Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

SUPPLEMENTARY INFORMATION

Ternary 12-electron $CBe_3X_3^+$ (X = H, Li, Na, Cu, Ag) clusters: planar tetracoordinate carbons and superalkali cations

Jin-Chang Guo,‡[ab] Lin-Yan Feng,‡[b] Chuan Dong,*[a] and Hua-Jin Zhai*[b]

[a]*Institute of Environmental Science, Center of Environmental Science and Engineering Research, Shanxi University, Taiyuan 030006, China*

[b]*Nanocluster Laboratory, Institute of Molecular Science, Shanxi University, Taiyuan 030006, China*

*E-mail: dc@sxu.edu.cn (C.D.), hj.zhai@sxu.edu.cn (H.J.Z.)

Table S1. Cartesian coordinates for optimized global-minimum (GM) clusters **1**–**5** of $CBe_3X_3^+$ (X = H, Li, Na, Cu, Ag) at the PBE0-D3/def2-TZVPP level, as well as those for their three lowest-lying ***n*B**–***n*D** isomers.

Table S2. Orbital composition analysis for occupied canonical molecular orbitals (CMOs) of $CBe_3H_3^+$ GM (**1**, C_{2v}, $^1A_1$) cluster.

Table S3. Orbital composition analysis for occupied CMOs of $CBe_3Li_3^+$ GM (**2**, C_{2v}, $^1A_1$) cluster.

Table S4. Orbital composition analysis for the lowest unoccupied molecular orbitals (LUMOs) of GM clusters **1**–**5** of $CBe_3X_3^+$ (X = H, Li, Na, Cu, Ag).

Figure S1. Calculated Wiberg bond indices (WBIs; blue color) and natural atomic charges (in |e|; red color) from natural bond orbital (NBO) analyses for GM clusters **1**–**5** of $CBe_3X_3^+$ (X = H, Li, Na, Cu, Ag).

Figure S2. Calculated WBIs (blue color) and bond distances (in Å; black color) between terminal X atom and adjacent Be atoms for GM structures **1**–**5** of $CBe_3X_3^+$ (X = H, Li, Na, Cu, Ag) clusters. Also presented is a C_{2v} $CBe_3Cu_3^+$ cluster, which is a transition state (TS).

Figure S3. Calculated root-mean-square deviations (RMSDs) of GM clusters **1**–**5** of $CBe_3X_3^+$ (X = H, Li, Na, Cu, Ag) during the Born-Oppenheimer molecular dynamics (BOMD) simulations at 300 K.

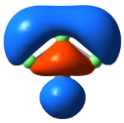
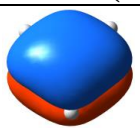
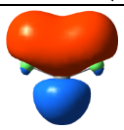
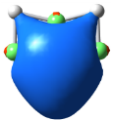
Figure S4. Chemical bonding of C_{2v} $CBe_3Na_3^+$ (**3**) cluster. (a) CMOs. (b) AdNDP scheme. Occupation numbers (ONs) are shown.

Figure S5. Chemical bonding of C_s $CBe_3Cu_3^+$ (**4**) cluster. (a) CMOs. (b) AdNDP scheme. ONs are shown.

Figure S6. Chemical bonding of C_{2v} $CBe_3Ag_3^+$ (**5**) cluster. (a) CMOs. (b) AdNDP scheme. ONs are shown.

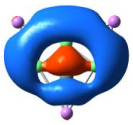
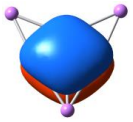
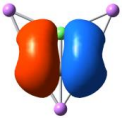
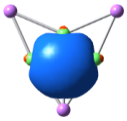
Figure S7. Nucleus independent chemical shifts (NICSs) for clusters **1**–**5**. NICS(0) (blue color) is calculated at the center of a triangle, whereas NICS(1) (red color) is at 1 Å above the center of a triangle or above the C center.

Table S2. Orbital composition analysis for occupied canonical molecular orbitals (CMOs) of $CBe_3H_3^+$ GM (**1**, C_{2v}, $^1A_1$) cluster. Main components are highlighted in **bold**.

Subsystem	CMO	C (%)		Be_3 (%)		H (%)[a]	H_2 (%)[a]
		s/p	total	s/p	total	s	s
Be-H-Be 3c-2e σ	 HOMO−2 (a_1)	2.9/30.0	**32.9**	6.1/14.4	**20.5**	8.9	**37.7**
	 HOMO−3 (b_2)	0.0/14.0	14.0	10.9/29.9	**40.8**	0.0	**45.2**
2π aromaticity	 HOMO (b_1)	0.0/65.4	**65.4**	0.0/34.6	**34.6**	0.0	0.0
6σ aromaticity	 HOMO−1 (b_2)	0.0/70.6	**70.6**	1.6/13.4	15.0	0.0	14.4
	 HOMO−4 (a_1)	1.7/40.6	**42.3**	12.9/6.8	**19.7**	11.6	**26.4**
	 HOMO−5 (a_1)	62.5/0.0	**62.5**	12.0/11.2	**23.2**	12.7	1.6

[a] H and H_2 represent the terminal and bridging H atoms, respectively.

Table S3. Orbital composition analysis for occupied CMOs of $CBe_3Li_3^+$ GM (**2**, C_{2v}, $^1A_1$) cluster. Main components are highlighted in **bold**.

