

Role of solvation structure in the shuttling of the hydrated excess proton[†]

RAJIB BISWAS and GREGORY A VOTH*

Department of Chemistry, James Franck Institute, and Institute for Biophysical Dynamics
The University of Chicago, Chicago, IL 60637, USA
E-mail: gavoth@uchicago.edu

MS received 9 February 2017; revised 14 April 2017; accepted 18 April 2017

Abstract. The classic Marcus electron transfer reaction model demonstrated that a barrierless electron transfer reaction can occur when both the reactant and product have almost similar solvation environment. In our recently developed proton model, we have incorporated the pre-solvation concept and showed that it indeed facilitates the proton diffusion in aqueous solution. In this work, we further quantify the degree of pre-solvation using different structural parameters, *e.g.*, tetrahedral order parameter, average numbers of hydrogen bonds. All the above said parameters exhibit a very strong correlation with the proton share parameter. The more Zundel-like configurations have almost identical solvation environment for both the water molecules and support the pre-solvation concept. However, in the case of Eigen-like configurations, the central hydronium and “special pair” water have distinctly different solvation structures.

Keywords. Empirical valence bond; reactive molecular dynamics; pre-solvation; proton transfer; proton transport.

1. Introduction

The aqueous transfer or “shuttle” of a hydrated excess proton between water molecules is extremely important to explore many important processes involved in biological^{1–4} and energy systems.^{5–8} In aqueous solution, an excess proton can interact with the surrounding water in a very fast time scale. The interaction strength can span continuously between a strong covalent interaction and a weaker hydrogen bond, which leads to the delocalization of excess positive charge defect. These excess proton water solvation structures can be by and large defined by a continuous evolution of different transient configurations within two limiting forms, the Eigen cation⁹ (hydronium solvated with three water molecules) and Zundel cation¹⁰ (proton equally shared between two water molecules). The fast transport of excess charge in case of the aqueous hydrated excess proton occurs *via* the Grotthuss mechanism,^{3,11,12} in which the excess proton is transferred by the breaking and forming of chemical bonds. Because of the rapid time scale and strong coupling of the structural evolution with proton

transfer process, it is extremely challenging to study the process experimentally and computationally as well.

Despite several challenges, the excess proton solvation and transport have been studied extensively by experiments^{13–19} and simulations.^{4,20–44} Ultrafast high-resolution spectroscopy^{13–19} and advanced computer simulation techniques,^{4,6–8,20–44} have enhanced our understanding of the proton transport mechanisms, particularly in the case of aqueous systems. The dynamical evolution of bonding topologies in terms of reorganization of water hydrogen bond (H-bond) network requires special attention for building a reasonable model to study proton transfer in aqueous solution. Because of the absence of bond breaking and bond formation features, classical molecular dynamics simulation does not allow to study proton solvation and transfer. On the other hand, in the case of *ab initio* molecular dynamics (AIMD) the explicit treatment of electronic degrees of freedom by the system Hamiltonian makes it one possible choice to study proton solvation and charge transfer more accurately.^{20,22,24,25,27,29,33,35,37,41–43,45} However, the AIMD method comes with a very high computational cost which, thus, limits the system size and time scales that can be studied. In addition to this, the intrinsic approximations accompanying with the level of density functional theory (DFT) employed in AIMD can also

*For correspondence

[†]Dedicated to the memory of the late Professor Charusita Chakravarty.

give rise to unphysical consequences, particularly in the case of liquid water.^{27,43,46,47}

However, despite these facts, the inherent capability of treating electronic polarization, chemical bond-breaking, and charge transfer by AIMD can provide significant information for parameterization of more efficient computational models.^{36,39} One such alternate approach based on the Multistate Empirical Valence Bond (MS-EVB) formalism has been shown to simulate excess proton solvation and transfer successfully while accurately capturing the essential physics and chemistry in different protonated systems.^{4,23,26,31,40} The MS-EVB and AIMD studies together find that the Eigen cation is the predominant solvation structure in bulk water and that proton transfer happens *via* an Eigen-Zundel-Eigen mechanism. In case of Eigen configurations, it has been found from the earlier simulation studies that one of the three water ligands in its first solvation shell always prefers to be closer to the hydronium moiety than the other two and is termed as “special pair” water.^{20,32} It has also been found that before the proton transfer event, the “special pair” water interchanges its identity rapidly within the three first shell water molecules (the “special pair” dance).^{32,34}

