Electronic Supplementary Information

A DFT Study on the Mechanism of the Sulfonic Acid + Alcohol Esterification Reaction

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Table of Contents

1. Relative stability of 5 and related pseudorotamers ................................................................. S2
2. Methanol assistance on neutral and acid-catalyzed Ad-E pathways ........................................ S2
3. Electronic and Gibbs free energies (calculated as the sum of electronic and thermal free energies, in Hartrees) in gas phase and methanol (IEF-PCM continuum model) for structures at B3LYP/aug-cc-pVTZ level ................................................................................................................................. S5
4. Cartesian coordinates (Å) for all structures. ............................................................................. S7
1. Relative stability of 5 and related pseudorotamers

Structure 5 as well as all possible related pseudorotamers (depending on the position occupied by every substituent around the pentacoordinated sulfur) were optimized in both gas phase and methanol solution. Interestingly, no energy minima for structures bearing an apical oxo group could be located after several extensive searches. Codes for all optimized pseudorotamers are gathered in Table S1.

Table S1 Pseudorotamers of 5

| Pseudorotamer | O= | Ph– | HO– | HO– | MeO– |
|---------------|----|-----|-----|-----|------|
| 5             | eq | eq  | eq  | ap  | ap   |
| 5a            | eq | eq  | ap  | ap  | eq   |
| 5b            | eq | ap  | eq  | eq  | ap   |
| 5c            | eq | ap  | eq  | eq  | ap   |

eq: equatorial; ap: apical

Structures of all optimized pseudorotamers and the corresponding relative Gibbs free energies (kJ mol⁻¹) in gas phase and solution are shown in Figure S1. As can be observed, structure 5 (bearing phenyl, oxo, and one hydroxy groups in equatorial positions) is clearly favored over all related pseudorotamers in gas phase and solution (by at least 22.7 kJ mol⁻¹ and 16.4 kJ mol⁻¹, respectively).

2. Methanol assistance on neutral and acid-catalyzed Ad-E pathways

The participation of one or several water molecules (i.e., water assistance) can lower the free energy barriers for some reactions (such as neutral and acid-promoted hydrolysis of formamide). In order to assess the possible role of methanol assistance on the neutral and acid-catalyzed Ad-E mechanism for the sulfonic acid + alcohol esterification has been studied here through discrete and continuum solvent models. Results on the one methanol molecule-assisted neutral Ad-E path are shown in Figure S2.
acceleration reported for the hydration of metaphosphoric acid.\textsuperscript{34}

As a result, a hydrogen-bonded (methanol)$_2$-methyl benzenesulfonate complex (S5) is obtained. The final dissociation of such a hydrogen-bonded complex yields methyl benzenesulfonate and two methanol molecules. The reaction energy for the whole methanol-assisted process is obviously identical to that corresponding to the non-assisted mechanism. Results on the two methanol molecules-assisted neutral Ad-E path are shown in Figure S3. The formation of the (methanol)$_2$-benzenesulfonic acid hydrogen-bonded complex (S6) is largely disfavored in Gibbs free energy terms.

The subsequent two methanol molecules-assisted methanol addition (through TS S7) involves a significant activation barrier (212.6 kJ mol$^{-1}$ in gas phase, 205.1 kJ mol$^{-1}$ in solution).

The two methanol molecules-coordinated pentacoordinate sulfur species (S8) is again rather unstable, as previously found for both non-coordinated and one water molecule-coordinated analogs.

A low activation barrier is found for the subsequent water elimination step through TS S9 (31.4 kJ mol$^{-1}$ in gas phase, 13.5 kJ mol$^{-1}$ in solution).

Results on the one methanol molecule-assisted acid-catalyzed Ad-E mechanism are shown in Figure S4. Thus, the formation of a cyclic benzenesulfonic acid-methanol-methyloxonium cation hydrogen-bonded complex (S11) is thermodynamically favored.

Instead, a large energy is required for the addition step through TS S12 (260.4 kJ mol$^{-1}$ in gas phase, 247.5 kJ mol$^{-1}$ in solution). Such an activation energy is similar to that of the non-assisted acid mechanism (256.8 kJ mol$^{-1}$ in gas phase, 260.1 kJ mol$^{-1}$ in solution).

The lack of a significant role of methanol assistance in the methanol addition to sulfonic acid contrasts with a previous theoretical study on the formamide hydration showing a little effect in the neutral mechanism, but a more important role in the pathway involving the H$_3$O$^+$ cation.\textsuperscript{31}

As a result of the addition step, a methanol-coordinated protonated methyl dihydrogen benzenesulfonate cation (S13) is obtained. Such a species is rather unstable (in comparison with the cyclic complex S11) (by 230.1 kJ mol$^{-1}$ in gas phase, by 228.6 kJ mol$^{-1}$ in solution).

A very low activation barrier is required for the subsequent water elimination through TS S14 (4.8 kJ mol$^{-1}$ in gas phase, 6.6 kJ mol$^{-1}$ in solution).

As a consequence a stable hydrogen-bonded methyl benzenesulfonate-oxonium cation-water complex (S15) is formed. The final dissociation yields methyl benzenesulfonate (B), methyloxonium cation (16) and water (9) as the reaction products.

As a general conclusion for all considered methanol-assisted mechanisms, very similar activation barriers are found. Thus,
methanol assistance cannot avoid the unfeasibility of both neutral and acid-catalyzed Ad-E mechanisms.

Figure S4  Acid-catalyzed water-assisted Ad-E mechanism. Relative Gibbs free energies (kJ mol$^{-1}$) in gas phase (in parenthesis) and solution (in square brakets) of involved structures are shown.

Notes and references
S1 S. Antonczak, M. F. Ruiz-López and J. L. Rivail, J. Am. Chem. Soc., 1994, 116, 3912–3921; S. Antonczak, M. Ruiz-López and J.-L. Rivail, J. Mol. Model., 1997, 3, 434–442.
3. Electronic and Gibbs free energies (calculated as the sum of electronic and thermal free energies, in Hartrees) in gas phase and methanol (IEF-PCM continuum model) for structures at B3LYP/aug-cc-pVTZ level.

| Code | Structure                                                                 | Electronic energy (gas phase) | Electronic energy (methanol) | Gibbs free energy (gas phase) | Gibbs free energy (methanol) |
|------|---------------------------------------------------------------------------|-------------------------------|------------------------------|-------------------------------|-------------------------------|
| 1    | benzenesulfonic acid                                                     | -856.288421036               | -856.300488755               | -856.208354                  | -856.220474                  |
| 2    | methanol                                                                | -115.776759287               | -115.78160367                | -115.748529                  | -115.753465                  |
| 3    | benzenesulfonic acid···methanol HB complex                               | -972.072865556               | -972.072865556               | -971.949354                  | -971.965605                  |
| 4    | benzenesulfonic acid + methanol addition TS                             | -971.995930573               | -972.005249928               | -971.870969                  | -971.880413                  |
| 5    | methyl dihydrogen benzeneorthosulfonate, pseudorotamer 5                 | -972.004708623               | -972.013709889               | -971.874941                  | -971.884971                  |
| 5a   | methyl dihydrogen benzeneorthosulfonate, pseudorotamer 5a               | -971.99563913                | -972.006703388               | -971.866286                  | -971.866286                  |
| 5b   | methyl dihydrogen benzeneorthosulfonate, pseudorotamer 5b               | -971.994046252               | -972.001965584               | -971.863066                  | -971.863066                  |
| 5c   | methyl dihydrogen benzeneorthosulfonate, pseudorotamer 5c               | -971.986013374               | -972.998475217               | -971.856968                  | -971.856968                  |
| 6    | methyl dihydrogen benzeneorthosulfonate, water elimination TS           | -971.997968843               | -972.007518690               | -971.871091                  | -971.881055                  |
| 7    | methyl benzenesulfonate···water HB complex                               | -972.077302355               | -972.090571508               | -971.952733                  | -971.970000                  |
| 8    | methyl benzenesulfonate                                                 | -895.602843373               | -895.613990999               | -895.496695                  | -895.508123                  |
| 9    | water                                                                    | -76.466196562                | -76.4729427575               | -76.462601                   | -76.469017                   |
| 10   | methyloxonium cation                                                    | -116.074455952               | -116.179571300               | -116.033814                  | -116.138579                  |
| 11   | benzenesulfonic acid···methyloxonium cation HB complex                   | -972.421245845               | -972.496927459               | -972.287624                  | -972.361047                  |
| 12   | protonated benzenesulfonic acid + methanol addition TS                  | -972.326672897               | -972.398826479               | -972.189785                  | -972.261966                  |
| 13   | protonated methyl dihydrogen benzeneorthosulfonate                      | -972.346667234               | -972.418515215               | -972.203865                  | -972.276590                  |
| 14   | protonated methyl dihydrogen benzeneorthosulfonate, water elimination TS| -972.332743157               | -972.402441009               | -972.196717                  | -972.265543                  |
| 15   | protonated methyl benzenesulfonate···water HB complex                    | -972.426461045               | -972.496159846               | -972.290991                  | -972.361632                  |
| 16   | oxonium cation                                                           | -76.738518512                | -76.859943078                | -76.722411                   | -76.843298                   |
| 17   | protonated benzenesulfonic acid                                          | -856.605184042               | -856.684858610               | -856.514464                  | -856.594174                  |
|      | benzenesulfonylium cation                                               | -780.103490061               | -780.184203921               | -780.035948                  | -780.116779                  |
| 18   | benzenesulfonylium cation···water complex                               | -856.596154636               | -856.674927631               | -856.507585                  | -856.584637                  |
| 19   | methanol···benzenesulfonylium cation···water complex                     | -972.395201205               | -972.466053836               | -972.261626                  | -972.332525                  |
| 20   | benzenesulfonylium cation···methanol complex                             | -895.916245998               | -895.991546256               | -895.800527                  | -895.874553                  |
| 21   | protonated methyl benzenesulfonate                                      | -895.929485740               | -896.00219587                 | -895.812955                  | -895.885404                  |
| 22   | methyloxonium cation···water pre-reactive complex                       | -192.556362559               | -192.653773709               | -192.499404                  | -192.598637                  |
| 23   | methyloxonium cation + water S2 TS                                      | -192.543183489               | -192.634586902               | -192.484527                  | -192.574690                  |
| S1   | benzenesulfonic acid···2 methanol HB complex                             | -1087.86148989               | -1087.87448037               | -1087.693681                  | -1087.707364                  |
| S2   | one methanol molecule-assisted benzenesulfonic acid + methanol addition TS | -1087.78736497               | -1087.79798744               | -1087.614734                  | -1087.626869                  |
| Code | Structure | Electronic energy (gas phase) | Electronic energy (methanol) | Gibbs free energy (gas phase) | Gibbs free energy (methanol) |
|------|-----------|-----------------------------|-----------------------------|-------------------------------|-------------------------------|
| S3   | methyl dihydrogen benzeneorthosulfonate···methanol HB complex | -1087.79448342 | -1087.80478467 | -1087.618247 | -1087.630316 |
| S4   | one methanol molecule-assisted methyl dihydrogen benzeneorthosulfonate, water elimination TS | -1087.79089812 | -1087.8091180 | -1087.617241 | -1087.628845 |
| S5   | methyl benzene sulfonate···methanol···water HB complex | -1087.86504757 | -1087.87800856 | -1087.696258 | -1087.712787 |
| S6   | benzenesulfonic acid···3 methanol HB complex | -1203.65038737 | -1203.66419537 | -1203.435454 | -1203.449262 |
| S7   | two methanol molecules-assisted benzenesulfonic acid + methanol addition TS | -1203.57563991 | -1203.59228955 | -1203.354489 | -1203.371138 |
| S8   | methyl dihydrogen benzeneorthosulfonate···2 methanol HB complex | -1203.58701804 | -1203.59721421 | -1203.372085 | -1203.382281 |
| S9   | two methanol molecules-assisted methyl dihydrogen benzeneorthosulfonate, water elimination TS | -1203.58118694 | -1203.59449520 | -1203.360036 | -1203.373344 |
| S10  | methyl benzene sulfonate···2 methanol···water HB complex | -1203.6509250 | -1203.66666734 | -1203.435159 | -1203.451734 |
| S11  | benzenesulfonic acid···methyloxonium cation···methanol HB complex | -1088.23683266 | -1088.30304591 | -1088.053218 | -1088.119085 |
| S12  | methanol-assisted protonated benzenesulfonic acid + methanol addition TS | -1088.14247653 | -1088.21323000 | -1087.954031 | -1088.024784 |
| S13  | protonated methyl dihydrogen benzeneorthosulfonate···methanol HB complex | -1088.15095930 | -1088.21742133 | -1087.965553 | -1088.032015 |
| S14  | methanol-assisted protonated methyl dihydrogen benzeneorthosulfonate, water elimination TS | -1088.14908666 | -1088.21669035 | -1087.960641 | -1088.028245 |
| S15  | methyl benzenesulfonate···oxonium cation···methanol HB complex | -1088.23993022 | -1088.30554635 | -1088.054757 | -1088.121267 |
4. Cartesian coordinates (Å) for all structures.

