Table S1. Force field parameters for Coulomb and Lennard-Jones potentials. Subscript abbreviations: W=water, HYD=hydronium ion, AMM=ammonia, AUM=ammonium ion, SA=sulfuric acid, HS=hydrogensulfate ion, DMI=dimethylammonium ion
(/H, /free = oxygen atom with or without hydrogen atom, respectively)
(/N, /C = hydrogen atom attached to N or C atom, respectively).

Atom	**q [e]**	**σ [Å]**	**ε [kJ mol^{-1}]**
O_W	-0.8476 [a]	3.166 [a]	0.6502 [a]
H_W	0.4238 [a]	0.00 [a]	0.0000 [a]
O_{HYD}	-0.4166 [b]	3.234 [b]	0.6200 [b]
H_{HYD}	0.4722 [b]	0.00 [b]	0.0000 [b]
N_{AMM}	-0.90	3.25 [c]	0.71128 [c]
H_{AMM}	0.30	2.50 [c]	0.12552 [c]
N_{AUM}	-0.76	3.25 [c]	0.71128 [c]
H_{AUM}	0.44	2.50 [c]	0.12552 [c]
S_{SA}	1.10	3.55 [c]	1.04600 [c]
$O_{SA/free}$	-0.46	3.00 [c]	0.71176 [c]
$O_{SA/H}$	-0.53	3.00 [c]	0.71176 [c]
H_{SA}	0.44	0.00 [c]	0.00000 [c]
S_{HS}	1.27	3.55 [c]	1.04600 [c]
$O_{HS/free}$	-0.67	3.00 [c]	0.71176 [c]
$O_{HS/H}$	-0.64	3.00 [c]	0.71176 [c]
H_{HS}	0.38	0.00 [c]	0.00000 [c]
N_{DMI}	-0.12	3.25 [c]	0.71128 [c]
$H_{DMI/N}$	0.31	2.50 [c]	0.12550 [c]
C_{DMI}	-0.20	3.50 [c]	0.27614 [c]
$H_{DMI/C}$	0.15	2.50 [c]	0.12552 [c]

[a] Berendsen, H. J. C., Grigera, J. R., and Straatsma, T. P.: The missing term in effective pair potentials, J. Phys. Chem., 91, 6269–6271, 1987.
[b] Dang, L.: Solvation of the hydronium ion at the water liquid/vapor interface, J. Chem. Phys., 119, 6351-6353, 2003.
[c] Canongia Lopes, J. N., Pádua, A. A. H., and Shimizu, K.: Molecular Force Field for Ionic Liquids IV: Trialkylimidazolium and Alkoxycarbonyl-Imidazolium Cations; Alkylsulfonate and Alkylsulfate Anions, J. Phys. Chem. B, 112, 5039-5046, 2008.

Table S2. Force field parameters for OPLS-AA bond strengths.
Subscript abbreviations: W=water, HYD=hydronium ion, AMM=ammonia, AUM=ammonium ion, SA=sulfuric acid, HS=hydrogensulfate ion, DMI=dimethylammonium ion
(/H, /free = oxygen atom with or without hydrogen atom, respectively)
(/N, /C = hydrogen atom attached to N or C atom, respectively).

Bonds	**r_e [Å]**	**k_e [kJ mol^{-1}Å^{-2}]**
O_W-H_W	1.000 [a]	4637 [a]
O_{HYD}-H_{HYD}	0.969 [a]	4030 [a]
N_{AMM}-H_{AMM}	1.003 [a]	3864.0 [a]
N_{AUM}-H_{AUM}	1.013 [a]	3660.3 [a]
S_{SA}-$O_{SA/free}$	1.411 [b]	6258.0 [c]
S_{SA}-$O_{SA/H}$	1.571 [b]	3083.8 [c]
S_{HS}-$O_{HS/free}$	1.438 [b]	5239.9 [c]
S_{HS}-$O_{HS/H}$	1.634 [b]	2328.3 [c]
O_{HS}-H_{HS}	0.949 [b]	4561.1 [c]
N_{DMI}-C_{DMI}	1.499 [a]	3071 [a]
H_{DMI}-N_{DMI}	1.010 [a]	3632 [a]

[a] computed using HF/6-31G* with scaling factor 0.899
[b] geometry from HF/6-31G(d),
[c] computed using HF/6-31G(d), scaled by 0.899^2

Table S3. Force field parameters for OPLS-AA bond angles.
Subscript abbreviations: W=water, HYD=hydronium ion, AMM=ammonia, AUM=ammonium ion, SA=sulfuric acid, HS=hydrogensulfate ion, DMI=dimethylammonium ion
(/H, /free = oxygen atom with or without hydrogen atom, respectively)
(/N, /C = hydrogen atom attached to N or C atom, respectively).

