Supporting Information

Infrared Photodissociation Spectroscopy of Protonated Acetylene and its Clusters

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Note: All computations were done at the MP2(fc) 6-311++G(2d,2p) level with GAMESS, unless noted otherwise. Tabulated frequencies are unscaled and have units cm^1(km/mol), simulated spectra have frequencies that are scaled by 0.95.

Table S1. The isomers of the $C_2H_3^+$ ion and their relative energies, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

Isomer	Total Energy (Hartrees)	Relative Energy (kcal/mol)
$C_2H_3^+$ classical	-77.3682369	+7.1
$C_2H_3^+$ non-classical	-77.3795656	+0.0

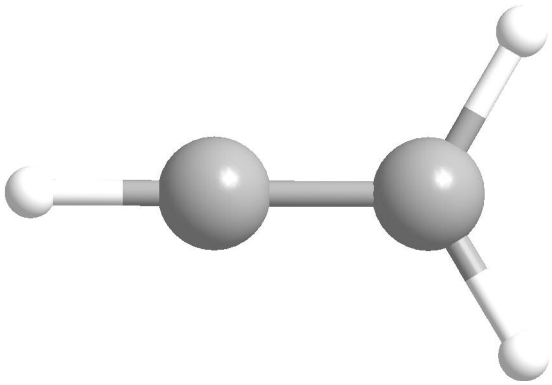

Figure S1. The structure of the $C_2H_3^+$ classical cation (ChemDraw object).

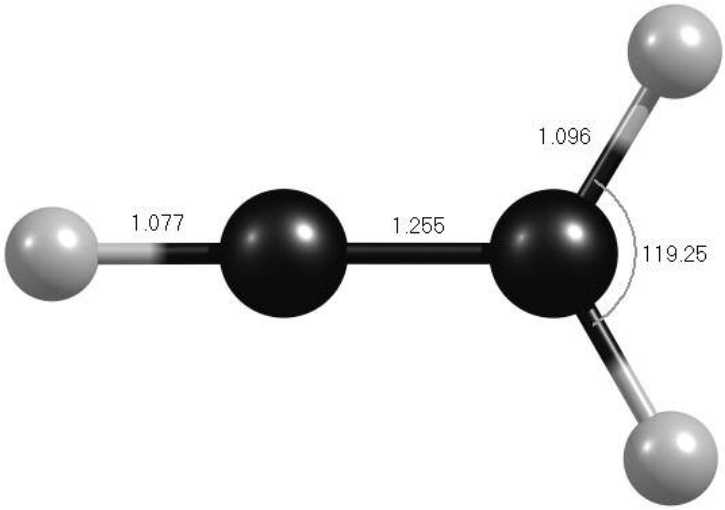

Figure S2. The structure of the $C_2H_3^+$ classical cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

The normal mode frequencies (unscaled) and intensities of the $C_2H_3^+$ classical cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS, are:

-67.4(42.3), 661.3(24.6), 812.8(134), 1110.4(0.9), 1182.4(84.5), 1765.7(85.4), 3025.1(307.2), 3102.3(232.4), 3327.8(112)

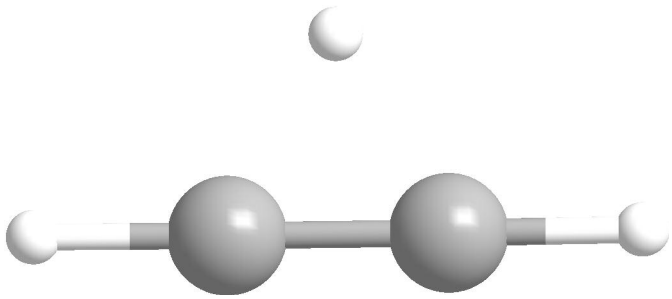

Figure S3. The structure of the $C_2H_3^+$ non-classical cation (ChemDraw object).

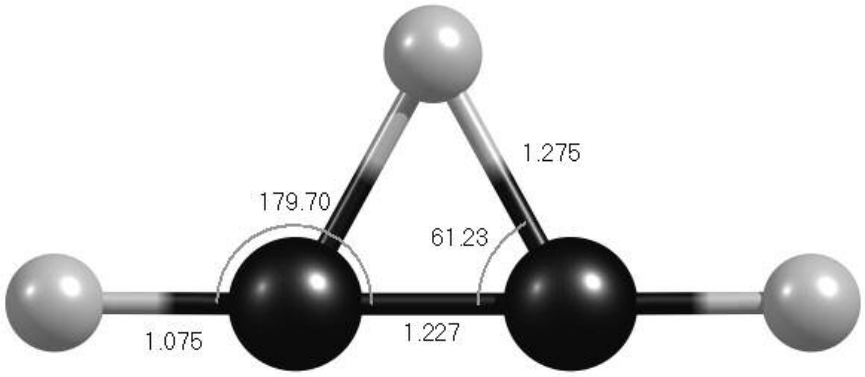

Figure S4. The structure of the $C_2H_3^+$ non-classical cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

The normal mode frequencies (unscaled) and intensities of the $C_2H_3^+$ non-classical cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS, are:

573.7(0), 693.8(25.9), 759.7(111.3), 921(47), 1316(8.8), 1923(5.7), 2368.8(102.5), 3294.1(399.4), 3397.4(0.1)

Table S2. The isomers of the $C_2H_3^+$ ion and their relative energies, calculated at the MP2(fc) aug-cc-pVTZ level of theory using GAMESS.

Isomer	Total Energy (Hartrees)	Relative Energy (kcal/mol)
$C_2H_3^+$ classical cation	-77.4011032	+8.4
$C_2H_3^+$ non-classical cation	-77.4145456	+0.0

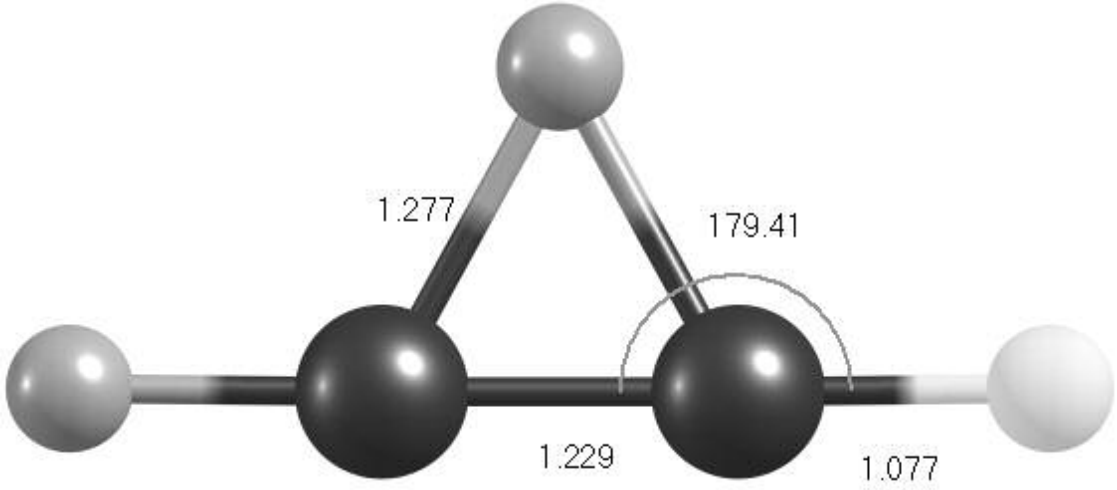

Figure S5 The calculated structure of the protonated acetylene cation with the proton bridging, calculated at the MP2(fc) aug-cc-pVTZ level of theory.

The normal mode frequencies (unscaled) and intensities of the $C_2H_3^+$ non-classical cation, calculated at the MP2(fc) aug-cc-pVTZ level of theory, are:

599.4(0), 700.5(23.2), 762.1(106.9), 913.5(45.2), 1320.9(9.8), 1926(6.5), 2390.4(99.3), 3292.4(409.9), 3392.5(0.1)

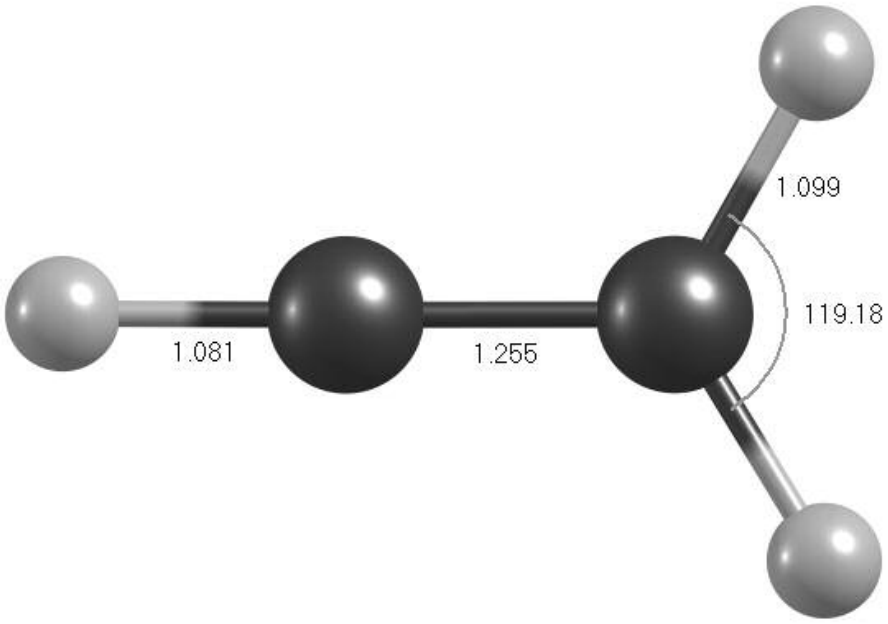

Figure S6. The structure of the protonated acetylene cation classical structure, calculated at the MP2(fc) aug-cc-pVTZ level.