Recent AIMD data and the latest version of the MS-EVB model (version 3.2) both showed that “pre-solvation” (*i.e.*, the hydronium is transiently solvated by four water molecules by accepting a weak hydrogen bond from the fourth water molecule) facilitates the proton shuttling and diffusion in aqueous solution.^{33,37,43,48} Since a water molecule typically forms four hydrogen bonds, in the pre-solvation picture, before the proton transfer happens, hydronium will also form four hydrogen bonds. This will create a similar solvation environment for both the hydronium and its nearby water molecules.^{33,37,43} Thus, if the excess proton transfers from hydronium to any one of its nearest water molecules in the pre-solvated condition, the newly formed water molecule will have similar coordination number as in the bulk water. This pre-solvation concept can be well understood by the classic Marcus picture of proton transfer.^{49,50} In the Marcus picture, the free energy of the system along the (slow) solvent coordinate is similar before and after a proton transfer reaction so that the transition can happen in the (fast) proton transfer coordinate. In the present work, we further quantify the degree of pre-solvation using different structural parameters, *e.g.*, a tetrahedral order parameter and average hydrogen bonds of proton donor and acceptor moieties.

The remaining sections of this paper are as follows: In section 2, we briefly discuss the method and the simulation details. Section 3 contains the main results of the present work, and conclusions are given in section 4.

2. Computational/theoretical

2.1 Theoretical framework of the MS-EVB model

It is a well-established fact that the delocalized nature of the excess proton charge or charge defect can be described by the MS-EVB approach in an efficient and accurate way.^{23,26,31,38} The complete description of the MS-EVB methodology can be found in earlier papers.^{23,26,31} In this article, we summarize the few key features and advances in the case of the latest version *i.e.*, MS-EVB 3.2.

In the MS-EVB formalism, for a given nuclear configuration, the ground state of the system $|\psi\rangle$ is represented by a linear combination of different “basis states” $|i\rangle$ corresponding to different bonding topologies:

$$|\psi\rangle = \sum_{i=1}^N c_i |i\rangle \quad (1)$$

where N is the total number of chemically motivated basis states and c_i 's are the EVB coefficients of i^{th} basis states. The coefficients (c_i) can be obtained by solving the eigenvalue-eigenfunction problem using the Hamiltonian matrix \mathbf{H} , which comprises of matrix elements $h_{ij} = \langle i | \mathbf{H} | j \rangle$, such that,

$$\mathbf{H}\mathbf{c} = E_0\mathbf{c} \quad (2)$$

Here, E_0 is eigenvalue corresponding to the ground state energy; \mathbf{c} represents eigenvector whose components are the EVB coefficients as shown in Eq. (1). The diagonal elements h_{ii} , contain terms that are, *e.g.*, (though not necessarily³⁹) described by classical force fields⁵¹ and are expressed as,

$$h_{ii} = V_{\text{H}_3\text{O}^+}^{\text{intra}} + \sum_{k=1}^{N_{\text{H}_2\text{O}}} V_{\text{H}_2\text{O}}^{\text{intra},k} + \sum_{k=1}^{N_{\text{H}_2\text{O}}} V_{\text{H}_3\text{O}^+, \text{H}_2\text{O}}^{\text{inter},k} + \sum_{k < k'}^{N_{\text{H}_2\text{O}}} V_{\text{H}_2\text{O}}^{\text{inter},kk'} \quad (3)$$

In addition to the functional forms of the intramolecular potential for hydronium ($V_{\text{H}_3\text{O}^+}^{\text{intra}}$) and the intra- and intermolecular potentials for water ($V_{\text{H}_2\text{O}}^{\text{intra},k}$, $V_{\text{H}_2\text{O}}^{\text{inter},kk'}$) similar to those of MS-EVB 3.0 and SPC/Fw,^{31,52} in the latest excess proton model, MS-EVB 3.2,⁴⁸ the intermolecular potential between water and hydronium, $V_{\text{H}_3\text{O}^+, \text{H}_2\text{O}}^{\text{inter},k}$ has an additional Lennard-Jones (LJ) interaction between the hydronium oxygen and water hydrogens to incorporate the pre-solvation concept, *i.e.*, to account for the weak hydrogen bond acceptor nature of hydronium oxygen as suggested by recent AIMD results.^{33,43}

To explore the effects of anharmonicity in the water O–H stretching modes on the structural and dynamical properties, particularly on the vibrational spectrum of the hydrated excess proton, we have also developed the anharmonic version of the latest proton model *i.e.*, aMS-EVB 3.2.⁴⁸ It is based on the flexible anharmonic water model aSPC/Fw developed by Park *et al.*⁴⁰ In addition to the MS-EVB 3.2 model, in this work,

we have quantified the degree of pre-solvation in aMS-EVB 3.2 model as well.

