Disintegration of finite carbon chains in electric fields

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Abstract

We use the density functional formalism to investigate the stability and disintegration of finite carbon chains in electric fields. Carbon chains are very stable, since they require energies in excess of 5 eV to fragment. Only in strong electric fields exceeding 4 V/Å, we find neutral chains to disintegrate, preferably by field emitting a monomer from the negatively polarized end. This critical field for fragmentation is found to decrease in chains that carry a net negative charge. We discuss the impact of these results on the evolution of atomic structures at the tip of carbon nanotubes grown in the carbon arc.

Carbon nanotubes [1-4], consisting of multiply nested graphene cylinders, up to 100 μm long and with a typical diameter of 10 nm, have been produced in macroscopic quantities [2] on a graphite cathode in a carbon arc. Recent reports of strong field electron emission from individually mounted carbon nanotubes [5] have suggested an exciting application of such systems in ultrafine flat panel displays [6,7]. The field emission current has been observed to depend strongly not only on the external electric field, but also a laser beam that would assist in annealing the tip.

These results have been interpreted in terms of the structure at the tube end, corresponding to either an open nanotube with an exposed "sharp" edge, or a nanotube terminated by a perfect dome. Very large electric currents, in the order of microamperes, that fluctuated in discrete steps, were associated with linear carbon chains attached to the tube end. Such chains could unravel, has been claimed, from the edges of individual chiral walls of a tube, being taught by the external electric field [5]. The large field emission currents could then be explained by a local enhancement of the elec-

tric field near sharp structures. Correspondingly, the observed reproducible quenching of the field emission current in a laser beam would follow from these sharp structures being extinguished in a laser beam. For this mechanism to be true, monatomic carbon chains have to be extremely stable in external fields.

Very little has been known so far about the stability of carbon chains in an electric field. In the following, we address this issue using density functional theory within the local density approximation (LDA) and compare the results to those obtained using the generalized gradient approximation (GGA). We find that thermal disintegration is very unlikely as it requires a dissociation energy of about 5 eV. We also find that excess negative charge causes a net stabilization of the chain, and that the optimum charge which minimizes the total energy increases slightly with increasing electric field. Since the field electron emission from a negatively charged chain is inverse to adding an extra electron to the chain, the electron affinity is a more appropriate to describe this process than the ionization potential. The preferential mechanism of field-

Table 1
Binding energy of unsaturated carbon chains with respect to isolated atoms. The values in parentheses refer to ring structures

Chain	E_b (eV/atom) (present LDA)	E_b (eV/atom) (present GGA)	E_b (eV/atom) (Hartree–Fock)[a]	E_b (eV/atom) (expt.)[b]
C_2	−3.4	−3.4	−2.8	−3.1 ± 0.05
C_3	−5.4	−5.0	−4.23	−4.63 ± 0.07
C_4	−5.5	−5.2	−4.33	−4.75 ± 0.1
C_5	−6.2	−5.7	−4.78	−5.3 ± 0.1
C_6	−6.3(−6.5)	−5.8	−4.81(−4.91)	
C_7	−6.6	−6.0	−5.03	

[a] Ref. [12].   [b] Refs. [14–16].

induced fragmentation consists of a field ion emission from the chain end carrying a net negative charge. We also find that negatively charged chains fragment more easily in an external field.

We use the local density functional formalism as implemented in the DMOL [1] [8] cluster code to describe the energetics of finite systems at $T = 0$. The LDA calculations use the von Barth and Hedin parameterization [9] of the exchange-correlation energy, whereas the GGA is based on the Becke–Perdew gradient correction scheme [10,11]. The all-electron Kohn–Sham wavefunctions of the chain are expanded in a local atomic orbital basis. In the double-numerical basis set [8], the C2s and C2p orbitals are represented by two wave functions each, and a 3d type wave function on each carbon atom is used to describe polarization. Our GGA calculations use a larger basis set, composed of four s-type, four p-type, and two d-type numerical functions. We do not make use of the frozen core approximation. Our energies are converged to 1.0×10^{-6} Ha. Test calculations using the local spin density approximation (LSDA) give essentially the same results as using LDA.