Subsystem	CMO	C (%)		Be_3 (%)		Li (%)[a]		Li_2 (%)[a]	
		s/p	total	s/p	total	s/p	total	s/p	total
Be-Li-Be 3c-2e σ	 HOMO (b_2)	0.0/13.5	13.5	12.3/66.1	**78.4**	0.0/0.0	0.0	7.3/0.8	8.1
	 HOMO−1 (a_1)	0.3/20.5	**20.5**	51.1/18.9	**70.0**	0.9/0.3	1.2	7.5/0.8	8.3
2π aromaticity	 HOMO (b_1)	0.0/67.2	**67.2**	0.0/32.5	**32.5**	0.0/0.2	0.2	0.0/0.1	0.1
6σ aromaticity	 HOMO−3 (a_1)	6.4/56.9	**63.3**	34.3/0.6	**34.9**	0.6/0.0	0.6	1.2/0.0	1.2
	 HOMO−4 (b_2)	0.0/72.3	**72.3**	13.4/12.3	**25.7**	0.0/0.2	0.2	0.4/0.2	0.6
	 HOMO−5 (a_1)	66.3/2.7	**69.0**	14.5/14.8	**29.3**	0.3/0.3	0.6	0.0/0.0	0.0

[a] Li and Li_2 represent the terminal and bridging Li atoms, respectively.

Table S4. Orbital composition analysis for the lowest unoccupied molecular orbitals (LUMOs) of GM clusters **1**–**5** of $CBe_3X_3^+$ (X = H, Li, Na, Cu, Ag). Main components are highlighted in **bold**.

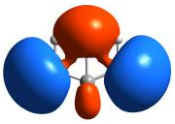
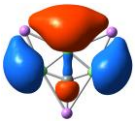
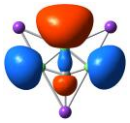
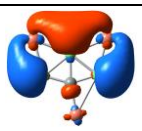
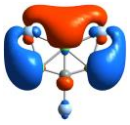
Species	LUMO	Symmetry	Be_3 (%)	X_3 (%)	C (%)
$CBe_3H_3^+$ (**1**)		a_1	**98.4**	1.5	0.1
$CBe_3Li_3^+$ (**2**)		a_1	**85.8**	**11.0**	**3.2**
$CBe_3Na_3^+$ (**3**)		a_1	**87.8**	**7.5**	**4.7**
$CBe_3Cu_3^+$ (**4**)		a′	**86.0**	**12.4**	1.6
$CBe_3Ag_3^+$ (**5**)		a_1	**86.4**	**12.3**	1.3

Figure S1. Calculated Wiberg bond indices (WBIs; blue color) and natural atomic charges (in |e|; red color) from natural bond orbital (NBO) analyses for GM clusters **1**–**5** of $CBe_3X_3^+$ (X = H, Li, Na, Cu, Ag).