2.2 Simulation details

The reactive molecular dynamics simulations using the MS-EVB 3.2 excess proton model were performed using a modified version of the LAMMPS⁵³ MD code. The simulation box consisted of 256 SPC/Fw⁵² water molecules with an excess proton and a chloride anion. The parameters for chloride ion were obtained from Dang.⁵⁴ The system is first equilibrated in a constant NVT ensemble by keeping the density and temperature at 1.0 g/cm^3 and 298 K. The temperature was kept constant by using a Nosé-Hoover chain of three thermostats,⁵⁵ along with 0.5 fs time step and a relaxation time of 0.05 ps. The long-range electrostatics were calculated using Ewald summation with a relative error of 10^{-5} in forces.⁵⁶ The cutoff value for the LJ interactions was set to 9 Å. Finally, the production data were collected with a constant NVE dynamics for a total length of 10 ns as obtained from 10 independent 1-ns long trajectories. In the case of aMS-EVB 3.2 model, we follow the same simulation strategy except in this case we use aSPC/Fw⁴⁰ water model.

3. Results and Discussion

The pre-solvation concept suggests that when two water molecules forming the special pair by solvating the excess proton structure have identical solvation environment, the proton can smoothly transfer from one water molecule to the other. This pre-solvation idea is very much similar to the Marcus picture of proton transfer,^{49,50} in which the free energy of the system along the solvent coordinate is comparable before and after a proton transfer event so that the transition can happen very easily in the proton transfer coordinate. In our earlier studies, we have shown that though the gas phase energy scan reflects an indication of the pre-solvation scenario,⁵⁷ it is not able to explain the exact path for the bulk phase.⁴³ The reactive molecular dynamics using MS-EVB approach can, however, capture the proton transfer events and the dynamical evolution of the solvation structures as well. In the case of reactive molecular dynamics simulation, after a proton transfer event, the acceptor water molecule can become hydronium moiety by accepting the excess proton. Thus, the atom index of each atom in the newly formed hydronium will be different from that of the old hydronium. In Figure 1, we show the evolution of hydronium-like oxygen atom index in case of the MS-EVB 3.2 proton model. It is evident from the figure that the excess proton is fluctuating from one water molecule to another in very fast time scale.

In order to gain insight about the pre-solvation concept, we first examine the proton sharing parameter, δ , as shown in Figure 2, and define a δ -dependent radial distribution function of hydronium oxygen and water hydrogen (shown in Figure 3). It is clear from the figure, that in the case of small δ , the radial distribution function shows small intensity around $r \sim 2.0 \text{ \AA}$, which corresponds to the fourth water molecules approaching towards hydronium oxygen.

To further quantify the solvation environment of the excess positive charge donor (hydronium) and the excess charge acceptor (special pair water), we analyze the local tetrahedral order parameter of the hydronium moiety and the special pair water separately. The local tetrahedral order parameter is described as,⁵⁸

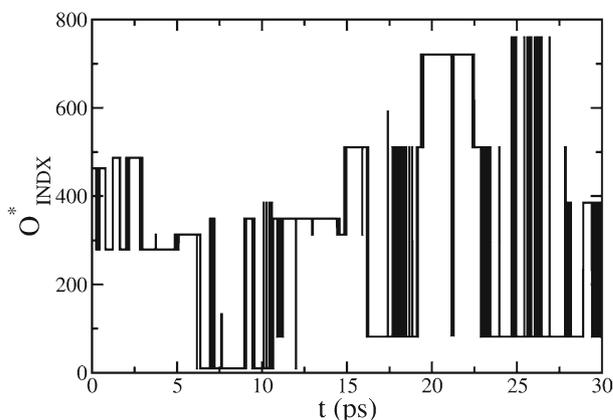


Figure 1. Time evolution of the oxygen index of the most hydronium-like oxygen atom, *i.e.*, the most dominant EVB states in case of MS-EVB3.2.

