SUPPLMENTARY INFORMATION

Proton mobility and stability of water clusters containing the bisulphate anion, $HSO_4^-(H_2O)_n$

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Cartesian coordinates (Å) and energies (Hartree) for the most stable isomeric structures, as calculated by B3LYP/6-311++G(2d,2p).

1B-1W
S 0.51238 -0.14360 0.00345
O 1.19792 1.36950 -0.25634
O 1.65889 -1.03750 0.15431
H 1.81703 1.48531 0.47333
O -0.28359 0.01869 1.23022
O -0.27975 -0.31524 -1.21325
O -2.96150 0.06228 0.01941
H -2.36862 -0.08119 -0.73205
H -2.30227 0.11164 0.72874
Electronic energy = -776.3638321
Sum of electronic and zero-point Energies = **-776.312806**

1B-2W
S -0.93512 -0.12632 0.08170
O -0.67133 0.97275 -1.11912
O -0.18987 -1.33753 -0.33279
H 0.24702 1.28496 -1.00221
O -0.35330 0.49557 1.28854
O -2.37620 -0.28689 0.08400
O 1.93995 1.58835 0.02617
H 1.27178 1.39788 0.71030
H 2.34510 0.71466 -0.11592
O 2.51479 -1.25457 -0.12874
H 2.65226 -1.46761 0.79765
H 1.53351 -1.33024 -0.24146
Electronic energy = -852.8491614
Sum of electronic and zero-point Energies = **-852.770956**

1B-3W
H 1.41250 0.13129 1.39294
O 2.32586 0.38786 1.15433
H 2.55868 -0.31014 0.51994
H 0.87630 1.40603 -1.30434
O 1.15964 2.15069 -0.75181
H 1.70143 1.70839 -0.06732
H 1.76596 -2.44825 -0.03180
O 2.04985 -1.84430 -0.72381
H 1.22188 -1.36350 -0.94967
O -0.33928 -0.55397 1.28065
O -2.42018 -0.82603 -0.01621
S -1.10646 -0.22168 0.06439
O -1.41546 1.38126 0.14722
H -0.56840 1.84297 -0.03381
O -0.26855 -0.37301 -1.15990
Electronic energy = -929.3319185
Sum of electronic and zero-point Energies = **-929.227896**

1B-4W
H -2.04561 1.30068 -0.91584
O -2.00209 0.84013 -1.77786
H -1.06284 0.61429 -1.85285
H -0.76399 1.93027 0.73272
O -1.72359 1.86956 0.86814
H -1.82865 1.01958 1.33860
H -2.27531 -0.98924 -1.16531
O -1.99900 -1.83460 -0.76350
H -1.03536 -1.77791 -0.85372
O 1.14576 -0.82188 1.17725
O 1.11779 1.44770 0.18360
S 1.31808 0.01722 -0.01580
O 2.93846 -0.06261 -0.35450
H 3.15782 -1.00195 -0.35536
O 0.64731 -0.53396 -1.20653
H -1.95563 -1.25819 1.09008
O -1.69412 -0.81206 1.91742
H -0.72377 -0.85125 1.88238
Electronic energy = -1005.8126407
Sum of electronic and zero-point Energies = **-1005.683189**

1B-5W

H 1.51876 1.25324 -1.18336
O 2.16670 1.85486 -0.77576
H 2.74022 1.24238 -0.28190
H -0.77843 2.37730 0.42979
O -0.00007 2.30356 1.01701
H 0.77830 2.37734 0.42981
H -1.51881 1.25318 -1.18339
O -2.16677 1.85478 -0.77579
H -2.74027 1.24229 -0.28192
O 0.00000 0.03021 -1.25899
O 1.22874 -1.88535 -0.32065
S 0.00003 -1.08677 -0.28453
O 0.00008 -0.38367 1.18363
H -0.00000 0.61111 1.09973
O -1.22869 -1.88535 -0.32059
H -2.68396 -0.96797 0.30984
O -3.32669 -0.35884 0.73256
H -2.93368 -0.20206 1.59613
H 2.93358 -0.20200 1.59609
O 3.32668 -0.35876 0.73256
H 2.68401 -0.96792 0.30979
Electronic energy = -1082.2955369
Sum of electronic and zero-point Energies = **-1082.140671**

