Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Stable global tubular boron clusters in Na_2B_{18} and $Na_2B_{18}^-$

Dong Xue,[a] Anita Das,[b] Wei-yan Liang,[a] Meng-hui Wang,[a] Zhong-hua Cui,*[a]

[a]*Institute of Atomic and Molecular Physics, Jilin Provincial Key Laboratory of Applied Atomic and Molecular Spectroscopy, Jilin University, Changchun, China*

[b]*Department of Chemistry, Indian Institute of Engineering Science and Technology, Shibpur, Howrah, India*

Email: zcui@jlu.edu.cn

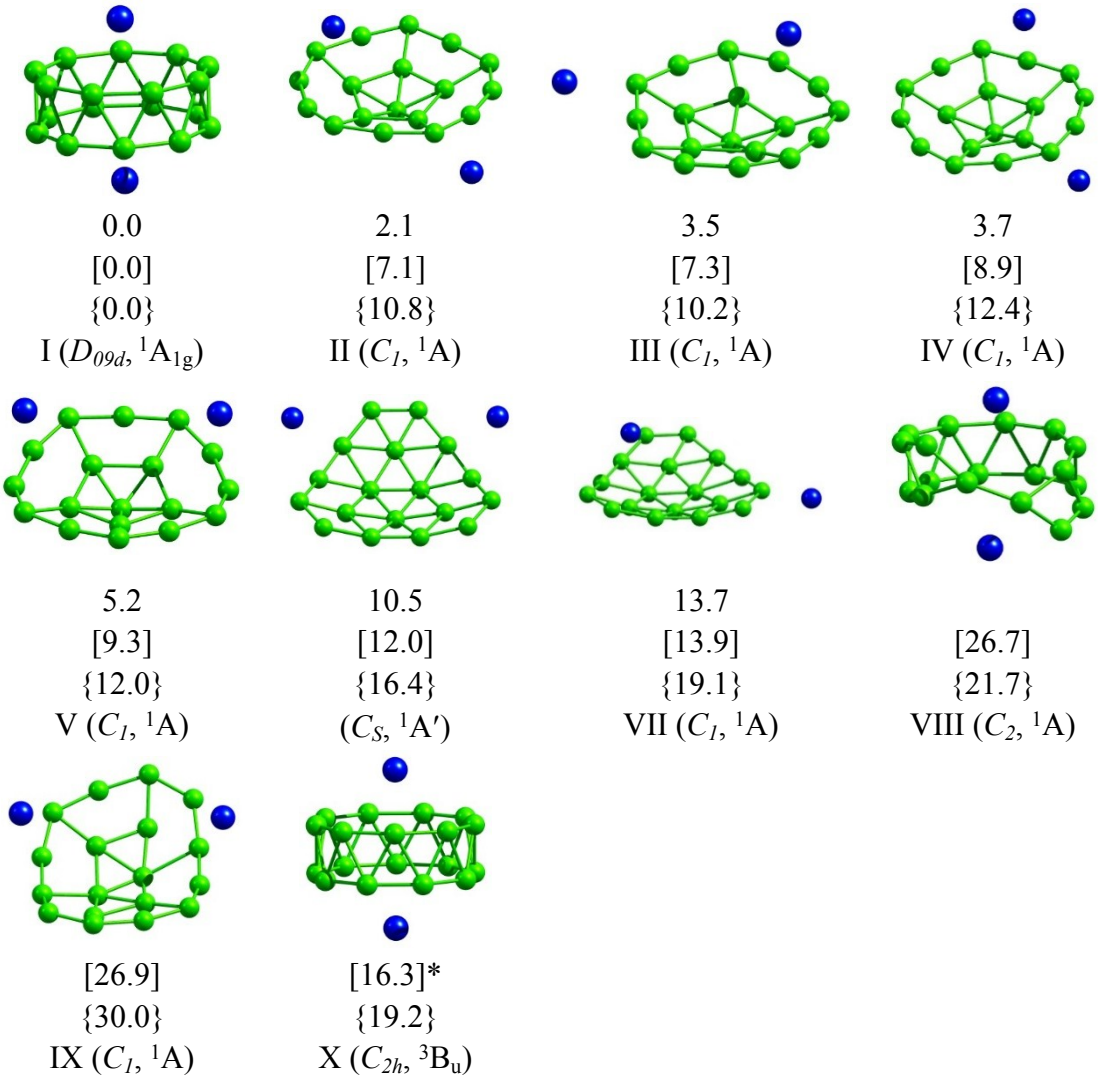


Figure S1. Structures of the lowest lying isomers of the Na_2B_{18} species at the TPSSh/6-311+G(d) level. Relative energies in kcal/mol were computed at the CCSD(T)/6-311+G(d)//TPSSh/6-311+G(d) level, TPSSh/6-311+G(d) (in square brackets), and B3LYP/6-311+G(d) (in curly brackets) levels. All energies are corrected for zero-point energies (ZPE) at their respective levels except for the CCSD(T) single-point calculations, which are ZPE corrected at TPSSh/6-311+G(d). "*" means that a small imaginary frequencies occurred in this level. The point group symmetries and spectroscopic states of lowest lying isomer are shown in parentheses.

