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Computed Electron Affinity of Carbon Clusters C_n up to $n = 20$ and Fragmentation Energy of Anions

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Vertical detachment energy and adiabatic electron affinity have been calculated for small carbon clusters C_n ($n = 2-20$), both for linear and monocyclic structures, in the framework of DFT formalism using the hybrid B3LYP functional with a basis set 6-31G* augmented of p diffuse functions. A good reproduction of experimental electron affinities has been obtained in that way for linear chains with $n = 5-20$ especially for odd members of the series. Results are poorer for monocyclic structures however experimental trends are reproduced. For both structures the lowest estimated fragmentation energy corresponding to the loss of C_3 remains larger than electron affinities for the sizes considered.

I. Introduction

In the wide field of cluster physics, which is largely motivated by the understanding of the nontrivial transition from simple atoms or molecules to bulk matter, carbon clusters occupy a very special position. On one hand, carbon clusters are rather common species in nature: as a product of combustion, in the atmosphere where small carbon particles represent a real environmental concern, in the interstellar medium where they are supposed to play a key role in the organic chemistry in space, . . . For instance pure carbon chains such as C_3[1] or C_5[2] have been detected in circumstellar envelopes of giant carbon stars, and larger species more difficult to observe are expected. On the other hand, since carbon atoms are linked by valence bonds, their electronic structure is particularly rich as compared to metal clusters. This is at the origin of the many different forms that carbon clusters may take: linear chains, monocyclic rings, . . . fullerenes.

From an experimental point of view, our group is interested in the study of the decay of energy-rich microscopic systems where the excitation energy exceeds the threshold for the emission of an electron. More specifically, we have tackled this problem by the study of the decay process of metal[3,4] or carbon[5] cluster anions excited above their photodetachment threshold analyzed via their photoelectron spectrum. In that case, major decay channels are either electron emission or, if energetically allowed, dissociation or evaporation of heavy fragments. Regarding electron emission, two qualitatively different channels have to be considered. First, if the emission process is fast enough to avoid internal redistribution of the energy, the electron is ejected with all the excess energy. This process corresponds to direct photoemission. Second, if ionization (or detachment) is not fast enough, a complete breakdown of the Born−Oppenheimer approximation occurs and the dynamics of the system is governed by the exchange of energy between the vibronic degrees of freedom. As a result, the electron does not carry away all the residual energy and may take a long time before being ejected. This phenomenon is described as thermionic emission[6] when the excitation energy is equipartitioned between the nuclear and electronic degrees of freedom. It has been observed mainly from metal[7−10] or carbon[11−14] clusters. In most metal cluster anions, electron emission is an open decay channel at moderate internal energy where fragmentation is not energetically allowed. This is no longer true in carbon clusters where electron affinities and dissociation energies are roughly of the same order of magnitude at moderate size. As far as the electron affinities are concerned, experimental values are reported in the literature for linear isomers ($n = 2-16$)[15,16] as well as for monocyclic rings ($n = 10-20$)[17] of interest here. On the contrary, dissociation energies are not very well-known and only partial theoretical data or crude experimental evaluations are available.[15,18]

Another problem arising in the interpretation of the experimental data is that the method of production of small carbon clusters, neutrals or anions, does not allow us, in general, to control precisely what kind of isomer is produced as a function of the cluster size. It is well-known for the neutral species that the most stable form is the linear chain up to size $n = 9$, while above $n = 10$ the monocyclic ring is more stable, until more complex structures take over at a larger size. The larger abundance of cyclic structures with respect to linear ones for clusters larger than C_{10}, confirmed by theoretical predictions,[19] is clearly visible in neutral cluster mass spectra where the C_{10} mass peak is particularly enhanced. However, stable forms of larger linear chains have been characterized spectroscopically like C_{13} for instance.[20]

The situation is slightly more complex for anions, although laboratory gas-phase spectra of linear anion chains have been reported.[21,22] Most anion cluster mass spectra exhibit also a particularly high intensity at size 10, but this may be due to the method of production (attachment of a slow electron to a highly abundant C_{10} species) rather than to a particular stability of a given isomer of C_{10}^-. On the other hand, ion mobility experiments[23] have shown that, under particular conditions, the linear chain is the most abundant species up to very large size above 50. Drawing from experimental observation the relative stability of the linear or cyclic isomer is thus rather illusive even when some kind of annealing process is allowed like in ref 9. For

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neutral species as well as anions, the more stable structure is not necessarily the most abundant in a given experiment depending on the conditions of production. Consequently the knowledge of structure and relative stability of linear chains is relevant even in a size range where rings are expected to be much more stable.