The normal mode frequencies (unscaled) and intensities of the $C_2H_3^+$ classical cation, calculated at the MP2(fc) aug-cc-pVTZ level of theory, are:

-168.5(40.6), 673(29.1), 813.2(121.4), 1094.3(1.2), 1168.5(86.1), 1769.6(85.1), 3027.4(312.5), 3105.8(232), 3318.3(113.5)

Table S3. The isomers of $C_2H_3^+Ar$ and their relative energies, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

Isomer	Total Energy (Hartrees)	Relative Energy (kcal/mol)
$C_2H_3^+Ar$ classical	-604.3501212	+7.8
$C_2H_3^+$ Ar non-classical	-604.3626211	+0.0

Table S4. The isomers of $C_2H_3^+Ar$ and their counterpoise corrected argon binding energies, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

Isomer	Argon Binding Energy (cm^{-1})
$C_2H_3^+$ Ar methyl classical	746
$C_2H_3^+Ar$ non-classical	1012

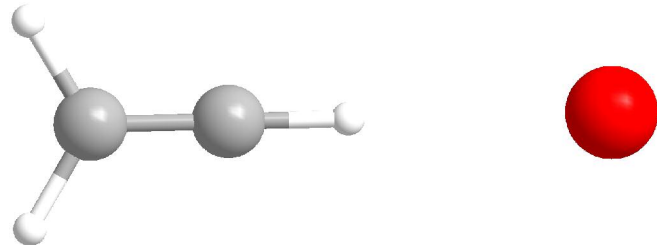

Figure S7. The structure of the $C_2H_3^+$ Ar classical cation (ChemDraw object).

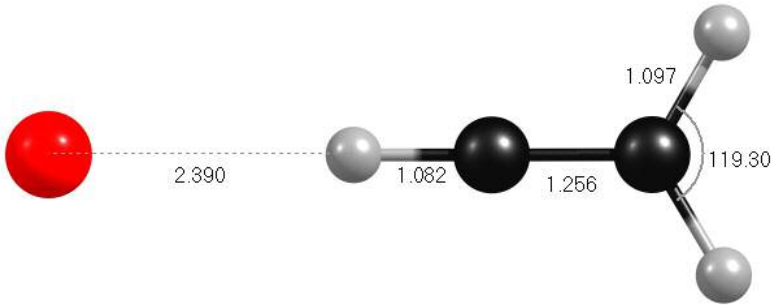

Figure S8. The structure of the $C_2H_3^+$ classical cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

The normal mode frequencies (unscaled) and intensities of the $C_2H_3^+$ Ar classical cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS, are:

20.1(7.3), 79.5(1.6), 89(35.5), 117.3(33), 709.3(5.9), 822.8(133.1), 1139.8(0.1), 1186.5(75.6), 1760.9(140.3), 3029.8(380.3), 3108.7(223.1), 3246.2(324.1)

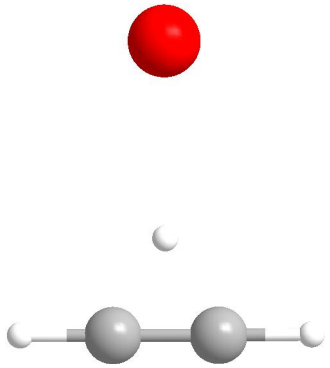

Figure S9. The structure of the $C_2H_3^+$ Ar non-classical cation (ChemDraw object).

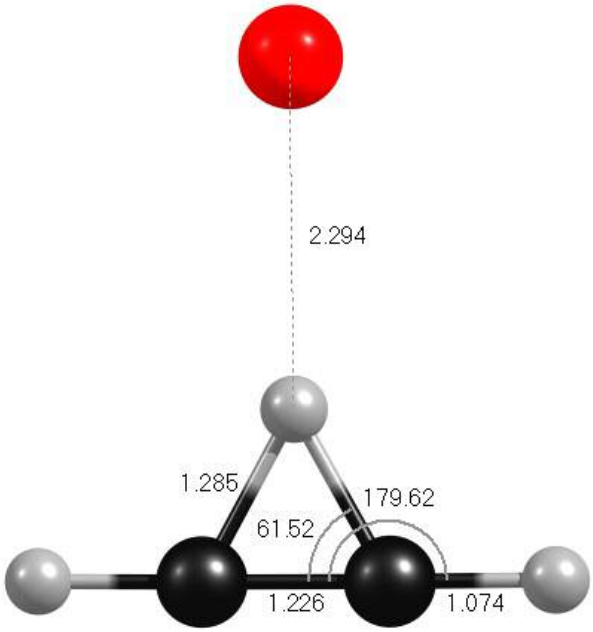

Figure S10. The structure of the $C_2H_3^+$ non-classical cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

The calcluated normal mode frequencies (unscaled) and intensities of the $C_2H_3^+$ Ar non-classical cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS, are:

89.8(8.6), 104.6(42.7), 286.8(35.5), 577.2(0), 688.1(22.6), 761.4(106.9), 915.3(30.6), 1309.7(12.3), 1928.6(14.4), 2241.9(467.4), 3304.3(376.9), 3407.1(0.8)

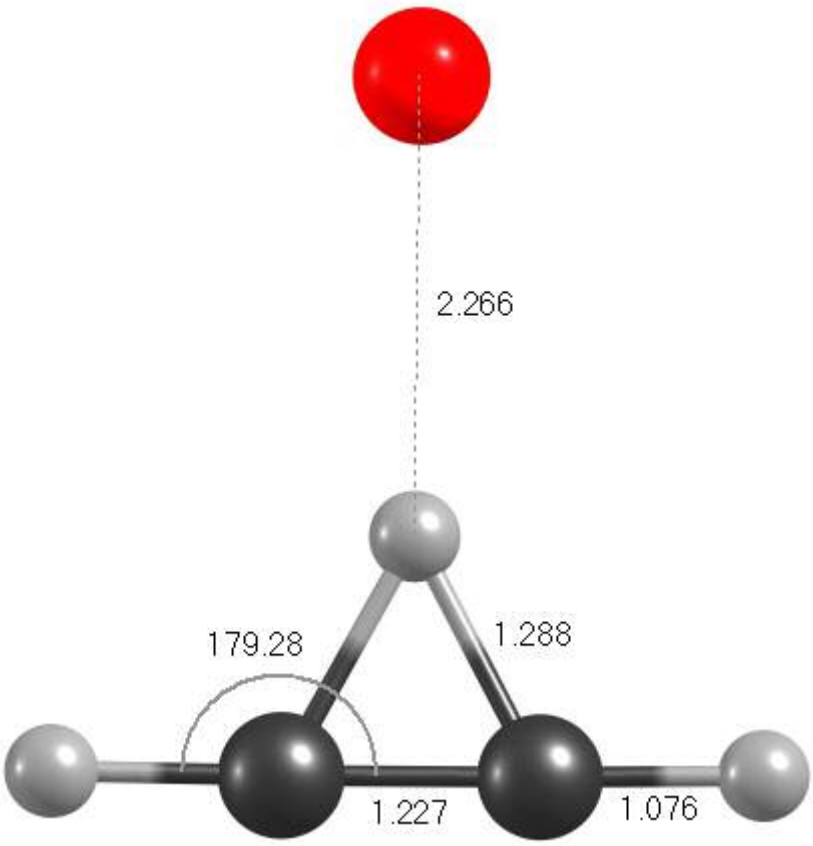

Figure S11. The structure of the non-classical cation with argon, calculated at the MP2(fc) aug-ccPVTZ level.

The normal mode frequencies (unscaled) and intensities of the $C_2H_3^+$ non-classical cation, calculated at the MP2(fc) aug-cc-pVTZ level of theory, are:

87.8(8.4), 117.1(42.9), 308.2(32.9), 601(0), 703.1(19.2), 762.3(100.9), 908.7(29.8), 1316.2(14.1), 1930.9(18.3), 2258(477.9), 3303(383.2), 3402.4(1)

Note: Using the aug-cc-pVTZ basis set, the classical protonated acetylene cation did not converge.

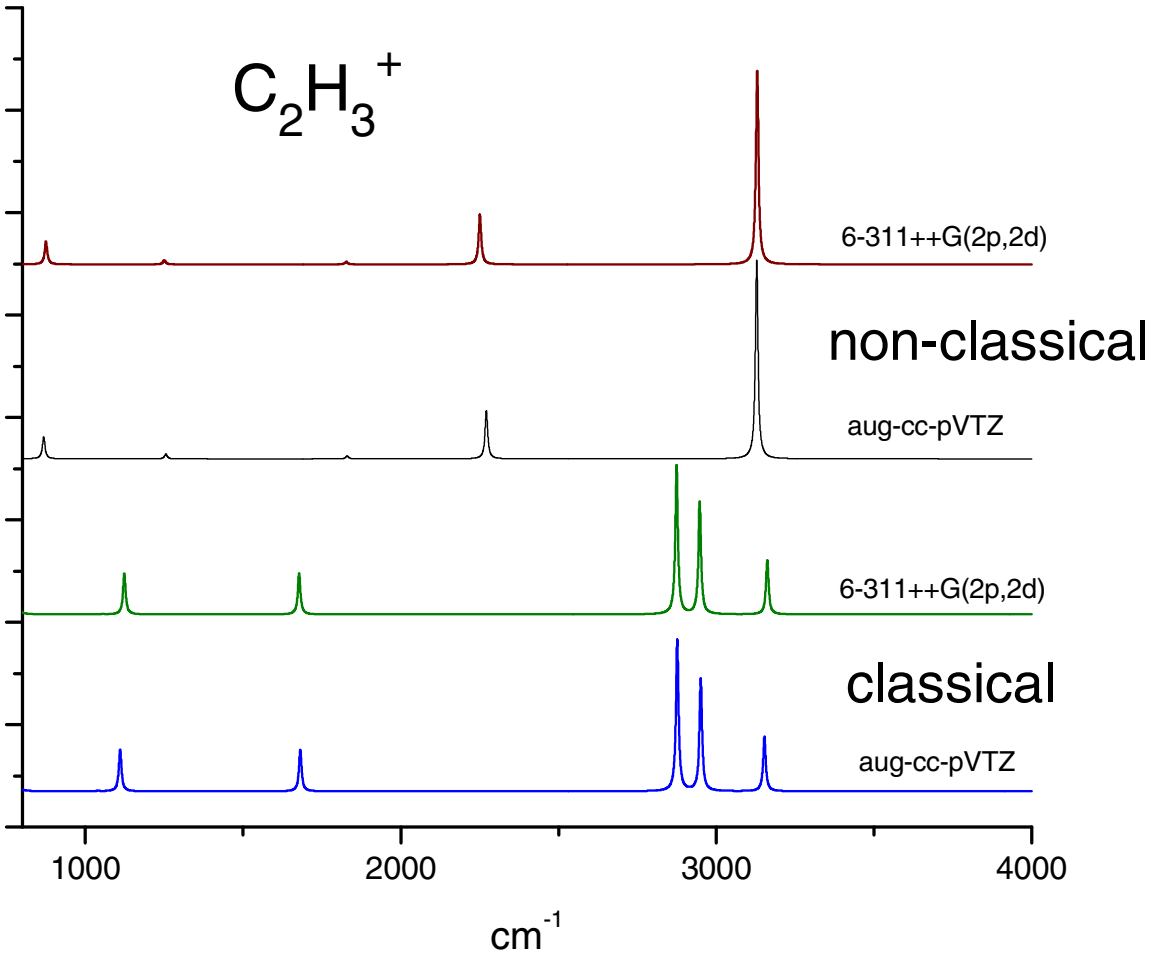

Figure S12. A comparison of simulated infrared spectra for the classical and non-classical $C_2H_3^+$ isomers at the MP2(fc) level with two different basis sets. The calculated frequencies have been scaled by 0.95.

