An investigation of oxidation and reduction of C_{60}, the excited states, energy gaps and stability using semi-empirical and ab initio methods

J.D. Santos[a], E. Longo[b], C.A. Taft[c],*

[a]Universidade Estadual de Goiás-UEG, Departmento de Química, Av. Jucelino Kubitschek, CEP 75110-380, Anápolis, Goiás, Brazil
[b]Laboratório Interdisciplinar de Eletroquímica e Cerâmica, Departamento de Química, Universidade Federal de São Carlos, Caixa Postal 676, 13565-905, São Carlos, SP, Brazil
[c]Centro Brasileiro de Pesquisas Físicas, Rua Dr Xavier Sigaud 150, Rio de Janeiro, RJ CEP 22290-180, Brazil

Abstract

We have used semi-empirical and ab initio methods to investigate the various oxidation and reduction states of C_{60} with their respective more energetically stable excited states resulting from variations of the charge from $+12$ to -12 electrons in the system with singlet, doublet, triplet and quadruplet multiplicities. We have analysed the various conformations, energy variations, $|HOMO - LUMO|$, system charges, average interatomic distances as well as regions of minimum energies resulting from the simulation of the possible reaction routes. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords*: Ab initio methods; $|HOMO - LUMO|$; Reduction of C_{60}

1. Introduction

The discovery of superconductivity in doped fullerenes has stimulated investigations of the electronic structures [1] and possible interactions between the C_{60} species [2–5]. A variation of charge and multiplicity of C_{60} in which the Buckminster has a large electronic affinity as well as oxidations and reductions in the presence of atoms and molecules has been reported [5–11].

Reactions of electron transfer involving fullerene cations in the gaseous phase has also been studied [12–21] in the presence of other species. The vacancies of C_{60} has transformed it into a good electron acceptor in which reactions have been studied [10–19] which involve different charges on the the C_{60}^{n+} cation. C_{60} films were examined eletrochemically indicating that C_{60} can undergo ionizations resulting in changes of the charges on this species [22–27]. The transfer or withdrawal of electrons from the neutral species of C_{60} results in a redistribution of the electronic energy levels, $|HOMO - LUMO|$, such that electric propieties related to band gaps may be modified. The cause of the variety of the oxidation–reduction numbers is due to the great number of π-electrons. This solid state system has non-conventional optical and electric structures indicated by numerous experimental techniques. Some of these properties have been applied to electronic applications, contributing to the development of new technologies.

It is consequently important to better understand

---

* Corresponding author. Tel.: +55-21-586-7100; fax: +55-21-541-2047.
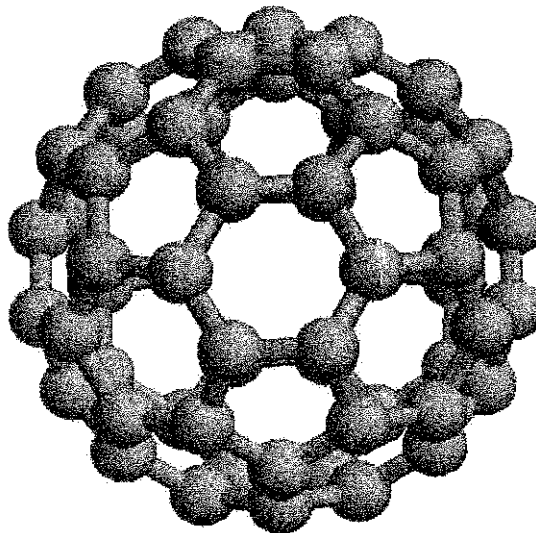
Fig. 1. The C_{60} molecule.

the ionization and excitation states of the [28–40] C_{60}. species. In the present work we do quantum mechanical calculations in order to analise the various oxidation and reduction states of C_{60} with their respective more energetically stable excited states resulting from a variation of the charge from $+12$ to -12 electrons in the system. The species with even charge values were analysed using singlet and triplet states whereas the odd species with doublets and quadruplets. We have compared the $|\text{HOMO} - \text{LUMO}|$ (GAP) using both semiempirical MNDO and ab initio methods with Huzinaga basis sets [38–40].

2. Computational methods

The C_{60} molecule of Fig. 1 was optimized for the ground state and the excited states using the MNDO method [39] in order to obtain the lowest total energy of the system adding or withdrawing systematically
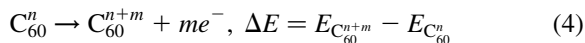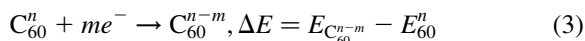
one electron from the system:

$$C_{60} + ne^- \rightarrow C_{60}^{n-} \tag{1}$$

and

$$C_{60} \rightarrow C_{60}^{n+} + ne^- \tag{2}$$

The first excited state was calculated for each case, in systems with even charges yielding energies for the singlet and triplet states. For systems with odd total charge, we determined the energies for the doublet and quadruplet states.

We analysed the exchange of energy from one species to another according to:

$$C_{60}^n + me^- \rightarrow C_{60}^{n-m}, \Delta E = E_{C_{60}^{n-m}} - E_{60}^n \tag{3}$$

$$C_{60}^n \rightarrow C_{60}^{n+m} + me^-, \ \Delta E = E_{C_{60}^{n+m}} - E_{C_{60}^n} \tag{4}$$

We investigated the variation of the energy levels $|\text{HOMO(H)}-\text{LUMO(L)}|$ $(\Delta|H\text{–}L| = |H\text{–}L|_{C_{60}^n} - |H\text{–}L|_{C_{60}^m})$ as well as a similar variation of the charge.

Table 1
Energy (eV) variations for $C_{60}^n (M = i_1, i_2) \overset{+1e^-}{\to} C_{60}^{n-1} (M = j_1, j_2)$ using the MNDO method

n (even)	ΔE_{ST}^n [a]	ΔE_{SD}^n [b]	ΔE_{SQ}^n [c]	ΔE_{TD}^n [d]	ΔE_{TQ}^n [e]	ΔE_{DQ}^{n-1} [f]
+12	+0.81	−43.05	−42.37	−43.85	−43.18	+0.68
+10	+1.32	−36.73	−36.08	−38.05	−37.40	+0.66
+8	+0.66	−32.69	−34.22	−33.35	−34.87	−1.52
+6	−0.74	−24.88	−24.28	−24.15	−24.27	−0.13
+4	−0.14	−18.29	−18.60	−18.15	−18.47	−0.32
+2	−0.13	−12.06	−9.66	−11.94	−9.53	+2.41
0	+3.23	−2.16	−0.34	−5.38	−2.88	+2.50
−2	−0.08	+3.31	+2.91	+3.39	+3.00	−0.40
−4	−0.33	+9.27	+9.22	+9.60	+9.55	−0.05
−6	−0.90	+15.07	+15.11	+15.97	+16.02	+0.05
−8	−1.90	+20.32	+24.99	+22.22	+21.88	−0.34
−10	−0.09	+27.87	+28.87	+27.96	+28.96	+0.99

n (odd)	ΔE_{DQ}^n [g]	ΔE_{DS}^n [h]	ΔE_{DT}^n [i]	ΔE_{QS}^n [j]	ΔE_{QT}^n [k]	ΔE_{ST}^{n-1} [l]
+11	+0.68	−39.30	−37.98	−39.98	−38.66	+1.32
+9	+0.66	−32.69	−34.22	−33.35	−34.87	−1.52
+7	+0.22	−26.84	−27.58	−27.06	−27.80	−0.74
+5	−0.13	−21.13	−21.26	−21.00	−21.14	−0.14
+3	−0.32	−15.02	−15.15	−14.70	−14.586	−0.13
+1	+2.41	−9.49	−6.27	−11.90	−8.67	+3.23
−1	+2.50	+0.34	+0.25	−2.16	−2.24	−0.08
−3	−0.40	+6.28	+5.95	+6.68	+6.35	−0.33
−5	−0.05	+13.15	+12.25	+13.20	+12.30	−0.90
−7	+0.05	+20.63	+18.73	+20.58	+18.68	−1.90
−9	−0.34	+24.65	+24.56	+24.99	+24.90	−0.09
−11	+0.99	+31.25	+32.01	+30.250	+31.013	+0.76