In addition, our experimental results[5] have shown that, regarding thermionic emission, carbon clusters are not very satisfactorily described by standard models describing the cluster as a small metallic sphere.[24] Of course, these models are well-suited for metal clusters[3,4] but not necessarily for covalent clusters or fullerenes.

All these considerations have motivated the calculations described in the following, aimed at obtaining the relative stability of the various isomers in the size range $n = 2-20$ with respect to the different decay channels: electron emission or dissociation in heavy fragments, both for linear and monocyclic structures. From this point of view, the calculation of the electron affinities will provide a stringent test of the theory since reliable measurements of these quantities are available in the literature,[15-17] and confirmed by our experimental measurements. More particularly, we will (i) clarify the competition between electron emission and heavy fragment emission as a function of the excitation energy; (ii) emphasize the relative stability of the linear or the monocyclic isomer as a function of the size for both neutral and anion clusters. Results of various calculations of the electron affinity of carbon clusters are available in the literature (among which are refs 15, and 25−32). Nevertheless, to our knowledge, no previous systematic investigation of the relative stability of linear and monocyclic structures of C_n^- with respect to electron emission or fragmentation in the whole range of sizes considered here has been published previously while the requirement for such investigation has been explicitly expressed in the literature.[33]

The origin of the large difference of behavior between carbon and metal clusters is partly attributable to the presence of a large gap in the density of states that complicates the electron dynamics and the internal conversion processes in carbon clusters. This aspect will not be considered here and we will focus only on the structure of the neutral and anion carbon clusters. Indeed, the description of the internal dynamics of such species requires a different approach that will be described separately.

II. Computational Approaches

Calculations have been performed for the total energy of small carbon cluster monoanions C_n^- ($n = 2-20$) and the corresponding neutral molecules. From these data, vertical detachment energy (VDE) and adiabatic electron affinity (AEA) as well as fragmentation energies have been derived. The VDE and AEA quantities are calculated as the energy necessary to take off an electron from an anion C_n^-, using for the neutral species C_n the same geometrical configuration as for C_n^- in the case of VDE while the change in the lowest energy structure from C_n^- to C_n is considered when evaluating AEA. This implies determining stable geometrical configurations for both monoanions and corresponding neutral molecules. Lowest-energy conformations were determined through a gradient process for two general cluster species, namely linear and monocyclic isomers.

For anions a two-step procedure was used. First the C_n^- energies involved in the minimization process were evaluated through the semiempirical method AM1.[34] Then, in a second step, these AM1-stable geometries were used as initial guesses in the optimization procedure, energies being calculated via a density functional theory (DFT) approach, using the hybrid exchange-correlation functional B3LYP. This energy functional is made up of the Lee−Yang−Parr correlation functional[35] and includes a linear combination of a small amount of "exact" Hartree−Fock-like exchange with the Becke's gradient-corrected exchange functional.[36] To simulate the experimental conditions for the photodetachment, the geometry optimization process for neutral clusters uses as initial guesses the corresponding stable anion structures previously determined.

Three different basis sets were used for the smallest sizes ($n = 2-10$): (a) a contracted Gaussian split-valence polarized basis set 6-31G*, (b) a larger basis set including one set of sp Gaussian diffuse functions 6-31+G*, (c) an intermediate basis set built up from the 6-31G* one by adding p Gaussian diffuse functions, that we labeled 6-31+(p)G*. For the larger sizes ($n = 11-20$) calculations were performed with both smaller and intermediate basis sets 6-31G* and 6-31+(p)G* respectively. All calculations have been carried out using the GAUSSIAN98 program package.[37]

