Supporting Information for

Linear Group 13 E≡E triple bonds

Zhong-hua Cui,*[1,3] Yu-qian Liu,[1] Runfeng Huang,[2] Meng-hui Wang,[1] Bing Yan,[1] Lili Zhao*[2]

[a]*Institute of Atomic and Molecular Physics, Key Laboratory of Physics and Technology for Advanced Batteries (Ministry of Education), Jilin University, Changchun, China*

E-mail: zcui@jlu.edu.cn

[b]*Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Nanjing Tech University, Nanjing, China*

E-mail: ias_llzhao@njtech.edu.cn

[c]*Beijing National Laboratory for Molecular Sciences*

I. Computational details

The PBE0[1]/def2-SVP level was used to minimize the initial structures of $E_2M_5^+$ (E=Group 13; M=Li, Na, K) with singlet and triplet and quintuplet potential energy surface (PES) analysis. For the low-lying energy isomers, we employed a large def2-QZVP basis set for better geometrical and frequency prediction. The relative energies of low-lying energy isomers of $E_2M_5^+$ were confirmed by the single-point CCSD(T)[2] /def2-QZVP calculations, where the T1 values are in a reasonable range (see supporting information, SI) for the single-reference method application. Since the insignificant difference from three M-based species, we only took $E_2Na_5^+$ for the detailed structural and electronic analysis in the main text. The MP2[3] and CCSD both with def2-QZVP were further considered for geometries and frequencies of the global minima. The natural bonding orbital (NBO)[4] and adaptive natural density partitioning (AdNDP) algorithm[5] analysis were made using Mulitwfn suite[6] at the CCSD/def2-QZVP level. The structure search is performed using the PSO algorithm within the revolutionary scheme, as implemented in the CALYPSO (Crystal structure Analysis by Particle Swarm Optimization) code.[7] All calculations were carried out with the GAUSSIAN09 program package.[8]

Bonding analysis of $E_2Na_5^+$ was performed at the unrestricted BP86/TZ2P level using ADF package.[9] The EDA-NOCV method combined the energy decomposition analysis (EDA) with natural orbital for chemical valence (NOCV) are applied.[10] The bonding analysis focuses on the instantaneous interaction energy ΔE_{int}, the energy difference between the energy of the molecule A-B and the energies of the prepared fragments A and B, which can be divided into three main components as follows.

$$\Delta E_{int} = \Delta E_{Pauli} + \Delta E_{elstat} + \Delta E_{orb}$$

where, the ΔE_{elstat} term corresponds to the classical electrostatic energy between those fragments and it is generally attractive in nature. The next attractive term is orbital interaction energy, ΔE_{orb}, which arises from the charge transfer and mixing of the occupied and unoccupied orbitals on the fragments and polarization effects. The only

repulsive contribution is the Pauli interaction energy (ΔE_{Pauli}) and it is originated from the repulsion between the occupied orbitals of the interacting fragments.

The EDA-NOCV calculation combines the energy and charge decomposition schemes and divides the deformation density, $\Delta\rho(r)$, associated with the bond formation into different components of a chemical bond. From the mathematical point of view, each NOCV, ψ_i is defined as an eigenvector of the deformation density matrix in the basis of fragment orbitals.

$$\Delta P_{\psi i} = \nu_i \psi_i$$

In EDA-NOCV, ΔEorb is given by the following equation,

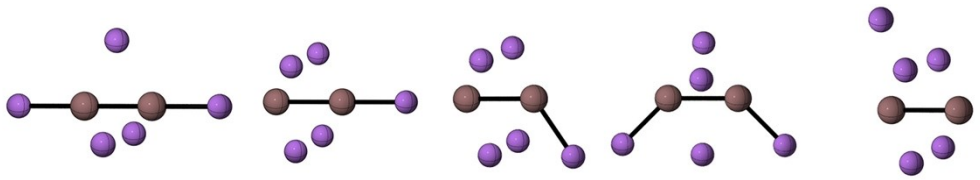
$$\Delta E_{orb} = \sum_k \Delta E_k^{orb} = \sum_{k=1}^{N/2} \nu_k [- F_{-k}^{TS} + F_k^{TS}]$$

where, $- F_{-k}^{TS}$ and F_k^{TS} are diagonal Kohn-Sham matrix elements corresponding to NOCVs with the eigenvalues $-\nu_k$ and ν_k, respectively. The ΔE_k^{orb} terms are assigned to a particular type of bond by visual inspection of the shape of the deformation density, $\Delta\rho_k$. The EDA-NOCV scheme thus provides both qualitative ($\Delta\rho_{orb}$) and quantitative (ΔE_{orb}) information about the strength of orbital interactions in chemical bonds.

Reference

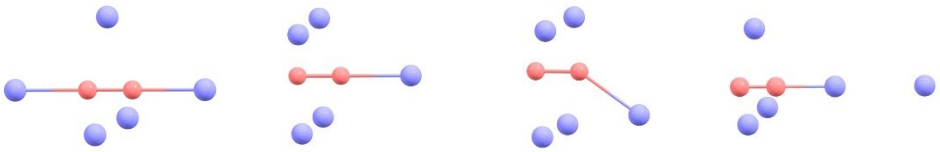
(1) Adamo, C.; Barone, V. Toward Reliable Density Functional Methods without Adjustable Parameters: The PBE0 Model. *J. Chem. Phys.* **1999,** *110*, 6158-6170.
(2) Purvis III, G. D.; Bartlett, R. J. A Full Coupled-Cluster Singles and Doubles Model: The Inclusion of Disconnected Triples. *J. Chem. Phys.* **1982,** *76*, 1910-1918.
(3) Frisch, M. J.; Head-Gordon, M.; Pople, J. A. A Direct MP2 Gradient Method. *Chem. Phys. Lett.* **1990,** *166*, 275-280.
(4) Martin, R. L. Natural Transition Orbitals. *J. Chem. Phys.* **2003,** *118*, 4775-4777.
(5) Zubarev, D. Y.; Boldyrev, A. I. Developing Paradigms of Chemical Bonding: Adaptive Natural Density Partitioning. *Phys. Chem. Chem. Phys.* **2008,** *10*, 5207-5217.
(6) Lu, T.; Chen, F. Multiwfn: A Multifunctional Wavefunction Analyzer. *J Comput Chem* **2012,** *33*, 580-592.
(7) (a) Wang, Y.; Ma, Y. CALYPSO Structure Prediction Method. *Chin. Sci. Bull.* **2015,** *60*, 2580-2587; (b) Wang, Y.; Lv, J.; Zhu, L.; Ma, Y. CALYPSO: A Method for Crystal Structure Prediction. *Comput. Phys. Commun.* **2012,** *183*, 2063-2070.