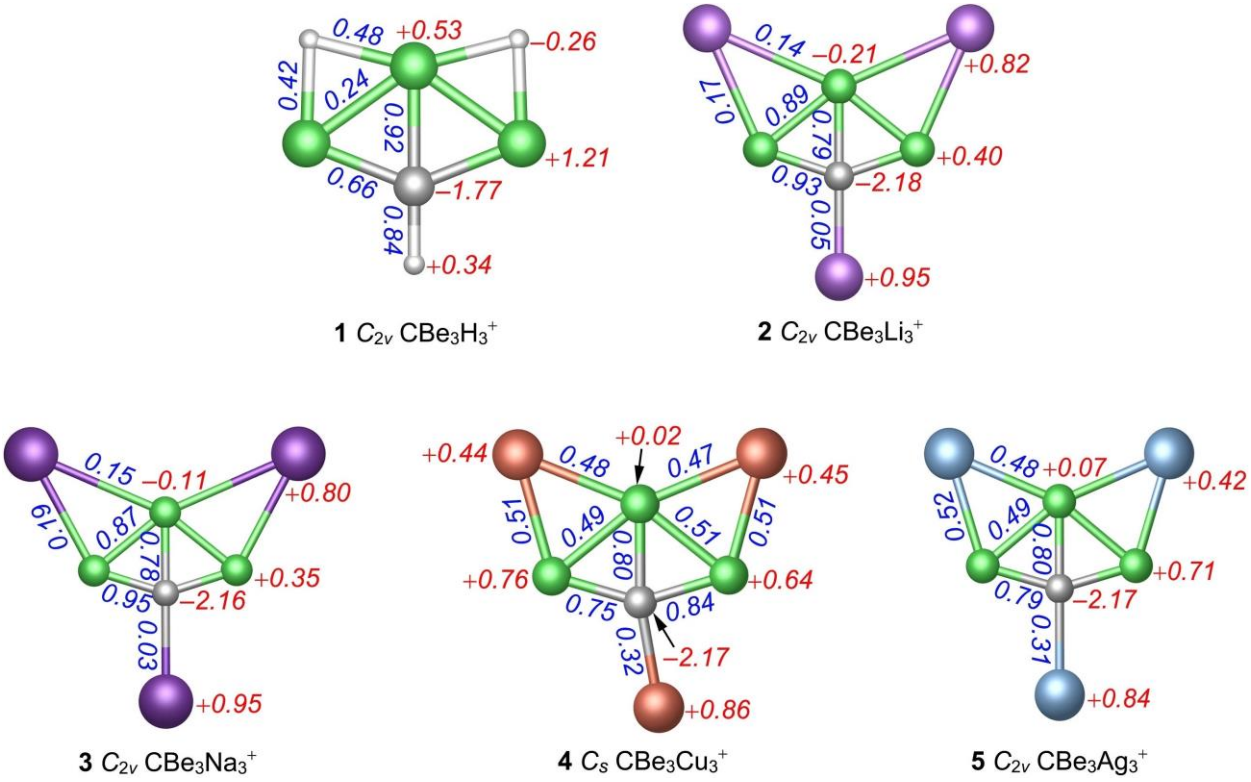
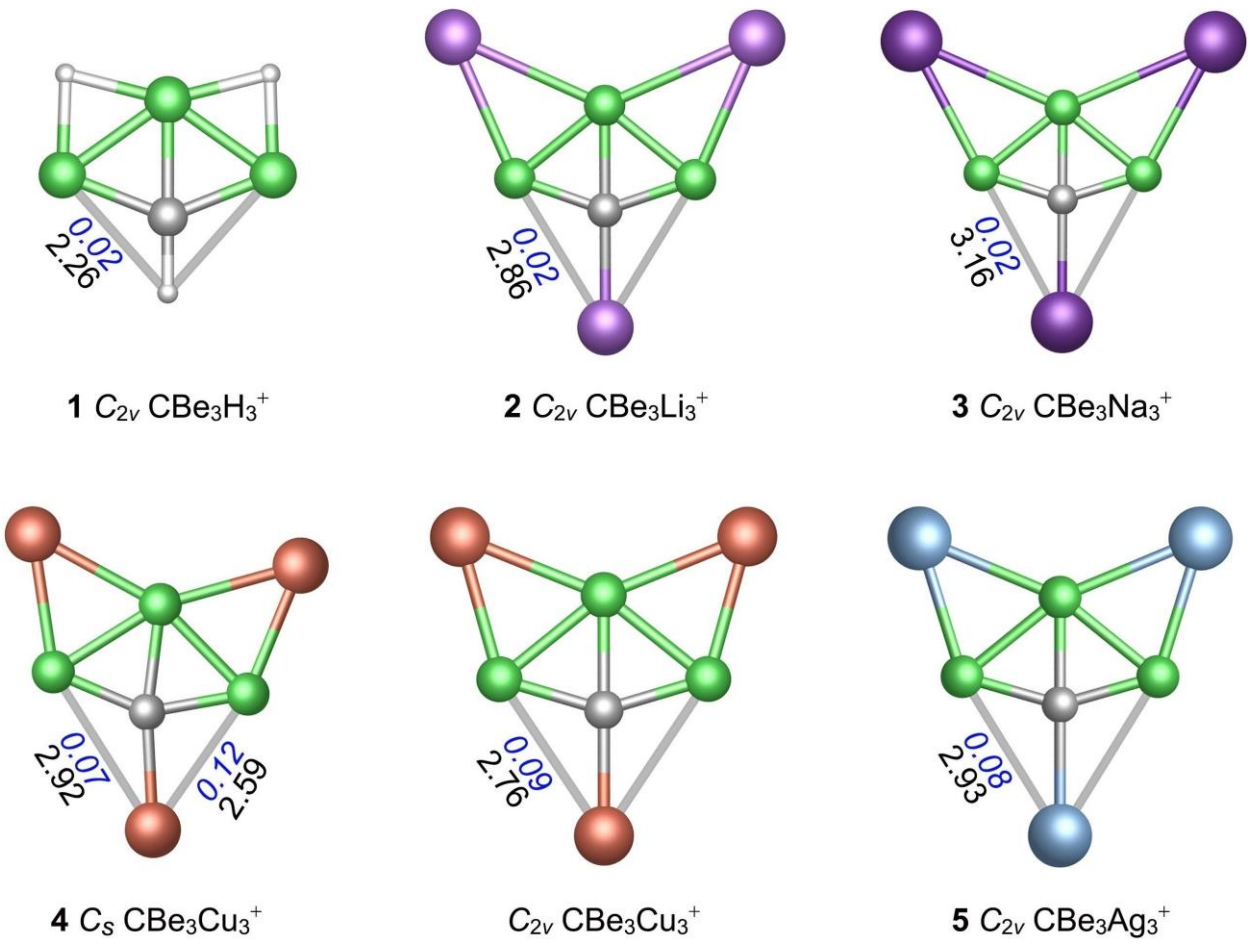


Figure S2. Calculated WBIs (blue color) and bond distances (in Å; black color) between terminal X atom and adjacent Be atoms for GM structures **1**–**5** of $CBe_3X_3^+$ (X = H, Li, Na, Cu, Ag) clusters. Also presented is a C_{2v} $CBe_3Cu_3^+$ cluster, which is a transition state (TS).



1 C_{2v} $CBe_3H_3^+$ **2** C_{2v} $CBe_3Li_3^+$ **3** C_{2v} $CBe_3Na_3^+$

4 C_s $CBe_3Cu_3^+$ C_{2v} $CBe_3Cu_3^+$ **5** C_{2v} $CBe_3Ag_3^+$

Figure S3. Calculated root-mean-square deviations (RMSDs) of GM clusters **1**–**5** of $CBe_3X_3^+$ (X = H, Li, Na, Cu, Ag) during the Born-Oppenheimer molecular dynamics (BOMD) simulations at 300 K.

