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Electronic Structure and Optical Properties of Compounds of C_{90} Fullerene Isomers with Chlorine

© A.I. Murzashev [1], N.V. Melnikova [2], A.P. Zhumanazarov [1], M.Yu. Kokurin [1], S.K. Paymerov [1]

[1] Mari State University, Yoshkar-Ola, Russia
[2] National Research Tomsk State University,
634050 Tomsk, Russia
e-mail: phdmelnikova@gmail.com, nanotubes59@mail.ru

Within the framework of Hubbard's model using an approximation of static fluctuations, the electronic structure and optical properties of compounds of C_{90} fullerene isomers with chlorine atoms are investigated. The energy spectrum of o-electron subsystem is shown to be divided into several unbound electronic subsystems when the number of the attached chlorine atoms becomes greater than (or about) 30. Each of subsystems behaves like a separate system in this case. The energy spectra and optical absorption spectra of ten different chlorine compounds $C_{90}@Cl_n$ have been calculated. Their optical properties are predicted.

Keywords: fullerene, fullerene chlorides, the Hubbard model, static fluctuation approximation, energy spectrum, optical absorption spectrum.

Introduction

Fullerenes and carbon nanotubes (CNT), discovered more than thirty years ago, are still of great interest to researchers. This interest is primarily due to the unique properties due to which these compounds can be used in various fields of science and human activity. However, despite such a long period of study, the nature of their unique electronic properties is not fully understood.

Experience shows that fullerenes can form compounds with both metals and non-metals. Compounds with metals, as a rule, are a fullerene, inside which either a metal atom or a cluster containing metal atoms is embedded [1]. Typically, such a cluster is a donor-type cluster, and such fullerenes are called endohedral, thereby emphasizing that the cluster is located inside the fullerene shell. In the first approximation, the electronic structure of such a system can be described as an electronic subsystem of π fullerene electrons with the addition of a certain number of valence electrons of an interstitial atom or an interstitial cluster [1].

Compounds of fullerenes with non-metal atoms or complexes containing non-metal atoms are another type of fullerene compounds [2–4]. As a rule, such complexes have an acceptor character. In this case, an exohedral type compound is formed, i.e., the complexes are attached to the outer shell of the fullerene from the outside, forming rigid σ bonds with the corresponding carbon atoms. In this case, there is a significant rearrangement of the π-electronic subsystem of the fullerene [3,4]. This is evidenced by the fact that the optical absorption spectra (OSA) of the systems $C_{60}@(CF_3)_{10}$ and $C_{70}@(CF_3)_{10}$, measured in [3,4], significantly depend on the nature of the distribution of CF_3

complexes over the fullerene shell. Thus, the rearrangement of the π-electronic subsystem can no longer be described as a simple introduction or removal of a certain number of electrons from the π-electronic subsystem. The fact is that the introduced acceptor complex changes the type of hybridization of the carbon atom associated with it from the sp^2- to sp^3-state. As a result, both the π electron and the π state are absent on this atom, i.e. this node becomes inaccessible to π electrons [5]. Calculations of energy spectra and OSA taking into account the foregoing, performed by us in the paper [5] as part of the Hubbard model, showed that the obtained OSA of the $C_{60}@(CF_3)_{10}$ and $C_{70}@(CF_3)_{10}$ systems with different distributions of CF_3 complexes at a good qualitative level coincide with the experimental spectra, in [3,4].

Obviously, all of the above also applies to exohedral fullerenes, which are compounds of fullerenes with chlorine atoms. Chlorine, being monovalent, takes one π electron from the carbon atom at the „attachment site" and the carbon atom passes into the hybridized state sp^3. As a result, the number of π electrons in the system decreases by one, and the "π-electron level disappears at the „ site, i.e. the carbon atom of this node becomes inaccessible to π electrons.

