

Supporting information

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

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Description of the criteria for hydrogen bond (H-bond) definition:

Following the recommendation of Luzar and Chandler,¹ we adopt a geometric criteria for H-bond definition: (a) the angle α is less than 30° , defined by the donor oxygen O_D , the acceptor oxygen O_A , and the donor hydrogen H_D ; (2) the distance $d_{O_A-O_D}$ between O_A and O_D is less than the first minimum in the radial distribution function (RDF) of O_A and O_D ; and (3) the distance $d_{O_A-H_D}$ between O_A and H_D is less than the first minimum in the RDF of O_A and H_D . The RDFs related to the H-bond definitions are shown in Figure S8 and S9.

Figures

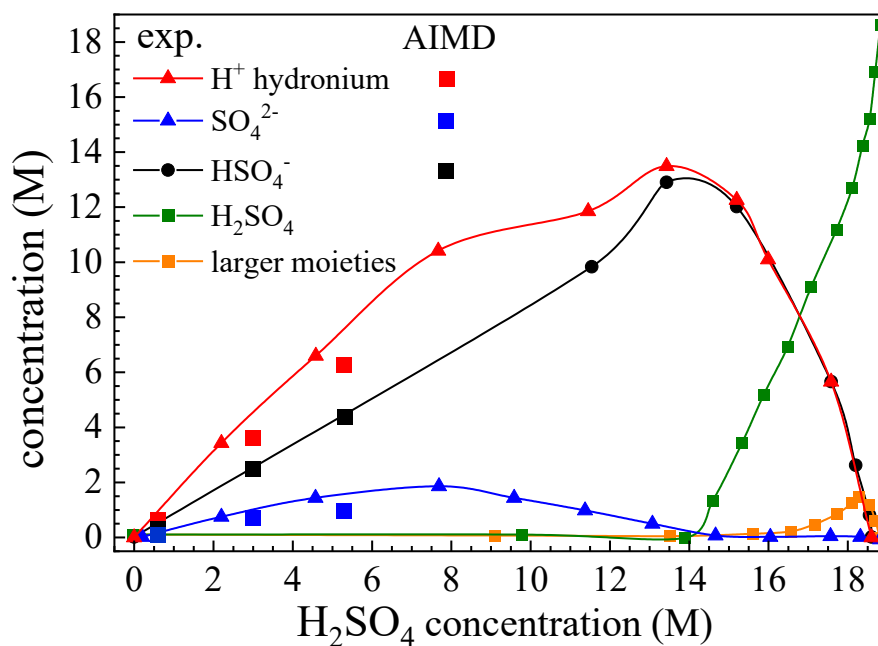


Figure S1. The various species present in sulfuric acid as a function of concentration from *ab initio* molecular dynamics (AIMD) simulations and from the literature.² The squares were calculated using AIMD at three concentrations.

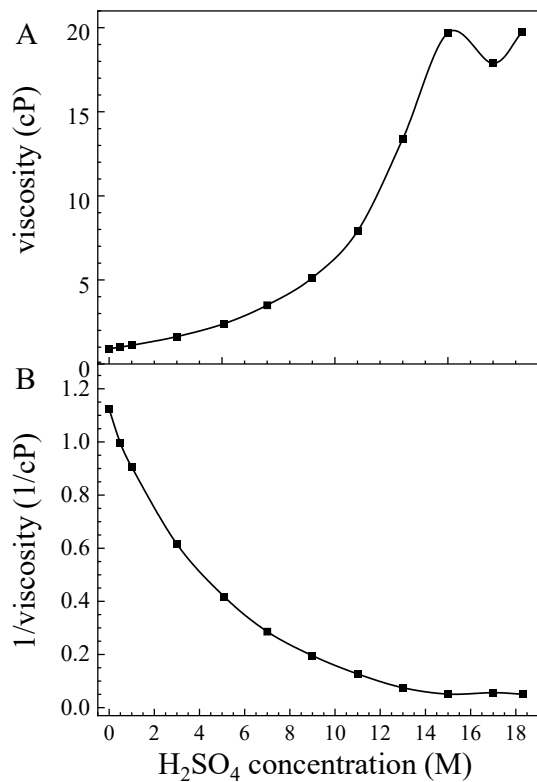


Figure S2. The viscosity (A) and the inverse of the viscosity (B) from the literature.³

