

Dirac-Fock-Slater calculations on the geometric and electronic structure of neutral and multiply charged C_{60} fullerenes

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Using a self-consistent relativistic molecular Dirac-Fock-Slater method we have determined the geometric structures and ionization energies of C_{60}^{x+} ($x=0-7$). The lengths of the bonds for the pentagonal edge (single bonds) and the bonds shared by hexagonal rings (double bonds) are found to increase as a function of charge state with an expansion of the cage. The binding energy per atom of C_{60}^{x+} ($x=0-7$) shows a quadratic dependence on the charge state of the C_{60} cluster and an extrapolation to higher charge states reveals that C_{60}^{x+} should still be bound up to $x=13$. Charging of the clusters are analyzed using a classical capacitance model and compared with results from other calculations. Calculated ionization potentials are found to increase linearly with the charge while the available experimental data with comparatively big uncertainties indicate a small quadratic dependence. [S0163-1829(97)00208-7]

I. INTRODUCTION

The possibilities for production of large amounts of fullerenes and, in particular, C_{60} and C_{70} by the electric arc evaporation technique¹ gave unique opportunities to characterize these types of carbon molecules also known as fullerenes. Although carbon clusters containing up to a few hundred atoms had been produced with the laser vaporization method² and detected with mass spectrometry more than six years before the uniqueness of, in particular, C_{60} and C_{70} were not noticed until Kroto, Heath, O'Brien, Curl, and Smalley³ also used the laser vaporization method but with somewhat different production conditions. Their proposed structure of C_{60} as a truncated icosahedron in the form of a cage with 60 vertices and 32 faces, 12 of which are pentagons and 20 hexagons is today well established. The high stability of C_{60} and other even containing carbon clusters was observed very early⁴ by laser irradiation with the observation of shrinking of the cage followed by the emission of C_2 units. All of these very early studies as the measurements of the electron affinity, EA,^{5,6} indicated a very high stability of, in particular, the even number carbon clusters. The measured value of EA was also very well described by local density calculations by one of the authors (A.R.).⁷ Detailed characterization of the fullerenes were however not feasible due to the lack of sufficient amounts of materials until Krätschmer and Huffman and students¹ developed the earlier mentioned electric arc evaporation technique. Very shortly thereafter a number of experiments were performed as the measurements of the ionization potential of C_{60} for the solid

phase in films⁸ and in the gas phase⁹ to be 7.6 ± 0.2 eV and 7.61 ± 0.02 eV, respectively. These values were in comparatively good agreement with the earlier mentioned local density calculations,⁷ which gave values of 6.9 eV and 7.8 eV using the $X\alpha$ exchange correlation potential with $\alpha=0.7$ (Ref. 10) and the parametrization of von Barth and Hedin,¹¹ respectively. Calculations for the ionization potential of singly charged C_{60} gave values of 10.1 eV ($\alpha=0.7$) and 10.8 eV (von Barth-Hedin). There exist today a number of measurements of the ionization potential of singly charged C_{60} with values in the range from 8.5–12.25 eV as summarized by Scheier *et al.*¹² and their own value of 11.4 ± 0.5 eV, which should be compared with the theoretical values given above. Scheier *et al.* summarized and remeasured also the ionization potential for C_{60}^{2+} with values in the range from 11.0–17.0 eV and their own value 16.6 ± 1.0 eV, respectively. More recent measurements of the ionization potential for C_{60}^{3+} by Wörgötter *et al.*¹³ gave a value of 27.4 ± 0.2 eV which has in measurements with better experimental data and use of an improved procedure for analysis of the experimental data¹⁴ has been changed to 19.2 ± 5 eV. Very recently Matt *et al.*¹⁴ extended also the studies to C_{60}^{5+} and obtained a value of 29.2 ± 8 eV for the ionization potential. All these more accurate experimental data of the ionization potentials indicate a small quadratic dependence as a function of the charge. The uncertainties of the data for the highly ionized clusters are however still somewhat high for a critical test of different calculations as will be discussed below.

