

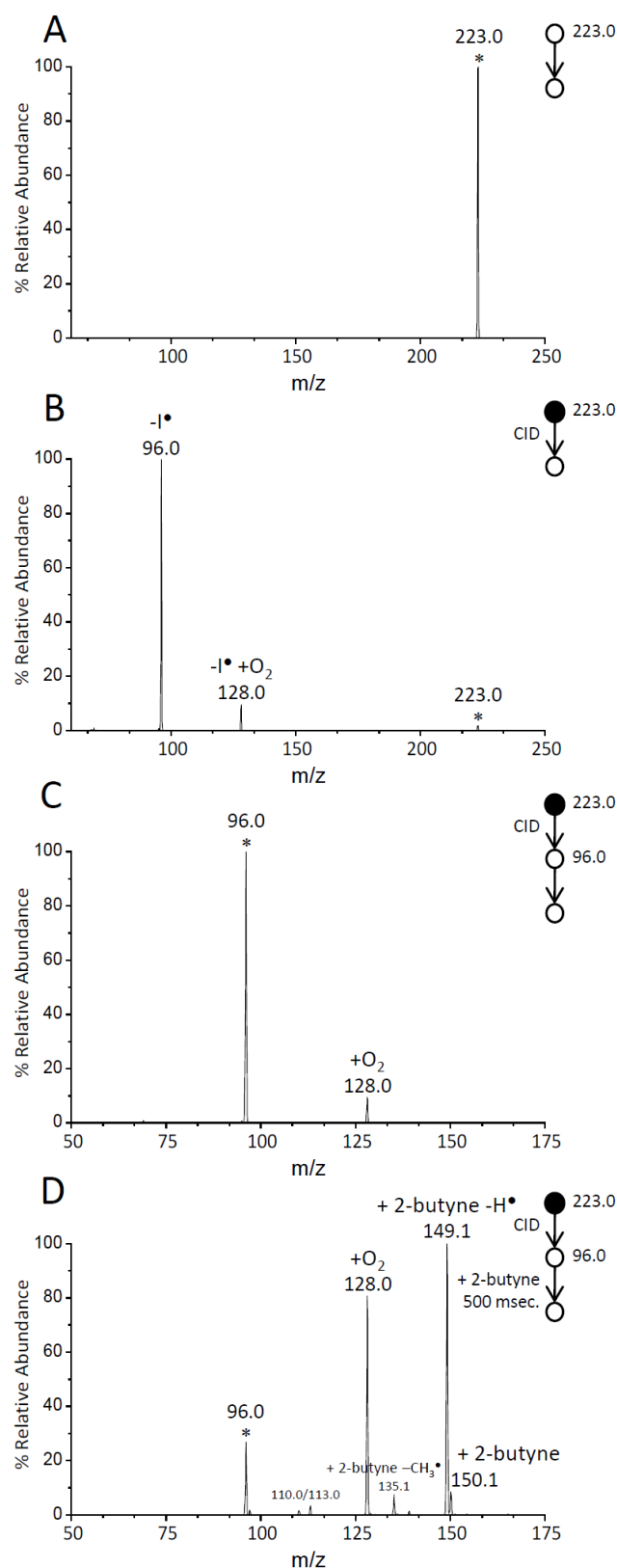


Figure S1: MS spectrum showing the gas-phase isolation of 4-Iodo-*N*-*d*₃-methylpyridine (7); (A) MS² CID spectrum of 7; (B) Subsequent isolation of the methylpyridinium radical cation; (C) Ion-molecule reaction of the methyl-*d*₃-pyridinium radical cation with 2-butyne at a reaction time of 500 milliseconds. An asterisk refers to the mass-selected precursor ion.

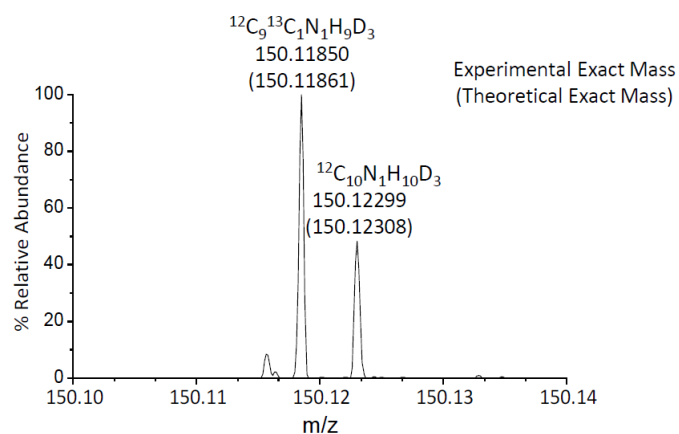


Figure S2: HRMS spectrum on the peak located at m/z 150 observed in the ion-molecule reaction of the methyl- d_3 -pyridinium radical cation with 2-butyne at a reaction time of 500 milliseconds (He Float 5, Injection Rate:10, Ion Gauge Pressure= 0.72) reveals that the peak at m/z 150 consists of two isobaric ions, comprising of the **1** + 2-butyne adduct and the ^{13}C **1** + 2-butyne-H loss product, present due to the natural abundance of ^{13}C in the 2-butyne.

