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Prediction of the hypervalent molecules: Investigation on the M_nC (M=Li, Na, K, Rb and Cs; *n*=1-8) clusters

Peng Shao,[a] Bo-Le Chen,[bc] Li-Ping Ding,[*d] Dao-Bin Luo[a], Cheng Lu[*b] and Xiao-Yu Kuang[c]

[a]*Department of Physics, Shaanxi University of Science & Technology, Xi'an 710021, China*

[b]*Department of Physics, Nanyang Normal University, Nanyang, 473061, China*

[c]*Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China*

[d]*Department of Optoelectronic Science & Technology, College of Elecrical & Information Engineering, Shaanxi University of Science & Technology, Xi'an 710021, China*

[*]Correspondence to: Li-Ping Ding, Shaanxi University of Science & Technology, Xi'an 710021, China.
E-mail address: scu_ding@163.com (Li-Ping Ding), lucheng@calypso.cn (Cheng Lu)

Table S1 The average distances of direct M-C bond and the vibration frequencies with most IR intensities of M_nC (M=Li, Na, K, Rb and Cs; *n*=1-8) clusters.

Cluster	Average distance (Å)	Frequency (cm^{-1})
Li_2C	1.951	148, 539, 733
Li_3C	1.916	107, 147, 539, 743
Li_4C	1.866	89, 155, 190, 192, 207, 508, 557, 654, 657
Li_5C	1.941	50, 209, 224, 269, 295, 492, 516, 634, 674
Li_6C	1.989	85, 211, 240, 285, 290, 465, 551, 575, 711
Li_7C	1.991	100, 200, 234, 257, 298, 329, 446, 495, 604, 631
Li_8C	1.996	69, 124, 136, 188, 212, 222, 307, 367, 585, 637
Na_2C	2.376	98, 231, 490
Na_3C	2.386	50, 122, 222, 414
Na_4C	2.284	58, 60, 79, 239, 419, 420
Na_5C	2.406	46, 83, 113, 122, 197, 213, 300, 420
Na_6C	2.409	75, 109, 131, 193, 220, 432,
Na_7C	2.419	35, 66, 74, 106, 110, 124, 135, 190, 216, 416
Na_8C	2.409	11, 35, 40, 72, 75, 108, 109, 130, 149, 219, 419
K_2C	2.726	88, 143, 321
K_3C	2.386	23, 64, 132, 221, 325
K_4C	2.659	58, 60, 154, 287
K_5C	2.814	14, 57, 97, 112, 133, 257, 284
K_6C	2.872	51, 80, 97, 109, 134, 294
K_7C	2.901	38, 50, 51, 74, 78, 87, 95, 122, 246, 276
K_8C	2.869	6, 19, 20, 25, 50, 53, 80, 85, 98, 108, 134, 291
Rb_2C	2.628	20, 32, 304
Rb_3C	3.082	16, 36, 38, 75, 182, 275
Rb_4C	3.150	9, 25, 29, 35, 47, 72, 136, 162, 248
Rb_5C	3.163	17, 28, 31, 49, 63, 77, 189, 249,
Rb_6C	3.192	30, 44, 58, 64, 79, 262
Rb_7C	3.247	16, 25, 28, 30, 39, 45, 50, 51, 53, 71, 207, 226
Rb_8C	3.180	5, 10, 12, 28, 44, 51, 56, 57, 58, 80, 253, 255
Cs_2C	3.267	31, 186, 191
Cs_3C	3.295	12, 26, 42, 55, 148, 235
Cs_4C	3.378	7, 17, 20, 27, 36, 51, 120, 150, 212
Cs_5C	3.417	8, 13, 31, 32, 33, 37, 49, 145, 170
Cs_6C	3.616	12, 13, 16, 22, 23, 25, 34, 45, 48, 104, 139, 170
Cs_7C	3.550	3, 11, 15, 18, 21, 24, 32, 35, 39, 48, 157, 174, 185
Cs_8C	3.569	10, 12, 20, 22, 25, 29, 32, 35, 47, 147, 156, 164

Table S2 Wiberg bond order between carbon and alkali atoms for the ground state Li_nC (n=1-8) clusters. The atom numeration to identify Li atoms is shown in Fig. S5.