The stability of multiply charged metal clusters has for a long time been the subject for extensive work as reviewed by

Echt and Märk.¹⁵ The works presented in this review and other studies^{16–20} have been focused on an understanding of the fragmentation pattern with a comparison with what is known from fission of nuclei. C_{60} is a very special cluster characterized as a spherical shell with an empty void which is of quite different structure compared with metal clusters. A very challenging problem has therefore been at which charge will the cage break up and fragment to smaller species as the emission of C_2 units. In addition to the studies mentioned above^{12–14} a number of experiments performed by Märk and co-workers^{21–24} found by electron impact the existence of C_{60}^{x+} ($x=1–7$), while studies by means for slow ion impact on neutral C_{60} by Walch *et al.*²⁵ indicated the existence of C_{60}^{x+} ($x=1–6$). More recently Jin *et al.*²⁶ detected stable C_{60}^{x+} up to a charge of $x=9$.

Results from the use of various methods of electronic structure calculations for C_{60} can be found in Refs. 7,27–30. In an earlier calculation³¹ we evaluated the successive ionization energies of C_{60} up to the 7th degree of ionization keeping the geometrical structure fixed. In this study we investigate the stability of the C_{60}^{x+} ($x=0–7$) by allowing its geometrical structures to rearrange in the I_h symmetry and evaluate also the ionization potentials by calculating the potential minimum for every degree of ionization. Recently a similar investigation using *ab initio* (Hartree-Fock) and semiempirical (modified neglect of differential overlap MNDO, AM1, and PM3) methods was published by Ciolowski *et al.*³² They predict D_{5h} , respectively, C_3 symmetry for C_{60}^{2+} resp. C_{60}^{4+} clusters. In contrast to their work the icosahedral I_h symmetry is used throughout all calculations presented here and the degenerated highest orbitals are statistically occupied.

A commonly discussed property for charged metal clusters and, in particular, for mesoscopic systems^{33,34} is the charging energies of the species and their capacitance. Such an analysis of the charged C_{60} clusters could be done by evaluating the change of the total energy compared with the

total energy of the neutral cluster as a function of excess charge.³⁰

II. METHOD

We calculate the total energy of the many-electron cluster within the (Dirac) Hartree-Fock-Slater (DFS) approximation.^{35,36} This approach is an approximation to the variationally determined Dirac-Fock procedure and an *ab initio* method with no adjustable parameters. Its derivation starts from the expression of the total energy E of the many-electron molecular system,

$$E = \sum_i \langle \phi_i | \mathbf{t} | \phi_i \rangle + \int \rho V^n d^3r + \frac{1}{2} \int \rho V^c d^3r + \frac{3}{4} \int \rho V^{\text{ex}} d^3r + \sum_{p>q} \frac{Z_p Z_q}{|R_p - R_q|}. \quad (1)$$

The single-particle wave functions ϕ_i for the N electrons in the molecule are four-component spinor functions, $\mathbf{t} = \alpha \cdot \mathbf{p} + \beta mc^2$ is the Dirac kinetic energy operator, α 4×4 matrix in spinor space; V^n represents the potential energy of the interaction of the electrons with the nuclei; and V^c is the direct Coulomb-interaction potential between the electrons. V^{ex} is the electron-electron exchange potential for which we used the Slater local density approximation,¹⁰

$$V^{\text{ex}}(\mathbf{r}) = -3\alpha \left[\frac{3}{8\pi} \rho(\mathbf{r}) \right]^{1/3}, \quad (2)$$

with fixed parameter $\alpha=0.7$. The electronic density is given by

$$\rho(\mathbf{r}) = \sum_i n_i \phi_i^\dagger(\mathbf{r}) \phi_i(\mathbf{r}), \quad (3)$$

where n_i are the occupation numbers.

