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Electronic and Atomic Structures of the Isomers of Endohedral and Exohedral Fullerene Complexes with Two Lithium Atoms

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Abstract—The electronic structures of all the possible isomers of endohedral and exohedral C_{60} fullerene complexes with two lithium atoms are theoretically investigated. It is found that the electronic structures of these compounds are characterized by an impurity filled-level state determining the band gap. The location of the impurity state and, correspondingly, the band gap of the exohedral fullerene complexes depend on the coordination mode and the distance between the alkali metal ions. A similar dependence is observed for the total energy of the exohedral fullerene complex under investigation. *© 2001 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

Fullerene molecules are capable of forming complexes with metals in which the metal atoms are arranged either inside the carbon cluster sphere (endohedral complex) or outside the fullerene cage (exohedral complex). Since the discovery of fullerenes, a large number of their complexes with metals have been prepared and studied experimentally [1–9].

The effects of the nature and the number of intercalated atoms on the electronic structure of fullerene complexes are widely covered in the literature [9–19]. However, the isomers of fullerene complexes with metals have not been adequately investigated. In recent works [1, 19], exohedral and endohedral fullerene complexes with different numbers of lithium atoms were prepared and studied experimentally and theoretically. Nonetheless, the influence of the lithium coordination in exohedral and endohedral metallocomplexes on their electronic structure is still not clearly understood.

2. METHODS AND OBJECTS OF INVESTIGATION

The calculations were performed by the semiempirical (MNDO) and *ab initio* Hartree–Fock (3-21G basis set) methods using the GAMESS [20] (*ab initio* calculations) and HyperChem 5.02 (semiempirical calculations) program packages.

In this work, we studied all the possible isomers of endohedral and exohedral C_{60} metallocomplexes with two lithium atoms ($Li_2@C_{60}$ and Li_2C_{60}, respectively) (Fig. 1). Among these isomers, we considered only one endohedral complex whose geometry corresponded to the state with the minimum energy. In the endohedral complex (Fig. 1b), the lithium atoms were arranged in the vicinity of the fullerene center along the C_2 axis, thus forming an Li_2 dimer (the distance between the lithium atoms was equal to ~3 Å). Moreover, we calculated 12 different isomers of the exohedral fullerene complex (Figs. 1c–1f). These isomers differed in the arrangement of the metal atoms with respect to particular faces of the carbon polyhedron. To every possible combination of polygons comprising a spherical C_{60} molecule there corresponded a certain mode of the lithium coordination. All the exohedral complexes can be divided into three groups depending on the position of lithium atoms with respect to the polygons forming the fullerene cage. In the first and second groups, alkali metal atoms were coordinated near pentagons (three isomers) and hexagons (five isomers), respectively. In complexes of the third group (four isomers), one lithium atom was placed over a pentagon and the other atom was located over a hexagon. Within each group, the isomers differed in the distance between the polygons near which the metal atoms were coordinated (Figs. 1c–1f). It should be noted that we also investigated exohedral complexes with lithium atoms located near edges and vertices of the carbon polyhedron. However, in the course of geometry optimization, the lithium atoms changed their mutual arrangement and occu-

