J. Phys. Chem. A **2004,** *108,* 6421−6429

Structure and Properties of the Open-Chain Calcium-Doped Carbon Clusters CaC_n, CaC_n^+, and CaC_n^- ($n = 1-8$)

Antonio Largo,* Pilar Redondo, and Carmen Barrientos

Departamento de Química Física, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain

Received: March 24, 2004; In Final Form: May 21, 2004

A DFT theoretical study of the CaC_n, CaC_n^+, CaC_n^- ($n = 1-8$) open-chain clusters has been carried out using the B3LYP method with both 6-311G(d) and 6-311+G(d) basis sets. For each species several molecular properties such as vibrational frequencies, dipole moments, and rotational constants are reported. For the CaC_n open-chain clusters the lowest-lying states correspond to triplet states for *n*-odd members, whereas in the *n*-even species the ground states were found to be singlets. Cationic clusters have doublet ground states with the exception of the smallest one, CaC^+. In CaC_n^- clusters, except for CaC_3^-, the ground state is alternate between quartets (for *n*-odd members) and doublets (for *n*-even members). The incremental binding energy diagrams show a clear odd−even alternation in the cluster stability in both neutral and anionic clusters with their *n*-even members being more stable than the corresponding *n*-odd ones, while the parity effects is less pronounced for the cationic clusters. This odd−even alternation was also found for the electron affinities, whereas there is not a clear alternation in the ionization potentials.

I. Introduction

In last few years the chemistry and physics of carbon clusters have been recognized as being important from both experimental and theoretical investigations. The reason for this experimental interest results from not only the diverse applications in fields as heterogeneous catalysis and soot formation during combustion, but also their relationship with fullerenes. In addition, carbon clusters have also attracted considerable interest in astrophysics from their identification in interstellar and circumstellar media by radiowave or infrared spectroscopy[1]. Many of these carbon clusters are found to be small in size, possessing only three or four atoms, however medium-sized species also exist appearing in the form of an archetypical cumulenic or acetylenic carbon chain, C_n, with one or two foreign atoms such as hydrogen, nitrogen, oxygen, or silicon attached to the extremities.[2,3] In the interstellar medium, the reactivity of small and medium-sized carbon clusters is forfeited by quasi-collisionless conditions, and carbon takes the highly stable, albeit under normal conditions highly reactive, form of linear chains.[4−6] On the other hand, the addition of heteroatoms provides a means to stabilize the carbon chain. Heteroatom-doped carbon clusters containing a first- or second-row element of the Periodic Table have been extensively studied in the past few years;[7−16] however, few studies deal with heavy-atom-doped carbon clusters.

The CaC molecule is of great importance in metal carbide astrophysics,[17,18] since on the basis of its natural abundance it became a strong candidate to be detected in space, and therefore it has received some attention from both theoretical[19−21] and experimental investigations.[22,23] In the past few years, we have carried out theoretical studies on both CaC_2[24] and CaC_3[25] systems in order to provide predictions of their molecular parameters that could help in their eventual experimental observation. In addition, we have also performed a theoretical study on the $MgC_n/MgC_n^+/MgC_n^-$ systems.[26,27] Calcium is isovalent with magnesium and to our knowledge no published works exist for larger CaC_n clusters. Therefore, in this work, we have carried out a theoretical study of the $CaC_n/CaC_n^+/CaC_n^-$ ($n = 1-8$) species in order to provide information about some molecular properties and also to make a comparative analysis with Mg-doped carbon clusters. Of course cyclic CaC_n clusters might also be relevant, but in order to obtain systematic trends, the present work will be restricted to open-chain clusters.

II. Computational Methods

The present study was performed employing the density functional theory (DFT), with the hybrid three-parameter Becke[28] (B3) exchange and the Lee, Yang, and Parr (LYP) correlation fuctional.[29] As is known, the DFT/B3LYP method has been widely applied to the study of many medium-sized heteroatom-doped carbon clusters, providing structures in good agreement with the experimental results.

In the calculations, we used in both geometry optimizations and frequency calculations the triple split-valence d-polarized 6-311G(d) basis set which employed the standard 6-311G triple-split-valence basis set[30] augmented with d-type polarization functions, and the 6-311+G(d) basis set which also includes diffuse functions.

Harmonic vibrational frequencies were computed from analytical gradient techniques and they were employed to estimate the zero-point vibrational energy and also to assess the nature of the stationary points.

All calculations were carried out using the Gaussian 98 set of programs.[31]

III. Results and Discussion

We will present results for the more stable open-chain geometries with the calcium atom sited at the end position, however other geometries for example species with the calcium in an intermediate position were also studied but are not presented here since they lie much higher in energy.

---

* To whom correspondence should be addressed.

10.1021/jp0486853 CCC: $27.50

TABLE 1: Electronic Energies, $\langle S^2\rangle$ Values, Vibrational Frequencies, Binding Energies (for the Ground States), Dipole Moments, Rotational Constants, and Relative Energies for CaC_n Clusters with the B3LYP/6-311G(d) (First Line) and B3LYP/6-311+G(d) (Second Line) Methods

isomer	state	$-E$ (au)	$\langle S^2\rangle$	vibrational frequencies (cm^{-1})	BE (eV)	μ (D)	rotational constants (GHz)	ΔE (kcal mol^{-1})
CaC	$^1\Delta$	715.441908		479		4.98	10.462	41.73
		715.447090		475		6.15	10.401	40.24
	$^3\Sigma$	715.508413	2.8332	482	2.05	3.26	10.387	0.00
		715.511206	2.8268	472	2.09	3.86	10.297	0.00
CaC_2	$^1\Sigma$	753.655282		136i(2)/488/1870	9.85	12.62	4.124	0.00
		753.662968		81i(2)/491/1863	9.99	13.55	4.120	0.00
	$^3\Sigma$	753.636805	2.0151	156i(2)/390/1962		3.97	3.666	11.58
		753.639944	2.0155	144i(2)/384/1953		4.33	3.649	14.42
CaC_3	$^1A'$	791.699644		97/231/293/407/1225/1930		7.29	74.310/1.928/1.879	13.19
		791.704341		96/264/294/396/1225/1923		8.14	89.217/1.900/1.860	13.12
	$^3\Pi$	791.720960	2.0154	87/89/278/330/410/1238/1878	15.43	7.39	1.737	0.00
		791.725565	2.0153	30/118/98/325/415/1235/1915	15.45	7.91	1.731	0.00
CaC_4	$^1\Sigma$	829.828633		146i(2)/181(2)/413/494(2)/1037/1911/2135	22.12	21.02	1.122	0.00
		829.838975		20i(2)/229(2)//410/543(2)/1034/1905/2120	22.26	21.66	1.118	0.00
	$^3\Pi$	829.822973	2.0132	65/71/186/242/300/462/526/974/1815/2098		9.06	1.013	3.39
		829.827973	2.0131	71/81/247/256/296/439/519/986/1824/2110		9.62	1.010	6.77
CaC_5	$^1\Delta$	867.863504		54/66/173/175/346/368/418/480/690/863/1503/1938/2028		22.20	0.695	29.35
		867.874748		62/68/181/198/364/397/425/570/781/861/1501/1937/2018		22.88	0.693	26.08
	$^3\Pi$	867.909556	2.0264	52/54/163/170/280/321/373/480/658/820/1488/1943/1982	28.13	10.05	0.649	0.00
		867.914944	2.0261	54/56/169/179/277/337/369/462/650/819/1485/1939/1966	28.10	10.63	0.648	0.00
CaC_6	$^1\Sigma$	906.006336		57(2)/173(2)/329(2)/349/637(2)/764/801(2)/1283/1909/2111/2208	34.44	27.08	0.473	0.00
		906.017045		14(2)/112(2)/262(2)/346/550(2)/760/803(2)/1280/1905/2106/2203	34.55	27.62	0.472	0.00
	$^3\Pi$	906.006345	2.0212	47/48/130/138/248/264/270/445/492/674/702/704/1246/1882/2045/2147		11.49	0.443	−1.63
	$^3A'$	906.011930	2.0209	46/131/136/251/261/269/443/489/656/675/701/1245/1880/2045/2149		12.08	0.443	2.11
CaC_7	$^1\Delta$	944.051680		38/42/109/123/211/216/323/363/422/523/627/671/697/921/1133/1619/1911/2029/2095		27.73	0.333	26.31
		944.062996		41/45/120/133/234/251/319/411/445/653/667/704/1008/1098/1130/1617/1906/2028/2029		27.62	0.332	24.32
	$^3\Pi$	944.092733	2.0366	37/38/103/109/206/217/253/340/375/490/592/621/745/859/1107/1599/1874/2025/2099	40.64	12.37	0.317	0.00
		944.098651	2.0363	37/39/102/110/205/217/250/334/368/473/577/619/703/803/1107/1600/1873/2023/2097	40.57	12.99	0.317	0.00
CaC_8	$^1\Sigma$	982.184109		36(2)/102(2)/203(2)/305(2)/306/545(2)/613/686(2)/1017/1032(2)/1416/1929/2031/2189/2224	46.87	33.00	0.246	0.00
	$^1A'$	982.195530		24/66/73/165/167/267/269/312/454/454/527/531/574/630/646/992/1402/1905/2009/2154/2200	46.95	29.46	50.168/0.251/0.250	0.00
	$^3\Pi$	982.187506	2.0286	32/32/88/88/169/184/242/280/290/439/476/552/611/626/940/965/982/1388/1896/2035/2090/2179		13.69	0.235	−3.50
		982.193585	2.0280	35/35/90/90/183/185/240/280/283/423/460/551/563/567/827/834/982/1387/1895/2035/2088/2178		14.34	0.235	1.76

