

# Structure and Dynamics of $\text{OH}^-$ (aq)

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## ABSTRACT

Topological defects in aqueous solution in the form of  $\text{H}^+$ (aq) and  $\text{OH}^-$ (aq) ions undergo anomalously fast transport via the structural Grotthuss diffusion mechanism. However, while the microscopic details of this process are well understood for  $\text{H}^+$ (aq), the corresponding picture for  $\text{OH}^-$ (aq) remains unresolved. Mechanistic scenarios proposed previously are critically reviewed with the help of the presolvation concept, which provides a unifying framework for understanding charge migration mechanisms in hydrogen-bonded networks. It is argued that  $\text{OH}^-$ (aq) features a nonclassical, in the Lewis sense, hypercoordinated solvation structure. The resulting mechanism deviates substantially from the traditional “mirror image” picture. Within the presolvation concept, it can also be suggested why alternative scenarios are inconsistent with experimental data.

## 1. Introduction

One of water's most unusual properties is its ability to transport charge defects created by hydronium,  $\text{H}_3\text{O}^+$ , and hydroxide ions,  $\text{OH}^-$ , at anomalously high rates,<sup>1</sup> a phenomenon that critically affects numerous chemically, biologically, and technologically important processes. Thus, an understanding of the elementary steps and the

mechanisms underlying this anomalous diffusion, particularly proton transfer (PT) in a hydrogen-bonded network with charge defects,  $\text{H}^+$ (aq) and  $\text{OH}^-$ (aq), is of fundamental significance.<sup>2</sup> Substantial experimental<sup>3–8</sup> and theoretical<sup>9–23</sup> investigation into the structural diffusion of  $\text{H}^+$ (aq) have yielded a rather consistent picture, which has become textbook knowledge.<sup>1</sup> This picture involves a continuous interconversion<sup>20</sup> between the 3-fold coordinated “Eigen complex”,  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_3$ , and the shared-proton “Zundel cation”,  $[\text{H}_2\text{O}\cdots\text{H}\cdots\text{OH}_2]^+$ , via PT. The resulting “structural diffusion” or “Grotthuss” mechanism<sup>1,24</sup> is driven by fluctuations that cause a hydrogen bond (HB) between the first and second solvation shells of  $\text{H}_3\text{O}^+$  to break, thereby reducing the coordination number of a water molecule in its first shell from four to three;<sup>10–12,20</sup> this leading-order picture may be refined<sup>22</sup> by including more solvation shells. Inclusion of nuclear quantum effects<sup>20</sup> leads to a “fluxional” defect, which is primarily due to zero-point motion, that is, proton tunneling does not play any significant role.

In stark contrast,  $\text{OH}^-$ (aq) structural diffusion is much less clear. Historically, efforts to investigate this problem as an independent question have been few since an ostensible mechanism had been inferred from that of  $\text{H}_3\text{O}^+$  by simply invoking a pseudosymmetry argument, which goes back to Danneel (1905) and Hückel (1928). The basis of this “mirror image” concept lies in the notion that  $\text{H}_3\text{O}^+$  is a water molecule with an excess proton, while  $\text{OH}^-$  is a  $\text{H}_2\text{O}$  with a missing proton (“proton hole”). Assuming similar solvation shell topologies, a mechanism of  $\text{OH}^-$  migration is inferred from that of  $\text{H}_3\text{O}^+$  by reversing HB polarities and the direction of PTs in schemes.<sup>5,6,25,26</sup> This mirror image or “proton hole” concept for  $\text{OH}^-$ (aq) migration is described in detail in ref 26 in close analogy to the structural diffusion picture derived earlier for the  $\text{H}^+$ (aq) case.<sup>12</sup> In this picture,  $\text{OH}^-$  accepts three HBs yet donates none, and structural diffusion is driven by the same type of second solvation shell effects that drive  $\text{H}^+$ (aq) migration. To the best of our knowledge, the only source in the literature where this symmetry argument is seriously questioned is an 1936 paper by Huggins.

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Dominik Marx (\*1963) studied Chemistry and Physics at the Universität Mainz (Germany) and at the University of California, Irvine. He received his *Diplom* (M.S.) in Chemistry, 1990, working with Karl Heinzinger at Max-Planck-Institut für Chemie on MD simulations of electrolytes and his Ph.D. (1992) under the supervision of Kurt Binder (Institut für Physik, Universität Mainz) on phase transitions in 2D off-lattice models using QMC methods. He was Postdoctoral Fellow at IBM Zurich Research Laboratory with Michele Parrinello (1993/94) and staff scientist at Max-Planck-Institut für Festkörperforschung; he obtained the *Habilitation* in Theoretical Physics at Universität Stuttgart (1998) and became Full Professor at Ruhr-Universität Bochum (Germany) in 1999. Chairs at the Universities of Frankfurt, Darmstadt, and Oxford were offered to him, and currently he is Distinguished Professor of Theoretical Chemistry and the Director of the Center for Theoretical Chemistry at University of Bochum. The focus of the Marx group is on computer simulation of structure, dynamics, and reactions of molecular systems, interpreted in a broad sense, involving quantum and quasi-classical, as well as classical, MD and MC techniques.

