

Ab initio simulation on the mechanism of proton transport in water

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Abstract

Ab initio simulations on proton transport in water have been conducted. Using the simulation results together with the experimental data in the literature, currently existing hypotheses, including the one proposed by Agmon [N. Agmon, The Grotthuss mechanism, Chem. Phys. Lett. 244 (5–6) (1995) 456–462], have been examined. Based on the results of the simulations including charge distributions and the movement of the positive charge centers inside the protonated water clusters during the proton diffusion process, one mechanism is found to dominate proton transport in water. The high mobility of protons inside water is mainly due to the high diffusion rate of H_5O_2^+ cations. The diffusion of H_5O_2^+ cations is mainly induced by the thermal movement of water molecules in the second solvation shell of the H_5O_2^+ cations and the Zundel polarization inside the cations. Furthermore, thermal effects play a dominant role during the transport process by affecting the reorientation of water molecules in the neighborhood of the second solvation shell of H_5O_2^+ cations to induce the Zundel polarization and by providing the energy for the cleavage of the hydrogen bond between a water molecule and a newly formed H_5O_2^+ cation. In addition, an external electrical field plays an important role in helping the water molecule reorient and lowering the Zundel polarization energy barrier. Because the weight fraction of H_5O_2^+ cations among the protonated water clusters decreases as the temperature increases, the proposed mechanism is considered to play a dominant role only at temperatures below 672 K.

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1. Introduction

The mobility of protons in water is 5–8 times greater than other cations [2]. This phenomenon is thought to be very important for proton permeation through membrane channels in biological organisms [3]. It is also assumed that this causes a high conductivity of the Nafion® series of membranes [4,5], which are used as one of the major components in proton exchange membrane (PEM) fuel cell systems.

This phenomenon has been studied since C.J.D. von Grotthuss firstly proposed a mechanism in 1806 [6]: Grotthuss assumed that pairs of oppositely-charged particles in a chain could rotate and join with the next pair, transferring one charge in one direction, the other charge in the opposite direction. Since then many other different hypotheses have also been proposed, such as the hopping mechanism [7,8], proton tunneling mechanism [9,10], solvation effect [14–18], etc. More recently,

Agmon [1] proposed that prototropic mobility or high proton mobility is a result of a series of isomerizations between the H_9O_4^+ cation and the H_5O_2^+ cation. He believed that it was the hydrogen bond cleavage and subsequent formation of a second-shell water molecule that drive the proton forward. All of these hypotheses have paved the way toward an understanding of this phenomenon. However, most of them still contradict the experimental data and/or molecular dynamic (MD) simulation results.

Agmon [1] made an excellent summary of all the previously proposed mechanisms and experimental observations. He concluded that: (1) proton mobility was incoherent; (2) the rate-limiting step was hydrogen bond cleavage rather than water cluster growth or proton motion; (3) the rotation of H_3O^+ suggested by Huckel [7] was not possible due to its high activation energy; (4) A proton-relay mechanism of H_9O_4^+ cation was excluded because of the nonequivalence of the oxygen sites and high energy threshold; (5) the mechanism proposed by Bernal and Fowler [19] or a proton hopping from a H_3O^+ cation moiety to a freely rotating nearest neighbor water molecule was eliminated because water molecules were not free rotators, but rather tightly involved in hydrogen bonding; (6) relay mecha-

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nisms were impossible since proton conductivity is about twice as slow in ice as in super-cooled water of equal temperature [1,20–22].

In the context of the mechanism proposed by Agmon [1] for proton transport in water, he envisioned proton migration as a multiple step process, beginning with hydrogen bond cleavage in front of a moving proton, and ending with the formation of a new hydrogen bond as depicted in Fig. 1. Originally, the positive charge center of the cluster in Fig. 1(a), excluding the leftmost water molecule, is located at the oxygen atom O(2).