The present paper is devoted to the theoretical study of the electronic and optical properties of the second type of compounds, namely, fullerene C_{90} isomers with chlorine, the synthesis of which is reported in the paper [2]. Energy spectrum calculations were carried out in the approximation of static fluctuations for the Hubbard model. Previously, this method was successfully used to describe the electronic properties of both CNT [6] and fullerenes [7].
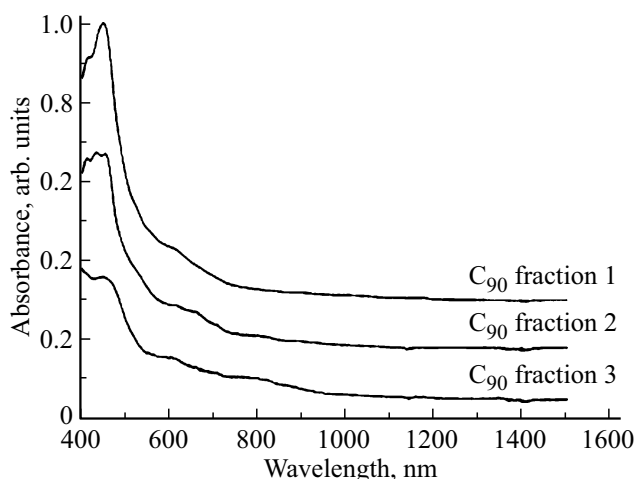
Figure 1. Optical absorption spectra of fullerene C_{90} isomer fractions synthesized in [2].
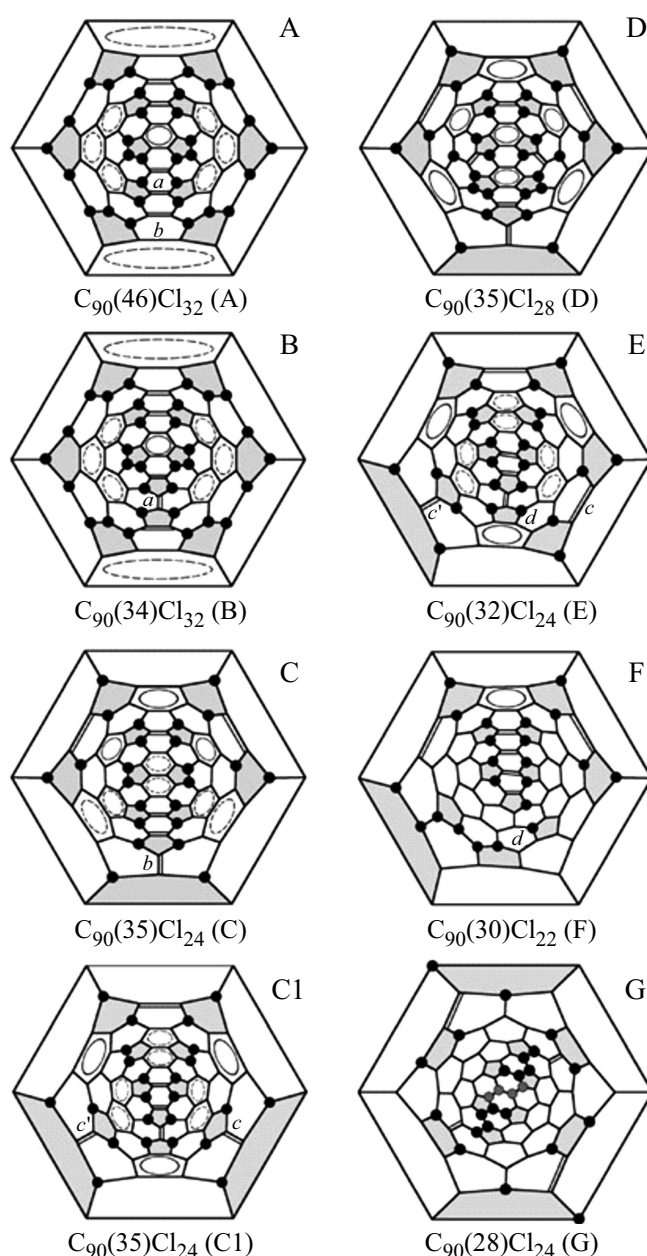

Figure 2. Schlegel diagrams of compounds included in fractions 1−3 after chlorination [2].

1. Energy spectrum and optical absorption spectra of C_{90} fullerene isomers

Three soot fractions containing the isomers № 46 (C_{2v}), № 34 (C_s), № 35 (C_s), № 32 (C_1), № 30 (C_1), № 28 (C_2) of the C_{90} fullerene (the numbering is given in accordance with the Atlas of fullerenes [8]). Fraction № 1 contained isomers № 46 and 35, fraction № 2 — isomers № 32 and 35, fraction № 3 — isomers № 28, 30 and 34. The measured OSA of these fractions are shown in the figure taken from [2] (Fig. 1). Subsequently, these three fractions were subjected to chlorination by the method described in detail in [2]. Analysis of the synthesized fractions showed that they contain the following compounds:

−$C_{90}(46)Cl_{32}$ (A), $C_{90}(34)Cl_{32}$ (B), $C_{90}(35)Cl_{28}$ (D) (fraction 1),

−$C_{90}(35)Cl_{24}$ (C), $C_{90}(32)Cl_{24}$(E), $C_{90}(35)Cl_{24}$ (C1) (fraction 2),

−$C_{90}(34)Cl_{32}$ (B), $C_{90}(30)Cl_{22}$ (F), $C_{90}(28)Cl_{24}$ (G) (fraction 3).

Numbers in parentheses are isomer numbers according to the Atlas of Fullerenes [8]. The Schlegel diagrams are shown in Fig. 2 (the places of addition of chlorine are indicated by solid circles). Taking into account the intrasite Coulomb interaction of π electrons at one site, we calculated the energy spectra and SOS of pure (without chlorine) isomers № 46 (C_{2v}), № 34 (C_s), № 35 (C_s), № 32 (C_1), № 30 (C_1), № 28 (C_2) of fullerene C_{90}, which are contained in fractions 1−3 (Fig. 3). As part of the approximation of static fluctuations for the Hubbard model, the energy spectra of fullerene isomers C_{90} contained in the indicated fractions were calculated.

To clarify the question of the applicability limits of the static fluctuation approximation for the Hubbard model, let us briefly dwell on the main provisions of this approximation. The Hubbard model, which takes into account the
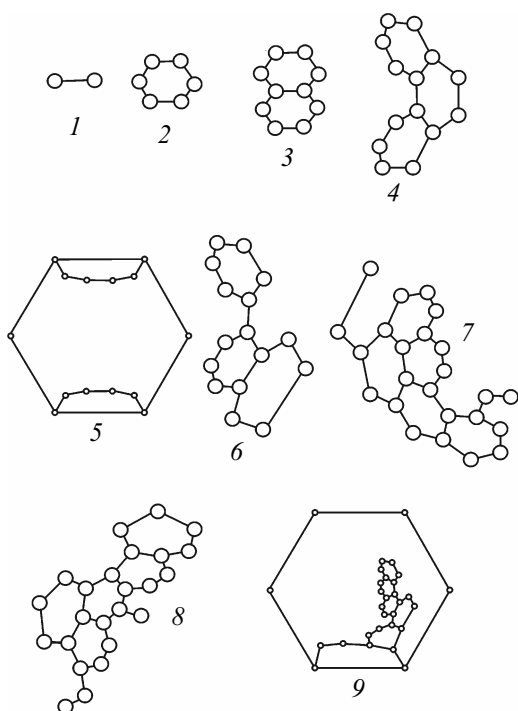
Coulomb repulsion of electrons at one site, which, according to [9] is large in systems with sp^2 , was proposed by Hubbard in 1963 [10]. As part of this model, it was possible to explain the metal-insulator transitions that take place in some compounds of transition metals. The Hamiltonian for this model is:

