Supporting Information

The Be-Be Bond In Action: Lessons From The Beryllium Ammonia Complexes $[Be(NH_3)_{0-4}]_2^{0,2+}$

*Isuru R. Ariyarathna and Evangelos Miliordos**

Department of Chemistry and Biochemistry, Auburn University, Auburn, AL 36849-5312, USA

Corresponding Author

* E-mail: emiliord@auburn.edu

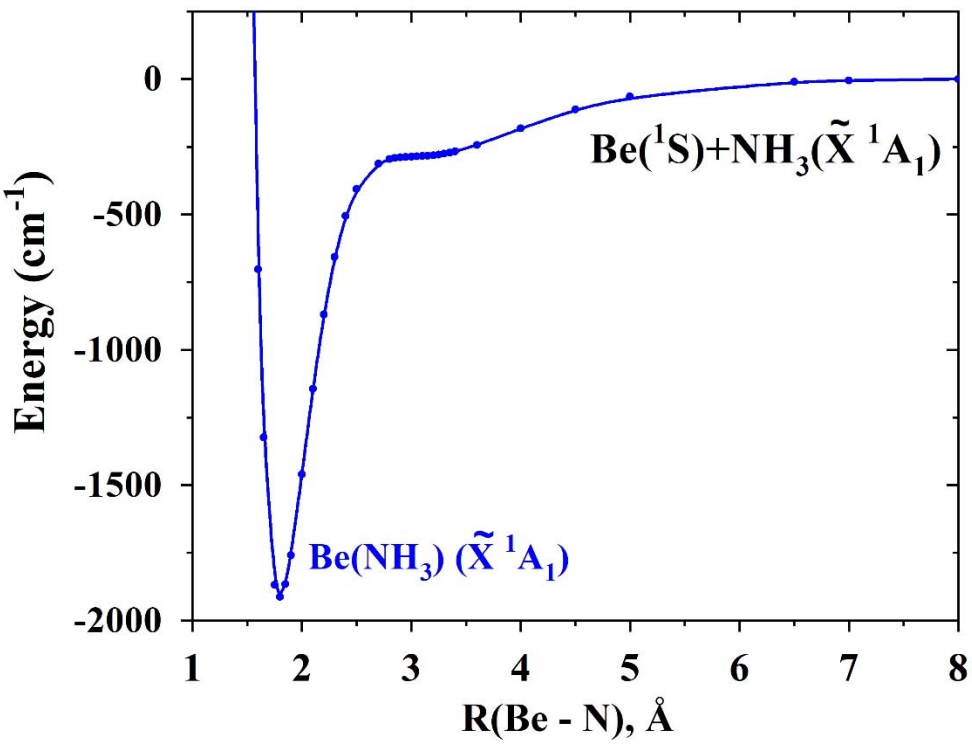

Figure S1. CCSD(T)/aug-cc-pVTZ potential energy profile of the ground electronic state of $Be(NH_3)$ as a function of the Be-N distance.