(8) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A., et al. Gaussian 09, Revision D.02, Gaussian, Inc., Wallingford CT, **2016**.
(9) (a) Te Velde, G. t.; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; van Gisbergen, S. J.; Snijders, J. G.; Ziegler, T. Chemistry with ADF. *J Comput Chem* **2001,** *22*, 931-967; (b) ADF 2020, SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands, http://www.scm.com.
(10) (a) Ziegler, T.; Rauk, A. On the Calculation of Bonding Energies by the Hartree Fock Slater Method. *Theor. Chim. Acta* **1977,** *46*, 1-10; (b) Zhao, L.; vonHopffgarten, M.; Andrada, D. M.; Frenking, G. Energy Decomposition Analysis. *WIREs Comput. Mol. Sci.* **2018,** *8*, e1345; (c) Zhao, L.; Hermann, M.; Schwarz, W. E.; Frenking, G. The Lewis Electron-Pair Bonding Model: Modern Energy Decomposition Analysis. *Nat. Rev. Chem.* **2019,** *3*, 48-63; (d) Mitoraj, M. P.; Michalak, A.; Ziegler, T. A Combined Charge and Energy Decomposition Scheme for Bond Analysis. *J. Chem. Theory Comput.* **2009,** *5*, 962-975.

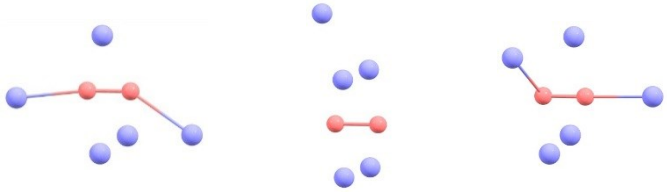


	I (D_{3h} $^1A_1'$)	II (C_{4v} $^1A_1$)	III (C_s $^3A'$)	IV (C_s $^3A''$)	V (C_{2v} $^3A_1$)
E=B	0.0 (0.0)	6.1 (5.8)	35.9	40.1*	40.5
E=Al	0.0 (0.0)	1.7 (1.8)	17.7	23.2	20.1
E=Ga	0.0 (0.0)	2.7 (1.9)	19.3	25.3	22.3
E=In	0.0# (0.0)	1.2 (0.6)	13.7	18.3	16.9
E=Tl	0.0# (0.0)	0.4 (-2.3)	13.7	21.1	18.3*

Figure S1. The structure and relative energy in kcal/mol low-lying energy isomers of $E_2Na_5^+$. The relative energies in kcal/mol were computed at the single-point CCSD(T)/def2-QZVP//PBE0/def2-QZVP. The values in parenthesis refer to the CCSD(T) optimizations using cc-pVTZ (cc-pVTZ-PP for In and Tl) basis sets. The point group symmetries and spectroscopic states are given. *C_1 symmetry. #Small imaginary frequency obtained by PBE0 method but a real minimum determined by both MP2 and CCSD methods.

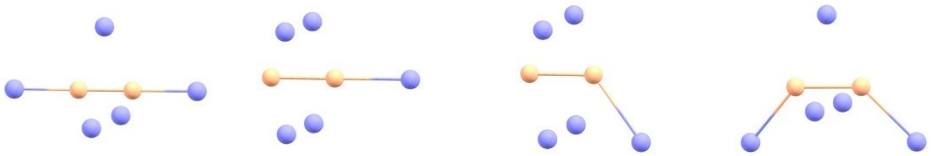


	D_{3h}, $^1A_1'$	C_{4v}, $^1A_1$	C_s, $^3A'$	C_1, ^3A
M = Li	0.0 (0.0)	8.8 (8.6)	39.8 (34.1)	46.8 (44.7)
M = Na	0.0 (0.0)	6.1 (6.3)	35.9 (32.3)	38.3 (36.0)
M = K	0.0 (0.0)	4.2 (4.8)	24.6 (22.0)[a]	28.2 (27.1)

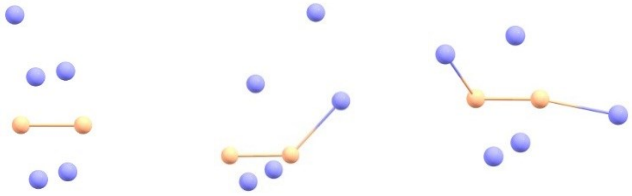


	C_1, ^3A	C_{2v}, $^3A_1$	C_s, $^1A_1'$
M = Li	47.1 (40.8)	48.5 (46.8)	9.3 (9.2)
M = Na	40.1 (36.4)	40.5 (38.9)	6.6 (6.8)
M = K	27.4 (25.2)	31.8 (31.2)	4.9 (5.5)

Figure S2. The low-lying energy isomers of $B_2M_5^+$ (M=Li, Na and K) species. The relative energies in kcal/mol were computed at the single-point CCSD(T)/def2-QZVP//PBE0/def2-QZVP and PBE0/def2-QZVP (in parenthesis) levels. All energies are corrected for zero-point energies (ZPE) at the PBE0/def2-QZVP level. The point group symmetries and spectroscopic states are given. The last structure is a transition state (TS). [a]C_1 symmetry.

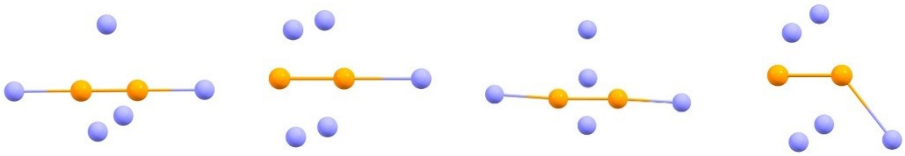


	D_{3h}, $^1A_1'$	C_{4v}, $^1A_1$	C_s, $^3A'$	C_s, $^3A''$
M = Li	0.8 (2.0)	0.0 (0.0)	15.9 (9.3)	21.9 (17.0)
M = Na	0.0 (0.0)	1.7 (1.7)	17.7 (12.8)	23.2 (18.2)
M = K	0.0 (0.0)	0.7 (0.0)	14.0 (9.9)	22.4 (16.4)

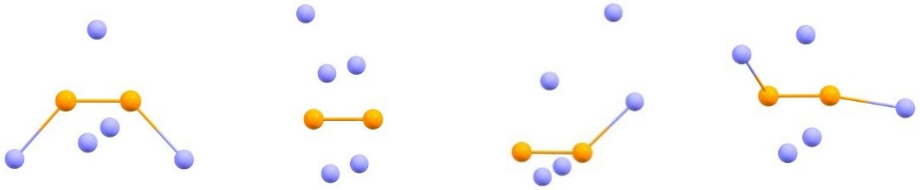


	C_{2v}, $^3A_1$	C_s, $^3A'$	C_s, $^1A_1'$
M = Li	22.2 (19.3)	32.1 (26.3)	4.1 (4.5)
M = Na	20.1 (17.1)	27.6 (22.1)	3.9 (3.8)
M = K	18.5 (15.3)	23.3 (19.3)	3.1 (2.5)

Figure S3. The low-lying isomers of $Al_2M_5^+$ (M=Li, Na and K) species. The relative energies in kcal/mol were computed at the single-point CCSD(T)/def2-QZVP//PBE0/def2-QZVP and PBE0/def2-QZVP (in parenthesis) levels. All energies are corrected for zero-point energies (ZPE) at the PBE0/def2-QZVP level. The point group symmetries and spectroscopic states are given. The last structure is a transition state (TS).

