

Supporting Information

On the Properties and Atmospheric Implication of Methylamine-Sulfuric Acid-Water Clusters

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S1. PW91/6-311++G(3df,3pd) Optimized Cartesian Coordinates (in Å) and Single Point

Energies (in Hartree) for the global minima of $\text{CH}_3\text{NH}_2(\text{H}_2\text{SO}_4)_m(\text{H}_2\text{O})_n$ ($m = 0-3$, $n = 0-3$)

Clusters. MA denotes CH_3NH_2 . SA denotes H_2SO_4 . W denotes H_2O .

The E[DF-MP2-F12] line represents Second-order Møller–Plesset Perturbation Theory-explicitly

Correlated Methods with Density Fitting single point energies for each isomer.

MA

E[DF-MP2-F12]	-95.70502023		
C	0.707392000000	-0.000020000000	0.018035000000
H	1.083818000000	-0.002279000000	1.056466000000
H	1.119402000000	-0.880443000000	-0.489865000000
H	1.118859000000	0.882974000000	-0.485785000000
N	-0.751193000000	-0.000019000000	-0.123345000000
H	-1.153978000000	0.815537000000	0.337213000000
H	-1.154106000000	-0.815533000000	0.337178000000

SA

E[DF-MP2-F12]	-699.5884088		
S	0.000000000000	0.000000000000	0.162139000000
O	0.000000000000	1.267836000000	0.829757000000
O	0.000000000000	-1.267836000000	0.829757000000
O	-1.253084000000	0.056558000000	-0.850086000000
O	1.253084000000	-0.056558000000	-0.850086000000
H	-1.451166000000	-0.855975000000	-1.134478000000
H	1.451166000000	0.855975000000	-1.134478000000

W

E[DF-MP2-F12]	-76.35789722		
O	0.000000000000	0.000000000000	0.118917000000
H	0.000000000000	0.764351000000	-0.475669000000
H	0.000000000000	-0.764351000000	-0.475669000000

1MA_1W

E[DF-MP2-F12]	-172.07522262		
C	-1.428003000000	-0.552678000000	-0.000319000000
H	-1.148528000000	-1.138208000000	0.882252000000

H	-2.521737000000	-0.424209000000	-0.001707000000
H	-1.146326000000	-1.138720000000	-0.881853000000
N	-0.667265000000	0.707108000000	0.000296000000
H	-0.905319000000	1.268068000000	0.817916000000
H	-0.904248000000	1.268255000000	-0.817510000000
O	2.010854000000	-0.263700000000	0.000665000000
H	1.124519000000	0.181976000000	0.000370000000
H	2.653677000000	0.458749000000	-0.004946000000

1MA_2W

E[DF-MP2-F12] -248.44802374

C	-2.106997000000	-0.193863000000	0.389951000000
H	-2.740843000000	-1.069201000000	0.178507000000
H	-1.681062000000	-0.320858000000	1.391599000000
H	-2.747363000000	0.695731000000	0.409747000000
N	-1.015195000000	0.004204000000	-0.572631000000
H	-1.381265000000	0.104819000000	-1.518676000000
H	-0.381590000000	-0.802363000000	-0.572806000000
O	1.241082000000	1.449357000000	0.012616000000
H	0.308783000000	1.115619000000	-0.175796000000
H	1.181580000000	1.967324000000	0.827704000000
O	1.638788000000	-1.282038000000	0.147415000000
H	1.724647000000	-0.296680000000	0.163490000000
H	2.426492000000	-1.599196000000	-0.315303000000

1MA_3W

E[DF-MP2-F12] -324.8232825

C	-2.441028000000	0.139727000000	0.540995000000
H	-3.048065000000	1.056535000000	0.489219000000
H	-3.115385000000	-0.723985000000	0.508970000000
H	-1.930600000000	0.126415000000	1.510119000000
N	-1.437288000000	0.030592000000	-0.528563000000
H	-0.786680000000	0.830503000000	-0.492250000000
H	-1.889508000000	0.051787000000	-1.442450000000
O	0.764371000000	1.963222000000	-0.078487000000
H	1.440338000000	1.240965000000	0.040196000000
H	1.168643000000	2.590127000000	-0.693902000000
O	0.374490000000	-1.922313000000	-0.070570000000
H	0.435244000000	-2.537386000000	-0.815023000000
H	-0.367840000000	-1.258169000000	-0.307549000000
O	2.400863000000	-0.191613000000	0.206068000000
H	1.709630000000	-0.911621000000	0.109652000000

H	2.773610000000	-0.312049000000	1.090899000000
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1MA_1SA

E[DF-MP2-F12] -795.3301591

C	-3.063024000000	0.535609000000	-0.022719000000
H	-3.733251000000	0.499509000000	0.840476000000
H	-2.477586000000	1.457968000000	0.010658000000
H	-3.647574000000	0.512106000000	-0.946316000000
N	-2.121405000000	-0.605126000000	0.007954000000
H	-2.586366000000	-1.513308000000	-0.022246000000
H	-1.442056000000	-0.556744000000	0.824661000000
S	0.976012000000	-0.103047000000	0.011793000000
O	0.174298000000	-0.296294000000	1.241593000000
O	2.266745000000	-0.753140000000	-0.036815000000
O	0.134077000000	-0.316897000000	-1.205724000000
O	1.266534000000	1.511673000000	0.045750000000
H	-1.345695000000	-0.534613000000	-0.753394000000
H	2.111076000000	1.643328000000	-0.420319000000

1MA_2SA

E[DF-MP2-F12] -1494.97179

C	0.947559000000	3.181782000000	-0.567388000000
H	0.995634000000	2.466861000000	-1.391743000000
H	0.133855000000	3.891973000000	-0.732991000000
H	1.899611000000	3.711729000000	-0.484894000000
N	0.696031000000	2.412981000000	0.681137000000
H	-0.222273000000	1.890108000000	0.631323000000
H	0.676336000000	3.016081000000	1.506752000000
S	1.730263000000	-0.727706000000	0.035173000000
O	1.044215000000	-0.149279000000	-1.147002000000
O	0.883613000000	-1.678302000000	0.773189000000
O	2.987770000000	-1.574960000000	-0.511485000000
O	2.379592000000	0.303534000000	0.853622000000
H	2.648395000000	-2.415609000000	-0.870820000000
H	1.436410000000	1.661094000000	0.816370000000
S	-2.189437000000	-0.195177000000	0.008636000000
O	-1.589596000000	0.977284000000	0.657775000000
O	-3.608611000000	-0.235266000000	-0.138917000000
O	-1.539168000000	-0.361583000000	-1.416198000000
O	-1.747756000000	-1.479809000000	0.799726000000
H	-0.523378000000	-0.305641000000	-1.344655000000
H	-0.735851000000	-1.544981000000	0.840405000000

1MA_3SA

E[DF-MP2-F12] -2194.597828

C	-0.085016000000	-0.592772000000	3.428668000000
H	0.200228000000	-1.442902000000	2.805663000000
H	0.733487000000	-0.329958000000	4.103228000000
H	-0.981448000000	-0.839197000000	4.002354000000
N	-0.380074000000	0.554962000000	2.527361000000
H	-0.658998000000	1.389360000000	3.050549000000
H	-1.173915000000	0.323325000000	1.864488000000
S	-2.886491000000	-0.243105000000	-0.381527000000
O	-4.248525000000	-0.481454000000	-0.730466000000
O	-2.531204000000	-0.038551000000	1.027491000000
O	-2.040431000000	-1.448707000000	-0.937785000000
O	-2.399173000000	1.009111000000	-1.206013000000
H	-1.124492000000	-1.482514000000	-0.521902000000
H	-1.582048000000	1.431573000000	-0.802899000000
S	1.640258000000	-1.897995000000	-0.335537000000
O	1.972663000000	-3.284226000000	-0.356003000000
O	0.348909000000	-1.468946000000	0.227984000000
O	2.757322000000	-1.128124000000	0.471191000000
O	1.748988000000	-1.345357000000	-1.801873000000
H	2.456601000000	-0.172275000000	0.620665000000
H	1.602482000000	-0.344847000000	-1.793371000000
S	1.130153000000	1.944979000000	-0.323027000000
O	1.474389000000	1.278481000000	-1.582636000000
O	-0.290073000000	2.187957000000	-0.074178000000
O	1.782851000000	1.298222000000	0.859503000000
O	1.733672000000	3.431893000000	-0.410426000000
H	0.448895000000	0.815125000000	1.942252000000
H	2.631977000000	3.379751000000	-0.787406000000

