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## A correlation study of large neutral and singly ionized carbon clusters

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**Abstract.** Electronic structures, binding energies and fragmentation energies have been calculated for neutral and positively charged carbon clusters containing up to twenty-eight atoms. The effects of electron correlation have been studied by invoking the concepts of many body perturbation theory. Magic numbers have been identified and different possible energy channels have been calculated and compared with other theoretical and experimental results.

### 1. Introduction

We have witnessed in recent years, a widespread interest in the theoretical and experimental investigations of atomic and molecular clusters (Jena *et al* 1987, Sugano *et al* 1987, Benedek *et al* 1988, Chapon *et al* 1989, Averback *et al* 1991). Of these systems, carbon clusters are of particular interest because of their importance in diverse processes such as catalysis, interstellar capacity and superconductivity. A summary of the available theoretical and experimental results on neutral and ionized carbon clusters, has been presented earlier by Ray (1987) and Islam and Ray (1989). A particular form of carbon, namely  $C_{60}$ , has recently received widespread attention from the scientific community (Kroto *et al* 1985, Curl and Smalley 1988, Kroto 1988, Saito and Oshiyama 1991). However, theoretical studies of the evolution of electronic structure and associated properties as a carbon cluster grows in size are indeed rare. In this paper, we extend our previous work to study large neutral and positively charged carbon clusters and include the effects of electron correlation at the second-order many body perturbation theory level. We first present the latest available results.

Lifshitz *et al* (1989) have produced  $C_n^+$  cluster ions by dissociative electron impact ionization of overcrowded perchloro hydrocarbons and studied these ions using a high-resolution reverse geometry mass spectrometer. Seifert *et al* (1988) have found the abundance distribution of positively charged carbon cluster ions from a laser-induced plasma. Creasy (1990) has used simple kinetic mechanisms to model the features of ionic carbon clusters that have been observed by laser vaporization mass spectrometry. A very comprehensive and up-to-date review has been presented by Weltner and Van Zee (1989).

## 2. Theory

The unrestricted Hartree-Fock (UHF) theory and the many body perturbation theory (MBPT) as used in this work, are well documented in the literature (Szabo and Ostlund 1982, Hehre *et al* 1986). Here, we present a basic equation to define some terms. In MBPT, the energy is given by the linked-diagram expansion (Bartlett and Silver 1974, Bartlett 1981, Goldstone 1957, Lowdin 1965):

$$\Delta E = E - E_0 = E_1 + E_{\text{corr}} = \sum_{n=0}^{\infty} \langle \Phi_0 | [V(E_0 - H_0)^{-1} V]^n | \Phi_0 \rangle_L \quad (1)$$

where  $\Phi_0$  is the single-determinant self-consistent-field (SCF) wavefunction,  $H_0$  is the sum of one-electron Fock operators,  $E_0$  is the sum of SCF orbital energies,  $V = H - H_0$  is the perturbation, where  $H$  is the usual electrostatic Hamiltonian. We have chosen  $\Phi_0$  to be the UHF wavefunction. The subscript L indicates the limitation to linked diagrams. Though one can include various categories of infinite-order summations from (1), the method is usually limited by termination at some order of perturbation theory. In this work, as implied before, we have carried out complete second-order (MP2) calculations.

## 3. Computational results and discussions

As mentioned before, our calculations are based on accurate all-electron *ab initio* molecular orbital techniques, specifically Hartree-Fock theory followed by detailed correlation investigations at the second-order many body perturbation theory level. One of the primary considerations involved in these calculations is determination of the type of basis set to be used. Gaussian-type basis sets used in *ab initio* molecular orbital computations usually involve some compromise between computational cost and accuracy. A considerable increase in computational efficiency can be achieved if the exponents of the Gaussian primitives are shared between different basis functions. At the split valence level, this is usually exploited by sharing primitive exponents between s and p functions for the valence functions. Accordingly, for carbon, we have used here the so-called 6-21G basis set (Hehre *et al* 1986), since the clusters involved are fairly large. The basis consists of an s-type inner-shell function with six Gaussians, an inner set of valence s- and p-type functions with two Gaussians and another outer sp set with one Gaussian. The computations were carried out on a Cray Y-MP/864 computer, using the program Gaussian 88, written by Frish *et al* (1988). The structures considered for  $C_n$  clusters are linear chains and cyclic rings in the shape of regular polygons. We chose these structures because covalently bonded species tend to minimize the number of dangling bonds. It is also known that polycyclic fragments of a graphite lattice are very unstable relative to simple polygons with the same number of atoms. Also, it is widely believed that for fairly large  $n$  ( $n \leq 40$ ),  $C_n$  clusters tend to have a ring structure (Ray 1987, Islam and Ray 1989, and references therein).