III. Results

A. Choice of a Basis Set. Within the B3LYP approach, the lowest-energy geometries and corresponding equilibrium energies were determined for the anions C_n^- and the corresponding neutral molecules C_n using the basis set 6-31G* for the sizes $n = 2-20$. When compared to the known experimental values a root-mean-squares (rms) value of 0.54 eV was obtained for the AEA for linear chains. To improve these preliminary results we performed again the calculations using the larger basis set 6-31+G*, diffuse functions being essential for an accurate description of anions. As a matter of fact, for $n = 2-10$ the agreement between calculated and experimental values of the AEA was significantly improved when going from the 6-31G* basis set to the larger one 6-31+G*, the rms value being reduced to 0.34 eV. Unfortunately we did not succeed in treating the C_n^-/C_n clusters with $n > 10$ in that way due to linear dependence problems. A compromise solution was found by designing a somewhat smaller basis set by adding to the 6-31G* basis, one set of Gaussian p diffuse functions keeping on the exponent (0.0438) taken from the 6-31+G* basis. For linear chains, the overall agreement between the AEA values calculated with this basis set and the experimental ones, while less good (rms = 0.44 eV) than with the larger basis set 6-31+G*, remains better than with the 6-31G* set especially for larger sizes. For the monocyclic geometries the AEA values obtained with the 6-31+(p)G* basis set were seen to be quite close to the corresponding values obtained with the 6-31+G* one. Using this intermediate basis set 6-31+(p)G* we were able to treat all the sizes under consideration here ($n = 2-20$) within the same framework for both linear and monocyclic clusters. This intermediate basis set has been used in all further calculations.

B. Linear Chains. For each size we determine first the lowest-energy geometrical configurations for both the anions and the corresponding neutral clusters as well as the corresponding equilibrium total energies.

a. Bond Lengths. Data concerning geometries are not fully reported here; optimized bond lengths are available at the address: *http://lasim.univ-lyon1.fr/allouche/cn.html* for both species C_n^- and C_n. The differences between the alternate long/short bond lengths of the anions are quite large within ∼0.07 Å, they are somewhat smaller for the odd-numbered species C_{2n+1}^- ∼0.05 Å. The effect of taking off an electron decreases these differences to ∼0.025 Å, a value in agreement with the

TABLE 1: (Equilibrium) Total Energies (in Hartree) Calculated at the B3LYP/6-31+(p)G* Level and Symmetry for Linear Anions C_n^- and Neutral Species C_n Vertical Detachment Energy (VDE), Adiabatic Electron Affinity (AEA), and Experimental Electron Affinity (EA) (in eV) for linear carbon clusters C_n

n	$E(C_n^-)$		$E(C_n)^g$		$E(C_n)^h$	VDE	AEA	EA^f
2	−76.037470	$^2\Sigma^+_g$	−75.8853281	$^1\Sigma^+_g$	−75.8856899	4.14	4.13 2.82[a]	3.39
3	−114.124074	$^2\Pi_g$	−114.048723	$^1\Sigma^+_g$	−114.049443	2.05	2.03 1.53[a]	1.98
4	−152.227786	$^2\Pi_g$	−152.051219	$^3\Pi_g$	−152.052450	4.80	4.77 3.52[a]	3.882
5	−190.313596	$^2\Pi_u$	−190.208891	$^1\Sigma^+_g$	−190.209808	2.85	2.82 2.49[a]	2.839
6	−228.407364	$^2\Pi_u$	−228.259888	$^3\Pi_g$	−228.264616	4.01	3.88 3.87[a] 4.160[b]	4.185
7	−266.489454	$^2\Pi_g$	−266.366900	$^1\Sigma^+_g$	−266.368149	3.33	3.30 2.95[a] 3.265[c]	3.358
8	−304.579316	$^2\Pi_g$	−304.424664	$^3\Pi_g$	−304.429463	4.21	4.08 4.07[a] 4.348[d]	4.379
9	−342.660139	$^2\Pi_u$	−342.525803	$^1\Sigma^+_g$	−342.527239	3.66	3.62 3.14[a]	3.684
10	−380.747650	$^2\Pi_u$	−380.587814	$^3\Pi_g$	−380.592607	4.35	4.22 4.16[a]	4.46
11	−418.827464	$^2\Pi_g$	−418.684757	$^1\Sigma^+_g$	−418.686276	3.88 3.90[e])	3.84	3.8
12	−456.913913	$^2\Pi_g$	−456.750171	$^3\Pi_g$	−456.754863	4.46	4.33	4.47
13	−494.993210	$^2\Pi_u$	−494.844198	$^1\Sigma^+_g$	−494.845748	4.05	4.01	4.06
14	−533.078883	$^2\Pi_u$	−532.911951	$^3\Pi_g$	−532.916603	4.54	4.42	4.6
15	−571.157925	$^2\Pi_g$	−571.003972	$^1\Sigma^+_g$	−571.005514	4.19	4.15	4.2
16	−609.242608	$^2\Pi_g$	−609.073039	$^3\Pi_g$	−609.077669	4.61	4.49	4.66
17	−647.321815	$^2\Pi_u$	−647.163794	$^1\Sigma^+_g$	−647.165359	4.30	4.26	
18	−685.406012	$^2\Pi_u$	−685.234152	$^3\Pi_g$	−685.238655	4.68	4.55	
19	−723.485073	$^2\Pi_g$	−723.323719	$^1\Sigma^+_g$	−723.325264	4.39	4.35	
20	−761.569446	$^2\Pi_g$	−761.394291	$^3\Pi_g$	−	4.77	−	

[a] Ref 15. [b] Ref 29. [c] Ref 28. [d] Ref 30. [e] Ref 31. [f] Refs 15, 16. [g] Geometry of C_n^-. [h] Optimized geometry from C_n^-.