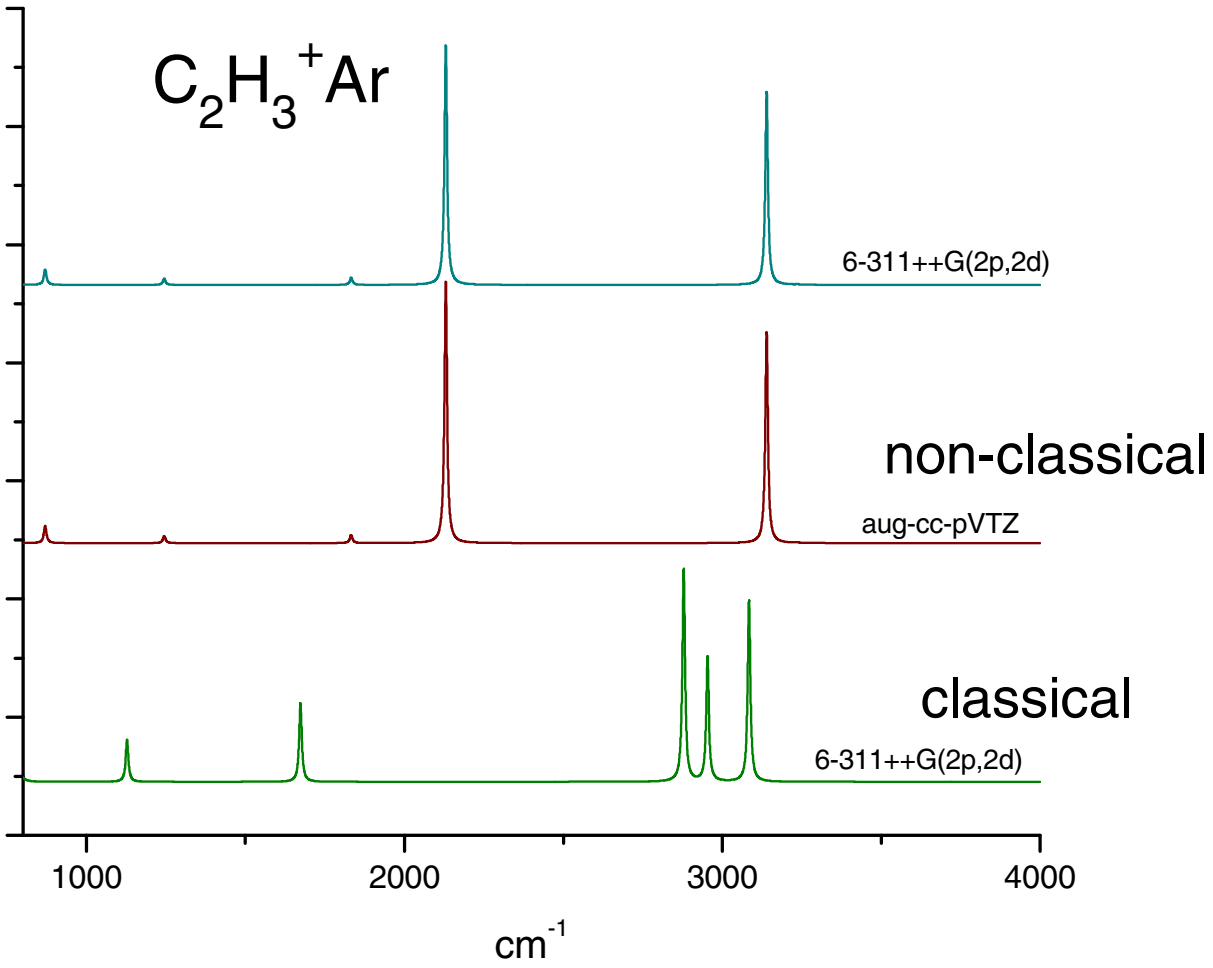

Figure S13. A comparison of simulated spectra for the classical and non-classical $C_2H_3^+$ isomers with argon at the MP2(fc) level with two different basis sets. The calculated frequencies have been scaled by 0.95. Using the aug-cc-pVTZ basis set, the classical isomer with argon did not converge.

Table S5. The isomers of $C_4H_5^+$ and their relative energies, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

Isomer	Total Energy (Hartrees)	Relative Energy (kcal/mol)
$C_4H_5^+$ methyl cyclopropane	-154.6570880	+0.0
$C_4H_5^+$ protonated cyclobutadiene	-154.6426901	+9.0
$C_4H_5^+$ allyl chain	-154.6288478	+17.7
$C_4H_5^+$ proton bound acetylene dimer	-154.5384998	+74.7

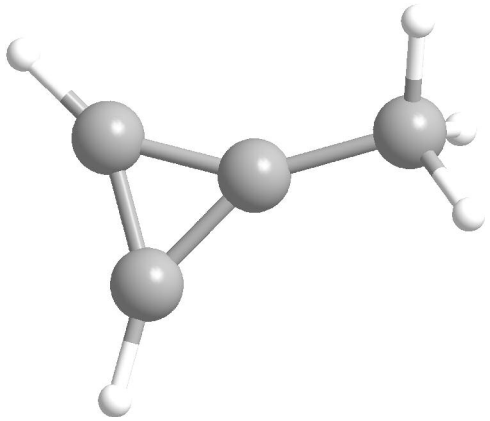

Figure S14. The structure of the $C_4H_5^+$ methyl cyclopropane cation (ChemDraw object).

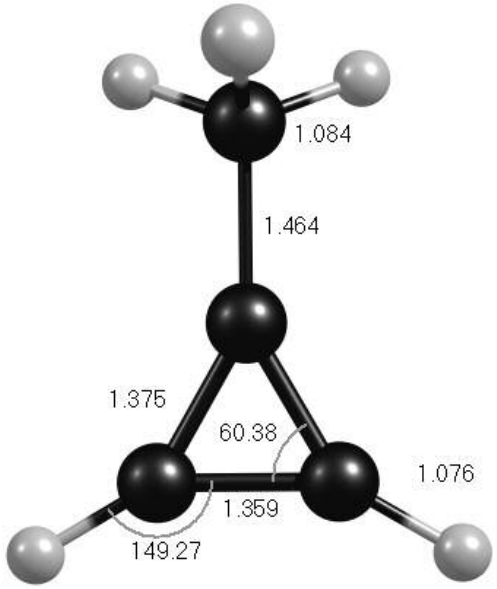

Figure S15. The structure of the $C_4H_5^+$ methyl cyclopropane cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

The normal mode frequencies (unscaled) and intensities of the $C_4H_5^+$ methyl cyclopropane cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS, are:

42.9(1.3), 357.9(2.2), 390.1(11.6), 770.4(4.6), 827.7(26.4), 952(0), 983.3(0.7), 992.7(17.5), 1050.9(20.3), 1096.7(15.5), 1298.2(9.2), 1407.5(32.3), 1416.6(46.4), 1477.2(23.7), 1501.3(10.7), 1738.8(27.6), 3081.1(28.1), 3172.3(8.3), 3222(6), 3270.7(78.3), 3310.5(39.6)

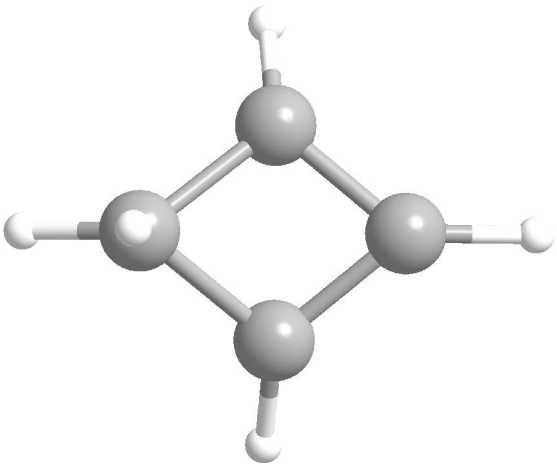

Figure S16. The structure of the $C_4H_5^+$ protonated cyclobutadiene cation (ChemDraw object).

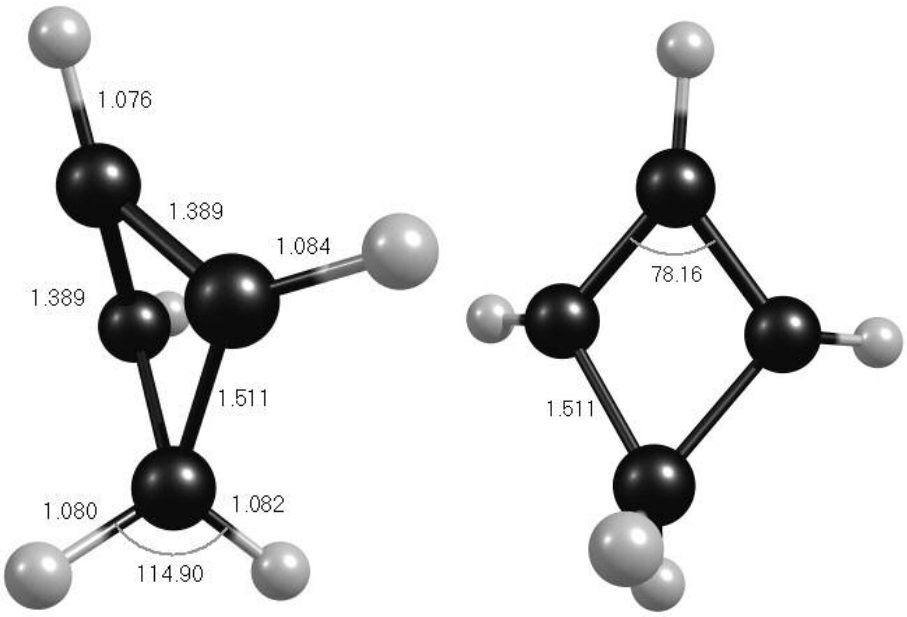

Figure S17. The structure $C_4H_5^+$ protonated cyclobutadiene cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS, with two different views.

