

atom is noticeably positively charged, explaining why these types of compounds are rarely isolated except as ylides. These considerations suggest that the chemical properties of species where $M' = \text{Si, Ge, and Sn}$ are quite different from their carbene parents.

This suggestion is also confirmed by the dramatic difference found in the dissociation energies and force constant associated with $\text{Mo}=\text{M}'$ bond strength between the carbene derivative and the rest of the compounds.

Finally, when the relative energy of the staggered and eclipsed conformers is examined, the conclusion is that the rotation of the $\text{M}'\text{H}_2$ group is practically free.

Acknowledgment. This work was supported by the Spanish Dirección General de Investigación Científica y Técnica, Project PB89-0561. We thank the staff of the Centro de Informática Científica de Andalucía for computational facilities.

Low-Lying Electronic Excited States of Buckminsterfullerene Anions

Fabrizia Negri, Giorgio Orlandi,* and Francesco Zerbetto

Contribution from Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via F. Selmi 2, 40126 Bologna, Italy. Received July 8, 1991

Abstract: We report Pople–Pariser–Parr (PPP) calculations of the energies of the lowest electronically excited states of six C_{60} anions ranging from the monoanion to the hexaanion. Multiplicities up to septet are included. The results for the monoanion are compared with the existing absorption spectrum. The stability of various anions and the possibility of obtaining them by electrochemical reduction are discussed. In most of the species studied, we find a remarkable density of electronic levels close to the electronic ground state. This density is due to the existence, in neutral C_{60} , of a triply degenerate lowest unoccupied molecular orbital (LUMO), together with a close-lying LUMO+1 of the same degeneracy.

1. Introduction

Fullerene compounds have very recently been isolated,¹ and fullerrite can now be considered one of the phases of carbon. It is made by molecules containing from 60 up to possibly several hundred carbon atoms, which shape themselves in the form of pentagons and hexagons to build spheroids. The archetype of these compounds is the highly symmetric C_{60} cluster, or Buckminsterfullerene (Bf), in which 12 pentagons and 20 hexagons are arrayed in the highest possible symmetry on the surface of a sphere.² The characterization of the physical and chemical properties of these molecules is now in progress and promises to yield remarkable results. Among other data that are presently becoming available, a particularly fascinating achievement was the reported electron transport, or conductivity, that C_{60} , and to a lesser extent C_{70} , show upon doping with alkali metals.³ Shortly after a communication on this subject was published,³ the same laboratory reported a transition temperature to superconductivity of 18 K for the potassium-doped Bf crystal.⁴ Very recently, two subsequent editorial comments⁵ have reported a dramatic increase of this transition temperature, which is presently claimed to be 42 K for the rubidium and thallium dopants and 57 K for the iodine dopant. To date, such a temperature is the highest for an organic material. The nominal composition of the sample that showed the higher conductivity was M_3C_{60} . This is possibly to be related to the crystal structure of C_{60} , which has a face-centered cubic packing with two vacant tetrahedral sites of radius 1.12 Å and one octahedral site of radius 2.06 Å.³ These sites can accommodate three alkali atoms, and the addition of a fourth atom modifies the original crystal lattice⁶ and possibly hinders the electron transport from one molecule to the other. Alternatively, the highest conductivity of the K_3C_{60} composition samples may be due to the different electronic structure of the various anions. Thus, a question to be addressed here is whether one can explain the trend observed in the conductivity and possibly offer suggestions on how to improve on the results of refs 3 and 4. The availability of the visible and near-infrared absorption spectrum of the C_{60}^- anions⁷ is another reason that prompted us to study these compounds.

Recently, we reported the vibrational frequencies of C_{60} together with the magnitude of the Jahn–Teller distortion in its monoanion.⁸ After the publication of some of the C_{60} and C_{70} vibrational frequencies,^{9,10} we calculated, with an upgraded QCFF/PI^{11,12}

with the magnitude of the Jahn–Teller distortion in its monoanion.⁸ After the publication of some of the C_{60} and C_{70} vibrational frequencies,^{9,10} we calculated, with an upgraded QCFF/PI^{11,12}

(1) Kratschmer, W.; Lamb, L. D.; Fostiropoulos, K.; Huffman, D. R. *Nature* 1990, 347, 354–358.

(2) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* 1990, 318, 162–163.

(3) Haddon, R. C.; Hebard, A. F.; Rosseinsky, M. J.; Murphy, D. W.; Duclos, S. J.; Lyons, K. B.; Miller, B.; Rosamilia, J. M.; Fleming, R. M.; Kortan, A. R.; Glarum, S. H.; Makhija, A. V.; Muller, A. J.; Eick, R. H.; Zahurak, S. M.; Tycko, R.; Dabbagh, G.; Thiel, F. A. *Nature* 1991, 350, 320–322.

