Supporting Information for

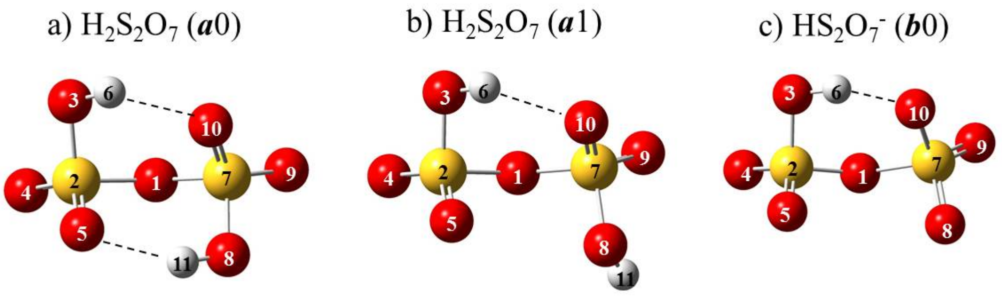
Disulfuric acid dissociated by two water molecules: Ab initio and density functional theory calculations

Seong Kyu Kim,[1,*] Han Myoung Lee,[2] Kwang S. Kim[2,*]

[1]*Department of Chemistry, Sungkyunkwan University, Suwon 440-746, Korea*

[2]*Center for Superfunctional Materials, Department of Chemistry, Ulsan Institute of Science and Technology (UNIST), Ulsan 689-798, Korea*

*Corresponding authors, skkim@skku.edu, kimks@unist.ac.kr



a) $H_2S_2O_7$ (***a***0) b) $H_2S_2O_7$ (***a***1) c) $HS_2O_7^-$ (***b***0)

Figure S1. Geometries of $H_2S_2O_7$ (a and b) and $HS_2O_7^-$ (c), optimized with SCS-MP2/aug-cc-pVTZ. For the $H_2S_2O_7$, ***a***0 is the geometry of the global minimum and ***a***1 is that of next lowest energy. Weak intramolecular H-bonds are shown with the broken straight lines. (This is a copy of Figure 1 in the main paper.)

Table S1. Selected geometry parameters, bond orders and energy values for the optimized $H_2S_2O_7$ and $HS_2O_7^-$. (This is an extended version of Table 1 in the main paper.)

	$H_2S_2O_7$		$HS_2O_7^-$
	***a*0**	***a*1**	***b*0**
bond length (Å);[a]			
O3-H6	0.9794	0.9774	0.9955
O8-H11	0.9794	0.9708	-
O10-H6	1.989	2.038	1.678
O1-S2	1.653	1.675	1.586
O1-S7	1.653	1.627	1.780
bond order;[b]			
O8-H11	0.676	0.682	-
O10-H6	0.013	0.002	0.060
O1-S2	0.666	0.704	0.784
O1-S7	0.666	0.617	0.485
S7-O8	0.835	0.825	1.264
angle (degree);[a]			
S2-O1-S7	117.6	120.3	121.3
S7-O8-O9-O10	25.0	26.8	22.8
O1-S7-O8-H11	-60.2	81.4	-
energy (hartree);[c]			
E_e	-1323.98347	-1323.97786	-1323.51836
ZPE	0.05540	0.05505	0.04300
energy (kcal/mol);[d]			
δE_e	0	3.15	-
δE_0	0	3.30	-
δH_{50K}	0	2.94	-
δH_{100K}	0	2.99	-
δH_{298K}	0	3.17	-
δG_{50K}	0	2.84	-
δG_{100K}	0	2.72	-
δG_{298K}	0	2.05	-
dipole moment (D);	2.137	2.267	1.790

[a] All the geometry values were obtained from SCS-MP2/aug-cc-pVTZ calculations.

[b] Wiberg bond order obtained from NBO analysis

[c] E_e is the electronic energy calculated with SCS-MP2/aug-cc-pVTZ. ZPE is the vibrational zero-point energy obtained from frequency analysis using the M062X/TZVP method.

[d] Relative to global minimum values. δE_e /δE_0 is the ZPE uncorrected/corrected internal energy relative to global minimum. δH_T and δG_T are the enthalpy and Gibbs free energy at temperature T relative to global minimum.