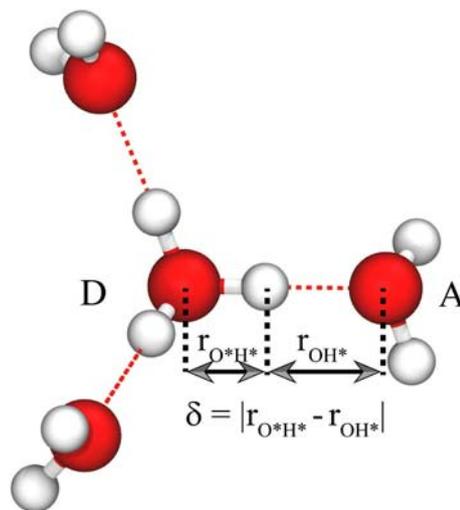


Figure 2. Excess charge donor (D), *i.e.*, the hydronium moiety, excess charge acceptor (A), *i.e.*, special pair water and the definition of proton sharing parameter δ .

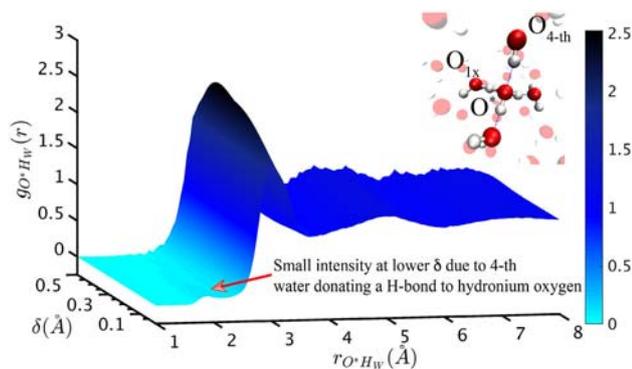


Figure 3. The proton sharing parameter (δ)-dependent radial distribution function of the most hydronium-like oxygen (O^*) and water hydrogen (H_W). The pre-solvation is reflected in terms of small intensity near $r \sim 2.0$ Å for low δ which represents the 4th water molecule donating a H-bond to the hydronium oxygen.

$$t_h \equiv 1 - \frac{3}{8} \sum_{j=1}^3 \sum_{k=j+1}^4 \left(\cos \psi_{jk} + \frac{1}{3} \right)^2. \quad (4)$$

where, ψ_{jk} is the angle formed by the lines joining the oxygen atom of the molecule under consideration and its nearest two oxygen atoms j and k . For perfect tetrahedral arrangement, t_h reaches its maximum value of

unity and for a non-interacting system, and the average value of t_h is zero.

In Figure 4, we show the angle distributions for both the excess proton models in case of $\delta < 0.1$ Å and $\delta > 0.4$ Å. It is clear from the figure that in the case of Zundel-like configurations (*i.e.*, $\delta < 0.1$ Å) both the hydronium ion and the special pair water have almost identical solvation environment. However, in the case of the Eigen-like configurations the angle distributions of hydronium moiety are distinctly different from that of the special pair water. We also find that the average t_h values of hydronium, and special pair water molecules for Zundel-like configurations are almost comparable (for MS-EVB 3.2 it is 0.72 vs. 0.69 and in the case of aMS-EVB 3.2, it is 0.71 vs. 0.68).

To further quantify the local structure around the donor oxygen and acceptor oxygen (as defined in Figure 2), we calculate the distribution of total hydrogen bond (H-bond) number for each center. We use a geometrical definition of H-bond, *i.e.*, the tagged proton of the O—H bond of interest is considered to have a hydrogen bond if intermolecular oxygen distance is less than 3.5 Å, and the angle between the intermolecular O—O distance vector and the O—H bond vector is less than 30°. ⁵⁹ In Figure 5, we represent the hydrogen bond