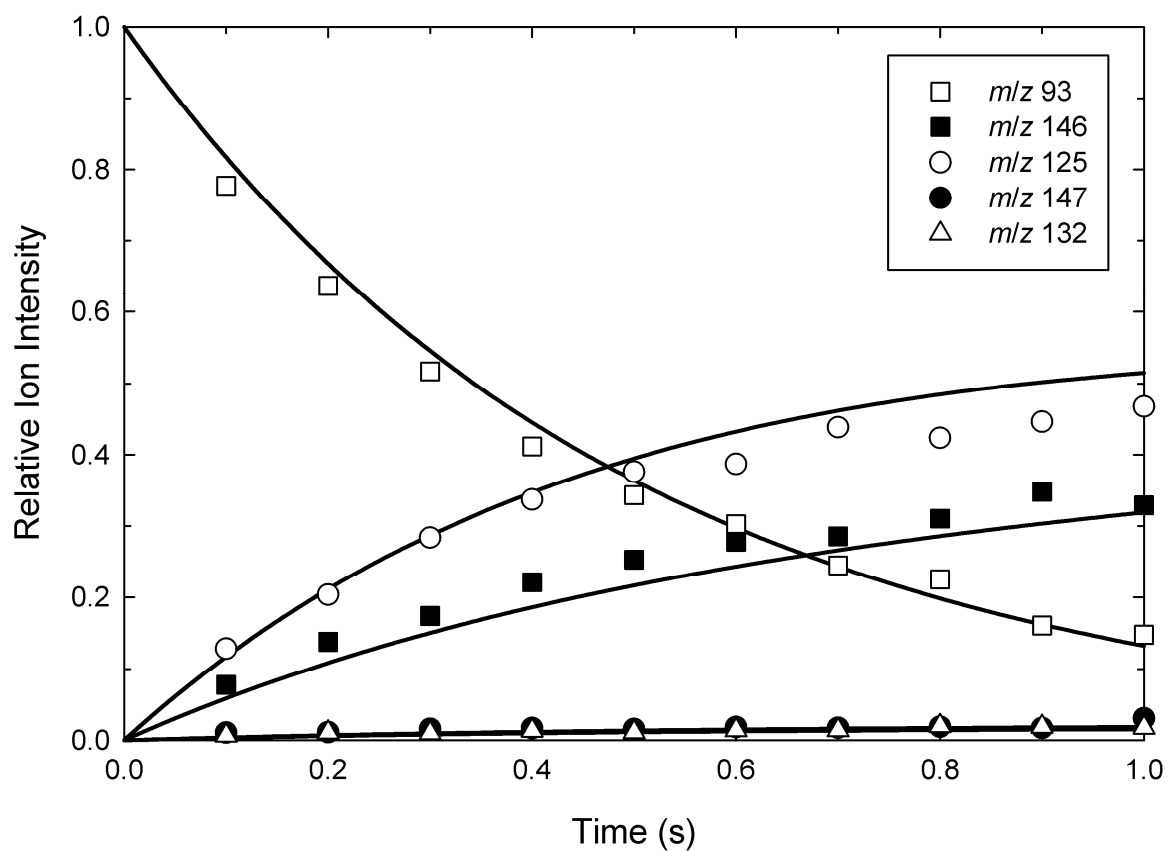


Figure S3: Relative ion intensities versus time (dot points) and rate constant fits (solid lines) for the *N*-methyl-pyridinium-4-yl radical cation (**1**, *m/z* 93) reaction with 2-butyne (2.06×10^9 molecule cm^{-3}) and O_2 .