In order to describe the physical behavior of a finite chain attached to a large carbon nanotube within a cluster calculation, we saturate the dangling bonds at one end by two H atoms which represent the proper termination in a graphitic network. This is not likely to affect the chain except for the C–C bond closest to the saturated chain end. We calculate the dissociation energy $D(n, m)$ of a mother chain C_nH_2 into two daughter fragments as

$$C_nH_2 \xrightarrow{D(n,m)} C_{n-m}H_2 + C_m . \tag{1}$$
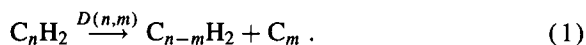
In the present study we will concentrate on the dissociation of C_nH_2 chains with $3 \leq n \leq 7$ into daughter fragments C_m containing $1 \leq m \leq 5$ atoms. The dissociation energy $D(n, m)$ is calculated using the total energy difference between the relaxed mother and daughter chains.

We find the carbon-hydrogen distance $d_{C-H} \approx 1.1$ Å in most chains. The H–C–H angle $\vartheta = 116.5°$ in odd-numbered chains is only slightly smaller than the value $\vartheta = 117.5°$ found in even-numbered chains. We do observe a C–C bond length alternation especially in odd-numbered chains and, to a lesser degree, in even-numbered chains. The typical alternation is between 1.268 Å and 1.301 Å, even though these values change slightly with the system size. Another interesting fact to note is that the bond length alternation becomes more pronounced in charged chains such as the negatively charged C_5H_2, where the bond lengths alternate between 1.26 Å and 1.33 Å. This suggests that the dominant electronic structure should bear resemblance with the bond-alternate polyyne isomer ($\cdots$–C $\equiv$ C–C $\equiv$ C–$\cdots$) in odd-numbered and charged chains, and the cumulenic isomer ($\cdots$ = C = C = C = $\cdots$) in even-numbered chains. The difference between the ground state electronic structure in even- and odd-numbered chains, reflecting the different π bonding, may play a role in the transport of electrons which originate from the chain anchor point in a negatively charged nanotube.

Table 1 shows the binding energy (or negative atomization energy) of free C_n chains and rings with no hydrogen attached. The increasing absolute value of the binding energy per atom indicates growing

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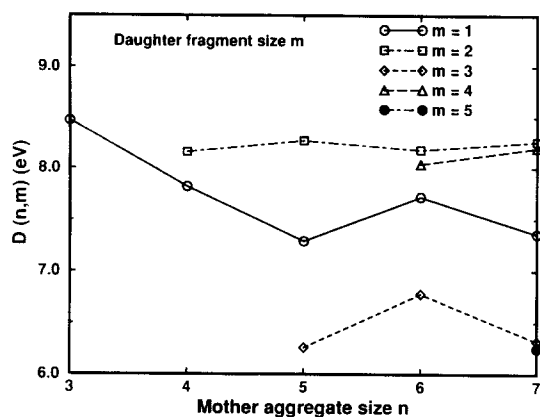[1] DMOL is a registered software product of Biosym Technologies.

Fig. 1. Dissociation energy $D(n,m)$ of neutral C_nH_2 chains into $C_{n-m}H_2$ and C_m fragments in zero field.

Fig. 2. Binding energy (per carbon atom) of C_4H_2, C_5H_2, and C_6H_2 chains as a function of a net excess charge q, in zero field.

stability with increasing cluster size. The data presented in Table 1 confirm the well-established trend that atomic aggregates are overbound in LDA, significantly less overbound in GGA, and underbound in Hartree-Fock calculations [12] when compared to experimental data, the discrepancy being smaller in smaller systems. Our LDA results suggest the C_6 ring with C_{6h} symmetry to be the most stable isomer which is energetically preferred to the chain by 0.2 eV/atom. (The corresponding Hartree-Fock calculation [12] suggests the ground state of C_6 to be a ring with D_{3h} symmetry that is energetically preferred by 0.1 eV/atom with respect to the chain.)

Fig. 1 illustrates the energetics of the fragmentation process of the C_nH_2 chain into daughter $C_{n-m}H_2$ and C_m chains. We find the dissociation energy $D(n,m)$ to exceed 6 eV for all the systems we considered[2], suggesting that disintegration of finite chains in absence of external fields should be observable only at very high temperatures. Our results suggest that it is easier by up to 2 eV to detach an odd-numbered fragment than an even-numbered fragment from a given chain. This is a consequence of odd-numbered fragments being relatively more stable, as seen in Table 1.