Angle	**θ [degrees]**	**k_0 [kJ mol^{-1}]**
H_W-O_W-H_W	109.4 [a]	383.0 [a]
H_{HYD}-O_{HYD}-H_{HYD}	113.1 [a]	451.4 [a]
H_{AMM}-N_{AMM}-H_{AMM}	107.18 [b]	334.01 [a]
H_{AUM}-N_{AUM}-H_{AUM}	109.47 [a]	518.26 [a]
$O_{SA/free}$-S_{SA}-$O_{SA/free}$	123.69 [b]	224.37 [c]
$O_{SA/H}$-S_{SA}-$O_{SA/free}$	107.32 [b]	364.56 [c]
$O_{SA/H}$-S_{SA}-$O_{SA/H}$	101.79 [b]	608.15 [c]
H_{SA}-$O_{SA/H}$-S_{SA}	110.50 [b]	396.82 [c]
$O_{HS/free}$-S_{HS}-$O_{HS/free}$	114.76 [b]	456.97 [c]
$O_{HS/H}$-S_{HS}-$O_{HS/free}$	103.45 [b]	814.48 [c]
H_{HS}-$O_{HS/H}$-S_{HS}	106.39 [b]	398.12 [c]
C_{DMI}-N_{DMI}-C_{DMI}	114.3 [b]	418.4 [d]
$H_{DMI/N}$-N_{DMI}-C_{DMI}	109.2 [b]	418.4 [d]
$H_{DMI/C}$-C_{DMI}-N_{DMI}	108.5 [b]	209.2 [d]
$H_{DMI/N}$-N_{DMI}-$H_{DMI/N}$	105.5 [b]	292.9 [d]

[a] computed using HF/6-31G* with scaling factor 0.899
[b] geometry from HF/6-31G(d) calculation
[c] computed using HF/6-31G(d), scaled by 0.899^2
[d] force constants from Rizzo, R. C. and Jorgensen, W. L.:
OPLS All-Atom Model for Amines: Resolution of the Amine Hydration Problem, J. Am. Chem. Soc., 121, 4827-4836, 1999.

Table S4. Force field parameters for OPLS-AA dihedral angles.
Subscript abbreviations: W=water, HYD=hydronium ion, AMM=ammonia, AUM=ammonium ion, SA=sulfuric acid, HS=hydrogensulfate ion, DMI=dimethylammonium ion
(/H, /free = oxygen atom with or without hydrogen atom, respectively)
(/N, /C = hydrogen atom attached to N or C atom, respectively).

Dihedral angle	V_1	V_2	V_3	V_4
$O_{SA/free}$-S_{SA}-$O_{SA/H}$-H_{SA}	0.0000	0.0000	0.0000	0.0000
$O_{SA/H}$-S_{SA}-$O_{SA/H}$-H_{SA}	-15.8628	-7.7970	2.3399	0.0000
$O_{HS/free}$-S_{HS}-$O_{SH/H}$-H_{HS}	0.0000	0.0000	0.0000	0.0000
$H_{DMI/C}$-C_{DMI}-N_{DMI}-$H_{DMI/N}$	0.0000	0.0000	0.0000	0.0000
$H_{DMI/C}$-C_{DMI}-N_{DMI}- C_{DMI}	0.0000	0.0000	3.3765	0.0000

Table S5a. The anharmonic (anharm) and harmonic (harm) frequencies, the ratios of these and the corresponding scaling factors obtained as an average of the ratios for all the free molecules in the study.

complex	anharm[a]	harm[b]	anharm / harm	scaling factor		complex	anharm[c]	harm[b]	anharm / harm	scaling factor
water[†]	1572.787	1566.849	1.003790	0.99079		sulfuric acid[†]	236.514	278.155	0.850297	0.99732
	3620.946	3658.622	0.989702				299.000	347.960	0.859295	
	3743.605	3824.327	0.978893				338.993	367.639	0.922082	
							394.270	431.617	0.913472	
ammonia	968.205	948.827	1.020424	0.98543			467.696	433.546	1.078768	
	1603.993	1630.076	0.983999				512.930	471.761	1.087268	
	1604.013	1630.732	0.983615				523.836	492.909	1.062744	
	3324.787	3409.962	0.975022				764.944	696.199	1.098743	
	3459.539	3548.630	0.974894				807.781	764.032	1.057261	
	3459.550	3549.678	0.974609				1145.336	1056.383	1.084205	
							1148.425	1174.666	0.977661	
dimethylamine	226.059	240.239	0.940977	1.00964			1166.732	1246.192	0.936238	
	265.985	252.002	1.055488				1417.091	1327.225	1.067709	
	385.423	374.270	1.029799				3552.058	3614.399	0.982752	
	756.730	650.839	1.162700				3556.261	3623.887	0.981339	
	929.450	888.239	1.046396							
	1011.843	1008.945	1.002872							
	1073.897	1046.927	1.025761							
	1144.918	1118.571	1.023554							
	1154.327	1118.791	1.031763							
	1229.867	1227.947	1.001564							
	1393.093	1392.670	1.000304							
	1418.146	1423.628	0.996149							
	1425.893	1429.165	0.997711							
	1439.577	1439.307	1.000187							
	1454.174	1470.503	0.988896							
	1463.350	1468.069	0.996786							
	1464.129	1448.244	1.010969							
	2846.132	2861.000	0.994803							
	2856.078	2869.764	0.995231							
	2967.274	2995.634	0.990533							
	2970.656	2999.810	0.990281							
	3015.713	3056.379	0.986695							
	3015.852	3051.928	0.988179							
	3368.046	3458.523	0.973839							

