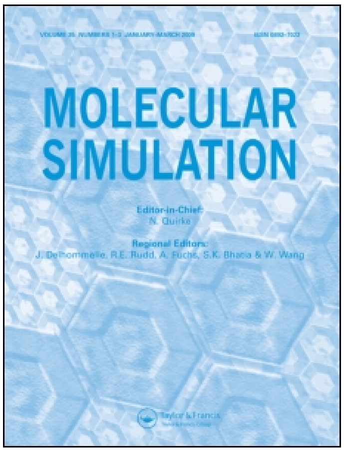

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Song Hi Lee[a]; Jayendran C. Rasaiah[b]
[a] Department of Chemistry, Kyungsung University, Pusan, South Korea [b] Department of Chemistry, University of Maine, Orono, ME, USA

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Local dynamics and structure of the solvated hydroxide ion in water

Song Hi Lee[a]* and Jayendran C. Rasaiah[b1]

[a]*Department of Chemistry, Kyungsung University, Pusan 608-736, South Korea;* [b]*Department of Chemistry, University of Maine, Orono, ME O4469, USA*

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Details of the structural diffusion mechanism in proton transfer (PT) reactions involving a hydroxide ion in water and the structure of the solvated ions and transfer intermediates are in dispute. Here, we elucidate the mechanism of PT involving a hydroxide ion in water by molecular dynamics simulations using a dissociating water model based on *ab initio* calculations. We find that the hydroxide ion in bulk water is present as the four-coordinated $OH^-(H_2O)_4$ complex, which loses a water molecule before a PT occurs through the formation of proton sharing intermediates in general agreement with the previously disputed first principles studies of small systems.

Keywords: proton transfer; hydroxide ion; OSS2 model; aqueous solution

1. Introduction

Proton transfer (PT) in water is of central importance to a wide range of chemical and biological processes [1–3]. The anomalously large mobility of hydrogen and hydroxide ions in aqueous solution compared to other ions [4,5] is explained by structural diffusion in which protons move successively between neighbouring molecules, one of which contains either an excess protonic charge or a negative charge defect, characterised as a 'proton hole' [6,7]. Simple hole–particle symmetry suggests that hydrogen ions move in the same direction as that of PT while hydroxide ions move in the opposite sense [7,8]. However, the mobility of the hydrogen ion is about 1.8 times that of the hydroxide ion. This indicates a dynamical asymmetry in the transport mechanisms of hydrogen and hydroxide ions in liquid water [7]. The origin of this is not fully understood, with conflicting opinions about the structure of the hydroxide ion and the mechanism of PT [9–12].

A hydrogen ion in a dilute aqueous solution exists as a range of structures from the Eigen cation [13–15] $H_9O_4^+$, consisting of a hydronium ion H_3O^+ hydrogen bonded to three water molecules, to the Zundel cation [16,17] $H_5O_2^+$ in which the excess proton is shared between two water molecules. Details of the mechanism of transport of the H^+ ion are broadly understood from first principles simulations of the excess proton in small systems of 32 water molecules [18–20] and from extended valence bond theory calculations of larger systems [21,22] but the corresponding details for hydroxide ion transport are in dispute [9–12,23]. Marx et al. [18] found that H^+ ion transport in aqueous solutions is driven by solvent fluctuations in the second solvation shell of the Eigen complex as suggested earlier by Agmon [19,20] with PT occurring via a Zundel intermediate.

