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Energy Spectrum and Optical Absorption Spectra of exohedral Fullerene $C_{70}Br_{10}$ within the Hubbard Model

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Energy spectrum exohedral fullerene $C_{70}Br_{10}$ with the C_s symmetry groups have been obtained within the Hubbard model and static fluctuation approximation. The energy states have been classified using the methods of group theory, and the allowed transitions in the energy spectra of molecule $C_{70}Br_{10}$ have been determined. On the basis of the energy spectrum of exohedral fullerene $C_{70}Br_{10}$ is given an interpretation of experimentally observed optical absorption bands molecule $C_{70}Br_{10}$.

Keywords: Hubbard model, Green's functions, energy spectrum, fullerenes, nanosystems, fullerene C_{70} , exohedral fullerene $C_{70}Br_{10}$.

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1. Introduction

In 1985, simultaneously with fullerene C_{60} , fullerene C_{70} was discovered [1], whose structure was studied using nuclear magnetic resonance (NMR) [2]. On the NMR spectrum ^{13}C fullerene C_{70} , five peaks were detected, in the ratio 10:20:10:20:10. From this spectrum it followed that fullerene C_{70} contains five groups of nonequivalent carbon atoms, which are in the ratio 10:20:10:20:10. From the results obtained, it was concluded that the fullerene molecule C_{70} , shown in Fig. 1, has symmetry D_{5h} .

From the Schlegel diagram, which is shown in Fig. 2, it can be seen that the fullerene C_{70} with the symmetry group D_{5h} has eight unequal bonds, denoted by the letters a, b, c, d, e, f, g, h ; and five groups of nonequivalent carbon atoms: $G_1 = \{1, 2, 3, 4, 5, 62, 63, 66, 67, 70\}$, $G_2 = \{6, 9, 12, 15, 18, 61, 64, 65, 68, 69\}$, $G_3 = \{7, 8, 10, 11, 13, 14, 16, 17, 19, 20, 43, 44, 47, 48, 51, 52, 55, 56, 59, 60\}$, $G_4 = \{21, 22, 25, 26, 29, 30, 33, 34, 37, 38, 41, 42, 45, 46, 49, 50, 53, 54, 57, 58\}$, $G_5 = \{23, 24, 27, 28, 31, 32, 35, 36, 39, 40\}$.

The G_1 set includes atoms, which are at vertices of junction of the two hexagons and one pentagon and, furthermore, each of these atoms has one adjacent neighbor of the same G_1 set. To the set G_2 belong to atoms that are located at the vertices of the junction of two hexagons and one pentagon, and each of them has no nearest neighbors from the same set G_2 . To set G_3 belong to the atoms that are located at the vertices of the junction of two hexagons and one pentagon, and each of them has one nearest neighbor from the same set G_3 . In this case, the edge to which both atoms belong is the boundary between two hexagons. To set G_4 belong to the atoms that are located at the vertices of the junction of two hexagons and one pentagon, and each

of them has one nearest neighbor from the same set G_4 , and the edge to which both atoms belong is the boundary between the hexagon and the pentagon. The G_5 set includes atoms, which are at vertices of junction of one hexagon and two pentagons, and each of these atoms has one adjacent neighbor of the same G_5 set.

Along with the study of the physical properties of fullerene C_{70} , studies of its chemical properties were also carried out; many different compounds of this fullerene were obtained. One of the first chemical compounds of

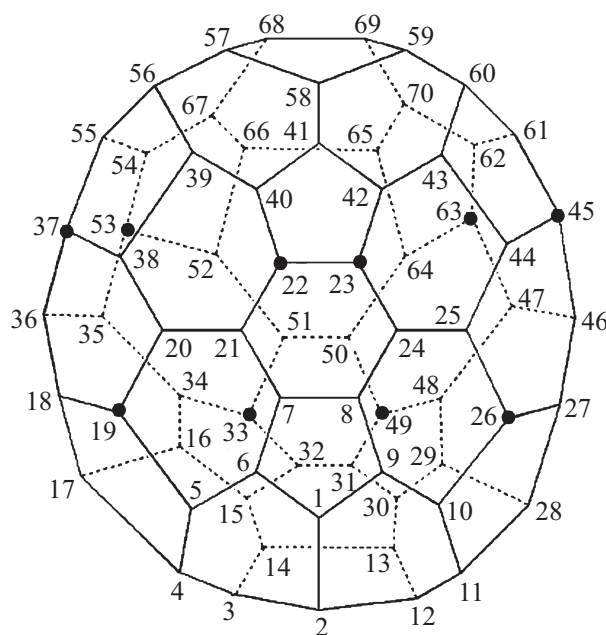


Figure 1. Schlegel Fullerene diagram C_{70} indicating the position of the carbon atoms and the bonds between the carbon atoms.

