Energy of compressed endoatoms and the energy capacity of small endohedral rare-gas fullerenes*

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The excess energies of the endoatoms within endofullerenes X@C_n (X = He, Ne, Ar; n = 20—50) as compared with the energies of the free atoms X were estimated using the simplest Thomas—Fermi model and density functional calculations at the B3LYP/6-311G* level. The energy capacities of the endofullerenes under study are primarily determined by the contributions of the compressed electronic systems of the endoatoms rather than the stretched fullerene cages.

Key words: compressed atoms, energy capacity, endofullerenes, the Thomas—Fermi method, density functional theory.

Atoms confined within fullerene cages are of considerable interest from the viewpoint of general problem of compressed atoms research.[1] In this respect, small endofullerenes X@C_n ($n < 60$, X is a rare gas atom) are suitable subjects of investigation. In such systems, a small size of the fullerene inner cavity creates prerequisites for compression of the endoatoms whose chemical inertness simplifies the analysis and makes it possible to treat the interaction between the carbon cage and the endoatom as a purely steric pressure.

In the present work, we studied endofullerenes X@C_n (X = He, Ne, Ar; n = 20—50). Among them, the synthesis of the systems He@C_n with $n \geq 20$,[2] Ne@C_n with $n \geq 30$, and Ar@C_n with $n \geq 40$ [2,3] seems not to be impossible. According to calculations,[2—5] endoatoms in these systems are in fact in the compressed state. Correspondingly, the calculated total energy of an endofullerene is higher than the sum of the total energies of the free fullerene cage and the free endoatom. Here we consider the nature and localization of the excess energy of these systems (their energy capacities).

Calculation Procedure

Application of the Thomas—Fermi model

To elucidate the nature the excess energy of the endoatom and to approximately estimate this energy, we will start with application of the Thomas—Fermi (TF) statistical model for an atom confined in an impenetrable sphere of radius R (see Refs 6 and 7). In our case it is sufficient to use the simplest version of this model without corrections for exchange and other complicating factors.

According to a known model,[6] the total energy E of an atom confined within an impenetrable sphere is given by

$$\tilde{E} = \frac{3}{7}\frac{Z^2e^2}{\mu}\left\{\varphi'(0) + \frac{2}{15}x_0^{1/2}[\varphi(x_0)^{5/2}]\right\}, \qquad (1)$$

where Z is the atomic number of the atom in question and e is the charge of an electron,

$$\mu = \frac{a_0}{4}\left(\frac{9\pi^2}{2Z}\right)^{1/3} = \frac{0.8853a_0}{Z^{1/3}},$$

(a_0 is the Bohr radius). The function $\varphi(x)$ is the solution of the conventional Thomas—Fermi equation, $x = r/\mu$ (r is the distance to the atomic nucleus), and $x_0 = R/\mu$.

The energy E_{TF} of compression of the atom (*i.e.*, the difference between the energy $\tilde{E}$ and the energy of free atom) in units of $\frac{3}{7}\frac{Z^2e^2}{\mu}$ is plotted *vs.* x_0 in Fig. 1 (curve *3*).[6]

In the case under study, we know all parameters in expression (1), except the radius R of the model sphere, which should allow for a finite thickness of the carbon cage wall. For the sake of simplicity we will assume that the radius R for any endofullerene is equal to its average radius R' minus the atomic radius of carbon ($R_C = 0.77$ Å). The energies E_{TF} of some endohedral rare-gas fullerenes calculated using this model are listed in Table 1. As in our previous work,[3] we considered endofullerenes C_{20} (the isomer with C_i symmetry), C_{24} (the isomer with D_{6d} symmetry), and C_{30} (the isomer with C_{2v} symmetry). Herein-

