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Electron-induced chemistry in microhydrated sulfuric acid clusters

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S1 Experimental setup

The experiments were performed on a versatile and unique experimental apparatus CLUB (cluster beam apparatus) which allows a variety of different experiments with a molecular beam of isolated clusters in vacuum. The apparatus and experiments have been described in numerous publications previously (e.g., mass spectrometry: (Lengyel et al., 2012; Kočišek et al., 2013a; Kočišek et al., 2013b); electron attachment: (Kočišek et al., 2016a; Kočišek et al., 2016b; Lengyel et al., 2016); etc.) and the details can be found in these references. The sketch of the CLUB apparatus is shown in Fig. S1 below. In the present work, the clusters were produced in the first vacuum chamber by supersonic expansion of the sulfuric acid vapor with buffer gas He, i.e. a mixture of H_2SO_4, H_2O and He gas phase molecules. The present mass spectrometry was performed in the 4th vacuum chamber TOFMS, where the cluster beam was crossed by a low-energy electron beam. Further details are given in the experimental section of the present paper. The other options and features of the CLUB apparatus shown in Fig. S1 were not exploited in the present experiments.

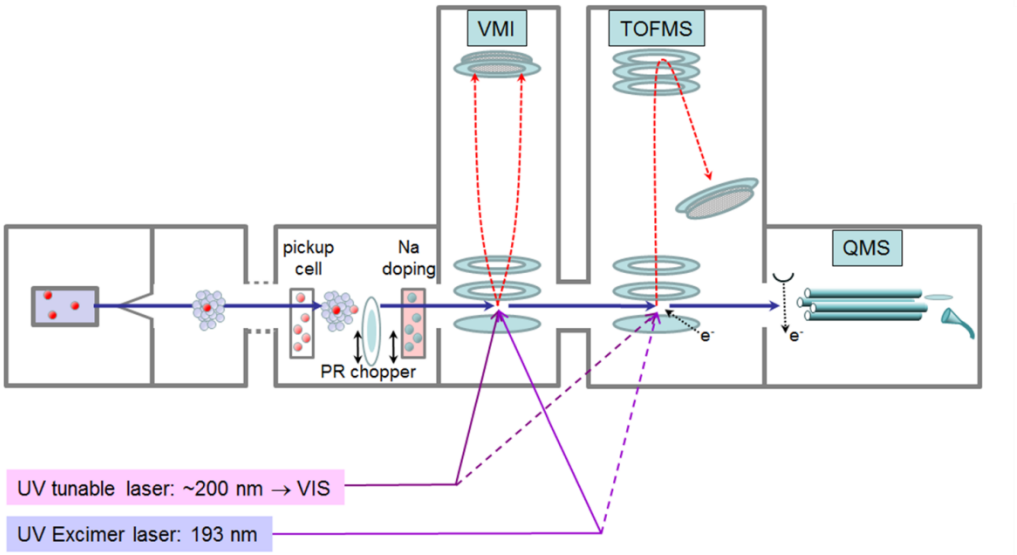

Figure S1: Schematic overview of the CLUB apparatus: VMI –velocity map imaging for photodissociation of molecules in clusters; TOFMS –reflectron time-of-flight mass spectrometer with various ionization methods, e.g., electron ionization, electron attachment, photoionization; QMS –quadrupole mass spectrometer with electron ionization.

S2 Dipole moment of $H_2SO_4(H_2O)_5$ clusters

Our M06-2X/aug-cc-pVDZ calculations exhibit only a small change in the cluster dipole moment upon the acidic dissociation of the sulfuric acid molecule on water cluster and could be overlapped by dynamic effects. The calculated dipole moments summarized in Figure S2 were in very broad range from ~0.3 D to ~4.6 D for $H_2SO_4(H_2O)_5$ clusters which depend rather on the cluster structure than on the acidic dissociation. Most likely, not only the energy minimum structure (see Figure S2 (a) for ion-pair and (e) for covalently-bonded H_2SO_4) but many different cluster structures are generated in the supersonic expansion.

