ions at the interface of H_2O and D_2O films, as described in the following. A crystalline ice film was grown on a Pt(111) crystal substrate at 140 K for a thickness greater than 110 ML (monolayer; $1 \text{ ML} = 1.1 \times 10^{15} \text{ molecules cm}^{-2}$) by depositing H_2O vapor through a capillary doser. The ice film was briefly annealed at 150–155 K to ensure its crystallization into a flat, continuous film structure with predominant ice Ih(0001) surfaces.²³ Then, excess H_3O^+ ions were added onto the film by the adsorption of HCl gas for about 0.3 ML of coverage, which ionized into H_3O^+ and Cl^- ions on the ice surface.²¹ Finally, a D_2O –ASW film was overlaid onto the sample for a 30–60 ML thickness by depositing D_2O vapor at low temperature ($\leq 95 \text{ K}$), which produced a “hydronium-sandwich” sample containing excess hydronium ions between the H_2O and D_2O films. Thermal diffusion of hydronium ions in ASW was negligible at $\leq 90 \text{ K}$.¹⁷ Likewise, a hydroxide-sandwich sample was prepared by providing excess hydroxide ions between the H_2O and D_2O films. The excess hydroxide ions were generated by the hydrolysis of Na atoms on a H_2O –ice film, which produced Na^+ and OH^- ions.²⁰ Each of the sample preparation stages was checked by performing surface analysis.

LES and RIS methods were used for identifying ionic and neutral species, respectively, on sample surfaces.^{21,22} In these methods, a Cs^+ beam collided with a sample surface at low incidence energy (35 eV), and a quadrupole mass spectrometer detected positive and negative ions emitted from the surface with its ionizer filament switched off. The detected ions were comprised of reflected Cs^+ primaries, RIS products that are association products of Cs^+ with neutral molecules on the surface, and LES ions resulting from collisional desorption (LES) of preexisting ions on the surface. The probing depth of LES and RIS methods for an ASW sample is 1 molecular layer.^{21,22} TPD experiments were used to detect gaseous molecules desorbing from the surface and to estimate the thickness of a sample.

To study the diffusion of hydronium or hydroxide ions, we activate these ions trapped in a sandwich layer by warming the samples. The ions are spread over the sample volume by diffusion, and some of them may reach the surface, which are detected by LES. Figure 1a and b shows LES signals measured from hydronium- and hydroxide-sandwich samples, respectively. As Figure 1a shows, a hydronium-sandwich sample had no ions on its surface after initial sample preparation at 95 K. Upon heating the sample at 160 K, the positive ion LES spectrum showed various hydronium ion isotopologues (H_3O^+ , H_2DO^+ , HD_2O^+ , and D_3O^+) appearing on the surface as a result of diffusion from the sample interior. The negative ion LES spectrum showed that the counter Cl^- ions also appeared on the surface. For a hydroxide-sandwich sample (Figure 1b), the negative ion spectrum showed that OH^- and OD^- ions appeared on the surface after heating at 160 K, which indicated the diffusion of hydroxide ions from the sample interior to its