Computational and theoretical studies [9–12,23] of the hydroxide ion in bulk water are not in agreement with the mechanism of transport or even the identity of the dominant solvated hydroxide ion species and intermediates in aqueous solution. In one scenario [9,23], the oxygen of the hydroxide ion is four coordinated through hydrogen bonds in a stable and relatively inert complex $OH^-[H_2O]_4$. Fluctuations lead to the loss of a water molecule to form the slightly less stable three-coordinated complex $OH^-[H_2O]_3$ followed by PT to the oxygen of the hydroxide ion from one of the three water molecules in the complex through a Zundel-like intermediate $[HO\cdots H\cdots OH]^-$ to create a new $OH^-[H_2O]_3$ complex at the donor site. The whole cycle can be repeated again (in a large enough system) after a suitable solvent fluctuation in which an OH^- ion is virtually transported in a direction opposite to that of PT without the actual movement of an oxygen atom in phase with PT. The process terminates when the newly formed $OH^-[H_2O]_3$ complex reverts back to the less active $OH^-[H_2O]_4$ by hydrogen bonding with an adjacent water molecule.

However, Quasi-chemical calculations and other *ab initio* quantum computer simulations [10,11] have suggested that the oxygen of the OH^- ion is three coordinated in its most stable form as expected from the Lewis picture of electron pair bonding. These uncertainties in the first principles simulations arise partly from small system sizes (usually of the order of about 32 water

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*Corresponding author. Email: shlee@ks.ac.kr

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molecules) and different approximations for the exchange functional in density functional theory which lead to different conclusions about the proportions of the three-and four-coordinated hydroxide ion species in solution. This translates into uncertainties in the mechanism of hydroxide ion transport.

2. Molecular model

Stillinger, Lemberg, David and Weber [24–28] have made several attempts at using dissociating water potentials in classical simulations. Recently, Ojamäe et al. [29] designed a family of potentials for solvated proton $H^+(H_2O)_n$ complexes in water called the OSS*n* potentials where $n = 1-3$ are fitted to *ab initio* MP2 calculations.

We use the OSS2 model of Ojamäe et al. for our simulations of protons and hydroxide ions in water. Although more accurate results could possibly be obtained with the OSS3 potential, the OSS2 model also gives good results judging by simulations of neat water. It is our preferred choice because of faster and less elaborate computer code implementation compared to the OSS3 model which contains three body dipole coupling terms.

The OSS2 model [15] is a polarisable model in which the induced dipole moment μ_i at each oxygen atom site i is obtained self consistently from

$$\mu_i = \alpha \left[\sum_{j \neq i}^{n_O + n_H} \frac{r_{ij} q_j}{r_{ij}^3} S_{ij}^{cd}(r_{ij}) + \sum_{j \neq i}^{n_O} \frac{T_{ij} \mu_j}{r_{ij}^3} S_{ij}^{dd}(r_{ij}) \right],$$

by imposing the conditions $\mathrm{d}V_{\mathrm{el}}/\mathrm{d}r_k = 0$ $(k = 1, 2, \ldots, n_O)$, where V_{el} is the electrostatic energy, n_O and n_H are the numbers of oxygen and hydrogen atoms, α is the polarisability of the atom and $S_{ij}^{cd}(r_{ij})$ and $S_{ij}^{dd}(r_{ij})$ are the cut-off functions for the charge–dipole and dipole–dipole interactions, respectively. Ewald summations were used in our simulations with the parameter for $\kappa = 5.0/L$ and the real-space cut distance r_{cut} and $K_{\max}$ chosen as $0.5L$ and 7, respectively, where L is the length of the box (~ 9.87 Å for 32 water molecules corresponding to a density of $0.998\,\mathrm{g\,cm^{-3}}$). The double summations in reciprocal space, which cannot be reduced to a single summation due to the cut-off functions, were ignored. This is reasonable as the distances in reciprocal space are larger than the length L of the box. To maintain electroneutrality a fictitious charge of opposite sign to the given OH^- or H^+ ion was placed at a corner of the simulation box. This charge never moves and only interacts with other charges through a Coulomb potential with Ewald summation. The time step was chosen as 0.2 fs. The simulations were first validated by checking our results against Ojamäe's work for pure water using the same OSS2 model. The calculated oxygen–hydrogen (O—H) radial distribution function and the hydration number $n(r)$ for hydrogen in the 216 molecule pure water system are nearly identical, even though Ojamäe et al. used a different method for the Ewald sums in the calculation of the induced dipole moment.