$$H = \varepsilon \sum_{i,\sigma} n_{i,\sigma} + B \sum_{i,j,\sigma} (a_{i\sigma}^+ a_{j\sigma} + a_{j\sigma}^+ a_{i\sigma}) + U \sum_{i,\sigma} n_{i,\uparrow} n_{i,\downarrow}.$$
(1)

Here ε — electron energy level, B — hopping integral, U — Coulomb integral, $n_{i,\sigma} = a_{i,\sigma}^+ a_{i,\sigma}$ — operator of the number of particles in a node i with spin σ, $a_{i\sigma}^+$ and

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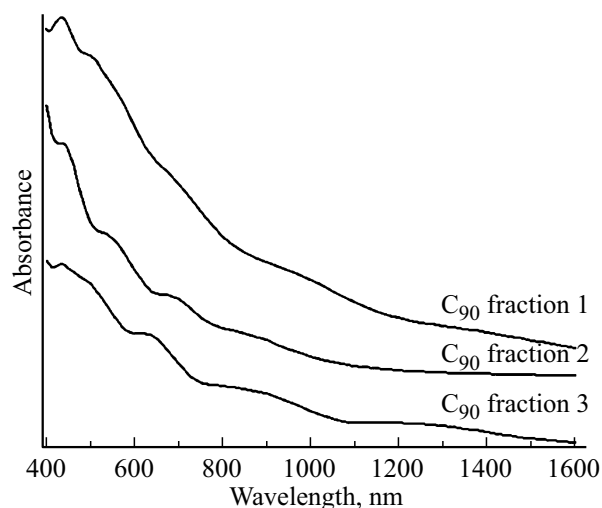
Figure 3. Optical absorption spectra of fractions 1−3 (before chlorination), calculated on the assumption that in each fraction the isomers included in their composition are present in equal amounts.

Cluster composition of the studied compounds

Compound	Composition	Compound	Composition
$C_{90}(46)Cl_{32}$ (A)	Cluster 1−5 Cluster 2−1 Cluster 4−2 Cluster 5−1	$C_{90}(35)Cl_{28}$ (D)	Cluster 1−7 Cluster 2−8
$C_{90}(34)Cl_{32}$ (B)	Cluster 1−5 Cluster 2−1 Cluster 4−2 Cluster 5−1	$C_{90}(32)Cl_{24}$ (E)	Cluster 1−6 Cluster 2−2 Cluster 3−1 Cluster 6−2
$C_{90}(35)Cl_{24}$ (C)	Cluster 1−6 Cluster 2−2 Cluster 3−1 Cluster 6−2	$C_{90}(30)Cl_{22}$ (F)	Cluster 1−4 Cluster 2−1 Cluster 7−1 Cluster 9−1
$C_{90}(35)Cl_{24}$ (C1)	Cluster 1−6 Cluster 2−2 Cluster 3−1 Cluster 6−2	$C_{90}(28)Cl_{24}$ (G)	Cluster 1−2 Cluster 2−2 Cluster 8−2

Figure 4. Schlegel diagrams of clusters into which isomers are broken down after chlorination.

$a_{i\sigma}$ — operators of creation and annihilation of electrons with spin σ on the ith node respectively. In (1) summation over i is performed over all sites of the system, and summation over j in the second term is performed over the sites that are neighboring to the site i. The first term — energy of π-electrons, the second — takes into account electron hops between neighboring sites, the third — Coulomb interaction of electrons at one site. Despite

the clarity, the Hubbard model is extremely complex in terms of obtaining calculated results. All problem solving methods within this model use the assumption that the width of the conduction band W is much smaller than the Coulomb integral U, $W \ll U$ [11]. In carbon nanosystems $W \sim 13$ eV [12], and the jump integral, taking into account screening, $U \sim 7$ eV [9]. This makes the well developed diagram technique for the Hubbard model [11] based on the $W \ll U$ assumption inapplicable. In [13,14] an approximation of static fluctuations was proposed to study carbon nanosystems as part of the Hubbard model. As part of this approximation, we write down the equation of motion for the creation operators taken in the Heisenberg representation:

$$\frac{da_{i\sigma}^{+}(\tau)}{d\tau} = \varepsilon_i a_{i\sigma}^{+}(\tau) + B \sum_{j=1} a_{j\sigma}^{+}(\tau) + U a_{i\sigma}^{+}(\tau)\Delta\hat{n}_{i\bar{\sigma}}(\tau).$$

(2)

Here $\bar{\sigma} = -\sigma$, and $\Delta\hat{n}_{i\bar{\sigma}} = \langle n_{i\bar{\sigma}}\rangle - \Delta n_{i\bar{\sigma}}$ — operator of fluctuation of particle number. It can be seen from (2) that in order to find $a_{i\sigma}^{+}(\tau)$ it is required to write the equation of motion for the operator $\Delta n_{i,\bar{\sigma}}(\tau)a_{i\sigma}^{+}(\tau)$. This will require writing equations of motion for higher order operators Instead, after writing (2), we will approximately assume that $[H_0, H] \approx 0$ (square brackets denote the commutator), where H_0 is — part of the Hamiltonian (1):

$$H_0 = \varepsilon \sum_{i,\sigma} n_{i,\sigma} + B \sum_{i,j,\sigma}(a_{i\sigma}^{+}a_{j\sigma} + a_{j\sigma}^{+}a_{i\sigma}).$$