The calcluated normal mode frequencies (unscaled) and intensities of the $C_4H_5^+$ cyclobutane cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS, are:

460.6(3), 655.1(15.9), 747.7(1.1), 917.1(16.4), 948.2(12.4), 991.8(12.5), 1019.4(3.6), 1038.9(0), 1110.7(9.2), 1113(4.3), 1152.5(12.7), 1216.2(0.1), 1245(16.9), 1375.1(35.5), 1479.7(5.3), 1529.1(9.3), 3171.5(9.6), 3221.2(19.3), 3221.5(40.2), 3267.8(14.6), 3303.1(43.4)

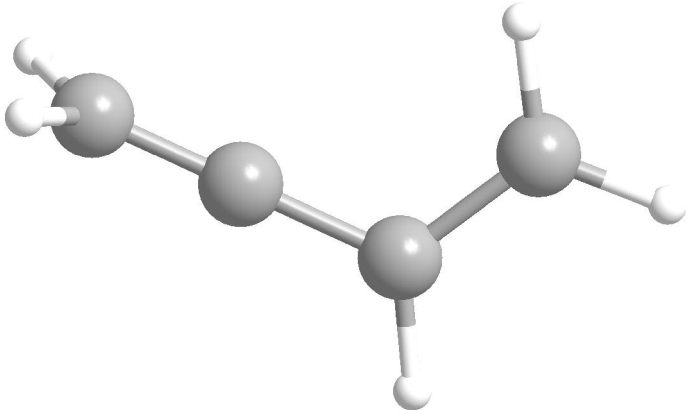

Figure S18. The structure of the $C_4H_5^+$ allyl chain cation (ChemDraw object).

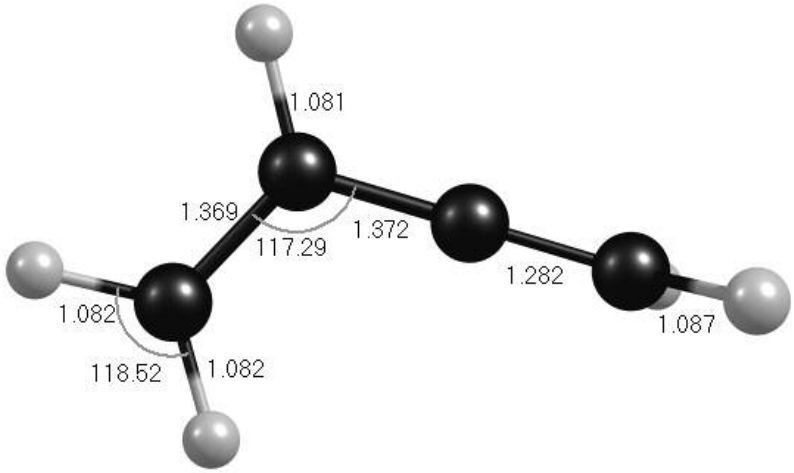

Figure S19. The structure of the $C_4H_5^+$ allyl chain cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

The normal mode frequencies (unscaled) and intensities of the $C_4H_5^+$ allyl chain cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS, are:

212.3(3.3), 238.5(6.9), 387.1(0.5), 555.5(6.2), 608.6(0), 850.1(62.4), 895.8(5.6), 926.9(5), 998.2(29.4), 1120.5(6.4), 1126.7(17.6), 1305.6(11.4), 1336(45.3), 1457.4(71.5), 1607.6(59.3), 1924.7(433.7), 3118.8(227.5), 3175.8(7.3), 3213.7(87.7), 3231.7(19.5), 3293.9(16.4)

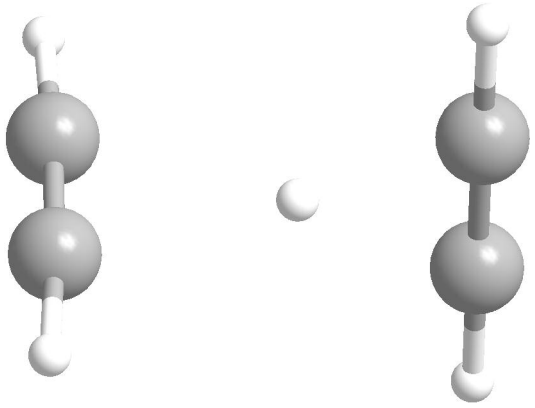

Figure S20. The structure of the $C_4H_5^+$ proton bound acetylene dimer cation (ChemDraw object).

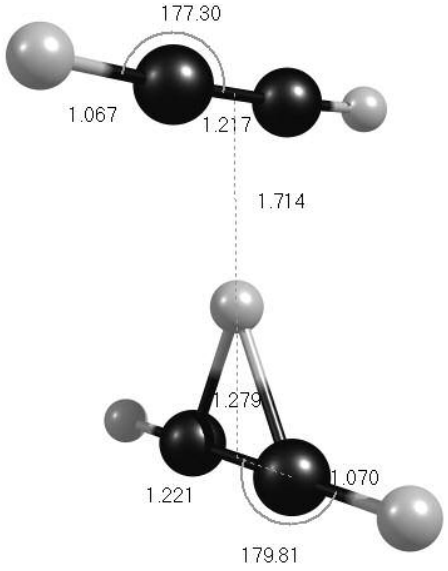

Figure S21. The structure $C_4H_5^+$ proton bound acetylene dimer cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

The normal mode frequencies (unscaled) and intensities of the $C_4H_5^+$ proton bound acetylene dimer cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS, are:

105.6(0), 160.4(1.8), 186.4(7), 208.2(269), 567.6(0.8), 594.5(8.2), 597(0), 609(0), 770.2(79.2), 773.7(88.3), 779(578.2), 841.8(302.1), 858.6(14.7), 1062.4(2293.1), 1156.9(2.2), 1943.3(3.1), 1945.5(2.7), 3341.1(299.8), 3373.7(209.4), 3440.5(3), 3468.7(2.8)

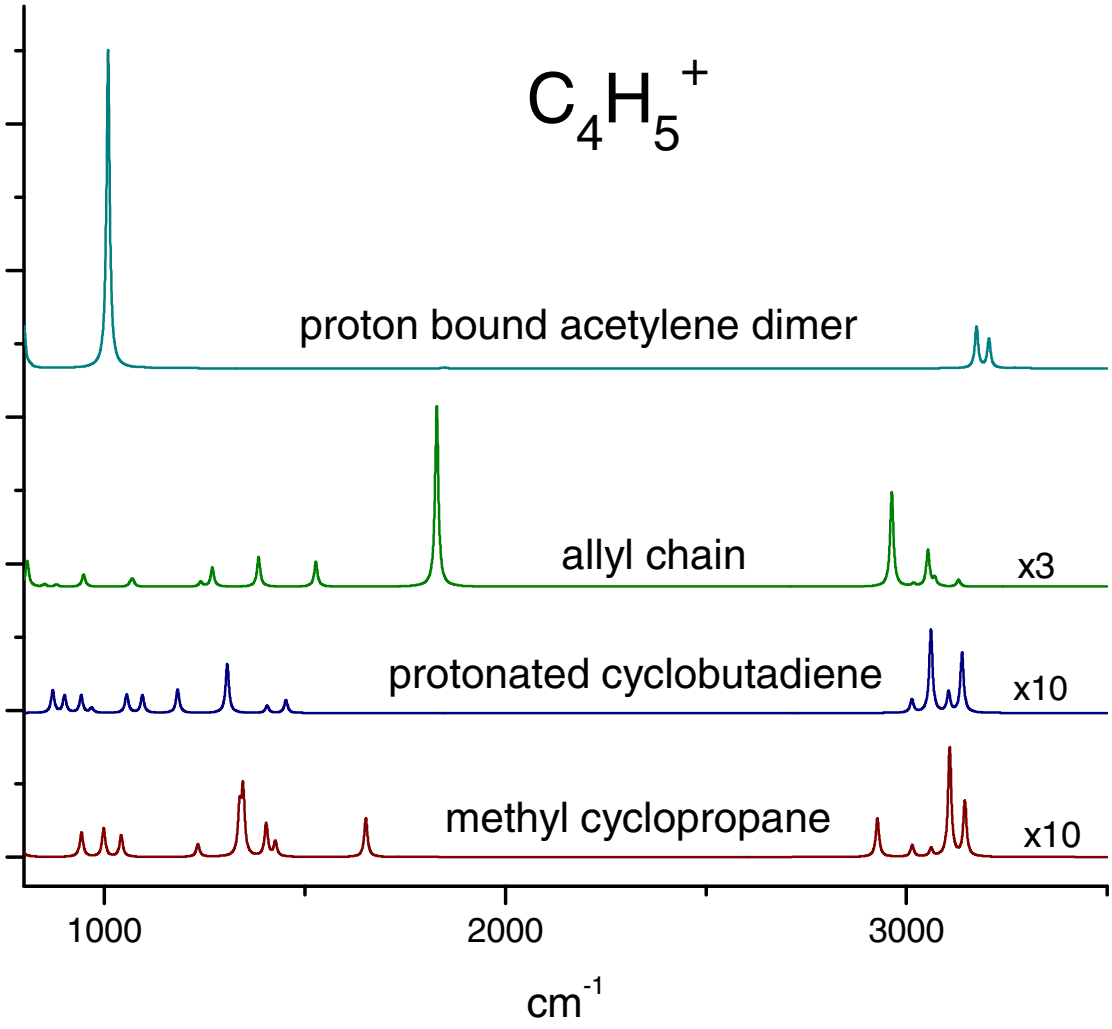

Figure S22. Simulated infrared spectra of the different $C_4H_5^+$ isomers. The frequencies have been scaled by 0.95.

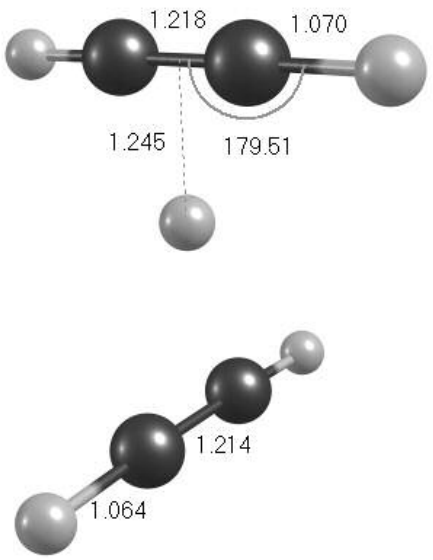

Figure S23. The structure $C_4H_5^+$ proton bound acetylene dimer cation, calculated at the MP2(full) aug-cc-pVTZ level of theory using Gaussian '03.

