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Parity Alternation Effects in the Stabilities of the Second-Row-Atom-Doped Linear Carbon Clusters $C_nX/C_nX^+/C_nX^-$ ($n = 1-10$; X = Na, Mg, Al, Si, P, S or Cl). A Comparative Study

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A comparative investigation has been carried out on second-row-atom-doped linear carbon clusters $C_nX/C_nX^+/C_nX^-$ ($n = 1-10$) using density functional theory (DFT-B3LYP) method in conjunction with 6-311+G* basis sets. For each linear $C_nX/C_nX^+/C_nX^-$ species, the low-lying states, total energies, geometries, incremental binding energies, ionization potentials, and electron affinities are considered. The incremental binding energy diagrams show that, doped by different heteroatoms X, $C_nX/C_nX^+/C_nX^-$ clusters exhibit different parity alternation effects in their stabilities, and these parity effects also appear in the ionization potential and electron affinity curves. For different kinds of the $C_nX/C_nX^+/C_nX^-$ clusters, the parity effects in their stabilities are discussed and compared. Systematic investigations of their electronic distributions find that the parity effects in their stabilities are attributed to the numbers of their valence π-electrons.

I. Introduction

In past decades pure carbon clusters have been extensively studied both experimentally and theoretically,[1−3] because detailed knowledge about the physical and chemical properties of these clusters is important for understanding a large variety of chemical systems. Carbon clusters with larger size, e.g., fullerenes, have been one of the most highlighted scientific research fields. The discovery[4] and successful preparation[5] of C_{60} and other fullerenes have spawned a new branch of chemistry. Even before the development of fullerene chemistry, the studies of smaller size carbon clusters engaged great interest.[1,3,6−8] The reason for this interest results from not only their role as intermediates in the chemical vapor deposition of carbon clusters[9] but also their role in astrochemistry.[10,11] In the interstellar medium, the reactivity of small carbon clusters is forfeited by quasicollisionless conditions, and carbon takes the highly stable, albeit highly reactive, form of linear chains.[12−14] In these linear carbon chains the atomic orbitals are sp-hybridized.[15,16] Lagow et al. have also synthesized bulk quantities of such carbon chains containing as many as 28 carbon atoms by stabilizing the terminal carbons with bulky organic end-capping groups.[17] According to their observations, they suggest that these long chains of sp-hybridized carbon atoms may constitute a “fourth stable allotrope of carbon”, after diamond, graphite, and fullerene.

Heteroatom-doped carbon clusters containing a first- or second-row element of the periodic table have attracted much attention in the past few years. Leleyter et al. have studied a series of heterocarbon cluster anions C_nX^- by various experimental techniques and the theoretical Hückel model, where the heteroatom X is a main group element such as N, F, Cl, H, Al, Si, S, or B.[18] According to their experiments, these C_nX^- anions exhibit a dramatic even−odd alternation in ion intensity, and generally the clusters with even numbers of carbon atoms have relatively higher signal intensities, except for C_nN^-. Zheng et al. have generated cluster anions C_nX^- (X = N, P, As, Sb, Bi),[19] C_nN^-,[20] C_nB^-,[21] C_nP^-,[22,23] and AlC_n^- [23] from laser ablation of appropriate samples and studied them by time-of-flight mass spectrometry. Since their observed signal intensities can be well fitted by a log-normal distribution curve, according to their statistical distribution model,[24] they predict that the C_nX^- clusters should have linear structures with the heteroatom X located on one end of the carbon chain. To explore their experimental observations, Zheng et al. have also done some ab initio quantum chemical computations at the Hartree−Fock (HF) level with 3-21G basis sets, and the calculated results are consistent with the observed even−odd alternation. Thinking that the HF/3-21G method is not good enough to give reasonable results for the C_nX^- systems, Zhan and Iwata (ZI) reinvestigated C_nN^-,[25] C_nB^-,[26] and C_nP^- [27] at different approximation levels such as Møller−Plesset (MP2), MP4SDTQ, and QCISD(T) methods with various basis sets. Although ZI predicted that some C_nX^- anions have slightly bent ground-state structures with the MP2/6-31G(d)[END+] method, most of the structural features calculated in the bent geometry do not exhibit significant differences from those computed with linear structure. Moreover, computations made by Pascoli and Lavendy (PL) at much higher levels of theory (CCSD(T)) have revealed that C_nP^- ($n = 2-7$) clusters should be linear.[28] PL also found that C_nN^- ($n = 2-7$) clusters are linear, too, in their ground state.[29] Besides anionic C_nX^- clusters, many cationic C_nX^+ and neutral C_nX clusters, such as C_nSi^+,[30,31] C_nS,[32] C_nS^+,[33] and C_nP^+ [34,35] are also extensively studied. Very recently, a series of papers published by Largo, Cimas, Redondo, and Barrientos (LCRB) presents their theoretical studies of the C_3Cl,[36] AlC_3,[37] $C_nCl/C_nCl^+/C_nCl^-$,[38] AlC_3^+,[39] MgC_3,[40] NaC_3,[41] and $AlC_n/AlC_n^+/AlC_n^-$ [42] clusters. From the calculation results above, it seems that the medium-sized heteroatom-doped carbon clusters have linear or nearly linear ground-state structures and an even−odd alternation in their stabilities.

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TABLE 1: Total Energies (in hartrees) and Numbers of Imaginary Vibrational Frequencies (in Parentheses) for the Lowest Lying States of Linear $C_nX/C_nX^+/C_nX^-$ Clusters with B3LYP/6-311+G* Method[a]