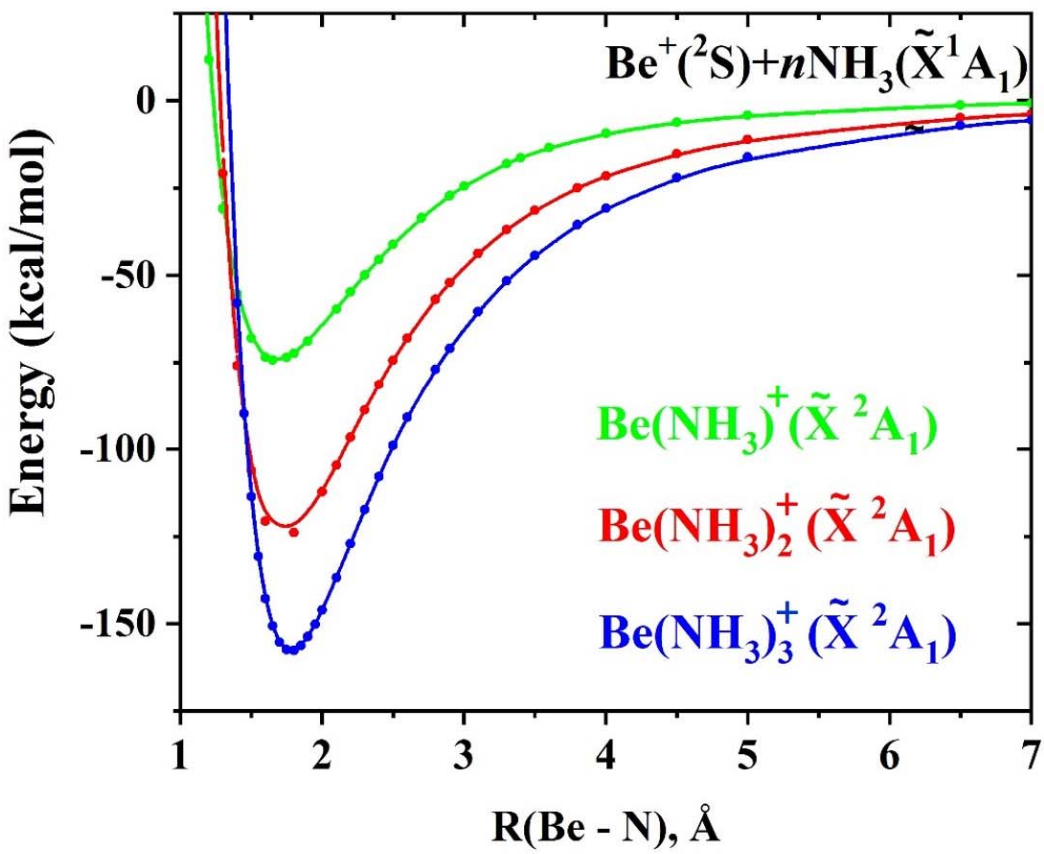

Figure S2. MRCI potential energy profiles of the ground electronic states of $Be(NH_3)_{1\text{-}3}^+$ as a function of the Be-N distance.

Optimized geometries and frequencies

CCSD(T)/ATZ geometry of $Be(NH_3)$

Be	0.0000000000	0.0000000000	-1.2192794947
N	0.0000000000	0.0000000000	0.5800659583
H	0.9542192705	0.0000000000	0.9469996293
H	-0.4771096353	0.8263781291	0.9469996293
H	-0.4771096353	-0.8263781291	0.9469996293

Frequencies CCSD(T)/ATZ: 455.87, 503.48, 503.63, 1244.15, 1630.75, 1630.82, 3350.99, 3497.34, 3497.45

CCSD(T)/ATZ geometry of $Be(NH_3)^+$

Be	0.0000000000	0.0000000000	-1.1451867434
N	0.0000000000	0.0000000000	0.5361238398
H	0.9464133107	0.0000000000	0.9297191231
H	-0.4732066553	0.8196179695	0.9297191231
H	-0.4732066553	-0.8196179695	0.9297191231

Frequencies CCSD(T)/ATZ: 710.4, 710.7, 772.6, 1403.2, 1641.9, 1642.2, 3380.9, 3471.0, 3471.3

CCSD(T)/ATZ geometry of $Be(NH_3)_2$

Be	0.0000000000	0.0000000000	-0.8958149874
N	0.0000000000	1.3554356722	0.1948237530
N	0.0000000000	-1.3554356722	0.1948237530
H	0.0000000000	-2.2345613064	-0.3189473572
H	-0.8296148503	-1.3537067687	0.8082152187
H	0.8296148503	-1.3537067687	0.8082152187
H	-0.8296148503	1.3537067687	0.8082152187
H	0.8296148503	1.3537067687	0.8082152187
H	0.0000000000	2.2345613064	-0.3189473572

Frequencies MP2/ATZ : 48.7, 64.4, 224.7, 521.4, 535.5, 562.6, 591.2, 700.8, 726.1, 1256.1, 1258.4, 1567.4, 1572.9, 1626.1, 1643.8, 3231.0, 3245.9, 3351.4, 3373.5, 3544.3, 3555.2

CCSD(T)/ATZ geometry of $Be(NH_3)_2^+$

N	0.0000000000	1.4627821986	-0.1092507598
H	0.0000000000	1.4299476399	-1.1297499244
H	-0.8083645385	2.0244190990	0.1642223054
H	0.8083645385	2.0244190990	0.1642223054
N	0.0000000000	-1.4627821986	-0.1092507598
H	0.0000000000	-1.4299476399	-1.1297499244
H	0.8083645385	-2.0244190990	0.1642223054
H	-0.8083645385	-2.0244190990	0.1642223054
Be	0.0000000000	0.0000000000	0.8022771468