TABLE I. The binding energies D_e and the geometric structures of C_{60}^{x+} ($x=0–7$). The bond distances in the pentagon, respectively, hexagon rings are r_p , respectively, r_h , and R is the radius of the Buckminsterfullerenes.

x (ionization)	Reference	r_p (a.u.)	r_h (a.u.)	R (a.u.)	D_e (eV)
0	this work	2.75	2.63	6.72	8.72
0	(Ref. 43)	2.76	2.62	6.70	
0	exp (Ref. 44)	2.76	2.65	6.71	
0	exp (Ref. 45)	2.75	2.63	6.72	
1	this work	2.76	2.65	6.74	8.45
1	(Ref. 43)	2.75	2.62	6.71	
2	this work	2.76	2.65	6.74	8.12
2	(Ref. 43)	2.75	2.63	6.71	
3	this work	2.76	2.66	6.75	7.72
3	(Ref. 43)	2.75	2.64	6.72	
4	this work	2.77	2.67	6.77	7.27
5	this work	2.77	2.68	6.79	6.77
6	this work	2.78	2.69	6.80	6.17
7	this work	2.78	2.70	6.82	5.60

The application of the variational procedure to the energy functional (1) leads to the single-particle DFS equations for the wave functions ϕ_i and energy eigenvalues ε_i ,

$$[t + V^n + V^c + V^{\text{ex}}]|\phi_i\rangle = \varepsilon_i|\phi_i\rangle, \quad i = 1, \dots, N. \quad (4)$$

In order to solve these equations we use the molecular-orbital linear combination of atomic orbitals (MO-LCAO) method and expand the molecular-orbital wave functions in symmetry-adapted wave function χ_j , which themselves are expanded in atomic orbitals $\xi_{n\nu}(\mathbf{r})$ which are atomic four-component Dirac spinors,^{37,38}

$$\phi_i(\mathbf{r}) = \sum_j \chi_j c_{ji} = \sum_j \sum_{n\nu} \xi_{n\nu}(\mathbf{r}) d_{n\nu j} c_{ji}, \quad (5)$$

with $n\nu = (\nu, n, \kappa, m)$. Here ν indicates the atomic site, and m and κ are the magnetic and Dirac quantum numbers. The symmetry orbitals are created with a projection operator technique using the icosahedral point group (I_h). The atomic basis functions $1s$, $2s$, $2p_{1/2}$, and $2p_{3/2}$ used for the construction of the symmetry orbitals are numerically obtained by solving the atomic DFS equations. Inserting (5) into (4) gives the matrix secular equation,

$$\mathbf{HC} = \varepsilon \mathbf{SC}, \quad (6)$$

where \mathbf{H} and \mathbf{S} are the Hamiltonian and overlap matrices, \mathbf{C} is the coefficient matrix (c_{ij}), and ε is the eigenvalue vector (ε_i). The matrix elements H_{ij} and S_{ij} are evaluated numerically using the modified version (adapted to relativistic numerical wave functions)³⁹ of the integration scheme of Boerrigter, Velde, and Baerends.⁴⁰ The direct Coulomb potential V^c is determined via an additional variational procedure⁴¹ which yields a minimal systematical error as well as a variationally consistent total energy. A solution of the secular equation with standard matrix routines gives the solution in terms of the eigenvalues (ε_i) and expansion coefficients (c_{ij}).

III. RESULTS AND DISCUSSIONS

Using the method described above we first evaluate the geometric and electronic structure of neutral C_{60} with a comparison with available experimental data and then the geometric structure of the multiply charged C_{60}^{x+} ($x=1-7$) ions. In these calculations the bond lengths for the pentagonal edge (single bonds) (r_p) and the bonds shared by hexagonal rings (double bonds) (r_h) are varied. Minimization of the potential energy for the neutral system gave (r_p)=2.75 a.u., (r_h)=2.63 a.u., and a binding energy of 8.72 eV per atom which is somewhat higher than the value of 4.95 eV obtained from large scale Hartree-Fock calculations by Lüthi and Almlöf.⁴² The overestimation of the binding energy is a well known result of the local density approximation (LDA) even for small molecules. These values of the bond lengths should be compared with the experimental values of $r_p=1.458 \text{ \AA}$ (2.76 a.u.) and $r_h=1.401 \text{ \AA}$ (2.65 a.u.) determined in gas phase electron diffraction.⁴⁴ Other experimental values are the solid state NMR measurements⁴⁵ which gave $r_p=2.75$ a.u. and $r_h=2.63$ a.u., while somewhat slightly different values $r_p=2.71$ a.u. and $r_h=2.63$ a.u. were derived from an x-ray study.⁴⁶ The results obtained for the neutral