1 [benzenesulfonic acid], in gas phase (at B3LYP/aug-cc-pVTZ level)
\begin{align*}
S, &\quad -0.380391048, -0.100617553, 0.1980938282 \\
O, &\quad -1.8351763102, -0.5262045357, -0.4070400718 \\
H, &\quad -1.68264961, -1.0278473281, -1.2207769991 \\
O, &\quad 0.6097520625, -0.9113413282, -0.4841084438 \\
O, &\quad -0.5388358907, -0.1290897369, 1.6304222881 \\
C, &\quad -0.2208654873, 1.5965515125, -0.333333359 \\
C, &\quad -0.8139950116, 2.5986059856, 0.4265745152 \\
C, &\quad 0.4985060348, 1.882743581, -1.4873520229 \\
C, &\quad -0.6905119816, 3.9167667703, 0.0085484095 \\
H, &\quad -1.3486127092, 2.3465837657, 1.3305218917 \\
C, &\quad 0.6160429271, 3.2067249741, -1.8923691037 \\
H, &\quad 0.9686324521, 1.0845887113, -2.0427862986 \\
C, &\quad 0.0207565755, 4.2195839869, -1.1484623643 \\
H, &\quad -1.1443612111, 4.7073116262, 0.5897803849 \\
H, &\quad 1.1779369344, 3.4583262622, -2.784515451 \\
H, &\quad 0.1170683735, 5.2486514917, -1.4667557636 \\
\end{align*}

1 [benzenesulfonic acid], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)
\begin{align*}
S, &\quad -1.4772464396, 0.001626565, -0.1605367138 \\
O, &\quad -1.9404152543, -0.1912880526, 1.3803117973 \\
H, &\quad -1.8864332329, 0.6547958883, 1.8528794131 \\
O, &\quad -1.9470095356, 1.2976678284, -0.615736063 \\
O, &\quad -1.9331193494, -1.2092923639, -0.8106910627 \\
C, &\quad 0.3008808042, 0.0077930121, -0.0778755787 \\
C, &\quad 0.975348706, -1.2076104313, -0.0069092473 \\
C, &\quad 0.9750839527, 1.2237175549, -0.0814375291 \\
C, &\quad 2.3614895185, -1.1968815724, 0.0667921918 \\
H, &\quad 0.4288444272, -2.138607201, -0.0167917467 \\
C, &\quad 2.3627317527, 1.2172900898, -0.0075957534 \\
H, &\quad 0.4277091638, 2.1518194061, -0.1479918459 \\
C, &\quad 3.052435354, 0.0118352707, 0.0677714334 \\
H, &\quad 2.901011908, -2.1318023408, 0.1196899449 \\
H, &\quad 2.9020551746, 2.1537961496, -0.0127961981 \\
H, &\quad 4.1321341559, 0.0130547163, 0.1234049583 \\
\end{align*}

2 [methanol], in gas phase (at B3LYP/aug-cc-pVTZ level)
\begin{align*}
H, &\quad 0.7625156054, -1.1572189366, 0. \\
O, &\quad -0.1052374465, -0.7448541863, 0. \\
C, &\quad 0.0539201827, 0.6696260877, 0. \\
H, &\quad -0.9463722232, 1.0976781284, 0. \\
H, &\quad 0.5818659758, 1.0228333684, 0.8907874089 \\
H, &\quad 0.5818659758, 1.0228333684, -0.8907874089 \\
\end{align*}

2 [methanol], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)
\begin{align*}
H, &\quad 0.766393827, -1.1526794175, 0. \\
O, &\quad -0.1065551923, -0.7483694584, 0. \\
C, &\quad 0.0549987171, 0.6722615014, 0. \\
H, &\quad -0.9477290516, 1.1024006096, 0. \\
H, &\quad 0.5824748889, 1.0186422973, 0.8898190699 \\
H, &\quad 0.5824748889, 1.0186422973, -0.8898190699 \\
\end{align*}

3 [benzenesulfonic acid···methanol HB complex], in gas phase (at B3LYP/aug-cc-pVTZ level)
\begin{align*}
S, &\quad 0.2596971931, 1.5329858944, 0.6011520699 \\
O, &\quad 0.5895582175, 1.9693852082, -0.9330105266 \\
\end{align*}
3 [benzenesulfonic acid···methanol HB complex], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

H, 0.0501715678, 2.7438402771, -1.14946169
O, 1.4847663297, 0.9297767142, 1.0790528838
C, -0.988147692, 0.2746735197, 0.407257274
C, -0.6172086766, -1.0014512664, -0.0052511028
C, -2.3121887224, 0.6043188798, 0.6822126353
C, -1.6079427706, -1.9636875192, -0.1495043166
H, 0.4180925344, -1.2456985829, -0.2003728828
C, -3.289129042, -0.3724000502, 0.534365764
H, 0.2556011251, -0.6441683402, 0.4470650323
O, 0.7336008241, -1.4899626202, 0.0150525581
C, 4.0465647841, -1.4753813527, -0.5259212072
H, 4.8068418962, -1.360476019, 0.2527060593
H, -2.4329240764, -1.020007619
H, 4.1764204306, -0.6788028714, -1.2650547562

4 [benzenesulfonic acid + methanol addition TS], in gas phase (at B3LYP/aug-cc-pVTZ level)

S, -0.3586479082, -0.8533262115, -0.0660902088
O, 0.814279543, -0.8702226843, 1.484800039
H, 0.3948239843, -1.6120674663, 1.9499458493
O, 1.3214395557, 0.036073328, -0.6920835619
C, 4.015137375, -0.0754933617, -0.049891867
C, -1.3193600231, 1.30941231, 0.0701109681
C, -2.3775119665, -0.8682500693, -0.1545327755
C, -2.5654256234, 1.9088965093, 0.088873727
H, -0.4152880495, 1.904131037, 0.139291169
H, -2.2898131845, -1.9393223716, -0.2563938198
C, -3.7155211777, 1.130510621, -0.0131198779
H, -2.6418255081, 2.98311052, 0.1785241941
H, -4.5170699999, -0.8522532138, -0.2208442753
H, -4.6807073185, 1.6045683384, -0.006404784
O, 0.2355597715, -2.2225226584, -0.5265731781
H, 2.9822654293, 0.9445748494, -0.1974208525
O, 3.7867639054, 1.4444494894, -0.007037794
C, 4.9059700499, 0.5711911896, -0.1272096537
H, 4.9933981099, 0.1677648792, -1.1398120324
H, 5.7992685742, 1.1537956156, 0.0910596794
H, 4.8530870847, -0.2612637605, 0.5799115363
[benzenesulfonic acid + methanol addition TS], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

S, 1.0825871714, -0.524968231, 0.222508567
O, 1.807616836, -0.9317205496, -1.117083561
O, 1.1819072257, 0.0245740083, 1.3473197162
H, 1.6531525089, -2.4920078628, -0.9450513748
O, -0.8110772516, -2.0859304619, -0.6862120077
C, 0.6699239466, -0.1843285587, 0.0813642398
C, 1.2512682217, 0.5963455998, 1.0686526916
C, 1.389507181, -0.720697474, -0.9756714266
C, 0.6163822252, 0.8467637136, -0.986762785
H, 0.6602071655, 0.9975330382, 1.8783579589
C, 2.7521454246, -0.4532453843, -1.0418035382
H, -0.597906189, -1.3262904121, -1.7284687099
C, 3.3633769373, -0.3269860692, -0.0650420822
H, 1.918095389, 1.4500471194, 0.7471345043
H, 3.333048667, -0.8581074516, -1.858219693
H, 1.4237114544, -0.5287794799, -0.123597318
C, -1.8852765683, 0.3774060561, -0.325270748
H, 1.2650853349, 2.8165183431, 0.4644273495
H, -0.2074040691, 3.1380402528, -0.1092678296
H, -2.8643022154, -1.1433749602, 0.1057278268
H, -1.8921879434, -0.5865959565, -1.4661358385
O, 1.2618674431, 1.2597722264, -0.8957588711

[methyl dihydrogen benzeneorthosulfonate, pseudorotamer 5], in gas phase (at B3LYP/aug-cc-pVTZ level)

S, -1.913186785, -0.3794896262, 0.0341241951
O, 1.5887543656, 1.1496178368, -0.4891459742
O, -2.6419763506, -0.8622250398, -0.104010902
H, 2.6196698475, -1.7942126718, 0.1770118209
O, 0.0518575276, -0.6312716954, -0.9691515451
H, 0.111170301, -2.3774565406, 0.3804921198
O, 0.8573900914, -1.9760405558, 0.8398611684
C, -0.7005175333, 0.390202492, 1.6224127332
C, -0.6362336384, 0.6240804102, 1.9025869349
C, 1.7154745402, 0.7204748468, 2.5085548032
C, -0.9663418973, 1.2097278833, 3.1190498727
H, 1.4006835407, 0.3591102295, 1.18629438
C, 1.3635688086, 1.2078683381, 3.7246303656
H, 1.7458131953, 0.5390081786, 2.2572025818
C, -0.297036492, 1.5428025763, 4.0302459473
5 [methyl dihydrogen benzeneorthosulfonate, pseudorotamer 5], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

S, -1.0528346688, 0.3689351758, 0.0287321655
O, -1.2559363257, -1.7275778348, -0.363467126
O, -2.04123989, 0.048332625, 1.4525320382
H, -1.7750251358, 1.2759834321, 1.9285988499
O, -1.752595817, 0.9458643111, -1.127769047
H, -1.0311332026, 2.6191789499, 1.1214428454
O, -0.6864424803, 1.973087544, 0.7493425201
C, 0.7290461277, 0.0586696492, -0.0028874921
C, 1.4278669671, 0.444957005, -1.1300434253
C, 1.34711654, -0.5359109146, 1.0912338691
C, 2.8002026451, 0.2224199695, -1.169139062
H, 0.9192250184, 0.9074977523, -1.9635727424
C, 2.721402826, -0.7452302727, 1.0372602836
H, 0.778623467, -0.8316329501, 1.9603538376
C, 3.4463233669, -0.368887941, -0.0885006837
C, 3.3607147424, 0.5137411397, -2.0464265467
H, 3.2211590817, -1.2064420278, 1.8776576625
H, 4.5136319521, -0.5370461818, -1.239673614
C, -2.5688121203, -1.7459207128, 0.6817903251
H, -2.9786101961, 1.2162587387, -1.541016815
H, -2.4527644568, -2.7995811448, -0.9252800409
H, -3.2437947036, 1.6463078097, 0.1694546463

5a [methyl dihydrogen benzeneorthosulfonate, pseudorotamer 5a], in gas phase (at B3LYP/aug-cc-pVTZ level)

S, -1.016799732, 0.1107703252, 0.7436740641
O, -1.8672110853, 1.2487792279, -0.0681468765
O, -1.2303032892, 1.0404489884, -0.5563359723
H, -1.8007548966, 1.7267430048, -0.1911457717
O, -1.66563894, -0.7538407783, 1.7463735253
C, 0.7486502367, 0.1083998902, -0.301012466
C, 1.4809073026, 0.1041682149, 0.5494047048
C, 1.3244965478, 1.2435226821, 0.2459547128
C, 2.836793973, -1.0471062688, 0.2472692434
H, 1.004494663, -1.9144300868, 0.9709046268
C, 2.6777190465, 1.2141189327, -0.5665899931
H, 0.735047358, 2.1322724956, -0.411544962
C, 3.434054718, 0.0756120665, -0.3161043152
H, 3.4229977275, 1.9339120119, 0.4454155663
H, 3.1394021076, 0.2090271729, -1.0034090621
H, 4.4877521521, 0.0624262675, -0.5589471256
C, -2.7646879702, 0.9481285212, -1.1582079409
H, -3.5055645476, 0.2076670015, -0.8682803185
H, -3.2538362641, 1.9016510715, -1.3461268382
H, -2.2228457218, 0.612859879, -2.0357950279
5a [methyl dihydrogen benzeneorthosulfonate, pseudorotamer 5a], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

S, -0.6095186667, 1.3655783415, 1.8360660479
O, -1.3217004826, 1.4067348487, 2.4864685664

5b [methyl dihydrogen benzeneorthosulfonate, pseudorotamer 5b], in gas phase (at B3LYP/aug-cc-pVTZ level)

S, -1.0105808207, 0.0356708431, 0.7030518878
O, -1.8720721055, 1.2448075163, 0.035651154

5b [methyl dihydrogen benzeneorthosulfonate, pseudorotamer 5b], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

S, -1.0105808207, 0.0356708431, 0.7030518878
O, -1.8720721055, 1.2448075163, 0.035651154
5c [methyl dihydrogen benzeneorthosulfonate, pseudorotamer 5c], in gas phase (at B3LYP/aug-cc-pVTZ level)

S, -0.6534955461, -0.5736583006, -0.8263761011
O, -2.2211795655, -1.362872771, -1.2017256375
O, -0.9072435222, -0.8522778786, 0.7646761225
O, -0.0278139561, -2.2211795655, -1.362872771, -1.2017256375
H, -0.9247283851, 0.880299617, -1.0128290619
C, 1.0905869851, -0.1390358306, -0.360208893
C, 1.5681517043, 1.1376538323, -0.6196180736
C, 1.9136786645, -1.0870235837, 0.2442973884
C, 2.8778332393, 1.4678959372, -0.2736541869
H, 0.9279879763, 1.8676361742, -1.080804669
H, 2.1264061048, -0.7512889698, 0.5875612176
H, 1.5448156982, 2.0810540469, 0.4488956973
C, 3.7026267759, 0.5281156986, 0.329019715
H, 3.2462502986, 2.4638222543, -0.4792183159
H, 3.8519211319, 1.4897664619, 1.0572519008
H, 4.7179887134, 0.7869404209, 0.596753963
O, -1.045359674, 0.7016595321, -1.4394962637
C, -2.1910591109, -1.1206969837, 1.382433907
H, -2.5322118681, 2.1212818908, 1.1432697157
H, -1.9804908014, -1.0305279252, 2.4453578569
H, -2.9299694035, -0.3831629671, 1.0858125982
H, -2.7558724792, -0.6572820022, -1.5837214813

5c [methyl dihydrogen benzeneorthosulfonate, pseudorotamer 5c], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

S, -0.849407167, 0.2492896436, 0.5259812119
O, -2.661302277, 0.0638290455, 0.4031075643
O, -0.8390737832, 1.3482206185, 0.9943277815
O, -0.9336547921, 0.8656811198, 1.013831832
H, -2.8422874727, 1.18606928, 1.1314108165
C, 0.9627483897, 0.0670309687, 0.2400480891
C, 1.4468273764, -0.8002776088, -0.732214638
C, 1.8257173593, 0.8190521991, 1.0203206214
C, 2.8171749364, -0.9129856099, -0.9225570587
H, 0.767904874, -1.3838704193, 1.3370266927
C, 3.1992553793, 0.6990615116, 0.8218745049
H, 1.4279342652, 1.4860336578, 1.7692481621
C, 3.6957561964, -0.1633115444, -0.145688117
H, 3.1985166737, -1.586627806, 1.677953423
H, 3.8769070543, 1.2842229526, 1.4286903474
H, 4.7629818008, -0.2532733061, -0.2963795646
O, -0.9404828716, 1.2213141407, 1.5988091217
C, -3.2380392747, -0.835635802, -0.5351747518
H, -4.3174296576, -0.7045798184, -0.4580595728
H, -2.9360329794, -0.629320521, -1.5667872665
H, -3.0023456267, -1.8838232317, -0.3239504578
H, -1.7247114636, -1.5353058511, 1.3431087873

5c [methyl dihydrogen benzeneorthosulfonate, pseudorotamer 5c], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

S, -0.8639402606, 0.2457209553, 0.5236477427
O, -2.643506074, 0.0656646667, 0.407712665
O, -0.830805534, -1.3431353707, 1.0146048545
O, -0.9247283851, 0.880299617, -1.0128290619
H, -1.8329981731, 1.1793938218, -1.1796889075

S12
6 [methyl dihydrogen benzeneorthosulfonate, water elimination TS], in gas phase (at B3LYP/aug-cc-pVTZ level)