More recently, however, a wealth of theoretical<sup>9–11,26–33</sup> and experimental<sup>34,35</sup> investigations into OH<sup>-</sup>(aq) structure and mobility have lead to a serious controversy about the microscopic transport mechanism. The aim of this paper is to critically examine and review the various viewpoints that have emerged over the past decade concerning OH<sup>-</sup> diffusion in water, employing a recently proposed theoretical framework.<sup>29</sup> Furthermore, three different mechanisms will be dissected in terms of solvation shell structures and diffusion coefficients using an extensive set of ab initio molecular dynamics simulations not only of OH<sup>-</sup>(aq) but also of H<sup>+</sup>(aq) and bulk water with the purpose of establishing an internally consistent protocol for all of the calculations. It will be shown that the mechanism for anomalous diffusion as originally presented in refs 29 and 30 retains substantial validity and is able to qualitatively reproduce known condensed-phase experimental results.

**A. Structural Diffusion in Aqueous Bases: Theoretical Picture.** Generalizing ideas about solvation shell fluctuations that drive H<sup>+</sup> migration in HB networks, a mechanistic rule based on a *presolvation concept* has been introduced.<sup>29</sup> This concept will provide a unifying framework and nomenclature for analyzing at the most fundamental molecular level the various mechanistic pictures that have been proposed<sup>26,29,33</sup> and for rationalizing why some of these theories<sup>26,33</sup> fail where others succeed<sup>29</sup> in providing a physically realistic description when compared to experimental data. At the very heart of our presolvation concept is the common notion that bulk water molecules prefer essentially a 4-fold tetrahedral coordination shell (subject to fluctuations and defects), a structural motif that explains a host of phenomena.<sup>36</sup> Most importantly, structural diffusion requires that in any PT reaction, the proton receiving species must first have a solvation pattern that corresponds to the species into which it will be transformed as a result of the reaction. Application to H<sup>+</sup>(aq) leads directly to a coordination number reduction from four to three HBs of a (proton-receiving) water molecule in the first shell of H<sup>+</sup>(aq) as predicted previously.<sup>10–12</sup> We note that a similar, though more qualitative, idea underlies Marcus' theory of electron transfer<sup>37</sup> and explanations of adiabatic PT in polar model solvents.<sup>38,39</sup>

Applying the presolvation concept to OH<sup>-</sup>(aq), one can obtain several possible transport mechanisms depending on the OH<sup>-</sup>(aq) coordination state. The finding<sup>10,11,29</sup> that the oxygen in OH<sup>-</sup>, being the proton-receiving species in aqueous bases, is on average hypercoordinated<sup>29</sup> by preferentially accepting four HBs (instead of only three as suggested by both the Lewis picture and localized molecular orbitals) suggests that structural diffusion of OH<sup>-</sup>(aq) should differ qualitatively from that of H<sup>+</sup>(aq). The initial step according to the presolvation concept would require a coordination number reduction of OH<sup>-</sup>(aq) itself by breaking a HB between its oxygen and a first shell water molecule; this leaves the OH<sup>-</sup> oxygen in a topology similar to that of bulk water. However, the presolvation concept requires that the topology of the full coordination shell of OH<sup>-</sup> resemble that of a water molecule. Conse-

quently, PT to OH<sup>-</sup> can only be completed when the OH<sup>-</sup> hydrogen also forms a HB. Indeed, a little reflection makes clear that this step places the OH<sup>-</sup> hydrogen in the solvation pattern of a water molecule. As the proton is transferred, that is upon transformation of OH<sup>-</sup> into an intact water molecule, this HB strengthens and leaves the nascent H<sub>2</sub>O molecule with two accepted and two donated HBs, as required for an ideal bulk water molecule. The rate-limiting step is the time needed for the coordination change and the relaxation into a tetrahedral configuration. This nontraditional mechanism (see panels e–h in Figure 1) was depicted for the first time in Figure 3 of ref 29. There is, moreover, growing theoretical evidence that the equilibrium structure of the  $n = 4$  cluster has four accepted molecules in the first shell but that zero-point and thermal motion can expell a water from the first to the second shell on an overall shallow potential energy surface.<sup>40–43</sup>

Other theoretical analyses<sup>26,32,33</sup> of the condensed phase, which include quasi-chemical theory and ab initio molecular dynamics approaches, as well as some experiments on small clusters,<sup>44,45</sup> have led to a suggestion that the OH<sup>-</sup> oxygen actually favors 3-fold coordination in aqueous solution. If this solvation pattern holds in the bulk, then two possible mechanisms can be derived from the presolvation concept. If the OH<sup>-</sup> hydrogen does not donate a HB, as argued in ref 26, then the 3-fold coordinated OH<sup>-</sup>(aq) indeed behaves as a mirror image<sup>5,6,25,26</sup> of the H<sup>+</sup>(aq) case. Thus, fluctuations must break a HB from the first to the second solvation shell of OH<sup>-</sup>(aq), thereby reducing the coordination number of a first shell water of OH<sup>-</sup> from four to three.<sup>26</sup> The obvious difficulty with this picture is that the nascent water molecule formed in the PT step does not possess the proper 4-fold tetrahedral water coordination pattern. Another mechanism is derived if the OH<sup>-</sup> hydrogen does donate a HB and favors 3-fold coordination of its oxygen.<sup>33</sup> In this case, the OH<sup>-</sup>, being the proton-receiving species in bases, naturally possesses a coordination pattern like that of a bulk water molecule. Thus, such a solvation pattern of OH<sup>-</sup>(aq) would, according to the presolvation concept, allow charge migration to occur readily with no rate-limiting step, apart from ultrafast local reorientations, and thus lead to an extraordinarily high structural diffusion rate (see panels b–d in Figure 1).