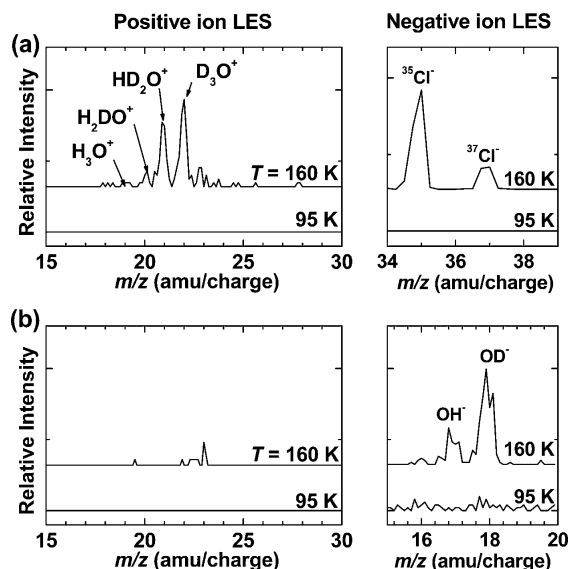


Figure 1. (a) LES mass spectra of positive (left frame) and negative ions (right frame) observed on a hydronium-sandwich sample [D_2O ($\sim 50 \text{ ML}$)/ H_3O^+ + $\text{Cl}^-/\text{H}_2\text{O}$ ($\geq 110 \text{ ML}$)/Pt(111)]. The spectral changes from $T = 95$ to 160 K indicate the migration of hydronium and chloride ions from the sample interior to its surface due to diffusion. (b) Analogous measurements for a hydroxide-sandwich sample [D_2O ($\sim 30 \text{ ML}$)/ Na^+ + $\text{OH}^-/\text{H}_2\text{O}$ ($\geq 110 \text{ ML}$)/Pt(111)] indicate the migration of hydroxide ions to the surface. The relative peak intensities in the displayed spectra are roughly proportional to the surface abundance of these ions.

surface. The positive ion spectrum revealed negligible appearance of Na^+ ions on the surface. The small-intensity signal at 23 amu/charge, which appeared for both hydronium- and hydroxide-sandwich samples at 160 K, was due to the surface scattering of impurity Na^+ ions contained in the Cs^+ beam,²⁴ rather than the diffusion of Na^+ ions to the surface. The appearances of hydronium, hydroxide, and Cl^- ions on the surfaces agree with their thermodynamic tendencies to reside on water surfaces.^{18,24–26} That is, these ions may diffuse in random directions inside of an ASW sample, but when they come close to the sample surface, they become attracted by the thermodynamic affinity forces from the surface and are accumulated there.¹⁵ On the other hand, because the Na^+ ions have thermodynamic preference for the interior of water,^{18,24} they become dispersed in the sample without being accumulated on the surface.

Temperature-programmed LES (TPLES) experiments were performed to measure the diffusion rates of hydronium and hydroxide ions. In these experiments, the sample temperature was increased linearly with time at a rate of $0.5 \text{ degree s}^{-1}$, and the growth kinetics of hydronium and hydroxide ion populations on the sample surface was monitored in real time with LES. Figure 2a and b presents TPLES measurements for the diffusion of hydronium and hydroxide ions, respectively, through a D_2O –ASW film with a 30 ML thickness. In Figure 2a, hydronium ions appear on the surface at a temperature above $\sim 140 \text{ K}$. Various hydronium ion isotopologues appear in the sequence of D_3O^+ , HD_2O^+ , H_2DO^+ , and H_3O^+ . The hydronium ion population as a whole continuously increases until $\sim 147 \text{ K}$, above which a steady surface population is reached. The saturation in surface hydronium ion population results from a kinetic balance between the upward migration of hydronium ions and the desorption of hydrogen chloride gas