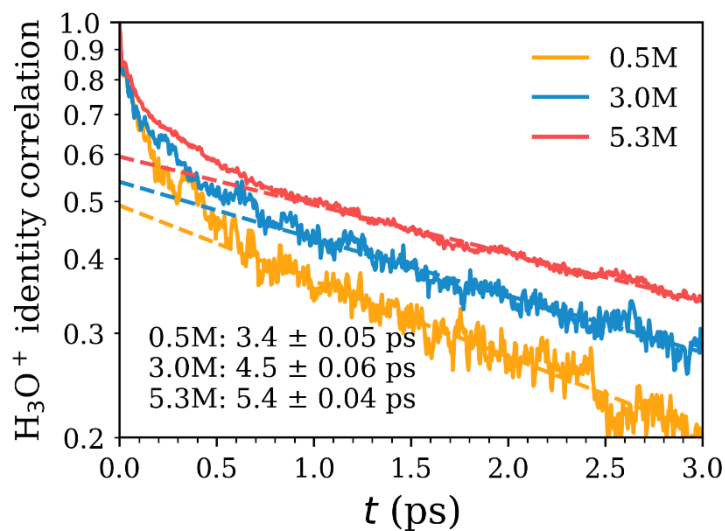


Figure S3. The hydronium identity correlation functions for sulfuric acid solution of three concentrations (0.54 M: orange line; 3.0 M: blue line; 5.3 M: red line). The intermediate time region ($1.0 \text{ ps} < t < 3.0 \text{ ps}$) was utilized to determine the lifetime t_{0^*} of hydronium through single exponential fittings applied to the correlation functions. The fitting results are shown in dashed lines.

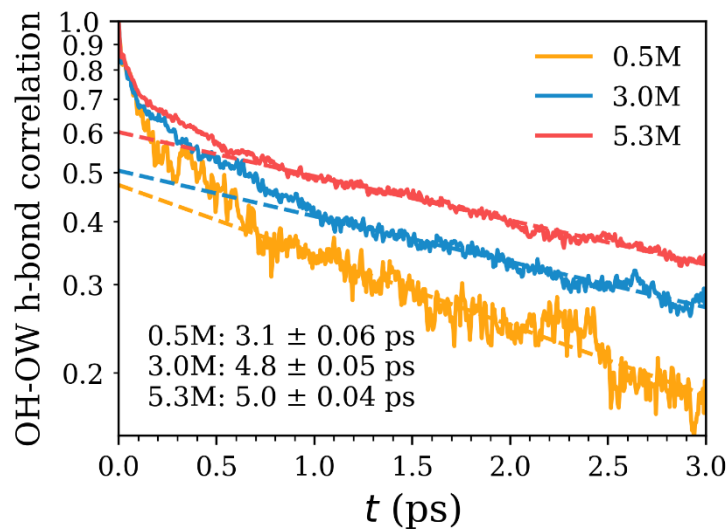


Figure S4. The hydronium-water (OH-OW) hydrogen bond (H-bond) correlation functions for sulfuric acid solution of three concentrations (0.54 M: orange line; 3.0 M: blue line; 5.3 M: red line). Here it is to be understood that “hydronium” refers to the hydronium-like hydrated excess proton structure. The intermediate time region ($1.0 \text{ ps} < t < 3.0 \text{ ps}$) was utilized to determine the lifetime of OH-OW H-bonds through single exponential fittings applied to the correlation functions. The fitting results are shown in dashed lines.

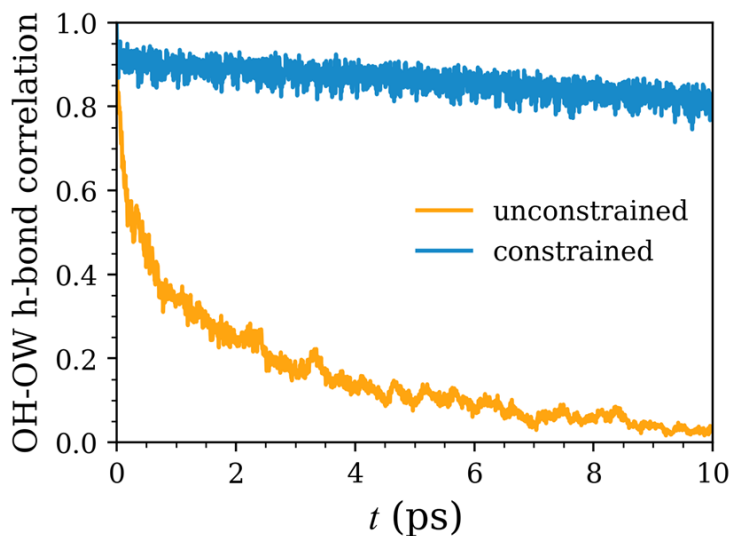


Figure S5. The correlation functions for the hydronium-water (OH-OW) hydrogen bonds (H-bonds) in a sulfuric acid solution with a concentration of 0.54 M are presented. The orange line represents the standard solution, namely the same as the orange line in Figure S4, while the blue line indicates the same concentration where all hydronium identities remain unchanged by imposing constraint on OH-HH bond lengths.