The total energies for the  $C_n$  clusters are reported in tables 1 and 2 and figure 1 indicates the binding energies per atom for the most stable carbon clusters as a function of cluster size. All the calculations were performed at a fixed bond length

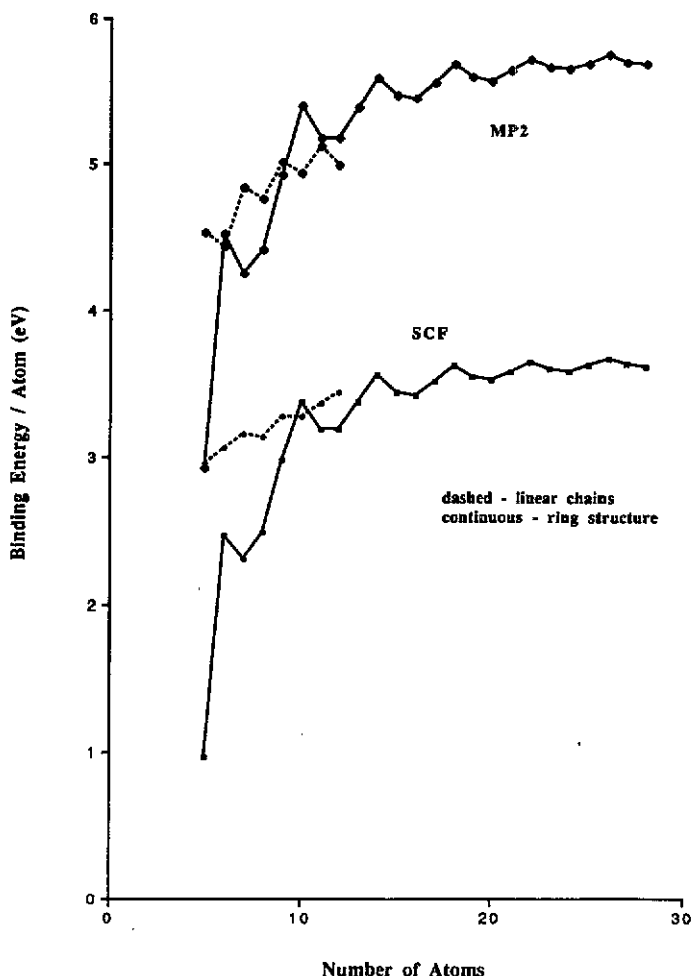


Figure 1. Binding energy/atom (eV) versus number of atoms for  $C_n$  clusters.

of 1.28 Å since the clusters involved are rather large and the binding energies have been calculated from:

$$E_b/n = (nE_1 - E_n)/n. \quad (2)$$

We first note that, based on our calculations, ring structures are generally preferred over linear chains for  $n \geq 10$ , again confirming the predictions of the semi-empirical calculations of Pitzer and Clementi (1959) in that a transition to neutral  $\pi$ -bonded rings should occur around  $C_{10}$ . For the sake of brevity, only the results up to  $n = 12$  are given for linear structure though the trends in stability are obvious. However,  $C_6$  is found to have a ring structure, in accordance with the calculations of Raghavachari and Binkley (1987) for small carbon clusters and the fact that graphite is planar and hexagonal.  $C_5$ – $C_{10}$  clusters are found to have singlet ground states while  $C_{11}$ – $C_{28}$  clusters have alternating triplet and singlet ground states. In particular, clusters with odd numbers of atoms have triplet ground states while clusters with an even number of atoms have singlet states. As far as the binding energy is

**Table 1.** Ground state total energies (au) for linear  $C_n$  clusters.

<i>n</i>	Singlet		Triplet	
	SCF Total energy (au)	MP2 Total energy (au)	SCF Total energy (au)	MP2 Total energy (au)
5	-188.838	-189.248	-188.728	-189.158
6	-226.594	-227.074	-226.629	-227.074
7	-264.426	-265.022	-264.467	-264.890
8	-302.197	-302.859	-302.229	-302.848
9	-340.016	-340.800	-340.094	-340.645
10	-377.796	-378.642	-377.828	-378.620
11	-415.606	-416.580	-415.635	-416.438
12	-453.018	-454.124	-453.426	-454.391