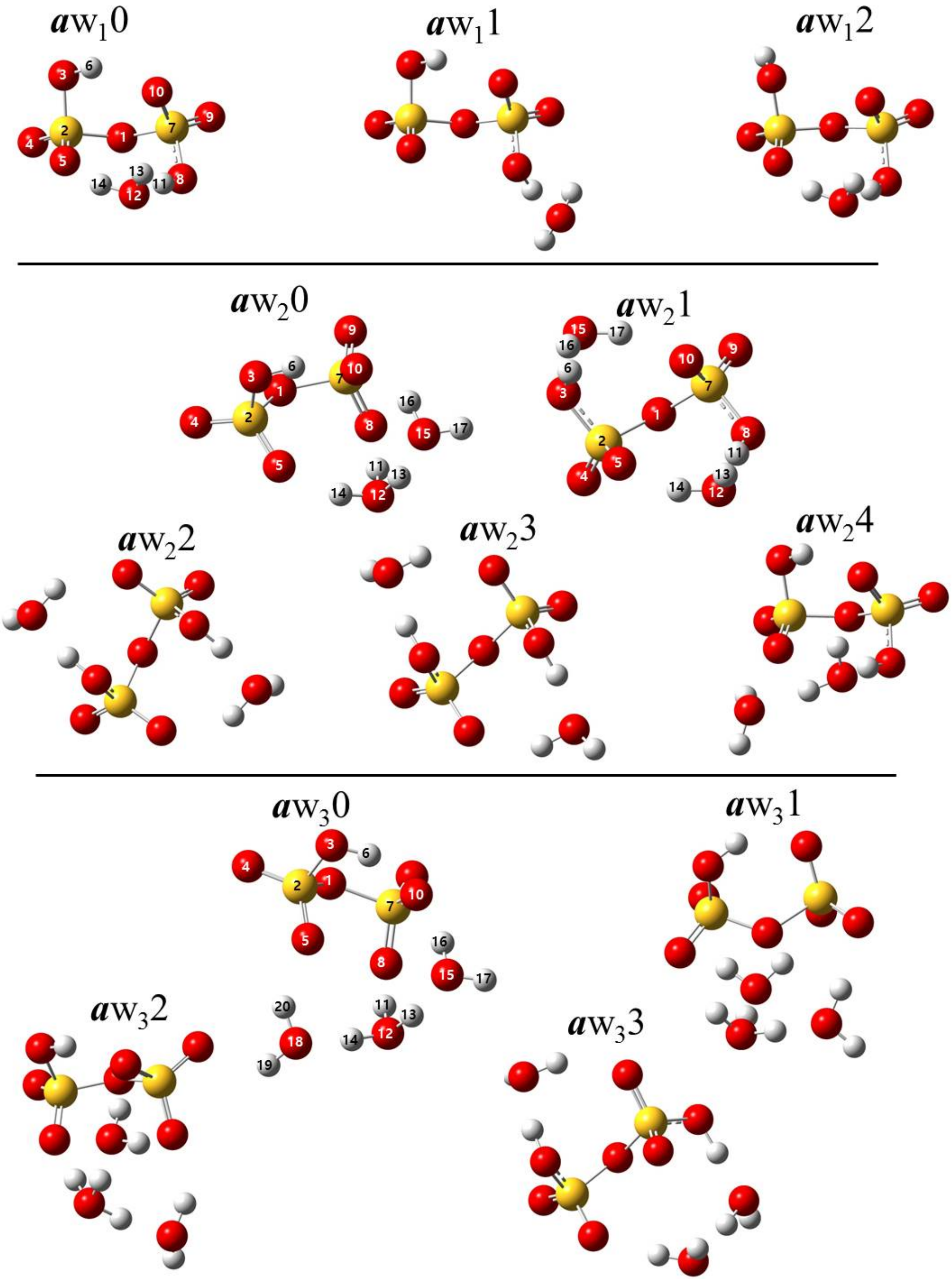


Figure S2. Geometries of $H_2S_2O_7(H_2O)_{1\text{-}3}$ low energy conformers, optimized with SCS-MP2/aug-cc-pVTZ. (This is a copy of Figure 2 in the main paper.)

