

FULLERENES AND ATOMIC CLUSTERS

Ab Initio Calculations of Endo- and Exohedral C₆₀ Fullerene Complexes with Li⁺ Ion and the Endohedral C₆₀ Fullerene Complex with Li₂ Dimer

S. A. Varganov^{1,2}, P. V. Avramov¹, and S. G. Ovchinnikov^{1,2}

¹ Kirenskiĭ Institute of Physics, Siberian Division, Russian Academy of Sciences,
Akademgorodok, Krasnoyarsk, 660036 Russia

² Siberian Aerospace Academy, Krasnoyarsk, 660014 Russia

Received March 31, 1999; in final form, June 22, 1999

Abstract—The results of *ab initio* Hartree–Fock calculations of endo- and exohedral C₆₀ fullerene complexes with the Li⁺ ion and Li₂ dimer are presented. The coordination of the Li⁺ ion and the Li₂ dimer in the endohedral complexes and the coordination of Li⁺ ion in the exohedral complex of C₆₀ fullerene are determined by the geometry optimization using the 3-21G basis set. In the endohedral Li⁺C₆₀ complex, the Li⁺ ion is displaced from the center of the C₆₀ cage to the centers of carbon hexa- and pentagons by 0.12 nm. In the Li₂ dimer encapsulated inside the C₆₀ cage, the distance between the lithium atoms is 0.02 nm longer than that in the free molecule. The calculated total and partial one-electron densities of states of C₆₀ fullerene are in good agreement with the experimental photoelectron and X-ray emission spectra. Analysis of one-electron density of states of the endohedral Li⁺@C₆₀ complex indicates an ionic bonding between the Li atoms and the C₆₀ fullerene. In the Li⁺C₆₀ and Li⁺@C₆₀ complexes, there is a strong electrostatic interaction between the Li⁺ ion and the fullerene.
© 2000 MAIK “Nauka/Interperiodica”.

Metallofullerenes—complexes of metal atoms with a fullerene molecule—are among the derivatives of C₆₀ fullerene. These compounds can be subdivided into two types depending on the position of metal atoms relative to the C₆₀ cage. In complexes of the first type, metal atoms are arranged outside the fullerene cage; these complexes were named exohedral. The endohedral complexes belong to the second class; in these complexes, metal atoms are encapsulated into the carbon sphere. Complexes of the first class are denoted as MC₆₀ and complexes of the second class, as M@C₆₀, where M is the metal atom.

Metallofullerenes are of interest because of their widespread application in various branches of science and technology. Actually, solids consisting of exohedral complexes of C₆₀ fullerene with some metals exhibit the highest superconducting transition temperatures, except copper-containing HTSC ceramics [1]. Endohedral complexes with the noncentral arrangement of encapsulated atoms can be used for the creation of a new type of ferroelastic materials [2].

In studying complexes of the two classes, one should first determine their geometry, in particular, the mode of the coordination of a metal atom at the carbon wall. At present, experimental studies of these complexes are hampered by the complexity of their synthesis in sufficient amounts and by difficulties of isomer separation.

The theoretical approaches to the determination of the coordination of metal atoms in exo- and endohedral

fullerene complexes involve both empirical methods based on the use of the Lennard-Jones interatomic potential [3, 4] and semiempirical and *ab initio* quantum-chemical calculations, which provide approximate solutions of the Schrödinger equation [5–10]. It was shown that many atoms in the endohedral complexes of C₆₀ can shift from the center of the fullerene cage. Nonetheless, the mode of atom coordination to the fullerene surface in both endohedral and exohedral complexes have not been understood yet. The problem of possible migration of the encapsulated atom along the inside or the outside surfaces of C₆₀ has also not been studied.