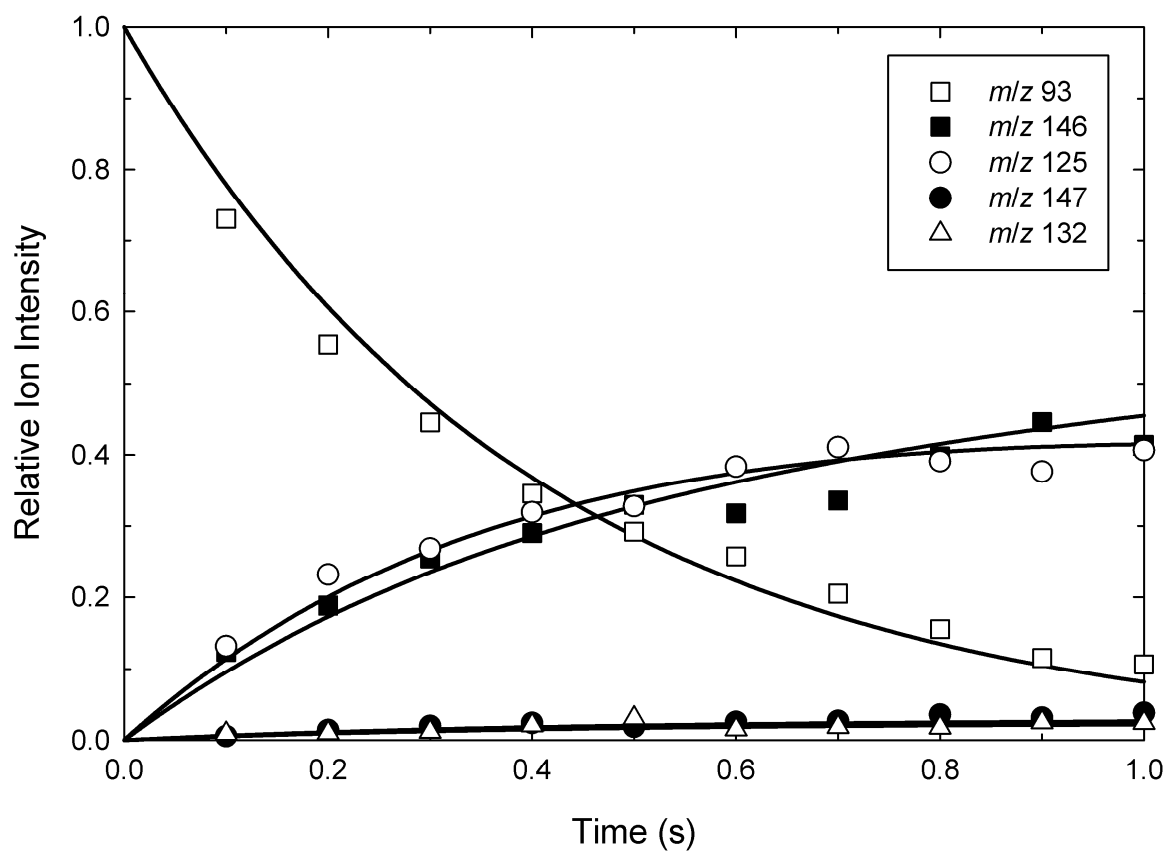


Figure S4: Relative ion intensities versus time (dot points) and rate constant fits (solid lines) for the *N*-methyl-pyridinium-4-yl radical cation (**1**, m/z 93) reaction with 2-butyne (3.43×10^9 molecule cm^{-3}) and O_2 .