(3)

The $[H_0, H] \approx 0$ approximation is called the static fluctuation approximation, since it [13] is equivalent to the fact that the fluctuation operator $\Delta n_{i,\bar{\sigma}}(\tau)$ does not depend on time, and therefore it can be set equal to $\Delta\tilde{n}_{i\bar{\sigma}}(\tau) = \Delta\tilde{n}_{i\bar{\sigma}}(0) = nn_{i\bar{\sigma}}(0) - n$, where $n = \langle n_{i\bar{\sigma}}\rangle$. Thus,
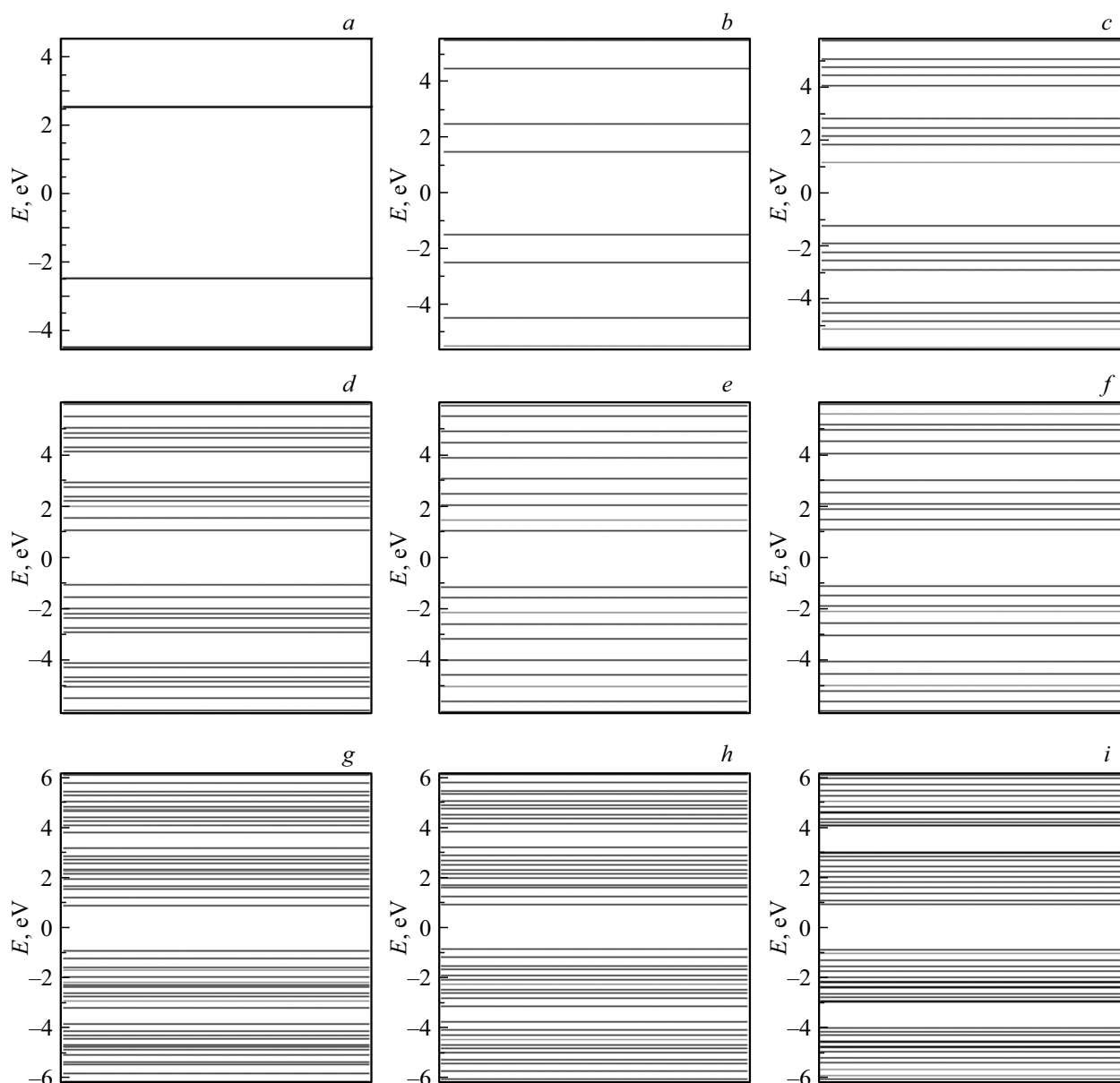
Figure 5. Energy spectra of clusters into which isomers are broken down after chlorination. The Latin letters *a–i* denote the energy spectra of clusters numbered 1−9, respectively.

this approximation, which is called the approximation of static fluctuations, greatly simplifies the problem of finding the energy spectrum of the system under study. Within this approximation the Coulomb interaction of electrons on one site is taken into account precisely. Also, their hops from node to node, which form the π-electronic zone, are accurately taken into account. This does not take into account the interference of these two processes. As a result, the approximation cannot describe the complex processes that take place in systems described by the Hubbard model. These processes, due to the screening of the local momentum of a partially localized π electron by other similar electrons, lead to the Kondo effect, and also, according to some researchers [15], to high-temperature superconductivity (HTSC) in cuprates and, possibly, in carbon nanosystems [16].