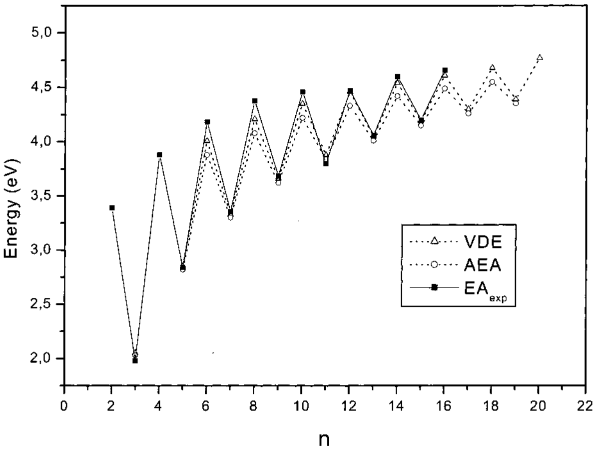

Figure 1. Electron affinities for linear carbon chains: calculated vertical (VDE) and adiabatic (AEA) values and experimental (EA) values.

cumulenic picture of neutral C_n clusters. Present values for the bond lengths of anions are compared with previous data, available to the best of our knowledge for $n = 2-10$. As could be expected they agree fairly well with results from B3LYP/6-31G* calculations,[25,26] our values being systematically larger by an average amount of 0.0018 Å (the discrepancy decreases when the size increases). Most differences are due to the larger basis set presently used. Present values are found to be closer to previous results from the higher-level large-scale coupled cluster calculations[27,29] (rms ∼ 0.006 Å) than to the values from the ROHF/DZP calculations[17](rms ∼ 0.018 Å).

b. Electron Affinities. For anions and corresponding neutral clusters total energies calculated at the B3LYP/6-31+(p)G* level are reported in Table 1, together with their differences defined as the AEA (geometries optimized for both anion and neutral) and the VDE (geometry optimized for C_n^- and subsequently used for C_n). The symmetry of the state under consideration is also reported in Table 1. Results for AEA and VDE are displayed comparatively to the experimental values of the electron affinity EA[15,16] on Figure 1. The experimentally observed even−odd alternation is well reproduced. As expected the electron affinity is seen to be larger for the C_{2n} clusters than for the C_{2n+1} ones due to the partially occupied π orbitals of linear even-numbered clusters. For sizes larger than 4 the overall agreement with experiment is better for VDE values than for AEA ones with rms(VDE) = 0.12 eV and rms(AEA) = 0.22 eV, a result which is consistent with the experimental derivation of the electron affinity from photoelectron spectra. The agreement is good especially for the C_{2n+1} ($n = 1-7$) clusters between the three values AEA, VDE, and EA with rms(VDE) = 0.046 eV and rms(AEA) = 0.053 eV. For the even-numbered species C_{2n} ($n = 3-8$) the overall agreement is significantly poorer with rms(VDE) = 0.12 eV and rms(AEA) = 0.25 eV. However the EA for the largest sizes ($n = 6-8$) are quite well reproduced by VDE values with rms = 0.045 eV.

For the two species C_2 and C_4 we did not succeed in obtaining satisfactory results within the present B3LYP/6-31+(p)G* approach. VDE and AEA values were found to be too large by amounts of 0.75 and 0.9 eV for C_2 and C_4, respectively. Using a larger basis set 6-31+G* led to a worse result for C_2 increasing the discrepancy to 0.93 eV contrarily to the case of C_4 for which a large improvement was obtained reducing the difference to 0.17 eV. It should be noted that for C_2, which may be considered as the most "electronically congested" molecule investigated here, the amount of "exact" HF-like exchange contained in the hybrid B3LYP functional may not be adequate, as was already pointed out in a systematic investigation of ionization potentials of unsaturated molecules.[38] As a matter of fact, using the BPW91 functional with the basis set 6-31+(p)G* led to an improvement of ~0.4 eV for the VDE value of C_2.