[a] ΔE_{ST}^n indicates variation of the energy due to transition of the system from a singlet state of charge n to a triplet state of the same charge.
[b] ΔE_{SD}^n indicates variation of the energy due to transition of the system from a singlet state of charge n to a quartet state of charge $n - 1$.
[c] ΔE_{SQ}^n indicates variation of the energy due to transition of the system from a singlet state of charge n to a quartet t state of charge $n - 1$.
[d] ΔE_{TD}^n indicates variation of the energy due to transition of the system from a triplet state of charge n to a doublet state charge $n - 1$.
[e] ΔE_{TQ}^n indicates variation of the energy due to transition of the system from a triplet state of charge n to a quartet t state charge $n - 1$.
[f] ΔE_{DQ}^{n-1} indicates variation of the energy due to transition of the system from a doublet state of charge n to a quartet t state charge $n - 1$.
[g] ΔE_{DQ}^n indicates variation of the energy due to transition of the system from a doublet state of charge n to a quartet state charge n.
[h] ΔE_{DS}^n indicates variation of the energy due to transition of the system from a doublet state of charge n to a singlet state charge $n - 1$.
[i] ΔE_{DT}^n indicates variation of the energy due to transition of the system from a doublet state of charge n to a triplet state charge $n - 1$.
[j] ΔE_{QS}^n indicates variation of the energy due to transition of the system from a quartet state of charge n to a singlet state charge $n - 1$.
[k] ΔE_{QT}^n indicates variation of the energy due to transition of the system from a quartet state of charge n to a triplet state charge $n - 1$.
[l] ΔE_{ST}^{n-1} indicates variation of the energy due to transition of the system from a singlet state of charge $n - 1$ to a triplet state of charge $n - 1$.

We have compared the results using the quantum mechanical ab initio methods (contracted Huzinaga basis) with those obtained from the semiempÍrical MNDO method. The simulations originated from a C_{60}^{+12} structure in the singlet and triplet states where they were optimized including a charge (-1) in the system. The new species was analysed by investigating its conformation, energy variation, charges, molecular levels as well as average interatomic distances. The general equations for each system are:

$$\Delta E_{i_1 i_2} \quad \begin{matrix} C_{60}^n (M = i_2) \\ C_{60}^n (M = i_2) \end{matrix} \overset{+1e^-}{\to} \begin{bmatrix} C_{60}^{n-1} (M = j_2) \\ C_{60}^{n-1} (M = j_1) \end{bmatrix}$$

$$\Delta E_{i_1 j_1}$$
$$\Delta E_{i_1 j_2}$$
$$\Delta E_{j_1 j_2}$$
$$\Delta E_{i_2 j_2}$$
$$\Delta E_{i_2 j_1} \tag{5}$$

Table 2
Energy (eV) variations for $C_{60}^n (M = i_1, i_2) \overset{+1e^-}{\to} C_{60}^{n-1} (M = j_1, j_2)$, using ab initio methods

n (even)	ΔE_{ST}^n [a]	ΔE_{SD}^n [b]	ΔE_{SQ}^n [c]	ΔE_{TD}^n [d]	ΔE_{TQ}^n [e]	ΔE_{DQ}^{n-1} [f]
0	+1.65	−3.55	−5.40	−5.20	−7.06	−1.85
−2	−0.55	+3.14	+2.59	+3.69	+3.14	−0.54
−4	−0.95	+9.12	+9.31	+10.07	+10.26	+0.19
−6	−0.04	+17.00	+16.84	+17.04	+16.88	−0.16
−8	−0.72	+23.46	+22.70	+24.178	23.42	−0.75
−10	−0.59	+29.67	+29.99	+30.27	+30.59	+0.32

n (odd)	ΔE_{DQ}^n [g]	ΔE_{DS}^n [h]	ΔE_{DT}^n [i]	ΔE_{QS}^n [j]	ΔE_{QT}^n [k]	ΔE_{ST}^{n-1} [l]
+1		−9.51	−7.86	–	–	+1.65
−1	−1.85	+0.68	+0.14	+2.54	+1.99	−0.55
−3	−0.54	+7.25	+6.30	+7.79	6.85	−0.95
−5	+0.19	+14.08	+14.05	+13.89	+13.86	−0.04
−7	−0.16	+20.34	+19.62	+20.50	+19.78	−0.72
−9	−0.75	+27.06	+26.46	+27.81	+27.21	−0.59
−11	+0.32	+34.21	+32.53	+33.89	+32.21	−1.68

[a] ΔE_{ST}^n indicates variation of the energy due to transition of the system from a singlet state of charge n to a triplet state of the same charge.
[b] ΔE_{SD}^n indicates variation of the energy due to transition of the system from a singlet state of charge n to a quartet state of charge $n − 1$.
[c] ΔE_{SQ}^n indicates variation of the energy due to transition of the system from a singlet state of charge n to a quartet t state charge $n − 1$.
[d] ΔE_{TD}^n indicates variation of the energy due to transition of the system from a triplet state of charge n to a doublet state charge $n − 1$.
[e] ΔE_{TQ}^n indicates variation of the energy due to transition of the system from a triplet state of charge n to a quartet t state charge $n − 1$.
[f] ΔE_{DQ}^{n-1} indicates variation of the energy due to transition of the system from a doublet state of charge n to a quartet t state charge $n − 1$.
[g] ΔE_{DQ}^n indicates variation of the energy due to transition of the system from a doublet state of charge n to a quartet state charge n.
[h] ΔE_{DS}^n indicates variation of the energy due to transition of the system from a doublet state of charge n to a singlet state charge $n − 1$.
[i] ΔE_{DT}^n indicates variation of the energy due to transition of the system from a doublet state of charge n to a triplet state charge $n − 1$.
[j] ΔE_{QS}^n indicates variation of the energy due to transition of the system from a quartet state of charge n to a singlet state charge $n − 1$.
[k] ΔE_{QT}^n indicates variation of the energy due to transition of the system from a quartet state of charge n to a triplet state charge $n − 1$.
[l] ΔE_{ST}^{n-1} indicates variation of the energy due to transition of the system from a singlet state of charge $n − 1$ to a triplet state of charge $n − 1$.

Here, i_1, i_2 are the multiplicities of the initial excited states and j_1, j_2 are the final states where the subscript $M = 1$ refers to the singlet state (S), $M = 2$ to the doublet state (D), $M = 3$ to the triplet state (T) and $M = 4$ to the quadruplet state (Q).