**Table 2.** Ground state total energies (au) for cyclic  $C_n$  clusters.

<i>n</i>	Singlet		Triplet	
	SCF Total energy (au)	MP2 Total energy (au)	SCF Total energy (au)	MP2 Total energy (au)
5	-188.412	-188.916	-188.474	-188.950
6	-226.496	-227.093	-226.417	-226.992
7	-264.181	-264.841	-264.205	-264.871
8	-302.003	-302.759	-302.112	-302.716
9	-339.894	-340.737	-339.914	-340.775
10	-377.830	-378.807	-377.734	-378.589
11	-415.535	-416.562	-415.541	-416.603
12	-453.315	-454.474	-453.427	-454.378
13	-491.177	-492.389	-491.178	-492.443
14	-529.057	-530.435	-529.014	-530.209
15	-566.793	-568.183	-566.784	-568.253
16	-604.556	-606.124	-604.533	-606.053
17	-642.414	-643.983	-642.400	-644.072
18	-680.260	-682.043	-680.311	-681.594
19	-718.021	-719.757	-717.999	-719.876
20	-755.772	-757.749	-755.942	-757.501
21	-793.633	-795.544	-793.605	-795.686
22	-831.453	-833.642	-831.508	-833.275
23	-869.238	-871.313	-869.201	-871.486
24	-906.976	-909.361	-907.189	-909.025
25	-944.845	-947.093	-944.802	-947.291
26	-982.642	-985.238	-982.758	-984.775
27	-1020.449	-1022.862	-1020.396	-1023.089
28	-1058.172	-1060.966	-1058.481	-1060.418

concerned, we note that at the SCF level, existence of magic numbers is predicted at  $n = 5, 7, 10, 14, 18, 22$  and  $26$ . MP2 calculations preserve this trend in that the same magic numbers are also observed at the correlated theory level. Again, this agrees partially with Pitzer and Clementi (1959) in that for small  $C_n$  clusters assumed linear and at thermodynamic equilibrium, their theory indicated increased relative stabilities

for odd clusters. We also note that the existence of magic numbers at  $n = 10, 14, 18, 22$  and  $26$  among the monocyclic rings is in accordance with the Hückel  $4n + 2$  rule for aromatic hydrocarbons. However, our results seem to slightly contradict the modified neglect of differential overlap (MNDO) calculations of Bernholc and Phillips (1986a, b) since they find that the most stable clusters are  $C_{10}$ ,  $C_{14}$ ,  $C_{15}$ ,  $C_{18}$ ,  $C_{19}$  and  $C_{23}$ . We note (Ray 1987) that our previous calculations at the Hartree-Fock theory level using a smaller 3-21G basis set predicted the existence of magic numbers at  $n = 10, 14, 18$  and  $20$ . The effect of invoking correlation is more pronounced in the nature of the ground states. 3-21G UHF calculations predict that  $C_6$ ,  $C_{10}$ ,  $C_{17}$  and  $C_{19}$  have singlet ground states while all other clusters have triplet ground states. As mentioned before, 6-21G MP2 calculations predict singlet ground states for smaller clusters and alternating triplet and singlet states for larger clusters. We do note, however, a saturation tendency in the binding energy; the binding energy of the  $C_{26}$  cluster is 5.75 eV/atom and that of the  $C_{28}$  cluster is 5.69 eV/atom; this is, however, still significantly less than the binding energy of bulk carbon, namely 7.37 eV/atom.