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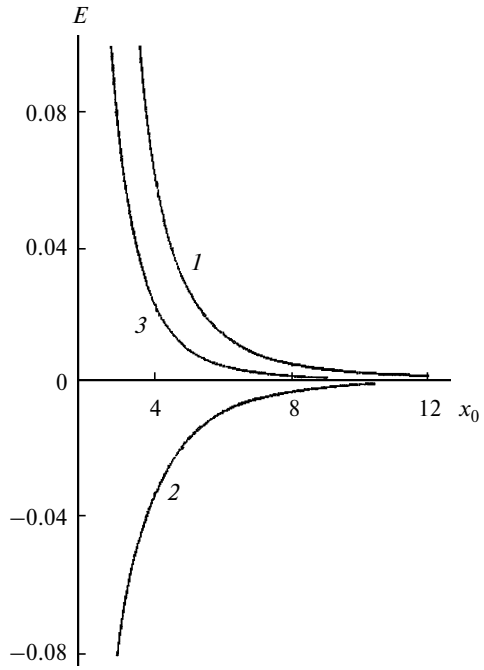

Fig. 1. Kinetic energy (*1*), potential energy (*2*), and total energy (*3*) of a compressed atom plotted *vs.* parameter x_0; the changes in these energies relative to free atom are shown (data taken from Ref. 6).

Table 1. Energy of confined atom compression in the Thomas—Fermi model

Endofullerene	R'	$R'-R_C$	$R'-R_C$	μ	x_0	E_{TF}
	Å		a.u.			
$Ne@C_{20}$	2.082	1.312	2.475	0.41	6.037	0.44
$Ar@C_{20}$	2.149	1.379	2.602	0.34	7.653	0.65
$Ne@C_{24}$	2.275	1.505	2.840	0.41	6.927	0.27
$Ar@C_{24}$	2.326	1.556	2.936	0.34	8.635	0.33
$Ne@C_{30}$	2.528	1.758	3.317	0.41	8.090	0.103

Note. R' is the average radius of endofullerene, μ and x_0 are parameters of the Thomas—Fermi model, and E_{TF} is the energy of confined atom compression in the Thomas—Fermi model.

after, the symmetry and the isomer numbering scheme are given according to the accepted classification.[8] We excluded from consideration all systems, for which the E_{TF} values cannot be found using the plot presented in Ref. 6, and endohedral compounds of helium, because for obvious reasons helium can not be described by the Thomas—Fermi method.

Quantum chemical calculations

It is clear that it is impossible to immediately compare the E_{TF} estimates obtained in this work with the experimental data. However, the E_{TF} values can be compared with the results of density functional calculations, which provide a reasonably correct description of fullerenes and the corresponding endohedral compounds.[2—5,9,10] Table 2 lists the total energies E_1 of the endofullerenes shown in Table 1 and of some other endohedral systems (see Ref. 3). The E_1 values of endofullerenes $X@C_{60}$ are given here for comparison; they were obtained using the same method as in Ref. 3. Table 2 also lists the total energies E_2 of the fullerene polyhedra (with the geometries corresponding to those in endofullerenes) and the total energies E_3 of free He, Ne, and Ar atoms calculated in the same approximation. Then the $E_{DFT} = E_1 - E_2 - E_3$ values can be considered as the desired estimates of the excess energies of the endoatoms in endofullerenes (ignoring the energy of chemical interaction between the rare gas endoatom and fullerene). In this work the E_1, E_2, and E_3 energies were calculated with the B3LYP three-parameter exchange-correlation functional[11] and a conventional 6-311G* split-valence basis set[11] using the GAUSSIAN-98 program.[11,12] When calculating the E_1 energy, the endoatom was placed at the center of the C_n molecule. Full geometry optimization of all endohedral systems under study showed that the endoatom retained its position.