2. Energy spectrum and optical absorption spectra of chlorine compounds with fullerene C_{90} isomers

Based on the energy spectra of isomers № 28, 30, 32, 34 and 46 (numbers according to the Atlas of Fullerenes [8]) of fullerene C_{90}, obtained in the approximation of static fluctuations, their OSA were constructed (Fig. 3). The spectra were built on the assumption that the fractions under consideration contain the same number of isomers indicated above. A comparison of the experimental (Fig. 1)
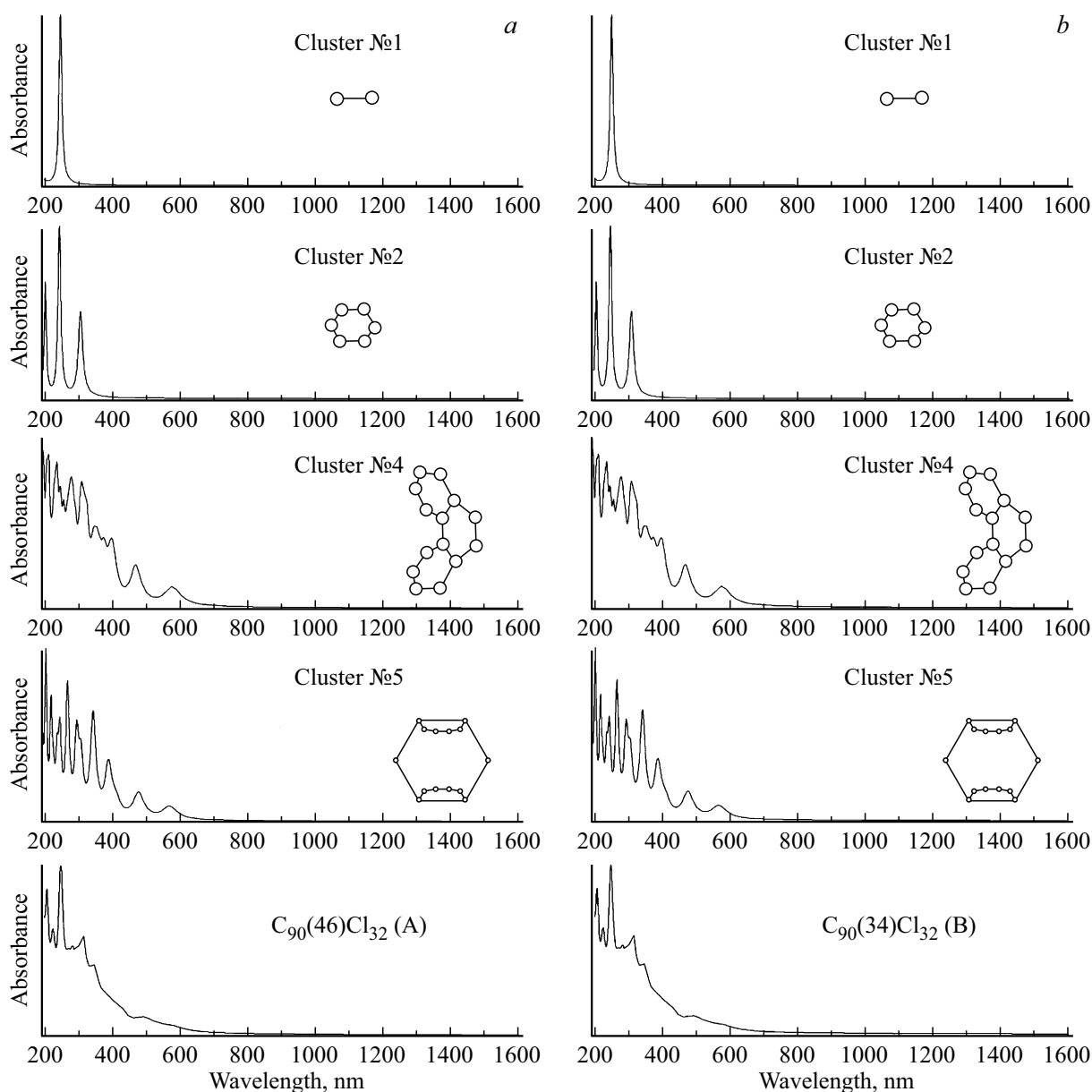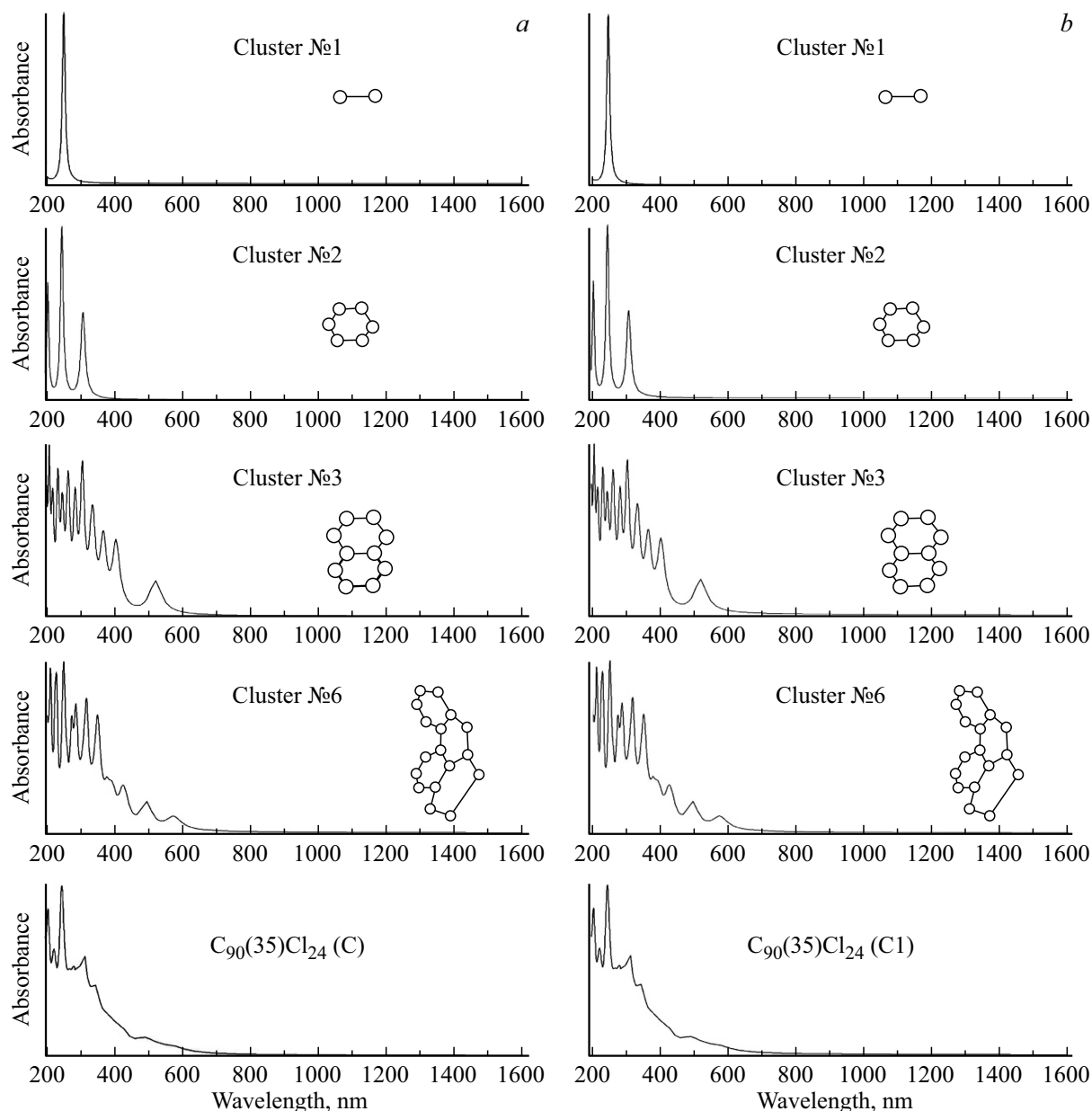
Figure 6. Optical absorption spectra of compounds CC$_{90}$(46)Cl$_{32}$ (A) (*a*) and C$_{90}$(34)Cl$_{32}$ (B) (*b*). Bottom — OSA of the connection, top — OSA of the clusters included in it.

