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Theoretical Study of the Toroidal Forms of Carbon and Related Endohedral Complexes with Lithium

A. A. Kuzubov[1, 2], P. V. Avramov[2], S. G. Ovchinnikov[1, 2], S. A. Varganov[2], and F. N. Tomilin[2, 3]*

[1]*Krasnoyarsk State Technical University, Krasnoyarsk, Russia;*

[2]*Kirensky Institute of Physics, Siberian Division, Russian Academy of Sciences, Akademgorodok, Krasnoyarsk, 660036 Russia*

[3]*Institute of Chemistry and Chemical Technology, Siberian Division, Russian Academy of Sciences, Krasnoyarsk, Russia*

*e-mail: felix@iph.krasn.ru*

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Abstract—The atomic and electron structures of toroidal carbon molecules (C_{240} and two C_{120} isomers) and related endohedral complexes with lithium ($Li_2@C_n$ and $Li_4@C_n$) were theoretically studied using both non-empirical (3–21G basis set) and semiempirical (MNDO) calculation schemes. For the metal-containing compounds, the behavior of lithium atoms embedded into internal cavities of the carbon framework was studied using methods of molecular dynamics. It is demonstrated that the structure of electron levels of metal-containing carbon complexes exhibits an embedded state in the forbidden band, which appears due to the presence of electrons accepted from metal atoms. The position of this embedded state and the bandgap width depend both on the initial carbon structure and on the amount of metal atoms incorporated. © *2001 MAIK "Nauka/Interperiodica".*

1. INTRODUCTION

To date, a large number of cluster compounds representing allotropic forms of carbon have been discovered. Exhibiting a large variety of structures and possessing unusual properties, these objects have drawn special attention of researchers. One of the families of carbon clusters represents toroidal forms of carbon. Molecules of this type, experimentally observed for the first time in 1992 [1], appear as closed surfaces composed of various carbon polygons, including pentagons, hexagons, and heptagons (Fig. 1). The presence of pentagons provides for a positive curvature of the surface, while heptagons account for a negative curvature. According to experimental data, toroidal carbon molecules may contain various numbers of atoms (from 80 to several thousands) and exhibit rather complicated shapes (Fig. 2).

Since 1992, a number of papers have been published devoted to theoretical investigation of toroidal carbon molecules. Itoh and Ihara [2–4] and Johnson [5] studied the dependence of the energies and electron structures of clusters on the amount of atoms and the geometric parameters of these objects (symmetry, internal and external diameters, etc.). In [6], Itoh and Ihara thoroughly studied C_{240} isomers (in that investigation, cluster geometries were optimized by the molecular dynamics method and the electron structures were calculated by the Hückel method). Dunlap [7] and Menner [8] studied the atomic and electron structures of still greater toroidal molecules: Dunlap described carbon tori containing 240, 540, and 576 atoms and obtained bandgap widths of 1, 0.04, and 0.02 eV, respectively; Menner studied a C_{1960} molecule, for which he obtained a bandgap width of 0.05 eV. Both researchers employed empirical potentials for the molecular geometry optimization and used the tight binding model for the electron structure calculations. In the general case, the distinctions between the electron structures of toroidal molecules were explained in terms of differences in atomic structures.
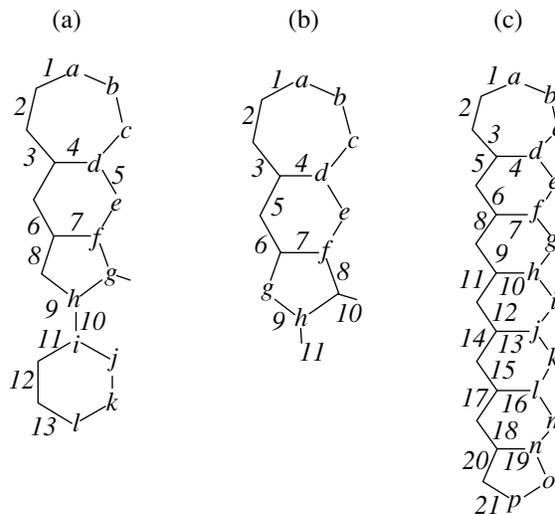
Fig. 1. Segments of toroidal carbon molecules: (a) C_{120} (long); (b) C_{120} (short); (c) C_{240}. Inequivalent atoms are indicated by letters and the bonds between these atoms are enumerated.

