

From Molecular Dynamics to the Conductivity of Sulfuric Acid: Ultrafast Optical Kerr Effect Experiments and Ab Initio Molecular Dynamics Simulations

Laura Kacenauskaite,^{||} Sijia Chen,^{||} Max Moncada Cohen, Gregory A. Voth,^{*} and Michael D. Fayer^{*}



Cite This: *J. Am. Chem. Soc.* 2025, 147, 27720–27730



Read Online

ACCESS |



Metrics & More

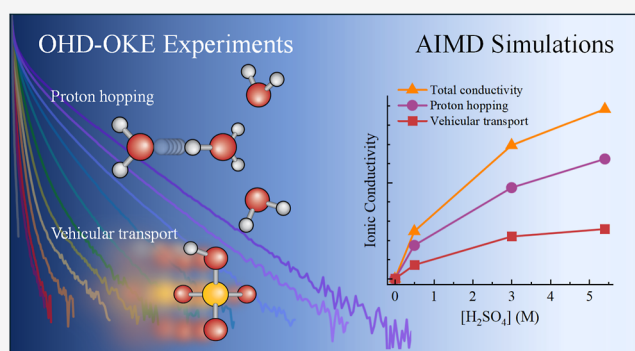


Article Recommendations



Supporting Information

ABSTRACT: Extensive use of sulfuric acid in technological applications calls for knowledge of its molecular scale properties. Here, we report a study of aqueous sulfuric acid solutions across a broad concentration range using optical heterodyne-detected optical Kerr effect (OHD-OKE) experiments and ab initio molecular dynamics (AIMD) simulations. The OHD-OKE experiments measured the time derivative of the polarizability–polarizability correlation function (PPCF). By comparison of distinct components of the OKE signal to the excess proton identity correlation functions calculated from AIMD simulations, it was found that the experimental t_3 components quantitatively agreed with the proton hopping time from one water to another, which suggested that the origin of t_3 was associated with proton hopping. The proton hopping distances within the t_3 time scale were used to determine the proton hopping diffusion constants at several concentrations. Using information from the literature and the Nernst–Einstein conductivity equation, it was shown that the vehicular mechanism was insufficient to describe the conductivity. The experimental concentration-dependent conductivities were reproduced by adding the AIMD proton hopping contribution to the conductivity, and proton hopping was shown to be the dominant component of the conductivity. Finally, the experimental concentration-dependent function, C_3/t_3 , where C_3 is the amplitude coefficient of the third PPCF component, closely tracked the concentration dependence of the hopping component of the conductivity.



1. INTRODUCTION

The exceptional solubility and conductivity of sulfuric acid in water make it an important component in the transition toward renewable energy production. In addition to its countless industrial applications,¹ sulfuric acid is one of the main components of redox flow batteries,² a technology increasingly used in large-scale energy storage facilities. As the generating capacity of intermittent sustainable energy sources such as wind and solar grows, so does the need for energy storage.³ As a result, the properties of redox flow batteries as a function of electrolyte composition are under intense study.⁴ However, the role of sulfuric acid is primarily optimized empirically rather than through an intricate interplay among molecular-level structures and dynamics that give rise to desirable properties.^{5–8} As the advancements in batteries rely more and more on a detailed understanding of molecular dynamics, methods to characterize microscale processes are essential. While previous extensive experimental and theoretical work provides methods to characterize and predict the properties of dilute acid solutions,^{9–12} highly concentrated solutions required for industrial applications are still lacking reliable theories to explain the dynamics of ion solvation,

proton transfer, and molecular interactions in poorly solvating environments.

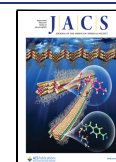
A great deal of experimental work has been done on concentrated acid solutions to provide a basis for theoretical simulations. Early physical chemistry measurements provided thermodynamic quantities as well as bulk properties of the solutions such as conductivity, viscosity, and heat capacity.^{13–16} Structural techniques like XRD, photoelectron spectroscopy, and X-ray and neutron scattering experiments estimated fractions of ionic species, radial distribution functions and solvation environments of the ions.^{17–22} Infrared absorption and Raman spectroscopy techniques have been used extensively to study low-temperature nonbulk solvated, surface-adsorbed, or hydrated sulfuric acid gas-phase clusters.^{23–28} These experiments can resolve individual vibrations

Received: April 14, 2025

Revised: June 18, 2025

Accepted: July 14, 2025

Published: July 25, 2025



of different species at very high resolution, providing detailed insight into molecular structure. As a way to evaluate the time-resolved behavior of species in concentrated acid solutions, NMR-based techniques like pulse field gradient, chemical shift, or diffusion coefficient measurements contribute to understanding the time scales of ion diffusivity.^{29–31} Recent advancements in ultrafast spectroscopy have opened new avenues for investigating fast molecular processes, facilitating the direct observation of molecular dynamics on femtosecond to picosecond time scales. 2D IR spectroscopy has been employed in hydrochloric and nitric acid studies, revealing time scales of ion pairing and proton transfer; optical Kerr effect experiments on structurally similar liquid sulfur dioxide provided timeframes for total orientational relaxation.^{32–35} At present, most current knowledge and hypotheses about ultrafast sulfuric acid dynamics are based on simulations.

Observation of molecular level dynamics is particularly useful in conjunction with *ab initio* molecular dynamics (AIMD) simulations. Initial theoretical work focused on hydration, ionization, and proton dynamics in sulfuric acid. The studies examined gas-phase clusters, which do not include the effects of extended hydrogen bond networks.^{11,36–38} Recent work by Sippola, Niskanen et al., Bazak et al., and others, through application and optimization of AIMD and DFT simulations, found correlations between viscosity and conductivity of solutions, described proton hopping mechanisms, simulated a range of spectroscopic features and suggested specific structures that dominate solutions as the concentration of the acid increases.^{14,21,31,39–42}

In the studies presented below, we use previous literature, AIMD simulations, and optical heterodyne-detected optical Kerr effect (OHD-OKE) experiments to determine the time dependence of dynamic processes of aqueous sulfuric acid solutions. From the experimental decays of polarizability–polarizability correlation function (PPCF), we identify specific components related to bulk water-like dynamics (t_1 and t_2), time scales of proton hopping (t_3) and provide a hypothesis for the origin of the slowest decay component (t_4) emerging at the concentrations with fewer than 4 water molecules per sulfuric acid. By comparing experimental results to our AIMD simulations, we were able to paint a comprehensive picture of ultrafast microscale dynamics in concentrated H_2SO_4 solutions and provide a molecular-level description of bulk physicochemical properties like viscosity and conductivity.

2. EXPERIMENTAL AND SIMULATION METHODS

2.1. Experimental Methods. 98.08% sulfuric acid (ACS grade) was purchased from Fisher and was used as received. Aqueous acid solutions were prepared gravimetrically using deionized, ultrafiltered water from Fisher. Samples were transferred to 1 cm path-length glass cuvettes, sealed, and used immediately at the controlled temperature of 24.4 °C for the OHD-OKE measurements. Experimental viscosities and conductivities of the solutions were obtained from the literature.¹⁶

OHD-OKE experiments used a home-built optical system featuring a Ti:sapphire oscillator seeding a regenerative amplifier (5 kHz, 120 fs pulses). Amplified pulses were split into a pump and a probe by a 98%/2% beam splitter. The pump and probe pulses were crossed in the sample. The linearly polarized pump induces transient birefringence in the sample. The probe pulse passes through crossed polarizers, one before and one after the sample. Heterodyned detection, phase, and polarization cycling were used for better sensitivity and signal-to-noise ratio. The phase of the probe pulse local oscillator was switched between + and – every other shot and the pump's polarization was rotated 90° every two shots. This four-shot

cycle enables signal processing with a lock-in amplifier and reduces scattered light. The signal reports the derivative of PPCF as a function of the delay time between the pump and probe pulses.⁴³ A detailed description of the experimental system and detection scheme is published.^{44,45} Experiments were conducted with 120 fs pulses and chirped 2 ps pulses to capture the faster and slower-decaying portion of the dynamics. Short and long pulse data sets were collected in triplicate for each sample, merged with an in-house program, normalized, and fit to tetra-exponential decays. Each merged data set was fit individually using the Levenberg–Marquardt algorithm with 1/y weighting. The average and standard deviation of the fitted time constants and amplitudes were calculated to provide error bars.