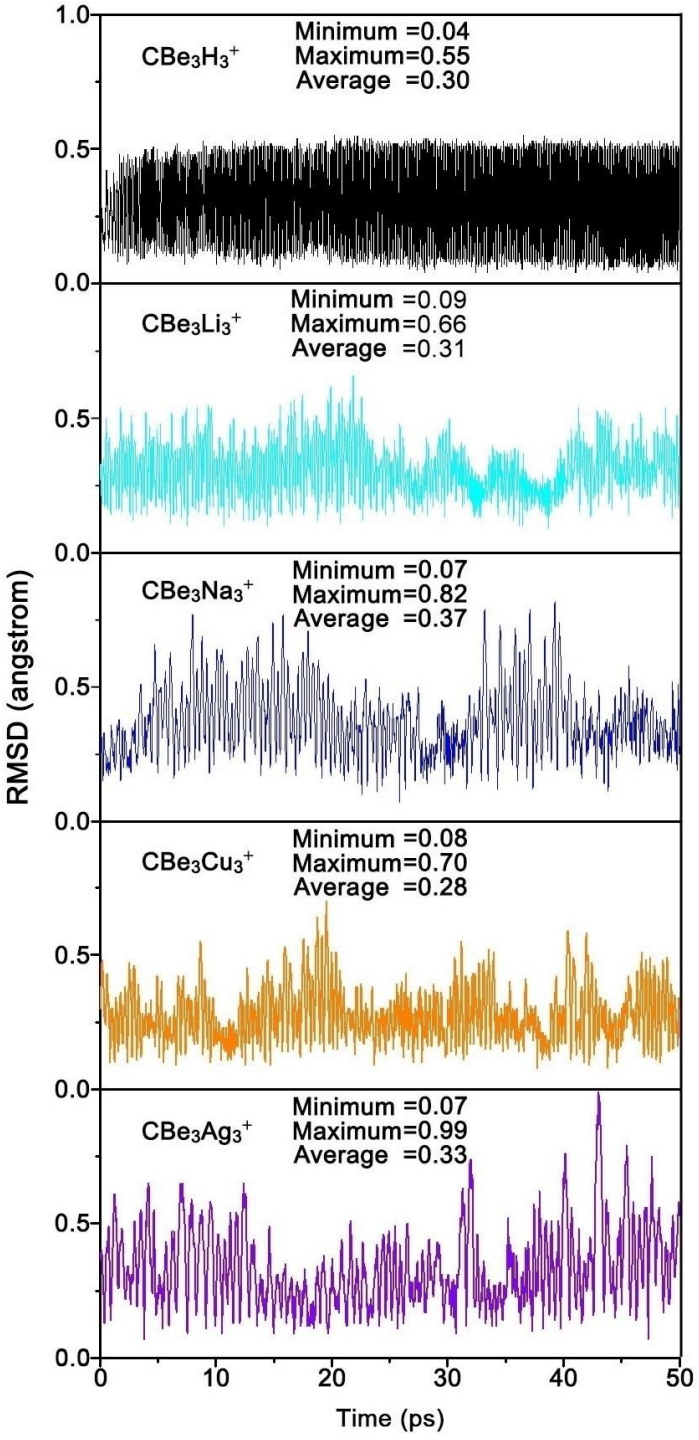


Figure S4. Chemical bonding of C_{2v} $CBe_3Na_3^+$ (**3**) cluster. (a) CMOs. (b) AdNDP scheme. Occupation numbers (ONs) are shown.

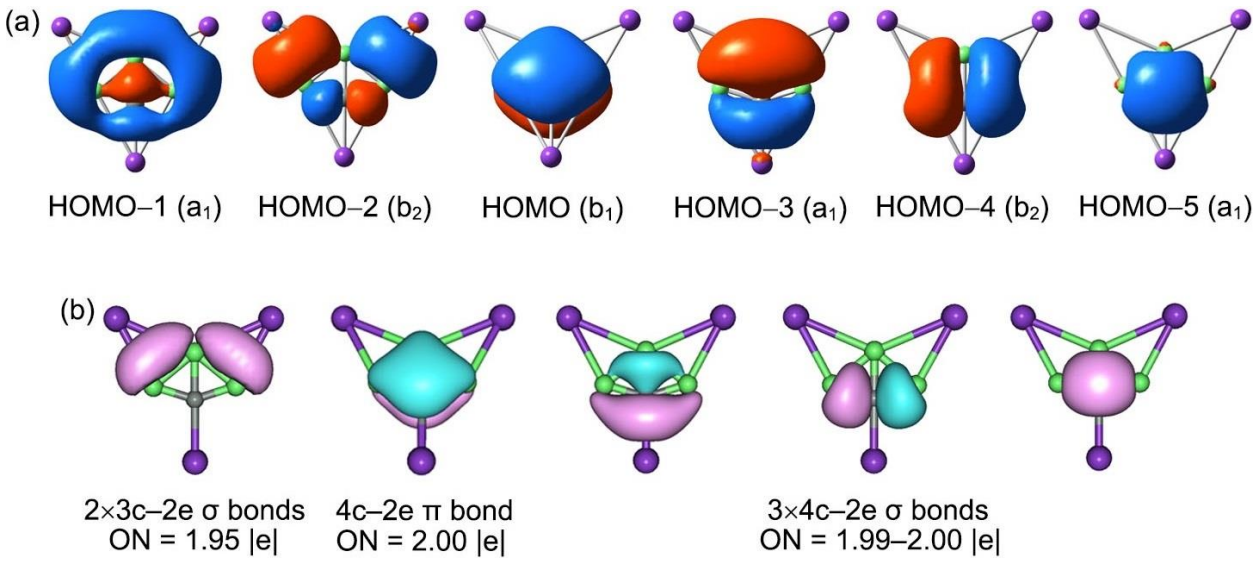


Figure S5. Chemical bonding of C_s $CBe_3Cu_3^+$ (**4**) cluster. (a) CMOs. (b) AdNDP scheme. ONs are shown.