(4) Hebard, A. F.; Rosseinsky, M. J.; Haddon, R. C.; Murphy, D. W.; Glarum, S. H.; Palstra, T. T. M.; Ramirez, A. P.; Kortan, A. R. *Nature* 1991, 350, 600–601.

(5) Baughman, R. H.; Ramakrishna, B. L.; Khare, S.; Murthy, N. S.; Bornemann, H. J.; Morris, D. E. *Science* 1991, 254, 826–828.

(6) Fleming, R. M.; Rosseinsky, M. J.; Ramirez, A. P.; Murphy, D. W.; Tully, J. C.; Haddon, R. C.; Siegrist, T.; Tycko, R.; Glarum, S. H.; Marsh, P.; Dabbagh, G.; Zahurak, S. M.; Makhija, A. V.; Hampton, C. *Nature* 1991, 352, 701–703.

(7) Kato, T.; Kodama, T.; Shida, T.; Nakagawa, T.; Matsui, Y.; Suzuki, S.; Shiromaru, H.; Yamauchi, K.; Achiba, Y. *Chem. Phys. Lett.* 1988, 144, 31–37.

(8) Negri, F.; Orlandi, G.; Zerbetto, F. *Chem. Phys. Lett.* 1988, 144, 31–37.

(9) Bethune, D. S.; Meijer, G.; Tang, W. C.; Rosen, H. J. *Chem. Phys. Lett.* 1990, 174, 219–222.

(10) Hare, J. P.; Dennis, T. J.; Kroto, H. W.; Taylor, R.; Allaf, W. A.; Balm, S.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* 1990, 412–413.

(11) Warshel, A.; Karplus, M. *J. Am. Chem. Soc.* 1972, 94, 5612–5625.

Warshel, A.; Levitt, M. *QCPE* 1974, No. 247.

(12) (a) Orlandi, G.; Zerbetto, F. *Chem. Phys.* 1986, 108, 187–195. (b) Zerbetto, F.; Zgierski, M. Z.; Orlandi, G.; Marconi, G. *J. Chem. Phys.* 1987, 87, 2505–2512. (c) Zerbetto, F.; Zgierski, M. Z.; Orlandi, G. *Chem. Phys. Lett.* 1987, 141, 138–142. (d) Zerbetto, F.; Zgierski, M. Z. *Chem. Phys. Lett.* 1988, 143, 153–162. (e) Zerbetto, F.; Zgierski, M. Z. *Chem. Phys. Lett.* 1988, 144, 437–444. (f) Zerbetto, F.; Zgierski, M. Z.; Negri, F.; Orlandi, G. *J. Chem. Phys.* 1988, 89, 3681–3688. (g) Zerbetto, F.; Zgierski, M. Z. *Chem. Phys. Lett.* 1988, 151, 526–530. (h) Zerbetto, F.; Zgierski, M. Z. *Chem. Phys. Lett.* 1989, 157, 515–520. (i) Negri, F.; Orlandi, G.; Zerbetto, F.; and Zgierski, M. Z. *J. Chem. Phys.* 1989, 91, 6215–6224. (j) Drew, J.; Zerbetto, F.; Szabo, A. G.; Morand, P. *J. Phys. Chem.* 1990, 94, 4439–4446. (k) Zerbetto, F.; Zgierski, M. Z. *J. Chem. Phys.* 1990, 93, 1235–1245. (l) Orlandi, G.; Zerbetto, F.; Zgierski, M. Z. *Chem. Rev.* 1991, 91, 867–891.

method (that is a Pople-Pariser-Parr (PPP)), the optimized structures and the vibrational frequencies of C_{70} and of two high-symmetry C_{84} clusters.¹³ The comparison of the vibrational frequencies experimentally available and those calculated by us showed an average error of $\sim 30\text{ cm}^{-1}$. In the present contribution to the understanding of fullerite, we use the quantum-chemical part of the QCFF/PI method to evaluate the energies of the lowest electronic excited states in six C_{60} anions (from the mono- to the hexaanion) that may be formed upon alkali-metal doping. All the multiplicities from singlet to septet are considered. The purpose is to determine the nature and the energy of the ground state, the energy gaps among the lowest electronic states, and the change of the density of states with increase of the negative charge.

This paper is organized as follows: in section 2, we present the quantum-chemical method used to perform all the calculations; in section 3, we discuss, as a prerequisite to the configuration interaction (CI) calculations, the energies of the molecular orbitals (MOs) of the six anions. The results are presented in section 4, where we discuss the spectrum of C_{60}^- , the stability of the various anions, and the high density of electronic states obtained by our calculations and attempt to furnish some insight into the properties of doped Bf.