S, -1.1203444735, -0.4565453109, 0.1578967297
O, -1.7914224741, -0.953999404, -1.1801249368
O, -1.887070055, 0.1974039281, 1.2051817021
O, -0.8742562899, -1.9715708114, 0.7526016554
C, 0.6435650557, -0.1549235468, 0.0539905376
C, -1.2067353868, 0.6904641466, 0.9954765835
C, -2.3893735857, -0.7792221878, 0.9325010105
C, -3.772621507, 0.912930372, 0.9441227195
O, -0.5891254081, 1.1655404986, 1.743376281
C, 2.7571253994, -0.5392864439, -0.972999207
C, -1.9167320702, 1.4321970492, -1.6511821617
C, 0.3500434782, 0.3016732286, -0.0378271093
H, 1.5568555902, 1.6707684341
H, -1.3578122171, -1.0127399466, -1.737160148
H, 4.4154352077, 0.4825237105, -0.0750941655
H, -1.832522046, 0.0320618794, -1.581684653
O, 1.2390288475, 1.2366356122, -1.0611476031
H, 0.819666767, 1.855803412, -0.6192931069
C, 2.0317279743, 2.7127758752, 1.180395898
C, -0.6401619431, 2.6382690353, 0.15933730236
H, -2.5752652453, -0.1626503202, 1.9463214628
H, -2.682969274, -2.9299583428, -0.3346781394

6 [methyl dihydrogen benzeneorthosulfonate, water elimination TS], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

S, 1.052656475, 0.2668327608, -0.0570838015
O, 1.7354860687, 0.3964018829, 1.3631145394
O, 1.6690750379, 0.8355955319, -0.2450520686
O, 1.343844318, -1.337913175, -0.1942644211
C, -0.7209662591, 0.0128122177, -0.0264002251
C, -1.4309059455, 0.3048649996, -1.1803948133
C, 1.3189678573, -0.4895229526, 1.118846918
C, 2.8022699746, 0.0780829136, -1.1809130018
H, -0.9318653634, 0.6999117481, -2.0527897554
C, 2.692677838, -0.7025792776, 1.0999167484
7 [methyl benzenesulfonyl···water HB complex], in gas phase (at B3LYP/aug-cc-pVTZ level)

S, -0.7375858217, -0.708211606, 2.0019889695
H, -3.4313285092, -0.421119032, -0.0448085964
H, -3.760425444, 0.2953998437, -2.0706924923
H, -3.181539822, -1.0905993047, 1.9823220472
H, -4.4988255018, -0.5911371752, -0.0514577059
H, 1.464620137, 1.3908744112, 1.4988853301
O, 0.52812823, 2.203412878, 0.62891055
H, 0.9643458382, 2.158984169, 0.026552283
C, 2.7121266953, -1.7676795274, -0.3895408112
H, 2.6538947908, -2.8457073897, -0.5017390998
H, 3.1253461012, -1.3197029413, -1.2901244683
H, 3.3187924597, -1.5150090804, 0.4774669297

7 [methyl benzenesulfonyl···water HB complex], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

S, 0.8390480677, 0.0236846062, -0.3155102469
O, 1.2287784489, 1.3718351929, -0.6996024496
H, 2.7521566451, 2.4949777013, -0.2632413368
O, 1.2826019901, -1.009641532, -1.1181736775
O, 1.4188955055, -0.1162796615, 1.1757766106
C, -0.927938322, -0.045697011, -0.1193564485
C, -1.6203991325, -1.1583553963, -0.5825038814
C, -1.5773371614, 1.023555485, 0.4933926616
C, -3.0014366578, -1.1974251344, -0.4266404066
H, -1.0910732862, -1.969098223, -1.0593879367
C, -2.9551695086, 0.9677374979, 0.6439659405
H, -1.0192603725, 1.8812932085, 0.8390341901
C, -3.6646242985, -0.1397224101, 0.1848478131
H, -3.5551774288, -2.0534126426, -0.7850926497
H, -3.4751057668, 1.7891341047, 1.1160731819
H, -4.7386793758, -0.1752118844, 0.3030323416
8 [methyl benzenesulfonate], in gas phase (at B3LYP/aug-cc-pVTZ level)
S, -1.5293036387, 0.0210391228, -0.3427997297
O, -2.0547797889, -0.1507700301, 1.1821042112
O, -1.9067247736, 1.3120455735, -0.8408808657
O, -1.9202913761, -1.2082308966, -0.9878636495
C, 0.2484579914, 0.0464924661, -0.152190815
C, 0.9136066147, -1.1494107158, 0.1016768318
C, 0.931384018, 1.2499933823, -0.2679957069
C, 2.2930187304, -0.1309149414, 0.2509884576
H, 0.3577169719, -2.0733971202, 0.1666823596
C, 2.3157169042, -0.125413724, -0.1175543267
H, 0.3907210015, 2.1575811576, -0.4879125001
C, -0.9921308938, 0.0684932279, 0.1432783962
H, -2.1834572098, -0.0285884544, 0.4448317306
H, 2.8618029907, 2.18265535, -0.2102446809
H, 4.0676504152, 0.0758699552, 0.2569068882
C, -0.0473611514, 1.0118689296, 2.0359220804
H, -2.6137354571, 1.8207359757, 1.5810121907
H, -2.5214871456, 0.6880864899, 2.957645882
H, -1.0250047442, 1.3317507339, 2.239464256

8 [methyl benzenesulfonate], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)
S, 0.12538833456, 0.3596886919, -0.4246991001
O, 0, 1.2947773508, 0.0047823716, 1.0104544403
O, 0, 1.732017187, -0.5955688187, -1.4096274251
O, 0, 1.5482402991, 1.7697754956, -0.5888380112
C, 0, -0.4973427456, 0.1321628719, -0.1884135082
C, 0, -1.2023539286, 1.0801102917, 0.5494387396
C, 0, -1.1227717309, -0.9797767431, -0.7406828799
C, 0, -2.5657069779, 0.9019415552, 0.7355705839
H, 0, -0.6967583036, 1.9047264879, 0.9619575094
C, 0, -2.4897682033, -1.1437740905, -0.5463830391
H, 0, -0.5539038193, -1.6946412047, -1.3154727842
C, 0, -3.2070800906, -0.2073128214, 0.1892040744
H, 0, -3.1276890858, 1.6299596636, 1.3031725829
H, 0, -2.99069063, -2.0015564154, -0.9720795856
H, 0, -4.2700972229, -0.338864254, 0.3362132261
C, 0, 1.9226423655, -1.385779875, 1.4289843842
H, 0, 2.4662261473, -1.9842719196, 0.7034132647
H, 0, 2.4415703253, -1.3785593168, 2.3814494836
H, 0, 0.9093064151, -1.7610919753, 1.5586804116

9 [water], in gas phase (at B3LYP/aug-cc-pVTZ level)
H, 0.7634939049, 0., -0.4641357136
H, -0.7634939049, 0., -0.4641357136
O, 0., 0., 0.1208598971

9 [water], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)
H, 0., 0.7620989914, −0.4693792381
H, 0., −0.7620989914, −0.4693792381
O, 0., 0.1197394762

10 [methylloxonium cation], in gas phase (at B3LYP/aug-cc-pVTZ level)
H, −0.2670366005, −1.1506144944, 0.7996494277
H, −0.2670366005, −1.1506144944, −0.7996494277
O, 0.0879944285, −0.7201125046, 0.
C, −0.0180094119, 0.7982185473, 0.
H, −0.8312679086, −0.3747393882, 0.2340822704
H, −0.0001213504, 0.9745711116, 0.1711151964
C, 1.2231199706, −0.6992128413, 0.4242957545
C, 1.1587579495, −1.7055459322, 0.0424638547
O, 2.0562227456, −0.1789550246, −0.0287767603

11 [benzenesulfonic acid···methylloxonium cation HB complex], in gas phase (at B3LYP/aug-cc-pVTZ level)
S, 0.6089184469, −0.6058736706, 0.2794296759
O, 1.0446131972, −0.0445169274, 1.5363889001
H, 2.593942251, 2.3377010871, 0.2356880207
C, 1.1872691154, −2.3341766055, 0.463297136
C, −1.1356474537, −0.6429771455, 0.0857128984
C, −0.6831938142, −0.7599689125, −1.1904370916
C, −1.9144280417, −0.5653275657, 1.2377799633
C, −3.0642406361, −0.8004187486, −1.3051410125
C, −1.0515869706, −0.814834008, −2.0645230557
C, −3.2941436345, −0.6504418167, 1.0963567227
H, −1.4550999178, −0.4690566523, 2.2104453602
C, −3.8636726276, −0.7238050564, −0.1674541583
C, −3.516103449, −0.890063876, −2.2824500321
H, −3.9220067418, −0.5420777036, 1.9733234501
H, −4.9395738722, −0.754741899, −0.2680543389
C, −3.3372496972, 2.492333544, −1.6677927506
H, 2.8806447611, 2.3138431577, −2.6344608124
H, 3.5924375732, 3.5402923516, −1.5541754899
C, 4.1980687008, 1.8485055045, −1.512575747
O, 2.2962465407, 2.1834725326, −0.6727312385
O, 1.2300867129, 0.0241043118, −0.9328565647
H, 1.8061259905, 1.1742443517, −0.7713476578

11 [benzenesulfonic acid···methylloxonium cation HB complex], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)
S, 0.4020332905, 0.8814083549, 0.111664529
O, 0.6933854495, 1.7124819853, −1.034322895
H, 3.5364193711, −0.5012659838, −1.6317680018
H, 0.9984142865, −2.229075375, 1.682759057
O, −0.1742800118, 1.7766593867, 1.4187405098

S16
| Element | Coordinates |
|---------|-------------|
| C       | -1.1868360792, 0.1203864868, -0.0103065669 |
| C       | -1.491178658, -0.9544785476, 0.8205873916 |
| C       | -2.0872532692, 0.6207696864, -0.9443313517 |
| C       | -2.746483329, -1.5378290974, 0.7082992777 |
| H       | -0.7684001007, -1.327685424, 1.5307255698 |
| C       | -3.359842279, 0.0211097203, -1.0429803158 |
| H       | -1.8164060493, 1.4508864998, -1.5788640957 |
| C       | -3.6622542464, -1.051042438, -0.2192261577 |
| C       | -4.0500632002, 0.3917425229, -1.7640491168 |
| H       | -4.636106777, -1.5129897378, -0.3014815316 |
| C       | -4.832460279, -1.3283512922, -0.0063922408 |
| H       | -4.1218587402, -1.9888267869, 0.7714715821 |
| H       | -5.2117726866, -1.8238826425, -0.6356049989 |
| C       | -3.305269374, -0.393359961, 0.3949301399 |
| O       | 2.5101225439, -0.631318059, -0.34902021 |

12 [protonated benzenesulfonic acid + methanol addition TS], in gas phase (at B3LYP/aug-cc-pVTZ level)

| Element | Coordinates |
|---------|-------------|
| S       | 1.11614403424, -0.4981646803, 0.2785543204 |
| O       | 1.9806834411, 0.3035588619, 1.3100586668 |
| H       | -0.6900876473, -1.2009826809, -1.8305356969 |
| C       | -2.6194742967, 0.5622031504, 1.0288031332 |
| H       | -0.5724043447, 0.7384521239, 2.0305611025 |
| C       | -3.2852134163, 0.1042648423, -0.104146609 |
| H       | -3.1140721753, -0.8839550435, -2.0059749714 |
| H       | -3.1661891312, 0.0453782897, 1.8257543734 |
| C       | -3.4588678868, 0.2360707175, -0.1850775609 |
| C       | 0.7705213912, 2.2240340555, -1.213424468 |
| H       | 0.0765928726, 2.5906671915, -0.4566840068 |
| H       | 1.3979329045, 3.0480497709, -1.5513276711 |
| H       | 0.2133878975, 1.8340530759, -2.0646072206 |
| O       | 1.6474106293, 1.2225198608, -0.6862963106 |
| O       | 1.8996470595, -1.1535840285, -0.9539927592 |
| H       | 2.1965587876, -0.4022062645, -1.5159850429 |

12 [protonated benzenesulfonic acid + methanol addition TS], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

| Element | Coordinates |
|---------|-------------|
| S       | 1.1614403424, -0.4981646803, 0.2785543204 |
| O       | 1.9806834411, 0.3035588619, 1.3100586668 |
| H       | -0.6900876473, -1.2009826809, -1.8305356969 |
| C       | -2.6194742967, 0.5622031504, 1.0288031332 |
| H       | -0.7212043447, 0.7384521239, 2.0305611025 |
| C       | -3.2852134163, 0.1042648423, -0.104146609 |
| H       | -3.1140721753, -0.8839550435, -2.0059749714 |
| H       | -3.1661891312, 0.0453782897, 1.8257543734 |
| C       | -3.4588678868, 0.2360707175, -0.1850775609 |
| C       | 0.7705213912, 2.2240340555, -1.213424468 |
| H       | 0.0765928726, 2.5906671915, -0.4566840068 |
| H       | 1.3979329045, 3.0480497709, -1.5513276711 |
| H       | 0.2133878975, 1.8340530759, -2.0646072206 |
| O       | 1.6474106293, 1.2225198608, -0.6862963106 |
| O       | 1.8996470595, -1.1535840285, -0.9539927592 |
| H       | 2.1965587876, -0.4022062645, -1.5159850429 |
13 [protonated methyl dihydrogen benzeneorthosulfonate], in gas phase (at B3LYP/aug-cc-pVTZ level)

S, 1.0415524435, -0.2570622902, 0.082658688
O, 1.5986211769, 1.245607054, -0.089554421
O, 1.7111746215, -0.376760332, 1.531658218
H, 1.588483881, -1.268640449, 1.8554189857
H, -0.3935213087, -1.9789690814, 0.538634314
O, 0.524784021, -1.924552256, 0.2400647831
C, -0.653794721, 0.3385679063, -0.0854432471
C, -1.4859305819, -0.2753745442, -0.1078751756
C, -1.06906297, 1.3943054837, 0.719841692
C, -2.7845843086, 0.200291248, -1.144341482
H, -1.1377226249, -1.0788795592, -1.649694386
C, -2.382594679, 1.826121891, 0.596118286
H, -0.3985197716, 1.8264831596, 1.423005593
C, -3.232883784, 1.2384636617, -0.3348809036
H, -3.4418813903, -0.2449870854, -1.8772381631
H, -2.7342760427, 2.6326137216, 1.2234108471
H, -4.248844985, 1.5939466668, -0.4328359664
C, 0.1555553983, 1.590673189, -0.0186022967
H, 1.7624969736, 1.0469320589, -0.5754022445
C, 0.3061235067, 2.6546973193, -0.2290031274
H, 0.3990353572, 1.3925737022, 0.9775054264
O, 1.8871782941, -0.7593792808, -1.173589104
H, 1.7392548158, -1.7151758882, -1.2929813158

13 [protonated methyl dihydrogen benzeneorthosulfonate], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

S, 0.9980959687, -0.3300356981, 0.0977934137
O, 1.2610818488, 1.1384260971, -0.553196372
O, 1.7985451062, 0.0915780172, 1.4137232774
H, 1.8954365706, -0.6851893939, 1.9930951579
H, 0.0166002089, -1.9803060704, 1.303915163
O, 0.7960951016, -1.9229480403, 0.7326141188
C, -0.7825649291, -0.0401158541, 0.0950103707
C, -1.583149561, -1.0031033931, -0.5990818258
C, -1.1025687164, -1.1335803, 0.549704863
C, -2.9498838635, -0.7646389365, -0.667212167
H, -1.1966037518, -1.9049295061, -1.019507209
C, -2.6655249643, 1.3306191544, 0.4984310686
H, -0.6470741545, 1.8661173521, 0.1005264228
14 [protonated methyl dihydrogen benzeneorthosulfonate, water elimination TS], in gas phase (at B3LYP/aug-cc-pVTZ level)