A powerful tool for investigating such issues is ab initio molecular dynamics (AIMD) combining MD with forces computed “on the fly” from electronic structure calculations based on density functional theory.<sup>46–48</sup> However, among several such simulations, which differ only in technical details, two distinct scenarios have emerged: a picture in which OH<sup>-</sup>(aq) is hypercoordinated with transport being driven by first solvation shell reorganization<sup>10,11,29–31</sup> and a picture in which OH<sup>-</sup>(aq) accepts three HBs, as a mirror image of H<sup>+</sup>(aq), but donates one in addition.<sup>33</sup>

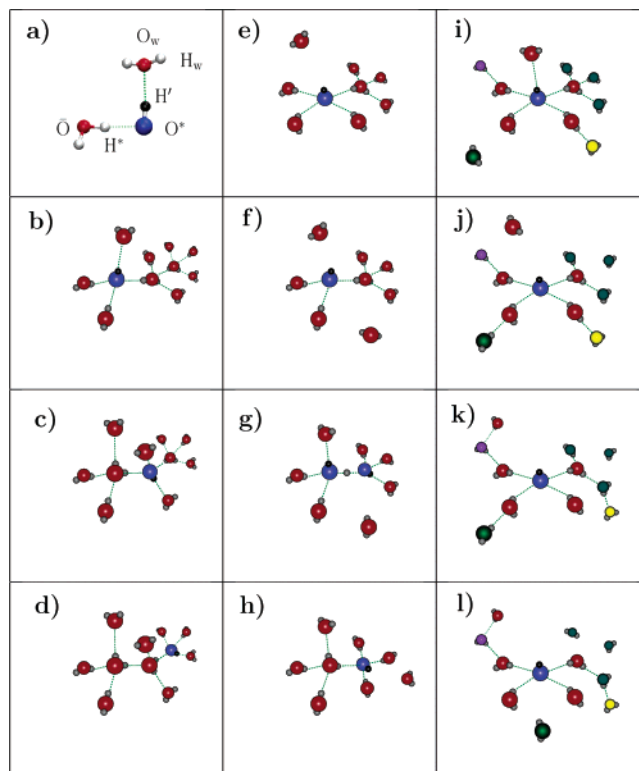
**B. Structural Diffusion in Aqueous Bases: Experimental Picture.** Currently, there is no experimental technique available that can resolve these issues in

mechanistic detail. Neutron scattering<sup>34,35</sup> provides evidence that OH<sup>-</sup> favors four accepted HBs and is able to donate a fifth in agreement with ref 29. On the other hand, cluster studies<sup>44,45</sup> using OH<sup>-</sup>·(H<sub>2</sub>O)<sub>*n*</sub> with *n* ≤ 7 and *n* ≤ 5 suggest only three accepted HBs so that additional water molecules are relegated to the second solvation shell. At first sight, this seems to agree with the traditional Lewis picture based on the existence of three accepting lone pairs. However, the mentioned quantum-chemical studies<sup>40–43</sup> demonstrate that subtle entropic effects, that is, zero-point vibrations and thermal fluctuations, play a decisive role in determining the solvation shell pattern of the *n* = 4 cluster. Finally, one could even question a priori whether medium-size clusters, OH<sup>-</sup>·(H<sub>2</sub>O)<sub>*n*</sub>, serve as a reliable model for fully hydrated OH<sup>-</sup>, that is, OH<sup>-</sup>(aq), particularly in view of the experimental evidence that OH<sup>-</sup> donates an additional, weak HB in the bulk environment,<sup>34,35</sup> which is clearly not able to form in small clusters.<sup>41,43</sup>