Next we focus on the disintegration of carbon chains, that are in contact to a negatively charged carbon nanotube, in the electric field of an arc. The

necessary prerequisite for such a study is to determine the most likely charge to be found on a given chain. In Fig. 2 we present our results for the binding energy of chains as a function of their net charge in field free space. The binding energy of a charged molecule in an electric field will depend on the point of origin of the electric field. For a carbon wire unraveling from a carbon nanotube one would expect the point of contact with the tube to be at zero potential [13]. Let us consider the electric field to be in the x direction. To avoid any ambiguity regarding the origin of the electrostatic field, we positioned all molecules so that that $\int d^3r\,\rho(r)x = 0$, where $\rho(r)$ is the charge density of the molecule in the field. No net electrostatic energy will then be associated with the system. The charged chains are optimized by keeping the terminating hydrogen atoms and the two carbon atoms closest to them fixed in the neutral system configuration. Our results suggest that chains with $4 \leq n \leq 6$ carbon atoms prefer to carry extra negative charge in zero field, which reflects the large electronegativity of carbon atoms. The optimum charge is found to be $q \approx -1$ e and to slightly increase with increasing chain length.

Energy differences between differently charged chains yield the ionization potential and the electron affinity of the chain, which we give in Table 2. We find the ionization potential to decrease with increasing chain length towards that of C_{60}, and to gradually converge to the bulk value that may resemble the work function of graphite. The Hartree-Fock results for hydrogen-free chains are in rough agreement with our values, but seem to overestimate the ionization

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[2] We note that our dissociation energy values, which are based on LDA total energy differences, could be overestimated by < 1 eV in longer chains, as suggested in Table 1. A more cautious lower bound on the dissociation energy is therefore ≈ 5 eV.
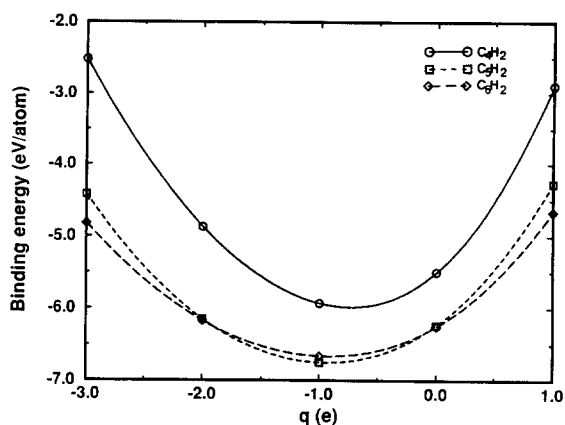
Table 2
Ionization potentials I and electron affinities A for carbon systems

System	IP (eV) (present LDA)	IP (eV) (Hartree-Fock)[a]	A (eV) (present LDA)
C_3H_2	11.0		
C_3		11.4	
C_4H_2	10.4		1.72
C_4		10.5	
C_5H_2	9.8		2.59
C_5		10.7	
C_6H_2	9.5		2.47
C_6		9.8	
C_7H_2	9.1		
C_7		10.0	
C(atom)	11.26[b]		
C_{60}	7.54[c]		2.74[d]
Graphite	5.0[b]		

[a] Ref. [12].
[b] Experimental data from Ref. [17].
[c] Experimental data from Ref. [18].
[d] Experimental data from Ref. [19].

potential and do not show a clear trend with increasing chain length. These values are relatively large so that field emission from neutral finite length chains appears to be very unlikely. This changes in the case of negatively charged chains, where the final state is charge neutral and the energy needed to remove an extra electron is equal to its electron affinity. Our results in Table 2 show the electron affinities to be much smaller than the ionization potentials, thus facilitating field electron emission from negatively charged chains. We also observe the electron affinity to increase with increasing chain length towards the electron affinity of C_{60}, and eventually approaching the bulk value that may resemble the work function of graphite. As we will discuss below, the electron affinity increases with increasing electric field due to polarization.