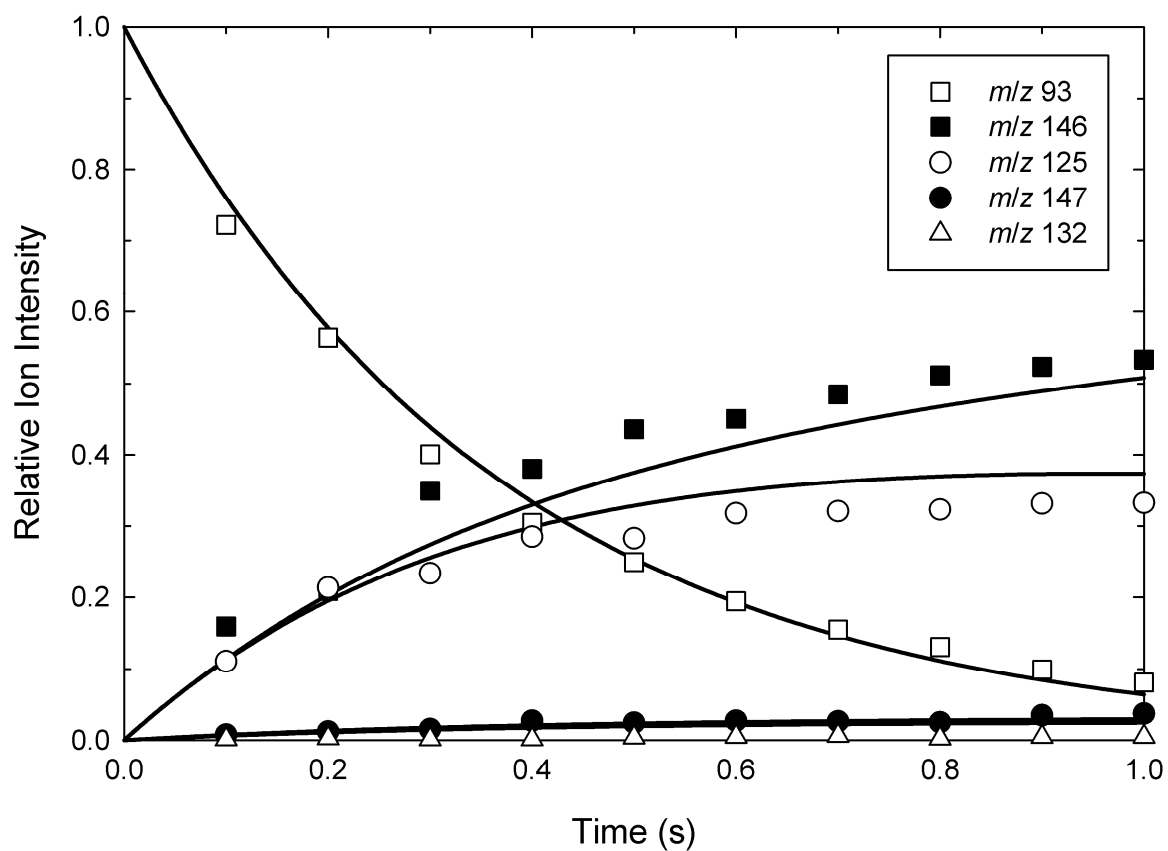


Figure S5: Relative ion intensities versus time (dot points) and rate constant fits (solid lines) for the *N*-methyl-pyridinium-4-yl radical cation (**1**, m/z 93) reaction with 2-butyne (4.12×10^9 molecule cm^{-3}) and O_2 .

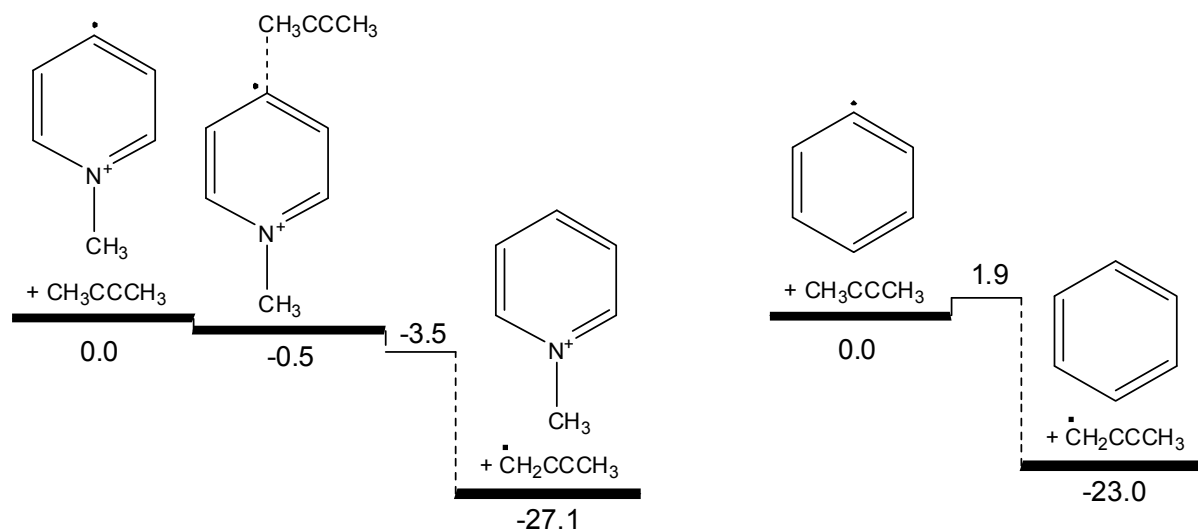


Figure S6: Theoretical energy surfaces for H atom abstraction from 2-butyne by the phenyl radical (2) and methyl-pyridiniumyl radical cation (1). Numbers refer to G3SX (for 2) and G3SX(MP3) (for 1) relative enthalpies at 0 K.