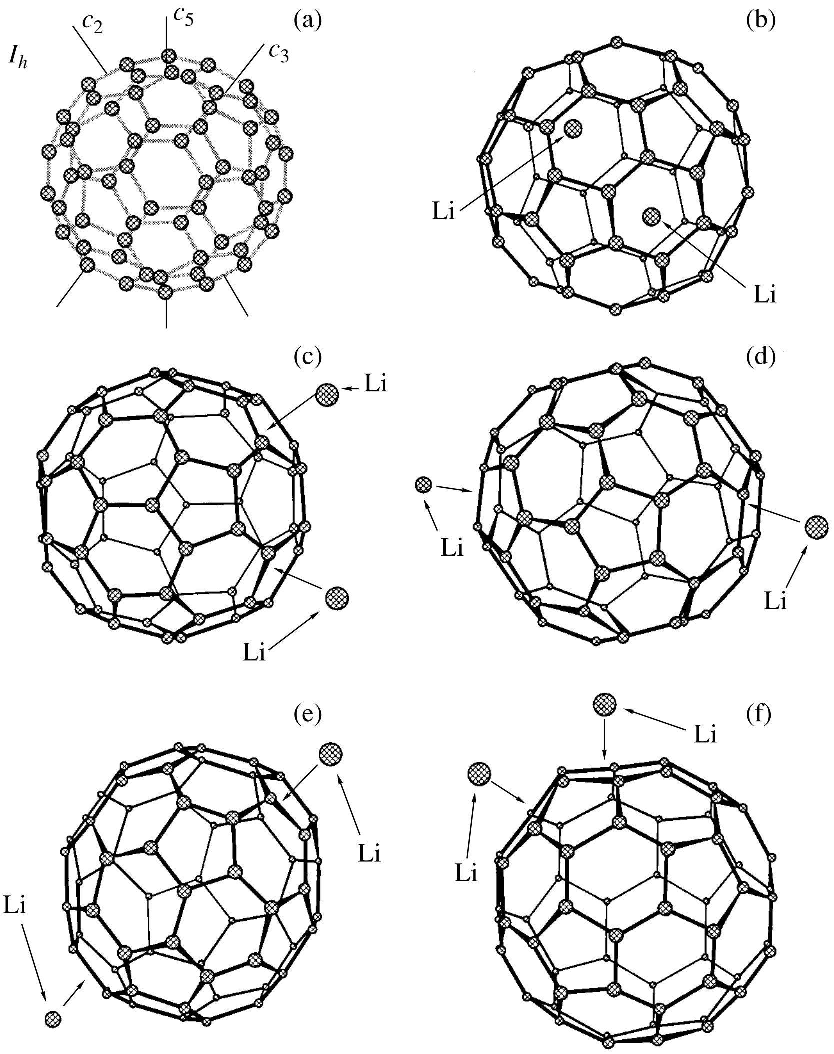

Fig. 1. Structures of a C_{60} molecule and different isomers of the fullerene complexes with two lithium atoms: (a) C_{60} molecule, (b) $Li_2@C_{60}$ endohedral complex, (c) exohedral complex with lithium atoms coordinated over the most closely spaced pentagons, (d) exohedral complex with lithium atoms coordinated over the most widely spaced hexagons, (e) exohedral complex with lithium atoms coordinated over the most widely spaced pentagons, and (f) exohedral complex with lithium atoms coordinated over the most closely spaced hexagons.

pied positions over the centers of the distorted polygons. In this case, the distance between the metal atom and the polygon plane was equal to ~2.3 Å.

Distortion of the high-symmetry carbon cage of the fullerene complex was observed in all the studied isomers. Upon attachment of lithium atoms to the fullerene molecule, the distance between carbon atoms in regular polygons typical of a C_{60} molecule increased differently.

In order to describe the electronic structure of the molecules under investigation, we constructed the total and partial densities of states. The theoretical densities of states were compared with the experimental photoelectron spectra. As follows from a comparison of the spectra of the valence band, the results of the *ab initio* and semiempirical calculations agree well with the experimental spectra. At the same time, the semiempirical methods offer an adequate description of the fullerene geometry, because the interatomic distances and bond angles determined in the semiempirical calculation are in better agreement with the experimental data as compared to the results obtained in the *ab initio* calculation with the 3-21G basis set [19].

The calculations were carried out for both the singlet and triplet states of the fullerene complexes. In all the cases under consideration, the energies of the singlet states of the fullerene complexes were less than those of the triplet states.