Analysing Eq. (5) we note that there are six possibilities for the variation of the energy as a function of the changes of state which are: $\Delta E_{i_1 i_2}^n$, $\Delta E_{j_1 j_2}^{n-1}$, $\Delta E_{i_1 j_1}^n$, $\Delta E_{i_1 j_2}^n$, $\Delta E_{i_2 j_1}^n$, $\Delta E_{i_2 j_2}^n$. The superscript (n) of ΔE refers to the magnitude of the charge.

3. Results and discussion

The energetic differences resulting from our MNDO and ab initio calculations are given in Tables 1 and 2, respectively. These two tables illustrate energetic variations for C_{60}^n molecules with multiplicity of i_1 or i_2. When this species is reduced we obtain C_{60}^{-1}, which as has a multiplicity of j_1 or j_2, and the variations of the possible routes through which the reaction could be simulated. In both tables the results were separated in two sections, i.e. one section where the initial system has even charges with singlet or triplet multiplicities and another section containing odd charges which could be initially in the doublet or quadruplet states. Consequently, the initial molecules with even charges (positive or negative), could proceed via three routes if they are in the singlet state, i.e. change multiplicity to the triplet state (ΔE_{ST}), reduction to a doublet (ΔE_{SD}) or a quadruplet (ΔE_{SQ}) state. Notwithstanding, if they are initially in the triplet state, they may be reduced to doublet (ΔE_{TD}) or a quadruplet (ΔE_{TQ}) state. After reduction, the C_{60}^{n-1} molecule with odd charge can have a doublet or quadruplet multiplicity (ΔE_{DQ}) which could be reduced to the singlet (ΔE_{DS}) or triplet (ΔE_{DT}) state,

Table 3

Average energies (eV) per charge $\overline{\Delta E_{ij}^n} = (\Delta E_{ij}^n/n)$, using the MNDO method for the reactions $C_{60}^n (M = i_1, i_2) \overset{+1e}{\rightarrow} C_{60}^{n-1} (M = j_1, j_2)$

n (even)	$\overline{\Delta E_{SD}^n}$ [a]	$\overline{\Delta E_{SQ}^n}$ [b]	$\overline{\Delta E_{TD}^n}$ [c]	$\overline{\Delta E_{TQ}^n}$ [d]
+12	−3.59	−3.53	−3.65	−3.65
+10	−3.67	−3.60	−3.80	−3.74
+8	−4.06	−4.02	−3.86	−3.83
+6	−4.15	−4.05	−4.03	−4.05
+4	−4.57	−4.65	−4.65	−4.62
+2	−6.03	−4.83	−5.97	−4.76
0	−2.16	+0.34	−5.38	−2.88
−2	+1.66	+1.46	+1.69	+1.50
−4	+2.32	+2.30	+2.40	+2.39
−6	+2.51	+2.52	+2.66	+2.67
−8	+2.54	+3.12	+2.78	+2.73
−10	+2.79	+2.88	+2.79	+2.89

n (odd)	$\overline{\Delta E_{DS}^n}$ [e]	$\overline{\Delta E_{DT}^n}$ [f]	$\overline{\Delta E_{QS}^n}$ [g]	$\overline{\Delta E_{QT}^n}$ [h]
+11	−3.57	−3.45	−3.63	−3.51
+9	−3.63	−3.80	−3.70	−3.87
+7	−3.83	−3.94	−3.87	−3.97
+5	−4.23	−4.25	−4.20	−4.23
+3	−5.00	−5.05	−4.90	−4.86
+1	−9.49	−6.27	−11.90	−8.67
−1	+0.34	+0.25	−2.16	−2.24
−3	+2.09	+1.98	+2.22	+2.11
−5	+2.63	+2.45	+2.64	+2.46
−7	+2.96	+2.67	+2.94	+2.66
−9	+2.73	+2.72	+2.77	+2.76
−11	+2.84	+2.91	+2.75	+2.81

[a] $\overline{\Delta E_{SD}^n}$ average variation of the energy per charge due to the transition of the system from a singlet state of charge n to a doublet state of charge $n-1$.

[b] $\overline{\Delta E_{SQ}^n}$ average variation of the energy per charge due to the transition of the system from a singlet state of charge n to a quartet state of charge $n-1$.

[c] $\overline{\Delta E_{TD}^n}$ average variation of the energy per charge due to the transition of the system from a triplet state of charge n to a doublet state of charge $n-1$.

[d] $\overline{\Delta E_{TQ}^n}$ average variation of the energy per charge due to the transition of the system from a triplet state of charge n to a quartet state of charge $n-1$.

[e] $\overline{\Delta E_{DS}^n}$ average variation of the energy per charge due to the transition of the system from a doublet state of charge n to a singlet state of charge $n-1$.

[f] $\overline{\Delta E_{DT}^n}$ average variation of the energy per charge due to the transition of the system from a doublet state of charge n to a triplet state of charge $n-1$.

[g] $\overline{\Delta E_{QS}^n}$ average variation of the energy per charge due to the transition of the system from a quadruplet state of charge n to a singlet state of charge $n-1$.

[h] $\overline{\Delta E_{QT}^n}$ average variation of the energy per charge due to the transition of the system from a quadruplet state of charge n to a triplet state of charge $n-1$.

Table 4

Average variations of the energies (eV) per charge $\Delta E_{ij}^n = (\Delta E_{ij}^n/n)$, using ab initio methods for the reactions $C_{60}^n (M = i_1, i_2) \overset{+1e}{\rightarrow} C_{60}^{n-1} (M = j_1, j_2)$

n (even)	$\overline{\Delta E_{SD}^n}$ [a]	$\overline{\Delta E_{SQ}^n}$ [b]	$\overline{\Delta E_{TD}^n}$ [c]	$\overline{\Delta E_{TQ}^n}$ [d]
0	−3.55	−5.40	−5.20	−7.06
−2	+1.57	+1.29	+1.85	+1.57
−4	+2.28	+2.33	+2.52	+2.56
−6	+2.83	+2.80	+2.84	+2.81
−8	+2.93	+2.84	+3.02	+2.93
−10	+2.96	+2.99	+3.02	+3.06

n (odd)	$\overline{\Delta E_{DS}^n}$ [e]	$\overline{\Delta E_{DT}^n}$ [f]	$\overline{\Delta E_{QS}^n}$ [g]	$\overline{\Delta E_{QT}^n}$ [h]
+1	−9.51	−7.86	–	–
−1	+0.68	+0.14	+2.54	+1.99
−3	+2.42	+2.10	+2.59	+2.28
−5	+2.82	+2.81	+2.64	+2.46
−7	+2.90	+2.80	+2.92	+2.83
−9	+3.00	+2.94	+3.09	+3.02
−11	+3.11	+2.95	+3.08	+2.92

[a] $\overline{\Delta E_{SD}^n}$ average variation of the energy per charge due to the transition from a doublet state of charge n to a quartet state of charge $n-1$.

[b] $\overline{\Delta E_{SQ}^n}$ average variation of the energy per charge due to the transition from a singlett state of charge n to a quadruplet state of charge $n-1$.

[c] $\overline{\Delta E_{TD}^n}$ average variation of the energy per charge due to the transition from a triplet state of charge n to a doublet state of charge $n-1$.

[d] $\overline{\Delta E_{TQ}^n}$ average variation of the energy per charge due to the transition from a triplet state of charge n to a quadruplet state of charge $n-1$.

[e] $\overline{\Delta E_{DS}^n}$ average variation of the energy per charge due to the transition from a doublet state of charge n to a singlet state of charge $n-1$.