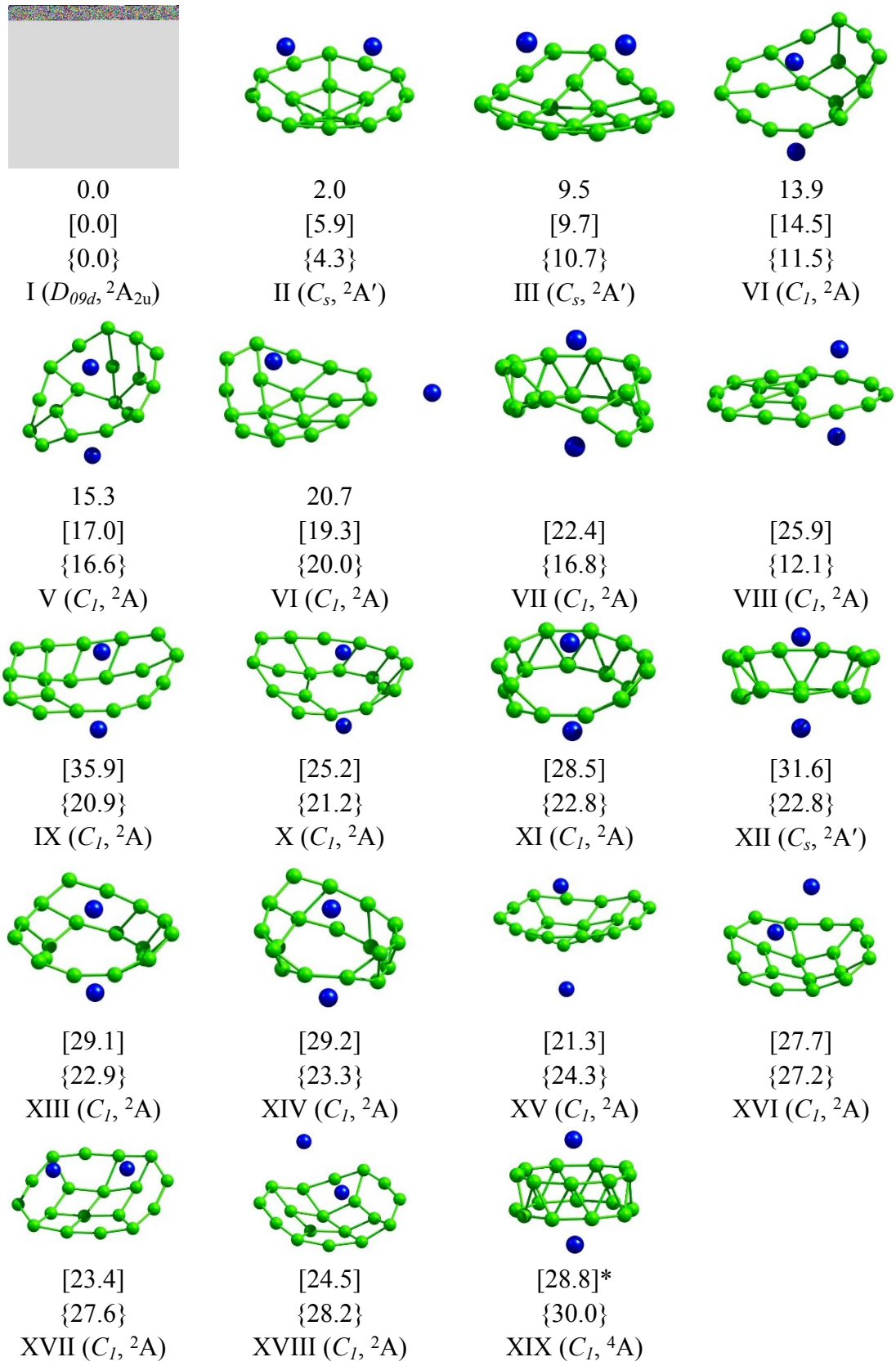


Figure S2. Structures of the lowest lying isomers of the $Na_2B_{18}^-$ species at the TPSSh/6-311+G(d) level. Relative energies in kcal/mol were computed at the

CCSD(T)/6-311+G(d)//TPSSh/6-311+G(d) level, TPSSh/6-311+G(d) (in square brackets), and B3LYP/6-311+G(d) (in curly brackets) levels. All energies are corrected for zero-point energies (ZPE) at their respective levels except for the CCSD(T) single-point calculations, which are ZPE corrected at TPSSh/6-311+G(d). "*" means that a small imaginary frequencies occurred in this level. The point group symmetries and spectroscopic states of lowest lying isomer are shown in parentheses.