2. Computational Procedure

All the calculations have been performed with the quantum-chemical part of the QCFF/PI method.¹¹ This is a Pople-Pariser-Parr Hamiltonian whose one-electron (α, β) and two-electron (γ) integrals are expressed as a function of the CC bond distance and were conceived to apply the zero differential overlap approximation to the calculation of a number of molecular properties, one of which is the energy of $\pi\pi^*$ electronic transitions. In its original formulation, the program could treat singly excited configurations arising from a closed-shell singlet. The modified version¹⁴ used in this work can perform a generalized half-electron self-consistent-field (HE-SCF)^{15,16} calculation on any electronic configuration. In this approach, the unpaired electrons are evenly distributed, regardless of the spin, in the partially occupied orbitals. The net result is that for the mono-, bi-, and trianion there are one-third, two-thirds, and one electron in each of the t_{1u} MOs. A difficulty arises starting from the tetraanion because the LUMO+1, a set of MOs of t_{1g} symmetry, is very close to the t_{1u} LUMO orbitals. We decided to perform both low-spin (with all of the excess electrons responsible for the anion charge in the t_{1u} orbitals) and high-spin (with the unpaired electrons distributed in the six $t_{1u} + t_{1g}$ orbitals) HE-SCF calculations. It is expected that the MOs generated by the two calculations should produce slightly different results in the subsequent limited CI. For example, in the case of the hexaanion, comparison of the low- and high-spin CI results might show an increased stability for the closed-shell singlet state calculated from the low-spin MOs, while the high-spin MOs should give an increased stability for the septet state.

Starting from the HE-SCF MOs, the energies of the electronic transitions are calculated by a general CI method based on determinants.¹⁶ Excitations up to sextuples are included, depending on the number of excess electrons. Spin multiplicities from singlet (or doublet) to sextet (or septet) are considered. The MO space used in the calculations is discussed in the next section.

The optimized geometrical structure of the C_{60} neutral cluster⁸ is used in all the calculations presented here. This neglects both the small molecular expansion that occurs with the introduction of each subsequent negative charge and the molecular deformations which may be caused by the Jahn-Teller or pseudo-Jahn-Teller effect. These two structural effects can effectively modify the ordering of close-lying electronic states; however, due to the high density of electronic states (vide infra), the conclusions of this work will be unaffected. We plan to study these structural modifications in the future.

3. Molecular Orbitals

3.1. Electronic Aufbau of Anions. In Figure 1, we present a qualitative scheme which shows the MOs of Bf and its anions. In the neutral molecule, the h_u MOs (or HOMO) are completely

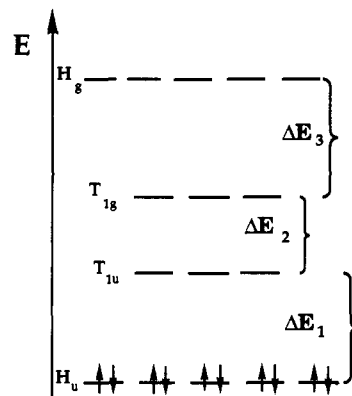


Figure 1. Qualitative representation of the molecular orbital energy levels in Buckminsterfullerene (C_{60}) and its anions. The h_u MOs are the HOMO in the neutral molecule.

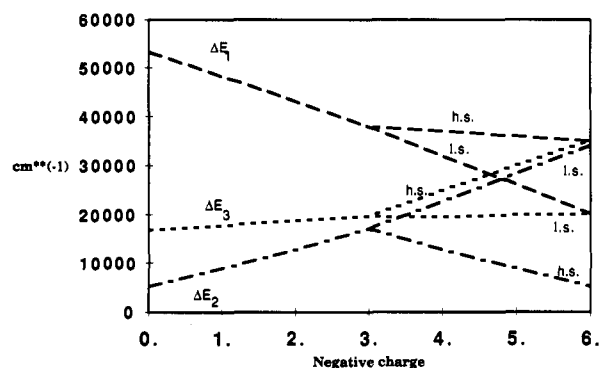


Figure 2. Half-electron self-consistent-field ΔE_1 , ΔE_2 , and ΔE_3 (see Figure 1) versus electronic charge for high- and low-spin C_{60} anions (see text).

occupied. With the anion formation, the t_{1u} orbitals begin being filled. The bianion and trianion are formed by adding a second and a third electron, respectively, to the same triply degenerate orbital. In principle, due to the closeness in energy of the t_{1u} and t_{1g} MOs, the fourth electron may fill either orbital (vide supra) in a way that resembles the electronic Aufbau of transition metal coordination complexes. The choice between the two possibilities depends both on the orbital energy gap ΔE_2 (see Figure 1) and on the exchange interactions between the electrons in the two sets of orbitals. The same two alternatives are also possible for the penta- and the hexaanions.