Table 2. Endoatom compression energies obtained from B3LYP/6-311G* calculations

Endofullerene	$-E_1$	$-E_2$	$-E_3$	E_{DFT}
	a.u.			
$He@C_{20}$	764.38451	761.58953	2.91303	0.11805
$Ne@C_{20}$	890.20135	761.56571	128.95091	0.31527
$Ar@C_{20}$	1288.18039	761.42713	527.55319	0.79993
$He@C_{24}$	916.86252	914.01465	2.91303	0.06516
$Ne@C_{24}$	1042.78461	914.00501	128.95091	0.17131
$Ar@C_{24}$	1440.95344	913.94632	527.55319	0.54607
$He@C_{30}$	1145.65513	1142.77250	2.91303	0.03040
$Ne@C_{30}$	1271.64507	1142.76902	128.95091	0.07486
$Ar@C_{30}$	1670.00197	1142.74670	527.55319	0.29792
$He@C_{32}$	1221.95431	1219.06342	2.91303	0.02214
$Ne@C_{32}$	1347.95798	1219.06149	128.95091	0.05442
$Ar@C_{32}$	1746.35732	1219.04542	527.55319	0.24129
$He@C_{40}$	1526.91806	1524.01227	2.91303	0.00724
$Ne@C_{40}$	1652.95058	1524.01203	128.95091	0.01236
$Ar@C_{40}$	2051.46148	1524.00852	527.55319	0.10023
$He@C_{50}$	1908.18924	1905.27855	2.91303	0.00234
$Ne@C_{50}$	2034.23024	1905.27848	128.95091	−0.00085
$Ar@C_{50}$	2432.79139	1905.27694	527.55319	0.03874
$He@C_{60}$	2289.50190	2286.59068	2.91303	0.00181
$Ne@C_{60}$	2415.54564	2286.59068	128.95091	−0.00405
$Ar@C_{60}$	2814.13409	2286.59066	527.55319	0.00976

Note. E_1 is the total energy of endofullerene $X@C_n$, E_2 is the total energy of the deformed carbon cage of the endofullerene having the geometry acquired in the endofullerene; E_3 is the energy of a free He, (Ne, Ar) atom, and E_{DFT} is the energy of atom compression.

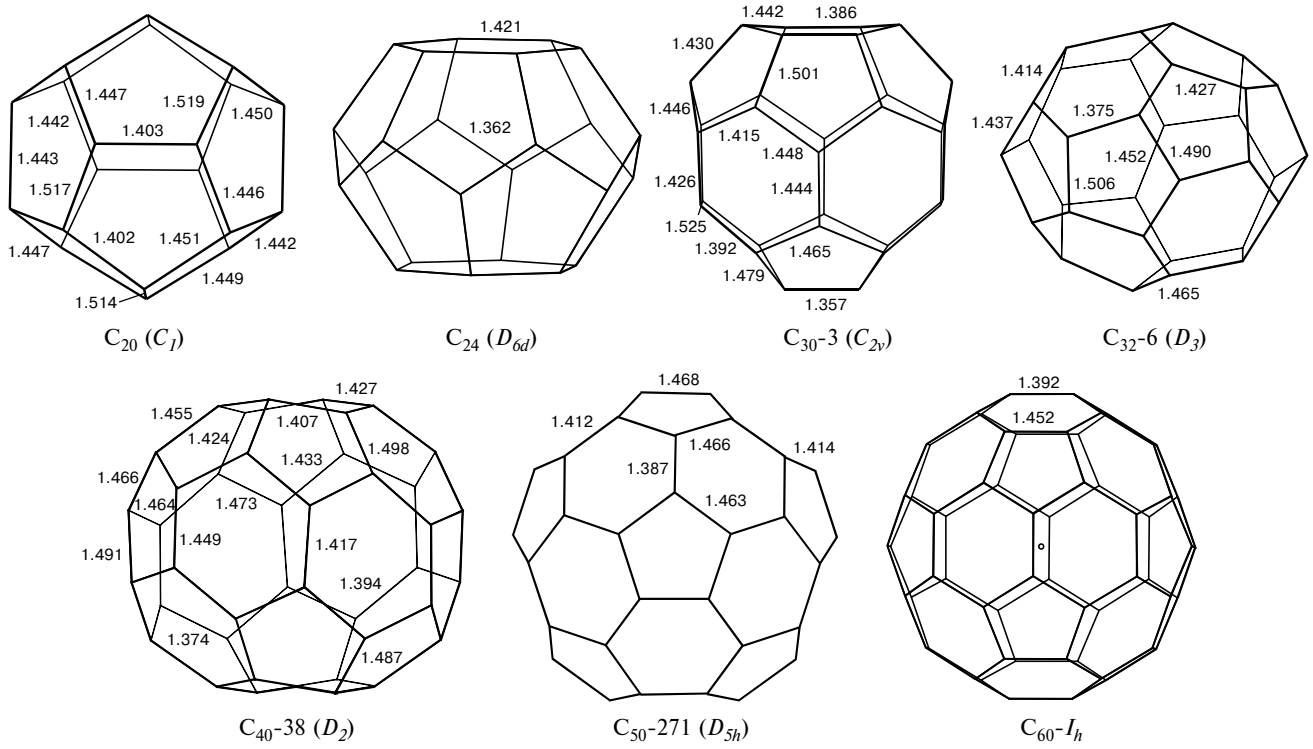

Fig. 2. Geometric parameters of the most stable fullerenes C_n obtained from B3LYP/6-31G* calculations. The lengths of inequivalent bonds and the number and symmetry of isomers are shown.