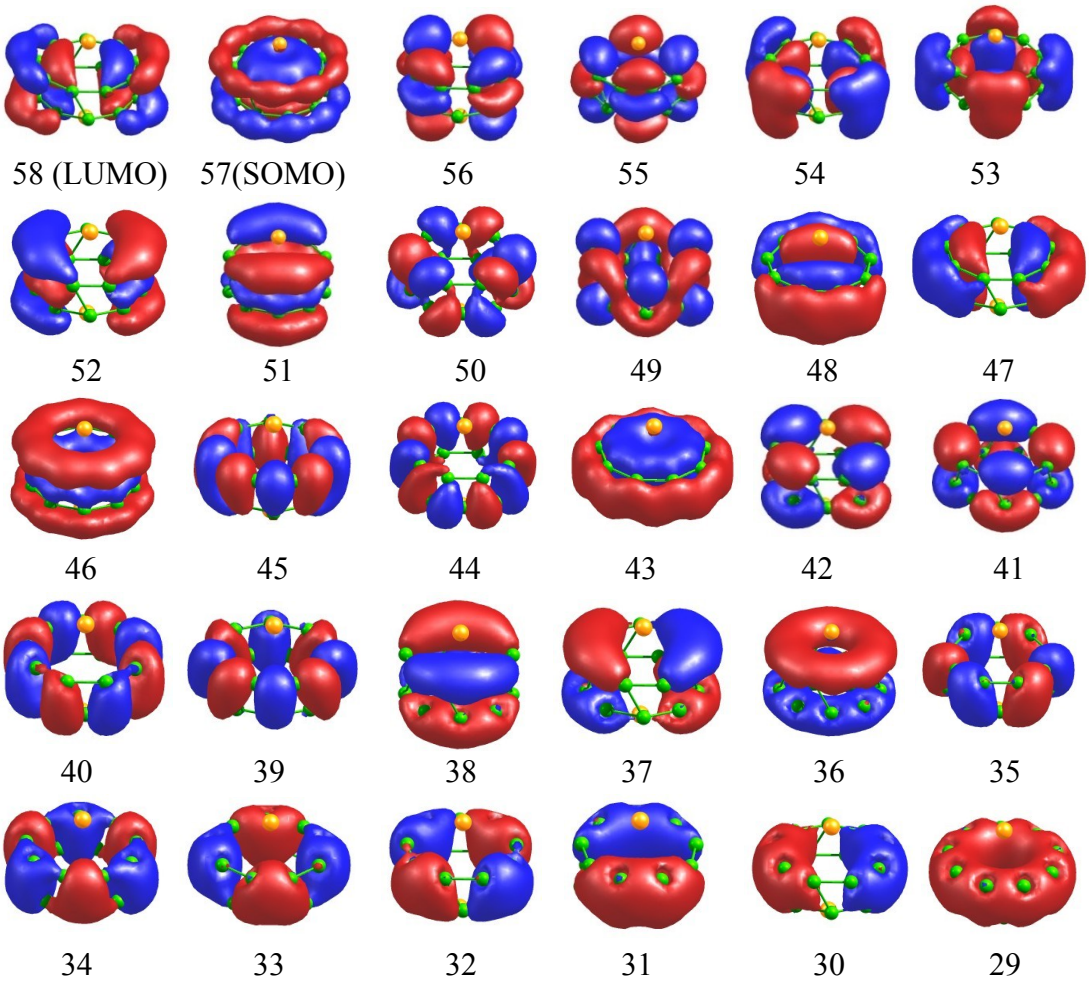
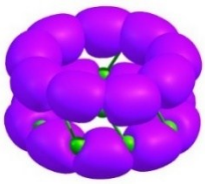
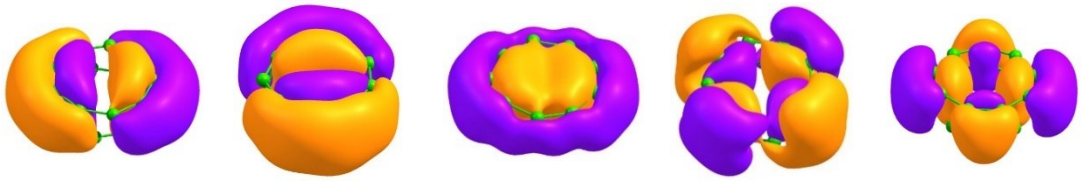


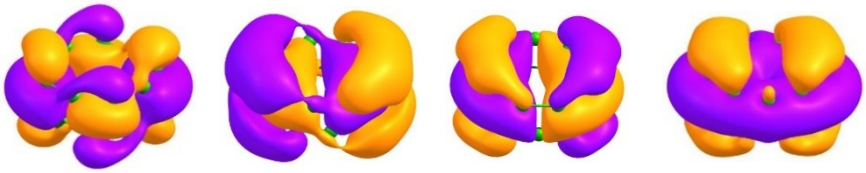
Figure S3. The valence molecular orbitals of the C_{2h} structure of $Na_2B_8^-$ obtained at the B3LYP/6-311+G(d) level.