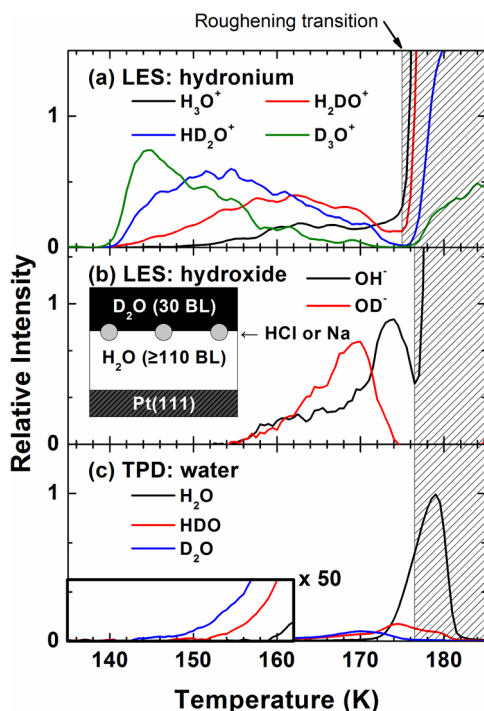


Figure 2. (a) TPLES measurements of hydronium ions appearing on the surface of a hydronium-sandwich sample [D_2O (~30 ML)/ H_3O^+ + $\text{Cl}^-/\text{H}_2\text{O}$ (≥ 110 ML)/ $\text{Pt}(111)$] via diffusion through a D_2O –ASW film. (b) Analogous measurements of hydroxide ions for a hydroxide-sandwich sample [D_2O (~30 ML)/ OH^- + $\text{Na}^+/\text{H}_2\text{O}$ (≥ 110 ML)/ $\text{Pt}(111)$]. (c) TPD of water from a hydroxide-sandwich sample, which has the same structure as that used for (b). The temperature ramping rate was $0.5 \text{ degree s}^{-1}$ in all measurements. The shaded area indicates the roughening transition region (see text).

from the surface via recombination of surface-accumulated hydronium and chloride ions, as explained previously.¹⁵

In Figure 2b, hydroxide ions arrive at the surface at a substantially higher temperature (~155 K) than hydronium ions. The relative intensities of OH^- and OD^- ions show that they have comparable populations on the surface at 155–162 K, and the OD^- population grows larger at higher temperature.

The TPLES curves abruptly rise at 175–177 K, following a momentary drop at a lower temperature. As explained previously,¹⁵ this behavior is due to a roughening transition of the ASW samples, which occurs when the sample thickness is reduced below a critical value by water sublimation, rather than due to an actual change in surface ion populations. The roughening transition causes the film to dewet the Pt substrate and exposes patches of water monolayer,²⁷ which sharply increases the LES efficiency on the surface. Accordingly, the diffusion kinetics is valid only below this transition temperature.

Figure 2c shows TPD of water measured from a hydroxide-sandwiched sample. The TPD curves of water isotopologues indicate that their desorption onset temperatures are in the order of $\text{D}_2\text{O} < \text{HDO} < \text{H}_2\text{O}$. Note that H_2O reaches the surface at ~159 K, which is due to self-diffusion from the $\text{D}_2\text{O}/\text{H}_2\text{O}$ interface. At this temperature, about 1 ML of water has desorbed from the film surface as estimated from TPD curve areas, corresponding to a reduction of sample thickness by $\leq 1\%$. This confirms that the surfacing of H_2O is due to self-diffusion rather than the evaporation of the D_2O overlayer. The same argument can apply to the diffusion of hydronium and hydroxide ions as well, shown in Figure 2a and b. The surfacing

temperatures of the hydronium ion (~140 K), hydroxide ion (~155 K), and H_2O (~159 K) indicate that their relative diffusion rates in ASW should be in the order of hydronium ion > hydroxide ion > water.

The D_2O –ASW overlayer may be crystallized during sample heating. It has been reported²⁸ that slow crystallization of a pure ASW film produces a small bump in the water TPD signal at 150–160 K, but this feature did not appear in the present experiments employing rapid temperature scans. For this reason, we consider that the crystallization process may be delayed to higher temperature (>160 K) in the present experiments.

The effects of the counter Na^+ and Cl^- ions on the diffusion kinetics study may be discussed. Because Na^+ and Cl^- ions have the opposite charges and different tendencies to reside in the interior or surface of ASW, these ions may influence the motion of hydronium and hydroxide ions in different ways. In the case of hydronium ion diffusion, we observed that the hydronium ion migrates to the surface slightly ahead of Cl^- or at comparable speeds.¹⁵ This refutes the possibility that the surfacing of hydronium ions is driven by the electrostatic forces of Cl^- ions. To examine the effects of Na^+ on hydroxide ion diffusion, we prepared the samples that additionally contained Br^- ions, which were provided from the ionization of NaBr .²⁴ Br^- has a tendency to float on an ASW surface,²⁴ like the hydroxide ion, and thus, it may serve as a reference anion for the study of hydroxide ion migration. The externally provided Br^- and its counter Na^+ ions were placed on the surface [Na^+ + $\text{Br}^-/\text{D}_2\text{O}/\text{Na}^+$ + $\text{OH}^-/\text{H}_2\text{O}/\text{Pt}(111)$]. We observed that the upward migration speed of hydroxide ions from a sandwich layer did not change noticeably due to the presence of these additional ions. These observations support that the electrostatic force effects are insignificant in the present diffusion study.

