Ab Initio Molecular Dynamics Simulations of an Excess Proton in a Triethylene Glycol–Water Solution: Solvation Structure, Mechanism, and Kinetics

Marshall T. McDonnell,† Haixuan Xu,‡ and David J. Keffer*‡

†Department of Chemical and Biomolecular Engineering, and ‡Department of Materials Science and Engineering, University of Tennessee, Knoxville, Tennessee 37996, United States

ABSTRACT: We investigate the solvation shell structures, the distribution of protonic defects, mechanistic details, kinetics, and dynamics of proton transfer for an excess proton in bulk water and for an excess proton in an aqueous solution of triethylene glycol (TEG) via Car−Parrinello molecular dynamics simulations. The PW91, PBE, and PBE with the Tkatchenko−Scheffler (TS) density-dependent dispersion functionals were used and compared for bulk water and the TEG−water mixtures. The excess proton is found to reside predominantly on water molecules but also resides on hydroxyl groups of TEG. The lifetimes associated with structural diffusion time scales of the protonated water were found to be on the order of ~1 ps. All three functionals studied support the presolvation requirement for structural diffusion. The highest level of theory shows a reduction in the free energy barrier for water−water proton transfer in TEG−water mixtures compared to bulk water. The effect of TEG shows no strong change in the kinetics for TEG−water mixtures compared to bulk water for this same level of theory. The excess proton displays burst-rest behavior in the presence of TEG, similar to that found in bulk water. We find that the TEG chain disrupts the hydrogen-bond network, causing the solvation shell around water to be populated by TEG chain groups instead of other waters, reducing the rigidity of the hydrogen-bond network. Methylene is a dominant hydrogen bond donor for the protonated water in hydrogen-bond networks associated with proton transfer and structural diffusion. This is consistent with previous studies that have found the hydronium ion to be amphiphilic in nature and to have higher proton mobility at oil−water interfaces.

I. INTRODUCTION

Polyethylene glycol (PEG) (also known as poly(ethylene oxide) (PEO) in its long chain form) is a water-soluble polymer that has been widely studied for its interesting properties in aqueous environments. These properties include interactions of its ethylene oxide (EO) chains in aqueous solutions,1−4 the ability to adsorb on surfaces and interfaces,5 and proton conductivity in polymer electrolytes.6−18 The interaction of water with the PEG chain backbone has been widely studied to date, both by experiment14,15,19 and simulation5,20−26 due to the interesting ability of PEG to form bridged hydrogen bonds (HBs) from EO monomer units to water molecules to other EO monomer units within the same chain.4 These properties give PEG a wide variety of applications such as biphasic (two-phase) liquid−liquid catalysis,27 electrochemical energy conversion as a proton exchange membrane additive,28−30 and in drug delivery via modification of therapeutic molecules (known as PEGylation).31−34

The conductivity of various ions with PEG in aqueous solution has also been of research interest in past years. In pharmaceutical applications, Capuano et al.35 studied the transport properties of NaCl in PEG-water mixtures to understand the combined effect of PEG and salt interactions in aqueous solution for extension to PEGylated proteins for drug delivery. Consta and Chung33,34 used hybrid Monte Carlo and classical molecular dynamics (MD) simulations to determine charge-induced conformational changes and ion release mechanisms of PEG chains in aqueous charged nanodroplets for applications in atmospheric aerosols and electrospray mass spectroscopy experiments. In fuel cell applications, Honma and co-workers35,36 synthesized organoic/inorganic nanocomposite hybrid polymer electrolyte membranes of SiO2/PEO via sol−gel processes. Sundholm and co-workers37−39 synthesized and characterized PEO sulfonic acids as a polymer electrolyte material. Ennari and co-workers40 performed computational studies of acidic aqueous PEO and PEO sulfonic acid solutions of the similar molecular weight as those of Sundholm and co-workers35,36. Classical MD simulations were used to study the structure, solvation and proton diffusion to determine the atomic-level effect of the

Supporting Information

*Corresponding author. E-mail: david.keffer@utk.edu (D.J.K.).

‡Contributed equally.

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observed that long-range proton transport occurs via periods of “burst” dynamics where the excess proton hops across multiple water molecules for a larger distance on a short time scale, followed by periods of long-lived “rest” (>5 ps) where it is stabilized by the local solvation structure on the picosecond (ps) time scale, still undergoing local proton hopping. To further clarify the role of both the weak hydrogen bond formation to the hydronium ion and proton hopping over multiple waters simultaneously to the molecular mechanism that gives rise to long-range proton transport, Tse et al. showed that concerted hops over multiple water molecules occur during both burst and rest periods and that the weak hydrogen bond formation to the hydronium was the stronger correlation to the burst behavior. Thus, long-range proton transport occurs via single and multiple hops and is mostly coupled to a favorable hydrogen bond network paired with a weak hydrogen bond formation to the hydronium to initiate the forward hopping, burst dynamics. From this refined state of understanding of proton transport in bulk water, a natural extension is to also study and refine proton transport in aqueous solutions and mixtures with other relevant molecular species that can have an effect on proton transfer mechanisms and transport.

With advances in computational resources and algorithms relevant to electronic structure calculations, larger systems such as study of proton transfer in aqueous polymer solutions can be modeled via CPMD simulations. The work by Ennari and co-workers17,39,68,69 used classical MD simulations with an empirical force field that does not explicitly contain the electronic degrees of freedom in its definition. This implies that bond breaking and formation required for structural diffusion of proton transport could not be simulated in such a way that is available in CPMD simulations. To overcome this limitation, the systems simulated included both a hydronium ion to model the vehicular diffusion and a particle with the mass and charge of a proton that, interacting via electrostatics, could move freely from surrounding water molecules to model the structural diffusion. This decomposition makes MD simulations of larger systems such as that required for long polymer chains viable but such simplification deviates from the real picture of structural diffusion. Mainly, it is not a single excess proton that hops from one water molecule to another but a much larger, multidynamic and multitime scale molecular mechanism that is still a current research challenge.

For this study, we have simulated bulk water with one excess proton and a triethylene glycol (TEG) aqueous solution with one excess proton using CPMD simulations. This model system provides further insight into the proton transport of systems with high PEG concentration and specifically the effect that PEG has on proton transport compared to bulk water. We analyze the structures of the hydrogen bond networks that are formed, the different protonic defect species that occur and their associated lifetimes, solvation shell species and associated lifetimes, mechanistic details of proton transfer, the free energy barriers for proton transfer between molecules, and the transport kinetics and dynamics for proton transport.

II. SIMULATION DETAILS

II.A. Simulation Size and Cell Setups. Density functional theory70 (DFT) based AIMD simulations, specifically CPMD simulations, were performed in the microcanonical ensemble (NVE) using the Quantum ESPRESSO (opEn-Source Package for Research in Electronic Structure, Simulation, and

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Optimization) software suite\textsuperscript{21} for an excess proton in bulk water and a TEG-water mixture. For the bulk water simulations, the system consisted of 32 water molecules and one excess proton in a cubic simulation cell of length 9.8652 Å, taken from previous studies.\textsuperscript{42} The TEG-water mixture consisted of 27 water molecules, an excess proton, and one TEG chain in a cubic simulation cell of length 10.0 Å. Both systems were subject to periodic boundary conditions for both classical and ab initio MD simulations.

The system size was chosen to ensure strong interaction and observable effect of the TEG chain with the excess proton. For a larger system, the aqueous TEG solution becomes more dilute, decreasing the observation of the TEG effect on proton transport. Thus, our system size helps increase interaction sampling of possible proton transport effects induced by the TEG chain. The simulation cell sizes were determined after classical MD simulations were used for rough equilibration and generation of the initial nuclear coordinates in the system, to be discussed further below. Using this system cell size, multiple AIMD simulations with different initial nuclear coordinates, were carried out to sample different phase space trajectories in order to increase the probability of seeing TEG interactions with the excess proton and also to increase the statistical sampling of structure and transport of the excess proton.