Eighteen 2c–2e B–B σ bonds ON=1.71~1.83 |e|

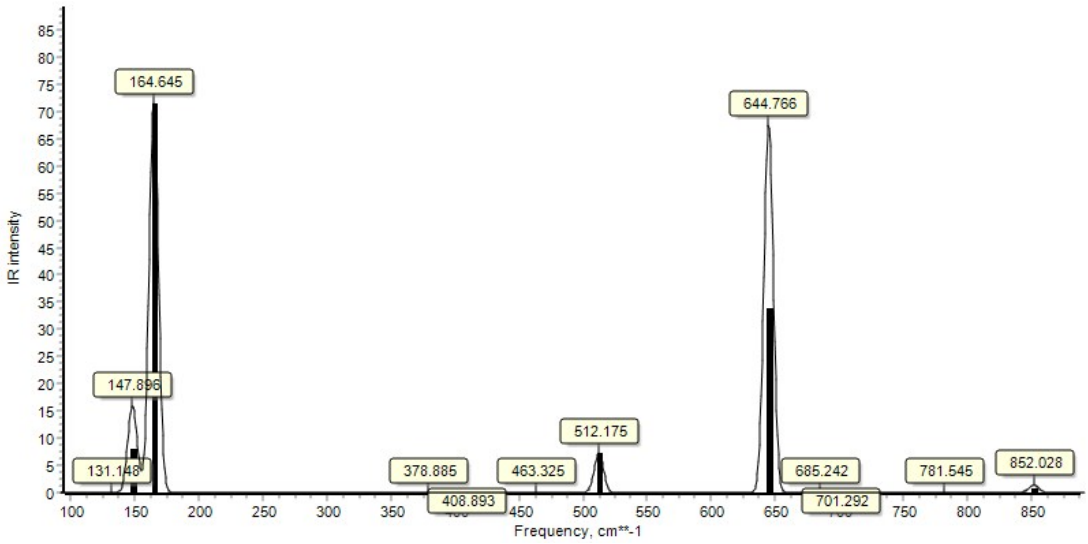


Five 18c–2e σ bonds ON=2.00 |e|

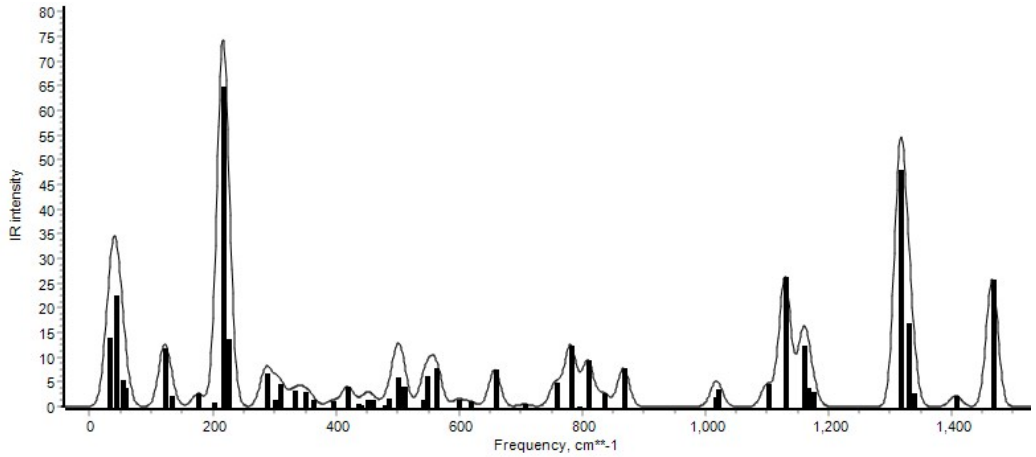


Four 18c–2e π bonds ON=2.00 |e|

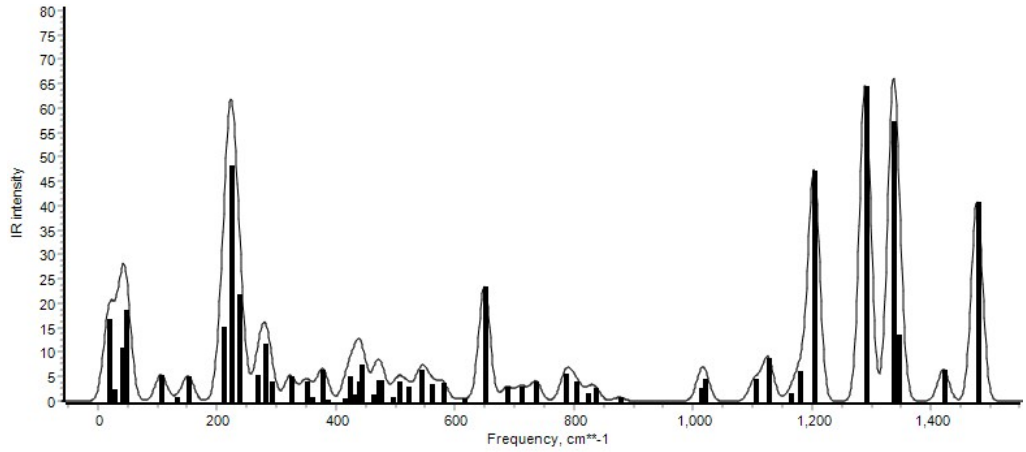
Figure S4. AdNDP analysis for B_{18} computed at the B3LYP/6-311+G(d) level, and ON stands for occupation number.



