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Structures and properties of small iron-doped carbon clusters

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ABSTRACT

A systemic study of the small iron-doped carbon clusters $FeC_n/FeC_n^-/FeC_n^+$(n = 1–10) has been performed with density functional theory (DFT) method at the B3LYP/6-311+G* level. Several properties including equilibrium geometries, electronic states, relative energies, vibrational frequencies, and dipole moments have been investigated for linear, cyclic and fanlike isomers. The stability of different structures and states has been discussed according to the relative energy for the same size, and the incremental binding energy for different size. For neutral FeC_n clusters, their ground states have fanlike structures for FeC_{2-4}, linear structure for FeC_5, and cyclic structures for FeC_{6-10}; for ionic FeC_n^-/FeC_n^+ clusters, they all have linear ground states, except FeC_7^-, FeC_9^-, FeC_2^+, and FeC_{10}^+.

1. Introduction

The study on small carbon clusters has been one of the most interesting subjects in chemistry and physics in last decades, for their role in astrophysics, in the chemistry of carbon star, in the formation of soot, in the chemical vapor deposition of carbide films [1,2]. In the interstellar medium, small carbon clusters take highly stable linear chains with their reactivity being forfeited by quasi-collisionless conditions [3,4]. Some of the carbon chains may be terminated by hydrogen atoms or other heteroatoms. Inclusion of heteroatoms provides a way to stabilize the carbon chains. Heteroatom-doped carbon clusters containing a first- or second-row element of the periodic table have been extensively studied both experimentally and theoretically [5–20].

Because of their interesting properties and potential applications, transition-metal-doped carbon clusters (TMDCCs) have also attracted much attention. For example, early 3d transition-metals can form stable gas-phase metal–carbon clusters, denominated as metallocarbohedrenes (met-cars) [21–25], while late 3d transition-metals are efficient catalysts for the formation of carbon nanotubes [26]. Moreover, some rare earth elements can be trapped into carbon clusters to form endohedral metallofullerenes [27]. Due to the complicated electronic structures of transition-metal atoms, experimental observations on transition-metal carbides are far from easy to interpret. Large number of local minima on their potential energy surfaces (PESs) make it is very difficult to determine the ground state structures of TMDCCs, though the geometry is one of the fundamental information in clusters research. With the hopefulness that the structures of the smaller TMDCCs may throw light on the growth mechanisms of the larger ones, many theoretical and experimental studies have been carried out on the ground state structures of the small TMDCCs [28–31]. The competition between their linear and cyclic arrangement has led a series of recent investigations on small TMDCCs, such as on dicarbide MC_2 [32] and MC_2^+(M = Sc–Zn) [33], on ScC_n [34,35], TiC_n [36,37], VC_n [38–40], ZnC_n [41,42], CoC_n [43,44], CrC_n [45], and so on.

Iron locates between early and late transition metals in the periodic table, and the properties of iron-doped carbon systems would be unlike other early and late TMDCCs. The FeC_n (n = 1–4) clusters have been studied by many theoretical and experimental groups [28–31,46–54], but different results were given for their ground state geometries. Computationally, the B3LYP/6-311+G* method (vide infra) has been widely applied to many TMDCCs [32–44]. In order to examine the ground state structures of the iron-doped small carbon clusters, we present a systemic study on $FeC_n/FeC_n^-/FeC_n^+$ (n = 1–10) using the B3LYP/6-311+G* method, with the focus on the competition between linear and cyclic structures. More recently, Ma et al. [55] have investigated the structures and magnetic moments of small FeC_n (n = 1–8) clusters by all-electron density functional method for molecules (DMOL), and predicted that most FeC_n have linear structures, with the iron atom bonded at one end, but our study predicted that most of the ground states for FeC_n (n = 1–10) clusters are cyclic or fanlike. Section 2 describes our computational method and Section 3 con-

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Table 1
Relative energies[a] (ΔE, in kcal/mol), numbers of imaginary vibrational frequencies (N_{imag}, given in parentheses), $\langle S^2 \rangle$ values, and dipole moments (μ(D)) for neutral FeC_n clusters at their different electronic states with the B3LYP/6-311+G* method.

	Linear structures					Cyclic/fanlike structures				
	State	Sym.	ΔE (N_{imag})	$\langle S^2 \rangle$	μ(D)	State	Sym.	ΔE (N_{imag})	$\langle S^2 \rangle$	μ(D)
FeC	${}^1\Sigma$	$C_{\infty v}$	52.99 (0)		1.86					
	${}^3\Delta$	$C_{\infty v}$	0.00 (0)	2.7381	2.71					
	${}^5\Pi$	$C_{\infty v}$	18.18 (0)	6.2451	3.20					
FeC_2	${}^1\Sigma$	$C_{\infty v}$	91.52 (0)		6.96	${}^1A_1$	C_{2v}	46.36 (0)		4.65
	${}^3A'$	C_s	50.23 (0)	3.0207	8.24	${}^3A''$	C_s	16.74 (0)	2.7142	4.97
	${}^5\Delta$	$C_{\infty v}$	12.35 (0)	6.0663	8.75	${}^5A_2$	C_{2v}	0.00 (0)	6.0336	6.21
FeC_3	${}^1\Sigma$	$C_{\infty v}$	45.03 (0)		6.68	${}^1A_1$	C_{2v}	37.40 (0)		3.88
	${}^3\Delta$	$C_{\infty v}$	2.57 (0)	2.7333	9.78	${}^3B_1$	C_{2v}	0.00 (0)	2.5600	4.09
	${}^5\Pi$	$C_{\infty v}$	14.01 (1)[b]	6.0540	9.77	${}^5B_1$	C_{2v}	15.72 (0)	6.3065	0.71
FeC_4	${}^1\Sigma$	$C_{\infty v}$	76.32 (0)		9.28	${}^1A_1$	C_{2v}	39.22 (0)		1.37
	${}^3\Phi$	$C_{\infty v}$	9.55 (0)	3.0595	9.22	${}^3B_1$	C_{2v}	29.50 (0)	3.0104	3.21
	${}^5\Delta$	$C_{\infty v}$	3.22 (0)	6.0712	13.01	${}^5A_1$	C_{2v}	0.00 (0)	6.0338	3.61
FeC_5	${}^1\Sigma$	$C_{\infty v}$	65.11 (0)		11.77	${}^1A_1$	C_{2v}	67.43 (0)		4.60
	${}^3\Delta$	$C_{\infty v}$	0.00 (0)	2.8961	13.18	${}^3A'$	C_s	10.14 (0)	3.2126	0.88
	${}^5A''$	C_s	4.21 (0)	6.0697	11.15	${}^5A_1$	C_{2v}	8.76 (0)	6.0281	1.92
FeC_6	${}^1\Delta$	$C_{\infty v}$	61.52 (0)		12.77	${}^1A'$	C_s	53.41 (0)		3.47
	${}^3\Pi$	$C_{\infty v}$	4.71 (0)	3.1151	11.23	${}^3A''$	C_s	16.93 (0)	2.7588	2.51
	${}^5\Delta$	$C_{\infty v}$	2.34 (0)	6.1049	16.28	${}^5A_1$	C_{2v}	0.00 (0)	6.0162	0.68
FeC_7	${}^1\Phi$	$C_{\infty v}$	58.05 (0)		10.42	${}^1A_1$	C_{2v}	50.65 (0)		0.59
	${}^3\Delta$	$C_{\infty v}$	11.44 (0)	3.0207	16.41	${}^3B_1$	C_{2v}	0.00 (0)	3.3189	1.03
	${}^5\Delta$	$C_{\infty v}$	19.08 (0)	6.0835	15.39	${}^5A_2$	C_{2v}	3.27 (0)	6.0837	2.79
FeC_8	${}^1\Sigma$	$C_{\infty v}$	86.63 (2)[b]		13.37	${}^1A'$	C_s	57.37 (0)		1.99
	${}^3\Phi$	$C_{\infty v}$	12.83 (1)[b]	3.1567	13.12	${}^3A'$	C_s	21.49 (1)[b]	2.9320	1.27
	${}^5\Delta$	$C_{\infty v}$	13.09 (0)	6.1408	19.45	${}^5A'$	C_s	0.00 (0)	6.0323	1.54
FeC_9	${}^1A'$	C_s	56.85 (0)		12.20	${}^1A'$	C_s	47.45 (0)		4.65
	${}^3A''$	C_s	4.78 (0)	3.0262	17.03	${}^3B_1$	C_{2v}	9.45 (0)	4.1152	1.02
	${}^5A$	C_1	8.03 (0)	6.0738	17.72	${}^5B_1$	C_{2v}	0.00 (0)	6.0302	2.75
FeC_{10}	${}^1A'$	C_s	79.45 (0)		16.81	${}^1A'$	C_s	58.53 (0)		4.20
	${}^3A''$	C_s	19.97 (0)	3.0801	17.39	${}^3A''$	C_s	15.60 (0)	3.0347	1.28
	${}^5A'$	C_s	17.92 (0)	6.0806	19.31	${}^5A_2$	C_{2v}	0.00 (0)	6.0405	3.21