Frequencies CCSD(T)/TZ: 16.7, 34.7, 239.8, 556.8, 633.7, 637.7, 689.2, 806.0, 843.8, 1375.4, 1383.4, 1642.2, 1645.8, 1659.7, 1668.5, 3409.3, 3410.7, 3506.6, 3507.8, 3510.5, 3510.6

CCSD(T)/ATZ geometry of $Be(NH_3)_3$

Be	0.0000000000	0.0000000000	0.6338912919
N	1.5865809723	0.0000000000	-0.0840450086
N	-0.7932904862	-1.3740194272	-0.0840450086
N	-0.7932904862	1.3740194272	-0.0840450086
H	1.5518992403	0.0000000000	-1.1250200801
H	2.1287653540	-0.8173965659	0.2018465820
H	2.1287653540	0.8173965659	0.2018465820
H	-1.7722688680	-1.4348665923	0.2018465820
H	-0.3564964859	-2.2522631582	0.2018465820
H	-0.7759496202	-1.3439841662	-1.1250200801
H	-1.7722688680	1.4348665923	0.2018465820
H	-0.3564964859	2.2522631582	0.2018465820
H	-0.7759496202	1.3439841662	-1.1250200801

Frequencies MP2/ATZ: 177.6, 177.6, 192.1, 211.8, 211.8, 247.0, 541.3, 553.5, 584.4, 584.4, 672.3, 672.3, 725.7, 791.4, 791.4, 1267.0, 1267.0, 1269.3, 1555.1, 1555.1, 1576.1, 1626.5, 1626.5, 1643.5, 3054.4, 3054.4, 3078.9, 3417.0, 3437.7, 3437.7, 3503.9, 3503.9, 3519.7

CCSD(T)/ATZ geometry of $Be(NH_3)_3^+$

Be	0.0000000000	0.0000000000	0.5286566381
N	1.6576229129	0.0000000000	-0.0782420529
N	-0.8288114565	-1.4355435525	-0.0782420529
N	-0.8288114565	1.4355435525	-0.0782420529
H	1.8276151644	0.0000000000	-1.0877983418
H	2.1555738047	-0.8054096238	0.2997361758
H	2.1555738047	0.8054096238	0.2997361758
H	-1.7752920970	-1.4640768627	0.2997361758
H	-0.3802817077	-2.2694864865	0.2997361758
H	-0.9138075822	-1.5827611607	-1.0877983418
H	-1.7752920970	1.4640768627	0.2997361758
H	-0.3802817077	2.2694864865	0.2997361758
H	-0.9138075822	1.5827611607	-1.0877983418

Frequencies at MP2/ATZ level: 96.4, 112.7, 112.7, 205.6, 205.6, 257.2, 475.7, 562.4, 562.4, 563.0, 651.7, 651.7, 796.6, 796.6, 826.3, 1337.9, 1337.9, 1352.0, 1635.6, 1646.7, 1646.7, 1666.1, 1666.1, 1686.0, 3420.3, 3427.5, 3427.5, 3546.0, 3546.0, 3548.1, 3571.0, 3571.0, 3571.5

CCSD(T)/TZ geometry of $Be(NH_3)$-$Be(NH_3)$ dimer

Be	-0.6216627946	-0.8617530542	0.0000000000
Be	0.6216627946	0.8617530542	0.0000000000
N	0.0941718869	-2.4790930886	0.0000000000
N	-0.0941718869	2.4790930886	0.0000000000
H	-0.6249007557	-3.1974910086	0.0000000000
H	0.6758435872	-2.6217815767	-0.8212545678
H	0.6758435872	-2.6217815767	0.8212545678
H	0.6249007557	3.1974910086	0.0000000000
H	-0.6758435872	2.6217815767	-0.8212545678
H	-0.6758435872	2.6217815767	0.8212545678

Frequencies at CCSD(T)/DZ level: 95.7, 96.5, 102.1, 169.5, 186.2, 389.0, 525.3, 541.6, 549.2, 637.8, 638.4, 668.1, 1242.6, 1246.9, 1617.8, 1621.8, 1646.3, 1652.5, 3435.7, 3436.2, 3564.1, 3565.1, 3575.9, 3585.1