2.2. AIMD Simulation Methods. The AIMD simulations based on electronic density functional theory (DFT) were conducted with the CP2K software package.^{46,47} The simulations were conducted with the revPBE^{48,49} generalized gradient approximation (GGA) DFT level with the Grimme DFT-D3 correction with zero damping.⁵⁰ A hybrid Gaussian and plane-wave (GPW) method⁵¹ was employed in the QUICKSTEP module⁴⁶ using the TZV2P-MOLOPT-GTH basis set⁵² and Goedecker–Teter–Hutter (GTH) pseudopotentials^{53,54} with a plane-wave cutoff kinetic energy of 400 Ry. The target accuracy of the self-consistent field (SCF) was 1.0×10^{-6} using the orbital transformation (OT) method.⁵⁵ All simulations were conducted in a constant NVT ensemble with the temperature controlled at 298 K using the Nosé–Hoover thermostat with an update frequency of 100 fs. The time step of the AIMD simulations was 0.5 fs. For acid concentrations of 0.54, 3.0, and 5.3 M, the initial simulation boxes contain 2, 8, and 16 HSO_4^- , 2, 8, and 16 H_3O^+ , and 199, 122, and 114 water molecules, respectively. To match experimental densities, the cubic box sizes were set to be 18.2 Å, 16.4 Å, 17.1 Å, respectively.⁵⁶ The initial configurations were prepared with PACKMOL.⁵⁷ The systems were first equilibrated using classical MD simulations for 10 ns. Force fields parameters for HSO_4^- , H_3O^+ , and water were taken from the work by Canales et al.,⁵⁸ Biswas,⁵⁹ and Wu et al.,⁶⁰ respectively. Bonds involving hydrogen atoms in the ions were restrained using the SHAKE algorithm. All classical MD simulations were performed using the LAMMPS MD software.⁶¹ The last snapshots of classical MD simulations were used to start AIMD simulations. First, all AIMD simulations were equilibrated for 15 ps. The production runs for the three systems were then 100 ps long each. The trajectories from the production runs were collected every 10 time steps, namely 5 fs, and used for further analyses. All snapshots were rendered using the VMD software package.⁶²

3. EXPERIMENTAL RESULTS AND DISCUSSION

In the OHD-OKE experiments, before the arrival of the pump pulse, the sample polarizability is macroscopically isotropic. However, on a local distance scale, sulfuric acid/water clusters will have anisotropic polarizabilities. The pump pulse induces an oscillating polarization along the principal axis of the anisotropic polarizability, which interacts with the pump pulse electric field, causing a very slight skewing of the local structure polarizability toward the direction of the pump E-field polarization. The minute alignment of the local structures with the pump polarization direction produces a macroscopic birefringence in the sample. The birefringence decay was detected as the delay time between the pump and probe pulses increases. In accord with linear response theory, the relaxation is caused by the equilibrium thermal functions of the medium. Therefore, the OHD-OKE decay measures the times and amplitudes of components of the equilibrium fluctuations as the pump-induced birefringence decays.

Figure 1 shows OHD-OKE signal decay data for pure water and different sulfuric acid concentrations from 0.5 to 18.3 M. As the concentration of sulfuric acid increases, the decay of the OKE signal slows significantly because of the strong interactions of water molecules with various dissociated sulfuric acid species, i.e., H_3O^+ , HSO_4^- , and SO_4^{2-} . Above ~14 M, the concentration of undissociated H_2SO_4 increases rapidly and becomes the dominant species (the Supporting Information, Figure S1).⁶³

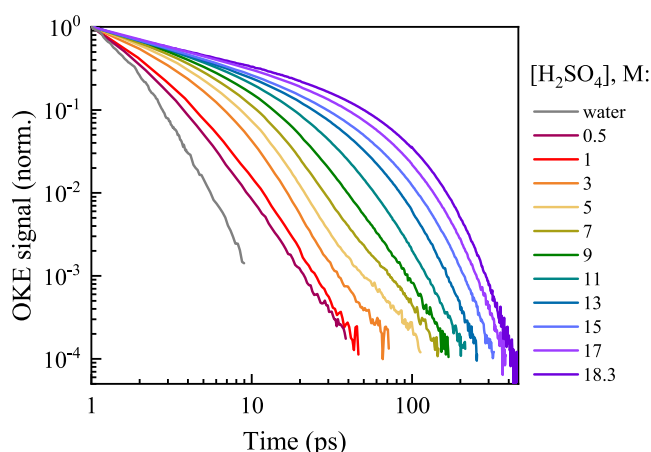


Figure 1. OHD-OKE decay data for various concentrations of sulfuric acid in water from 0.5 to 18.3 M and pure water on a log–log plot. The data cover four decades of amplitude decay and times from subpicosecond to 400 ps.

The OHD-OKE data for the H_2SO_4 solutions at all concentrations studied fit well to tetraexponential decay functions

$$r(t) = R'(t) = A_1 \exp(-t/t_1) + A_2 \exp(-t/t_2) + A_3 \exp(-t/t_3) + A_4 \exp(-t/t_4) \quad (1)$$

where $R'(t)$ is the decaying OHD-OKE signal (the time derivative of the polarizability–polarizability correlation function), the t_i 's are the decay time constants, and A_i 's are the associated amplitudes. The integration of eq 1 gives the polarizability–polarizability correlation

$$R(t) = A_1 t_1 \exp(-t/t_1) + A_2 t_2 \exp(-t/t_2) + A_3 t_3 \exp(-t/t_3) + A_4 t_4 \exp(-t/t_4) \quad (2)$$

Because the sign of the signal in the experiments is arbitrary, we take $R(t)$ to be positive. The prefactors in eq 2 can be normalized and relabeled in the following manner

$$C_i = \frac{A_i t_i}{A_1 t_1 + A_2 t_2 + A_3 t_3 + A_4 t_4} \quad (3)$$

The C_i 's, which sum to 1, are the correlation coefficients, i.e., the normalized relative fractions of the PPCF associated with each time component.

The time constants and PPCF coefficients are shown in Figure 2A,B (points; the connecting curves are guides to the eye.) The four time constants divide into two groups of two.

The two fast time constants, t_1 and t_2 , are similar to their pure water values, approaching the pure water values as the sulfuric acid concentration is reduced toward zero. The pure water decay (Figure 1, gray curve) decays as a biexponential. The pure water time constants and correlation coefficients are shown on the graphs at 0.0 concentration. t_1 is 0.52 ps in pure water. It is unchanged until 11 M, where it begins to increase, reaching 0.78 ps at 18.3 M. t_2 is 1.3 ps in pure water and increases starting at 3 M, reaching a value of 3.6 ps at 18.3 M. The pure water values are very similar to 2D IR spectral diffusion measured time constants, which are 0.4 and 1.7 ps.^{64,65} Pure water MD simulations of spectral diffusion show that the fast component is mainly hydrogen bond length fluctuations (oxygen – oxygen separation fluctuations of $\text{O}\cdots\text{H}-\text{O}$), and the slow component is randomization of the H-bond network.⁶⁴ Although OHD-OKE and 2D IR measure different correlation functions, the similarities in the time constants suggest that they reflect the same dynamics. Figure 2B shows the coefficients (sum normalized to 1). The coefficients C_1 and C_2 drop as the sulfuric acid concentration is increased. At higher sulfuric acid concentrations, the remaining water hydroxyls will

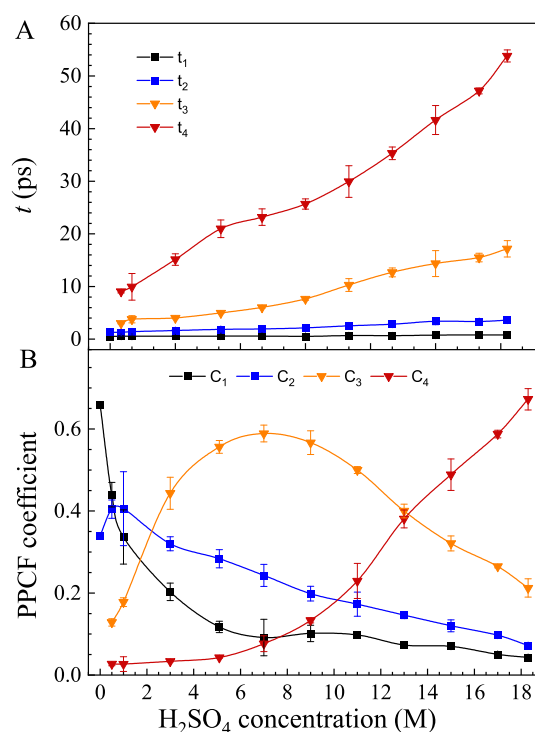


Figure 2. Decomposition of the polarizability–polarizability correlation function (PPCF) decays into four components of the tetraexponential decays. (A) The decay times as a function of concentration. (B) The amplitudes (coefficients of the PPCF) of the four components with their sum normalized to 1. The two fastest components have corresponding decays in pure water. The two slower decays do not have corresponding decays in pure water.

increasingly make H-bonds to sulfuric acid hydroxyls, which can be responsible for the increasing decay times.

The remaining decay components, t_3 and t_4 , do not have counterparts in pure water. As shown in Figure 2A, t_3 increases from 3 to 17.2 ps over the concentration range from 0.5 to 18.3 M, and t_4 increases from 9.1 to 53.8 ps over the same concentration range. Figure 2B shows that C_3 increases initially, reaching a maximum value at ~ 7 M, then decreases, while C_4 increases monotonically. C_4 gains significant amplitude when C_3 peaks and continues to increase as C_3 decreases. In the following section, these specific features will be discussed in the light of AIMD simulations.

In contrast to a simple acid like hydrochloric acid, sulfuric acid has significantly higher solubility and a more complex structure, resulting in a wider variety of ions and moieties, ranging from SO_4^{2-} to undissociated H_2SO_4 . At very high concentrations, species like H_3SO_4^+ can exist.⁶³ While well-established dissociation constants can be used to predict ion ratios in low concentration solutions, specific ions, their lifetimes, and their fractions are hard to determine at higher concentrations. There are MD simulations at midrange to high concentrations, but they give varying results.^{9,66} It is generally agreed that H_2SO_4 is a strong acid, fully dissociated at low to midrange concentrations, resulting in H^+ and HSO_4^- ions. H^+ will be in the form of hydrated excess proton, i.e., hydronium cations.⁶⁷ The second dissociation constant is relatively small, about 1 order of magnitude greater than weak organic acids, so SO_4^{2-} is only present to a small extent. It peaks in concentration at ~ 8 M (Figure S1). As the sulfuric acid concentration approaches the solubility limit, ions, including hydronium, decrease in concentration, as there are insufficient water molecules for solvation or to form hydronium.