3.2. Orbital Excitation Energies. To determine the electronic configurations to be taken into account in the CI treatment, three orbital energy differences (see Figure 1) need to be considered. With reference to the electronic occupation of the orbitals in the neutral compound, these are the LUMO - HOMO energy gap (ΔE_1), and the two subsequent gaps, namely, the LUMO+1 - LUMO (ΔE_2) and LUMO+2 - LUMO+1 (ΔE_3). In Figure 2, we show all these energy differences (calculated with the HE-SCF procedure) versus the number of negative charges (n_e) in the anions. These energies are not related to observables such as ionization potentials or electron affinities because, due to the closeness of the t_{1u} and t_{1g} orbitals, C_{60} anions wave functions can only be described by a multideterminant approach such as CI or multiconfiguration self-consistent field (MCSCF). However, these energy gaps allow the choice of the MO space to be used to calculate the energies of the ground and electronic excited states of C_{60} anions.

In the following, we find that, due to the nature of the MOs of C_{60} , the ΔE_2 energy gap is usually lower than the others. To clarify the consequences of this, the anions need to be separated in three groups:

(i) To the first group belong the anions with up to three negative charges. For these species, the first three orbital excitation energies are ΔE_2 , $\Delta E_2 + \Delta E_3$, and ΔE_1 . In all three species, the ΔE_2 energies are at most half the value of the other two excitation

(13) Negri, F.; Orlandi, G.; Zerbetto, F. *J. Am. Chem. Soc.* **1991**, *113*, 6037-6040.

(14) Negri, F.; Orlandi, G. *J. Phys. Chem.* **1989**, *93*, 4470-4477.

(15) Dewar, M. J. S.; Hashmall, J. A.; Venier, C. G. *J. Am. Chem. Soc.* **1968**, *90*, 1953-1957.

(16) Armstrong, D. R.; Fortune, R.; Perkins, P. G.; Stewart, J. J. P. *J. Chem. Soc., Faraday Trans 2* **1972**, *68*, 1839-1846.

Table I. Electronic Energy (eV), up to 0.75 eV, of the Lowest Excited States of C_{60}^{n-} ($n = 1, 2, 3$)

ES ^a	energy	ES ^a	energy
Anion C_{60}^{1-}			
1^2T_{1u}	0.00 (-1.69) ^b		
1^2T_{1g}	0.64		
Anion C_{60}^{2-}			
1^1A_g	0.00 (-0.16) ^b		
1^1A_u	0.16	1^3T_{1g}	0.19
1^1H_g	0.30	1^3T_{1u}	0.52
		1^3H_u	0.57
Anion C_{60}^{3-}			
		1^4A_u	0.00 (5.00) ^b
1^2T_{1u}	0.42	1^4A_g	0.10
1^2H_u	0.43	1^4H_g	0.45
1^2T_{1g}	0.62		

^aES, electronic state. ^bThe energy relative to that of the neutral C_{60} molecule is in parentheses.

energies. Thus only the electronic configurations in the $t_{1u}-t_{1g}$ space are considered. In the calculation, all the possible excitations in the $t_{1u}-t_{1g}$ space are generated, so that singly excited determinants are considered for C_{60}^- , singly plus doubly excited determinants are used for C_{60}^{2-} , and so on with up to sextuply excited determinants included in the calculation for the hexaanion. The number of determinants arising from this space is 6 for the monoanion, 36 for the bianion, and 90 for the trianion. Obviously enough, only one S_z component for any given spin multiplicity is considered. The monoanion, for which the visible and near-IR spectrum is available,⁷ was treated also by a larger CI comprising 431 detors from a $8 \times 8 \pi, \pi^*$ orbital space. We expect that the results obtained by this CI will be of an accuracy comparable (although lower) to that of the CI calculations on the neutral Bf .⁸ In this way, we check the accuracy of the results obtained with the reduced CI, which involves a very small number of determinants (6) in the monoanion;

(ii) The second group contains the tetra- and the pentaanion. Starting from $n_e = 4$, two kinds of HE-SCF are possible (vide supra): the low-spin calculation is characterized by n_e electrons in t_{1u} orbitals, the high-spin ones are performed by distributing n_e electrons in six orbitals. For the high-spin case, the same considerations made at point i about the ΔE_i 's apply (see Figure 2) and only the determinants arising from the $t_{1u}-t_{1g}$ space need to be included. When the energy gaps for the low-spin MOs of the tetra- and the pentaanion are examined, one finds that ΔE_1 and ΔE_2 excitation energies have similar values. In view of this fact, it is advisable to assess the validity of including in the CI only determinants from the $t_{1u}-t_{1g}$ space in the description of the energies and the wave functions of the lowest excited states of Bf anions. We do this through a comparison of the results of two CI calculations: in the first only the determinants arising from the $t_{1u}-t_{1g}$ space are considered; in the second the singly excited determinants of the one-electron excitation from the h_u-t_{1u} space are also included. The numbers of determinants in the $t_{1u}-t_{1g}$ space are 225 and 300 for the tetra- and the pentaanion, respectively;

(iii) The third group contains only the hexaanion. For this species, the considerations of point ii hold, with the difference that in the low-spin configuration the t_{1u} orbital is now completely occupied and the h_u-t_{1u} single excitations are no longer possible. Thus, for both the low-spin and the high-spin CI, only the 400 determinants arising from the $t_{1u}-t_{1g}$ space are considered in the calculations.