The geometry of complexes is responsible for their electronic structure. One of the most efficient techniques for studying the electronic structure of molecules and solids is spectroscopy (photoelectron, inverse photoelectron, and X-ray spectroscopy). The spectroscopic data are often interpreted based on the results of calculations of the electronic structure of the systems under consideration. Although the nature of photoelectron and X-ray spectra is rather complicated, in many cases, they are satisfactorily reproduced in the calculations of the ground states of complexes in the single-electron approximation. For the C₆₀ fullerene, this is evident if we compare the total densities of states calculated *ab initio* by the Hartree–Fock method [11] and using the density functional theory [12] with the experimental data of photoelectron and inverse photoelectron spectroscopy. The results of calculations for C₆₀

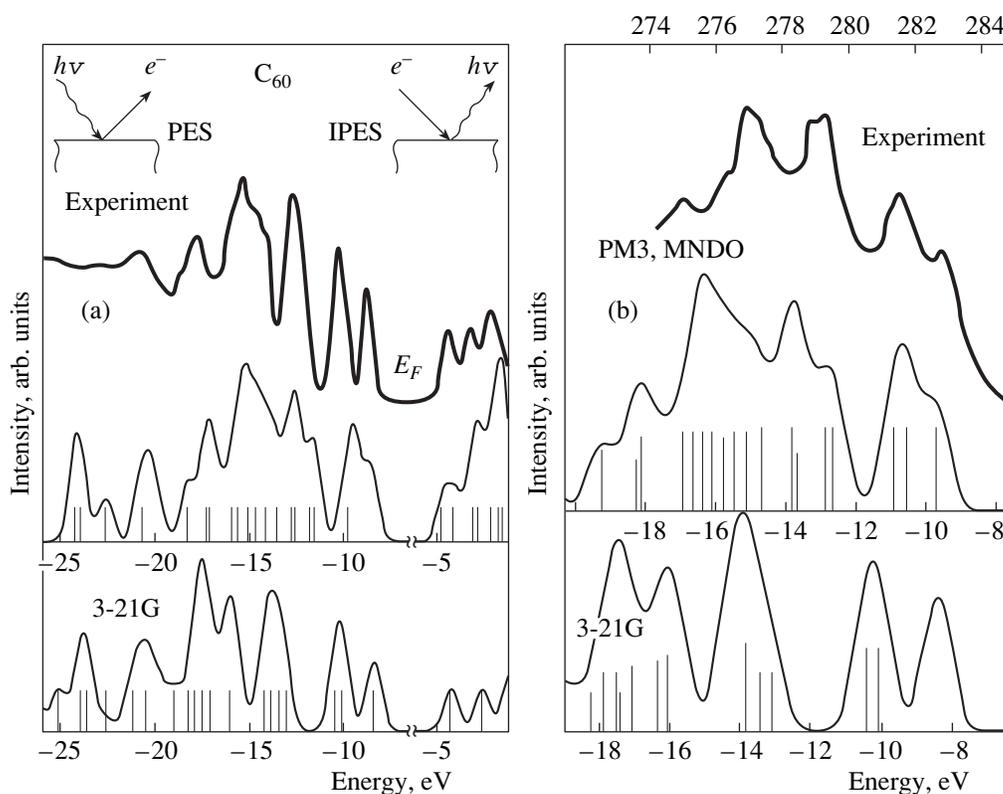


Fig. 1. (a) Photoelectron and inverse photoelectron spectra and (b) X-ray K_{α} emission spectrum of carbon in C_{60} fullerene. Experimental spectra are taken from (a) [12] and (b) [13].

fullerene, fluorinated $C_{60}F_{24}$ fullerene [13], polymeric fullerene [14], and graphite nanotubes [15] by the semiempirical PM3 method in the Hartree–Fock approximation demonstrate a good agreement between the calculated partial densities of states and the experimental X-ray emission spectra of the above compounds.

In this work, we report the results of *ab initio* Hartree–Fock calculations of endo- and exohedral complexes of C_{60} fullerene with the Li^+ ion and the endohedral complex of C_{60} with the Li_2 dimer. The analysis of the electronic structure of complexes was performed using the calculated total and partial densities of states.