The normal mode frequencies (unscaled) and intensities of the $C_4H_5^+$ proton bound acetylene dimer cation, calculated at the MP2(full) aug-cc-pVTZ level of theory using Gaussian '03, are:

100.4(0), 169.5(1.4), 187.1(6), 212.7(173), 591.8(0.2), 634.5(8.9), 637.3(0), 645.7(0), 770.2(82.9), 772.2(77.5), 820.7(0), 835.8(13), 846.8(249.4), 1172.3(4.6), 1212.3(2664.5), 1959.5(0.2), 1961(2.5), 3311.4(311.3), 3343.8(209.9), 3417.4(1.5), 3470.1(2.5)

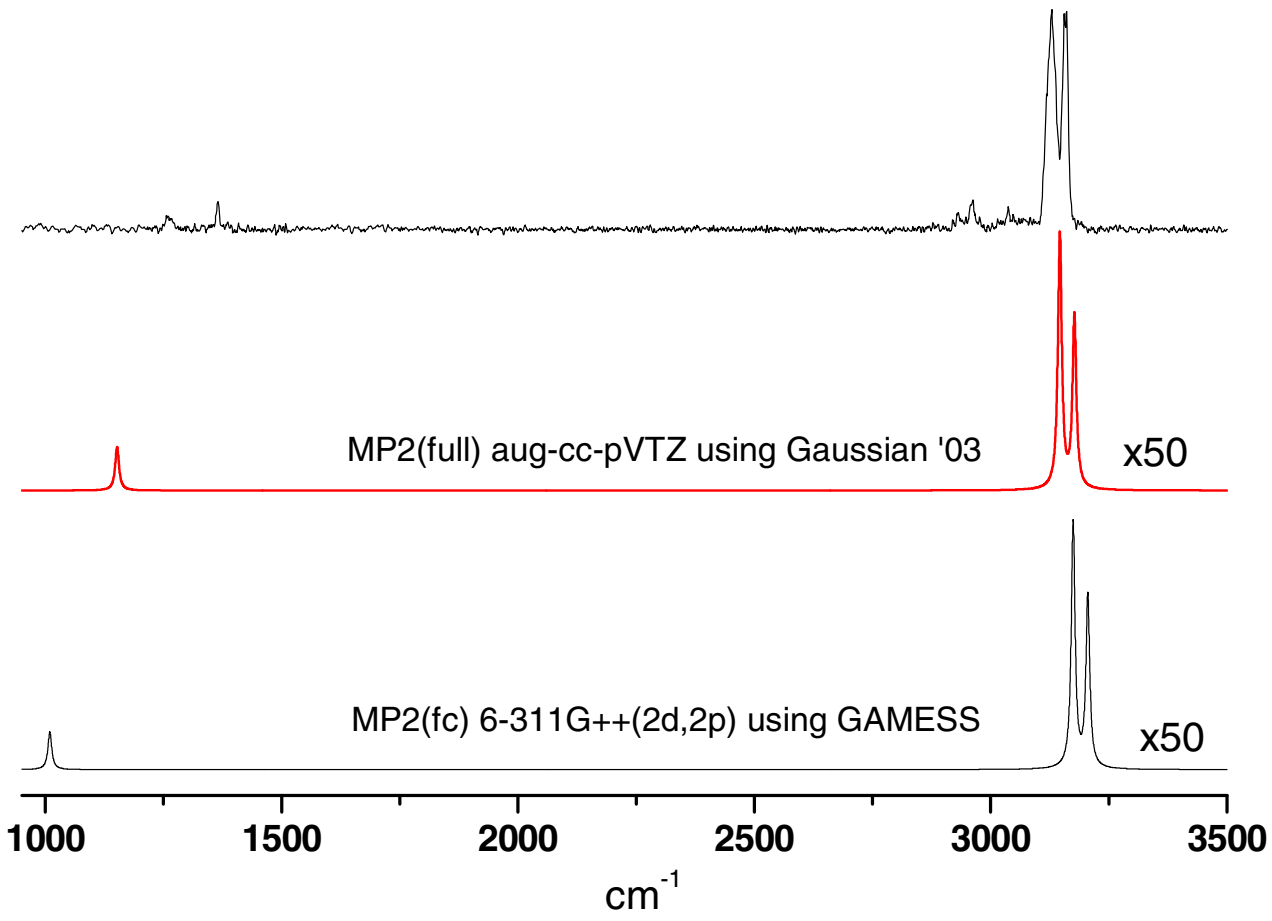

Figure S24. A comparison of the experimental spectra for the loss of argon from the proton bound acetylene dimer with argon and a simulated spectra for the proton bound acetylene dimer without argon done at two different levels of theory. The band intensities in the 3200 cm^{-1} region have been multiplied by 50 to make their intensities agree with that in the experiment.

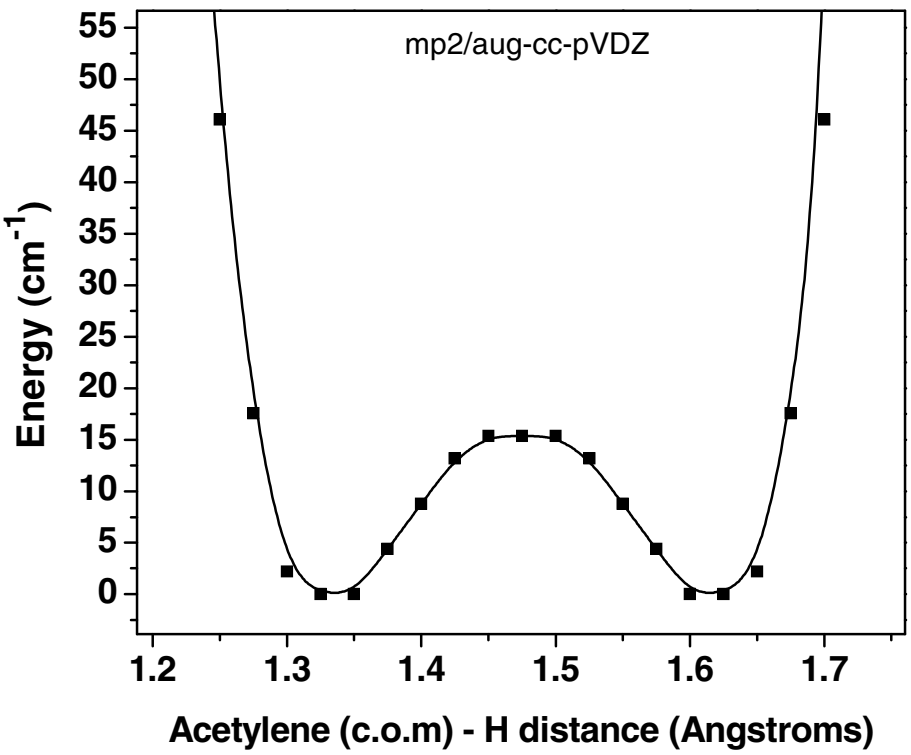

Figure S25. The relaxed potential energy surface for the proton moving between the pi bonds of the two acetylene molecules, calculated at the MP2(full) aug-cc-pVDZ level of theory with Gaussian '03.

Table S6. The isomers of $C_4H_5^+Ar$ and their relative energies.

Isomer	Total Energy (Hartrees)	Relative Energy (kcal/mol)
$C_4H_5^+$ Ar methyl cyclopropane	-681.6383009	+0.0
$C_4H_5^+Ar$ protonated cyclobutadiene	-681.6242292	+8.8
$C_4H_5^+$ Ar allyl chain	-681.6092811	+18.2
$C_4H_5^+$ Ar proton bound acetylene dimer	-681.5193943	+74.7

Table S7. The isomers of $C_4H_5^+Ar$ and their counterpoise corrected argon binding energies.

Isomer	Argon Binding Energy (cm^{-1})
$C_4H_5^+$ Ar methyl cyclopropane cation	596
$C_4H_5^+Ar$ protonated cyclobutadiene	669
$C_4H_5^+$ Ar allyl chain	426
$C_4H_5^+$ Ar proton bound acetylene dimer	532

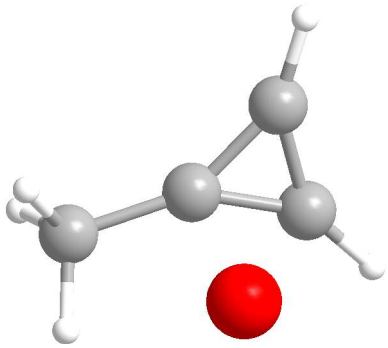

Figure S26. The structure of the $C_4H_5^+$Ar methyl cyclopropane cation (ChemDraw object).

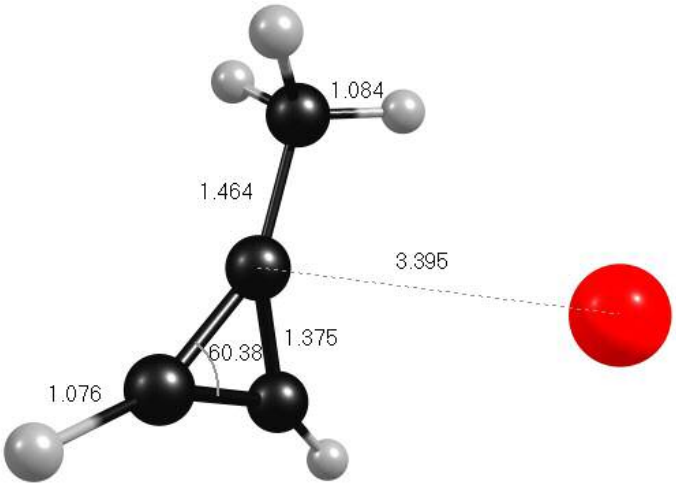

Figure S27. The structure of the $C_4H_5^+$ Ar methyl cyclopropane cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

The normal mode frequencies (unscaled) and intensities of the $C_4H_5^+$ Ar methyl cyclopropane cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS, are:

21.3(0.6), 40.1(4.6), 58.2(7.5), 75.6(0.8), 357.4(2.1), 386.6(9.7), 770.8(4.6), 823(26.2), 948.2(0), 983.4(0.7), 923(17.5), 1049.2(23.2), 1096.9(14.8), 1298.8(8.9), 1407.5(26.2), 1417.1(50.7), 1477.2(25.4), 1500.5(11.4), 1740.1(25.4), 3081(26.6), 3172.9(6.8), 3223(5.5), 3271.1(76.1), 3311(39.3)

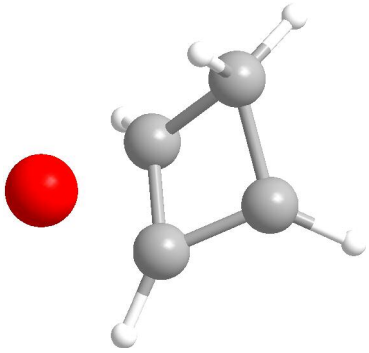

Figure S28. The structure of the $C_4H_5^+$ Ar protonated cyclobutadiene cation (ChemDraw object).