CCSD(T)/TZ geometry of $Be(NH_3)^+$-$Be(NH_3)^+$ dimer

Be	0.0000000000	0.0000000000	-1.0432434013
Be	0.0000000000	0.0000000000	1.0432434013
N	0.0000000000	0.0000000000	-2.7080439564
N	0.0000000000	0.0000000000	2.7080439564
H	0.9420523001	0.0000000000	-3.1157697444
H	-0.4710261501	-0.8158412236	-3.1157697444
H	-0.4710261501	0.8158412236	-3.1157697444
H	-0.9420523001	0.0000000000	3.1157697444
H	0.4710261501	-0.8158412236	3.1157697444
H	0.4710261501	0.8158412236	3.1157697444

Frequencies: 2.9, 114.0, 114.3, 243.8, 244.0, 327.7, 771.2, 771.3, 787.9, 787.9, 824.6, 1026.6, 1441.4, 1443.7, 1640.8, 1641.1, 1641.2, 1641.5, 3372.7, 3375.0, 3450.4, 3450.4, 3450.6, 3450.6

CCSD(T)/TZ geometry of $Be(NH_3)_2$-$Be(NH_3)_2$ dimer

Be	-0.3549557546	0.9726425387	0.0000000000
N	-0.1107323798	2.0749772736	-1.4173717756
H	-0.3157696481	1.4643503801	-2.2011452259
H	-0.7584167981	2.8544025063	-1.4749273563
H	0.8395142557	2.4182473789	-1.5320691098
N	-0.1107323798	2.0749772736	1.4173717756
H	0.8395142557	2.4182473789	1.5320691098
H	-0.3157696481	1.4643503801	2.2011452259
H	-0.7584167981	2.8544025063	1.4749273563
N	0.1107323798	-2.0749772736	-1.4173717756
H	0.7584167981	-2.8544025063	-1.4749273563
H	-0.8395142557	-2.4182473789	-1.5320691098
H	0.3157696481	-1.4643503801	-2.2011452259
N	0.1107323798	-2.0749772736	1.4173717756
H	0.7584167981	-2.8544025063	1.4749273563
H	0.3157696481	-1.4643503801	2.2011452259
H	-0.8395142557	-2.4182473789	1.5320691098
Be	0.3549557546	-0.9726425387	0.0000000000

Frequencies at MP2/ATZ level: -23.2, 75.8, 78.1, 84.7, 84.9, 105.5, 161.5, 167.3, 195.5, 209.6, 272.3, 328.1, 446.6, 482.2, 488.1, 505.8, 559.4, 614.1, 622.4, 636.2, 677.2, 696.0, 791.7, 840.5, 1224.8, 1232.6, 1234.2, 1247.1, 1562.4, 1614.6, 1624.8, 1636.2, 1637.4, 1649.0, 1664.8, 1945.9, 3380.0, 3414.0, 3438.1, 3456.6, 3566.3, 3572.0, 3579.1, 3600.1, 3614.1, 3614.6, 3614.9, 4299.5

CCSD(T)/TZ geometry of $Be(NH_3)_2^+$-$Be(NH_3)_2^+$ dimer

Be	0.0000000000	0.0000000000	1.0852119958
N	-0.9571633360	1.0282636890	2.1295046483
H	-1.8038741755	1.3565832082	1.6665159572
H	-1.2685205744	0.6257610216	3.0152620295
H	-0.4542306317	1.8810531259	2.3866134883
N	0.9571633360	-1.0282636890	2.1295046483
H	1.2685205744	-0.6257610216	3.0152620295
H	1.8038741755	-1.3565832082	1.6665159572
H	0.4542306317	-1.8810531259	2.3866134883
N	-0.9571633360	-1.0282636890	-2.1295046483
H	-1.2685205744	-0.6257610216	-3.0152620295
H	-0.4542306317	-1.8810531259	-2.3866134883
H	-1.8038741755	-1.3565832082	-1.6665159572
N	0.9571633360	1.0282636890	-2.1295046483
H	0.4542306317	1.8810531259	-2.3866134883
H	1.8038741755	1.3565832082	-1.6665159572
H	1.2685205744	0.6257610216	-3.0152620295
Be	0.0000000000	0.0000000000	-1.0852119958