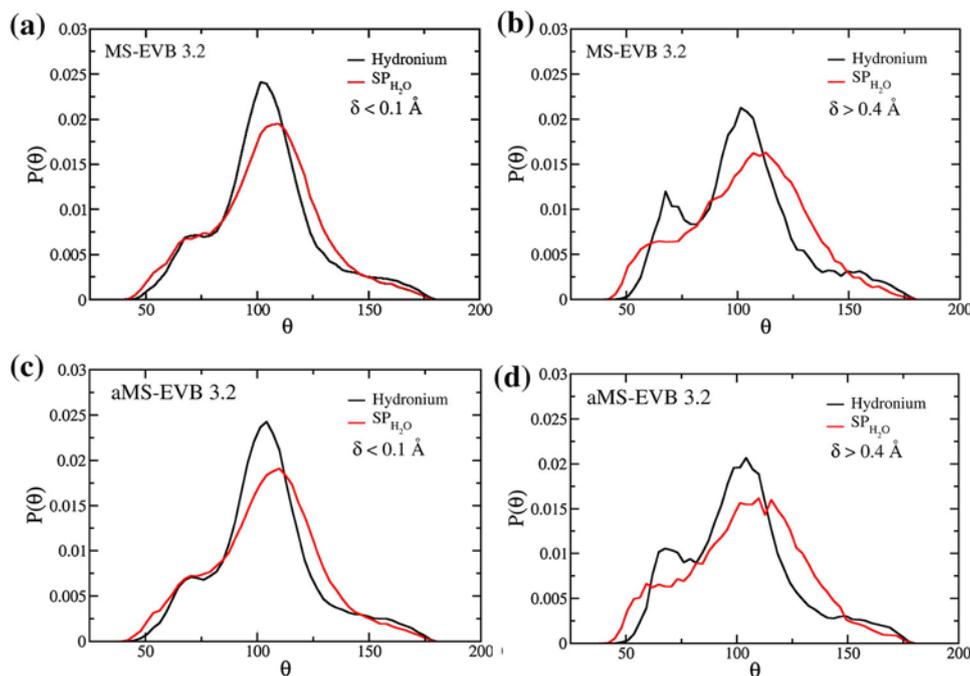


Figure 4. Angle distributions for tetrahedral order parameter in case of excess proton donor (hydronium) is shown in *black* and in case of excess proton acceptor (the special pair water) is represented in *red*. *Top panel* shows the results for the MS-EVB 3.2 and *bottom panel* for the aMS-EVB 3.2 proton models. Results for the configurations having $\delta < 0.1$ Å are shown in (a) and (c); and, the configurations having $\delta > 0.4$ Å are represented in (b) and (d).

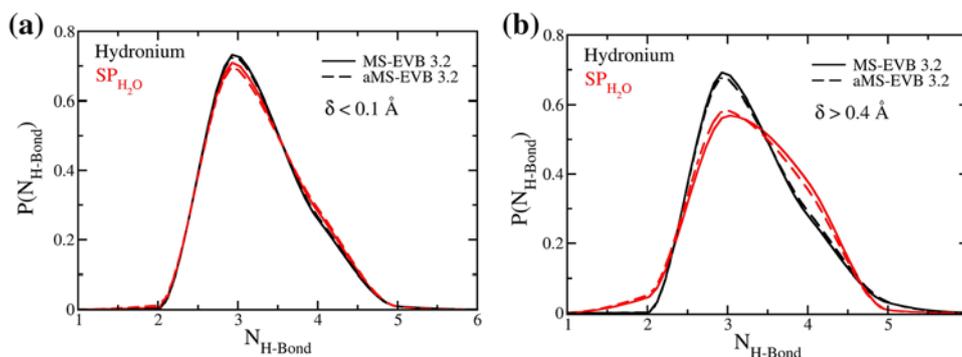


Figure 5. Distribution of number of H-bond in case of, (a) Zundel-like configurations (structure with $\delta < 0.1 \text{ \AA}$), and (b) Eigen-like configurations with $\delta > 0.4 \text{ \AA}$. For both the proton models in case of Zundel-like configurations hydronium and special pair water have similar number of H-bonds. However, in case of Eigen-like configurations the scenario is completely different.

number distribution in the case of Zundel-like configurations and Eigen-like configurations having $\delta > 0.4 \text{ \AA}$. It is evident from Figure 5(a) that in the Zundel-like configurations hydronium and special pair water have identical H-bond distributions. This reflects that when two water molecules equally share the proton, both the water molecules are experiencing similar solvation environments and as a result proton can transfer from one water molecule to the other by experiencing very small barrier. Thus, a pre-defined solvent orientation is highly coupled with the proton transfer events. This observation becomes more evident when we study the H-bond distributions for configurations with $\delta > 0.4 \text{ \AA}$ (shown in Figure 5(b)). From Figure 5(b) it is clear that when the excess charge is more localized on the hydronium, the special pair water and hydronium have completely different local structure.