The movement of the water molecule with O(21) causes the cleavage of the hydrogen bond between H(20) and O(11). Consequently, the structure becomes horizontally symmetrical and the positive charge center relocates to the midpoint between O(2) and O(11) (Fig. 1(b)); when the water molecule with O(24) approaches O(2), a new hydrogen bond forms between H(23) and O(2); the structure of the cluster transforms as if the cluster structure shown in Fig. 1(a) flips horizontally, resulting in the structure shown in Fig. 1(c). As a result, the positive charge center moves from O(2) to O(11). A significant literature on *ab*

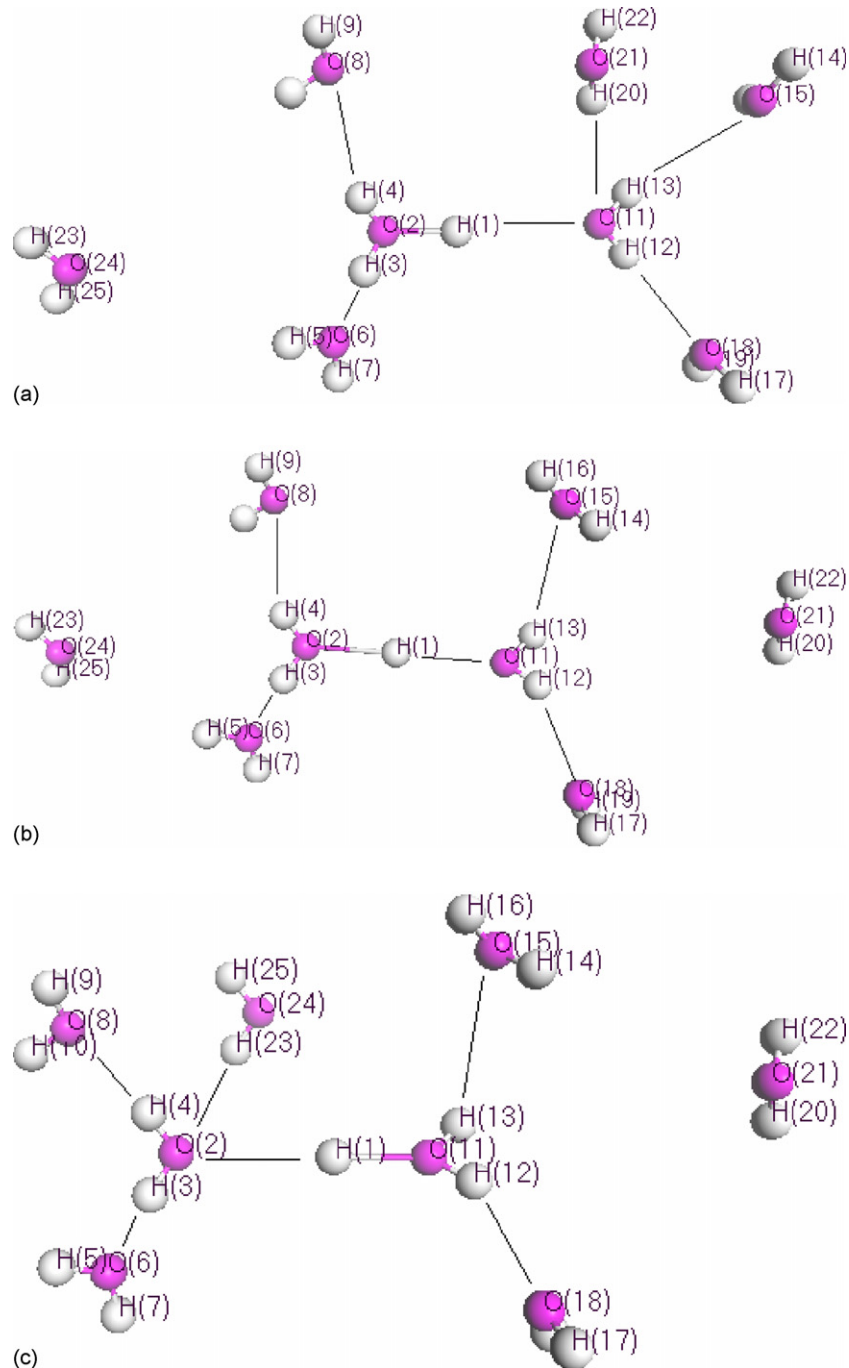


Fig. 1. The Grotthuss mechanism proposed by Agmon [1]. (a) The original structure of a cluster of a hydronium and water molecules. (b) The structure after the hydrogen bond breaks between H(20) and O(11). (c) The final structure after the hydrogen bond forms between H(23) and O(2).