The sequential increase and decrease of various hydronium (D_3O^+ , HD_2O^+ , H_2DO^+ , and H_3O^+) ions, shown in Figure 2a, parallel the increasing abundance of D-enriched water molecules on the surface, shown in Figure 2c. This suggests that hydronium ions undergo efficient H/D exchange with water molecules. On the other hand, OH^- and OD^- have similar populations at 155–162 K (Figure 2b), even though H_2O is absent from the surface or has only a very small population. This suggests that OH^- ions migrate to the surface without experiencing H/D exchange with water. To quantify the efficiency of H/D exchange reactions, we have calculated the $\text{H}/(\text{H} + \text{D})$ ratios (HDRs) for the hydronium ion, hydroxide ion, and water on the surface, and they are plotted in Figure 3. The HDR for water on a pure ASW sample is also shown for comparison. Figure 3a shows that the hydronium ion and water exhibit essentially the same HDRs in the entire temperature range of investigation, indicating efficient proton exchange between the hydronium ion and water. The HDR of water on a hydronium-sandwich sample is significantly higher than that on a pure ASW sample at <170 K, which indicates that excess protons promote the H/D exchange of water. All of these observations are consistent with the established diffusion mechanism of the hydronium ion via proton transfer.^{10–15} In contrast, the HDR of the hydroxide ion is significantly higher than that of water at 154–168 K (Figure 3b). Below 154 K, hydroxide ion diffusion hardly occurs. Above 168 K, the hydroxide ion experiences H/D exchange as efficiently as water. Yet, the presence of excess hydroxide ions in the sample does not increase the H/D exchange efficiency of water from that

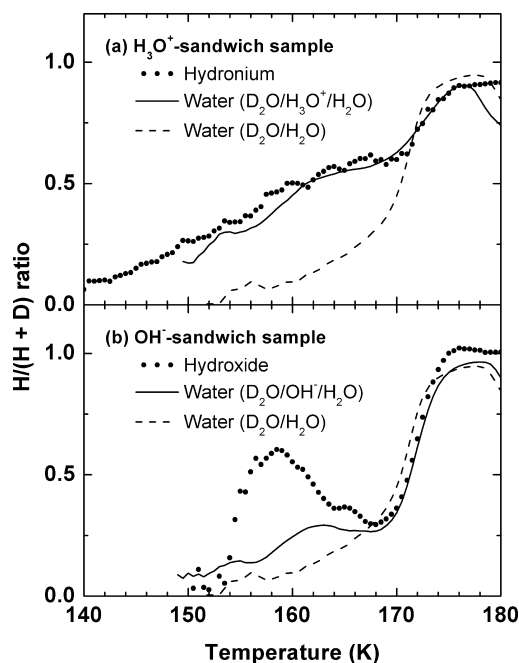


Figure 3. (a) HDR for the hydronium ion and water measured on a hydronium-sandwich sample surface as a function of temperature. (b) HDR for the hydroxide ion and water measured on a hydroxide-sandwich sample. Plots are based on the LES and TPD data shown in Figure 2. For comparison, the HDR for water on a pure ASW sample [D_2O (~ 30 ML)/ H_2O (≥ 110 ML)/Pt(111)] is also shown with the broken lines.

observed for a pure ASW surface. Note that if OH^- moves via a proton transfer mechanism, then OD^- must form in accordance with the HDR of water molecules. Therefore, the higher HDR of hydroxide ion than water is compelling evidence that the hydroxide ion moves without proton transfer.