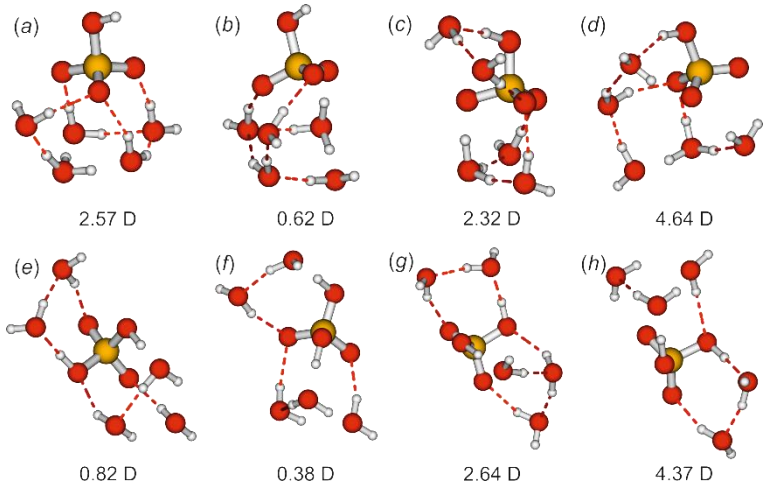

Figure S2: Selected local minima of neutral, $H_2SO_4\cdots H_2O$, (a-d) and ion-pair, $HSO_4^-\cdots H_3O^+$, (e-h) structures in $H_2SO_4(H_2O)_5$ clusters and the corresponding dipole moments calculated at the M06-2X/aug-cc-pVDZ level of theory.

S3 Thermochemistry

Table S1: Reaction energies (in kJ mol^{-1}) for the HSO_4^- dissociation channels after electron attachment to H_2SO_4/H_2O clusters optimized at the M06-2X/aug-cc-pVDZ level of theory.

N	$H_2SO_4(H_2O)_N$	$(H_2SO_4)_2(H_2O)_N$
0	–8.6	–132.2
1	–16.2	–117.2
2	–30.3	–120.5
3	–39.6	–99.8
4	–43.5	–106.5
5	–46.3	–88.9

Table S2: Free energies (in kJ mol^{-1}, at T=298K and p^0=1atm) of binary nucleation of H_2O/H_2SO_4 clusters

$H_2SO_4(H_2O)_{n-1} + H_2O \rightarrow H_2SO_4(H_2O)_n$ $\Delta_rG^0(1)$

$H_2SO_4 + nH_2O \rightarrow H_2SO_4(H_2O)_n$ $\Delta_rG^0(2)$

n =	$\Delta_rG^0(1)$ our results	$\Delta_rG^0(1)$ (Kurtén et al., 2007)	$\Delta_rG^0(2)$ our results	$\Delta_rG^0(2)$ (Henschel et al., 2014)	$\Delta_rG^0(2)$ (Loukonen et al., 2010)
1	–11.3	–11.76	–11.3	–10.88	–12.26
2	–7.1	–7.82	–18.4	–18.41	–26.19
3	–3.3	–9.92	–21.8	–24.39	–29.75
4	–9.6	–3.77	–31.4	–29.50	–33.93
5	–5.0	–	–36.4	–28.49	–41.88