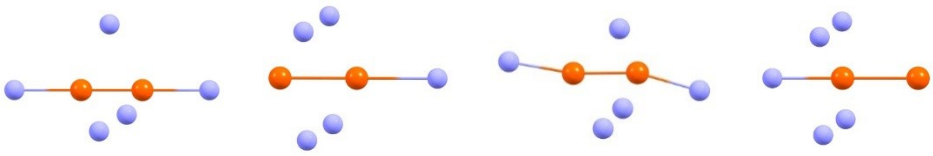


	D_{3h}, $^1A_1'$	C_{4v}, $^1A_1$	C_s, $^1A'$	C_s, $^3A'$
M = Li	0.0 (0.0)	1.8 (0.1)	0.7 (0.1)[a]	18.7 (10.4)
M = Na	0.0 (0.0)	2.7 (2.2)	–	19.3 (13.4)
M = K	0.0 (0.0)	1.2 (0.4)	–	16.1 (10.6)

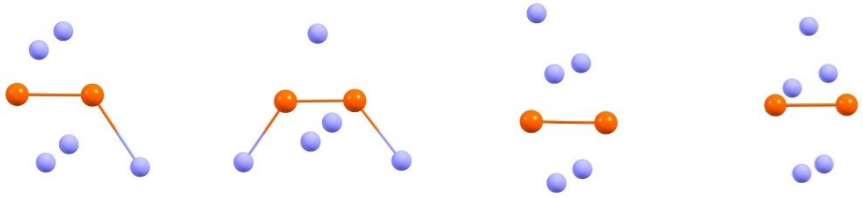


	C_s, $^3A''$	C_{2v}, $^3A_1$	C_s, $^3A'$	C_s, $^1A_1'$
M = Li	23.8 (17.1)	25.4 (20.4)	34.7 (26.1)	4.7 (3.5)
M = Na	25.3 (19.4)	22.3 (18.1)	29.2 (21.9)	4.6 (3.9)
M = K	22.8 (17.3)[b]	20.1 (16.5)	24.5 (19.3)	3.5 (2.6)

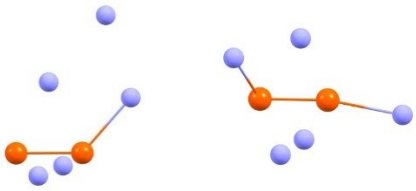
Figure S4. The low-lying isomers of $Ga_2M_5^+$ (M=Li, Na and K) species. The relative energies in kcal/mol were computed at the single-point CCSD(T)/def2-QZVP//PBE0/def2-QZVP and PBE0/def2-QZVP (in parenthesis) levels. All energies are corrected for zero-point energies (ZPE) at the PBE0/def2-QZVP level. The point group symmetries and spectroscopic states are given. The last structure is a transition state (TS). "–"Not available. [a]Change to the global minimum at the MP2/de2-QZVP level. [b]C_1 symmetry.



	D_{3h}, $^1A_1'$	C_{4v}, $^1A_1$	C_s, $^1A'$	C_{4v}, $^1A_1$
M = Li	1.2 (2.5)	0.0 (0.0)	2.1 (1.8)[a]	7.5 (4.0)[a]
M = Na	0.0 (0.0)*	1.2 (0.4)	0.0 (0.6)[a]	–
M = K	0.0 (0.0)	0.5 (0.1)	–	–

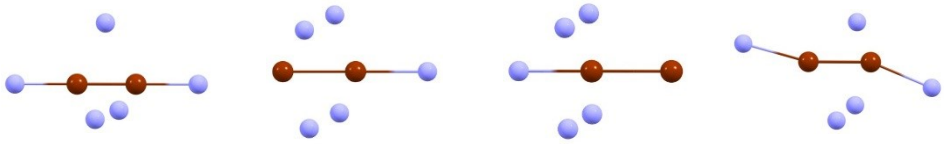


	C_s, $^3A'$	C_s, $^3A''$	C_s, $^3A''$	C_s, $^3A''$
M = Li	15.3 (9.1)	20.2 (15.4)	22.1 (19.7)	22.7 (15.9)
M = Na	13.7 (10.4)	18.3 (16.2)	16.9 (15.9)[b]	18.5 (14.2)
M = K	11.3 (8.3)	19.5 (14.4)	16.5 (14.5)[b]	–

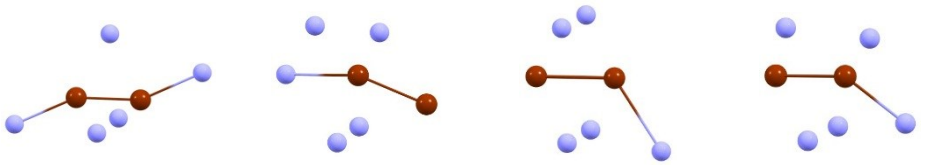


	C_s, $^3A'$	C_s, $^1A_1'$
M = Li	–	4.9 (5.3)
M = Na	23.2 (19.1)	4.1 (3.8)
M = K	21.1 (17.5)	2.9 (2.4)

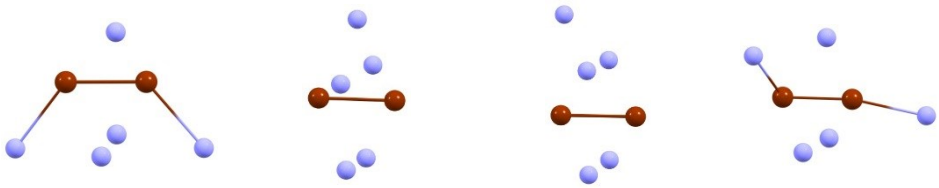
Figure S5. The low-lying isomers of $In_2M_5^+$ (M=Li, Na and K) species. The relative energies in kcal/mol were computed at the single-point CCSD(T)/def2-QZVP//PBE0/def2-QZVP and PBE0/def2-QZVP (in parenthesis) levels. All energies are corrected for zero-point energies (ZPE) at the PBE0/def2-QZVP level. The point group symmetries and spectroscopic states are given. The last structure is a transition state (TS). "–"Not available. *Imaginary frequency. [a]Change to the global minimum or the second lowest-energy structure at the MP2/de2-QZVP level. [b]C_{2v} symmetry. The single point CCSD(T) energy of $In_2K_5^+$ computed using the MOLPRO package without ZPE correction.