(a)

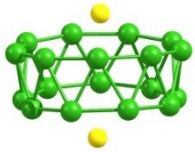


(b)



(c)

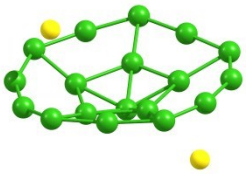
Figure S5. Calculated infrared (IR) absorption spectra (in cm^{-1}) of (a) tubular structure (b) second and (c) third lowest isomer of Na_2B_{18} computed at the B3LYP/6-311+G(d) level.



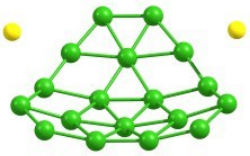
[0.0]
Li01 (C_1,^{1}A)*

[4.3]
Li02 (C_1,^{1}A)

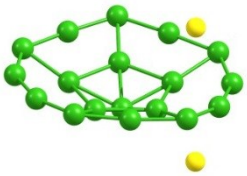
[6.6]
Li03 (C_1,^{1}A)



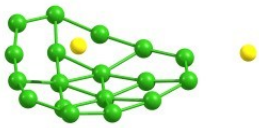
[6.8]
Li04 (C_1,^{1}A)



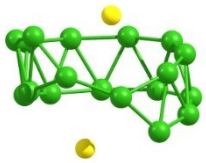
[8.2]
Li05 (C_s,^{1}A')



[8.4]
Li06 (C_1,^{1}A)

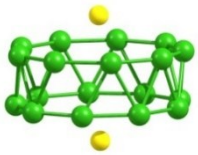


[11.8]
Li07 (C_1,^{1}A)

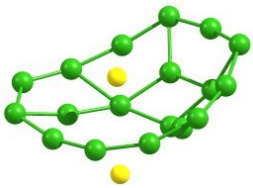


[20.7]
Li08 (C_2,^{1}A)

(a) Li_2B_{18}



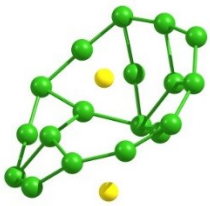
[0.0]
Li-01 (C_{2h},^{2}B$_u$)



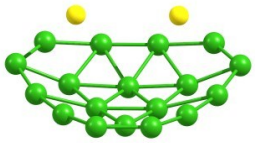
[10.0]
Li-02 (C_1,^{2}A)

[10.1]
Li-03 (C_s,^{2}A')

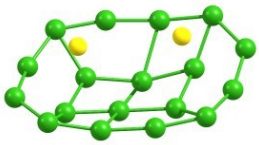
[10.9]
Li-04 (C_1,^{2}A)



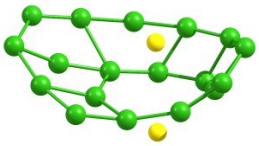
[12.0]
Li-05 (C_1,^{2}A)



[13.1]
Li-06 (C_s,^{2}A')

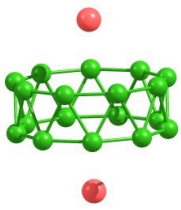


[16.0]
Li-07 (C_1,^{2}A)

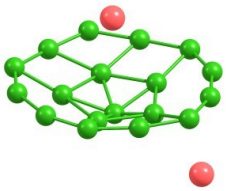


[16.1]
Li-08 (C_1,^{2}A)

(b) $Li_2B_{18}^-$

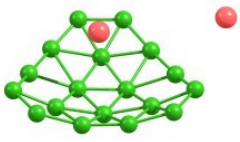


[0.0]
K01 (D_{9d},^{1}A$_{1g}$)

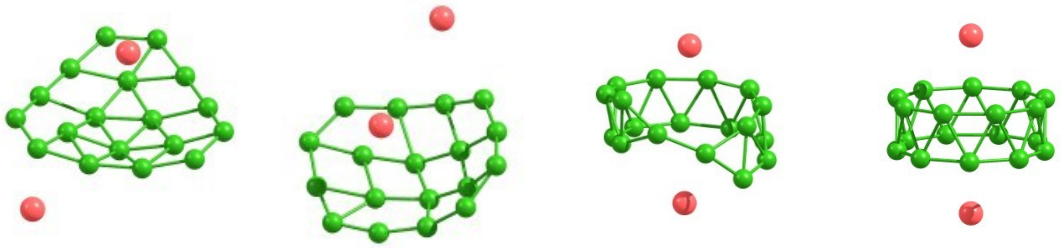


[1.2]
K02 (C_1,^{1}A)

[2.8]
K03 (C_1,^{1}A)

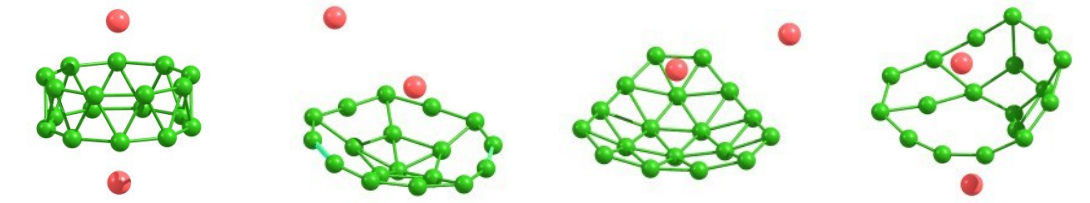


[5.3]
K04 (C_1,^{1}A)