Of much greater interest are the derivatives of toroidal carbon molecules, in particular, metal-containing complexes. No data on such objects have been reported so far, although investigation of the geometry of toroidal molecules containing metal atoms in cavities, the electron structure of such complexes, and the behavior of incorporated metal atoms is a very interesting task.

We have theoretically studied the toroidal forms of carbon and related electron-doped derivatives (endohedral complexes with lithium) using the methods of quantum chemistry and molecular dynamics, aiming at establishing regularities in the spatial and electron structures of these molecules.

2. OBJECTS AND METHODS OF INVESTIGATION

We have theoretically studied the toroidal molecules containing 120 and 240 carbon atoms (Figs. 1, 2). In the case of C_{120}, we studied two isomers differing in values of their internal and external diameters and in arrangement of pentagons and heptagons. The structures of C_{120} (with elongated segments) and C_{240} compounds were proposed in [2, 3]. In addition to this C_{120} isomer denoted C_{120} (long), we have also studied another C_{120} isomer referred to hereinafter as "short." The coordinates of inequivalent atoms in the C_{120} (short) isomer are given in Table 1.

In addition to the toroidal carbon structures, we studied the related metal-containing complexes with lithium (Figs. 2d, 2f), in particular, compounds containing two and four alkali metal atoms inside the carbon clusters. In this study, the main attention was paid to determining the positions of metal atoms, the behavior of these atoms at a given temperature (300 K in this model calculation), and the influence of embedded metal atoms upon the electron structure of the toroidal carbon framework.

The calculations were performed using semiempirical (MNDO) and nonempirical (3–21G basis set) calculation schemes. The latter method was applied only to C_{120} isomers and used to assess the applicability of various calculation schemes to the clusters studied. The calculations of toroidal molecules were performed with symmetry limitations: C_5 for C_{120} (long) and C_{240}; D_{5d} for C_{120} (short). No such limitations were posed on the metal-containing complexes, which allowed all possible coordinations of the metal atoms to be determined. To check for the fact that a given system occurred in a local energy minimum, we calculated the vibrational spectra of compounds. The absence of complex modes was indicative of the occurrence of a local minimum. Containing large numbers of atoms, the systems under consideration may possess several local minima. For determining the global minimum of energy, we considered various initial positions of atoms which led, in the course of optimization, to atomic configurations corresponding to various local minima. An analysis of these
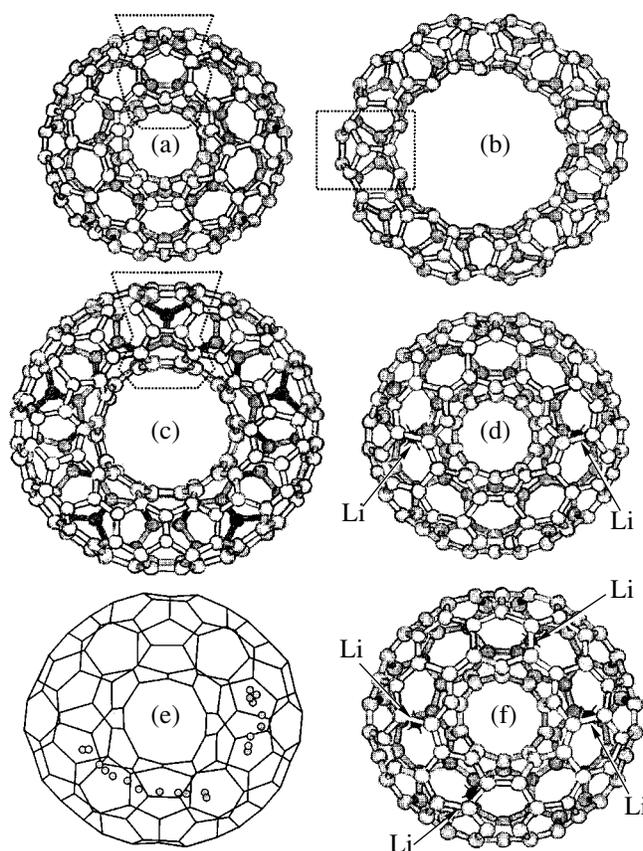
Fig. 2. Schematic diagrams showing the structures of toroidal carbon molecules and related complexes with lithium: (a) C_{120} (long); (b) C_{120} (short); (c) C_{240}; (d) $Li_2@C_{120}$ (long); (e) trajectories of the lithium atom in the course of molecular modeling of the $Li_2@C_{120}$ (long) complex; (f) $Li_4@C_{120}$ (long) complex. Dashed contours in (a)–(c) frame molecular segments depicted in Fig. 1.