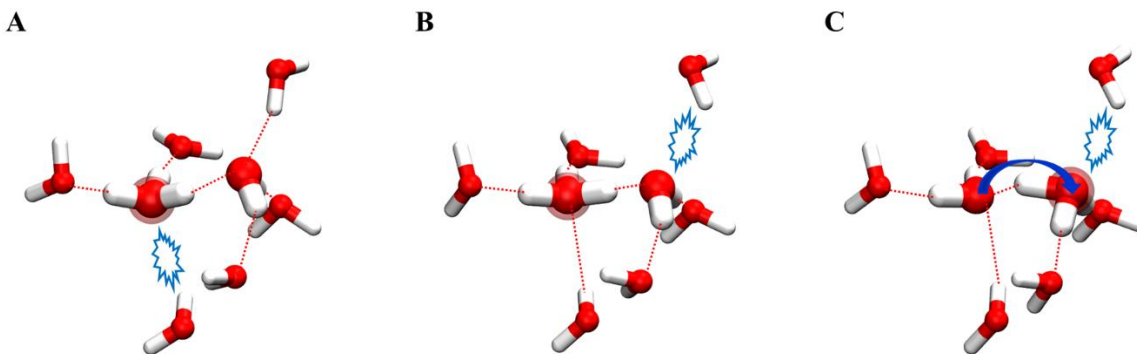


Figure S6. Representative snapshots of a typical proton transfer event with surrounding hydrogen bond network rearrangement. Oxygen atoms are shown in red, hydrogen atoms are in white, while hydronium oxygens are distinguished by an red shade. Hydrogen bonds formed between hydronium and water are indicated by red dashed lines, while broken hydrogen bonds are marked with sparkling stars. The arrow in (c) indicates the direction of proton transfer. (a) Before a hopping event, the initial hydronium does not form a hydrogen bond with a fourth water, as indicated by the blue spark. Here, the fourth water means the water which is going to form a hydrogen bond with the initial hydronium. (b) When a proton transfer event approaches, the fourth water moves closer to the initial hydronium and rotates to form a hydrogen bond. Meanwhile, one of the resulting hydronium's hydrogen bonds breaks, indicated by the blue spark. (c) Finally, a proton transfer event happens, the initial hydronium establishes a strong hydrogen bond with its fourth water, while the hydrogen bond between the resulting hydronium and its own fourth water is broken.