1B-6W
H 1.63978 -1.52644 -1.23615
O 2.25797 -2.16089 -0.83574
H 1.66411 -2.74336 -0.32924
H 2.79535 0.77970 0.35378
O 2.72740 0.00057 0.94160
H 2.79567 -0.77853 0.35377
H 1.63915 1.52714 -1.23615
O 2.25707 2.16185 -0.83572
H 1.66292 2.74405 -0.32921
O 0.37274 0.00008 -1.23810
O -1.49346 -1.22653 -0.20046
S -0.68062 -0.00017 -0.20307
O 0.08424 0.00005 1.21850
H 1.08099 0.00023 1.09488
O -1.49406 1.22579 -0.20049
H -0.52854 2.70987 0.34387
O 0.10272 3.36467 0.70744
H 0.26815 3.03795 1.59646

H 0.26952 -3.03807 1.59647
O 0.10419 -3.36473 0.70741
H -0.52734 -2.71017 0.34393
H -3.62769 -0.74306 -0.15673
O -4.24566 -0.00061 -0.13818
H -3.62726 0.74152 -0.15675
Electronic energy = -1158.7762874
Sum of electronic and zero-point Energies = **-1158.595963**

1B-7W
H -2.33385 -1.85603 0.03471
O -3.14451 -1.31900 0.11899
H -3.10232 -0.72099 -0.66002
H -2.39186 0.23289 2.74879
O -2.08507 0.37544 1.85040
H -2.58676 -0.26796 1.26870
H 3.20513 -0.61843 -0.57213
O 3.81317 0.12919 -0.75112
H 3.41919 0.56883 -1.51027
O -0.50073 -2.36741 0.02178
O 0.22017 -0.32859 -1.14011
S 0.52602 -1.33066 -0.09605
O 0.50280 -0.50611 1.32425
H -0.41565 -0.19791 1.50756
O 1.90104 -1.82136 -0.14459
H 0.60420 1.53975 -0.94157
O 0.72317 2.47376 -0.69536
H 1.35617 2.42601 0.04439
H -2.44178 1.33490 -1.36251
O -2.49673 0.50537 -1.87746
H -1.58717 0.16559 -1.84657
H -1.06066 2.74435 -0.22611
O -2.02144 2.66372 -0.05449
H -2.08076 2.07905 0.71477
O 2.57376 1.65566 1.35386
H 3.17173 1.22242 0.71724
H 1.94308 0.95294 1.57057
Electronic energy = -1235.2575894
Sum of electronic and zero-point Energies = **-1235.050562**

1B-8W
H -2.72124 -1.64963 -0.41749
O -3.47909 -1.04272 -0.32295

H -3.28585 -0.33550 -0.97702
H -2.90928 -0.03038 2.59905
O -2.48017 0.21016 1.77458
H -2.96972 -0.26927 1.04235
H 3.17335 -1.04893 0.08921
O 3.82475 -0.32871 0.13697
H 3.61783 0.20444 -0.65147
O -0.94474 -2.34207 -0.32068
O 0.13334 -0.25701 -1.03137
S 0.19620 -1.44545 -0.13618
O 0.06077 -0.83996 1.38109
H -0.85138 -0.48976 1.51741
O 1.50460 -2.08146 -0.11305
H 0.52455 1.43267 -0.29335
O 0.80787 2.30987 0.02430
H 1.35200 2.08910 0.80805
H -2.34340 1.72084 -1.23030
O -2.41131 0.99782 -1.88417
H -1.54805 0.55793 -1.82528
H -1.02346 2.79750 0.32170
O -1.99855 2.76584 0.34422
H -2.20347 2.06569 0.98143
O 2.30361 1.06123 2.07223
H 2.96980 0.64059 1.48908
H 1.60559 0.39283 2.11918
H 2.22104 1.85540 -1.51362
O 2.59944 1.13646 -2.04259
H 1.88834 0.47816 -2.02852
Electronic energy = -1311.7382951
Sum of electronic and zero-point Energies = **-1311.504943**