4. AIMD SIMULATION RESULTS AND ANALYSIS

AIMD simulations can provide valuable insight into the solution structures and dynamics at the molecular level.⁶⁸ To

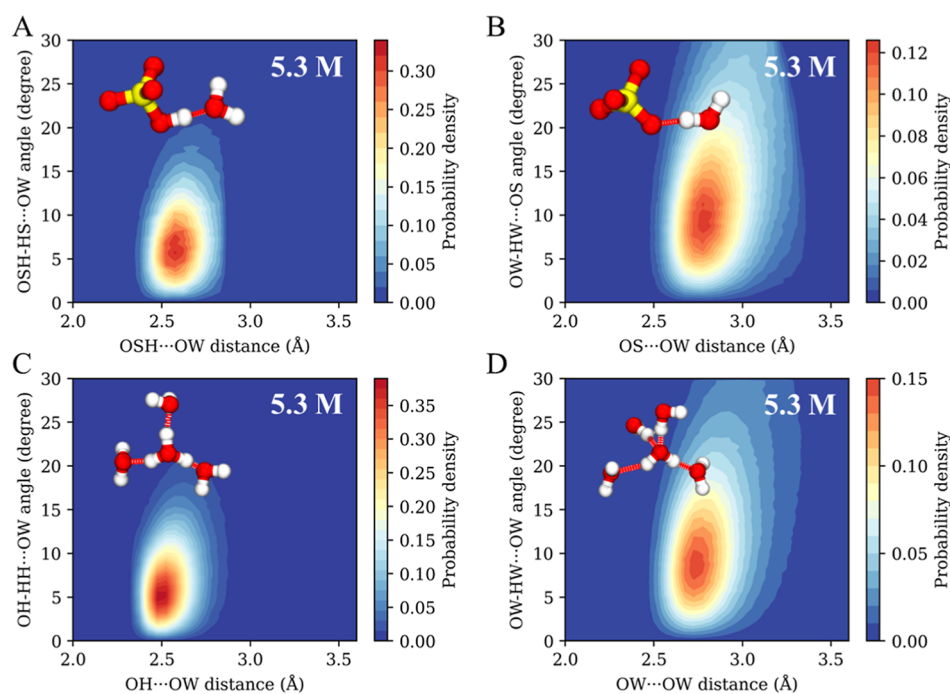


Figure 3. Probability density distribution plots for hydrogen bonds formed by (A) protonated oxygen in bisulfate and water, (B) unprotonated oxygen in bisulfate or sulfate and water, (C) hydronium and water, and (D) water and water, in 5.3 M sulfuric acid solutions. The probability density is normalized such that the integral over the entire 2D domain satisfies $\sum_{x,y} \Delta x \Delta y P(x,y) = 1$, where $P(x,y)$ is the probability density at bin center x and y , and Δx , Δy are the corresponding bin widths. In the current plot, Δx and Δy are 0.05 Å and 0.5°, respectively. “OS”, “OSH”, and “HS” represent unprotonated oxygen atoms in sulfate or bisulfate, protonated oxygen atoms in bisulfate, and hydrogen atoms in bisulfate. “OH” and “HH” represent oxygen atoms and hydrogen atoms in hydronium. “OW” and “HW” represent water’s oxygen and hydrogen atoms. Representative configurations of each kind of hydrogen bond are shown in each plot’s insets, where hydrogen bonds are highlighted in dashed red lines. Oxygen nuclei are red, hydrogen nuclei are white, and sulfur nuclei are yellow.

understand the solvation nature of sulfuric acid solutions and the origin of various time scales observed in the OHD-OKE measurements, the AIMD simulations described earlier were performed for three concentrations: 0.54, 3.0, and 5.3 M. As mentioned above, t_1 and t_2 have their counterparts in pure water. On the other hand, t_3 and t_4 are new components existing exclusively in sulfuric acid solutions. Because t_4 represents slow structural motions with time scales of tens of picoseconds, it is hard to capture them quantitatively with computationally demanding AIMD simulations. Therefore, our AIMD simulations mainly focused on identifying the origin of the t_3 time scales. A previous study on the hydrated excess proton in water (aka hydronium H_3O^+) has shown, in agreement with experimental results, that its dominant solvated structure is a “distorted” Eigen cation, H_9O_4^+ , which continuously undergoes a “special pair dance.”^{69,70} In the special pair dance, one of the H-bonds formed between the three water molecules in the first solvation shell, and the inner hydronium core is shorter and stronger than the other two, forming the “special pair.” The identity of the special pair interchanges rapidly within the three equivalent hydrated (H-bonded) water molecules on a subpicosecond time scale. Due to the dynamic and delocalized nature of the hydrated excess proton in water, the term “hydronium” cation (the classical, quasi-static interpretation) does not accurately describe this entity. Instead, it is better understood as a “hydronium-like” hydrated excess proton structure which consistently undergoes proton hops from one water molecule to another. In the following context, this structure could be referred to as a hydronium-like hydrated excess proton, but for conciseness, we

will use the term hydronium, keeping in mind the more detailed definition, which describes a dynamic structure, rather than a static, classical hydronium cation.

However, the case of sulfuric acid solutions is more complicated. In sulfuric acid solutions at low concentrations, there are two possible acceptors of excess protons—water molecules, forming hydronium and sulfate SO_4^{2-} anions forming bisulfate HSO_4^- anions. To assign the excess protons to the appropriate acceptor, we stipulated that an excess proton belongs to its closest oxygen atom, either water molecule oxygen atoms or sulfate anion oxygen atoms. A proton hopping event occurs when there is a change in the closest oxygen atom associated with an excess proton from one oxygen atom to another.

First, we explored the solvation structures of different ions, especially the formation of H-bonds by ions and water molecules. The definition of eligible H-bonds can be found in the [Supporting Information \(SI\)](#).

Anions (bisulfate and sulfate) can form two types of hydrogen bonds with water, as illustrated in [Figure 3A,B](#). In the first type, depicted in the inset of [Figure 3A](#), protonated oxygen atoms in bisulfate ions (OShs) act as H-bond donors, while water oxygen atoms (OWs) act as H-bond acceptors. In the second type, shown in the inset of [Figure 3B](#), oxygen atoms (OSs) in sulfate/bisulfate ions act as H-bond acceptors, with water oxygen atoms serving as H-bond donors. As shown in [Figure 3C](#), hydronium typically forms three H-bonds with water by donating its three hydrogen atoms (HHs) to OWs. To compare the strength of different types of hydrogen bonds, we calculated the probability density distributions as a function

of the distance between donors and acceptors and the angles formed by hydrogens, donors, and acceptors. The results of the 5.3 M solutions are shown in Figure 3. The results of the 0.5 and 3.0 M solutions are in the Supporting Information. A comparison between Figure 3A,B shows that OSHs form stronger hydrogen bonds with OWs than OSs with OWs. The strengths are indicated by the shorter distance (2.58 Å vs 2.78 Å), smaller angle (7.3° vs 8.8°), and higher probability density (0.29 vs 0.12). Similar observations were made when comparing hydronium and water, where the most likely distance (2.48 Å vs 2.73 Å), angle (4.8° vs 8.3°), and highest probability density (0.38 vs 0.15) follow the same trend. These findings suggest that protonated oxygens (OSHs and hydronium oxygens, OHs) form stronger hydrogen bonds to mitigate the stronger electrostatic interactions resulting from the additional positive charges.

We then calculated the hydronium identity correlation functions, defined below

$$C(t) = \frac{\langle \sum_i h_i(t) h_i(0) \rangle}{\langle \sum_i h_i(0) \rangle} \quad (4)$$

where $h_i(t)$ is 1 if the i th water oxygen is protonated (namely hydronium oxygen) at time t and 0 otherwise, and $\langle \bullet \rangle$ represents the ensemble average. The hydronium identity correlation functions exhibit a rapid decay in the first 0.5 ps due to proton rattling between hydronium and water molecules. The permanent proton hopping contributes to the subsequent decay. To extract the lifetime of hydronium t_{OW}^* ,

we did a single exponential fit, $C(t) = ae^{-t/t_{\text{OW}}^*}$, to the intermediate time region (1.0 to 3.0 ps). The lifetime of hydronium is the average time a proton resides on the same water oxygen, i.e., before a proton hop occurs. This does not mean that all proton hops occur exactly at this time; rather, it is an ensemble average over faster and slower events. Thus, the hydronium lifetime represents how frequently, on average, the proton hops from one water molecule to another.

The correlation function of the 0.54 M solution and its exponential fit are shown in Figure 4A. The correlation functions for all three concentrations are in Figure S3.

The lifetime values of hydronium for the concentrations of 0.54, 3.0, and 5.3 M are 3.4, 4.5, and 5.4 ps, respectively. Figure 4B shows these values are very close to the experimental OHD-OKE t_3 values, demonstrating the correlation between t_3 and the average hydronium to water proton hopping times.

To further investigate the dynamics of hydronium, we calculated the correlation functions of hydronium-water H-bonds, as shown in Figure S4. Applying the single exponential fitting methodology to the H-bond correlation functions, the OH–OW H-bond lifetime values were found to be 3.0, 4.8, and 5.0 ps, which are very close to the hydronium lifetime values. This similarity suggests that proton hopping and H-bond rearrangement are strongly correlated dynamic processes.