1. METHODS

The calculations were performed by the *ab initio* Hartree–Fock method within the 3-21G basis set using the Direct procedure. The Gamess program [16] and a Dual Pentium-II 266 MHz PC RAM 128 MB were used.

The total densities of states were obtained by the following method. First, the energy spectrum of a complex was constructed. In this complex, each molecular orbital was represented by a line, and the line intensities were assumed equal to unity. Next, each line was replaced by a Gaussian distribution with a halfwidth of

0.4 eV, and the distributions were convoluted at each energy to sum up their intensities.

In constructing the partial density of states of atomic orbitals x , the intensity of each line corresponding to the molecular orbital y was assumed equal to the sum of squared coefficients of the atomic orbitals x in the MO LCAO expansion of the orbital y . Next, the partial density of states spectra were constructed by the algorithm similar to that for constructing the total density of states spectra.

2. RESULTS AND DISCUSSION

To assess the correspondence between the calculated electronic structure of C_{60} fullerene and the experimental data, we constructed total and partial densities of states. The experimental photoelectron and inverse photoelectron spectra of the surface of a C_{60} film [12] and the total density of states spectra obtained in *ab initio* calculations with the 3-21G basis set are shown in Fig. 1a. Figure 1b displays the partial densities of states for the p AO of carbon atoms in the C_{60} fullerene, which were constructed from the results of *ab initio* calculations, and also the experimental K_{α} emission spectrum of carbon in C_{60} [13]. For comparison, the figures also present total and partial densities of states calculated by semiempirical MNDO and PM3 methods. It can be

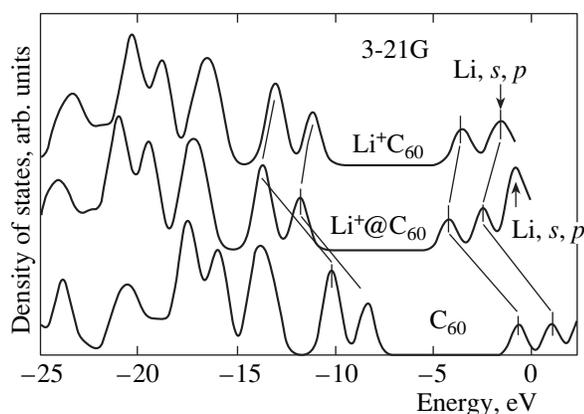


Fig. 2. Total densities of states of the $\text{Li}^+\text{@C}_{60}$ and Li^+C_{60} complexes.

seen that the results of calculations satisfactorily agree with the experimental data.

The positions of critical points in the potential energy surface of the endo- and exohedral complexes of C_{60} with the Li^+ ion were localized by the geometry optimization procedure using the quasi-Newton–Rafson method. In different calculations, different initial coordination modes of the lithium ion at the surface of the C_{60} fullerene were used. From the reasons of symmetry, the lithium ion was placed near the center of a hexagon of carbon atoms (on the C_3 axis), near the center of a pentagon of carbon atoms (on the C_5 axis), near an edge between two hexagons (on the C_2 axis), near an edge between a hexagon and a pentagon (on the σ_v symmetry plane), near a carbon atom (on another σ_v plane), and at the center of C_{60} . The geometry optimization was performed within the C_{3v} , C_{5v} , C_{2v} , C_s , C_s , and T_h symmetry groups, respectively. The results of calculations of the $\text{Li}^+\text{@C}_{60}$ and Li^+C_{60} metallocomplexes are listed in Table 1. The following designations are used: $E_{\text{C}_{60}}$ is the total energy of C_{60} , E_{Li} is the total energy of the Li atom, $E_{\text{LiC}_{60}}$ is the total energy of the