Two different states were considered for the linear or quasi-linear isomers. In the neutral clusters we studied both singlet and triplet CaC_n potencial surfaces, whereas in the cationic and anionic clusters the study included the corresponding doublet and quartet potential surfaces.

It should be pointed out that for some of the structures reported in this work the B3LYP method, as well as single-reference based methods such as HF, MP2, QCISD, etc., provides nondegenerate π frequencies. This is the case for structures corresponding to $^2\Pi$, $^3\Pi$, or $^4\Pi$ electronic states. On the other hand for the $^1\Sigma$, $^2\Sigma$, $^3\Sigma$, and $^4\Sigma$ linear states, the degenerate π frequencies are denoted in Tables 1−3 as (2). As general criteria we will only report the properties for structures corresponding to real minima on the respective potential surface, that is with all their vibrational frequencies real. The only exception is the CaC_2 species, since the different neutral, cationic, and anionic compounds have imaginary frequencies. This special case has been studied in detail in a recent paper,[24] where it has been shown that all these species have nonlinear ground states corresponding to T-shape structures. In the case of neutral CaC_4 a similar situation is found, and we report a singlet linear state with imaginary frequencies.

III.1. Structures, Energies, and Spectroscopic Parameters. Tables 1−3 list the $\langle S^2\rangle$ values, vibrational frequencies, binding energies, dipole moments, rotational constants, and absolute and relative energies for the different CaC_n/CaC_n^+/CaC_n^- species that could be useful for experimentalists in their spectral analysis of these species. In addition in Figures 1−3, the equilibrium geometries for the more stable open-chain isomers are given.

CaC_n Clusters. Except for the first member CaC, the $\langle S^2\rangle$ values for the triplet states, shown in Table 1, are uniform and deviate slightly from the pure spin values, always less than 2%. Consequently it can be considered that the B3LYP wave functions are nearly spin-pure, and spin contamination should not be a problem in these cases. The only exception with significant spin contamination, CaC, is probably due to a low-lying quintet state ($^5\Sigma$), which in fact is a competitive candidate to the ground state (see below).

From Table 1, it is also readily seen that the neutral clusters with *n*-odd have triplet ground states, whereas *n*-even neutral clusters present singlet ground states. The triplet−singlet difference is large enough for *n*-odd clusters to be confident in the state ordering. In the case of *n*-even clusters the singlet−triplet energy difference is much smaller, and furthermore

TABLE 2: Electronic Energies, $\langle S^2\rangle$ Values, Vibrational Frequencies, Binding Energies (for the Ground States), Dipole Moments, Rotational Constants, and Relative Energies for CaC_n^+ Clusters with the B3LYP/6-311G(d) (First Line) and B3LYP/6-311+G(d) (Second Line) Methods

isomer	state	$-E$ (au)	$\langle S^2\rangle$	vibrational frequencies (cm^{-1})	BE (eV)	μ (D)	rotational constants (GHz)	ΔE (kcal mol^{-1})
CaC^+	$^2\Pi$	715.243506	0.8067	379		6.02	9.068	28.02
		715.244329	0.8022	383		6.18	9.081	28.13
	$^4\Sigma$	715.288640	3.7523	583	2.23	6.87	11.566	0.00
		715.289614	3.7523	579	2.21	6.97	11.527	0.00
CaC_2^+	$^2\Sigma$	753.416956	0.7739	54i(2)/481/1983	9.52	9.47	3.991	0.00
		753.418968	0.7741	47(2)/478/1998	9.49	9.54	3.980	0.00
	$^4A''$	753.304114	3.7595	113/200/1539		1.37	226.390/2.996/2.957	69.45
		753.305043	3.7598	116/200/1529		1.45	231.716/2.992/2.954	70.02
CaC_3^+	$^2\Pi$	791.491831	0.7624	97/98/296/380/402/1221/1942	15.34	14.19	1.851	0.00
		791.495002	0.7622	91/103/298/338/397/1218/1926	15.33	14.29	1.846	0.00
	$^4\Sigma$	791.453261	3.8135	115(2)/422/446(2)/1336/1720		10.64	1.898	24.43
		791.455711	3.8129	115(2)/418/440(2)/1335/1722		10.65	1.893	24.96
CaC_4^+	$^2A'$	829.592220	0.7875	77/110/235/373/471/492/1003/1733/1922	21.88	17.72	829.679/1.083/1.081	0.00
		829.595530	0.7850	78/107/233/370/452/489/1000/1752/1918	21.82	16.95	1026.404/1.079/1.077	0.00
	$^4A''$	829.517874	3.7863	54/132/133/193/425/428/940/1604/2055		5.24	1003.479/0.930/0.929	46.01
		829.520144	3.7863	53/143/161/245/376/447/937/1613/2052		5.56	1012.161/0.930/0.929	46.77
CaC_5^+	$^2\Pi$	867.680379	0.7711	62/63/163/173/336/343/352/480/675/843/1473/1991/2018	28.04	19.63	0.681	0.00
		867.684531	0.7707	60/64/165/179/340/346/350/448/665/841/1474/1991/2021	27.97	19.71	0.680	0.00
	$^4\Sigma$	867.641495	3.8624	67(2)/189(2)/353/414(2)/550(2)/866/1566/1734/1948		14.85	0.688	24.30
		867.644757	3.8612	67(2)/195(2)/349/418(2)/540(2)/864/1563/1741/1947		14.76	0.687	24.78
CaC_6^+	^2A	905.776364	0.7863	50/102/122/219/236/325/439/487/659/677/735/1256/1844/1989/2076	34.44	22.52	2515.780/0.463/0.463	0.00
		905.780738	0.7764	30/69/73/193/202/321/436/468/658/682/731/1256/1859/1986/2106	34.34	22.78	24892.807/0.462/0.262	0.00
	$^4\Sigma$	905.715857	3.8083	49(2)/135(2)/198/263(2)/434(2)/666(2)/690/1245/1758/2018/2152		6.56	0.423	37.88
		905.718953	3.8081	52(2)/133(2)/196/261(2)/425(2)/619(2)/690/1246/1758/2019/2155		6.86	0.423	38.68
CaC_7^+	$^2\Pi$	943.864813	0.7795	43/44/109/112/202/213/306/355/362/499/602/652/752/886/1120/1579/1937/2050/2109	40.59	24.86	0.329	0.00
		943.869689	0.7790	42/43/110/115/205/219/303/356/361/499/596/649/708/819/1120/1579/1935/2048/2109	40.48	24.91	0.329	0.00
	$^4\Sigma$	943.826665	3.9067	44(2)/11(2)/233(2)/310/402(2)/535(2)/662/812(2)/1135/1629/1681		19.08	0.331	23.63
		943.830611	3.9053	44(2)/119(2)/238(2)/308/397(2)/531(2)/660/764(2)/1134/1633/1678		18.92	0.330	24.24
CaC_8^+	$^2\Pi$	981.959213	0.7854	35/37/80/93/131/179/250/281/290/435/490/588/620/634/955/1000/1014/1393/1864/1928/2069/2171	46.92	27.89	0.243	0.00
		981.964330	0.7851	35/36/84/91/144/181/248/252/288/402/431/431/467/586/656/681/999/1393/1870/1940/2067/2070	46.83	27.99	0.243	0.00
	$^4\Sigma$	981.907375	3.8281	32(2)/90(2)/168(2)/197/282(2)/426(2)/540/578(2)/949(2)/989/1407/1794/2023/2068/2158		8.28	0.230	32.08
		981.911110	3.8277	34(2)/90(2)/169(2)/196/279(2)/404(2)/500(2)/539/783(2)/989/1407/1794/2024/2069/2159		8.56	0.230	33.67