3. Results and discussion

Figure 1 shows four snapshots of a PT sequence from our simulations of 31 water molecules with a single OH^- after equilibration. In panel (a) the hydroxide ion is indeed present as the $OH^-(H_2O)_4$ complex which in our calculations is the most stable form before PT occurs as shown in panels (b) and (d). The four water molecules (at the ends of the four yellow coloured bonds shown in panel (a)) are in a plane as predicted by Tuckerman et al. [9]. Each of the four water molecules coordinated with the oxygen atom of OH^- is on average tetrahedrally coordinated; one to the OH^- ion and the others to water molecules. One such water molecule is shown in panel (a).

To explain the mechanism, the four-coordinated oxygen atom of the OH^- ion is characterised as O$*$ and the hydrogen atom as H$'$. The hydrogen atom of the $(O{*}H')^-$ ion can also be hydrogen bonded to a water molecule. This five coordinated structure (not shown) exists only transiently in our simulations. Thermal fluctuations cause a water molecule to be detached from the four-coordinated $(O{*}H')^-$ ion complex to form $[O{*}H'^-(H_2O)_3]$ which is accompanied by shrinking of the three hydrogen bonded O$*$—O distances which

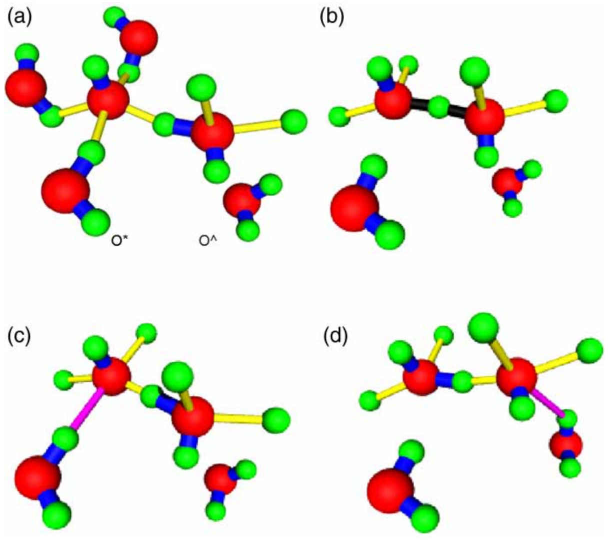

Figure 1. Representative configurations of OH^- ion showing the mechanism of PT leading to the transport of the hydroxide ion in a simulation of one OH^- ion in 31 water molecules using the OSS2 potential. (a) $O{*}H'^-(H_2O)_4$ complex showing four coordination of O$*$. (b) $OH^-(H_2O)_3$ intermediate with H$'$ between O$*$ and O^ showing three coordination of O$*$. (c) Return to (a) from three-coordinated intermediate. (d) Completion of PT via $OH^-(H_2O)_3$ intermediate (see the text).

nevertheless fluctuate as expected in a dynamical system. The hydrogen in the bond linking the shortest distance between two adjacent oxygen atoms $O{*}—O^{\wedge}$ is the most likely one to undergo PT and moves closer to the oxygen atom of the $(O{*}H')^-$ ion to form the Zundel-like intermediate $[(H'O{*})^- \cdots H \cdots O^{\wedge}H]$ in panel (b). A fluctuation in position of this hydrogen can return it to its former site restoring the original $(O{*}H')^-$ and a water molecule as shown in panel (c), or it can move in the opposite direction to produce a new water molecule ($H_2O{*}$) and a new $O^{\wedge}H^-$ ion at the adjacent oxygen atom, as shown in panel (d), which is already three coordinated with water molecules. Several transitions back and forth between these two sets are observed. In our simulation of the hydroxide ion in 31 water molecules, PT is finally complete when the newly formed three-coordinated hydroxide ion is stabilised by the formation of the four coordinated but relatively inert $OH^-[H_2O]_4$ structure seen in panel (d) due to the presence of a water molecule in the vicinity.