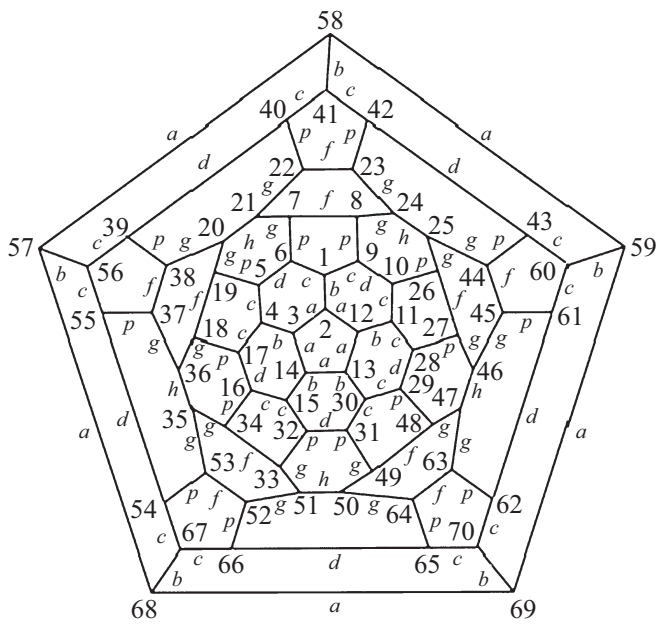


Figure 2. Schlegel Fullerene diagram C_{70} indicating the position of the carbon atoms and the bonds between the carbon atoms.

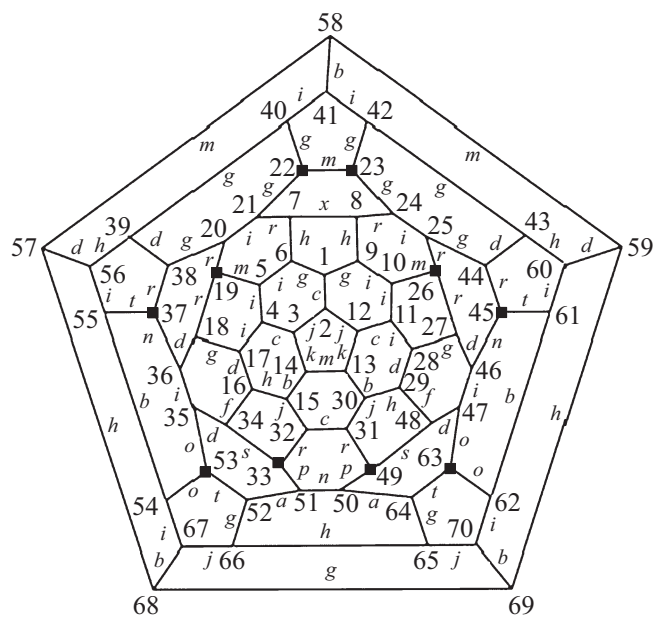


Figure 3. Schlegel diagram of exofullerene $C_{70}Br_{10}$ indicating the position of carbon atoms, bonds between carbon atoms and carbon atoms with which bromine atoms are bound.

fullerenes C_{70} and C_{60} were their halides [3,4]. Quite a lot of papers [5–7] are devoted to the study of the physical and chemical properties of the fullerene C_{70} . In addition to studying the halides of fullerenes C_{70} and C_{60} , quite a lot of work is devoted to the study of halides of other fullerenes as well: C_{50} [8], C_{90} [9], C_{96} [10], etc. The increased interest in fullerene halides is due to the fact that they have a number of properties that are valuable for practical

purposes. For example, $C_{50}Cl_{10}$ is a promising material for nonlinear optics, since this compound has a fairly high static polarizability and a second hyperpolarizability [11]. It should also be noted that halogenated fullerenes are promising as multifunctional additives to petroleum products that can simultaneously improve their antioxidant and anti-wear performance characteristics [12]. In addition, fullerene halides are important compounds that are used to produce a wide variety of materials [13]. To obtain new materials based on fullerene halides, knowledge of the chemical and physical properties of these compounds is necessary.