[a] The total energies of ground states for FeC_n ($n = 1–10$) are: −1301.63666, −1339.75624, −1377.81920, −1415.91565, −1453.99438, −1492.09132, −1530.19083, −1568.28567, −1606.36496, −1644.47790 a.u., respectively.

[b] When we reinvestigate these systems using 6-311G* basis set (in which diffuse sp-functions are excluded), they all have no imaginary vibrational frequency, indicating that they should be minima.

tains our results and discussions. A short conclusion is given in Section 4.

2. Theoretical methods

All the calculations were carried out using density functional theory (DFT) method at the B3LYP/6-311+G* level, where B3LYP was constructed from Becke's three-parameter non-local exchange functional [56] along with the Lee, Yang, and Parr non-local correlation functional [57], and 6-311G specifies the standard split-valence triple-ζ 6-311G basis set for C atom, the Wachters–Hay all electron basis set [58,59], using the scaling factors of Raghavachari and Trucks [60], for Fe atom. Because of the inclusion both cations and anions in the study, the 6-311G basis sets were augmented with d-type polarization functions and diffuse sp-type functions. For Fe atom, the diffuse functions were also recommended by Raghavachari and Trucks. Many previous studies have shown the computational efficiency and accuracy of the B3LYP/6-311+G* method in researching TMDCCs [32–44]. Harmonic vibrational frequencies were computed from analytic gradient techniques to estimate the nature of the stationary points. All calculations were carried out with the Gaussian 03 program [61]. The default integration grid (75, 302) of Gaussian 03 was mainly applied, but we also used the finer grid (99, 590) to check some suspicious results when necessary.

3. Results and discussion

We have searched for the linear, cyclic and fanlike isomers of neutral and ionic iron-doped carbon clusters. As the C–C bond is stronger than the C–Fe bond, for the linear structures, only the structures with the iron atom located at one end of the carbon chain have been considered. For the cyclic configurations, the iron atom is bonded to the two terminal carbon atoms of the carbon chain, while for the fanlike structures, the iron atom is side-bonded to the entire carbon chain. For each structure, three electronic states with different multiplicities, i.e. the singlet, triplet and quintet states for neutral FeC_n, the doublet, quartet and sextuplet states for ionic FeC_n^-/FeC_n^+, are considered. For larger FeC_n/FeC_n^-/FeC_n^+ ($n > 4$) clusters, the lowest-lying fanlike isomers are energetically less stable than the cyclic ones, while for smaller FeC_3/FeC_3^-/FeC_3^+ and FeC_4/FeC_4^-/FeC_4^+, the geometrical optimizations from the "guessing" cyclic structures converge to the fanlike isomers. In this article, for non-linear structure, only the lowest-lying isomer, either cyclic or fanlike, is shown for each spin multiplicities. In Table 1 we list the relative energies, electronic states, $\langle S^2 \rangle$ expectation values, and dipole moments for the lowest-lying linear and cyclic/fanlike FeC_n species on their three PESs at the B3LYP/6-311+G* level, while the corresponding optimized geometries for the ground states are shown in Fig. 1. The properties of anionic FeC_n^- and cationic FeC_n^+ are presented in Tables 2 and 3 , respectively,

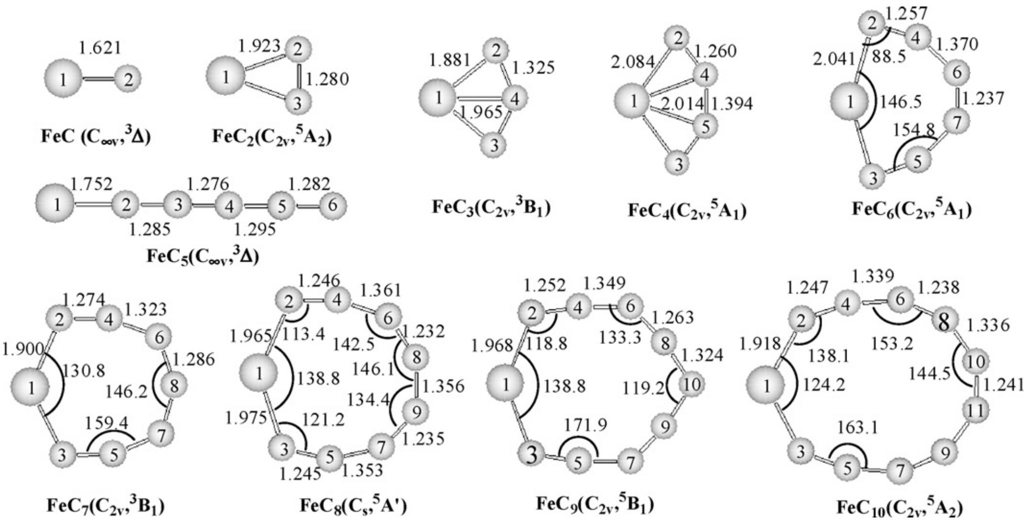

Fig. 1. Optimized geometries (in Å and degrees) for the ground states of FeC_n.

Table 2
Relative energies[a] (ΔE, in kcal/mol), numbers of imaginary vibrational frequencies (N_{imag}, given in parentheses), $\langle S^2 \rangle$ values, and dipole moments (μ(D)) for anionic FeC_n^- clusters at their different electronic states with the B3LYP/6-311+G* method.