4. Conclusions

In our earlier work, we have already shown that the presence of 4th water molecule, weakly H-bonded to the hydronium-like oxygen, actually facilitates the aqueous phase proton transfer process. In this work, we further quantify the extent of pre-solvation in proton transfer events by studying the solvent orientation and hydrogen bond numbers. The latest two new MS-EVB excess proton models have been studied for the pre-solvation picture. First, with the help of a proton sharing parameter-dependent (δ -dependent) radial distribution function, we show that the hydronium can indeed behave as a weak hydrogen bond acceptor. Furthermore, the local tetrahedral order parameter and angle distribution both suggest that, in Zundel configurations, the hydronium and special pair water have almost identical

solvation structure. A similar conclusion is also supported by the δ -dependent H-bond distributions.

We therefore conclude from the present work that the hydrated excess proton transfer events in liquid water are even more highly coupled with local solvent orientations than previously thought. These results, while interesting in their own right, will also allow us to develop even more accurate reactive MD models and methods in the future for the excess proton in aqueous media.

Acknowledgements

This research was supported in part by the Department of Energy (DOE), Office of Basic Energy Sciences (BES), Division of Chemical Sciences, Geosciences, and Biosciences, (DOE-BES Grant No. DE-SC0005418), and by the National Science Foundation (NSF Grant No. CHE-1465248). The computational resources in this work were provided by the University of Chicago Research Computing Center (RCC).

References

1. Decoursey T E 2003 Voltage-gated proton channels and other proton transfer pathways *Physiol. Rev.* **83** 475
2. Wraight C A 2006 Chance and design - Proton transfer in water, channels and bioenergetic proteins *BBA-Bioenergetics* **1757** 886
3. Cukierman S 2006 Et tu, Grotthuss! and other unfinished stories *BBA-Bioenergetics* **1757** 876
4. Swanson J M J, Maupin C M, Chen H, Petersen M K, Xu J, Wu Y and Voth G A 2007 Proton Solvation and Transport in Aqueous and Biomolecular Systems: Insights from Computer Simulations *J. Phys. Chem. B* **111** 4300
5. Kreuer K D, Paddison S J, Spohr E and Schuster M 2004 Transport in proton conductors for fuel-cell applications: Simulations, elementary reactions, and phenomenology *Chem. Rev.* **104** 4637

