

Endohedral fullerene Sm@C₈₀: electronic structure, optical properties

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Taking into account the strong intra-node Coulomb interaction (~ 10 eV), the energy spectrum of endohedral metallofullerene Sm@C₈₀ is calculated. Based on the theoretical energy spectrum, the optical absorption spectrum of this compound is obtained. Comparison of the theoretical curves of the optical absorption spectrum obtained at different values of charge transfer from the embedded Sm atom with the experimental one with the corresponding experimental curve did not allow to establish the value of charge transfer. But despite this, the qualitative coincidence of the experimental curve with the theoretical ones indicates the adequacy of our model proposed for studying the electronic structure of endohedral fullerenes.

Keywords: fullerene, intra-site Coulomb interaction, Hubbard model, energy spectrum, optical absorption spectrum.

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1. Introduction

The focus on the study of fullerenes has recently moved from the investigation of pure fullerenes towards fullerene-based compounds. The first fullerene-based compounds, that were synthesized and experimentally studied, included endohedral metallofullerenes whose structure may be described as follows: metal atom inside fullerene shell [1]. In such structure, a part of valence electrons of the metal atom apparently flow to the fullerene shell. In fullerene, an interface between occupied and vacant electron states is known to be inside the π -electron band formed by those valence electrons of carbon that are not involved in formation of hard σ -bonds forming the fullerene scaffold. Valence electrons of the metal atom fall exactly in this π -band. At a first approximation, it can be suggested with good accuracy that „excess“ electrons occurring in this band do not change the energy level positions of π -electrons. Therefore electronic structure of the endohedral fullerene may be treated as π -electron system of fullerene having some number of excess electrons that have moved from the metal atom.

Earlier, in [2–5], such approximation was used to study the electronic structure and to build the optical absorption spectra (OAS) of the endohedral systems based on C₇₂, C₈₂ and C₉₀ fullerenes. Comparison of the OAS curves obtained in the studies mentioned above with the experimental OAS has shown their close qualitative agreement suggesting that both the model described above and calculation methods used in [2–5] are applicable.

This paper is focused on theoretical investigation of the electronic structure and optical properties of the endohedral metallofullerene Sm@C₈₀ whose synthesis was reported in [6]. Endohedral fullerene Sm@C₈₀ was deposited herein from carbon black produced by electric-arc evaporation of Sm₂O₃doped graphite rods. It has been found that basic

C₈₀, according to An Atlas of Fullerenes [7], is isomer № 3 with symmetry C_{2v}. In [6], OAS of the synthesized metallofullerene was measured, curve of absorption rate vs. wavelength λ is shown in Figure 1. The same methods as in [2–5] were used to calculate the energy spectrum and OAS of this metallofullerene was obtained.

2. Model and method

Carbon in fullerenes and carbon nanotubes is in sp^2 -hybridized state. Three of its four valence electrons form hard bonds with adjacent atoms (σ -bonds), these bonds form the system structure, and the fourth nonhybridized electron, being relatively free and partially localized on

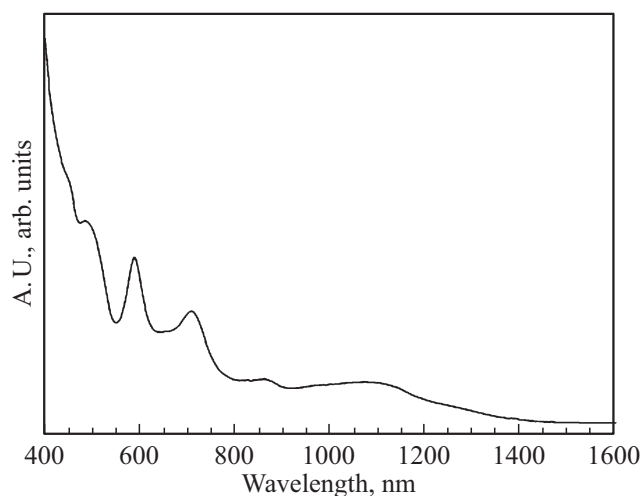


Figure 1. Optical absorption spectrum of Sm@C₈₀ based on isomer № 3 of C₈₀ [6].