The identity of the solvated complexes of the hydroxide ion and the likelihood of PT can be determined by selecting two sets of configurations for which the displacement coordinate [9] $\delta = |R_{O*H} - R_{OH}|$ is small ($\delta < 0.1$ Å) and large ($\delta > 0.5$ Å) before or after PT. Here, R_{O*H} and R_{OH} are the respective distances of the shared proton from O*, the oxygen of the hydroxide ion and O, the oxygen of a water molecule to which it is hydrogen bonded. A small δ indicates a potential pathway for PT (panel (b) of Figure 1) and a large value of δ suggests the opposite (panels (a) and (d) of Figure 1).

Figure 2 shows the radial distribution functions g_{O*H} and g_{O*O} and the corresponding coordination numbers n_{O*H} and n_{O*O} with respect to the oxygen atom O* of the hydroxide ion $O{*}H^-$ in 31 water molecules for a configuration in which the displacement coordinate (a) $\delta > 0.5$ Å and (b) $\delta < 0.1$ Å. Figure 2(a) shows that for large δ the oxygen O* of the hydroxyl ion accepts on average four hydrogen bonds in complete agreement with the AIMD study of Tuckerman et al. [9]. Visual observations (panel (a) Figure 1) show that the four hydrogen atoms are in a plane slightly below the oxygen atom of the hydroxyl ion. However, our studies for configurations with large δ suggest that the hydroxyl ion $O{*}H'$ does not donate its hydrogen H′ to form the additional weak H bond observed in [9], so that the total coordination number n_{O*O} remains at 4 instead of ~4.5 reported by Tuckerman et al. [9]. For the displacement coordinate $\delta < 0.1$ Å (Figure 2(b)) the first peak in the O*—O pair correlation function g_{O*O} at 2.72 Å for $\delta > 0.5$ Å is split into two peaks at 2.44 and 2.90 Å, respectively, and the first intra-molecular peak in the O*—H pair correlation function g_{O*H} at 1.72 Å for $\delta > 0.5$ Å is also split into peaks at 1.21 and 1.89 Å, respectively. The peak at the shorter distance (2.44 Å) in the O*—O pair correlation function characterises the hydrogen bonded pair (bonds shown in black in panel (b) of Figure 1 in the main text) across which PT can occur and the corresponding peak in the O*—H pair correlation function at 1.21 Å shows a hydrogen atom approximately midway between this pair of oxygen atoms. This splitting is also observed in AIMD simulations of Tuckerman et al. [9].

In our previous MD simulation [30] of a protonated water in 31 water molecules, the H_3O^+ ion exists as the Eigen cation $H_3O^+(H_2O)_3$ (Figure 3(a)) before PT occurs. This complex is solvated by water molecules which form a second solvation shell. Thermal fluctuations break the H bond of a water molecule in the second solvation shell of H_3O^+, leaving the three-coordinated H_3O^+ with shorter hydrogen bonded O—O distances. To explain the mechanism of PT, the oxygen in the three-coordinated H_3O^+ is characterised as O*. The hydrogen atom linking the shortest O*—O distance in a hydrogen bond is the most likely one to undergo PT by moving closer to the oxygen of the solvating water molecule, designated as $O^{\wedge}$, to form the Zundel intermediate $[H_2O{*} \cdots H \cdots O^{\wedge}H_2]^+$. This 'most