The proton hopping process is also strongly coupled with the rearrangement of the surrounding H-bond network. An additional AIMD simulation was performed at the 0.54 M concentration to examine the effect of proton hopping on OH–OW H-bonds. During this simulation, the identities of the hydronium ions were maintained (i.e., no hopping allowed) by constraining the bond lengths of the initial hydroniums from the beginning. The resulting OH–OW H-bond correlation function in this constrained AIMD simulation, together with the one of unconstrained simulation,

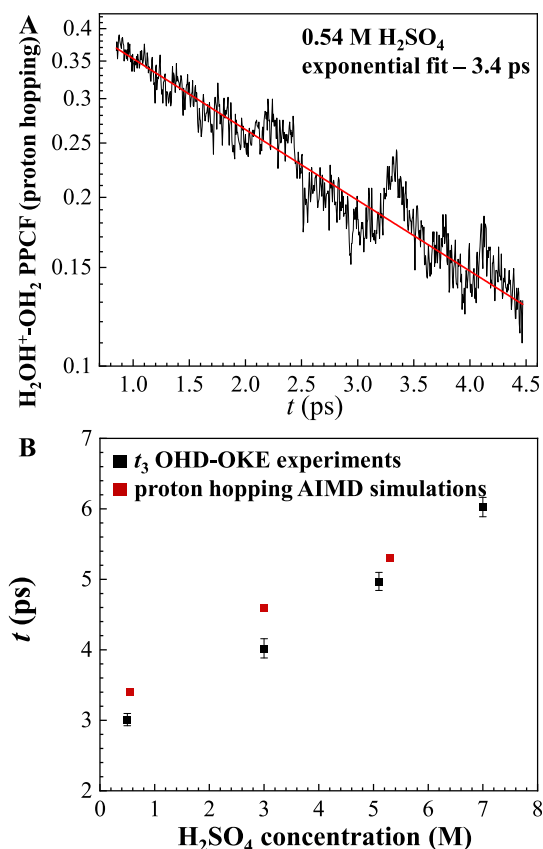


Figure 4. (A) AIMD simulation results for hydronium-oxygen identity correlation function on a semilog plot. This correlation function describes the transfer of a proton from hydronium to a hydrogen bonded water molecule, i.e., proton hopping. The decay is for 0.54 M solution. The red line is the exponential fit to the decay. The time constant is 3.4 ps. (B) A plot of t_3 decay constants from the OHD-OKE experiments (black points) and the AIMD hydronium-oxygen identity correlation function decay time constants (red points) for several concentrations. These results demonstrate that t_3 is the time constant for proton hopping, which is accurately determined by the AIMD simulations.

is shown in Figure S5. With hydronium identity change prohibited, over 80% of OH–OW hydrogen bonds stay intact for 10 ps. This result is unsurprising, considering the strong OH–OW H-bond strength shown in Figure 3C. Without proton hopping, the H-bond rearrangement around hydronium is greatly limited. In fact, a proton hopping event is always accompanied by a rearrangement of the H-bonds involving hydronium and its solvation water molecules, as well as in the broader local solvent network. This dynamic interplay is characteristic of the Grotthuss mechanism. For example, a proton transfer event, where the excess proton hops from the initial hydronium oxygen to the resulting hydronium oxygen, involves a reduction in the coordination number of the resulting hydronium oxygen (from 4-fold to 3-fold), while the initial hydronium may increase its coordination by accepting a weak H-bond on its lone pair side just prior to the transfer. This behavior is illustrated in the Figure S6 and aligns with previous findings by Berkelbach et al.⁷¹ and Tse et al.⁷² Our results reinforce the view that proton hopping is tightly coupled with the significant H-bond network rearrangements³⁵ occurring on the t_3 time scale.

The Grotthuss mechanism, namely proton hopping, affects the surrounding H-bond relaxation dynamics and may contribute significantly to the diffusivity of hydrated excess protons. Compared to other monovalent cations, hydronium exhibits a significantly higher diffusion rate, for example, H^+ $9.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ vs Na^+ $1.3 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ at room temperature.⁷³ There are two mechanisms of hydronium's diffusion in aqueous solutions: (i) the vehicular diffusion, in which the hydronium identity does not change and the hydronium diffuses as a whole, and (ii) the proton hopping diffusion, in which the excess proton hops from one water oxygen to another and the hydronium identity changes as a result. To quantify the contribution of proton hopping diffusion to the total diffusion of hydronium, we calculated the mean square displacements (MSDs) of hydroniums due to proton hopping within their lifetimes, as described above. Additional details about the calculations of MSDs due to proton hopping are found in the [Supporting Information](#). The MSDs due to hydronium proton hopping within their lifetimes are 12.06 Å², 8.55 Å², and 8.03 Å², for concentrations of 0.54, 3.0, and 5.3 M, respectively. While the lifetime of hydronium increases with higher concentrations, the MSDs caused by proton hopping decrease, indicating fewer proton hopping events within the hydronium lifetimes. This supposition is confirmed by histograms of the number of hopping events within the hydronium lifetime, as shown in [Figure S12](#). In a 0.54 M solution, hydronium ions have approximately a 50% probability of experiencing at least two proton hopping events within their lifetime. In contrast, the probabilities in 3.0 and 5.3 M solutions are roughly 35% and 30%, respectively.

5. COMPARISONS BETWEEN EXPERIMENTAL AND SIMULATION RESULTS

In the previous section, one component of the PPCF was demonstrated to be associated with the transfer of a proton from hydronium to a hydrogen bonded water molecule (hydronium identity correlation function). As discussed above, the decay times of the hydronium identity correlation function simulated at three concentrations agree very well with the OHD-OKE t_3 component at the respective concentrations, as shown in [Figure 4B](#). The simulated values are 3.4, 4.5, and 5.4 ps, and the experimental values for almost the same concentrations are 3.1, 4.1, and 5.1 ps. The quality of the agreement validates the simulations and identifies t_3 as the proton hopping time. The OH–OW H-bond correlation functions of unconstrained and constrained AIMD simulations also demonstrate that the proton hopping process is correlated with the surrounding H-bond network rearrangement.

Variations in the concentrations of the dissociated species and their dynamics as the concentration increases affect properties on the molecular scale, which result in significant changes in bulk solution properties. One important bulk property is the conductivity. For an ionic solution, the conductivity, which is associated with ion diffusivity, can be described by the Nernst–Einstein equation⁷⁴

$$\sigma = \sum_i \frac{D_i C_i Z_i^2}{RT} \quad (5)$$

where D_i is the diffusion constant of the i th ionic species, C_i is the carrier density (concentration), Z_i is the elementary charge, R is the molar gas constant, and T is the absolute temperature. The sum is over all species. For transport in which the ion diffusion is the result of the ions moving through the solution, i.e., the vehicular mechanism, the diffusion constant can be obtained with reasonable accuracy from the Stokes–Einstein Equation

$$D_i = \frac{k_B T}{6\pi a_i \eta} \quad (6)$$

where k_B is Boltzmann's constant, a_i is the radius of the i th diffusing ion, and η is the viscosity. Therefore, the conductivity for the vehicular mechanism is inversely proportional to the viscosity ([Figure S2](#)) and proportional to the carrier density, i.e., charged species' concentrations ([Figure S1](#)). While the Nernst–Einstein and Stokes–Einstein equations offer a practical approximation for the vehicular contribution to conductivity, their validity can diminish at high ionic strengths due to strong ion–ion correlations, local solvent structuring, and deviations from ideal spherical behavior.^{75–79} These factors may lead to overestimated diffusion coefficients and conductivity, thereby contributing to the slight overestimation of the total conductivity observed in our study, as discussed below. Although MD simulations can be used to directly compute conductivity using the Einstein equation,⁸⁰ this approach is not suitable in the context of our AIMD study. Conductivity is a collective property that requires extensive sampling to achieve statistical convergence,⁸¹ which is unfeasible with the relatively short ~ 100 ps time scale of AIMD simulations. Therefore, in this work, we adhere to conductivity estimates derived from the Nernst–Einstein and Stokes–Einstein equations.

When proton hopping is included, the protons have two diffusion constants: the vehicular hydronium diffusion constant and the proton hopping diffusion constant. The proton hopping diffusion constant is obtained using

$$D_H = \frac{\text{MSD}(t_3)}{6t_3} \quad (7)$$

Here, $\text{MSD}(t_3)$ is the MSD of hydroniums resulting from proton hopping within their lifetimes, t_3 , as described in [Section 4](#).

[Figure 5A](#) shows the experimental conductivity values (black points) and the calculated vehicular contributions to the conductivity for HSO_4^- (blue points), SO_4^{2-} (green points), the hydronium vehicular contribution (purple points) for the three concentrations used for the AIMD simulations. The viscosity vs sulfuric acid concentration and its inverse are shown in [Figure S2A,B](#), respectively. The radii for the three species were obtained from the literature.⁸² The orange points are the sum of the three contributions (see [eq 5](#)). These results show that the vehicular mechanism accounts for approximately one-third of the total conductivity for the three concentrations studied.

[Figure 5B](#) includes the contribution from proton hopping, as shown by the red points. The hydronium concentrations were calculated using the AIMD simulations (square points in [Figure S1](#)) for the hopping conductivity. The AIMD concentrations are close to the experimental concentrations compiled from the literature, much of which uses spectroscopic methods from the late 1940s. These concentrations are appropriate for comparison with the MSD hopping calculations. The orange points are again the sum of the contributions but now include the hopping contribution. The addition of the hopping contribution brings the calculated conductivities quite close to the experimental conductivities, with a consistent overestimation.

The overestimation of the total conductivity is probably caused by errors in determining the vehicular contributions from all species. The proton hopping contributions were calculated from AIMD simulations and the experimental t_3 . The simulations of the proton hopping times at the three sulfuric acid concentrations of 0.54, 3, and 5.3 M are very close to the measured t_3 values ([Figure 4B](#)). Using AIMD simulations, the concentrations of the three ionic species at the three sulfuric acid concentrations were determined. They are very close to the reported values, as shown in [Figure S1](#). Given that the hopping times and the concentrations are in good agreement with experiments, the hopping MSDs, which depend on the hopping times and the spatial distribution of ions, should also be accurate.