Table 1
The coordinates and charge distribution inside the protonated water cluster as shown in Fig. 1(a): the cluster included all the molecules except the leftmost one

Atom number	Atom symbol	Charge, q (e)	Coordinates			xq	yq	zq
			x	y	z			
1	H	0.514459	0.945585	0.009402	1.359944	0.486465	0.004837	0.699635
2	O	-0.85789	0.002751	0.019616	1.037778	-0.00236	-0.01683	-0.8903
3	H	0.569679	-0.52815	-0.71828	1.436454	-0.30087	-0.40919	0.818318
4	H	0.546789	0.007695	-0.02485	0.039924	0.004208	-0.01359	0.02183
5	H	0.492236	-2.29727	-1.67294	2.29173	-1.1308	-0.82348	1.128072
6	O	-0.91078	-1.37361	-1.89144	2.144115	1.251051	1.722674	-1.95281
7	H	0.480854	-1.37707	-2.73193	1.679051	-0.66217	-1.31366	0.807378
8	O	-0.98071	0.260505	-0.10812	-1.52582	-0.25548	0.106031	1.49638
9	H	0.494087	1.217188	-0.09292	-1.63691	0.601397	-0.04591	-0.80878
10	H	0.515222	-0.08234	0.642575	-2.01564	-0.04242	0.331069	-1.0385
11	O	-0.83051	2.523012	0.026445	1.625285	-2.09538	-0.02196	-1.34981
12	H	0.459546	2.831773	0.828287	2.062741	1.30133	0.380636	0.947924
13	H	0.44486	2.859402	-0.7196	2.135216	1.272034	-0.32012	0.949872
14	H	0.486427	3.844791	2.961551	2.302721	1.87021	1.440578	1.120106
15	O	-0.93723	3.395178	2.35395	2.891401	-3.18207	-2.2062	-2.70991
16	H	0.48139	2.683236	2.864599	3.278959	1.291683	1.378989	1.578458
17	H	0.467169	3.147362	-2.15481	4.000596	1.47035	-1.00666	1.868954
18	O	-0.89501	3.478128	-2.13903	3.101597	-3.11294	1.914446	-2.77594
19	H	0.469524	4.432243	-2.14279	3.188364	2.081044	-1.00609	1.497013
20	H	0.421943	3.081864	-0.04187	-0.31458	1.300371	-0.01767	-0.13273
21	O	-0.91943	3.040741	-0.04668	-1.2694	-2.79575	0.042923	1.167125
22	H	0.487357	3.517259	-0.8304	-1.5437	1.714161	-0.4047	-0.75233

Middle point between O(11) and O(2): $x_m = (x_2 + x_{11})/2 = 1.262882$; $y_m = (y_2 + y_{11})/2 = 0.023031$; $z_m = (z_2 + z_{11})/2 = 1.331532$. Charge center: $x_c = \sum xq / \sum q = 1.064057$; $y_c = \sum yq / \sum q = -0.28388$; $z_c = \sum zq / \sum q = 1.689957$.

initio simulations [23–25] and MS-EVB simulations [26] have further discussed the proton transport mechanisms. Some literature concentrated only on the calculations of protonated clusters [27–29]. Recent simulations by Lapid et al. [25] have expanded the mechanism by considering larger water clusters around the $H_5O_2^+$ cation transferring complex than those shown in Fig. 1 but the results did not support the mechanism proposed by Agmon [1].

In the present work, we carried out *ab initio* chemical structure calculations to evaluate the charge distribution when a proton approaches a water molecule. Then, based on the displacement of the positive charge center, Agmon's assumption on the proton translocation and distribution is examined. Further, we studied the positive charge center displacement before and after the $H_5O_2^+$ ion combines with one water molecule and loses another. Based on these results, together with the experi-

mental data in the literature, only one of the previously proposed mechanisms for proton transport in water is confirmed.