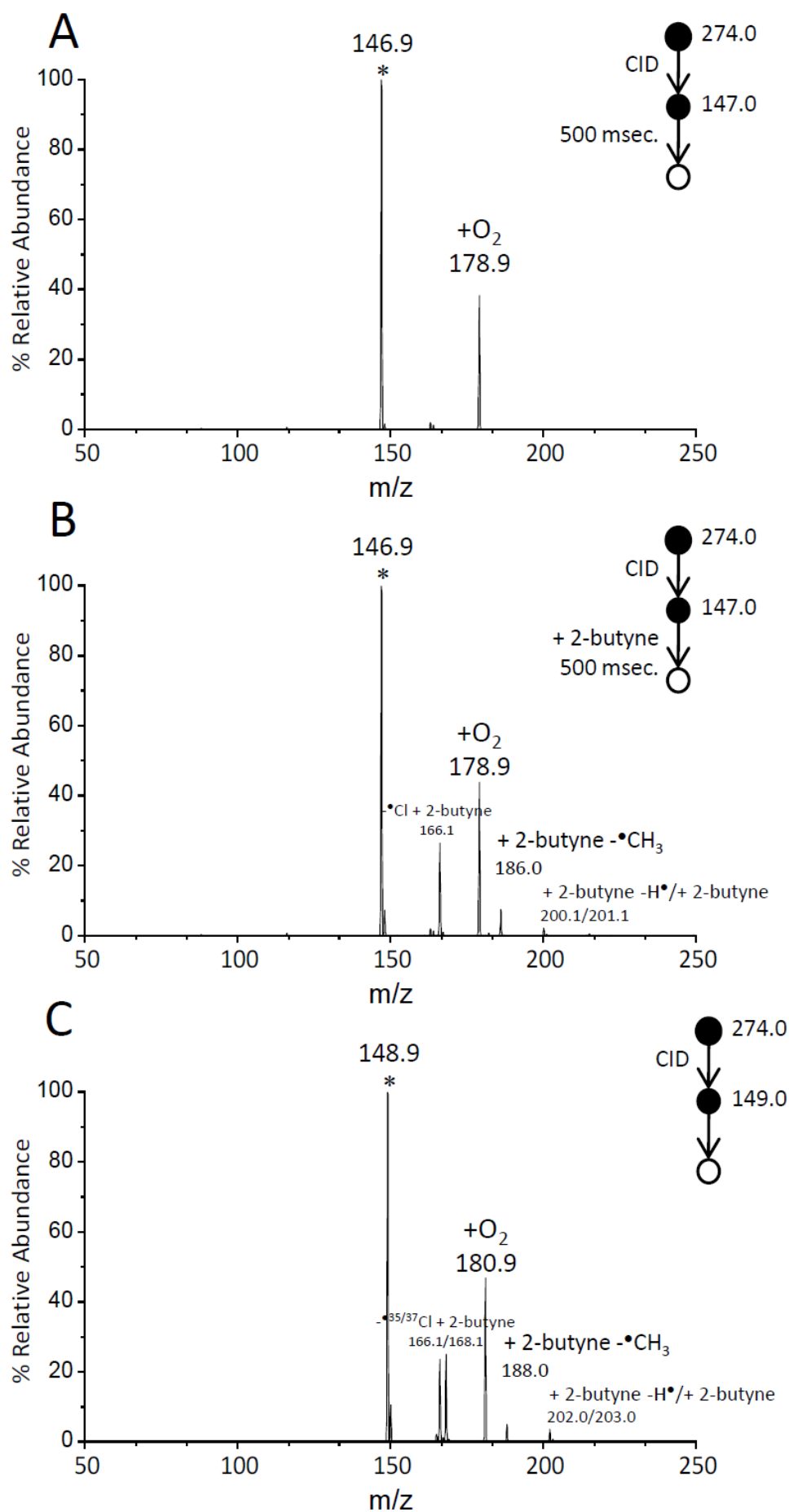


Figure S7: MS spectrum showing the gas-phase reactivity of protonated 3,5-dichloro-methylpyridinium radical cation ($\text{C}_5\text{H}_3\text{N}^{35}\text{Cl}_2^+$) at a reaction time of 500 milliseconds: with no neutral introduced into the ion-trap (A) and in the presence of 2-butyne (B). (C) MS spectrum showing the gas-phase reactivity of protonated 3,5-dichloro-methylpyridinium radical cation ($\text{C}_5\text{H}_3\text{N}^{35}\text{Cl}^{37}\text{Cl}^+$) at a reaction time of 500 milliseconds in the presence of 2-butyne.

Vibrational frequencies, cm⁻¹ (B3LYP/6-31G(2df,p))

la		lb		lc		ld	
16.85	1489.08	18.03	1487.90	33.11	1493.22	46.05	1489.80
49.86	1506.51	56.27	1493.14	61.17	1505.88	52.93	1495.81
86.14	1540.69	83.91	1515.26	83.09	1515.41	86.48	1511.89
103.98	1578.77	126.08	1543.83	135.69	1544.37	131.72	1545.36
127.14	1663.17	141.84	1637.37	177.37	1587.88	158.80	1647.82
199.47	1714.54	178.81	1690.17	200.44	1672.44	207.32	1682.12
215.11	2991.12	200.26	3029.26	214.51	3013.24	226.63	3024.24
242.19	3035.20	299.17	3036.21	275.37	3061.46	251.82	3031.47
303.46	3065.69	299.29	3070.46	354.49	3074.03	281.31	3071.31
338.97	3071.07	345.81	3073.14	388.77	3120.74	339.02	3086.64
356.51	3085.15	367.00	3087.42	414.77	3160.38	391.06	3088.60
416.90	3095.41	412.33	3122.75	429.46	3164.19	414.60	3130.28
444.46	3148.03	442.99	3152.30	498.92	3170.56	431.75	3140.27
452.47	3152.34	464.29	3153.64	537.67	3181.98	475.39	3156.98
550.58	3179.98	556.94	3166.37	583.43	3221.80	563.97	3157.75
564.37	3215.62	564.87	3179.76	597.89	3225.99	582.66	3179.23
673.74	3227.55	669.36	3218.66	675.69	3233.51	669.48	3220.53
682.60	3230.75	708.76	3221.28	684.22	3238.18	680.50	3228.53
747.18	3243.19	718.89	3235.29	757.30	3267.70	738.71	3241.75
813.49		803.89		768.95		806.08	
866.50		846.85		804.25		844.17	
874.78		887.05		823.12		876.53	
911.18		897.43		878.51		900.24	
988.30		920.87		882.86		932.35	
999.88		979.32		897.74		987.69	
1012.49		1008.94		1000.28		1044.07	
1014.02		1044.08		1004.04		1049.91	
1044.35		1060.10		1017.29		1058.18	
1057.66		1065.70		1037.54		1078.63	
1072.45		1077.36		1069.12		1080.07	
1088.76		1090.51		1084.56		1097.63	
1105.62		1148.46		1139.82		1144.97	
1150.63		1161.34		1150.19		1146.63	
1180.77		1194.45		1164.88		1188.12	
1218.03		1207.06		1176.94		1207.59	
1237.63		1262.95		1218.56		1253.55	
1309.29		1318.69		1241.25		1289.47	
1329.03		1366.15		1263.27		1357.62	
1379.00		1379.22		1326.82		1394.90	
1386.01		1403.40		1369.41		1408.65	
1406.77		1419.02		1394.96		1419.32	
1434.80		1453.02		1410.17		1439.01	
1445.32		1459.05		1441.82		1457.21	
1458.67		1465.36		1457.19		1470.72	
1481.57		1475.84		1471.55		1476.65	
1484.47		1479.33		1478.46		1482.26	
1485.85		1487.03		1486.33		1484.91	