1MA_1SA_1W

E[DF-MP2-F12] -871.7124211

S	1.192088000000	0.022397000000	0.066446000000
O	2.168781000000	0.940969000000	0.616323000000
O	0.263226000000	0.606481000000	-0.929588000000
O	2.027590000000	-1.123774000000	-0.746803000000
O	0.452728000000	-0.798387000000	1.063735000000
H	2.840673000000	-0.691222000000	-1.062605000000
H	-2.193231000000	0.498181000000	0.467375000000
N	-2.115241000000	-0.537464000000	0.672664000000

H	-2.670198000000	-0.768408000000	1.498703000000
H	-1.053976000000	-0.696956000000	0.886618000000
C	-2.517960000000	-1.337274000000	-0.512594000000
H	-2.395311000000	-2.401252000000	-0.294408000000
H	-1.857286000000	-1.057427000000	-1.336875000000
H	-3.557138000000	-1.125685000000	-0.778427000000
O	-1.863986000000	2.019751000000	-0.232057000000
H	-1.690284000000	2.819073000000	0.285250000000
H	-0.968925000000	1.690925000000	-0.534733000000

1MA_1SA_2W

E[DF-MP2-F12] -948.0940835

S	-1.362671000000	0.015119000000	0.143505000000
O	-0.480562000000	-0.009197000000	1.332601000000
O	-1.303516000000	-1.242274000000	-0.625206000000
O	-2.881882000000	0.119212000000	0.704053000000
O	-1.240722000000	1.235552000000	-0.657169000000
H	-3.095999000000	-0.737683000000	1.115256000000
H	1.973970000000	0.841754000000	-0.272058000000
N	2.048190000000	-0.020233000000	0.327791000000
H	1.949226000000	-0.860790000000	-0.298031000000
H	1.151641000000	-0.017387000000	0.892194000000
C	3.264681000000	-0.049133000000	1.167015000000
H	3.260309000000	-0.950514000000	1.785635000000
H	3.283214000000	0.832938000000	1.812579000000
H	4.155253000000	-0.051045000000	0.532249000000
O	1.244561000000	2.222290000000	-1.043871000000
H	1.338649000000	2.456620000000	-1.977727000000
H	0.288471000000	1.960643000000	-0.932162000000
O	1.174606000000	-2.196700000000	-1.112868000000
H	1.250805000000	-2.379652000000	-2.059812000000
H	0.221897000000	-1.931431000000	-0.971152000000

1MA_1SA_3W

E[DF-MP2-F12] -1024.471345

O	-1.262459000000	-1.003029000000	1.024067000000
S	-1.592549000000	-0.001291000000	-0.007683000000
O	-1.250406000000	1.373278000000	0.406503000000
O	-3.209106000000	-0.040768000000	-0.174906000000
H	-3.595947000000	0.197639000000	0.686940000000
O	-1.137876000000	-0.348843000000	-1.358355000000
N	2.283639000000	0.010917000000	0.006204000000

H	1.888390000000	-0.142291000000	0.974938000000
H	1.856159000000	0.907954000000	-0.359974000000
H	1.916273000000	-0.774875000000	-0.598496000000
C	3.761946000000	0.065785000000	0.009840000000
H	4.165242000000	-0.864809000000	0.418683000000
H	4.098018000000	0.905440000000	0.624500000000
H	4.127993000000	0.198855000000	-1.011947000000
O	0.979650000000	2.318733000000	-0.761875000000
H	0.792504000000	2.444237000000	-1.703967000000
H	0.098550000000	2.063334000000	-0.366892000000
O	1.005983000000	-0.533308000000	2.393406000000
H	0.115792000000	-0.716738000000	1.978267000000
H	0.839833000000	0.185533000000	3.020559000000
O	1.066842000000	-1.853646000000	-1.623028000000
H	0.179729000000	-1.399362000000	-1.578329000000
H	0.900074000000	-2.754734000000	-1.310315000000

1MA_2SA_1W

E[DF-MP2-F12] -1571.348988

C	0.843348000000	3.379317000000	0.022033000000
H	0.120119000000	4.185510000000	-0.122870000000
H	1.770844000000	3.774156000000	0.443914000000
H	1.052721000000	2.892748000000	-0.933276000000
N	0.273912000000	2.353458000000	0.935684000000
H	-0.630436000000	1.970832000000	0.532580000000
H	0.957628000000	1.545325000000	1.047378000000
S	-2.262412000000	0.036111000000	-0.214384000000
O	-3.609897000000	-0.427029000000	-0.363969000000
O	-2.022175000000	1.482929000000	-0.219734000000
O	-1.593635000000	-0.463973000000	1.112774000000
O	-1.415333000000	-0.651733000000	-1.353066000000
H	0.071459000000	2.737281000000	1.861654000000
H	-0.437097000000	-0.370476000000	-1.294843000000
S	1.979332000000	-0.496273000000	-0.130195000000
O	2.080472000000	0.342512000000	1.081388000000
O	1.071185000000	0.090322000000	-1.134749000000
O	3.409514000000	-0.396623000000	-0.885391000000
O	1.772152000000	-1.919423000000	0.155487000000
H	4.047438000000	-0.930207000000	-0.376940000000
H	0.298675000000	-2.555870000000	0.730162000000
O	-0.619316000000	-2.782865000000	1.046365000000
H	-0.998801000000	-3.357082000000	0.363356000000
H	-1.284482000000	-1.472661000000	1.067328000000

1MA_2SA_2W

E[DF-MP2-F12] -1647.727157

C	-0.009930000000	3.762791000000	0.377836000000
H	-0.905290000000	4.126002000000	0.888588000000
H	0.882838000000	4.057446000000	0.935166000000
H	0.033884000000	4.188987000000	-0.627266000000
N	-0.062127000000	2.285550000000	0.266388000000
H	0.797389000000	1.892821000000	-0.217597000000
H	-0.106671000000	1.827572000000	1.183115000000
S	-2.448592000000	-0.104342000000	-0.204904000000
O	-2.113041000000	-1.274818000000	-1.039141000000
O	-1.854596000000	-0.107982000000	1.138818000000
O	-2.258129000000	1.175148000000	-0.911654000000
O	-4.033409000000	-0.231719000000	0.104703000000
H	-0.919544000000	1.948353000000	-0.255702000000
H	-4.493503000000	-0.356041000000	-0.745779000000
S	2.454443000000	-0.086792000000	-0.205655000000
O	2.113729000000	1.161265000000	-0.898983000000
O	1.919296000000	-0.140950000000	1.168231000000
O	2.196853000000	-1.316739000000	-0.982486000000
O	4.066101000000	0.014342000000	-0.094769000000
H	0.852445000000	-2.151372000000	-0.821801000000
H	4.404420000000	-0.871526000000	0.130020000000
O	0.017721000000	-1.975948000000	1.862189000000
H	0.788262000000	-1.353394000000	1.793220000000
H	-0.763214000000	-1.368410000000	1.808729000000
O	0.021899000000	-2.658121000000	-0.517344000000
H	-0.796354000000	-2.143587000000	-0.837975000000
H	0.014806000000	-2.470125000000	0.567989000000

1MA_2SA_3W

E[DF-MP2-F12] -1724.107905

C	-2.288071000000	3.555123000000	-0.498948000000
H	-2.186463000000	3.810383000000	-1.557075000000
H	-3.334796000000	3.333381000000	-0.274913000000
H	-1.959257000000	4.400560000000	0.110686000000
N	-1.452431000000	2.375564000000	-0.182393000000
H	-0.428373000000	2.529653000000	-0.367420000000
H	-1.711354000000	1.527428000000	-0.718683000000
S	1.803768000000	1.018083000000	-0.186374000000
O	3.251613000000	0.851765000000	-0.235571000000