results allowed the global minimum of energy to be determined, which was additionally verified by comparison with molecular dynamics data. All structures were calculated in both singlet and triplet states using a GAMESS program [9].

Table 1. The coordinates of inequivalent atoms (Å) in the C_{120} (short) isomer calculated using the MNDO method for a molecule with the $D5d$ symmetry

x	y	z
0.0000	4.6992	1.2477
0.0000	6.0552	1.6057
0.7582	7.1114	0.2071
0.6784	5.1688	1.4971
1.5186	6.4116	–1.2346
1.2622	6.7170	1.1064
1.2650	4.1822	0.7031

Table 2. Interatomic distances (Å) between inequivalent atoms in various toroidal carbon molecules

Bond number	C_{120} (long)		C_{120} (short)		C_{240}
	MNDO	3–21*G*	MNDO	3–21*G*	
1	1.477	1.474	1.471	1.454	1.433
2	1.378	1.333	1.417	1.364	1.413
3	1.485	1.472	1.513	1.507	1.469
4	1.386	1.341	1.357	1.312	1.371
5	1.466	1.447	1.523	1.531	1.448
6	1.420	1.385	1.457	1.425	1.489
7	1.479	1.464	1.516	1.539	1.423
8	1.477	1.461	1.461	1.415	1.427
9	1.477	1.458	1.510	1.520	1.450
10	1.411	1.374	1.434	1.405	1.388
11	1.495	1.490	1.402	1.346	1.478
12	1.466	1.447			1.483
13	1.485	1.472			1.498
14					1.431
15					1.456
16					1.483
17					1.470
18					1.407
19					1.494
20					1.468
21					1.482
22					1.395

Table 3. Energies (per atom) and bandgap widths of various toroidal carbon molecules and related complexes with lithium atoms

Object	$\Delta E_{\text{HO–LU}}$, eV	$-E$/atom, eV
C_{120} (long), MNDO	6.454	127.18
C_{120}, 3–21*G*	7.809	1024.34
C_{120} (long), 3–21*G* (opt. MNDO)	7.138	1024.31
$Li_2@C_{120}$ (long)	1.611	125.19
$Li_4@C_{120}$ (long)	2.114	123.27
C_{120} (short) MNDO	5.828	126.62
C_{120} (short), 3–21*G*	7.181	1023.85
C_{120} (short), 3–21*G* (opt. MNDO)	6.201	1023.81
$Li_2@C_{120}$ (short)	2.686	124.57
$Li_4@C_{120}$ (short)	4.634	122.58
C_{240}	4.422	127.27
$Li_2@C_{240}$	4.304	126.29
$Li_4@C_{240}$	3.603	125.31

The behavior of lithium atoms in metal-containing complexes was studied using the method of molecular dynamics. Requiring no empirical intermolecular and interatomic potentials, this method is widely employed at present for investigation of the dynamic properties of molecular systems [10]. In this study, the behavior of lithium atoms in complexes with carbon was simulated by a demonstrative version of the HyperChem 5.02 program capable of performing calculations with the aid of semiempirical (MNDO, PM3) potentials.