[a]calculated at the MP2/aug-cc-pVTZ level of theory
[b]calculated at the BLYP/DZP level of theory
[c]calculated at the MP2/aug-cc-pV(T+d)Z level of theory
[†]anharmonic frequencies from Kurtén, T., Noppel, M., Vehkamäki, H., Salonen, M., and Kulmala, M.: Quantum chemical studies of hydrate formation of H_2SO_4 and $H_2SO_4^-$, Boreal Environ. Res., 12, 431-453, 2007.

Table S5b. The anharmonic (anharm) and harmonic (harm) frequencies, the ratios of these and the corresponding scaling factors obtained as an average of the ratios for all mono- and dihydrates of sulfuric acid.

complex	anharm[a]	harm[b]	anharm / harm	scaling factor		complex	anharm[a]	harm[b]	anharm / harm	scaling factor
monohydrate	42.146	88.639	0.475480	0.90305		dihydrate	24.571	96.285	0.255191	0.84271
of sulfuric	111.976	211.265	0.530028			of sulfuric	40.134	103.357	0.388305	
acid	166.186	245.007	0.678291			acid	117.328	224.669	0.522226	
	207.775	282.675	0.735030				122.427	263.137	0.465260	
	239.724	298.504	0.803086				179.470	315.442	0.568948	
	280.650	343.465	0.817113				181.700	276.882	0.656235	
	347.192	388.616	0.893407				202.620	271.986	0.744966	
	389.700	457.978	0.850915				208.956	325.042	0.642858	
	456.157	460.430	0.990720				279.529	366.827	0.762019	
	496.392	475.724	1.043446				281.068	394.748	0.712019	
	513.645	490.415	1.047369				367.463	445.456	0.824915	
	524.672	681.391	0.770001				392.760	460.288	0.853292	
	747.410	802.726	0.931090				475.340	483.845	0.982422	
	768.184	708.551	1.084161				483.530	474.390	1.019267	
	851.753	937.107	0.908918				489.340	754.878	0.648237	
	1152.514	1186.428	0.971415				521.129	514.876	1.012144	
	1157.388	1033.084	1.120323				531.088	715.607	0.742150	
	1325.355	1278.739	1.036455				760.008	893.263	0.850822	
	1415.081	1500.907	0.942817				767.353	849.747	0.903037	
	1577.944	1577.408	1.000340				800.888	770.289	1.039725	
	2952.250	2847.791	1.036681				855.318	918.851	0.930856	
	3544.724	3416.078	1.037659				1146.327	1024.735	1.118657	
	3560.141	3611.292	0.985836				1276.031	1171.983	1.088779	
	3696.444	3762.207	0.982520				1310.676	1380.310	0.949552	
							1410.153	1442.995	0.977240	
							1581.357	1563.219	1.011603	
							1581.971	1574.202	1.004935	
							2982.259	2855.580	1.044362	
							2995.663	2888.370	1.037147	
							3525.475	3366.552	1.047207	
							3528.257	3388.203	1.041336	
							3692.712	3757.829	0.982672	
							3693.161	3764.344	0.981090	

[a]calculated at the MP2/aug-cc-pV(T+d)Z level of theory
[b]calculated at the BLYP/DZP level of theory
[†]anharmonic frequencies from Kurtén, T., Noppel, M., Vehkamäki, H., Salonen, M., and Kulmala, M.: Quantum chemical studies of hydrate formation of H_2SO_4 and $H_2SO_4^-$, Boreal Environ. Res., 12, 431-453, 2007.

Table S6. The scaling factors s, used for the entropy and the translational, rotational and vibrational parts of the enthalpy, the deviation from unity of these scaling factors (x) and the scaling factors s_{ZPE} used for zero-point vibrational energy calculations.

complex	s	$x = 1 - s$	$s_{ZPE} = 1 - 0.5x$
water	0.99079	0.00921	0.99540
ammonia	0.98543	0.01457	0.99271
dimethylamine	1.00964	-0.00964	1.00482
sulfuric acid	0.99732	0.00268	0.99866
monohydrate of sulfuric acid[a]	0.90305	0.09695	0.95152
dihydrate of sulfuric acid[b]	0.84271	0.15729	0.92136

[a]for other dimer structures ($(H_2SO_4)_2$, $H_2SO_4 \bullet NH_3$ and $H_2SO_4 \bullet (CH_3)_2NH$) the scaling factors of the monohydrate were used

[b]for larger structures the scaling factors of dihydrate were used