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

SUPPLEMENTARY INFORMATION

Ternary 14-electron XB_2Be_2 (X = Si, Ge, Sn, Pb) clusters: planar tetracoordinate silicon (ptSi) system and its ptGe/Sn/Pb congeners

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Table S1. Cartesian coordinates for optimized global-minimum (GM) clusters **1**–**4** of the XB_2Be_2 (X = Si, Ge, Sn, Pb) systems at the PBE0-D3/def2-QZVP level.

Table S2. Composition analysis for occupied canonical molecular orbitals (CMOs) of SiB_2Be_2 GM cluster **1**. Main components are highlighted in **bold**.

Table S3. Composition analysis for CMOs of PbB_2Be_2 GM cluster **4**. Main components are highlighted in **bold**.

Figure S1. Optimized structures of GM clusters **1**−**4** and three lowest-lying isomers (***n*B**–***n*D**) for the XB_2Be_2 (X = Si, Ge, Sn, Pb) systems at the PBE0-D3/def2-QZVP level. Relative energies are listed in kcal mol^{-1} at the PBE0-D3/def2-QZVP and single-point CCSD(T)/def2-QZVP//PBE0-D3 /def2-QZVP (in square brackets) levels. Shown in curly brackets are complementary energetics data at the single-point CCSD(T)/def2-QZVP

//B3LYP-D3/def2-QZVP level. All three sets of relative energies include zero-point energy (ZPE) corrections at PBE0-D3 or B3LYP-D3.

Figure S2. Wiberg bond indices (WBIs; in black color) and natural atomic charges (in |e|; red color) for GM clusters **1**−**4**, calculated at the PBE0-D3/def2-QZVP level.

Figure S3. Comparative root-mean-square deviations (RMSDs) of cluster **1** during the Born-Oppenheimer molecular dynamics (BOMD) simulations at room temperature (298 K) and at a higher temperature (1200 K).

Figure S4. Chemical bonding analyses for GM cluster **4**. (a) Occupied CMOs. (b) AdNDP scheme. Occupation numbers (ONs) are shown.

Figure S5. Electron localization functions (ELFs), ELF_σ and ELF_π, for GM cluster **4**. (a) ELF_σ for peripheral Lewis-type two-center two-electron (2c-2e) σ bonds. (b) ELF_π for global 2π electrons. (c) ELF_σ for global 2σ electrons.

Table S1. Cartesian coordinates for optimized global-minimum (GM) clusters **1**–**4** of the XB_2Be_2 (X = Si, Ge, Sn, Pb) systems at the PBE0-D3/def2-QZVP level.

1 SiB_2Be_2 (C_{2v}, $^1A_1$)

Si	0.00000000	0.00000000	0.81445500
Be	0.00000000	1.93405800	0.08620500
Be	0.00000000	-1.93405800	0.08620500
B	0.00000000	0.77415100	-1.20920100
B	0.00000000	-0.77415100	-1.20920100

2 GeB_2Be_2 (C_{2v}, $^1A_1$)

Ge	0.00000000	0.00000000	0.56283600
Be	0.00000000	1.93517700	-0.27962800
Be	0.00000000	-1.93517700	-0.27962800
B	0.00000000	0.77561700	-1.57737300
B	0.00000000	-0.77561700	-1.57737300

3 SnB_2Be_2 (C_{2v}, $^1A_1$)

Sn	0.00000000	0.00000000	0.48193500
Be	0.00000000	2.00600900	-0.65138100
Be	0.00000000	-2.00600900	-0.65138100
B	0.00000000	0.77444500	-1.88857000
B	0.00000000	-0.77444500	-1.88857000

4 PbB_2Be_2 (C_{2v}, $^1A_1$)

Pb	0.00000000	0.00000000	0.34915700
Be	0.00000000	2.00395000	-0.90326700
Be	0.00000000	-2.00395000	-0.90326700
B	0.00000000	0.77337500	-2.14047400
B	0.00000000	-0.77337500	-2.14047400

Table S2. Composition analysis for occupied canonical molecular orbitals (CMOs) of SiB_2Be_2 GM cluster **1**. Main components are highlighted in **bold**.