From the discussion so far, it is clear that results from different theoretical and experimental approaches concerning solvated OH<sup>-</sup> and OH<sup>-</sup>(aq) remain inconclusive. Fortunately, there is older data that can be brought to bear on the present controversy. It is well established<sup>1</sup> that the mobility and thus the obtained diffusion coefficient of H<sup>+</sup>(aq) is larger than that of OH<sup>-</sup>(aq),  $9.31 \times 10^{-9}$  vs  $5.30 \times 10^{-9}$  m<sup>2</sup>/s at 298 K, respectively. Recalling that the self-diffusion coefficient of water is  $2.26 \times 10^{-9}$  m<sup>2</sup>/s, it is evident that diffusion of OH<sup>-</sup>(aq) is much faster than water self-diffusion but at the same time slower than H<sup>+</sup>(aq) migration. The diffusion coefficients for the fully deuterated systems at 298 K are  $6.69 \times 10^{-9}$ ,  $3.12 \times 10^{-9}$ , and  $1.86 \times 10^{-9}$  m<sup>2</sup>/s for D<sub>3</sub>O<sup>+</sup>, OD<sup>-</sup>, and D<sub>2</sub>O, respectively.<sup>17,49</sup> Thus, apart from mild H/D isotope effects deuteration only reduces the impact of quantum fluctuations without altering the basic fact that  $D_{\text{H}^+} > D_{\text{OH}^-} > D_{\text{H}_2\text{O}}$ . A preponderance of the experimental data suggests that comparing computed diffusion coefficient ratios for the fully deuterated systems to experiment should be a robust way to scrutinize simulated scenarios qualitatively, irrespective of quantitative detail. Indeed, careful examination of the different ab initio simulation techniques that have been employed to study hydroxide migration,<sup>29,33</sup> in light of these important data, allow us to perform “virtual” experiments that answer the question: How does a predominantly 3-fold vs 4-fold coordinated solvation shell for hydroxide affect its transport mechanism in most general terms and which yields a physically meaningful picture in light of the existing experimental data?

## II. Comparing and Assessing Various Scenarios

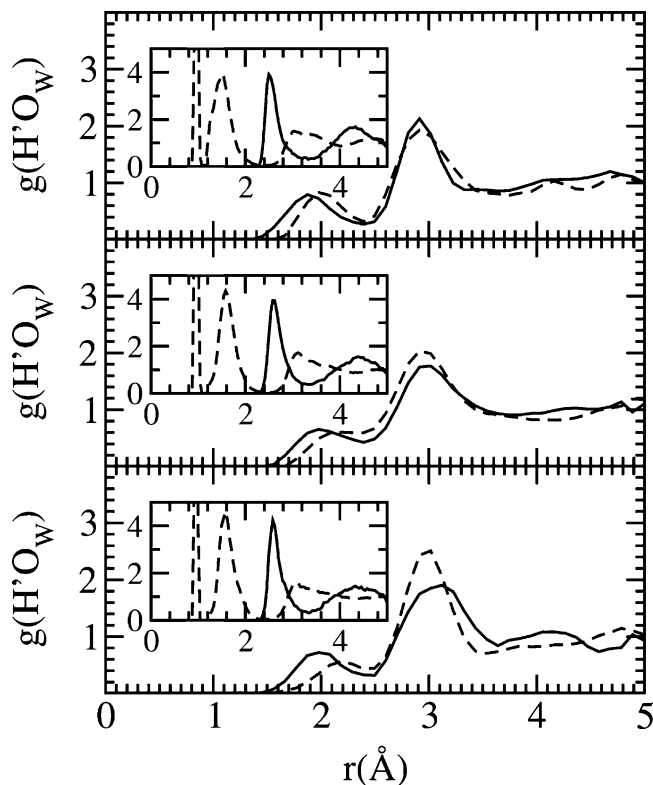
**A. Conceptual Approach and Simulations.** A comprehensive AIMD study of OH<sup>-</sup> in ambient water was carried out using three popular density functionals, PW91, BLYP, and HCTH/120. In addition, analogous simulations of bulk water and H<sup>+</sup> in H<sub>2</sub>O were carried out to extract diffusion coefficient ratios and perform a comparative analysis. Both



**FIGURE 1.** Panel a shows the labeling convention of the defect site. Panels b–d depict in schematic fashion the OH<sup>-</sup>(aq) diffusion mechanism for PW91; panels e–h and i–l depict the mechanism for BLYP and HCTH, respectively. The time ordering proceeds from top to bottom in each column. Only the most important species in the periodic simulation box are shown; the defect is highlighted in blue and black. In the case of HCTH, for ease in following the vehicular diffusion mechanism, different coloring schemes are used for water molecules in the second solvation shell.

BLYP and PW91 were used in recent OH<sup>-</sup>(aq) studies,<sup>29–33</sup> whereas HCTH represents yet another functional family; note that PBE and revPBE, also used in ref 33, are very similar to PW91. All simulations were performed using the Car–Parrinello technique,<sup>46</sup> the CPMD code,<sup>47</sup> and a 9.865 Å periodic cubic box with one OH<sup>-</sup> (or H<sub>3</sub>O<sup>+</sup>) ion and 31 water molecules or 32 H<sub>2</sub>O. The electronic structure was represented within the Kohn–Sham density functional theory<sup>47</sup> and a plane-wave basis. For the BLYP and HCTH functionals, Troullier–Martins norm-conserving pseudopotentials with a cutoff of 70 Ry were employed, whereas the PW91 simulations employed Vanderbilt ultrasoft pseudopotentials at 30 Ry as in ref 33. The fictitious electron mass was 800 au, and the mass of deuterium was used throughout with a 5 au time step. Each system was carefully equilibrated at 300 K followed by 20–50 ps of unthermostated dynamics of production for each case for a total of ~500 ps. Additional checks on the fictitious mass and the system size gave no appreciable change in the conclusions to be presented below.