decreases as the number of carbon atoms increases. It is worth noting that for CaC_6 and CaC_8 it is crucial to include diffuse functions. With the 6-311G(d) basis set the triplet states are predicted to lie lower in energy, whereas with the 6-311+G(d) basis set singlets are placed below the corresponding triplet states.

The alternation in stability between singlet and triplet states for CaC_n clusters can be explained in terms of their electronic configuration. Linear calcium-doped carbon clusters, CaC_n, present $4n + 2$ (n being the number of carbon atoms) valence electrons, and the corresponding electronic configurations match the following patterns:

$$\{\text{core}\}1\sigma^2...1\pi^4...(n+2)\sigma^1\left(\frac{n+1}{2}\right)\pi^1 \quad n \text{ odd members}$$

$$\{\text{core}\}1\sigma^2...1\pi^4...\frac{n}{2}\pi^4(n+1)\sigma^2 \quad n \text{ even members}$$

except for CaC: $\{\text{core}\}1\sigma^2 2\sigma^2 1\pi^4$.

The CaC_n clusters with even n contain $2n + 2$ σ valence electrons and $2n$ π valence electrons. The $2n + 2$ σ valence electrons fully occupy $n + 1$ σ orbitals, and in these species, the $2n$ (four-multiple) π valence electrons constitute a closed shell. Thus, the configurations correspond to a closed shell and give $^1\Sigma$ electronic states.

On the other hand, the n-odd CaC_n species (with the only exception of the smallest member CaC) present $2n + 3$ valence electrons of σ-type and $(2n - 1)$ valence π-electrons. $2n + 2$ valence σ-electrons, of the $2n + 3$ total σ-electrons, fully occupy $n + 1$ orbitals, and the one σ-electron valence remaining leads to a half-filled σ-orbital, σ^1. One (for $n = 3, 7$) or three (for $n = 5$) of the $2n - 1$ π-electrons are distributed over a pair of π-orbitals, corresponding to π^1 or π^3 distributions. Both the $\sigma^1\pi^1$ and $\sigma^1\pi^3$ configurations will give $^3\Pi$ electronic states in these cases.

As can be seen in Figure 1, the two basis sets considered in this study lead to equilibrium geometries very similarly, and consequently, we can conclude that the employment of diffuse

TABLE 3: Electronic Energies, $\langle S^2\rangle$ Values, Vibrational Frequencies, Binding Energies (for the Ground States), Dipole Moments, Rotational Constants, and Relative Energies for CaC_n^- Clusters with the B3LYP/6-311G(d) (First Line) and B3LYP/6-311+G(d) (Second Line) Methods

isomer	state	$-E$ (au)	$\langle S^2\rangle$	vibrational frequencies (cm^{-1})	BE (eV)	μ (D)	rotational constants (GHz)	ΔE (kcal mol^{-1})
CaC^-	$^2\Pi$	715.517129	2.1409	459		1.44	10.778	16.46
		715.523869	2.1503	440		2.67	10.749	17.09
	$^4\Sigma$	715.543241	3.7607	404	3.14	1.83	9.566	0.00
		715.550992	3.7607	391	3.16	1.03	9.461	0.00
CaC_2^-	$^2\Sigma$	753.718379	0.7526	112i(2)/438/1877	11.71	6.41	3.870	0.00
		753.730220	0.7523	50i(2)/438/1871	11.80	7.90	3.853	0.00
	$^4\Pi$	753.638519	3.7638	264i/196i/340/1941		0.93	3.506	50.06
		753.648579	3.7634	293i/204i/337/1937		1.82	3.500	51.18
CaC_3^-	$^2A''$	791.775684	1.0735	93/251/347/363/1208/1751	17.08	2.09	372.750/1.746/1.737	0.00
		791.785842	1.2040	106/262/358/428/1200/1722	17.09	4.13	381.569/1.765/1.757	0.00
	$^4\Sigma$	791.769809	3.7769	109(2)/377/439(2)/1233/1729		7.87	1.825	4.29
		791.782538	3.7793	104(2)/383/417(2)/1235/1708		9.67	1.825	2.49
CaC_4^-	$^2\Sigma$	829.919774	0.7509	42(2)/252(2)/356/561(2)/981/1932/2111	24.73	11.64	1.064	0.00
		829.933863	0.7505	53(2)/258(2)/352/552(2)/975/1927/2109	24.82	13.01	1.060	0.00
	$^4\Delta$	829.842821	3.7595	72/85/257/264/266/458/537/958/1762/2027		1.81	0.992	47.71
		829.852047	3.7603	78/100/258/266/330/486/564/952/1764/2014		1.38	0.989	50.94
CaC_5^-	$^2\Pi$	867.969619	0.7776	60/74/189/204/254/366/428/655/801/1117/1491/1906/1955		2.44	0.615	7.39
		967.978372	0.7773	61/67/191/201/201/368/393/515/641/801/1492/1906/1956		1.72	0.614	9.04
	$^4\Sigma$	867.979617	3.8021	59(2)/189(2)/322/411(2)/535(2)/826/1478/1826/1877	30.18	11.94	0.667	0.00
		867.992576	3.8037	60(2)/193(2)/321/410(2)/534(2)/828/1481/1813/1872	30.20	13.58	0.666	0.00
CaC_6^-	$^2\Sigma$	906.114730	0.7507	39(2)/135(2)/284(2)/302/524(2)/698(2)/715/1231/1944/2101/2197	37.64	15.60	0.454	0.00
		906.128129	0.7504	44(2)/143(2)/288(2)/298/533(2)/712(2)/712/1226/1940/2097/2193	37.58	16.94	0.453	0.00
	$^4\Delta$	906.039759	3.7604	50/55/146/149/255/285/319/413/513/631/679/682/1245/1751/1892/2009		7.40	0.444	45.94
		906.049917	3.7607	50/52/142/147/256/285/319/391/511/583/672/678/1239/1712/1853/1980		9.75	0.445	47.60
CaC_7^-	$^2\Pi$	944.157287	0.7878	38/39/111/111/182/225/227/357/387/497/596/598/752/858/1099/1613/1838/2000/2087		3.49	0.305	13.79
		944.166236	0.7875	39/39/111/111/180/221/226/350/377/468/574/597/692/693/1098/1613/1837/1999/2085		2.72	0.304	15.76
	$^4\Sigma$	944.179008	3.8278	40(2)/114(2)/229(2)/284/405(2)/537(2)/635/766(2)/1099/1611/1735/1950/2004	43.15	15.72	0.322	0.00
		944.191695	3.8285	41(2)/117(2)/223(2)/282/403(2)/550(2)/633/790(2)/1097/1609/1726/1946/1999	43.08	17.14	0.322	0.00
CaC_8^-	$^2\Sigma$	982.305128	0.7506	29(2)/86(2)/188(2)/267/301(2)/505(2)/567/653(2)/975/978(2)/1366/1968/2043/2188/2215	50.28	19.32	0.238	0.00
		982.317973	0.7504	31(2)/86(2)/190(2)/264/279(2)/476(2)/487(2)/564/704(2)/972/1362/1965/2037/2185/2212	50.25	20.62	0.238	0.00
	$^4\Delta$	982.238193	3.7634	33/35/91/95/179/191/259/303/341/409/504/553/557/639/886/961/980/1407/1748/1894/1949/1990		14.21	0.237	40.48
		982.250084	3.7644	34/34/92/94/172/195/263/305/345/386/500/561/569/643/904/960/980/1408/1737/1900/1929/2000		16.59	0.237	42.53