O	1.303936000000	2.364156000000	-0.480752000000
O	1.286629000000	0.018266000000	-1.328435000000
O	1.198451000000	0.504905000000	1.098086000000
H	0.291528000000	-0.118324000000	-1.268894000000
H	1.376272000000	-0.943467000000	1.270972000000
S	-1.758086000000	-1.456765000000	-0.222845000000
O	-1.348173000000	-0.334163000000	-1.101698000000
O	-0.707409000000	-2.482554000000	-0.078437000000
O	-2.369140000000	-1.038627000000	1.037485000000
O	-2.923397000000	-2.142535000000	-1.110933000000
H	-1.750790000000	0.418646000000	2.050111000000
H	-3.325528000000	-2.850539000000	-0.574361000000
O	-1.323471000000	1.274885000000	2.280791000000
H	-1.507510000000	2.068904000000	0.843475000000
H	-0.368548000000	1.081709000000	2.173993000000
O	1.482155000000	-1.991687000000	1.215048000000
H	2.331349000000	-2.091594000000	0.616130000000
H	0.646718000000	-2.276943000000	0.701305000000
O	3.631244000000	-1.869874000000	-0.155765000000
H	3.579822000000	-2.190411000000	-1.069429000000
H	3.651962000000	-0.876442000000	-0.236518000000

1MA_3SA_1W

E[DF-MP2-F12] -2270.971272

C	0.638073000000	-1.888400000000	3.268637000000
H	1.481193000000	-1.457109000000	3.813674000000
H	-0.169326000000	-2.136324000000	3.961755000000
H	0.964551000000	-2.789044000000	2.744421000000
N	0.146300000000	-0.914922000000	2.260421000000
H	0.895453000000	-0.657818000000	1.566295000000
H	-0.167026000000	-0.032604000000	2.678966000000
S	-2.532557000000	-1.140979000000	-0.296686000000
O	-1.967883000000	-1.864844000000	0.844288000000
O	-1.883814000000	-1.435320000000	-1.592015000000
O	-4.013113000000	-1.758823000000	-0.395219000000
O	-2.695120000000	0.311946000000	-0.073426000000
H	-4.438728000000	-1.405207000000	-1.198537000000
H	-0.672169000000	-1.298761000000	1.710106000000
S	2.679484000000	-0.905875000000	-0.541353000000
O	4.106847000000	-0.998347000000	-0.386399000000
O	1.972399000000	-0.011092000000	0.425775000000
O	2.220459000000	-0.679316000000	-1.928582000000
O	2.020276000000	-2.333068000000	-0.068925000000

H	0.850365000000	-0.215460000000	-2.231700000000
H	2.489843000000	-3.043156000000	-0.543821000000
S	-0.133479000000	2.748396000000	0.232125000000
O	-0.493697000000	4.064866000000	0.652535000000
O	-0.324526000000	2.401456000000	-1.177944000000
O	1.358674000000	2.517042000000	0.655895000000
O	-0.870509000000	1.645570000000	1.103564000000
H	1.661794000000	1.573181000000	0.451492000000
H	-1.624566000000	1.173921000000	0.578512000000
O	-0.094770000000	0.167858000000	-2.458084000000
H	-0.826436000000	-0.476917000000	-2.118671000000
H	-0.194463000000	1.052057000000	-1.964367000000

1MA_3SA_2W

E[DF-MP2-F12] -2347.350502

C	-0.082120000000	-0.308218000000	3.754583000000
H	-1.105676000000	-0.213954000000	4.125099000000
H	0.565559000000	0.404725000000	4.270368000000
H	0.279592000000	-1.324306000000	3.928834000000
N	-0.059715000000	-0.031080000000	2.296970000000
H	0.902326000000	-0.093508000000	1.884229000000
H	-0.386075000000	0.924678000000	2.058977000000
S	-2.694904000000	-0.779910000000	-0.077253000000
O	-2.832604000000	0.560298000000	0.515113000000
O	-2.528189000000	-0.813538000000	-1.523279000000
O	-1.696875000000	-1.609634000000	0.664308000000
O	-4.064620000000	-1.564714000000	0.268889000000
H	-0.682008000000	-0.684331000000	1.757724000000
H	-4.768510000000	-1.197657000000	-0.297935000000
S	0.004964000000	2.620737000000	-0.496725000000
O	-0.300650000000	3.939406000000	-0.959694000000
O	-0.076350000000	1.477269000000	-1.381478000000
O	1.418834000000	2.684417000000	0.192785000000
O	-0.915808000000	2.287762000000	0.793424000000
H	1.795658000000	1.757224000000	0.323917000000
H	-1.696472000000	1.703339000000	0.510311000000
S	2.682357000000	-0.861354000000	-0.037226000000
O	2.274826000000	0.266118000000	0.842945000000
O	2.520565000000	-0.620152000000	-1.463760000000
O	4.265519000000	-0.935191000000	0.269209000000
O	2.098928000000	-2.133832000000	0.440243000000
H	4.676294000000	-1.495832000000	-0.414888000000
H	0.863897000000	-2.715471000000	-0.404826000000

O	0.004941000000	-2.905357000000	-0.914195000000
H	-0.724113000000	-2.557844000000	-0.311817000000
H	0.010947000000	-2.171473000000	-1.778034000000
O	0.000767000000	-1.208740000000	-2.689009000000
H	-0.813846000000	-0.700221000000	-2.473772000000
H	0.760218000000	-0.632959000000	-2.449241000000

S2. Harmonic frequencies (in cm^{-1}) and IR intensities of the global minima of

$\text{CH}_3\text{NH}_2(\text{H}_2\text{SO}_4)_m(\text{H}_2\text{O})_n$ ($m = 0-3$, $n = 0-3$) clusters. MA denotes CH_3NH_2 . SA denotes H_2SO_4 .

W denotes H_2O .

MA

#	Frequency	Infrared
1	296.8589	31.2110
2	805.5308	143.1931
3	947.4758	0.1389
4	1040.5371	9.9757
5	1133.9745	4.8968
6	1306.9243	0.2015
7	1410.0738	1.6327
8	1450.1503	6.9690
9	1471.0266	4.5780
10	1612.1078	19.4192
11	2908.7853	94.7134
12	3005.8658	28.4441
13	3044.5748	25.1136
14	3425.3575	1.9827
15	3499.7479	1.0939

SA

#	Frequency	Infrared
1	240.8819	87.9780
2	323.5798	53.1432
3	352.0313	3.8278
4	417.4161	16.3338
5	467.3803	38.6993
6	508.1864	30.0170
7	521.5307	15.7790
8	761.9952	104.0364
9	817.6411	306.6215

10	1109.7609	64.2912
11	1125.8517	85.2865
12	1177.0560	148.9375
13	1424.6537	258.1877
14	3661.0041	157.3770
15	3664.9216	41.4376

W

#	Frequency	Infrared
1	1593.2507	64.3936
2	3719.9515	1.9142
3	3821.6846	47.9041

IMA_1W

#	Frequency	Infrared
1	42.3531	76.8918
2	75.0817	4.2116
3	106.5308	20.4551
4	222.7950	9.7104
5	333.0274	14.2233
6	468.0770	75.4452
7	789.5849	62.0039
8	869.1727	142.8190
9	960.1643	0.5800
10	1029.6406	10.7670
11	1146.7989	5.4227
12	1306.3202	0.3779
13	1413.9826	2.3698
14	1452.3851	4.6318
15	1470.0834	6.3845
16	1608.1584	27.1525
17	1633.9421	22.2285
18	2944.9911	81.8971
19	3030.5710	14.8066
20	3065.4151	14.1818
21	3289.7154	884.4611
22	3426.2910	1.6733
23	3500.6628	4.7181
24	3787.4082	39.2643