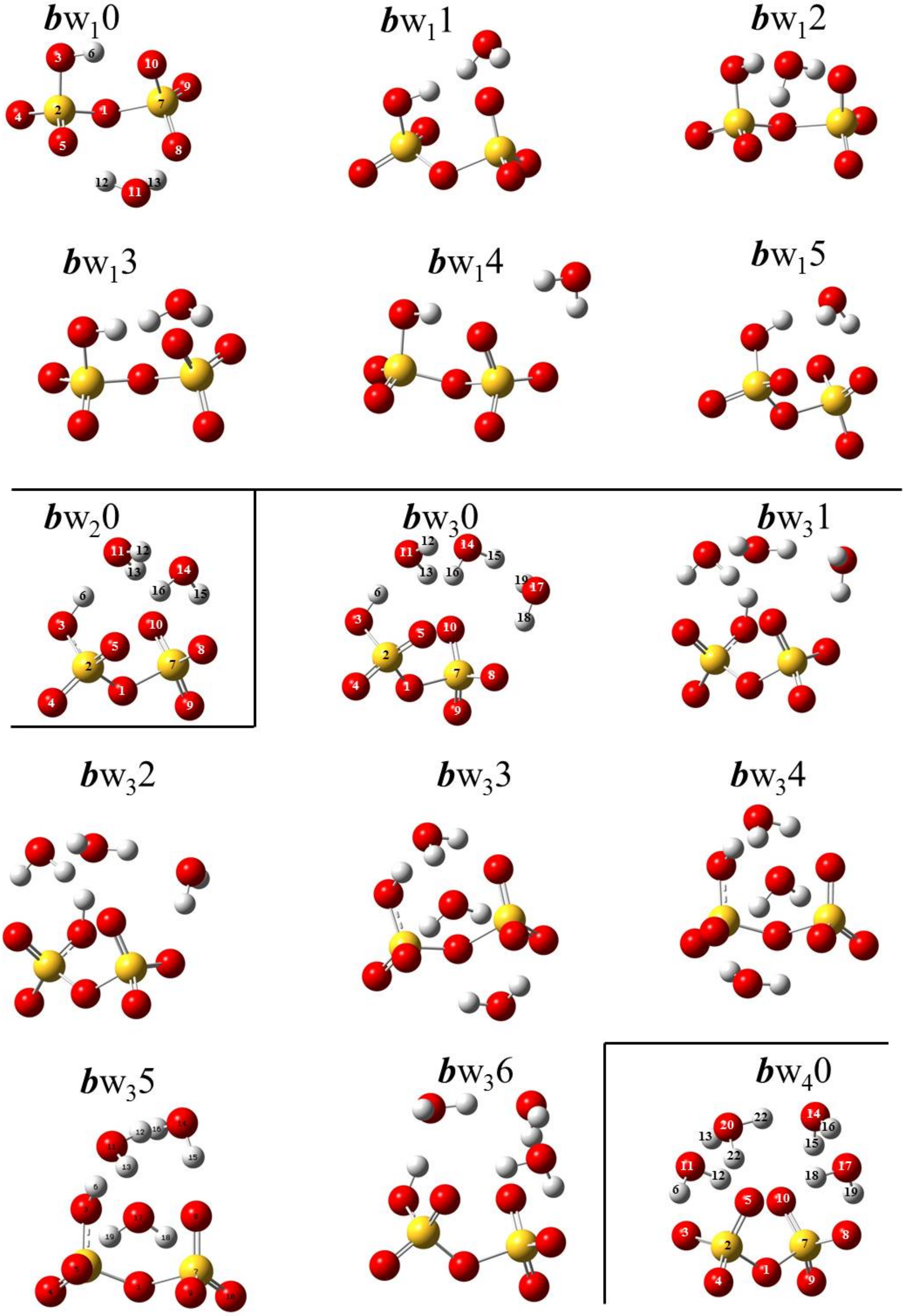


Figure S3. Geometries of $[HS_2O_7(H_2O)_{1\text{-}4}]^-$ low energy conformers, optimized with SCS-MP2/aug-cc-pVTZ. (This is an extended version of Figure 3 in the main paper.)

Table S2. Internal binding energy, enthalpy change and Gibbs free energy change for low energy conformers of $H_2S_2O_7(H_2O)_{1\text{-}3.}$ (This is an extended version of Table 2 in the main paper.)