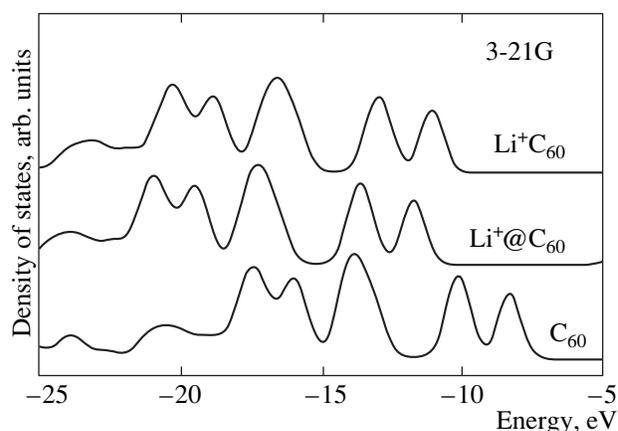


Fig. 3. Partial densities of the p states of carbon in the $\text{Li}^+\text{@C}_{60}$ and Li^+C_{60} complexes.

LiC_{60} metallocomplex, and $E_{\text{form}} = E_{\text{LiC}_{60}} - (E_{\text{C}_{60}} + E_{\text{Li}})$ is the energy of complex formation.

The position of the Li ion in the center of C_{60} does not correspond to a stationary point on the potential energy surface of the complex. The results of calculations for this coordination are presented in order to estimate the energy effect upon the displacement of the lithium ion from the center of C_{60} . The results of calculations indicate that the complexes are thermodynamically stable (the energies of complex formation are negative). It can be seen that the most stable endo- and exohedral complexes are obtained when the lithium atom is arranged at the center of a carbon hexagon. The total energy of the complex is significantly decreased upon the displacement of the lithium ion from the center of the C_{60} cage. The displacement of the lithium atom is about 0.12 nm regardless of the direction.

The total densities of states of the $\text{Li}^+\text{@C}_{60}$ and Li^+C_{60} complexes are presented in Fig. 2. It can be seen for the endohedral complex that the interaction between the Li^+ ion and the C_{60} sphere results in a pronounced shift of the energy levels without splitting of the levels of Li and of the p AO of carbon atoms (Fig. 3). This is indicative of the absence of chemical

Table 1. Calculated properties of the $\text{Li}^+\text{@C}_{60}$ and Li^+C_{60} complexes

Geometry, symmetry	Complex type	E , a.u.	$r_{\text{Li-C}_{60}}$, nm	E_{form} , a.u.	E_{form} , kcal/mol
Center of pentagon, C_{5v}	Endo	-2266.2867802	0.1179	-0.0518927	-32.5632
Center of hexagon, C_{3v}	Endo	-2266.2887585	0.1204	-0.0538710	-33.8046
Hexagon-hexagon edge, C_{2v}	Endo	-2266.2867882	0.1217	-0.0519007	-32.5682
Center of C_{60} , T_h	Endo	-2266.2790085	0.0000	-0.0441210	-27.6864
Center of hexagon, C_{3v}	Endo	-2266.2885003	0.5301	-0.0536128	-33.6426

Note: $E_{\text{Li}^+} = -7.1870945$ a.u., $E_{\text{C}_{60}} = -2259.047793$ a.u.

Table 2. Calculated properties of the Li⁺@C₆₀ complex

Geometry, symmetry	E , a.u.	$r_{\text{Li-Li}}$, nm	E_{form} , a.u.	E_{form} , kcal/mol
Center of pentagon, C_{5v}	-2273.8284520	0.3008	-0.0114048	-7.15663
Hexagon-hexagon edge, C_{2v}	-2273.8404428	0.3111	-0.0233956	-14.681

Note: $E_{\text{Li}_2} = -14.7692542$ a.u., $E_{\text{C}_{60}} = -2259.047793$ a.u., and $r_{\text{Li-Li}} = 0.2815$ nm.