1B-9W
H 1.44555 1.44270 -1.17085
O 2.00050 2.19982 -0.92898
H 2.84217 1.79510 -0.63142
H -0.77873 2.65199 0.36619
O -0.00045 2.55751 0.95727
H 0.77813 2.65253 0.36672
H -1.44529 1.44198 -1.17173
O -2.00027 2.19906 -0.92985
H -2.84193 1.79438 -0.63215
O 0.00073 0.00878 -1.06804
O 1.22489 -1.70628 0.20061

S 0.00026 -0.89135 0.10493
O 0.00093 0.02896 1.41147
H 0.00020 1.03188 1.18983
O -1.22539 -1.70479 0.20061
H 3.98569 0.30621 0.68670
O 4.25806 0.69371 -0.16479
H 4.06216 -0.00790 -0.81040
H 2.45532 -1.12526 1.52704
O 3.07011 -0.64076 2.10871
H 2.48891 -0.03208 2.57445
H 2.61566 -0.86837 -2.56566
O 3.10871 -1.34311 -1.89065
H 2.43495 -1.56072 -1.21799
H -2.61965 -0.87123 -2.56715
O -3.11044 -1.34442 -1.88942
H -2.43476 -1.56001 -1.21800
H -4.06261 -0.00824 -0.80962
O -4.25795 0.69398 -0.16450
H -3.98542 0.30704 0.68720
H -2.45452 -1.12343 1.52771
O -3.06958 -0.63926 2.10938
H -2.48875 -0.03067 2.57569
Electronic energy = -1388.2135652
Sum of electronic and zero-point Energies = **-1387.957593**

1B-10W
H 3.47350 -0.35475 -0.75532
O 4.12350 -0.58799 -0.07398
H 3.85716 -1.48786 0.18765
H 2.54790 1.95219 0.91807
O 2.59284 1.16228 1.50139
H 3.28000 0.59118 1.09883
H 1.82512 2.29223 -1.02493
O 2.05314 3.04459 -0.45962
H 1.19826 3.44665 -0.20380
O 1.61043 0.20631 -1.40324
O 0.55230 -1.90492 -0.69661
S 0.44317 -0.43445 -0.78766
O 0.36793 0.10218 0.72284
H 1.26609 0.48303 1.03360
O -0.83940 -0.01949 -1.38644
H -0.36622 3.79877 1.43871
O -0.41219 4.05138 0.51287

H -1.12923 3.48584 0.13598
H 2.00211 -2.71711 0.06993
O 2.79603 -3.05913 0.52916
H 2.52914 -3.13566 1.44892
O -3.23283 -1.35153 -1.33542
H -3.53545 -1.48679 -2.23634
O -3.93249 0.57938 0.82680
H -3.98478 -0.03165 0.07764
H -2.47952 -2.75418 -0.12626
H -0.98336 -2.85216 0.12590
H -2.36051 -0.90390 -1.41104
O -1.83894 -3.10628 0.51095
H -3.31975 0.12773 1.44268
O -2.26098 2.37798 -0.59850
H -2.89290 1.90002 -0.02438
H -1.69832 1.66752 -0.94744
O -1.97382 -0.85883 2.29638
H -1.98900 -1.71917 1.83496
H -1.17505 -0.43801 1.94656
Electronic energy = -1464.6944002
Sum of electronic and zero-point Energies = **-1464.411998**

Structures for proposed mechanism of H/D exchange in bisulphate-water clusters. Cartesian coordinates (Å) and energies (Hartree), by B3LYP/6-311++G(2d,2p).

1B-1W
H 1.41538 -0.82064 -0.11043
H 2.82182 -0.00002 0.80590
O 2.47082 0.00000 -0.08793
O -1.57264 0.00003 -1.06344
S -0.60143 0.00000 0.01506
O -1.14658 -0.00004 1.36444
O 0.37235 1.22034 -0.15813
O 0.37235 -1.22033 -0.15819
H 1.41538 0.82064 -0.11038
Electronic energy = -776.3433911
Sum of electronic and zero-point Energies = **-776.296377**