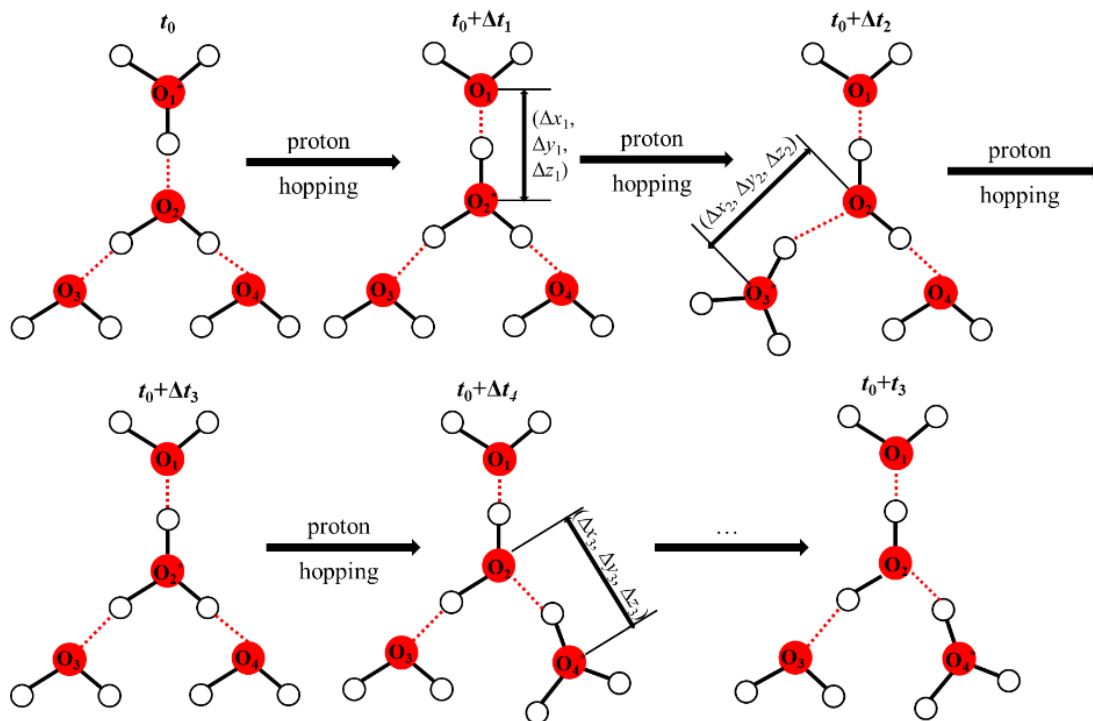


Figure S7. We calculate the mean square displacement (MSD) due to proton hopping within hydronium lifetimes. Here it is to be understood that “hydronium” refers to the hydronium-like hydrated excess proton structure. Given the similarity between calculated hydronium lifetimes and OHD-OKE t_3 values, we account for proton hopping events within the t_3 timescale—3.1 ps, 4.1 ps, and 5.1 ps for concentrations of 0.54 M, 3.0 M, and 5.3 M, respectively. For simplicity, we used 3.0 ps, 4.0 ps, and 5.0 ps. To estimate the MSD due to proton hopping events and exclude the proton rattling effect, we define an essential hopping step where a hydronium identity changes and does not revert. We sum the displacements of all essential hopping steps within t_3 to calculate MSD. For example, as shown in Figure S6, the hydronium identity changes as follows: $O1 \rightarrow O2 \rightarrow O3 \rightarrow O2 \rightarrow O4$. Although $O3$ has become hydronium oxygen after the excess proton hopping from $O2$ to it, the proton finally hops back to $O2$. Therefore, the hopping from $O2$ to $O3$ and $O3$ to $O2$ are not seen as essential hopping steps, and its related displacement, $(\Delta x_2, \Delta y_2, \Delta z_2)$, is not taken into account of the total displacement. Only the displacements happening of the essential hopping events $O1 \rightarrow O2$ and $O2 \rightarrow O4$ are taken into account. Therefore, the total displacement happening in the t_3 time length is $(\Delta x_1 + \Delta x_3, \Delta y_1 + \Delta y_3, \Delta z_1 + \Delta z_3)$, and the MSD is $(\Delta x_1 + \Delta x_3)^2 + (\Delta y_1 + \Delta y_3)^2 + (\Delta z_1 + \Delta z_3)^2$.

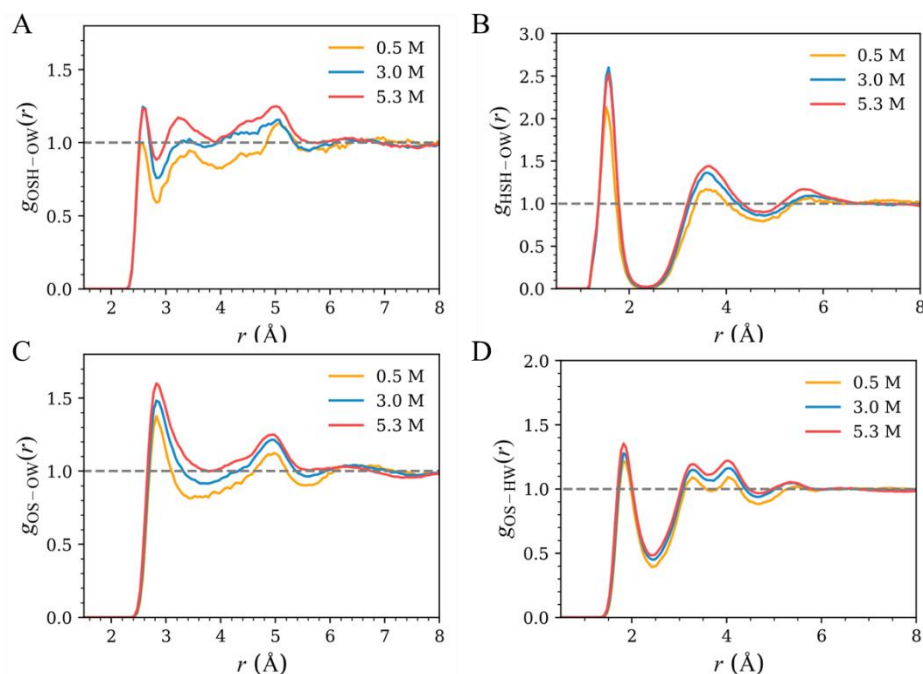


Figure S8. Radial distribution functions of (a) protonated bisulfate oxygen and water oxygen (OSH-OW), (b) the hydrogen in bisulfate oxygen and water oxygen (HSH-OW), (c) unprotonated bisulfate/sulfate oxygen and water oxygen (OS-OW), and (d) unprotonated bisulfate/sulfate oxygen and water hydrogen (OS-HW).