It should be noted that the bromides of this fullerene are obtained most simply from the fullerene halides C_{70} . For example, the bromide $C_{70}Br_{10}$ is obtained in two stages. Initially, with the interaction of fullerene C_{70} with liquid bromine at room temperature, monosolvated bromide $C_{70}Br_{10} \times Br_2$ is formed. Then, when heated $C_{70}Br_{10} \times Br_2$ to $70^\circ C$, the bromide $C_{70}Br_{10}$ is formed, the output of which is approximately 91% [14].

The conducted studies [15] have shown that the molecule $C_{70}Br_{10}$ has a symmetry of C_s , and the bromine atoms are associated with those carbon atoms that, as can be seen from Fig. 1, they are located in the equatorial region of fullerene C_{70} . From the Schlegel diagram for the molecule $C_{70}Br_{10}$, shown in Fig. 3, it can be seen that bromine atoms are bound to carbon atoms that belong to the set G_4 , and in each hexagon, which consists of four atoms belonging to the set G_4 and two atoms belonging to the set G_5 , contains two carbon atoms bound to bromine atoms.

The Hubbard model [27] is commonly used to characterize the electron properties of the carbon fullerenes and nanotubes [16–26]. Within the framework of this model, the energy spectra and optical absorption spectra of fullerene were obtained in the approximation of static fluctuations (ASF). C_{20} with symmetry groups I_h , D_{5d} and D_{3d} [16], fullerene C_{24} with symmetry groups O_h , D_6 and D_{6d} [17], fullerene C_{26} with symmetry group D_{3h} [18], fullerene C_{28} with the symmetry group T_d [19], fullerene C_{36} with symmetry group D_{6h} [20], fullerene C_{50} and exofullerene $C_{50}Cl_{10}$ with symmetry group D_{5h} [21], fullerene C_{60} [22], fullerene C_{70} [23], fullerene C_{80} with the symmetry group I_h [24], and in work [26] the electronic properties of carbon nanotubes were investigated. The results obtained in [21–24] agree fairly well with experimental data.

The aim of this work is to study the energy spectrum of an exohedral fullerene $C_{70}Br_{10}$ with a symmetry group C_s in the framework of the Hubbard model in the approximation of static fluctuations.

2. Energy spectrum of the fullerene C_{70} .

As known, the electronic properties of carbon fullerenes and nanotubes generally depend on the behavior of

π -electrons in these molecules. To describe the π -electron system of the fullerene C₇₀Br₁₀, we will use the Hubbard model [10]:

$$H = \sum_{\sigma,i} \varepsilon_i n_{i\sigma} + \sum_{\sigma,i \neq j} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + \frac{1}{2} \sum_{\sigma,i} U_i n_{i\sigma} n_{i\bar{\sigma}}, \quad (1)$$

where $c_{i\sigma}^{\dagger}, c_{i\sigma}$ — the operators of creation and annihilation of electrons with the σ spin at the i site; $n_{i\sigma}$ — the operator of the number of particles with the σ spin at the i site; ε_i — the energy of the one-electron atomic state at the i site; t_{ij} — the transfer integral characterizing electron hops from the i site to the j site; U_i — the energy of the Coulomb repulsion of two electrons at the i -m site; $\bar{\sigma} = -\sigma$.

To find numerical values for the transfer integrals that are included in the Hubbard model Hamiltonian (1) and correspond to the molecule C₇₀Br₁₀, we use the following relation [23,24]:

$$t_{ij} = -8.17065 \cdot \exp(-1.69521 \cdot x_{ij}), \quad (2)$$

where x_{ij} — the distance between two carbon atoms, one of which is located at the site i , and the other — at the site j .

X-ray diffraction studies have shown that the distances between carbon atoms in a fullerene bromide molecule C₇₀Br₁₀ [15] have the following values:

$$\begin{aligned} x_a &= 1.37(2) \text{ \AA}, x_b = 1.38(2) \text{ \AA}, x_c = 1.39(2) \text{ \AA}, \\ x_d &= 1.40(2) \text{ \AA}, x_f = 1.41(2) \text{ \AA}, x_g = 1.42(2) \text{ \AA}, \\ x_h &= 1.43(2) \text{ \AA}, x_i = 1.44(2) \text{ \AA}, x_j = 1.45(2) \text{ \AA}, \\ x_k &= 1.46(2) \text{ \AA}, x_m = 1.48(2) \text{ \AA}, x_n = 1.49(2) \text{ \AA}, \\ x_o &= 1.50(2) \text{ \AA}, x_p = 1.51(2) \text{ \AA}, x_r = 1.41(2) \text{ \AA}, \\ x_s &= 1.53(2) \text{ \AA}, x_t = 1.54(2) \text{ \AA}, x_x = 1.59(2) \text{ \AA}. \end{aligned} \quad (3)$$