	Binding energy [a]							Method for E_e [b]
	$-\Delta E_e(-\Delta E_0)$	$-\Delta H_{50K}$	$-\Delta H_{100K}$	$-\Delta H_{298K}$	$-\Delta G_{50K}$	$-\Delta G_{100K}$	$-\Delta G_{298K}$	
$H_2S_2O_7(H_2O)_1$;								
a$\mathrm{w}_1$0	12.9(11.1)	11.4	11.6	11.8	10.1	8.65	2.53	SCS-MP2/aug-cc-pVTZ
	12.6(10.8)	11.2	11.4	11.6	9.84	8.42	2.29	SCS-MP2/aug-cc-pVQZ
	14.0(12.2)	12.5	12.7	13.0	11.2	9.78	3.66	CCSD(T)/aug-cc-pVTZ
	12.5(10.7)	11.0	11.2	11.4	9.67	8.25	2.12	SCS-MP2/CBS
	13.7(11.8)	12.2	12.4	12.6	10.8	9.42	3.29	CCSD(T)/CBS
a$\mathrm{w}_1$1	10.1(8.44)	8.72	8.84	8.73	7.52	6.26	1.12	SCS-MP2/aug-cc-pVTZ
	9.90(8.27)	8.55	8.67	8.56	7.35	6.09	0.95	SCS-MP2/aug-cc-pVQZ
	10.7(9.05)	9.33	9.45	9.34	8.13	6.87	1.73	CCSD(T)/aug-cc-pVTZ
	9.78(7.79)	8.43	8.55	8.44	7.23	5.97	0.83	SCS-MP2/CBS
	10.4(8.79)	9.08	9.20	9.09	7.87	6.61	1.47	CCSD(T)/CBS
a$\mathrm{w}_1$2	10.0(8.24)	8.58	8.76	8.83	7.25	5.85	-0.07	SCS-MP2/aug-cc-pVTZ
	9.78(7.98)	8.32	8.50	8.57	7.00	5.59	0.33	SCS-MP2/aug-cc-pVQZ
	10.6(8.83)	9.17	9.35	9.42	7.84	6.44	0.52	CCSD(T)/aug-cc-pVTZ
	9.59(7.79)	8.13	8.32	8.38	6.81	5.40	0.52	SCS-MP2/CBS
	10.2(8.42)	8.76	8.95	9.01	7.44	6.03	0.11	CCSD(T)/CBS
$H_2S_2O_7(H_2O)_2$;								
a$\mathrm{w}_2$0 [c]	25.4(20.8)	21.5	22.0	22.7	18.8	15.8	2.88	SCS-MP2/aug-cc-pVTZ
	25.0(20.5)	21.2	21.6	22.4	18.4	15.5	2.52	SCS-MP2/aug-cc-pVQZ
	27.4(22.80)	23.5	24.0	24.7	20.7	17.8	4.86	CCSD(T)/aug-cc-pVTZ
	24.8(20.2)	20.9	21.4	22.1	18.1	15.2	2.26	SCS-MP2/CBS
	26.9(22.3)	23.0	23.5	24.2	20.2	17.3	4.33	CCSD(T)/CBS
a$\mathrm{w}_2$1 [d]	24.2(20.6)	21.3	21.7	22.0	18.6	15.7	3.53	SCS-MP2/aug-cc-pVTZ
	23.7(20.2)	20.8	21.2	21.5	18.1	15.3	3.08	SCS-MP2/aug-cc-pVQZ
	26.3(26.76)	23.4	23.8	24.1	20.7	17.9	5.67	CCSD(T)/aug-cc-pVTZ
	23.4(19.9)	20.5	20.9	21.2	17.8	15.0	2.76	SCS-MP2/CBS
	25.6(22.1)	22.7	23.1	23.4	20.0	17.2	4.98	CCSD(T)/CBS
a$\mathrm{w}_2$2 [d]	24.0(20.3)	21.0	21.4	21.7	18.3	15.4	3.04	SCS-MP2/aug-cc-pVTZ
	23.4(19.7)	20.4	20.8	21.1	17.7	14.8	2.45	SCS-MP2/aug-cc-pVQZ
	26.1(22.5)	23.1	23.5	23.8	20.4	17.5	5.17	CCSD(T)/aug-cc-pVTZ
	22.9(19.3)	20.0	20.4	20.7	17.2	14.4	2.02	SCS-MP2/CBS
	25.2(21.5)	22.2	22.6	22.9	19.5	16.6	4.25	CCSD(T)/CBS
a$\mathrm{w}_2$3 [d]	23.3(19.5)	20.2	20.6	20.9	17.4	14.5	1.93	SCS-MP2/aug-cc-pVTZ
	22.7(18.9)	19.6	20.0	20.4	16.9	13.9	1.36	SCS-MP2/aug-cc-pVQZ
	25.4(21.6)	22.3	22.7	23.0	19.5	16.6	4.02	CCSD(T)/aug-cc-pVTZ
	22.3(18.5)	19.2	19.6	20.0	16.4	13.5	0.95	SCS-MP2/CBS
	24.5((20.7)	21.4	21.8	22.2	18.6	15.7	3.14	CCSD(T)/CBS
a$\mathrm{w}_2$4	23.0(19.1)	19.8	20.2	20.9	17.1	14.2	1.58	SCS-MP2/aug-cc-pVTZ
	22.6(18.7)	19.4	19.8	20.5	16.7	13.9	1.36	SCS-MP2/aug-cc-pVQZ
	25.0(21.1)	21.8	22.3	22.9	19.1	16.2	3.61	CCSD(T)/aug-cc-pVTZ
	22.3(18.4)	19.0	19.5	20.1	16.3	13.5	0.84	SCS-MP2/CBS
	24.4(20.5)	21.2	21.6	22.3	18.5	15.6	2.96	CCSD(T)/CBS
$H_2S_2O_7(H_2O)_3$;								
a$\mathrm{w}_3$0 [c]	38.0(30.8)	31.8	32.5	33.4	22.7	23.3	4.06	SCS-MP2/aug-cc-pVTZ

aw$_3$1 [c]	37.0(29.9)	31.0	31.7	32.6	26.7	22.2	2.49	SCS-MP2/aug-cc-pVTZ
aw$_3$2 [c]	37.2(29.8)	30.8	31.5	32.4	26.7	22.2	2.83	SCS-MP2/aug-cc-pVTZ
aw$_3$3	35.6(28.3)	31.0	31.6	32.4	26.8	22.4	3.38	SCS-MP2/aug-cc-pVTZ

[a] Given in kcal/mol. ΔE_e is the difference of electronic energy (E_e) between the cluster and the individual molecules, while the difference of vibrational zero point energy (ZPE) is included for ΔE_0. For ΔH_T and ΔG_T, the difference of thermal correction at temperature T is included. No correction for basis set superposition error was made. The ZPE and thermal corrections were obtained from M062X/TZVP calculations.

[b] For $H_2S_2O_7(H_2O)_1$ and $H_2S_2O_7(H_2O)_2$ conformers, E_e values were also obtained from single point calculations with SCS-MP2/aug-cc-pVQZ and CCSD(T)/aug-cc-pVTZ for geometries optimized with SCS-MP2/aug-cc-pVTZ, and their corresponding binding energies are listed in the second and the third rows of each conformer section. For all conformers, binding energies calculated with SCS-MP2/aug-cc-pVTZ are listed in the first row of each conformer section.