IMA_2W

#	Frequency	Infrared
1	56.1485	0.5930
2	94.5836	6.0487
3	124.1963	11.5298
4	158.2696	25.3892
5	189.4312	79.7402
6	218.3016	10.3993
7	245.6460	34.5533
8	260.2163	54.1276
9	425.8447	99.3587
10	453.8817	26.9474
11	518.2165	109.4960
12	759.4683	182.0553
13	920.3214	178.2272
14	931.0438	2.9008
15	1032.0745	9.8938
16	1042.5538	9.5115
17	1154.1987	10.1894
18	1318.8023	2.6196
19	1411.6683	3.0750
20	1453.1687	4.4929
21	1473.4849	4.6644
22	1611.7984	47.4904
23	1622.6614	32.6372
24	1635.5397	9.7713
25	2943.8810	205.3804
26	3006.8825	982.4535
27	3020.6141	55.3713
28	3056.3693	23.1242
29	3353.3767	182.9606
30	3374.8441	534.4070
31	3480.1182	23.5823
32	3778.6028	38.2715
33	3789.6256	44.9651

1MA_3W

#	Frequency	Infrared
1	37.3951	0.1898
2	77.3256	3.0303
3	91.4419	2.6012
4	104.6542	2.0664
5	138.7598	1.1079
6	185.2715	7.8366

7	229.1689	84.5753
8	237.5275	23.8995
9	268.4354	32.6366
10	276.1866	104.1431
11	302.3619	27.4334
12	316.5717	129.8027
13	443.8738	31.5567
14	488.1777	22.7579
15	509.5551	65.6127
16	629.1609	44.9646
17	837.3922	61.9555
18	920.1342	85.7229
19	956.3198	115.7273
20	985.8179	65.2054
21	1035.3934	9.9070
22	1117.9907	11.8910
23	1179.7475	17.4222
24	1330.0429	4.0414
25	1411.1636	5.0007
26	1451.4125	5.0512
27	1470.6400	4.9562
28	1614.1662	53.6830
29	1629.8122	15.1106
30	1634.6838	23.4242
31	1658.5165	14.8880
32	2724.4768	1651.6441
33	2951.1164	41.2166
34	3024.0654	22.3195
35	3059.6111	19.4519
36	3116.8109	1048.6012
37	3239.2331	915.2326
38	3276.2714	368.8506
39	3464.2213	17.3800
40	3777.2758	38.5403
41	3778.6950	42.8138
42	3786.9848	40.5878

IMA_1SA

#	Frequency	Infrared
1	36.7332	4.4994
2	60.2092	1.6885
3	101.7744	8.7048
4	118.2142	6.2039

5	142.9139	63.5267
6	210.1058	3.6404
7	315.9899	108.8810
8	364.0157	13.9876
9	432.8180	20.8019
10	459.3271	4.9561
11	531.1291	12.3718
12	552.5232	22.9923
13	569.8025	139.2250
14	744.1821	194.3881
15	893.6311	83.2680
16	943.4568	48.6869
17	986.4435	242.4663
18	1017.2553	10.2684
19	1079.6772	125.4706
20	1112.5822	88.1370
21	1203.7356	43.6950
22	1277.2452	0.1589
23	1293.9403	519.4709
24	1411.5995	26.4200
25	1457.2818	8.0741
26	1463.4807	8.2607
27	1562.9241	180.1741
28	1565.4104	261.8428
29	1596.7691	308.8300
30	2465.8789	743.5635
31	2865.2931	1081.2762
32	3014.5641	2.9207
33	3096.4364	5.0099
34	3104.3377	1.4249
35	3463.9075	42.8807
36	3695.0608	77.9807

IMA_2SA

#	Frequency	Infrared
1	30.6525	1.6807
2	48.0556	6.1153
3	77.5841	0.8265
4	85.5457	1.7708
5	96.4050	1.4555
6	109.2761	2.5074
7	126.6182	0.2646
8	158.4754	5.4585

9	168.4593	7.4511
10	178.3942	40.8718
11	185.2687	37.2348
12	233.3495	56.6024
13	265.1635	92.4546
14	376.8167	4.9687
15	380.6168	26.1831
16	393.9817	2.6745
17	439.2815	19.7597
18	500.0136	23.3524
19	519.2611	9.4387
20	530.5817	11.7017
21	533.4819	17.9748
22	541.4611	15.2431
23	557.7725	37.9126
24	577.4473	40.1767
25	769.1161	24.1837
26	794.0230	164.8314
27	832.1531	81.3384
28	877.5802	66.5375
29	890.6162	135.4998
30	939.2730	31.5390
31	976.7535	7.7701
32	996.4513	14.8056
33	1018.3246	284.9601
34	1098.5608	3.8628
35	1115.4871	313.7209
36	1144.6223	305.2239
37	1223.2508	392.5876
38	1265.6350	64.9718
39	1271.7446	1.9457
40	1289.8120	87.9659
41	1296.7903	170.2058
42	1410.0514	202.7305
43	1413.0544	49.5941
44	1458.3924	7.6653
45	1466.4282	7.4697
46	1548.1138	40.2711
47	1621.5192	15.2190
48	1664.3623	93.9614
49	2752.0023	413.1268
50	2819.5812	419.8427
51	2876.7124	1083.0349
52	2973.2384	3397.8465

53	3020.8218	12.1038
54	3108.4318	1.5919
55	3115.4558	0.3383
56	3444.3592	52.8054
57	3675.2991	92.2272

IMA_3SA

#	Frequency	Infrared
1	30.2450	0.2320
2	44.6516	1.8666
3	52.3735	2.6542
4	63.6373	2.7498
5	67.6629	1.4469
6	73.3306	1.0809
7	89.0004	3.0422
8	96.9796	0.8796
9	102.5245	0.7639
10	110.9268	5.4136
11	118.9015	4.3085
12	146.2917	2.3165
13	154.9917	9.6063
14	162.0167	0.5487
15	175.2485	27.5010
16	185.6467	7.1741
17	195.2014	57.9609
18	212.4436	68.8170
19	247.0326	53.9458
20	364.3649	3.7411
21	368.0429	8.7624
22	379.8822	6.3198
23	400.5493	5.3882
24	403.1019	2.4779
25	426.0523	16.9696
26	460.4761	5.9941
27	511.5730	3.4611
28	517.3833	7.9029
29	521.1729	10.8797
30	527.1295	30.9674
31	530.7157	45.9562
32	537.4692	28.9816
33	544.5836	16.0559
34	556.0270	47.8529
35	567.4949	20.6401

36	730.2131	23.4979
37	753.9852	42.9610
38	789.7057	127.8195
39	808.7865	68.3655
40	823.8702	50.8080
41	828.1874	92.4866
42	854.6488	70.6084
43	889.4739	143.6252
44	898.7471	228.1326
45	924.9878	19.9986
46	976.9034	19.8292
47	994.1101	47.6053
48	1006.3357	292.0892
49	1096.0782	270.6946
50	1104.0947	120.4920
51	1113.8038	83.9594
52	1138.1153	513.2678
53	1220.1237	85.6609
54	1242.7232	292.1180
55	1255.5642	180.7013
56	1259.6590	5.9097
57	1272.5627	60.4292
58	1275.4268	8.0849
59	1288.9975	149.5275
60	1391.9323	355.1955
61	1407.4177	217.2594
62	1413.1192	59.6834
63	1457.1578	12.2020
64	1466.8027	8.9530
65	1542.8666	50.9043
66	1625.8571	21.9012
67	1646.4439	29.1205
68	2830.4144	863.1051
69	2923.2968	291.2823
70	2995.6166	691.7428
71	3020.3302	149.0114
72	3037.0603	405.9481
73	3089.1328	2060.3976
74	3111.1084	16.1808
75	3119.1350	5.5578
76	3134.5147	2741.6446
77	3435.9663	50.5289
78	3670.6672	104.0173