S, -1.34889077803, 0.3913472256, -0.114124914
H, -3.5886602624, -1.4901803579, -1.1493155756
H, -3.0865443447, 2.226484031, 0.9313344822
H, -4.5551097097, 0.5617015857, -0.1604893747
C, 2.5945500894, 1.6906229599, -0.7235620755
H, 3.228037078, 0.99569914, -1.2716776052
H, 2.4377581743, 2.593635379, -1.3043869892
H, 3.0257475553, 1.9323862283, 0.2492646838
O, 1.7914824189, -1.029896601, -1.097290072
H, 1.8191859164, -1.9846314788, -0.9530298181

14 [protonated methyl dihydrogen benzeneorthosulfonate, water elimination TS], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

S, -1.1548043301, -0.5328182173, 0.002879573
O, -2.0388503639, 0.2265542225, -1.0087780683
H, -2.0467948238, 1.149047489, -0.4164263112
O, -1.1261331421, -1.9540136781, -0.6623867828
C, 0.5988562444, -0.2503381089, 0.0006170498
C, 1.3272406766, -0.6005680535, 1.1302627115
C, 1.160913451, -0.2803617376, -1.1542748582
C, 2.7014580748, -0.4035995412, 1.0871100655
H, 1.8544688958, -1.017874645, 2.0069052634
C, 2.537327931, 0.4667586929, -1.1638993044
H, 0.560023392, 0.5348683736, -2.015424473
C, 3.3003871255, 0.1280473766, -0.0508167215
H, 3.3005971238, -0.669033154, 1.9461861812
H, 3.008786753, 0.8757781159, -2.045832824
H, 4.3704335406, 0.278486556, -0.0707431428
O, -1.476262903, 1.3419488878, 0.8594059232
O, -1.784456844, -0.9721459907, 1.3752636271
H, -1.9546024918, -1.288625234, 1.8627919289
C, -2.3696655713, -2.6888086404, -0.974646738
H, -2.0135733888, -3.6014272972, -1.437764819
H, -2.9025209929, -2.901969985, -0.053424257
H, -2.9670080371, -2.1050234554, -1.6671064085
H, -0.7309772354, 1.9436741985, 0.9738131193

14 [protonated methyl dihydrogen benzeneorthosulfonate, water elimination TS], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

S, -1.004418843, 0.188533054, -0.000445305
O, 1.7175021551, 0.4823390301, 1.33439072
H, 1.4368237934, 1.548851634, 1.3068863208
O, 1.3566416816, -1.3356590378, -0.1709773204
C, -0.7627020426, -0.01161225, -0.01875209
C, -1.454744454, 0.272438768, -1.1878505945
C, -1.3608954623, -0.4697875889, 1.1477004361
C, -2.8291986116, 0.0740954254, -1.1772020887
H, -0.9530381978, 0.6271670296, -2.0751690907
C, -2.7375013191, -0.651117011, 1.1279303699
H, -0.7861325483, -0.6776647281, 2.0375659442
C, -3.4650346772, -0.3817986713, -0.0268186584
H, -3.3983801927, 0.2788698624, -2.0720414413
H, -3.235371572, 0.0046536479, 2.0186351123
H, -4.5356743305, 0.527837418, -0.030465067
O, 0.7764514998, 2.2724174011, 0.2865834938
O, 1.6560598529, 0.6801397511, -1.3432733667
H, 1.5915853814, 1.661923508, -1.3445813665
C, 2.7573568968, -1.8001070717, -0.1321242976
H, 2.6756867504, -2.8661072253, -0.3054531773
H, 3.321057334, -1.319528248, -0.924834697
H, 3.1767745378, -1.5931018567, 0.8461865797
H, -0.1246477741, 2.5283055959, 0.457859065

15 [protonated methyl dihydrogen benzeneorthosulfonate···water HB complex], in gas phase (at B3LYP/aug-cc-pVTZ level)
S, 0.86947, -0.24301, 0.22884
O, 1.35612, 0.06083, 1.54566
H, 2.709, 3.15231, 0.5021
O, 1.13622, -1.70323, -0.25328
C, -0.86723, -0.09585, 0.05817
C, -1.4444, -0.14554, -1.21111
C, -1.61175, 0.06048, 1.22518
C, -2.8205, -0.03464, -1.30087
H, -0.83935, -0.26514, -2.09781
C, -2.9901, 0.17089, 1.10663
H, -1.12748, 0.0974, 2.18957
C, -3.58898, 0.12241, -0.14765
H, -3.29828, -0.06959, -2.27002
H, -3.5928, 0.29454, 1.99465
H, -4.66342, 0.2086, -0.23013
O, 2.10566, 2.96739, -0.22739
H, 2.2711, 3.62602, -0.91222
C, -3.5176, -2.23135, -0.22844
H, 3.39659, 3.27163, -0.5053
H, 3.1151, -1.69629, -0.95986
H, 2.91846, 2.1376, 0.77614
O, 1.5577, 0.58909, -0.88532
H, 1.79539, 1.55868, 0.59744

15 [protonated methyl dihydrogen benzeneorthosulfonate···water HB complex], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)
S, 0.8243200405, -0.2851401934, 0.1958930341
O, 1.257054108, -0.3934171937, 1.5721953869
H, 3.63846261575, 2.5224790396, 0.2602167454
O, 0.9866435819, -1.6522592047, 0.5834545849
C, -0.9151757034, -0.0336524687, 0.0487900271
C, -1.4357299559, 0.4731656209, -1.1397427598
C, -1.7155423856, -0.353388187, 1.1406012878
C, -2.8078328739, 0.6552353155, -1.2291126952
H, -0.7889855919, 0.7182585794, -1.9682344905
C, -3.086045693, -1.600296839, 1.0308080772
H, -1.2777878363, -0.7359307455, 2.050100447
C, -3.6278905511, 0.3401318685, -0.1487305652
H, -3.2351302598, 1.0473110778, -2.1406424333
H, -3.7269112488, -0.3982270838, 1.8672896064
H, -4.6957594797, 0.4887618933, -0.2264645278
O, 2.7235617893, 2.6389827792, 0.3003843583
H, 2.4916114987, 3.4566811708, -0.1687104707
C, 2.3346504558, -2.220671192, -0.6967781866
H, 2.1852881079, -3.14667483, -1.2410813102
H, 2.9706894505, -1.5425774241, -1.2562335819
H, 2.7324829686, -2.4174681639, 0.2945314859
O, 1.5382172021, 0.7371338831, -0.6291094629
H, 2.178889159, 1.7563580698, -0.107435432

16 [oxonium cation], in gas phase (at B3LYP/aug-cc-pVTZ level)
H, -0.8163045293, -0.4712936476, 0.2265398663
H, -0.0000000006, 0.942587282, 0.2265398663
H, 0.8163045353, -0.4712936372, 0.2265398663
O, 0., -0.0000000009, -0.0429598951

16 [oxonium cation], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)
H, -0.0000000787, 0.927998, -0.224395
H, -0.8036698033, -0.4639990681, -0.224395
H, 0.803669882, -0.4639989319, -0.224395
O, 0., 0., 0.084148

17 [protonated benzenesulfonic acid], in gas phase (at B3LYP/aug-cc-pVTZ level)
S, -0.5852039241, -0.0503841858, -0.0338463939
O, 1.48401212, -0.5793111132, -1.2052162305
H, 1.6797606104, -1.3540381703, -1.137599744
O, 0.7216489738, -0.8990251792, -0.3438826182
H, 1.3139567483, -0.9401718218, 0.4296884145
O, -0.0825136037, -0.2664298453, 1.288401436
C, -0.3055177812, 1.612312966, -0.466772152
C, -0.6837263904, 2.5770923553, 0.4675775344
C, 0.2731308257, 1.1912894948, -1.7016864325
C, -0.4692220943, 3.907391667, 0.1393497486
H, -1.1292089925, 2.968421576, 1.4105807149
C, 0.4724822191, 3.255334373, -1.9994010519
H, 0.5552511757, 1.147052855, -2.4024434671
C, 0.1030325964, 4.2414587594, -1.0840289795
H, -0.7512079453, 4.6799012449, 0.8397973337
H, -0.9163741887, 3.5302739973, -2.9452128213
H, 0.2648798238, 5.2816768282, -1.3299671108

17 [protonated benzenesulfonic acid], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)
S, -1.394006, 0.135164, -0.004735
O, -1.788859, -0.714577, -1.254127
H, -2.753723, -0.844219, -1.345164
O, -1.960427, -0.810832, 1.122618
H, -1.964542, -0.377488, 1.99733
O, -1.921693, 1.464224, 0.044763
C, 0.348924, 0.039139, -0.007605
C, 1.052456, 1.241138, -0.018957
C, 0.967284, -1.211874, 0.016747
C, 2.438186, 1.177929, -0.010027
H, 0.535331, 2.188107, -0.304549
C, 2.351124, -1.243639, 0.023413
H, 0.39208, -2.1255, 0.029557
C, 3.080282, -0.055525, 0.010285
H, 3.011962, 2.092694, -0.018912
H, 2.860986, -2.195471, 0.040864
H, 4.160309, -0.094285, 0.017479
benzenesulfonylium cation, in gas phase (at B3LYP/aug-cc-pVTZ level)
S,0.,0.,-1.61417517
O,0.,-1.27672928,-2.25724307
O,0.,1.27672928,-2.25724307
C,0.,0.,0.09584283
C,0.,1.24325997,0.75924073
C,0.,-1.24325997,0.75924073
C,0.,1.22135308,2.13772673
H,0.,2.17038592,0.20560365
C,0.,-1.22135308,2.13772673
H,0.,-2.17038592,0.20560365
C,0.,0.,2.81944483
H,0.,2.15127812,2.68755165
H,0.,-2.15127812,2.68755165
H,0.,0.,3.90104583

benzenesulfonylium cation, in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)
S,0.,0.,-1.6037517081
O,0.,-1.271725796,-2.2585171267
O,0.,1.271725796,-2.2585171267
C,0.,0.,0.0981379241
C,0.,1.2429480331,0.7594483948
C,0.,-1.2429480331,0.7594483948
C,0.,1.220720597,2.1366374138
H,0.,2.1684329153,0.2056929471
C,0.,-1.220720597,2.1366374138
H,0.,-2.1684329153,0.2056929471
C,0.,0.,2.8173914543
H,0.,2.149375066,2.6857700446
H,0.,-2.149375066,2.6857700446
H,0.,0.,3.8980766824

[benzenesulfonylium cation···water complex], in gas phase (at B3LYP/aug-cc-pVTZ level)
S,0.4273739318,-1.3401186303,0.
O,0.7104010754,-1.9198403317,1.2750341299
O,0.7104010754,-1.9198403317,-1.2750341299
H,-1.9909060085,-2.4610889867,0.7783158583
H,-1.9909060085,-2.4610889867,-0.7783158583
O,-1.748183763,-1.9379031033,0.
C,0.1763387614,0.3645499519,0.
C,0.0874251197,1.0218655666,-1.2353603329
C,0.0874251197,1.0218655666,1.2353603329
C,-0.0839296123,2.393023718,-1.2168656031
H,0.1647892612,0.4758988102,-2.1635419521
C,-0.0839296123,2.393023718,1.2168656031
H,0.1647892612,0.4758988102,2.1635419521
C,-0.1710045628,3.0711979373,0.
H,-0.1469651037,2.9362981489,-2.14845328
H,-0.1469651037,2.9362981489,2.14845328
H,-0.3064190307,4.1440055338,0.

[benzenesulfonylium cation···water complex], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)
S,-1.011046376,0.5788324566,-0.5475078812
O,-1.6379235644,-0.2678388326,-1.5158409946
19 [methanol···benzenesulfonylium cation···water complex], in gas phase (at B3LYP/aug-cc-pVTZ level)
O, -1.3785941051, 1.936874955, -0.2863110771
H, -2.5702561708, 0.3267341155, 1.4982175299
O, -1.8373987636, -0.2266742269, 1.1870422936
C, 0.6386028052, 0.1864401316, -0.1969907082
C, 1.3898114461, 1.0979436703, 0.5507440029
C, 1.1510724532, -1.0168247078, -0.6906619474
C, 2.7144391112, 0.7841135884, 0.7957676164
H, 0.9528348047, 2.01483554, 0.9144452797
C, 2.4792267508, -1.3011990798, -0.4273983192
H, 0.5344724897, -1.6924507339, -1.2627565192
C, 2.5262071904, -1.4767946914, 1.3633819689
H, 2.911282517, -2.2183153444, -0.7989967971
H, 4.2884310431, -0.6416803176, 0.5115722864
H, -2.182281046, -1.1234413363, 0.1047820805

19 [methanol···benzenesulfonylium cation···water complex], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)
O, -1.6656020005, 0.5765246191, -1.1732232402
O, -1.4375708634, 1.0816140386, 1.3235828862
S, -1.0113095295, 0.4874600221, 0.0943147561
H, -2.358892153, -1.306305443, 1.4136509297
H, -0.2679447356, 3.3740156349, -1.342851166
H, -0.0392878323, 3.6644253233, 0.1451858226
O, -1.8122170163, -1.4683149834, 0.6310453316
O, -0.2000534062, 2.9579167052, -0.5098029827
C, 0.6423913978, -0.0302827375, 0.0449013676
C, 1.3772347377, -0.0128502906, 1.2327465634
C, 1.1721823571, -0.4376766089, -1.1817961162
C, 2.6990258269, -0.4186563632, 1.1755214788
H, 0.929848989, 0.3159281472, 2.1585273435
C, 2.4967078315, -0.838966082, -1.2073376331
H, 0.5717280077, -0.423413406, -2.0787243062
C, 3.2527499865, -0.8299223778, -0.036113915
H, 3.2990314822, -0.4122243947, 2.0738728717
H, 2.9420005084, -1.1524572803, -2.1401763838
H, 4.286623882, -1.144522997, -0.0685106132
C, -2.5674927274, -2.2199885028, -0.3623503098
H, -2.9153758785, -3.1397730764, 0.102303391
H, -3.4015937202, -1.6311172801, -0.7357430402
H, -1.875547219, -2.453319039, -1.1643051914

19 [methanol···benzenesulfonylium cation···water complex], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)
O, -1.6568690302, 0.6226530068, -1.1552499042
O, -1.4143365596, 1.0906544286, 1.3355026204
S, -1.0370823377, 0.4306764726, 0.1209108961
H, -2.321227775, -1.2548158011, 1.4176779582
H, -0.2121343764, 3.4645066861, -1.2446396247
H, 0.2075328704, 3.6425003149, 0.2133663281
O, -1.8358742534, -1.3799456465, 0.5853997443
O, 0.2163417447, 3.0081838364, -0.5119899165
C, 0.6224738871, -0.0890265468, 0.0549811204
C, 1.3611977529, -0.8985228787, 1.2383507255
C, 1.1471975079, -0.4745376437, -1.1786240915
20 [benzenesulfonylium cation···methanol complex], in gas phase (at B3LYP/aug-cc-pVTZ level)