[f] $\overline{\Delta E_{DT}^n}$ average variation of the energy per charge due to the transition from a doublet state of charge n to a triplet state of charge $n-1$.

[g] $\overline{\Delta E_{QS}^n}$ average variation of the energy per charge due to the transition from a quadruplet state of charge n to a singlet state of charge $n-1$.

[h] $\overline{\Delta E_{QT}^n}$ average variation of the energy per charge due to the transition from a quadruplet state of charge n to a triplet state of charge $n-1$.

if it is initially in the doublet state, otherwise it could have ΔE_{QS}, ΔE_{QT} variations.

The values of the variations of the systems with positive charge when reduced are negative, indicating that the addition of an electron increases the stability of the system, for even as well as for odd charges
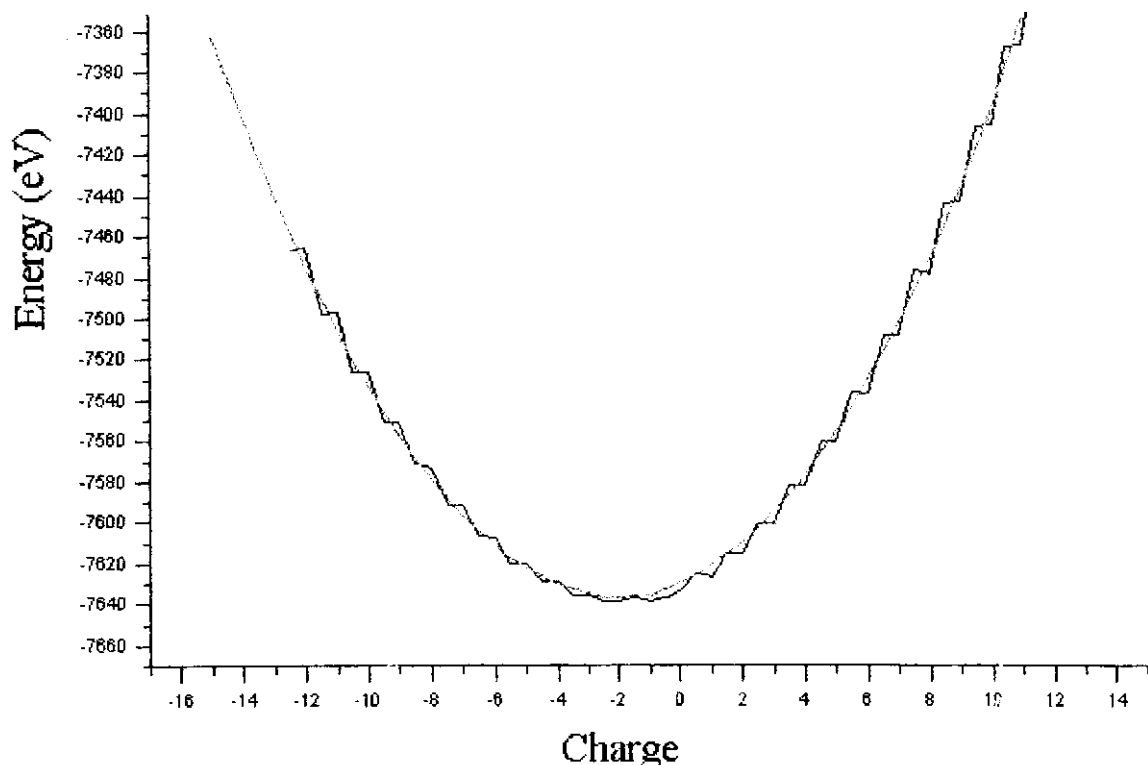
Fig. 2. Total energy variations for $C_{60} \pm ne^- \rightarrow C_{60}^{\pm n}$, where n varies from -12 to $+12$, with multiplicities ($M = 1, 2, 3, 4$) using the MNDO method.

using both MNDO and ab initio methods. When the consecutive reductions lead to negative charges the variations remain negative until the reduction of C_{60}^{-1} to C_{60}^{-2}, whereas they become positive for systems with odd as well as even charges.

Analyzing the results of Tables 1 and 2 we observe that the singlet excitation to the triplet (even n) state only occurs for negative ΔE_{ST} whereas there will be a competition to occupy less energetic levels among the different states, i.e. ΔE_{SD}, ΔE_{SQ}, ΔE_{TD}, ΔE_{TQ}. Similar reasoning can be made for the excitation of the doublet to the quadruplet (odd n) state.

Tables 3 and 4 illustrate the average variations of the energies per charge for the reactions in which the reductions occur, for systems with even and odd as well as positive and negative charges. These tables indicate that the simulated reactions could lead to more stable states. The most stable electron transfer with change of multiplicity is that of the quadruplet to the singlet state. The variations of energies related

only to the change of multiplicities in systems with the same charge are positive.

Analysing Tables 3 and 4 we observe that in the regions of positive charge (odd or even), the variations of the energies per charge are negative. Figs. 2 and 3 indicate that from C_{60}^0 to C_{60}^{-6} yields a region of minimum energy facilitating the transfer of charge for the buckyball, in agreement with experimental results [30]. In order to add more electrons to C_{60} would involve a large quantity of energy that would difficult the electron transfer process.

Analysing the complete process from C_{60}^{+12} to C_{60}^{-12}, one arrives at the conclusion that starting from C_{60}^0, the oxidation and reduction process indicates that the variation rate of energy as a function of withdrawal or donation of electrons ($\Delta E / \Delta n$), is larger for oxidation.

In Fig. 2, we observe that the curve obtained is parabolic, in which the region of the minimum energy is close to the systems with charges in the region (-3)
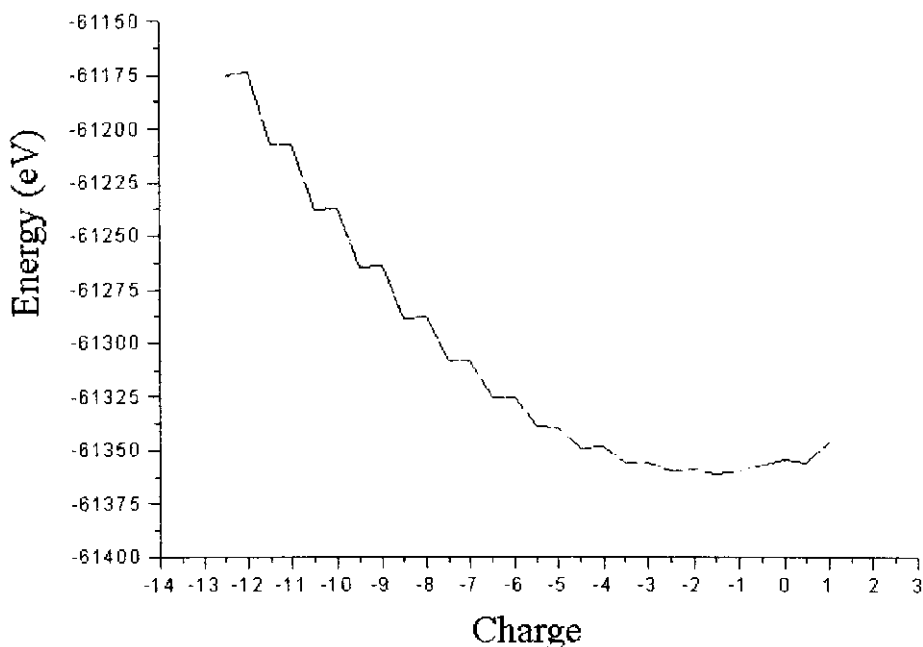
Fig. 3. Total energy for variations $C_{60} \pm ne^- \rightarrow C_{60}^{\pm n}$, where $\bar{n}$ varies from -12 to $+1$, with multiplicities ($M = 1, 2, 3, 4$) using the ab initio method.

to (-1), whereas we observe that there exist the possibility that these reduced systems could have unpaired electrons, such as doublets, triplets or quadruplets, increasing thus the reactivity of such a system, if it enter in contact with other molecules or atoms.