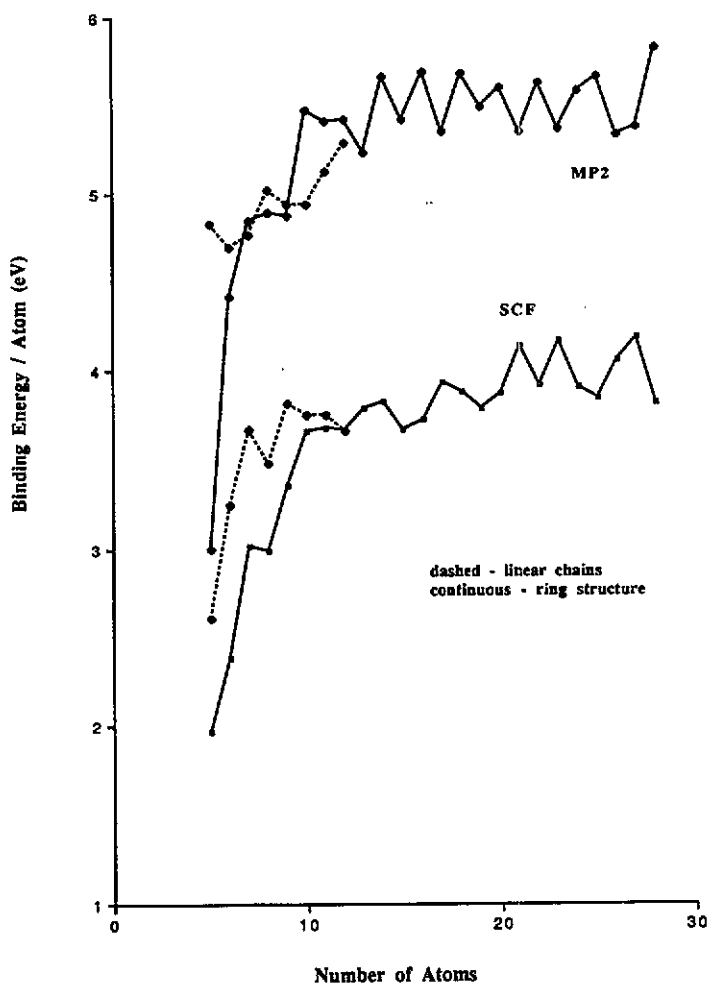
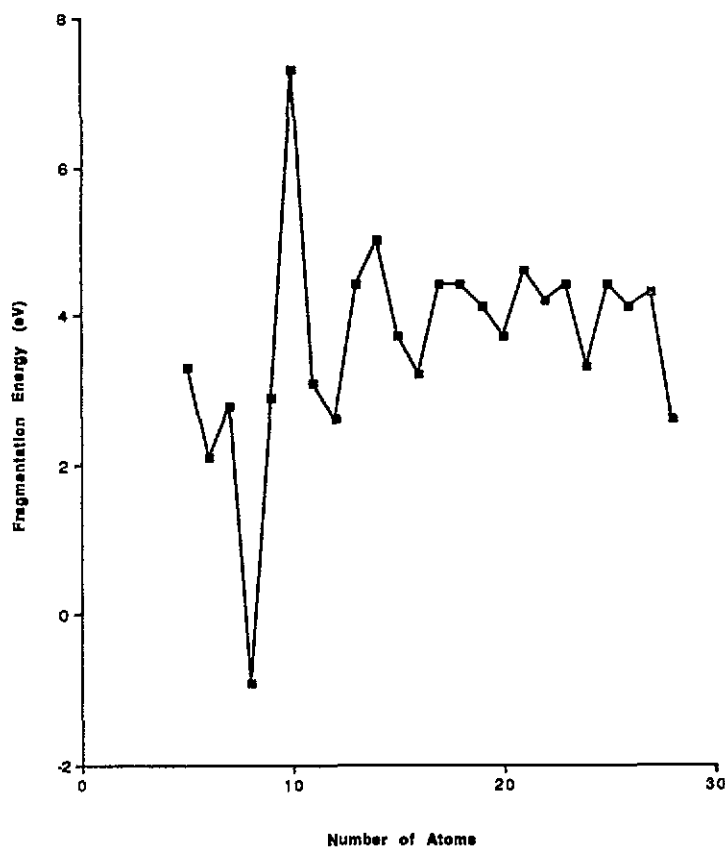


Figure 2. Binding energy/atom (eV) versus number of atoms for  $C_n^+$  clusters.

Table 3. Ground state total energies (au) for linear  $C_n^+$  clusters.

n	Doublet		Quartet	
	SCF Total energy (au)	MP2 Total energy (au)	SCF Total energy (au)	MP2 Total energy (au)
5	-188.376	-188.907	-188.506	-188.804
6	-226.274	-226.735	-226.343	-226.717
7	-264.161	-264.610	-264.146	-264.587
8	-301.900	-302.541	-301.978	-302.495
9	-339.794	-340.381	-339.781	-340.356
10	-377.573	-378.245	-377.578	-378.244
11	-415.370	-416.183	-415.332	-416.138
12	-453.128	-454.128	-453.129	-454.053

We now consider singly ionized  $C_n^+$  clusters. The total energies for linear and cyclic  $C_n^+$  clusters are given in tables 3 and 4 and figure 2 gives the binding energy per atom of the charged clusters at the SCF and MP2 levels. The binding energies

Figure 3. Fragmentation energy/atom (eV) versus number of atoms for  $C_n$  clusters.

have been calculated from:

$$E_{\text{c}}^+ / n = [E_1^+ + (n - 1) E_1 - E_n^+] / n. \quad (3)$$

We find again that a general transition to ring structures occurs at  $n = 10$ , in accordance with the experimental study of McElvany *et al* (1987) and that all singly charged carbon clusters for  $n \leq 9$  are linear. The only exception is  $\text{C}_7^+$ , which is found to have a ring structure. All the smaller clusters up to  $n = 11$  are found to have doublet ground states while no pattern is indicated in the ground states of the larger clusters. The situation with 'magic numbers' or particularly, stable  $\text{C}_n^+$  clusters, is, however, not so clear. According to our calculations, at the SCF level, 'pronounced' maxima occur at  $n = 9, 14, 17, 21, 23$  and  $27$  while at the MP2 level, maxima occur at  $n = 8, 10, 14, 16, 18, 20, 22, 25$  and  $28$ . Thus, correlation is found to have a significant effect on the stabilities of charged clusters. We believe that this is due to the unpaired electron in a  $\text{C}_n^+$  system. The experimental situation here is quite ambiguous in that experiments by Rohlfing *et al* (1984) predict abundance spectra at  $n = 11, 15, 19$  and  $23$  while the experiments by Joyes and Leleyter (1984) predict maxima at  $n = 5, 7, 10, 14, 19, 22$  and  $26$ . Further experimental work followed by detailed correlation investigations at a higher level of theory is clearly necessary to study the distributions of  $\text{C}_n^+$  clusters.