S4 Ion-yield curves for selected ionic fragments

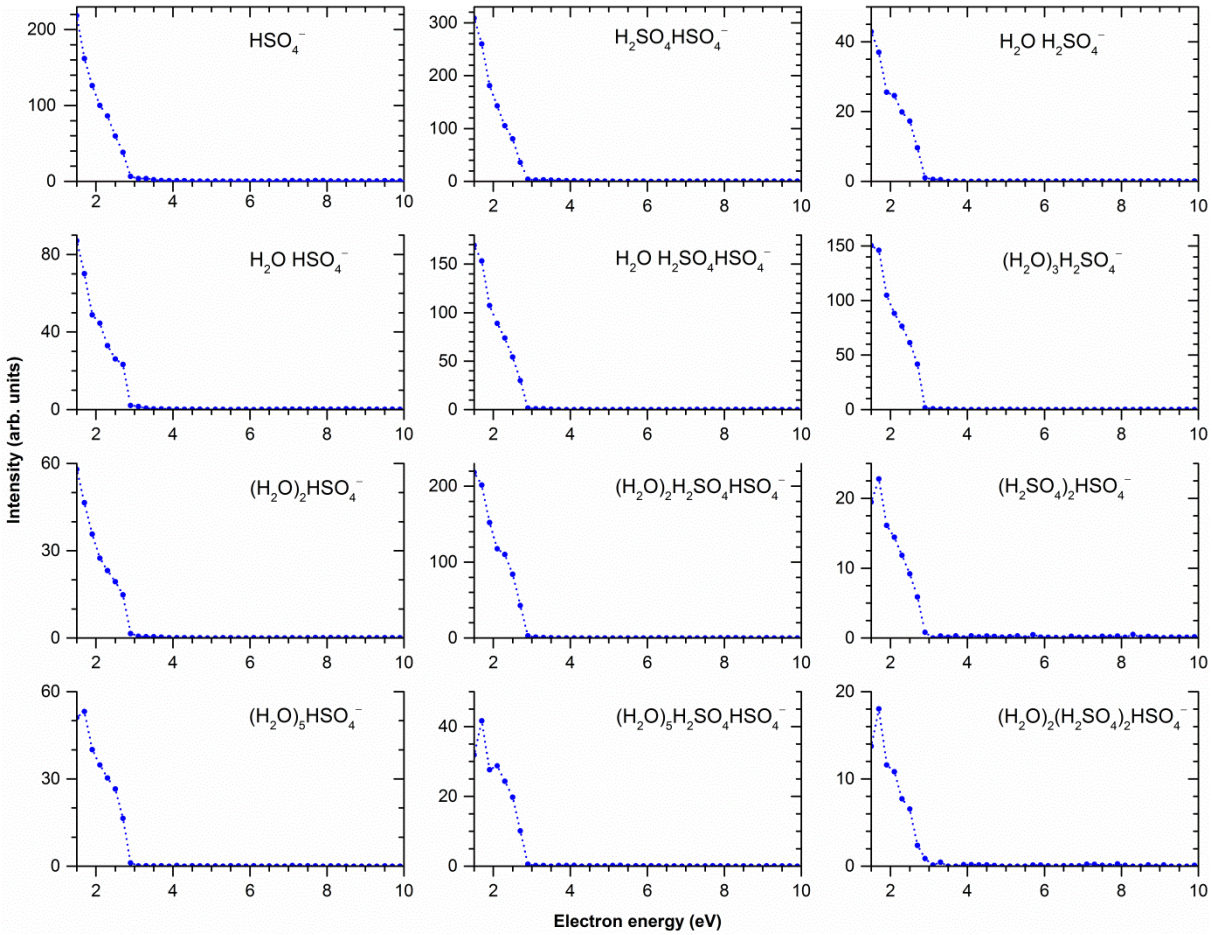

Figure S3: Ion-yield curves for selected ionic fragments with different degree of hydration.

S5 Benchmarking the electronic structure calculations

Table 1 summarizes the benchmark calculations of electron affinity of HSO_4, ionization potential of H_2SO_4, and reaction enthalpies for deprotonation of gas-phase H_2SO_4 calculated at different levels of theory. The M06-2X/aug-cc-pVDZ energies are comparable with the CCSD/aug-cc-pVDZ values with the exception of the IP(H_2SO_4). The comparison of double-zeta with triple-zeta basis sets of the M06-2X functional shows that there is essentially constant shift from the experimental values and therefore we do not expect any significant shift in reaction energies even upon hydration. The calculated reaction enthalpies for deprotonation of gas-phase H_2SO_4 are in good agreement with the experimental value. The error of the DFT method is 0.1-0.2 eV. Please note that, in the present work, chemical trends with respect to hydration are of the main concern, and a possible systematic shift of few tenths of eV does not influence our conclusions.