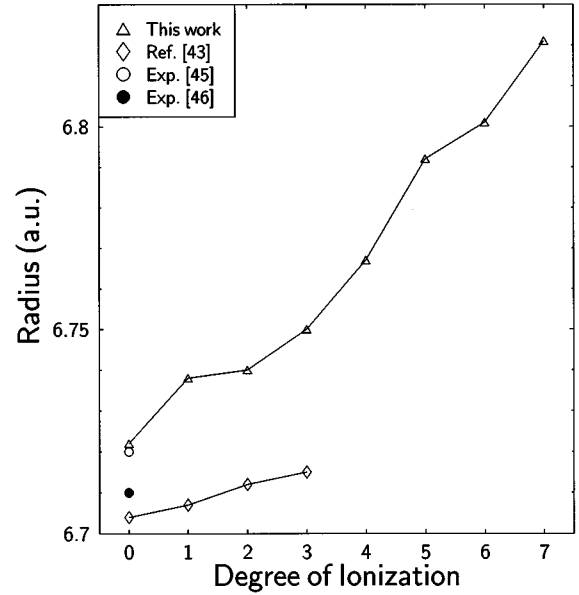


FIG. 1. Radius of the Buckminsterfullerene with respect to the degree of ionization. \triangle this work, \diamond Ref. 43, \circ experiments (Refs. 45,46).

and ionized C_{60} in terms of r_p , r_h , the radius of the cage, and the bond energy per atom, D_e , is presented in Table I. The evaluated bond lengths in this work are in good agreement with the experimental values for the neutral C_{60} as well as with the semiempirical results of Yamaguchi *et al.*⁴³ for C_{60}^{x+} ($x=0-3$).

The results of the ionized systems have been analyzed assuming the C_{60}^{x+} ions to be a composition of x C^+ ions and $(60-x)$ neutral C constituents. Thus the binding energies are calculated as the difference between the total energy of the ionized molecule C_{60}^{x+} and x times the total energy of the C^+ ion plus $(60-x)$ times the total energy of the neutral C. The binding energies obtained are fitted to a product

$$V(x, y) = D_e \{ \exp[2a(r_p - x)] - 2 \exp[a(r_p - x)] \} \\ \times \{ \exp[2b(r_h - y)] - 2 \exp[b(r_h - y)] \} \quad (7)$$

of two Morse potentials. These are the values of the bond energy per atom D_e given in the last column of Table I.

In Fig. 1 the radii of the neutral and ionized C_{60} are drawn with respect to the degree of ionization with a comparison with the results of Yamaguchi *et al.*⁴³ Two experimental values for the radius of the neutral C_{60} are marked with empty⁴⁵ and filled circles.⁴⁶ Both calculations exhibit an increase of the C_{60} radius with respect to the degree of ionization. The semiempirical results of Yamaguchi *et al.*⁴³ show a linear relation whereas our results rather fit to a quadratic behavior.

The binding energy per atom versus the degree of ionization is presented in Fig. 2. Our calculations are shown as triangles and clearly reveal a quadratic behavior. A fit to a quadratic equation of these values in the range from the neutral to seventh degree of ionization indicates by extrapolation an estimate of stable C_{60}^{x+} clusters up to $x=13$. Such a value relies on the evaluated quadratic behavior obtained in these calculations which might change for calculations of