Whereas the equilibrium excess charge was found to depend only slightly on the chain length, its dependence on the external electric field is much more pronounced. In Fig. 3 we show results for the binding energy of a C_6H_2 chain as a function of the electric field for different excess charges. In all our calculations we assume the chain to be aligned with the field, its hydrogen end pointing in the field direction. The chain is equilibrated in different fields by keeping the terminating hydrogen atoms and the two carbon atoms
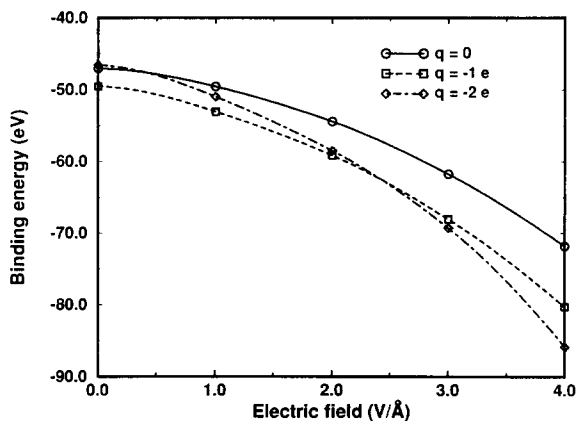

Fig. 3. Binding energy of the C_6H_2 chain as a function of the external electric field, for different negative excess charges q. The chain is assumed to be aligned with the field, its hydrogen end pointing in the field direction.

Table 3
The ionization potentials $I(C_6H_2^-)$ and $I(C_6H_2^{2-})$ as a function of the external electric field (see footnote 3). We consider the chain to be aligned with the field, its hydrogen end pointing in the field direction

Field (V/Å)	$I(C_6H_2^-)$	$I(C_6H_2^{2-})$
0.0	2.47	-2.92
1.0	3.49	-2.07
2.0	4.72	-0.66
3.0	6.31	1.24
4.0	8.44	4.59

closest to them fixed in the zero field configuration. Independent of its net charge, the chain gains polarization energy in the external field. Our results show that indeed the energy gain scales approximately with the square of the applied field, as expected for a constant polarizability (which does, however, depend on the net charge). In a low electric field, the chain prefers to hold one electron, in agreement with the zero field results discussed above. The larger polarizability of a negatively charged chain causes a crossover in the binding energy curves, indicating that a chain carrying two electrons is most stable in fields exceeding 2.2 V/Å. The next potential crossover to a chain carrying three electrons in a still higher field does not occur, since under these conditions the chain disintegrates, as we discuss below.