6. Jorn R, Savage J and Voth G A 2012 Proton Conduction in Exchange Membranes across Multiple Length Scales *Acc. Chem. Res.* **45** 2002
7. Tse Y-L S, Herring A M, Kim K and Voth G A 2013 Molecular Dynamics Simulations of Proton Transport in 3M and Nafion Perfluorosulfonic Acid Membranes *J. Phys. Chem. C* **117** 8079
8. Savage J, Tse Y-L S and Voth G A 2014 Proton Transport Mechanism of Perfluorosulfonic Acid Membranes *J. Phys. Chem. C* **118** 17436
9. Eigen M 1964 Proton Transfer, Acid-Base Catalysis, and Enzymatic Hydrolysis. Part I: ELEMENTARY PROCESS *Angew. Chem. Int. Edit.* **3** 1
10. Zundel G 2000 Hydrogen Bonds with Large Proton Polarizability and Proton Transfer Processes in Electrochemistry and Biology *Adv. Chem. Phys.* **111** 1
11. von Grothuss C J T 1806 Sur la décomposition de l'eau et des corps qu'elle tient en dissolution à l'aide de l'électricité galvanique *Ann. Chim.* **58** 54
12. Agmon N 1995 The Grothuss Mechanism *Chem. Phys. Lett.* **244** 456
13. Garczarek F and Gerwert K 2006 Functional waters in intraprotein proton transfer monitored by FTIR difference spectroscopy *Nature* **439** 109
14. Roberts S T, Petersen P B, Ramasesha K, Tokmakoff A, Ufimtsev I S and Martinez T J 2009 Observation of a Zundel-like transition state during proton transfer in aqueous hydroxide solutions *Proc. Natl. Acad. Sci. U.S.A.* **106** 15154
15. Roberts S T, Ramasesha K, Petersen P B, Mandal A and Tokmakoff A 2011 Proton Transfer in Concentrated Aqueous Hydroxide Visualized Using Ultrafast Infrared Spectroscopy *J. Phys. Chem. A* **115** 3957
16. Fayer M D 2013 *Ultrafast Infrared Vibrational Spectroscopy* (Boca Raton, Florida: CRC Press)
17. Mandal A, Ramasesha K, De Marco L and Tokmakoff A 2014 Collective vibrations of water-solvated hydroxide ions investigated with broadband 2DIR spectroscopy *J. Chem. Phys.* **140** 204508
18. Fournier J A, Johnson C J, Wolke C T, Weddle G H, Wolk A B and Johnson M A 2014 Vibrational spectral signature of the proton defect in the three-dimensional H₂O₂₁ cluster *Science* **344** 1009
19. Thämer M, De Marco L, Ramasesha K, Mandal A and Tokmakoff A 2015 Ultrafast 2D IR spectroscopy of the excess proton in liquid water *Science* **350** 78
20. Tuckerman M, Laasonen K, Sprik M and Parrinello M 1995 Ab-Initio Molecular-Dynamics Simulation of the Solvation and Transport of Hydronium and Hydroxyl Ions in Water *J. Chem. Phys.* **103** 150
21. Lobaugh J and Voth G A 1996 The Quantum Dynamics of an Excess Proton in Water *J. Chem. Phys.* **104** 2056
22. Tuckerman M E, Marx D, Klein M L and Parrinello M 1997 On the Quantum Nature of the Shared Proton in Hydrogen Bonds *Science* **275** 817
23. Schmitt U W and Voth G A 1999 The Computer Simulation of Proton Transport in Water *J. Chem. Phys.* **111** 9361
24. Marx D, Tuckerman M E, Hutter J and Parrinello M 1999 The Nature of the Hydrated Excess Proton in Water *Nature* **397** 601
25. Tuckerman M E, Marx D and Parrinello M 2002 The nature and transport mechanism of hydrated hydroxide ions in aqueous solution. *Nature* **417** 925
26. Day T J F, Soudackov A V, Cuma M, Schmitt U W and Voth G A 2002 A Second Generation Multistate Empirical Valence Bond Model for Proton Transport in Aqueous Systems *J. Chem. Phys.* **117** 5839
27. Izvekov S and Voth G A 2005 Ab initio molecular-dynamics simulation of aqueous proton solvation and transport revisited *J. Chem. Phys.* **123** 044505
28. Lapid H, Agmon N, Petersen M K and Voth G A 2005 A bond-order analysis of the mechanism for hydrated proton mobility in liquid water *J. Chem. Phys.* **122** 014506
29. Marx D 2006 Proton transfer 200 years after von Grothuss: Insights from ab initio simulations. *ChemPhysChem* **7** 1848
30. Chandra A, Tuckerman M E and Marx D 2007 Connecting solvation shell structure to proton transport kinetics in hydrogen-bonded networks via population correlation functions *Phys. Rev. Lett.* **99** 145901
31. Wu Y J, Chen H N, Wang F, Paesani F and Voth G A 2008 An improved multistate empirical valence bond model for aqueous proton solvation and transport *J. Phys. Chem. B* **112** 467
32. Markovitch O, Chen H, Izvekov S, Paesani F, Voth G A and Agmon N 2008 Special pair dance and partner selection: Elementary steps in proton transport in liquid water *J. Phys. Chem. B* **112** 9456
33. Berkelbach T C, Lee H S and Tuckerman M E 2009 Concerted Hydrogen-Bond Dynamics in the Transport Mechanism of the Hydrated Proton: A First-Principles Molecular Dynamics Study *Phys. Rev. Lett.* **103** 238302
34. Swanson J M J and Simons J 2009 Role of Charge Transfer in the Structure and Dynamics of the Hydrated Proton *J. Phys. Chem. B* **113** 5149
35. Marx D, Chandra A and Tuckerman M E 2010 Aqueous Basic Solutions: Hydroxide Solvation, Structural Diffusion, and Comparison to the Hydrated Proton *Chem. Rev.* **110** 2174
36. Knight C, Maupin C M, Izvekov S and Voth G A 2010 Defining Condensed Phase Reactive Force Fields from ab Initio Molecular Dynamics Simulations: The Case of the Hydrated Excess Proton *J. Chem. Theory Comput.* **6** 3223
37. Tuckerman M E, Chandra A and Marx D 2010 A statistical mechanical theory of proton transport kinetics in hydrogen-bonded networks based on population correlation functions with applications to acids and bases *J. Chem. Phys.* **133** 124108
38. Knight C and Voth G A 2012 The Curious Case of the Hydrated Proton *Acc. Chem. Res.* **45** 101
39. Knight C, Lindberg G E and Voth G A 2012 Multiscale reactive molecular dynamics *J. Chem. Phys.* **137** 22A525
40. Park K, Lin W and Paesani F 2012 A Refined MS-EVB Model for Proton Transport in Aqueous Environments *J. Phys. Chem. B* **116** 343
41. Hassanali A, Giberti F, Cuny J, Kuhne T D and Parrinello M 2013 Proton transfer through the water gossamer *Proc. Natl. Acad. Sci. U.S.A.* **110** 13723
42. Hassanali A A, Giberti F, Sosso G C and Parrinello M 2014 The role of the umbrella inversion mode in proton diffusion *Chem. Phys. Lett.* **599** 133