	Linear structures					Cyclic/fanlike structures				
	State	Sym.	ΔE (N_{imag})	$\langle S^2 \rangle$	μ(D)	State	Sym.	ΔE (N_{imag})	$\langle S^2 \rangle$	μ(D)
FeC^-	$^{2}\Delta$	$C_{\infty v}$	0.00 (0)	1.7801	0.62					
	$^{4}\Pi$	$C_{\infty v}$	11.27 (0)	4.2414	1.89					
	$^{6}\Sigma$	$C_{\infty v}$	21.83 (0)	8.8968	3.47					
FeC_2^-	$^{2}\Pi$	$C_{\infty v}$	31.52 (0)	1.7780	8.82	$^{2}A''$	C_s	27.68 (0)	2.3165	3.30
	$^{4}\Delta$	$C_{\infty v}$	0.00 (0)	4.2118	7.71	$^{4}B_1$	C_{2v}	12.55 (0)	3.7922	7.44
	$^{6}\Delta$	$C_{\infty v}$	4.18 (0)	8.7679	6.47	$^{6}B_2$	C_{2v}	6.98 (0)	8.7666	3.32
FeC_3^-	$^{2}\Delta$	$C_{\infty v}$	0.00 (0)	2.5517	7.25	$^{2}B_1$	C_{2v}	13.81 (0)	2.5409	0.85
	$^{4}\Sigma$	$C_{\infty v}$	6.39 (0)	4.8788	4.39	$^{4}B_1$	C_{2v}	7.03 (0)	4.7284	0.54
	$^{6}\Pi$	$C_{\infty v}$	13.75 (0)	8.9598	5.71	$^{6}B_2$	C_{2v}	16.93 (0)	8.9621	1.42
FeC_4^-	$^{2}\Pi$	$C_{\infty v}$	30.64 (0)	1.8101	13.89	$^{2}B_1$	C_{2v}	39.92 (0)	1.7648	4.26
	$^{4}\Delta$	$C_{\infty v}$	0.00 (0)	4.2901	12.22	$^{4}B_1$	C_{2v}	16.58 (0)	3.8028	4.31
	$^{6}\Delta$	$C_{\infty v}$	1.58 (0)	8.7778	9.94	$^{6}A_1$	C_{2v}	12.88 (0)	8.7685	1.27
FeC_5^-	$^{2}\Delta$	$C_{\infty v}$	0.00 (0)	2.7553	10.98	$^{2}A_2$	C_{2v}	27.40 (0)	2.1270	1.29
	$^{4}A''$	C_s	10.07 (0)	4.6260	9.26	$^{4}A'$	C_s	13.24 (0)	4.4207	2.88
	$^{6}\Pi$	$C_{\infty v}$	12.32 (0)	9.0443	8.27	$^{6}B_1$	C_{2v}	10.39 (0)	8.8087	2.13
FeC_6^-	$^{2}\Delta$	$C_{\infty v}$	25.11 (0)	2.2050	13.53	$^{2}A''$	C_s	40.20 (0)	1.7226	4.07
	$^{4}\Delta$	$C_{\infty v}$	0.00 (0)	4.2352	16.11	$^{4}B_1$	C_{2v}	22.71 (0)	4.1117	4.08
	$^{6}\Delta$	$C_{\infty v}$	2.28 (0)	8.7861	12.92	$^{6}B_2$	C_{2v}	22.17 (0)	8.7872	2.70
FeC_7^-	$^{2}\Delta$	$C_{\infty v}$	4.16 (0)	2.8793	14.51	$^{2}A_1$	C_{2v}	14.61 (0)	2.0740	0.15
	$^{4}\Phi$	$C_{\infty v}$	24.80 (0)	4.4220	19.77	$^{4}A_2$	C_{2v}	0.00 (0)	4.1340	1.89
	$^{6}\Sigma$	$C_{\infty v}$	23.50 (0)	8.8478	20.70	$^{6}A_1$	C_{2v}	16.97 (1)[b]	8.8022	4.69
FeC_8^-	$^{2}\Sigma$	$C_{\infty v}$	25.44 (0)	2.2470	15.50	^{2}A	C_1	36.20 (0)	2.4004	1.72
	$^{4}\Delta$	$C_{\infty v}$	0.00 (0)	4.1871	19.81	$^{4}A''$	C_s	11.93 (1)[b]	3.9349	0.94
	$^{6}\Delta$	$C_{\infty v}$	3.01 (0)	8.7930	15.73	$^{6}A_1$	C_{2v}	21.60 (0)	8.7810	2.97
FeC_9^-	$^{2}\Delta$	$C_{\infty v}$	0.83 (2)[b]	2.9673	17.96	$^{2}B_2$	C_{2v}	21.68 (0)	2.9244	0.09
	$^{4}A'$	C_s	3.76 (0)	5.4829	14.11	$^{4}B_1$	C_{2v}	0.00 (0)	4.8235	2.05
	$^{6}A'$	C_s	10.54 (0)	9.0491	17.21	$^{6}A_1$	C_{2v}	0.20 (0)	8.7918	1.30
FeC_{10}^-	$^{2}A'$	C_s	25.10 (1)[c]	2.3824	11.25	$^{2}A''$	C_s	23.29 (0)	1.7319	2.91
	$^{4}A'$	C_s	0.00 (0)	4.1488	23.37	$^{4}A''$	C_s	0.38 (0)	3.8515	2.81
	$^{6}\Delta$	$C_{\infty v}$	3.78 (2)[b]	8.7984	18.47	$^{6}B_2$	C_{2v}	14.96 (0)	8.7925	2.28

[a] The total energies of ground states for FeC_n^- ($n = 1$–10) are: −1301.68325, −1339.82276, −1377.89373, −1416.01780, −1454.09181, −1492.20877, −1530.29049, −1568.39663, −1606.47416, −1644.58276 a.u., respectively.

[b] When we reinvestigate these systems using 6-311G* basis set (in which diffuse sp-functions are excluded), they all have no imaginary vibrational frequency, indicating that they should be minima.

[c] We tried our best to find a minimum according to this imaginary frequency, but all of our efforts failed (some calculations have convergence problems and others converge to energetically higher states), which makes this imaginary frequency doubtful.

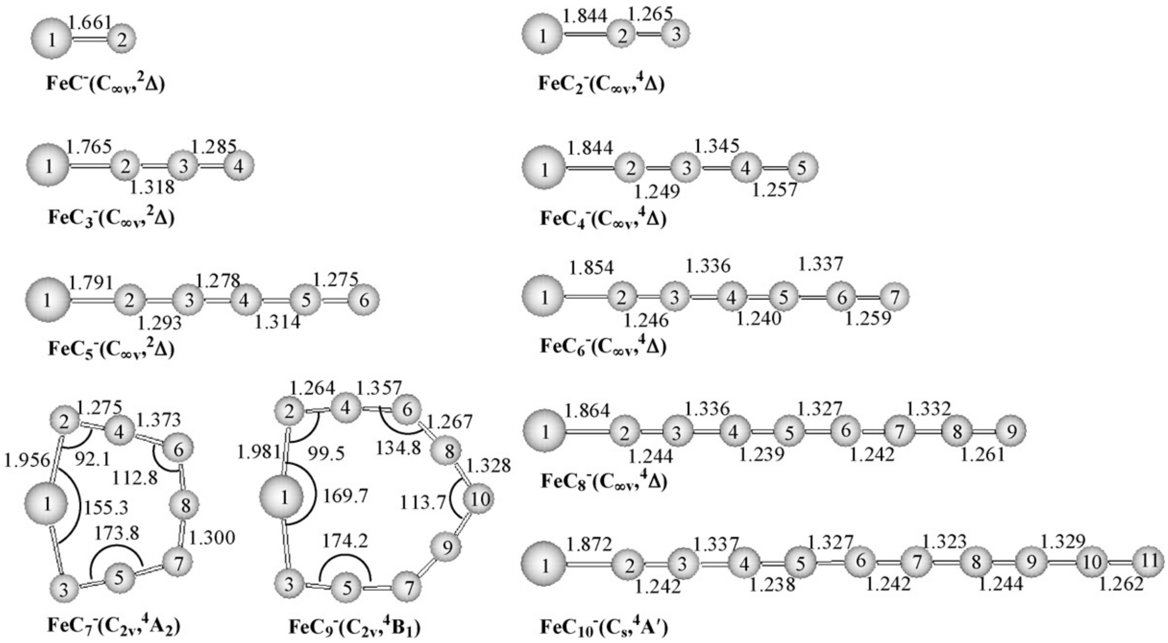

Fig. 2. Optimized geometries (in Å and degrees) for the ground states of FeC_n^-.