3. CALCULATIONS OF TOROIDAL MOLECULES

Before studying various carbon clusters and related complexes, it is necessary to consider differences in the spatial and electron structures of these molecules as determined from various methods (semiempirical and nonempirical). For buckminsterfullerene, the most accurate values of bond lengths were obtained using semiempirical methods (PM3, MNDO) [11]. A nonempirical calculation using a 3–21*G* basis set leads to a double bond length 0.04 Å shorter than that given by the semiempirical methods (the same difference is observed for C_{60}). The length of a bond with the bond order (determined according to [9]) about unity was virtually the same (Table 2, Fig. 1).

Changes in the electron structure were not less significant. The electron levels determined from semiempirical calculations were much closer to each other than those obtained from nonempirical methods (Fig. 3). Despite this shift, the structure of levels in the valence band region remained qualitatively unchanged. Nevertheless, the shift led to a certain difference in estimates of the bandgap width (Table 3) obtained from semiempirical and nonempirical methods (e.g., the difference was 1.35 eV for both C_{120} isomers).

A comparative analysis of data for the C_{120} isomers (Table 3) showed that the C_{120} (short) molecule is energetically less favorable (by 66.8 and 58 eV according to estimates obtained using the MNDO method and the nonempirical calculation employing 3–21*G* basis set, respectively). We explain this discrepancy in terms of small diameter of the internal cavity in this isomer leading to higher bond stresses in the cluster. As a result, the bond lengths in the polygons of C_{120} (short) have proved to be smaller than those in the corresponding polygons of C_{120} (long). Despite this difference, the proportional bond ratios in the like cycles of both isomers were very close.

Each pentagon or heptagon in C_{240} molecules, in contrast to those in C_{120} isomers, is surrounded by hexagons; this circumstance significantly changed the bond lengths in some polygons (Table 2, Fig. 1). However, certain features typical of the interatomic distances in C_{120} are also retained in C_{240}. In particular, the shortest bonds are those shared by heptagons and hexagons (bonds *4* in all structures) and those originating from the vertices of pentagons (bonds *10* in C_{120} and *22* in C_{240}).

4. ENDOHEDRAL COMPLEXES WITH LITHIUM

Upon optimization of the molecular geometry of the carbon complexes containing two lithium atoms, the incorporated metal atoms resided at the opposite ends of the internal cavity of the carbon clusters. Embedded in the C_{120} (long) molecule, lithium atoms are spaced by 7.79 Å and coordinated against bonds *5* of the carbon molecule (Figs. 1, 2d). In the C_{120} (short) isomer, the distance between embedded metal atoms is 10.9 Å and these atoms are located in the cavity near bonds *11*. In the $Li_2@C_{240}$ complex, lithium atoms spaced 10.5 Å apart are located near bonds *22*. It must be noted that, in all cases, lithium atoms occur at virtually equal distances from walls of the internal cavity.

In the complexes containing four lithium atoms, the incorporated particles were differently coordinated in the two C_{120} isomers. In the $Li_4@C_{120}$ (long) complex, alkali metal atoms exhibited coupling: atoms in the couple are spaced 4.48 Å apart and the distance between two couples is 6.44 Å (Fig. 2f). The $Li_4@C_{120}$ (short) complex adopted a configuration with maximum possible distances between alkali metal atoms: 8 Å between nearest neighbors and 11.6 Å between opposite atoms. In the $Li_4@C_{240}$ molecule, lithium atoms are also distributed in the internal cavity so as to be maximum spaced (with the distances 7.5 and 10.39 Å between nearest neighbors and opposite atoms, respectively).