Table 3 shows the ionization potentials $I(C_6H_2^-)$ and $I(C_6H_2^{2-})$, giving the energy needed to remove
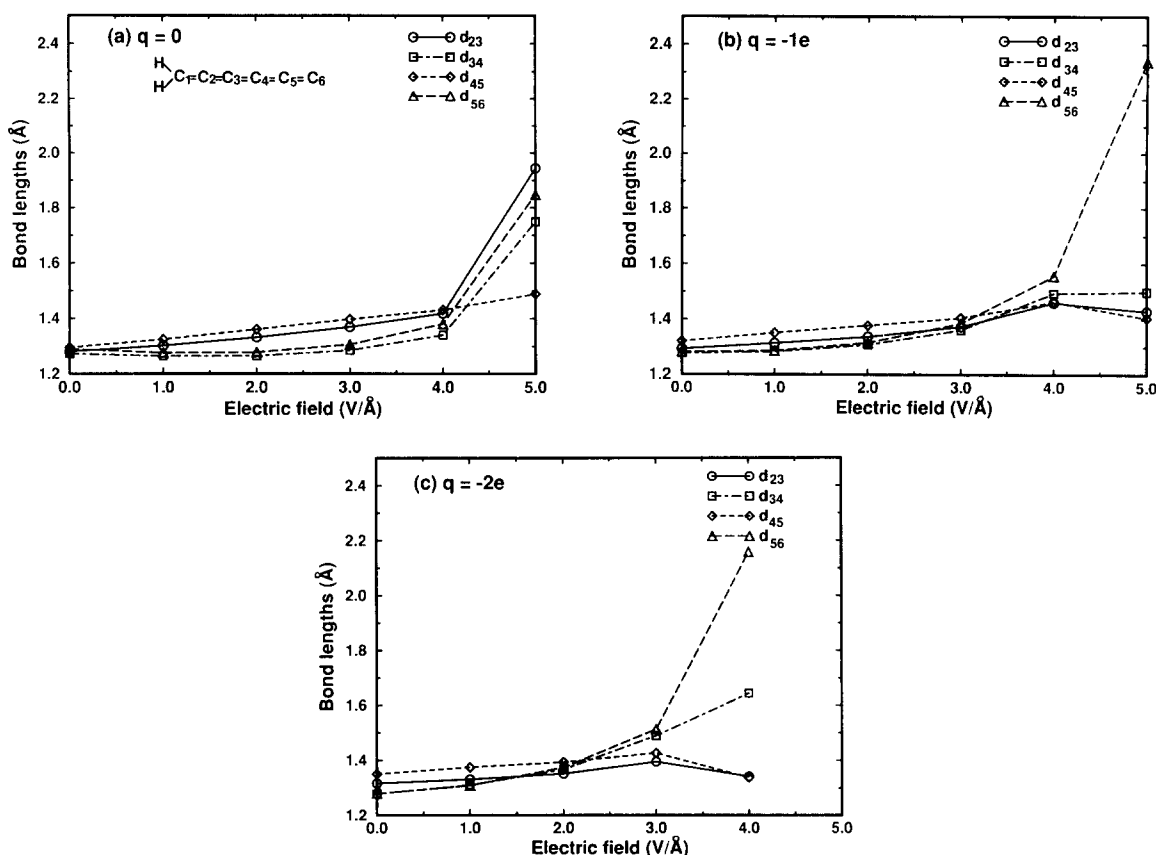
Fig. 4. Interatomic bond lengths d_{ij} in the C_6H_2 chain as a function of the external electric field, for a net charge on the chain (a) $q = 0$, (b) $q = -1$ e, and (c) $q = -2$ e. The chain is assumed to be aligned with the field, its hydrogen end pointing in the field direction.

an electron from a charged system in nonzero external field [3]. These quantities are equal to the electron affinities $A(C_6H_2)$ and $A(C_6H_2^-)$, respectively, and are based on our equilibrium structures presented in Fig. 3. The fact that $I(C_6H_2^-) > 0$ for all field values reflects the above discussed fact that a C_6H_2 chain prefers to carry at least one extra electron. Our data also indicate that $I(C_6H_2^{2-}) > 0$ only for $F > 2$ V/Å, reflecting the preference for a double negatively charged state in these higher fields. The efficiency of the field emission process will be governed by the ionization from the

charged ground state. We find the ionization potential first to increase, and the field emission to decrease, with increasing field in the range 0 V/Å$< F < 2$ V/Å. For $F > 3$ V/Å, the chain gains an extra electron in the ground state, causing the ionization potential to first drop abruptly and to increase gradually with further increasing field.

Fig. 4 shows the effect of an external electric field on the individual bond lengths in a C_6H_2 chain as a function of the net charge. The labeling of the carbon sites is explained in the inset. As shown in Fig. 4(a), we find the bond lengths in a neutral chain to increase gradually up to a field of 4 V/Å. In fields exceeding 4 V/Å, the C_2–C_3, C_3–C_4, and C_5–C_6 bonds are broken. With increasing electric field, an increasingly negative charge is accumulated at the C_6 site, filling the antibonding orbitals of the C_5–C_6 bond. At the point of fracture, we find a net charge $q(C_6) = -2.04$ e. This

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[3] The ionization potential and electron affinity of a molecule in a uniform external field are ill-defined quantities since the reference energy of the electron will depend on its final position. In practice this problem never arises since the electric field is only locally homogeneous and the electrostatic potential zero far away from the molecule. The calculated ionization potential (electron affinity) values are based on the assumption that the electron has been moved to (from) a position of zero potential energy.

charge is supplied by depleting the bonding orbitals at the hydrogen end, leading to a net Coulomb repulsion and eventual fracture of the C_2–C_3 and C_3–C_4 bonds.