Previous calculated values of EA are also reported in Table 1. Watts and Bartlett (WB)[15] published calculated electron affinities for carbon-chain clusters with sizes from 2 to 10. They used coupled cluster theory including triple excitation with basis sets containing polarization and diffuse functions for geometries optimized through restricted open shell Hartree–Fock methods with a double-ζ plus polarization basis set (ROHF/DZP//DZP+sp UHF-CCSD(T)). Present results of AEA are larger than those from WB except for the sizes $n = 6,8,10$ for which both results are quite close. Our results are in better agreement with experimental data, except for the sizes $n = 2,4$ for which present values are not satisfactory owing to the limitations of our method mentioned above. For the clusters C_6, C_7, and C_8 results from large-scale open coupled cluster calculations are available.[29,28,30] Present VDE values are in better agreement with both these high level results and experimental data than are the AEA values. The agreement is quite good with a relative difference of ~4% for C_6, ~2% for C_7, and ~4% for C_8. Our value for VDE(C_{11}) agrees fairly well with the previous one from a B3LYP/6-31+G*[31] with a difference of 0.02 eV. To our knowledge no previous theoretical results have been published for the larger sizes $n = 12-20$.

c. Fragmentation Energies. To compare the energy necessary to remove an electron from an anion C_n^- with the energy required to remove a heavy fragment from C_n^-, fragmentation energies have been calculated following the scheme:

$$C_{n+m}^- \rightarrow C_n^- + C_m \text{ for various values of } m = 2, 3, 4, 5, \ldots 10$$

These fragmentation energies are estimated through:

$$E_{\text{frag}}^{\ m} = E(C_{n+m}^-) - E(C_n^-) - E(C_m)$$

The fragmentation energies are found to be higher for the loss of C_{2k} than for the loss of C_{2k+1}, the lowest ones corresponding to the loss of C_3. This is in agreement with the previously reported result[25] showing that aggregation reactions between carbon-chain anions C_n^- and neutral clusters C_m are more exothermic for $m = 2k$ than for $m = 2k + 1$. No alternation with respect to odd/even numbered anions is observed for the energies for the loss of C_{2k}, these energies decrease smoothly and regularly as the size increases. The situation is different for the loss of C_{2k+1} for which the fragmentation energy alternates, being higher for C_{2n}^- than for C_{2n+1}^-. This alternation is attenuated with the increase in the chain size but remains significant up to $n = 20$ for neutral fragments C_3 up to C_9. Present results agree reasonably with the trends previously pointed out for the fragmentation channels C_2 and C_3.[15]

In Figure 2 we have plotted the experimental EA as well as the calculated VDE values, in comparison with the estimated lowest fragmentation energies corresponding to the loss of C_3 and C_5. At every cluster size, the C_3 energy loss $E_{\text{frag}}^{\ 3}$, reported in Table 2, is found larger than 5.2 eV while EA is always smaller than 4.5 eV. In every case, the ejection of a heavy fragment from a linear carbon chain anion requires at least 0.7 eV more than the ejection of an electron. Provided that the excitation energy is properly chosen, the competition between detachment and fragmentation of carbon chain anions may be avoided in a photoexcitation experiment. Regarding the experiments described in ref 5, photon energy of 4.025 eV was used, ensuring that only photodetachment may occur for most species, fragmentation being not energetically allowed for carbon chain anions in that case.

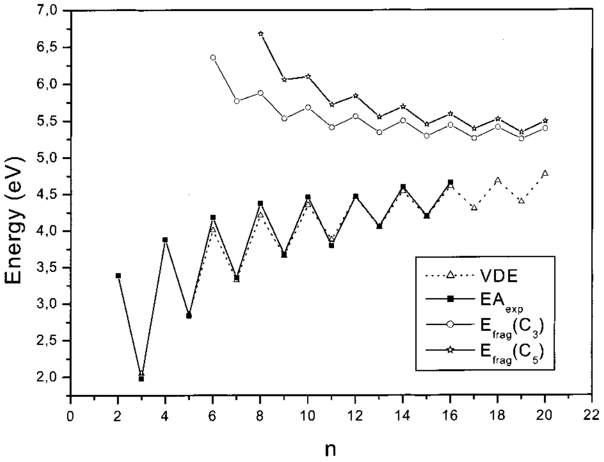

Figure 2. Fragmentation energies for the loss of C_3 and C_5 from linear anions C_n^- compared with electron affinities (calculated VDE and experimental EA).