S, -1.0127616064, 0.5395309646, -0.545250952
O, -1.620658554, -0.3184137027, -1.5160932818
O, -1.3892882369, 1.8941029098, -0.2724339854
H, -2.4577495372, 0.4601456679, 1.5138073876
O, -1.897061497, -0.2524590347, 1.1679865311
C, 0.6430010522, 0.1644636335, -0.1940869776
C, 1.3841744526, 1.0772590903, 0.5645169357
H, 1.1767959103, -1.0237524812, -0.7056825273
C, 2.7134402404, 0.7796285741, 0.8063669208
H, 0.9361307037, 1.9879390661, 0.9326608677
C, -2.59288969, -1.292238958, -0.4464303717
H, 0.5735538923, -1.6939064126, -1.2995044465
C, 3.2694693307, -0.3975046841, 0.3059047175
H, 3.1848979766, 1.4662365579, 1.3803956704
H, 2.9579035148, -2.194599296, -0.8357477031
H, 4.3098803039, -0.6179618675, 0.5008116245
C, 2.655489816, -1.5026365366, 1.0624870488
H, 3.0748345574, -1.7045743072, 0.2.0437921724
H, -3.432329741, -1.40938181, 0.3089237882
H, -1.939738401, -2.2710496165, 0.7932015806

20 [benzenesulfonylium cation···methanol complex], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

S, -1.0424498831, 0.5050745973, -0.5246483382
O, -1.630594995, -0.3472124605, -1.5154307599
O, -1.3931350355, 1.8813077951, -0.3229931389
H, -2.4426923493, 0.4989666047, 1.4821152808
O, -1.8726953546, -0.2151029323, 1.1178188457
C, 0.6247165888, 0.1407283469, -0.1796754354
C, 1.3537896661, 1.044100496, 0.5966522035
C, 1.1731043638, -0.10248293546, -0.7185472143
C, 2.6879345629, 0.7596869675, 0.8305948528
H, 0.893864598, 1.9361888698, 0.9928112728
C, 2.5108204284, -1.2814516433, -0.4693253455
H, 0.5748861584, -1.6952964703, -1.3156785405
C, 3.2604723792, -0.3958447965, 0.3010994701
H, 3.2818751302, 1.4395002117, 1.4228233149
H, 2.967556654, -2.1702357147, -0.8786778804
H, 4.3036176912, -0.6065594429, 0.4895907237
C, -2.6217472115, -1.4828381491, 1.0622736113
H, -3.0284531976, -1.6326555343, 2.0572198956
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### 21 [protonated methyl benzenesulfonate], in gas phase (at B3LYP/aug-cc-pVTZ level)

| Atom | x-coordinate | y-coordinate | z-coordinate |
|------|--------------|--------------|-------------|
| S    | 0.1387669002 | 0.1274267395 | -0.06475680 |
| O    | 0.1827689038 | -0.695320576 | 1.17263426 |
| C    | 1.716669387 | -0.3451123344 | -0.26348404 |
| C    | -0.5303244566 | 2.1794608787 | 0.06203497 |
| C    | -2.3663875544 | -1.2449103628 | -0.04648813 |
| O    | -0.4096789208 | -2.1343204094 | -0.13070323 |
| C    | 3.27326514 | 0.8212978379 | 1.50653670 |
| H    | -0.9676743338 | 2.4754733665 | 0.75460404 |
| H    | 0.8786123669 | 0.1706206711 | 1.56535998 |

### 21 [protonated methyl benzenesulfonate], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

| Atom | x-coordinate | y-coordinate | z-coordinate |
|------|--------------|--------------|-------------|
| S    | 0.0581927766 | 0.3392372943 | 0.20509461 |
| O    | 0.6618221213 | 0.6082558027 | -0.85998333 |
| O    | -0.5506031569 | -0.3868219639 | 1.52021128 |
| C    | 0.6663315845 | 1.7121302634 | 0.14065789 |
| C    | 0.6638949042 | 0.0849382694 | 0.04397826 |
| C    | 1.4472783763 | 1.1986211513 | -0.24710817 |
| C    | 1.1885306628 | -1.1962198924 | 0.21605202 |
| C    | 2.8162664737 | 0.1011986444 | -0.37302700 |
| H    | 1.0017953491 | 2.1738029745 | -0.36909167 |
| C    | 2.557014915 | 1.3451785494 | 0.08336739 |
| C    | 0.5562839392 | -2.0383144274 | 0.44667248 |
| C    | 3.3650849469 | -2.2562846487 | -0.20931745 |
| H    | 3.4500527678 | 1.8560142291 | -0.59811477 |
| H    | 2.9949222157 | 2.3335084874 | 0.21015802 |
| H    | 4.4326108025 | -0.3924112132 | -0.3806448 |
| C    | -3.1375414437 | -0.7144558143 | -1.00855261 |
| C    | -3.2531634574 | -1.3158565909 | -1.90074661 |
| C    | -3.5372575694 | -1.2137174941 | -0.13340764 |
| C    | -3.5515517517 | 0.2786934917 | -1.14331881 |

### 22 [oxonium cation···water pre-reactive complex], in gas phase (at B3LYP/aug-cc-pVTZ level)

| Atom | x-coordinate | y-coordinate | z-coordinate |
|------|--------------|--------------|-------------|
| H    | 2.3991095524 | 0.5324670587 | 0.6757874234 |
| H    | 2.4053351024 | -0.8061125599 | -0.1885949707 |
| O    | 0.197999671709 | 0.196111334956 | -0.0659809464 |
| O    | 0.138722236322 | 1.039956912885 | 0.0577303353 |
| H    | 0.145995597874 | -0.477124348137 | -0.9105937341 |
| H    | 0.179469209965 | -0.56344356603 | 0.89839922573 |

S25
22 [onium cation···water pre-reactive complex], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)
H, 2.449134114582, -0.120485576863, -0.824275364966
H, 2.416918141786, 0.672199915266, 0.547749386105
O, -0.070157558808, 0.051782552382
H, -0.909409360730, -0.544633248906
H, 0.193043838764, 0.10465731774
H, 0.22412599268835, -0.546093471901
C, 0.517541220654, -0.009310662041, -0.019609924378
H, 2.916682158176, -0.745462844136, 0.217640617726
H, 2.956490165056, 0.632888562230, -0.434876690303
O, -0.2372140489744, 0.027709623343, 0.034414412479

23 [methyloxonium cation + water S\textsubscript{2}N\textsubscript{2} TS], in gas phase (at B3LYP/aug-cc-pVTZ level)
H, -0.3152263049, -2.4464583896, -0.8115795118
H, 0.6218678378, 2.4308039582, 0.5468017398
O, -0.0737573232, -1.9898255038, 0.0390708792
H, -0.9340440425, -0.0044056505, -0.5419002496
H, 0.9340440425, 0.0044056505, -0.5419002496
H, 0.0, 0.0, 1.0636430404
C, 0.0, 0.0, -0.0109394367
H, 0.1352263049, 2.4464583896, -0.8115795118
H, -0.6126014604, 2.4308039582, 0.5468017398
O, 0.0737573232, 1.9898255038, 0.0390708792

23 [methyloxonium cation + water S\textsubscript{2}N\textsubscript{2} TS], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)
H, -0.0776711829, -2.3482211619, -0.8470353256
H, 0.6126014604, -2.3639604729, 0.534548199
O, -0.1314628724, 0.9829671527, 0.0472342009
H, -0.9313693958, 0.0282543121, -0.5228626849
H, 0.9313693958, 0.0282543121, -0.5228626849
H, 0.0, 0.0, 1.0837001062
C, 0.0, 0.0, -0.0100282607
H, 0.0776711829, 2.3482211619, -0.8470353256
H, -0.6126014604, 2.3639604729, 0.534548199
O, 0.1314628724, 1.9829671527, 0.0472342009

S1 [benzenesulfonic acid···2 methanol HB complex], in gas phase (at B3LYP/aug-cc-pVTZ level)
S, -0.727038, -1.559813, 0.283788
O, -0.530163, -1.611484, -0.433374
C, 2.3736, -1.92495, -0.407136
O, 0.673757, -2.651588, 0.194906
H, 0.998905, -1.772958, 2.394573
O, -0.291837, -1.406961, 1.843271
C, -1.552765, -0.021172, -0.071937
C, -2.923424, -0.043313, -0.304235
C, -0.811118, 1.155866, -0.122971
C, -3.569937, 1.151635, 0.595853
H, -3.463302, 0.977719, -0.26782
C, -1.476325, 2.339669, -0.412646
S1 [benzenesulfonic acid···2 methanol HB complex], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

H, 0.256267, 1.168998, 0.056981
C, -2.848068, 2.338662, -0.648456
H, -4.634332, 1.151563, -0.785257
H, -0.913916, 3.261658, -0.457556
H, -3.355142, 3.266283, -0.877171
C, 3.159803, 2.442851, 1.344766
H, 2.692972, 3.382712, 1.638073
H, 3.152163, 1.769593, 2.208137
H, 4.2007, 2.648399, 1.073979
O, 3.241011, -0.662672, -0.438616
H, 2.811607, 1.063902, -0.011149
O, 2.422317, 1.917969, 0.253514
C, -0.7115414693, -1.545255032, 0.08524894
O, 0.4923074426, -1.5500629441, -0.7294469252
H, 2.3217485618, -1.0550612437, -0.504576372
O, -1.6407970797, -2.6533330707, -0.112506763
H, -0.8414050058, -1.6800003879, 2.232349409
O, -0.1388855824, -1.4741471241, 1.5944698573
C, -1.5789669349, -0.086035447, -0.1347372387
C, -2.9690191547, -0.0228190794, -0.1602638278
C, -0.8477283478, 1.1682431496, -0.2773504891
C, -3.6445253364, 1.1789043658, -0.3364143034
H, -3.507503585, -0.9519719216, -0.0524043285
C, -1.5399801893, 2.3589278579, -0.4496114817
H, 0.2332928338, 1.1650890085, -0.2563556052
C, -2.9322326797, 2.3644482341, -0.4797497334
H, 4.7247619163, 1.1850964797, -0.3634660349
H, 0.9901872641, 3.2824156657, -0.5632861667
H, -3.4624655176, 3.2965323849, -0.6175248682
C, 3.0688370353, 2.4431465954, 1.2774229611
H, 2.8067675901, 3.4936315201, 1.3958560494
H, 2.5464144251, 1.8685390731, 2.0482935858
H, 4.1464212549, 2.3372459925, 1.4346522827
H, 2.8016104336, -0.6747937978, -0.3894629075
H, 2.9194427995, 1.1063499842, -0.1573628438
O, 2.6827613963, 2.0453959085, -0.0328708073
C, 4.0598639112, -1.1449634903, -1.4361300294
H, 4.1677719461, -2.2306190295, -1.3974124179
H, 3.8635212103, -0.8568763559, -2.4200028703
H, 5.0361262223, -0.6895751984, -1.28586769

S2 [one methanol molecule-assisted benzenesulfonic acid + methanol addition TS], in gas phase (at B3LYP/aug-cc-pVTZ level)

S, 1.4176704598, 1.5265194415, -0.4420805809
O, 2.4792351065, 1.0286046943, -1.446197421
H, 2.8241033624, -0.0285617011, -1.3539928305
O, 1.6987641661, 1.6578895868, 0.978805639
H, 2.3211221897, 3.496757416, -0.4719829964

S27
O, 1.5543687836, 3.1221388091, -0.927542836
C, -0.2693961808, 1.5020565025, -1.0687830385
C, -1.2796033099, 1.8939199457, -0.2053125397
C, -0.5136194463, 1.155781093, -2.3884544173
H, -2.5857723211, 1.9219431553, -0.6842607349
H, -1.0531711350, 2.1791676242, 0.8114595107
C, -1.8223452643, 1.1948531959, -2.850439899
H, 0.2970838676, 0.8648758468, -3.093218065
C, -2.8578538145, 1.5731736909, -2.009317738
H, -3.3871623507, 2.2233519569, -0.023844765
H, -2.0315798481, 0.929188024, -3.8777287007
H, -3.8745944727, 1.5998022275, -2.3678665646
C, 0.3840245861, -0.8736936069, 1.0378303601
H, -0.6130884641, -0.4316590086, 1.1489939255
H, 0.262242302, -1.9611982792, 1.0507426067
H, 0.9865747096, -0.5788827768, 1.9011185253
O, 3.0608549834, -1.3095532226, -1.1383582464
H, 2.1515842396, -1.2497827872, -0.629724114
O, 0.9812489413, -0.49571434, -0.1796773091
C, 2.9777464643, -2.1633406661, -2.2796366081
H, 2.0803066904, -1.9570670236, -2.8676073159
H, 3.8580981987, -1.9963957618, -2.8976240613
H, 2.9632466125, -3.2057451313, -1.9606286577

S2 [one methanol molecule-assisted benzenesulfonic acid + methanol addition TS], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)
S, -0.3651891203, -1.0715787658, -0.2860678434
O, -1.4714871667, -0.4917627896, -1.1870351865
H, -2.327556281, 0.0927605291, -0.6939532583
O, -0.6184291908, -2.1798915799, 0.6304460281
H, -0.2060365926, -2.6822535946, -1.758683357
O, 0.3548943222, -1.9159827872, -1.5548438639
C, 1.1308096379, -0.072397373, -0.164257447
C, 2.166548176, -0.5531176325, 0.6212251864
C, 1.2284906367, 1.1106112852, -0.8819046979
C, 3.3402475939, 0.1922822806, 0.6974060539
H, 2.0707469288, -1.4870792296, 1.1549125121
C, 2.4094032337, 1.8374938713, -0.7985675722
H, 0.4072234052, 1.4591422198, -1.4899400925
C, 3.4622330828, 1.3827482652, -0.0086173355
C, 0.1574874649, -0.1663961461, 1.3073963234
H, 2.5042504639, 2.7608256174, -1.3528332914
H, 4.3770272212, 1.9555442198, 0.052547867
C, -0.7341010119, -0.0094918351, 2.4622964164
H, 0.3451350313, -0.06031221, 2.6446821672
H, -1.1353419957, 0.8016808911, 3.0760303648
H, -1.1808083296, -0.9503769733, 2.7947729158
O, -3.1610778127, 0.7401146421, 0.0174137867
H, -2.419437593, 0.7256791795, 0.7287404966
O, 1.0200101317, 0.2667091548, 1.1096198187
C, -3.4548154402, 2.0756515072, -0.431648771
H, -2.5418599887, 2.6024138338, -0.7101482162
H, -4.1105282659, 1.9994371799, -1.294836431
H, -3.963108633, 2.6176281566, 0.3631187246