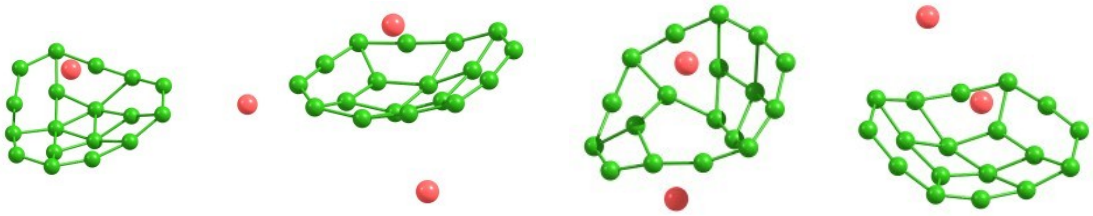


[7.0] K05 (C_1,^{1}A) [23.1] K06 (C_1,^{1}A) [28.0] K07 (C_2,^{1}A) [20.3] K08 (C_1, ^3A_u)

(c) K_2B_{18}



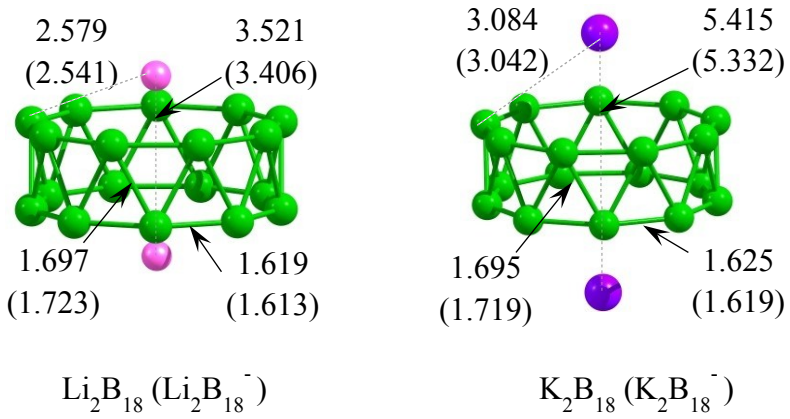
[0.0] K-01 (C_{2h},^2B_u) [5.6] K-02 (C_1,^{2}A) [7.9] K-03 (C_1,^{2}A) [10.1] K-04 (C_1,^{2}A)



[11.5] K-05 (C_s,^{2}A') [12.5] K-06 (C_1,^{2}A) [12.9] K-07 (C_1,^{2}A) [15.7] K-08 (C_1,^{2}A)

(d) $K_2B_{18}^-$

Figure S6. Structures and relative energies (kcal/mol) of the lowest lying isomers of the (a) Li_2B_{18}, (b) $Li_2B_{18}^-$, (c) K_2B_{18}, and (d) $K_2B_{18}^-$ species at the TPSSh/6-311+G(d) level. All energies are corrected for zero-point energies (ZPE). "*" means that a small imaginary frequencies occurred in this level. The point group symmetries and spectroscopic states of lowest lying isomer are shown in parentheses.



Li_2B_{18} ($Li_2B_{18}^-$) K_2B_{18} ($K_2B_{18}^-$)

Figure S7. Structures of M_2B_{18} and $M_2B_{18}^-$ (M=Li, K) computed at the TPSSh/6-311+G(d) level. All distances are in Å and the values shown in parenthesis refer to the anionic $M_2B_{18}^-$ system.

Table S1. The calculated vertical detachment energies (VDE) from the ground state for $Na_2B_{18}^-$. All energies are in eV.

Feature	Final state and electronic configuration	VDE TD-B3LYP
X	$^1A_{1g}$; $7A_{1g}^2\ 5E_{1u}^4\ 3E_{1g}^4\ 4E_{1g}^4\ 6A_{2u}^0$	1.65
A	$^3E_{1u}$; $7A_{1g}^2\ 5E_{1u}^4\ 3E_{1g}^4\ 4E_{1g}^3\ 6A_{2u}^1$	2.63
B	$^1E_{1u}$; $7A_{1g}^2\ 5E_{1u}^4\ 3E_{1g}^4\ 4E_{1g}^3\ 6A_{2u}^1$	2.75
C	$^3E_{1u}$; $7A_{1g}^2\ 5E_{1u}^4\ 3E_{1g}^3\ 4E_{1g}^4\ 6A_{2u}^1$	3.30
D	$^1E_{1u}$; $7A_{1g}^2\ 5E_{1u}^4\ 3E_{1g}^3\ 4E_{1g}^4\ 6A_{2u}^1$	3.60
E	$^3E_{1g}$; $7A_{1g}^2\ 5E_{1u}^3\ 3E_{1g}^4\ 4E_{1g}^4\ 6A_{2u}^1$	5.19
F	$^1E_{1g}$; $7A_{1g}^2\ 5E_{1u}^3\ 3E_{1g}^4\ 4E_{1g}^4\ 6A_{2u}^1$	5.43

The first two VDEs were calculated at the B3LYP/6-311+G(2df)//B3LYP/6-311+G* level of theory as the lowest transition from the doublet state of the anion into the final lowest singlet and triplet states of the neutral species. Then the vertical excitation energies of the neutral species in the lowest singlet and triplet states (at the TD-B3LYP level) were added to the first two VDEs, respectively, in order to obtain higher VDEs.