Table S3: Electron affinity of HSO_4, ionization potential of H_2SO_4, and enthalpy of deprotonation at various levels of theory (all in kJ mol^{-1}). DZ and TZ represent aug-cc-pVDZ and aug-cc-pVTZ, respectively. Enthalpies were calculated at 298.15 K within the harmonic approximation.

	B3LYP/DZ	M06-2X/DZ	M06-2X/TZ	MP2/DZ	CCSD/DZ	Experiment
EA(HSO_4)	453	474	483	503	478	458±10 (Wang et al., 2000)
IP(H_2SO_4)	1103	1117	1137	1195	1209	1196±5 (Snow and Thomas, 1990)
ΔH($H_2SO_4 \rightarrow H^+ + HSO_4^-$)	1318	1304	1300	1294	1309	1295±23 (Wang et al., 2000)

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Structures optimized at the M06-2X/aug-cc-pVDZ level of theory (coordinates in Å)

H2SO4,

S	0.000064	-0.000011	0.150574
O	-0.008803	1.287414	0.823392
O	0.008537	-1.287472	0.823344
O	-1.253357	-0.047337	-0.873079
O	1.253426	0.047310	-0.873222
H	-1.477412	0.867560	-1.107276
H	1.477544	-0.867564	-1.107433

H2SO4.H2O,

S	-0.002092	0.478526	0.019730
O	-1.122963	1.157172	-0.631673
O	1.114572	1.190582	0.618755
O	-0.562309	-0.538977	1.107359
O	0.584738	-0.519520	-1.120247
H	-1.483379	-0.811275	0.821010
H	1.486119	-0.765134	-0.858585
O	-2.970064	-0.852470	0.101511
H	-3.213990	-1.565378	-0.497780
H	-2.837433	-0.066926	-0.451981

H2SO4.2H2O,

S	0.000000	0.467392	0.000000
O	-1.127912	1.182899	-0.598603
O	1.127912	1.182899	0.598603
O	-0.544571	-0.525972	1.126354
O	0.544571	-0.525972	-1.126354
H	-1.457398	-0.819564	0.845467
H	1.457398	-0.819564	-0.845467
O	-2.952264	-0.863317	0.087315
H	-3.167318	-1.556293	-0.545456
H	-2.804014	-0.059401	-0.435852
O	2.952264	-0.863317	-0.087315
H	3.167318	-1.556293	0.545456
H	2.804014	-0.059401	0.435852

H2SO4.3H2O,

O	1.534809	1.462137	-1.001570
H	1.781577	0.721103	-1.570209
H	2.010710	1.291324	-0.171101
S	-1.254013	-0.027940	0.145515
O	-2.676737	-0.212944	0.334029
O	-1.037139	1.389948	-0.533069
O	-0.755988	-1.052734	-0.979924
O	-0.331366	-0.161830	1.295309
H	-0.055388	1.501559	-0.728110
H	0.213448	-1.230135	-0.856840
O	1.907043	-1.412438	-0.785868
H	2.255817	-1.097554	0.069469
H	2.246433	-2.302996	-0.917273
O	2.326583	0.197862	1.379342
H	2.786076	0.330487	2.212974
H	1.369934	0.132151	1.580426