Frequencies MP2/ATZ level: -21.6, 13.0, 25.4, 63.4, 63.5, 129.9, 132.4, 182.1, 261.9, 300.1, 315.7, 340.6, 576.5, 606.3, 607.5, 630.3, 631.2, 656.7, 710.9, 726.3, 790.5, 792.2, 824.5, 913.8, 1380.5, 1380.6, 1387.6, 1392.9, 1648.9, 1650.6, 1651.3, 1653.8, 1670.1, 1670.5, 1672.1, 1672.1, 3429.8, 3430.0, 3431.3, 3431.8, 3524.9, 3524.9, 3526.2, 3526.2, 3552.5, 3552.6, 3553.0, 3553.5

MP2/ATZ geometry of $[Be(NH_3)_3]$-$[Be(NH_3)_3]$ dimer

Be	0.000000	0.000000	1.089000
N	0.000000	1.628072	1.867049
H	-0.813000	2.156529	1.539974
H	0.813000	2.156529	1.539974
H	0.000000	1.696232	2.883866
N	-1.409952	-0.814036	1.867049
H	-2.274109	-0.374186	1.539974
H	-1.461109	-1.782343	1.539974
H	-1.468980	-0.848116	2.883866
N	-1.409952	0.814036	-1.867049
H	-2.274109	0.374186	-1.539974
H	-1.468980	0.848116	-2.883866
H	-1.461109	1.782343	-1.539974
N	-0.000000	-1.628072	-1.867049
H	-0.813000	-2.156529	-1.539974
H	0.813000	-2.156529	-1.539974
H	-0.000000	-1.696232	-2.883866
Be	-0.000000	-0.000000	-1.089000
N	1.409952	0.814036	-1.867049
H	2.274109	0.374186	-1.539974
H	1.461109	1.782343	-1.539974
H	1.468980	0.848116	-2.883866
N	1.409952	-0.814036	1.867049
H	1.468980	-0.848116	2.883866
H	2.274109	-0.374186	1.539974
H	1.461109	-1.782343	1.539974

Frequencies:

-11.2, 51.4, 51.4, 153.5, 153.5, 157.6, 177.9, 181.1, 183.9, 183.9, 185.8, 185.9, 188.3, 188.4, 239.8, 239.8, 250.8, 341.3, 471.1, 504.4, 504.4, 510.6, 510.6, 528.3, 531.0, 552.8, 609.9, 609.9, 654.3, 654.3, 710.4, 710.4, 747.5, 774.4, 774.4, 888.2, 1260.7, 1260.7, 1265.6, 1265.6, 1276.9, 1283.9, 1616.2, 1616.2, 1622.9, 1622.9, 1626.3, 1630.3, 1635.3, 1635.3, 1635.8, 1639.9, 1639.9, 1640.5, 3331.4, 3331.4, 3340.0, 3347.4, 3347.4, 3350.0, 3448.5, 3448.5, 3453.8, 3453.8, 3467.1, 3473.4, 3495.2, 3508.7, 3508.7, 3512.8, 3512.8, 3515.9

MP2/ATZ geometry of $[Be(NH_3)_3]^+$-$[Be(NH_3)_3]^+$ dimer

Be	0.287861	1.126623	0.000000
N	2.060083	1.536525	0.000000
H	2.532686	1.131933	0.804988
H	2.532686	1.131933	-0.804988
H	2.321382	2.523276	0.000000
N	-0.287861	2.136431	1.399139
H	0.049203	1.766489	2.284907
H	-1.301717	2.111609	1.479966
H	-0.039517	3.126492	1.406834
N	0.287861	-2.136431	1.399139
H	-0.049203	-1.766489	2.284907
H	0.039517	-3.126492	1.406834
H	1.301717	-2.111609	1.479966
N	-2.060083	-1.536525	0.000000
H	-2.532686	-1.131933	0.804988
H	-2.532686	-1.131933	-0.804988
H	-2.321382	-2.523276	0.000000
Be	-0.287861	-1.126623	0.000000
N	0.287861	-2.136431	-1.399139
H	-0.049203	-1.766489	-2.284907
H	1.301717	-2.111609	-1.479966
H	0.039517	-3.126492	-1.406834
N	-0.287861	2.136431	-1.399139
H	-0.039517	3.126492	-1.406834
H	0.049203	1.766489	-2.284907
H	-1.301717	2.111609	-1.479966