Now, substituting (3) into the relationship (2), we obtain the numerical values for the transfer integrals for the fullerene C₇₀Br₁₀ with the C_s symmetry group:

$$\begin{aligned} t_a &= -0.82863 \text{ eV}, & t_b &= -0.81470 \text{ eV}, \\ t_c &= -0.80101 \text{ eV}, & t_d &= -0.78754 \text{ eV}, \\ t_f &= -0.77430 \text{ eV}, & t_g &= -0.76129 \text{ eV}, \\ t_h &= -0.74849 \text{ eV}, & t_i &= -0.73591 \text{ eV}, \\ t_j &= -0.72354 \text{ eV}, & t_k &= -0.71138 \text{ eV}, \\ t_m &= -0.68766 \text{ eV}, & t_n &= -0.67611 \text{ eV}, \\ t_o &= -0.66474 \text{ eV}, & t_p &= -0.65357 \text{ eV}, \\ t_r &= -0.64258 \text{ eV}, & t_s &= -0.63178 \text{ eV}, \\ t_t &= -0.62116 \text{ eV}, & t_x &= -0.57068 \text{ eV}. \end{aligned} \quad (4)$$

To find the energy spectrum of a molecule C₇₀Br₁₀, we use the method of Green's anticommutatory functions [28]:

$$\langle\langle c_{f\sigma}^{\dagger} | c_{f\sigma} \rangle\rangle = \theta(\tau) \langle [c_{f\sigma}^{\dagger}(\tau), c_{f\sigma}(0)]_+ \rangle, \quad (5)$$

where $f = 1, \dots, N$; N — a number of sites of the quantum system.

As you know [28] to find the energy spectrum of a quantum system, it is enough to calculate the poles of Fourier images of anticommutatory Green's functions. It can be shown [22,23] that the Fourier image of Green's anticommutatory function (5) in the ASF has the following form:

$$\langle\langle c_{j\sigma}^{\dagger} | c_{j\sigma} \rangle\rangle_E = \frac{i}{2\pi} \sum_{m=1}^p \frac{F_{j,m}}{E - E_m + i\hbar},$$

$$E_k = \varepsilon + e_k, E_{k+p/2} = E_k + U, F_{j,m} = q_{m,\sigma} \cdot Q_{j,m},$$

$$Q_{j,k+p/2} = Q_{j,k}, k = 1, \dots, p/2, \quad (6)$$

$$q_{m,\sigma} = \begin{cases} 1 - \frac{n}{2}, & m = 1, \dots, p/2, \\ \frac{n}{2}, & m = \frac{p}{2} + 1, \dots, p, \end{cases}$$

where p — the number of the energy states of the quantum system, E_m — the energy of the m -th state of the quantum system, $F_{j,m}$ — the spectrum density of the m -th energy state.

An important characteristic of the energy spectrum of a quantum system is the degree of degeneracy of its energy states, which can be found by knowing the spectral density of these states, which is contained in the Green's function (6) [22,23]:

$$g_i = \sum_{j=1}^N Q_{i,j}, \quad (7)$$

where g_i — the degree of degeneracy of the i -th energy level, N — the number of sites of the nanosystem.

To find the anticommutatory Green's functions, first of all it is necessary to determine the dependence of the creation operators on time. To do this, using the Hamiltonian (1) and the Schlegel diagram shown in Fig. 3, as in [16–24], we write for the operators $c_{1\sigma}^{\dagger}(\tau), c_{1\sigma}^{\dagger}(\tau)n_{1\bar{\sigma}}(\tau), \dots, c_{70\sigma}^{\dagger}(\tau), c_{70\sigma}^{\dagger}(\tau)n_{70\bar{\sigma}}(\tau)$, given in the Heisenberg representation, the

equations of motion in the ASF:

$$\left\{ \begin{aligned} \frac{dc_{1\sigma}^+}{d\tau} &= \varepsilon c_{1\sigma}^+ + t_c c_{2\sigma}^+ + t_g (c_{6\sigma}^+ + c_{9\sigma}^+) + U c_{1\sigma}^+ n_{1\bar{\sigma}}, \\ \frac{d(c_{1\sigma}^+ n_{1\bar{\sigma}})}{d\tau} &= (\varepsilon + U) c_{1\sigma}^+ n_{1\bar{\sigma}} + t_c c_{2\sigma}^+ n_{2\bar{\sigma}} \\ &\quad + t_g (c_{6\sigma}^+ n_{6\bar{\sigma}} + c_{9\sigma}^+ n_{9\bar{\sigma}}), \\ &\dots\dots\dots \\ \frac{dc_{70\sigma}^+}{d\tau} &= \varepsilon c_{70\sigma}^+ + t_j c_{65\sigma}^+ + t_i c_{62\sigma}^+ + t_b c_{69\sigma}^+ + U c_{70\sigma}^+ n_{70\bar{\sigma}}, \\ \frac{d(c_{70\sigma}^+ n_{70\bar{\sigma}})}{d\tau} &= (\varepsilon + U) c_{70\sigma}^+ n_{70\bar{\sigma}} + t_j c_{65\sigma}^+ n_{65\bar{\sigma}} \\ &\quad + t_i c_{62\sigma}^+ n_{62\bar{\sigma}} + t_b c_{69\sigma}^+ n_{69\bar{\sigma}}, \end{aligned} \right. \quad (8)$$

where $\tau = it, t$ — time.

Before solving the system of equations (8), it is also necessary to set the numerical values of the parameters ε and U . In the work [22], based on the experimentally observed optical absorption spectrum of fullerene C₆₀, numerical values of these parameters were found in the framework of the Hubbard model in the ASF: $\varepsilon = -7.824$ eV, $U = 5.662$ eV. We note that the numerical value of the parameter $U = 5.662$ eV agrees with the results presented in the paper [29], where $U \approx 5$ eV was obtained.

Now, having solved the system of differential equations (8) taking into account the numerical values of the transfer integrals (4) and the parameters $\varepsilon = -7.824$ eV and $U = 5.662$ eV, we obtain expressions for the creation operators $c_{1\sigma}^+(\tau), \dots, c_{70\sigma}^+(\tau)$. Substituting these solutions in (5), we get Green's anticommutatory functions. Then, having obtained Fourier images from Green's anticommutatory functions, we obtain expressions that coincide in appearance with the relation (6). Using the solution of the system of equations, as well as relationships (7) and (6), we obtain the numerical values for E_k, \bar{e}_k and g_k , see Table 1, where \bar{e}_k — the energy value of the k -th level in relation to $\varepsilon + U/2$, which, as it is clear from the relationship (6), is correlated to the magnitude E_k as follows:

$$E_k = \varepsilon + \frac{U}{2} + \bar{e}_k, \quad (9)$$

where

$$\bar{e}_k = \begin{cases} e_k - \frac{U}{2}, & k = 1, \dots, p/2, \\ e_k + \frac{U}{2}, & k = \frac{p}{2} + 1, \dots, p. \end{cases} \quad (10)$$

As it follows from the relationships (9) and (10), the energy states of the fullerene C₁₀ form two Hubbard subbands, wherein the lower Hubbard subband is formed by the energy states focused near the energy ε , while the upper Hubbard subband is formed by the energy states focused near the energy $\varepsilon + U$. The energy states forming the energy spectrum of the molecule C₇₀Br₁₀ with the symmetry