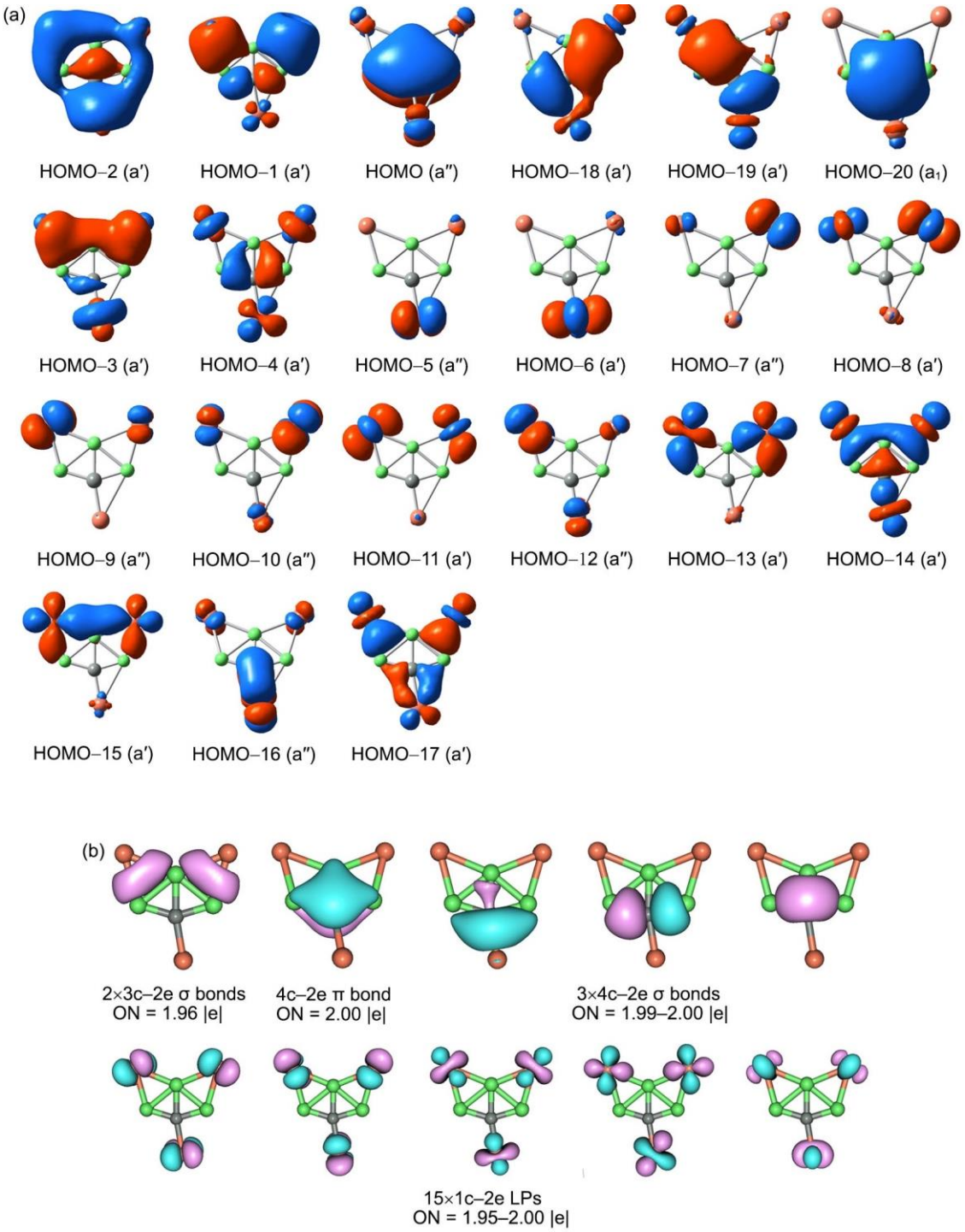


Figure S6. Chemical bonding of C_{2v} $CBe_3Ag_3^+$ (**5**) cluster. (a) CMOs. (b) AdNDP scheme. ONs are shown.