n	CC_n	NaC_n	MgC_n	AlC_n
0	^{3}P −37.857 27	^{2}S −162.286 78	^{1}S −200.093 26	^{2}P −242.386 40
1	$^{1}\Sigma_g$ −75.901 59 (0)	$^{4}\Sigma$ −200.211 69 (0)[b]	$^{3}\Sigma$ −238.003 00 (0)[c]	$^{4}\Sigma$ −280.364 70 (0)[d]
2	$^{1}\Sigma_g$ −114.076 91 (0)	$^{2}\Sigma$ −238.349 93 (2)[e]	$^{1}\Sigma$ −276.131 17 (0)[f]	$^{2}\Sigma$ −318.498 32 (0)[g]
3	$^{3}\Sigma_g$ −152.131 94 (0)	$^{2}\Pi$ −276.437 85 (0)	$^{3}\Pi$ −314.209 97 (0)	$^{2}\Pi$ −356.568 95 (0)
4	$^{1}\Sigma_g$ −190.254 54 (0)	$^{2}\Pi$ −314.542 18 (0)	$^{3}\Pi$ −352.312 52 (1)[h]	$^{2}\Pi$ −394.670 51 (1)
5	$^{3}\Sigma_g$ −228.318 05 (0)	$^{2}\Pi$ −352.629 10 (0)	$^{3}\Pi$ −390.399 30 (0)	$^{2}\Pi$ −432.757 99 (0)
6	$^{1}\Sigma_g$ −266.430 52 (0)	$^{2}\Pi$ −390.726 99 (1)[h]	$^{3}\Pi$ −428.496 43 (0)	$^{2}\Pi$ −470.854 72 (0)
7	$^{3}\Sigma_g$ −304.500 38 (0)	$^{2}\Pi$ −428.813 59 (0)	$^{3}\Pi$ −466.583 15 (0)	$^{2}\Pi$ −508.941 88 (0)
8	$^{1}\Sigma_g$ −342.607 26 (0)	$^{2}\Pi$ −466.909 12 (0)	$^{3}\Pi$ −504.678 22 (0)	$^{2}\Pi$ −547.036 80 (0)
9	$^{3}\Sigma_g$ −380.681 24 (2)[h]	$^{2}\Pi$ −504.995 87 (0)	$^{3}\Pi$ −542.764 97 (2)[h]	$^{2}\Pi$ −585.124 01 (2)[h]
10	$^{1}\Sigma_g$ −418.784 39 (0)	$^{2}\Pi$ −543.089 89 (2)[h]	$^{3}\Pi$ −580.858 98 (2)[h]	$^{2}\Pi$ −623.217 78 (2)[h]
n	SiC_n	C_nP	C_nS	C_nCl
0	^{3}P −289.394 17	^{4}S −341.281 73	^{3}P −398.133 07	^{2}P −460.166 88
1	$^{3}\Pi$ −327.406 08 (0)[i]	$^{2}\Sigma$ −379.329 60 (0)[j]	$^{1}\Sigma$ −436.249 39 (0)	$^{2}\Pi$ −498.172 22 (0)
2	$^{1}\Sigma$ −365.569 68 (0)	$^{2}\Pi$ −417.415 38 (0)	$^{3}\Sigma$ −474.276 39 (0)	$^{2}\Pi$ −536.248 51 (0)
3	$^{3}\Sigma$ −403.622 69 (0)	$^{2}\Pi$ −455.509 94 (0)	$^{1}\Sigma$ −512.406 68 (0)	$^{2}\Pi$ −574.329 72 (1)
4	$^{1}\Sigma$ −441.744 91 (0)	$^{2}\Pi$ −493.600 48 (1)[h]	$^{3}\Sigma$ −550.460 92 (0)	$^{2}\Pi$ −612.431 16 (1)
5	$^{3}\Sigma$ −479.806 99 (0)	$^{2}\Pi$ −531.693 64 (0)	$^{1}\Sigma$ −588.579 06 (0)	$^{2}\Pi$ −650.517 73 (2)
6	$^{1}\Sigma$ −517.919 20 (0)	$^{2}\Pi$ −569.782 31 (0)	$^{3}\Sigma$ −626.643 10 (0)	$^{2}\Pi$ −688.615 54 (2)
7	$^{3}\Sigma$ −555.987 88 (0)	$^{2}\Pi$ −607.875 08 (0)	$^{1}\Sigma$ −664.753 85 (2)[h]	$^{2}\Pi$ −726.702 38 (2)
8	$^{1}\Sigma$ −594.094 63 (0)	$^{2}\Pi$ −645.963 19 (0)	$^{3}\Sigma$ −702.823 60 (2)	$^{2}\Pi$ −764.797 91 (2)
9	$^{3}\Sigma$ −632.167 42 (2)[h]	$^{2}\Pi$ −684.055 52 (2)[h]	$^{1}\Sigma$ −740.929 44 (0)	$^{2}\Pi$ −802.885 00 (2)
10	$^{1}\Sigma$ −670.270 76 (2)[h]	$^{2}\Pi$ −722.143 55 (2)[h]	$^{3}\Sigma$ −779.003 24 (2)[h]	$^{2}\Pi$ −840.979 14 (2)[h]
n	CC_n^+	NaC_n^+	MgC_n^+	AlC_n^+
0	^{2}P −37.432 85	^{1}S −162.087 57	^{2}S −199.809 27	^{1}S −242.165 42
1	$^{4}\Pi_g$ −75.459 43 (0)	$^{3}\Pi$ −199.955 54 (0)[k]	$^{4}\Sigma$ −237.708 20 (0)[l]	$^{3}\Sigma$ −280.044 40 (0)[m]
2	$^{2}\Sigma_u$ −113.625 77 (0)	$^{3}\Pi$ −238.045 08 (0)[n]	$^{2}\Sigma$ −275.842 81 (0)[o]	$^{3}\Sigma$ −318.159 61 (2)
3	$^{2}\Pi_g$ −151.716 80 (0)	$^{1}\Sigma$ −276.193 35 (0)	$^{2}\Sigma$ −313.922 49 (0)	$^{1}\Sigma$ −356.269 51 (0)
4	$^{2}\Sigma_u$ −189.828 64 (0)	$^{3}\Sigma$ −314.256 34 (0)	$^{2}\Pi$ −352.017 60 (2)	$^{3}\Sigma$ −394.342 34 (0)
5	$^{2}\Pi_u$ −227.943 75 (0)	$^{1}\Sigma$ −352.383 80 (0)	$^{2}\Sigma$ −390.119 63 (0)	$^{1}\Sigma$ −432.466 14 (0)
6	$^{2}\Sigma_u$ −266.029 56 (0)	$^{3}\Sigma$ −390.452 67 (0)	$^{2}\Pi$ −428.205 22 (2)	$^{3}\Sigma$ −470.538 22 (1)[h]
7	$^{2}\Pi_g$ −304.152 62 (0)	$^{1}\Sigma$ −428.569 48 (0)	$^{2}\Sigma$ −466.310 36 (0)	$^{1}\Sigma$ −508.657 69 (0)
8	$^{2}\Pi_g$ −342.254 71 (2)	$^{3}\Sigma$ −466.642 87 (0)	$^{2}\Pi$ −504.390 33 (1)	$^{3}\Sigma$ −546.733 48 (0)
9	$^{2}\Pi_u$ −380.352 32 (2)[h]	$^{1}\Sigma$ −504.753 41 (2)[h]	$^{2}\Sigma$ −542.497 93 (2)[h]	$^{1}\Sigma$ −584.846 56 (2)[h]
10	$^{2}\Pi_u$ −418.450 99 (0)	$^{3}\Sigma$ −542.829 77 (2)[h]	$^{4}\Sigma$ −580.576 17 (2)[p]	$^{3}\Sigma$ −622.924 59 (2)[h]
n	SiC_n^+	C_nP^+	C_nS^+	C_nCl^+
0	^{2}P −289.096 05	^{3}P −340.900 00	^{4}S −397.746 96	^{3}P −459.686 38
1	$^{4}\Sigma$ −327.078 24 (0)[q]	$^{3}\Pi$ −378.930 28 (0)[r]	$^{2}\Sigma$ −435.826 73 (0)[s]	$^{1}\Sigma$ −497.836 86 (0)
2	$^{2}\Sigma$ −365.211 05 (0)[t]	$^{1}\Sigma$ −417.076 04 (0)	$^{2}\Pi$ −473.892 72 (0)	$^{3}\Sigma$ −535.862 41 (2)
3	$^{2}\Pi$ −403.288 55 (0)	$^{3}\Sigma$ −455.156 53 (1)[h]	$^{2}\Sigma$ −512.026 29 (0)[u]	$^{1}\Sigma$ −574.015 68 (0)
4	$^{2}\Sigma$ −441.399 76 (0)[v]	$^{1}\Sigma$ −493.284 22 (0)	$^{2}\Pi$ −550.113 98 (0)	$^{3}\Sigma$ −612.083 39 (2)
5	$^{2}\Pi$ −479.493 81 (0)	$^{3}\Sigma$ −531.364 76 (1)	$^{2}\Sigma$ −588.223 65 (0)[w]	$^{1}\Sigma$ −650.217 89 (2)[h]
6	$^{2}\Pi$ −517.593 38 (1)	$^{1}\Sigma$ −569.481 90 (0)	$^{2}\Pi$ −626.319 50 (0)	$^{3}\Sigma$ −688.290 86 (2)
7	$^{2}\Pi$ −555.689 68 (0)	$^{3}\Sigma$ −607.563 08 (0)	$^{2}\Pi$ −664.420 95 (2)	$^{1}\Sigma$ −726.413 25 (2)
8	$^{2}\Pi$ −593.786 15 (0)	$^{1}\Sigma$ −645.674 15 (0)	$^{2}\Pi$ −702.516 30 (2)	$^{3}\Sigma$ −764.489 07 (2)
9	$^{2}\Pi$ −631.880 71 (2)[h]	$^{3}\Sigma$ −683.756 01 (2)[h]	$^{2}\Pi$ −740.614 18 (0)	$^{1}\Sigma$ −802.604 14 (2)
10	$^{2}\Pi$ −669.975 38 (2)[h]	$^{1}\Sigma$ −721.863 10 (2)[h]	$^{2}\Pi$ −778.708 12 (2)[h]	$^{3}\Sigma$ −840.682 09 (2)
n	CC_n^-	NaC_n^-	MgC_n^-	AlC_n^-
0	^{4}S −37.907 30	^{1}S −162.308 27	^{2}P −200.085 04	^{3}P −242.400 57
1	$^{2}\Sigma_g$ −76.062 21 (0)	$^{3}\Sigma$ −200.242 98 (0)	$^{4}\Sigma$ −238.050 98 (0)	$^{3}\Pi$ −280.406 94 (0)[x]
2	$^{2}\Pi_g$ −114.158 28 (0)	$^{1}\Sigma$ −238.405 92 (0)	$^{2}\Sigma$ −276.226 65 (0)	$^{1}\Sigma$ −318.610 94 (0)
3	$^{2}\Pi_g$ −152.270 75 (0)	$^{3}\Pi$ −276.481 13 (1)[y]	$^{2}\Pi$ −314.279 13 (0)[z]	$^{3}\Sigma$ −356.663 90 (0)
4	$^{2}\Pi_u$ −190.363 22 (0)	$^{1}\Sigma$ −314.613 33 (2)[h]	$^{2}\Sigma$ −352.425 53 (0)	$^{1}\Sigma$ −394.808 34 (0)
5	$^{2}\Pi_u$ −228.465 78 (0)	$^{3}\Pi$ −352.679 93 (0)[aa]	$^{4}\Sigma$ −390.484 43 (0)	$^{3}\Sigma$ −432.866 54 (0)
6	$^{2}\Pi_g$ −266.555 66 (0)	$^{1}\Sigma$ −390.815 76 (0)	$^{2}\Sigma$ −428.618 67 (0)	$^{1}\Sigma$ −470.996 87 (0)
7	$^{2}\Pi_g$ −304.654 39 (0)	$^{3}\Sigma$ −428.879 27 (0)	$^{4}\Sigma$ −466.682 54 (0)	$^{3}\Sigma$ −509.060 54 (0)
8	$^{2}\Pi_u$ −342.743 45 (0)	$^{1}\Sigma$ −467.011 25 (0)	$^{2}\Sigma$ −504.807 91 (0)	$^{1}\Sigma$ −547.182 88 (0)
9	$^{2}\Pi_u$ −380.839 97 (2)	$^{3}\Sigma$ −505.078 18 (1)[h]	$^{4}\Sigma$ −542.875 29 (2)[h]	$^{3}\Sigma$ −585.250 29 (2)[h]
10	$^{2}\Pi_g$ −418.928 56 (0)	$^{1}\Sigma$ −543.202 39 (2)	$^{2}\Sigma$ −580.994 68 (2)[h]	$^{1}\Sigma$ −623.367 25 (2)[h]
n	SiC_n^-	C_nP^-	C_nS^-	C_nCl^-
0	^{4}S −289.442 92	^{3}P −341.315 20	^{2}P −398.213 69	^{1}S −460.303 73
1	$^{2}\Sigma$ −327.490 54 (0)[bb]	$^{1}\Sigma$ −379.438 67 (0)	$^{2}\Pi$ −436.259 64 (0)	$^{3}\Sigma$ −498.223 31 (0)
2	$^{2}\Pi$ −365.631 61 (0)	$^{3}\Sigma$ −417.515 93 (0)	$^{2}\Pi$ −474.375 36 (0)	$^{1}\Sigma$ −536.371 24 (0)
3	$^{2}\Pi$ −403.720 78 (0)	$^{1}\Sigma$ −455.645 30 (0)	$^{2}\Pi$ −512.467 89 (1)	$^{3}\Sigma$ −574.397 76 (2)
4	$^{2}\Pi$ −441.830 42 (0)	$^{3}\Sigma$ −493.716 35 (0)	$^{2}\Pi$ −550.577 22 (0)	$^{1}\Sigma$ −612.558 46 (2)
5	$^{2}\Pi$ −479.919 51 (0)	$^{1}\Sigma$ −531.835 95 (0)	$^{2}\Pi$ −588.668 25 (0)	$^{3}\Sigma$ −650.608 48 (2)
6	$^{2}\Pi$ −518.020 46 (1)[h]	$^{3}\Sigma$ −569.908 29 (0)	$^{2}\Pi$ −626.770 68 (0)	$^{1}\Sigma$ −688.749 51 (2)
7	$^{2}\Pi$ −556.110 55 (0)	$^{1}\Sigma$ −608.022 58 (0)	$^{2}\Pi$ −664.860 62 (0)	$^{3}\Sigma$ −726.808 73 (2)
8	$^{2}\Pi$ −594.207 35 (0)	$^{3}\Sigma$ −646.096 58 (0)	$^{2}\Pi$ −702.959 42 (1)[h]	$^{1}\Sigma$ −764.937 70 (2)
9	$^{2}\Pi$ −632.297 80 (2)[h]	$^{1}\Sigma$ −684.207 03 (2)[h]	$^{2}\Pi$ −741.048 46 (0)	$^{3}\Sigma$ −803.002 28 (2)
10	$^{2}\Pi$ −670.392 42 (2)[h]	$^{3}\Sigma$ −722.282 48 (2)[h]	$^{2}\Pi$ −779.145 17 (2)[h]	$^{1}\Sigma$ −841.123 66 (2)[h]