and theoretical (Fig. 3) spectra shows that they coincide qualitatively. This indicates the adequacy of the model and methods used by us to calculate the energy spectrum and construct OSA for fullerenes of different symmetry. These models and methods are described in detail in the papers [5,17–19].

The energy spectra of compounds of C$_{90}$ fullerene isomers with chlorine atoms were calculated using the methods mentioned above. When calculating the spectra, it is required to take into account that at the attachment site, the atom passes from the sp^2- to the sp^3-state. As a result, both the π electron and the π state are absent at this site. Consequently, as part of the approximation of static fluctuations, from the fullerene sites accessible to π

electrons, it is required to exclude sites at which chlorine atoms are attached. This approach was implemented when calculating the energy spectra of compounds C$_{60}$@(CF$_3$)$_{10}$ and C$_{70}$@(CF$_3$)$_{10}$ [5]. The optical absorption spectra of these compounds, obtained on the basis of energy spectra, are in good qualitative agreement with the experimental ones [3,4]. When studying the compounds declared in this paper, we will proceed in a similar way.

Before starting the calculations, it is required to find out the structure of the compound with „excluded" sites obtained as a result of chlorination. In all compounds that are part of fractions 1−3, the number of chlorine atoms reaches the values I∼ 30. As a result, the system of atoms of each compound is divided into clusters of atoms in the
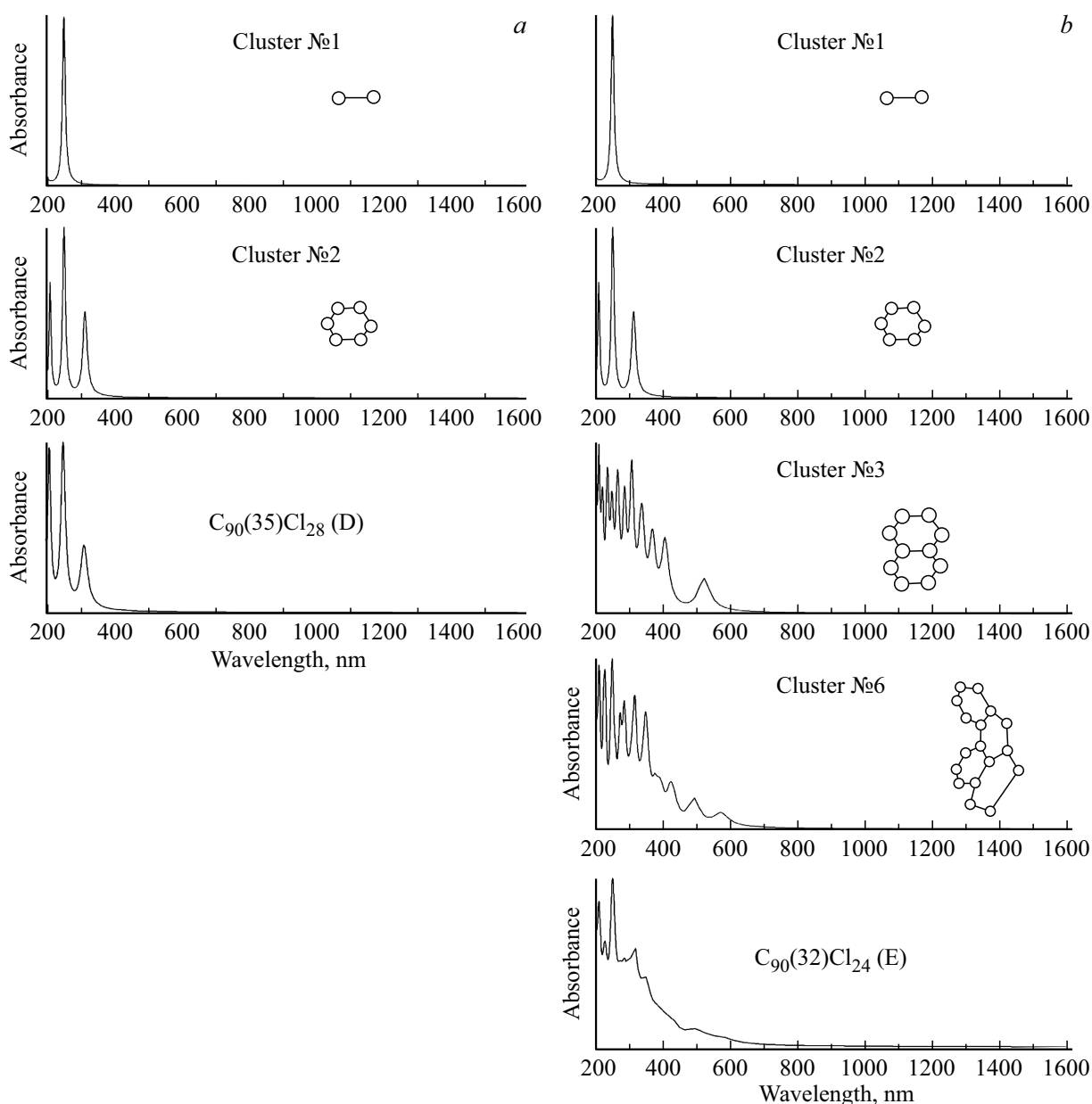
Figure 7. Optical absorption spectra of compounds $CC_{90}(35)Cl_{24}$ (A) (*a*) and $C_{90}(35)Cl_{24}$ (B) (*b*). Bottom — OSA of the connection, top — OSA of the clusters included in it.

sp^2 state. Let us call these clusters π clusters separated by atoms in the sp^3 state. The division into clusters is a consequence of the fact that the probability of hopping of π electrons from one π cluster to another as part of the model is negligible. Thus, the energy spectrum of compounds will be a set of energy spectra of clusters. It is obvious that, due to the impossibility of absorption with the transition of π electrons between clusters, the OSA of the compounds under consideration should be calculated as the OSA of individual noninteracting π clusters. Analysis shows that compounds $C_{90}(46)Cl_{32}$ (A), $C_{90}(34)Cl_{32}$ (B), $C_{90}(35)Cl_{24}$ (C), $C_{90}(35)Cl_{24}$ (C1), $C_{90}(35)C_{I28}$ (D), $C_{90}(32)Cl_{24}$ (E), $C_{90}(30)Cl_{22}$ (F), $C_{90}(28)Cl_{24}$ (G), being

parts of the fractions 1−3 are divided into π clusters the Schlegel diagrams of which are shown in Fig. 4. The table shows which clusters the compounds A, B, C, C1, D, E, F and G consist of.