[c] deprotonated geometry [d] C_2 symmetry.

Table S3. Internal binding energy, enthalpy change and Gibbs free energy change for low energy conformers of $[HS_2O_7(H_2O)_{1\text{-}4}]^-$. (This is an extended version of Table 3 in the main paper.)

	Binding energy [a]						
	$-\Delta E_e(-\Delta E_0)$	$-\Delta H_{50K}$	$-\Delta H_{100K}$	$-\Delta H_{298K}$	$-\Delta G_{50K}$	$-\Delta G_{100K}$	$-\Delta G_{298K}$
$[HS_2O_7(H_2O)_1]^-$;							
bw$_1$0	11.4(9.20)	9.52	9.68	9.57	8.18	6.77	0.96
bw$_1$1	10.6(8.11)	8.44	8.63	8.57	7.06	5.59	-0.54
bw$_1$2	10.7(7.99)	8.35	8.59	8.81	6.93	5.41	-1.16
bw$_1$3	9.86(7.78)	8.07	8.22	8.08	6.78	5.43	-0.14
bw$_1$4	9.70(7.59)	7.88	8.05	7.93	6.60	5.24	-0.38
bw$_1$5	7.07(9.74)	7.42	7.66	7.87	6.02	4.52	-1.96
$[HS_2O_7(H_2O)_2]^-$;							
bw$_2$0	25.8(20.2)	21.0	21.5	22.2	18.1	14.9	1.08
$[HS_2O_7(H_2O)_3]^-$;							
bw$_3$0	36.5(28.7)	29.7	30.5	31.3	25.5	20.9	0.93
bw$_3$1	35.5(28.1)	29.2	30.0	30.8	24.9	20.2	0.06
bw$_3$2 [c]	35.0(28.0)	29.1	29.9	31.0	24.8	20.1	-0.30
bw$_3$3	35.3(28.0)	29.0	29.7	30.2	24.8	20.3	0.94
bw$_3$4	35.8(27.9)	29.0	29.7	30.5	24.6	20.0	-0.23
bw$_3$5	34.9(27.6)	28.8	29.5	30.6	24.4	19.7	-0.89
bw$_3$6	35.5(27.6)	28.6	29.3	30.1	24.4	19.8	-0.04
$[HS_2O_7(H_2O)_4]^-$;							
bw$_4$0 [b]	48.5(37.8)	39.2	40.3	41.9	33.4	27.2	-0.35

[a] Refer to footnote of Table S2. [b] deprotonated geometry. [c] near deprotonated geometry

Table S4. Variation of selected geometry parameters.[a] (This supplements Figure 4 in the main paper.)

	lowest energy $H_2S_2O_7(H_2O)_n$					lowest energy $[HS_2O_7(H_2O)_{n,}]^-$ conformers					
	a0	***a***w$_1$0	(***a***w$_2$1)[e]	***a***w$_2$0	***a***w$_3$0	***b***0	***b***w$_1$0	***b***w$_2$0	***b***w$_3$0	(***b***w$_3$2)[e]	***b***w$_4$0
bond order;[b]											
O8-H11	0.676	0.561	0.576	0.144	0.109	-	-	-	-	-	-
O10-H6	0.013	0.018	0.000	0.027	0.025	0.060	0.060	0.001	0.001	0.000	0.000
O1-S2	0.666	0.682	0.660	0.747	0.753	0.784	0.785	0.779	0.768	0.767	0.676
O1-S7	0.666	0.646	0.660	0.566	0.561	0.485	0.489	0.495	0.517	0.514	0.609
S7-O8	0.835	0.890	0.876	1.102	1.118	1.264	1.230	1.191	1.193	1.171	1.148
charge;[c]											
HSO_4	-0.471	-0.497	-0.542	-0.546	-0.567	-0.657	-0.651	-0.678	-0.664	-0.678	-0.851
SO_3	-0.077	-0.135	-0.323	-0.323	-0.337	-0.343	-0.343	-0.363	-0.376	-0.375	-0.441
H	0.548	0.546	0.558	0.545	0.544	0.547	0.548	0.550	0.552	0.555	0.558
HS_2O_7	-0.548	-0.631	-0.680	-0.869	-0.904	-1.000	-0.994	-1.040	-1.040	-1.053	-1.262
H_3O	-	0.631	0.619	0.820	0.804	-	0.542	0.582	0.589	0.599	0.749
S7 orbital;[d]											
3s	0.92	0.91	0.91	0.91	0.90	0.91	0.91	0.90	0.90	0.90	0.90
3p+4p+5d	2.12	2.11	2.10	2.10	2.10	2.12	2.11	2.11	2.11	2.11	2.11
3d+4d	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18	0.18
Angle;											
S2-O1-S7	117.6	120.7	125.2	121.9	120.3	121.3	121.5	127.0	125.5	125.8	127.2
S7-O8-O9-O10	25.02	24.88	25.65	24.60	24.33	22.82	22.75	23.14	23.94	23.84	27.0