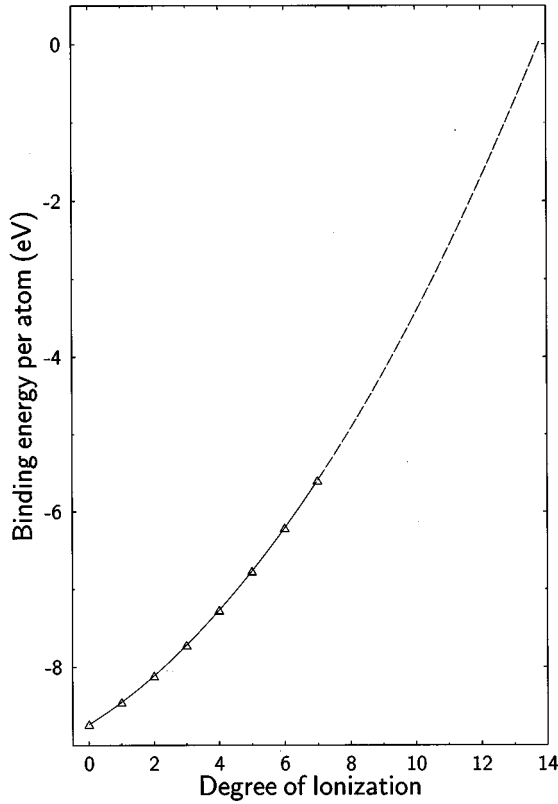


FIG. 2. Dissociation energy of C_{60}^{x+} ($x=0-7$). The curve is a fit of \triangle points (this work) to a quadratic equation.

systems of higher ionicity and if dynamics would be included in the calculations. This value of stability should be compared with the result from recent slow ion impact experiment by Jin *et al.*²⁶ who determined the critical charge to be at least 9. Theoretical investigations by Seifert *et al.*²⁰ reveal the critical charge to be $x=16$, while Ciolowski *et al.*³² estimated from their calculations a stability up to $x=28$, which are too high compared with our value of stability. However, from the analysis of the vibrational frequency spectrum, Ciolowski *et al.*³² suggest that only the C_{60}^{10+} has a minimum on the potential energy hypersurface as higher charge states show a large part of imaginary frequencies in the vibrational density of states which are related to decay channels.

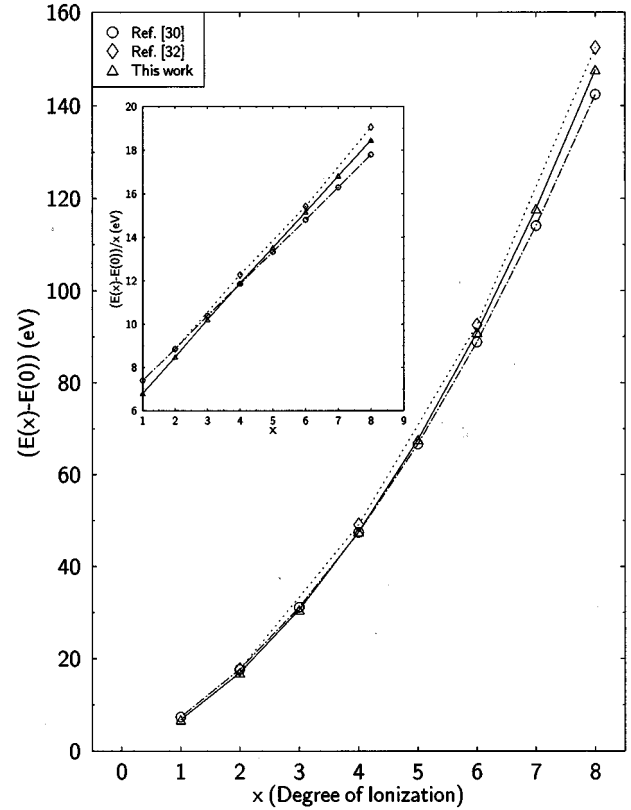


FIG. 3. The difference of the total energies of C_{60} and C_{60}^{x+} ($x=0-6$) as a function of excess charge. Inset: The differences divided by the charge as a function of the excess charge. \circ Ref. 30, \diamond Ref. 32, and \triangle this work.

Ciolowski *et al.*³² analyzed their result by evaluating the differences in the total energy of the neutral C_{60} and the multiply ionized C_{60}^{x+} ($x=2,4,6,8$) fullerenes. We have done a similar analysis in Fig. 3, using the results obtained in this work by comparing the results of Ciolowski *et al.*³² and Yannouleas and Landman.³⁰ A plot of these differences divided by the charge as a function of the excess charge is also given as an inset in Fig. 3. The lines have somewhat different slopes but the agreement is rather good although we kept the I_h symmetry in our calculations. Rewriting the linear plot as done by Yannouleas and Landman³⁰ gives the following equation:

TABLE II. Ionization energies of C_{60}^{x+} ($x=0-7$).