II.B. Classical MD for Generating Initial Conditions for AIMD. Classical MD simulations using the Optimized Potentials for Liquid Simulations - All Atom (OPLS-AA) empirical force field\textsuperscript{72–74} for the TEG molecule and the Transferable Intermolecular Potential - Three Point (TIP3P) water model\textsuperscript{76} with flexible OH bonds\textsuperscript{76} for the water molecule and the hydronium molecules were performed prior to the AIMD simulations to generate initial nuclear coordinates for initialization of the AIMD systems. For the classical MD simulations, the hydronium charges were taken from the work of Urata et al.\textsuperscript{77} The long-range Coulombic interactions were computed using the k-space method, long-range particle–particle particle-mesh solver\textsuperscript{78} with a relative error in the force tolerance of 10\textsuperscript{−5} kcal/mol. Geometric mixing rules were used for computing pair-style force field parameters of different atom types. The simulation cell was +1 charged due to the hydronium ion (not a charge neutral system). The pairwise and Coulombic forces used a cutoff of 10.0 Å. To initialize the system, the TEG chain, water molecule and hydronium ion were put on a simple cubic lattice arrangement of very low density (\(\sim 0.3\) g/cm\(^3\)) initially to reduce aphysical initial configurations of high energy using the open-source Moltemplate molecule building and force field database code.\textsuperscript{79} The Large-Scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) open-source code was used to perform all classical MD simulations.\textsuperscript{80,81} The reversible reference system propagator algorithm (rRESPA) by Tuckerman et al.\textsuperscript{82} was used for integrating the equations of motion. The largest time step was 1 fs (fs) for pairwise interactions and a smallest time step was 0.2 fs for bonding interactions. The system was initialized by first performing energy minimization with an energy convergence tolerance of 10\textsuperscript{−5} kcal/mol and a force convergence tolerance of 10\textsuperscript{−7} kcal/mol. After minimization, the system was run in the isobaric–isothermal ensemble (NPT) for 250 ps using the Nosé–Hoover thermostat and barostat\textsuperscript{83,84} with the equations of motion formalism from the work of Shinoda et al.\textsuperscript{85} the hydrostatic equations of Martyna et al.\textsuperscript{86} the strain energy proposed by Parrinello and Rahman,\textsuperscript{87} and the time integrator closely following the one from Tuckerman et al.\textsuperscript{88} The thermostat was set at 300 K with a relaxation timelength of 0.1 ps. The barostat was set at 1 atm with a relaxation timelength of 1 ps with a drag applied to the Nosé–Hoover equations to dampen the large pressure oscillations that can occur in going from low density to high density. This protocol gave a converged density of \(\sim 1.05\) g/cm\(^3\) for the system. This density appears to be within reasonable agreement with experiment, lying between the density of pure water (0.99 g/cm\(^3\)) and the density of pure TEG (1.12 g/cm\(^3\)) at STP. With a TEG mole fraction of \(\sim 0.0357\) and at \(\sim 300\) K, we are in relatively good agreement with the recent work of Begum et al.\textsuperscript{89} who report a density of 1.0412 g/cm\(^3\) for a mole fraction of TEG equal to 0.05023 and at 303.15K for TEG–water mixtures. Keeping the density fixed, the system then underwent thermal annealing via temperature ramping from 300 to 900 K within 250 ps and then run in the canonical ensemble for a fixed temperature of 900 K for 500 ps and then quenched back to 300 K for 500 ps. This allowed the system to cross possible high energy barriers that may not be overcome at low temperatures and to explore more of the phase space within the simulation time. The initial configurations for AIMD simulations were taken from the final 500 ps at 300 K of the classical MD simulations at one of the five equally spaced (100 ps) configurations.

II.C. AIMD. For the TEG–water mixture, three different DFT conditions were set up, each with either a different exchange-correlation (XC) functional used in the quantum mechanical treatment of the electronic degrees of freedom, a different pseudopotential used to describe the interaction between the valence electrons and the ions (nuclei and their core electrons), or the inclusion of nonlocal electron correlation effects that are responsible for the van der Waals (vdW)/dispersion interactions, or vdW-inclusion/dispersion DFT. The first set of conditions, deemed the PW91 set, used the Perdew–Burke–Ernzerhof (PBE) XC functional,\textsuperscript{49,50} Vanderbilt ultrasoft pseudopotentials for core electron-valence electron interactions,\textsuperscript{92,93} and no vdW/dispersion interactions. The second set of conditions, deemed the PBE set, used the Perdew, Burke, and Ernzerhof (PBE) GGA-type XC functional,\textsuperscript{49,50} Martins–Troullier (MT) norm-conserving pseudopotentials,\textsuperscript{86} and no vdW/dispersion interactions. The third set of conditions, deemed the PBE+TS-vdW set, used the same as the PBE set but included the Tkatchenko–Scheffler density-dependent vdW/dispersion functional (TS-vdW).\textsuperscript{97,98} For the bulk water simulations, four sets of DFT XC functionals were used: the PW91 XC functional with Vanderbilt ultrasoft pseudopotentials, the Beck, Lee, Yang, Parr (BLYP)\textsuperscript{99,100} XC functional with MT pseudopotentials, the PBE XC functional with MT pseudopotentials, and the PBE XC functional with the Tkatchenko–Scheffler density-dependent vdW/dispersion functional (TS-vdW).\textsuperscript{97,98} The choice of including the BLYP functional for the bulk water simulations was made to allow for comparison with results in the literature.\textsuperscript{101,102}

For each set of DFT conditions, four to five independent AIMD simulations of the TEG–water mixture were run, totaling 13 different simulations across all XC functionals. Since the system is positively charged due to the hydronium ion, a negatively charged jellium/background charge\textsuperscript{103} was applied to the system to give a charge-neutral cell. The Kohn–Sham orbitals were expanded in plane waves with a kinetic energy cutoff 80 Ry for all three sets of DFT conditions. This cutoff is also consistent with previous work for determining accurate
The charge density was expanded in plane waves with an energy cutoff of 320 Ry for the PBE and vdW-PBE setups and 960 Ry cutoff for the PW91 setup since ultrasoft pseudopotentials trade-off a smaller Kohn–Sham orbital cutoff for a larger charge density cutoff. The electronic subsystem was sampled at the Γ-point at the first Brillouin zone. This is also consistent with previous literature, specifically in the work of Galli et al. where electronic structure calculations of both a 64 water molecule cell and, by repeating the 64 molecule cell periodically twice in each direction, a 512 water molecule cell, showed energy per molecule changes were less than 0.01 kcal/mol and the force was equivalent per atom within $10^{-5}$ a.u. between both systems.

For all the CPMD simulations, a time step of 0.075 fs and a fictitious electronic mass of 300 au was chosen due to testing from previous studies of CPMD for water simulations. The small time step and electronic mass are due to the light hydrogen nucleus within the system. To ensure adiabaticity between the ions and the electrons, the fictitious kinetic energy of the orbitals was monitored and showed to be constant and remained close to zero. This test is a measure of how close the system stays to the ground-state Born–Oppenheimer (BO) energy surface. If incorrect parameters are used, the electrons will exchange energy with the ions (destroying adiabaticity) and this kinetic energy will increase, undermining the integrity of the CPMD simulation.

For the bulk water AIMD simulations, the simulations were first run with 10 ps in the canonical (NVT) ensemble and followed by 50 ps of NVE for data production for each XC functional. The TEG–water mixture AIMD simulations were first carried out in the NVT ensemble for 13 ps of equilibration and then run in the NVE ensemble for a minimum of 10 ps for data production for each of the simulations. The length of each simulation varied but it was ensured that 50 ps of data production per XC functional set were obtained. The collective total for each XC functional were ~95 ps for the PBE set, ~68 ps for the PW91 set, and ~52 ps for the PBE+TS-vdW set. The system was initialized by first relaxing the electronic wave function by relaxing the electronic degrees of freedom with frozen, immobile ions. Then, the system wave function was relaxed by mobilizing the ions, allowing the ionic and electronic dynamical degrees of freedom to converge on the ground-state energy simultaneously. This was performed via geometry optimization using dampened dynamics with a total energy convergence tolerance and a fictitious electronic kinetic energy convergence tolerance of $10^{-7}$ and $10^{-4}$ Hartree a.u., respectively. For the equilibration stage of the TEG–water mixtures in the NVT ensemble, Nose–Hoover chain thermostats were implemented, each with a chain length of four. To achieve rapid equipartition of the thermal energy, one Nose–Hoover chain was applied per atom (“massive” Nose–Hoover thermostat). Four different thermostat frequencies were used to stimulate both the slow and fast intramolecular, oxygen–hydrogen vibrational motions. The ionic temperature was monitored and was found to be well-averaged around ~300 K after 3 ps. This was the followed by an additional 10 ps of NVT equilibration and then switched to the NVE ensemble for a minimum of 10 ps for data production.

III. RESULTS AND DISCUSSION

III.A. Comparative Analysis of Solvation Structure via Radial Distribution Functions. Our analysis begins with a description of the solvation structure found around H$_2$O and H$_3$O$^+$ molecules for both the bulk water and TEG–water mixture systems using radial distribution functions (RDF), g(r).

Figure 1. Radial distribution functions of oxygen and hydrogen of water and hydronium ion in bulk water and TEG–water mixtures at 300 K. The different figures are as follows: (a) O (water)–O (water), (b) O (water)–H (all hydrogens), (c) O (hydronium)–O (water), and (d) O (hydronium)–H (all hydrogens). The Journal of Physical Chemistry B

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to illustrate key differences in local liquid structure between the bulk water system and the TEG–water mixture, and also to highlight affinity of H$_2$O and H$_3$O$^+$ for specific groups along the TEG polymer chain specific to the TEG–water mixture. In Figure 1, the RDFs for oxygen of H$_2$O and H$_3$O$^+$ with different species are shown.

For understanding the solvation structure around water molecules, we first analyze the correlation between the O of H$_2$O, annotated O (H$_2$O), with other O (H$_2$O) RDF, or $g_{O(H_2O)-O(H_2O)}(r)$ in Figure 1a. The oxygen–oxygen RDF in Figure 1a shows that the first peak around 2.75 Å is the same for the bulk water and the TEG–water mixture and all density functionals. The first minimum occurs around 3.2–3.3 Å with the location being found at greater distance from the oxygen with an increasing level of theory for the XC functional. The second peak occurs at around 4.2–4.3 Å, appears to vary less for the XC functional in the TEG–water mixture.

In Figure 1b, the RDF between the oxygen of water, O (H$_2$O), and surrounding H, $g_{O(H_2O)-H}(r)$ is shown. The first peak occurs due to covalently bonded hydrogen atoms. We see that the second and third peaks occur around 1.75 and 3.2 Å, respectively, for both bulk and TEG–water mixture, regardless of the XC functional. The peak height decreases with increasing level of theory and from bulk water to the TEG–water mixture, indicating a weakening of the HB network.