[a] Values are not corrected for zero point energies (ZPE). [b] Its $^{2}\Pi$ state is 0.99 eV (22.7 kcal/mol) less stable. [c] Its $^{3}\Pi$ state is 1.05 eV (24.3 kcal/mol) less stable. [d] Its $^{2}\Pi$ state is 1.41 eV (32.9 kcal/mol) less stable. [e] Its $^{2}\Pi$ state is 0.18 eV (4.1 kcal/mol) less stable. [f] Its $^{3}\Pi$ state is 0.38 eV (8.8 kcal/mol) less stable. [g] Its $^{2}\Pi$ state is 0.66 eV (15.1 kcal/mol) less stable. [h] With B3LYP/6-311G* method, all these structures have no imaginary vibrational frequency. [i] Its $^{3}\Sigma$ state is 0.30 eV (6.8 kcal/mol) less stable. [j] Its $^{2}\Pi$ state is 0.66 eV (15.3 kcal/mol) less stable. [k] Its $^{1}\Sigma$ state is 1.37 eV (31.5 kcal/mol) less stable. [l] Its $^{2}\Sigma$ state is 1.90 eV (43.8 kcal/mol) less stable. [m] Its $^{1}\Sigma$ state is 1.58 eV (36.3 kcal/mol) less stable. [n] Its $^{3}\Sigma$ state is 0.31 eV (7.1 kcal/mol) less stable. [o] Its $^{2}\Pi$ state is 0.41 eV (9.5 kcal/mol) less stable. [p] Its $^{2}\Pi$ state is 0.06 eV (1.5 kcal/mol) less stable. [q] Its $^{2}\Pi$ state is 1.29 eV (29.8 kcal/mol) less stable. [r] Its $^{2}\Pi$ state is 0.53 eV (12.3 kcal/mol) less stable. [s] Its $^{2}\Pi$ state is 1.27 eV (29.3 kcal/mol) less stable. [t] Its $^{2}\Pi$ state is 0.87 eV (20.0 kcal/mol) less stable. [u] Its $^{2}\Pi$ state is 0.42 eV (9.7 kcal/mol) less stable. [v] Its $^{2}\Pi$ state is 0.15 eV (3.6 kcal/mol) less stable. [w] Its $^{2}\Pi$ state is only 0.06 eV (1.4 kcal/mol) less stable. [x] Its $^{1}\Sigma$ state is 0.12 eV (2.7 kcal/mol) less stable. [y] Its $^{3}\Sigma$ state is 0.68 eV (15.7 kcal/mol) less stable. [z] Its $^{4}\Sigma$ state is 0.08 eV (1.8 kcal/mol) less stable. [aa] Its $^{3}\Sigma$ state is 0.18 eV (4.1 kcal/mol) less stable. [bb] Its $^{2}\Pi$ state is 0.26 eV (5.9 kcal/mol) less stable.

TABLE 2: Numbers of Valence σ- and π-Electrons for Linear $C_nX/C_nX^+/C_nX^-$ Clusters with B3LYP/6-311+G* Method[a]

	1		2		3		4		5		6		7		8		9		10	
n	σ	π	σ	π	σ	π	σ	π	σ	π	σ	π	σ	π	σ	π	σ	π	σ	π
CC_n	4	4	8	4	10	6	12	8	14	10	16	12	18	14	20	16	22	18	24	20
NaC_n	3	2	5	4	8	5	10	7	12	9	14	11	16	13	18	15	20	17	22	19
MgC_n	4	2	6	4	9	5	11	7	13	9	15	11	17	13	19	15	21	17	23	19
AlC_n	5	2	7	4	10	5	12	7	14	9	16	11	18	13	20	15	22	17	24	19
SiC_n	5	3	8	4	10	6	12	8	14	10	16	12	18	14	20	16	22	18	24	20
PC_n	5	4	8	5	10	7	12	9	14	11	16	13	18	15	20	17	22	19	24	21
SC_n	6	4	8	6	10	8	12	10	14	12	16	14	18	16	20	18	22	20	24	22
ClC_n	6	5	8	7	10	9	12	11	14	13	16	15	18	17	20	19	22	21	24	23
NaC_n^+	3	1	5	3	8	4	10	6	12	8	14	10	16	12	18	14	20	16	22	18
MgC_n^+	3	2	5	4	9	4	10	7	13	8	14	11	17	12	18	15	21	16	23	18
AlC_n^+	4	2	6	4	10	4	10	8	14	8	16	10	18	12	20	14	22	16	24	18
SiC_n^+	5	2	7	4	10	5	11	8	14	9	16	11	18	13	20	15	22	17	24	19
PC_n^+	5	3	8	4	10	6	12	8	14	10	16	12	18	14	20	16	22	18	24	20
SC_n^+	5	4	8	5	9	8	12	9	13	12	16	13	18	15	20	17	22	19	24	21
ClC_n^+	6	4	8	6	10	8	12	10	14	12	16	14	18	16	20	18	22	20	24	22
NaC_n^-	4	2	6	4	9	5	10	8	13	9	14	12	16	14	18	16	20	18	22	20
MgC_n^-	5	2	7	4	10	5	11	8	13	10	15	12	17	14	19	16	21	18	23	20
AlC_n^-	5	3	8	4	10	6	12	8	14	10	16	12	18	14	20	16	22	18	24	20
SiC_n^-	5	4	8	5	10	7	12	9	14	11	16	13	18	15	20	17	22	19	24	21
PC_n^-	6	4	8	6	10	8	12	10	14	12	16	14	18	16	20	18	22	20	24	22
SC_n^-	6	5	8	7	10	9	12	11	14	13	16	15	18	17	20	19	22	21	24	23
ClC_n^-	6	6	8	8	10	10	12	12	14	14	16	16	18	18	20	20	22	22	24	24

[a] The core $1s^2$ electrons of carbon atom and $1s^22s^22p^6$ electrons of second-row-atom X are excluded.

Despite these numerous theoretical works reported, each of them only deals with one kind of $C_nX^{(\pm)}$ species, and few of them concern $C_nX^{(\pm)}$ clusters with different heteroatoms. What is the relationship between the stabilities for different heteroatom-doped carbon clusters? How do the heteroatom affect the stabilities of $C_nX^{(\pm)}$ clusters? Besides, studies for larger $NaC_n^{(\pm)}$ and $MgC_n^{(\pm)}$ clusters have not been found in the literature to date to our knowledge. Herein we present a systematic investigation on the second-row-atom-doped carbon clusters $C_nX/C_nX^+/C_nX^-$ ($n = 1-10$; X = Na, Mg, Al, Si, P, S, or Cl). Their stabilities, ionization potentials (IP), and electron affinities (EA) are all considered, with special attention focused on the comparison between different kinds of $C_nX^{(\pm)}$ species. To simplify our study, only heteroatom-terminated linear chain structures are investigated in present work. This is because (1) most of the $C_nX^{(\pm)}$ clusters are linear in their ground state, as shown in the theoretical studies mentioned above, and (2) for the $C_nX^{(\pm)}$ clusters having nonlinear ground state structures, the energy gap between the linear isomer and the bent ground state is usually very small,[38] so use of the total energies of the linear structures instead of the bent structures does not change the trends about the relative stabilities.[25]

II. Theoretical Methods

The linear isomers of the $C_nX/C_nX^+/C_nX^-$ ($n = 1-10$; X = Na, Mg, Al, Si, P, S, or Cl) clusters were fully optimized using density functional theory (DFT) method at the B3LYP/6-311+G* level, where B3LYP was formed from Becke's three-parameter nonlocal exchange functional[43] along with the Lee, Yang, and Parr nonlocal correlation functional.[44] Considering the computational efficiency and accuracy, DFT/B3LYP method has been well documented by its successful application to many medium-sized heteroatom-doped carbon clusters.[28−35,38,42] The 6-311G specifies the standard split-valence triple-ζ 6-311G basis sets for C atom and the McLean−Chandler (12s9p)/[6s5p] basis sets for all second-row atoms (Na, Mg, Al, Si, P, S, and Cl).[45,46] Because of the inclusion of both cations and anions in this study, the 6-311G basis sets were augmented with d-polarization functions and diffuse sp-functions. It has been shown that such basis sets are able to give accurate results for $C_nX/C_nX^+/C_nX^-$ clusters.[28,38,42]

To assess the nature of the stationary points, harmonic vibrational frequencies were computed from analytic gradient techniques. All calculations were carried out with the Gaussian 98 program suite.[47] Spin-restricted wave functions were used for all closed-shell systems, and spin-unrestricted references were employed for the open-shell species. Stability calculations[48,49] were performed to ensure the wave function computed corresponds to the lowest energy solution for the system investigated.