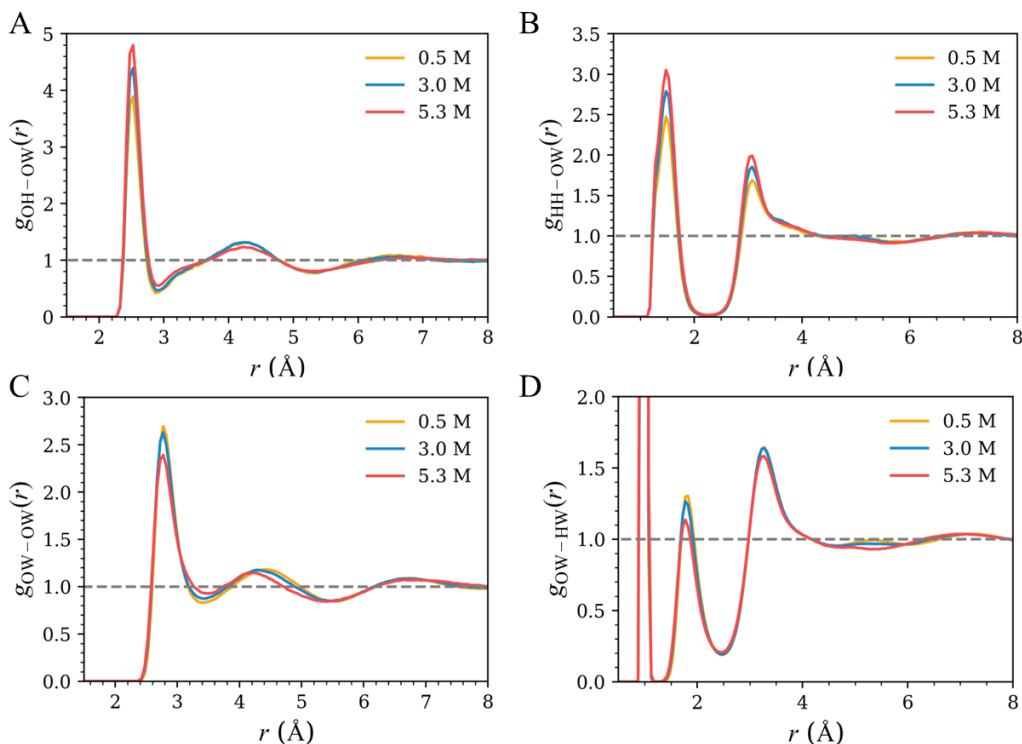


Figure S9. Radial distribution functions of (a) hydronium oxygen and water oxygen (OH-OW), (b) hydronium hydrogen and water oxygen (HH-OW), (c) water oxygen and water oxygen (OW-OW), and (d) water oxygen and water hydrogen (OW-HW). Here it is to be understood that “hydronium” refers to the hydronium-like hydrated excess proton structure.