Ie		If		Ig		TSb	
25.21	1489.63	84.11	1480.95	35.78	1478.41	26.26	1499.29
35.64	1511.02	88.60	1486.28	75.08	1483.08	42.36	1540.86
76.85	1540.64	122.56	1500.05	160.83	1490.07	56.65	1573.27
117.02	1552.63	154.40	1538.72	187.55	1545.83	70.56	1671.99
160.12	1564.03	204.79	1584.79	192.12	1669.22	99.59	2126.36
179.90	1677.07	245.36	1618.08	240.04	1699.17	108.47	3020.69
249.58	3032.50	257.25	2876.39	262.53	2778.10	141.51	3071.52
322.01	3066.95	331.05	3015.02	333.36	2987.94	173.95	3083.83
355.24	3084.94	401.41	3043.23	382.92	3027.07	301.23	3102.94
378.76	3150.70	427.37	3074.05	435.35	3054.12	306.69	3103.41
389.09	3169.18	456.87	3093.54	453.11	3058.40	340.74	3157.79
421.90	3175.03	518.70	3099.86	499.52	3076.76	395.49	3178.85
462.87	3177.99	568.68	3140.09	527.02	3132.91	408.52	3225.98
509.45	3187.83	573.13	3158.01	550.28	3134.93	415.25	3228.73
567.63	3226.35	647.94	3183.60	631.02	3176.35	439.38	3239.15
640.41	3227.92	680.14	3211.66	705.17	3212.38	501.68	3248.83
674.35	3245.05	729.37	3212.33	738.02	3218.73	513.36	3264.49
701.16	3247.88	747.65	3218.36	748.27	3219.68	555.68	3274.91
736.51	3267.02	776.93	3246.56	803.49	3232.15	660.37	
813.48		794.14		817.59		678.70	
843.80		832.61		885.02		741.32	
854.22		920.43		900.01		816.06	
933.99		927.34		945.11		868.04	
944.59		949.87		954.41		874.27	
971.24		986.46		962.93		887.87	
983.51		1027.50		1008.28		988.95	
988.27		1044.61		1029.48		992.17	
1030.00		1063.79		1051.26		995.81	
1033.81		1066.70		1061.42		1015.68	
1053.61		1079.42		1070.20		1039.23	
1080.42		1145.63		1115.67		1063.09	
1101.35		1150.75		1133.62		1081.20	
1146.55		1157.54		1137.08		1148.91	
1185.42		1170.82		1155.43		1175.47	
1221.33		1194.28		1188.21		1217.97	
1249.15		1230.25		1208.21		1234.55	
1279.70		1266.79		1226.92		1303.25	
1315.49		1272.84		1266.61		1323.16	
1351.32		1317.16		1297.50		1372.74	
1359.60		1330.02		1299.29		1401.17	
1377.50		1367.53		1329.55		1416.11	
1407.40		1385.78		1392.15		1428.83	
1456.06		1421.53		1421.10		1451.89	
1466.52		1422.64		1431.41		1455.34	
1478.63		1455.59		1441.33		1457.94	
1485.12		1470.70		1471.70		1481.91	
1486.44		1477.82		1475.90		1486.97	