Table 4. Ground state total energies (au) for cyclic  $\text{C}_n^+$  clusters.

n	Doublet		Quartet	
	SCF Total energy (au)	MP2 Total energy (au)	SCF Total energy (au)	MP2 Total energy (au)
5	-188.163	-188.565	-188.260	-188.570
6	-226.211	-226.674	-226.082	-226.674
7	-263.994	-264.630	-264.026	-264.469
8	-301.754	-302.505	-301.815	-302.482
9	-339.646	-340.359	-339.678	-340.315
10	-377.538	-378.442	-377.388	-378.306
11	-415.341	-416.303	-415.230	-416.200
12	-453.106	-454.182	-453.129	-454.188
13	-491.072	-491.969	-490.982	-491.980
14	-528.797	-530.074	-528.682	-529.988
15	-566.432	-567.742	-566.515	-567.835
16	-604.334	-605.874	-604.387	-605.809
17	-642.365	-643.527	-642.264	-643.555
18	-680.030	-681.649	-679.932	-681.605
19	-718.005	-719.304	-717.769	-719.410
20	-755.825	-757.225	-755.626	-757.378
21	-793.642	-795.070	-793.483	-794.935
22	-831.261	-833.165	-831.350	-832.941
23	-869.277	-870.838	-869.189	-870.813
24	-907.091	-908.756	-906.864	-908.911
25	-944.609	-946.875	-944.825	-946.565
26	-982.608	-984.438	-982.622	-984.444
27	-1020.543	-1022.365	-1020.457	-1022.329
28	-1057.974	-1060.703	-1058.254	-1060.213



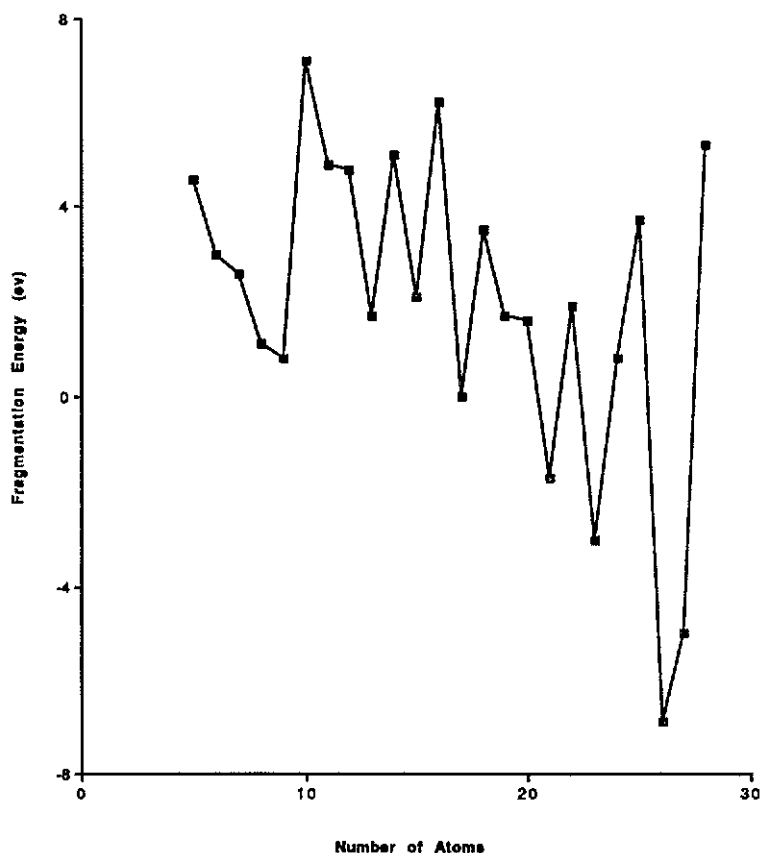


Figure 4. Fragmentation energy/atom (eV) versus number of atoms for  $C_n^+$  clusters.