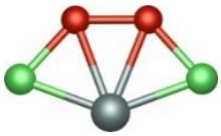
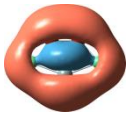
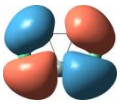
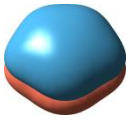
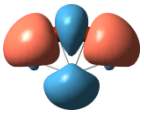
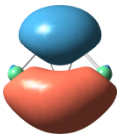
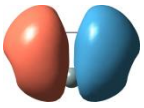
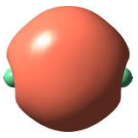
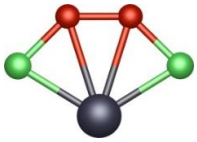
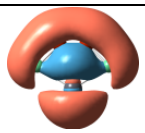
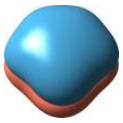
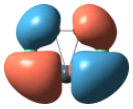
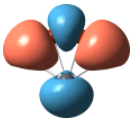
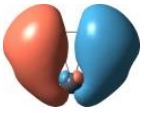
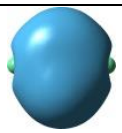
	Si (%)		Be (%)		B (%)	
	3s	3p	2s	2p	2s	2p
 HOMO	3.5	**22.7**	**18.2**	2.9	**10.0**	**42.7**
 HOMO-1	0.0	**37.8**	2.4	**27.5**	**13.5**	**18.3**
 HOMO-2	0.0	**34.7**	0.0	**14.0**	0.0	**51.3**
 HOMO-3	6.1	6.9	**10.6**	**10.0**	2.7	**63.1**
 HOMO-4	**36.5**	4.8	3.0	9.1	**24.6**	**20.6**
 HOMO-5	0.0	**23.5**	**17.1**	4.1	**24.2**	**29.1**
 HOMO-6	**25.4**	5.8	6.3	4.9	**39.4**	**16.1**

Table S3. Composition analysis for CMOs of PbB_2Be_2 GM cluster **4**. Main components are highlighted in **bold**.

	Pb (%)		Be (%)		B (%)	
	6s	6p	2s	2p	2s	2p
 HOMO	3.4	**19.0**	**12.9**	5.3	7.9	**50.7**
 HOMO-1	0.0	**25.9**	0.0	**16.9**	0.0	**57.0**
 HOMO-2	0.0	**40.6**	9.2	**27.6**	**10.6**	**10.4**
 HOMO-3	5.4	7.2	**13.8**	4.7	0.6	**67.5**
 HOMO-4	0.0	**11.1**	**22.0**	2.2	**27.2**	**34.2**
 HOMO-5	**39.0**	2.8	0.0	6.8	**36.2**	**11.2**
 HOMO-6	**33.2**	2.8	8.3	5.0	**33.1**	**12.1**

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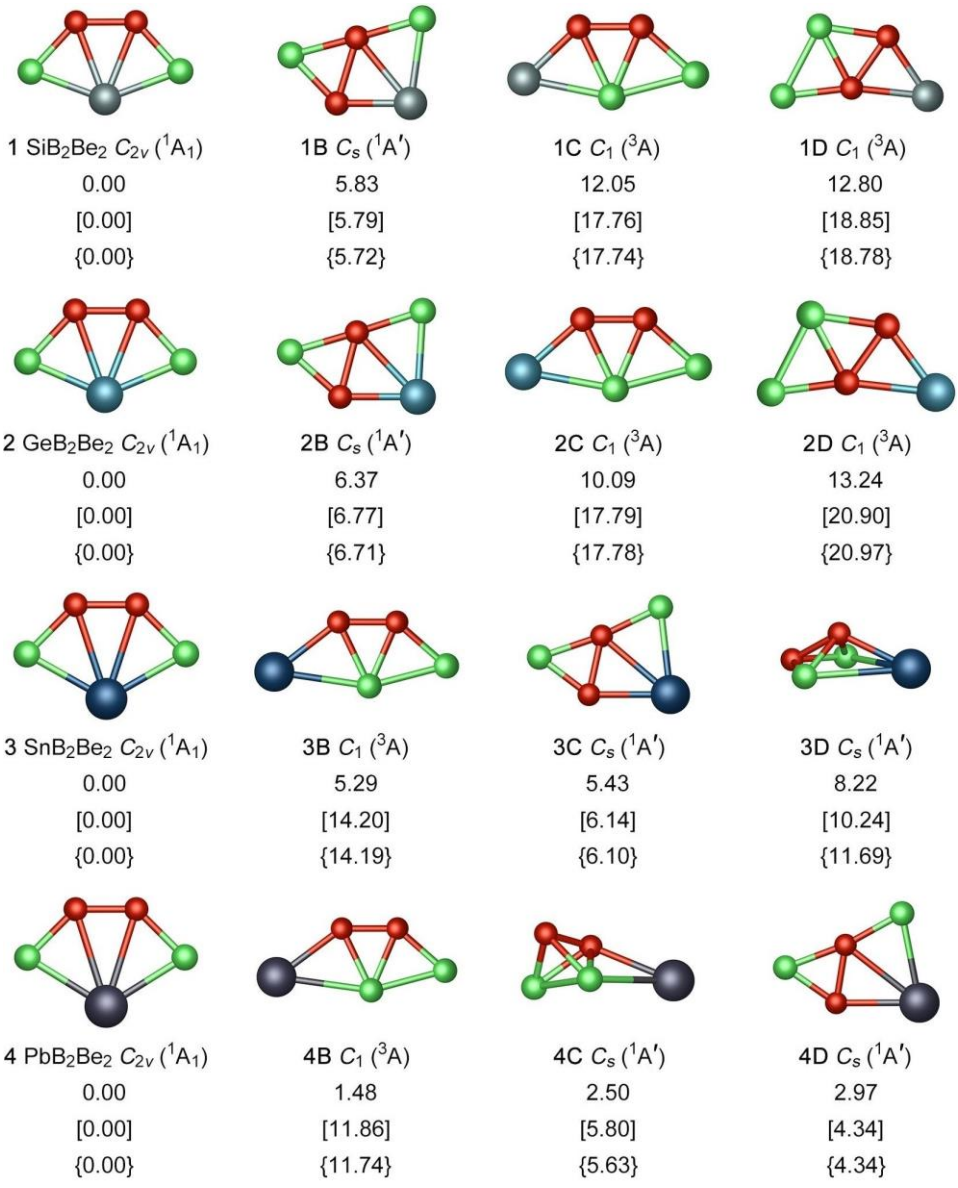