III. Results and Discussion

A. Overview of the Total Energies and Electronic States for Linear $C_nX/C_nX^+/C_nX^-$ Clusters. We have studied the linear isomers of all second-row-atom-doped carbon clusters $C_nX/C_nX^+/C_nX^-$ in both their singlet and triplet states for the even-electron-number systems, while for the clusters having odd numbers of electrons both their doublet and quartet states were considered. The spin contamination is not serious because the $\langle S^2 \rangle$ values are uniform and only slightly deviate from the pure spin values, and the B3LYP wave functions are nearly spin-pure. We have indicated this in Table 1, which shows the lowest lying states and their total electronic energies for the clusters investigated.

As can be seen in Table 1, second-row-atom-doped carbon clusters $C_nX/C_nX^+/C_nX^-$ show many interesting characters:

(i) For most of the $C_nX/C_nX^+/C_nX^-$ clusters, their X-terminated linear conformations have all real vibrational frequencies, expressing that they are minima on the corresponding potential energy surfaces (PES). Their stability has been testified to by many previous studies.[14,20,21,28−30,32−34,42]

It should be noted that, for larger $C_nX/C_nX^+/C_nX^-$ ($n = 9-10$) clusters, B3LYP/6-311+G* calculations usually predict their linear isomers having two imaginary vibrational frequencies. Because of the large overlap between the diffuse functions, the 6-311+G* basis sets become overly complete for some carbon chain systems.[25−27] Thus, we recompute these systems with 6-311G* basis sets, in which diffuse sp-functions are excluded. At the B3LYP/6-311G* level of computations, most of these linear isomers have no imaginary vibrational frequency, indicating that they should be stable.

All the $C_nCl/C_nCl^+/C_nCl^-$ clusters in linear form are saddle points on the corresponding PES because of their imaginary vibrational frequencies, except for some smaller clusters such as CCl, CCl^+, CCl^-, C_2Cl, C_3Cl^+, and C_2Cl^-. As shown in the study of LCRB,[38] most of the $C_nCl/C_nCl^+/C_nCl^-$ ($n = 1-7$) clusters adopt Cl-terminated quasi-linear structures for the ground-state geometries.

(ii) When some smaller $C_nX/C_nX^+/C_nX^-$ ($n = 1-2$) clusters are excluded, doublet electronic states with Π symmetry are more stable than the corresponding quartet states for most of the odd-electron-number systems (except for MgC_n^- and MgC_n^+, vide infra), while for most of the even-electron-number systems the lowest energy states alternate between singlet $^1\Sigma$ and triplet $^3\Sigma$, again with the Mg-containing system (MgC_n) being the exception.

Different from other even-electron-number systems, linear MgC_n ($n > 2$) clusters are all in triplet $^3\Pi$ electronic states. On the other hand, for linear MgC_n^- clusters, the lowest energy states alternate between doublet $^2\Sigma$ for n-even members and $^4\Sigma$ for n-odd ones, with the only exception of MgC_3^- (its $^4\Sigma$ state is less stable than the $^2\Pi$ doublet state by 0.08 eV). For MgC_n^+, although their lower energy states are doublets, most of them have Σ symmetry. These all are very different from other odd-electron-number systems.

B. Electronic Configurations. To understand why the lowest energy states for linear $C_nX/C_nX^+/C_nX^-$ clusters are as shown above, we collect their valence electron numbers in Table 2. Here, we exclude the core $1s^2$ electrons of carbon atom and the core $1s^22s^22p^6$ electrons of second-row-atom X. For comparison, Table 2 also includes the valence electron numbers of linear CC_n clusters (we use CC_n, instead of C_n, to be consistent with C_nX).

First, the clusters SiC_n are considered. Except for the two core 1s electrons of each carbon atom and the 10 core $1s^22s^22p^6$ electrons of the second-row atom, SiC_n cluster has $4n + 4$ valence electrons. Based on molecular orbital theory, quantum chemical computations predict that linear SiC_n clusters have the following electronic configurations:

SiC_3: (core) $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 4\sigma^2 5\sigma^2 2\pi^2$

SiC_4: (core) $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2 6\sigma^2 2\pi^4$

SiC_5: (core) $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 1\pi^4 6\sigma^2 2\pi^4 7\sigma^2 3\pi^2$

SiC_6: (core) $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 1\pi^4 2\pi^4 7\sigma^2 8\sigma^2 3\pi^4$

SiC_7: (core) $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 1\pi^4 2\pi^4 8\sigma^2 3\pi^4 9\sigma^2 4\pi^2$

SiC_8: (core) $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma^2 1\pi^4 2\pi^4 9\sigma^2 3\pi^4 10\sigma^2 4\pi^4$

SiC_9: (core) $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma^2 9\sigma^2 1\pi^4 2\pi^4 3\pi^4 10\sigma^2 11\sigma^2 4\pi^4 5\pi_u{}^2$

SiC_{10}: (core) $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 5\sigma^2 6\sigma^2 7\sigma^2 8\sigma^2 9\sigma^2 10\sigma^2 1\pi^4 2\pi^4 3\pi^4 11\sigma^2 4\pi^4 12\sigma^2 5\pi_u{}^4$

This is summarized by

$$\begin{cases} \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\dfrac{n+1}{2}\right)\pi^2 & n\text{-odd members} \\ \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\dfrac{n}{2}\right)\pi^4 & n\text{-even members} \end{cases}$$

(except for SiC).

Thus, except for the smallest member SiC, linear SiC_n cluster contains $2n + 4$ valence σ-electrons and $2n$ valence π-electrons, as shown in Table 2. The $2n + 4$ valence σ-electrons fully occupy $n + 2$ σ-orbitals. For the species with even n, the $2n$ π-electrons constitute a closed shell and result in a $^1\Sigma$ electronic state. For the cluster with odd n, however, two of the $2n$ π-electrons are distributed over a pair of degenerate π-orbitals, corresponding to a half-filled π-orbital, so that the lowest energy state of this open-shell configuration is $^3\Sigma$.

Phosphorus atom has one more electron than silicon atom, so phosphorus-doped carbon cluster C_nP should have $4n + 5$ valence electrons. The electronic configurations for linear C_nP clusters can be generalized as

$$\begin{cases} \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\dfrac{n+1}{2}\right)\pi^3 & n\text{-odd members} \\ \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\dfrac{n+2}{2}\right)\pi^1 & n\text{-even members} \end{cases}$$

(except for CP: (core) $1\sigma^2\ 2\sigma^2\ 3\sigma^1\ 1\pi^4$).

There are $2n + 4$ valence $\boldsymbol{\sigma}$-electrons and $2n + 1$ valence $\boldsymbol{\pi}$-electrons (as shown in Table 2). After the $2n + 4$ valence σ-electrons fully occupy $n + 2$ σ-orbitals, one (for n-even species) or three (for n-odd species) of the $2n + 1$ $\boldsymbol{\pi}$-electrons are distributed over a pair of π-orbitals, corresponding to π^1 or π^3 distributions. Both of them will result in $^2\Pi$ electronic states for linear C_nP clusters.

For sulfur-doped linear carbon clusters C_nS, there are $4n + 6$ valence electrons and the electronic configurations are

$$\begin{cases} \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\dfrac{n+1}{2}\right)\pi^4 & n\text{-odd members} \\ \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\dfrac{n+2}{2}\right)\pi^2 & n\text{-even members} \end{cases}$$

There are $2n + 4$ valence σ-electrons and $2n + 2$ valence π-electrons (as shown in Table 2). When n is even, two of the π-electrons are distributed over a pair of degenerate π-orbitals, leading to a half-filled π-orbital and a $^3\Sigma$ electronic state. When n is odd, the $2n + 2$ π-electrons fully occupy $(n + 1)/2$ π-orbitals, corresponding to a closed shell and a $^1\Sigma$ state. This is opposite the case for the linear SiC_n clusters.

Linear chlorine-doped carbon clusters C_nCl have $4n + 7$ valence electrons, which are distributed over the valence orbitals as follows:

$$\begin{cases} \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\dfrac{n+3}{2}\right)\pi^1 & n\text{-odd members} \\ \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\dfrac{n+2}{2}\right)\pi^3 & n\text{-even members} \end{cases}$$

There are $2n + 4$ valence σ-electrons and $2n + 3$ valence π-electrons (as shown in Table 2). Again, both the π^3 (for n-even species) and π^1 (for n-odd species) configurations will result in $^2\Pi$ electronic states for linear C_nCl.