2. Simulation results and discussions

2.1. Simulation of Agmon's proposed mechanism

Ab initio simulation of Agmon's proposition was carried out by using the unrestricted Hartree–Fock Self-Consistent (UHF) [30–32] method and with the 6-31G (d) basis [33,34]. To simulate the circumstances around the protonated water cluster; the IEFPCM solvent model was included. The structure of the water–proton cluster shown in Fig. 1(a) was optimized using energy minimization procedure. The charge distribution for this structure was obtained by using the CHelpG method. The results are shown in Table 1.

Table 2
The coordinates and charge distribution inside the protonated water cluster as shown in Fig. 3(a)

Atom number	Atom charge	Coordinates			Charge, q (e)	xq	yq	zq
		x	y	z				
1	H	1.682654	0.819287	-0.12962	0.532684	0.896323	0.436421	-0.06905
2	O	1.25615	-0.04215	-0.06249	-0.66622	-0.83687	0.028078	0.041635
3	H	0.231982	-0.00112	-0.00612	0.512125	0.118804	-0.00057	-0.00313
4	H	1.671468	-0.56911	0.631432	0.513148	0.85771	-0.29204	0.324018
5	O	-1.26847	0.039238	-0.05285	-0.84394	1.070507	-0.03311	0.044605
6	H	-1.74309	0.551787	0.596648	0.467187	-0.81435	0.257788	0.278746
7	H	-1.74447	-0.77758	-0.16956	0.485009	-0.84608	-0.37713	-0.08224

Charge center coordinates: $x_c = 0.446046$; $y_c = 0.019427$; $z_c = 0.534586$.

From the computational results, the midpoint between O(2) (the oxygen atom supposed to lose the proton) and O(11) (the oxygen atom supposed to obtain the proton) is (1.262882, 0.023031, 1.331532), and the charge center of the cluster is located at (1.064057, -0.28388, 1.689957). The distance between the midpoint and the charge center is only 0.512047 Å, while the distance between the two oxygen atoms is 2.587842 Å. It is clear that the charge center is initially located near the midpoint between O(2) and O(11), rather than at O(2) as assumed by Agmon [1]. During the cleavage and formation of the hydrogen bonds at the second solvation shell of this cation, the positive charge moves to the right, a distance of 1.024094 Å, to a point between O(2) and O(11), rather than from O(2) to O(11) as proposed by Agmon [1]. *Ab initio* calculations by Li et al. [35] also support that the positive charge is distributed among the surrounding water molecules for H_3O_4^+ . Thus, it is difficult for Agmon's hypothesis to account for the high proton mobility in water.

2.2. Charge distribution and energy

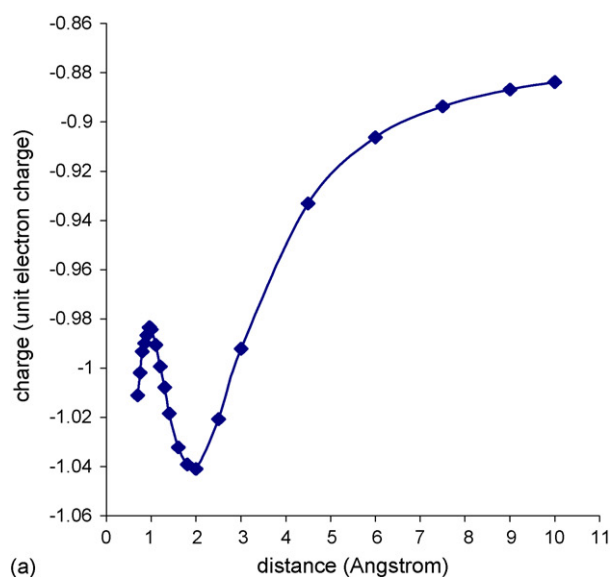
By using the UHF procedure/6-31G(d) basis, *ab initio* simulation was carried out for a small system consisting of a water molecule and a proton. The simulation results show that the energy of this system and the charge distribution among the different atoms change as the distance between the proton and water molecule changes, as shown in Fig. 2.

From Fig. 2, when the distance is much larger than 0.9648 Å, the bond breaks, and the water molecule and the proton are dissociated. When the distance is about 0.9648 Å, it is considered to be a H_3O^+ cation. In order for the hydronium cation to dissociate into a water molecule and a proton, nearly 0.3 hartrees energy is needed, an almost unconquerable barrier under ambient conditions. From Fig. 2(a) and (b), it can be concluded that charge redistribution takes place among the different atoms due to the quantum effect when a proton approaches towards or departs from a water molecule.