	D_{3h}, $^1A_1'$	C_{4v}, $^1A_1$	C_{4v}, $^1A_1$	C_s, $^1A'$
M = Li	1.7 (7.3)*	0.0 (2.7)	1.7 (0.0)[a]	3.7 (5.7)[a]
M = Na	0.0 (2.8)*	0.4 (0.0)	–	2.8 (1.3)[a]
M = K	0.0 (1.0)*	0.9 (0.0)	–	–



	C_s, $^1A'$	C_s, $^1A'$	C_s, $^3A'$	C_s, $^3A''$
M = Li	–	–	15.4 (11.9)	16.6 (12.9)
M = Na	0.8 (2.5)[a]	4.3 (0.6)[a]	13.7 (8.7)	–
M = K	–	–	11.4 (6.5)	–



	C_s, $^3A''$	C_s, $^3A''$	C_s, $^3A''$	C_s, $^1A_1'$
M = Li	21.7 (17.8)	21.8 (16.3)	–	5.8 (9.5)
M = Na	21.1 (14.2)	17.6 (12.2)[b]	18.3 (15.2)[c]	3.8 (5.2)
M = K	19.7 (13.0)	–	17.7 (13.7)	3.3 (2.7)

Figure S6. The low-lying isomers of $Tl_2M_5^+$ (M=Li, Na and K) species. The relative energies in kcal/mol were computed at the single-point CCSD(T)/def2-QZVP//PBE0/def2-QZVP and PBE0/def2-QZVP (in parenthesis) levels. All energies are corrected for zero-point energies (ZPE) at the PBE0/def2-QZVP level. The point group symmetries and spectroscopic states are given. The last structure is a transition state (TS). "–"Not available. *Imaginary frequency. [a]Change to the global minimum or the second lowest-energy structure at the MP2/de2-QZVP level. [b]D_{5h} symmetry. [c]C_1 symmetry.

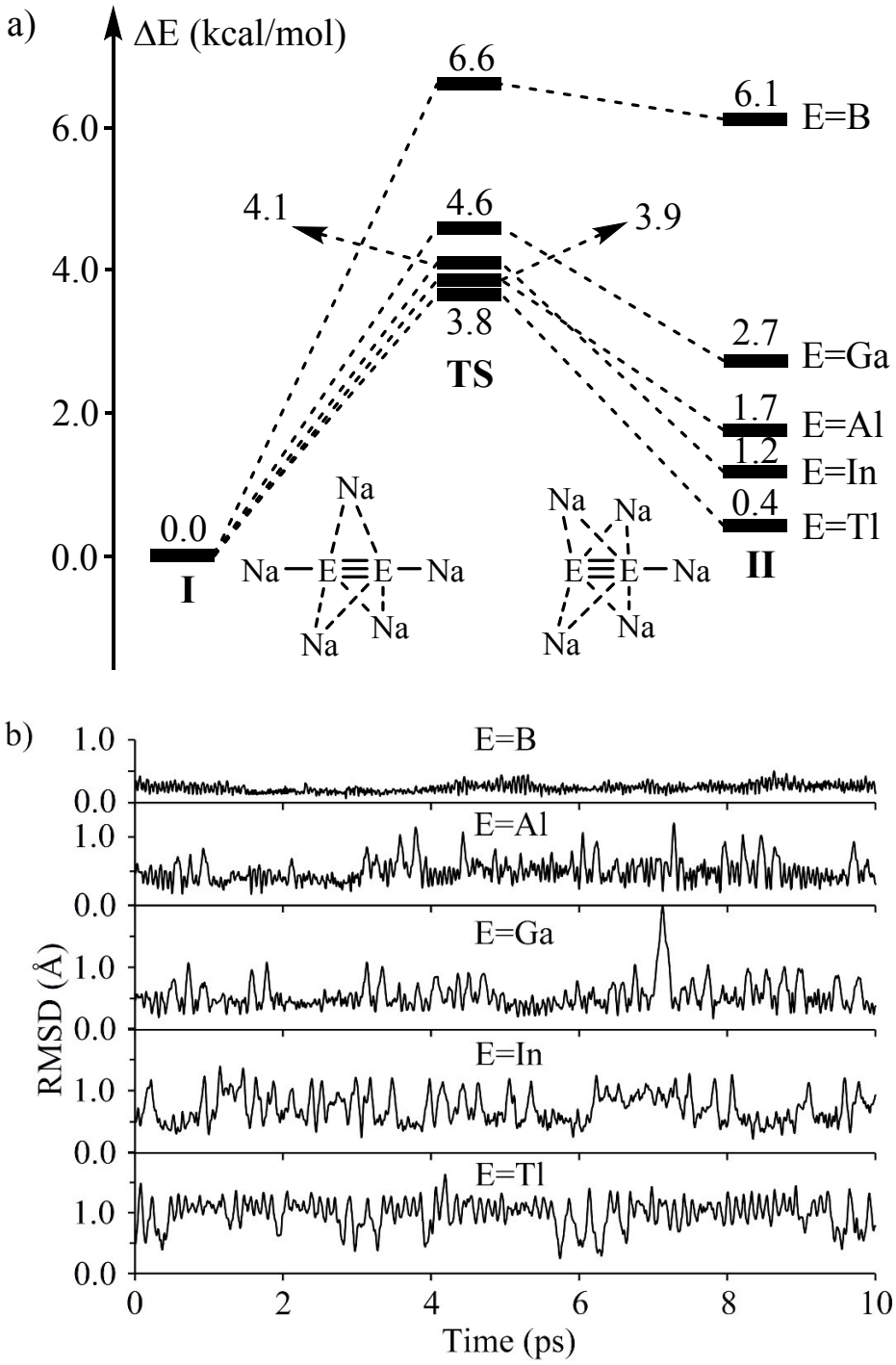


Figure S7. a) the direct conversion between two lowest-energy isomers (**II** ↔ **I**), and b) the RMSD vs simulation time of $E_2Na_5^+$ at 400 K obtained at the PBE0/def2-SVP level.