Frequencies: -3.4, 107.2, 107.2, 144.7, 149.8, 149.8, 155.9, 160.2, 173.0, 173.0, 182.0, 182.0, 213.0, 213.0, 238.4, 238.4, 279.8, 327.8, 468.5, 489.7, 489.7, 490.9, 490.9, 514.7, 520.7, 523.8, 606.7, 606.7, 650.0, 650.0, 728.1, 728.1, 775.1, 775.1, 798.3, 850.3, 1334.0, 1334.1, 1335.2, 1335.2, 1349.6, 1357.5, 1647.6, 1651.3, 1666.3, 1666.3, 1666.4, 1666.4, 1667.0, 1667.0, 1671.9, 1671.9, 1688.9, 1693.2, 3434.8, 3436.8, 3439.1, 3439.1, 3439.3, 3439.3, 3548.4, 3549.3, 3549.3, 3549.8, 3549.8, 3551.6, 3575.2, 3575.2, 3575.4, 3575.5, 3575.5, 3576.8

MP2/(Be, N: TZ and H: ATZ) geometry of $[Be(NH_3)_4]$-$[Be(NH_3)_4]$ dimer

Be	-0.000000	0.000000	3.088767
Be	-0.000000	-0.000000	-3.088767
N	-0.000000	1.619581	2.481942
N	-1.402598	-0.809790	2.481942
N	1.402598	-0.809790	2.481942
N	1.402598	0.809790	-2.481942
N	-1.402598	0.809790	-2.481942
N	-0.000000	0.000000	4.818695
N	-0.000000	-0.000000	-4.818695
H	-0.000000	1.606245	1.450356
H	-1.391049	-0.803122	1.450356
H	1.391049	-0.803122	1.450356
H	1.391049	0.803122	-1.450356
H	-1.391049	0.803122	-1.450356
H	-0.824816	2.154748	2.777544
H	0.824816	2.154748	2.777544
H	-1.453658	-1.791685	2.777544
H	-2.278474	-0.363062	2.777544
H	2.278474	-0.363062	2.777544
H	1.453658	-1.791685	2.777544
H	2.278474	0.363062	-2.777544
H	1.453658	1.791685	-2.777544
H	-1.453658	1.791685	-2.777544
H	-2.278474	0.363062	-2.777544
H	-0.000000	-0.952540	5.205595
H	0.824924	0.476270	5.205595
H	-0.824924	0.476270	5.205595
H	-0.824924	-0.476270	-5.205595
H	0.000000	0.952540	-5.205595
H	0.824924	-0.476270	-5.205595
N	-0.000000	-1.619581	-2.481942
H	-0.000000	-1.606245	-1.450356
H	-0.824816	-2.154748	-2.777544
H	0.824816	-2.154748	-2.777544

Frequencies B3LYP/DFT: -14.0, 19.4, 19.5, 23.3, 23.3, 34.6, 162.4, 162.5, 172.8, 172.8, 173.0, 173.0, 183.2, 183.2, 183.5, 183.5, 183.6, 185.8, 186.2, 190.8, 225.4, 230.4, 230.4, 231.2, 231.2, 232.9, 261.6, 263.8, 278.7, 281.0, 292.2, 292.9, 302.5, 325.9, 455.5, 455.6, 571.9, 574.4, 582.1, 589.9, 595.9, 598.4, 599.1, 599.1, 599.6, 599.6, 606.4, 606.5, 629.3, 629.4, 639.4, 639.4, 640.0, 640.0, 730.7, 730.7, 731.2, 731.2, 857.4, 857.4, 860.9, 860.9, 867.1, 872.4, 1285.3, 1288.4, 1292.2, 1292.3, 1292.9, 1293.6, 1571.9, 1574.4, 1581.9, 1581.9, 1582.1, 1585.6, 1595.9, 1595.9, 1595.9, 1597.4, 3178.3, 3178.3, 3183.6, 3183.6, 3218.7, 3223.3, 3263.2, 3263.2, 3263.8, 3267.7, 3278.7, 3281.0, 3301.1, 3301.1, 3302.5, 3325.9