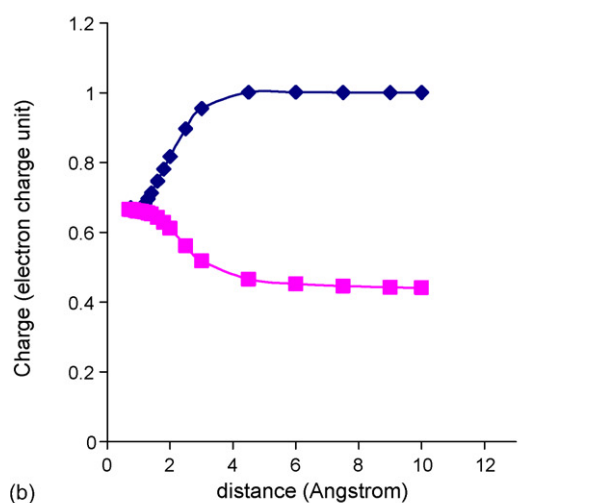
2.3. The transport media for the prototropic process

Many researchers assumed that prototropic mobility was caused by the thermal mobility of the hydrated cations ([11–15,19]). Starting with an optimized structure of a protonated cation $\text{H}^+(\text{H}_2\text{O})_n$, one additional water molecule is placed near the cation, and then the structure of the protonated cluster $\text{H}^+(\text{H}_2\text{O})_n + \text{H}_2\text{O}$ is optimized. Because of the quantum effect shown in Fig. 2, the charge redistributions accompanying the variation of the hydrogen bond strength occur when the hydrated cation interacts with the water molecule. If the newly formed $\text{H}^+(\text{H}_2\text{O})_{n+1}$ cation loses a water molecule inside the previous cation $\text{H}^+(\text{H}_2\text{O})_n$, the positive charge center moves as shown in Fig. 3. All the simulations are run with UHF methods/6-31G (d) basis and with dipole solvation model.

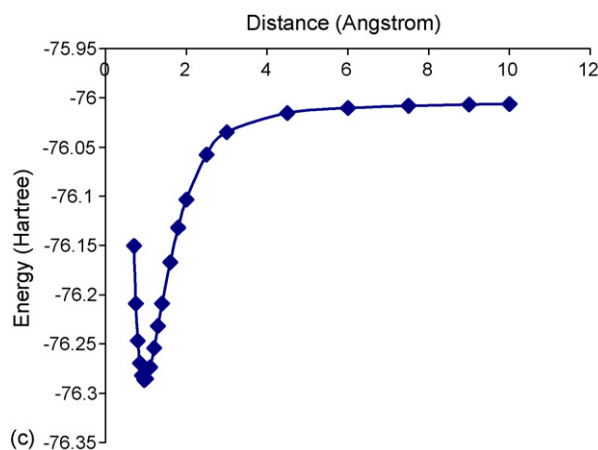
Both *ab initio* simulations and molecular dynamics simulations on hydronium–water clusters [36–38] lead to the conclusion that the hydrated protons form defects in the hydrogen-bonded network containing both H_3O_4^+ and H_5O_2^+ . Sobolewski



(a) Charge of the oxygen atom versus the distance between the oxygen atom and the proton.



(b) Charge of the hydrogen atom and the proton vs. the distance between the oxygen atom and the proton.



(c) Energy of the system vs. the distance between the oxygen atom and the proton.

Fig. 2. The energy and charge distribution vs. the distance between the oxygen atom and the proton. (a) Charge of the oxygen atom versus the distance between the oxygen atom and the proton. (b) Charge of the hydrogen atom and the proton vs. the distance between the oxygen atom and the proton. (c) Energy of the system vs. the distance between the oxygen atom and the proton.