functions is not essential in the computation of structures for these neutral clusters.

The first member of the series, calcium carbide, has been widely theoretically studied. Thus, it could be interesting to discuss this species individually. The characterization of the ground state of CaC has received some attention in the last few years. In fact, initially, there was a debate about the symmetry of the ground state with a competition between $^3\Sigma^-$ and $^5\Sigma^-$ electronic states. Castro et al.[32] from a many-body perturbation theory including all contributions up to fourth-order (MBPT-(4)) characterized a $^3\Sigma^-$ to be the ground state, although it was not considered the $^5\Sigma^-$ state as a possible candidate. Subsequently, the two lower-lying $^3\Sigma^-$ and $^5\Sigma^-$ electronic states were investigated by Da Silva et al.[33] using restricted Hartree-Fock (RHF), generalized valence bond (GVB) and configuration interaction (CI) calculations to establish the relative ordering of these states. From their study, they concluded that the ground state for the CaC molecule was the high-spin $^5\Sigma^-$ state. Serrano and Canuto[34] by using coupled cluster methodology with single and double substitutions and quasiperturbative account for triple excitations (CCSD(T)) suggested that the lowest-lying state of CaC was $^3\Sigma^-$.

Recently the $^3\Sigma^-$ as the ground state of the CaC molecule was confirmed by different studies. Takada et al.[35] carried out a multireference singles and doubles configuration interaction (MRSDCI) characterization of the ground state of CaC, and they found the ground state of symmetry $^3\Sigma^-$ with the first excited state, $^5\Sigma^-$, lying 695 cm^{-1} higher in energy, and finally Kerkines et al.[36] and Papakondylis and Mavridis[37] from a multireference Brillouin−Wigner coupled cluster (MRBWCCSD) method definitively showed that the ground state is of $^3\Sigma^-$ symmetry with the $^5\Sigma^-$ state lying 1500−2500 cm^{-1} higher.

Calcium carbide was observed in the laboratory for the fist time by Ziurys and co-workers[38] using millimeter/submillimeter direct absorption spectroscopy. From their study they concluded that the spectra exhibited clear triplet patterns, evidencing that the ground state of this species is indeed $^3\Sigma^-$. Then the last few years' debate on the identity of the ground state could be

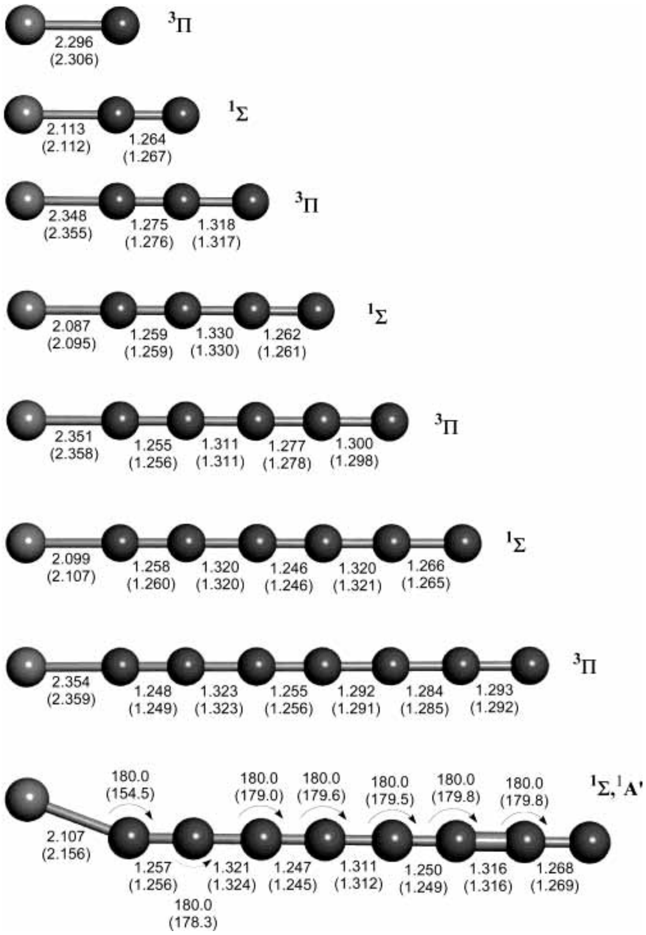

Figure 1. Equilibrium geometries of CaC_n ($n = 1-8$) clusters at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) (in parentheses) levels of theory.

considered complete, confirming beyond any doubt that the ground state is of $^3\Sigma^-$ symmetry.

We have studied the singlet, triplet, and quintet CaC potential surfaces, and our B3LYP calculations also predicted a $^3\Sigma^-$ ground state with a $^5\Sigma^-$ lying quite close in energy (about 3.51 kcal/mol at the B3LYP/6-311+G(d) level).

The valence electronic configuration for CaC is $\{\text{core}\}7\sigma^2 8\sigma^2 3\pi^2$ which could be represented by the following valence bond structure:

$$\mathrm{Ca} \rightarrow \overset{\bullet}{\underset{\bullet}{\mathrm{C}}}:$$

The computed Ca−C distance is 2.306 Å [6-311+G(d) basis set], a value in excellent agreement with the recently determined experimental value[38] ($r_0 = 2.3015$ Å), this distance is shorter than those predicted theoretically by Serrano et al.[34] (2.348 Å) from a CCSD(T) calculation, by Takada el al[35] (2.369 Å) and by Pelegrini et al.[39] (2.378 Å) from a multireference singles and doubles configuration interaction (MRSDCI) methodology; and by Papakondylis and Mavridis[37] (2.369 Å) from their MRCI study.