The variations of distances, charges and $|HOMO - LUMO|$ are illustrated in Figs. 3 and 4 and Table 2,
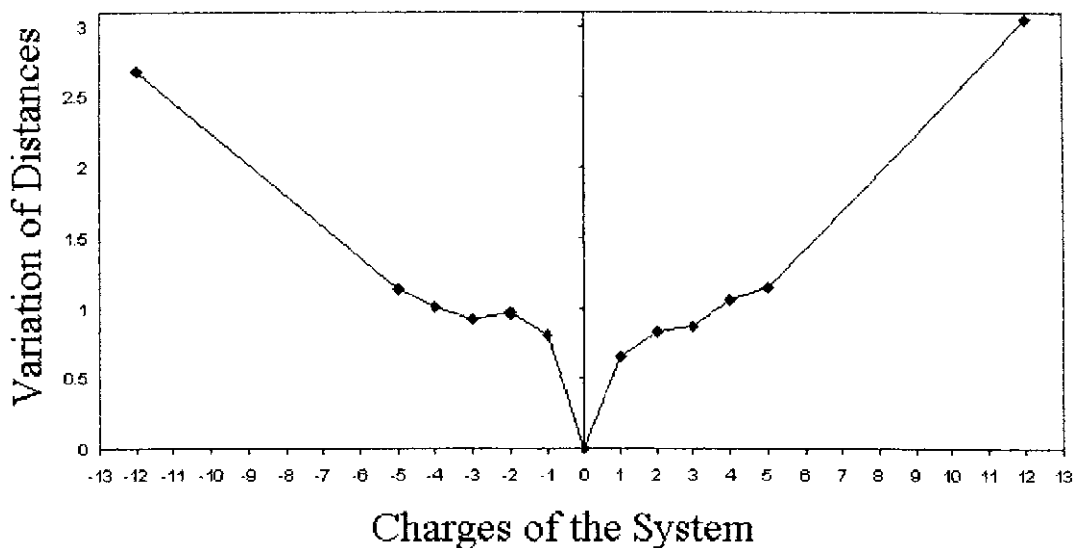
Fig. 4. Average of the percent variations of the distances as a function of the charges on C_{60}^n, $n = +12$ to -12.
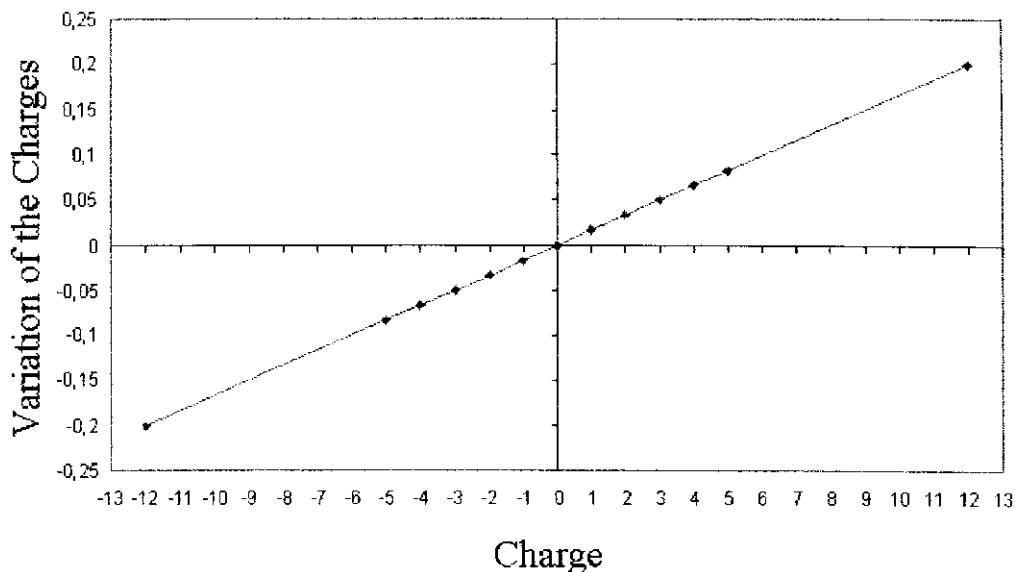
Fig. 5. Average of the variations of the charges of the system C_{60}^{n} as a function of reduction or oxidation, where $n = +12$ to -12.

respectively. There is controversy regarding the energy of the ground state of C_{60}^{-2} and C_{60}^{-3}. Experimental work indicate that for the C_{60}^{-2} state the triplet is the most stable state, in contrast to the doublet for the C_{60}^{-3} state. In this work we observed the triplet state for C_{60}^{-2} and quadruplet for the C_{60}^{-3}. This result for C_{60}^{-3} is in agreement with previous theoretical calculations published in the literature.

Fig. 4 shows that after reduction or oxidation of C_{60}, of ± 12 eletrons, the interatomic distance increases slightly $\sim 3\%$ at most. This trend repeats itself with the same intensity whether 12 electrons are added or withdrawn from the system. For C_{60}^{+12} or C_{60}^{-12} the interatomic distances vary between 1474 and 1399 Å. Such a molecule is a conglomerate of hexagons and pentagons where ressonant structures exist such as carbon sp^2. In general the average interatomic distances increase at most to 1518 Å. Among the averages of the percent variations of distances, one should take into consideration that the C_{60} molecule

Table 5

Distribution of the systems as a function of the number of filled and partially-filled levels with their multiplicities: singlet, doublet, triplet and quadruplet (P12S, P10S, P8S, P6S, P4S, P2S indicates C_{60} with positive charges (P), $+12$, $+10$, $+8$, $+6$, $+4$, $+2$, singlet statet (S); P12T, P10T, P8T, P6T, P4T, P2T indicates C_{60} with positive charges (P), $+12$, $+10$, $+8$, $+6$, $+4$, $+2$, triplet state (T); P11D, P9D, P7D, P5D, P3D, P1D indicates C_{60} with positive charges (P), $+11$, $+9$, $+7$, $+5$, $+3$, $+1$, doublet state (D); P11Q, P9Q, P7Q, P5Q, P3Q, P1Q indicates C_{60} with positive charges (P), $+11$, $+9$, $+7$, $+5$, $+3$, $+1$, quartet state (Q); ZS indicates neutral C_{60} (Z), singlet state (S); ZT indicates neutral C_{60} (Z), triplet state (T); N2S, N4S, N6S, N8S, N10S, N12S indicates C_{60} with negative charges (N), -2, -4, -6, -8, -10, -12, singlet state (S); N2T, N4T, N6T, N8T, N10T, N12T indicates C_{60} with negative charges (N), -2, -4, -6, -8, -10, -12, triplet state (T); N1D, N3D, N5D, N7D, N9D, N11D indicates C_{60} with negative charges (N), -1, -3, -5, -7, -9, -11, doublet state (D); N1Q, N3Q, N5Q, N7Q, N9Q, N11Q indicates C_{60} with negative charges (N), -1, -3, -5, -7, -9, -11, quartet state (Q); (*) indicate systems with the lowest energies (charges $+12$ to -12))