**B. Solvation Shell Structures.** To locate the OH<sup>-</sup> charge defect, designated (O\*H<sup>-</sup>), the oxygen, O\*, with a single hydrogen, H', covalently bound to it is identified for each configuration (see Figure 1, panel a, for the labeling scheme). Note that H' can, in principle, donate a HB to a



**FIGURE 2.** Radial distribution functions of H'O<sub>w</sub> using PW91 (top), BLYP (center), and HCTH (bottom) for  $|\delta| \leq 0.1$  Å (solid) and  $|\delta| \geq 0.5$  Å (dashed). Insets show the corresponding full O\*O<sub>w</sub> and O\*H<sub>w</sub> (including the H' hydrogen) radial distribution functions in solid and dashed lines, respectively.

nearby water molecule, [O\*H'...OH<sub>2</sub>]<sup>-</sup>. For each HB involving O\*, a displacement coordinate,  $\tilde{\delta} = R_{O_aH} - R_{O_bH}$ , is defined, where  $R_{O_aH}$  and  $R_{O_bH}$  are the distances between the shared proton and the two oxygens yielding a PT coordinate  $\delta$  defined in each configuration by selecting the HB with the smallest  $\tilde{\delta}$  value. This particular HB, O\*...H\*Ō, is considered to be the “most active” or most likely to experience PT,<sup>20,29</sup> and the water molecule with Ō has a propensity for donating the proton H\* upon transfer. Finally, unspecified (solvent) water molecules are designated by O<sub>w</sub> and H<sub>w</sub>.

The O\*O<sub>w</sub> and O\*H<sub>w</sub> radial distribution functions generated by PW91, BLYP, and HCTH are quite similar (see insets of Figure 2). In particular, all functionals yield the expected contraction of the first solvation shell around the defect; however, the contraction is clearly more pronounced for PW91 than for BLYP and HCTH. The running coordination numbers of O\*O<sub>w</sub> (O\*H<sub>w</sub>) yield 4.2, 4.8, and 4.7. (3.4, 3.9, and 4.0) at the first minimum for the PW91, BLYP, and HCTH functionals, respectively. This analysis is refined (see main panels of Figure 2) by investigating the HBs involving H' separately for configurations close to PT events as characterized by  $|\delta|$ -values approaching zero ( $|\delta| \leq 0.1$  Å), as well as in the opposite limit of strongly bound OH<sup>-</sup> units ( $|\delta| \geq 0.5$  Å). It is crucial to observe that the HB donated by the charge defect, H'...O<sub>w</sub>, is always present in the case of PW91 irrespective of the dynamical situation, that is, a pronounced peak is present around 1.8–2.0 Å in both limits according to

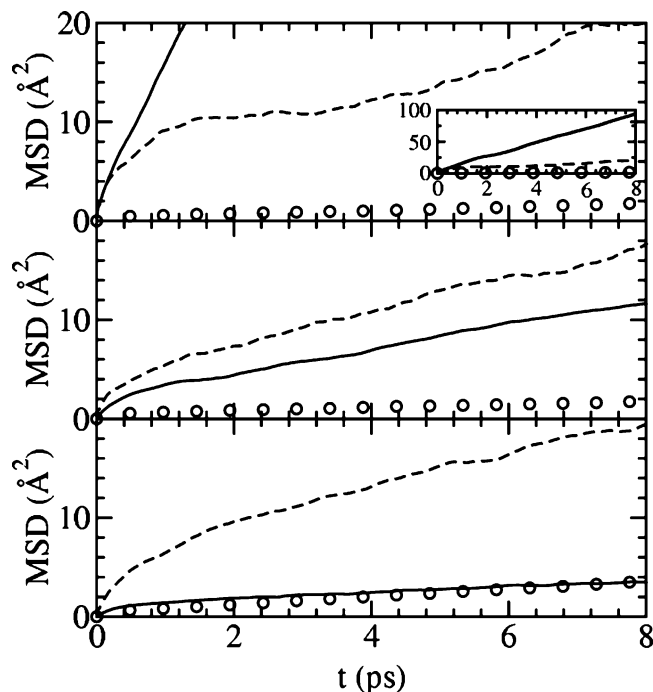
Figure 2. In the case of BLYP, H' donates this bond only transiently close to PT, that is, for small  $|\delta|$ , whereas the peak degenerates into a broad plateau for large  $|\delta|$ .

In all three cases, the most probable number of HBs donated by H' is unity, but the largest average H' coordination number is found for PW91, 0.72, followed by BLYP and HCTH with 0.67 and 0.61, respectively. Importantly, the number of accepted HBs, that is, the average O\* coordination number, differs qualitatively. In the case of PW91, the most probable state is that with three accepted waters, whereas BLYP, as well as HCTH, favors 4-fold coordination. This qualitative difference of the O\* solvation obtained from integrating the appropriate radial distribution functions from Figure 2 is analyzed in more detail with the help of an O\* coordination number,  $n_w^*(|\delta|)$ , as a function of the PT coordinate  $|\delta|$  and weighted by the corresponding fraction of contributing configurations. For BLYP,  $n_w^*(|\delta|)$  is found to be largest far from PT events, that is, for  $|\delta| \gg 0$ , and to decrease significantly close to PT, that is, as  $|\delta| \rightarrow 0$ . This signifies that there is a clear change in the coordination number when the proton is transferred and that the low-coordination intermediate states visited during PT are only visited transiently. In stark contrast,  $n_w^*(|\delta|)$  does not vary much along  $|\delta|$  for PW91 implying that the number of accepted HBs by O\* is essentially independent of PT; note that even  $n_w^*(|\delta| \approx 0) > n_w^*(|\delta| \gg 0)$  in this case.