[a] Obtained with SCS-MP2/aug-cc-pVTZ calculations

[b] Wiberg bond order obtained from NBO analysis

[c] Sum of atomic charges from NBO analysis. HSO_4 means the sum of atomic charges of H6, S2, O3, O4, O5. SO_3 means the sum of atomic charges of S7, O8, O9, O10. H means the atomic charge of H6. HS_2O_7 means the sum of charges of O1 through O10. H_3O means the sum of charges of H11, O12, H13, H14 for $[H_2S_2O_7(H_2O)_n]$ or H6, O11, H12, H13 for $[HS_2O_7(H_2O)_n]^-$.

[d] Hybrid orbital character of S7

[e] ***a***w$_2$1 is listed since its energy is almost same as the lowest energy conformer. ***b***w$_3$2 is listed since H_6 is almost deprotonated.

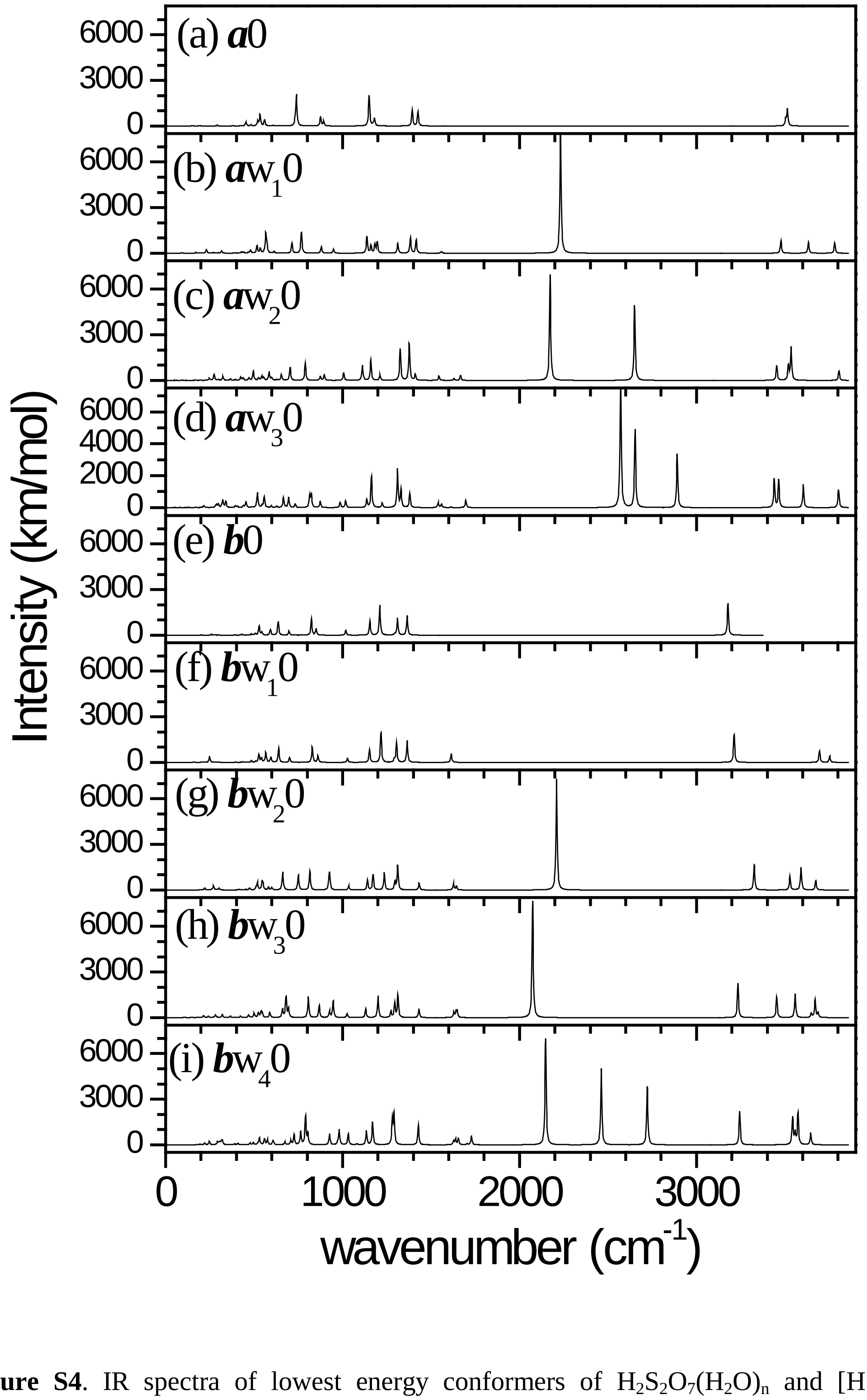


Figure S4. IR spectra of lowest energy conformers of $H_2S_2O_7(H_2O)_n$ and $[HS_2O_7(H_2O)_n]^-$, calculated with the M062X/TZVP method. (Frequency scale factor: 0.943)