4. Results and Discussion

4.1. Spectrum of C_{60}^- . In Table I, we show the lowest electronic states of the three anions C_{60}^{n-} , $n = 1, 2, 3$. As expected from the orbital ordering reported in Figure 1, the ground state of the monoanion is calculated to be 2^2T_{1u} . The only excited state found using the restricted CI, 2^2T_{1g} , is 0.64 eV higher in energy and corresponds to the $t_{1u}-t_{1g}$ electronic excitation. The electronic states of C_{60}^- obtained with the larger CI are reported in Table II. The lowest excited state D_1 is found at a considerably lower

Table II. Lowest Electronic States of C_{60}^- , with the Larger CI (see text)

doublets				quartets		
	Sym	energy, eV	f	Sym	energy, eV	
D_0	T_{1u}	0.00		Q_1	G_u	2.67
D_1	T_{1g}	0.37	0.33	Q_2	H_u	2.73
D_2	H_g	2.58	0.37	Q_3	H_u	2.74
D_3	H_g	2.64	0.13	Q_4	G_g	2.78
D_4	H_u	2.76		Q_5	T_{2g}	2.80
D_5	A_u	2.88		Q_6	A_g	2.80
D_6	G_u	2.91		Q_7	T_{1g}	2.86
D_7	T_{1u}	2.91		Q_8	G_g	2.88
D_8	H_u	2.93		Q_9	H_g	2.88
D_9	G_u	2.96		Q_{10}	T_{1u}	2.92
D_{14}	T_{2g}	3.09	0.07			
D_{15}	H_g	3.10	0.14			

energy, namely, at 0.37 eV. The next excited states are found at an energy higher than 2.57 eV; at least seven states appear in the energy interval 2.57–2.96 eV. Among these, only the states D_1 (2^2T_{1g}), D_2 (2^2H_g), D_3 (2^2H_g), with energies of 0.37, 2.58, and 2.64 eV, respectively, are associated with symmetry-allowed $D_0 \rightarrow D_n$ transitions. The next allowed transition is due to $D_0 \rightarrow D_{14}$ and requires a photon energy of 3.09 eV. The absorption spectrum of C_{60}^- in the visible and near-IR region has been reported recently together with CNDO/S calculations of electronic states.⁷ It shows two well-resolved bands at 1076 (1.15 eV) and 952 nm (1.30 eV), the former being the more intense. A large, intense, unresolved band begins to develop at ~ 450 nm (2.75 eV). Since the energy of the observed transitions is ~ 1.5 eV below the calculated energies of D_2 and D_3 and ~ 1 eV above D_1 , at first sight it seems that these theoretical results are of little help in interpreting the observed spectrum. However, if we take into account that the lowest excited state of the neutral C_{60} was calculated (with a larger CI) at 2.58 eV and is observed at 1.74 eV¹⁷ and that correlation effects are more important for the open-shell than for the closed-shell systems, we are led to attribute the two bands observed at 1.15 and 1.30 eV to the states D_2 and D_3 calculated at 2.58 and 2.64 eV, respectively. Notice that the calculated intensity ratio $I(D_0 \rightarrow D_2)/I(D_0 \rightarrow D_3)$ is very similar to the observed intensity ratio $I(1076\text{nm})/I(952\text{nm})$. A doublet of electronic states at 1.04 and 1.08 eV was found also by the CNDO/S calculations of ref 7. The two prominent bands observed in absorption at 1076 and 952 nm could correspond to these two states. Another possibility mentioned in ref 7 is that only the band at 1076 nm belongs to an electronic transition and that the band at 952 nm, like other weaker bands, is due to the vibrational structure. The CNDO/S results displayed in Figure 1 of ref 7 do not extend in the IR spectral range and therefore they do not support or disprove the lowest excited state we find at 0.37 eV. The band corresponding to this state, which we have derived also by CNDO/S calculations, is expected to be very prominent in the IR region because of its high oscillator strength. Notice that the fundamentals of the vibrations that couple vibronically D_0 with D_1 (that is all the "u"-type vibrations) can all borrow intensity from the $D_0 \rightarrow D_1$ electronic transition. Furthermore, because of the quasi-degeneracy, the energies of the same fundamentals are perturbed by the nearby state D_1 . Thus, the presence of the low-lying D_1 state is expected to strongly perturb the IR spectrum.