TSc		TSd		TSe		TSf	
46.43	1489.10	49.02	1492.25	32.48	1494.40	31.57	1494.03
86.03	1515.83	57.11	1512.34	47.37	1511.40	82.74	1506.08
113.91	1573.63	94.67	1577.27	75.20	1571.75	92.05	1552.30
133.11	1652.76	142.02	1643.61	95.47	1643.88	188.30	1567.74
159.09	1686.65	153.13	1667.96	204.46	1671.13	219.51	1627.81
181.76	1750.90	187.03	1719.48	226.09	1717.07	227.26	1684.50
212.92	3016.70	293.15	3029.13	244.49	3027.98	246.04	3033.82
229.06	3036.04	306.88	3070.75	296.59	3070.97	323.93	3063.66
312.77	3069.97	348.90	3077.26	359.32	3090.50	333.77	3070.89
351.22	3087.38	352.55	3092.43	402.33	3097.28	402.80	3088.08
402.82	3088.95	426.91	3132.78	408.74	3134.82	407.86	3130.32
409.17	3091.45	444.83	3150.27	445.20	3154.44	462.74	3134.34
443.26	3143.66	445.91	3156.58	459.34	3156.78	471.95	3140.42
494.41	3150.98	543.25	3171.85	495.96	3175.43	477.50	3155.93
570.79	3179.16	577.86	3177.26	592.16	3177.71	580.34	3178.38
579.20	3213.53	589.63	3213.05	620.66	3217.67	607.95	3213.85
692.12	3220.05	686.88	3218.69	669.19	3227.43	693.43	3222.63
694.62	3232.50	737.60	3231.48	724.04	3243.87	711.73	3235.25
754.69		746.22		761.80		752.13	
825.27		824.41		825.07		799.86	
867.45		852.58		839.60		855.17	
899.57		886.14		880.24		877.51	
905.93		914.63		912.16		907.24	
981.01		973.56		964.96		938.60	
985.41		984.87		988.02		987.99	
1035.58		1004.21		1033.58		1053.38	
1052.12		1035.40		1051.11		1054.48	
1053.45		1055.27		1059.60		1064.92	
1079.23		1062.47		1073.35		1075.88	
1083.52		1076.79		1088.27		1084.94	
1094.09		1092.88		1105.29		1109.48	
1149.45		1146.53		1135.56		1147.08	
1158.28		1159.87		1146.90		1180.16	
1193.30		1195.17		1193.98		1198.86	
1207.76		1208.19		1202.68		1214.44	
1291.14		1249.46		1244.41		1253.78	
1329.46		1271.70		1260.71		1277.09	
1383.76		1323.90		1303.73		1287.47	
1394.27		1360.25		1357.84		1361.83	
1415.18		1369.47		1392.05		1375.01	
1441.27		1403.49		1405.69		1420.02	
1448.50		1440.31		1443.15		1422.70	
1454.64		1449.45		1448.26		1450.60	
1475.19		1468.46		1466.34		1470.99	
1479.30		1469.31		1471.33		1481.69	
1480.17		1478.90		1482.94		1482.15	
1482.16		1484.44		1487.69		1483.82	

TSg		TSh		TSi		TSj	
32.99	1504.81	41.60	1506.72	20.10	1493.38	32.56	1492.89
40.06	1544.85	68.25	1536.54	54.07	1511.48	56.40	1512.01
78.70	1575.05	91.30	1555.59	91.46	1542.70	85.49	1542.05
93.11	1660.20	139.75	1578.74	109.82	1581.00	103.59	1577.06
140.28	1701.78	184.41	1688.39	192.10	1675.58	131.73	1675.06
205.50	1854.58	190.84	2176.65	212.80	1978.16	202.29	1982.35
245.91	3016.81	238.11	3024.94	216.06	3036.10	224.79	3035.98
258.49	3070.89	278.82	3060.98	246.21	3071.62	234.10	3071.15
347.48	3083.67	333.85	3065.58	290.01	3096.53	318.18	3095.66
388.09	3085.38	358.04	3091.09	315.53	3129.22	343.92	3131.40
397.92	3094.73	392.76	3136.24	345.13	3152.60	381.29	3152.73
416.84	3155.93	426.20	3147.15	411.75	3153.34	413.44	3154.68
482.47	3178.45	458.40	3172.84	417.09	3180.99	418.41	3180.47
497.27	3186.63	478.08	3185.64	443.78	3206.32	451.62	3218.81
571.19	3219.72	562.08	3217.32	452.54	3217.47	466.11	3219.71
622.51	3226.32	624.78	3224.97	568.54	3228.42	558.76	3228.54
671.41	3234.52	674.17	3231.61	608.26	3231.71	604.44	3232.56
676.23	3244.93	692.00	3240.51	672.35	3243.06	621.18	3243.32
749.68		743.67		676.38		673.64	
816.82		813.41		677.06		678.38	
864.01		853.73		758.96		754.28	
876.53		865.08		816.93		816.49	
939.50		940.40		869.59		867.11	
984.15		972.98		880.80		877.79	
988.26		980.12		926.63		919.80	
994.28		989.32		944.11		942.94	
1005.01		1033.32		985.15		978.09	
1052.08		1042.71		989.88		988.20	
1060.61		1049.64		1001.79		999.57	
1063.77		1078.40		1057.01		1054.63	
1081.74		1081.21		1061.16		1060.39	
1114.11		1147.38		1083.06		1083.16	
1148.33		1172.61		1086.47		1089.72	
1149.87		1190.05		1150.83		1150.47	
1180.62		1201.70		1178.24		1179.20	
1218.98		1224.59		1217.07		1218.09	
1238.62		1239.25		1237.08		1239.19	
1311.61		1328.53		1239.65		1244.59	
1343.34		1359.76		1318.08		1322.09	
1375.42		1381.97		1340.96		1341.46	
1388.17		1408.98		1378.87		1379.00	
1428.90		1459.91		1410.44		1410.54	
1442.04		1468.67		1439.44		1442.29	
1455.98		1484.16		1459.42		1459.54	
1461.51		1485.83		1481.59		1481.90	
1483.71		1490.43		1484.98		1485.30	
1486.93		1490.96		1487.26		1485.68	