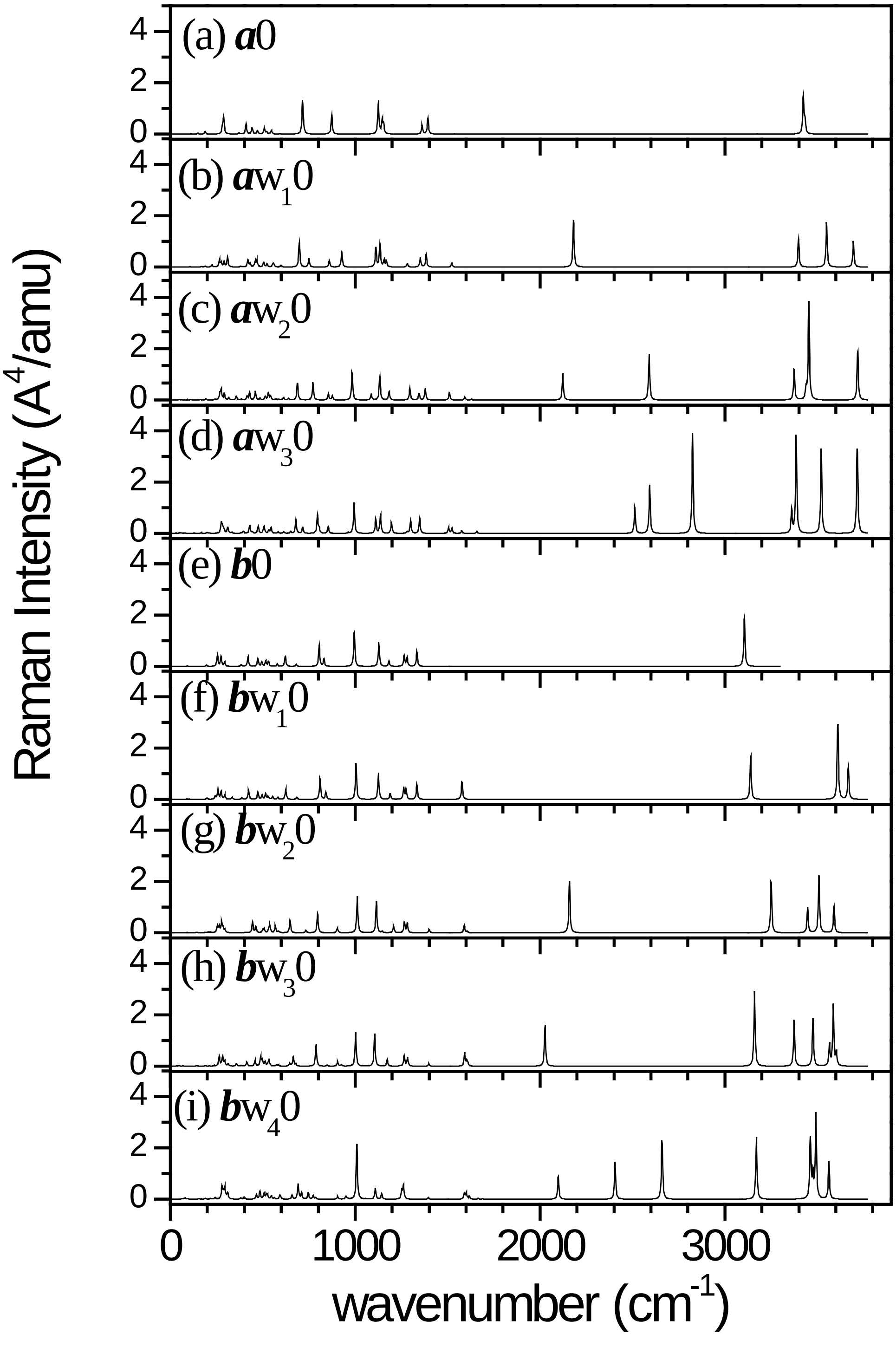


Figure S5. Raman spectra of lowest energy conformers of $H_2S_2O_7(H_2O)_n$ and $[HS_2O_7(H_2O)_n]^-$, calculated with the M062X/TZVP method. (Frequency scale factor: 0.943)

Table S5. Selected vibrations of lowest energy conformers of of $H_2S_2O_7(H_2O)_{0\text{-}3}$, calculated with the M062X/TZVP method.

