SUPPLEMENTARY MATERIAL - TABLE A

Unscaled Mp2/6-311++G(d,p) harmonic vibrational frequencies of the various stationary points on the doublet and quartet PES of $(CH_4S)^+$ system. Zero point energies are given in kcal/mol.

Species	Frequecies in cm^{-1}	ZPE
1	231.7, 727.6, 819.6, 879.1, 1129.6, 1374.2, 1438.8, 1449.2, 2731.5, 3073.0, 3165.2	28.9
2	157.4, 535.9, 753.3, 775.2, 867.9, 1117.1, 1194.1 1436.9, 2718.7, 2735.6, 3216.3, 3371.9	26.9
1/2	1611.8i, 503.0, 671.9, 753.1, 831.2, 1096.3, 1113.3, 1424.8, 2241.4, 2748.1, 3206.7, 3375.0	25.7
1/3	761.3i, 388.3, 419.2, 867.1, 941.5, 1045.7, 1153.2 1167.7, 1508.6, 2755.8, 3178.5, 3302.4	23.9
1/5	798.3i, 284.8, 450.4, 749.9, 887.7, 903.3, 1008.1 1095.4, 1240.5, 2713.8, 2836.4, 3241.4	22.0
1/6	480.2i, 480.2i, 92.1, 136.8, 136.8, 759.5, 1442.5 1442.5, 2646.7, 3154.5, 3342.7, 3342.7	23.6
2/3	1023.3i, 301.4, 391.9, 869.7, 910.1, 1053.1, 1105.9 1158.7, 1506.9, 2749.7, 3186.2, 3315.7	23.7
2/7	90.6i, 104.2, 128.3, 154.9, 302.6, 475.0, 603.4 627.6, 1209.8, 2694.9, 2715.1, 4495.1	19.3
2/8	1695.0i, 559.2, 597.6, 835.6, 880.9, 991.9, 1026.6 1181.1, 1467.5, 2747.7, 3175.3, 3308.8	23.9
2/10	72.3i, 48.4, 120.3, 303.8, 744.7, 831.2, 872.5 993.1, 1211.9, 2679.2, 2690.7, 3273.9	19.7
11	109.6, 109.6, 134.8, 1291.6, 1375.6, 1375.6, 1546.1, 1546.1, 3044.7, 3179.0, 3179.0	28.7
11/12	2038.2i, 324.2, 387.2, 943.5, 983.6, 1097.6 1355.9, 1437.8, 1455.4, 2720.7, 3044.8, 3158.2	24.2

SUPPLEMENTARY MATERIAL - TABLE B

Unscaled Mp2/6-311++G(d,p) harmonic vibrational frequencies of the various stationary points on the singlet and triplet PES of $(CH_3S)^+$ system. Zero point energies are given in kcal/mol.

Species	Frequecies in cm^{-1}	ZPE
14t	753.0, 881.9, 881.9, 1370.5, 1395.0, 1395.0, 3039.4, 3151.6, 3151.6	22.9
15t	342.7, 600.7, 794.1, 842.8, 899.9, 1385.3, 2652.1, 3164.5, 3313.5	20.0
16t	253.4, 770.2, 828.7, 880.4, 1010.6, 1209.3, 2696.5, 2703.4, 3278.8	19.5
14t/15t	1673.2i, 600.8, 774.5, 813.6, 848.2, 1367.2, 2278.0, 3150.0, 3306.7	18.8
15t/16t	1688.5i, 353.8, 756.5, 812.0, 995.3, 1080.8, 2195.5, 2691.4, 3248.5	17.3
14t/17t	374.1i, 293.6, 430.0, 831.5, 1064.4, 1103.3, 1435.0, 3112.0, 3230.4	16.4
14t/18t	439.6i, 221.3, 341.1, 351.4, 588.3, 909.6, 1138.8, 3167.6, 4020.3	15.3
15t/17t	1387.1i, 329.4, 577.9, 820.8, 1038.8, 1080.6, 1419.7, 3095.5, 3212.9	16.5
15t/19t	976.1i, 454.1, 488.1, 739.9, 937.1, 983.0, 1101.7, 2660.3, 3247.8	15.2
15t/20t*	814.6i, 277.9, 488.9, 530.5, 728.6, 961.8, 1072.0, 2793.6, 3910.9	15.4
16t/19t	790.1i, 289.1, 415.4, 763.1, 900.3, 998.4, 1110.0, 2670.5, 3265.9	14.9
16t/18t	1009.9i, 443.3, 591.9, 659.3, 845.9, 928.2, 1096.3, 3205.7, 3316.6	15.8
15s	873.7, 898.6, 1074.8, 1103.7, 1152.0, 1505.4, 2736.8, 3177.7, 3305.3	22.6
16s	191.7, 707.3, 790.1, 882.0, 1085.2, 1265.5, 2619.6, 2767.4 3120.2	19.2
15s/16s	1222.4i, 708.9, 880.3, 1004.7, 1133.7, 1194.9, 2096.6, 2684.0, 3081.3,	18.3
14s/18s	844.7i, 583.8, 855.5, 915.4, 1140.7, 1528.0, 1673.1, 3022.6, 3236.1	18.5
15s/20s	304.0i, 203.4, 369.5, 418.0, 536.3, 698.6, 1129.4, 2548.3, 4212.3	14.5
16s/18s	1225.4i, 694.3, 767.4, 969.1, 997.9, 1032.4, 1893.7, 2358.7, 3105.9	16.9

SUPPLEMENTARY MATERIAL - TABLE C

Unscaled Mp2/6-311++G(d,p) harmonic vibrational frequencies of the various stationary points on the doublet PES of $(CH_2S)^+$ system and on the singlet and triplet PES's of $(CHS)^+$ system. Zero point energies are given in kcal/mol.

Species	Frequecies in cm^{-1}	ZPE
22	824.6, 1117.2, 1148.9, 1449.7, 3102.4, 3214.3	15.5
23	748.6, 977.5, 981.4, 1198.2, 2659.8, 3254.1	14.0
24	428.2, 577.6, 605.7, 1209.6, 2694.9, 2715.8	11.8
22/23	2125.9i, 346.8, 833.1, 1402.0, 2308.5, 3190.2	11.6
23/24	2099.4i, 571.5, 781.6, 1225.3, 2049.9, 2456.1	10.1
22/25	1228.7i, 544.1, 990.4, 1032.6, 1590.7, 3334.4	10.7
23/25	1184.0i, 392.0, 821.2, 996.8, 1586.7, 3350.2	10.2
24/26*	727.4i, 290.7, 477.0, 710.6, 963.9, 2735.2	7.4
27t	882.4, 1070.5, 3169.9	7.3
28t	979.6, 1154.0, 2612.0	6.8
27t/28t	2013.6i, 1213.0, 2287.0	5.0
27s	775.4, 775.4, 1408.6, 3305.2	8.9
28s	437.5, 1194.6, 2198.4	5.5
27s/28s	675.6i, 1265.4, 2071.6	4.8

* represents HF/6-31G** level.