4.2. Lowest Electronic States in the Six Anions. In Table I are listed the lowest ($E < 0.75$ eV) electronic states of C_{60}^{n-} , for $n = 1, 2, 3$, calculated with the smaller CI. As can be seen, the number of states increases markedly for C_{60}^{2-} and C_{60}^{3-} . The bianion shows low-lying excited states of both singlet and triplet multiplicity. Its ground state is calculated to be a singlet of A_g symmetry. For monoconfigurational wave functions, the Hund principle requires that the ground state of a two-electron system has triplet multiplicity. Since in this case both the wave function of the 1^1A_g state and that of the 3^1T_{1g} state contain a large con-

(17) Yang, S. H.; Pettiette, C. L.; Conceicao, J.; Cheshnowsky, O.; Smalley, R. E. *Chem. Phys. Lett.* **1991**, *139*, 233–238.

Table III. Electronic Energy (eV), up to 0.75 eV, of the Lowest Excited States of C_{60}^{n-} , ($n = 4, 5, 6$)^{a,b}

ES	EE	ES	EE	ES	EE	ES	EE
Anion C_{60}^{4-}							
1^1A_g	0.00	1^3T_{1g}	0.00 (14.23) ^c				
1^1A_u	0.14	1^3T_{1u}	0.20	1^5T_{1u}	0.16		
1^1H_g	0.15	1^3H_u	0.32	1^5T_{1g}	0.49		
2^1A_g	0.37	2^3T_{1u}	0.41	1^5H_g	0.54		
1^1H_u	0.53	1^3A_u	0.57				
		3^3T_{1u}	0.57				
		4^3T_{1u}	0.57				
		1^3H_g	0.74				
Anion C_{60}^{5-}							
		1^4A_g	0.00 (26.9) ^c				
1^2T_{1u}	0.01	1^4A_u	0.19	1^6T_{1u}	0.11		
1^2T_{1g}	0.30	1^4T_g	0.21	1^6T_{1g}	0.75		
2^2T_{1g}	0.46	1^4H_g	0.24				
1^2H_g	0.46	1^4H_u	0.40				
2^2T_{1u}	0.55	2^4H_u	0.72				
1^2A_g	0.60	1^4T_u	0.73				
3^2T_{1g}	0.60						
4^2T_{1g}	0.60						
Anion C_{60}^{6-}							
1^1A_g	0.00 (43.05) ^c						
1^1A_u	0.22	1^3A_u	0.24	1^5A_g	0.19	1^7A_u	0.01
2^1A_g	0.36	1^3T_{1u}	0.39	1^5T_{1g}	0.53		
1^1H_u	0.58	1^3H_u	0.42	1^5H_g	0.54		
3^1A_g	0.63	1^3H_g	0.62				
1^1H_g	0.74	1^3T_{1g}	0.72				

^aThe HE-SCF high-spin MOs (see text) are used in the calculations. ^bES, electronic state; EE, electronic energy. ^cThe energy relative to that of the neutral C_{60} molecule is in parentheses.

Table IV. Electronic Energy (eV), up to 0.75 eV, of the Lowest Excited States of C_{60}^{4-} ^a

ES ^b	energy ^c	ES ^b	energy ^c	ES ^b	energy ^c
1^1A_g	0.09 (0.09)	1^3T_{1g}	0.00 (0.00)		
1^1H_g	0.15 (0.15)	1^3T_{1u}	0.22 (0.22)	1^5T_{1u}	0.17 (0.17)
2^1A_g	0.22 (0.22)	1^3H_u	0.34 (0.34)	1^3T_{1g}	0.50 (0.50)
1^1A_u	0.36 (0.36)	2^3T_{1u}	0.43 (0.43)	1^5H_g	0.57 (0.57)
1^1H_u	0.56 (0.56)	1^3A_u	0.58 (0.58)		
		3^3T_{1u}	0.58 (0.58)		
		4^3T_{1u}	0.58 (0.58)		
		1^3H_g	0.75 (0.75)		

^aThe HE-SCF low-spin MOs (see text) are used in the calculations. ^bES, electronic state. ^cIn parentheses, we show the values of the electronic transition calculated with inclusion of the singly excited configurations arising from the h_u-t_{1u} space.

tribution of double excitation from the t_{1u} to the t_{1g} orbitals, the Hund principle does not hold necessarily. The trianion is calculated to have an electronic pattern rather similar to the bianion; the main difference is that the state of higher multiplicity, namely, 4A_u , is now the electronic ground state, in agreement with the Hund principle. The number of low-lying electronic states for the bi- and the trianion is similar.

In Table III, we list the energies of the lowest electronic states of tetra-, penta-, and hexaanions calculated on the basis of MOs obtained from a HE-SCF calculation of the proper high-spin configuration (vide supra). To evaluate the influence of the choice of the MOs, we also performed the calculations using the HE-SCF MOs obtained for low-spin configurations. The results obtained in this way for C_{60}^{4-} are shown in Table IV.