Isomers	C-Li2	C-Li3	C-Li4	C-Li5	C-Li6	C-Li7	C-Li8	C-Li9
Li_2C	1.210	1.210						
Li_3C	1.028	1.028	1.028					
Li_4C	1.019	1.019	1.019	1.019				
Li_5C	0.819	0.819	0.819	0.819	0.840			
Li_6C	0.712	0.712	0.712	0.712	0.712	0.712		
Li_7C	0.649	0.727	0.727	0.649	0.727	0.649	0.089	
Li_8C	0.687	0.687	0.687	0.687	0.687	0.108	0.687	0.108

Table S3 Wiberg bond order between carbon and alkali atoms for the ground state Na_nC (n=1-8) clusters. The atom numeration to identify Na atoms is shown in Fig. S5.

Isomers	C-Na2	C-Na3	C-Na4	C-Na5	C-Na6	C-Na7	C-Na8	C-Na9
Na_2C	1.098	1.098						
Na_3C	0.708	0.709	0.740					
Na_4C	0.983	0.983	0.983	0.983				
Na_5C	0.713	0.713	0.693	0.713	0.713			
Na_6C	0.689	0.689	0.689	0.689	0.689	0.689		
Na_7C	0.625	0.108	0.649	0.649	0.625	0.649	0.649	
Na_8C	0.133	0.674	0.000	0.646	0.646	0.674	0.646	0.674

Table S4 Wiberg bond order between carbon and alkali atoms for the ground state K_nC (n=1-8) clusters. The atom numeration to identify K atoms is shown in Fig. S5.

Isomers	C-K2	C-K3	C-K4	C-K5	C-K6	C-K7	C-K8	C-K9
K_2C	0.904	0.904						
K_3C	0.821	0.845	0.935					
K_4C	0.920	0.920	0.920	0.920				
K_5C	0.623	0.623	0.623	0.623	0.652			
K_6C	0.634	0.634	0.634	0.634	0.634	0.634		
K_7C	0.068	0.490	0.490	0.490	0.471	0.471	0.471	
K_8C	0.000	0.628	0.592	0.622	0.586	0.592	0.628	0.115

Table S5 Wiberg bond order between carbon and alkali atoms for the ground state Rb_nC (n=1-8) clusters. The atom numeration to identify Rb atoms is shown in Fig. S5.

Isomers	C-Rb2	C-Rb3	C-Rb4	C-Rb5	C-Rb6	C-Rb7	C-Rb8	C-Rb9
Rb_2C	0.968	0.968						
Rb_3C	0.397	0.434	0.434					
Rb_4C	0.397	0.352	0.397	0.352				
Rb_5C	0.570	0.570	0.570	0.570	0.481			
Rb_6C	0.641	0.641	0.641	0.641	0.641	0.641		
Rb_7C	0.480	0.480	0.067	0.480	0.480	0.480	0.480	
Rb_8C	0.588	0.128	0.588	0.638	0.583	0.638	0.056	0.632

Table S6 Wiberg bond order between carbon and alkali atoms for the ground state Cs_nC (n=1-8) clusters. The atom numeration to identify Cs atoms is shown in Fig. S5.

Isomers	C-Cs2	C-Cs3	C-Cs4	C-Cs5	C-Cs6	C-Cs7	C-Cs8	C-Cs9
Cs_2C	0.896	0.896						
Cs_3C	0.407	0.379	0.379					
Cs_4C	0.396	0.369	0.333	0.333				
Cs_5C	0.602	0.487	0.602	0.602	0.602			
Cs_6C	0.250	0.250	0.316	0.316	0.251	0.251		
Cs_7C	0.053	0.484	0.500	0.500	0.500	0.484	0.478	
Cs_8C	0.000	0.293	0.266	0.235	0.000	0.293	0.293	0.293

Fig. S1 The ground state structures and second low-lying isomers of Li_nC (a), Na_nC (b), K_nC (c), Rb_nC (d) and Cs_nC (e) (n=1-8) clusters.The grey, pink, purple, green, blue and brown spheres represent the C, Li, Na, K, Rb and Cs atoms, respectively.