It should be pointed out that the bond distance in CaC is shorter than that found in some molecules containing Ca−C bond such as $CaCH_3$ (2.349 Å) or CaCCH (2.320 Å). This short bond distance found in CaC may reflect some degree of multiple bond character,[38] being present the theoretically predicted "half-bond". Da Silva et al.[33] pointed out that the stabilization in the electronic configuration of CaC was achieved through a σ bond between the carbon and calcium atoms. Two valence electrons occupy a nonbonding σ orbital located primarily on the carbon atom, and the two unpaired electrons reside in a π orbital set that has a certain degree of bonding character. This "half-bond" overcomes the exchange stabilization that is important in the $^5\Sigma$ state, and thus, the $^3\Sigma$ term becomes lowest in energy.

In the case of $n = 2$, both $^1\Sigma$ and $^3\Sigma$ present imaginary frequencies. Redondo et al.[40] carried out a theoretical study of the possible structures of calcium dicarbide, and from their calculations using the perturbative MP2 and multireference MP2 formalisms they concluded that the ground state has a triangular geometry of C_{2v} symmetry. A recent theoretical study[24] at different levels of theory has confirmed this prediction. Thus, we will not discuss here this species in detail. We will only recall that a wide variety of theoretical methods (including B3LYP, MP2, QCISD(T), CCSD(T), and CASSCF) agree in that the lowest-lying singlet and triplet states of CaC_2 have imaginary vibrational π frequencies, and therefore should be considered as transition states rather than as true minima.[24] Furthermore, all theoretical methods show that the energy decreases monotonically from the linear species to the cyclic one,[24] therefore suggesting that there are no stable bent minima. In the previously referred theoretical study[24] it was also shown that the same behavior is observed for linear CaC_2^+ and CaC_2^-, both having imaginary frequencies and therefore corresponding in fact to transition states.

By looking at Figure 1, it can be seen that the CaC_n clusters with n-odd present bigger Ca−C bond distances (running from 2.306 Å for CaC to 2.359 Å for CaC_7) than those with n-even (2.095 Å for CaC_4 to 2.156 Å for CaC_8).

The C−C bond distances are all in the range 1.245−1.330 Å and can be assigned to moderately strong double bonds, suggesting that the most important valence structure for these clusters is a cumulene-type structure. On the other hand a clear alternation in the C−C bond distances can be observed, $C_{odd}-C_{even}$ being shorter than $C_{even}-C_{odd}$. This fact suggests that there is some polyacelylenic character in this type of compound's alternating triple C−C bonds.

In n-odd clusters ($^3\Pi$ electronic states) with $n \geq 3$ we find spin densities for calcium close to 1.0 e$^-$, for C_1 the spin density is in the range 0.3−0.6 e$^-$ and the rest of the spin density is distributed among the other odd carbon atoms, mainly at the terminal carbon atom.

Consequently the valence structures contributing to the description of these clusters can be depicted as

$$\bullet\mathrm{Ca} - \dot{\mathrm{C}}(=\mathrm{C})_{n-2}{=}\mathrm{C}: \quad n \text{ odd}$$

$$\bullet\mathrm{Ca}(-\mathrm{C}{\equiv}\mathrm{C})_{(n-1)2} - \dot{\mathrm{C}}:$$

In the case of n-even clusters the short Ca−C bond lengths can be assigned to moderately strong double bonds; consequently, the most important valence structure for these clusters is a cumulene-type structure:

$$\mathrm{Ca}(=\mathrm{C})_{n-1}{=}\mathrm{C}: \quad n \text{ even}$$

with the lone pair on the terminal carbon atom.

Dipole moments of CaC_n clusters are quite high, reflecting the relatively high ionic character of the Ca−C bonds. As can be seen in Table 1 the dipole moments regularly increase with the number of carbon atoms considering n-odd and n-even clusters separately. As can be expected lowest-lying singlets present larger dipole moments than the triplet ones.

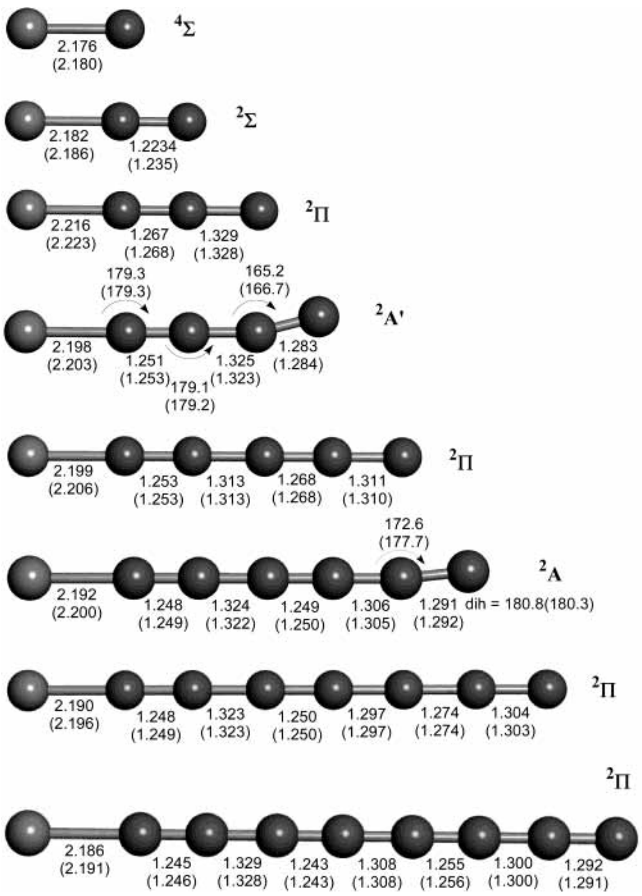

Figure 2. Equilibrium geometries of CaC_n^+ ($n = 1-8$) clusters at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) (in parentheses) levels of theory.

The most important difference observed between CaC_n clusters and their isovalent analogues containing magnesium is that MgC_n clusters have triplet ground states[26] (except MgC_2, which has a $^1\Sigma$ ground state), whereas CaC_n compounds with even n have singlet ground states (even though the singlet−triplet difference is rather small). C−C bond distances are quite similar for both families of compounds containing calcium and magnesium, especially for those corresponding to an odd number of carbon atoms ($^3\Pi$ electronic ground states in both cases) where C−C distances are virtually coincident.

CaC_n^+ Clusters. The geometrical parameters for the lowest-lying states of CaC_n^+ open-chain clusters are shown in Figure 2, and the corresponding properties (absolute and relative energies, rotational constants, vibrational frequencies, and dipole moments) are given in Table 2.

Once again our DFT results for these open-shell states seem to be reliable enough, since spin contamination is smaller than 5% in all cases.

With the only exception of CaC^+, where the scheme is different since carbon is only bonded to calcium, all CaC_n^+ clusters present doublet ground states, (with $^2\Pi$ symmetry in CaC_2^+ and $^2\Sigma$ in the remaining species). The energy differences between doublet and quartet states seem high enough as to be confident in the predictions.