Compared with chlorine atom, aluminum atom has four less electrons, so aluminum-doped carbon cluster AlC_n has $4n + 3$ valence electrons. For linear AlC_n, the electronic configurations are

$$\begin{cases} \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\dfrac{n+1}{2}\right)\pi^1 & n\text{-odd members} \\ \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\dfrac{n}{2}\right)\pi^3 & n\text{-even members} \end{cases}$$

(except for AlC: (core) $1\sigma^2\ 2\sigma^2\ 1\pi^2\ 3\sigma^1$ and AlC_2: (core) $1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 1\pi^4\ 4\sigma^1$).

Among the $4n + 3$ valence electrons, there are $2n + 4$ valence σ-electrons and $2n - 1$ valence π-electrons (as shown in Table 2). Since π-orbitals are doubly degenerate, four electrons can fully occupy a pair of π-orbitals, so the four valence π-electron difference between AlC_n and C_nCl does not change the ground electronic states. Similar to linear C_nCl, linear AlC_n clusters also have $^2\Pi$ electronic states, except for smaller members (AlC has $^4\Sigma$ and AlC_2 has $^2\Sigma$).

Magnesium atom has one less electron than aluminum atom. Linear magnesium-doped carbon clusters MgC_n have $4n + 2$ valence electrons and the following electronic distributions:

$$\begin{cases} \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^1\left(\frac{n+1}{2}\right)\pi^1 & n\text{-odd members} \\ \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots \left(\frac{n}{2}\right)\pi^3(n+2)\sigma^1 & n\text{-even members} \end{cases}$$

(except for MgC: (core) $1\sigma^2$ $2\sigma^2$ $1\pi^2$ and MgC_2: (core) $1\sigma^2$ $2\sigma^2$ $1\pi^4$ $3\sigma^2$).

That is, linear MgC_n clusters contain $2n + 3$ valence σ-electrons and $2n - 1$ valence π-electrons (as shown in Table 2) except for smaller members MgC and MgC_2. Unlike the cases of AlC_n, SiC_n, C_nP, C_nS, and C_nCl, in which the valence electron differences change the valence π-electron numbers and the valence σ-electron numbers remain fixed, the one-electron difference between MgC_n and AlC_n results in different valence σ-electron numbers. Both the π^3 σ^1 (for the n-even members) and σ^1 π^1 (for the n-odd members) configurations will give $^3\Pi$ electronic states for linear MgC_n clusters.

Linear sodium-doped carbon clusters NaC_n have $4n + 1$ valence electrons. The electronic configurations are

$$\begin{cases} \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots (n+1)\sigma^2\left(\frac{n+1}{2}\right)\pi^1 & n\text{-odd members} \\ \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots (n+1)\sigma^2\left(\frac{n}{2}\right)\pi^3 & n\text{-even members} \end{cases}$$

(except for NaC: (core) $1\sigma^2$ $2\sigma^1$ $1\pi^2$ and NaC_2: (core) $1\sigma^2$ $2\sigma^2$ $3\sigma^1$ $1\pi^4$).

There are $2n + 2$ valence σ-electrons and $2n - 1$ valence π-electrons (as shown in Table 2). Again, the one-electron difference between NaC_n and MgC_n changes their valence σ-electron numbers. Similar to linear C_nCl and AlC_n, both the π^3 (for n-even members) and π^1 (for n-odd members) electronic distributions will result in $^2\Pi$ electronic ground states for linear NaC_n clusters.

The valence σ- and π-electron numbers for the second-row-atom-doped linear carbon cluster C_nX can also be derived from its two fragments: C_n and X. Similar to SiC_{n-1}, C_n cluster has $4n$ valence electrons, $2n + 2$ valence σ-electrons and $2n - 2$ valence π-electrons. Among the $2n + 2$ valence σ-electrons, there are $2n - 2$ bonding σ-electrons, occupying $n - 1$ bonding σ-orbitals, and four lone-pair electrons, belonging to two terminal carbon atoms (see Figure 1 for the valence molecular orbitals of linear C_7 cluster, as an example). When a C_n cluster is doped by an X atom, one of the two terminal carbon atoms will be penultimate, so that one of its lone-pair electrons must occupy an energetically higher π-orbital, leaving the σ-orbital hole to accommodate the electron from the X atom and to form a new σ-bond. Thus, among all valence electrons of linear C_nX, there are $2n + 1$ valence σ-electrons and $2n - 1$ valence π-electrons coming from the C_n fragments. Sodium atom has only one valence electron ($3s^1$), so linear NaC_n has $2n + 2$ valence σ-electrons and $2n - 1$ valence π-electrons, resulting in $^2\Pi$ electronic state. Similarly, linear MgC_n has $2n + 3$ valence σ-electrons and $2n - 1$ valence π-electrons, resulting in $^3\Pi$ electronic state, and linear AlC_n has $2n + 4$ valence σ-electrons and $2n - 1$ valence π-electrons, resulting in $^2\Pi$ electronic state. Since linear C_nX has $n + 2$ energetically lower σ-orbitals at most (n bonding σ-orbitals and 2 lone-pair σ-orbitals), for linear SiC_n, after the $n + 2$ σ-orbitals are fully occupied, one of the four valence electrons ($3s^23p^2$) from silicon atom must be distributed in an energetically higher π-orbital. Thus, linear SiC_n has $2n + 4$ valence σ-electrons and $2n$ valence π-electrons, resulting in $^3\Sigma$ states for n-odd members and $^1\Sigma$ states for n-even ones. Similarly, linear C_nP has $2n + 4$ valence σ-electrons and $2n + 1$ valence π-electrons, resulting in the $^2\Pi$ electronic state; linear C_nS has $2n + 4$ valence σ-electrons and $2n + 2$ valence π-electrons, resulting in $^1\Sigma$ states for n-odd members and $^3\Sigma$ states for n-even ones; linear C_nCl has $2n + 4$ valence σ-electrons and $2n + 3$ valence π-electrons, resulting in the $^2\Pi$ electronic state.

Removing an electron from neutral C_nX gives cationic C_nX^+ clusters, while attaching an electron to neutral C_nX gives anionic C_nX^- clusters. Because chemical processes usually occur in frontier molecular orbitals, the electronic configurations for the second-row-atom-doped linear carbon cluster ions C_nX^+/C_nX^- can be obtained from the electronic distributions of the corresponding neutral linear C_nX clusters by removing an electron from or attaching an electron to their frontier orbitals, which are

$$NaC_n^{\,+}\!: \begin{cases} \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots \left(\frac{n-1}{2}\right)\pi^4(n+1)\sigma^2 & n = 3, 5, 7, 9 \\ \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots (n+1)\sigma^2\left(\frac{n}{2}\right)\pi^2 & n = 4, 6, 8, 10 \end{cases}$$

NaC^+: (core) $1\sigma^2$ $2\sigma^1$ $1\pi^1$; NaC_2^+: (core) $1\sigma^2$ $2\sigma^2$ $1\pi^3$ $3\sigma^1$

$$NaC_n^{\,-}\!: \begin{cases} \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots \left(\frac{n+1}{2}\right)\pi^1(n+2)\sigma^1 & n = 3, 5 \\ \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots (n+1)\sigma^2\left(\frac{n+1}{2}\right)\pi^2 & n = 1, 7, 9 \\ \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots (n+1)\sigma^2\left(\frac{n}{2}\right)\pi^4 & n = 2, 4, 6, 8, 10 \end{cases}$$

$$MgC_n^{\,+}\!: \begin{cases} \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots \left(\frac{n-1}{2}\right)\pi^4(n+2)\sigma^1 & n = 3, 5, 7, 9 \\ \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots (n+1)\sigma^2\left(\frac{n}{2}\right)\pi^3 & n = 4, 6, 8 \\ \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots \left(\frac{n}{2}\right)\pi^2(n+1)\sigma^1 & n = 10 \end{cases}$$

MgC^+: (core) $1\sigma^2$ $2\sigma^1$ $1\pi^2$; MgC_2^+: (core) $1\sigma^2$ $2\sigma^2$ $3\sigma^1$ $1\pi^4$

$$MgC_n^{\,-}\!: \begin{cases} \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\frac{n+1}{2}\right)\pi^1 & n = 3 \\ \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots \left(\frac{n+1}{2}\right)\pi^2(n+2)\sigma^1 & n = 1, 5, 7, 9 \\ \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots \left(\frac{n}{2}\right)\pi^4(n+2)\sigma^1 & n = 2, 4, 6, 8, 10 \end{cases}$$

$$AlC_n^{\,+}\!: \begin{cases} \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots \left(\frac{n-1}{2}\right)\pi^4(n+2)\sigma^2 & n = 3, 5, 7, 9 \\ \text{(core) } 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\frac{n}{2}\right)\pi^2 & n = 6, 8, 10 \end{cases}$$

AlC^+: (core) $1\sigma^2$ $2\sigma^2$ $1\pi^2$

AlC_2^+: (core) $1\sigma^2$ $2\sigma^2$ $3\sigma^1$ $1\pi^4$ $4\sigma^1$; the state with (core) $1\sigma^2$ $2\sigma^2$ $3\sigma^2$ $4\sigma^2$ $1\pi^2$ distribution is 1.36 eV energetically less stable