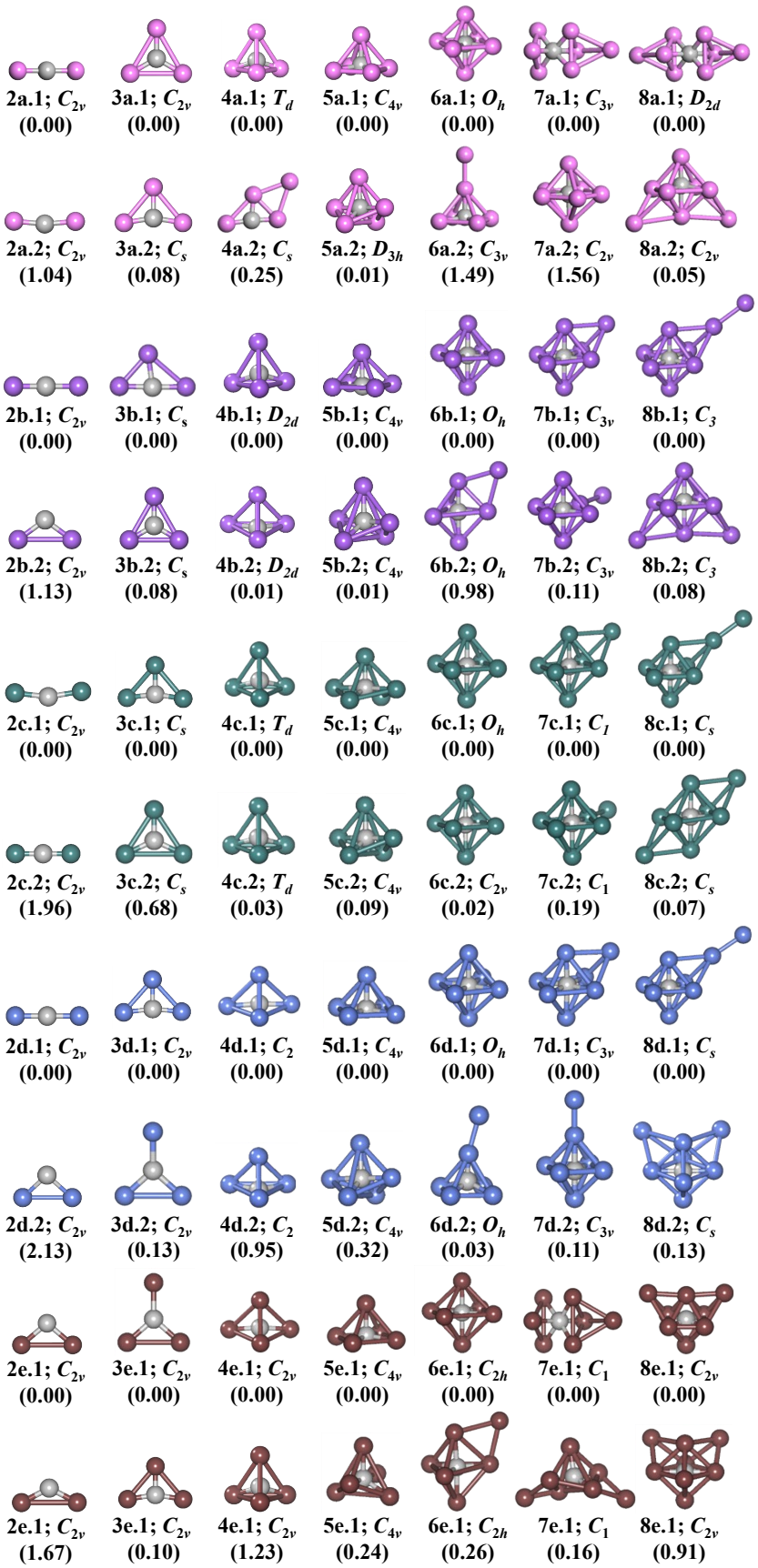

Fig. S2 Contour maps of the HOMOs of the ground state M_nC (M=Li, Na and K; *n*=3, 7-8) clusters.

