# Strong Carbon – Noble Gas Covalent Bond and Fluxionality in Hypercoordinate Compounds

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## SUPPORTING INFORMATION

**Table S1.** Vibrational modes (in $cm^{-1}$) computed at the CCSD(T)/def2-TZVP level.

| ν | $CH_4He^{2+}$ | $CH_4Ne^{2+}$ | $CH_4Ar^{2+}$ | $CH_4Kr^{2+}$ | $CH_4Xe^{2+}$ | $CH_4Rn^{2+}$ |
|---|---|---|---|---|---|---|
| 1 | 712.6079 | 420.3711 | 606.9756 | 557.2035 | 516.3135 | 445.7527 |
| 2 | 909.1061 | 720.8941 | 787.9108 | 696.9451 | 545.4223 | 489.8312 |
| 3 | 923.4879 | 815.2974 | 801.0899 | 774.6904 | 738.113 | 716.984 |
| 4 | 1055.8543 | 969.2108 | 911.853 | 867.7708 | 815.6047 | 782.4142 |
| 5 | 1060.3472 | 995.9897 | 1022.6994 | 1020.677 | 997.4863 | 987.958 |
| 6 | 1213.7408 | 1154.3162 | 1251.2854 | 1246.1762 | 1238.2602 | 1229.0865 |
| 7 | 1272.5143 | 1198.1464 | 1279.533 | 1281.9632 | 1288.9217 | 1287.2196 |
| 8 | 1500.7985 | 1536.715 | 1545.2365 | 1552.1084 | 1551.7349 | 1553.9434 |
| 9 | 1893.3463 | 1824.375 | 2068.5309 | 2126.4268 | 2208.5027 | 2242.59 |
| 10 | 2352.7944 | 2383.5884 | 2503.0562 | 2542.6227 | 2576.5237 | 2596.3457 |
| 11 | 2796.8171 | 2813.9623 | 2909.8044 | 2932.0994 | 2955.3932 | 2968.4924 |
| 12 | 2870.2891 | 2913.6744 | 2965.5511 | 2982.6324 | 2996.857 | 3009.4948 |

**Table S2.** Moment of Inertia (*I*, in amu.$Å^2$) computed at the CCSD(T)/def2-TZVP level.

| *I* | $CH_4He^{2+}$ | $CH_4Ne^{2+}$ | $CH_4Ar^{2+}$ | $CH_4Kr^{2+}$ | $CH_4Xe^{2+}$ | $CH_4Rn^{2+}$ |
|---|---|---|---|---|---|---|
| XX | 7.590424 | 25.761183 | 26.545415 | 33.560320 | 38.204431 | 41.914489 |
| YY | 78.316797 | 10.140773 | 26.776697 | 36.905488 | 50.134306 | 57.782924 |
| ZZ | 57.708748 | 29.707826 | 41.454371 | 54.450764 | 66.382668 | 74.782079 |

**Table S3.** Rotational constants (*B*, in GHz) computed at the CCSD(T)/def2-TZVP level.

| *B* | $CH_4He^{2+}$ | $CH_4Ne^{2+}$ | $CH_4Ar^{2+}$ | $CH_4Kr^{2+}$ | $CH_4Xe^{2+}$ | $CH_4Rn^{2+}$ |
|---|---|---|---|---|---|---|
| XX | 66.581128 | 19.617849 | 19.038279 | 15.058826 | 13.228283 | 12.057382 |
| YY | 78.316797 | 49.83634 | 18.873837 | 13.693871 | 10.080503 | 8.7461653 |
| ZZ | 57.708748 | 17.011645 | 12.191212 | 9.2813943 | 7.6131169 | 6.7580229 |

**Table S4.** IQA Values (in $kcal.mol^{-1}$) for all systems computed at the CCSD(T)/Jorge-TZP/CCSD(T)/def2-TZVP level. Vc: Coulomb (Ionic) contribution; Vx: Exchange (Covalent) contribution.

| **Systems** | **$CH_4He^{2+}$** | **$CH_4Ne^{2+}$** | **$CH_4Ar^{2+}$** | **$CH_4Kr^{2+}$** | **$CH_4Xe^{2+}$** | **$CH_4Rn^{2+}$** |
|---|---|---|---|---|---|---|
| **Vc (C - Ng)** | -11.3 | -3.7 | 4.2 | -7.0 | -63.6 | -83.4 |
| **Vx (C - Ng)** | -78.1 | -61.2 | -127.9 | -134.8 | -134.2 | -125.9 |
| **$\Delta E_{int}$ (C - Ng)** | -89.4 | -64.9 | -123.7 | -141.8 | -197.8 | -209.3 |
| **Vc (C - Ha)** | -11.9 | -7.6 | -11.7 | -19.3 | -29.3 | -29.4 |
| **Vx (C - Ha)** | -123.7 | -125.3 | -133.9 | -136.3 | -139.1 | -140.6 |
| **$\Delta E_{int}$(C - Ha)** | -135.6 | -132.9 | -145.6 | -155.7 | -168.5 | -170.0 |
| **Vc (C - Hb)** | -26.6 | -18.9 | -20.1 | -26.4 | -36.7 | -36.8 |
| **Vx (C - Hb)** | -94.5 | -93.6 | -98.6 | -100.1 | -101.8 | -102.4 |
| **$\Delta E_{int}$(C - Hb)** | -121.1 | -112.5 | -118.7 | -126.5 | -138.6 | -139.2 |

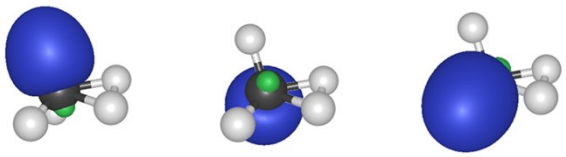
**Table S5.** Atomic descriptors computed for noble gas atoms at the CCSD(T)/def2-TZVP level.