Based on the RDFs for oxygen atoms of water, the presence of TEG shows an overall reduction in RDF peak height and softening of the local water structure. This occurs most likely due to the TEG chain species being located in the first solvation shell, causing softening of the first solvation structure and disrupting the HB network. This disruption is best shown in the reduction of the second peak of the O of H$_2$O and any H, signifying that H atoms are less likely to be locked into hydrogen bonds with oxygen of water molecules. Also, we see that inclusion of vdW/dispersion interactions also reduce the peak height, indicating a further softening of the water structure. It has become well-known that the PBE level of theory gives an overstructured oxygen–oxygen RDF for water due to the key limitations in GGA-DFT. These limitations manifest in theoretical descriptions of water as overstructuring, giving a representation of supercooled liquid water at ambient conditions. Recently, DiStasio et al. determined that including vdW/dispersion interactions strengthen the interaction between a given water molecule and those found in its first and second solvation shells. The stronger interaction with second solvation shell water molecules allow them to move inward to interstitial regions, weakening the HBs in the first solvation shell and allowing first solvation shell water molecules to move outward. Thus, we attribute this softening of structure with the dispersion-included PBE+TS-vdW level of theory due to weakened HBs and stronger interaction with second solvation shell species, displacing first solvation shell water molecules compared to the PBE level of theory. The most evident feature is the increase in the RDF value for the first minimum in the $g_{O(H_2O)-O(H_2O)}(r)$ in Figure 1a. This is due to interstitial water molecules between the first and second solvation shell, i.e. the water molecules migration outward, from first to second solvation shells, and inward, from second to first solvation shells.

For the solvation structure around H$_3$O$^+$, we analyze the RDF of O in H$_3$O$^+$ with O in H$_2$O, $g_{O(H_3O^+)-O(H_2O)}(r)$ (Figure 1c), and with H atoms, $g_{O(H_3O^+)-H}(r)$ (Figure 1d). In $g_{O(H_3O^+)-O(H_2O)}(r)$, we observe the first peak around 2.5 Å for both systems and all levels of theory. The first minimum occurs...
at approximately 2.9–3.0 Å with increasing peak height for the TEG–water mixture and increasing level of theory. The second peak occurs at around 4.2–4.3 Å. In Figure 1d, the O of H₂O and any hydrogen RDF has a first peak for covalently bonded hydrogen atoms. Comparing to the O of H₂O and any hydrogen RDF in Figure 1b, we observe a broadening of the first peak farther from the oxygen atom. The second peak for the bulk water systems occur at ~1.80 Å. This peak is the hydrogen of a HB donor. Comparing Figure 1b to d, we see the expected reduction in the second peak height for bulk water due to H₂O accepting two HBs while H₃O⁺ can only accept one HB. For the TEG–water mixture, no strong peak is observed at ~1.80 Å across all levels of theory but instead shows an increasing slope starting around 1.6 Å. Thus, the hydrogen of the HB donor is less localized than that for bulk water and is located within any range from 1.6 to 2.6 Å.

In Figure 2, we show the RDFs for oxygen atoms of H₂O and H₃O⁺ with oxygen atoms of the TEG chain, specifically the ether (ROR) oxygen and hydroxyl (ROH) oxygen. We begin with the RDFs of the O of H₂O with the TEG atoms to better understand the direct interaction of water molecules with the TEG chain and the effects of TEG on the solvation structure around water molecules. In Figure 2a, $g_{O(H₂O)-O(ROR)}(r)$ shows the first peak at around 2.70 to 2.75 Å. The first peak of the PW91 XC functional occurs closer to the oxygen of water, indicating a stronger attraction between ether and water compared to the PBE and PBE+TS-vdW functionals. Also, the minimum between the water and ether is farther away for the PBE and PBE+TS-vdW XC functionals, indicating that the PW91 has a more rigid structure between the water molecules and the ether backbone compared to the other XC functionals.

In Figure 2b, we examine the correlation of O of H₂O with the O of the ROH group. We observe that $g_{O(H₂O)-O(ROH)}(r)$ has a first peak located around 2.7 Å and that there is a decrease in the peak height. The highest peak belongs to PBE, the next highest belongs to PW91, and the PBE+TS-vdW with the lowest peak. The trend that we observe is that the ultrasoft pseudopotential used for PW91 could effect this interaction and thus the RDF. Also, that the inclusion of dispersion effects seem to have a drastic decrease in RDF size, going from the PBE to the PBE+TS-vdW XC functionals, indicating the importance of including dispersion for this system. This shows overall there is a softening of the second solvation shell structure around H₂O via including dispersion.

For Figure 2c and d, we show the RDF for O of H₂O with the ether O and hydroxyl O of TEG, respectively. In Figure 2c, the ether O of TEG is shown to be in the first solvation shell of H₂O for the PBE+TS-vdW XC functional but not for the PW91 and PBE levels of theory. There appears to be a strong interaction between the ether oxygen of TEG and H₂O that is not captured by modeling without dispersion effects. In Figure 2d, the hydroxyl O of TEG is in the first solvation shell of H₂O for the PW91 and PBE levels of theory but not for the PBE+TS-vdW XC functional. Interestingly, the PBE+TS-vdW XC functional gives an almost feature-less RDF between a H₃O⁺ and the hydroxyl group of TEG, whereas, the PW91 and PBE RDFs have apparent peaks at ~2.5 and ~4.5 Å. The strongest interaction of H₂O⁺ with the hydroxyl group occurs with the PW91 level of theory. Overall, for H₂O⁺, the PW91 and PBE XC functionals give a H₂O⁺ solvated mostly by H₂O but also by hydrogen O of TEG in the first solvation shell and PBE+TS-vdW gives H₂O⁺ solvated by H₂O and ether groups of TEG.

### III. B. Protonic Defect Species Occurrence and Lifetime Analysis

One interesting effect that TEG has on proton transfer in aqueous solution is the different protonated and deprotonated species, or protonic defect species, that can occur and their associated lifetimes. We analyze the trajectory for these species by, first, assigning every hydrogen atom to the geometrically closest oxygen or carbon atom for every frame to identify it as a water molecule or a molecular group of the TEG chain (i.e., ether, hydroxyl, or methylene). Then, the molecule/molecular group is identified as having either an excess or lack of a hydrogen atom, indicating a protonic defect species.

In Table 1, we show the different species that occur over all simulations of the aqueous TEG solutions with occurrence percentages, cumulative occurrence percentages, and lifetimes of each species. For the lifetimes, the mean value is reported with one standard deviation being noted as (±σ). Proton rattling, where upon two consecutive proton transfer events,
the protonic defect is returned to the original species, is both included and excluded. The reasoning for excluding proton rattling is, if one includes the proton rattling events in analysis, the transient protonic defect species and surrounding solvation take over the recorded observations. One can exclude these proton rattling events, recording only those where two consecutive proton transfer events lead to a different protonated atom to determine structures that are associated with long-range, structural diffusion.

For all three XC functionals used, we note three common trends for the protonic defect species occurrences. First, H$_3$O$^+$ is the dominant species that occurs for more than 99% of the simulation time. Second, the second most likely protonated species besides H$_3$O$^+$ to not exist simply as a proton rattling species, implying it has a role in proton transfer events that correlate to structural diffusion. Third, the OH$^-$ ion and RO$^-$ occur with only a small fraction of a percent and only exist in proton rattling occurrences.

For the lifetimes of these species that occur, we point out a few key notes in Table 1. First, the H$_3$O$^+$ lifetime occurs well within one standard deviation for all three XC functionals, signifying no strong change among levels of theory, for both cases of proton rattling. Yet, the mean and the standard deviation of the lifetimes do increase with increasing the level of theory, pointing to longer lifetimes of H$_3$O$^+$ in the system. Note, the standard deviation is larger than the mean of the lifetime. A lifetime cannot be negative, thus putting a lower bound on the lifetime and implying a larger standard deviation.

The OH$^-$ ion show a very short lifetime among the protonated species. Interestingly, we also see more occurrences and longer lifetimes of the protonated hydroxyl group of TEG with long-range, structural diffusion. Interestingly, we also see more occurrences and longer lifetimes of the protonated hydroxyl group of TEG with proton rattling included but approximately equal when proton rattling is excluded. This implies that for the PBE XC functional, the proton reside on the hydroxyl group longer during proton rattling events compared to the PBE+TS-vdW XC simulations. Yet, overall, the proton rattling occurs for the same length of time before the proton travels to another atom, undergoing structural diffusion. Interestingly, we also see more occurrences and shorter lifetimes of the protonated hydroxyl group of TEG with the PW91 level of theory for both including and excluding proton rattling. This indicates a much stronger interaction between the H$_3$O$^+$ and the hydroxyl group for PW91, consistent with Figure 1d.

Next, we observe that for the protonated hydroxyl group of TEG, the occurrences and lifetimes are lower for the inclusion of dispersion effects when proton rattling is included but approximately equal when proton rattling is excluded. This implies longer lifetimes. Distributions of the H$_3$O$^+$ lifetimes in TEG–water mixtures with proton rattling included are shown in the Supporting Information in Figures S1–S3 for the three functionals for clarity.

### Table 2. Occurrences and Lifetimes of Special Pairs Made up of the Protonated Species (Z$_{protonated}$) and the Special Partner of the Protonated Species (Z$_{shared}$) Found in Aqueous H$^+$ and Triethylene Glycol (TEG) Systems$^a$

<table>
<thead>
<tr>
<th>functional</th>
<th>proton rattling</th>
<th>Z$_{protonated}$</th>
<th>Z$_{shared}$</th>
<th>%</th>
<th>𝐁$^a$</th>
<th>lifetime (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PW91</td>
<td>excluded</td>
<td>H$_2$O$^+$</td>
<td>H$_2$O</td>
<td>97.32</td>
<td>97.32</td>
<td>1.16 (±1.57)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H$_2$O$^+$</td>
<td>ROH</td>
<td>95.95</td>
<td>95.95</td>
<td>2.45 (±2.42)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ROH$^+$</td>
<td>H$_2$O</td>
<td>0.50</td>
<td>100</td>
<td>0.06$^a$</td>
</tr>
<tr>
<td>PBE</td>
<td>excluded</td>
<td>H$_2$O$^+$</td>
<td>H$_2$O</td>
<td>98.76</td>
<td>98.79</td>
<td>1.85 (±0.06)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H$_2$O$^+$</td>
<td>ROH</td>
<td>99.86</td>
<td>99.80</td>
<td>0.08 (±0.16)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ROH$^+$</td>
<td>H$_2$O</td>
<td>0.14</td>
<td>100</td>
<td>0.02$^a$</td>
</tr>
<tr>
<td>PBE+TS-vdW</td>
<td>excluded</td>
<td>H$_2$O$^+$</td>
<td>H$_2$O</td>
<td>99.51</td>
<td>99.51</td>
<td>1.53 (±2.51)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>H$_2$O$^+$</td>
<td>ROH</td>
<td>99.97</td>
<td>99.97</td>
<td>0.01$^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ROH$^+$</td>
<td>H$_2$O</td>
<td>0.03</td>
<td>100</td>
<td>0.01$^a$</td>
</tr>
</tbody>
</table>

$^a$Proton rattling effects are excluded. $^b$Single lifetime measurement.