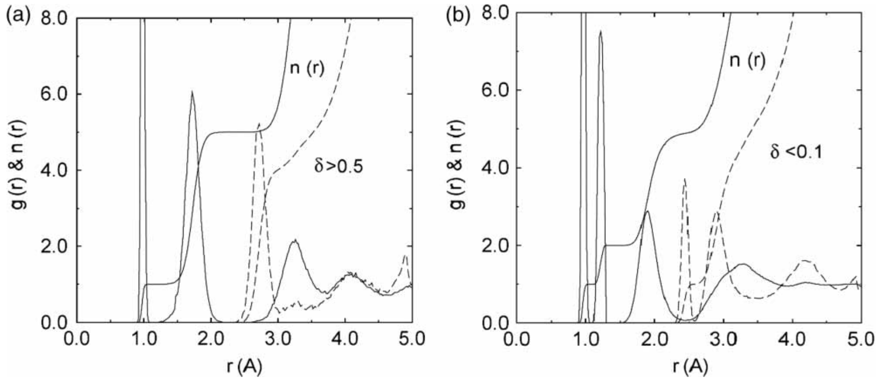

Figure 2. The radial distribution functions g_{O*H} and g_{O*O} (solid and dashed line respectively) and the corresponding coordination numbers n_{O*H} and n_{O*O} with respect to the oxygen atom O* of the hydroxide ion $O{*}H^-$ in 31 water molecules for configuration in which the displacement coordinate (a) $\delta > 0.5$ Å before or after PT and (b) $\delta < 0.1$ Å (Zundel-like intermediate).

active' H fluctuates between two O's (Figure 3(b)). If the O^ returns to its former state by forming a hydrogen bond with an extraneous water molecule (a H bond shown in pink colour in Figure 3(c)), the most active H atom goes back to O∗ and PT does not occur. Alternatively, if the O∗ atom of the original Eigen complex, now present in the Zundel form, becomes four coordinated by forming a H bond with a fourth water molecule (a H bond shown in pink colour in Figure 3(d)), the most active H within the Zundel complex moves to O^ and PT occurs to form a new H_3O^+ ion that is stabilised in the next step by the formation of an Eigen complex (not shown). The initial existence of a water near the old H_3O^+ is essential for PT to occur since the newly formed H bond (pink colour in Figure 3(d)) stabilises the conversion of the old $(H_3O*)^+$ to form a new four-coordinated water molecule after PT has occurred.

The pre-existence of a water molecule near the Eigen complex $H_3O^+[H_2O]_3$ is necessary for PT to occur in an adjacent water molecule via the Zundel intermediate, whereas PT from a water molecule to the hydroxide ion OH^- ion, via the three-coordinated intermediate, requires the pre-existence of a water molecule near the newly forming OH^-. Our simulations of H^+ ion and OH^- ion transport using the dissociating OSS2 model are in general agreement with the results of first principles AIMD simulations [9,18] of the same systems containing 32 water molecules, but the size limitations of small system may preclude the observation of consecutive PTs and transport properties. We found that the OSS2 model could behave like a glass under ambient conditions, as suggested to us by N. Agmon [31], but the same mechanism of proton transport is observed at higher temperatures (500 K) or lower densities ($0.542\,g\,cm^{-3}$) where glass formation is absent.

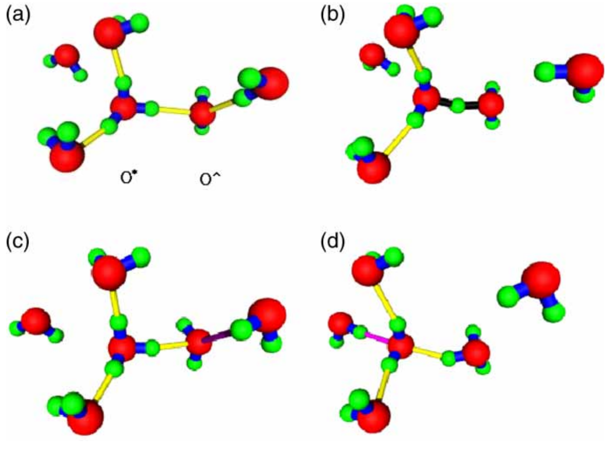

Figure 3. Representative configurations showing the mechanism of PT leading to the transport of a hydrogen ion in a simulation of one H_3O^+ ion in 31 water molecules using the OSS2 potential. (a) H_3O^+ ion stabilised as an Eigen complex $H_3O^+(H_2O)_3$ showing three coordination of H_3O^+ and a water molecule in the second solvation shell. (b) Loss of water in the second solvation shell in (a) and the formation of the Zundel intermediate $H_5O_2^+$. (c) Return to (a) from the Zundel intermediate in the absence of PT. (d) Completion of PT via the Zundel intermediate to form a new H_3O^+ ion.