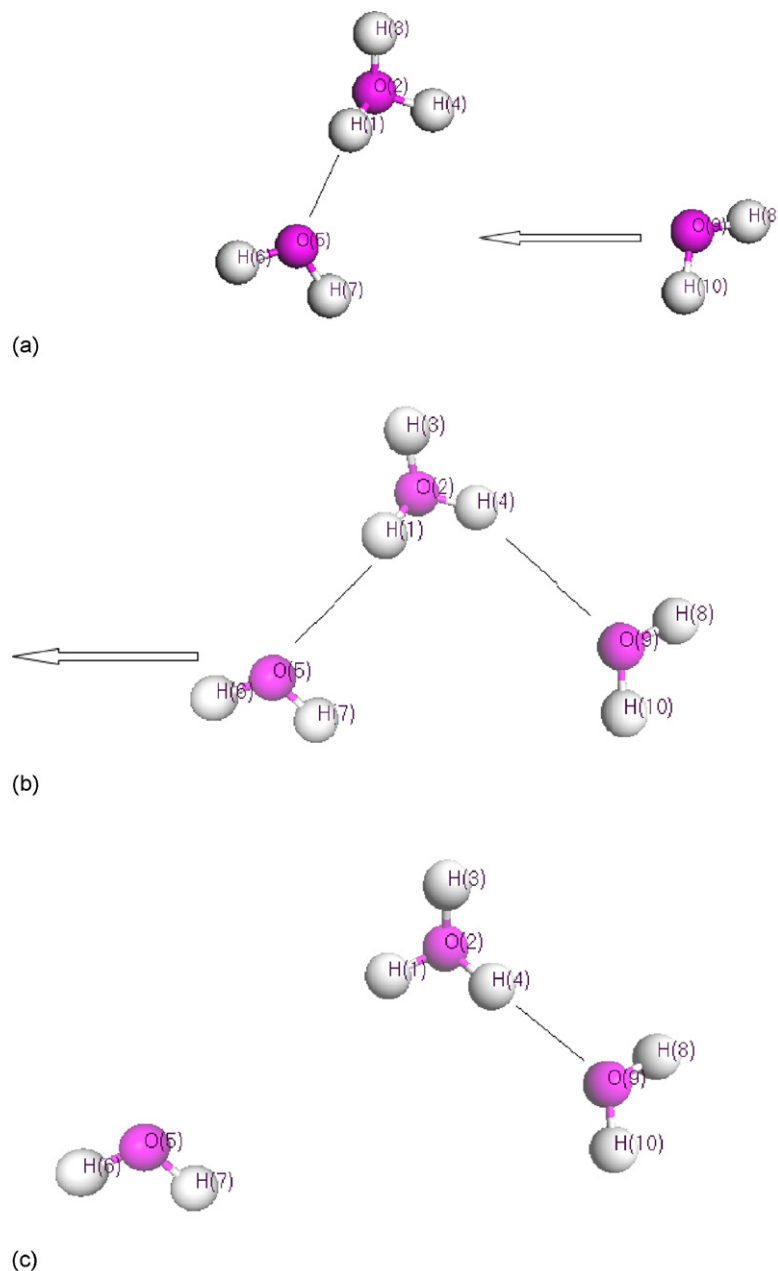


Fig. 3. Prototropic mechanism using Zundel cations as the transport media. (a) $H^+(H_2O)_2 + H_2O$. (b) $H^+(H_2O)_3$. (c) $H_2O + H^+(H_2O)_2$.

and Domcke [38] further pointed out that Eigen-type structure $H_3O^+W_n$ is more stable than the Zundel-type structure $H_5O_2^+W_n$. Thus, the proton transport mechanism is through the cation $H_5O_2^+W_n$. Using $H_5O_2^+$ cations as the proton transport media, the charge distribution and the coordinates of the different atoms at the different transport processes are shown in Tables 2–4. Based on these results, the charge center in Fig. 3(a) is located at (0.446046, -0.019427, 0.534586). It is near the middle point between point O(5) and O(2). When there is one more water molecule near the point O(2), the charge redistributes and the charge center moves 1.796724 Å to point (0.001479, 0.350705, 0.613383) in the new coordinates in Fig. 3(b). At the same time the bond between atom O(5) and H(1) becomes weaker while the bond between H(4) and O(9) becomes stronger.

If the bond between O(5) and H(1) breaks, the charge center moves to point (0.506539, 0.027269, 0.461696) according to the coordinates in Fig. 3(c). If the position of the oxygen atom O(2) is the same during this process, the total displacement for the charge center from Fig. 3(a) to (c) is 2.489779 Å.