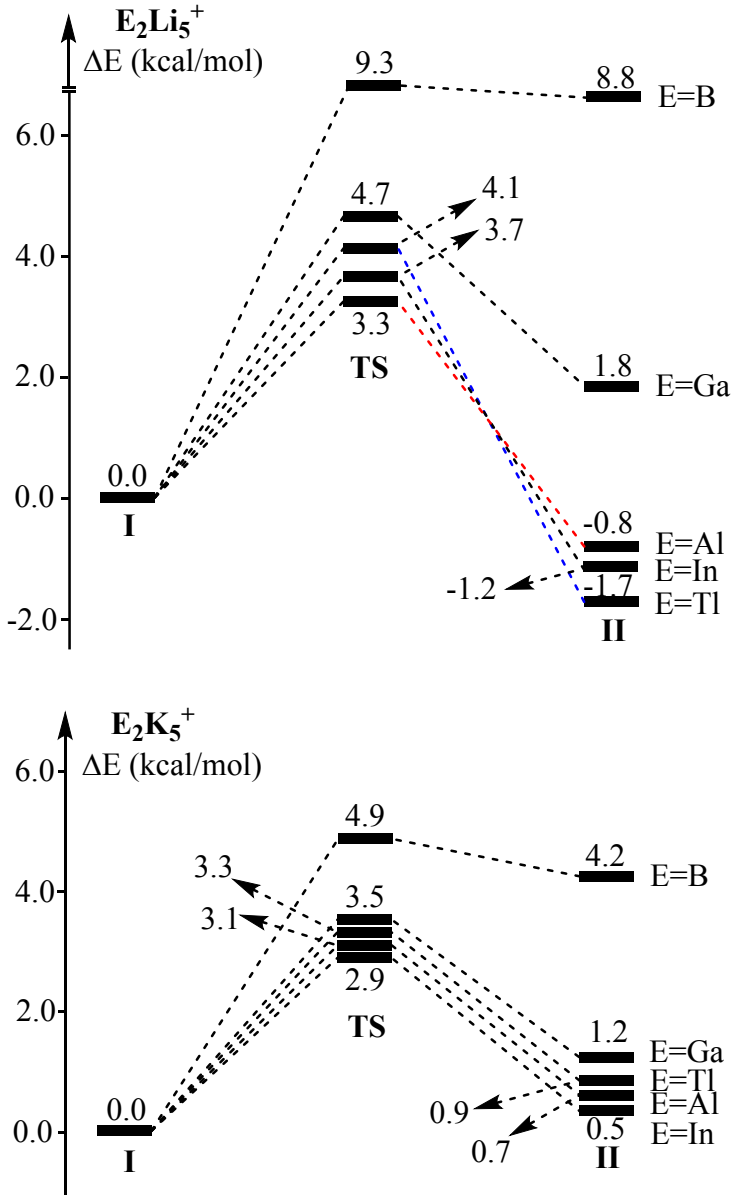


Figure S8. The direct conversion between two lowest-energy isomers (**II** ↔ **I**) of $E_2Li_5^+$ and $E_2K_5^+$ computed at the CCSD(T)/def2-QZVP//PBE0/def2-QZVP level. The single point CCSD(T) of $In_2K_5^+$ using the MOLPRO package.

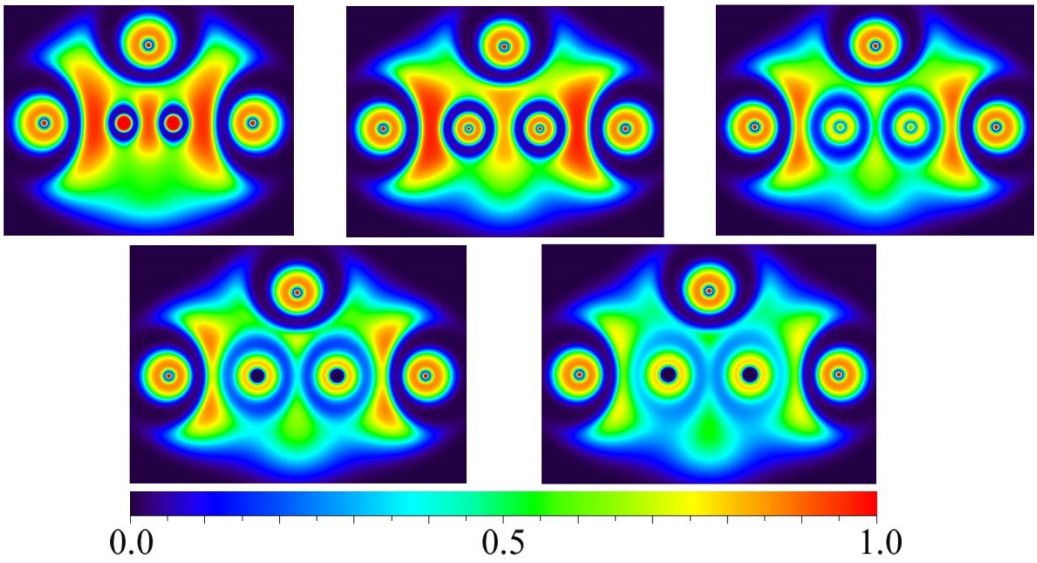


Figure S9. The ELF contour map of the D_{3h}-symmetry $E_2Na_5^+$ clusters.

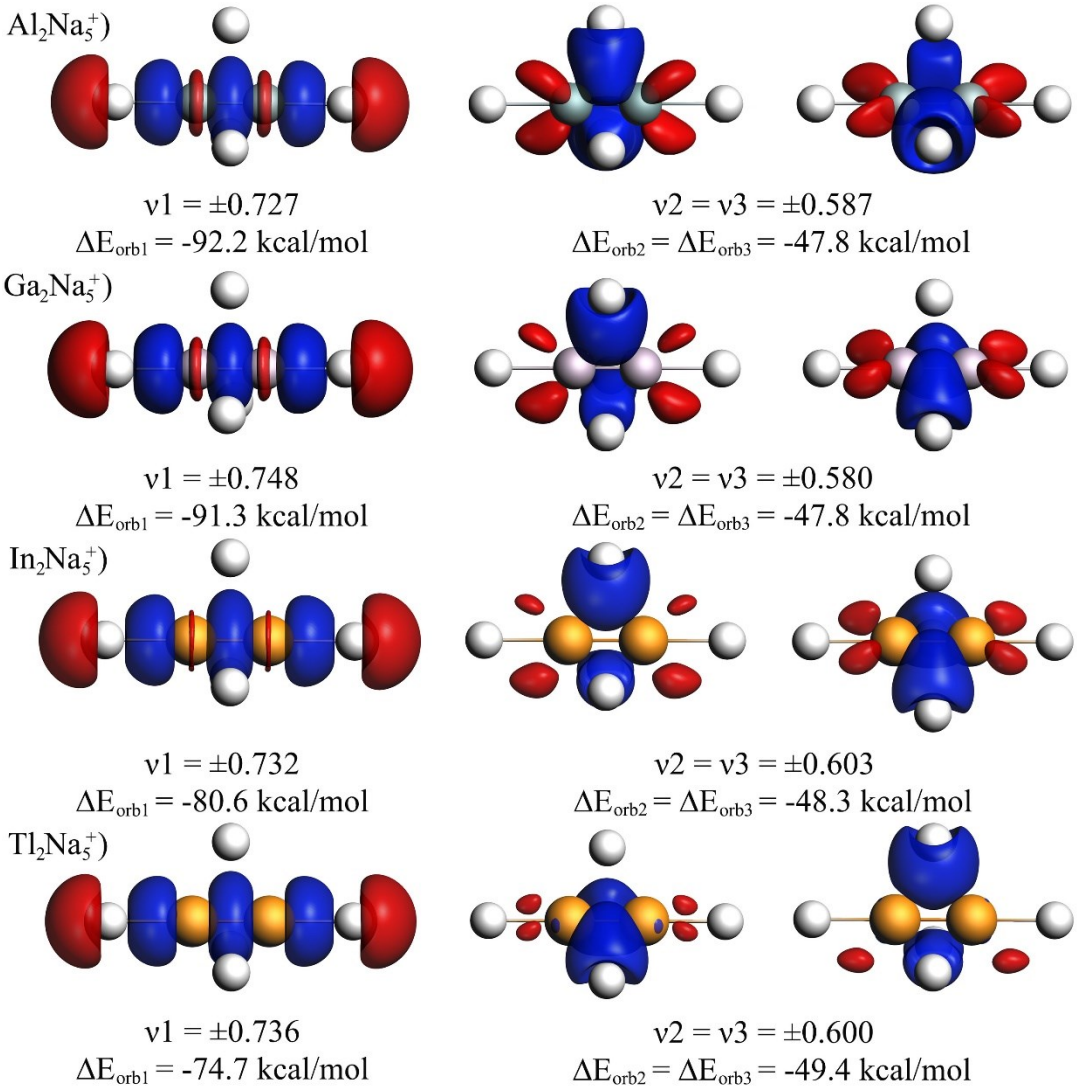


Figure S10. Plot of deformation densities $\Delta\rho_{1\text{-}3}$ of the pairwise orbital interactions between two ENa^{-} (Quartet) and one Na_3^{3+} (Singlet) fragments in $E_2Na_5^{+}$ (E=Al, Ga, In, Tl), associated interaction energies ΔE_{orb} (in kcal/mol) and eigenvalues ν. The eigenvalues ν indicate the size of the charge flow, and the direction of charge flow is red→blue.