The vehicular diffusion constants for the three ions were obtained using the Stokes–Einstein equation, which assumes spherical particles with stick boundary conditions. While reasonably accurate, there can be deviations from the SE results in these concentrated ionic solutions

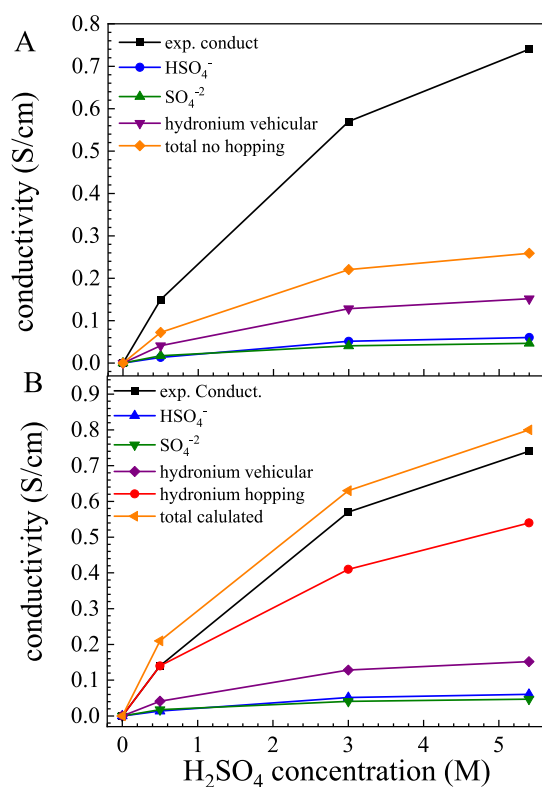


Figure 5. (A) The experimental conductivity (black points) for the three concentrations studied with the AIMD simulations. Calculated contributions to the vehicular conductivity of the various charged species and the total calculated vehicular conductivity (orange points). Vehicular conductivity does not account for the experimental conductivity. (B) The experimental conductivity (black points), the calculated contributions to the vehicular conductivity of the various charged species, and the calculated proton hopping contribution to the conductivity (red points). The total calculated conductivity (orange points) reproduces the experimental conductivity well. The proton hopping contributions are larger than the sum of the vehicular contributions.

with extensive H-bonding. In addition, some studies have suggested a small but non-negligible anticorrelation between proton hopping diffusion and proton vehicular diffusion and ion pairing at higher concentrations.^{83,84} These effects could lead to the slowing of vehicular diffusion.

To match the experimental conductivity, the vehicular contribution was scaled by 0.81, with the hopping contribution left unchanged. The scaling factor was determined so that the sum of vehicular and hopping-associated conductivity best agreed with the experimental data points at the three concentrations at which the AIMD calculations were performed. We assume that this scaling factor applies at all concentrations. Figure 6 shows the vehicular contribution to the conductivity at all concentrations (blue points) scaled by 0.81. The scaled vehicular conductivity was subtracted from the experimental conductivity (black points) to provide a reasonable approximation of the hopping contribution to the conductivity at all concentrations (red points). The green points are the AIMD hopping conductivities at the three calculated concentrations with no adjustments. The inputs are the AIMD calculated MSD and the experimentally measured hopping times, t_3 , to give the diffusion constants and the AIMD calculated concentrations. The fact that the green points fall on the hopping curve (red points) demonstrates the procedure's accuracy, i.e., scaling and subtracting the vehicular component of the conductivity from the experimental conductivity to give the hopping contribution to the conductivity. The hopping conductivity curve is accurate from low concentration to the

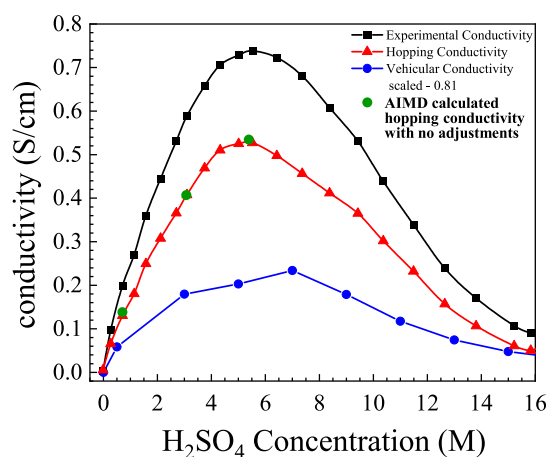


Figure 6. Experimental conductivity (black points). The vehicular contribution to conductivity (blue points) was calculated using the same method as that used for Figure 5 (see text). The red points are the proton hopping contribution to the conductivity obtained by subtracting the vehicular contribution for the experimental conductivity.

conductivity peak and somewhat higher sulfuric acid concentrations. It should be a reasonable but untested approximation up to ~16 M. At all but the highest concentration (>16 M), proton hopping is the main contribution to the total conductivity.

The AIMD simulations demonstrate that the OHD-OKE time constant t_3 is the proton hopping time (see Figure 4B). C_3 is the coefficient of t_3 in the PPCF (see eq 3). C_3 reflects the contribution to the PPCF that comes from proton hopping. Figure 7 compares the

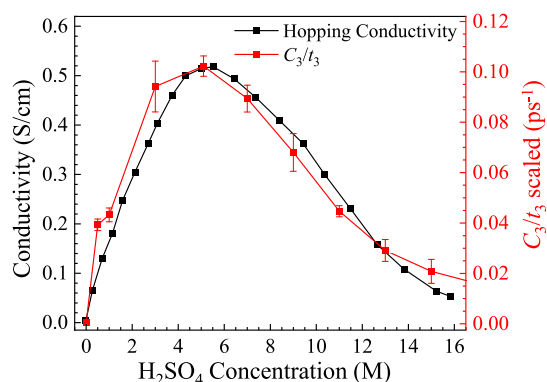


Figure 7. Proton hopping contribution to the conductivity from Figure 6 (black points, left axis) and C_3/t_3 from the OHD-OKE experiments (red points, right axis). (Figure 2) as a function of concentration.

concentration dependence of the proton hopping contribution to the conductivity (black points; see red points Figure 6) and a plot of the function C_3/t_3 (red points), which was scaled to match the maximum amplitude of the hopping conductivity curve. The C_3/t_3 plot is remarkably close to the proton hopping contribution to the conductivity. The hopping conductivity is proportional to the hopping diffusion constants times the hydronium concentrations (eq 5). The hopping diffusion constant, D_H (eq 7), is proportional to the MSD divided by t_3 . These relations suggest that C_3 is proportional to the hopping MSD times the hydronium concentration. From the AIMD simulations, we know that t_3 is the hopping time. The hopping causes the decay of the third component of the PPCF. Then, the amplitude of this component is related to how far the Figure 6 shows that the conductivity peaks at 5.5 M sulfuric acid concentration. The AIMD simulations in Figures 5B and 6 show that the major

contribution to the conductivity is caused by hydronium to water proton hopping. There is an interesting and compelling hypothesis for the peak conductivity concentration. Figure 8A shows the number of

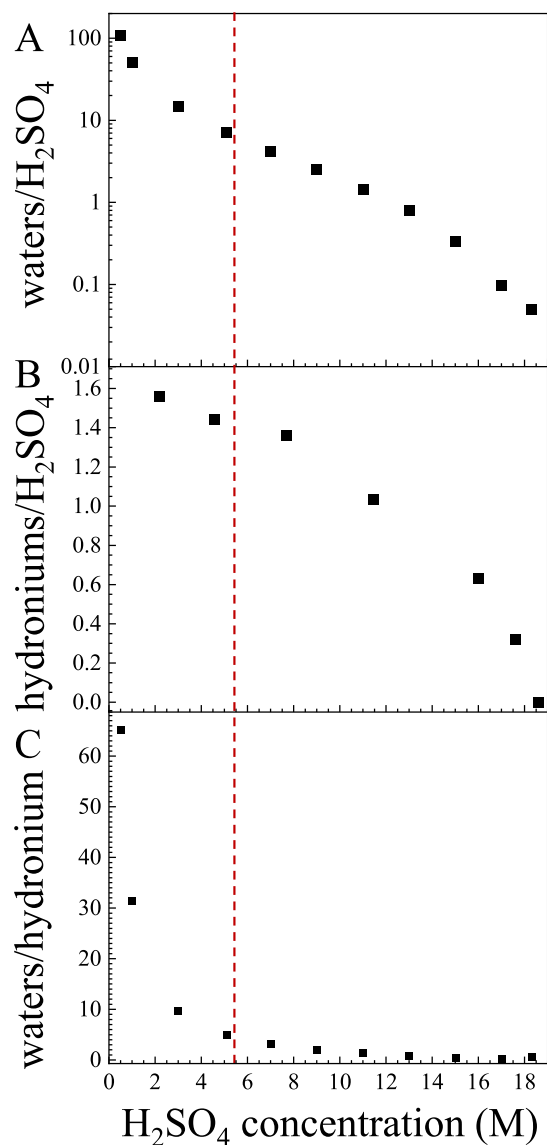


Figure 8. (A) A semilog plot of the number of water molecules per sulfuric acid as a function of the sulfuric acid concentration. (B) The number of hydronium per sulfuric acid as a function of the sulfuric acid concentration. (C) The number of water molecules per hydronium as a function of the sulfuric acid concentration. The dashed red line is the sulfuric acid concentration at which the conductivity peaks.

water molecules per sulfuric acid. The red dashed line is the concentration of the peak of the conductivity. Note the proton hops and how many hydroniums there are that give rise to the hopping semilog scale. The ratio is dropping rapidly and is down over an order of magnitude by 5.5 M. However, Figure 8B shows that the number of hydroniums per sulfuric acid is changing gradually around 5.5 M sulfuric acid. Hydronium is essential for proton hopping. As the sulfuric acid concentration increases well above the peak in the conductivity (Figure 6), there is still a significant amount of hydronium. For example, there is ~ 1 hydronium per sulfuric acid at 11.5 M.