Table 3

Relative energies[a] (ΔE, in kcal/mol), numbers of imaginary vibrational frequencies (N_{imag}, given in parentheses), $\langle S^2 \rangle$ values, and dipole moments (μ(D)) for cationic FeC_n^+ clusters at their different electronic states with the B3LYP/6-311+G* method.

	Linear structures					Cyclic/fanlike structures				
	State	Sym.	ΔE (N_{imag})	$\langle S^2 \rangle$	μ(D)	State	Sym.	ΔE (N_{imag})	$\langle S^2 \rangle$	μ(D)
FeC^+	$^2\Delta$	$C_{\infty v}$	0.00 (0)	1.4955	2.42					
	$^4\Sigma$	$C_{\infty v}$	13.35 (0)	4.1569	2.14					
	$^6\Sigma$	$C_{\infty v}$	39.69 (0)	8.8288	2.06					
FeC_2^+	$^2A'$	C_s	27.76 (0)	2.6945	2.73	$^2A_1$	C_{2v}	28.26 (0)	1.8793	2.47
	$^4A'$	C_s	41.23 (0)	4.7796	4.03	$^4A_2$	C_{2v}	27.42 (0)	4.4571	4.24
	$^6\Delta$	$C_{\infty v}$	2.89 (0)	8.8304	3.73	$^6A_1$	C_{2v}	0.00 (0)	8.7825	3.81
FeC_3^+	$^2\Delta$	$C_{\infty v}$	36.19 (0)	0.7981	5.38	$^2A_1$	C_{2v}	55.32 (0)	0.7670	2.11
	$^4\Sigma$	$C_{\infty v}$	0.00 (0)	3.8983	5.62	$^4B_1$	C_{2v}	10.96 (0)	3.9108	2.69
	$^6\Delta$	$C_{\infty v}$	48.88 (0)	8.9646	2.45	$^6A'$	C_s	43.37 (0)	8.8104	3.40
FeC_4^+	[b]	$C_{\infty v}$	12.89 (0)	2.6505	5.04	$^2A_1$	C_{2v}	33.98 (0)	1.7548	0.70
	$^4A'$	C_s	2.27 (0)	4.6751	7.79	$^4A_2$	C_{2v}	22.19 (0)	4.2566	1.30
	$^6\Sigma$	$C_{\infty v}$	0.00 (0)	8.8048	7.68	$^6A_1$	C_{2v}	20.10 (0)	8.7986	1.98
FeC_5^+	$^2\Delta$	$C_{\infty v}$	22.83 (0)	1.6586	7.05	$^2A_2$	C_{2v}	56.61 (0)	3.1579	1.61
	$^4\Sigma$	$C_{\infty v}$	0.00 (0)	3.9067	7.60	$^4B_1$	C_{2v}	31.40 (0)	3.9986	2.70
	$^6A'$	C_s	26.32 (0)	8.7888	7.01	$^6B_1$	C_{2v}	38.80 (0)	8.7930	1.34
FeC_6^+	$^2\Sigma$	$C_{\infty v}$	73.89 (0)	0.7740	5.59	$^2A'$	C_s	34.68 (0)	2.5063	0.90
	$^4\Pi$	$C_{\infty v}$	2.25 (0)	4.6522	10.70	$^4A'$	C_s	19.56 (0)	4.5886	2.11
	$^6\Sigma$	$C_{\infty v}$	0.00 (0)	8.8314	9.71	$^6A'$	C_s	20.78 (0)	8.7938	2.85
FeC_7^+	$^2\Delta$	$C_{\infty v}$	36.86 (0)	0.8003	9.26	$^2B_1$	C_{2v}	43.81 (0)	0.9617	0.12
	$^4\Sigma$	$C_{\infty v}$	0.00 (0)	3.9171	9.56	$^4A_2$	C_{2v}	10.89 (0)	4.1551	1.51
	$^6A'$	C_s	22.59(0)	8.8089	9.38	$^6B_1$	C_{2v}	24.61 (0)	8.8165	2.19
FeC_8^+	$^2A'$	C_s	4.97 (0)	2.7932	9.01	$^2A'$	C_s	23.22 (0)	3.2245	1.33
	$^4A''$	C_s	1.31 (0)	4.7551	12.42	$^4B_2$	C_{2v}	5.75 (0)	4.4978	0.13
	$^6\Sigma$	$C_{\infty v}$	0.00 (0)	8.8567	11.73	$^6A'$	C_s	13.27 (0)	8.7827	1.95
FeC_9^+	$^2A''$	C_s	24.07 (0)	1.6707	10.63	$^2A_2$	C_{2v}	29.26 (0)	1.6153	3.19
	$^4A''$	C_s	0.00 (0)	3.8717	10.75	$^4B_1$	C_{2v}	11.90 (0)	4.7691	1.45
	$^6A'$	C_s	21.24 (0)	8.8276	12.80	$^6B_1$	C_{2v}	14.74 (0)	8.7826	1.78
FeC_{10}^+	$^2A'$	C_s	6.95 (0)	2.8194	10.75	$^2A'$	C_s	15.68 (0)	2.8339	0.12
	$^4A'$	C_s	4.40 (0)	4.8032	14.54	$^4A_2$	C_{2v}	0.00 (0)	4.5667	1.78
	$^6A'$	C_s	3.46 (0)	8.8811	13.69	$^6A_1$	C_{2v}	4.43 (0)	8.7900	2.61

[a] The total energies of ground states for FeC_n^+ ($n = 1$–10) are: −1301.34889, −1339.42908, −1377.53993, −1415.61465, −1453.72937, −1491.80683, −1529.91536, −1567.99512, −1606.10193, −1644.18653 a.u., respectively.

[b] The electronic state of this double state is unable to determine because some of its orbitals have unidentified symmetries.