Table S1. Dissociation pathway in kcal/mol of $E_2M_5^+$ computed at the PBE0/def2-QZVP level.

(1) $E_2M_5^+ \rightarrow E_2M_4 + M^+$			(2) $E_2M_5^+ \rightarrow E_2M_4^+ + M$		
E=B	M=Li	88.0	E=B	M=Li	57.8
		95.3			65.9
	M=Na	75.7		M=Na	44.7
		82.0			49.0
	M=K	60.9		M=K	34.5
		65.9			37.0
E=Al	M=Li	69.9	E=Al	M=Li	40.5
		75.4			45.2
	M=Na	62.0		M=Na	32.8
		67.6			37.2
	M=K	52.5		M=K	28.1
		61.9			33.3
E=Ga	M=Li	71.1	E=Ga	M=Li	42.3
		76.6			46.1
	M=Na	61.6		M=Na	33.0
		67.9			37.4
	M=K	51.9		M=K	28.2
		61.9			33.7
E=In	M=Li	67.1	E=In	M=Li	39.9
		72.9			41.8
	M=Na	58.7		M=Na	31.3
		65.2			35.0
	M=K	50.5		M=K	27.0
		59.1			31.6
E=Tl	M=Li	64.6	E=Tl	M=Li	38.3
		71.8			40.4
	M=Na	55.4		M=Na	28.5
		63.3			33.2
	M=K	48.0		M=K	24.9
		57.1			30.3

Table S2. Smallest frequencies (V_{min}, cm^{-1}), NPA charge on E and Li atoms (Q, |e|), Bonding properties (B, Wiberg bond index (WBI) in parenthesis and bond distances (Å)) of the D_{3h} symmetry $E_2Li_5^+$ (**I**) obtained at the PBE0/def2-QZVP level.

$E_2Li_5^+$	V_{min}	Q_E	Q_{Li}	B_{E-E}	B_{E-Li}	B_{Li-Li}
E=B	90.9	-1.68	0.88 0.86	1.513 (2.96)	2.143 (0.18) 2.167 (0.11)	3.517 (0.01)
E=Al	12.5	-1.63	0.83 0.86	2.410 (2.71)	2.611 (0.27) 2.723 (0.12)	4.229 (0.00)
E=Ga	33.7	-1.65	0.85 0.87	2.341 (2.74)	2.513 (0.23) 2.654 (0.12)	4.126 (0.00)
E=In	18.7	-1.59	0.84 0.83	2.675 (2.58)	2.646 (0.24) 2.838 (0.15)	4.336 (0.00)
E=Tl	-5.7 -5.5	-1.61	0.86 0.83	2.750 (2.55)	2.599 (0.20) 2.825 (0.15)	4.274 (0.00)

The first line in each row is the M atom contacted linearly with E

Table S3. Smallest frequencies (V_{min}, cm^{-1}), NPA charge on E and Li atoms (Q, |e|), Bonding properties (B, Wiberg bond index (WBI) in parenthesis and bond distances (Å)) of the D_{3h} symmetry $E_2Na_5^+$ (**I**) obtained at the PBE0/def2-QZVP level.

$E_2Na_5^+$	V_{min}	Q_E	Q_{Na}	B_{E-E}	B_{E-Na}	B_{Na-Na}
E=B	45.0	-1.57	0.82 0.83	1.526 (2.96)	2.459 (0.25) 2.514 (0.13)	4.149 (0.01)
E=Al	20.1	-1.51	0.77 0.83	2.429 (2.60)	2.891 (0.32) 3.022 (0.15)	4.794 (0.00)
E=Ga	20.3	-1.52	0.78 0.83	2.360 (2.61)	2.812 (0.29) 2.964 (0.15)	4.709 (0.00)
E=In	-3.7 -3.7	-1.48	0.78 0.80	2.697 (2.45)	2.942 (0.30) 3.129 (0.18)	4.891 (0.01)
E=Tl	-19.6 -19.6	-1.47	0.79 0.79	2.771 (2.36)	2.921 (0.26) 3.125 (0.19)	4.851 (0.01)

The first line in each row is the M atom contacted linearly with E

Table S4. Smallest frequencies (V_{min}, cm^{-1}), NPA charge on E and Li atoms (Q, |e|), Bonding properties (B, Wiberg bond index (WBI) in parenthesis and bond distances (Å)) of the D_{3h} symmetry $E_2K_5^+$ (**I**) obtained at the PBE0/def2-QZVP level.

$E_2K_5^+$	V_{min}	Q_E	Q_K	B_{E-E}	B_{E-K}	B_{K-K}
E=B	31.6	-1.51	0.82 0.79	1.539 (2.93)	2.889 (0.23) 2.884 (0.16)	4.814 (0.02)
E=Al	20.6	-1.56	0.81 0.83	2.432 (2.70)	3.314 (0.25) 3.401 (0.15)	5.502 (0.01)
E=Ga	21.3	-1.53	0.81 0.82	2.364 (2.66)	3.232 (0.23) 3.339 (0.16)	5.409 (0.01)
E=In	14.8	-1.57	0.82 0.83	2.697 (2.60)	3.362 (0.23) 3.508 (0.15)	5.610 (0.00)
E=Tl	-1.2 -1.2	-1.56	0.82 0.83	2.770 (2.51)	3.335 (0.22) 3.501 (0.16)	5.570 (0.00)

The first line in each row is the N atom contacted linearly with E

Table S5. Calculated E≡E stretching frequency (cm^{-1}) of $E_2M_5^+$ obtained at the CCSD/def2-QZVP level.

Stretching mode	$E_2M_5^+$	Previous reported
B≡B	1230.4	1658.3 (OCBBOC)
Al≡Al	429.2	
Ga≡Ga	298.9	
In≡In	217.2	
Tl≡Tl	194.8	

Table S6. EDA-NOCV results of $E_2Na_5^+$ using the interacting fragments (two ENa^- and one Na_3^{3+}) at the BP86/TZ2P level of theory. Energy values are given in kcal/mol.