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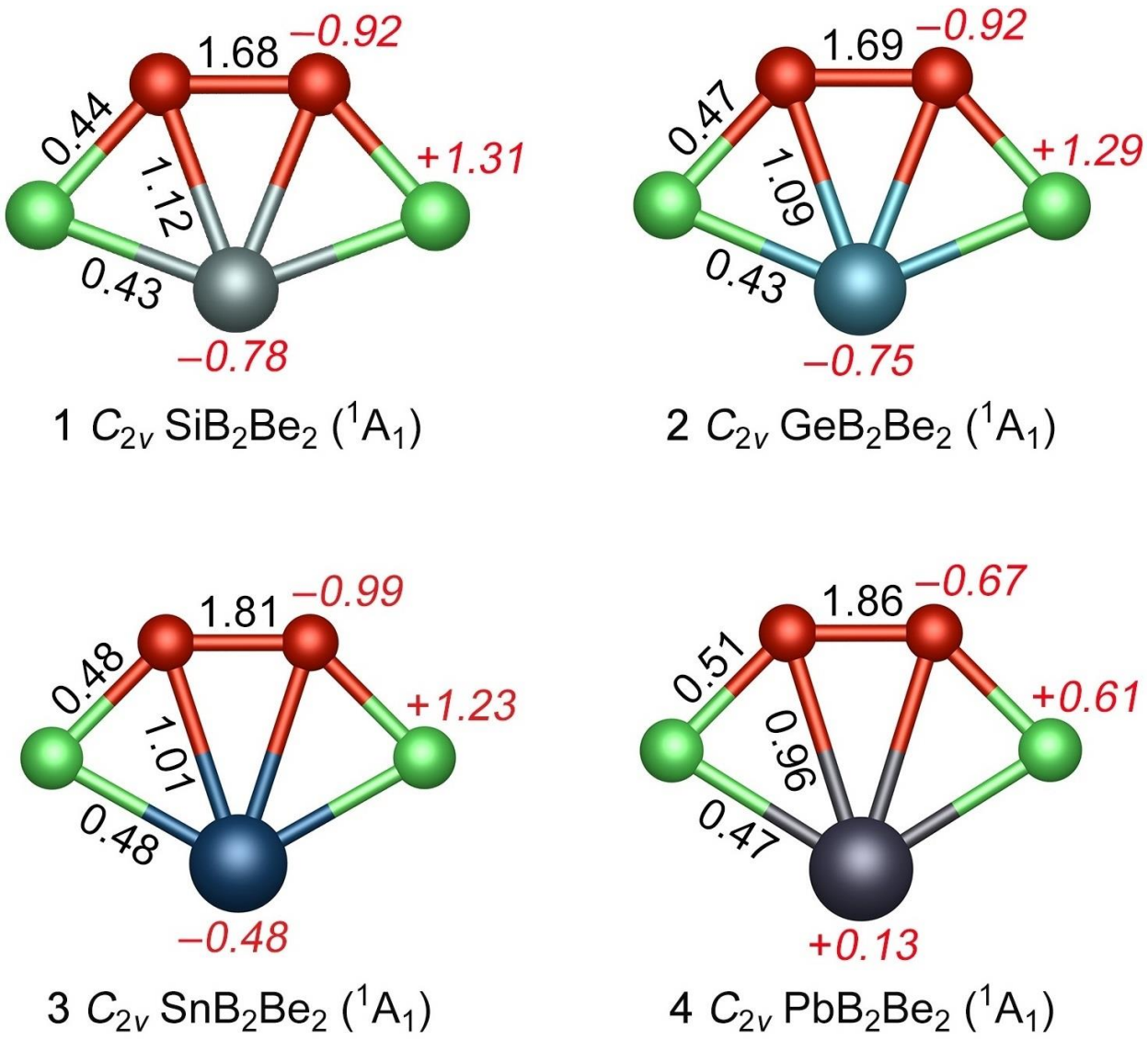