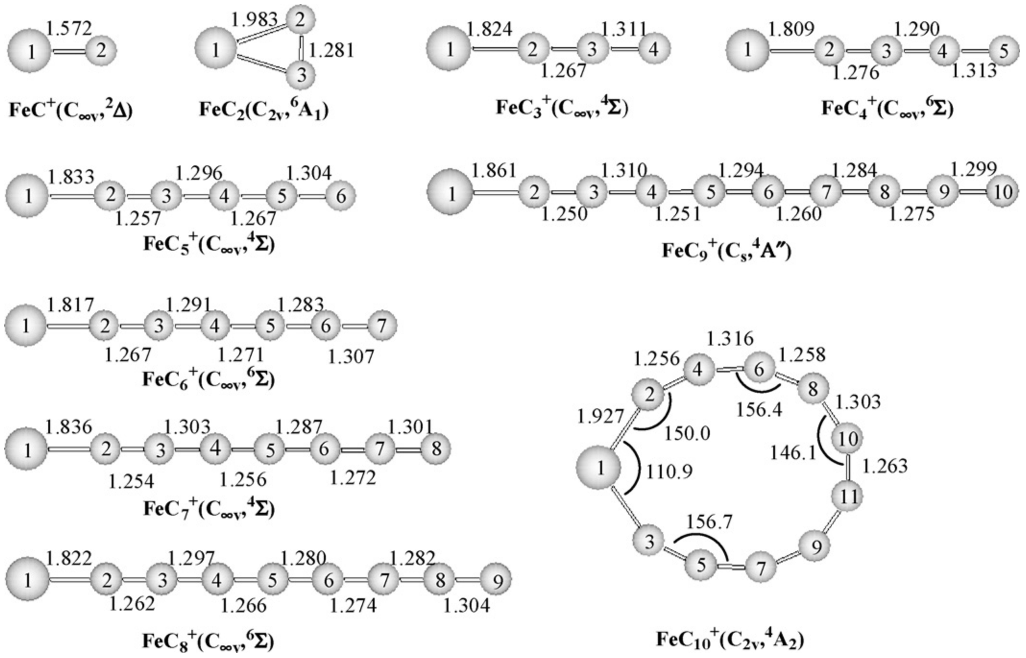

Fig. 3. Optimized geometries (in Å and degrees) for the ground states of FeC_n^+.

and the corresponding structures of ground states are exhibited in Figs. 2 and 3.

3.1. Neutral clusters

For the first member FeC, the ground state is found to be $^3\Delta$, with its bond length being 1.621 Å, which is similar to the experimental value, 1.5924 Å, reported by Brugh and Morse [49] with optical spectroscopy of jet-cooled. Similarly, Noya et al. [52] and Ma et al. [55] gave approximate bond length of 1.61 and 1.575 Å with the DFT and DMOL methods, respectively. However, Nash et al. [48] reported it was 1.92 Å with HF-MP4, 1.54 Å with local density approximation (LDA) and 1.57 Å with non-local (NL) method, respectively.

As the unit of the met-car, FeC_2 has been investigated extensively. There was a detail study reported by Arbuznikov et al. [50], which shows that its C_{2v} structure is more stable in comparison with the linear $C_{\infty v}$ structure, and the ground state was predicted to be $^5A_2$ with ionic Fe^{2+}–C_2^{2-} formalism at the DFT-B3LYP and CASPT2 levels, or $^7A_2$ at the CASSCF level. Using the HF/MIDI* method, Cao [47] also proposed the $^7A_2$ state with C_{2v} symmetry as the ground state. Moreover, other theoretical studies [32,48,52,53,55] also indicated that the ground state of FeC_2 was in C_{2v} form, and the electronic state was quintet except that Nash et al. [48] obtained the triplet ground state using DFT method with LDA. Experimentally, FeC_2 was considered qualitatively to be linear at somewhat lower resolution [28] but in C_{2v} symmetry at higher level [30] by Fan with anion photoelectron spectroscopy. According to our calculations, the stability of FeC_2 grows as the multiplicity increases both for linear and cyclic isomers, and the cyclic $^5A_2$ state is energetically more stable than the linear $^5\Delta$ state by 12.35 kcal/mol, which is in excellent agreement with the result of Arbuznikov et al. [50]. The ground $^5A_2$ state is same as that reported by Rayon et al. [32] and Arbuznikov et al. [50], but differs from that of Hendrickx and Clima [53], in which the $^5A_2$ state is predicted to be higher in energy than the $^5A_1$ only by 1.43 kcal/mol with the CASSCF/CASPT2 approach. According to our optimization, the Fe–C and C–C bond distances are 1.923 and 1.280 Å, respectively, which are also close to those of Arbuznikov et al. [50].

For FeC_3 cluster, Fan et al. [29] gave inconsistent results with different DFT methods, namely, the ground state of FeC_3 was in fanlike form with C_{2v} symmetry at the LDA level but in linear arrangement at the NL level. Five years latter, Wang and Li [31] confirmed the lowest-lying state of FeC_3 should be in C_{2v} symmetry with hybrid B3LYP method, which are consistent with the results of Nash et al. [48], Noya et al. [52] and Hendrickx and Clima [53]. In present work, the lowest-energy structure of FeC_3 is also found in C_{2v} symmetry fanlike form, with the iron atom bond to all the three carbon atoms. The Fe–C bond lengths are 1.965 (Fe1–C4) and 1.881 Å (Fe1–C2, Fe1–C3), respectively. The electronic state is $^3B_1$. The lowest-lying linear state $^3\Delta$ is only 2.57 kcal/mol energetically higher than the ground $^3B_1$ state, indicating that the linear and fanlike isomers of FeC_3 would be coexistent. This is also reflected in the works of Noya et al. [52]. Although Ma et al. [55] predicted the linear isomer was more stable than the fanlike one, the binging energy difference between the two isomers is only 2.58 kcal/mol (0.112 eV). The stability of the different states are in the order of triplet > quintet > singlet for both linear and cyclic/fanlike structures. Similarly, Noya et al. [52] also found that the triplet state is more stable than the quintet one both in the linear and cyclic/fanlike forms.

For the ground state of FeC_4, both previous [52] and our DFT calculations predicted a quintuple state with a fanlike conformation, in which the iron atom interacting with the whole carbon chain. At the B3LYP/6-311+G* level, the linear $^5\Delta$ and $^3\Phi$ states are only energetically higher than the $^5A_1$ global minimum by 3.22 and 9.55 kcal/mol, respectively. The second lowest-lying non-linear state $^3B_1$ is 29.50 kcal/mol less stable than the ground $^5A_1$ state. In contrast to our fanlike ground structure, Ma et al. [55] reported a linear ground structure with DMOL method.

Different from the FeC_{2-4} clusters, the lowest-energy structure of FeC_5 is found to be linear herein, which is in agreement with the result of Ma et al. [55]. The ground state is $^3\Delta$. The optimized bond lengths for the ground $^3\Delta$ state are R(Fe1–C2) = 1.752, R(C2–C3) = 1.285, R(C3–C4) = 1.276, R(C4–C5) = 1.295 and R(C5–C6) = 1.282 Å, respectively. Compared with the bond lengths shown by Ma et al. [55], all our corresponding C–C bonds are shorter, while our Fe–C bond is longer. Another low-lying state in linear form is quintet. When the $C_{\infty v}$ symmetry is fixed, this quintuple state has an imaginary vibrational frequency. Following the normal mode of the imaginary frequency leads to a C_s symmetry bend structure with a $^5A''$ state. In this bend structure, the smallest bend angle is ∠Fe1C2C3 = 152.6°. Compared with the ground $^3\Delta$ state, this $^5A''$ state is only 4.21 kcal/mol less stable in energy.