The results of our calculations showed that the introduction of alkali metal (i.e., electron donor) atoms into carbon clusters leads to distortion of the framework structure. This is manifested by increasing bond lengths in the carbon cluster at the metal coordination sites. Because of the large size of carbon clusters studied, changes in carbon–carbon bond lengths become less pronounced with increasing distance from lithium atoms. The increase in the carbon–carbon bond lengths in the metal-containing clusters in comparison with that in the metal-free initial toroidal molecules is evidence of an antibonding character of the vacant states occupied by the electrons accepted from embedded metal atoms.

The process of complex formation with alkali metal atoms leads to a change in electron structure of the toroidal carbon molecules. In contrast to the pure carbon tori, where the lowest energy states are singlets, a minimum energy in the complexes of C_{120} with two or four lithium atoms [except for $Li_4@C_{120}$ (short)] is attained in the triplet states. An energy difference between triplet and singlet states for $Li_2@C_{120}$ (long), $Li_4@C_{120}$ (long), $Li_2@C_{120}$ (short), and $Li_4@C_{120}$ (long) amounts to 1.26, 0.05, 0.06, and 0.34 eV, respectively. In order to establish a reason for this behavior, it is necessary to consider the vacant levels of C_{120} isomers. The lowest vacant state (see Figs. 4a, 4b) is level *A*, which is followed by a doubly degenerate level E_1; in the complexes containing two metal atoms, these levels exhibit inversion. Two electrons introduced with lithium atoms fill the vacant electron states of the carbon framework,
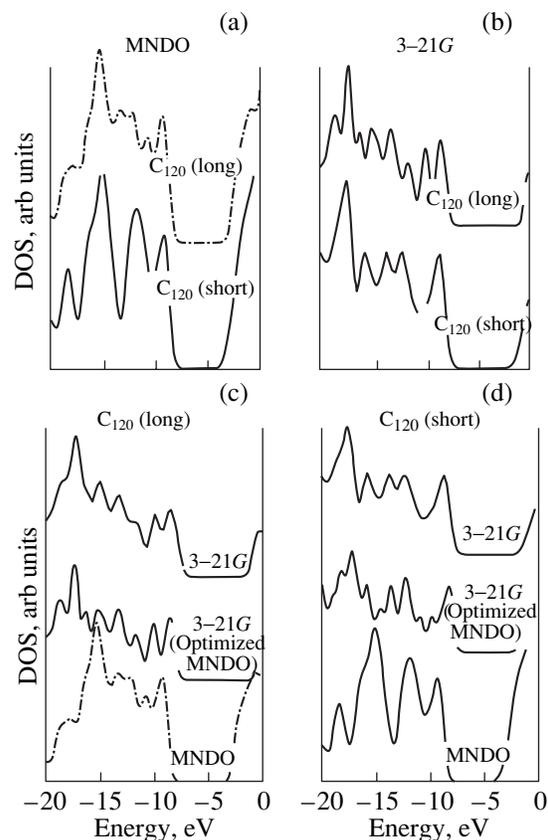

Fig. 3. Densities of states in toroidal carbon cluster structures calculated from various methods: (a) C_{120} (long) and C_{120} (short), MNDO; (b) C_{120} (long) and C_{120} (short), 3–21*G*; (c) C_{120} (long), MNDO, 3–21*G* optimized by MNDO, and 3–21*G*; (d) C_{120} (short), MNDO, 3–21*G* optimized by MNDO, and 3–21*G*.

occupying first the two orbitals corresponding to a lowest vacant state of the E_1 level. According to the Hund rule, this leads to the appearance of a triplet. The inversion of levels also takes place in $Li_4@C_{120}$ (short), where the embedded state (similar to that described above) is represented by two levels accommodating four electrons (accepted from alkali metal atoms) which form a singlet. No such alteration in the arrangement of levels takes place in the $Li_4@C_{120}$ (long) complex, where two (of the four) electrons occupy level *A* and two other electrons occupy the two levels previously forming the degenerate E_1 level, thus yielding a ground triplet state.