As it can be seen in Table III, starting from the tetraanion, the number of electronic states with excitation energy less than 0.75 eV increases dramatically. In C_{60}^{4-} , the calculation yields a triplet T_{1g} ground state accidentally degenerate with an A_g singlet state. There are also quintet states close to the electronic ground state. The pentaanion is calculated to have a pattern of electronic states whose density closely resembles that of the tetraanion. Once again the calculation yields a (quasi) degeneracy of the ground state as the two lowest states 1^4A_g and 1^2T_{1u} separated only by 0.01 eV. In the hexaanion, four possible multiplicities from singlet

Table V. Number of Electronic Levels ($E < 0.75$ eV) and Lowest Electronic Energy Gap

negative charge	no. of levels	ΔE_{0-1}	negative charge	no. of levels	ΔE_{0-1}
1	12	0.64	4	148	0.00
2	40	0.16	5	176	0.01
3	50	0.10	6	117	0.01

to septet are possible. Again, the two lowest electronic states, 1^1A_g and 1^7A_u , are quasi-degenerate.

In Table IV, we show the energies of the electronic states of C_{60}^{4-} calculated with low-spin MOs (vide supra). In parentheses, we give the energies calculated with the inclusion of the singly excited configurations arising from the h_u-t_{1u} space. As can be seen, these two different amounts of CI yield little or no difference with respect to the results obtained with high-spin MOs and reported in Table II. The same applies to the CI results of the penta- and hexaanion, which, for this reason, are not reported. Thus it appears that the electronic energies in the more charged anions are moderately sensitive, with respect to the monoanions, to the increase in the size of the CI matrix.

The calculations show that these species are characterized by a large number of energetically low-lying electronically excited states that are due to the presence in the neutral molecule of two sets of triply degenerate unoccupied MOs very close to each other, both of them available to the electrons of the dopant and their excitations. In Table V, we summarize the number of electronic levels calculated within 0.75 eV from the ground state, which is simply obtained by multiplying the symmetry degeneracy by the spin multiplicity and summing over all the electronic states. This number gives an idea of the remarkable high density of electronic states in Bf anions and especially in the tetra- and the pentaanions.

The large number of low-lying electronic states is expected to contribute in a notable way to the IR spectrum of these compounds, both directly and indirectly, by lending intensity to the vibrational levels of the electronic ground state. Thus, the infrared intensity distribution in the anions is expected to be quite different from that of the parent neutral molecule.

With the exception of the monoanion, the calculations also show that it is difficult to determine with certainty the multiplicity and the spatial symmetry of the electronic ground state of these species because of the quasi-degeneracy of the two lowest electronic states and of the approximations involved in these calculations. As we mentioned above, all the calculations were performed using the optimized structure of the neutral molecule, by this neglecting both the molecular expansion that occurs upon the introduction of each successive electron and the possible Jahn-Teller and pseudo-Jahn-Teller effects; the CI treatment comprises only a moderate number of determinants. The removal of these approximations can effectively modify the ordering of closely lying states. On the other hand, in this high-density regime of electronic states, no computational procedure, be it semiempirical or ab initio, can yield with absolute certainty either the level ordering or the exact energy of any electronic state.

Besides the computational difficulties, the comparison of theoretical results with experimental data is complicated by the fact that the energy ordering of the electronic states of the free anions may be modified by the counterions which are necessary to maintain electrical neutrality and to stabilize the crystal lattice of doped C_{60} . It is conceivable that the ordering of the electronic states can be modified by changing the nature of the counterions. Thus, one can expect that different dopants can yield C_{60} anions with different ground states and possibly with rather different properties.

The above considerations assume tacitly the Born-Oppenheimer (BO) approximation to be valid. Due to vibroelectronic interactions, the low-lying electronic excited states of C_{60} anions should mix to a significant degree with the fundamental vibrational levels of the electronic ground state that are located in the same region (up to 0.2 eV), leading to a breakdown of the BO approximation. It follows that these are ideal systems to study non-BO effects, such Jahn-Teller and pseudo-Jahn-Teller effects. Furthermore,

Table VI. Calculated Free Energy Changes for Isolated Molecules, Δg , Molecular Solvation Free Energy, Δg_{solv} , Total Free Energy Changes, Δg_{t} , and Electrochemical Standard Potentials, ϵ° , for the Reduction of Neutral Bf and Its Anions

	n_e						
	1	-1	-2	-3	-4	-5	-6
Δg , eV	0.00	-1.69	-0.16	5.00	14.24	26.91	43.05
Δg_{solv} , eV	0.00	-1.65	-6.58	-14.80	-26.32	-41.12	-59.21
Δg_{t} , eV	0.00	-3.34	-6.74	-9.80	-12.08	-14.21	-16.16
ϵ° , V	-1.10	-1.00	-1.38	-2.16	-2.31	-2.49	

an appropriate discussion of the nature of the ground state and of the infrared spectrum of these anions requires consideration of vibronic rather than solely electronic or vibrational states.