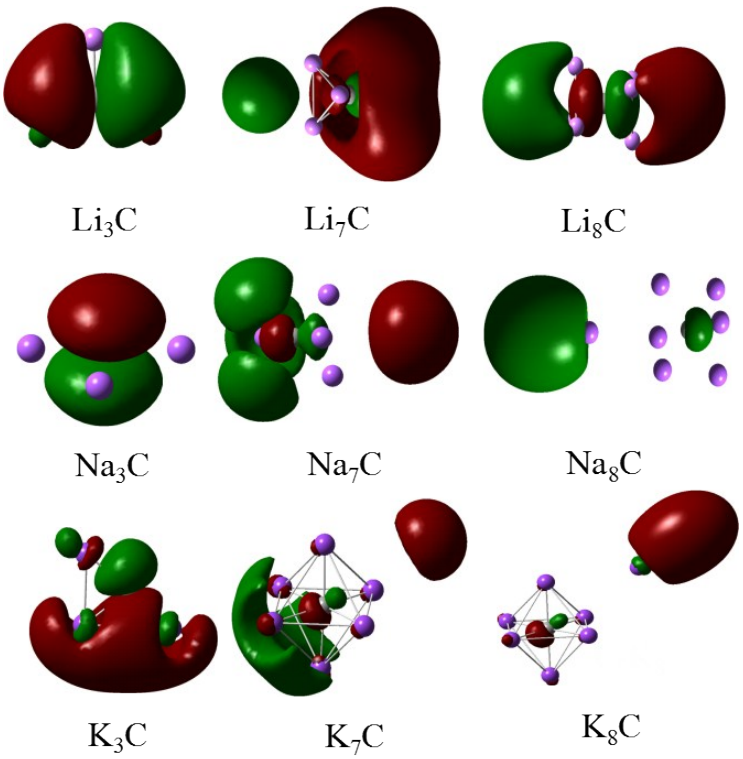

Fig. S3 Contour maps of the HOMOs of the ground state M_nC (M= Rb and Cs; *n*=1-8) clusters.

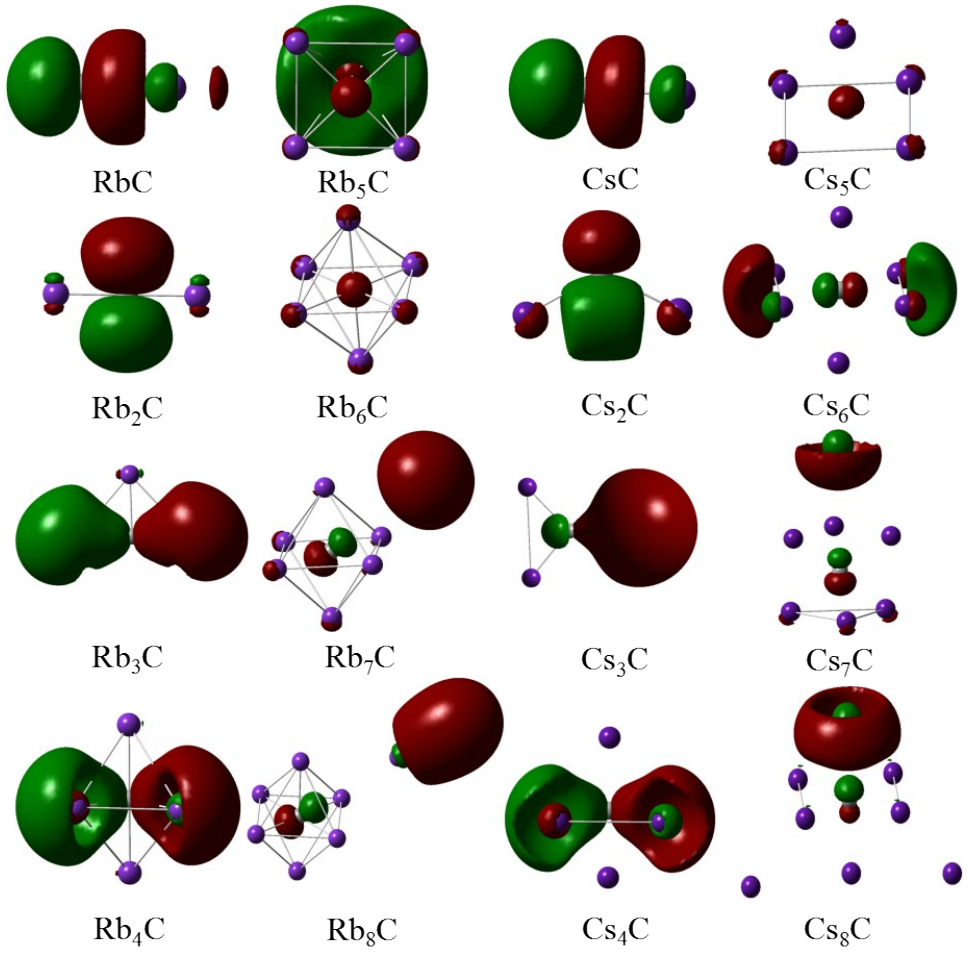

Fig. S4 The atom numeration to identify alkali atomss for the ground state structures of Li_nC (a), Na_nC (b), K_nC (c), Rb_nC (d) and Cs_nC (e) (n=1-8) clusters.