From the HDR curves shown in Figure 3b, one can estimate the relative efficiencies with which hydroxide ions move with and without proton transfer. About half of OH^- ions are converted to OD^- as a result of H/D exchange with water during travel from the sandwich layer to the surface at ~ 160 K. At this temperature, the HDR of water (f_w) on the sample surface is 0.20 ± 0.03 , as estimated from the TPD curves of water isotopologues, shown in Figure 2c. The f_w value at the $\text{H}_2\text{O}/\text{D}_2\text{O}$ interface should be close to 0.50 in the early stage of the diffusion because the diffusion fluxes of H_2O and D_2O are equal. Hydroxide ion transport can be considered as a series of successive encounter events of hydroxide ions with different water molecules, regardless of whether it is the Brownian motion of hydroxide molecules or a proton hopping channel. The probability (P) that OH^- does not undergo H/D exchange with deuterated water while crossing one water molecular layer is expressed by eq 1

$$P = x + (1 - x)f_w \quad (1)$$

where x is the branching ratio for the molecular transport channel without proton transfer. In our observation, Figure 3b, the probability that OH^- does not undergo H/D exchange after passing through 30 ML of ASW at 160 K is 0.55 ± 0.05 , which is the HDR of the hydroxide ion at this temperature. If we assume that the hydroxide ion interacts with 30 water molecules along this travel path and that f_w decreases from 0.50 to 0.20 ± 0.03 linearly through the 30 ML ASW film due

to self-diffusion, then we can deduce $x = 0.96 \pm 0.01$ from the relationship $P^{30} = 0.55 \pm 0.05$. The use of a differently changing f_w function does not much change the estimate for x from 0.96. A hydroxide ion moving through a 30 ML film in random-walk diffusion may in fact interact with far more than 30 water molecules before it reaches the surface. In this respect, $x = 0.96 \pm 0.01$ may well be regarded as a lower limit of the branching ratio for the molecular hydroxide transport channel. This analysis clearly shows that the molecular hydroxide transport channel operates almost exclusively for hydroxide ion diffusion in ASW at 160 K, and the proton transfer channel is effectively blocked.

In summary, the present study reveals the following properties for the diffusion of hydronium and hydroxide ions in ASW at 140–180 K. (i) The relative diffusion speeds of these species are in the order of hydronium ion > hydroxide ion > water molecule. This order in ASW is the same as that observed for aqueous solutions at room temperature. (ii) The hydronium ion migrates via a proton transfer process with rapid proton exchange with water. This mechanism has been well established in previous works,^{10–15} and the present result just confirms the occurrence of the same mechanism for ASW at high temperature (>140 K). (iii) The hydroxide ion moves via a molecular transport mechanism without proton transfer.

Evidently, the diffusions of hydronium and hydroxide ions in ASW involve fundamentally different molecular mechanisms. The hydroxide ion moves via molecular diffusion through the intermolecular spaces of ASW, whereas the hydronium ion migrates via successive proton transfers along the H-bond network of the lattice. This finding is in stark contrast to the current view of the diffusion mechanism of hydroxide ions in aqueous solution that hydroxide ions also move via proton transfer, although the critical solvation structures for the proton transfers are different for hydronium and hydroxide ions.^{5–7} An interesting question that arises here is to what extent such asymmetric transport properties of hydronium and hydroxide ions are transferable to aqueous solution at room temperature. ASW and liquid water have similar molecular packing structures, and their self-diffusivities are possibly connected to each other.¹⁹ In this respect, we may expect that the water solvation structures related to molecular hydroxide diffusion in ASW also form in liquid water and contribute to the diffusion of aqueous hydroxide ions. A combined experimental and theoretical research effort using quantum mechanical molecular dynamics simulations is currently underway in our laboratories to compare the diffusion mechanisms in ASW and liquid water.

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Notes

The authors declare no competing financial interest.

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