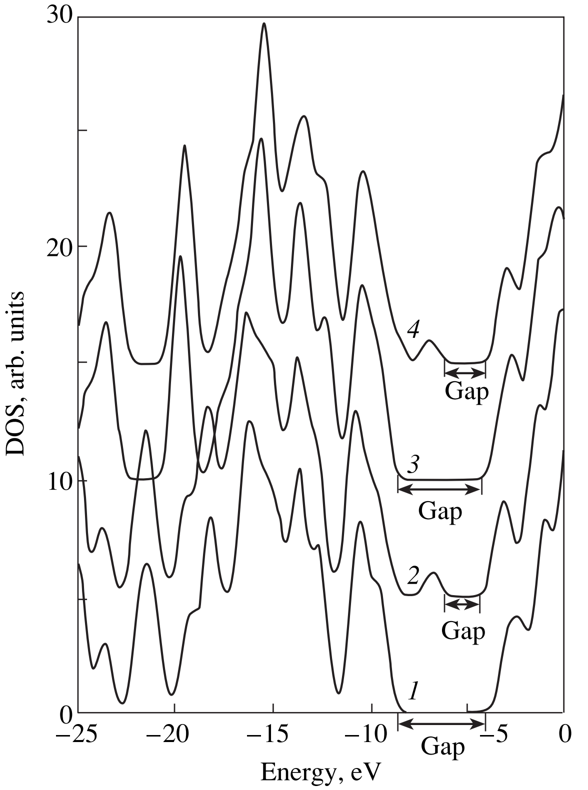

Fig. 2. Total densities of states for (*1*) C_{60}, (*2*) C_{60}^{2-}, (*3*) $Li_2@C_{60}^{2+}$, and (*4*) $Li_2@C_{60}$.

3. RESULTS AND DISCUSSION

The analysis performed in this work revealed considerable differences between the electronic structures of the studied complexes and the electronic structure of the C_{60} molecule. The attachment of lithium atoms to the fullerene molecule led to relief of the multiple degeneracy of the electronic levels, which is characteristic of undoped C_{60} fullerenes. This can be explained by a substantial lowering in the symmetry of the fullerene complexes as compared to the initial high-symmetry C_{60} molecule. Consequently, the previously degenerate energy levels of the carbon cage were grouped into packets in the fullerene complexes. The energy-level separation in each packet was equal to ~0.01–0.5 eV, depending on the symmetry of the isomer. In some cases, this resulted in a mixing of different packets of energy levels at the valence band top. In addition to the differences between the symmetries of the metallocomplexes and the C_{60} molecule, the positive charge of lithium ions also contributes to the shift of the energy levels. In the fullerene complexes with alkali metals, electrons are transferred from the metal to the carbon cage of the molecule. As a result, the carbon cage acquires a negative charge, whereas the lithium atoms become positively charged (the charge of each lithium ion is ~0.6). Therefore, the C_{60} fullerene with an extra pair of electrons in the field of positively charged lithium ions can be treated as a model of the metallocomplexes under investigation. With the aim of verifying this model, we calculated the $Li@C_{60}^{2+}$ system. A comparative analysis of the total densities of states for the ions and isomers of the metallocomplexes demonstrated that the energy levels of the ions lie below the corresponding levels of the complexes. However, being aligned on the energy scale, their electronic level patterns are virtually identical (Fig. 2).

Another difference between the electronic structures of the metallocomplexes and the C_{60} molecule is in the occurrence of an extra filled level (i.e., an impurity state), which lies ~1–3 eV above the packets of filled levels and 3.5–5 eV below the vacant energy levels (the energy of the impurity state in the studied complexes is equal to ~–7 eV). The formation of the impurity state is explained by the occurrence of two electrons of lithium atoms on the carbon cage of the fullerene complex. This is confirmed by the model calculations of the C_{60}^{2-} ion (singlet). A comparison of the total densities of states for the model ion and one of the structural isomers of the fullerene complex with two lithium atoms (Fig. 2) showed that the impurity state is observed for both structures with an extra pair of electrons.