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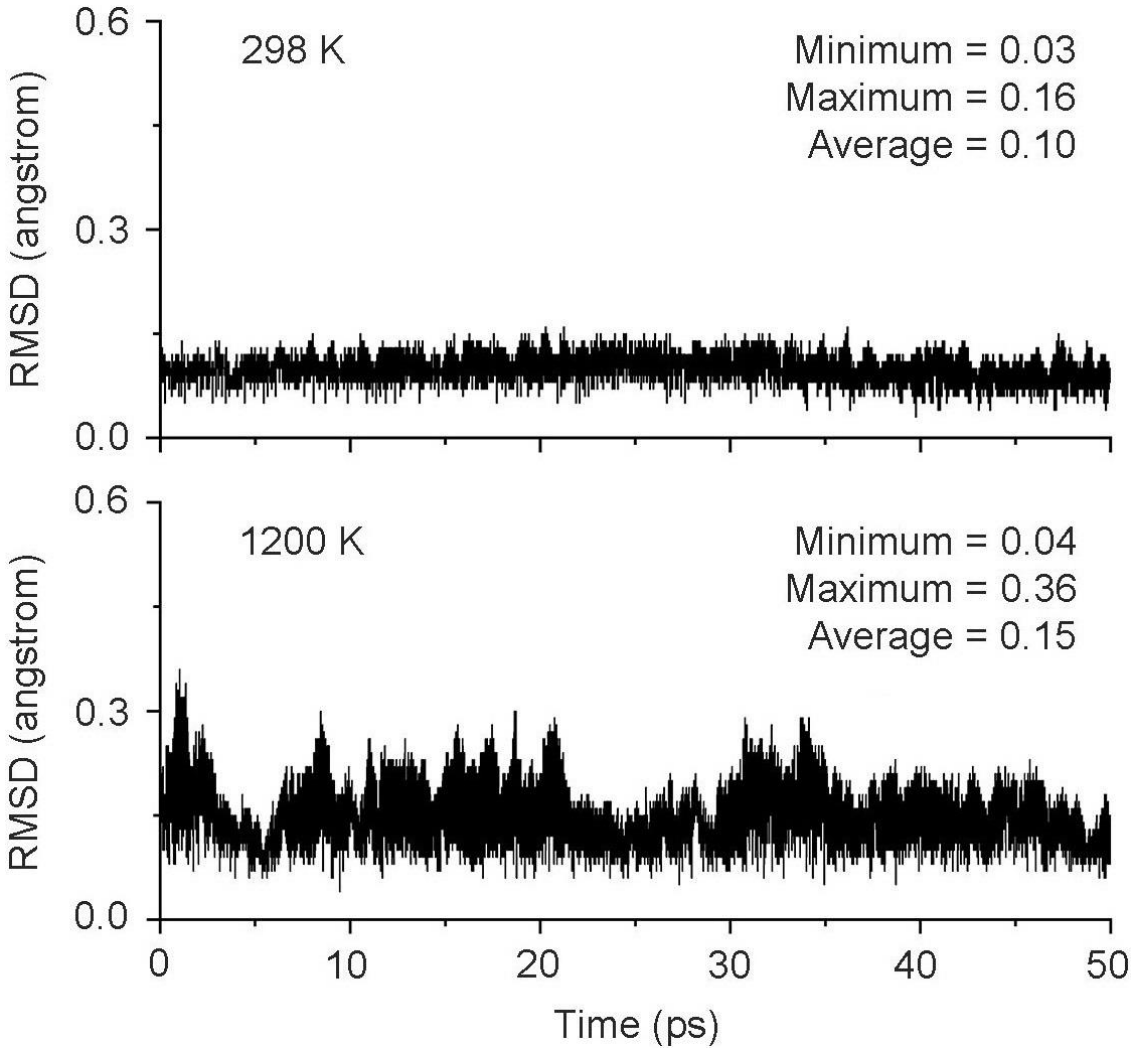