x	Theory			Experiment			
	(Ref. 30) (eV)	(Ref. 20) (eV)	This work (eV)	(Ref. 14) (eV)	(Ref. 47) (eV)	(Ref. 48) (eV)	(Ref. 49) (eV)
0	7.40	8.50	6.80	7.60 ± 0.5	7.58 ± 0.4	8.1 ± 0.5	
1	10.31	11.7	10.16	11.4 ± 0.5	11.43 ± 0.4	10.3	12.25 ± 0.5
2	13.28	14.6	13.67	16.6 ± 1.0		14.8 ± 0.1	17.0 ± 0.7
3	16.25	18.0	16.92	19.2 ± 5.0			
4	19.22		20.07	29.2 ± 8.0			
5	22.20		23.35				
6	25.24		26.78				
7	28.31		29.91				

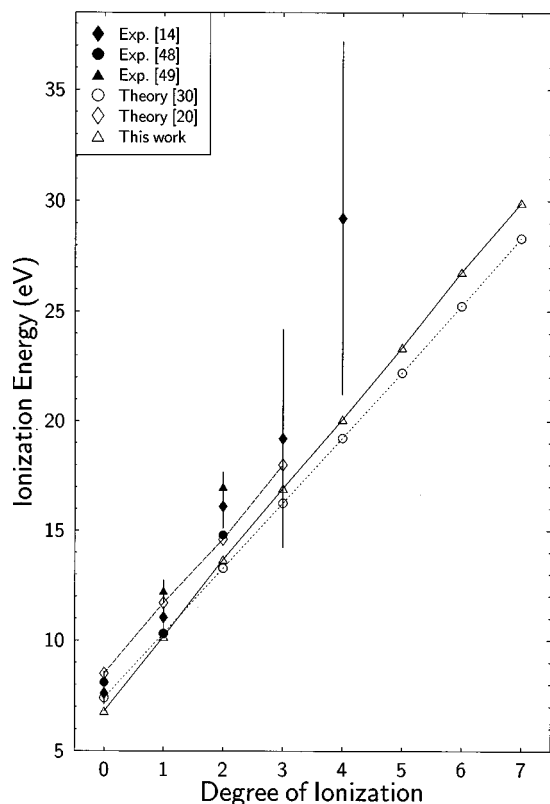


FIG. 4. Ionization potential of C_{60}^{x+} ($x=0-7$).

$$E(x) = E(0) + \frac{x(x-1)e^2}{2C} - xA_I. \quad (8)$$

From the least square fit of the different lines of the inset in Fig. 3 we get a capacitance of 8.17 a.u. from our results, a value of 8.03 a.u. from the results of Ciolowski *et al.*,³² and a value of 9.16 a.u. from the values given by Yannouleas and Landman,³⁰ which should be compared with their value of 8.86 a.u. Using a stabilized-jellium model with a smeared

out of the charge as used by Yannouleas and Landman³⁰ seems therefore to give about a 10% higher capacitance compared with standard LCAO type calculations.

The x th ionization potential is calculated as the difference of the total energies of the systems $C_{60}^{(x-1)+}$ and C_{60}^{x+} in the minima of their corresponding potential energy surfaces. The ionization potentials are presented in Table II and Fig. 4, together with the experimentally (filled points) known values^{14,47-49} as well as the results of a stabilized-jellium LDA calculation³⁰ and the theoretical results of Seifert *et al.*²⁰ (unfilled points). The experimental data for different ionization potentials indicate a small quadratic dependence as a function of charge although the experimental uncertainties are rather big. These experimental data should be compared with the different theoretical results which show a linear relationship as a function of the degree of ionization. The new value of the ionization energy for the 3+ ion as reported by Matt *et al.*,¹⁴ using an improved evaluation procedure, is however in much better agreement with our results compared with the earlier quoted value by Scheier and co-workers.⁵⁰ Access to experimental data of higher accuracy is therefore necessary for a more critical test of the calculations.

IV. SUMMARY

We have studied the electronic and geometric structure and the ionization energy of multiply charged C_{60} fullerenes. The previously estimated linear increase of the ionization energy is again reproduced. From our calculation a stable structure of the charged C_{60} up to charge 13 is expected to exist.

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