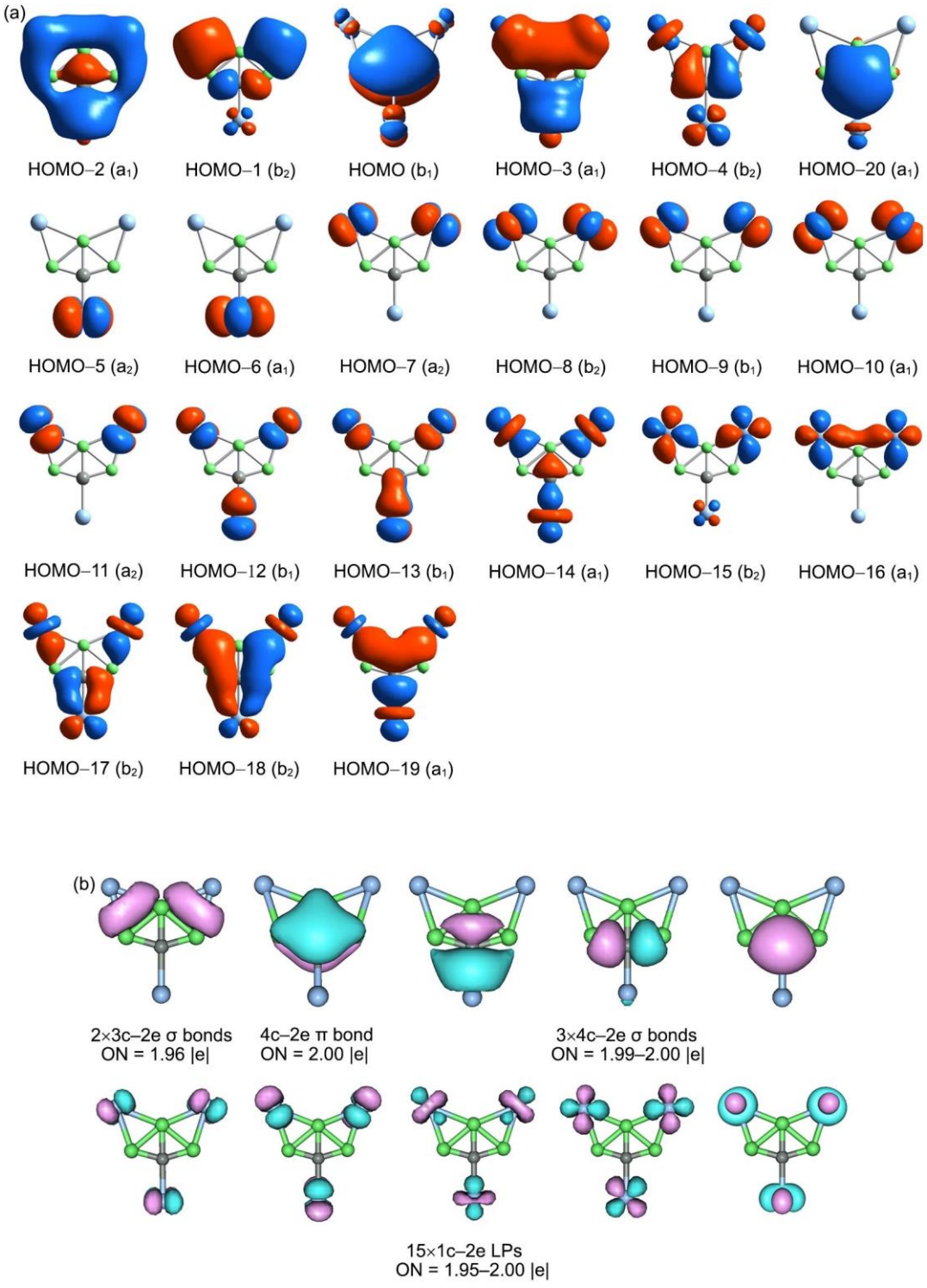


Figure S7. Nucleus independent chemical shifts (NICSs) for clusters **1**–**5**. NICS(0) (blue color) is calculated at the center of a triangle, whereas NICS(1) (red color) is at 1 Å above the center of a triangle or above the C center.