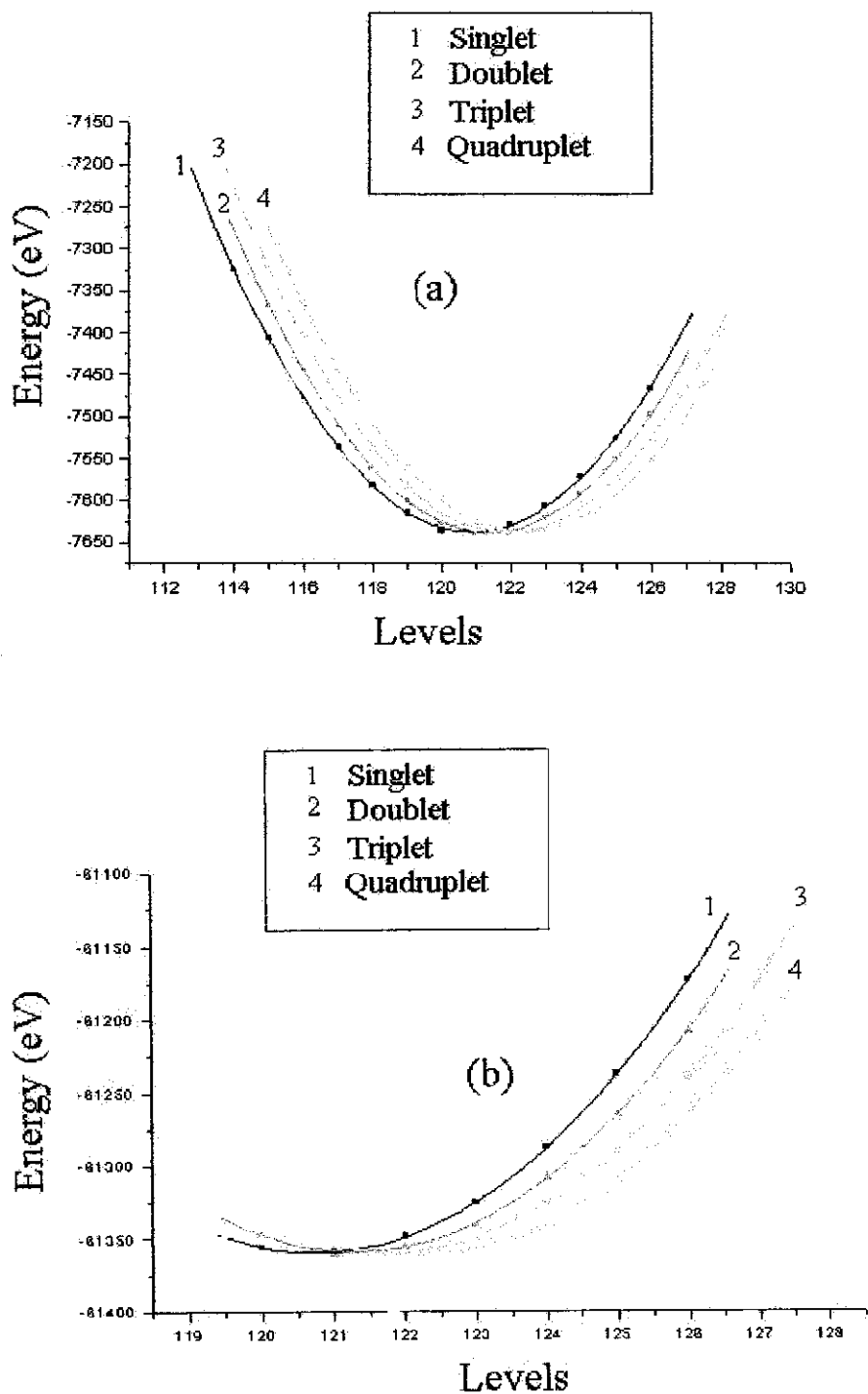| N/M	114	115	116	117	118	119	120	121	122	123	124	125	126	127
0	* P12S	* P10S	P8S	P6S	P4S	P2S	* ZS	N2S	N4S	N6S	N8S	N10S	* N12S	
1	–	* P11D	* P9D	* P7D	P5D	P3D	* P1D	* N1D	N3D	N5D	* N7D	N9D	* N11D	
2	–	P12T	P10T	* P8T	* P6T	* P4T	* P2T	ZT	* N2T	* N4T	* N6T	* N8T	* N10T	N12T
3	–		P11Q	P9Q	P7Q	* P5Q	* P3Q	P1Q	N1Q	* N3Q	* N5Q	N7Q	* N9Q	N11Q

Fig. 6. The variation of total energy as a function of the number of filled levels and multiplicities ($M = 1, 2, 3, 4$) (a) MNDO (b) Ab initio.

is a closed symmetrical geometrical form. In this manner, if there is any increase of the distances in one region there may be a reduction in another region.

In the graph of Fig. 5, we observe the average variations of the charges in the molecules C_{60}^n, $n = +12$ to -12, yielding equal negative and positive structures such that the evolution of the average values have a linear behaviour whereas Average charge $= \{\sum charges/no. \ of \ atoms\}$. We note that if the averages are positive, then the number of atoms with positive charge exceed those of the negative charges or these have a weight, whose magnitude is greater that that of the atoms with negative charges.

Table 5 describes 50 systems investigated, distributed in numbers of filled and partially filled levels, number of unpaired electrons and multiplicity whereas the prefix P indicates positive, Z indicates zero, N indicates negative and the systems with pairs of charges can be singlets or triplets and the odd systems can be doublets or quadruplets. Starting with the oxidized $+12$ singlet system and reducing continuously to -12, we have the route of least energy ([*] in Table 5) along which all these reductions can occur. Only four of these have the singlet state, for the doublet state we find seven systems with stability. The triplet state has nine systems and the quadruplet has five systems with lower energy. We thus have 25

systems with lower energies with their respective multiplicities.

The graph of Fig. 6 indicates the energies as a function of the number of filled and partially filled levels which yields the variation of energy with the singlet, doublet, triplet and quadruplet multiplicities indicating the regions of minimum energies determined by molecules such as. C_{60}^- (doublet), C_{60}^{-2} (triplet), C_{60}^{-3} (quadruplet) and C_{60}^0 (singlet). Similar results are shown in Fig. 7, whereas the surface and curves at each level are given as a function of the energy, number of levels and multiplicity. On the surface one observes a minimum near the region determined by the number of levels (120–122) whereas the level of least energy is found near the singlet and doublet multiplicities.