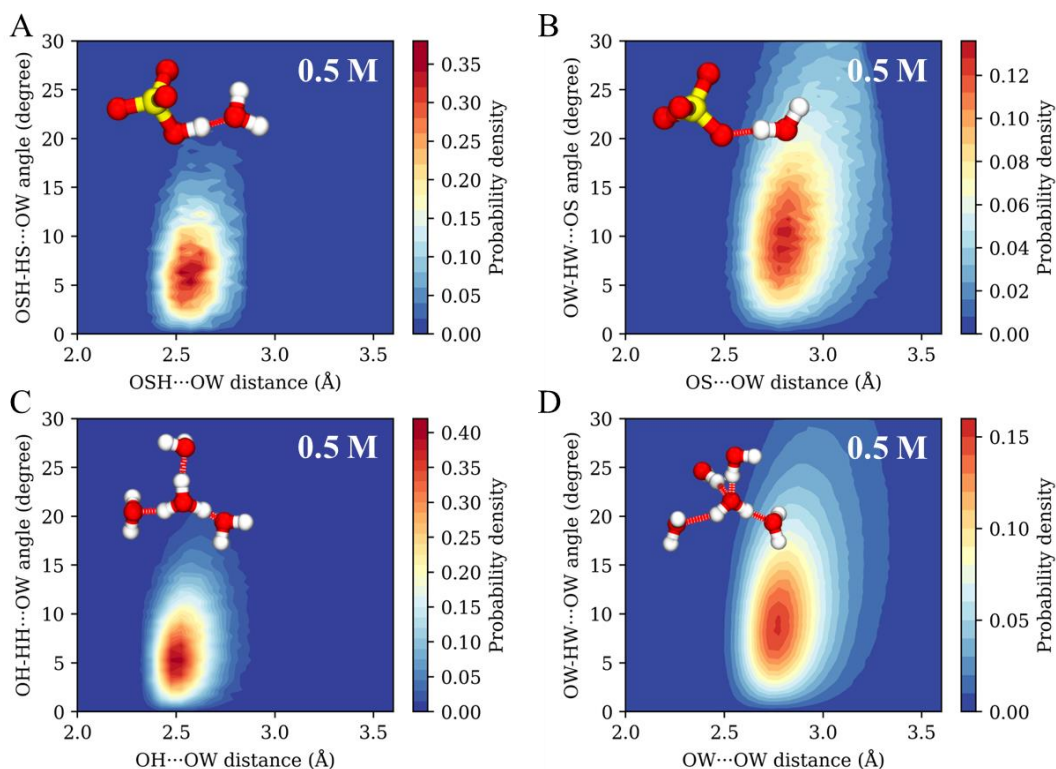


Figure S10. Probability density distribution plots for hydrogen bonds formed by (a) protonated oxygen in bisulfate and water, (b) unprotonated oxygen in bisulfate or sulfate and water, (c) hydronium and water, and (d) water and water, in 0.54 M sulfuric acid solutions. “OS” and “HS” represent oxygen atoms in sulfate or bisulfate and hydrogen atoms in bisulfate. “OH” and “HH” represent oxygen atoms and hydrogen atoms in hydronium. “OW” and “HW” represent oxygen atoms and hydrogen atoms in water. Representative configurations of each kind of hydrogen bonds are shown in the insets of each plot, where hydrogen bonds are highlighted in dashed red lines. Oxygen nuclei are in red, hydrogen nuclei are in white, and sulfur nuclei are in yellow. Here it is to be understood that “hydronium” refers to the hydronium-like hydrated excess proton structure.

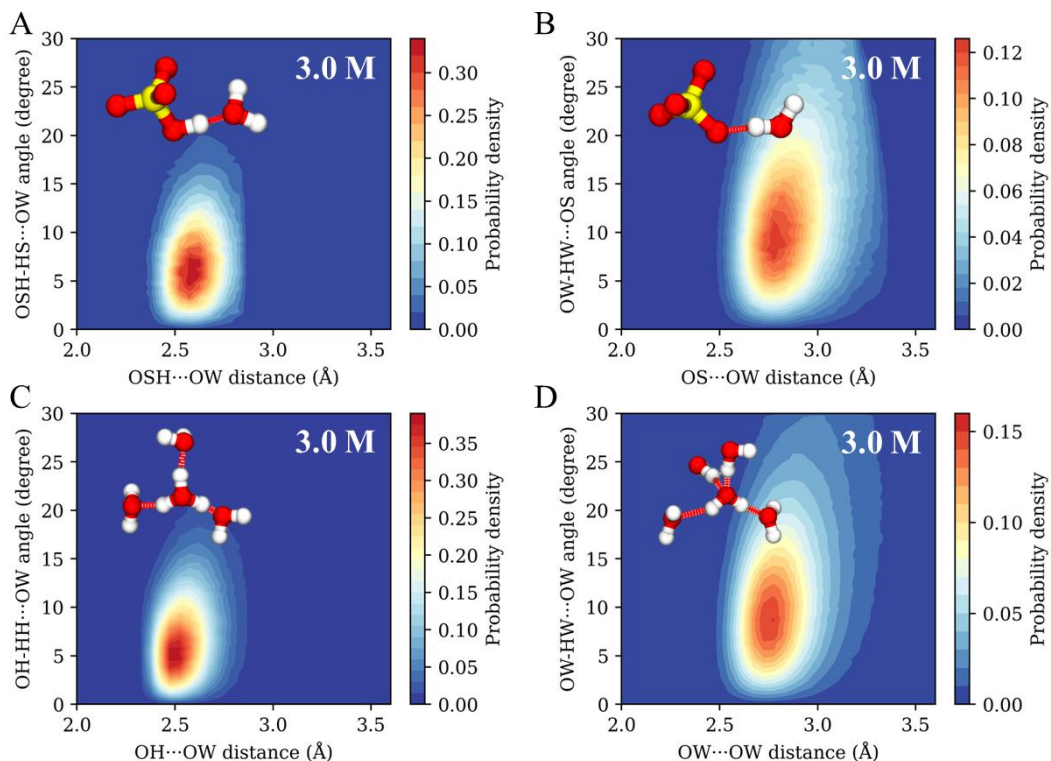


Figure S11. Probability density distribution plots for hydrogen bonds formed by (a) protonated oxygen in bisulfate and water, (b) unprotonated oxygen in bisulfate or sulfate and water, (c) hydronium and water, and (d) water and water, in 3.0 M sulfuric acid solutions. “OS” and “HS” represent oxygen atoms in sulfate or bisulfate and hydrogen atoms in bisulfate. “OH” and “HH” represent oxygen atoms and hydrogen atoms in hydronium. “OW” and “HW” represent oxygen atoms and hydrogen atoms in water. Representative configurations of each kind of hydrogen bonds are shown in the insets of each plot, where hydrogen bonds are highlighted in dashed red lines. Oxygen nuclei are in red, hydrogen nuclei are in white, and sulfur nuclei are in yellow. Here it is to be understood that “hydronium” refers to the hydronium-like hydrated excess proton structure.