	ENa^- (Doublet) + ENa^- (Doublet) + Na_3^{3+} (Singlet)				
	E=B	E=Al	E=Ga	E=In	E=Tl
ΔE_{int}	-716.9	-580.9	-585.5	-561.4	-553.5
ΔE_{Pauli}	480.3	301.5	345.9	331.7	355.4
ΔE_{elstat}[a]	-740.3 (61.8%)	-590.1 (66.9%)	-636.3 (68.3%)	-620.7 (69.5%)	-643.0 (70.7%)
ΔE_{orb}[a]	-456.9 (38.2%)	-292.3 (33.1%)	-295.2 (31.7%)	-272.4 (30.5%)	-266.0 (29.3%)
ΔE_{orb1}[b]	-279.1 (60.9%)	-192.3 (65.7%)	-191.2 (64.7%)	-177.9 (65.2%)	-170.9 (64.2%)
ΔE_{orb2}[b]	-45.8 (10.0%)	-41.6 (14.2%)	-41.1 (13.9%)	-41.9 (15.4%)	-42.4 (15.9%)
ΔE_{orb3}[b]	-121.4 (26.5%)	-53.3 (18.2%)	-54.3 (18.4%)	-45.8 (16.8%)	-43.9 (16.5%)
$\Delta E_{orb(rest)}$[b]	-11.7 (2.5%)	-5.4 (1.9%)	-8.9 (3.0%)	-7.1 (2.6%)	-8.9 (3.3%)

[a]The values in parentheses give the percentage contribution to the total attractive interactions $\Delta E_{elstat} + \Delta E_{orb}$

[b]The values in parentheses give the percentage contribution to the total orbital interactions ΔE_{orb}

Table S7. Energy components of interacting quantum atoms (IQA) analysis in kcal/mol for the D_{3h}-symmetry $E_2Na_5^+$ (E = group 13 elements) systems, where inter-atomic interaction energy (V_{Total}) can be evaluated and decomposed into electrostatic (ionic, V_{Ionic}) and exchange (covalent, $V_{Coval.}$) contributions.

$E_2Na_5^+$	E=B	E=Al	E=Ga	E=In	E=Tl
V_{Total} (E-E)	-97.91	-53.97	-54.07	-52.04	-59.49
$V_{Coval.}$ (E-E)	-282.64	-166.53	-174.47	-159.43	-168.55
V_{Ionic} (E-E)	184.73	112.57	120.40	107.38	109.06
V_{Total} (E-Na)	-173.00	-124.31	-127.80	-119.25	-126.34
$V_{Coval.}$ (E-Na)	-36.46	-32.20	-30.67	-31.87	-34.61
V_{Ionic} (E-Na)	-136.53	-92.12	-97.13	-87.38	-91.73
V_{Total} (E-Na′)	-135.31	-98.44	-100.86	-89.39	-96.90
$V_{Coval.}$ (E-Na′)	-19.66	-18.84	-18.03	-18.17	-19.22
V_{Ionic} (E-Na′)	-115.64	-79.59	-82.83	-71.22	-77.69

I. Coordinates obtained at the CCSD/def2-QZVP level.

$B_2Na_5^+$

Lowest Frequencies -- 45.4533 cm^{-1}
Sum of electronic and zero-point Energies= -858.767429 (Hartree)
Sum of electronic and thermal Energies= -858.756209 (Hartree)
Sum of electronic and thermal Enthalpies= -858.755265 (Hartree)
Sum of electronic and thermal Free Energies= -858.805526 (Hartree)

B	0.000000000	0.000000000	0.764898000
B	0.000000000	0.000000000	-0.764898000
Na	0.000000000	0.000000000	-3.267646000
Na	0.000000000	0.000000000	3.267646000
Na	0.000000000	2.437606000	0.000000000
Na	2.111029000	-1.218803000	0.000000000
Na	-2.111029000	-1.218803000	0.000000000

$Al_2Na_5^+$

Lowest Frequencies -- 27.2346 cm^{-1}
Sum of electronic and zero-point Energies= -1293.286994 (Hartree)
Sum of electronic and thermal Energies= -1293.273761 (Hartree)
Sum of electronic and thermal Enthalpies= -1293.272817 (Hartree)
Sum of electronic and thermal Free Energies= -1293.331720 (Hartree)

Al	0.000000000	0.000000000	1.215675000
Al	0.000000000	0.000000000	-1.215675000
Na	0.000000000	0.000000000	-4.147635000
Na	0.000000000	0.000000000	4.147635000
Na	0.000000000	2.818419000	0.000000000
Na	2.440823000	-1.409210000	0.000000000
Na	-2.440823000	-1.409210000	0.000000000

$Ga_2Na_5^+$

Lowest Frequencies -- 34.4781 cm^{-1}
Sum of electronic and zero-point Energies= -4656.407433 (Hartree)
Sum of electronic and thermal Energies= -4656.393853 (Hartree)
Sum of electronic and thermal Enthalpies= -4656.392908 (Hartree)
Sum of electronic and thermal Free Energies= -4656.453637 (Hartree)

Ga	0.000000000	0.000000000	1.170158000
Ga	0.000000000	0.000000000	-1.170158000
Na	0.000000000	0.000000000	-4.014042000
Na	0.000000000	0.000000000	4.014042000
Na	0.000000000	2.755516000	0.000000000

Na	2.386347000	-1.377758000	0.000000000
Na	-2.386347000	-1.377758000	0.000000000

$In_2Na_5^+$

Lowest Frequencies -- 20.8605 cm^{-1}

Sum of electronic and zero-point Energies= -1188.636688

Sum of electronic and thermal Energies= -1188.622650

Sum of electronic and thermal Enthalpies= -1188.621706

Sum of electronic and thermal Free Energies= -1188.685122

In	0.000000000	0.000000000	1.338470000
In	0.000000000	0.000000000	-1.338470000
Na	0.000000000	0.000000000	-4.312100000
Na	0.000000000	0.000000000	4.312100000
Na	0.000000000	2.858960000	0.000000000
Na	2.475932000	-1.429480000	0.000000000
Na	-2.475932000	-1.429480000	0.000000000

$Tl_2Na_5^+$

Lowest Frequencies -- 16.7585 cm^{-1}

Sum of electronic and zero-point Energies= -1153.474582 (Hartree)

Sum of electronic and thermal Energies= -1153.460435 (Hartree)

Sum of electronic and thermal Enthalpies= -1153.459491 (Hartree)

Sum of electronic and thermal Free Energies= -1153.524470 (Hartree)

Tl	0.000000000	0.000000000	1.352890000
Tl	0.000000000	0.000000000	-1.352890000
Na	0.000000000	0.000000000	-4.288430000
Na	0.000000000	0.000000000	4.288430000
Na	0.000000000	2.816520000	0.000000000
Na	2.439178000	-1.408260000	0.000000000
Na	-2.439178000	-1.408260000	0.000000000

II. Coordinates and vibrational frequencies (cm^{-1}) of the D_{3h} symmetry $E_2M_5^+$obtained at the MP2/def2-QZVP level.