$\mathrm{AlC_4}^+$: (core) $1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 5\sigma^1\ \pi^4\ 2\pi^4\ 6\sigma^1$; the state with (core) $1\sigma^2\ 2\sigma^2\ 3\sigma^2\ 4\sigma^2\ 1\pi^4\ 5\sigma^2\ 6\sigma^2\ 2\pi^2$
distribution is only 0.17 eV energetically less stable

$$\mathrm{AlC}_n^-:\begin{cases}(\text{core})\ 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\frac{n+1}{2}\right)\pi^2 & n=3,5,7,9\\ (\text{core})\ 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\frac{n}{2}\right)\pi^4 & n=2,4,6,8,10\end{cases}$$

AlC^-: (core) $1\sigma^2\ 2\sigma^2\ 1\pi^3\ 3\sigma^1$

$$\mathrm{SiC}_n^+:\begin{cases}(\text{core})\ 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\frac{n+1}{2}\right)\pi^1 & n=3,5,7,9\\ (\text{core})\ 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\frac{n}{2}\right)\pi^3 & n=6,8,10\\ (\text{core})\ 1\sigma^2 \ldots 1\pi^4 \ldots \left(\frac{n}{2}\right)\pi^4\ (n+2)\sigma^1 & n=2,4\end{cases}$$

SiC^+: (core) $1\sigma^2\ 2\sigma^2\ 3\sigma^1 1\pi^2$

$$\mathrm{SiC}_n^-:\begin{cases}(\text{core})\ 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\frac{n+1}{2}\right)\pi^3 & n=3,5,7,9\\ (\text{core})\ 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\frac{n+2}{2}\right)\pi^1 & n=2,4,6,8,10\end{cases}$$

SiC^-: (core) $1\sigma^2\ 2\sigma^2\ 3\sigma^1 1\pi^4$

$$\mathrm{C}_n\mathrm{P}^+:\begin{cases}(\text{core})\ 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\frac{n+1}{2}\right)\pi^2 & n=3,5,7,9\\ (\text{core})\ 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\frac{n}{2}\right)\pi^4 & n=2,4,6,8,10\end{cases}$$

CP^+: (core) $1\sigma^2\ 2\sigma^2\ 3\sigma^1 1\pi^3$

$$\mathrm{C}_n\mathrm{P}^-:\begin{cases}(\text{core})\ 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\frac{n+1}{2}\right)\pi^4 & n=1,3,5,7,9\\ (\text{core})\ 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\frac{n+2}{2}\right)\pi^2 & n=2,4,6,8,10\end{cases}$$

$$\mathrm{C}_n\mathrm{S}^+:\begin{cases}(\text{core})\ 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\frac{n+1}{2}\right)\pi^3 & n=7,9\\ (\text{core})\ 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^1\left(\frac{n+1}{2}\right)\pi^4 & n=1,3,5\\ (\text{core})\ 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\frac{n+2}{2}\right)\pi^1 & n=2,4,6,8,10\end{cases}$$

$$\mathrm{C}_n\mathrm{S}^-:\begin{cases}(\text{core})\ 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\frac{n+3}{2}\right)\pi^1 & n=1,3,5,7,9\\ (\text{core})\ 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\frac{n+2}{2}\right)\pi^3 & n=2,4,6,8,10\end{cases}$$

$$\mathrm{C}_n\mathrm{Cl}^+:\begin{cases}(\text{core})\ 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\frac{n+1}{2}\right)\pi^4 & n=1,3,5,7,9\\ (\text{core})\ 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\frac{n+2}{2}\right)\pi^2 & n=2,4,6,8,10\end{cases}$$

$$\mathrm{C}_n\mathrm{Cl}^-:\begin{cases}(\text{core})\ 1\sigma^2 \ldots 1\pi^4 \ldots (n+2)\sigma^2\left(\frac{n+3}{2}\right)\pi^2 & n=1,3,5,7,9\\ (\text{core})\ 1\sigma^2 \cdots 1\pi^4 \ldots (n+2)\sigma^2\left(\frac{n+2}{2}\right)\pi^4 & n=2,4,6,8,10\end{cases}$$

On the other hand, we can also get some electronic configurations for the linear isomers of ionic $\mathrm{C}_n\mathrm{X}^+$ and $\mathrm{C}_n\mathrm{X}^-$ from their isovalent neutral counterparts. For example, the valence electron numbers of ionic AlC_n^- and $\mathrm{C}_n\mathrm{P}^+$ are same as neutral SiC_n, so linear AlC_n^- and $\mathrm{C}_n\mathrm{P}^+$ have electronic configurations similar to that of linear SiC_n. This is also the case for (SiC_n^-, $\mathrm{C}_n\mathrm{S}^+$, and $\mathrm{C}_n\mathrm{P}$), ($\mathrm{C}_n\mathrm{P}^-$, $\mathrm{C}_n\mathrm{Cl}^+$, and $\mathrm{C}_n\mathrm{S}$), and ($\mathrm{C}_n\mathrm{S}^-$ and $\mathrm{C}_n\mathrm{Cl}$), but not for the Na- and Mg-containing species.

C. Stabilities. Although the total electronic energy of a molecule is the most important criterion for its stability, it is only good in comparison with its structural isomers. To gauge the relative stability of the clusters with different sizes, we adopt the concept of incremental binding energy,[28,30,34,50] labeled as ΔE^{I}, as suggested by Pascoli and Lavendy. ΔE^{I}_n is defined as the consecutive binding energy difference between adjacent $\mathrm{C}_n\mathrm{X}/\mathrm{C}_n\mathrm{X}^+/\mathrm{C}_n\mathrm{X}^-$ and $\mathrm{C}_{n-1}\mathrm{X}/\mathrm{C}_{n-1}\mathrm{X}^+/\mathrm{C}_{n-1}\mathrm{X}^-$ clusters, and can be determined by the reaction energies of

$$\mathrm{C}_n\mathrm{X} \rightarrow \mathrm{C}_{n-1}\mathrm{X} + \mathrm{C} \qquad \text{(DN1)}$$

$$\mathrm{C}_n\mathrm{X}^+ \rightarrow \mathrm{C}_{n-1}\mathrm{X}^+ + \mathrm{C} \qquad \text{(DN2)}$$

$$\mathrm{C}_n\mathrm{X}^- \rightarrow \mathrm{C}_{n-1}\mathrm{X}^- + \mathrm{C} \qquad \text{(DN3)}$$

The incremental binding energies versus the carbon atom numbers for second-row-atom-doped linear carbon clusters $\mathrm{C}_n\mathrm{X}/\mathrm{C}_n\mathrm{X}^+/\mathrm{C}_n\mathrm{X}^-$ are presented in Figure 2. Because of their differences in electronic distributions and ground states, smaller $\mathrm{CX}/\mathrm{CX}^+/\mathrm{CX}^-$ and $\mathrm{C_2X}/\mathrm{C_2X}^+/\mathrm{C_2X}^-$ clusters will not be included in the following discussions. From Figure 2 we make several observations:

(i) A strong even−odd alternation exists in the stability of linear SiC_n clusters, with the *n*-even members being much more stable than the *n*-odd ones. This stability alternation is a result of the number of available valence π-electrons. As already ascertained above, linear SiC_n cluster contains $2n$ valence π-electrons. For even n, these π-electrons fully populate $n/2$ doubly degenerate π-orbitals, resulting in a $\cdots\pi^4$ electronic configuration and a $^1\Sigma$ state, while for odd n the highest occupied molecular orbital (HOMO) with π-symmetry is half-filled with two electrons, resulting in a $\cdots\pi^2$ electronic configuration and a $^3\Sigma$ state. As is well-known, the former situation (fully filled π-orbitals) is energetically much more stable than the latter one (half-filled π-orbitals), which simply explains our results. The incremental binding energy difference of the adjacent clusters decreases monotonically with an increasing number of carbons, indicating that the distinctness of the clusters with different parities reduces following the growth of the carbon chain.

(ii) For linear $\mathrm{C}_n\mathrm{S}$, there also exists a strong alternation effect in the cluster stability, but opposite to linear SiC_n, linear $\mathrm{C}_n\mathrm{S}$ clusters with odd n are much more stable than those with *n*-even ones. Since linear $\mathrm{C}_n\mathrm{S}$ cluster possesses $2n + 2$ valence π-electrons, for its *n*-even member, the π-symmetry HOMO is half-filled, corresponding to a $^3\Sigma$ electronic ground state, while for its *n*-odd member, the $(n + 1)/2$ valence π-orbitals are fully occupied, corresponding to a $^1\Sigma$ electronic state. Apparently, the clusters with closed shell are always systematically much more stable than the clusters with half-filled orbitals.