S28
S3 [methyl dihydrogen benzeneorthosulfonate···methanol HB complex], in gas phase (at B3LYP/aug-cc-pVTZ level)

| Atom | X      | Y      | Z       |
|------|--------|--------|---------|
| S    | 0.0    | -0.5781230803 | -0.218591301 | -1.5572490795 |
| O    | -1.0450873081 | 0.181536716 | -0.0832208919 |
| H    | -1.8566866802 | 0.766789084 | -0.0696511813 |
| O    | -1.2118875408 | -1.2648235734 | -2.3649992475 |
| O    | 0.6884631527 | -1.1356843433 | -0.8788904179 |
| C    | 0.7183182797 | 0.8432815597 | -2.2391394667 |
| C    | 1.1057364598 | 0.616740482 | -3.5495578855 |
| C    | 1.2929595153 | 1.8320740671 | -1.4585606603 |
| C    | 2.1014672578 | 1.4183546059 | -4.095498706 |
| O    | 0.0    | -1.0442948991 | -0.1703703768 | -4.128557937 |
| C    | 2.2846815799 | 2.6278222927 | -2.0207445953 |
| H    | 0.9237660609 | 1.9738821686 | -0.4340384887 |
| C    | 2.683347489 | 2.4238810886 | -3.3354122172 |
| H    | 0.4178705449 | 1.2529442403 | -5.1162286945 |
| H    | 0.7450888533 | 3.4041627382 | -1.4250732775 |
| O    | -2.2145842518 | 0.600341896 | -2.8948754827 |
| C    | 0.332942157 | -2.366330067 | -0.2346059792 |
| H    | 0.2813753517 | -2.8127393325 | 0.0570034568 |
| H    | -0.1924915576 | -3.0331771749 | -0.9172776037 |
| H    | -0.2736504967 | -2.1918624582 | 0.6551928673 |
| C    | 0.30653531892 | 3.1175969503 | 0.5695623148 |
| H    | -0.8532237869 | 3.7755575951 | 0.1972061472 |
| C    | 0.29942955 | 3.5864288066 | 0.3910618627 |
| H    | 0.32001829027 | 2.9825426575 | 1.6405110795 |

S3 [methyl dihydrogen benzeneorthosulfonate···methanol HB complex], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

| Atom | X      | Y      | Z       |
|------|--------|--------|---------|
| S    | -0.325643624 | 0.8027037905 | 0.3328705209 |
| O    | -1.5132943806 | 0.4243430893 | -0.6597656788 |
| H    | 2.1735747133 | -0.2238388882 | -0.260267204 |
| O    | 0.4427831513 | 1.7871129094 | 1.4202940754 |
| O    | 0.2747779093 | 1.8650901465 | -0.8664761288 |
| C    | 1.1961716903 | -0.1458069598 | 0.0805947191 |
| C    | 2.7061803035 | 0.1309134402 | 0.9110504544 |
| C    | 1.2555634101 | -1.1129034417 | -0.910259916 |
| C    | 3.4458995682 | -0.5935067061 | 0.7399083654 |
| H    | 2.1979421195 | 0.8930148111 | 1.67357151 |
| C    | 2.4381126873 | -1.8283122304 | -1.0675874439 |
| H    | 0.4059766432 | -1.3071489961 | -1.5480922629 |
| C    | 3.5306386609 | -1.5712513971 | -0.2455866303 |
| H    | 4.29380678 | -0.3886292805 | 1.3786197735 |
| H    | 2.5019226109 | -2.5856937918 | -1.8365315552 |
| H    | 4.4466540826 | -2.1308490313 | -0.3741350699 |
| O    | -3.3050671128 | -1.2648590008 | 0.2790457909 |
| H    | -2.7128360951 | -1.5352545218 | 0.9953437366 |
| O    | -0.8875057207 | -0.5585244367 | 1.3846021001 |
| H    | -0.8348683898 | -0.2069891339 | 2.2808525333 |
| C    | -0.4473988542 | 0.3066979832 | -1.1337523041 |
| H    | 0.121004182 | 3.5952380497 | -1.8985155467 |
S4 [one methanol molecule-assisted methyl dihydrogen benzeneorthosulfonate, water elimination TS], in gas phase (at B3LYP/aug-cc-pVTZ level)

S, -0.5172095565, 3.6924382943, -0.242309233
H, -1.4477328301, 2.857317475, -1.5131817589
C, -3.7027571074, -2.407236449, -0.4938472242
H, -4.2843853918, -3.0978458327, 0.1167323439
H, -2.8371681436, -2.9263063538, -0.9077081903
H, -4.3232103038, -2.0401804647, -1.3070304864

S4 [one methanol molecule-assisted methyl dihydrogen benzeneorthosulfonate, water elimination TS], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

S, -0.4285728833, 0.636769663, -1.5095033854
O, -0.8687899708, 0.7948502272, -0.0346172547
H, -1.6206716017, 1.5893226429, 0.1986999791
O, -1.3226168821, 0.1321130292, -2.5435911255
O, -0.5099848324, -0.7034747935, -1.1994514559
H, 1.0679616256, 1.5366432287, -1.9518351199
C, 1.4225551696, 1.5816458378, -3.2898600866
C, 1.8413992432, 2.1130424995, -0.9589931711
C, 2.5940735544, 2.24080134, -3.6417762738
H, 0.7982635633, 1.1153877979, -4.0381698162
C, 3.0086805297, 0.7711988374, -1.328878615
H, 1.5443690899, 2.0481256432, 0.0770572588
C, 3.3848291428, 2.8371637875, -2.665423973
H, 2.8866320978, 2.8653883684, -4.6817628142
H, 3.6250722641, 3.2289328648, -0.5673320375
H, 4.2945348303, 3.3499368323, -2.9461024861
O, -2.4579546292, 2.6011903106, 0.291103185
H, -2.1085045559, 2.8129347459, -0.671985549
O, -1.242750551, 2.5220631028, -1.815209482
H, -1.7374011052, 2.3980048094, -2.6311832625
C, -0.1668440536, -1.9246932451, -0.8722708171
H, 0.6166696217, -2.6721191882, -0.775427492
H, -0.8547765089, -2.2098548647, -1.6668746524
H, -0.7026782023, -1.8300485541, 0.0722574956
C, -2.1090485638, 3.6260770522, 1.221459733
H, -1.0615542573, 3.9194011106, 1.1820638722
H, -2.7406399664, 4.5000868618, 1.0613518982
H, -2.2783891815, 3.2485250499, 2.2283609837

S4 [one methanol molecule-assisted methyl dihydrogen benzeneorthosulfonate, water elimination TS], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

S, 0, 0.4543730956, 0.8025967085, 0.2646759875
O, 0, -1.58253351, 0.3538372629, -0.6892692361
H, 0, -2.3026358669, -0.4387704887, -0.3252923411
O, 0, -0.7186641476, 1.5995210772, 1.461659419
O, 0, 0.1039752484, 1.9842756306, -0.779071444
C, 0, 1.1149583393, -0.603175655, 0.0565782372
C, 0, 1.2827460756, 0.2108081705, 0.961470262
C, 0, 1.2801247174, -0.9283721911, -1.0102774671
C, 0, 3.3544746251, 0.4228503972, 0.7888807473
H, 0, 1.9701018645, 0.8948976689, 1.7823970905
C, 0, 2.5124227576, -1.5544047802, -1.1660415176
H, 0, 0.4735082356, -1.1162613481, -1.7031288297
C, 0, 3.546686456, -1.3042903217, -0.2701293247
H, 0, 4.1573509522, -0.2241457951, 1.4849986295
H, 0, 2.6602884141, -2.2361589577, -1.9919451216
H, 0.45018371552, -1.7941565835, -0.3980675024
O, 0.0, -3.0063972738, -1.369588268, 0.239531482
H, 0.0, -2.2290403097, -1.4157561805, 0.9113976852
O, 0.0, -0.8748805436, -0.8840107352, 1.3656302336
H, 0.0, -0.884106408, -0.5468343897, 2.2673595056
C, 0.0, -0.7313172649, 3.1329474813, -1.0003255803
H, 0.0, -0.1678053932, 3.778753396, -1.67030702
H, 0.0, -0.926321668, 3.6557101659, -0.0655074065
H, 0.0, -1.6701666288, 2.845852458, -1.4724096171
C, 0.0, -3.146270406, -2.5910005808, -0.5060795685
H, 0.0, -3.5321769711, -3.371567614, 0.14696161763
H, 0.0, -3.854330147, -2.4118158489, -1.3110653091

**SS [methyl benzenesulfonate···methanol···water HB complex], in gas phase (at B3LYP/aug-cc-pVTZ level)**

S, 0.0, -0.2447948224, -0.3483526649, -0.2676157863
O, 0.0, -0.9655252422, 0.9190373879, -0.2690695761
H, 0.0, -2.693414698, 1.5861908168, -0.6896784096
O, 0.0, -0.3490011304, -1.2086834184, -1.4284801709
O, 0.0, -0.6491234329, -1.1755168668, 1.0497995587
C, 0.0, 1.4611869766, -0.0382358978, 0.130995359
C, 0.0, 2.4287517272, -0.9133869242, -0.3472509987
C, 0.0, 1.7911133408, 1.0747885423, 0.8951554314
C, 0.0, 3.7612535156, -0.6671101761, -0.0425231943
H, 0.0, 2.139431276, -1.7590544876, -0.9534931422
C, 0.0, 3.1271282912, 1.307384446, 1.1939661896
H, 0.0, 1.0172717199, 1.7450486663, 1.2379001242
C, 0.0, 4.1082645786, 0.4380567171, 0.7274244552
H, 0.0, 4.5269721709, -1.3358953395, -0.4100275045
H, 0.0, 3.401327188, 2.1686148636, 1.7865857949
H, 0.0, 5.1475057446, 0.6259645741, 0.960531674
O, 0.0, -3.6065929949, 1.9075984488, -0.7468925184
H, 0.0, -4.5433745153, 0.6563734543, 0.1984720276
O, 0.0, -4.8992209181, -0.0793980592, 0.734849388
H, 0.0, -5.6691753682, -0.3956778155, 0.2552775559
C, 0.0, -1.9437678509, -1.8498292417, 1.034892426
H, 0.0, -1.984920681, 2.3705737302, 1.9859841472
H, 0.0, -1.9747928483, -2.5597698995, 0.2114825387
H, 0.0, -2.758869925, -1.133154518, 0.9621152849
C, 0.0, -3.6367390048, 3.2896747229, -0.4087769017
H, 0.0, -3.0457818076, 3.8833618867, -1.1108863803
H, 0.0, -4.6736715947, 3.6153469996, -0.4655797119
H, 0.0, -3.2696259605, 3.467291648, 0.6057656963

**SS [methyl benzenesulfonate···methanol···water HB complex], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)**

S, 0.0, -0.1907563671, -0.3090231824, -0.1956684504
O, 0.0, -0.9528161893, 0.9192323354, 0.0168206209
H, 0.0, -2.6920147274, 1.4862454028, -0.4501130032
O, 0.0, -0.3460457679, -0.9851547081, -1.4722366421
O, 0.0, -0.5296872916, -1.3356222724, 0.9933302832
C, 0.0, 1.5210038082, -0.0203937388, 0.1662803
C, 2.4765223844, -0.8404844284, -0.4245211608
C, 1.866780007, 1.0197354797, 1.0224084542
S32

S6 [benzenesulfonic acid···3 methanol HB complex], in gas phase (at B3LYP/aug-cc-pVTZ level)

S, -1.574786327, -1.6107316307, 0.0128310927
O, -0.3591416373, -1.8073888084, -0.7518762613
H, 1.5067200798, -2.000496207, -0.4965815855
O, -2.7452281697, -2.4272220948, -0.2298358928
O, -1.1666426438, -1.8562416809, 1.5556918047
C, -2.0190031793, 0.1112546368, -0.021686532
C, -3.666572587, 0.455420896, -0.0071461029
C, -1.012901261, 1.070977466, -0.054049277
C, -3.7080378913, 1.8018737213, -0.0197705006
H, -4.1235898902, -0.3145900084, -0.0018595543
C, -1.3702680357, 2.4120138927, -0.0603383411
H, 0.0302840947, 0.7954840524, -0.0838265423
C, -2.7133885066, 2.7747074753, -0.0419081967
H, -4.7505071287, 2.0886348382, -0.016363213
H, -0.5838183328, 3.1523282654, -0.0815127979
H, -2.9875725466, 3.8210253065, -0.0500770394
O, 2.472599692, -2.0042665566, -0.413696515
H, 3.0937565858, -0.4841861344, 0.2556369362
O, 3.3946838612, 0.3600990275, 0.6491596048
H, 2.4854287358, 1.8334017511, 0.1472333921
O, 1.9738015317, 2.6064200106, -0.1597911858
H, -1.8841900683, -2.1707244268, 2.0553891711
C, 2.7943505248, 3.3822489815, -1.0513205321
H, 3.1164920097, 2.8200539403, -1.8982814989
H, 2.2098490975, 4.2388291236, -1.3512820326
H, 3.6853077912, 3.7576340184, -0.5088378158
C, 3.0397181857, -2.6393109274, -1.5569456837
H, 4.1212243284, -2.6100790581, -1.4407775338
H, 2.7221748187, -3.682152712, -1.6261055144
H, 2.7706570767, -2.1216650725, -2.4808900432
C, 3.8263879164, 0.1333693034, 1.9842684378
H, 4.1109640213, 1.0954444925, 2.407319846
H, 3.0321559566, -0.2969148281, 2.6006630738
S6 [benzenesulfonic acid···3 methanol HB complex], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)
H, -1.076930, -1.565967, 0.147284
O, 0.0726, -1.356877, -0.718695
H, 1.931866, -1.608733, -0.498535
O, -1.825165, -2.804505, 0.058212
O, -0.449381, -1.442222, 1.630946
C, -2.182029, -0.180064, 0.012513
C, -3.552483, -0.414426, 0.025740
C, -1.648125, 1.101288, -0.102292
C, -4.414110, 0.670521, -0.082081
H, -3.933013, -1.420755, 0.111476
C, -2.525793, 2.172033, -0.206020
H, -0.579441, 1.270380, -0.111583
C, -3.901850, 1.958186, -0.196779
H, -5.482299, 0.5068, -0.078580
H, -2.132748, 3.174735, -0.296458
H, -4.576331, 2.799014, -0.280994
O, 2.896608, -1.646358, -0.398060
H, 3.482893, -0.035861, 0.025669
O, 3.748216, 0.876336, 0.269903
H, 2.304059, 1.940046, 0.137993
O, 1.503980, 2.495543, 0.045339
H, -1.079866, -1.770916, 2.292108
C, 1.822868, 3.622236, -0.761646
H, 2.159653, 3.27061, 1.760118
H, 0.919651, 4.221717, -0.868174
H, 2.597217, 4.245565, -0.303953
C, 3.457615, -2.353861, -1.507789
H, 4.535349, -2.379192, -1.363879
H, 3.083028, -3.378206, -1.548160
H, 3.238349, -1.853616, -2.453285
C, 4.474182, 0.840728, 1.497877
H, 4.739973, 1.864439, 1.754584
H, 3.874038, 0.421137, 2.309085
H, 5.391992, 0.256671, 1.397956