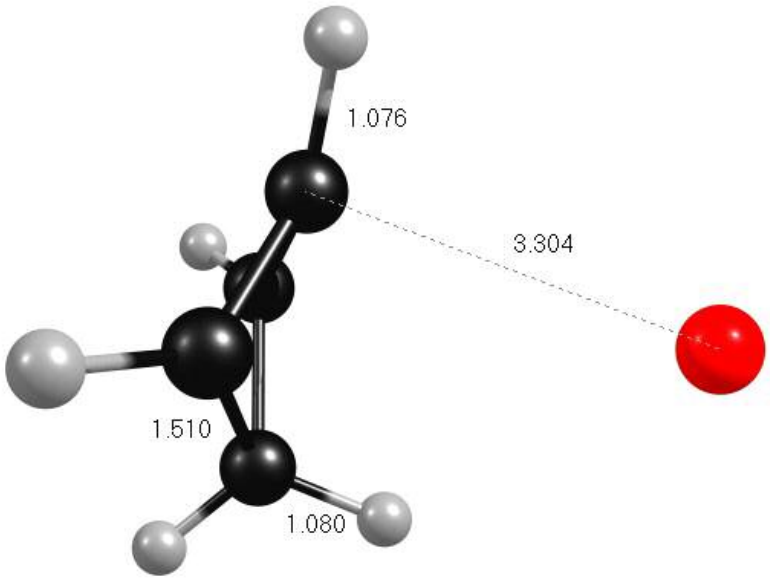

Figure S29. The structure $C_4H_5^+$ Ar protonated cyclobutadiene cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

The calculated normal mode frequencies (unscaled) and intensities of the $C_4H_5^+$ Ar protonated cyclobutadiene are:

43.5(0.1), 62.7(10.7), 64.7(0.5), 462.2(3), 657.9(17.7), 749.3(1), 918.3(13.5), 947.5(11.8), 989.7(12.4), 1020(3.6), 1037.9(0), 1109.8(8.2), 1112.2(5.2), 1151.9(9.9), 1215(0), 1245.7(17.7), 1374.6(35.2), 1478.7(3.8), 1526.2(10.4), 3170.4(9.3), 3221.4(21.6), 3221.9(36.1), 3267.1(15.5), 3303.3(42.3)

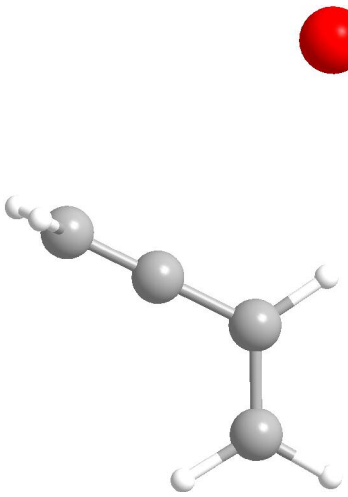

Figure S30. The structure of the $C_4H_5^+Ar$ allyl chain cation (ChemDraw object).

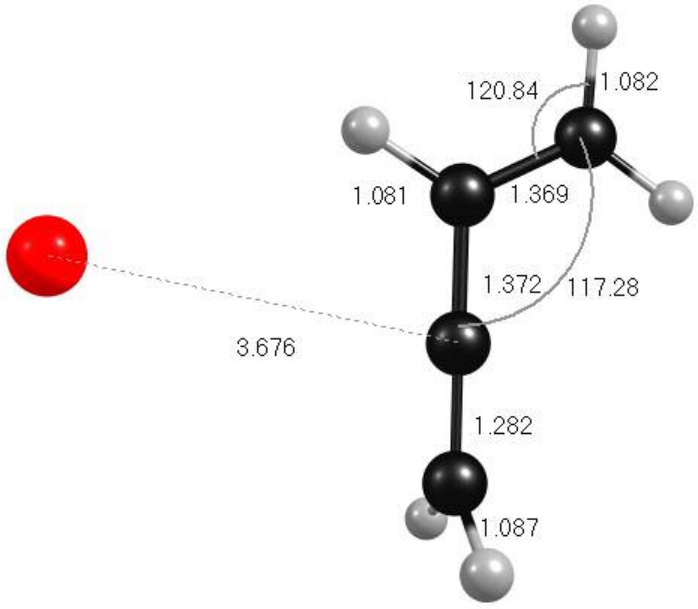

Figure S31. The structure $C_4H_5^+$ Ar allyl chain cation calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

The normal mode frequencies (unscaled) and intensities of the $C_4H_5^+$ Ar allyl chain cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS are:

7.2(0.7), 28.7(2.1), 51(8.5), 210.1(3), 235.8(7.1), 385.2(0.3), 554.6(6.8), 607.9(0), 847.1(63.4), 895.5(5.1), 926.9(5.1), 998.5(25.8), 1119.4(4.8), 1126.9(17.2), 1302.9(6.2), 1335.5(44.8), 1456.5(78.6), 1607.3(58.7), 1925.3(424.7), 3119.7(222.3), 3176.3(7.4), 3214.6(85.8), 3234.2(21.8), 3294.3(15.9)

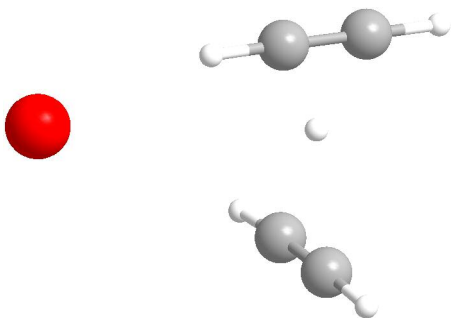

Figure S32. The structure of the $C_4H_5^+$ Ar proton-bound acetylene dimer cation (ChemDraw object).

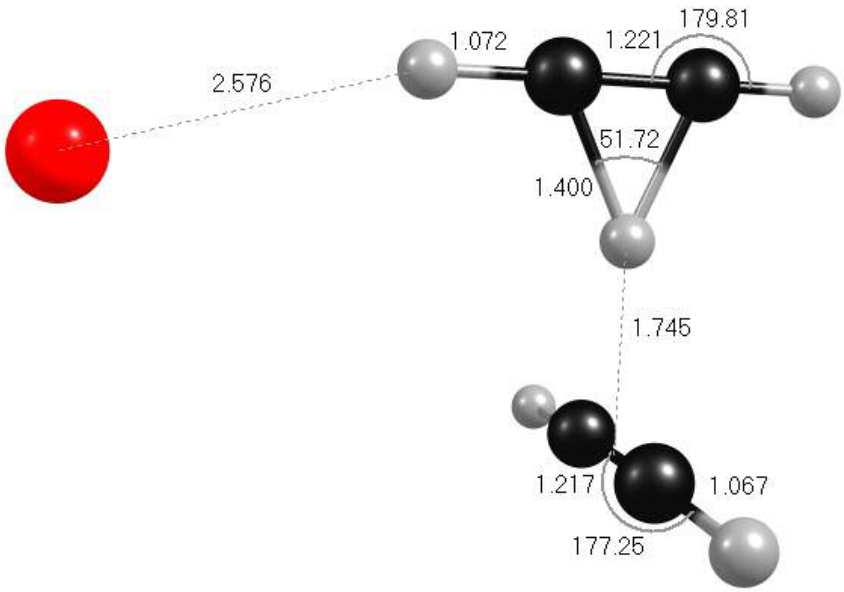

Figure S33. The structure $C_4H_5^+$ Ar proton-bound acetylene dimer cation calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

The normal mode frequencies (unscaled) and intensities of the $C_4H_5^+$ Ar proton bound acetylene dimer cation, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS, are:

7.9(2.1), 34.1(0.3), 66.3(14.7), 110(0.1), 160.1(1.7), 187.6(7.8), 211.9(186.9), 564.5(0.6), 600.8(0.7), 607.3(0.7), 613(15.6), 771.9(88.4), 780.9(61), 818.7(39.1), 838(21.7), 842.8(411.6), 1148(2195.4), 1176.8(297.4), 1939.9(3.6), 1945.7(1.9), 3220.3(449.9), 3376.5(201.6), 3429.2(1.2), 3471(3)

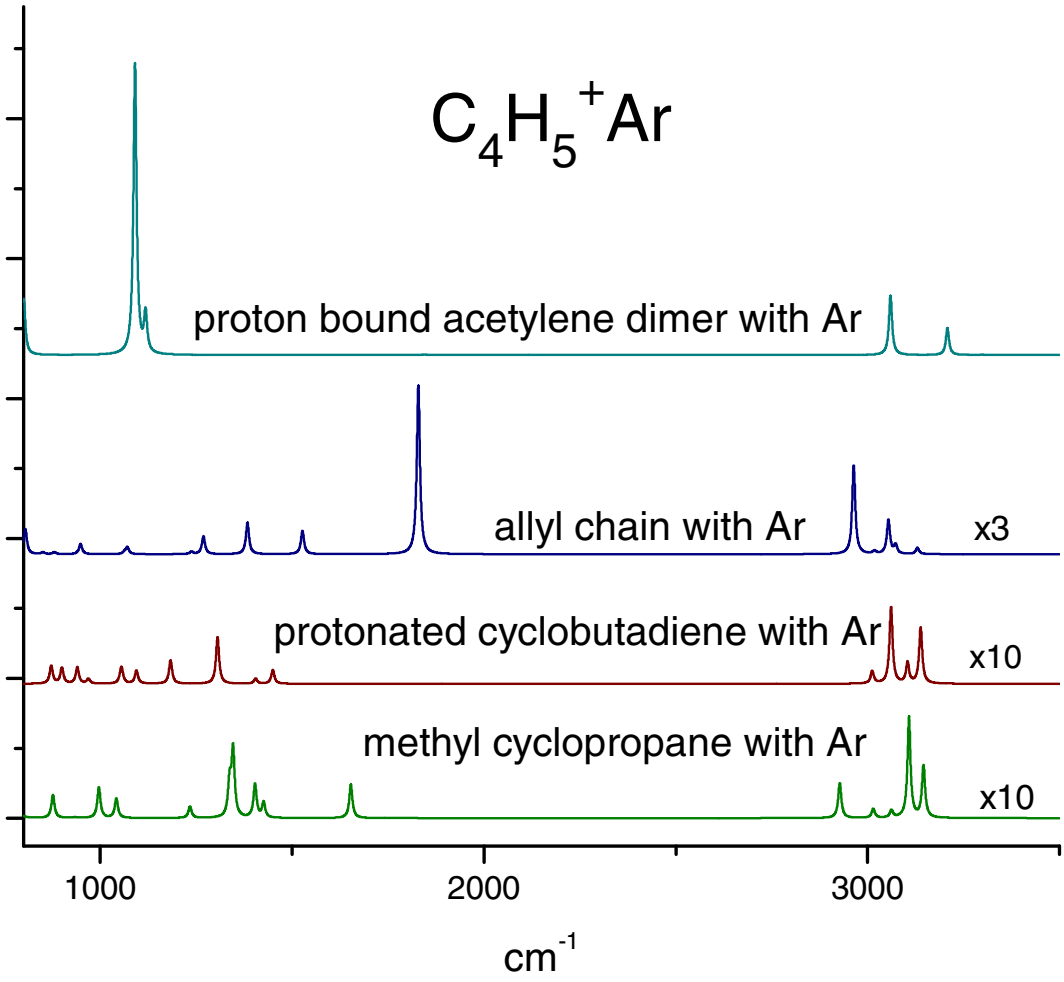

Figure S34. Simulated spectra of the different $C_4H_5^+Ar$ isomers. The frequencies have been scaled by 0.95.