The energy spectra of № 1−9 clusters calculated as part of the static fluctuation approximation for the Hubbard model with parameters $\tilde{U} \sim 7.0\,\text{eV}$, $B \sim 1.0\,\text{eV}$ [5,17–19] are shown in Fig. 5. The energy spectra of clusters contain from four to sixty energy levels. Energy levels with negative energies of π electrons „of the lower Hubbard subband" correspond to a single occupation of the node, and with positive energies of π electrons „of the upper Hubbard subband" to double occupation of the node. The states „of
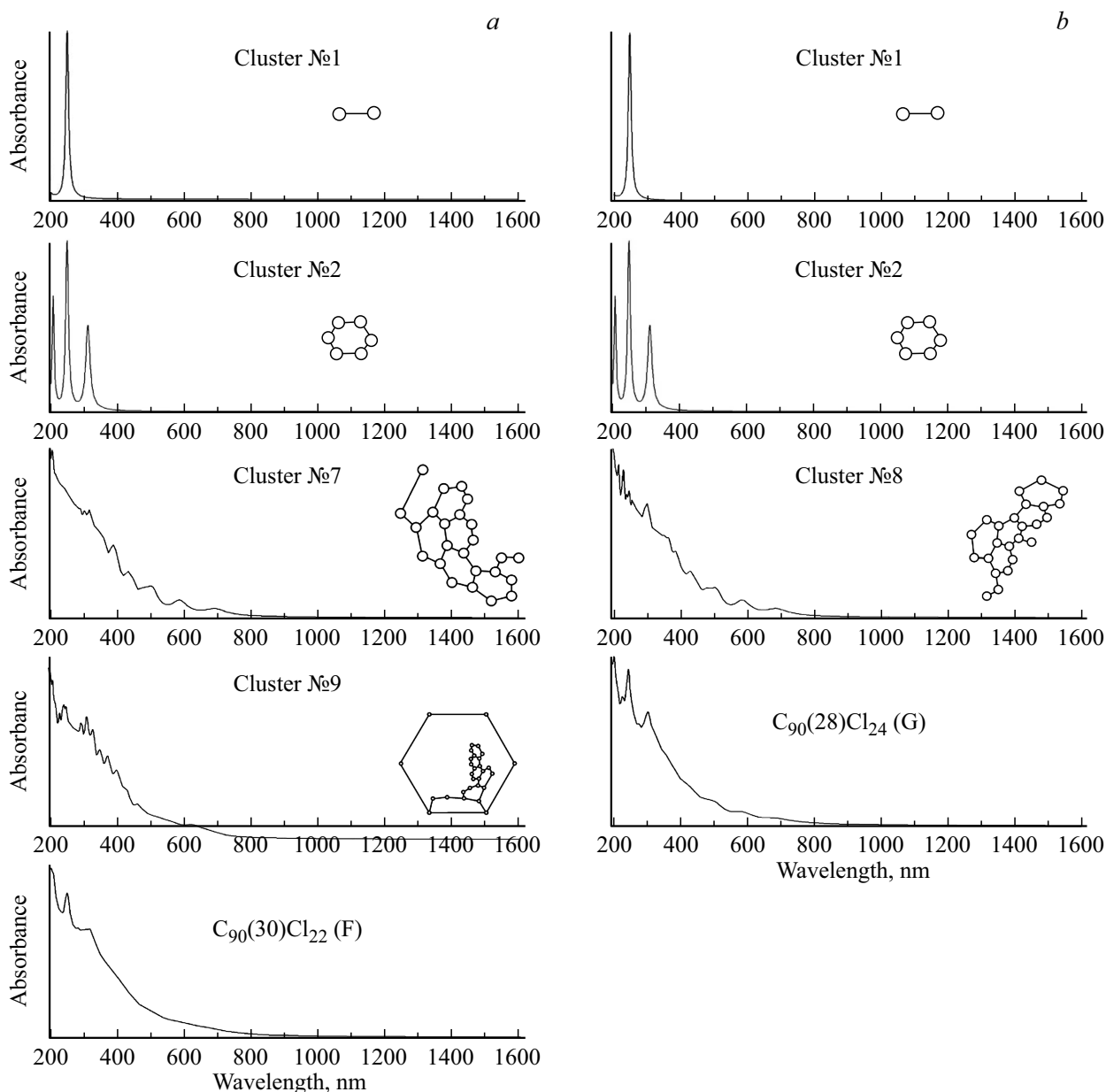
Figure 8. Optical absorption spectra of compounds $C_{90}(35)Cl_{28}$ (D) (*a*) and $C_{90}(32)Cl_{24}$(E) (*b*). Bottom — OSA of the connection, top — OSA of the clusters included in it.

the lower Hubbard subzone" are completely filled, „of the upper" are vacant. The LFMO-UVMO gaps (lower filled molecular orbital − upper vacant molecular orbital) in the energy spectra of № 1−9 clusters decrease with increasing number of atoms in the cluster from 5 eV for the № 1 cluster to 1.51 eV for the № 9 cluster.

Obviously, due to the splitting of the compounds $C_{90}(46)Cl_{32}$ (A), $C_{90}(34)Cl_{32}$ (B), $C_{90}(35)Cl_{24}$ (C), $C_{90}(35)Cl_{24}$ (C1), $C_{90}(35)Cl_{28}$ (D), $C_{90}(32)Cl_{24}$ (E), $C_{90}(30)Cl_{22}$ (F), $C_{90}(28)Cl_{24}$ (G) on independent clusters, optical absorption in these systems occurs due to optical transitions between states of π electrons exclusively inside the electronic subsystems of clusters. The optical

absorption spectra of the clusters and the total absorption spectra obtained from the calculated energy spectra with allowance for the selection rules are shown in Fig. 6−9. It can be seen from the figures that in the OSA of all compounds there are short-wavelength absorption bands with a wavelength of $\sim 200-300$ nm, due to transitions in № 1 and 2 clusters, which are „regular" systems with two and six atoms. The maximum absorption edge wavelength is $\sim 600-700$ nm. Of particular interest is the compound $C_{90}(35)Cl_{28}$ (D) (Fig. 8, *a*), which consists exclusively of „regular" systems № 1 and 2. The OSA of this compound contains only three pronounced absorption bands with maxima at 200, 250, and 300 nm. Obviously,

Figure 9. OSA of compounds $C_{90}(30)Cl_{22}$ (F) (left) and $C_{90}(28)Cl_{24}$(G) (right). Bottom — OSA of the connection, top — OSA of the clusters included in it.

this compound is of interest for use as an active element in laser technology.

Conclusion

Thus, it has been shown that in highly chlorinated fullerenes, carbon atoms at the attachment sites pass from the hybridized state sp^2 to the state sp^3, as a result of which the π electron system breaks up into several independent subsystems. Among these subsystems there can be simple „regular" systems, dimer and hexagon, which have pronounced absorption bands with maxima at wavelengths $\sim 200-300$ nm. Among all the systems

studied, in our opinion, the compound $C_{90}(35)Cl_{28}$ (D), the π electronic subsystem of which is divided exclusively into dimers and hexagons, is of greatest interest. Therefore, the total OSA of this compound has only three narrow absorption bands with maxima at wavelengths of 200, 250, and 300 nm. This circumstance makes such a compound very interesting in terms of its application as a working fluid in laser technologies.

Conflict of interest

The authors declare that they have no conflict of interest.

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