### Table 3. Occurrences and Lifetimes of Solvating Shell Species (H$_{A\lambda}$) around the Protonated Species (Z$_{protonated}$) Found in Aqueous H$^+$ and Triethylene Glycol (TEG) Systems$^a$

<table>
<thead>
<tr>
<th>functional</th>
<th>Z$_{protonated}$</th>
<th>H$_{A\lambda}$</th>
<th>H$_{A\lambda}$</th>
<th>H$_{A\lambda}$</th>
<th>%</th>
<th>𝐁$^a$</th>
<th>lifetime (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PW91$^a$</td>
<td>H$_2$O$^+$</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>86.40</td>
<td>86.40</td>
<td>0.81 (±1.46)</td>
</tr>
<tr>
<td></td>
<td>H$_2$O$^+$</td>
<td>ROH</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>97.32</td>
<td>97.32</td>
<td>0.82 (±1.34)</td>
</tr>
<tr>
<td></td>
<td>H$_2$O$^+$</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>3.06</td>
<td>99.22</td>
<td>0.62 (±0.01)</td>
</tr>
<tr>
<td></td>
<td>ROH$^+$</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>0.50</td>
<td>99.72</td>
<td>0.03 (±0.02)</td>
</tr>
<tr>
<td>PBE$^a$</td>
<td>H$_2$O$^+$</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>85.75</td>
<td>85.75</td>
<td>1.52 (±2.84)</td>
</tr>
<tr>
<td></td>
<td>H$_2$O$^+$</td>
<td>ROH</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>93.75</td>
<td>93.75</td>
<td>1.10 (±1.42)</td>
</tr>
<tr>
<td></td>
<td>H$_2$O$^+$</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>3.11</td>
<td>99.86</td>
<td>0.49 (±0)</td>
</tr>
<tr>
<td></td>
<td>ROH$^+$</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>0.14</td>
<td>100</td>
<td>0.01</td>
</tr>
<tr>
<td>PBE+TS-vdW$^a$</td>
<td>H$_2$O$^+$</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>90.12</td>
<td>90.12</td>
<td>1.52 (±2.32)</td>
</tr>
<tr>
<td></td>
<td>H$_2$O$^+$</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>5.95</td>
<td>96.07</td>
<td>0.72</td>
</tr>
<tr>
<td></td>
<td>H$_2$O$^+$</td>
<td>ROH</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>98.28</td>
<td>98.28</td>
<td>0.21 (±0.20)</td>
</tr>
<tr>
<td></td>
<td>H$_2$O$^+$</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>1.70</td>
<td>99.98</td>
<td>1.36</td>
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<tr>
<td></td>
<td>ROH$^+$</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>H$_2$O</td>
<td>0.02</td>
<td>100</td>
<td>1.27$^a$</td>
</tr>
</tbody>
</table>

$^a$Proton rattling effects are excluded. $^b$12 different solvation shells found when proton rattling included. $^c$Single lifetime measurement. $^d$13 different solvation shells found when proton rattling included.
equal during these event, implying these are proton sharing event versus proton transfer event.

Using our values for the probability of H⁺ to reside on water or the hydroxyl/ROH of TEG in Table 1, we calculate the change in the free energy of transfer for H⁺ from water to ROH to be 7.2, 10.2, and 13.8 in kJ/mol for the PW91, PBE, and PBE +TS-vdW levels of theory, respectively, with an average value of 10.4 kJ/mol over all three XC functionals. This gives excellent agreement compared to the experimental values for both 10.4 kJ/mol for methanol and 10.5 kJ/mol for ethanol, in Tables 2 and 3, respectively, from the work of Marcus109 that reports the standard Gibbs free energy for the transfer of ions from water to aqueous alcohol mixtures for varying mass fraction of the alcohol content using the extra-thermodynamic assumption. Note, we used the assumption that we can mimic the ROHs of TEG as methanol and ethanol. Discussion and tabulation of the reported values in Table S2 can be found in section II of the Supporting Information.

III.C. Special Pair Occurrence and Lifetime Analysis.
Another effect of introducing TEG is the different special pairs that can form between atoms, helping identify the most active protons of the system. The term special pair originally referred to the protonated H₂O⁺ and its hydrogen-bonded water molecule in the first solvation shell that was under-coordinated with similar hydration, yet this identity has changed with time. For further detail and insight, the reader is directed to the work of Markovitch et al.66 where, using the multistate empirical valence bond (MS-EVB) approach, they investigated the role of the special pair in the proton transport process and its dynamics throughout the system, termed the “special pair dance”.

For the present work, we begin by expanding on the previous section analysis, in that once the protonic defect species is determined, the “most-active” proton of the system is identified using the asymmetric stretch coordinate, given as δ = R₄₋₅ + R₆₋₅, where R₄₋₅ and R₆₋₅ are the HB distances for the shared proton (H⁺) between two atoms, a and b. The hydrogen atom which gives the smallest value of δ between the protonic defect species atom and the HB acceptor atom is identified as H⁺ and these two forms the special pair.

In Table 2, the different special pair types that occur over all simulations of the aqueous TEG solutions are listed with occurrence percentages, cumulative occurrence percentages, and lifetimes of each species. For the lifetimes, the mean value is reported with one standard deviation being noted as (~σ). Proton rattling events have been excluded to highlight special pairs relevant to structural diffusion. For all special pairs that occur with proton rattling events included, the reader is directed to Table S2 in the Supporting Information.

The trends of the special pairs follows closely with those of the protonic defect species analysis, as expected. First, the special pair between two water molecules (H₂O⁺ and H₂O) occurs more than 97% for the entire simulation time over all levels of theory. The second and third highest occurring special pairs are direct results from proton transfer between a water molecule and a hydroxyl group of TEG (H₂O⁺ with ROH and ROH₂ with H₂O). These are expected since the second highest occurring protonic defect species across all levels of theory was the protonated hydroxyl group of TEG and the only other protonated species that occurs when proton rattling is excluded for structural diffusion events.

The lifetimes of the H₂O⁺–H₂O special pairs appear to be in the range of ~1–2 ps across all levels of theory. These lifetimes have a very widespread over the simulations, shown by the PBE having lifetimes up to ~5 ps within one standard deviation. For the H₂O⁺–ROH and ROH₂–H₂O complexes, the general trend is a decrease in the occurrences with increasing level of theory. For the lifetimes of the H₂O⁺–ROH, the same general trend is observed with decreasing lifetimes for increasing level of theory. The occurrence of a special pair and the lifetime of that pair are correlated, most likely due to favorable stability of the structure for the given XC functional. The ROH₂–H₂O complex does not show a strong trend due to only a single occurrence for all XC functionals when proton rattling events have been excluded.

III.D. Solvation Shell Occurrence and Lifetime Analysis.
The results for analysis of the molecular groups that populate the hydrogen-bond acceptors, also called the ligand sites for the Eigen cation for protonated water molecules, are presented and discussed below to expand on the understanding of the solvation shells that are present around the given protonated species. Similar to the previous analysis of protonated species and special pairs, Table 3 shows all of the occurrences of solvation shells and their lifetimes for all levels of theory with proton rattling events excluded to highlight solvation likely present during structural diffusion events. We observe that the dominant species is the Eigen cation, occurring more than 85% of the simulation time sampled for all levels of theory. The lifetimes of this solvation shell seem to be dependent on the XC functional used but independent of dispersion inclusion.

Consistent with the RDFs of Figure 2d and the special pair analysis in Table 2, we see that the second dominant solvation shell structure is one that contains the hydroxyl group for the PW91 and PBE XC functionals but not for the PBE+TS-vdW XC functional. Instead, the second dominant solvation shell structure for the PBE+TS-vdW XC functional simulations is one with a vacant ligand site. The fact that this occurs for the dispersion inclusion functional leads one to conclude that the overstructuring of water that has been discussed for GGA XC functionals (PW91 and PBE) suppresses this solvation structure due to overly strong hydrogen bonding interactions for this given temperature. It appears that including dispersion increases the probability of observing a vacancy in the solvation structure, most likely due to stronger interactions with more distant molecular groups that can help stabilize this structure. Yet, the GGA XC functionals do have this as the third dominant solvation shell, implying that this solvation pattern is only suppressed but not prohibited.

Interestingly, the methylene group is present in the PW91 and PBE+TS-vdW solvation shell structures but only as a minority species. Yet, the lifetimes are very high for this solvation shell. Upon analyzing the solvation shell structures including proton rattling, it is observed that these may be long-lived proton rattling events, where the protonic defect resides on another atom with a different solvation shell for an extended amount of time before returning back to this solvation shell. The lifetime reported is therefore the collective lifetime of this solvation shell and all others observed during proton rattling events, which is not reflected in the occurrence of this solvation shell. The fact that this lifetime is long-lived (~1 ps for PBE+TS-vdW and ~4 ps for PW91) indicates that this is a solvation shell structure that can lead to proton “traps”, giving rise to rest periods and reduce overall structural diffusion. One explanation could be that when this solvation shell occurs, the excess proton has a reduced amount of paths along the hydrogen bond.
network to escape. An analysis of the hydrogen bond ring statistics, as in similar work, relative to this structure could determine the validity of this hypothesis but is not explored in the current work. All solvation shells present when proton rattling is included is shown in Table S3 in the Supporting Information.