S7 [two methanol molecules-assisted benzenesulfonic acid + methanol addition TS], in gas phase (at B3LYP/aug-cc-pVTZ level)
S, 0.301735, -1.404859, 0.259904
O, -0.936816, -1.448490, -0.591145
H, -2.125082, -0.903373, -0.326959
O, 0.382295, -2.005180, 1.586875
H, 1.063260, -3.384722, -0.151334
O, 1.162559, -2.549727, -0.627408
C, 1.502855, -0.146639, -0.222081
C, 2.568752, 0.099629, 0.629885
C, 1.380691, 0.482084, -1.451221
C, 3.531991, 1.023039, 0.239245
H, 2.645814, -0.421232, 1.572884
C, 2.352626, 1.401056, -1.826520
H, 0.546067, 0.259772, -2.098232
C, 3.425739, 1.673996, -0.984420
S7 [two methanol molecules-assisted benzenesulfonic acid + methanol addition TS], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

S, 0.278571, -1.307536, 0.236084
O, -0.910435, -1.353587, -0.729097
H, -2.004793, -0.930759, -0.449424
O, 0.313347, -2.060585, 1.496653
H, 0.867390, 0.313347, -0.126298, -0.449424
C, 1.578339, -1.648998, -0.879059
H, 4.622338, 0.869474, 0.829196
H, 3.208102, 2.217077, -2.517698
H, 3.632847, 2.345041, -1.141664
C, -0.126298, -0.449424
H, 0.878620, 0.874136, 2.397192
H, -0.795924, 1.356178, 2.697043
H, -0.280462, -0.302170, 3.050710
O, -0.563134, -0.185917, 1.047450
H, -1.497709, 1.462185, 0.321669
O, -2.248709, 1.907967, -0.136037
H, -3.000063, 0.504903, -0.284701
O, -3.130421, -0.493702, -0.346928
C, -2.758188, 2.991673, 0.647495
H, -3.653281, 3.360231, 0.151340
H, -3.20984, 2.667365, 1.655955
H, -2.027523, 3.799536, 0.706979
C, -3.997295, -0.854603, -1.445981
H, -4.979828, -0.424612, -1.270845
S8 [methyl dihydrogen benzeneorthosulfonate···2 methanol HB complex], in gas phase (at B3LYP/aug-cc-pVTZ level)

S,0,0.20506,-1.133082,0.327356
O,0,-0.922492,-1.192214,-0.784874
H,0,-1.768926,-0.669869,-0.585319
O,0,0.156447,-1.908233,1.571097
O,0,1.154439,-2.182319,-0.595979
C,0,1.485247,0.110274,0.025716
C,0,2.422497,0.324542,1.02276
C,0,1.508994,0.802139,-1.173337
O,0,1.416161,1.271867,0.806992
H,0,2.378724,-0.238012,1.944273
C,0,2.50581,1.752074,-1.370757
H,0,0.774914,0.599981,-1.939261
C,0,3.45723,1.987252,-0.385041
H,0,4.155858,1.44873,1.573136
H,0,2.539946,2.301572,-2.301602
H,0,4.232299,2.723763,-0.546727
O,0,-0.746857,0.255387,1.07967
H,0,-1.695536,1.715869,0.765349
O,0,-2.440892,2.285504,0.481614
H,0,-3.105609,0.922928,-0.393543
O,0,-3.216413,0.015035,-0.752362
C,0,0.75953,-3.551963,-0.688764
O,0,1.551537,-4.049203,-1.245018
C,0,0.669534,-3.995924,0.300471
H,0,-0.181681,-3.653666,-1.231126
H,0,-0.854828,-0.043062,2.017431
C,0,-4.336674,-0.615093,-0.134213
H,0,-5.259612,0.282066,-0.937057
H,0,-4.405527,-1.625986,-0.530887
H,0,-4.220228,-0.666693,0.950989
C,0,-1.957515,3.529635,-0.010039
H,0,-1.257879,3.395186,-0.839478
H,0,-2.8149,4.098424,-0.365272
H,0,-1.463483,4.101304,0.779536

S8 [methyl dihydrogen benzeneorthosulfonate···2 methanol HB complex], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

S,0.1913630354,-1.1219790372,0.330886309
O,-0.9419817967,-1.1589926499,-0.7745939422
H,-1.7913024631,-0.636274678,-0.5624550371
O,0.1569854066,-1.943293737,1.5503816001
O,1.1291749881,-2.1720169173,-0.6313324618
C,1.4890948772,0.1085368856,0.0430241102
C,2.4688848145,0.2515666912,1.0126424775
C,1.4743653184,0.8687688317,-1.1148537323
C,3.4700946096,1.195016006,0.8089634661
H,2.4548630012,-0.3556770386,1.9062096904
C,2.4807312705,1.8117162361,-1.3003294361
H,0.7030832059,0.7327317966,-1.8583918348
C,3.4761906541,1.9749788235,-0.3429989195
S9 [two methanol molecules-assisted methyl dihydrogen benzenoethersulfonate, water elimination TS], in gas phase (at B3LYP/aug-cc-pVTZ level)

S, -0.4149287137, 1.0205439863, -0.4575388686
O, 0.719625815, 1.3497866966, 0.5009145006
H, 1.8823453956, 0.9283516397, 0.3742349847
O, -0.4370464877, 1.4883132459, -1.8398017001
O, -1.5185740268, 2.0682959347, 0.2501842707
C, -1.4769906328, -0.3465972212, 0.0440452516
C, -2.4440173518, -0.7799441509, -0.8482614995
C, -1.3336954116, -0.9005518805, 1.3042639734
C, -3.2876359476, -1.8138577704, -0.4620146876
H, -2.5300413731, -0.3224029653, -1.8230534248
C, -2.1838339593, -1.9363725359, 1.6750996166
H, 0.576555777, -0.5338041212, 1.9809703883
C, -3.1580715162, -2.3942108787, 0.7955114377
H, -4.0470661121, -2.1652904793, -1.1471516629
H, -2.0832282469, -2.3827540644, 2.6550409726
H, -3.8165899686, -3.1999457245, 1.0895728498
O, 0.7401709817, -0.5714237497, -1.100133292
H, 1.8797687464, -1.4506684955, -0.6000835454
O, 2.7475348831, -1.7846447728, -0.1667518109
H, 3.0562189883, -0.3850313732, 0.2064348221
O, 0.083126596, 0.6222569814, 0.4496045256
C, -1.2787699115, 3.4691265399, 0.0957108822
H, -2.1101340621, 3.9658199278, 0.5910476201
H, -1.2585304433, 3.7471386334, -0.9578407129
H, -0.3429781175, 3.7608243893, 0.574687443
C, -3.5035849442, -2.5135612218, -1.1036771942
H, 3.0093444447, -3.4226703345, -1.411010887
H, 4.4664930266, -2.7959979028, -0.623369957
H, 3.7574238714, -1.9187851439, -1.9933582146
C, -3.5482456663, 0.8804774615, 1.7566782948
H, 3.0601820558, 0.2613465281, 2.5094029934
S9 [two methanol molecules-assisted methyl dihydrogen benzeneorthosulfonate, water elimination TS], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

S, -0.397194978, 0.9950433646, -0.5141800747
O, 0.7140243854, 1.3701290134, 0.4653489655
H, 1.8651087508, 0.9357344371, 0.3906007261
O, -0.4829095203, 1.5336703139, -1.8806651451
O, -1.5291887546, 2.0468220951, 0.2294698447
C, -1.4841867197, -0.3533885004, 0.0101032775
C, -2.4849162616, -0.7652187754, -0.8559149101
C, -1.3008605878, -0.9334759534, 1.2547074822
C, -3.3251538504, -1.7996696367, -0.4581612202
H, -2.6067290531, -0.2937008844, -1.8203976111
H, -2.0177700781, -1.1228309783
H, -3.8187539034, -0.4387050153, -1.1483264588
H, 1.8935864799, -1.521095163, -0.6031594397
O, 2.7051976696, -1.8548214657, -0.1403494385
H, 3.0432209113, -0.3778201881, 0.2736657545
O, 2.9965917942, 0.6159431566, 0.4717545444
C, -1.2889734796, 3.4509418998, 0.1305492888
H, -2.1131373313, 3.936082653, 0.6501484513
H, -1.2766142771, 3.775097791, -0.9097590106
H, -0.3496044802, 3.7273290948, 0.6117348033
C, 3.5395672891, -2.5735983973, -1.0542452013
H, 3.0337902307, -3.4732613445, -1.4072718162
H, 2.8624911331, -0.5200809926
H, 3.8161251344, -1.9569865352, -1.9119028577
C, 3.5887601377, 0.935421407, 1.7524977213
H, 3.0751783257, 0.4084760806, 2.5546425964
H, 3.4997979604, 2.0081641741, 1.892539718
H, 4.6375953735, 0.6535212873, 1.727394003
H, 0.6808609775, -0.3414833788, -2.1053074258

S10 [methyl benzenesulfonate···2 methanol···water HB complex], in gas phase (at B3LYP/aug-cc-pVTZ level)

S, 1.078193, -0.540299, -0.078533
O, 0.204225, 0.503772, -0.600429
H, -1.679177, 0.732011, -0.34521
O, 0.949699, -1.88359, -0.6046
O, 0.922191, -0.58524, 1.52761
C, 2.765555, 0.010168, -0.165897
C, 3.774134, -0.94377, -0.233389
C, 3.038947, 1.372736, -0.180468
C, 5.092754, -0.515562, -0.308459
H, 3.524785, -1.994532, -0.238913
C, 4.362686, 1.785707, -0.254545
H, 2.230934, 2.08816, -0.145441
S10  [methyl benzenesulfonate···2 methanol···water HB complex], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

C, 5.385169, 0.844513, -0.316463
H, 5.89887, -1.243478, -0.36522
H, 4.594006, 2.841559, -0.268961
H, 6.413947, 1.172403, -0.377014
O, 2.587472, 0.786696, -0.012114
H, -3.963448, -0.129679, -0.72917
O, -4.81581, -0.519843, -1.00478
O, -6.468548, 1.278869, 0.380773
H, -5.987747, 0.608768, -0.143309
C, -0.300215, -1.183915, 2.040937
H, -1.167859, -0.608078, 1.724249
H, -0.192352, -1.441444, 3.119899
H, -0.376728, -2.215669, 1.704908
C, -2.904346, 2.147966, 0.293488
H, -2.91161, 2.789915, -0.381967
H, -3.945829, 2.174699, 0.605484
H, -2.274992, 2.524238, 1.103844
C, -4.808443, -1.912832, -0.726465
H, -4.67629, -2.114851, 0.340905
H, -5.771324, -2.315678, -1.036485
H, -4.021781, -2.428555, -1.284548
H, -7.13775, 1.632325, -0.210731

S38
H, $-4.709286, -2.011783, 0.111623$
H, $-5.455154, -2.045961, -1.495834$
H, $-3.690265, -2.041119, -1.345778$
H, $-7.494314, 1.219663, -1.147554$

S11  [benzenesulfonic acid···methyloxonium cation···methanol HB complex], in gas phase (at B3LYP/aug-cc-pVTZ level)
S, $0.1793975909, -0.1295415865, 0.6610105418$
O, $-0.5106710346, -1.305463079, 0.145469526$
H, $-2.3176211318, -1.3731835487, -0.4609457015$
H, $-2.0736420199, 1.40922484, 0.2133404018$
O, $-0.4646016231, 1.1726282803, 0.5002103634$
C, $1.8327089969, -0.0672136481, 0.0455243848$
C, $2.5898107997, 0.0788646894, 0.2838779652$
C, $2.3344404261, -1.1643210785, -0.6483871067$
C, $3.8912945777, 1.1157511622, -0.1914197113$
H, $2.1715327903, 1.9183291738, 0.819012507$
C, $3.6408008824, -1.1046608307, -1.1166711652$
H, $1.7185191886, -2.0332896733, -0.8245296127$
C, $4.4137038716, 0.0281077111, -0.8875378787$
H, $4.4973351123, 1.9939031127, -0.0207400991$
H, $4.0505730832, -1.9424861821, -1.6622140321$
H, $5.4295250036, 0.066775171, -1.2553033311$
C, $-3.4351151495, 2.340097173, -1.0252552311$
H, $-3.2530021471, 3.3155418314, -0.5871444322$
H, $4.4958445201, 2.002373739, -1.2013437536$
H, $2.8660767756, 2.2075248069, -1.941642817$
O, $-3.1941961975, -1.0100169843, -0.6853691082$
H, $-3.1919207065, 0.2927320628, -0.3392808455$
O, $-0.3071852331, 1.3364685891, -0.0370770178$
O, $0.3123629902, -0.2648622098, 2.2556379834$
H, $0.603778089, -1.1560691235, 2.5081501192$
C, $-4.2593724197, -1.9075024354, -0.2820476513$
H, $-5.1935314619, -1.440889427, -0.5832353285$
H, $-4.140582886, -2.8546263869, -0.8018544794$
H, $-4.2479552955, -2.0593366094, 0.7957697891$

S11  [benzenesulfonic acid···methyloxonium cation···methanol HB complex], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)
S, $0.1640924582, -0.2211081288, 0.7050787471$
O, $-0.5232790766, -1.338652916, 0.0734739809$
H, $-2.3411948226, -1.3675253486, -0.5004554407$
H, $2.0947966724, 1.3945674735, 0.2421560032$
O, $-0.472315563, 1.0922340849, 0.6942769628$
C, $1.810637893, -0.0878669824, 0.066617919$
C, $2.5196260621, 1.090553877, 0.2847883231$
C, $2.351609903, -1.1644085672, -0.628410295$
C, $3.8114280546, 1.1841081349, -0.2120901579$
H, $2.072002557, 1.9143544216, 0.8201523032$
C, $3.6464156713, -1.0507438364, -1.1181376408$
H, $1.7739725292, -2.0620503809, -0.7880151508$
C, $4.3720142563, 0.1173099019, -0.9097053118$
H, $4.3779640384, 2.0910399083, -0.057312744$
H, $4.0837060976, -1.8739952838, -1.6643541522$
H, $5.3786751017, 0.1991878697, -1.294989215$
| Atom | X-Coordinate | Y-Coordinate | Z-Coordinate |
|------|--------------|--------------|--------------|
| C    | -3.3253279942 | 2.3271835023 | -1.118410064 |
| H    | -3.1814775599 | 3.3079087536 | -0.6726937268 |
| H    | -4.3628521091 | 2.1829174021 | -1.3894725152 |
| H    | -2.6677498734 | 2.176069813 | -1.962942802 |
| O    | -3.2157883654 | -1.0043807536 | -0.7325491108 |
| H    | -3.1842205941 | 0.2901044992 | -0.38781924 |
| O    | -3.0326070016 | 1.3370582593 | -0.0748231519 |
| O    | 0.3297019173 | -0.527012787 | 2.271034445 |
| H    | -5.2126655584 | 2.1829174021 | -1.3894725152 |
| H    | -4.20917699 | -2.8230659358 | -0.6237566176 |
| H    | -2.6677498734 | 2.1765069813 | -1.962942802 |
| O    | -3.2157883654 | -1.0043807536 | -0.7325491108 |
| H    | -3.1842205941 | 0.2901044992 | -0.38781924 |
| O    | -3.0326070016 | 1.3370582593 | -0.0748231519 |
| O    | 0.3297019173 | -0.527012787 | 2.271034445 |
| H    | -5.2126655584 | 2.1829174021 | -1.3894725152 |
| H    | -4.20917699 | -2.8230659358 | -0.6237566176 |
| H    | -4.2028809773 | -1.8823459748 | 0.8947111146 |