It is clear from the above discussion that these three density functional models (PW91, BLYP, HCTH) capture the solvation patterns at the heart of the controversy, thereby allowing us to perform the “virtual” experiment to test each mechanistic picture: PW91 (HCTH) favors 3-fold (4-fold) coordination of O\*, while BLYP favors a 4-fold state that can be transformed *transiently* into a 3-fold state. Furthermore all three models predict the formation of the H'...O<sub>w</sub> hydrogen bond with slightly different probabilities. As will be shown in the following, these quite subtle changes in the solvation shell structure will result in vastly different charge migration dynamics.

**C. Diffusion: OH<sup>-</sup>(aq) vs H<sup>+</sup>(aq) vs H<sub>2</sub>O.** The mean-square displacements in Figure 3 demonstrate that all three functionals predict an astonishingly similar behavior for both water self-diffusion and H<sup>+</sup>(aq) structural diffusion. For OH<sup>-</sup>(aq), on the other hand, dramatic qualitative differences are readily observed: BLYP yields a displacement vs time that is slower than that of H<sup>+</sup>(aq) but much faster than pure water in agreement with experiment;<sup>1</sup> with HCTH, the structural diffusion of OH<sup>-</sup>(aq) is slightly slower than water self-diffusion; finally, PW91 OH<sup>-</sup>(aq) overshoots H<sup>+</sup>(aq) by a considerable amount (see inset).

Since it is difficult to obtain reliable absolute values for diffusion coefficients from AIMD, in particular as a function of temperature,<sup>50</sup> we opt to compare their ratios to experiment. Experimentally, it is well established that H<sup>+</sup>(aq) structural diffusion is by far the fastest diffusion process in ambient water, followed by OH<sup>-</sup>(aq) structural diffusion and finally by water self-diffusion.<sup>1,7,49</sup> In particular, migration of H<sup>+</sup>(aq) is about two times faster than that of OH<sup>-</sup>(aq) for fully deuterated systems (see Table



**FIGURE 3.** Mean-square displacement of O\* for OH<sup>-</sup> (solid), H<sub>3</sub>O<sup>+</sup> (dashed), and O<sub>w</sub> for H<sub>2</sub>O (○) as a function of time using PW91 (top), BLYP (center), and HCTH (bottom). Water self-diffusion is obtained from independent bulk simulations, and the deuterium mass was used throughout for technical reasons.

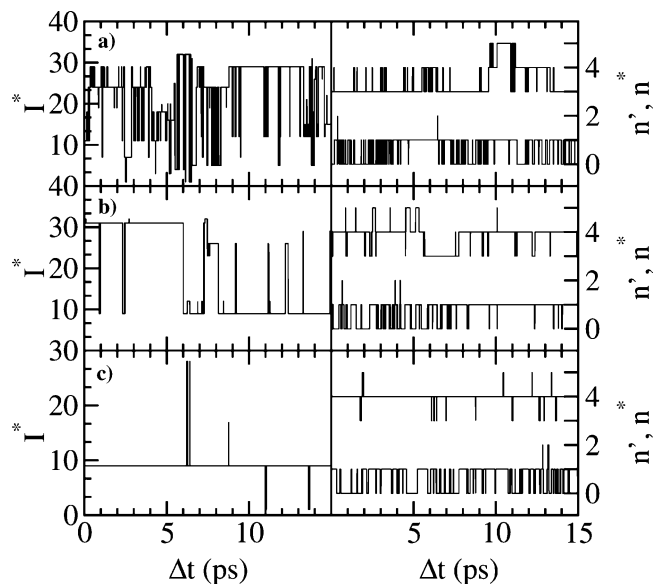
**Table 1. Diffusion Coefficients in Units of 10<sup>-9</sup> m<sup>2</sup>/s (i.e., 10<sup>-1</sup> Å<sup>2</sup>/ps) Obtained from the Slopes of the Mean-Square Displacements Shown in Figure 3<sup>a</sup>**

quantity	PW91	BLYP	HCTH	experiment
$D_{\text{OH}^-}$	18.5	1.92	0.44	3.12
$D_{\text{H}^+}$	3.24	2.83	3.25	6.69
$D_{\text{H}_2\text{O}}$	0.30	0.25	0.64	1.86
$D_{\text{OH}^-}/D_{\text{H}^+}$	5.88	0.68	0.14	0.47

<sup>a</sup> Water self-diffusion is obtained from independent bulk simulations, and the deuterium mass was used throughout for technical reasons. Experimental data<sup>7,49</sup> are those of the fully deuterated systems.