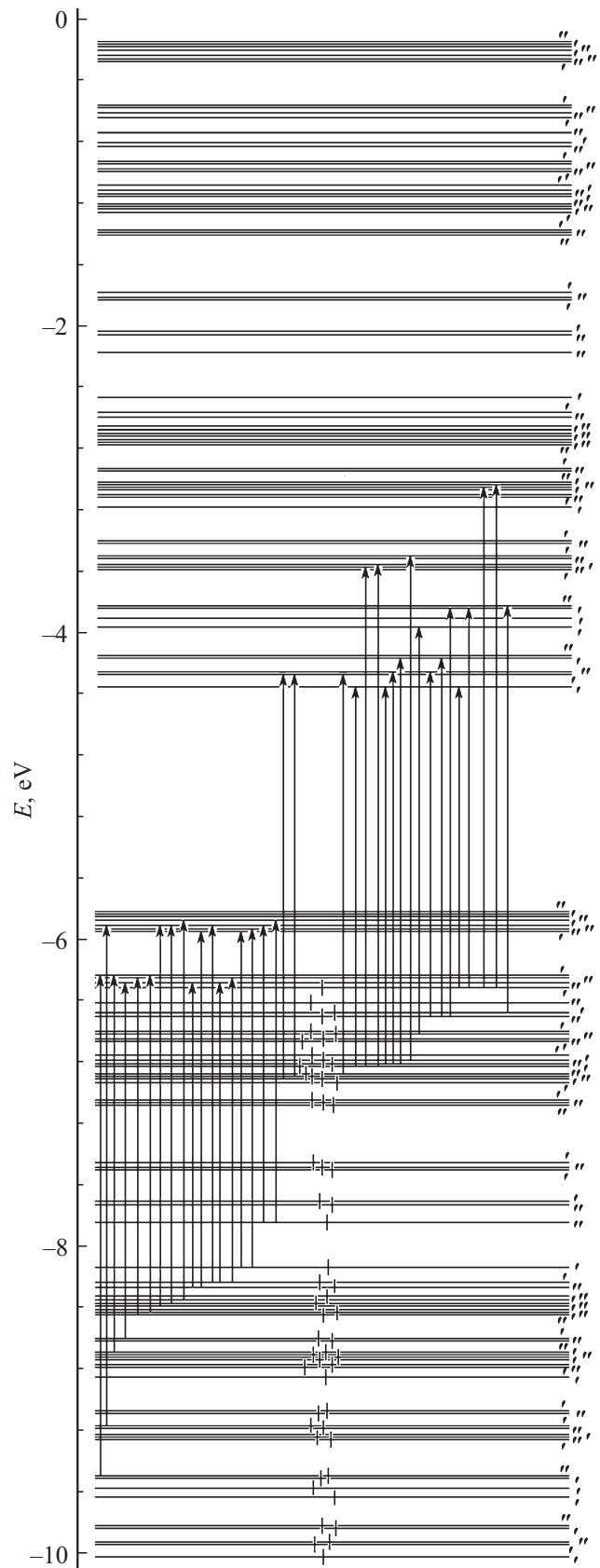


Figure 4. Energy spectrum of the molecule C₇₀Br₁₀.