The explanation is illustrated in Figure 8C. The number of water molecules per hydronium drops rapidly. At 5.5 M sulfuric acid, there

are 4.5 water molecules per hydronium. It takes 3 water molecules to form a hydronium's first H-bonded solvation shell. At 5.5 molar sulfuric acid, almost all of the water is tied up solvating hydronium. At 7 M, there are only 3 waters per hydronium. At 5.5 M, the concentration of hydroniums is still rapidly increasing (See Figure S1). It does not peak until 14 M. Although, at the higher concentrations, protons can be solvated by both water and HSO_4^- . These contact ion pairs may be responsible for the slowest component of the tetra-exponential OHD-OKE decay. The C_4 coefficient is very small below 5 M, and increases rapidly for higher concentrations (see Figure 2B).

Above 5.5 M, it will be increasingly difficult for a proton to hop to a water as most water molecules are part of another hydronium solvation shell. The water molecules will not be uniformly distributed, so proton hopping can occur. However, for long-range diffusion, which is necessary for conductivity, a type of percolation problem will occur. There will be pockets of hydroniums with water enabling hopping. However, as connections among these pockets become increasingly scarce and the sizes of these pockets decrease, conductivity will fall off. The peak in the conductivity, 5.5 M, occurs when there are just slightly more water molecules than needed to solvate the hydroniums, which is consistent with the hypothesis.

6. CONCLUDING REMARKS

This paper described the investigation of sulfuric acid's molecular-level properties using ultrafast optical heterodyne detected optical Kerr effect (OHD-OKE) experiments and AIMD simulations to identify specific nanoscopic dynamics and structures. Molecular level dynamics and chemical constituents determine bulk properties. Here, we used the results of the experiments and simulations to address the molecular-level processes responsible for bulk conductivity.

The OHD-OKE experiments were conducted over the 0.5 to 18.3 M concentration range. At the lowest concentrations, the number of water molecules greatly exceeds the number of sulfuric acids. At the highest concentration, there is only one water per ten sulfuric acids. Tetra-exponential decays were observed at all sulfuric acid concentration. In the sulfuric acid solutions, the two fast decays, t_1 and t_2 , are closely related to their pure water counterparts. In addition, two much slower decays, t_3 and t_4 , do not occur in pure water.

t_3 is of particular interest here because it falls in the time range that is amenable to detailed analysis with the AIMD simulations. The AIMD simulations were used to determine the identity correlation functions of the hydronium-like hydrated excess proton and its lifetimes at three concentrations, 0.54 M, 3.0 M, and 5.3 M. The calculated excess proton (hydronium-like structure) lifetimes are in excellent agreement with the measured t_3 decay times (see Figure 4). Through detailed analysis, the simulations conclusively identify t_3 as the hydronium-like excess proton hopping time from one water to another.

The solvation structures of different ions were explored through AIMD simulations, revealing that protonated oxygens (i.e., protonated oxygens in bisulfate ions and hydronium oxygens) form stronger hydrogen bonds compared to unprotonated oxygens. To better understand hydronium-like hydrated excess proton dynamics, we analyzed the correlation functions of hydronium-water hydrogen bonds, revealing lifetimes comparable to that of hydrated excess proton itself. Additional AIMD simulations at 0.54 M showed that constraining proton hopping significantly suppresses H-bond rearrangement, with over 80% of OH–OW bonds remaining intact for 10 ps. These findings highlighted the critical role of

proton transfer in facilitating local hydrogen-bond network dynamics.

A method was implemented to determine the proton hopping MSD using the AIMD simulations. The MSD and the experimental hopping time, t_3 , were used to determine the proton hopping diffusion constant at the three concentrations. The diffusion constants were combined with the AIMD determined hydronium-like hydrated excess proton concentrations. The proton hopping contributions to the total conductivities were calculated using the Nernst–Einstein equation. Stokes–Einstein equation was used to calculate the vehicular diffusion constants. The diffusion constant and literature values of the concentrations of the ions as a function of sulfuric acid concentration were used to determine the vehicular contribution from all ions to the conductivity. Adding the proton hopping and vehicular portions of the conductivity gave the total conductivity for the three concentrations used for the AIMD simulations.

Figures 5 and 6 show the results of these calculations. The total calculated conductivity is close to the experimental conductivity but slightly too large. It was assumed that the error was due to the vehicular conductivity and the anticorrelation between hopping diffusion and vehicular diffusion of the hydrated excess protons (hydronium-like structures). The vehicular conductivity was scaled by 0.81, so the results gave the experimental conductivity at the three concentrations used for the simulations when added to the proton hopping conductivity. The accuracy of this procedure, at least through the peak of the conductivity, was demonstrated by the agreement of the green points on the hopping conductivity curve that were calculated with no adjustable parameters using the results of the AIMD simulations and the experimental value of t_3 .

The third term of the polarizability–polarizability correlation function is the proton hopping exponential decay, t_3 , with coefficient C_3 . Figure 7 shows that sulfuric acid concentration dependence of the function C_3/t_3 comes very close to matching the experimental conductivity curve from 0.5 to 16 M when the former is scaled to match the peak of the conductivity curve (see Figure 7). This result implies that C_3 is proportional to the proton hopping MSD times the hydronium concentration.

The net result of this study is an increased molecular level understanding of the structural dynamics of sulfuric acid solutions and the relationship of the dynamics and structures to the bulk conductivity.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.5c06194>.

Description of the criteria for H-bond definition, Figures S1 through S13, Tables S1 & S2, references (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Gregory A. Voth – Department of Chemistry, Chicago Center for Theoretical Chemistry, Institute for Biophysical Dynamics, and James Franck Institute, The University of Chicago, Chicago, Illinois 60637, United States; orcid.org/0000-0002-3267-6748; Phone: 773 702-9092; Email: gavoth@uchicago.edu

Michael D. Fayer – Department of Chemistry, Stanford University, Stanford, California 94305, United States; orcid.org/0000-0002-0021-1815; Phone: 650 723-4446; Email: fayer@stanford.edu

Authors

Laura Kacenauskaitė – Department of Chemistry, Stanford University, Stanford, California 94305, United States; Nano-Science Center & Department of Chemistry, University of Copenhagen, Copenhagen 2100, Denmark

Sijia Chen – Department of Chemistry, Chicago Center for Theoretical Chemistry, Institute for Biophysical Dynamics, and James Franck Institute, The University of Chicago, Chicago, Illinois 60637, United States; orcid.org/0000-0003-2060-4920

Max Moncada Cohen – Department of Chemistry, Stanford University, Stanford, California 94305, United States; orcid.org/0000-0003-1633-6732

Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/jacs.5c06194>

Author Contributions

^{||}Laura Kacenauskaitė and Sijia Chen contributed equally to this research. Gregory A. Voth: theory; Michael D. Fayer: experiment.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

L.K. acknowledges generous support from Villum Fonden (award number 41380). This work was supported by the National Science Foundation, Division of Chemistry, award number 2319637 (L.K., M.M.C. and M.D.F.). This research was also partly supported by the Air Force Office of Scientific Research under award number FA9550-21-1-0380 (G.A.V. and S.C.). The computational resources for this research were provided by the University of Chicago Research Computing Center (RCC).

■ REFERENCES

- (1) Ashar, N. G.; Golwalkar, K. R. Current Status of Manufacture of Sulfuric Acid. In *A Practical Guide to the Manufacture of Sulfuric Acid, Oleums, and Sulfonating Agents*; Springer, 2013; pp 4–7..
- (2) Skyllas-Kazacos, M.; Chakrabarti, M. H.; Hajimolana, S. A.; Mjalli, F. S.; Saleem, M. Progress in Flow Battery Research and Development. *J. Electrochem. Soc.* **2011**, *158* (8), R55.
- (3) Sharmoukh, W. Redox flow batteries as energy storage systems: materials, viability, and industrial applications. *RSC Adv.* **2025**, *15* (13), 10106–10143.
- (4) Shoaib, M.; Vallayil, P.; Jaiswal, N.; Iyapazham Vaigunda Suba, P.; Sankararaman, S.; Ramanujam, K.; Thangadurai, V. Advances in Redox Flow Batteries - A Comprehensive Review on Inorganic and Organic Electrolytes and Engineering Perspectives. *Adv. Energy Mater.* **2024**, *14* (32), 2400721.
- (5) Zhao, Y.; Liu, L.; Qiu, X.; Xi, J. Revealing sulfuric acid concentration impact on comprehensive performance of vanadium electrolytes and flow batteries. *Electrochim. Acta* **2019**, *303*, 21–31.
- (6) Shin, J.; Kim, C.; Jeong, B.; Vaz, N.; Ju, H. New operating strategy for all-vanadium redox flow batteries to mitigate electrolyte imbalance. *J. Power Sources* **2022**, *526*, 231144.
- (7) Ge, L.; Liu, T.; Zhang, Y.; Liu, H. Optimized the vanadium electrolyte with sulfate-phosphoric mixed acids to enhance the stable operation at high-temperature. *Front. Chem. Sci. Eng.* **2024**, *18* (2), 14.
- (8) Lawton, J. S.; Tiano, S. M.; Donnelly, D. J.; Flanagan, S. P.; Arruda, T. M. The Effect of Sulfuric Acid Concentration on the

Physical and Electrochemical Properties of Vanadyl Solutions. *Batteries* **2018**, *4* (3), 40.