In the case of FeC_6, the ground state is cyclic $^5A_1$ state. The stability of FeC_6 reduces as the multiplicity decreases. Except the two single states, which are higher than the ground state $^5A_1$ exceeding 50 kcal/mol, all the other isomers locate above the $^5A_1$ ground state no more than 20 kcal/mol. Take linear $^5\Delta$ state for example, it is only 2.34 kcal/mol energetically higher than the $^5A_1$ ground state.

Our B3LYP/6-311+G* calculations show that FeC_7 prefers cyclic structure to the linear one. The C_{2v} symmetry cyclic structure in its $^3B_1$ state has the lowest energy and all real vibrational frequencies, indicating it should be the ground state of FeC_7. The C_{2v} symmetry cyclic structure with $^5A_2$ state also has lower energy, which is only 3.27 kcal/mol energetically higher than the $^3B_1$ ground state. The geometrical parameters for the $^5A_2$ state are R(Fe1–C2) = 1.905, R(C2–C4) = 1.269 Å, R(C4–C6) = 1.347 Å, R(C6–C8) = 1.293 Å, ∠C2Fe1C3 = 131.9°, ∠Fe1C2C4 = 110.0° and ∠C2C4C6 = 168.1°, respectively. The lowest-lying linear state is also in triplet ($^3\Delta$). It is energetically higher than the ground $^3B_1$ state by 11.44 kcal/mol.

The global minimum of FeC_8 is its cyclic $^5A'$ state with C_s symmetry. When C_{2v} geometry is constrained, the cyclic $^5A_1$ state has an imaginary frequency of $48i$ cm^{-1}. The $^5A'$ and $^5A_1$ states have almost equal energy, with the latter being only 0.01 kcal/mol less stable. We also found another isoenergetic saddle point with C_{2v} symmetry and $^5B_1$ state. This $^5B_1$ state has an imaginary frequency of only $18i$ cm^{-1}. Following the normal mode of imaginary frequency also gives the $^5A'$ ground state. The optimized geometry for the $^5B_1$ state is very close to that for the $^5A_1$ state, with the maximal difference in bond length being only 0.002 Å in Fe1–C2 and bond angle being only 0.3° in ∠C2Fe1C9. For the linear isomers, two lowest states $^3\Phi$ and $^5\Delta$ are less stable than the ground $^5A'$ state by 12.83 and 13.09 kcal/mol, respectively.

For FeC_9, the ground state is its $^5B_1$ state in cyclic form with C_{2v} symmetry. The triple $^3B_1$ state in C_{2v} symmetry is 9.45 kcal/mol higher in energy than the ground $^5B_1$ state. All the open chain structures of FeC_9 slightly bend from the straight line, though all the angles formed by three consecutive atoms are close to 180.0°. When we constrain these structures to $C_{\infty v}$ arrangement, they all have imaginary frequency(ies). The quasi-linear structure lies above the ground $^5B_1$ state by 4.78 kcal/mol in its triple $^3A''$ state and by 8.03 kcal/mol in its quintuple ^5A state. The single state $^1A'$, either in quasi-linear form or in cyclic form, is unstable compared with the ground $^5B_1$ state, with the relative energy being up to 56.85 or 47.45 kcal/mol, respectively.

For FeC_{10}, its quintuple $^5A_2$ state with cyclic form is the global minimum in its PES. The second lowest-lying is its cyclic $^3A''$ state, which lies above the ground $^5A_2$ state by 15.60 kcal/mol. Similar to FeC_9, all the open chain structures of FeC_{10} also slightly bend from the straight line. The lowest quasi-linear state $^5A'$ is energetically higher than the ground $^5A_2$ state by 17.92 kcal/mol.

In summary, at the B3LYP/6-311+G* level, neutral iron-doped small carbon clusters FeC_n have fanlike ground states for $FeC_{2–4}$, linear ground state for FeC_5, and cyclic ground states for $FeC_{6–10}$, although systemic calculations performed with DMOL [55] showed that the ground states of $FeC_{3–8}$ preferred linear configurations to cyclic/fanlike ones. For the n-odd clusters, the ground states are triplets except for FeC_9, and the stability for different states follows the order of singlet < quintet < triplet except the cyclic arrangement in the FeC_5 and FeC_9. For the n-even clusters, all the ground states are cyclic quintets, and the order of stability for different states is singlet < triplet < quintet except for the linear FeC_8, in which triple state is only 0.26 kcal/mol more stable than the quintuple one.

Compared with their corresponding ground states, the lowest-lying linear states of FeC_n also have lower energies, with their relative energies being 12.35 (FeC_2), 2.57 (FeC_3), 3.22 (FeC_4), 0.00 (FeC_5), 2.34 (FeC_6), 11.44 (FeC_7), and 12.83 kcal/mol (FeC_8), respectively. As can be seen in Table 1, these lowest-lying linear states alternate between triplet $^3\Delta$ (for n-odd member) and quintet $^5\Delta$ (for the n-even member) except FeC_8. This alternation can be related to their electronic configuration. When the core $1s^2$ electrons for each carbon atom and $1s^22s^22p^63s^23p^6$ electrons for iron atom are excluded, the electronic configurations for the linear states above can be described as follows:

$$\{\text{core}\}1\sigma^2\ldots(n+1)\sigma^2 1\pi^4\ldots\left(\frac{n+1}{2}\right)\pi^4(n+2)\sigma^1 1\delta^3,\quad n-\text{odd}$$

$$\{\text{core}\}1\sigma^2\ldots(n+1)\sigma^2 1\pi^4\ldots\frac{n}{2}\pi^4(n+2)\sigma^1\left(\frac{n+2}{2}\right)\pi^2 1\delta^3,$$

n − even

Neutral FeC_n clusters have $4n+8$ valence electrons, which contains $2n+3$ σ-electrons, $2n+2$ π-electrons and 3 δ-electrons. The $2n+2$ σ-electrons fully occupy $n+1$ σ-orbitals and another σ-electron leads to a $(n+2)$ σ^1 occupation. The 3 δ-electrons are distributed over a pair of degenerate δ-orbitals. For the species with odd n, the $2n+2$ valence π-electrons fully occupy a $(n+1)/2$ π-orbitals, and the configuration results in a $^3\Delta$ state. However, for the clusters with even n, two of the $2n+2$ 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 configuration is $^5\Delta$.

3.2. Anionic clusters

Anionic FeC_n^- clusters were obtained when an electron is attached to neutral FeC_n. For FeC^-, the ground state is $^2\Delta$, and the Fe–C bond length is 1.661 Å, which is longer than that of FeC (1.621 Å).

Our B3LYP/6-311+G* calculations show that FeC_2^- has linear $^4\Delta$ ground state, which is energetically lower than linear $^6\Delta$ and cyclic $^6B_2$ states by 4.18 and 6.98 kcal/mol, respectively. However, Cao's results showed that FeC_2^- had a cyclic $^6B_2$ ground state with C_{2v} symmetry at the HF/MIDI*, CISD and CISD+Q levels [47]. With CASSCF/CASPT2 method, Hendrickx and Clima [53] also predicted that FeC_2^- had cyclic sextuple ground state, but it was $^6A_1$, with the next two states $^6B_1$ and $^6B_2$ being energetically less stable than the ground $^6A_1$ state by 13.42 and 13.74 kcal/mol, respectively.