To further examine the stabilities of the ionized clusters, we computed the fragmentation energy given by Rao *et al* (1986):

$$\begin{aligned}\Delta E_{n,m} &= E(n-m) + E(m) - E(n) & n > m \geq 1 \\ \Delta E_{n,m}^+ &= E^+(n-m) + E(m) - E^+(n) & n > m \geq 1\end{aligned}\quad (4)$$

for neutral and ionized clusters respectively. The numbers in the parentheses denote the number of atoms in that particular cluster. Depending upon the value of  $n$  and  $m$ , the fragmentation can proceed in many different channels and calculation of the value  $\Delta E_{n,m}$  for different values of  $n$  and  $m$  gives us the best possible channel for fragmentation. If  $\Delta E_{n,m}$  is positive, the cluster needs that much energy to go through dissociation in that channel. If  $\Delta E_{n,m}$  is negative, the cluster would fragment spontaneously—'Coulomb explosion' would occur. However, a negative value of  $\Delta E_{n,m}$  does not mean that the dissociation will necessarily occur since this is also dependent upon the activation barrier.

The possible fragmentation channels for  $C_n$  clusters at the MP2 level ( $n \leq 28$ ) are shown in table 5 and the lowest fragmentational energies have been plotted in figure 3. We find that up to  $n = 10$ , the dominant fragmentation channels contain a

Table 5. Fragmentation energies (eV) for  $C_n$  clusters.

$n$	$C_{n-1} + C_1$	$C_{n-2} + C_2$	$C_{n-3} + C_3$	$C_{n-4} + C_4$	$C_{n-5} + C_5$	$C_{n-6} + C_6$	$C_{n-7} + C_7$	$C_{n-8} + C_8$	$C_{n-9} + C_9$	$C_{n-10} + C_{10}$
5	3.3	5.5								
6	4.4	2.1	3.9							
7	6.7	5.5	2.8							
8	4.2	5.3	3.7							
9	7.0	5.6	6.3							
10	8.8	10.2	8.4							
11	3.1	6.3	7.3							
12	5.1	2.6	5.4		7.9					
13	7.8	7.3	4.4		8.9					
14	8.4	10.6	9.7		13.1					
15	3.7	6.5	8.2		9.8	10.6				
16	5.1	3.2	5.6		6.1	10.1				
17	7.2	6.7	4.4		10.2	8.2				
18	7.8	9.4	8.5		9.6	11.1				
19	4.1	6.3	7.5		9.5	11.3				
20	5.2	3.7	5.5		12.9	10.3				
21	6.9	6.5	4.6		6.0	7.7				
22	7.5	8.8	7.9		9.2	6.2				
23	4.4	6.2	7.1		11.6	10.0				
24	5.2	4.0	5.4		8.7	9.2				
25	6.7	6.3	4.7		6.1	7.3				
26	7.2	8.3	7.5		8.8	6.1				
27	4.6	6.2	6.9		10.8	9.3				
28	5.3	4.3	5.4		8.4	8.7				
29					6.3	7.0				
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Table 6. Fragmentation energies (eV) for  $C_n^+$  clusters.

$n$	$C_{n-1}^+ + C_1$	$C_{n-2}^+ + C_2$	$C_{n-3}^+ + C_3$	$C_{n-4}^+ + C_4$	$C_{n-5}^+ + C_5$	$C_{n-6}^+ + C_6$	$C_{n-7}^+ + C_7$	$C_{n-8}^+ + C_8$	$C_{n-9}^+ + C_9$	$C_{n-10}^+ + C_{10}$
5	4.6	6.7	8.8	4.7						
6	4.0	3.0	4.6	5.0	5.4					
7	5.8	4.1	2.7	2.6	7.5	6.8				
8	6.2	6.4	4.3	1.1	5.5	9.3	6.3			
9	4.3	4.9	4.6	0.8	2.1	5.4	6.9			
10	10.3	9.0	9.2	7.1	7.8	8.0	9.0	6.3		
11	4.9	9.5	7.8	6.2	8.7	8.3	6.2	13.0	9.6	
12	5.5	4.8	9.0	5.5	8.5	9.8	7.1	9.6	10.8	5.6
13	3.0	2.9	1.7	4.2	5.2	7.0	6.1	7.5	8.1	7.5
14	11.2	8.5	8.0	5.1	12.1	12.0	11.5	5.8	3.4	2.3
15	2.1	7.7	4.6	2.4	3.9	9.8	7.4	13.1	10.0	5.8
16	9.7	6.2	11.4	6.5	8.8	9.2	12.8	9.4	8.2	3.3
17	0.0	4.0	0.1	3.5	3.2	4.3	2.5	12.9	5.8	9.0
18	11.2	5.5	9.2	3.5	11.4	10.0	8.8	8.6	12.7	3.2
19	2.2	7.7	1.7	3.6	2.4	9.2	5.4	9.5	4.6	8.2
20	7.7	4.3	9.5	1.6	8.0	5.7	10.2	6.8	7.5	6.1
21	0.3	2.4	-1.5	1.9	-1.4	3.9	-0.7	9.0	2.2	3.5
22	11.2	5.9	7.6	1.9	9.9	5.4	-0.7	6.3	10.5	-1.1
23	-0.3	5.3	-0.4	-0.5	-1.6	5.2	-1.6	6.3	-1.0	4.6
24	10.6	4.7	9.9	2.4	6.9	4.6	9.1	3.9	7.5	1.4
25	7.7	12.7	6.4	9.8	6.8	10.1	5.6	4.8	5.5	0.8
26	-3.1	-1.0	3.6	-4.5	-0.7	-0.7	0.3	12.6	2.4	6.4
27	6.5	-2.2	-0.6	2.2	-1.3	5.5	-0.9	-1.7	-2.3	-6.4
28	17.8	18.7	9.6	16.8	12.1	12.1	16.6	2.6	13.4	0.1
								12.7		6.7