1B-2W
H -0.80178 1.26771 -0.36567
H -2.25085 1.52276 0.81549
O -2.16848 1.21150 -0.08954
H -2.25434 -0.00000 -0.05411
O -2.16847 -1.21151 -0.08954
H -2.25081 -1.52276 0.81550
O 2.33358 0.00001 -0.33747
S 0.94517 0.00000 0.06427
O 0.64347 -0.00002 1.48982
O 0.25725 -1.23821 -0.60376
O 0.25725 1.23823 -0.60372
H -0.80178 -1.26770 -0.36570
Electronic energy = -852.8229196
Sum of electronic and zero-point Energies = **-852.752205**

1B-3W
H -0.84195 0.23182 1.27380
H -2.50323 -0.47867 1.52111
O -2.15951 0.36361 1.21153
H -2.25665 0.35938 -0.00001
O -2.15947 0.36368 -1.21154
H -2.50313 -0.47860 -1.52117
O 2.12790 -0.87118 0.00002
S 0.68914 -0.74537 -0.00001
O -0.11206 -1.96241 -0.00010
O 0.27769 0.13116 -1.23368

O 0.27764 0.13101 1.23376
H -0.84191 0.23194 -1.27377
H 1.05415 2.20864 0.74476
O 1.22437 2.79951 0.00001
H 1.05407 2.20846 -0.74458
Electronic energy = -929.2990812
Sum of electronic and zero-point Energies = **-929.204928**

1B-4W
H 0.20660 -0.54741 1.57810
O -0.95728 -0.52865 1.89468
H -1.39069 -1.16832 1.28240
H -1.55735 2.38914 1.13722
O -1.38800 1.57762 0.65539
H -1.22688 0.41413 1.48255
O 1.36352 -0.47706 1.21268
O 0.62773 -0.85245 -1.09789
S 1.50390 -0.03436 -0.24966
O 0.96763 1.45339 -0.28667
H -0.00793 1.52720 0.08414
O 2.89701 0.02387 -0.62477
H -2.44171 -1.16297 -0.63807
O -1.90174 -1.90549 -0.30576
H -1.01657 -1.71370 -0.66825
H -2.56471 0.70605 -1.98950
O -3.05501 0.59040 -1.17111
H -2.49400 1.05268 -0.48648
Electronic energy = -1005.7918843
Sum of electronic and zero-point Energies = **-1005.668015**

1B-5W
H 0.38949 -1.98434 -0.15065
O -0.64806 -2.38468 -0.04223
H -1.14870 -1.94605 -0.79033
H -1.14358 -1.07893 2.70171
O -1.15026 -0.78533 1.78861
H -0.94601 -1.82902 0.80885
O 1.57501 -1.39345 -0.18305
O 0.61108 0.64229 -1.14544
S 1.52777 0.12215 -0.08828
O 0.87681 0.46505 1.28904
H -0.08033 -0.13008 1.53897
O 2.85579 0.69568 -0.11297

H -0.36781 2.08325 -0.57502
O -0.93716 2.71425 -0.08475
H -0.54183 2.69231 0.79292
H -2.33658 -0.26561 -1.24075
O -1.75849 -0.77628 -1.84741
H -0.92487 -0.26677 -1.83277
H -2.42627 1.50280 0.11363
O -2.97789 0.70632 0.23036
H -2.49260 0.19723 0.90863
Electronic energy = -1082.2749447
Sum of electronic and zero-point Energies = **-1082.125753**

1B-6W
H -1.42274 -1.90455 0.23762
O -2.33669 -1.45569 0.50246
H -2.54705 -0.85856 -0.28913
H -1.26986 0.05961 2.91526
O -1.27535 0.20152 1.96628
H -1.98037 -0.75047 1.24764
O -0.04074 -2.30127 -0.04315
O 0.30608 -0.25564 -1.33773
S 0.88438 -1.14134 -0.28561
O 0.90782 -0.30923 1.05123
H -0.15976 -0.05169 1.51557
O 2.25232 -1.54798 -0.55057
H 0.61854 1.59694 -1.23254
O 0.69576 2.53953 -0.98769
H 1.43750 2.53245 -0.36062
H -2.40159 1.08653 -0.99160
O -2.45848 0.23619 -1.48206
H -1.51828 0.03729 -1.66917
H -0.98563 2.60921 -0.17283
O -1.87567 2.41813 0.19017
H -1.70182 1.83447 0.94780
O 2.83965 1.70061 0.83552
H 3.46588 1.27597 0.24168
H 2.19762 0.98477 1.02434
Electronic energy = -1158.7566522
Sum of electronic and zero-point Energies = **-1158.581104**