Removing one electron from neutral linear CaC_n clusters produces CaC_n^+ clusters. Since chemical processes occur in frontier molecular orbitals, the electronic configurations for the cationic species can be derived from the electronic distributions of the corresponding neutral linear clusters by subtracting one electron from their frontier orbital (one valence σ-electron in n-odd clusters and one valence π-electron in n-even ones), and thus the electronic configurations for n-odd and n-even CaC_n^+ clusters, except for the first members of the series, can be summarized as

$$\{\text{core}\}1\sigma^2...1\pi^4...(n+1)\sigma^2\left(\frac{n+1}{2}\right)\pi^1 \qquad n \text{ odd members } (n = 3,5,7)$$

$$\{\text{core}\}1\sigma^2...1\pi^4...\frac{n}{2}\pi^3(n+1)\sigma^2 \qquad n \text{ even members } (n = 4, 6, 8)$$

Both the $\sigma^2\pi^1$(for the n-odd members) and the $\pi^3\sigma^2$ (for the n-even members) configurations will give $^2\Pi$ electronic states in the linear geometries and $^2A'$ in nonlinear ones.

Doublet open-chain CaC_n^+ clusters are linear with the exception of $n = 4$ and $n = 6$ (although in this last case the bond angle is close to 180°). Because of the higher electronegativity of carbon respect calcium atom, the carbon chain is quasi-neutral whereas that calcium atom bears a positive charge. On the other hand the C−C bond distances are typical of cumulene-type structures

$$\overset{+}{\text{Ca}} - \dot{\text{C}}(=\text{C})_{n-2}=\text{C}: \quad n \geq 3$$

although some polyacetylenic character appears with alternant triple C−C bonds starting in the C_1-C_2 bond:

$$\overset{+}{\text{Ca}}(-\text{C}\equiv\text{C})_{(n-1)/2}-\dot{\text{C}}: \quad n \text{ odd}; n = 3, 5, 7$$

$$\overset{+}{\text{Ca}}(-\text{C}\equiv\text{C})_{(n-2)/2}-\text{C}\equiv\dot{\text{C}} \quad n \text{ even}; n = 4, 6, 8$$

CaC_n^- Clusters. In Figure 3 we presented the optimized geometries for the different CaC_n^- clusters, and the corresponding molecular properties are summarized in Table 3.

As in both their neutral and cationic counterparts spin contamination is smaller than 5% in these anionic clusters.

Inclusion of diffuse functions has not a significant effect in the geometries of CaC_n^- clusters. However diffuse functions produce an important modification in several molecular properties. Thus, dipole moments are incremented in about 1 D when diffuse functions are included. The influence of diffuse functions in the predicted relative energies is also relevant and variations of up to 3 kcal/mol can be observed when diffuse functions are added.

It is readily seen in Table 3 that n-odd clusters (excepting CaC_3^-) have doublet ground states, whereas n-even ones present quartet ground states.

CaC_n^- clusters have one more electron than their corresponding neutrals. In n-odd clusters the extra electron is incorporated to the ($n + {}^1/_2$) π-orbital of their neutral counterparts, whereas in the n-even ones, the electron goes to a new $n + 2$ σ-orbital, since in CaC_n clusters the electronic distribution corresponds to a closed shell. Consequently the electronic configurations for anionic linear clusters can be generalized as

$$\{\text{core}\}1\sigma^2...1\pi^4...\left(\frac{n+1}{2}\right)\pi^2(n+2)\sigma^1 \quad n \text{ odd members}$$

$$\{\text{core}\}1\sigma^2...1\pi^4...\frac{n}{2}\pi^4(n+2)\sigma^1 \quad n \text{ even members}$$

except for CaC_3^-.

The $\pi^2\sigma^1$ electronic distribution for clusters with odd n results in $^4\Sigma$ electronic states (except for CaC_3^- which has a nonlinear

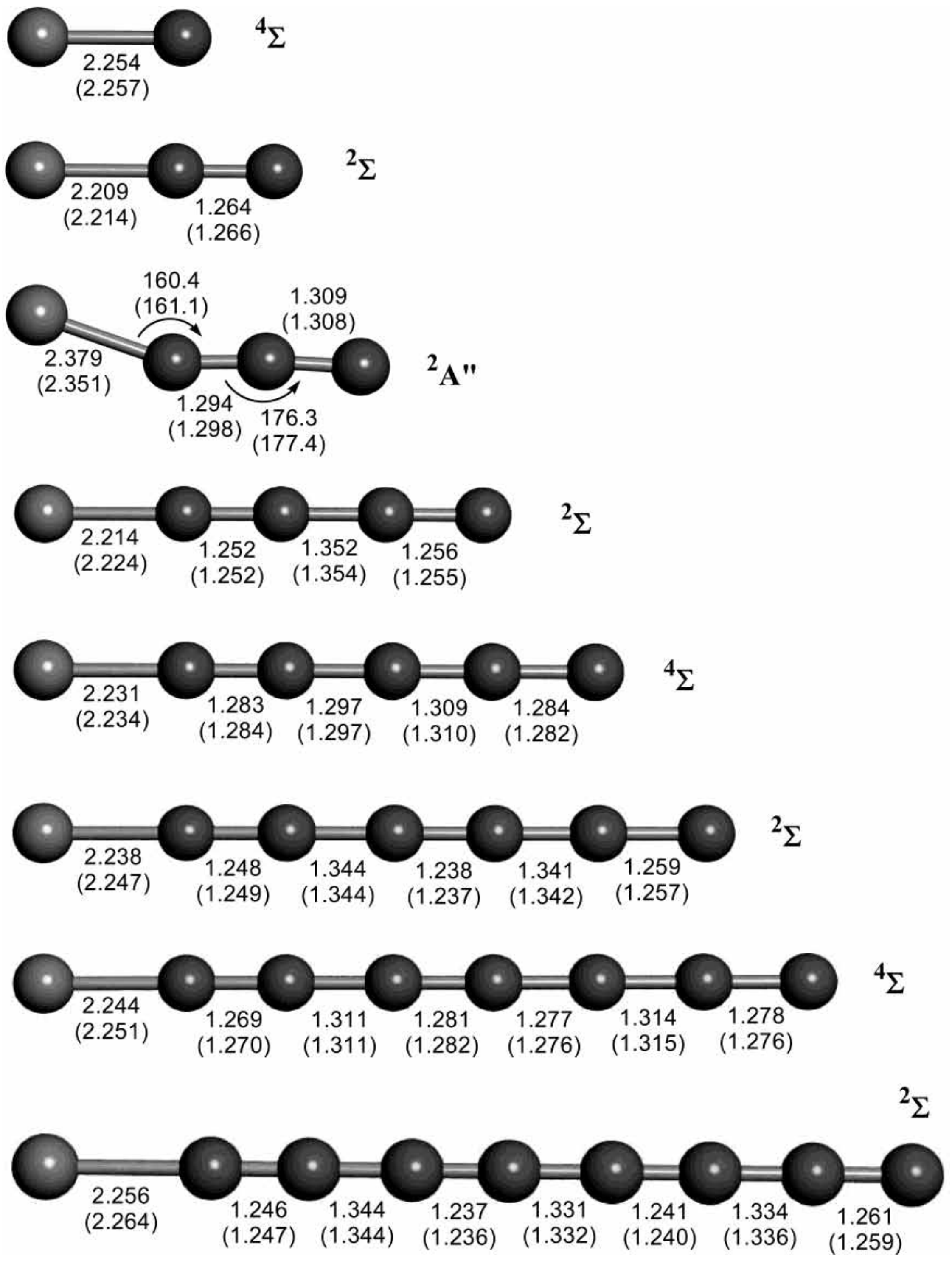

Figure 3. Equilibrium geometries of CaC_n^- ($n = 1-8$) clusters at the B3LYP/6-311G(d) and B3LYP/6-311+G(d) (in parentheses) levels of theory.

geometry corresponding to a $^2A''$ electronic state, correlating in linear geometries with a $^2\Pi$ state), whereas the $\pi^4\sigma^1$ configurations give $^2\Sigma$ electronic ground states for the n-even members.