C. Monocyclic Anions. *a. Geometries.* Stable geometries have been derived for the cyclic anion clusters C_n^- for $n = 4$, 6–20 and for the corresponding neutral species C_n starting from the optimized geometries of the C_n^-. Full data concerning optimized geometries for monocyclic anions are available at the address: *http://lasim.univ-lyon1.fr/allouche/cn.html.* Using the 6-31+(p)G* basis, we obtained stable geometries for the cyclic C_7^-, C_8^-, and C_9^- anions while no stable cyclic structures were found for these anions using the 6-31G* basis.[25] No stable geometry was obtained for the cyclic C_5^- from either basis. To our knowledge, calculated geometries have been reported only for the sizes $n = 4$, 6,[25] $n = 10$,[32] and $n = 11$.[31] For C_4^- and C_6^- we obtain ring structures with equal distances R_{CC} slightly smaller than the previous results from a B3LYP/6-31G* calculation[25] with differences $\Delta R_{CC}(C_4^-) = 0.004$ Å and $\Delta R_{CC}(C_6^-) = 0.019$ Å. For C_{10}^- the alternation between long/short bond lengths previously pointed out from DFT calculations using Becke's functional[39] and 6-311G(d) basis set[32] is reproduced, present values for R_{CC} being slightly larger by an averaged amount of 0.006 Å. For C_{11}^- present results for R_{CC} display an alternation between long/short values, they are in good agreement with previously published results from B3LYP/6-31G* calculations[31] with a rms of 0.002 Å.

b. Electron Affinities. Energies of the stable geometries obtained for C_n^- and C_n (minimization process initiated with the stable geometry of C_n^-), from which we derive the VDE values, are displayed in Table 3 as well as energies of C_n evaluated for the stable geometry of C_n^-, from which we derive the AEA values. VDE and AEA values are reported in Table 3 together with experimental values for the EA available for sizes from $n = 10$ to $n = 20$.[17] They are plotted together for comparison in Figure 3. Differences between calculated VDE and AEA are larger than for linear chains and they reach values larger than 0.4 eV for $n = 7$, 10, 14. The agreement with experiment is better for VDE than for AEA values which is not surprising owing to the experimental derivation of the electron affinity from photoelectron spectra. The experimental odd/even alternation is qualitatively reproduced for $n = 11-20$. When compared quantitatively with experimental EA the

TABLE 2: Calculated Fragmentation Energy (in eV) of Linear Chain Anions C_n^- for the Loss of C_3

n	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
$E_{\mathrm{frag}}{}^3$	6.36	5.77	5.88	5.53	5.68	5.41	5.56	5.34	5.50	5.29	5.44	5.26	5.41	5.25	5.39

TABLE 3: (Equilibrium) Total Energies (in Hartree) Calculated at the B3LYP/6-31+(p)G* Level and Symmetry for Monocyclic Anions C_n^- and Neutral Species C_n Vertical Detachment Energy (VDE), Adiabatic Electron Affinity (AEA) and Experimental Electron Affinity (EA) (in eV) for Monocyclic Carbon Clusters C_n

n	$E(C_n^-)$		$E(C_n)^g$		$E(C_n)^h$	VDE	AEA	EA^i
4	−152.164729	$^2B_{2g}$	−152.071906	^1A_g	−152.072902	2.53	2.50	
6	−228.350323	$^2A'$	−228.249027	$^1A'$	−228.256750	2.76	2.55	
7	−266.400125	$^2A_1$	−266.274707	$^1A_1$	−266.321074	3.41	2.15	
8	−304.474466	$^2B_{2u}$	−304.376639	$^1B_{1u}$	−304.379390	2.66	2.59	
9	−342.606873	$^2B_2$	−342.479484	$^1A_1$	−342.491570	3.47	3.14	
10	−380.733118	$^2A'$	−380.635223	$^1A'$	−380.671993	2.66	1.66	2.3
11	−418.800794	$^2A''$	−418.710519	$^1A'$	−418.713357	2.46 2.49^a	2.38 1.87^a	2.85
12	−456.886662	$^2A''$	−456.787576	$^1A'$	−456.794533	2.70	2.51	2.55
13	−495.002500	$^2A_1$	−494.872091	$^1A_1$	−494.877746	3.55	3.39	3.6
14	−533.106284	^2A_g	−533.009024	$^1A_1$	−533.024408	2.65	2.23	2.5
15	−571.176244	$^2B_1$	−571.068466	^1A_u	−571.070485	2.93	2.88	3.2
16	−609.258942	^2A_u	−609.148115	$^1A_1$	−609.156909	3.02	2.78	2.5
17	−647.364387	$^2B_2$	−647.220506	$^1A_1$	−647.235000	3.91	3.52	3.6
18	−685.462285	$^2A_1$	−685.357338	$^1A_1$	−685.366924	2.86	2.59	2.75
19	−723.533709	$^2A_2$	−723.413340	$^1A_1$	−723.414845	3.28	3.23	3.52
20	−761.612221	$^2A_1$	−761.502689	$^1A_1$	−761.508070	2.98	2.83	2.7