Let us now elucidate the nature of the energy level under consideration. For this purpose, it is necessary to investigate in more detail the electronic structure of the C_{60} molecule. Of particular interest is the valence band top of this compound. It is expedient to compare the structure of the electronic levels of the C_{60} fullerene and the electronic structures of the molecules characterized by the π-electron system, for example, benzene, anthracene, pyrine, etc. (Fig. 3).

Molecular electronic levels in the benzene molecule can be classified into two groups: the σ levels, which involve mixed contributions from the p_x, p_y, and s atomic orbitals of carbon and hydrogen atoms, and the π states, which are formed only by the carbon p_z orbitals. Analysis of the partial densities of states demonstrates clear separation between the peaks associated with the π-electron system (two maxima) and the peaks of all the remaining electronic levels (Fig. 3a). An increase in the number of atoms in the molecule (anthracene or pyrine) results in an increase in the number of peaks attributed to the π-electron system, even though the location and nature of the energy levels remain virtually unchanged (Fig. 3b).

Since the spherical C_{60} molecule has a surface curvature, the atomic orbitals lying in the plane of the molecular surface ($p_{\parallel}$) overlap with atomic orbitals aligned perpendicular to this surface ($p_{\perp}$). As a result, the fullerene molecule contains no σ- or π-type levels inherent in planar aromatic molecules (Fig. 3c). For the systems with different charges on the carbon cage of the fullerene complex, the ratios of the contributions from the $p_\perp$ and $p_\parallel$ electrons to energy levels of the valence band top also differ (see table). For the C_{60} molecule, the ratio $p_\perp/p_\parallel$ is equal to 1.1. A change in the charge of the system leads to a decrease in the $p_\perp/p_\parallel$ ratio, except for the C_{60}^{2-} cluster with a multiplicity of 1. It is evident that the ratio of the contributions from the $p_\perp$ and $p_\parallel$ electrons to a particular energy level determines its nature.

In the C_{60} molecule, the upper filled level is the quintuply degenerate bonding state h_u and the lower vacant level is the triply degenerate antibonding state t_{1u}. For singlet states of the fullerene complexes with two lithium atoms, the electron pair of the metal occupies one of the three previously triply degenerate levels (the t_{1u} state), which is split upon attachment of the lithium atoms. The nature of the impurity filled-level state remains unchanged; i.e., this is an antibonding orbital [21, 22]. This is also confirmed by the differences between the spatial structures of the fullerene metallocomplexes and the C_{60} molecule: the interatomic distances in the isomers of the metallocomplex under investigation are longer than those in the C_{60} molecule. The C_{60} molecule is characterized by two types of bonds. Bonds of the first type have a length of ~1.44 Å and are shared by hexagons and adjacent pentagons (the 6–5 bonds). Bonds of the second type have a length of ~1.39 Å and are shared by two adjacent hexagons (the 6–6 bonds). In the studied complexes, the majority of bonds between the carbon atoms become inequivalent. The observed increase in the distance between the carbon atoms is associated with the fact that the carbon orbitals make the main contribution to the impurity state of an antibonding nature. After the formation of the metallocomplex, changes in the 6–6 bond lengths of the carbon cage are most pronounced ($\Delta R_{\max}$ ~ 0.1 Å). However, for the most part, the bonds between hexagons in all the studied isomers, as before, remain shorter than those between the hexagons and pentagons.

The electronic structures of the isomers of the metallocomplexes differ in the location of the impurity filled-level state. In the exohedral complexes with the most widely spaced lithium atoms (Fig. 1d), the impurity filled level most closely approaches the vacant levels. In the case when the lithium atoms are arranged over adjacent polygons (Fig. 1f), the shift of the impurity filled level toward the packet of vacant levels is minimum. The impurity levels for other Li_2C_{60} isomers, including the endohedral complex, are intermediate in location between the above extreme cases. The distance between the lithium atoms in the isomers of the exohedral complexes has a determining effect on the location of the impurity state and, as a consequence, on the band gap (Figs. 4, 5).

As was noted above, the exohedral complexes can be divided into three groups depending on the position of the coordinated lithium ions with respect to particular faces of the fullerene polyhedron.