(iii) For linear $\mathrm{C}_n\mathrm{P}$, all its members have almost the same incremental binding energies, expressing that their relative stabilities are similar. This can also be interpreted by their valence π-electron numbers. Linear $\mathrm{C}_n\mathrm{P}$ cluster has $2n + 1$ valence π-electrons. Its *n*-even member has a $\cdots\pi^1$ electronic configuration, and its *n*-odd member has a $\cdots\pi^3$ electronic configuration. None of them corresponds to a fully filled HOMO, so the stabilities for both *n*-odd and *n*-even species

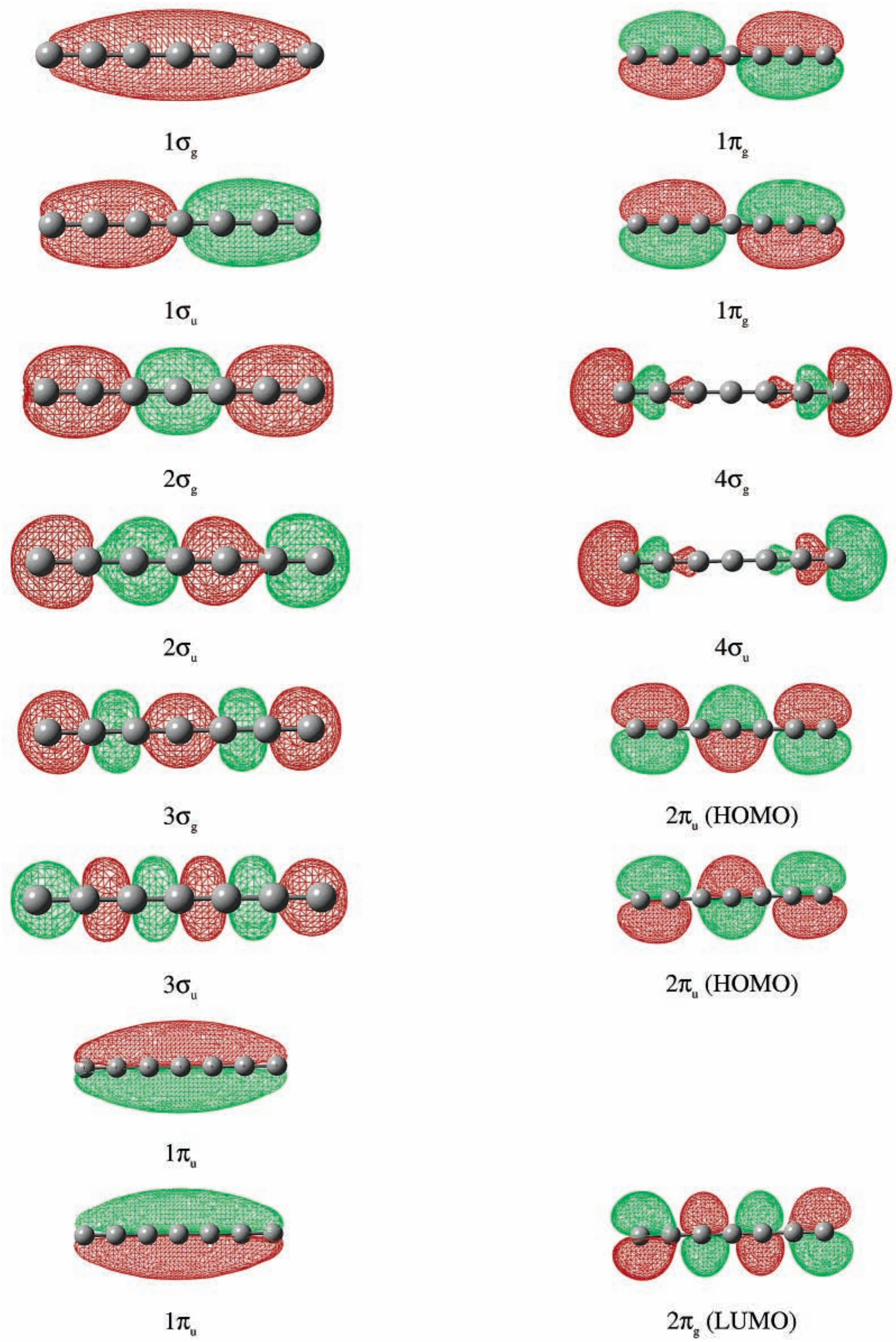

Figure 1. Valence molecular orbitals of linear C_7 cluster. Seven core orbitals, formed by seven 1s orbitals of the carbon atoms, are excluded and not numbered.

should not differ much. As for the very weak odd−even alternation in ΔE^{I} of linear C_nP, one can refer to PL's article[28] for a detailed discussion.

(iv) For linear C_nCl, AlC_n, MgC_n, and NaC_n clusters, the even−odd parity effect in their relative stability is also very weak. There are $2n + 3$ valence π-electrons in linear C_nCl and $2n - 1$ valence π-electrons in linear AlC_n, MgC_n, and NaC_n. Again, none of them can fully occupy the π-type HOMO, resulting in their stability being similar.

It is interesting to note that linear AlC_n, MgC_n, and NaC_n have similar alternation effects in cluster relative stability. Usually, if there is a one-electron difference between two kinds of linear C_nX clusters, the parity effect in their relative stability will be drastically different, such as (SiC_n and C_nP), (C_nP and C_nS), and (C_nP and C_nCl), because this electron always changes the electronic configuration in the π-type HOMO. It is this electronic distribution that determines the relative stability of linear $C_nX^{(\pm)}$ clusters. However, for linear MgC_n and AlC_n (or

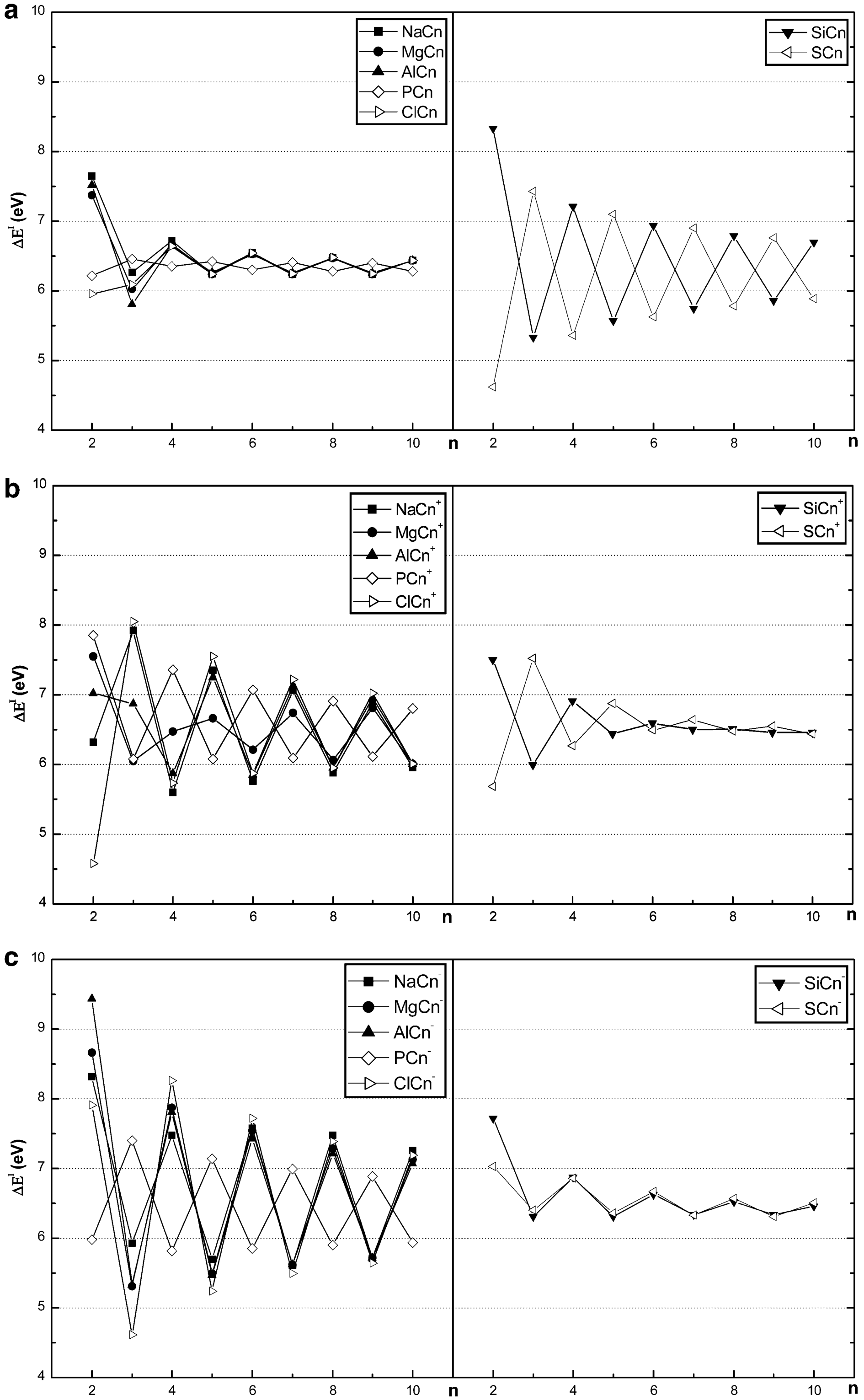

Figure 2. Incremental binding energies for linear $C_nX/C_nX^+/C_nX^-$ clusters vs number of carbon atoms. (a) C_nX; (b) C_nX^+; (c) C_nX^-.

MgC_n and NaC_n), the one-electron difference only changes the valence σ-electron numbers, leaving the valence π-electron numbers fixed. Further analysis finds that the highest occupied σ-orbital for linear MgC_n and AlC_n is a lone-pair orbital, which belongs to only the heteroatom X, so whether this σ-orbital is filled does not change any trend about the relative stability of the clusters involved.