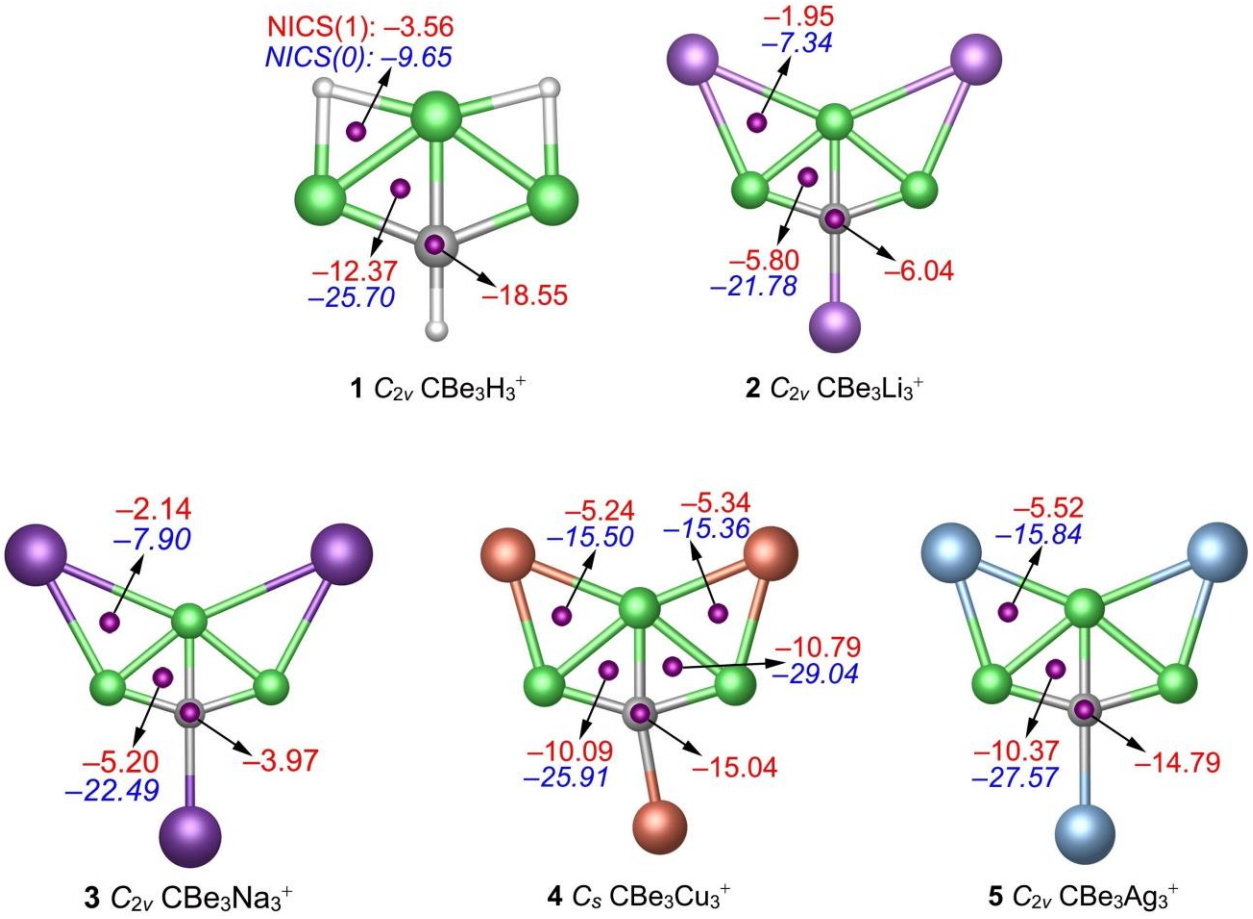


Table S1. Cartesian coordinates for optimized global-minimum (GM) clusters **1**–**5** of $CBe_3X_3^+$ (X = H, Li, Na, Cu, Ag) at the PBE0-D3/def2-TZVPP level, as well as those for their three lowest-lying ***n*B**–***n*D** isomers.

1 $CBe_3H_3^+$ (C_{2v}, $^1A_1$)

C	0.00000000	0.68946800	0.00000000
Be	1.50563800	0.09090700	0.00000000
Be	−1.50563800	0.09090700	0.00000000
Be	0.00000000	−0.98514800	0.00000000
H	0.00000000	1.78155400	0.00000000
H	1.45917300	−1.35251200	0.00000000
H	−1.45917300	−1.35251200	0.00000000

1B (C_s, $^1A'$)

C	0.43562100	0.43755500	0.00000000
Be	0.43562100	−0.86670100	0.95232300
Be	0.43562100	−0.86670100	−0.95232300
Be	−1.19185500	0.92474000	0.00000000
H	0.90331500	1.42428800	0.00000000
H	−2.48505500	1.20294400	0.00000000
H	0.25046100	−2.01791600	0.00000000

1C (C_s, $^1A'$)

C	0.20110500	0.30487000	0.00000000
Be	0.20110500	−0.65076400	1.39292400
Be	0.20110500	−0.65076400	−1.39292400
Be	−1.02911200	1.30444100	0.00000000
H	0.09721600	−1.39114500	2.48395100
H	0.09721600	−1.39114500	−2.48395100
H	1.10655300	0.94141900	0.00000000

1D (C_s, $^1A'$)

C	0.00000000	0.88277700	0.00000000
Be	−1.68682600	0.89960600	0.00000000
Be	1.59678200	−2.56002900	0.00000000
Be	0.68184200	−0.58753200	0.00000000

H	−3.01197600	0.81105100	0.00000000
H	0.32239200	1.44205500	0.89152200
H	0.32239200	1.44205500	−0.89152200

2 $CBe_3Li_3^+$ (C_{2v}, $^1A_1$)

C	0.00000000	0.82001500	0.00000000
Be	1.50099500	0.30918000	0.00000000
Be	−1.50099500	0.30918000	0.00000000
Be	0.00000000	−0.89640900	0.00000000
Li	−2.52061900	−2.00660700	0.00000000
Li	2.52061900	−2.00660700	0.00000000
Li	0.00000000	2.74391700	0.00000000

2B (C_s, $^1A'$)

C	0.17143500	0.16157800	0.00000000
Be	−1.31549000	0.86410100	0.00000000
Be	0.76745800	−0.98586900	0.94496500
Be	0.76745800	−0.98586900	−0.94496500
Li	0.76745800	2.07262500	0.00000000
Li	1.84587500	−3.24724300	0.00000000
Li	−3.24877000	2.32831100	0.00000000

2C (C_s, $^1A'$)

C	−0.06699600	0.39199400	0.00000000
Be	1.07304500	−0.81122900	0.00000000
Be	−1.25044000	0.98158000	0.95965300
Be	−1.25044000	0.98158000	−0.95965300
Li	2.26156000	−2.94640000	0.00000000
Li	1.02665000	2.10706800	0.00000000
Li	−1.25044000	−1.48056200	0.00000000

2D (C_1, ^1A)

C	0.60754800	−0.22962200	−0.07617000
Be	1.16278000	0.97633100	0.85338200
Be	−0.72240200	0.75460600	0.61936100
Be	−0.79801000	−0.90330200	−0.41648000
Li	−3.21122300	−0.28833500	0.12692400