2.4. Other factors affecting proton mobility

Lagodzinskaya et al. [39] stated that both the rate of proton migration and the rotational correlation time increase exponentially as the temperature decreases linearly. The proton conductivity is about twice as slow in ice as in super-cooled water at the same temperature [1,20,21,22]. Recent experimental results indicate that protons in ice between 30 and 190 K are

Table 3

The coordinates and charge distribution inside the protonated water cluster as shown in Fig. 3(b)

Atom number	Atom symbol	Coordinates			Charge, q (e)	xq	yq	zq
		x	y	z				
1	H	-0.00116	1.607724	0.633743	0.476032	-0.00055	0.765328	0.301682
2	O	0.000107	0.909756	-0.02488	-0.70125	-7.5E-05	-0.63797	0.017444
3	H	-0.84494	0.367672	-0.00667	0.538425	-0.45493	0.197964	-0.00359
4	H	0.845535	0.368151	-0.00516	0.538455	0.455283	0.198233	-0.00278
5	O	-2.17068	-0.46989	-0.05463	-0.88654	1.924388	0.416571	0.048435
6	H	-2.48284	-0.95345	0.704388	0.476709	-1.18359	-0.45452	0.335788
7	H	-2.93839	-0.09995	-0.47895	0.483914	-1.42193	-0.04837	-0.23177
8	O	2.170351	-0.46955	-0.05366	-0.88652	-1.92407	0.416266	0.047574
9	H	2.488564	-0.94555	0.707717	0.476923	1.186853	-0.45096	0.337527
10	H	2.935006	-0.10716	-0.48966	0.483852	1.420109	-0.05185	-0.23692

Charge center coordinates: $x_c = 0.001479$; $y_c = 0.350705$; $z_c = 0.613383$.

Table 4

The coordinates and charge distribution inside the protonated water cluster as shown in Fig. 3(c)

Atom number	Atom symbol	Coordinates			Charge, q (e)	xq	yq	zq
		x	y	z				
1	H	1.647461	-0.52843	0.689879	0.517574	0.852683	-0.2735	0.357063
2	O	1.278873	-0.05258	-0.05755	-0.67274	-0.86035	0.03537	0.038715
3	H	1.736108	0.828138	-0.21106	0.54632	0.948471	0.452428	-0.1153
4	H	0.276491	-0.00335	-0.02172	0.525734	0.145361	-0.00176	-0.01142
8	H	-1.29066	0.050158	-0.04208	-0.87661	1.131407	-0.04397	0.036884
9	O	-1.78667	0.435881	0.673973	0.472578	-0.84434	0.205988	0.318505
10	H	-1.77912	-0.7129	-0.33409	0.487147	-0.86669	-0.34729	-0.16275

Charge center coordinates: $x_c = 0.506539$; $y_c = 0.027269$; $z_c = 0.461696$.

immobilized [40]. The reorientation time of water molecules at such low temperatures is much longer than that at normal temperatures [39]. Johari and Jones [41] also found that the orientation polarization time increases with decrease in temperature, and it takes more than 5 min when the temperature is below 119 K. Furthermore, it is stated that the water molecule reorientation takes 1–2 ps at room temperature [42], and the proton hopping times are of similar magnitude, i.e. $\tau_p = 1.5$ ps [43]. From all of the above, it can be concluded that proton mobility is closely related to water molecule reorientation and the reorientation time decreases with increasing temperature.

The barrier for proton transport is removed or greatly reduced in an electrical field [35,44]. Huggins [11] believes that some of the molecular units are free to reorient themselves in an electrical field. An external electrical field lowers the barrier for proton transport in water by helping the water molecule reorient along the desired direction and reducing the energy barrier for proton transfer through $H_5O_2^+$.

To further explain the process of proton transport by the $H_5O_2^+$ cation mobility, we classify hydrogen bonds into three different types: the strong, the weak and the medium. The strong bond is between a H^+ and a H_2O inside a $H_5O_2^+$ cation, the weak bond is between two water molecules, and the medium bond is the one between a hydrated cation and a water molecule (such as the one on the second solvation shell of a hydrated cation). It is believed that it is the exchange between the three kinds of hydrogen bonds that leads to the formation and cleavage of the

hydrogen bonds in the second solvation shell, which in turn drive protons forward.