Agmon et al. have interpreted the free energy of proton transfer from water to methanol, concluding that the solvation shell around the hydronium ion does not show preference to water or methanol and that either are likely candidates for hydrogen-bond acceptors. For our simulations, to determine if the hydroxyl group is also equally likely to populate the solvation shell relative to water, we determine what the probability of finding ROH on the ligand sites to varying degree. Second, in determining the target probability, we have assumed that the chain can both sterically hinder interaction with the hydroxyl group from other molecules in the system and also that the additional methylene groups in the chain could invoke repulsive behavior, already discussed. These effects would suppress the probability of finding ROH on the ligand sites relative to this structure could determine the validity of this hypothesis but is not explored in the current work. All solvation shells present when proton rattling is included is shown in Table S3 in the Supporting Information.

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(second-solvation shell) around the Zundel ion and, the work of Shevchuk et al.\textsuperscript{116} that use complex network analysis to track several coordinates of interest of the HB network relevant to proton transport. We determine the hydrogen bonded atoms that surround the special pair complex based on the criteria that the distance between HB acceptor (A) and donor (B) is less \( R_{AB} < 3.5 \) Å and the angle between the HB acceptor, hydrogen of the HB, and the HB donor \( \alpha(A \cdots H \cdots B) < 30^\circ \). Using a tree-structure data type, we “grow” the tree for the HBs surrounding the special pair by levels where the levels indicate the solvation shells. We can then compare tree-structures to determine equality, i.e. equivalent HB networks around the same special pair. We report the occurrences of each HB network around a given special pair and its associated lifetimes, shown in Table 4, only including HB networks that occur when proton rattling has been excluded. Only the five highest occurring of these HB networks are listed for brevity in the Table 4, with the total number of HB networks found listed in the footnotes for both excluding and including proton rattling. All of the HB networks found for TEG−water mixtures with proton rattling excluded are listed in the Supporting Information, in Tables S4−S6. In Figure 3, we give an illustration for the labels found in Table 4.

Since most HB networks surround a water−water special pair, this is the species shown in Figure 3.

![Figure 3. Hydrogen-bond network around a water−water special pair.](image)

From Table 4, we can determine the most significant HB networks present for structural diffusion proton transfer events. The \( \text{H}_2\text{O}^-\text{H}_2\text{O} \) special pair dominates the center of the HB networks found due to the high occurrence of this complex listed in Table 2 for all XC functionals. It is observed that the most likely hydrogen-bond donor for the hydronium, HB\( _{\text{prot}} \), is either a vacancy or CH\(_2\). This observation is in line with previous literature,\textsuperscript{117–120} that the hydronium ion has an “amphiphilic” nature, due to possessing both hydrophilic character via HBs formed with water molecules and also a hydrophobic character due to the lone pair of oxygen not forming a HB with water molecules due to the overall positive charge on the cation. Thus, instead of forming HBs with water at the HB donor site, the hydronium ion orients such that the hydrophobic lone electron pair either remains vacant or creates a HB to the hydrophobic CH\(_2\) of TEG and the hydrophilic hydrogens form HBs with other hydrophilic molecules and monomers (water molecules, ethers, and hydroxyls). Note, for this HB network analysis, the tree-structure has initially been setup to only capture “waterlike” hydrogen-bond networks based on H\(_2\)O−H\(_2\)O being the most likely observed special pair, seen in Table 2. This was to allow for easier comparison of similar hydrogen-bond networks and to reduce the already high number of entities identified. Relaxation of this constraint could be easily implemented but is not pursued in the current work. In the Supporting Information, we report the HB networks for the bulk water simulations where proton rattling has been excluded (Tables S7−S10), included (Tables S11−S14) and all HB networks found in TEG−water mixtures where proton rattling has been included (Tables S15−S17).

Following similar analysis used for the solvation shell ligand sites, we examine the relative probability of a molecule/molecular group to occupy HB network sites. Table 5 gives the percentage of occurrence of a given species on any of the 6 sites in the HB network, on any of the 4 HB acceptor sites, and on either of the 2 HB donor sites. Table 5 should be understood as follows. From the first row, for the PW91 XC functional, 49% of the hydrogen bond networks around a special pair have at least one methylene group in one of the six sites shown in Figure 3; 0.6% of the hydrogen bond networks have at least one methylene group in one of the four acceptor sites shown in Figure 3; and 48.5% of the hydrogen bond networks have at least one methylene group in one of the two donor sites shown in Figure 3. We note that water occurs in at least one acceptor site for all HB networks (thus a 100% occurrence for the total and acceptor columns of Table 5) and occurs at the donor site with ∼45% probability for all functionals.

Focusing on the preference for methylene in the HB network, we first determine that there is an ∼70% probability for CH\(_2\) to occur in the HB network based solely on concentration. Again, for discussion of the concentration-based probability union relation used, the reader is referred to section V of the Supporting Information. We see that based on the simulations, the CH\(_2\) group occurrence is XC functional-dependent, varies over the different simulation runs for each XC functional set seen in the large standard deviations, and that it does not appear to have an equal probability to occur when we compare to our probability to see it in any of the HB network sites. Yet, we notice that CH\(_2\) groups mainly sit on donor sites. Thus, if we reformulate our above analysis to only look at the donor sites instead, the probability for CH\(_2\) groups to be at either site based on concentration is ∼31%. From previously discussed assumptions of this analysis, if we look at the “cavity” occurrence, there is an overwhelmingly high chance of having no hydrogen bond donor present. This implies that our assumption for computing the probability based on concentration overestimates the probability for the HB donor site since we do not take into account the lack of a hydrogen bonded species at these sites. Therefore, CH\(_2\) groups have preference to be located at the HB donor sites relative to other molecule groups, observed previously in Table 4. Similarly, for the ROR or ROH to occupy any of the HB acceptor sites based on concentration is ∼22%. Thus, we can say ROH has a preferential probability be in the HB acceptor sites relative to other molecules. Surprisingly, the ether ROR has almost no probability for the PW91 and PBE XC functionals but a 20% probability when dispersion effects are included. This can also be seen in Figure 2c. Yet, we see that ROR actually has a relatively high preference over other molecules to be in the HB acceptor sites for only the PBE+TS-vdW XC functional.

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Table 5. Occurrence Percentages of a Given Molecule Species in the Total Hydrogen Bond Network, the Hydrogen Bond Acceptor Sites (H_A), and the Donor Sites (H_D)\(^a\)

<table>
<thead>
<tr>
<th>molecule group</th>
<th>functional</th>
<th>total %</th>
<th>SD</th>
<th>H_A %</th>
<th>SD</th>
<th>H_D %</th>
<th>SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_2)</td>
<td>PW91</td>
<td>49.0</td>
<td>±22</td>
<td>0.6</td>
<td>±1.1</td>
<td>48.5</td>
<td>±23</td>
</tr>
<tr>
<td></td>
<td>PBE</td>
<td>27.1</td>
<td>±10</td>
<td>0.6</td>
<td>±0.6</td>
<td>26.6</td>
<td>±9</td>
</tr>
<tr>
<td></td>
<td>PBE+TS-vdW</td>
<td>31.5</td>
<td>±4</td>
<td>3.3</td>
<td>±5</td>
<td>28.5</td>
<td>±7</td>
</tr>
<tr>
<td>ROH</td>
<td>PW91</td>
<td>19.2</td>
<td>±15</td>
<td>18.8</td>
<td>±15</td>
<td>0.4</td>
<td>±0.5</td>
</tr>
<tr>
<td></td>
<td>PBE</td>
<td>25.4</td>
<td>±12</td>
<td>20.0</td>
<td>±10</td>
<td>5.3</td>
<td>±7</td>
</tr>
<tr>
<td></td>
<td>PBE+TS-vdW</td>
<td>10.3</td>
<td>±15</td>
<td>8.2</td>
<td>±13</td>
<td>2.2</td>
<td>±2</td>
</tr>
<tr>
<td>ROR</td>
<td>PW91</td>
<td>1.5</td>
<td>±2</td>
<td>1.5</td>
<td>±2</td>
<td>86.1</td>
<td>±4</td>
</tr>
<tr>
<td></td>
<td>PBE</td>
<td>0.9</td>
<td>±1</td>
<td>0.9</td>
<td>±1</td>
<td>84.1</td>
<td>±3</td>
</tr>
<tr>
<td></td>
<td>PBE+TS-vdW</td>
<td>20.2</td>
<td>±16</td>
<td>20.2</td>
<td>±16</td>
<td>80.3</td>
<td>±2</td>
</tr>
<tr>
<td>“…”</td>
<td>PW91</td>
<td>81.9</td>
<td>±1</td>
<td>10.6</td>
<td>±5</td>
<td>80.3</td>
<td>±2</td>
</tr>
<tr>
<td></td>
<td>PBE</td>
<td>88.4</td>
<td>±3</td>
<td>17.0</td>
<td>±4</td>
<td>86.1</td>
<td>±4</td>
</tr>
<tr>
<td></td>
<td>PBE+TS-vdW</td>
<td>86.6</td>
<td>±2</td>
<td>16.2</td>
<td>±4</td>
<td>84.1</td>
<td>±3</td>
</tr>
</tbody>
</table>

“The molecular groups are the ether (ROR), methylene (CH\(_2\)) and hydroxyl (ROH) groups of TEG and a “cavity”. The standard deviations are reported also (SD).