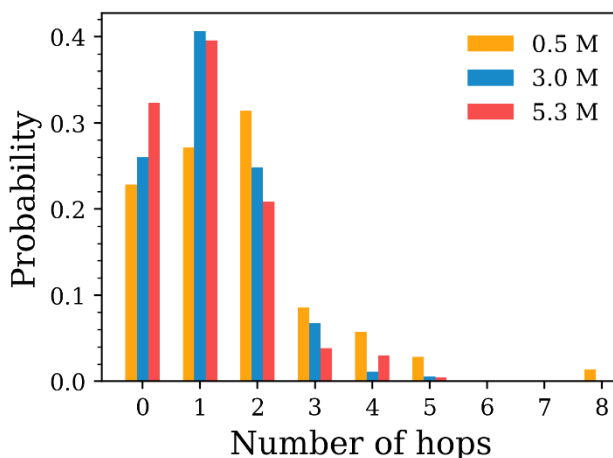


Figure S12. Probability distribution of numbers of hydronium proton hop events happening within hydronium lifetime in sulfuric acid solutions of different concentrations. Here it is to be understood that “hydronium” refers to the hydronium-like hydrated excess proton structure.

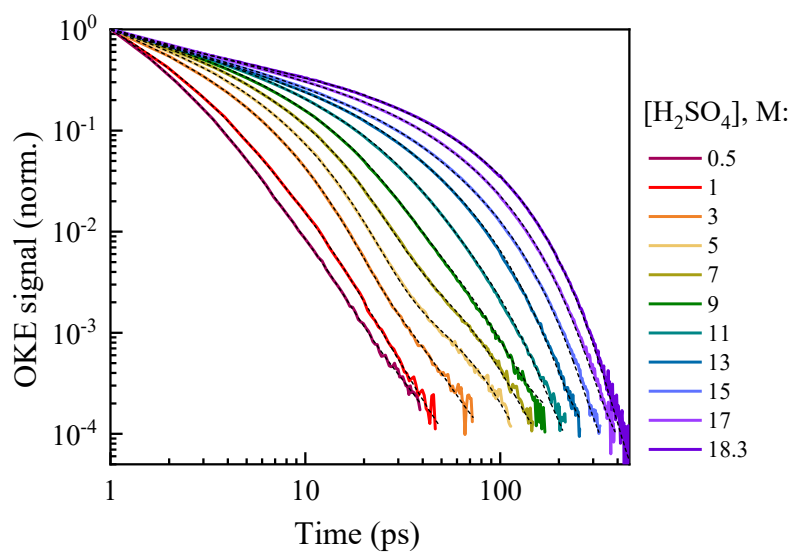


Figure S13. OHD-OKE decays of aqueous sulfuric acid solutions of various concentrations with fits to Eqn. 1 superimposed (black dashed lines).