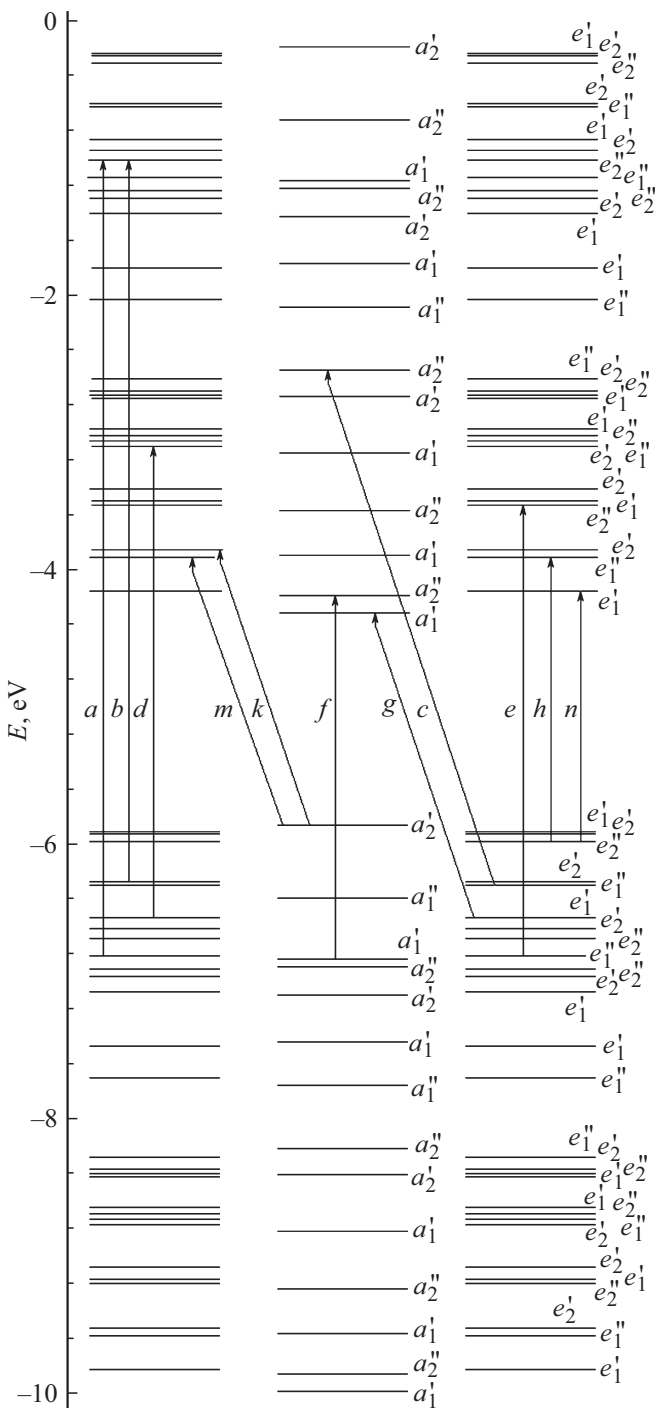


Figure 5. Fullerene energy spectrum C_{70} [23].

group C_s can be classified by irreducible representations of the group C_s . The energy spectrum of a molecule $C_{70}Br_{10}$ is depicted in Fig. 4, where the icon ' corresponds to an irreducible representation a' , and the icon '' corresponds to an irreducible representation a'' . It can be seen from Fig. 4 that the degree of degeneracy of all energy states of a molecule $C_{70}Br_{10}$ is equal to one. This is due to the fact that all irreducible representations of the group C_s are one-

dimensional: a' and a'' [30]. In work [23] the fullerene energy spectrum was obtained C_{70} with the symmetry group D_{5h} , see Fig. 5. Energy states of fullerene C_{70} in Fig. 5 are classified according to one-dimensional a'_1, a'_2, a''_1, a''_2 and two-dimensional e'_1, e'_2, e''_1, e''_2 irreducible representations of the group D_{5h} . In Fig. 5, for convenience, the transitions forming the optical absorption spectrum of fullerene are depicted C_{70} , doubly degenerate states correspond to the energy levels of the first and third column, and non-degenerate states correspond to the energy levels of the second column.

Comparing the energy spectra of fullerene bromide $C_{70}Br_{10}$ with symmetry group C_s and fullerene C_{70} with the symmetry group D_{5h} , see fig. 4 and 5, we see that the decrease in symmetry caused by the addition of bromine atoms to fullerene C_{70} , led to the splitting of doubly degenerate energy states. From Fig. 4 it is also seen that the exohedral fullerene $C_{70}Br_{10}$ has ten energy states in the lower Hubbard subband free. It is due to the fact that when the molecule $C_{70}Br_{10}$ is formed, the ten valence electrons of the fullerene C_{70} are spent to form strong chemical bonds with the bromine atoms.

The optical absorption spectrum is an important physical characteristic of any molecule. Using the above energy spectrum of the exohedral fullerene $C_{70}Br_{10}$ with the C_s symmetry group, it is possible to find the transitions which form the optical spectrum of this molecule. The group theory [30] may be used to demonstrate that a molecule with symmetry group C_s has the following allowed transitions in its energy spectrum:

In the work [31], experimental studies were conducted to study the optical absorption spectrum of bromide $C_{70}Br_{10}$ in benzene, in 1,2-dichlorobenzene and in 1,2-dimethylbenzene. The conducted studies have shown that in the optical absorption spectrum of bromide $C_{70}Br_{10}$, six absorption bands can be distinguished, as can be seen from Fig. 6: a, b, c, d, f, g , represented by in table 1. Knowing the energy spectrum of the

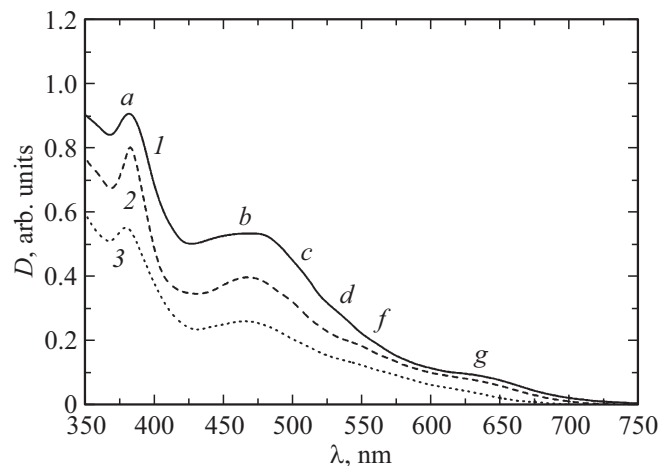


Figure 6. Absorption spectrum $C_{70}Br_{10}$ in benzene (curve 1), in 1,2-dichlorobenzene (2), in 1,2-dimethylbenzene (3) [31].