conformer	cm^{-1}	IR/Raman activity [a]	depolarization ratio	mode assignment [b]	OH stret group [c]
a0	715	6/19	0.01	SOS def	
	745	60/2	0.75	SOS as stret	
	1123	52/2	0.75	(as) SOH bend	
	1361	30/6	0.75	(as) OSO as stret.	
	1393	27/11	0.30	(as) SOH bend + (as) OSO as stret	
	3424	12/43	0.03	(sy) OH stret	A
	3433	33/15	0.75	(sy) OH stret	A
a$w_1$0	697	19/14	0.02	SOS def	
	750	41/5	0.10	SOS as stret	
	1112	33/13	0.06	SOH bend + OSO as stret	
	2181	253/40	0.29	O-H--O as stret	B
	3398	24/32	0.16	OH stret	A
	3549	22/54	0.13	OH stret	C
	3694	19/32	0.40	HOH as stret.	C
a$w_2$0	687	25/10	0.06	SOS def + H_2O wag	
	771	33/10	0.05	SOS as stret + H_2O wag	
	1132	40/15	0.10	SO_3 sy stret + SOH wag	
	1295	61/8	0.57	SO_3 as stret + H_3O umb	
	1346	74/5	0.60	H_3O umb	
	2123	203/22	0.61	O-H--O as stret	D
	2590	147/43	0.20	H_3O sy stret	D
	3375	28/36	0.22	OH stret	A
	3439	29/12	0.57	(as) OH stret (H_3O)	D
	3454	66/118	0.16	(sy) OH stret	C
	3718	19/63	0.32	HOH as stret	C
a$w_3$0	795	22/11	0.03	SOS as stret + H_2O wag	
	993	13/19	0.01	SO_3 sy stret	
	1136	59/12	0.15	SOH bend	
	1280	70/1	0.54	H_3O umb	
	2512	266/25	0.73	O-H--O as stret	D
	2592	144/45	0.53	H_3O as stret	D
	2825	98/97	0.12	H_3O sy stret	D
	3361	53/26	0.62	OH stret	A
	3385	51/112	0.15	OH stret	C
	3512	42/101	0.19	OHO sy stret	C
	3714	16/57	0.35	OHO as stret	C
	3716	19/61	0.32	OHO as stret	C

[a] IR activity in 10 km/mol and Raman activity in (A^4/amu).

[b] as: antisymmetric, sy: symmetric, stret: stretching, bend: bending, def: deformation, wag: wagging, umb: umbrella. When as or sy notation is given in front of a motion (stret, bend), it means the internal coordinate of that motion is antisymmetric or symmetric. When as or sy notation is given in parenthesis in front of atoms in motion, it means two groups of atoms move antisymmetrically or symmetrically.

[c] group A: O-H stretching in acid, group B: O-H--O antisymmetric stretching in between acid and water, group C: O-H stretching in water(s), group D: H_3O stretching

Table S6. Selected vibrations of lowest energy conformers of of $[HS_2O_7(H_2O)_{0\text{-}4}]^-$, calculated with the M062X/TZVP method.

conformer	cm^{-1}	IR/Raman activity [a]	depolarization ratio	mode assignment [b]	OH stret group [c]
***b*0**	805	31/12	0.04	SOS as stret	
	994	10/22	0.01	SO_3 sy stret	
	1128	27/15	0.09	OSO sy stret	
	3105	62/53	0.22	OH stret	A
***b*w$_1$0**	810	31/13	0.02	SOS as stret	
	1004	8/23	0.02	SO_3 sy stret	
	1125	24/17	0.07	OSO sy stret	
	3139	55/48	0.21	OH stret	A
	3611	22/95	0.15	HOH sy stret	C
	3667	12/41	0.40	HOH as stret.	C
***b*w$_2$0**	797	37/12	0.05	SOS as stret	
	1011	8/22	0.02	SO_3 sy stret	
	1114	19/20	0.08	SO_3 as stret + SOH wag	
	2159	215/43	0.21	O-H--O as stret	B
	3249	51/59	0.17	O-H--O as stret	C
	3447	27/29	0.26	OH stret	C
	3509	46/71	0.21	OH stret	C
	3590	19/33	0.29	HOH as stret	C
***b*w$_3$0**	788	40/13	0.04	SOS as stret	
	1002	8/21	0.02	SO_3 sy stret	
	1104	17/20	0.09	SO_3 sy stret + SOH wag	
	2026	229/34	0.17	O-H--O as stret	B
	3161	66/81	0.17	OH stret	C
	3375	40/54	0.22	OH stret	C
	3477	47/58	0.28	OH stret	C
	3566	8/26	0.13	HOH syn stret	C
	3587	35/75	0.21	OH stret	C
	3603	9/17	0.54	HOH as stret	C
***b*w$_4$0**	1009	21/34	0.01	SO_3 sy stret + SO stret	
	2098	210/19	0.49	O-H--O as stret	D
	2405	149/33	0.70	H_3O as stret	D
	2660	116/57	0.06	H_3O sy stret	D
	3170	64/66	0.19	OH stret	C
	3461	14/21	0.71	(as) OH stret	C
	3463	41/54	0.13	(sy) OH stret	C
	3477	22/27	0.51	OH as stret	C
	3492	63/102	0.15	(sy) OH stret	C
	3563	23/44	0.30	OH stret	C

[a,b,c] Refer to footnotes in Table S5.