4.3. Relative Stability of Anions with Respect to the Neutral Fullerene. In Tables I and III we also report the calculated energies of the six anions in their ground states, measured with respect to the ground state of the neutral molecule. Comparing these energies, it appears that the electron affinity of C_{60} and of C_{60}^- is positive, while for the remaining anions the electron affinity is negative. Thus, in the gas phase, only C_{60}^- should be stable. Smalley et al.¹⁷ estimated from photoelectron spectra an EA of ca. 2.60–2.80 eV for C_{60} . This is consistent with the fact that NO_2 , which has an EA of 2.27 eV,¹⁸ does not extract an electron from C_{60}^- .¹⁹ This is in agreement also with the positive EA of C_{60} reported here and with its reaction chemistry, which is similar to that of electron-poor alkenes and arenes. Organometallic derivatives of C_{60} with Pt and Ru²⁰ and with Os²¹ have been reported.

In solution, the interaction with the solvent stabilizes all the anions with a solvation energy increasing with the charge. Thus anions with higher charges may be also observable in solution. The stability of these anions is not a surprise since their negative charge, per carbon atom, is ≤ 0.1 . A crude estimate of the average

solvation free energy per molecule Δg_{solv} can be obtained by the Born relation²²

$$\Delta g_{\text{solv}} = \frac{\Delta G_{\text{solv}}}{N} = -n_e^2 \left(\frac{e^2}{2R} \right) \left(1 - \frac{1}{D} \right) \quad (1)$$

where N is the Avogadro number, n_e and R are the number of negative charges and the radius of the sphere which represents the solute molecule, respectively, and D is the dielectric constant of the solvent. The values of the solvation free energy of the six anions for a solvent with a dielectric constant of 50 and R equal to the radius of the fullerene (3.59 Å) plus the radius of a carbon atom (0.7 Å) are given in Table VI. Neglecting the entropy contributions, which are expected to have similar values in the isolated anions, the electronic energies relative to the neutral C_{60} can be taken as the average free energy change per molecule Δg . Thus, addition of the calculated electronic energies to the molecular solvation free energies yields the average molecular free energy change Δg_{t} , for the six anions. From these, taking into account the absolute potential for the reduction at the hydrogen electrode (4.44 V²³), we get the electrochemical standard potentials for the reductions of C_{60} and its anions. These standard potentials, which are listed in Table VI, fall in the range of -1 + -2 V. Keeping in mind their qualitative nature, these results suggest that Bf anions can be obtained by electrochemical reductions in proper solvents. Recently it has been reported^{24–26} that C_{60} anions have been prepared electrochemically, up to the tetraanion.²⁶ The observed^{24–26} reduction potentials $\epsilon^{1/2}$ follow a trend in qualitative agreement with the calculated standard potentials.

Acknowledgment. Financial support from the National Research Council (CNR Roma) is gratefully acknowledged.

(18) McDonald, R. N.; Chowdhury, A. K.; Setser, D. W. *J. Am. Chem. Soc.* **1980**, *102*, 6491–6498.

(19) Ervin, K. M.; Ho, J.; Lineberger, W. C. *J. Phys. Chem.* **1988**, *92*, 5405–5412.

(20) Fagan, P. J.; Calabrese, J. C.; Malone, B. *Science* **1991**, *252*, 1160–1161.

(21) Hawkins, J. M.; Meyer, A.; Lewis, T. A.; Loren, S.; Hollander, F. J. *Science* **1991**, *252*, 312–313.

(22) Bockris, M. O'M.; Reddy, A. K. N. *Modern Electrochemistry*; Plenum Press: New York, 1970; Vol. 1, pp 49–59.

(23) *Standard Potentials in Aqueous Solution*; Bard, A. J., Parson, R., Jordan, J., Eds.; Marcel Dekker, Inc.: New York, 1985; pp 18–19.

(24) Haufler, R. E.; Conceicao, J.; Chibanta, L. P. F.; Chai, Y.; Byrne, N. E.; Flanagan, S.; Haley, M. M.; O'Brien, S. C.; Pan, C.; Xiao, Z.; Billups, W. E.; Ciufolini, M. A.; Hauge, R. H.; Margrave, J. L.; Wilson, L. J.; Curl, R. F.; Smalley, R. E. *J. Phys. Chem.* **1990**, *94*, 8634–8636.

(25) Cox, D. M.; Behal, S.; Disko, M.; Gorun, S. M.; Greaney, M.; Hsu, C. S.; Kollin, E. B.; Millar, J.; Robbins, J.; Robbins, W.; Sherwood, R. D.; Tindall, P. *J. Am. Chem. Soc.* **1991**, *113*, 2940–2944.

(26) Dubois, D.; Kadish, K. M.; Flanagan, S.; Haufler, R. E.; Chibanta, L. P. F.; Wilson, L. J. *J. Am. Chem. Soc.* **1991**, *113*, 4364–4366.