43. Tse Y L, Knight C and Voth G A 2015 An analysis of hydrated proton diffusion in ab initio molecular dynamics *J. Chem. Phys.* **142** 014104
44. Peng Y, Swanson J M J, Kang S-g, Zhou R and Voth G A 2015 Hydrated Excess Protons Can Create Their Own Water Wires *J. Phys. Chem. B* **119** 9212
45. Marx D and Hutter J 2009 In *Ab Initio Molecular Dynamics: Basic Theory and Advanced Methods* (New York: Cambridge University Press)
46. Yoo S, Zeng X C and Xantheas S S 2009 On the phase diagram of water with density functional theory potentials: The melting temperature of ice I-h with the Perdew-Burke-Ernzerhof and Becke-Lee-Yang-Parr functionals *J. Chem. Phys.* **130** 221102
47. Yoo S and Xantheas S S 2011 Communication: The effect of dispersion corrections on the melting temperature of liquid water *J. Chem. Phys.* **134** 121105
48. Biswas R, Tse Y L, Tokmakoff A and Voth G A 2016 Role of Presolvation and Anharmonicity in Aqueous Phase Hydrated Proton Solvation and Transport *J. Phys. Chem. B* **120** 1793
49. Ando K and Hynes J T 1997 Molecular Mechanism of HCl Acid Ionization in Water: Ab initio Potential Energy Surfaces and Monte Carlo Simulations *J. Phys. Chem. B* **101** 10464
50. Ando K and Hynes J T 1999 Acid-Base Proton Transfer and Ion Pair Formation in Solution *Adv. Chem. Phys.* **110** 381
51. All the terms in a diagonal element are described by the classical force fields, with the exception of the intermolecular term between hydronium and water in which contains two extra “repulsive terms”. See the original MS-EVB3 paper
52. Wu Y J, Tepper H L and Voth G A 2006 Flexible simple point-charge water model with improved liquid-state properties *J. Chem. Phys.* **124** 024503
53. Plimpton S 1995 Fast Parallel Algorithms for Short-Range Molecular Dynamics *J. Comp. Phys.* **117** 1
54. Dang L X 1995 Mechanism and Thermodynamics of Ion Selectivity in Aqueous-Solutions of 18-Crown-6 Ether - a Molecular-Dynamics Study *J. Am. Chem. Soc.* **117** 6954
55. Martyna G J, Klein M L and Tuckerman M 1992 Nose-Hoover Chains - the Canonical Ensemble Via Continuous Dynamics *J. Chem. Phys.* **97** 2635
56. Allen M P and Tildesley D J 1989 In *Computer Simulation of Liquids* (New York: Oxford University Press)
57. Jagoda-Cwiklik B, Cwiklik L and Jungwirth P 2011 Behavior of the Eigen Form of Hydronium at the Air/Water Interface *J. Phys. Chem. A* **115** 5881
58. Chau P L and Hardwick A J 1998 A new order parameter for tetrahedral configurations *Mol. Phys.* **93** 511
59. Luzar A and Chandler D 1996 Effect of environment on hydrogen bond dynamics in liquid water *Phys. Rev. Lett.* **76** 928