Calculations performed for the metal-containing C_{240} complexes showed that singlet states are energetically more favorable than triplet states (the gain being 0.38 and 0.1 eV in $Li_2@C_{240}$ and $Li_4@C_{240}$, respectively). In this case, sequential filling of singly degenerate levels *A* is preferred (Fig. 4c).

In all metal-containing complexes studied, the set of levels filled by electrons accepted from incorporated lithium atoms (embedded state) is situated ~1–4 eV

(a) (b) (c)
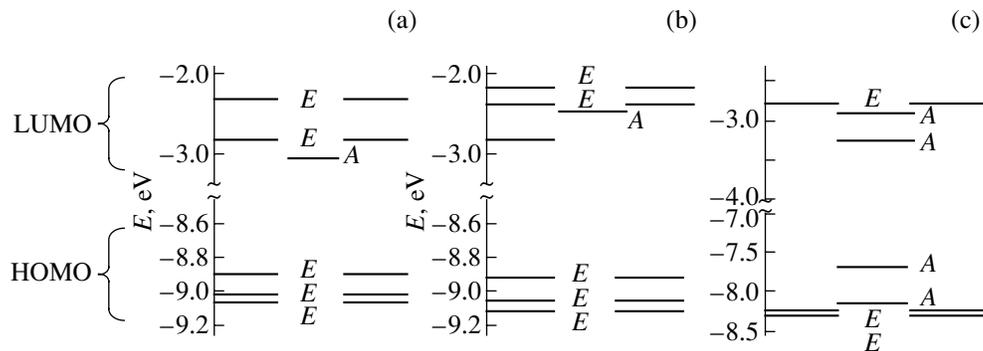
Fig. 4. Electron energy level structure in the valence band of toroidal carbon molecules: (a) C_{120} (short); (b) C_{120} (long); (c) C_{240}.

above the other filled levels. Thus, the passage of electrons from metal atoms to the carbon framework of the complex leads to formation of the embedded state (Fig. 5). A similar process was observed in the metal

Fig. 5. Densities of states in metal-containing complexes $Li_n@C_m$ calculated from the MNDO method: (a) C_{120} (long), $Li_2@C_{120}$ (long), and $Li_4@C_{120}$ (long); (b) C_{120} (short), $Li_2@C_{120}$ (short), and $Li_4@C_{120}$ (short); (c) $Li_2@C_{120}$ (long) simulated by molecular dynamics method for lithium atoms spaced at (*1*) $R_{min} = 2.95$ Å and (*2*) $R_{max} = 7.75$ Å; (d) C_{240}, $Li_2@C_{240}$, and $Li_4@C_{240}$.
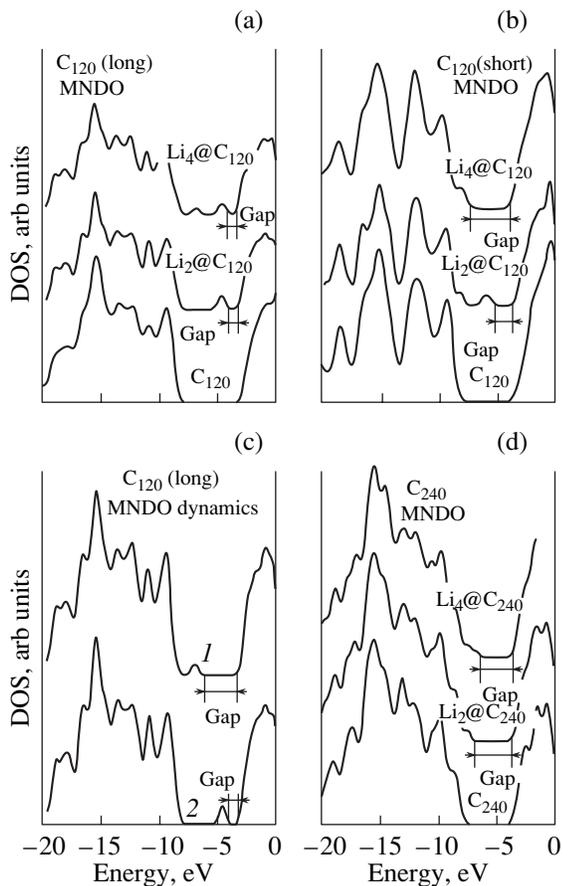
complexes of C_{60} fullerenes [1]. The shift of electron levels under the action of positively charged lithium atoms is less pronounced in the toroidal carbon molecules than in C_{60}, which is related to the greater dimensions of the former clusters. However, we may suggest that the same factor accounts for the inversion of energy levels leading to the triplet state formation in the case of toroidal molecules. This is confirmed by the results of calculation of the isoelectron C_{120}^{-2} ion, where no such inversion of levels takes place.