TSk		TSi		TSm		TSn		Tso	
42.81	1483.72	58.20	1486.49	25.50	1505.67	78.64	1487.02	47.85	1488.88
103.82	1512.24	101.50	1493.18	37.00	1545.61	107.56	1503.88	97.90	1495.44
117.36	1551.53	138.67	1513.03	79.47	1575.63	128.30	1535.28	150.09	1524.12
153.69	1592.47	182.69	1583.79	134.11	1596.03	184.42	1598.27	189.55	1564.85
217.26	1626.35	207.76	1620.78	155.61	1674.03	195.78	1681.49	204.78	1643.54
237.99	3036.08	253.38	1658.71	183.77	1690.12	213.38	2174.72	257.65	1682.20
268.63	3072.40	267.56	3025.73	285.25	3071.00	245.84	3029.19	271.24	3022.04
328.63	3092.69	341.53	3039.04	335.04	3080.88	302.65	3039.35	339.74	3035.44
385.94	3112.19	403.31	3072.34	357.58	3085.84	331.03	3048.71	365.09	3055.92
400.15	3138.20	429.84	3091.51	403.45	3154.01	435.23	3056.94	399.58	3068.26
453.94	3154.09	465.08	3094.21	414.98	3155.11	456.57	3094.41	446.58	3089.27
499.77	3156.82	469.37	3140.05	463.82	3164.65	482.63	3118.57	472.90	3140.01
587.19	3169.06	503.78	3158.76	538.44	3176.46	511.23	3141.13	485.56	3151.93
599.53	3182.79	539.78	3178.76	587.29	3179.13	564.06	3164.56	493.91	3175.70
600.97	3199.09	584.27	3220.54	600.69	3223.07	588.39	3209.22	580.40	3220.88
638.57	3222.00	590.03	3223.56	627.72	3224.00	657.19	3218.01	585.63	3222.29
694.53	3233.21	666.78	3226.06	675.13	3235.05	708.08	3230.95	662.91	3224.74
754.71	3241.44	762.12	3236.64	732.71	3237.71	735.72	3240.98	743.50	3235.98
775.03		767.61		795.08		763.58		764.33	
797.22		778.60		820.27		769.35		778.99	
809.03		807.96		853.17		815.05		804.29	
850.32		864.42		862.82		877.15		858.77	
868.62		894.10		884.52		891.77		911.54	
946.58		948.70		940.57		950.24		947.04	
957.64		965.88		986.86		955.04		963.48	
1000.41		973.07		988.01		965.04		972.58	
1045.05		973.86		994.40		1029.98		978.82	
1048.93		1031.60		1047.16		1062.25		1030.64	
1065.64		1070.30		1050.19		1071.45		1068.44	
1071.79		1096.56		1061.65		1082.93		1090.44	
1094.72		1102.56		1064.97		1107.23		1102.80	
1119.89		1147.07		1084.02		1143.17		1144.95	
1149.40		1150.97		1122.64		1160.16		1149.72	
1168.76		1154.75		1149.30		1189.10		1154.69	
1196.19		1192.98		1180.96		1198.75		1195.21	
1220.07		1233.00		1218.97		1227.27		1233.56	
1250.86		1258.11		1242.80		1259.10		1257.81	
1320.06		1275.85		1286.74		1271.42		1271.50	
1364.96		1324.15		1315.92		1313.23		1321.51	
1367.56		1365.50		1352.34		1346.87		1350.55	
1419.08		1371.75		1359.42		1365.44		1375.77	
1439.77		1421.02		1378.48		1419.73		1418.66	
1452.87		1427.18		1419.62		1431.05		1420.51	
1458.06		1453.51		1442.93		1453.45		1452.55	
1476.69		1479.29		1457.64		1474.34		1478.30	
1480.04		1479.94		1483.25		1476.14		1480.99	
1481.09		1481.46		1486.10		1478.95		1484.27	

Moments of inertia, amu Å² (B3LYP/6-31G(2df,p))

	K-rotor (1D)	J-rotor (2D)
Ia	174.97	950.24
Ib	165.46	984.99
Ic	217.62	819.06
Id	217.38	844.20
Ie	162.94	943.42
If	215.22	709.07
Ig	214.05	713.81
TSb	193.71	1023.66
TSc	191.90	896.07
TSd	152.79	975.44
TSe	209.02	843.80
TSf	221.74	796.12
TSg	202.82	916.51
TSh	175.04	955.37
TSi	194.83	914.83
TSj	202.50	888.50
TSk	214.39	735.31
TSl	208.51	717.69
TSm	144.98	963.18
TSn	209.40	731.31
TSo	207.61	719.68