Table 6. Continued.

$n$	$C_{n-11}^+ + C_{11}$	$C_{n-12}^+ + C_{12}$	$C_{n-13}^+ + C_{13}$	$C_{n-14}^+ + C_{14}$	$C_{n-15}^+ + C_{15}$	$C_{n-16}^+ + C_{16}$	$C_{n-17}^+ + C_{17}$	$C_{n-18}^+ + C_{18}$	$C_{n-19}^+ + C_{19}$	$C_{n-20}^+ + C_{20}$
12	8.1									
13	7.4	5.9								
14	10.4	13.4	9.3							
15	4.8	7.4	7.8	3.0						
16	9.9	9.4	9.3	9.1	9.0					
17	5.9	4.7	1.6	0.8	5.3	3.9				
18	11.3	12.0	8.1	4.4	8.3	11.4	7.8			
19	7.2	8.3	6.3	1.9	2.8	5.3	6.3	2.1		
20	10.7	9.9	8.3	5.7	5.9	5.4	5.9	6.2	5.8	
21	0.7	5.9	2.3	0.2	2.2	1.1	-1.5	-1.7	2.4	0.9
22	7.0	6.8	9.3	5.2	7.7	8.3	5.1	1.9	5.4	8.4
23	1.3	1.7	-1.3	0.6	1.2	2.3	0.8	-3.0	-2.5	0.0
24	8.9	6.7	4.5	0.9	7.5	6.7	5.7	3.6	3.5	2.9
25	5.4	11.5	6.6	3.8	4.9	10.1	7.1	5.5	7.2	6.0
26	0.2	-2.8	0.6	-4.9	-3.0	-3.3	-0.2	-3.8	-1.7	-1.1
27	-3.1	1.5	-4.1	-1.4	-2.1	-1.7	-4.1	-1.6	-1.4	-0.4
28	14.8	9.7	11.6	5.3	12.8	10.6	8.9	5.9	12.1	11.2

$n$	$C_{n-21}^+ + C_{21}$	$C_{n-22}^+ + C_{22}$	$C_{n-23}^+ + C_{23}$	$C_{n-24}^+ + C_{24}$	$C_{n-25}^+ + C_{25}$	$C_{n-26}^+ + C_{26}$	$C_{n-27}^+ + C_{27}$
22	5.2						
23	1.2	-2.5					
24	3.7	4.4	3.7				
25	3.7	3.9	7.7	6.1			
26	-4.0	-6.9	-3.6	-0.6	-3.7		
27	-1.5	-5.0	-4.8	-2.3	-0.9	-4.4	
28	10.5	8.9	8.4	7.8	8.8	9.7	8.8