1B-7W
H -1.99541 -1.78274 0.06874
O -2.86389 -1.23617 0.20148

H -2.88104 -0.62686 -0.61120
H -2.01050 0.12693 2.75709
O -1.85701 0.28351 1.82264
H -2.53032 -0.56179 1.00906
H 3.17834 -0.66765 -0.48151
O 3.82638 0.05212 -0.64409
H 3.50074 0.47390 -1.44433
O -0.57717 -2.31121 -0.01779
O 0.18992 -0.31705 -1.21827
S 0.47265 -1.24822 -0.08812
O 0.38286 -0.42056 1.23349
H -0.72517 -0.06470 1.54349
O 1.82305 -1.81219 -0.14679
H 0.57375 1.53356 -1.02143
O 0.67859 2.47261 -0.77985
H 1.29888 2.43014 -0.02779
H -2.43829 1.27452 -1.26925
O -2.49270 0.42595 -1.76506
H -1.55707 0.14542 -1.81611
H -1.07233 2.68588 -0.24541
O -2.02088 2.56168 -0.02439
H -2.00726 1.98710 0.75758
O 2.44001 1.65693 1.33187
H 3.08755 1.21413 0.75460
H 1.78232 0.95878 1.49031
Electronic energy = -1235.2400367
Sum of electronic and zero-point Energies = **-1235.038468**

1B-8W
H -2.38357 -1.59445 -0.38230
O -3.20171 -0.97883 -0.25953
H -3.04381 -0.24500 -0.94141
H -2.59918 -0.18183 2.58453
O -2.29457 0.10877 1.72182
H -2.91969 -0.49408 0.69713
H 3.09232 -1.09960 0.18156
O 3.77261 -0.40594 0.24252
H 3.61627 0.11832 -0.56237
O -1.01295 -2.26491 -0.38380
O 0.13109 -0.21794 -1.09174
S 0.14331 -1.35976 -0.11361
O -0.06738 -0.73933 1.30184
H -1.17310 -0.32032 1.52985

O 1.41994 -2.06493 -0.09817
H 0.52893 1.45506 -0.36188
O 0.79951 2.33335 -0.03050
H 1.30850 2.10441 0.77512
H -2.32100 1.67891 -1.17661
O -2.38467 0.93988 -1.82195
H -1.48384 0.56238 -1.81706
H -1.01996 2.75696 0.29878
O -1.99375 2.67872 0.34626
H -2.14303 1.97525 0.99864
O 2.15359 1.04351 2.07914
H 2.85608 0.61322 1.55052
H 1.43216 0.39507 2.04423
H 2.29227 1.79864 -1.52407
O 2.64759 1.04536 -2.01838
H 1.91338 0.41152 -1.97707
Electronic energy = -1311.7213331
Sum of electronic and zero-point Energies = **-1311.493323**

1B-9W
H 1.19729 1.15158 -1.16272
O 1.70787 1.98101 -0.91530
H 2.58813 1.65566 -0.54784
H -0.75178 2.60403 0.17779
O 0.06044 2.52859 0.75904
H 0.96277 2.36006 -0.04867
H -1.37492 1.35564 -1.24096
O -1.88257 2.15162 -0.99903
H -2.71016 1.79064 -0.60504
O 0.04470 -0.03780 -1.17872
O 1.30865 -1.65096 0.16946
S 0.00977 -0.91867 0.05466
O -0.14233 -0.02891 1.27834
H -0.02782 1.58141 1.09255
O -1.13132 -1.85329 -0.02568
H 3.68357 0.48274 0.81157
O 3.93734 0.88987 -0.04410
H 3.90942 0.14155 -0.67365
H 2.32292 -1.03200 1.52128
O 2.86520 -0.50468 2.14917
H 2.19472 -0.00245 2.62262
H 2.81478 -1.02450 -2.52891
O 3.25384 -1.29444 -1.71812