(9) Borah, S. Spatially resolved hydration shells and dynamics of different sulfur species in water from first-principle molecular dynamics simulations. *J. Mol. Liq.* **2020**, *312*, 113387.

(10) Kundu, A.; Mamatkulov, S. I.; Brünig, F. N.; Bonthuis, D. J.; Netz, R. R.; Elsaesser, T.; Fingerhut, B. P. Short-Range Cooperative Slow-down of Water Solvation Dynamics Around $\text{SO}_4^{2-}\text{-Mg}^{2+}$ Ion Pairs. *ACS Phys. Chem. Au* **2022**, *2* (6), 506–514.

(11) Toivola, M.; Napari, I.; Vehkamäki, H. Structure of water-sulfuric acid clusters from molecular dynamics simulations. *Boreal Environ. Res.* **2009**, *14*, 654–661.

(12) Giaque, W. F.; Hornung, E. W.; Kunzler, J. E.; Rubin, T. R. The Thermodynamic Properties of Aqueous Sulfuric Acid Solutions and Hydrates from 15 to 300°K. *J. Am. Chem. Soc.* **1960**, *82* (1), 62–70.

(13) Zeleznik, F. J. Thermodynamic Properties of the Aqueous Sulfuric Acid System to 350 K. *J. Phys. Chem. Ref. Data* **1991**, *20* (6), 1157–1200.

(14) Sippola, H. Thermodynamic modelling of concentrated sulfuric acid solutions. *CALPHAD: Comput. Coupling Phase Diagrams Thermochem.* **2012**, *38*, 168–176.

(15) Rhodes, F. H.; Barbour, C. B. The Viscosities of Mixtures of Sulfuric Acid and Water. *J. Ind. Eng. Chem.* **1923**, *15* (8), 850–852.

(16) Darling, H. E. Conductivity of Sulfuric Acid Solutions. *J. Chem. Eng. Data* **1964**, *9* (3), 421–426.

(17) Margarella, A. M.; Perrine, K. A.; Lewis, T.; Faubel, M.; Winter, B.; Hemminger, J. C. Dissociation of Sulfuric Acid in Aqueous Solution: Determination of the Photoelectron Spectral Fingerprints of H_2SO_4 , HSO_4^- , and SO_4^{2-} in Water. *J. Phys. Chem. C* **2013**, *117* (16), 8131–8137.

(18) Andreani, C.; Petrillo, C. Neutron and X-ray diffraction patterns of aqueous sulphuric acid solutions. *Mol. Phys.* **1987**, *62* (3), 765–773.

(19) Randall, J. T. An X-Ray Study of Sulphuric and Orthophosphoric Acids. *Nature* **1936**, *138* (3498), 842.

(20) Kameda, Y.; Hosoya, K.; Sakamoto, S.; Suzuki, H.; Usuki, T.; Uemura, O. Hydrogen-bonded structure in aqueous sulfuric acid solutions. *J. Mol. Liq.* **1995**, *65–66*, 305–308.

(21) Niskanen, J.; Sahle, C. J.; Ruotsalainen, K. O.; Müller, H.; Kavčič, M.; Žitnik, M.; Bučar, K.; Petric, M.; Hakala, M.; Huotari, S. Sulphur K β emission spectra reveal protonation states of aqueous sulfuric acid. *Sci. Rep.* **2016**, *6*, 21012.

(22) Kinnibrugh, T.; Fister, T. Structure of Sulfuric Acid Solutions Using Pair Distribution Function Analysis. *J. Phys. Chem. B* **2022**, *126* (16), 3099–3106.

(23) Bell, R. M.; Jeppesen, M. A. The Raman Spectrum of Sulphuric Acid. *J. Chem. Phys.* **1935**, *3*, 245–247.

(24) Horn, A. B.; Jessica Sully, K. ATR-IR spectroscopic studies of the formation of sulfuric acid and sulfuric acid monohydrate films. *Phys. Chem. Chem. Phys.* **1999**, *1* (16), 3801–3806.

(25) Lund Myhre, C. E.; Christensen, D. H.; Nicolaisen, F. M.; Nielsen, C. J. Spectroscopic Study of Aqueous H_2SO_4 at Different Temperatures and Compositions: Variations in Dissociation and Optical Properties. *J. Phys. Chem. A* **2003**, *107* (12), 1979–1991.

(26) Hintze, P. E.; Kjaergaard, H. G.; Vaida, V.; Burkholder, J. B. Vibrational and Electronic Spectroscopy of Sulfuric Acid Vapor. *J. Phys. Chem. A* **2003**, *107* (8), 1112–1118.

(27) Sinha, R. K.; Chiavarino, B.; Fornarini, S.; Lemaire, J.; Maitre, P.; Crestoni, M. E. Protonated Sulfuric Acid: Vibrational Signatures of the Naked Ion in the Near- and Mid-IR. *J. Phys. Chem. Lett.* **2010**, *1* (11), 1721–1724.

(28) Zhou, J.; Santambrogio, G.; Brümmer, M.; Moore, D. T.; Wöste, L.; Meijer, G.; Neumark, D. M.; Asmis, K. R. Infrared spectroscopy of hydrated sulfate dianions. *J. Chem. Phys.* **2006**, *125* (11), 111102.

(29) Han, K. S.; Bazak, J. D.; Chen, Y.; Graham, T. R.; Washton, N. M.; Hu, J. Z.; Murugesan, V.; Mueller, K. T. Pulsed Field Gradient

Nuclear Magnetic Resonance and Diffusion Analysis in Battery Research. *Chem. Mater.* **2021**, *33* (22), 8562–8590.

(30) Klenø, J. G.; Kristiansen, M. W.; Nielsen, C. J.; Pedersen, E. J.; Williams, L. R.; Pedersen, T. Diffusion Coefficients in Cold Sulfuric Acid Solution. *J. Phys. Chem. A* **2001**, *105* (37), 8440–8444.

(31) Bazak, J. D.; Wong, A. R.; Duanmu, K.; Han, K. S.; Reed, D.; Murugesan, V. Concentration-Dependent Solvation Structure and Dynamics of Aqueous Sulfuric Acid Using Multinuclear NMR and DFT. *J. Phys. Chem. B* **2021**, *125* (19), 5089–5099.

(32) Lewis, N. H. C.; Fournier, J. A.; Carpenter, W. B.; Tokmakoff, A. Direct Observation of Ion Pairing in Aqueous Nitric Acid Using 2D Infrared Spectroscopy. *J. Phys. Chem. B* **2019**, *123* (1), 225–238.

(33) Jaye, A. A.; Hunt, N. T.; Meech, S. R. Temperature- and solvation-dependent dynamics of liquid sulfur dioxide studied through the ultrafast optical Kerr effect. *J. Chem. Phys.* **2006**, *124* (2), 024506.

(34) Fournier, J. A.; Carpenter, W. B.; Lewis, N. H. C.; Tokmakoff, A. Broadband 2D IR spectroscopy reveals dominant asymmetric H_5O_2^+ proton hydration structures in acid solutions. *Nat. Chem.* **2018**, *10* (9), 932–937.

(35) Yuan, R.; Napoli, J. A.; Yan, C.; Marsalek, O.; Markland, T. E.; Fayer, M. D. Tracking Aqueous Proton Transfer by Two-Dimensional Infrared Spectroscopy and ab Initio Molecular Dynamics Simulations. *ACS Cent. Sci.* **2019**, *5* (7), 1269–1277.

(36) Yamaguchi, M.; Ohira, A. Ab initio molecular dynamics simulation of infrared absorption spectra of crystalline sulfuric acid mono- and tetra-hydrates. *Comput. Theor. Chem.* **2016**, *1089*, 54–58.

(37) Matsubara, H.; Ebisuzaki, T.; Yasuoka, K. Microscopic insights into nucleation in a sulfuric acid-water vapor mixture based on molecular dynamics simulation. *J. Chem. Phys.* **2009**, *130* (10), 104705.

(38) Re, S.; Osamura, Y.; Morokuma, K. Coexistence of Neutral and Ion-Pair Clusters of Hydrated Sulfuric Acid $\text{H}_2\text{SO}_4(\text{H}_2\text{O})_n$ ($n = 1\text{--}5$). A Molecular Orbital Study. *J. Phys. Chem. A* **1999**, *103* (18), 3535–3547.

(39) Choe, Y.-K.; Tsuchida, E.; Ikeshoji, T. Vibrational analysis of aqueous sulfuric acid: A computational study. *Int. J. Quantum Chem.* **2009**, *109* (9), 1984–1990.

(40) Ishiyama, T.; Morita, A. Molecular Dynamics Simulation of Sum Frequency Generation Spectra of Aqueous Sulfuric Acid Solution. *J. Phys. Chem. C* **2011**, *115* (28), 13704–13716.

(41) Choe, Y.-K.; Tsuchida, E.; Ikeshoji, T. Electrical property of a sulfuric acid-water mixture from the first-principles molecular dynamics simulation. *Comput. Phys. Commun.* **2007**, *177* (1), 38–39.

(42) Chen, S.; Yoon, B.; Wu, J.; Voth, G. A. Metastable Shared Proton Complexes in Aqueous Sulfuric Acid Solutions. *J. Phys. Chem. Lett.* **2025**, *16* (13), 3281–3286.