Table 6. Top Five Most Occurring Hydrogen-Bond Networks around Reactant and Product during Proton Transfer for TEG–Water Mixtures\(^a\)

<table>
<thead>
<tr>
<th>functional</th>
<th>Z(^{\text{prex}})</th>
<th>Z(^{\text{prex}})</th>
<th>HB(_{A_p})</th>
<th>HB(_{A_p})</th>
<th>HB(_{D_p})</th>
<th>HB(_{A_x})</th>
<th>HB(_{A_x})</th>
<th>A %</th>
<th>Σ%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PW91(^b)</td>
<td>H(_2)O</td>
<td>H(_2)O</td>
<td>H(_2)O</td>
<td>H(_2)O</td>
<td>...</td>
<td>H(_2)O</td>
<td>H(_2)O</td>
<td>15.19</td>
<td>15.19</td>
</tr>
<tr>
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<td>H(_2)O</td>
<td>H(_2)O</td>
<td>H(_2)O</td>
<td>H(_2)O</td>
<td>...</td>
<td>H(_2)O</td>
<td>H(_2)O</td>
<td>14.82</td>
<td>30.02</td>
</tr>
<tr>
<td></td>
<td>H(_2)O</td>
<td>H(_2)O</td>
<td>H(_2)O</td>
<td>H(_2)O</td>
<td>H(_2)O</td>
<td>H(_2)O</td>
<td>...</td>
<td>14.25</td>
<td>44.26</td>
</tr>
<tr>
<td></td>
<td>H(_2)O</td>
<td>H(_2)O</td>
<td>H(_2)O</td>
<td>H(_2)O</td>
<td>CH(_2)</td>
<td>H(_2)O</td>
<td>H(_2)O</td>
<td>11.52</td>
<td>55.79</td>
</tr>
<tr>
<td></td>
<td>H(_2)O</td>
<td>H(_2)O</td>
<td>H(_2)O</td>
<td>H(_2)O</td>
<td>CH(_2)</td>
<td>H(_2)O</td>
<td>H(_2)O</td>
<td>4.45</td>
<td>60.24</td>
</tr>
<tr>
<td></td>
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<td>6.00</td>
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Therefore, we conclude that ROH has preference over other molecule groups to be at the acceptor sites, CH\(_2\) groups have preference over other molecule groups to be in the donor sites, and ROR has a XC functional-dependence that ranges from very low probability to preference when dispersion effects are included.

In Table 6, we report the HB networks that occur during proton transfer events. This helps determine how TEG is incorporated into the HB network to facilitate proton transport. Only the top five highest occurring HB networks are listed for brevity. Only the number of occurrences are listed for these HB networks since they are only captured at the instance of a proton transfer event. The CH\(_2\) of TEG is again in the top three most observed the HB networks, consistent with a similar observation in Table 4. This implies that proton transfer could possibly take place along the axis parallel to the TEG chain with the chain CH\(_2\) groups being HB donors, providing the necessary solvation around the special pair for proton transfer. This observation appears to be in line with the high proton mobility that is found at oil–water interfaces, shown in the work of Zhang et al.\(^{121}\) They showed via experiment and AIMD simulations of an interface of n-decane and water with an excess proton that the amphiphilic hydronium was attracted to the interface and retained high lateral mobility along the interface that exceed the bulk mobility for proton carriers.

The hydroxyl of TEG is present for PBE in Table 6 but not PW91. From Figure 2d, it appears that PW91 would also have HB networks that contain hydroxyls. Yet, Tables 1 and 2 and Figure 2d together give the picture that when the excess proton is located on a water and approaches the hydroxyl group, the hydroxyl group has a higher probability to become protonated for the PW91 as opposed to only occupying the solvation shell for the PBE case. The ether of TEG shows a high probability for occupying the solvation shell for PBE+TS-vdW, seen previously in Table 5. However, since this species does not appear in Table 3, we believe this HB network to be present for proton rattling events and not for longer range, structural diffusion proton transfer events. In the Supporting Information,
we show all HB networks during proton transfer events for the bulk water (Tables S18–S21) and TEG–water mixtures (Tables S22–S24).

III.F. Mechanistic Picture for Proton Transfer among Water Molecules. One would also like to know the effect of TEG on the mechanistic picture of proton transfer for water–water hops. Previous studies have shown that for proton transport in bulk water that, using the asymmetric stretch reaction coordinate \( \delta \) to identify the most likely oxygen to receive a transferring proton, the hydrogen-bonding patterns of this oxygen and the protonated oxygen had great similarity, termed the “presolvation” concept, previously discussed. This analysis was further refined in a recent study where, having knowledge of the entire trajectory, the focus was shifted from the atom most likely to receive a transferring proton instead to the atom that will receive the next transferring proton. In the work of Berkelbach et al., the RDF of atom A relative to atom B, \( \xi_{AB}(r) \), and corresponding integrated coordination number (ICN), 

\[
\eta_{AB}(r) = 4\pi\rho_b \int_0^r R^2 \xi_{AB}(R) dR,
\]

where \( \rho_b \) is the number density of atom B, were sampled at intervals to give a time progression of these functions leading up to a proton transfer event. They showed that the presolvation concept retained validity under this refined analysis for the concerted mechanism of proton transfer. In bulk water, the importance of the hydronium ion accepting a hydrogen bond to initiate long-range structural diffusion has been demonstrated in the work described by Berkelbach et al. and again in recent work by Tse et al. We employ this analysis for our system, comparing across different XC functionals and both for the bulk water and TEG–water mixtures. Figure 4 highlights the results using the PBE+TS-vdW XC functional for the TEG–water mixtures. The RDFs (Figures S5–S8) and the ICNs (Figures S9–S12 and S4) for proton transfer from water to water for bulk water, the RDFs for proton transfer from water to water (Figures S13–S15) and the ICNs for proton transfer from water to water (Figures S16–S17 and S25), from water to hydroxyl (Figures S18–S20), and from hydroxyl to water (Figures S21–S23) are provided in the Supporting Information using all XC functionals. For all XC functionals, the water-to-water ICNs for bulk water show evidence of the “presolvation” concept.

In Figure 4, we show the ICNs when proton rattling is excluded for the donating (Figure 4a) and receiving (Figure 4b) entities with the PBE+TS-vdW XC functional prior to the proton transfer event. Presolvation is captured in Figure 4 by noting the similarity between the ICNs in the range associated with HBs of the donating and receiving entities in the time immediately preceding (20–0 fs) the proton transfer event. For the PW91 and PBE levels of theory, shown in Figures S16 and S17, respectively, the protonated oxygen clearly gains a HB and the receiving oxygen clearly loses a HB. However, at the PBE+TS-vdW level of theory, we observe smaller changes in ICN in Figure 4a for the protonated species and even less for the receiving oxygen in Figure 4b, indicating little difference in the solvation leading up to the proton transfer event. To explain the difference in solvation, we compared the ICNs in the range of 20–0 fs for PBE (Figure S17) and for PBE+TS-vdW (Figure 4). An explicit comparison of 20–0 fs ICNs for different XC functionals is given in the Supporting Information in Figures S24 and S25 for bulk water and TEG–water mixtures, respectively. We observe that the ICNs for PBE and PBE+TS-vdW are roughly equivalent at 20–0 fs prior to proton transport. Thus, for PBE+TS-vdW simulations, prior to the proton transfer the HB is already partially broken for the receiving oxygen and the HB that must be present for the protonated oxygen is already partially formed. This can be attributed to the softening of the HB network due to inclusion of dispersion effects for PBE+TS-vdW XC functional. The PW91 and PBE XC functionals overstructure the oxygen–hydrogen bond in \( \text{H}_2\text{O} \), as seen previously in Figure 1b, compared to the PBE+TS-vdW XC functional, allowing the latter to have a persistent HB network that provides the necessary HB for the donating entity. Using the GGA-type XC functionals, we see that there is a larger dynamic change of the hydrogen bond network to either form or break a HB prior to the proton transfer event. Thus, an equivalent solvation is required for proton transfer, but the dynamics of the HB network leading up to this event are different due to including dispersion effects that soften the HB structures.

Overall, the ICNs for both the protonated water molecule and the protonated receiving water molecule were lower than the bulk water ICNs. This further supports the fact that the HB networks are different in the TEG–water mixture compared to bulk water, which we also observed in the analysis of the HB networks during reaction in Table 6. The reduction in the ICNs is consistent with Table 6 in that the most common HB networks found during reaction for any XC functional did not
find a HB donor for either the protonated or previously protonated species.