bonding between the lithium ion and the fullerene cage. In this case, the interaction between the lithium ion and the charged C₆₀ sphere is primarily electrostatic. The same is true for the exohedral complex with the only difference that the interaction in this complex is somewhat weaker. This can be explained by the fact that the stability of the 1s shell of lithium is very high, and the electron transfer from the lithium ion to the carbon sphere with the formation of an ionic bond is hampered. Therefore, for the lithium atom bearing one electron in the 2s shell, the interaction pattern should change dramatically. Thus, we can conclude that the electronic structures calculated for the fullerene metallocomplexes with alkali metal ions are inadequate approximations to the electronic structures of metallocomplexes with alkali metal atoms.

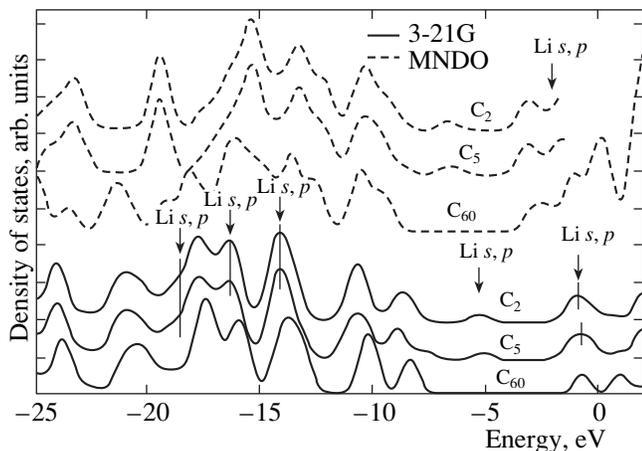
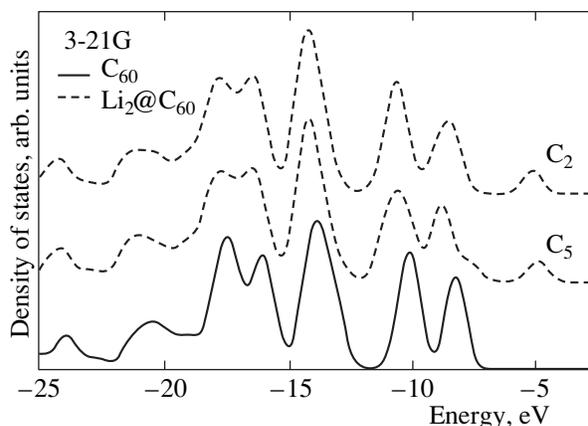
We performed *ab initio* calculations for two modes of coordination of the Li₂ dimer in the endohedral C₆₀ fullerene complex. In the first mode, the dimer was arranged on the C₅ symmetry axis (lithium atoms were placed near the centers of carbon pentagons) and, in the second case, on the C₂ axis (lithium atoms were placed near edges between two carbon hexagons). The results of calculations are listed in Table 2. The designations are the same as in Table 1; $r_{\text{Li-Li}}$ is the distance between the lithium atoms in the dimer. In two coordination modes, the energy of complex formation is essentially negative, which is indicative of the thermodynamic stability of the complexes. For both modes of coordina-

tion, the distance between the lithium atoms is longer than that in the free Li₂ dimer. This enables us to suggest chemical bonding in the fullerene complex.

Figure 4 presents the total densities of states for the endohedral Li⁺@C₆₀ complex. The orbitals of C₆₀ are split for both total and partial densities of p states of carbon atoms (Fig. 5). This splitting is due to the lowering of the symmetry of the C₆₀ cage upon incorporation of the lithium atoms and partial removal of the degeneracy of the single-electron states of fullerene. For both coordination modes of the dimer, the energy levels of the complex are shifted relative to their positions in the C₆₀ fullerene. This indicates the ionic bonding between Li₂ and C₆₀.