4. Summary

Classical simulations using the OSS2 model potential derived from *ab initio* calculations can be used to understand the mechanism of PT in bulk water. PT of the hydroxide ion in bulk water starts from the four-coordinated species and proceeds through a three-coordinated intermediate accompanied by specific solvent reorganisation which must take place for PT to occur. For hydrogen ions, the starting point is the Eigen complex and PT proceeds through a Zundel intermediate. These conclusions and the asymmetry in the transport mechanism of hydrogen and hydroxide ions in bulk water are in broad agreement with first principles AIMD simulations of H^+ ions by Tuckerman et al. [9] and of OH^- ions by Marx et al. [18].

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Note

1. Email: rasaiah@maine.edu

References

[1] J.T. Hynes, *The protean proton in water*, Nature 397 (1999), pp. 565–566.
[2] G.A. Voth, *Computer simulation of proton solvation and transport in aqueous and biomolecular systems*, Acc. Chem. Res. 39 (2006), pp. 143–150.
[3] C.A. Wraight, *Chance and design: proton transfer in water, channels and bioenergetic proteins*, Biochem. Biophys. Acta. 1757 (2006), pp. 886–912.
[4] S. Koneshan, J.C. Rasaiah, R.M. Lynden-Bell, and S.H. Lee, *Solvent structure, dynamics, and ion mobility in aqueous solutions at 25°C*, J. Phys. Chem. B. 102 (1998), pp. 4193–4204.
[5] J.C. Rasaiah and R.M. Lynden-Bell, *Computer simulation studies of the structure and dynamics of ions and non-polar solutes in water*, Phil. Trans. R. Soc. Lond. A 359 (2001), pp. 1545–1574.
[6] R. Ludwig, *New insight into the transport mechanism of hydrated hydroxide ions in water*, Angew. Chem., Int. Ed. 42 (2003), pp. 258–260.
[7] F.H. Stillinger and T.A. Weber, *Asymmetry between protons and proton holes in gas-phase neutralization reactions*, Mol. Phys. 46 (1982), pp. 1325–1333.
[8] D. Riccardi, P. König, X. Prat-Resina, H. Yu, M. Elstner, T. Frauenheim, and Q. Cui, *Proton holes in long-range proton transfer reactions in solution and enzymes: a theoretical analysis*, J. Am. Chem. Soc. 128 (2006), pp. 16302–16311.

[9] M.E. Tuckerman, D. Marx, and M. Parrinello, *The nature and transport mechanism of hydrated hydroxide ions in aqueous solution*, Nature 417 (2002), pp. 925–929.

[10] D. Asthagiri, L.R. Pratt, J.D. Kress, and M.A. Gomez, *The hydration state of* HO^- *(aq)*, Chem. Phys. Lett. 380 (2003), pp. 530–535.

[11] D. Asthagiri, L.R. Pratt, J.D. Kress, and M.A. Gomez, *Hydration and mobility of* HO^-, Proc. Natl. Acad. Sci. USA 101 (2004), pp. 7229–7233.

[12] N. Agmon, *Mechanism of hydroxide mobility*, Chem. Phys. Lett. 319 (2000), pp. 247–252.

[13] E. Wicke, M. Eigen, and Th. Ackermann, *Über den Zustand des Protons (Hydroniumions) in wäβriger Lösung*, Z. Physik. Chem. (N.F.) 1 (1954), pp. 340–364.