Fig. 4(b) shows that the fragmentation behavior is very different in a chain carrying an extra electron. The bonds stretch upon charging even in zero field, due to the filling of antibonding orbitals and incomplete screening of the internuclear repulsion. As in the neutral chain, all bond lengths increase as the field increases up to a critical value that is somewhat lower than in the neutral system. The excess charge preferentially accumulates at the hydrogen free end of the chain. It fills the antibonding orbitals in the C_5–C_6 bond which eventually breaks. The C_6 atom carries away a charge of $q = -2.9\ e$, reducing the net charge on the remaining fragment[4]. As shown in Fig. 4(b), this shortens the bond lengths in the daughter fragment and hence stabilizes it.

In a $C_6H_2^{2-}$ chain carrying two extra electrons, the critical field for fragmentation decreases significantly to ≈ 3 V/Å, as shown in Fig. 4(c). As in the chain carrying only one extra electron, the C_6 is detached first. At the same time, however, the C_3–C_4 bond breaks as well, yielding C, C_2 and C_3H_2 as fragments. Even though C_3H_2 is also the preferred daughter fragment of neutral C_6H_2 in zero field, as shown in Fig. 1, the thermal and the field-induced fragmentation mechanisms are very different.

In conclusion, we have studied the disintegration of finite carbon chains in an external electric field. We found carbon chains to be extremely stable, as they require a minimum of 5 eV to dissociate in zero field. Chains are likely to carry a net negative charge which increases their polarizability in electric fields. We find the onset of field-induced fragmentation to occur in very high fields of 3 V/Å, the detailed fragmentation mechanism depending sensitively on the net charge of the chain. As mentioned earlier, our results are obtained for systems at zero temperature. We expect therefore that in hot clusters thermally activated fragmentation may occur at lower fields.

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[4] The usual interpretation of fractional charges on atomic aggregates is based on a large ensemble of identical systems. Even though the *expectation value* of the aggregate charge in a composite system may be noninteger, the charge on each individual fragment is, of course, quantized.

References

[1] S. Iijima, Nature 354 (1991) 56.

[2] T.W. Ebbesen and P.M. Ajayan, Nature 358 (1992) 220;

[3] T.W. Ebbesen, Ann. Rev. Mater. Sci. 24 (1994) 235.

[4] T.W. Ebbesen, P.M. Ajayan, H. Hura and T. Tanigaki, Nature 367 (1994) 519.

[5] A.G. Rinzler, J.H. Hafner, P. Nikolaev, L. Lou, S.G. Kim, D. Tománek, P. Nordlander, D. T. Colbert and R.E. Smalley, Science 269 (1995) 1550.

[6] Walt A. de Heer, W.S. Bacsa, A. Châtelain, T. Gerfin, R. Humphrey-Baker, L. Forro and D. Ugarte, Science 268 (1995) 845.

[7] Walt A. de Heer, A. Châtelain and D. Ugarte, Science 270 (1995) 1179.

[8] B. Delley, J. Chem. Phys. 92 (1990) 508.

[9] U. von Barth and L. Hedin, J. Phys. C 5 (1972) 1629.

[10] A.D. Becke, Phys. Rev. A 38 (1988) 3089.

[11] J.P. Perdew, Phys. Rev. B 33 (1986) 8822.

[12] K. Raghavachari and J.S. Binkley, J. Chem. Phys. 87 (1987) 2191.

[13] L. Lou, P. Nordlander, and R.E. Smalley, Phys. Rev. B 52 (1995) 1429.

[14] J. Drowart, R.P. Burns, G. DeMaria, and M.G. Inghram, J. Chem. Phys. 31 (1959) 1131.

[15] K.P. Huber and G. Herzberg, Constants of Diatomic Molecules (Van Nostrand Reinhold, New York, 1979).

[16] D.R. Stull and H. Prophet, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand. 37 (1971).

[17] CRC Handbook of Chemistry and Physics, 62th Ed. (CRC Press 1982).

[18] I.V. Hertel, H. Steger, J. de Vries, B. Weisser, C. Menzel, B. Kamke and W. Kamke, Phys. Rev. Lett. 68 (1992) 784.

[19] S.H. Yang, C.L. Pettiette, J. Conceico, O. Chesnovsky and R.E. Smalley, Chem. Phys. Lett. 139 (1987) 233.