As can be seen from Figs. 5a, 5b, and 5d, the embedded level positions depend on the amount of incorporated metal atoms. As the number of such atoms increases, the embedded state in C_{240} complexes (Fig. 5d) shifts toward vacant levels. This displacement leads to a decrease in the bandgap width (Table 3). The metal-containing complexes based on C_{120} (short) exhibit an opposite pattern (Fig. 5b, Table 3), whereby the embedded state is situated closer to the vacant levels in $Li_2@C_{120}$ (short) than in the complex with four metal atoms. In the complexes based on C_{120} (long) with either two or four lithium atoms (Fig. 5a, Table 3), the embedded state shifts so as to completely shorten the forbidden band (1.8 eV). Thus, we may conclude that the appearance of the embedded state in the electron structure is a general property of all lithium-intercalated toroidal carbon compounds.

5. MOLECULAR DYNAMICS OF METAL-CONTAINING COMPLEXES OF TOROIDAL CARBON MOLECULES WITH LITHIUM

We have employed the molecular dynamics method to study the behavior of the incorporated alkali metal atoms inside a carbon cluster framework. The calculations were performed for both singlet and triplet states of the complexes containing two or four lithium atoms.

In C_{120} (short) isomers with any number of incorporated atoms and any multiplicity of the ground sate, the guest atoms performed small oscillations in a potential well at an energy minimum determined in the course of

the geometry optimization. The oscillating atoms did not leave the space bounded by *d–e–f* hexagon (Figs. 1, 2). This behavior is explained by the small internal diameter of this carbon cluster. In addition, a toroidal molecule of this type contains adjacent cavities with a diameter of ~2.8 Å connected by 2.2-Å windows. These windows play the role of barriers keeping lithium atoms within strictly confined regions inside the carbon molecule.

A significantly different pattern is observed for the guest metal atoms incorporated into the C_{120} (long) isomer. Since this isomer structure is characterized by a considerably greater internal diameter (~4 Å) as compared to that in C_{120} (short) and the inner surface is free of nodes (as well as that in C_{120} (short)), the incorporated metal atoms can move freely over the whole cavity of the carbon core. Nevertheless, the inner surface still has potential minima of two types. The first (global) minimum is situated in the vicinity of bond *5* (Figs. 1, 2d). The second minimum (with a higher energy) is at the center of a *d–e–f* hexagon (Fig. 1). Simulations of the behavior of lithium atoms in $Li_2@C_{120}$ and $Li_4@C_{120}$ complexes in the triplet state showed guest atoms passing from one minimum to another. These transitions were only performed between neighboring minima and did not significantly affect the positions of incorporated atoms. The same behavior was typical of lithium atoms in simulations of $Li_4@C_{120}$ complexes in the singlet state.