All C−C bond lengths for n-odd CaC_n^- clusters are rather close and in the range 1.27−1.31 Å typical of cumulenic structures.

$$\bullet\mathrm{Ca}-\dot{\mathrm{C}}(=\mathrm{C})_{n-2}=\dot{\mathrm{C}}^{-}\colon \quad n \text{ odd}$$

In contrast, for n-even species, an alternation in the C−C bond distances is found with $C_{odd}-C_{even}$ distances being shorter than $C_{even}-C_{odd}$ ones. Thus in these cases, the polyacetylenic character seems to be predominant. Consequently the dominant valence structure contributing to their description could be summarized as

$$\bullet\mathrm{Ca}(-\mathrm{C}\equiv\mathrm{C})_{n-2}-\mathrm{C}\equiv\mathrm{C}\colon^{-} \quad n \text{ even}$$

III.2. Stabilities. To compare the relative stability of the clusters with different sizes, we have adopted the concept of incremental binding energy as suggested by Pascoli and

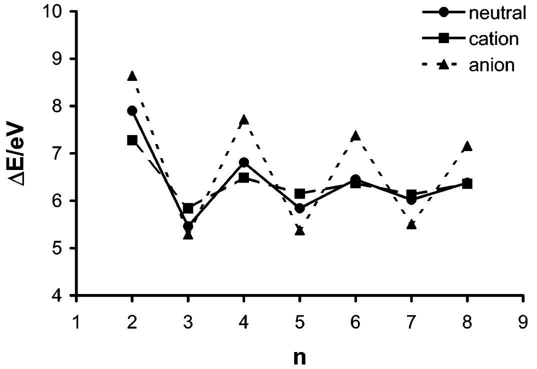

Figure 4. Incremental binding energies (eV) for the CaC_n, CaC_n^+ and CaC_n^- clusters vs the number of carbon atoms.

Lavendy.[13] The incremental binding energy can be defined as the change in energy accompanying the following processes:

$$CaC_n \rightarrow CaC_{n-1} + C$$

$$CaC_n^+ \rightarrow CaC_{n-1}^+ + C$$

$$CaC_n^- \rightarrow CaC_{n-1}^- + C$$

and can be calculated as the consecutive binding energy differences between adjacent $CaC_n/CaC_n^+/CaC_n^-$ and $CaC_{n-1}/CaC_{n-1}^+/CaC_{n-1}^-$ clusters.

The incremental binding energies vs the number of carbon atoms are represented in Figure 4. We have always taken, in each case, the lowest-lying state.

An even−odd alternation in the cluster stability in the CaC_n, CaC_n^+, and CaC_n^- clusters can be observed, with their n-even members being more stable than the corresponding odd $n - 1$ and $n + 1$ ones. This even−odd alternation is clear in anionic CaC_n^-, moderate in neutral CaC_n, and very weak in cationic CaC_n^+ clusters. In this last case, except for the first members of the series, the incremental binding energies are in the range 5.84−6.49 eV.

The parity effects in cluster relative stability can be attributed to the number of available valence π-electrons, mainly the electron number in π-type highest occupied molecular orbital (HOMO).[16]

As we pointed out before, n-even CaC_n clusters ($^3\Pi$) have $\pi^4\sigma^2$ electronic configurations constituting a closed shell. However, except for the smaller member CaC, species with odd n ($^1\Sigma$ states) present $\sigma^1\pi^1$ electronic configurations thus the π-type HOMO is not fully filled with only one electron. Since the situation of fully filled π-orbitals (n-even clusters) is energetically more favorable than the unfilled π-orbitals (n-odd clusters), an even−odd alternation arises in the stability of CaC_n clusters with the n-even members being more stable than the n-odd ones.

For linear CaC_n^- clusters, the parity effect is similar from that of the corresponding neutral counterparts. The CaC_n^- clusters have $4n + 3$ valence electrons, in n-odd species ($^4\Sigma$ electronic states) there are $2n + 2$ valence σ-electrons and $2n - 1$ π valence electrons, whereas n-even CaC_n^- clusters ($^2\Sigma$ states) contain $2n + 3$ valence σ-electrons and $2n$ valence π-electrons. Thus, the highest occupied molecular orbital (HOMO) with π-symmetry is fully populated. The last situation (fully filled π-orbitals) is energetically much more favorable than the former.

The CaC_n^+ clusters present $4n + 1$ valence electrons: $2n + 2$ valence σ-electrons and $2n - 1$ π valence electrons. The $2n + 2$ σ valence electrons fully occupy $n + 1$ σ orbitals, the $2n - 1$ valence π-electrons cannot fully occupy the π-type HOMO, and the cationic cluster stability will be similar; consequently, the incremental binding energy curve does not exhibit a clear odd−even alternation.

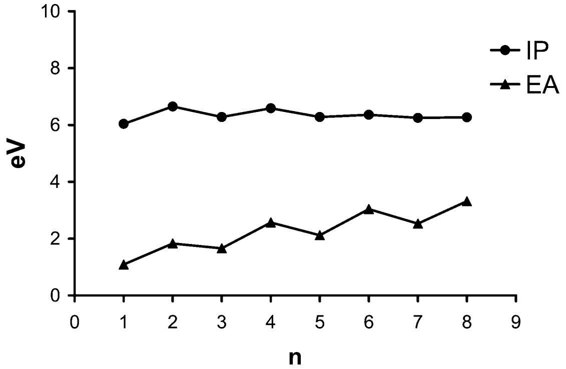

Figure 5. Ionization potentials (IP) and electron affinities (EA), in eV, of CaC_n clusters vs the number of carbon atoms.

Compared to their magnesium isovalent clusters, CaC_n compounds exhibit a rather similar behavior. MgC_n clusters,[26] as well as their cationic and anionic derivatives, show the same parity effect in stability, n-odd species being more stable than their n-even counterparts. Furthermore, the magnitude of the incremental binding energies is quite similar for both magnesium and calcium compounds, and also the difference in stability between consecutive members in the series is much higher for the anionic clusters than for neutral and cationic species in both cases.

III.3. Ionization Potentials and Electron Affinities. Comparing the total energies of CaC_n/CaC_n^+ and CaC_n/CaC_n^- species, we have computed respectively the ionization potentials (IP) and the electron affinities of the different CaC_n clusters. These properties are calculated in the adiabatic form, from the total energies of the neutral and charges species at their optimized geometries including the zero-point vibrational corrections. In Figure 5, the IP and EA values as a function of the number of carbon atoms are depicted. Because n-even CaC_n clusters are more stable than n-odd ones, an even−odd alternation is found, with n-even species presenting higher IPs and EAs than n-odd ones. However both figures are not similar. Whereas variations in the IPs are rather smooth, with values in the range 6.09−6.65 eV, a clear odd−even parity effect in the EAs values is found. This behavior is related to the stablility of CaC_n/CaC_n^+ and CaC_n/CaC_n^- clusters. As it was pointed out, CaC_n^- clusters present a strong even−odd alternation effect, and the parity effect is also evident in neutral clusters resulting in a clear even−odd effect in EAs. However, CaC_n^+ clusters present similar stabilities; thus, the parity effect in the IP curve is much less pronounced.

From Figure 5, it can be observed that there is a tendency to lower IPs and higher EAs as the number of carbon atom in the clusters increases, suggesting that it could be feasible to make extrapolations for advanced members in the series.