^{a} Ref 31. ^{g} Geometry of C_n^-. ^{h} Optimized geometry from C_n^-. ^{i} Ref 17.

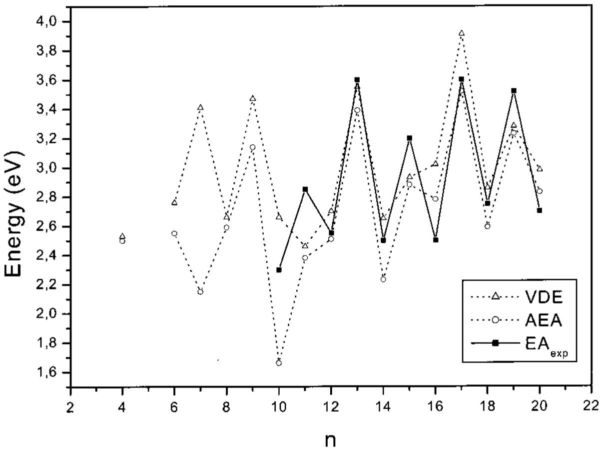

Figure 3. Electron affinities for monocyclic carbon clusters: calculated vertical (VDE) and adiabatic (AEA) values and experimental (EA) values.

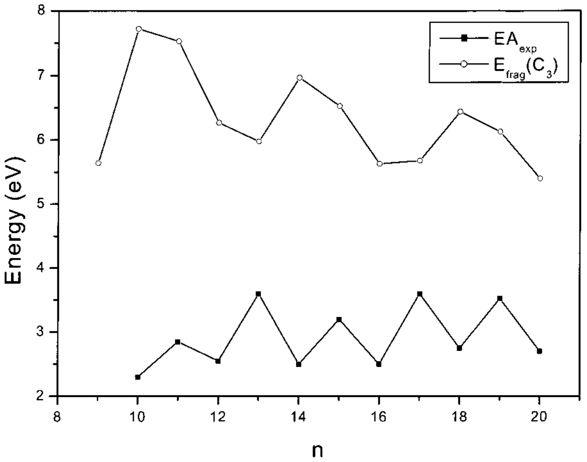

Figure 4. Fragmentation energies for the loss of C_3 from monocyclic anions C_n^- compared with experimental electron affinities EA.

following rms were obtained: 0.30 eV for VDE and 0.34 eV for AEA, with mean relative differences of ∼9% for VDE and of ∼10% for AEA. The relatively large discrepancies between experimental and theoretical values, together with the large difference between VDE and AEA, are obviously connected to the larger difference of the stable geometry of the neutral with respect to the anion in the monocyclic rings as compared to the linear chains. This renders the determination of experimental electron affinities more inaccurate for the ring isomers.

To our knowledge, calculated values of the electron affinity of monocyclic carbon clusters were published only in the case of C_{11}. The literature values obtained from B3LYP/6-31G* and 6-31+G* calculations[31] are AEA = 1.87 eV(6-31G*) in poorer agreement with experiment (2.85 eV) than our result (2.38 eV) and VDE = 2.49 eV(6-31+G*) in good agreement with our result (2.46 eV). Differences are mainly due to the different basis sets used.

From the calculated energy values of the monocyclic carbon anions and of the linear carbon chains we roughly estimated fragmentation energies (fragmentation channels corresponding to the ejection of small linear neutral chains are open at a noticeable lower energy), following the scheme:

$$E_{\mathrm{frag}}{}^m = E[C_{n+m}^-\ (\mathrm{ring})] - E[C_n^-\ (\mathrm{ring})] - E[C_m\ (\mathrm{chain})]$$

Similarly to the case of linear chains, the lowest fragmentation energy was found for the loss of the chain C_3, it remains larger than 5.5 eV, a value higher than the experimental electron affinity by an amount of ∼2 eV. This is illustrated in Figure 4. From this point of view, the competition between fragmentation and detachment is even more favorable to the detachment process in monocyclic rings as compared to linear chains. Under the experimental conditions of ref 5, the effect of fragmentation may thus entirely be ruled out both for linear chains and monocyclic rings.