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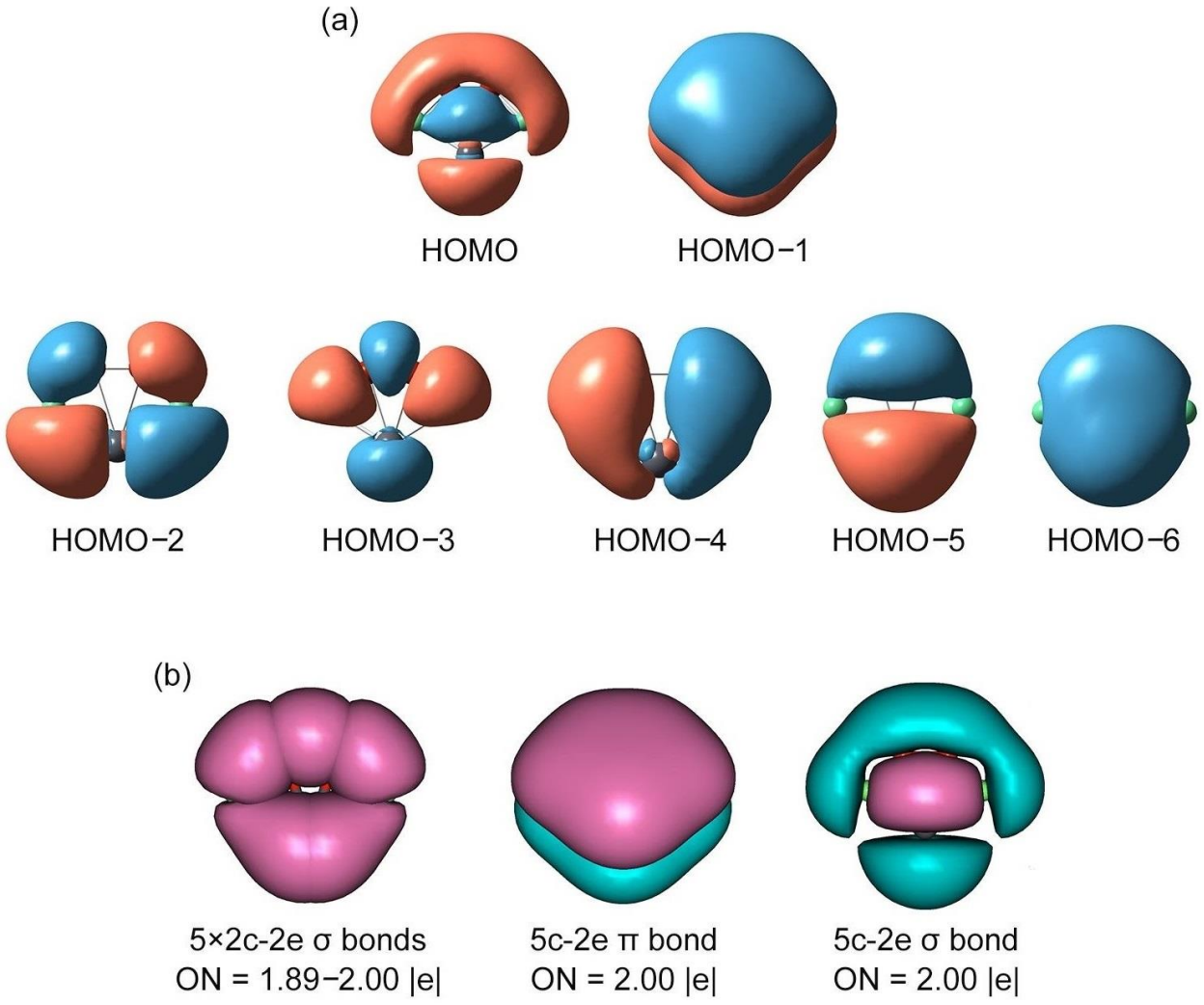

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