(v) For linear C_nX^+/C_nX^- ions, the parity effect in cluster relative stability is distinctly different from that of the corresponding linear C_nX neutral counterparts. For example, all linear ionic SiC_n^+/SiC_n^- and C_nS^+/C_nS^- clusters have very weak parity effect in their relative stability, while for linear neutral SiC_n and C_nS molecules, the alternation effect is very strong. On the other hand, the odd−even (or even−odd) alternations are very strong for linear C_nP^+/C_nP^-, C_nCl^+/C_nCl^-, AlC_n^+/AlC_n^-, MgC_n^+/MgC_n^-, and NaC_n^+/NaC_n^- ions (for linear C_nP^+, C_nCl^-, AlC_n^-, MgC_n^-, and NaC_n^- ions, their *n*-even members are much more stable than the corresponding odd $n - 1$ and $n + 1$ ones, while for linear C_nP^-, C_nCl^+, AlC_n^+, MgC_n^+ and NaC_n^+ ions, their *n*-odd members are much more stable than the correspond-

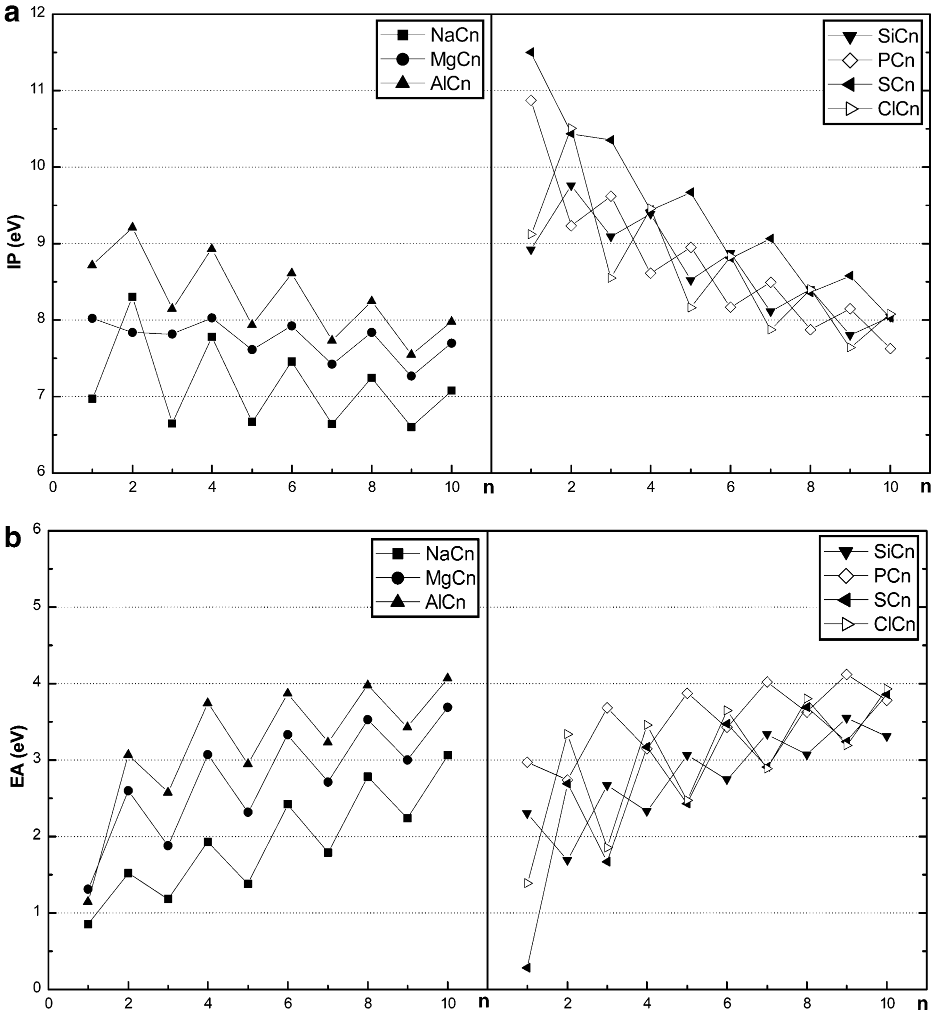

Figure 3. Ionization potentials (IP) and electron affinities (EA) of linear C_nX clusters vs number of carbon atoms.

ing even $n - 1$ and $n + 1$ ones), but for the corresponding linear C_nP, C_nCl, AlC_n, MgC_n, and NaC_n clusters, the parity effects in their stabilities are less pronounced. These results are also closely related to the valence π-electron numbers. In their linear isomers, cationic C_nX^+ clusters have one less valence π-electron than the corresponding neutral C_nX, and anionic C_nX^- clusters have one more valence π-electron than the corresponding neutral C_nX. It is this one valence π-electron difference that changes the filling of the π-type HOMO and the cluster relative stability.

(vi) Compared with linear C_nP^+ cations, linear C_nP^- anions have the alternation effect in relative stability reversed. Both linear C_nP^+ and C_nP^- have similar structures and compositions. Their only difference is the two electrons resulting from the opposite charge carried by the single-charged species. It is these two electrons that invert the parity of the alternation effect between linear C_nP^+ and C_nP^-. This is also the case for linear C_nCl^+, $AlC_n{}^+$, $MgC_n{}^+$, and $NaC_n{}^+$ cations with their corresponding anions. One can easily understand these results by their valence π-electron numbers, too.

All the parity alternations predicted here are consistent with the experimental observations reported by Leleyter et al.[18] and by Zheng et al.[19,22,23]

D. Ionization Potentials and Electron Affinities.

The parity effect in cluster stability for linear $C_nX^{(\pm)}$ also appears in the ionization potentials (IP) and the electron affinities (EA) curves, as depicted in Figure 3. Here, the IPs and EAs are evaluated as the total energy differences in the following manner:

$$\mathrm{IP}(C_nX) = E(\text{optimized linear } C_nX^+ \text{ cation}) - E(\text{optimized linear } C_nX \text{ neutral})$$

$$\mathrm{EA}(C_nX) = E(\text{optimized linear } C_nX \text{ neutral}) - E(\text{optimized linear } C_nX^- \text{ anion})$$

For linear SiC_n, the clusters containing an even number of carbon atoms have higher IP and lower EA than the odd $n - 1$ and $n + 1$ congeners, which can be reasoned from the relative stability of linear SiC_n, $SiC_n{}^+$, and $SiC_n{}^-$ clusters—n-even SiC_n neutrals have much higher stability than the n-odd ones, while for linear $SiC_n{}^+$ and $SiC_n{}^-$ ions, all their n-even and n-odd members have similar stability. Compared with linear SiC_n, linear C_nS clusters have a reversed even−odd alternation, resulting in lower IPs and higher EAs for n-even C_nS clusters than the odd $n - 1$ and $n + 1$ members. For linear C_nP, all the n-even and n-odd members have similar stability, while cationic C_nP^+ has its n-even members much more stable and anionic C_nP^- has its n-even members much less stable, so n-even C_nP clusters have both lower IP and EA than the odd $n - 1$ and $n + 1$ ones. Oppositely, for linear NaC_n, MgC_n, AlC_n, and C_nCl clusters, their n-even members have both higher IP and EA than the odd $n - 1$ and $n + 1$ congeners, which can also be understood by relative stability of the clusters involved. It is interesting to note that IP(NaC$_n$) < IP(MgC$_n$) < IP(AlC$_n$) and EA(NaC$_n$) < EA(MgC$_n$) < EA(AlC$_n$), which are consistent with the metallic order of Na > Mg > Al. On the other hand, for all C$_n$X clusters, there is a tendency to lower IPs and higher EAs as n increases.

IV. Conclusion

Theoretical studies of the second-row-atom-doped linear carbon clusters shows that, doped by different heteroatom X, C$_n$X/C$_n$X$^+$/C$_n$X$^-$ clusters have different parity effect in their stabilities. Both linear SiC$_n$ and C$_n$S clusters have strong parity effect in their relative stabilities, but the alternation trends are opposite. For linear SiC$_n$, the n-even members are much more stable than the n-odd ones, while for linear C$_n$S, the n-odd members are much more stable than the n-even ones. For linear C$_n$P, C$_n$Cl, NaC$_n$, MgC$_n$, and AlC$_n$ clusters, the alternation in their relative stabilities is very smooth. Compared with linear C$_n$X neutrals, the corresponding linear C$_n$X$^+$/C$_n$X$^-$ ions have distinctly different parity effects in their stabilities. For linear C$_n$P$^+$/C$_n$P$^-$, C$_n$Cl$^+$/C$_n$Cl$^-$, AlC$_n$$^+$/AlC$_n$$^-$, MgC$_n$$^+$/MgC$_n$$^-$, and NaC$_n$$^+$/NaC$_n$$^-$ ions, very strong alternation effect in their stabilities is observed: linear C$_n$P$^+$, C$_n$Cl$^-$, AlC$_n$$^-$, MgC$_n$$^-$, and NaC$_n$$^-$ ions have their n-even members being much more stable than the corresponding n-odd ones, while oppositely linear C$_n$P$^-$, C$_n$Cl$^+$, AlC$_n$$^+$, MgC$_n$$^+$, and NaC$_n$$^+$ ions have their n-odd members being much more stable than the corresponding n-even ones. For linear SiC$_n$$^+$/SiC$_n$$^-$ and C$_n$S$^+$/C$_n$S$^-$ ions, the parity effect in their stabilities is less pronounced. Systematic investigations of their electronic distributions find that the parity effects mentioned above are attributed to the numbers of their valence π-electrons. The odd−even (or even−odd) parity effects in cluster stabilities for linear C$_n$X/C$_n$X$^+$/C$_n$X$^-$ clusters are also apparent in the ionization potential and electron affinity curves.

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