While the strong hydrogen bond between a H^+ and a H_2O inside a $H_5O_2^+$ cation is the impetus for Zundel polarization, the weaker hydrogen bonds between water molecules and between a water molecule and a $H_5O_2^+$ cation also play a critical role in the transport process of protons. Increase in temperature and pressure helps the removal of the newly formed cation $H_5O_2^+$ by weakening the weak and medium hydrogen bonds. This helps to explain why proton mobility increases with increasing temperature and pressure [42].

Of all the existing theories for prototropic mobility, proton transport through the cation $H_5O_2^+$ is the only theory that does not contradict any existing experimental and simulation results. The picture can be envisioned as follows. Inside the water solvent, a proton is surrounded by water molecules. Because of the high solvation energy of the reaction $H^+ + H_2O \rightarrow H_3O^+$, a proton combines with a water molecule and quickly forms a hydronium; the reverse process rarely occurs due to the high energy barrier. Similarly, because of the exothermal properties of the reactions, H_3O^+ cations continue to combine with water molecules to form cations of $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$. Furthermore, due to the symmetry structures, $H_5O_2^+$ cations and $H_9O_4^+$ cations are more stable than $H_7O_3^+$ cations. A $H_7O_3^+$ cation combines with a water molecule and becomes a $H_9O_4^+$ cation, or dissociates a water molecule and becomes a $H_5O_2^+$ cation. Regardless, all three

types of cations decompose and recombine into each other constantly.

According to Lobaugh and Voth [45], when a water molecule is close to a H_5O_2^+ cation, solvent-induced proton transport occurs and a structure similar to H_7O_3^+ is formed. The Zundel polarization is assumed to play the main role during this process. H_7O_3^+ cations are unstable and will dissociate to form new H_5O_2^+ cations and new water molecules. During this process, the proton moves forward. The formation and cleavage of hydrogen bonds are critical for the high proton mobility. Water molecule orientation is the determining factor for inducing the Zundel polarization during this process. An external electrical field helps the water molecules reorient along the desired direction and lowers the barrier for Zundel polarization inside H_5O_2^+ cations. Higher temperature not only reduces the reorientation time but also facilitates the departure of the newly formed H_5O_2^+ cations.

While it is assumed that protons are transported in water by the mobility of H_5O_2^+ cations, Kuznetsov et al. [46] pointed out that the experimental data [47,48] show that the excess proton mobility reaches maximum near 422 K and decreases as the temperature increases. This agrees well with the protonated water cluster weights evaluated by Gierer and Wirtz [48], which show that the weight of H_5O_2^+ decreases quadratically as the temperature increases and nearly disappears at 672 K, above which proton transport through Zundel cations is not the dominant mechanism.

3. Conclusion

In this paper, a solvation model based *ab initio* computations on the charge distribution inside a protonated water cluster and the energy involved for proton transport in water by the mobility of H_3O^+ , H_5O_2^+ , H_7O_3^+ , H_9O_4^+ cations have been carried out. Based on the computational results and the existing experimental data, the following conclusions on the mechanism of proton transport in water can be made.

It is most likely that the high mobility of protons in water is due to the high mobility of H_5O_2^+ cations, and the high mobility of H_5O_2^+ cations is mainly induced by the thermal movement of water molecules in the second solvation shell of H_5O_2^+ cations and the Zundel polarization inside the cations. Furthermore, thermal effects play a dominant role during the transport process by determining the reorientation time of the water molecules in the neighborhood of the second solvation shell of H_5O_2^+ cations and also by providing the energy for the cleavage of the hydrogen bond between a water molecule and a H_5O_2^+ cation. An external electrical field lowers the proton transport barrier by helping water molecules orient along the desired direction and by lowering the energy barrier for proton transfer inside H_5O_2^+ cations.

When the temperature is higher than 422 K, proton mobility decreases as the temperature increases because the weight of H_5O_2^+ cations decrease quadratically with the increase of the temperature. When the temperature is over 672 K, the content of H_5O_2^+ cations is very low and proton transport through Zundel cations is not the dominant mechanism.

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