Table S8. The isomers of the $C_6H_7^+$ ion and their relative energies, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

Isomer	Total Energy (Hartrees)	Relative Energy (kcal/mol)
$C_6H_7^+$ methyl cyclopropane cation acetylene complex	-231.8008485	+0.0
$C_6H_7^+$ protonated cyclobutadiene acetylene complex	-231.7873425	+8.5
$C_6H_7^+$ allyl chain acetylene complex	-231.7715866	+18.3
$C_6H_7^+$ proton-bound acetylene dimer acetylene complex	-231.6836323	+73.4

Table S9. The isomers of $C_6H_7^+$ and their counterpoise corrected acetylene binding energies.

Isomer	Acetylene Binding Energy (cm^{-1})
$C_6H_7^+$ methyl cyclopropane acetylene complex	2386
$C_6H_7^+$Ar protonated cyclobutadiene acetylene complex	2643
$C_6H_7^+$ allyl chain acetylene complex	2149
$C_6H_7^+$ proton bound acetylene dimer acetylene complex	2765

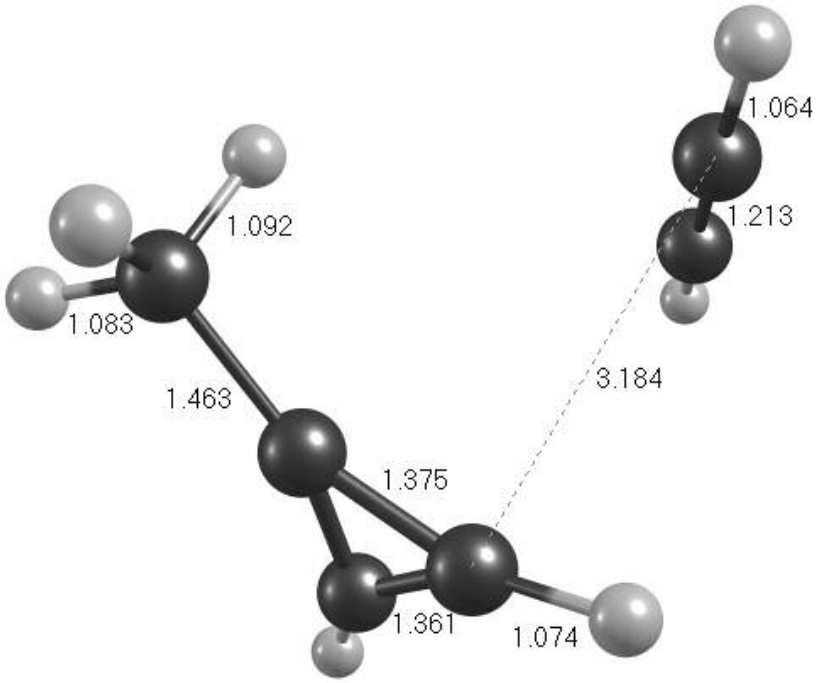

Figure S35. The structure of the $C_4H_5^+$ methyl cyclopropane cation acetylene complex, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

The normal mode frequencies (unscaled) and intensities of the $C_4H_5^+$ methyl cyclopropane cation acetylene complex, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS, are:

35.2(1.1), 55.1(1), 78(3), 84.6(1.6), 106.6(0.3), 120.9(8), 357.8(2.1), 385.1(13.1), 601.4(0), 611.6(1.7), 760.2(82.1), 770.5(19.2), 776(96.3), 816.3(23), 933.2(2.1), 982.8(0.4), 996(16.9), 1046.5(18.3), 1096.1(12.8), 1300.9(10.5), 1400.9(21.3), 1413.8(45.2), 1479.9(18.9), 1500.6(11.1), 1744.6(24.4), 1953.3(5.4), 3079.2(20.3), 3168.8(7.4), 3222.1(4.5), 3278.7(66.5), 3320.3(36.5), 3408.5(124), 3499.5(2.6)

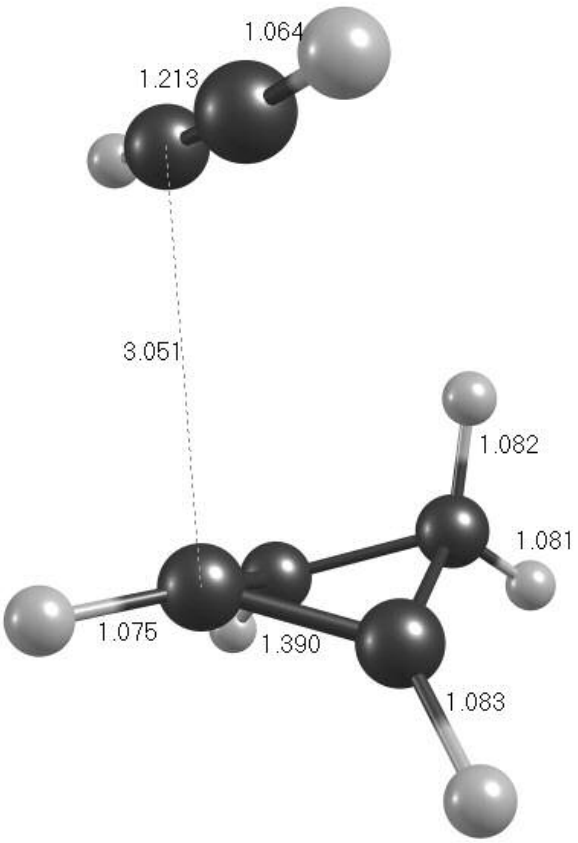

Figure S36. The structure of the $C_4H_5^+$ protonated cyclobutadiene cation acetylene complex, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

The normal mode frequencies (unscaled) and intensities of the $C_4H_5^+$ protonated cyclobutadiene cation acetylene complex, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS, are:

28.1(0.2), 71.2(1.7), 102.4(0.4), 108.1(0), 111.1(14.8), 471.2(9.3), 598.2(0), 612.1(1.1), 667.4(14.5), 749.9(1), 757.9(83.7), 777.2(110.2), 910.8(3.9), 945.6(12.5), 976.1(14.3), 1022(1.9), 1031.8(0.1), 1102.6(6.3), 1113.4(7.2), 1156.6(5.8), 1209.3(0), 1245.4(12.2), 1365.5(31.6), 1475(6.6), 1520.4(12), 1951.4(8.4), 3159.4(12.7), 3226.9(31.6), 3227(21.9), 3262.2(15.7), 3312.1(39.5), 3407.8(126.4), 3498.7(2.6)

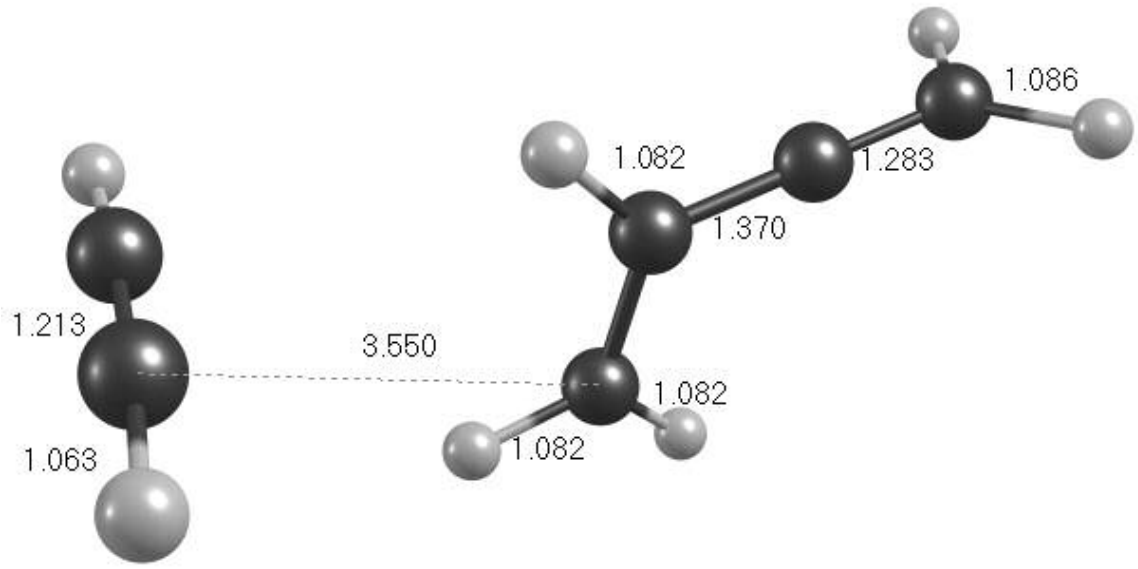

Figure S37. The structure of the $C_4H_5^+$ allyl chain cation acetylene complex, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

The normal mode frequencies (unscaled) and intensities of the $C_4H_5^+$ allyl chain cation acetylene complex, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS, are:

39.6(0), 51.2(1.3), 61.1(0.4), 101.2(9.2), 102.8(0.5), 209.9(4.4), 232.4(3.9), 370(0.3), 528.3(4.2), 572.4(0), 579(2), 586.6(0.1), 721.9(83.7), 734.9(119.1), 803.9(62.9), 855.2(4.2), 879.4(7.6), 964.7(21.9), 1056.9(5.8), 1080.9(12.1), 1233(6.1), 1271.7(46.9), 1373.5(68.3), 1517.5(95), 1829.7(453.8), 1858.4(2.8), 2968.7(226.9), 3010.5(6.5), 3057.7(47.3), 3059.1(79.9), 3125.6(25.9), 3241.8(124.8), 3328(2.8)