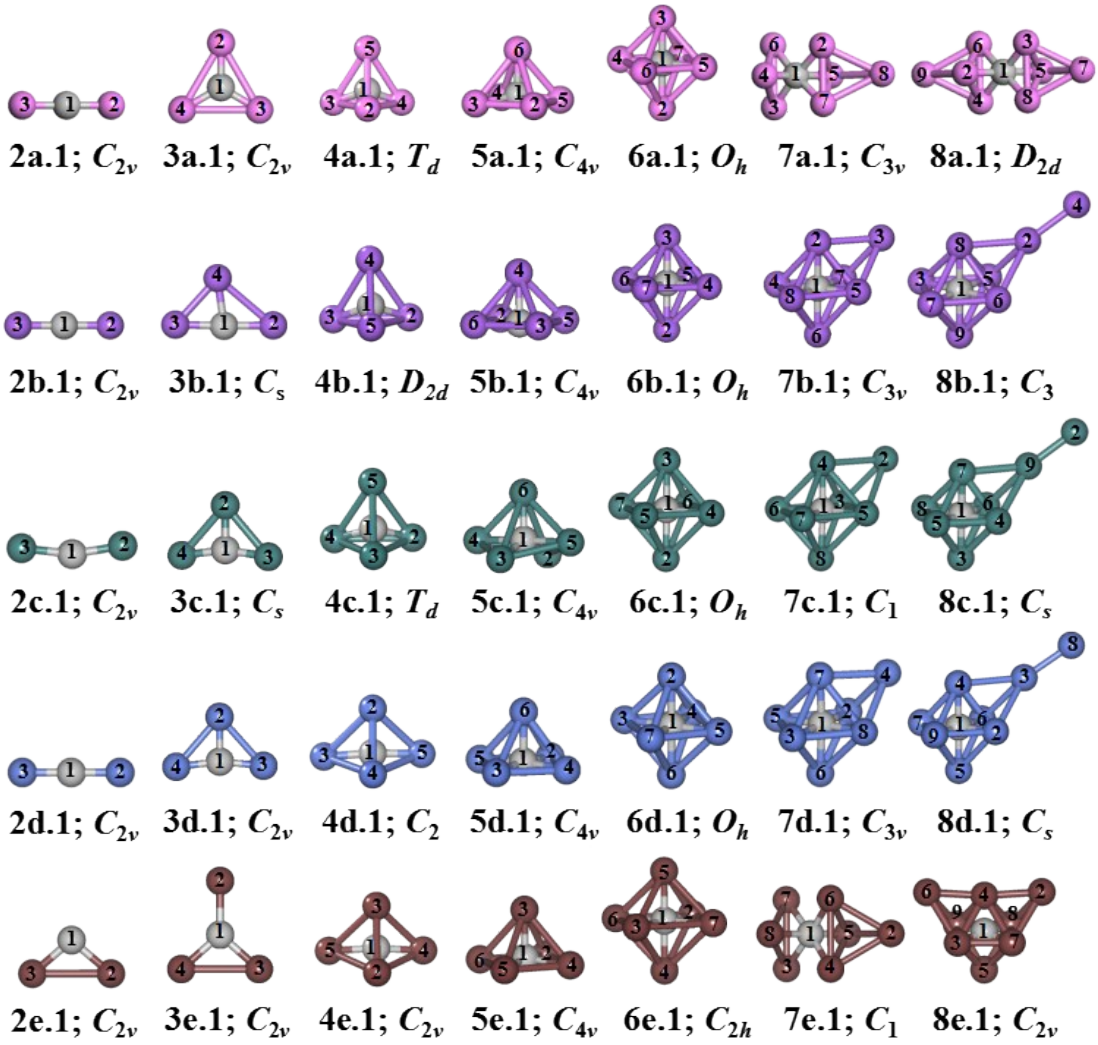

Fig. S5 Electron localization function plots of the ground state M_nC (M=Li, Na and K; *n*=2-4, 7 and 8) clusters.