**III.G. Free Energy Profiles of Proton Transfer.** The free energy barriers for proton transfer between two water molecules have been calculated to determine the effects of TEG in the TEG–water mixtures. We first calculate the two-dimensional probability density functions, \( P(R_{O^*-O^*}, \delta) \), using the oxygen–oxygen distance \( (R_{O^*-O^*}) \) between the oxygens of a water–water special pair and the asymmetric stretch \( (\delta) \) as reaction coordinates to describe proton transport. An example of \( P(R_{O^*-O^*}, \delta) \) for proton transport between water molecules for a single PBE+TS-vdW XC functional simulation is shown in Figure 5. In the Supporting Information, the plots for \( P(R_{O^*-O^*}, \delta) \) are shown for both bulk water (Figures S26–S29) and PW91 and PBE XC functional TEG–water mixtures (Figures S30–S31). Upon integrating over the \( R_{O^*-O^*} \) coordinate, we have the one-dimensional probability density function of the asymmetric stretch reaction coordinate, \( P(\delta) \). Since \( \delta \) is the reaction coordinate that describes proton transport, we can calculate the free energy barrier as

\[
\Delta F(\delta) = -k_B T \ln \left[ \int P(R_{O^*-O^*}, \delta) \, dR_{O^*-O^*} \right]
= -k_B T \ln P(\delta)
\]

The free energy barrier averages and standard deviations \((\pm \sigma)\) were calculated to be 0.21 \((\pm 0.08)\), 0.38 \((\pm 0.07)\), and 0.42 \((\pm 0.13)\) kcal/mol for PW91, PBE, and PBE+TS-vdW, respectively. These averages and standard deviations were calculated using the 4–5 simulations for a given XC functional set. For our bulk water simulations, we found the free energy barriers of the single 50 ps simulations to be 0.26, 0.59, 0.40, and 0.64 kcal/mol for PW91, BLYP, PBE, and PBE+TS-vdW, respectively. The BLYP XC functional for bulk water was chosen to compare with previous results in the literature.\(^{101,102}\)

Thus, the free energy barriers of the TEG–water mixtures for the PW91 and PBE XC functional are equal to that of bulk water \((\text{within one } \sigma)\) and the PBE+TS-vdW gives a lower free energy barrier in TEG–water mixtures compared to bulk water. In Figure 6, we show the free energy profiles for visual comparison of bulk water to TEG–water mixture. Interestingly, by comparing the PBE and PBE+TS-vdW free energy profiles for TEG–water mixture in Figure 6, the inclusion of dispersion effects are observed to increase the free energy barrier for both TEG–water mixtures and bulk water. Yet, the PBE and PBE+TS-vdW free energy barriers for TEG–water mixtures do fall with one standard deviation of each other.

**III.H. Kinetics of Proton Transfer among Water Molecules.** We investigate the effects of TEG on the kinetics of proton transport between water molecules by utilizing the population time correlation function (TCF) approach from the recent work of Chandra et al.\(^{101,102}\) The formulation of these population TCFs is analogous to that of the previously derived hydrogen bond correlation functions and kinetics.\(^{122,123}\) This approach has proven to be advantageous for a variety of proton transport mechanisms in hydrogen-bonded systems such as an excess proton and a hydroxide ion in water,\(^{101,102,124}\) an excess proton and a hydroxide ion in water–ammonia mixtures,\(^{125}\) and an excess proton in water–HCl mixtures.\(^{126}\) Time scales of proton transfer and proton transfer rate constants are determined using both the history-independent, or intermittent, time correlation function, \( C(t) \), and the history-dependent, or continuous, time correlation function, \( C_\tau(t) \). To construct these time correlation functions (TCFs), we define the population functions \( h(t) \) and \( H(t) \). We denote the protonic defect species atom as O\(^*\). Then, we define \( h(t) = 1 \) if a specific oxygen atom is O\(^*\) at time \( t \) and \( h(t) = 0 \) otherwise. \( H(t) = 1 \) if an atom is O\(^*\) for a time interval \( t \), given that the atom was initially O\(^*\) at the beginning of the interval. Then, using these population functions, we can define our intermittent TCF as

\[
C(t) = \frac{\langle h(0) h(t) \rangle}{\langle h \rangle}
\]

Thus, \( C(t) \) gives us the probability that an atom that was O\(^*\) at \( t = 0 \) will be O\(^*\) at \( t \), without regard to proton transfer events in the interval \( t \). The continuous TCF is defined as

\[
C_\tau(t) = \frac{\langle h(0) H(t) \rangle}{\langle h \rangle}
\]

which gives the probability that at atom that was O\(^*\) at \( t = 0 \) will remain O\(^*\) on the time interval \( t \). Importantly, from \( C_\tau(t) \), we can directly calculate the average exchange time of O\(^*\), \( \tau_{\text{exch}} \), as
$$\tau_{\text{exch}} = \int_0^\infty C_c(t) \, dt$$  (4)

In Figure 7, we show $C_c(t)$ including and excluding proton rattling events, respectively, for all XC functionals used for both bulk water and TEG–water mixture. Similarly, in Figure 8, we show the same plots for $C_i(t)$. When rattling is included in $C_c(t)$, such as in Figure 8a, ultrafast processes are accessible such as short-lived complexes that exist in bulk water measured by femtosecond vibrational spectroscopy. However, experimental research continues to determine what complexes are short-lived and what are metastable, discussed more below. By excluding proton rattling, we analyze the time scale for true charge displacements via structural diffusion in the system. The difference between including and excluding proton rattling is less for $C_i(t)$ compared to $C_c(t)$ due to the continuous-time-independence of $C_i(t)$.

Previously, it has been thought that the interconversion from Zundel to Eigen configurations was an ultrafast process on the sub-100 fs time scale. However, in recent experimental work by Thämer et al., ultrafast two-dimensional (2D) IR spectroscopy was used to probe the lifetime of the Zundel proton complex and suggested that the Zundel configuration is not merely a transition state between Eigen configurations but a metastable configuration that has a lower limit lifetime of ~480 fs. The reader is encouraged to consult a recent article for further discussion of the impact of the work by Thämer et al., its contrast to theoretical results, and the future role of 2D infrared spectroscopy in further unraveling the elusive proton complexes in water. From the current work, our analysis of TCFs is consistent with ultrafast processes on the sub-100 fs time scale.

The slow and fast decay times, $\tau_{\text{slow}}$ and $\tau_{\text{fast}}$, respectively, associated with proton transfer can be well-defined by a biexponential function fit of $C_i(t)$.

$$C_i(t) = a_{\text{slow}} e^{-t/\tau_{\text{slow}}} + a_{\text{fast}} e^{-t/\tau_{\text{fast}}}$$  (5)

with $a_{\text{slow}} + a_{\text{fast}} = 1$. Similarly, from eqs 16 and 17 of the work by Tuckerman et al., we can also fit a biexponential to $C_i(t)$ to determine parameters $a_0$, $a_1$, and $a_2$ in eq 6 below to then determine the forward rate constant for proton transfer, $k_{\text{PT}}^{\text{PT}}$, in eq 7 below.

$$C_i(t) = a_0 e^{-a_1 t} + (1 - a_0) e^{-a_2 t}$$  (6)

$$k_{\text{PT}}^{\text{PT}} = a_0 a_1 + a_2 (1 - a_0)$$  (7)

This biexponential decay model for $C_i(t)$ of proton transport in water has shown to be in good agreement up to approximately 30 ps. However, the work of Chen et al. showed that approaching the long-time limit, $C_i(t)$ initially displays an exponential decay ($t < 30$ ps), then transitions to slower, nonexponential decay ($30$ ps $< t < 100$ ps), and finally reaching power law decay at the asymptotic limit ($t > 100$ ps). Yet, the simulations in the work presented here are far from reaching this power law asymptotic limit and well within the exponential decay regime.

In Tables 7 and 8, the kinetics for proton transfer are presented for bulk water and TEG–water mixtures, respectively. We have computed $\tau_{\text{exch}}$ via eq 4, $\tau_{\text{fast}}$, $\tau_{\text{slow}}$, and $a_{\text{slow}}$ via eq 5, and $1/k_{\text{PT}}^{\text{PT}}$ via eqs 6 and 7 (including parameters for fitting...
Table 7. Kinetics of Aqueous H⁺ System

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<th>$\tau_{\text{exch}}$</th>
<th>$\sigma_{\text{slow}}$</th>
<th>$\tau_{\text{fast}}$</th>
<th>$\tau_{\text{slow}}$</th>
<th>$1/k_{\text{PT}}$</th>
<th>$a_0$</th>
<th>$1/\alpha_1$</th>
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<td>0.40</td>
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<td>0.98</td>
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<td>0.57</td>
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<td>--</td>
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<td>1.05</td>
<td>0.09</td>
<td>14.58</td>
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<td>0.53</td>
<td>3.53</td>
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<tr>
<td>PBE+TS-vdW</td>
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<td>1.82</td>
<td>1.30</td>
<td>0.65</td>
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"Relaxation times, parameters, and inverse rates (in ps) for H⁺ including and excluding rattling events.

Table 8. Kinetics of Aqueous H⁺ and Triethylene Glycol (TEG) System

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<th>$\sigma_{\text{slow}}$</th>
<th>$\tau_{\text{fast}}$</th>
<th>$\tau_{\text{slow}}$</th>
<th>$1/k_{\text{PT}}$</th>
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<th>$1/\alpha_1$</th>
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<td>1.01</td>
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<td>1.00</td>
<td>--</td>
<td>1.02</td>
<td>1.01</td>
<td>0.50</td>
<td>0.50</td>
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<td>0.56</td>
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<td>0.19</td>
<td>0.52</td>
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<td>1.84</td>
<td>0.68</td>
<td>0.62</td>
<td>3.90</td>
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"Relaxation times and inverse rates (in ps) for H⁺ including and excluding rattling events.

For bulk water in Table 7, the fast time scale associated with including proton rattling events gives lifetimes, $\tau_{\text{fast}} < 100$ fs for XC functionals that display biexponential decay behavior, in agreement with experiment and previous simulation results. The only outlier that had exhibited simple exponential decay was the PBE+TS-vdW, which still displayed decay lifetimes of $\sim 160$ fs. The exchange lifetimes qualitatively agree with previous simulation results. The difference is most likely due to the lighter mass of the hydrogen atom used in the present simulations (here, using the mass of hydrogen instead of deuterium). The exchange lifetime appears to be $\tau_{\text{exch}} \approx 1$ ps for all four XC functionals when analyzing the kinetics associated with structural diffusion via excluding proton rattling. The shortest lifetime appears to be for PW91, with $\tau_{\text{exch}} = 0.73$ ps and the longest lifetime is for PBE+TS-vdW, with $\tau_{\text{exch}} = 0.139$ ps. These lifetimes are consistent with those in Table 1 and the free energy barriers observed in Figure 6 for PW91 and PBE+TS-vdW in bulk water.