Li	0.59615100	1.34838700	−1.50392200
Li	1.87681900	−1.70432100	0.12098600

3 $CBe_3Na_3^+$ (C_{2v}, $^1A_1$)

C	0.00000000	0.98320100	0.00000000
Be	1.51291600	0.50502200	0.00000000
Be	−1.51291600	0.50502200	0.00000000
Be	0.00000000	−0.72468500	0.00000000
Na	0.00000000	3.27488200	0.00000000
Na	2.83681800	−1.95747100	0.00000000
Na	−2.83681800	−1.95747100	0.00000000

3B (C_s, $^1A'$)

C	0.01400800	0.20334100	0.00000000
Be	0.35617300	−1.39754700	0.00000000
Be	0.35617300	1.43899900	0.95590400
Be	0.35617300	1.43899900	−0.95590400
Na	1.31299800	4.07959600	0.00000000
Na	0.51641000	−4.09803100	0.00000000
Na	−2.22560100	−0.63082400	0.00000000

3C (C_s, $^1A'$)

C	0.60203100	−0.64459300	0.00000000
Be	−0.69795700	0.36894500	0.00000000
Be	1.77326600	−1.21962600	0.96654500
Be	1.77326600	−1.21962600	−0.96654500
Na	−0.51781500	−2.83975700	0.00000000
Na	1.77326600	1.65079200	0.00000000
Na	−2.61967700	2.29340000	0.00000000

3D (C_1, ^1A)

C	0.79216500	−0.01875800	0.04920600
Be	1.29910600	0.65409900	1.42186100
Be	−0.55771200	0.22349700	1.16885400
Be	−0.52525400	−0.56548900	−0.66612000
Na	−3.25236400	−0.84672200	−0.05176900
Na	0.37543900	2.44958200	−0.42471700

Na	2.36623800	−1.70612200	−0.25020700

4 $CBe_3Cu_3^+$ (C_s, $^1A'$)

C	−0.20659900	−0.98605400	0.00000000
Be	−1.67235100	−0.36006300	0.00000000
Be	1.36979700	−0.70734800	0.00000000
Be	0.00000000	0.69142700	0.00000000
Cu	2.19210500	1.30057800	0.00000000
Cu	−1.99193200	1.78708300	0.00000000
Cu	−0.11569800	−2.83179000	0.00000000

4B (C_s, $^1A'$)

C	0.27252400	1.17604400	0.00069600
Be	1.47699500	0.66752900	0.96004800
Be	1.47678000	0.66827900	−0.95935300
Be	−1.34384700	1.36182700	0.00028400
Cu	−3.06010300	0.09445300	−0.00028200
Cu	−0.56513400	−0.65921200	0.00026400
Cu	3.34679400	−0.05064800	−0.00026000

4C (C_s, $^1A'$)

C	−0.31307500	1.43234400	0.00000000
Be	0.51351200	−0.01762600	0.00000000
Be	−1.41042300	0.69110700	0.96529400
Be	−1.41042300	0.69110700	−0.96529400
Cu	0.75509000	2.95240200	0.00000000
Cu	−1.41042300	−1.33539900	0.00000000
Cu	1.03836000	−2.10157000	0.00000000

4D (C_{2v}, $^1A_1$)

C	0.00000000	−2.49098200	0.00000000
Be	1.13500300	−1.36582300	0.00000000
Be	0.00000000	−4.01311100	0.00000000
Be	−1.13500300	−1.36582300	0.00000000
Cu	−2.40706300	0.41592000	0.00000000
Cu	0.00000000	0.61384600	0.00000000
Cu	2.40706300	0.41592000	0.00000000

5 $CBe_3Ag_3^+$ (C_{2v}, $^1A_1$)

C	0.00000000	0.99886400	0.00000000
Be	1.53556100	0.56077700	0.00000000
Be	−1.53556100	0.56077700	0.00000000
Be	0.00000000	−0.68679500	0.00000000
Ag	2.20581300	−1.61072700	0.00000000
Ag	−2.20581300	−1.61072700	0.00000000
Ag	0.00000000	3.05694000	0.00000000

5B (C_s, $^1A'$)

C	−0.67018400	−0.98184300	0.00000000
Be	0.37222600	−1.74134000	0.97488900
Be	0.37222600	−1.74134000	−0.97488900
Be	−1.81212200	0.17162800	0.00000000
Ag	−2.25822500	2.36357500	0.00000000
Ag	0.37222600	1.05479700	0.00000000
Ag	2.06242100	−3.01123900	0.00000000

5C (C_{2v}, $^1A_1$)

C	0.00000000	−2.65819700	0.00000000
Be	1.15806200	−1.55961900	0.00000000
Be	0.00000000	−4.17910500	0.00000000
Be	−1.15806200	−1.55961900	0.00000000
Ag	−2.67196500	0.17495400	0.00000000
Ag	2.67196500	0.17495400	0.00000000
Ag	0.00000000	0.61057200	0.00000000

5D (C_s, $^1A'$)

C	1.41440100	1.43701500	0.00000000
Be	0.19631400	2.46459400	0.00000000
Be	2.59767900	2.40153400	0.00000000
Be	0.00000000	0.46644700	0.00000000
Ag	2.03323500	−0.69021200	0.00000000
Ag	−0.46692500	−1.79781800	0.00000000
Ag	−1.98465800	1.85074500	0.00000000