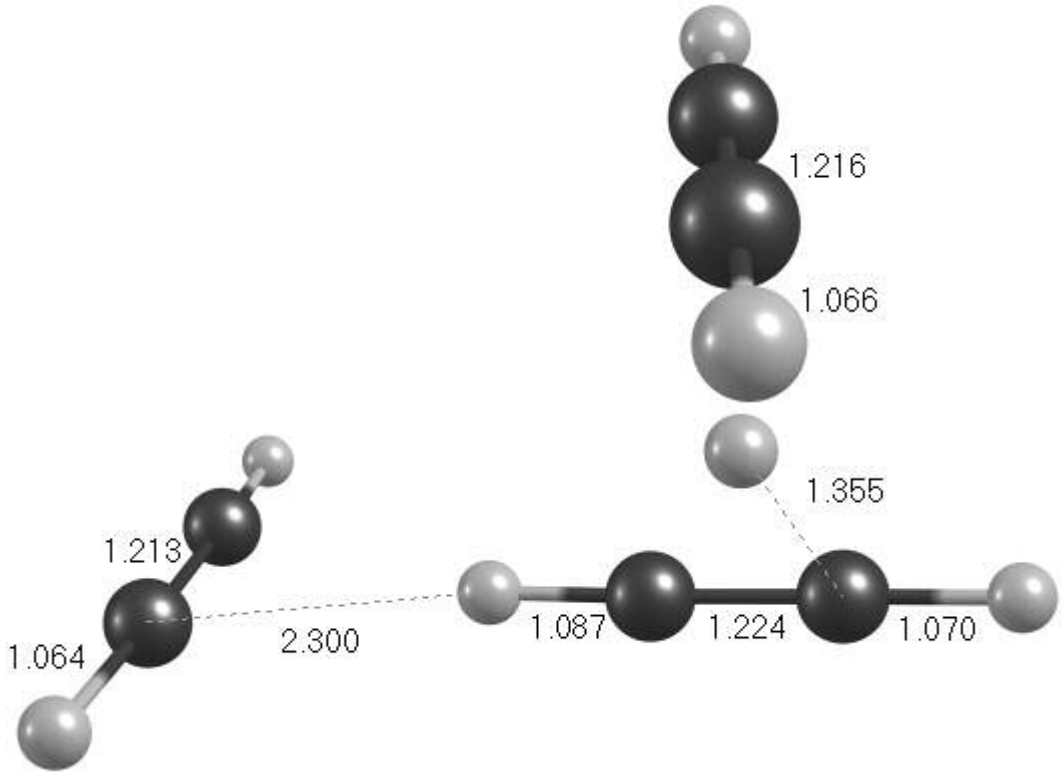

Figure S38. The structure of the $C_4H_5^+$ proton bound acetylene dimer acetylene complex, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

The normal mode frequencies (unscaled) and intensities of the $C_4H_5^+$ proton bound acetylene dimer cation acetylene complex, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS, are:

18.1(0), 30.9(0.7), 55.2(0.4), 106.6(0.2), 141.6(23.9), 153.1(0.5), 164.6(2.4), 195.6(12.4), 205(87.9), 557.7(0.2), 599.4(0), 602.5(0), 613.6(6), 637.1(12.3), 650.9(15.8), 758.7(84.3), 767.4(90.7), 770.6(7.3), 787.5(111.8), 816.9(115), 868.9(45.7), 919.6(34.9), 1210.1(6), 1445.8(2227.4), 1916.2(34.6), 1948(0.4), 1956.5(4.3), 3117.6(961.4), 3386.1(175.2), 3398.8(49.9), 3406.6(138.5), 3479.6(2.9), 3498.2(1.8)

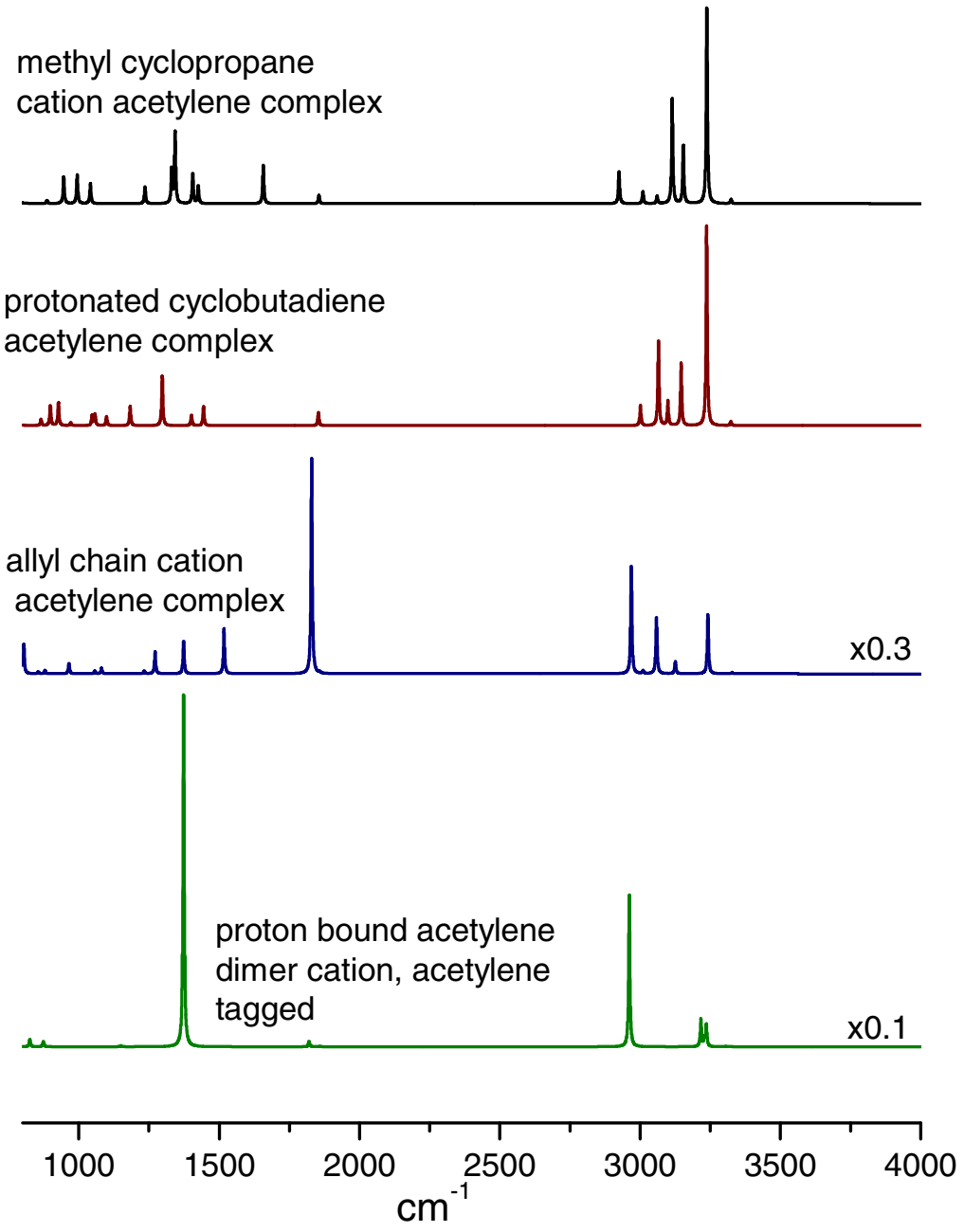

Figure S39. Simulated infrared spectra (unscaled) for the isomers of the $C_6H_7^+$ ion and their relative energies, calculated at the MP2(fc) 6-311++G(2d,2p) level of theory using GAMESS.

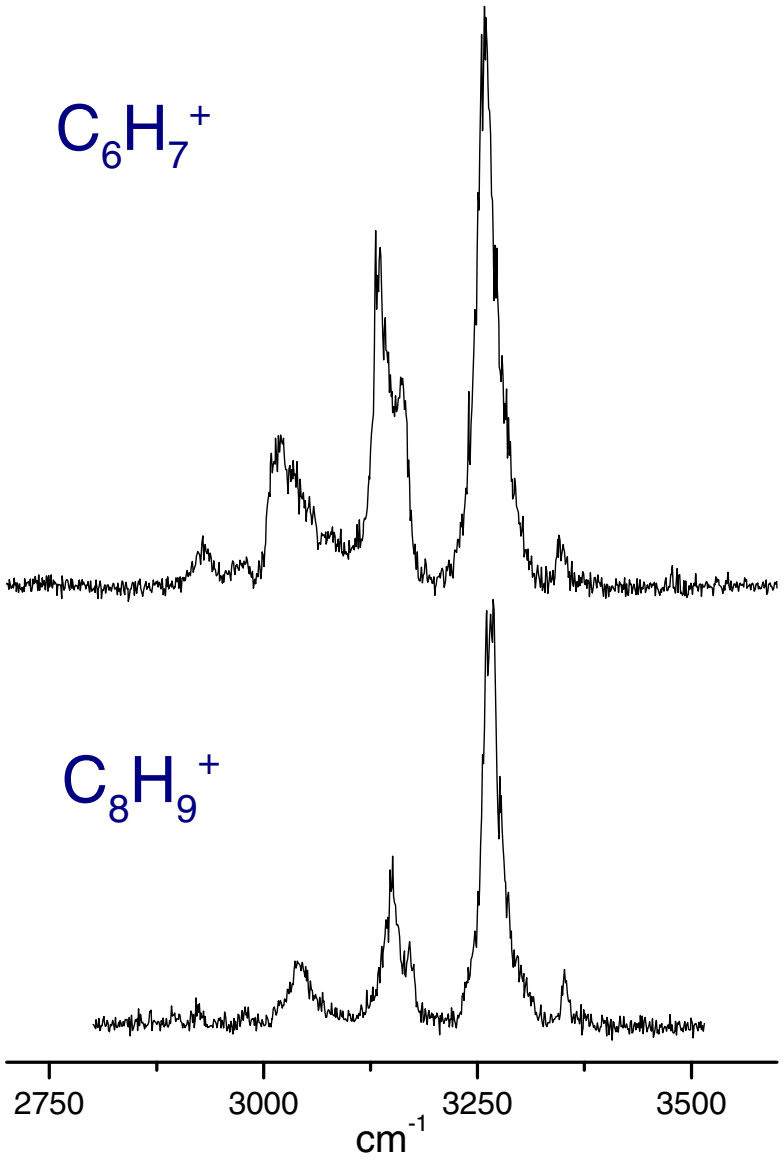

Figure S40. The experimental spectra for $C_6H_7^+$ and $C_8H_9^+$.