| Atom | IE | EA | Hardness | Softness | Chem Pot | Electrophilicty |
|---|---|---|---|---|---|---|
| He | 24.35 | 22.38 | 0.98 | 1.02 | 23.37 | 277.88 |
| Ne | 21.32 | 20.77 | 0.28 | 3.63 | 21.04 | 803.27 |
| Ar | 15.54 | 14.77 | 0.38 | 2.60 | 15.15 | 298.33 |
| Kr | 13.97 | 12.30 | 0.83 | 1.20 | 13.14 | 103.41 |
| Xe | 12.26 | 8.96 | 1.65 | 0.61 | 10.61 | 34.14 |
| Rn | 11.53 | 7.27 | 2.13 | 0.47 | 9.40 | 20.75 |

**Table S6.** Activation energies (in kcal.mol$^{-1}$) for the reorganization of C – H bonds in $CH_4Ng^{2+}$ (Ng = He and Ne) at the DFT and CCSD(T) levels.

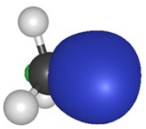
| System | $\Delta E^{\ddagger}_{\omega B97xD}$ | $\Delta E^{\ddagger}_{CCSD(T)}$ |
|---|---|---|
| $CH_4He^{2+}$ | 0.89 | 0.53 |
| $CH_4Ne^{2+}$ | 1.01 | -0.32 |

**Figure S1.** AdNDP orbitals and occupation numbers (ON, in |e|) for $CH_5^+$.



3 x 2c-2e C-H σ bonds

ON : 1.92 - 1.99 |e|



1 x 3c-2e C-H-H σ bonds

ON : 2.00 |e|

## CARTESIAN COORDINATES

| $CH_4^{2+}$ | | | |
|---|---|---|---|
| C | 0.126647000 | -0.000167000 | 0.000001000 |
| H | 0.662798000 | 1.003158000 | 0.000023000 |
| H | -1.042305000 | -0.520076000 | 0.000046000 |
| H | 0.660907000 | -1.003898000 | -0.000026000 |
| H | -1.041283000 | 0.521817000 | -0.000047000 |

| $CH_5^+$ | | | |
|---|---|---|---|
| C | 0.000000000 | 0.000000000 | 0.000000000 |
| H | 0.000000000 | 0.000000000 | 1.100076000 |
| H | 1.013459000 | 0.000000000 | -0.646616000 |
| H | -0.076963000 | 1.054686000 | -0.303390000 |
| H | -0.697201000 | -0.683091000 | -0.476176000 |
| H | 1.054492000 | -0.567857000 | 0.104104000 |

| $CH_4He^{2+}$ | | | |
|---|---|---|---|
| C | 0.078615000 | -0.159801000 | 0.000309000 |
| H | 0.005406000 | -0.745374000 | -0.960755000 |
| H | 0.792866000 | 0.715882000 | 0.523834000 |
| H | 0.005089000 | -0.741900000 | 0.962847000 |
| He | -1.034070000 | 0.508061000 | -0.000929000 |
| H | 0.793088000 | 0.714073000 | -0.525924000 |

| $CH_4Ne^{2+}$ | | | |
|---|---|---|---|
| C | 0.808897454 | -0.134666545 | 0.000156399 |
| H | 0.950507757 | -0.675223105 | -0.975144815 |
| H | 1.051570948 | 0.991533837 | 0.506586895 |
| H | 0.948874673 | -0.669281043 | 0.979041026 |
| Ne | -0.885463020 | 0.017128623 | -0.000080915 |
| H | 1.050292128 | 0.989683346 | -0.510612343 |

| $CH_4Ar^{2+}$ | | | |
|---|---|---|---|
| C | 1.118590871 | -0.119320349 | 0.000135398 |
| H | 1.438186661 | -0.662849528 | -0.919758267 |
| H | 1.538181830 | 0.923496380 | 0.498694014 |
| H | 1.438078402 | -0.660121032 | 0.921654113 |
| Ar | -0.703634775 | 0.010752954 | -0.000031157 |
| H | 1.539433806 | 0.921843114 | -0.500841428 |

| $CH_4Kr^{2+}$ | | | |
|---|---|---|---|
| C | 1.499856000 | -0.116046000 | 0.000434000 |
| H | 1.846176000 | -0.647757000 | -0.914235000 |
| H | 1.936914000 | 0.912512000 | 0.498225000 |
| H | 1.848017000 | -0.659329000 | 0.907210000 |
| Kr | -0.460486000 | 0.004995000 | -0.000045000 |
| H | 1.947258000 | 0.911022000 | -0.492170000 |

| $CH_4Xe^{2+}$ | | | |
|---|---|---|---|
| C | 1.777143745 | -0.109820462 | 0.000550862 |
| H | 2.158980278 | -0.646702129 | -0.894196307 |
| H | 2.248650215 | 0.895446255 | 0.492526976 |
| H | 2.158998953 | -0.646486193 | 0.895003239 |
| Xe | -0.360854183 | 0.003078089 | -0.000039472 |
| H | 2.256633981 | 0.890448017 | -0.494507608 |

| $CH_4Rn^{2+}$ | | | |
|---|---|---|---|
| C | 1.980373415 | -0.107864824 | 0.000462408 |
| H | 2.367632851 | -0.642437505 | -0.891653610 |
| H | 2.465926170 | 0.886986357 | 0.491559100 |
| H | 2.369680201 | -0.644792069 | 0.889976452 |
| Rn | -0.250664913 | 0.001902845 | -0.000009423 |
| H | 2.471702833 | 0.883787486 | -0.491846028 |