(43) Ruhman, S.; Williams, L. R.; Joly, A. G.; Kohler, B.; Nelson, K. A. Nonrelaxational inertial motion in carbon disulfide liquid observed by femtosecond time-resolved impulsive stimulated scattering. *J. Phys. Chem.* **1987**, *91* (9), 2237–2240.

(44) Sturlaugson, A. L.; Arima, A. Y.; Bailey, H. E.; Fayer, M. D. Orientational dynamics in a lyotropic room temperature ionic liquid. *J. Phys. Chem. B* **2013**, *117* (47), 14775–14784.

(45) Sturlaugson, A. L.; Fruchey, K. S.; Fayer, M. D. Orientational Dynamics of Room Temperature Ionic Liquid/Water Mixtures: Water-Induced Structure. *J. Phys. Chem. B* **2012**, *116* (6), 1777–1787.

(46) VandeVondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing, T.; Hutter, J. Quickstep: Fast and accurate density functional calculations using a mixed Gaussian and plane waves approach. *Comput. Phys. Commun.* **2005**, *167* (2), 103–128.

(47) Kühne, T. D.; Iannuzzi, M.; Del Ben, M.; Rybkin, V. V.; Seewald, P.; Stein, F.; Laino, T.; Khaliullin, R. Z.; Schütt, O.; Schiffmann, F.; et al. CP2K: An electronic structure and molecular dynamics software package - Quickstep: Efficient and accurate electronic structure calculations. *J. Chem. Phys.* **2020**, *152* (19), 194103.

(48) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868.

- (49) Zhang, Y.; Yang, W. Comment on "Generalized Gradient Approximation Made Simple". *Phys. Rev. Lett.* **1998**, 80 (4), 890.
- (50) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, 132 (15), 154104.
- (51) Lippert, G.; Hutter, J.; Parrinello, M. A hybrid Gaussian and plane wave density functional scheme. *J. Mol. Phys.* **1997**, 92, 477–487.
- (52) VandeVondele, J.; Hutter, J. Gaussian basis sets for accurate calculations on molecular systems in gas and condensed phases. *J. Chem. Phys.* **2007**, 127 (11), 114105.
- (53) Goedecker, S.; Teter, M.; Hutter, J. Separable dual-space Gaussian pseudopotentials. *Phys. Rev. B* **1996**, 54 (3), 1703–1710.
- (54) Krack, M. Pseudopotentials for H to Kr optimized for gradient-corrected exchange-correlation functionals. *Theor. Chem. Acc.* **2005**, 114 (1), 145–152.
- (55) VandeVondele, J.; Hutter, J. An efficient orbital transformation method for electronic structure calculations. *J. Chem. Phys.* **2003**, 118 (10), 4365–4369.
- (56) Lide, D. R. *CRC Handbook of Chemistry and Physics*, 85th Ed.; Taylor & Francis, 2004.
- (57) Martínez, L.; Andrade, R.; Birgin, E. G.; Martínez, J. M. PACKMOL: a package for building initial configurations for molecular dynamics simulations. *J. Comput. Chem.* **2009**, 30 (13), 2157–2164.
- (58) Canales, M.; Guàrdia, E. Computer simulation study of ion-water and water-water hydrogen bonds in sulfuric acid solutions at low temperatures. *J. Mol. Liq.* **2022**, 347, 118351.
- (59) Biswas, R.; Tse, Y. L.; Tokmakoff, A.; Voth, G. A. Role of Presolvation and Anharmonicity in Aqueous Phase Hydrated Proton Solvation and Transport. *J. Phys. Chem. B* **2016**, 120 (8), 1793–1804.
- (60) Wu, Y.; Tepper, H. L.; Voth, G. A. Flexible simple point-charge water model with improved liquid-state properties. *J. Chem. Phys.* **2006**, 124 (2), 024503.
- (61) Thompson, A. P.; Aktulga, H. M.; Berger, R.; Bolintineanu, D. S.; Brown, W. M.; Crozier, P. S.; in 't Veld, P. J.; Kohlmeyer, A.; Moore, S. G.; Nguyen, T. D.; et al. LAMMPS - a flexible simulation tool for particle-based materials modeling at the atomic, meso, and continuum scales. *Comput. Phys. Commun.* **2022**, 271, 108171.
- (62) Humphrey, W.; Dalke, A.; Schulten, K. VMD: Visual molecular dynamics. *J. Mol. Graph.* **1996**, 14 (1), 33–38.
- (63) Romero, M. Low Temperature Studies for the sulphuric acid decomposition step in the HyS and SI Thermochemical Cycles. PhD thesis, University of Sheffield, 2014.
- (64) Asbury, J. B.; Steinell, T.; Stromberg, C.; Corcelli, S. A.; Lawrence, C. P.; Skinner, J. L.; Fayer, M. D. Water Dynamics: Vibrational Echo Correlation Spectroscopy and Comparison to Molecular Dynamics Simulations. *J. Phys. Chem. A* **2004**, 108 (7), 1107–1119.
- (65) Park, S.; Fayer, M. D. Hydrogen bond dynamics in aqueous NaBr solutions. *Proc. Natl Acad. Sci. U S A* **2007**, 104 (43), 16731–16738.
- (66) Hammerich, A. D.; Buch, V. Ab Initio Molecular Dynamics Simulations of the Liquid/Vapor Interface of Sulfuric Acid Solutions. *J. Phys. Chem. A* **2012**, 116 (23), 5637–5652.
- (67) Knight, C.; Voth, G. A. The Curious Case of the Hydrated Proton. *Acc. Chem. Res.* **2012**, 45 (1), 101–109.
- (68) Hassanali, A. A.; Cuny, J.; Verdolino, V.; Parrinello, M. Aqueous solutions: state of the art in ab initio molecular dynamics. *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.* **2014**, 372, 20120482.
- (69) Calio, P. B.; Li, C.; Voth, G. A. Resolving the Structural Debate for the Hydrated Excess Proton in Water. *J. Am. Chem. Soc.* **2021**, 143 (44), 18672–18683.
- (70) Markovitch, O.; Chen, H.; Izvekov, S.; Paesani, F.; Voth, G. A.; Agmon, N. Special pair dance and partner selection: elementary steps in proton transport in liquid water. *J. Phys. Chem. B* **2008**, 112 (31), 9456–9466.
- (71) Berkelbach, T. C.; Lee, H. S.; Tuckerman, M. E. Concerted hydrogen-bond dynamics in the transport mechanism of the hydrated proton: a first-principles molecular dynamics study. *Phys. Rev. Lett.* **2009**, 103 (23), 238302.
- (72) Tse, Y. L.; Knight, C.; Voth, G. A. An analysis of hydrated proton diffusion in ab initio molecular dynamics. *J. Chem. Phys.* **2015**, 142 (1), 014104.
- (73) Yuan-Hui, L.; Gregory, S. Diffusion of ions in sea water and in deep-sea sediments. *Geochim. Cosmochim. Acta* **1974**, 38 (5), 703–714.
- (74) Newman, J.; Thomas-Alyea, K. E. *Electrochemical Systems*; Wiley, 2004.
- (75) Borucka, Z. A. B.; O'M, J.; Kitchener, J. A. Self-diffusion in molten sodium chloride: a test of the applicability of the Nernst-Einstein equation. *Proc. Roy. Soc. Lond. Math. Phys. Sci.* **1957**, 241 (1227), 554–567.
- (76) Blazquez, S.; Abascal, J. L. F.; Lagerweij, J.; Habibi, P.; Dey, P.; Vlugt, T. J. H.; Moulton, O. A.; Vega, C. Computation of Electrical Conductivities of Aqueous Electrolyte Solutions: Two Surfaces, One Property. *J. Chem. Theory Comput.* **2023**, 19 (16), 5380–5393.
- (77) Li, P.; Lu, H.; Fu, Y. Q. An extended Stokes-Einstein model for condensed ionic water structures with topological complexity. *J. Phys.: Condens. Matter* **2022**, 34 (47), 475101.
- (78) Angell, C. A. Diffusion—Conductance Relations and Free Volume in Molten Salts. *J. Phys. Chem.* **1965**, 69 (2), 399–403.
- (79) Sherman, D. M.; Collings, M. D. Ion association in concentrated NaCl brines from ambient to supercritical conditions: results from classical molecular dynamics simulations. *Geochem. Trans.* **2002**, 3 (1), 102.
- (80) Müller-Plathe, F. Permeation of polymers — a computational approach. *Acta Polym.* **1994**, 45 (4), 259–293.
- (81) Kubisiak, P.; Eilmes, A. Estimates of Electrical Conductivity from Molecular Dynamics Simulations: How to Invest the Computational Effort. *J. Phys. Chem. B* **2020**, 124 (43), 9680–9689.
- (82) Kadhim, M. J.; Gamaj, M. I. Estimation of the Diffusion Coefficient and Hydrodynamic Radius (Stokes Radius) for Inorganic Ions in Solution Depending on Molar Conductivity as Electro-Analytical Technique-A Review. *J. Chem. Rev.* **2020**, 2 (3), 182–188.
- (83) Xu, J.; Izvekov, S.; Voth, G. A. Structure and Dynamics of Concentrated Hydrochloric Acid Solutions. *J. Phys. Chem. B* **2010**, 114 (29), 9555–9562.
- (84) Tse, Y.-L. S.; Herring, A. M.; Kim, K.; Voth, G. A. Molecular Dynamics Simulations of Proton Transport in 3M and Nafion Perfluorosulfonic Acid Membranes. *J. Phys. Chem. C* **2013**, 117 (16), 8079–8091.