The graphs of Figs. 8–10 show variations of the $|HOMO - LUMO|$ as a function of the singlet, doublet, triplet and quadruplet states as well as the number of filled and partially filled levels. Fig. 9 indicates that the maximum values are always in the region of 120 levels (filled or partially filled), determined by the molecules $C_{60}^0(S)$, $C_{60}^{+1}(D)$, $C_{60}^{+2}(T)$, $C_{60}^{+3}(Q)$. The $|HOMO - LUMO|$ is high in the singlet state but decreases in the doublet, triplet and quadruplet states where the values diminish to less than 2 eV. The least decrease is observed in the double state $C_{60}^{+1}(D)$.
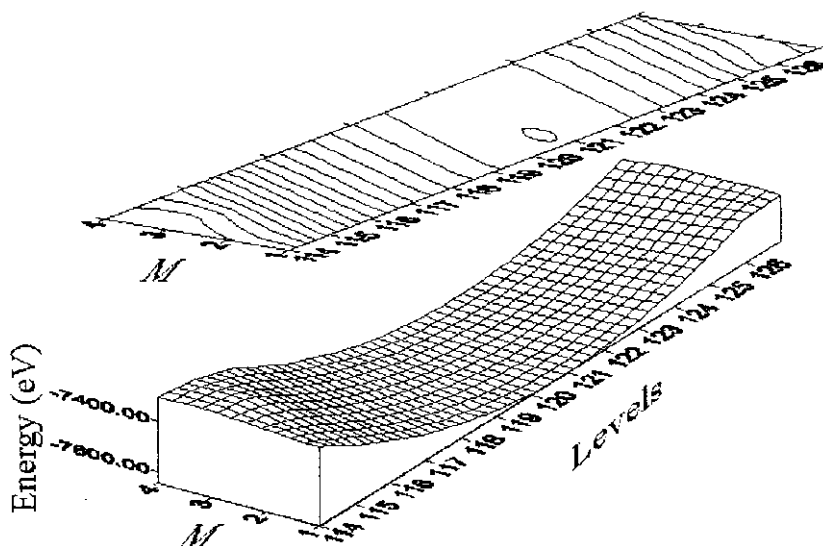
The general trend indicates that, independent of the

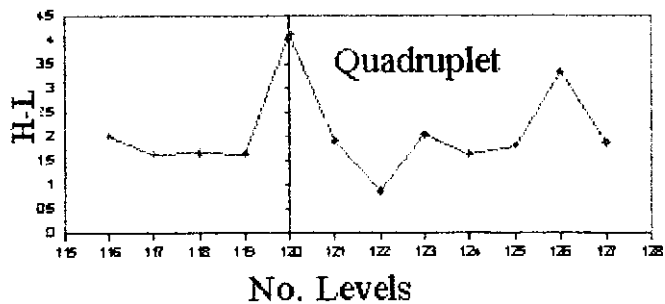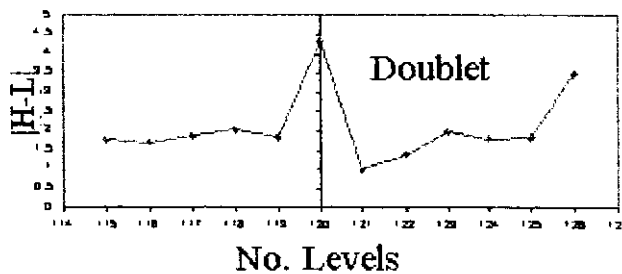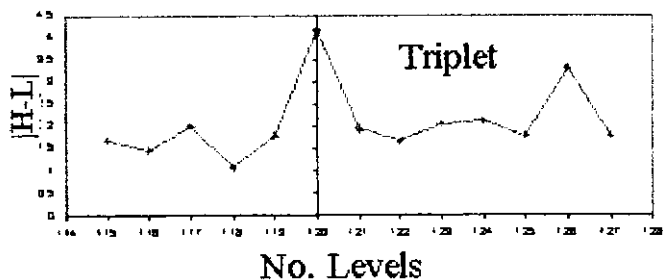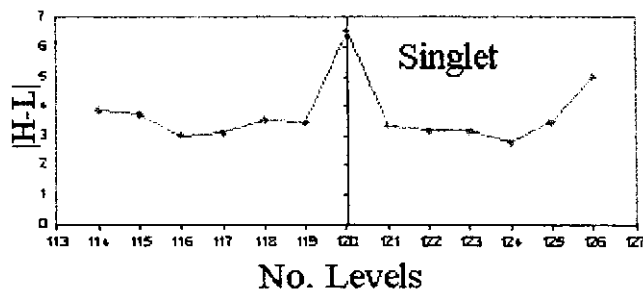Fig. 7. Total energy (eV) vs multiplicities vs number of filled levels.

Fig. 8. Variation of $|\text{HOMO(H)} - \text{LUMO(L)}|$ as a function of the filled and partially filled levels with singlet, doublet, triplet and quadruplet C_{60}^{n}, multiplicities using the MNDO method.
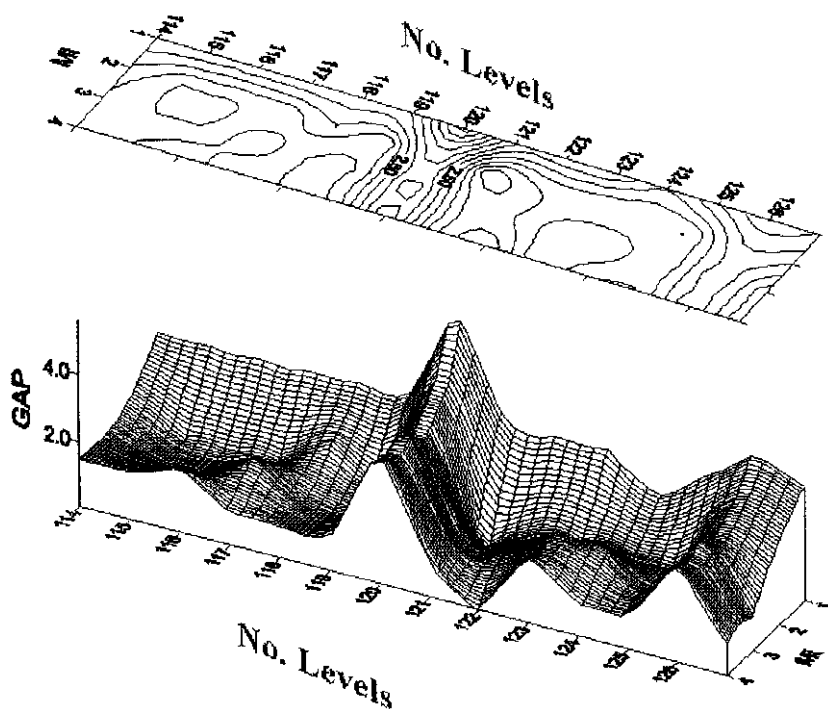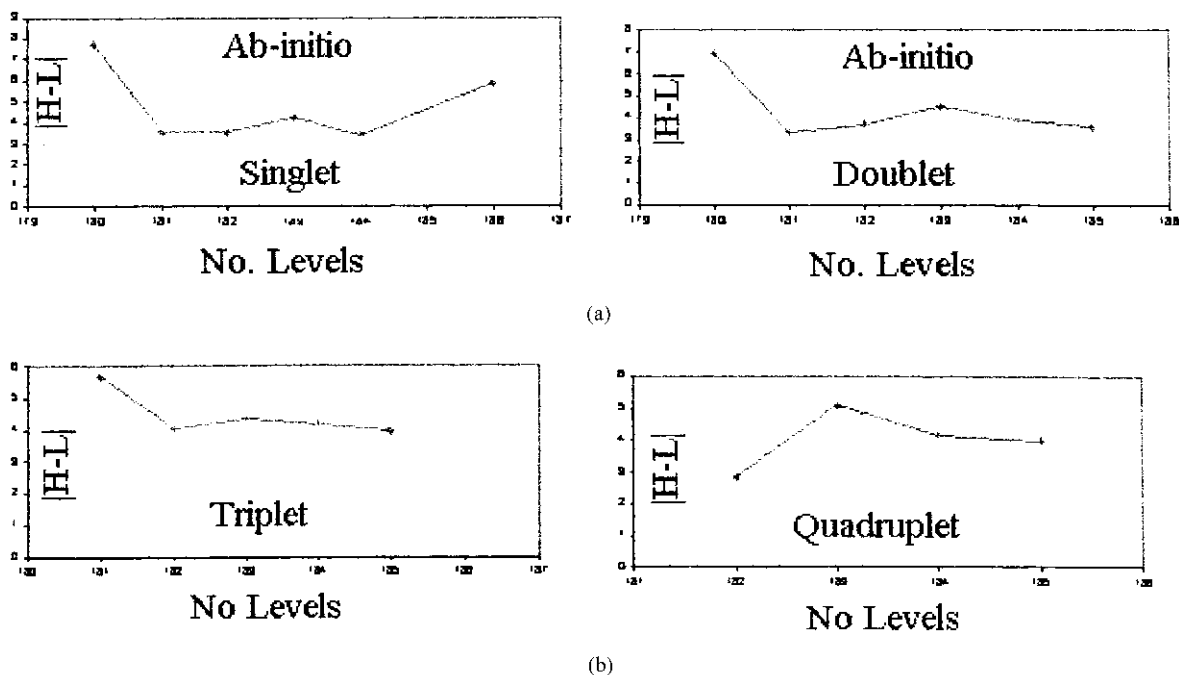
Fig. 9. Variation of $\left|\text{HOMO(H)} - \text{LUMO(L)}\right|$ vs number of levels vs ($M = 1, 2, 3, 4$) for the systems C_{60}^{n}, $n = +12$ à -12.