[14] M. Eigen, W. Kruse, G. Maass, and L. DeMayer, *Rate constants of protolytic reactions in aqueous solution*, Prog. React. Kin. 2 (1964), pp. 285–318.

[15] M. Eigen, *proton transfer acid-base catalysis and enzyme hydrolysis*, Angew. Chem., Int. Ed. Engl. 3 (1964), pp. 1–19.

[16] G. Zundel and H. Metzger, *Energiebänder der tunnelnden Überschuβ-Protenon in flüssigen Säuren. Eine IR-spektroskopische Untersuchung der Natur Gruppierungen* $H_5O_2^+Z$, Physik. Chem. (N.F.) 58 (1968), pp. 225–245.

[17] G. Zundel, *Easily polarizable hydrogen bonds – their interactions with the environment – IR continuum and anomalous large conductivity*, in *The hydrogen bond-recent developments in theory and experiments. II Structure and Spectroscopy*, P. Schuster, G. Zundel & C. Sandorfy, eds., North-Holland, Amsterdam, 1976, pp. 683–766.

[18] D. Marx, M.E. Tuckermann, and M. Parrinelleo, *The nature of the hydrated excess proton in water*, Nature 397 (1999), pp. 601–604.

[19] N. Agmon, *The Grotthuss mechanism*, Chem. Phys. Lett. 244 (1995), pp. 456–462.

[20] N. Agmon and M. Gutman, *Proton solvation and proton mobility (Proceedings of a Research Workshop of the Israel Science Foundation)*, Foreword Isr. J. Chem. 39 (1999), pp. III–IIV.

[21] R. Vuilleumier and D. Borgis, *Transport and spectroscopy of the hydrated proton: a molecular dynamics study*, J. Chem. Phys. 111 (1999), pp. 4251–4265.

[22] U.W. Schmitt and G.A. Voth, *The computer simulation of proton transport in water*, J. Chem. Phys. 111 (1999), pp. 9361–9381.

[23] M.E. Tuckerman, A. Chandra, and D. Marx, *Structure and dynamics of* OH^-*(aq)*, Acc. Chem. Res. 39 (2006), pp. 151–158.

[24] H.L. Lemberg and F.H. Stillinger, *Central-force model for liquid water*, J. Chem. Phys. 62 (1975), pp. 1677–1690.

[25] F.H. Stillinger and C.W. David, *Polarization model for water and its ionic dissociation products*, J. Chem. Phys. 69 (1978), pp. 1473–1484; F.H. Stillinger and C.W. David, *Study of the water octamer using the polarization model of molecular interactions*, J. Chem. Phys. 73 (1980), pp. 3384–3389.

[26] F.H. Stillinger and T.A. Weber, *Computer simulation proton hydration dynamics*, Chem. Phys. Lett. 79 (1981), pp. 259–260.

[27] F.H. Stillinger and T.A. Weber, *Polarization model study of isotope effects in the gas phase hydronium–hydroxide neutralization reaction*, J. Chem. Phys. 76 (1982), pp. 4028–4036.

[28] T.A. Weber and F.H. Stillinger, *Reactive collisions of* H_3O^+ *and* OH^- *studied with the polarization model*. J. Phys. Chem. 86 (1982), pp. 1314–1318; T.A. Weber and F.H. Stillinger, *Dynamical study of the* $H_5O_2^+ + H_3O_2^-$ *neutralization reaction using the polarization model*, J. Chem. Phys. 77 (1982), pp. 4150–4155.

[29] L. Ojamäe, I. Shavitt, and S.J. Singer, *Potential models for simulations of the solvated proton in water*, J. Chem. Phys. 109 (1998), pp. 5547–5564.

[30] S.H. Lee, *Local dynamics and structure of solvated proton in water*, Bull. Kor. Chem. Soc. 30 (2009), pp. 499–501.

[31] N. Agmon, *Private communication*.