D. Relative Stability of Small Chain and Monocyclic-Carbon Cluster Anions. From our calculated data relevant to anions, we evaluated the relative stability

$$\Delta E_n = E_n(\mathrm{monocyclic}) - E_n(\mathrm{linear})\ \text{for}\ n = 4, 6{-}20$$

Values of ΔE_n are reported in Table 4 and displayed on Figure 5. Chains are found to be more stable than monocyclic forms

TABLE 4: Energy Difference $\Delta E = E(\text{monocyclic } C_n^-) - E(\text{linear } C_n^-)$ (in eV)

n	ΔE
4	1.72
6	1.55
7	2.43 2.11[a]
8	2.85
9	1.45
10	0.40
11	0.73
12	0.74
13	−0.25
14	−0.75
15	−0.50
16	−0.44
17	−1.16
18	−1.53
19	−1.32
20	−1.16

[a] Ref 40.

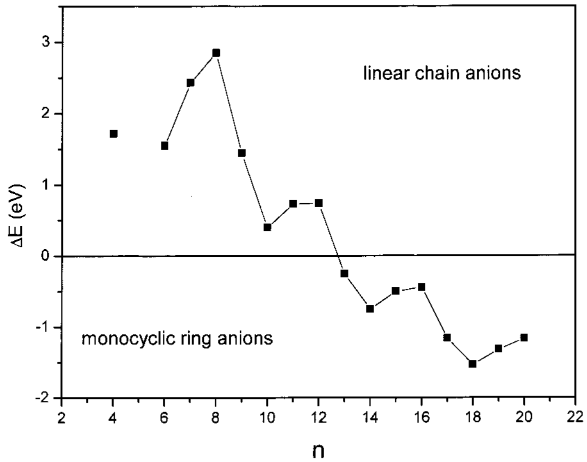

Figure 5. Relative stability of monocyclic vs linear isomers of C_n^-: energy differences $\Delta E = E(\text{monocyclic } C_n^-) - E(\text{linear}C_n^-)$.

up to $n = 12$, the reverse situation is observed for $n = 13-20$. Roughly stated, for $n < 10$, $\Delta E_n > 1$ eV and a predominance of linear configurations may be assumed; for $10 \leq n \leq 16$, $|\Delta E_n| < 0.75$ eV with positive ($n = 10-12$) and negative ($n = 13-16$) values, consistent with a competition between linear and monocyclic forms; finally for $17 \leq n \leq 20$, ΔE_n is always negative with $|\Delta E_n| > 1$ eV which is compatible with a relative predominance of monocyclic forms in that size range.[40] For neutral clusters ($n \geq 6$) the transition from a linear chain to a monocyclic ring is found to take place for $n = 10$, in agreement with mass spectrometry observations. Neutral carbon clusters with size $n \geq 10$ are more stable in the monocyclic ring structure.[19,41] Finally, clear indication of a 4-fold periodicity related to the particularly high stability of neutral C_n clusters with $n = 4N + 2$ as provided by semiempirical calculations[42] was visible for $N = 2, 3, 4$.

IV. Conclusion

With the aim of investigating the relative stability of anions C_n^- (linear chains and monocyclic structures) with respect to electron emission or fragmentation, lowest-energy geometrical configurations have been derived for carbon cluster anions of small size ($n = 2-20$) in a B3LYP/6-31+(p)G* approach for both linear and monocyclic structures. From the equilibrium energies vertical detachment energies VDE as well as adiabatic electron affinities AEA have been calculated and fragmentation energies have been derived.

By comparison to experimental values of the electron affinity EA, the following conclusions can be made.

- For linear anion chains, except for C_2 and C_4, the present approach describes rather accurately experimental data, especially for the odd members of the C_n^- series. The lowest fragmentation energy which corresponds to the loss of C_3 remains larger than the electron affinity for all sizes considered.
- For monocyclic anion rings, the present approach while providing poorer results than for linear chains, reproduces the trends of experimental data with a mean relative difference of ~10%. The estimated lowest fragmentation energy which corresponds to the loss of C_3 is found to be by far larger than the electron affinity.
- The calculated relative stability of linear and monocyclic structures is consistent with some predominance of linear anion chains for sizes smaller than 12 and of monocyclic anion rings for sizes larger than 17 as well as with the well-known predominance of monocyclic neutral structures from C_{10} onward.

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