Table S2. The calculated vertical detachment energies (VDE) from the second lowest isomer of $Na_2B_{18}^-$. All energies are in eV.

Feature	Final state and electronic configuration	VDE TD-B3LYP
X	^{1}A'; 21A"^{2} 29A'^{2} 22A"^{2} 23A"^{2} 30A'^{2} 31A'^{2} 24A"^{2} 32A'^{2} 33A'^{0}	2.55
A	^{3}A'; 21A"^{2} 29A'^{2} 22A"^{2} 23A"^{2} 30A'^{2} 31A'^{2} 24A"^{2} 32A'^{1} 33A'^{1}	3.89
B	^{1}A'; 21A"^{2} 29A'^{2} 22A"^{2} 23A"^{2} 30A'^{2} 31A'^{2} 24A"^{2} 32A'^{1} 33A'^{1}	3.66
C	^{3}A"; 21A"^{2} 29A'^{2} 22A"^{2} 23A"^{2} 30A'^{2} 31A'^{2} 24A"^{1} 32A'^{2} 33A'^{1}	4.10
D	^{1}A"; 21A"^{2} 29A'^{2} 22A"^{2} 23A"^{2} 30A'^{2} 31A'^{2} 24A"^{1} 32A'^{2} 33A'^{1}	3.79
E	^{3}A'; 21A"^{2} 29A'^{2} 22A"^{2} 23A"^{2} 30A'^{2} 31A'^{1} 24A"^{2} 32A'^{2} 33A'^{1}	4.20
F	^{1}A'; 21A"^{2} 29A'^{2} 22A"^{2} 23A"^{2} 30A'^{2} 31A'^{1} 24A"^{2} 32A'^{2} 33A'^{1}	3.92
G	^{3}A'; 21A"^{2} 29A'^{2} 22A"^{2} 23A"^{2} 30A'^{1} 31A'^{2} 24A"^{2} 32A'^{2} 33A'^{1}	4.33
H	^{1}A'; 21A"^{2} 29A'^{2} 22A"^{2} 23A"^{2} 30A'^{1} 31A'^{2} 24A"^{2} 32A'^{2} 33A'^{1}	4.14
I	^{3}A"; 21A"^{2} 29A'^{2} 22A"^{2} 23A"^{1} 30A'^{2} 31A'^{2} 24A"^{2} 32A'^{2} 33A'^{1}	4.49
J	^{1}A"; 21A"^{2} 29A'^{2} 22A"^{2} 23A"^{1} 30A'^{2} 31A'^{2} 24A"^{2} 32A'^{2} 33A'^{1}	4.13
K	^{3}A"; 21A"^{2} 29A'^{2} 22A"^{1} 23A"^{2} 30A'^{2} 31A'^{2} 24A"^{2} 32A'^{2} 33A'^{1}	6.14
L	^{1}A"; 21A"^{2} 29A'^{2} 22A"^{1} 23A"^{2} 30A'^{2} 31A'^{2} 24A"^{2} 32A'^{2} 33A'^{1}	5.80
M	^{3}A'; 21A"^{2} 29A'^{1} 22A"^{2} 23A"^{2} 30A'^{2} 31A'^{2} 24A"^{2} 32A'^{2} 33A'^{1}	6.13
N	^{1}A"; 21A"^{2} 29A'^{1} 22A"^{2} 23A"^{2} 30A'^{2} 31A'^{2} 24A"^{2} 32A'^{2} 33A'^{1}	5.81

The first two VDEs were calculated at the B3LYP/6-311+G(2df)//B3LYP/6-311+G* level of theory as the lowest transition from the doublet state of the anion into the final lowest singlet and triplet states of the neutral species. Then the vertical excitation energies of the neutral species in the lowest singlet and triplet states (at the TD-B3LYP level) were added to the first two VDEs, respectively, in order to obtain higher VDEs.

Table S3. The calculated vertical detachment energies (VDE) from the third lowest isomer of $Na_2B_{18}^-$. All energies are in eV.