H2SO4.4H2O,

O	0.369118	1.579893	-0.259299
H	1.202090	1.605634	0.346984
S	0.347838	0.202507	-1.049951
O	1.673499	-0.093974	-1.603650
O	0.109356	-0.873963	0.093257
H	-0.835252	-0.743440	0.484336
O	-0.815844	0.274657	-1.940218
O	3.128602	-1.008646	0.656279
H	2.514904	-1.630884	1.062595
H	2.800389	-0.920750	-0.255144
O	-2.695346	1.776866	-0.432679
H	-2.179271	1.430809	-1.181062
H	-2.166168	2.514883	-0.109840
O	2.413802	1.506984	1.243770
H	2.769558	0.589206	1.141609
H	3.139971	2.102662	1.033068
O	-2.207302	-0.418736	1.025772
H	-2.499986	0.413818	0.577955
H	-2.891058	-1.073226	0.850620

H2SO4.5H2O,

O	2.530094	-0.488264	0.456179
O	2.766862	1.149864	-1.439462
O	1.747942	-2.556670	-1.273177
O	-0.058200	0.544141	0.545237
S	-0.833135	-0.036079	-0.582157
O	-0.673560	0.720459	-1.870133
O	-0.672560	-1.504548	-0.771780
O	-2.372431	0.198128	-0.113351
O	0.908546	2.840738	-0.960190
H	1.624235	-0.272759	0.750816
H	2.451809	-1.361197	0.030348
H	1.818091	-3.515374	-1.300637
H	0.205597	2.354613	-1.433529
H	0.670757	2.675538	-0.036384
H	0.813063	-2.344304	-1.056790
H	-2.948688	-0.173522	-0.798367
H	2.094086	1.898372	-1.246379
H	2.755855	0.515316	-0.617185
H	2.352817	0.566049	-2.187776
H	1.724621	-1.281620	-2.713774
O	1.610395	-0.384716	-3.074888
H	0.679306	-0.153067	-2.895336

2H2SO4,

S	1.745825	0.029839	-0.059980
O	3.329326	0.099758	-0.237040
O	1.225540	1.341119	-0.440342
O	1.681857	-0.172605	1.515730
O	1.235030	-1.168892	-0.740880
H	3.685237	-0.804701	-0.247897
H	0.719563	-0.220633	1.736599
S	-1.924079	-0.019868	0.098364
O	-1.563209	-1.143575	-0.981219
O	-3.351604	-0.059240	0.306312
O	-1.584903	1.348763	-0.655891
O	-0.981346	-0.160287	1.227890
H	-0.592141	-1.293207	-0.969850
H	-0.616274	1.506078	-0.611788

2H2SO4.1H2O,

S	-1.353553	-0.511414	-0.087013
O	-1.227393	-0.561068	1.499813
O	-1.128619	0.883270	-0.538941
O	-2.864381	-0.884391	-0.260993
O	-0.530691	-1.558253	-0.696590
H	-0.279978	-0.347271	1.693110
H	-3.405755	-0.031417	-0.155546
S	2.251621	0.254920	0.108457
O	2.223385	-1.111167	-0.718891
O	1.345124	0.113600	1.267819
O	1.594297	1.312963	-0.894274
O	3.636755	0.618520	0.292603
H	1.294006	-1.430291	-0.763406
H	0.613364	1.264162	-0.813656
O	-3.918220	1.453703	-0.075381
H	-3.105060	1.963084	-0.204107
H	-4.331662	1.791292	0.726718

2H2SO4.2H2O,

S	1.133014	-0.781556	-0.436442
O	1.107072	-0.548213	1.139465
O	2.498648	-1.195467	-0.751781
O	0.831395	0.660660	-1.022179
O	0.001521	-1.622536	-0.845083
H	0.188558	-0.231213	1.368849
H	1.648914	1.315414	-0.812327
S	-2.450541	0.296644	0.340762
O	-1.979223	1.026965	-1.004861
O	-1.338323	0.400646	1.313497
O	-2.605880	-1.226151	-0.102257
O	-3.764970	0.783930	0.683121
H	-1.000647	0.985115	-1.071389
H	-1.718447	-1.558502	-0.372102
O	4.165046	0.366943	0.940214
H	3.793831	-0.421900	0.511638
H	3.970992	0.264946	1.878140
O	2.749942	2.106272	-0.451276
H	3.281491	2.434290	-1.184733
H	3.352697	1.559276	0.121564