Finally it should also be pointed out that both IP and EA diagrams for CaC_n compounds exhibit a rather similar parity effect than their isovalent analogues MgC_n.[26] The main difference is that CaC_n compounds have much smaller IP's (around 6 eV in most cases) than MgC_n species (with IPs close to 8 eV[26]). This essentially reflects the lower IP of calcium atom compared to magnesium, since by obtaining the cations the electron is essentially lost by the heteroatom.

IV Conclusions

Open-chain calcium-doped carbon clusters CaC_n, CaC_n^+, and CaC_n^- ($n = 1-8$) have been studied through the density functional theory at B3LYP/6-311G(d) and B3LYP/6-311+G-(d) theoretical methods.

For the neutral open-chain clusters the ground state is found to be a triplet ($^3\Pi$) for n-odd members and a singlet ($^1\Sigma$) for the n-even ones. In the case of cationic species the lowest-lying states were found to be doublet with the exception of $n = 1$. Finally for the CaC_n^- clusters an odd−even alternation was found, n-odd species presenting quartet ground states (excepting CaC_3^-) and n-even ones having doublet ones.

We use the concept of incremental binding energy to estimate the relative stability of the different CaC_n, CaC_n^+, and CaC_n^- clusters. A clear even−odd alternation in the cluster stability was found for neutral CaC_n and anionic CaC_n^- clusters with their n-even members being more stable than the corresponding $n - 1$ and $n + 1$ ones, while for cationic CaC_n^+ clusters the alternation effect is much less pronounced.

We have also estimated the ionization potentials and electronic affinities of the different CaC_n clusters to check the relative stability found from the incremental binding energy. The electron affinities also exhibit a clear odd−even effect, whereas in the ionization potential the alternation is practically nonexistent.

In addition computations on some molecular properties such as vibrational frequencies, dipole moments and rotational constants, which could be useful for experimentalists, have also been carried out.

Acknowledgment. The authors thank The Ministerio de Ciencia y Tecnologia of Spain (Grant BQU2001-3660-C02-02) and the Junta de Castilla y León (Grant VA 085/03) for financial support.

References and Notes

(1) Williams, D. A. Molecules and Grains in Space; Nenner, I., Ed.; *AIP Conf. Proc.* **1994**, 312.

(2) Cherchneff, I. M.; Glassgold, A. E.; Mamon, G. A. *Astrophys. J.* **1993**, *410*, 188.

(3) Cherchneff, I. M. *Astrophys. J. Suppl. Ser.* **1995**, *224*, 379.

(4) Moazzen-Ahmadi, N.; Zerbetto, F. *J. Chem. Phys.* **1995**, *103*, 6343.

(5) Liu, Z. Y.; Tang, Z. C.; Huang, R. B.; Zhang, Q.; Zheng, L. S. *J. Phys. Chem A* **1997**, *101*, 4019.

(6) Tang, Z. C.; BelBruno, J. J. *Int. J. Mass Spectrom.* **2001**, *208*, 7.

(7) Largo, A.; Cimas, A.; Redondo, P.; Barrientos, C. *Int. J. Quantum Chem.* **2001**, *84*, 127.

(8) Largo, A.; Redondo, P.; Barrientos, C. *J. Phys. Chem. A* **2002**, *106*, 4217.

(9) Pascoli, G.; Lavendy, H. *Int. J. Mass. Spectrom.* **1998**, *173*, 41.

(10) Pascoli, G.; Lavendy, H. *Int. J. Mass. Spectrom.* **1988**, *177*, 31.

(11) Pascoli, G.; Lavendy, H. *Int. J. Mass. Spectrom.* **1998**, *181*, 11.

(12) Pascoli, G.; Lavendy, H. *Int. J. Mass. Spectrom.* **1998**, *181*, 135.

(13) Pascoli, G.; Lavendy, H. *J. Phys. Chem. A* **1999**, *103*, 3518.

(14) Pascoli, G.; Lavendy, H. *Chem. Phys. Lett.* **1999**, *312*, 333.

(15) Pascoli, G.; Lavendy, H. *Eur. Phys. J. D.* **2002**, *19*, 339.

(16) Li, G.; Tang, Z. *J. Phys. Chem.* **2003**, *107*, 5317.

(17) Cernicharo, J.; Gottlieb, C. A.; Guelin, M.; Thadeus, P.; Vrtilek, J. M. *Astrophys. J. Lett.* **1989**, *341*, L25.

(18) Bernath, O. F.; Rogers, S. A.; O'Brien, L. C.; Brazier, C. R.; McLean, A. D. *Phys. Rev. Lett.* **1988**, *60*, 197.

(19) Castro, M. A.; Canuto, S.; Müller-Plathe, *Astrophys. J.* **1991**, *367*, L69.

(20) Silva, C. O.; Teixeira, F. E. C.; Azevedo, J. A. T.; Silva, E. C.; Nascimento, M. A. C. *Int. J. Quantum Chem.* **1996**, *60*, 433.

(21) Serrano, A.; Canuto, S. *Chem. Phys. Lett.* **1997**, *269*, 193.

(22) Serrano, A.; Canuto, S.; Castro, M. A. *J. Mol. Struct. (THEOCHEM)* **1999**, *489*, 29.

(23) Takada, H. H.; Pelegrini, M.; Roberto-Neto, O.; Machado, F. B. C. *Chem. Phys. Lett.* **2002**, *363*, 283.

(24) Redondo, P.; Barrientos, C.; Largo, A. *Chem. Phys. Lett.* **2003**, *382*, 150.

(25) Largo, A.; Redondo, P.; Barrientos, C.; Ziurys, L. M. *Chem. Phys. Lett.* **2002**, *355*, 509.

(26) Redondo, P.; Barrientos, C.; Cimas, A.; Largo, A. *J. Phys. Chem. A* **2003**, *107*, 4676.

(27) Redondo, P.; Barrientos, C.; Cimas, A.; Largo, A. *J. Phys. Chem. A* **2003**, *107*, 6317.

(28) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(29) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(30) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(31) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millan, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.;. Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelly, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, Gaussian Inc.: Pittsburgh, PA, 1998.

(32) Castro, M. A.; Canuto, S.; Müller-Plathe, F. *Phys. Rev. A* **1992**, *46*, 4415.

(33) Da Silva, C. O.; Teixeira, F. E. C.; Azevedo, J. A. T.; Da Silva, E. C.; Nascimento, M. A. C. *Int. J. Quantum Chem.* **1996**, *60*, 433.

(34) Serrano, A.; Canuto, S. *Chem. Phys. Lett.* **1997**, *269*, 193.

(35) Takada, H. H.; Pelegrini, M.; Roberto-Neto, O.; Machado, F. B. C. *Chem. Phys. Lett.* **2002**, *363*, 283.

(36) Kerkines, I. S. K.; Pittner, J.; Čarsky, P.; Mavridis, A.; Hubač, I. *J. Chem. Phys.* **2002**, *117*, 9733.

(37) Papakondylis, A.; Mavridis, A. *J. Phys. Chem. A* **2003**, *107*, 7650.

(38) Halfen, D. T.; Apponi, A. J.; Ziurys, L. M. *Astrophys. J.* **2002**, *577*, L67.

(39) Pelegrini, M.; Roberto-Neto, O.; Ornellas, F. R.; Machado, F. B. C. *Chem. Phys. Lett.* **2004**, *383*, 143.

(40) Redondo, P.; Ellinger, Y.; Berthier, G.; Cimiraglia, R. *Astron. Astrophys.* **1991**, *247*, L1.