Feature	Final state and electronic configuration	VDE TD-B3LYP
X	^{1}A'; 28A'^{2} 22A"^{2} 29A'^{2} 23A"^{2} 30A'^{2} 31A'^{2} 24A"^{2} 32A'^{2} 33A'^{0}	2.68
A	^{3}A'; 28A'^{2} 22A"^{2} 29A'^{2} 23A"^{2} 30A'^{2} 31A'^{2} 24A"^{2} 32A'^{1} 33A'^{1}	3.81
B	^{1}A'; 28A'^{2} 22A"^{2} 29A'^{2} 23A"^{2} 30A'^{2} 31A'^{2} 24A"^{2} 32A'^{1} 33A'^{1}	3.49
C	^{3}A"; 28A'^{2} 22A"^{2} 29A'^{2} 23A"^{2} 30A'^{2} 31A'^{2} 24A"^{1} 32A'^{2} 33A'^{1}	3.85
D	^{1}A"; 28A'^{2} 22A"^{2} 29A'^{2} 23A"^{2} 30A'^{2} 31A'^{2} 24A"^{1} 32A'^{2} 33A'^{1}	3.57
E	^{3}A'; 28A'^{2} 22A"^{2} 29A'^{2} 23A"^{2} 30A'^{2} 31A'^{1} 24A"^{2} 32A'^{2} 33A'^{1}	3.87
F	^{1}A'; 28A'^{2} 22A"^{2} 29A'^{2} 23A"^{2} 30A'^{2} 31A'^{1} 24A"^{2} 32A'^{2} 33A'^{1}	3.63
G	^{3}A'; 28A'^{2} 22A"^{2} 29A'^{2} 23A"^{2} 30A'^{1} 31A'^{2} 24A"^{2} 32A'^{2} 33A'^{1}	4.20
H	^{1}A'; 28A'^{2} 22A"^{2} 29A'^{2} 23A"^{2} 30A'^{1} 31A'^{2} 24A"^{2} 32A'^{2} 33A'^{1}	4.02
I	^{3}A"; 28A'^{2} 22A"^{2} 29A'^{2} 23A"^{1} 30A'^{2} 31A'^{2} 24A"^{2} 32A'^{2} 33A'^{1}	5.06
J	^{1}A"; 28A'^{2} 22A"^{2} 29A'^{2} 23A"^{1} 30A'^{2} 31A'^{2} 24A"^{2} 32A'^{2} 33A'^{1}	4.74
K	^{3}A'; 28A'^{2} 22A"^{2} 29A'^{1} 23A"^{2} 30A'^{2} 31A'^{2} 24A"^{2} 32A'^{2} 33A'^{1}	5.35
L	^{1}A'; 28A'^{2} 22A"^{2} 29A'^{1} 23A"^{2} 30A'^{2} 31A'^{2} 24A"^{2} 32A'^{2} 33A'^{1}	5.07
M	^{3}A"; 28A'^{2} 22A"^{1} 29A'^{2} 23A"^{2} 30A'^{2} 31A'^{2} 24A"^{2} 32A'^{2} 33A'^{1}	5.50
N	^{1}A"; 28A'^{2} 22A"^{1} 29A'^{2} 23A"^{2} 30A'^{2} 31A'^{2} 24A"^{2} 32A'^{2} 33A'^{1}	5.24

The first two VDEs were calculated at the B3LYP/6-311+G(2df)//B3LYP/6-311+G* level of theory as the lowest transition from the doublet state of the anion into the final lowest singlet and triplet states of the neutral species. Then the vertical excitation energies of the neutral species in the lowest singlet and triplet states (at the TD-B3LYP level) were added to the first two VDEs, respectively, in order to obtain higher VDEs.

Table S4. Coordinates

Na_2B_{18}

Na	2.232560000	0.000000000	0.000000000
Na	-2.232560000	0.000000000	0.000000000
B	-0.740516000	0.000000000	-2.373811000
B	0.740516000	0.000000000	2.373811000
B	0.740516000	1.525857000	1.818445000
B	0.740516000	2.337748000	0.412208000
B	0.740516000	2.055781000	-1.186906000
B	0.740516000	0.811891000	-2.230653000
B	0.740516000	-0.811891000	-2.230653000
B	0.740516000	-2.055781000	-1.186906000
B	0.740516000	-2.337748000	0.412208000
B	0.740516000	-1.525857000	1.818445000
B	-0.740516000	1.525857000	-1.818445000
B	-0.740516000	2.337748000	-0.412208000
B	-0.740516000	2.055781000	1.186906000
B	-0.740516000	0.811891000	2.230653000
B	-0.740516000	-0.811891000	2.230653000
B	-0.740516000	-2.055781000	1.186906000
B	-0.740516000	-2.337748000	-0.412208000
B	-0.740516000	-1.525857000	-1.818445000

$Na_2B_{18}^-$

B	2.050440000	-1.183822000	0.755251000
B	0.000000000	2.367645000	0.755251000
B	-2.050440000	-1.183822000	0.755251000
B	-2.331675000	-0.411137000	-0.755251000
B	1.521893000	-1.813721000	-0.755251000
B	0.809782000	2.224858000	-0.755251000
B	2.331675000	-0.411137000	-0.755251000
B	-0.809782000	2.224858000	-0.755251000
B	-1.521893000	-1.813721000	-0.755251000
B	-2.331675000	0.411137000	0.755251000
B	0.809782000	-2.224858000	0.755251000
B	1.521893000	1.813721000	0.755251000
B	2.331675000	0.411137000	0.755251000
B	-1.521893000	1.813721000	0.755251000
B	-0.809782000	-2.224858000	0.755251000
B	-2.050440000	1.183822000	-0.755251000
B	0.000000000	-2.367645000	-0.755251000
B	2.050440000	1.183822000	-0.755251000
Na	0.000000000	0.000000000	-2.146179000
Na	0.000000000	0.000000000	2.146179000