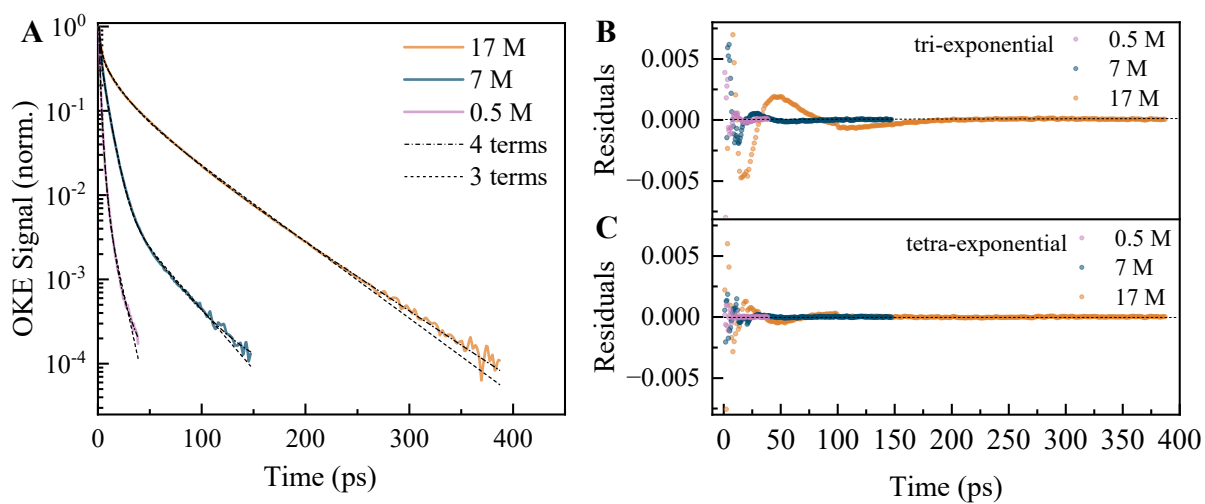


Figure S14. Comparison of multi-exponential fitting models. (a) Fits to tetra-exponential (dash-dot lines) and tri-exponential (dashed lines) models at low, intermediate, and high concentration. (b-c) Comparison of the residuals of the tri-exponential (b) and tetra-exponential (c) model fits showing better performance of the tetra-exponential model.

Tables

Concentration (M)	t_1 (ps)	t_2 (ps)	t_3 (ps)	t_4 (ps)
0	0.52	1.3	--	--
0.5	0.54 ±0.08	1.27 ±0.07	3.01 ±0.09	9.05 ±0.27
1	0.53 ±0.07	1.41 ±0.18	3.78 ±0.68	9.94 ±2.54
3	0.55 ±0.08	1.63 ±0.22	4.02 ±0.14	15.12 ±1.10
5.1	0.58 ±0.13	1.84 ±0.23	4.97 ±0.13	20.97 ±1.68
7	0.57 ±0.11	1.94 ±0.21	6.025 ±0.14	23.18 ±1.56
9	0.52 ±0.08	2.13 ±0.32	7.628 ±0.25	25.68 ±0.97
11	0.66 ±0.07	2.53 ±0.49	10.28 ±1.22	29.95 ±2.99
13	0.64 ±0.06	2.82 ±0.25	12.69 ±0.85	35.304 ±1.20
15	0.76 ±0.11	3.39 ±0.66	14.35 ±2.47	41.63 ±2.77
17	0.77 ±0.08	3.34 ±0.38	15.51 ±0.81	47.16 ±0.55
18.3	0.78 ±0.06	3.59 ±0.37	17.16 ±1.55	53.8 ±1.14

Table S1. Time constants obtained from tetra-exponential fits of the OHD-OKE decays of sulfuric acid solutions. Error bars were calculated from the standard deviation of triplicate experiments.

Concentration (M)	C_1 (a.u.)	C_2 (a.u.)	C_3 (a.u.)	C_4 (a.u.)
0	0.66	0.34	--	--
0.5	0.44 ±0.03	0.40 ±0.02	0.13 ±0.01	0.027 ±0.004
1	0.34 ±0.07	0.41 ±0.09	0.18 ±0.01	0.027 ±0.018
3	0.20 ±0.02	0.32 ±0.02	0.44 ±0.04	0.033 ±0.001
5.1	0.12 ±0.01	0.28 ±0.02	0.56 ±0.02	0.043 ±0.002
7	0.09 ±0.04	0.24 ±0.03	0.59 ±0.02	0.076 ±0.019
9	0.10 ±0.02	0.20 ±0.02	0.57 ±0.03	0.13 ±0.01
11	0.10 ±0.006	0.17 ±0.03	0.50 ±0.01	0.23 ±0.04
13	0.07 ±0.002	0.15 ±0.01	0.40 ±0.02	0.38 ±0.02
15	0.07 ±0.006	0.12 ±0.01	0.32 ±0.02	0.49 ±0.01
17	0.05 ±0.004	0.10 ±0.003	0.26 ±0.003	0.59 ±0.01
18.3	0.04 ±0.001	0.07 ±0.003	0.21 ±0.02	0.67 ±0.03

Table S2. Correlation coefficients obtained from tetra-exponential fits of the OHD-OKE decays of sulfuric acid solutions. Error bars were calculated from the standard deviation of triplicate experiments.

Supplemental References

1. Luzar, A.; Chandler, D., Structure and hydrogen bond dynamics of water–dimethyl sulfoxide mixtures by computer simulations. *J. Chem. Phys.* **1993**, 98 (10), 8160-8173.
2. Romero, M. Low Temperature Studies for the sulphuric acid decomposition step in the HyS and SI Thermochemical Cycles. PhD thesis, University of Sheffield, **2014**.
3. Das, A.; Dev, S.; Shangpliang, H.; Nonglait, K. L.; Ismail, K., Electrical Conductance and Viscosity of Concentrated H₂SO₄/H₂O Binary Systems at Low Temperatures: Correlation with Phase Transitions. *J. Phys. Chem. B.* **1997**, 101 (20), 4166-4170.