(a)

(b)

Fig. 10. Variation of $\left|\text{HOMO(H)} - \text{LUMO(L)}\right|$ as a function of the number of filled and partially filled levels, with (a) singlet and doublet, (b) triplet and quadruplet multiplicities, using the ab initio method.

state of oxidation or reduction, the largest $|\text{HOMO} - \text{LUMO}|$ correspond to the singlet state. The important regions are near the 120 number of filled and partially filled levels. From the surfaces and Tables described above we can follow, starting from the C_{60}^{+12} surface and reducing continuously the system, the route on the surface on which the reactions occur leading to the C_{60}^{-12} species.

Acknowledgements

References

[1] C.A. Taft, T.C. Guimarães, A.C. Pavão, W.A. Lester Jr., Int. Rev. Phys. Chem. 18 (1999) 163.

[2] D.K. Bohme, Int. Rev. Phys. Chem. 13 (1994) 163.

[3] V.V.Y. Kriyno, Y.I.L. Shamovsk, E.E. Tornau, A. Rosengren, Synth. Met. 70 (1995) 1493.

[4] E. Tosatti, N. Manini, Chem. Phys. Lett. 223 (1994) 61.

[5] R.T. Fu, K. Nassi, W. Ghang, H.J. Ye, X. Sun, Synth. Met. 70 (1995) 1505.

[6] R.A. Evarestov, D.K. Grigorev, V.A. Veryazov, Fiz. Tverd Tela 37 (1995) 3328.

[7] G.P. Zhang, X. Sun, T.F. George, J. Chem. Phys. 106 (1997) 6398.

[8] G. Duskesas, S. Larsson, Theor. Chem. Acc. 97 (1997) 110.

[9] M.C. Bohm, J. Schulte, R. Schlogl, Z. Naturforsch., A 52 (1997) 331.

[10] O.V. Boltalina, E.V. Dashkova, L.N. Sidokov, Chem. Phys. Lett. 256 (1996) 253.

[11] R.J.O.M. Hoofman, G.P. Vanderlaan, M.P. Dehaas, Synth. Met. 86 (1997) 2355.

[12] H. Iikura, S. Mori, M. Sawamura, J. Org. Chem. 62 (1997) 7912.

[13] P. Jenniskens, G. Mulas, I. Porceddu, Astrophysics 327 (1997) 337.

[14] J.Z. Li, J. Univ. Sci. Technol. B 5 (1998) 241.

[15] S. Okada, S. Saito, A. Oshiyama, Phys. Rev. Lett. 83 (1999) 1986.

[16] M.M. Garcia, R. Cruz-almanza, F. Lara-ochoa, et al., Fullerene Sci. Technol. 7 (1999) 897.

[17] W.T. Ford, T. Nishioka, F. Qiu, J. Org. Chem. 64 (1999) 6257.

[18] X.F. Tan, D.I. Schuster, S.R. Wilson, Abstr. Pap. Am. Chem. Soc. 217 (1999) 195.

[19] W.J. Wang, H.S. Chiu, L.J. Yu, B.C. Wang, Synth. Met. 70 (1965) 195.

[20] N. Minami, Kazaoui, R. Ross, Synth. Met. 70 (1995) 1397.

[21] K. Saito, T. Wakamatsu, H. Yokoyama, Thin Solid Films 285 (1996) 481.

[22] Y. Yoshida, N. Tanigaki, K. Yase, Thin Solid Films 282 (1996) 80.

[23] T. Ohgami, Y. Shimada, H. Kubota, Physica B 239 (1997) 32.

[24] A.K. Evans, J. Phys. Chem. B 102 (1998) 7016.

[25] V.D. Natsik, S.V. Lubenets, L.S. Fomenko, Phys. Status Solidi 157 (1996) 303.

[26] G.C. Pandey, A.C. Boccara, D. Fournier, Fullerene Sci. Technol. 5 (1997) 1067.

[27] P. Colet, Photon Spectra 32 (1998) 120.

[28] S.J. Hasegawa, T. Miyamae, K. Yakushi, Phys. Rev. B 58 (1998) 4927.

[29] K. Datta, M. Banerje, A.K. Mukherjee, Phys. Chem. Phys. 1 (1999) 2919.

[30] M.A. Lantz, S.J. O'Shea, M.E. Welland, Surf. Sci. 437 (1999) 99.

[31] A. Sakai, Y. Yamakoshi, N. Miyata, Fullerene Sci. Technol. 7 (5) (1999) 743.

[32] G.E. Scuseria, Science 271 (1996) 942.

[33] K. Ruud, H. Agren, T. Helgaker, Chem. Phys. Lett. 285 (1998) 205.

[34] M. Venuti, M. Stener, G. De Alti, J. Chem. Phys. 111 (1999) 4589.

[35] H.S. Cho, S.I. Yang, S.K. Kim, J. Phys. Chem. B 103 (1999) 6504.

[36] Y. Yu, Z.M. Zhang, X.X. Pan, Spectrosc. Lett. 32 (1999) 535.

[37] K.P. Bohnen, R. Heid, Phys. Rev. Lett. 83 (1999) 1167.

[38] I.N. Levine, Quantum Chemistry, 4th ed., Prentice-Hall, Englewood Cliffs, NJ, 1991.

[39] M.J.S. Dewar, M.L. Mckee, J. Am Chem. Soc. 99 (1977) 5231.

[40] S. Huzinaga, J. Andzelm, M. Klobukowski, Radzio-Andzelm, Y. Sakai, H. Tatewaki, Gaussian Basis Sets for Molecular Calculations, Elsevier, Amsterdam, 1984.