1MA_1SA_1W

#	Frequency	Infrared
1	21.6782	3.3432
2	50.8855	2.7945
3	88.9142	7.6910
4	111.2853	3.2532
5	129.7434	73.4043
6	139.8686	1.0019
7	169.2871	0.8229
8	209.7288	5.0926
9	261.5049	54.2467
10	307.8537	65.8807
11	323.4081	99.1545
12	380.1149	21.0838
13	426.7388	19.5129
14	482.5030	97.7826
15	523.2402	34.1672
16	542.8370	49.1094
17	561.9550	56.2602
18	612.1271	27.2025
19	753.6008	217.8676
20	846.9334	119.8848
21	955.2340	38.9646
22	996.4035	147.8447
23	1001.9142	46.0790
24	1005.5865	114.5122
25	1088.1758	160.9981
26	1130.4377	166.6909
27	1254.7674	36.3467
28	1281.8851	237.4643
29	1288.0457	139.0272
30	1408.2649	3.6472
31	1457.4297	5.3991
32	1464.0194	4.2151
33	1556.9266	28.2214
34	1601.5773	53.8345
35	1634.2077	9.9484
36	1676.4856	97.1892
37	2340.8247	1785.6915
38	2847.8363	834.6728
39	3014.5974	5.9056
40	3100.2179	4.1856
41	3108.1649	0.0219

42	3183.6772	1163.9845
43	3452.1309	32.8773
44	3695.0222	80.5090
45	3779.0385	63.0471

IMA_1SA_2W

#	Frequency	Infrared
1	34.2302	3.5287
2	54.9868	0.5419
3	70.2285	1.4299
4	89.6504	6.3847
5	95.7932	7.2277
6	110.0269	2.7533
7	145.1708	3.7973
8	158.2105	56.7830
9	199.3166	16.7650
10	220.8501	20.0234
11	229.2318	24.8688
12	252.5449	128.4049
13	254.4924	52.9532
14	281.0331	61.9244
15	305.8062	13.3222
16	397.8228	15.9978
17	419.8479	10.8477
18	466.2040	7.9465
19	491.6249	142.1826
20	529.0150	34.3155
21	545.3551	35.1373
22	565.1290	20.5670
23	641.6210	35.9280
24	765.9185	199.9216
25	808.3883	188.4747
26	837.5334	37.4218
27	987.5387	14.7778
28	990.4256	12.5288
29	1014.6057	235.3127
30	1028.5302	1.0007
31	1107.2885	116.7062
32	1145.3736	290.1711
33	1227.8058	285.9198
34	1268.2812	29.6719
35	1278.3473	32.9517
36	1415.1759	3.4634

37	1461.7196	6.0333
38	1463.0568	5.4539
39	1601.4668	209.4624
40	1621.3377	11.8065
41	1640.5475	8.2596
42	1654.8623	92.8720
43	1675.5592	70.9336
44	2838.0266	612.2903
45	2937.4242	624.3997
46	2955.6810	905.6964
47	3016.6395	19.4566
48	3094.3758	4.7099
49	3099.6309	1.3936
50	3197.9630	827.3089
51	3237.3992	1496.6057
52	3685.0139	72.3041
53	3783.5149	41.6981
54	3784.8201	82.1745

1MA_1SA_3W

#	Frequency	Infrared
1	37.2713	3.3906
2	39.8500	3.1431
3	44.6341	1.5306
4	61.3643	8.8637
5	64.2767	7.2751
6	76.9916	2.8972
7	112.8462	2.8258
8	115.0751	2.2570
9	152.5339	0.0619
10	157.8463	47.2264
11	201.1201	7.1344
12	206.0481	27.9574
13	241.9070	64.0299
14	256.7831	2.7841
15	270.7253	52.0970
16	272.7279	48.2378
17	317.4622	30.3529
18	323.0985	104.6419
19	334.6410	107.5935
20	399.2965	20.7960
21	411.3334	1.9782
22	456.3208	60.5075

23	492.7280	31.8405
24	495.5108	43.5559
25	537.5583	66.5700
26	551.0588	38.5172
27	554.3376	50.2533
28	720.6420	0.2727
29	760.9128	219.3417
30	822.5028	178.5201
31	832.6239	175.6536
32	864.2534	8.6661
33	1014.4595	30.8582
34	1015.7289	31.3302
35	1016.6872	194.5197
36	1026.3397	8.7209
37	1105.5085	109.9290
38	1168.0741	312.3567
39	1223.4305	271.1800
40	1306.0251	1.9847
41	1308.0938	4.8060
42	1413.2974	2.0474
43	1462.9138	5.6709
44	1463.5929	5.7967
45	1598.9581	164.2158
46	1620.7998	16.4732
47	1623.4678	13.4522
48	1639.9172	0.9081
49	1686.6648	26.9741
50	1687.8591	26.9418
51	2819.4538	790.8546
52	2841.0697	740.1550
53	2888.7247	1036.6087
54	3013.5242	0.5940
55	3094.4761	3.3077
56	3094.7490	3.2095
57	3192.8798	765.5593
58	3206.4099	850.4740
59	3239.0642	1617.9311
60	3683.8155	69.2681
61	3768.6851	57.6052
62	3772.5514	58.6064
63	3773.8202	50.2807

1MA_2SA_1W

#	Frequency	Infrared
1	36.1189	6.6917
2	46.2745	0.4254
3	63.0841	2.1206
4	70.0291	0.1722
5	81.5121	6.6930
6	88.0615	3.3030
7	100.8256	2.1865
8	108.5442	1.2745
9	123.7094	7.4463
10	150.6134	54.7216
11	165.9816	2.4122
12	174.7785	1.6631
13	196.0201	38.4761
14	236.9989	52.0448
15	260.9287	77.2295
16	294.2254	57.6602
17	362.7602	74.7703
18	367.5174	2.1512
19	390.9617	14.3902
20	422.7951	11.2890
21	444.7497	83.5459
22	499.8677	5.1080
23	514.3646	29.9172
24	523.4092	27.2190
25	534.5663	12.4670
26	538.0292	29.3996
27	552.4815	31.0154
28	558.0016	31.3586
29	570.7827	40.5885
30	766.4955	120.1471
31	787.0502	239.6843
32	834.9083	58.3421
33	889.1237	32.4148
34	915.0839	187.9828
35	939.7488	25.8913
36	991.8505	15.5522
37	999.8224	5.4453
38	1019.2469	266.2878
39	1098.0577	189.6895
40	1112.2116	149.8800
41	1145.4496	156.9593
42	1175.4169	358.0240
43	1220.6060	275.8731

44	1267.6385	91.1248
45	1273.4149	7.5489
46	1288.1579	3.5140
47	1358.4788	298.5089
48	1398.8671	109.6629
49	1414.7479	1.3965
50	1457.7633	8.1829
51	1466.0443	8.1328
52	1540.8687	31.2540
53	1615.4083	23.5841
54	1625.7842	7.1915
55	1660.4830	30.4471
56	2301.6588	1976.3624
57	2733.0346	659.5568
58	2816.1050	1026.7268
59	2874.9114	2590.6230
60	3020.7870	1.9392
61	3107.9887	1.8591
62	3114.4901	0.0916
63	3245.3630	1148.6263
64	3443.8155	45.4459
65	3680.5020	89.1846
66	3757.6773	81.9428

1MA_2SA_2W

#	Frequency	Infrared
1	28.9035	2.2574
2	37.8272	0.2192
3	39.6483	2.0850
4	53.9770	0.1772
5	57.2246	2.3471
6	61.5388	3.7098
7	91.1327	2.8146
8	93.3895	2.8490
9	96.0174	3.7548
10	146.7086	3.6981
11	149.9604	8.2043
12	155.2677	40.9250
13	157.8984	10.8305
14	162.7565	38.3365
15	164.5905	22.6478
16	211.2778	99.0791
17	227.4539	8.9022

18	232.7461	22.0304
19	272.5931	141.0700
20	375.1367	9.8184
21	381.5240	4.0506
22	430.1738	2.8854
23	436.5400	66.0546
24	446.8770	24.2533
25	480.5958	4.5132
26	503.1459	9.0679
27	522.8075	25.8490
28	534.9251	14.2243
29	543.4600	37.0418
30	546.5199	33.0782
31	563.2762	66.3092
32	576.9486	55.6854
33	697.4993	75.2524
34	756.3579	59.5328
35	762.2272	147.9175
36	788.8906	190.3439
37	796.4173	96.4267
38	945.4204	9.4526
39	954.9036	241.9365
40	972.3230	11.3891
41	985.2022	6.4325
42	1014.9819	22.3183
43	1016.0942	451.7307
44	1020.7621	17.5174
45	1099.9902	124.7126
46	1100.9065	55.6084
47	1158.2330	74.2708
48	1164.5716	215.5069
49	1205.7677	73.1454
50	1219.1730	584.5124
51	1269.6762	34.6528
52	1277.7930	19.6712
53	1396.2845	491.2430
54	1416.0489	0.0473
55	1461.7721	8.0882
56	1462.8763	9.4358
57	1581.7728	89.0524
58	1625.4437	63.8158
59	1634.2207	6.7034
60	1647.0985	83.5367
61	1662.5015	32.6648