Results and Discussion

For many reasons, one should not expect that the E_{DFT} estimates listed in Table 2 will be equal to the E_{TF} energies from Table 1. Indeed, not only two different approximations used in our calculations, but also a marked deviation of the shape of the small fullerenes from the sphere (Fig. 2) play a significant role (this was included in the quantum chemical calculations but ignored in the Thomas—Fermi model). Nevertheless, the E_{TF} and E_{DFT} values are in reasonable agreement, which allows one to qualitatively interpret the endoatom contributions to the energy capacities of the endofullerenes as the work of compression of inhomogeneous electron gas in the endoatom by the stretched fullerene carbon cages. As should be expected, these contributions increase with an increase in the atomic number of the confined atom and decrease as the fullerene size increases. According to calculations for hypothetical endofullerenes Ne@C_n and Ar@C_n (n = 20, 24), these contributions are unrealistically large (10—20 eV) compared to ~3 eV for He@C_{20}, Ne@C_{30} and Ar@C_{40} (see Tables 1 and 2; 1 a.u. ≈27.2 eV); the synthesis of the three last-named systems seems not to be impossible.[3]

The contributions of the carbon cages to the total excess energies of the endofullerenes can also be found with ease. Table 3 lists the calculated total energies $E_{total}(C_n)$ of the carbon cages of the free endofullerenes

Table 3. Energies of stretching of endofullerene carbon cages obtained from B3LYP/6-311G* calculations

Endofullerene	$-E_2$	$-E_{total}(C_n)$	$E_2 - E_{total}(C_n)$
	a.u.		
He@C_{20}	761.58953	761.59305	0.00352
Ne@C_{20}	761.56571	761.59305	0.02734
Ar@C_{20}	761.42713	761.59305	0.16592
He@C_{24}	914.01465	914.01628	0.00163
Ne@C_{24}	914.00501	914.01628	0.01127
Ar@C_{24}	913.94632	914.01628	0.06996
He@C_{30}	1142.77250	1142.77330	0.00080
Ne@C_{30}	1142.76902	1142.77330	0.00428
Ar@C_{30}	1142.74670	1142.77330	0.02660
He@C_{32}	1219.06342	1219.06382	0.00040
Ne@C_{32}	1219.06149	1219.06382	0.00233
Ar@C_{32}	1219.04542	1219.06382	0.01840
He@C_{40}	1524.01227	1524.01232	0.00005
Ne@C_{40}	1524.01203	1524.01232	0.00029
Ar@C_{40}	1524.00852	1524.01232	0.00380
He@C_{50}	1905.27855	1905.27856	0.00001
Ne@C_{50}	1905.27848	1905.27856	0.00008
Ar@C_{50}	1905.27694	1905.27856	0.00162
He@C_{60}	2286.59068	2286.59069	0.00001
Ne@C_{60}	2286.59068	2286.59069	0.00001
Ar@C_{60}	2286.59066	2286.59069	0.00003

Note. E_2 is the total energy of the deformed endofullerene carbon cage having the geometry acquired in the endofullerene and $E_{total}(C_n)$ is the total energy of the corresponding free fullerene.

under study, the total energies E_2 of the deformed cages of the endofullerenes, and the differences between them. A comparison of these differences with the corresponding data in Tables 1 and 2 shows that the excess energy of endofullerenes is localized on the endoatoms. The contributions of the stretched fullerene polyhedra are much smaller (sometimes, by an order of magnitude). Of course, here we left too low energies (10^{-3}—10^{-4} a.u. or lower) out of consideration. Based on these data, it is impossible to draw substantiated conclusions about the actual relative magnitude of such energies. We can only state that endoatoms in endofullerenes are practically uncompressed and the cages of the corresponding endofullerenes are not stretched.

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