For FeC_3^-, different theoretical studies [29,31,53,54] predicted different results for its ground state structure. Wang and Li [31] suggested it was a C_{2v} symmetry ring structure with preliminary DFT calculation, but a linear configuration was obtained by Fan et al. [29] with the NL method, by Cao et al. [54] with the B3LYP, CCSD(T)//CISD and MRMP2//CASSCF methods, and by Hendrickx and Clima [53] with the CASSCF/CASPT2 method. With the B3LYP/6-311+G* approach, we also got a linear structure for the global minimum of FeC_3^-, but different from the ground $^4\Sigma^-$ state of Cao et al. [54] and Hendrickx and Clima [53], our ground state is $^2\Delta$. The bond lengths in this ground $^2\Delta$ state are R(Fe1–C2) = 1.765, R(C2–C3) = 1.318 and R(C3–C4) = 1.285 Å, respectively. In our calculations, the $^4\Sigma$ state is energetically less stable than the ground $^2\Delta$ state by 6.39 kcal/mol. The lowest-lying cyclic state $^4B_1$ is slightly higher (0.64 kcal/mol) in energy than the $^4\Sigma$ state.

The global minimum of FeC_4^- is in linear $^4\Delta$ state with $C_{\infty v}$ symmetry. Comparing with the cyclic form of neutral FeC_4, anionic

FeC_4^- shows large difference in geometry, which is in agreement with the broad spectrum of FeC_4^-, and supported by the gas phase ion chromatography experiment of Helden et al. [28] and the NL calculation of Fan et al. [12]. The Fe–C bond length is 1.844 Å and the C–C bond distances are in the range of 1.249-1.345 Å for this ground $^4\Delta$ state.

For FeC_5^-, the ground state is $^2\Delta$ with $C_{\infty v}$ symmetry. The Fe–C bond length is 1.791 Å, and the C–C bond distances are in the range of 1.275–1.314 Å, representing some extent property of C=C double bond.

Similar to FeC_2^- and FeC_4^-, FeC_6^- and FeC_8^- also have linear $^4\Delta$ ground state with $C_{\infty v}$ symmetry. The Fe–C bond lengths are 1.854 and 1.864 Å in FeC_6^- and FeC_8^-, respectively. The C–C bond distances exhibit an alternation with the C_{even}–C_{odd} lengths shorter than the C_{odd}–C_{even} ones, which are in the range of 1.240–1.337 Å for FeC_6^-, and 1.239–1.336 Å for FeC_8^-.

Both FeC_7^- and FeC_9^- have cyclic ground state structures. For FeC_7^-, the ground state is $^4A_2$, with other two cyclic states $^2A_1$ and $^6A_1$ being less stable than the ground $^4A_2$ state by 14.61 and 16.97 kcal/mol, respectively. Linear $^2\Delta$ state also has lower energy, which is energetically higher than the ground $^4A_2$ state only by 4.16 kcal/mol. All other linear states of FeC_7^- have much higher energies. For FeC_9^-, the ground state is $^4B_1$, which is energetically more stable than cyclic $^6A_1$ state and linear $^2\Delta$ state by only 0.20 and 0.83 kcal/mol, respectively. Clearly, higher level calculations are necessary to confirm which state is more stable for FeC_9^-.

For FeC_{10}^-, the ground state is in quasi-linear form with $^4A'$ state. When it is constrained to linear form, there are two degenerate π imaginary frequencies. Following the normal mode of the imaginary frequencies related to the $^4A'$ ground state. It should be mentioned that the cyclic $^4A''$ state with C_s symmetry is only 0.38 kcal/mol higher in energy than the ground $^4A'$ state, indicating that these two states are almost isoenergetic. The Fe–C bond length in $^4A'$ state is 1.872 Å, and the C–C bond distances are in the range of 1.238–1.337 Å, which exhibit an alternation with the C_{even}–C_{odd} lengths shorter than C_{odd}–C_{even} ones.

Generally, anionic FeC_n^- clusters have linear or quasi-linear ground states except FeC_7^- and FeC_9^-, which have cyclic ones. The electronic states are $^2\Delta$, $^4\Delta$, $^2\Delta$, $^4\Delta$, $^2\Delta$, $^4\Delta$, $^4A_2$, $^4\Delta$, $^4B_1$ and $^4A'$ for FeC_{1-10}^-, respectively, and the linear states can be deduced from their electronic configurations as followed:

$$\{\text{core}\}1\sigma^2\ldots(n+2)\sigma^2 1\pi^4\ldots\left(\frac{n+1}{2}\right)\pi^4 1\delta^3, \quad n-\text{odd}$$

$$\{\text{core}\}1\sigma^2\ldots(n+2)\sigma^2 1\pi^4\ldots\frac{n}{2}\pi^4\left(\frac{n+2}{2}\right)\pi^2 1\delta^3, \quad n\text{-even}$$

3.3. Cationic clusters

For cationic FeC^+, the most stable state is $^2\Delta$, and the Fe–C bond length is 1.572 Å. For FeC_2^+, the sextuple state has the lowest energy for both linear and cyclic configurations. The ground state is the cyclic $^6A_1$ state, with the linear $^6\Delta$ state being 2.89 kcal/mol higher in energy. The optimized geometrical parameters for the $^6A_1$ ground state are R(Fe–C) = 1.983 and R(C–C) = 1.281 Å. With several methods, Rayon et al. [33] also proposed the ground electronic state of FeC_2^+ is $^6A_1$. When n = 3–8, the linear isomer with a terminal iron atom is the lowest-energy conformation for each member of the FeC_n^+ series and the electronic ground state is quadruple $^4\Sigma$ for n-odd member and sextuple $^6\Sigma$ for n-even member. The $^4\Sigma$ state is resulted from the

$$\{\text{core}\}1\sigma^2\ldots(n+2)\sigma^2 1\pi^4\ldots\left(\frac{n+1}{2}\right)\pi^4(n+2)\sigma^1 1\delta^2$$

configuration, and the $^6\Sigma$ state is from the

$$\{\text{core}\}1\sigma^2\ldots(n+1)\sigma^2 1\pi^4\ldots\frac{n}{2}\pi^4(n+2)\sigma^1\left(\frac{n+2}{2}\right)\pi^2 1\delta^2$$

configuration. The Fe–C bond length increases as the number of carbon atoms increases for the n-odd and n-even series, with the former (1.824–1.836 Å for n-odd clusters) being longer than the latter (1.809–1.822 Å for n-even ones). The C–C distances (1.254–1.313 Å) present the property of moderate carbon–carbon double bond, and there is an alternation in the n-odd clusters with the C_{even}–C_{odd} bond shorter than C_{odd}–C_{even} bond. For FeC_9^+, the lowest-energy structure is in quasi-linear form and the electronic state is $^4A''$. When it is constrained to linear form, the $^4\Sigma$ state has two degenerate π imaginary frequencies. For FeC_{10}^+, the global minimum reverse to cyclic form, which is in $^4A_2$ state and is energetically more stable than quasi-linear $^6A'$ state by only 3.46 kcal/mol.