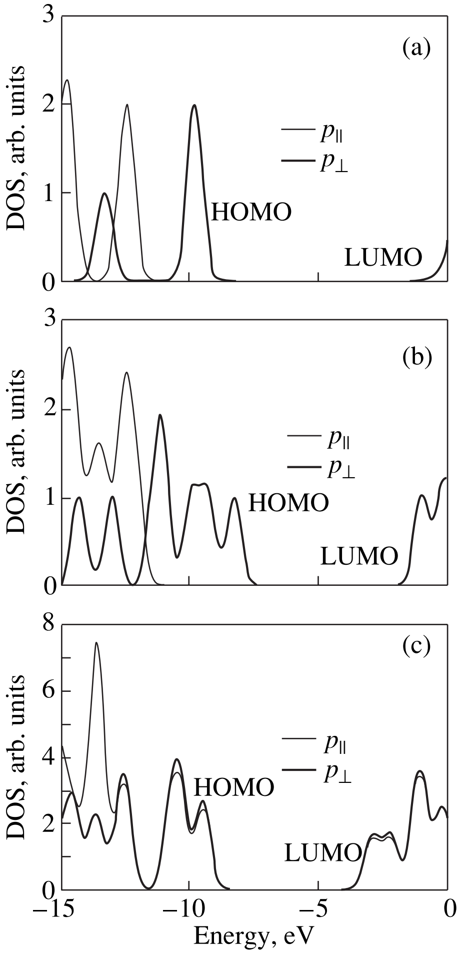

Fig. 3. Partial densities of states for (a) C_6H_6, (b) $C_{14}H_{10}$, and (c) C_{60} molecules.

For each group of exohedral complexes, the band gap decreases with an increase in the distance between the lithium atoms. The dependence of the band gap on

Ratios of the contributions from the $p_\perp$ and $p_\parallel$ electrons to energy levels of the valence band top for different carbon clusters

Carbon cluster	Ratio $p_\perp/p_\parallel$ in HOMO
C_{60}	1.11
C_{60}^{1}	0.65
C_{60}^{2} MULT 1	0.98
C_{60}^{-1}	0.92
C_{60}^{-2} MULT 1	1.19
C_{60}^{-2} MULT 3	0.84

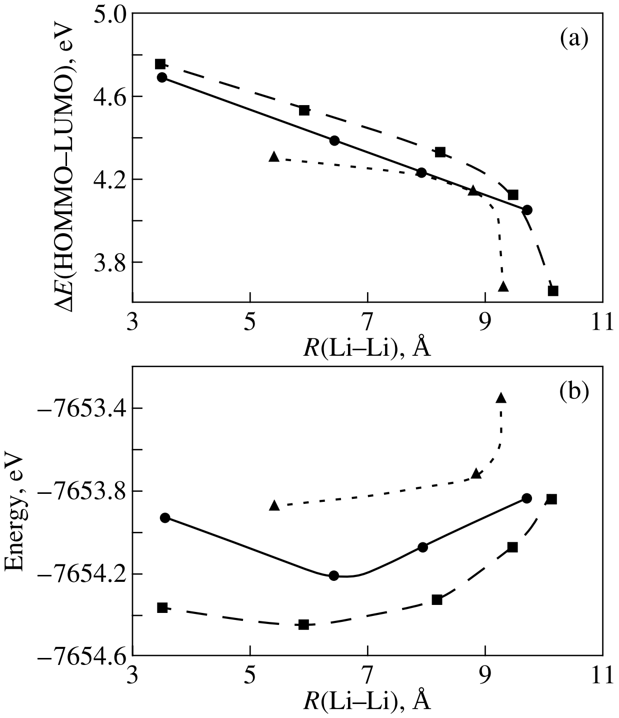

Fig. 4. Dependences of (a) the band gap and (b) the total energy of the molecule on the distance between the lithium atoms coordinated in the immediate vicinity of different polygons (pentagon–pentagon, hexagon–hexagon, and hexagon–pentagon).

the distance between lithium atoms has a linear character, except for the case of the two isomers in which the lithium atoms are located at a maximum distance from each other. In these two cases (when the lithium atoms are coordinated near either two opposite pentagons or two opposite hexagons), the band gap decreases drastically.