1). Clearly, out of the three functionals used, BLYP, which favors a 4-fold coordination pattern for OH<sup>-</sup>(aq) (without excluding 3-fold), reproduces these basic facts. By contrast, PW91, which predicts a predominantly 3-fold coordination pattern, actually reverses the relative magnitude of the OH<sup>-</sup>(aq) and H<sup>+</sup>(aq) diffusion rates, yielding a ratio  $D_{\text{OH}^-}/D_{\text{H}^+} \approx 6$  instead of  $\sim 0.5$  as observed experimentally. Finally, HCTH, which strongly favors 4-fold coordination of O\*, yields a OH<sup>-</sup>(aq) diffusion that is slower than water self-diffusion.

**D. Charge Migration Mechanisms.** From the above analyses, three different OH<sup>-</sup>(aq) charge transport mechanisms are extracted from the trajectories. The mechanisms are represented, from top to bottom, in simple schematic form in the columns of Figure 1. PW91, left column, strongly favors three accepted HBs by O\* in addition to a fourth one that is frequently donated by the OH<sup>-</sup> hydrogen, H' according to Figure 2, leading to representative configurations as illustrated in Figure 1, panels b–d. Panel b in Figure 1 shows the tetrahedral



**FIGURE 4.** Index of the OH<sup>-</sup> oxygen O\*,  $l^*$ , and the instantaneous number of its accepted and donated HBs,  $n^*$  (upper curve) and  $n'$  (lower curve), respectively, shown for segments of the trajectories using PW91 (top, a), BLYP (center, b), and HCTH (bottom, c).

environment of OH<sup>-</sup>(aq). In this configuration, a neighboring water molecule, here to the right, can readily transfer a proton to OH<sup>-</sup> upon a suitable fluctuation and thereby exchange O\* and H', and this is illustrated as we move to panel c. But even at the new vertex site, OH<sup>-</sup> is perfectly tetrahedrally solvated and, therefore, is in a perfect state to receive a proton from one of its first shell water molecules, leading readily to the next PT event illustrated in panel d of Figure 1. Thus, not only does the coordination pattern predicted by PW91 lead to a scenario where OH<sup>-</sup> is most of the time perfectly embedded in the HB network of bulk water like any intact water molecule, but the presolvation concept is able to predict the mechanism that results from this fact. When OH<sup>-</sup>(aq) accepts three hydrogen bonds and donates one much of the time, it is not a topological defect, meaning that no coordination number change is required to prepare it for receiving a proton. Hence, the defect can move through the network with practically no hindrance. It turns out that PT events and HB fluctuations in the first shell of OH<sup>-</sup>(aq) are largely uncorrelated as demonstrated by Figure 4a, which is consistent with ref 33. This analysis explains naturally why PT occurs on an ultrafast time scale in a model such as PW91 in which OH<sup>-</sup> predominantly accepts three HBs and donates one and thus rationalizes the unphysically large diffusion coefficient of OH<sup>-</sup> in comparison to both H<sub>2</sub>O self-diffusion and H<sub>3</sub>O<sup>+</sup> structural diffusion (Figure 3a and Table 1).

In the HCTH trajectory, OH<sup>-</sup>(aq) almost always accepts four HBs in addition to donating one (Figure 2), leading to a saturated solvation shell. Contrary to the PW91 case, HCTH OH<sup>-</sup> is rarely solvated in such a way as to receive an additional proton. This is illustrated in the right-most column of Figure 1 (see panel i). The resulting charge defect dynamics depicted in Figure 4c makes clear that structural diffusion is extremely slow and highly correlated

with switches from four to three accepted bonds around O\*. The slow diffusive dynamics in Figure 3c suggests that OH<sup>-</sup> moves mainly like a simple ion, that is, by carrying a rather tightly bound and bulky solvation shell with it as illustrated by moving down the right-most column in Figure 1. This observation explains straightforwardly why the diffusion coefficient of OH<sup>-</sup> in water is slower than that of H<sub>2</sub>O in water. Thus, HCTH produces mainly slow vehicle diffusion of a long-lived solvation aggregate, OH<sup>-</sup>·(H<sub>2</sub>O)<sub>*n*</sub>, interrupted by fast structural diffusion steps, the latter, however, being highly rare events!

The coordination pattern of OH<sup>-</sup> captured by BLYP predicts a mechanism that can account for the dynamical solvation shell changes from the resting state (four accepted and no donated HB) to the active state (three accepted and one donated HB) from above (see main panel in Figure 2b). Most importantly, the most probable state clearly is the one that accepts four bonds, as illustrated in the middle column of Figure 1 (see panel e); an additional non-hydrogen-bonded water molecule might already be located close to H'. As we move down the middle column to panel f, we see that fluctuations in the second solvation shell reduce the number of accepted HBs from four to three in the first shell of OH<sup>-</sup> and, almost simultaneously, another HB is donated by H'. Only in this configuration (see panel g) characterized by three accepted and one donated HBs is the proton-receiving species, that is, OH<sup>-</sup>, presolvated like a regular water molecule. In this state, a proton from a neighboring water molecule can transfer to OH<sup>-</sup> (see also panel g). After this PT step, the charge defect has migrated along a HB and is now located, in a 4-fold coordinated state, at a neighboring vertex site (panel h). There, it relaxes to a resting state configuration similar to the one depicted in panel e. This mechanism<sup>29</sup> leads to a charge defect dynamics (see Figure 4b) where, in accordance with the presolvation concept, a first shell coordination number change of O\* from four to three accepted bonds, in addition to the donation of another HB by H', are strongly correlated with PT. This implies a rate limitation by those HB fluctuations that ultimately break an accepted bond in the first solvation sphere of O\* in conjunction with donating a HB by H'.