H 2.51352 -1.51121 -1.10438
H -2.82207 -0.92629 -2.50242
O -3.21677 -1.32179 -1.72087
H -2.44457 -1.55527 -1.15564
H -3.93878 0.05525 -0.59529
O -4.05222 0.78385 0.04373
H -3.69893 0.41615 0.87701
H -2.79147 -1.42030 1.86051
O -2.74721 -0.53585 2.24038
H -1.82794 -0.28177 2.02119
Electronic energy = -1388.2064989
Sum of electronic and zero-point Energies = **-1387.951828**

1B-10W
H 3.28171 -0.44322 -0.77433
O 3.95012 -0.65814 -0.09593
H 3.67268 -1.54762 0.20165
H 2.43529 1.95308 0.54247
O 2.63961 1.11573 1.41628
H 3.28382 0.47492 1.00138
H 1.79404 1.82421 -0.98087
O 2.09363 2.59577 -0.41302
H 1.27389 3.10954 -0.14960
O 1.55238 0.22060 -1.40756
O 0.46560 -1.89509 -0.78471
S 0.37171 -0.40967 -0.71871
O 0.37648 0.03540 0.72840
H 1.76045 0.62807 1.31427
O -0.88726 0.05616 -1.37377
H -0.11507 3.75560 1.37705
O -0.08140 3.87772 0.42422
H -0.87636 3.37563 0.07705
H 1.81201 -2.68608 0.04260
O 2.58645 -3.04224 0.53803
H 2.27517 -3.11632 1.44387
O -3.30575 -1.13999 -1.27102
H -3.61262 -1.25626 -2.17299
O -3.80088 0.79351 0.93620
H -3.92924 0.20683 0.17604
H -2.57123 -2.63315 -0.15597
H -1.07326 -2.79819 0.04118
H -2.40313 -0.74260 -1.34747
O -1.92705 -3.05180 0.43569

H -3.18274 0.28459 1.50407
O -2.07870 2.45125 -0.56743
H -2.72085 2.04013 0.04810
H -1.60288 1.67527 -0.92662
O -1.88003 -0.79074 2.25874
H -1.99151 -1.65619 1.82452
H -1.08304 -0.43879 1.82014
Electronic energy = -1464.6863851
Sum of electronic and zero-point Energies = **-1464.405356**

Cluster temperatures

It is possible to estimate the temperatures (more specifically, the finite size heat bath microcanonical temperature) of the clusters in a cluster beam experiment using statistical physics [refs S1, S2, S3]. This has previously been done for pure water clusters for the current experimental setup [ref 5]. The clusters studied are formed by successive evaporation of H_2O from larger clusters. The underlying assumption of the temperature estimate is that the clusters are small enough that each successive evaporation leads to an order of magnitude decrease in the evaporation rate constant due to lower temperature. The lifetime of the cluster at its current size is then essentially the same as the total time since the formation of the cluster (in practice, the time when the cluster entered high vacuum).

The maximum temperature of a cluster that survives the passage of the instrument intact can be expressed as $T_{max,\,n} = D_n/(k_B \times \ln(wn^{2/3}t))$, where w denotes a frequency factor, n is the cluster size, D is the dissociation energy, and T is the finite size heat bath microcanonical temperature. The frequency factor is mainly a property of the leaving fragment i.e. H_2O, and can be approximated to be the same for the present clusters as for pure water clusters (1.33×10^{-16} at 150 K)[reference 56] . A maximum cluster temperature for $HSO_4^-(H_2O)_n$ with n = 1 – 11, estimated from the dissociation energies found in Table 1, ranges from 120 to 190 K in our cluster ion beam, depending on size and dissociation energy.

References

S1. Hansen, K. and U. Naher, Evaporation and cluster abundance spectra. Physical Review A, 1999. 60(2): p. 1240-1250.

S2. Naher, U. and K. Hansen, Temperature of Large Clusters. Journal of Chemical Physics, 1994. 101(6): p. 5367-5371.

S3. Sunden, A.E.K., et al., *Heat capacities of freely evaporating charged water clusters.* Journal of Chemical Physics, 2009. **130**(22):224308 p. 1–7.