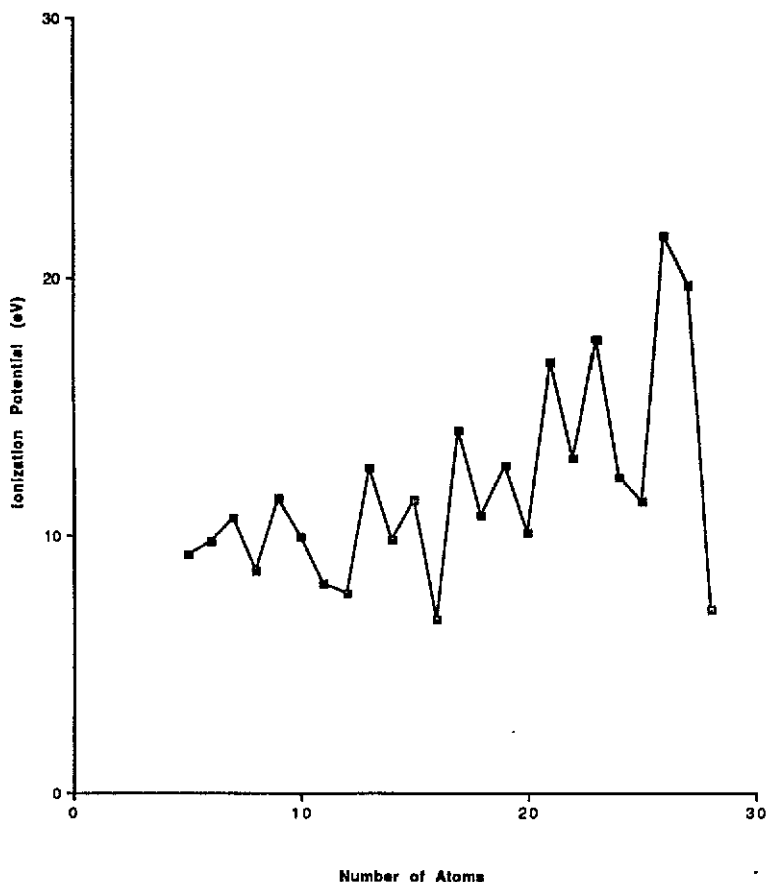


Figure 5. Ionization potential (eV) for carbon clusters.

$C_4$  unit, indicating that  $C_4$  is a particularly stable cluster. We also find that  $\Delta E_{n,m}$  for  $C_8$  is negative, implying that it could disintegrate into two  $C_4$  units. As far as the larger clusters are concerned, we note that the possible fragmentation channel for  $C_{11}$ , is  $C_{10} + C_1$ ; for  $C_{12}$ , it is  $C_{10} + C_2$ ; for  $C_{13}$ , it is  $C_{10} + C_3$ ; for  $C_{14}$ , it is  $C_{10} + C_4$ . This indicates that  $C_{10}$  is a very stable cluster, confirming the existence of a magic number at  $n = 10$ . Similarly, the best possible fragmentation channel for  $C_{15}$  is  $C_{14} + C_1$ ; for  $C_{16}$ , it is  $C_{14} + C_2$ ; for  $C_{17}$ , it is  $C_{14} + C_3$  and for  $C_{18}$ , it is  $C_{14} + C_4$ , all indicating that  $C_{14}$  is a particularly stable cluster. Similarly, if one considers  $C_{19}$ – $C_{22}$  clusters,  $C_{18}$  is found to be very stable. For larger clusters, the pattern is mixed; for example, for  $C_{24}$  and  $C_{28}$  clusters, the best possible fragmentation channels contain  $C_{10}$  and  $C_{14}$  but  $C_{24}$ – $C_{27}$  clusters all contain  $C_4$  as a by-product.

The possible fragmentation channels for  $C_n^+$  clusters at the MP2 level are shown in table 6 and fragmentation energies are plotted in figure 4. For  $C_5^+$ , our fragmentation energy is 4.6 eV whereas the experimental results of Bloomfield *et al* (1987), predict a photofragmentation energy threshold of 4.98 eV. For  $C_6^+$ – $C_9^+$ , our values lie between 0.8 eV and 3.0 eV while the results of Bloomfield *et al* (1987) predict a threshold of 3.53 eV. For  $C_{10}^+$ – $C_{20}^+$ , our values oscillate between 1.6 eV and 6.2 eV, while

Bloomfield *et al* (1987) claim that the values are all less than 3.53 eV. Part of this discrepancy can be attributed to the levels of correlation included and the size of the basis set. In addition, further experimental work is clearly necessary for  $C_n^+$  clusters. We also note that up to  $n = 10$ , the best possible fragmentation channels for all  $C_n^+$  clusters contain either a  $C_4$  or a  $C_4^+$  unit. For  $C_{11}^+ - C_{14}^+$  clusters, the channel contains a  $C_{10}^+$  unit, implying that  $C_{10}^+$  is a particularly stable cluster. The same conclusions apply to the  $C_{14}^+$  cluster. For larger clusters, the pattern is mixed as for neutral  $C_n$  clusters.

We next considered the ionization potentials (IP) of the  $C_n$  clusters at the MP2 level given by

$$IP = E_n^+ - E_n. \quad (5)$$

A plot of the IPs is given in figure 5. No pattern is indicated, except that a general oscillatory tendency is observed between odd and even clusters. Also we do not observe any tendency towards saturation up to  $n = 28$ . Also, unlike the transition metal clusters where the ionization potentials fall to within 0.5 eV of the bulk metal work function by a cluster size of about 15 atoms, for a cluster as large as  $C_{28}$ , the ionization potential of 7.17 eV is significantly higher than the work function of graphite (3.9–4.9 eV). This is a sign of the unique extended  $\pi$  bonding which characterizes carbon clusters.

In conclusion, we investigated linear chains and cyclic rings of carbon clusters and predicted the existence of magic numbers by accurate *ab initio* molecular orbital techniques.

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