At this stage, a comparison of the simulation results to the mirror image picture is in order. It has been suggested<sup>26</sup> that the resulting proton hole mechanism might proceed without the formation of the donated HB, H'···O<sub>w</sub>. In this mechanism,<sup>26</sup> the OH<sup>-</sup>(aq) accepts three HBs and donates none and, therefore, is never coordinated like a bulk water molecule, even during proton transfer (see Figure 3 therein). In consideration of this proposal, it must be stressed that (i) the PT step would produce a water molecule with the wrong solvation pattern and (ii) the three standard functionals employed unanimously predict that the H'···O<sub>w</sub> HB must form when the proton is transferred. Therefore, there is little substantive evidence to support mechanistic proposals that do not consider donation of a HB by OH<sup>-</sup>(aq). As an experimental corollary, small OH<sup>-</sup>·(H<sub>2</sub>O)<sub>*n*</sub> clusters, known

to not form this H'···O<sub>w</sub> HB,<sup>40–43,45</sup> are most likely not a useful approach to understand charge migration in bulk aqueous bases.

### III. Conclusions and Outlook

Using three popular density functionals, we have been able to perform a “virtual experiment” on how different proposed solvation patterns for OH<sup>-</sup>(aq) influence the microscopic transport mechanism. In a situation where OH<sup>-</sup> accepts three HBs and often donates one, as predicted by the PW91 functional, the local topology of such a tetrahedral defect is close to the one of an intact water molecule, and only slight reorientational motion in the first solvation shell is necessary to induce PT, resulting in ultrafast migration. This picture is unphysical since the diffusion coefficient of OH<sup>-</sup>(aq) is found to exceed that of H<sup>+</sup>(aq) considerably, in clear contradiction to the experimental facts. In stark contrast, HCTH leads to OH<sup>-</sup>(aq) that overwhelmingly accepts four quite tightly bound water molecules and donates one bond, thereby preventing OH<sup>-</sup> from accessing a solvation pattern that allows for PT. Hence, with HCTH, diffusion occurs primarily by the vehicle or hydrodynamic mechanism where a rather long-lived aggregate, [OH<sup>-</sup>·(H<sub>2</sub>O)<sub>*n*</sub>](aq), is moving akin to simple ions such as Na<sup>+</sup>(aq) or Cl<sup>-</sup>(aq), PT and structural diffusion becoming rare events. This model yields a diffusion constant of OH<sup>-</sup>(aq) similar to the self-diffusion of water, which also contradicts experiment.

Finally, the solvation pattern predicted by BLYP yields a physically reasonable diffusion coefficient for OH<sup>-</sup>(aq) being much larger than that of water but also smaller than that of H<sup>+</sup>(aq) as expected experimentally. By accepting four HBs, the dominant complex formed by OH<sup>-</sup>(aq) is a hypercoordinated one. However, fluctuations can activate this inert resting state by breaking one of the accepted HBs in the first solvation shell of OH<sup>-</sup> and forming a new donated HB from its hydrogen. This transiently creates a tetrahedral solvation topology such that PT can occur readily once the active state is formed. Thus, the HB lifetime governs this dynamical gating and imposes the proper rate limitation for structural diffusion of OH<sup>-</sup>(aq). More generally, this analysis of the three functionals allows us to trace back the qualitatively different mechanisms of PW91, BLYP, and HCTH to different populations of OH<sup>-</sup> molecules that accept three or four HBs in the first shell.

This overall consistent picture has important ramifications. First, it suggests that the solvation pattern of OH<sup>-</sup>(aq) is not analogous to that of H<sup>+</sup>(aq), implying that its structural diffusion mechanism cannot be a simple mirror image picture of the latter. Instead, support for the mechanism proposed in ref 29 is provided. Second, it has been demonstrated that the “presolvation concept” sketched in ref 29 not only predicts a structural diffusion mechanism that is consistent with experiment but also offers a microscopic understanding of the failures of the other mechanisms. Finally, this analysis supports the notion that OH<sup>-</sup> in ambient water, OH<sup>-</sup>(aq), is mostly hypercoordinated in the sense of preferentially accepting

four HBs in addition to being able to transiently donate one, which is distinctly different from microsolvated clusters, OH<sup>-</sup>·(H<sub>2</sub>O)<sub>n</sub>. The detailed predictions presented here should be a challenge to time-resolved spectroscopic experiments to be carried out directly in the liquid phase.

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