S12 [methanol-assisted protonated benzenesulfonic acid + methanol addition TS], in gas phase (at B3LYP/aug-cc-pVTZ level)

| Atom | X-Coordinate | Y-Coordinate | Z-Coordinate |
|------|--------------|--------------|--------------|
| S    | -0.3432532842 | -0.962785944 | -0.259838285 |
| O    | 1.5036618235 | -0.5148369876 | -1.0966484623 |
| H    | -2.5490731274 | 0.1469511187 | -0.5596499313 |
| H    | -2.7966359327 | -2.6128604706 | -1.6918016585 |
| O    | -0.3477079906 | -1.9396502101 | -1.386397972 |
| C    | 1.1883281641 | -0.0082977844 | -0.1988678885 |
| C    | 2.3757097977 | -0.6571234566 | 0.1083307734 |
| C    | 1.1207628206 | 1.3451696595 | -0.4956280596 |
| C    | 3.5422375878 | 0.0983046229 | 0.1300434249 |
| H    | 2.4000767882 | -1.7160750085 | -0.3154587069 |
| C    | 2.3034695487 | 2.0735240146 | -0.4951462627 |
| H    | 0.1820081643 | 1.8188542741 | -0.7391896184 |
| C    | 3.5073425089 | 1.4541223944 | -0.1752056677 |
| H    | 4.4790666953 | -0.381977206 | 0.3737530374 |
| H    | 2.2806820559 | 3.1247128705 | -0.7448075698 |
| H    | 4.4220105529 | 2.029866109 | -0.1686564849 |
| C    | 0.2699769292 | 0.2827336063 | 2.337102161 |
| H    | 0.4374461105 | 1.097888246 | 2.1905531516 |
| H    | -0.971983624 | 0.5532195843 | 3.1252768188 |
| H    | 0.2782702072 | -0.6056456565 | 2.6589305483 |
| O    | -3.3047366439 | 0.662790107 | 0.0375271022 |
| H    | 2.7556513213 | 0.8320086693 | 0.8343273373 |
| O    | -1.0440926599 | 0.0429758383 | 1.1519095956 |
| O    | -0.5361970728 | -2.2462537591 | 0.6991708272 |
| H    | -1.0678301043 | -1.9654096315 | 1.4630105192 |
| C    | -3.907844379 | 1.8613946647 | -0.5524966047 |
| H    | -4.6059989609 | 2.263298003 | 0.1736779526 |
| H    | -3.1357149395 | 2.5837458329 | -0.8031166123 |
| H    | -4.434295 | 1.5282343564 | -1.4396430933 |

S12 [methanol-assisted protonated benzenesulfonic acid + methanol addition TS], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

| Atom | X-Coordinate | Y-Coordinate | Z-Coordinate |
|------|--------------|--------------|--------------|
| S    | -0.3519231107 | -1.0016890018 | -0.2819696284 |
| O    | 1.5102862002 | -0.5624150618 | -1.1112107387 |
| H    | -2.5996141733 | -2.214069223 | -0.5477512741 |
| H    | -0.2227824925 | -2.6053414653 | -1.7729375052 |
| O    | 0.3880905142 | -1.9206685671 | -1.4606648642 |
| C    | 1.1541741217 | -0.0029580568 | -0.203358901 |
| C    | 2.3601509529 | -0.6007993369 | 0.1302343463 |
S41

C, 1.0378096834, 1.3477030521, -0.4958864043
C, 3.4954368108, 0.2003997497, 0.1768477448
H, 2.4202216411, -1.655849531, 0.3490292751
C, 2.189454859, 2.1250209693, -0.467133708
H, 0.0836927556, 1.784875578, -0.7482011564
C, 3.4116811225, 1.5551046668, -0.1258945801
H, 4.4447703961, -0.2414619656, 0.4437653428
H, 2.1251916217, 3.1765798375, -0.7074524726
H, 4.3009776765, 2.1686966505, -0.0958747246
C, -0.2804057758, 0.1071428739, 2.3378784555
H, 0.4013789618, 0.949562527, 2.2322640499
H, -0.997431905, 0.3201939125, 3.1286271402
H, 0.2888707603, -0.780886907, 2.6173495543
O, -3.2727908426, 0.7356573225, 0.0635921828
H, -2.7215472519, 0.8109984023, 0.8741741477
O, -1.046337373, -0.0953166304, 1.1402339198
O, -0.4760338246, -2.3428081994, 0.6087978263
H, -1.032221975, -2.139115804, 1.380482485
C, -3.7195425631, 2.0331826549, -0.4669166616
H, -4.3637782351, 2.4713715069, 0.2854244588
H, -2.8575006386, 2.6594204762, -0.6717327958
H, -4.2736540164, 1.8100052008, -1.3702888505

S13 [protonated methyl dihydrogen benzeneorthosulfonate···methanol HB complex], in gas phase (at
B3LYP/aug-cc-pVTZ level)
S, 1.7746843378, -1.8522071995, -1.639399134
O, 1.7753754869, -3.194713053, -0.8652952553
H, 2.6828808774, -3.7257151526, -0.8175981184
O, 0.1647333769, -1.6674435246, -1.5088798606
C, 1.9944856282, -0.2636990198, -0.8002156401
C, 1.369935801, 0.862407254, -1.3226418219
C, 2.7842324648, -0.2266257208, 0.3435506839
C, 1.5697544548, 2.0756264649, -0.6762100565
H, 0.7476081369, 0.8015205363, -2.2018320753
C, 2.9413614456, 0.9932776638, 0.9896068647
H, 3.2472878788, -1.18974539, 0.7374758944
C, 2.3445212364, 2.1398749173, 0.4767980752
H, 1.1058801819, 2.9678163622, -1.0718711914
H, 3.5326028275, 1.0425721867, 1.8927448228
H, 2.4807731707, 3.0866454604, 0.9799931142
O, 3.7681598036, -4.676691524, -0.7196790368
H, 4.6497452742, -4.3280338707, -0.8831115094
O, 3.5214586984, -2.0281373386, -1.8360626471
O, 1.6536349254, -1.8945620261, -3.2418212623
H, 2.539526954, -2.0757219075, -3.6007201666
C, 3.8030398526, 5.805919867, 0.1833857678
H, 2.7779710464, -6.1461052501, 0.2934277592
H, 4.404043142, -6.6029638785, -0.2487581018
H, 4.2002485165, 5.512955083, 1.1538537824
C, -0.7770217425, -2.6562554322, -2.004086888
H, -0.596191542, -3.6185120272, -1.5338629053
H, 1.7483920943, -2.2727063056, -1.708935263
H, -0.7151951262, -2.7299407592, 3.0862506572
H, 3.9369908963, -1.1558403464, -1.842274006

S41
S13 [protonated methyl dihydrogen benzeneorthosulfonate···methanol HB complex], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

S, 0.376416, 0.751028, 0.206880
O, 1.591958, 0.390487, -0.588706
H, 2.499382, -0.540188, -0.098609
O, -0.221130, 1.876808, -0.852526
C, -1.180247, -0.154750, 0.028003
C, -2.353355, 0.411963, 0.504159
C, -1.136587, -1.400725, -0.580178
C, -3.531375, -0.313922, 0.366977
H, -2.356225, 1.386762, 0.967662
C, -2.329537, -2.099332, -0.724717
H, -0.206912, -1.816206, -0.939253
C, -3.520347, -1.560858, -0.248541
H, -4.456633, 0.104199, 0.736953
H, -2.321942, -3.066598, -1.206437
H, -4.442157, -2.114473, -0.357987
O, 3.172339, -1.247838, 0.347119
H, 2.678709, -1.564115, 1.125624
O, 0.891027, -0.423787, 1.485174
O, 0.456052, 1.888734, 1.343048
H, 0.845967, 1.476053, 2.133900
C, 0.617244, 2.957623, -1.312715
H, 1.475596, 2.569776, -1.855771
H, -0.013656, 3.537470, -1.980109
O, 0.941826, 3.578861, -0.480754
H, 0.1257, -0.740230, 1.983229
C, -3.597269, -2.339905, -0.540154
H, 4.274893, -2.964613, 0.029198
H, 2.727892, -2.894782, -0.877460
H, 4.111037, -1.866252, -1.367678

S14 [methanol-assisted protonated methyl dihydrogen benzeneorthosulfonate, water elimination TS], in gas phase (at B3LYP/aug-cc-pVTZ level)

S, 0.3555537652, 0.689722501, 0.1765859708
O, 1.5548805573, 0.3071706278, -0.6535989784
H, 2.4430941726, -0.4798255763, -0.1748075799
O, -0.2008409096, 1.8695932768, -0.7923605471
C, -1.2303128356, -0.1618417994, 0.0159077715
C, -3.591812725, 0.4282775531, 0.5664165007
C, -1.2602551751, -1.3714609618, -0.6632568366
C, -3.5700719244, -0.2423531264, 0.4362934911
H, -2.3057059085, 1.3810577464, 1.0715647218
C, -2.4864717533, -2.01163141, -0.7976289801
H, -0.365753588, -1.7964507276, -1.0938132294
C, -3.6337486387, -1.4528257667, -0.247016842
H, -4.4639356787, 0.1928312807, 0.8598615066
H, -2.540986418, -2.9466071289, -1.3367789013
H, -4.5820071436, -1.960598736, -0.3494963257
O, 3.2126922061, -1.1500441384, 0.3282962637
H, 2.6973348066, -1.5224252482, 1.0661131322
O, 0.8732920808, -0.6042085401, 1.4198161035
O, 0.5409840252, 1.7290658462, 1.3862085444
H, 0.905531129, 1.2229397152, 2.1346304437
C, 0.6455928514, 2.9758242, -1.2011954272
S14 [methanol-assisted protonated methyl dihydrogen benzeneorthosulfonate, water elimination TS], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

S, 0.37620208, 0.75234909, 0.20833302
O, 1.59514217, 0.38877572, -0.57945750
H, 2.49331773, -0.54651032, -0.11147938
O, -0.21711630, 1.87215124, -0.85972921
H, -1.17968992, -0.15453791, 0.02847902
H, -2.35345992, 0.41249809, 0.50260802
C, -1.13624166, -1.39806156, -0.58463633
H, -3.53119992, -0.31375891, 0.36506502
H, -2.35700592, 1.38784809, 0.96493002
H, -2.32782892, -2.10016291, -0.72326498
H, -2.0510992, -1.81684791, -0.93592898
C, -3.51925392, -1.56144491, -0.24889898
H, -4.45691892, 0.10465009, 0.73356502
H, -2.31951692, -3.06802091, -1.20377998
H, -4.44081492, -2.11543291, -0.35855798
O, 3.07615803, -1.26497505, 0.45181261
H, 2.43235514, -1.42117599, 1.18610190
O, 0.89765391, -0.44161767, 1.52375099
O, 0.44950614, 1.89633623, 1.33891220
H, 0.83982455, 1.48985706, 2.13271296
C, 0.62243077, 2.95135476, -1.32151953
H, 1.48640050, 2.56142697, -1.85407046
H, -0.00415016, 3.52409179, -1.99905174
H, 0.93823581, 3.58008213, -0.49181334
H, 0.12799985, -0.80482199, 1.98005625
C, 3.50993052, -2.45761183, -0.28967490
H, 4.12148354, -3.04435175, 0.38511825
H, 2.64122118, -3.01233521, -0.62885773
H, 4.09637675, -2.09083935, -1.12315765

S15 [methyl benzenesulfonate···oxonium cation···methanol HB complex], in gas phase (at B3LYP/aug-cc-pVTZ level)

S, -0.1078760174, 0.7040932538, -0.0406640331
O, -0.7079121415, 0.8006809465, 1.2862035847
H, -3.7082150232, -0.2230708259, 2.5649965121
O, 0.3003885874, 2.1438406805, -0.5595711672
C, 1.4706936775, -0.0740972916, 0.0165596538
C, 1.935616104, -0.6249679503, -1.1508996963
C, 2.1537762421, -0.1016128952, 1.2289776347
C, 3.2440319806, -1.2220161589, -1.0919198837
H, 1.4380785548, -0.590171827, -2.0762192997
C, 3.4028206283, -0.7058338978, 1.2656539133
H, 1.7185771975, 0.3326949711, 2.1165642396
C, 3.9441053962, -1.2613944239, 0.1108313368
S15 [methyl benzenesulfonate···oxonium cation···methanol HB complex], in solution (at PCM(methanol)/B3LYP/aug-cc-pVTZ level)

S, -0.105171, 0.69688, -0.064933
O, -0.704598, 0.8242, 1.25839
H, -3.92636, 0.222219, 2.176858
O, 0.306221, 2.133589, -0.608169
C, 1.485848, -0.063685, 0.030341
C, 2.006304, -0.682216, -1.102563
C, 2.172601, -0.023938, 1.23979
C, 3.257798, -1.274944, -1.013562
H, 1.445803, -0.705518, -2.025043
C, 3.422381, -0.623618, 1.308899
H, 1.737708, 0.455996, 2.10367
C, 3.962085, -1.244528, 0.186719
H, 3.679885, -1.762723, -1.880344
H, 3.971237, -0.60716, 2.239402
H, 4.935479, -1.710648, 0.248347
O, -3.211516, -0.35123, 1.87453
H, -2.387696, 0.169931, 1.911373
H, -3.314518, -0.795102, 0.510616
O, -3.232564, -1.061836, -0.508839
O, -0.921559, 0.032596, -1.092217
H, -2.356087, -0.688821, -0.821726
C, -0.766697, 3.102045, -0.842765
H, -1.294876, 3.297299, 0.086216
H, -0.252887, 3.992473, -1.185078
H, -1.437804, 2.727248, -1.610364
C, -3.347514, -2.503536, -0.751582
H, -3.288322, -2.649254, -1.823645
H, -2.548814, -3.027146, -0.235338
H, -4.319855, -2.800906, -0.377231