The situation when the metallocomplex has several isomers should be reflected in the photoelectron and optical spectra. Since the impurity levels in the electronic structure of the particular isomers of the metallocomplex differ in location, their superposition should manifest itself in the spectra. This brings about the broadening of the peak associated with the impurity state and, hence, the narrowing of the band gap.

In the exohedral complexes, the total energy, like the band gap, depends on the distance between the lithium ions and their mutual arrangement with respect to particular polygons. For each group of the studied isomers, an increase in the distance between lithium atoms leads to an increase in the total energy. The exception is provided by the isomers in which lithium atoms are arranged over adjacent polygons (either over two hexagons or over a hexagon and an adjacent pentagon). It seems likely that the increase in the total energy for these complexes is caused by the strong electrostatic repulsion between positively charged lithium ions.

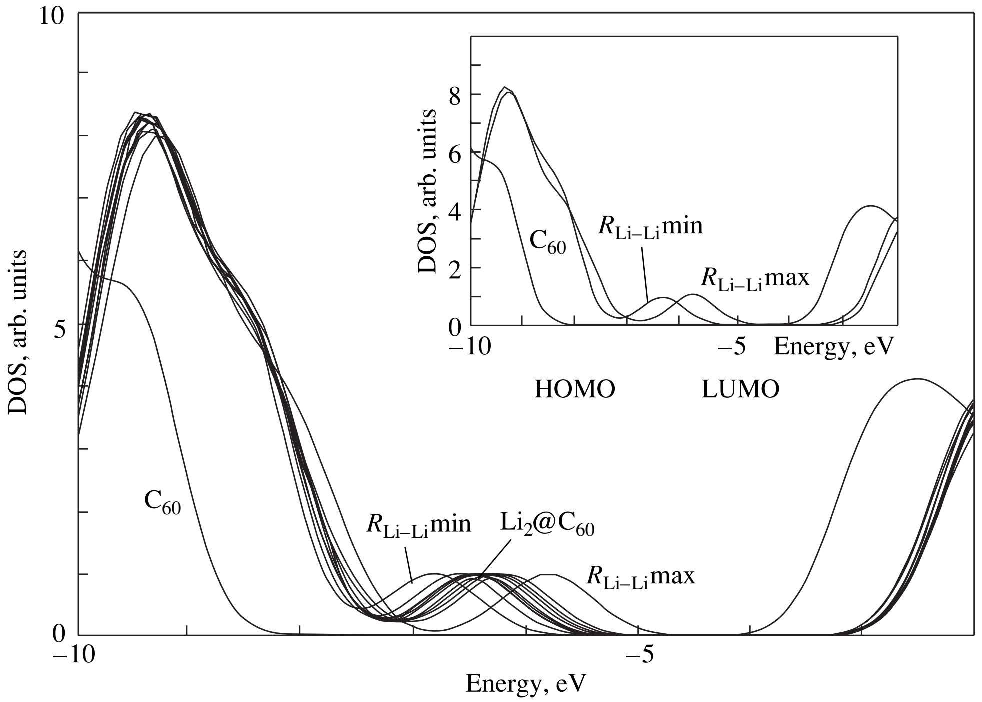

Fig. 5. Total densities of states for different Li_2C_{60} isomers.

4. CONCLUSION

Thus, the calculations demonstrated that the electronic structures of the isomers of exohedral metallocomplexes can differ in the band gap and the total energy depending on the lithium coordination. The occurrence of several isomers in the system should bring about broadening of the impurity state due to the superposition of the corresponding states of particular isomers and, as a consequence, the narrowing of the band gap, which should be reflected in the photoelectron and optical spectra of the metallocomplexes under investigation.

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