An interesting feature is the appearance of a peak in the density of state of the complex almost in the middle of the energy gap of C₆₀. The contributions of s and p AO of Li to this peak are small; nonetheless, it can be seen from Fig. 4 that this peak consists primarily of the split AOs of carbon. The chief distinguishing feature between complexes with various coordination modes of Li₂ inside the C₆₀ cage is that the p states of carbon atoms that correspond to HOMO in the density of state of the complex in which Li₂ lies along the C₅ axis of symmetry are split.

Thus, the results of *ab initio* Hartree-Fock calculations are as follows.


Fig. 4. Total densities of states of the Li₂@C₆₀ complex.

Fig. 5. Partial densities of the p states of carbon in the Li₂@C₆₀ complex.

In the endohedral complex of C_{60} with the lithium ion, the Li^+ cation is shifted from the center of fullerene cage by 0.12 nm. The most favorable ion coordination in both endohedral and exohedral complexes is the coordination toward a hexagon center.

The interaction between the carbon sphere and lithium atoms in the endohedral $C_{60}@Li_2$ complex is of the ionic character. The distance between the lithium atoms increases from 0.30 to 0.32 nm when they are placed inside the C_{60} cage.

It was also shown that the presentation of the results of quantum-chemical calculations as total and partial densities of states is convenient for the analysis of the electronic structure of large systems such as fullerenes and their derivatives.

ACKNOWLEDGMENTS

This work was performed at the Shared-Access Center for "Quantum-Chemical Calculations of Nanoclusters," which was supported by the Federal Program for Basic Research in Higher Education (project no. 69). We acknowledge financial support by the Russian Foundation for Basic Research (project no. 97-03-33684a), the State Program on Fullerenes and Atomic Clusters (project no. 97018), the Interinstitutional Program for Basic Research in Russian Universities (project no. 2049), and the State Program for High-Temperature Superconductivity (project no. 99019).

REFERENCES

1. A. P. Ramírez, *Supercond. Rev.* **1** (1–2), 1 (1994).

2. Y. Wang and D. Tomanek, *Chem. Phys. Lett.* **208** (1–2), 79 (1993).
3. J. Breton, J. González-Platas, and C. Girardet, *J. Chem. Phys.* **99** (5), 4036 (1993).
4. L. Pang and F. Brisse, *J. Phys. Chem.* **97** (33), 8562 (1993).
5. J. Cioslowski and E. D. Fleischmann, *J. Chem. Phys.* **94** (5), 3730 (1991).
6. A. H. H. Chang, W. C. Ermler, and R. M. Pitzer, *J. Chem. Phys.* **94** (7), 5004 (1991).
7. F. de Proft, C. van Alsenoy, and P. Geerlings, *J. Phys. Chem.* **100** (18) 7440 (1996).
8. Y. Maruyama, K. Ohno, and K. Esfarjani, *Sci. Rep. RITU A* **41** (2), 183 (1996).
9. T. Aree and S. Hannongbua, *J. Phys. Chem. A* **101**, 5551 (1997).
10. S. Patchkovskii and W. Thiel, *J. Chem. Phys.* **106** (5), 1796 (1997).
11. A. H. H. Chang, W. C. Ermler, and R. M. Pitzer, *J. Chem. Phys.* **95** (23) 9288 (1991).
12. J. H. Weaver, *Acc. Chem. Res.* **25** (3), 143 (1992).
13. L. G. Bulusheva, A. V. Okotrub, and N. E. Yudanov, *J. Phys. Chem. A* **101**, 10018 (1997).
14. A. V. Okotrub, L. G. Bulusheva, and Yu. V. Shvetsov, *Phys. Low-Dim. Struct.* **5**, **6**, 103 (1997).
15. L. G. Bulusheva, Candidate's Dissertation in Chemistry (Novosibirsk, 1998).
16. M. W. Schmidt, K. K. Baldrige, and J. A. Boatz, *J. Comp. Chem.* **14**, 1347 (1993).

Translated by E. Rykova