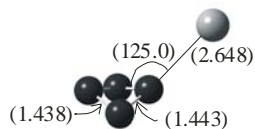


## Supporting Information

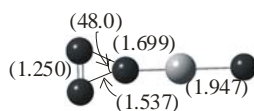
Optimized geometries of 10 high lying structures of singlet and triplet GaN<sub>4</sub><sup>+</sup> species at B3LYP/LANL2DZ level of theory, grey spheres Ga, black spheres N.



A.1s1-s / <sup>1</sup>A'/C<sub>3v</sub>

D<sub>e</sub><sup>1</sup> = 171.8(168.7) kcal/mol

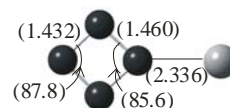
T<sub>e</sub><sup>2</sup> = 209.4 kcal/mol



B.3s2-s / <sup>3</sup>A<sub>2</sub>/C<sub>2v</sub>

282.7(278.1)

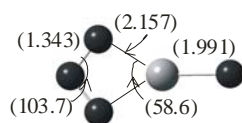
218.1



C.1s3-s / <sup>1</sup>A<sub>1</sub>/C<sub>2v</sub>

158.6(155.6)

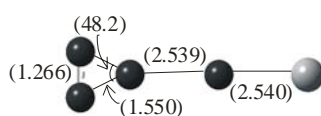
222.7



D.3s4-s / <sup>3</sup>A''/C<sub>s</sub>

D<sub>e</sub> = 277.7(273.8) kcal/mol

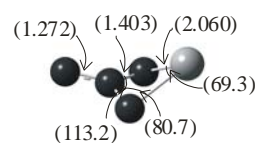
T<sub>e</sub> = 223.2 kcal/mol



E.3s5-s / <sup>3</sup>B<sub>2</sub>/C<sub>2v</sub>

269.2(267.0)

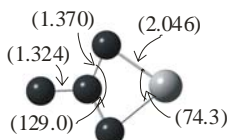
231.7



F.1s6-s / <sup>1</sup>A'/C<sub>s</sub>

122.6(118.3)

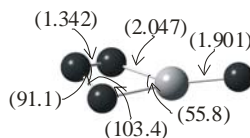
258.7



G.1s7-s / <sup>1</sup>A<sub>1</sub>/C<sub>2v</sub>

D<sub>e</sub> = 114.2(110.1) kcal/mol

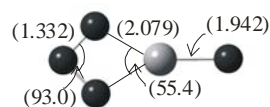
T<sub>e</sub> = 267.0 kcal/mol



H.1s8-s / <sup>1</sup>A'/C<sub>s</sub>

109.7(105.4)

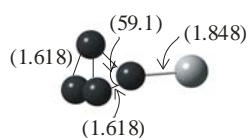
271.5



I.1s9-s / <sup>1</sup>A<sub>1</sub>/C<sub>2v</sub>

105.9(101.7)

275.4



J.3s10-s / <sup>3</sup>A''/C<sub>s</sub>

D<sub>e</sub> = 220.0(215.7) kcal/mol

T<sub>e</sub> = 280.9 kcal/mol

<sup>1</sup>D<sub>e</sub>(BSSE) with respect to Ga<sup>+</sup>(<sup>1</sup>S and <sup>3</sup>P) + 4N(<sup>4</sup>S) for the singlet and triplet states, respectively.

<sup>2</sup>T<sub>e</sub> with respect to the ground structure 1m1 of the paper.