62	1778.9497	783.3557
63	1786.0514	789.4535
64	2774.1838	190.5909
65	2843.4648	1916.8656
66	2864.3154	2385.3693
67	2954.9861	627.2650
68	3019.5888	1.1113
69	3105.1345	0.9429
70	3107.3924	2.3737
71	3333.3042	887.2218
72	3374.6796	681.4186
73	3411.9839	37.7982
74	3677.5724	88.8823
75	3682.4783	81.2978

1MA_2SA_3W

#	Frequency	Infrared
1	41.4986	5.3342
2	45.9311	2.9081
3	49.4697	0.2714
4	68.0250	1.7266
5	75.9226	5.3004
6	84.7741	3.8790
7	92.1143	2.1693
8	93.5583	2.1811
9	98.3167	3.0455
10	110.3211	3.6081
11	133.7675	3.7167
12	153.3742	0.8312
13	157.0833	0.0558
14	169.9447	1.8405
15	170.9163	17.3988
16	185.8784	30.7563
17	187.1362	66.2130
18	229.2340	25.6734
19	240.1961	50.8373
20	291.8947	78.5761
21	299.9276	43.6377
22	328.4618	94.5730
23	350.2463	85.8857
24	380.1656	0.4555
25	397.9537	8.0895
26	408.2254	18.9729

27	434.6823	5.1368
28	440.8036	0.1541
29	504.3794	27.4780
30	527.4739	47.4289
31	538.0647	22.8412
32	542.7232	1.9212
33	550.1325	88.8374
34	557.4967	16.2553
35	565.3111	56.8557
36	588.3622	48.1331
37	695.5582	173.9730
38	741.3062	103.4531
39	768.8359	160.8333
40	789.0223	136.1059
41	801.5244	104.6654
42	809.2168	104.8303
43	841.8787	35.3302
44	858.1664	66.2049
45	951.5122	83.5794
46	957.4419	42.3081
47	983.3640	70.0958
48	999.7242	13.6059
49	1013.4996	300.5211
50	1023.9082	4.2343
51	1097.5277	56.2942
52	1111.6379	346.0217
53	1172.8009	285.1045
54	1214.5535	347.0034
55	1217.2684	194.6979
56	1257.3914	58.2639
57	1271.6830	37.2343
58	1293.8107	190.3920
59	1357.2188	278.2342
60	1415.8004	2.0966
61	1461.2996	6.2611
62	1463.9543	7.4228
63	1602.9515	225.7126
64	1617.6430	19.1300
65	1639.0573	59.8460
66	1657.7038	25.7431
67	1660.5113	78.8649
68	1686.4767	37.2351
69	1742.9823	126.2501
70	2263.3299	1563.0754

71	2544.6816	1815.3381
72	2662.9481	964.9818
73	2883.5194	813.8315
74	2960.2471	601.5308
75	3016.5432	1.0828
76	3071.3117	1852.4752
77	3099.9430	2.7070
78	3102.4261	9.4188
79	3231.5983	306.9084
80	3253.6294	950.0429
81	3480.9005	452.0371
82	3570.8751	352.8780
83	3675.7302	86.7415
84	3758.4993	69.9826

1MA_3SA_1W

#	Frequency	Infrared
1	28.6078	1.4045
2	36.7635	1.3020
3	37.6981	1.7790
4	48.2477	0.1968
5	56.9289	0.4012
6	65.3850	2.7700
7	71.0680	7.0669
8	73.7976	0.3505
9	82.5287	0.2467
10	85.3699	2.9950
11	99.2209	0.6555
12	114.2856	0.6445
13	128.1247	7.1538
14	146.2029	1.4404
15	151.4670	9.7989
16	171.8580	47.1770
17	176.7680	13.3899
18	208.7088	33.0585
19	211.1967	84.8026
20	233.2130	21.5070
21	240.0179	34.6682
22	268.8532	53.5993
23	294.9705	150.3798
24	359.3286	1.0438
25	381.6645	4.7333
26	391.7038	4.3678

27	412.6947	20.2455
28	431.6292	10.1003
29	437.8699	3.5824
30	494.7321	3.3909
31	510.7047	17.7515
32	522.8349	23.1030
33	526.6778	67.7525
34	532.9393	8.8921
35	538.8150	28.8691
36	544.2067	28.8273
37	557.0505	77.7634
38	573.8607	31.9599
39	578.8013	22.0530
40	744.1441	118.1738
41	751.1274	14.3943
42	795.8501	170.9545
43	821.5112	24.2039
44	830.6758	108.5432
45	852.2670	94.4324
46	879.9639	243.4600
47	895.8708	11.3027
48	914.7358	148.3410
49	928.2695	18.8162
50	980.2610	6.0220
51	996.1594	233.2584
52	1006.1233	10.0466
53	1023.5883	333.1019
54	1075.6590	43.5134
55	1105.7303	32.7497
56	1114.3660	178.1178
57	1132.8197	179.0730
58	1161.0915	427.6186
59	1218.8336	551.5385
60	1245.9258	86.3361
61	1256.5284	25.0945
62	1260.0220	243.7648
63	1275.9255	52.3806
64	1287.3222	101.6061
65	1310.9724	452.4488
66	1374.8251	294.2324
67	1416.3047	1.1887
68	1458.9367	10.2437
69	1463.0493	10.0190
70	1564.3075	82.2182

71	1635.7573	19.6803
72	1648.6527	9.5693
73	1655.0052	26.4132
74	1676.8008	7.0763
75	2422.9418	2109.3942
76	2592.3649	489.1281
77	2678.0868	2371.1827
78	2861.5584	2123.0974
79	2912.0901	1168.9583
80	2933.7200	668.7062
81	3014.4355	2035.5001
82	3025.3225	422.4354
83	3109.7341	0.5081
84	3115.7876	0.6455
85	3410.8043	70.6208
86	3672.5168	97.5793
87	3679.3733	89.0643

1MA_3SA_2W

#	Frequency	Infrared
1	28.0141	6.6414
2	34.8932	3.5785
3	49.5039	1.4601
4	50.5952	0.3843
5	56.6148	0.9646
6	59.5654	3.2685
7	66.4851	0.8291
8	72.0414	3.0682
9	72.1351	0.8440
10	81.9806	1.9478
11	95.3417	4.3940
12	101.8455	1.8286
13	106.3429	4.5815
14	120.5392	2.0460
15	124.0185	1.3091
16	144.5983	17.1595
17	157.4530	0.8000
18	162.8542	8.6496
19	167.8302	28.0080
20	183.6828	79.3138
21	185.3899	50.0539
22	203.1511	47.0939
23	207.8427	31.8934

24	216.6851	20.9516
25	242.8957	77.9404
26	365.1491	12.2944
27	387.3627	8.6234
28	392.6110	16.2717
29	396.4119	33.6662
30	404.8313	60.5445
31	417.8269	11.0774
32	426.9571	1.6114
33	473.8160	48.8139
34	511.1729	3.4256
35	515.9899	35.0966
36	519.2263	20.5324
37	522.7158	34.9692
38	530.9646	23.1991
39	536.6152	15.6465
40	548.0649	94.2906
41	555.2084	18.8090
42	561.2051	15.1199
43	580.4352	51.8566
44	654.5236	7.8796
45	680.1359	4.0578
46	721.5391	148.3682
47	762.9815	189.4302
48	781.5708	265.9948
49	791.8672	150.4478
50	823.3950	32.2576
51	833.3001	136.1133
52	877.0211	226.3900
53	910.4589	45.4833
54	942.9947	4.7092
55	972.4775	6.3669
56	974.9087	11.5858
57	1001.0721	456.8552
58	1009.3572	83.6872
59	1014.4683	119.3140
60	1091.2309	52.3634
61	1092.5447	102.8790
62	1143.7422	67.1214
63	1157.2321	77.7209
64	1163.9081	223.2380
65	1230.7089	365.2009
66	1236.6511	39.9746
67	1249.2524	42.2385