3.4. Incremental binding energy

To compare the relative stability of FeC_n with different sizes, we adopt the concept of incremental binding energy, labeled as ΔE^I, as suggested by Pascoli and Lavendy [15]. ΔE^I is defined as the consecutive binding energy difference between adjacent $FeC_n/FeC_n^-/FeC_n^+$ and $FeC_{n-1}/FeC_{n-1}^-/FeC_{n-1}^+$ clusters, which can be depicted as the reaction energies of following processes:

$$FeC_n \rightarrow FeC_{n-1} + C$$

$$FeC_n^- \rightarrow FeC_{n-1}^- + C$$

$$FeC_n^+ \rightarrow FeC_{n-1}^+ + C$$

The incremental binding energies *vs.* the carbon atom numbers are shown in Fig. 4 for the lowest-lying linear states, the lowest-lying cyclic/fanlike states, and the ground states of the Fe-doped clusters. For linear isomers, we can observe a slight even–odd alternation in stability for neutral FeC_n clusters especially in the first members in the series, with even n members being slightly more stable than the adjacent odd $n-1$ and $n+1$ ones. Similarly, n-even linear FeC_n^- isomers are also more stable than the adjacent n-odd FeC_n^- ones, and the amplitude of the alternation is much obvious. Linear FeC_n^+ isomers also show parity effect in their incremental binding energies, but opposing to FeC_n^-, n-odd FeC_n^+ species are more stable than the adjacent n-even FeC_n^+ ones. For cyclic/fanlike $FeC_n/FeC_n^-/FeC_n^+$ clusters, the parity effect only present for their smaller members ($n \leq 6$), with the tendency similar to the corresponding linear ones, but it is difficult to find a general trend for their larger members. Since most ground states of the $FeC_n/FeC_n^-/FeC_n^+$ clusters have linear structures or have their energies closer to the lowest-lying linear states, the even–odd alternations in stability for the ground states of the Fe-doped clusters are very similar to those for the lowest-lying linear states.

3.5. Ionization potentials and electron affinities

Comparing the total energies for the ground states of FeC_n, FeC_n^- and FeC_n^+, we obtained the ionization potentials (IPs) and the electron affinities (EAs) of the FeC_n clusters. Fig. 5 shows the IP and EA values as a function of the number of carton atoms. Both IPs and EAs reported herein are calculated in the adiabatic form, from the ground state energies of the neutral and ionic species at their optimized geometries. It can be readily seen from Fig. 5 that IPs show a clear even-odd alternation with higher values for the n-even species. As mentioned above, n-even neutral FeC_n have higher stabilities than n-odd FeC_n, while n-even cationic FeC_n^+ are less stable than n-odd FeC_n^+, both of them result in higher IPs of n-even

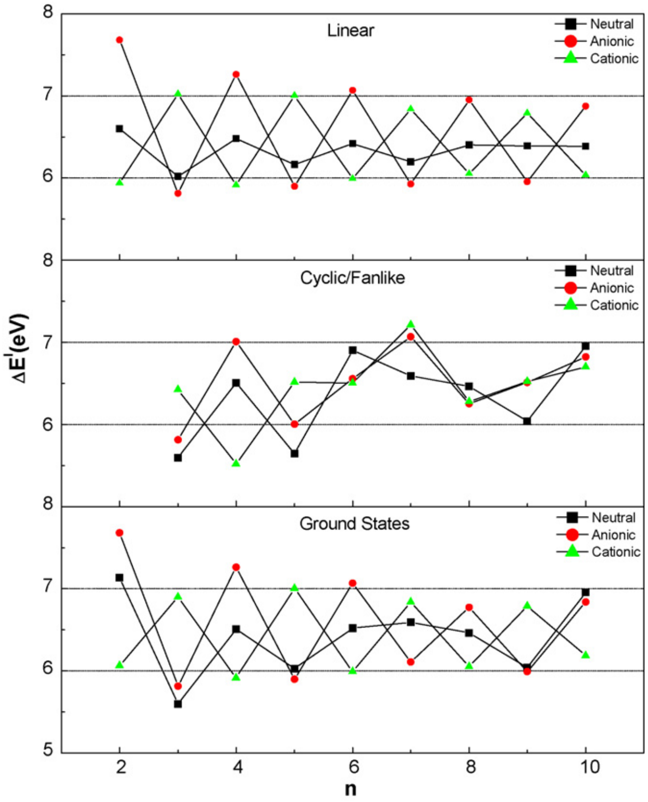

Fig. 4. Incremental binding energies for $FeC_n/FeC_n^-/FeC_n^+$ *vs.* the number of carbon atoms.

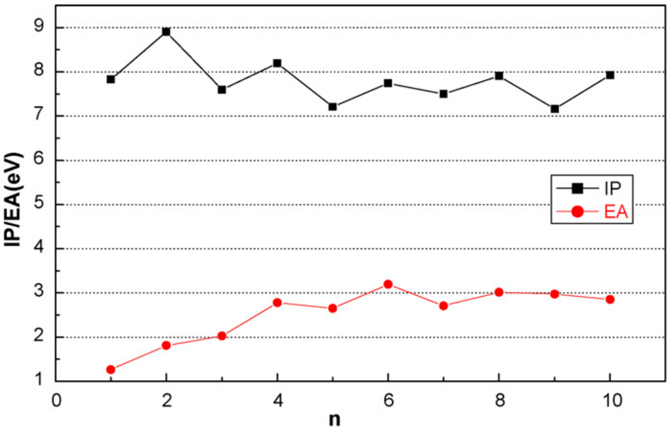

Fig. 5. Ionization potentials (IP) and electron affinities (EA) of FeC_n *vs.* the number of carbon atoms.

FeC_n. The EA values increase from FeC (1.27 eV) to FeC_4 (2.78 eV), but vary smoothly from FeC_5 to FeC_{10}, which is also the reflection of the incremental binding energies of related FeC_n and FeC_n^- clusters.

4. Conclusion

A theoretical study has been carried out on linear and cyclic iron-doped carbon clusters $FeC_n/FeC_n^-/FeC_n^+$ ($n = 1–10$) with DFT method at the B3LYP/6-311+G* level.

Geometrically, neutral FeC_n prefer cyclic/fanlike structures to linear ones, except for FeC_5, which has a linear lowest-energy structure. Oppositely, ionic FeC_n^- and FeC_n^+ have linear or quasi-linear ground states, except anionic FeC_7^-, FeC_9^- and cationic FeC_2^+ and FeC_{10}^+, which all have cyclic lowest-lying states. On the other hand, for FeC_9^-, the energy difference between ground $^4B_1$ state and linear $^2\Delta$ (or cyclic $^6A_1$) state is less than 1.00 kcal/mol, indicating that they all are almost isoenergetic; for FeC_{10}^-, the quasi-linear $^4A'$ state and the cyclic $^4A''$ state are also isoenergetic. Considering their spin multiplicities, the ground states are triple for n-odd FeC_n, quintuple for n-even FeC_n; double ($n = 1, 3, 5$) or quadruple ($n = 7, 9$) for n-odd FeC_n^-, quadruple for n-even FeC_n^-; quadruple for the n-odd FeC_n^+, and sextuple for n-even FeC_n^+, FeC^+ and FeC_{10}^+ being exceptions.

According to the incremental binding energies, strong even–odd alternations in the cluster stability exist for iron-doped small carbon clusters. For neutral FeC_n and anionic FeC_n^-, their n-even members are much more stable than the corresponding odd $n-1$ and $n+1$ ones, with FeC_7 being the only exception. Oppositely, for cationic FeC_n^+, their n-old members are much more stable than the corresponding even $n-1$ and $n+1$ ones. The parity effects in the cluster stability also reflect in the ionization potential and electron affinity curves.

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