$B_2Li_5^+$
MP2= -86.737785
Frequencies= 93.8918
Coordinate:

B	0.000000000	0.000000000	0.762585000
B	0.000000000	0.000000000	-0.762585000
Li	0.000000000	0.000000000	-2.942599000
Li	0.000000000	0.000000000	2.942599000
Li	0.000000000	2.061737000	0.000000000
Li	1.785517000	-1.030868000	0.000000000
Li	-1.785517000	-1.030868000	0.000000000

$B_2Na_5^+$
MP2= -858.7805421
Frequencies= 45.4120
Coordinate:

B	0.000000000	0.000000000	0.766291000
B	0.000000000	0.000000000	-0.766291000
Na	0.000000000	0.000000000	-3.290419000
Na	0.000000000	0.000000000	3.290419000
Na	0.000000000	2.445437000	0.000000000
Na	2.117811000	-1.222719000	0.000000000
Na	-2.117811000	-1.222719000	0.000000000

$B_2K_5^+$
MP2= -3045.2939323
Frequencies= 29.7079
Coordinate:

B	0.000000000	0.000000000	0.769806000
B	0.000000000	0.000000000	-0.769806000
K	0.000000000	0.000000000	-3.804210000
K	0.000000000	0.000000000	3.804210000
K	0.000000000	2.903680000	0.000000000
K	2.514660000	-1.451840000	0.000000000
K	-2.514660000	-1.451840000	0.000000000

$Al_2Li_5^+$
MP2= -521.2007097
Frequencies= 35.5352
Coordinate:

Al	0.000000000	0.000000000	1.217565000

Al	0.000000000	0.000000000	-1.217565000
Li	0.000000000	0.000000000	-3.860269000
Li	0.000000000	0.000000000	3.860269000
Li	0.000000000	2.470053000	0.000000000
Li	2.139128000	-1.235026000	0.000000000
Li	-2.139128000	-1.235026000	0.000000000

$Al_2Na_5^+$
MP2= -1293.2858486
Frequencies= 27.2676
Coordinate:

Al	0.000000000	0.000000000	1.223348000
Al	0.000000000	0.000000000	-1.223348000
Na	0.000000000	0.000000000	-4.174243000
Na	0.000000000	0.000000000	4.174243000
Na	0.000000000	2.813658000	0.000000000
Na	2.436700000	-1.406829000	0.000000000
Na	-2.436700000	-1.406829000	0.000000000

$Al_2K_5^+$
MP2=-3479.8263697
Frequencies=20.4157
Coordinate:

Al	0.000000000	0.000000000	1.226445000
Al	0.000000000	0.000000000	-1.226445000
K	0.000000000	0.000000000	-4.661767000
K	0.000000000	0.000000000	4.661767000
K	0.000000000	3.292701000	0.000000000
K	2.851563000	-1.646351000	0.000000000
K	-2.851563000	-1.646351000	0.000000000

$Ga_2Li_5^+$
MP2= -3884.3668431
Frequencies= 51.7901
Coordinate:

Ga	0.000000000	0.000000000	1.160928000
Ga	0.000000000	0.000000000	-1.160928000
Li	0.000000000	0.000000000	-3.687140000
Li	0.000000000	0.000000000	3.687140000
Li	0.000000000	2.393381000	0.000000000
Li	2.072729000	-1.196690000	0.000000000
Li	-2.072729000	-1.196690000	0.000000000

$Ga_2Na_5^+$

MP2= -4656.4466972
Frequencies= 34.0326
Coordinate:

Ga	0.000000000	0.000000000	1.166433000
Ga	0.000000000	0.000000000	-1.166433000
Na	0.000000000	0.000000000	-4.016455000
Na	0.000000000	0.000000000	4.016455000
Na	0.000000000	2.744102000	0.000000000
Na	2.376462000	-1.372051000	0.000000000
Na	-2.376462000	-1.372051000	0.000000000

$Ga_2K_5^+$
MP2= - 6842.9833134
Frequencies= 22.0166
Coordinate:

Ga	0.000000000	0.000000000	1.169867000
Ga	0.000000000	0.000000000	-1.169867000
K	0.000000000	0.000000000	-4.495349000
K	0.000000000	0.000000000	4.495349000
K	0.000000000	3.223066000	0.000000000
K	2.791257000	-1.611533000	0.000000000
K	-2.791257000	-1.611533000	0.000000000

$In_2Li_5^+$
MP2= -416.6338318
Frequencies= 34.6986
Coordinate:

In	0.000000000	0.000000000	1.321164000
In	0.000000000	0.000000000	-1.321164000
Li	0.000000000	0.000000000	-3.970606000
Li	0.000000000	0.000000000	3.970606000
Li	0.000000000	2.494457000	0.000000000
Li	2.160263000	-1.247228000	0.000000000
Li	-2.160263000	-1.247228000	0.00000000

$In_2Na_5^+$
MP2= -1188.7217774
Frequencies= 20.8133
Coordinate:

In	0.000000000	0.000000000	1.328117000
In	0.000000000	0.000000000	-1.328117000
Na	0.000000000	0.000000000	-4.292702000
Na	0.000000000	0.000000000	4.292702000
Na	0.000000000	2.828361000	0.000000000

Na	2.449433000	-1.414181000	0.000000000
Na	-2.449433000	-1.414181000	0.000000000

$In_2K_5^+$
MP2=-3374.43653876
Frequencies= 66.28
Coordinate:

In	0.0000000000	-0.0000000884	1.3972142175
In	0.0000000000	-0.0000000884	-1.3972142175
K	0.0000000000	3.3634631815	0.0000000000
K	0.0000000000	0.0000000933	-4.9137984972
K	2.9128444233	-1.6817320957	0.0000000000
K	-2.9128444233	-1.6817320957	0.0000000000
K	0.0000000000	0.0000000933	4.9137984972

$Tl_2Li_5^+$
MP2= -381.5177766
Frequencies= 52.5080
Coordinate:

Tl	0.000000000	0.000000000	1.337310000
Tl	0.000000000	0.000000000	-1.337310000
Li	0.000000000	0.000000000	-3.931605000
Li	0.000000000	0.000000000	3.931605000
Li	0.000000000	2.445251000	0.000000000
Li	2.117650000	-1.222626000	0.000000000
Li	-2.117650000	-1.222626000	0.000000000

$Tl_2Na_5^+$
MP2= -1153.6048856
Frequencies= 24.8903
Coordinate:

Tl	0.000000000	0.000000000	1.341525000
Tl	0.000000000	0.000000000	-1.341525000
Na	0.000000000	0.000000000	-4.272312000
Na	0.000000000	0.000000000	4.272312000
Na	0.000000000	2.784157000	0.000000000
Na	2.411151000	-1.392079000	0.000000000
Na	-2.411151000	-1.392079000	0.000000000

$Tl_2K_5^+$
MP2= -3340.14467515
Frequencies= 21.2636
Coordinate:

Tl	0.000000000	0.000000000	1.342215000

Tl	0.000000000	0.000000000	-1.342215000
K	0.000000000	0.000000000	-4.746312000
K	0.000000000	0.000000000	4.746312000
K	0.000000000	3.277273000	0.000000000
K	2.838202000	-1.638636000	0.000000000
K	-2.838202000	-1.638636000	0.000000000