68	1254.9947	28.4219
69	1270.4837	25.8540
70	1287.0587	76.7422
71	1368.6682	1261.5377
72	1393.8317	82.9096
73	1416.4975	2.1508
74	1462.0487	9.4940
75	1462.6303	8.0668
76	1485.9847	876.9317
77	1569.2529	72.9857
78	1603.4631	642.4853
79	1647.9628	94.2183
80	1664.0163	64.1641
81	1693.8201	57.8864
82	1769.1748	74.6515
83	2889.3138	175.1812
84	2913.6919	738.5276
85	2983.4313	2269.3789
86	2984.9049	881.0369
87	3022.4254	77.4073
88	3062.1329	1370.3923
89	3099.0625	1033.0768
90	3110.1993	20.4485
91	3110.4101	5.4849
92	3211.1147	532.5748
93	3499.4758	214.2979
94	3551.3040	552.5159
95	3672.5713	100.2243
96	3675.5729	94.2664

S3. Differences between the PW91 and DF-MP2-F12 binding energies (electronic energies)

for the clusters

The binding energy (ΔE) was calculated as the energy difference between the cluster and infinitely separated constituents:

$$\Delta E = E[CH_3NH_2(H_2SO_4)_m(H_2O)_n] - E[CH_3NH_2] - m * E[H_2SO_4] - n * E[H_2O]$$

	ΔE (PW91 & DF-MP2-F12)	ΔE (PW91)	deviation
CH ₃ NH ₂ (H ₂ O)	-5.6069	-6.1414	-0.5345

CH ₃ NH ₂ (H ₂ O) ₂	-12.6130	-13.8008	-1.1878
CH ₃ NH ₂ (H ₂ O) ₃	-20.8149	-24.1428	-3.3279
CH ₃ NH ₂ (H ₂ SO ₄)	-21.2231	-19.0531	2.1700
CH ₃ NH ₂ (H ₂ SO ₄) ₂	-52.4808	-46.3661	6.1147
CH ₃ NH ₂ (H ₂ SO ₄) ₃	-74.7288	-64.7892	9.9396
CH ₃ NH ₂ (H ₂ SO ₄)(H ₂ O)	-33.7650	-31.6328	2.1322
CH ₃ NH ₂ (H ₂ SO ₄)(H ₂ O) ₂	-46.1326	-44.3737	1.7589
CH ₃ NH ₂ (H ₂ SO ₄)(H ₂ O) ₃	-55.9399	-54.7233	1.2166
CH ₃ NH ₂ (H ₂ SO ₄) ₂ (H ₂ O)	-62.5619	-57.6920	4.8699
CH ₃ NH ₂ (H ₂ SO ₄) ₂ (H ₂ O) ₂	-72.9669	-69.5714	3.3955
CH ₃ NH ₂ (H ₂ SO ₄) ₂ (H ₂ O) ₃	-84.2752	-80.8020	3.4732
CH ₃ NH ₂ (H ₂ SO ₄) ₃ (H ₂ O)	-82.9566	-76.5412	6.4154
CH ₃ NH ₂ (H ₂ SO ₄) ₃ (H ₂ O) ₂	-93.8536	-86.0536	7.8000

The deviations were obtained by the results of PW91 method subtracting the corresponding results of PW91 & DF-MP2-F12 method. From the table above, except for the results of the clusters containing three sulfuric acid molecules and CH₃NH₂(H₂SO₄)₂ cluster, the deviations are smaller than 5 kcal/mol.

S4. Method Validation

In order to verify the validity of the results calculated by PW91 & DF-MP2-F12, another seven methods (MP2, PW91, PBE1PBE, B3LYP, CAM-B3LYP, M062X and wB97XD) which are the general theoretical methods previous employed in atmospheric cluster calculations were performed for the relative small clusters, H₂O, CH₃NH₂, H₂SO₄, CH₃NH₂(H₂SO₄)(H₂O) (refer to J. Phys. Chem. 2009, 113, 680–689; Proc. Natl. Acad. Sci. USA, 2009, 106, 17650-17654; J. Chem. Phys. 2013, 139, 064312; Phys. Chem. Chem. Phys., 2013, 15, 16442-16445; Phys. Chem. Chem. Phys., 2015, 17, 9552-9563; J. Phys. Chem. A 2015, 119, 3035-3047.). The results of all the functionals would be compared with that of MP2 to investigate their performance.

In this work, we focus on the binding energy (ΔE) and the Gibbs free energy (ΔG). They were calculated as the energy difference between the cluster and infinitely separated constituents:

$$\Delta E = E[CH_3NH_2(H_2SO_4)(H_2O)] - E[CH_3NH_2] - E[H_2SO_4] - E[H_2O]$$

$$\Delta G = G[CH_3NH_2(H_2SO_4)(H_2O)] - G[CH_3NH_2] - G[H_2SO_4] - G[H_2O]$$

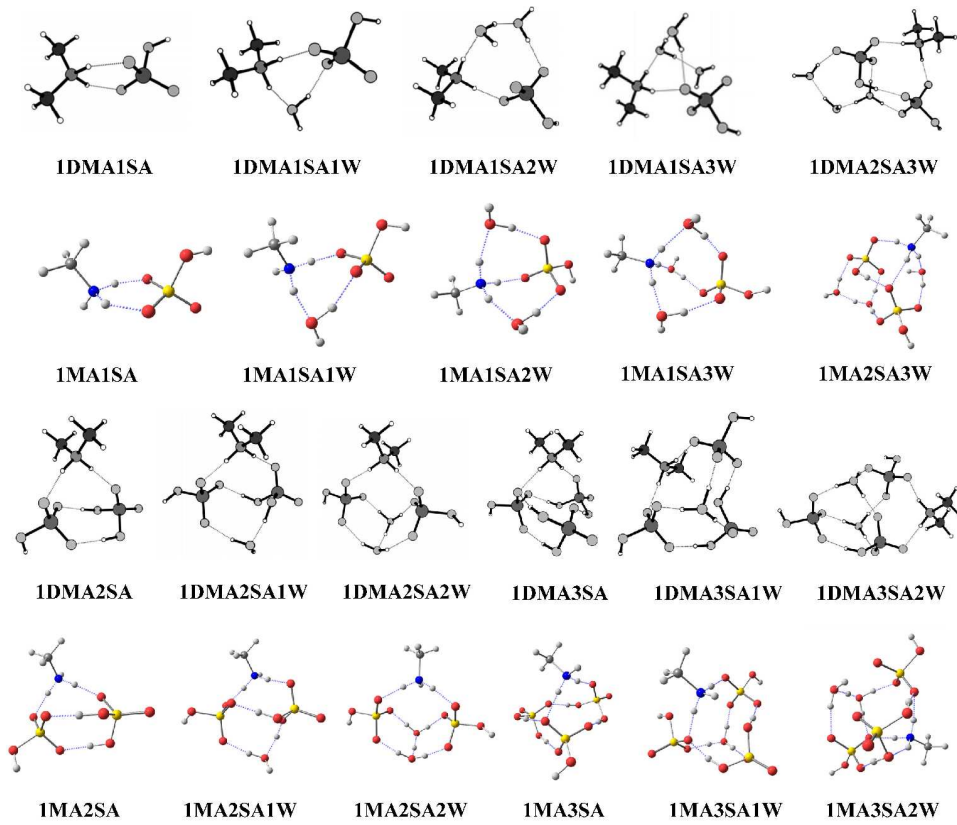
The divisions of each functional, $\Delta\Delta E$ and $\Delta\Delta G$, were calculated by the results of MP2 subtracting the results of the corresponding functional.