However, an essentially different pattern was observed for $Li_2@C_{120}$ complexes in the singlet state. Here, the incorporated alkali metal atoms, also passing from one minimum to another, shifted toward each other to form a pair spaced ~3 Å apart. After that, atoms of the couple jointly performed transitions between adjacent minima, thus migrating over the internal cavity. The Li–Li distance in the couple exhibited oscillations, but the maximum spacing between atoms never exceeded 6.3 Å. This behavior, as well as the resulting appearance of a nonzero orbital angular momentum of ions in the molecule at elevated temperatures, are explained by a change in the total orbital angular momentum of electrons. Indeed, the total angular moment of the system, representing a sum of the electron orbital angular momentum, nuclear angular momentum, and spin, has to be conserved. An increase in the temperature leads to changes in the effective internuclear distances and, hence, modifies the electron wavefunction of the system so that $\psi(r, R_0) \neq \psi(r, R_T)$, because the set of nuclear coordinates entering as parameters into this wavefunction also changes with the temperature ($\{R_0\} \neq \{R_T\}$). Therefore, the whole system (remaining in the state of the same multiplicity) must compensate for a change in the electron orbital angular momentum. This is achieved by changing the ion orbital angular momentum, as manifested by the motion of lithium atoms in the singlet state. The nonzero value of the spin component leads to a change in the proportion between the electron and ion orbital

angular momenta and in the onset temperature for the motion of atoms inside the cavity. This circumstance explains the absence of motions of the incorporated Li atoms in $Li_2@C_{120}$ complexes in the triplet state. A similar effect is observed upon changing the number of incorporated atoms in the same carbon framework.

Thus, the $Li_2@C_{120}$ complexes in the singlet state exhibit various atomic configurations with different electron structures depending on the temperature. Figure 5c shows two such structures, corresponding to the maximum and minimum distances between lithium atoms. The temperature-induced variations in the electron spectra must be accompanied by superposition of the electron structures corresponding to different configurations, so that some of the related spectral features must be smeared. This refers, in particular, to the embedded state. As the lithium atoms are removed from one another, the embedded state shifts toward vacant orbitals; on the contrary, a decrease in the spacing between metal atoms drives the embedded state away from the vacant levels. The difference between the positions of the embedded state reaches ~2 eV.

It should be noted, however, that a multiplet character of the system cannot be revealed without allowance for the correlation effects. Therefore, interpretations of the temperature dependence of the experimental photoelectron spectra allow us to judge the spin state of the carbon complexes studied.

The complexes of toroidal carbon C_{240} with different (two or four) numbers of lithium atoms exhibited no significant motions of incorporated metal atoms in either the singlet or triplet state. This can be explained by the presence of deep potential minima (absent in C_{120} tori of smaller diameter) on the inner surface of the carbon framework.

6. CONCLUSIONS

Toroidal carbon molecules possess significantly different atomic and electron structures. Factors such as the number of atoms in the cluster, symmetry, dimensions (internal and external diameters), and order of cycles connected in a segment affect both the structure of electron energy levels and the bandgap width.

The introduction of alkali metal atoms into internal cavities of the toroidal carbon molecules leads to analogous changes in the atomic and electron structures of all objects studied. The presence of lithium atoms increased the interatomic distances in the carbon framework of the complex as compared to those in the initial structure. The electron structure exhibited an embedded state in the forbidden band. The position energy of this state depends on a number of factors (amount of incorporated atoms, structure of the initial carbon molecule, multiplicity, etc.). On the whole, the effect of incorporated metal atoms reduces to the decrease in the bandgap width related to the appearance of the embedded state. The molecular dynamics data indicate that, under certain conditions (sufficiently large size of the internal cavity, the absence of barriers

or minima on the inner surface, or singlet ground state), the experimental spectra would exhibit smearing of the peak corresponding to the embedded levels, which is related to the mobility of metal ions in cavities of the carbon tori.

Files with film of the molecular dynamics are accessible on the server of the Kirensky Institute of Physics (Kirensky.iph.krasn.ru). The authors are ready to provide these data on request via e-mail (felix@iph.krasn.ru).

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