From Table 8, there is a noticeable effect when incorporating TEG, specifically in the exchange lifetimes for excluded proton rattling, thus time scales for structural diffusion. For the PW91 XC functional, there is an increase in exchange lifetime from bulk to TEG–water mixtures. This is caused by an increase in the slow process lifetime. The PBE XC functional lifetimes also increase going from bulk water to TEG–water mixtures but with a much smaller change in the lifetime, being $\sim 1$ ps for both bulk water and TEG–water mixtures. The PBE+TS-vdW functional lifetimes decrease going from the bulk water to the TEG–water mixtures. However, we see that this is due to contamination of the fast process since $\sigma_{\text{slow}}$ decreases to $\sim 60\%$, implying an increase in the effect of the fast dynamic processes associated with $\tau_{\text{fast}}$. Overall, the TEG–water mixture shows an increased lifetime for proton transfer using the PW91 XC functional due to an increase in slow processes associated with structural diffusion and shows relatively little change in the lifetimes for PBE and PBE+TS-vdW XC functionals, with only slight decrease being accounted to the decrease of the fast processes associated with proton rattling events for PBE+TS-vdW.

III.I. Hopping Dynamics and Mean Square Displacements for Proton Transport. The displacement of the protonic defect throughout the trajectories was extracted to determine 1) the observation of burst-rest dynamics previously discussed and 2) the mean square displacements (MSDs) for the protonated atom. For all TEG–water mixture MSDs of the protonated atom, we have not yet reached the linear regime where reliable self-diffusion coefficients based on the Einstein relation can be calculated. We reserve this for a future effort where reliable values can be reported.

Figure 9 shows the proton hopping dynamics via displacement of the protonated atom relative to the initial position of the first protonated atom in the trajectory for selected...
trajectories of the XC functional simulation sets. The red line indicates trajectories that display an overall “rest” behavior during the simulation while the blue line indicates trajectories that show burst-rest dynamics, similar to recent simulation work of an excess proton in bulk water.62,65 Previous work showed that rest periods consisted of long-lived proton traps, being >5 ps.65 We do observe such long rest dynamic period in our simulations, specifically in the PW91 functional simulations in Figure 9. The length of burst periods and rest periods seem to be shorter for our protonated atom in TEG–water mixtures compared to the displacements of the hydronium oxygen in bulk water in Figure 2 of Tse et al.62 Yet, our simulation lengths are almost an order of magnitude shorter, in exchange for increasing number of trajectories per XC functional. We believe extended simulations of the present trajectories would be required before a conclusion on whether the TEG–water mixture could shorten these burst and rest periods relative to those observed in bulk water. The observance of trajectories with either a long-lived rest period or that have occurrences of burst and rest periods seems overall to be less dependent on the XC functional used and more dependent on initial conditions of the trajectory and simulation length. Emphasis is placed on using a number of trajectories for these types of analysis due to the variety of burst-rest dynamic behavior that can be observed during a simulation and the long length that these periods can have, such as rest periods for ~100 ps of the excess proton in bulk water simulation observed in Figure 2 of Tse et al.65 The Supporting Information presents all trajectories for all XC functionals of TEG–water mixtures (Figure S32) and bulk water (Figure S33) for comparison of burst-rest dynamics in different simulation trajectories and XC functionals used. Similar burst-rest behavior is displayed for all XC functionals tested for bulk water.

In Figure 10, the average MSDs over all trajectories for a given XC functional set are shown. The MSDs are extended to the longest time length simulated for a given XC functional set, implying that average over all the simulations was guaranteed up to 10 ps, since this was a minimum for simulated time length. Yet, past 10 ps, only a subset of all trajectories were used for the averaging. We note that the PW91 XC functional set has the MSD with the smallest slope, which can be attributed to the long rest behavior seen in the trajectories shown in Figures 9 and S32. Included in the Supporting Information are the MSDs of each individual simulation trajectory and the corresponding average MSDs using only 10 ps of each trajectory in Figure S34 and the bulk water MSDs in Figure S35.

IV. CONCLUSION

In this work, we investigated the effects of TEG on the distribution of protonic defect structures, special pair formation, solvation structure around water and protonic defect structures, hydrogen-bond network patterns, mechanistic details for proton transfer, proton transfer kinetics and proton dynamics via ab initio molecular dynamics simulations using a variety of exchange-correlation functionals, including dispersion effects.

For the structural effects of TEG associated proton transport, we observe the following. The protonic defect structure that occurs most is found to be the protonated water molecule, $H_2O^+$, with the hydroxyl group of TEG being the second highest occurring species. The TEG chain disrupts the hydrogen-bond network, causing the solvation shell around water to be populated by TEG chain groups instead of other waters, reducing the rigidity of the HB network. The predominant special pair is water–water special with the water–hydroxyl special pair being the second most common. The solvation shell analysis showed that the hydroxyl groups of TEG populate the hydrogen-bond acceptor sites with decreasing probability with increasing level of theory. The hydrogen-bond network analysis around the special pair showed that hydroxyl groups populate the hydrogen-bond acceptor sites with relatively equal probability to other molecules/molecular groups and the methylene groups populate the hydrogen-bond donor sites preferentially compared to other molecules. A myriad of hydrogen-bonding networks were found, showing that methylene groups of TEG are hydrogen-bond donors in hydrogen bond networks that are associated with long-range structural diffusion. This observation leads to the hypothesis that proton transport could possibly occur along the axis parallel to the PEG backbone with methylene groups providing as hydrogen-bond donors in the solvation around special pairs.

For the mechanistic and dynamical effects of TEG on proton transport, we observe the following. All three functionals studied support the presolvation requirement for structural diffusion in the presence of TEG, even with very different hydrogen-bond networks. The detailed mechanistic dynamics of presolvation appear to differ when dispersion effects are included due to softening of the hydrogen bonding structure with increasing level of theory. A favorable reduction in the free energy barrier for proton transfer was observed for the PBE +TS-vdW level of theory for TEG–water mixture compared to bulk water, while not including dispersion effects for PW91 and PBE gives equal barriers between TEG–water mixtures and bulk water. The kinetics show that the structural diffusion time scale differences for TEG–water mixtures to bulk water are relatively equal for both PBE and PBE+TS-vdW levels of theory but unfavorably increase for the PW91 level of theory. The excess proton displays burst-rest dynamic behavior, similar to that observed in bulk water.

In speculation, we believe that, for systems where there is a strong correlation to hydration and proton migration, PEG monomers can take the place of water molecules in necessary
solvation shell structures and potentially have modestly favorable effects on proton transport. This would imply that in systems whose proton conductivity suffers due to low hydration, PEG can have an enhancement effect on the structural diffusion of protons. Also, as a polymer, given an optimal orientation of the PEG chain, the structural diffusion could show directional preference along the polymer backbone. Further study of hydration effects for proton migration with a given polymer orientation could shed light on this hypothesis. This should help in design principles of systems trying to enhance proton migration with a dependence on hydration.

As a final note, our results have been obtained from a finite-size system of 27 water molecules, one excess proton and one TEG chain. The system size effects were not investigated in this study. It would be quite useful to extend the work performed here by increasing the system size in such a way that would not negatively impact seeing interactions of the excess proton with TEG. Also, increasing chain length and varying TEG composition in the TEG-mixture would be of interest to determine chain-dependent and compositional effects. No quantum nuclear effects were treated in the simulations. This quantum treatment of the nuclei has been shown to flatten out the free energy barrier for proton transfer in bulk water, making it effectively “barrierless”. Including these nuclear quantum effects via path-integral molecular dynamics would be interesting due to possibly more protonic defect structures that could become more energetically favorable at ambient temperature.

**ASSOCIATED CONTENT**

1. **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcb.6b02445.

- Distributions of H$_3$O$^+$ lifetimes for TEG–water mixtures, Gibb’s free energy change for H$^+$ transfer from water to alcohol, special pairs including proton rattling, solvation shells including proton rattling, probability union for occupied sites derivation and discussion, HB networks in bulk water and their associated lifetimes including and excluding proton rattling, HB networks that occur during proton transfer bulk water and TEG–water mixtures, time-progression RDFs for proton transfer from water to water for bulk and TEG–water mixtures, time-progression ICNs for proton transfer from water to water for bulk water and TEG–water mixtures, time-progression ICNs for proton transfer from water to hydroxyl groups and from hydroxyl groups to water for TEG–water mixtures, ICNs for the interval of 20–0 fs leading up to proton transfer from water to water for all three XC functionals in bulk water and TEG–water mixtures, PDFs for reaction coordinates of proton transfer for bulk water and TEG–water mixtures, proton hopping dynamics displaying burst-rest dynamics, and mean square displacements of protonated defect species for bulk water and TEG–water mixtures (PDF)

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: dkeffer@utk.edu. Phone: 865-974-5322.*

**Notes**

The authors declare no competing financial interest.

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**ABBREVIATIONS**

TEG, triethylene glycol; PEG, polyethylene glycol; PEO, poly(ethylene oxide); EO, ethylene oxide; HB, hydrogen-bond; MD, molecular dynamics; AIMD, ab initio molecular dynamics; CPMD, Car–Parrinello molecular dynamics; DFT, density functional theory; OPLS-AA, Optimized Potentials for Liquid Simulations - All Atom; TIP3P, Transferable Intermolecular Potential - Three Point; XC, exchange-correlation; vdW, van der Waals; PW91, Perdew–Wang 91; PBE, Perdew, Burke, and Ernzerhof; GGA, generalized-gradient approximation; MT, Martin–Troullier; RDF, radial distribution function; PDF, probability density function; TCF, time correlation function; MSD, mean square displacement

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