Table 1. Experimental and theoretical values of wavelengths λ and energies E corresponding to absorption bands in the optical spectrum of a molecule $C_{70}Br_{10}$

Bands absorptions	λ , nm [31]	E , eV [31]	Theor. E , eV
<i>a</i>	380	3.269	3.268
<i>b</i>	470	2.643	2.643
<i>c</i>	505	2.460	2.465
<i>d</i>	535	2.322	2.326
<i>f</i>	565	2.199	2.195
<i>g</i>	635	1.956	1.958

Table 2. Transitions forming absorption bands *a*, *b*, *c*, *d*, *f*, *g*

ΔE	ΔE , eV	ΔE	ΔE , eV	ΔE	ΔE , eV
a		$E_{78}-E_{57}$	2.6499	$E_{64}-E_{33}$	2.3339
$E_{81}-E_{49}$	3.2650	$E_{72}-E_{46}$	2.6506	f	
$E_{82}-E_{49}$	3.2652	c		$E_{62}-E_{26}$	2.1935
$E_{63}-E_9$	3.2655	$E_{71}-E_{50}$	2.4540	$E_{63}-E_{27}$	2.1953
$E_{66}-E_{14}$	3.2677	$E_{66}-E_{30}$	2.4652	$E_{64}-E_{35}$	2.2054
$E_{92}-E_{60}$	3.2717	$E_{66}-E_{29}$	2.4662	$E_{65}-E_{35}$	2.2058
$E_{93}-E_{60}$	3.2730	$E_{78}-E_{60}$	2.4664	g	
$E_{84}-E_{51}$	3.2745	$E_{63}-E_{23}$	2.4710	$E_{66}-E_{36}$	1.9328
b		$E_{67}-E_{31}$	2.4719	$E_{61}-E_{34}$	1.9519
$E_{76}-E_{55}$	2.6311	$E_{71}-E_{49}$	2.4721	$E_{71}-E_{60}$	1.9579
$E_{79}-E_{58}$	2.6383	d		$E_{67}-E_{36}$	1.9628
$E_{73}-E_{50}$	2.6383	$E_{61}-E_{25}$	2.3164	$E_{61}-E_{33}$	1.9817
$E_{72}-E_{48}$	2.6403	$E_{73}-E_{57}$	2.3256	$E_{62}-E_{34}$	1.9839
$E_{74}-E_{50}$	2.6427	$E_{66}-E_{34}$	2.3291		
$E_{72}-E_{47}$	2.6469	$E_{74}-E_{57}$	2.3301		

$C_{70}Br_{10}$, molecule, its experimentally observed spectrum of optical absorption can be interpreted as follows. The bands of the optical absorption spectrum that correspond to the experimentally observed energies $E_a, E_b, E_c, E_d, E_f, E_g$ presented in Table 1 can be interpreted as bands formed by transitions presented in Table 2. As can be seen from Table 2, the energies of these transitions are close to the experimental values [31].

3. Conclusion

Thus, the optical absorption of the exohedral fullerene $C_{70}Br_{10}$, which is observed experimentally, agrees fairly well with the optical absorption spectrum of this molecule, which is obtained from the energy spectrum of the molecule $C_{70}Br_{10}$ within the Hubbard model in the static fluctuation approximation.

We note also that in [21–24] the energy spectra of fullerenes C_{60} , C_{70} , endohedral fullerenes $Lu_3N@C_{80}$ and $Y_3N@C_{80}$, and exohedral fullerene $C_{50}Cl_{10}$ were studied, also performed in the scope of the Hubbard model in the approximation of static fluctuations. These studies showed that the optical absorption spectra of these molecules,

which were observed experimentally, also agree fairly well with the optical absorption spectra of the molecules C_{60} , C_{70} , $Y_3N@C_{80}$, $Y_3N@C_{80}$ and $C_{50}Cl_{10}$, which have been obtained within the Hubbard model in the static fluctuation approximation. This allows one to state that the Hubbard model in the static fluctuation approximation characterizes fairly well the electron properties of carbon nanosystems.

Conflict of interest

The author declares that he has no conflict of interest.

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