The results are shown in the table below. W, MA, SA and 1MA1SA1W denote the water, methylamine, sulfuric acid molecules and the $CH_3NH_2(H_2SO_4)(H_2O)$ cluster, respectively. From the table, especially from the data of $\Delta\Delta E$ and $\Delta\Delta G$, we can get that compared with the other functionals the results of PW91 & DF-MP2-F12 which is the method we used in this work and PW91 are closer to the results of MP2. For the clusters calculated in our work, the order of the other methods in terms of difference with MP2 is: wB97XD, M062X, CAM-B3LYP, PBE1PBE and B3LYP. Although the method of PW91 & DF-MP2-F12 we used should be better in theory, PW91 has the best performance here. The $\Delta\Delta E$ and $\Delta\Delta G$ of the Pw91 method are 1.16 kcal/mol and 1.12 kcal/mol, respectively. While that of the PW91 & DF-MP2-F12 method are 1.17 kcal/mol and 1.21 kcal/mol, respectively. The $\Delta\Delta E$ and $\Delta\Delta G$ differences of these two methods are 0.01 kcal/mol and 0.09 kcal/mol. As the table below shown, all of the functional methods have resulted in the underestimation of the results to some extent. The PW91 & DF-MP2-F12 method we used has corrected the problem of underestimate by other functional methods, but also caused a litter overestimation. Compared with the best performance, PW91, the divisions, 0.01 kcal/mol and 0.09 kcal/mol, of PW91 & DF-MP2-F12 method we used are so small that our method is also apposite.

method	Isomer	E(hartre e)	G(hartre ee)	ΔE (kcal/ mol)	ΔG (kcal/ mol)	$\Delta\Delta E$ (kcal/ mol)	$\Delta\Delta G$ (kcal/ mol)
MP2	W	-76.30	-76.32				
	MA	-95.60	-95.62				
	SA	-699.37	-699.39				
	1MA1SA1W	-871.32	-871.36	-32.59	-14.14		
PW91+ DF-MP2 -F12	W	-76.34	-76.35				
	MA	-95.64	-95.67				
	SA	-699.55	-699.58				
	1MA1SA1W	-871.58	-871.62	-33.77	-15.35	1.17	1.21
PW91	W	-76.42	-76.43				
	MA	-95.79	-95.81				
	SA	-700.30	-700.33				
	1MA1SA1W	-872.55	-872.59	-31.43	-13.01	-1.16	-1.12
WB97X D	W	-76.42	-76.43				
	MA	-95.80	-95.82				
	SA	-700.28	-700.31				
	1MA1SA1W	-872.55	-872.59	-31.12	-12.54	-1.47	-1.60
M062X	W	-76.41	-76.42				
	MA	-95.78	-95.80				
	SA	-700.25	-700.28				
	1MA1SA1W	-872.48	-872.52	-31.04	-12.66	-1.55	-1.47
CAM-B 3LYP	W	-76.41	-76.43				
	MA	-95.78	-95.80				
	SA	-700.30	-700.33				
	1MA1SA1W	-872.55	-872.59	-30.54	-12.14	-2.05	-2.00
PBE1PB E	W	-76.36	-76.37				
	MA	-95.71	-95.74				
	SA	-699.93	-699.96				
	1MA1SA1W	-872.05	-872.09	-29.73	-11.24	-2.86	-2.89
B3LYP	W	-76.44	-76.46				
	MA	-95.84	-95.86				
	SA	-700.39	-700.42				
	1MA1SA1W	-872.71	-872.75	-26.78	-8.57	-5.81	-5.56

S5. The structural patterns of the two bases (methylamine and dimethylamine) clusters

The gray graphs represent the structures of dimethylamine - sulfuric acid – water clusters (refer to the reference 71). The color images representative the structures of methylamine - sulfuric acid - water clusters. MA, DMA, SA and W denote CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, H_2SO_4 and H_2O molecules, respectively.



S6. Method for hydrate distribution

The number concentration of a hydrate, e.g. one H_2SO_4 with n water molecules can be given as:

$$\rho(1, n) = K_1 K_2 \cdots K_n \left(\frac{\rho_{\text{water}}^{\text{free}}}{\rho} \right)^n \rho_{\text{H}_2\text{SO}_4}^{\text{free}} \quad (1)$$

Where K_m are the equilibrium constants

$$K_m = e^{\frac{\Delta G_m}{RT}} \quad (2)$$

with ΔG_m the formation free energy of an m -hydrate formed from one water molecule and $(m-1)$ -hydrate, T the temperature and R the molar gas constant. The free monomer concentration of water is approximately given by

$$\rho_{\text{water}}^{\text{free}} = \frac{S}{k_B T} P_{\text{water}}^{\text{eq}} \quad (3)$$

where S is the saturation ratio (here S is defined as a ratio of the proper partial pressure of the water vapor to the saturation vapor pressure and thus the relative humidity is defined as $\text{RH} = 100\% \times S$), k_B the Boltzmann constant, T the temperature in Kelvins and $P_{\text{water}}^{\text{eq}}$ the saturation vapor pressure of water (Seinfeld and Pandis, 1998) in Pascals. This is a valid approximation, since the hydration of the small clusters does not significantly affect the amount of free water molecules available, as there are always several orders of magnitude more water molecules in the atmosphere than any other condensing species.

The reference concentration ρ can be given in terms of some reference pressure P (here $P = 1$ atm), the Boltzmann constant k_B and the temperature T as

$$\rho = \frac{P}{k_B T} \quad (4)$$

As we are interested in the relative fractions of the different hydrates of the cluster cores, the absolute concentrations of the nonhydrated core clusters are not needed. For example, in the particular case of hydration of one sulfuric acid molecule, the concentration of free sulfuric acid $\rho_{\text{H}_2\text{SO}_4}^{\text{free}}$ is eventually cancelled out from the final expressions. Thus, the relative concentration of some m -hydrate in this case is then given as

$$\begin{aligned}
\frac{\rho(1,m)}{\rho_{H_2SO_4}^{total}} &= \frac{\rho(1,m)}{\rho(1,0) + \rho(1,1) + \dots + \rho(1,n)} \\
&= \frac{K_1 K_2 \dots (S \frac{P_{water}^{eq}}{p})^m}{1 + K_1 S \frac{P_{water}^{eq}}{p} + \dots + K_1 K_2 \dots K_n (S \frac{P_{water}^{eq}}{p})^n}
\end{aligned} \tag{5}$$

where the hydration level m can take values between 1 and n , n being the amount of water molecules in the most extensively hydrated case

In addition, saturated water vapor pressures we used here are 3.169 KPa at 298.15 K and 0.611 KPa at 273.15 K.

S7. Basis set and functional assessment of polarizabilities

Calculated polarizabilities are very dependent on diffuse functions and the choice of DFT functional. To assess the performance of different functionals and basis sets preliminary results are benchmarked against coupled cluster ccsd(t). All calculations were done in Gaussian09.

Table 1 Calculated isotropic mean polarizabilities ($\bar{\alpha}$) of H₂O using different DFT functionals and basis sets.

	CCSD(T)	CAM-B3LYP	B3LYP	M06-2X	PW91
aug-cc-pvdz	9.26	9.39	9.52	8.97	10.00
aug-cc-pvtz	9.59	9.74	9.89	9.32	10.45
aug-cc-pvqz	9.67	9.87	10.02	9.54	10.56

Table 2 Calculated isotropic mean polarizabilities ($\bar{\alpha}$) of H₂SO₄ using different DFT functionals and basis sets.

	CCSD(T)	CAM-B3LYP	B3LYP	M06-2X	PW91
aug-cc-pvdz	35.46	36.49	37.05	35.48	38.78
aug-cc-pvtz	35.24	36.68	37.24	35.91	38.89
aug-cc-pvqz		36.73	37.28	36.02	38.80

Table 3 Calculated isotropic mean polarizabilities ($\bar{\alpha}$) of CH₃NH₂ using different DFT functionals and basis sets.

	CCSD(T)	CAM-B3LYP	B3LYP	M06-2X	PW91
aug-cc-pvdz	25.73	25.95	26.42	25.72	27.15
aug-cc-pvtz	25.80	26.20	26.69	25.63	27.55
aug-cc-pvqz		26.24	26.75	25.91	27.61