2H2SO4.3H2O,

S	1.911406	0.302172	1.004299
O	2.002457	-0.519031	-0.354128
O	3.251986	0.516643	1.497074
O	1.163196	-0.684751	2.002934
O	1.013037	1.465973	0.766709
H	1.082924	-0.652053	-0.723374
H	0.231275	-0.829764	1.678738
S	-1.640653	-0.938902	-0.382259
O	-0.465014	-0.686075	-1.281778
O	-2.024913	-2.497877	-0.553992
O	-2.837837	-0.154923	-0.791105
O	-1.312562	-0.843515	1.068651
H	-2.305329	-2.646579	-1.470978
O	-2.325283	2.390213	-0.373368
H	-2.018102	2.289516	0.620738
H	-1.448985	2.403053	-0.944100
H	-2.714090	1.496154	-0.584884
O	-0.187319	2.160939	-1.662509
H	0.493477	2.109950	-0.966892
H	-0.257542	1.239238	-1.962555
O	-1.484569	1.913077	1.941515
H	-1.722947	0.978659	2.051025
H	-0.517672	1.880340	1.817961

2H2SO4.4H2O,

S	1.784275	0.547719	-0.487643
O	0.376649	1.048498	-0.879104
O	-0.981482	-1.044910	-1.422991
H	-0.520105	-0.142336	-1.325710
O	2.488009	-0.033265	-1.644329
O	1.504115	-0.718557	0.461352
O	1.067604	-2.379082	-2.044191
H	-0.208564	-1.691632	-1.666255
O	-0.628815	2.820358	0.642983
H	-1.347252	2.233968	1.056338
S	-1.585857	-0.132154	1.888293
O	-0.168479	0.160378	2.261477
O	-1.715621	-1.338022	1.009703
O	-2.321114	1.068096	1.404662
H	0.921306	-0.429200	1.224166
O	2.489556	1.589776	0.284729
H	1.374637	-2.963366	-1.340778
H	1.718500	-1.643959	-2.049245
H	-1.320159	-1.237200	-0.482771
H	-0.185312	2.196170	-0.033581
H	0.100541	3.046060	1.335600
O	-2.369059	-0.507824	3.251984
H	-2.013358	-1.347082	3.583243
H	1.775657	4.057102	2.168376
O	1.340476	3.198028	2.166567
H	1.931806	2.593921	1.671787

2H2SO4.5H2O,

S	2.463316	-0.007738	-0.264464
O	1.490393	-0.370175	0.797581
O	3.883207	-0.484662	0.361638
O	2.600433	1.455901	-0.521683
O	2.285757	-0.790802	-1.528680
H	4.582422	-0.267420	-0.274512
S	-2.346417	-0.293625	0.162067
O	-1.629343	-0.359861	-1.151363
O	-3.794822	-0.921159	-0.223972
O	-2.596308	1.106970	0.615838
O	-1.768006	-1.142111	1.232780
H	-4.357598	-0.882783	0.564910
O	0.165337	-2.193356	-1.420715
H	1.026470	-1.660524	-1.541397
H	0.229414	-2.605931	-0.459033
H	-0.579199	-1.512094	-1.369709
O	0.612327	2.885592	0.249474
H	1.428177	2.386092	-0.074238
H	0.269836	2.362126	1.089286
H	-0.121548	2.805885	-0.467326
O	-0.201685	1.490133	2.156993
H	-1.136652	1.294638	1.972911
H	0.271242	0.659281	1.979821
O	-1.311766	2.570989	-1.373026
H	-1.984887	2.240590	-0.746780
H	-1.170761	1.803888	-1.945146
O	0.302146	-2.945633	0.961722
H	-0.519241	-2.509320	1.258325
H	0.989487	-2.323997	1.251641