Energy spectrum of isomer №3 (C_{2v}) of C_{80} . (In each cell, the first value is the level energy, the second value is the irreducible representation, including the energy level)

5.3354, B1	4.2630, B1	2.5623, A2	1.5767, A2	0.4146, "B1"	1.4870, "B1"	-3.1877, "A2"	-4.1733, "A2"
5.3178, B2	4.2532, B2	2.4622, B2	1.5766, B1	-0.4322, "B2"	-1.4968, "B2"	-3.2878, "B2"	-4.1734, "B1"
5.3174, A2	4.1649, A1	2.3685, A1	1.5587, A1	-0.4326, "A2"	-1.5851, "A1"	-3.3815, "A1"	-4.1913, "A1"
5.3082, A1	4.0857, B1	2.3188, A2	1.4518, A1	-0.4418, "A1"	-1.6643, "B1"	-3.4312, "A2"	-4.2982, "A1"
5.2688, B2	4.0831, A1	2.1703, B2	1.1538, B16	-0.4812, "B2"	-1.667, "A1"	-3.5797, "B2"	-4.5962, "B1"
5.1747, B2	4.0378, B2	2.1420, B1	1.1519, A1	-0.5753, "B2"	-1.7122, "B2"	-3.6080, "B1"	-4.5981, "A1"
5.1080, A2	4.0123, A2	2.1397, A1	1.1517, B2	-0.6420, "A2"	-1.7377, "A2"	-3.6103, "A1"	-4.5983, "B2"
5.0584, A1	3.9938, B2	2.1378, B1	1.0826, A2	-0.6916, "A1"	-1.7562, "B2"	-3.6122, "B1"	-4.6674, "A2"
4.9188, B1	3.9613, B1	2.1301, A1	1.0306, A1	-0.8312, "B1"	-1.7887, "B1"	-3.6199, "A1"	-4.7194, "A1"
4.7866, A2	3.9359, B2	2.1028, A2	1.0163, B2	-0.9634, "A2"	-1.8141, "B2"	-3.6472, "A2"	-4.7337, "B2"
4.7772, B1	3.7750, A1	2.0604, A2	0.9974, B1	-0.9728, "B1"	-1.9750, "A1"	-3.6896, "A2"	-4.7526, "B1"
4.7270, B2	3.7750, A2	2.0604, B2	0.7077, A2	-1.0230, "B2"	-1.9750, "A2"	-3.6896, "B2"	-5.0423, "A2"
4.6479, B2	3.6800, B1	2.0328, B2	0.6552, B2	-1.1021, "B2"	-2.0700, "B1"	-3.7172, "B2"	-5.0948, "B2"
4.6283, A2	3.5521, B2	2.0283, B1	0.6495, A1	-1.1217, "A2"	-2.1979, "B2"	-3.7217, "B1"	-5.1005, "A1"
4.6169, A1	3.5362, A1	1.9750, A1	0.6311, A1	-1.1331, "A1"	-2.2138, "A1"	-3.7750, "A1"	-5.1189, "A1"
4.5775, A1	3.1696, A1	1.7556, A2	0.6149, B1	-1.1725, "A1"	-2.5804, "A1"	-3.9944, "A2"	-5.1351, "B1"
4.3866, B1	3.1038, B1	1.6330, A1	0.3522, B2	-1.3634, "B1"	-2.6462, "B1"	-4.1170, "A1"	-5.3978, "B2"
4.3312, A2	3.0506, B2	1.6320, B1	0.3374, B1	-1.4188, "A2"	-2.6994, "B2"	-4.1180, "B1"	-5.4126, "B1"
4.3132, A1	2.9516, A2	1.6318, B2	0.3271, A1	-1.4368, "A1"	-2.7984, "A2"	-4.1182, "B2"	-5.4229, "A1"
4.2977, A2	2.5928, B1	1.5825, B2	0.1750, A1	-1.4523, "A2"	-3.1572, "B1"	-4.1675, "B2"	-5.5750, "A1"

the system sites, is capable of jumping between adjacent sites, thus, forming π -band. The boundary between vacant and populated electron states in such systems (carbon systems with sp^2 -hybridization) is in π -band. Using this approach with the Hueckel approximation, energy spectrum of C_{60} [8] was calculated before the synthesis. The energy spectrum of the graphite plane at the same approximation was calculated by Wallace as early as in 1948 [9]. It should be mentioned that the Hueckel approach considers only electron jumps between the adjacent sites and fully ignore their Coulomb interaction on the same site. The fact that the Coulomb interaction of electrons in carbon systems with sp^2 -hybridization, π -electrons, may play a significant role was for the first time addressed in [10]. The calculations herein have shown that the intrasite Coulomb interaction integral U in such systems may achieve ~ 10 – 15 eV. It is apparent that systems with such U values may be correctly described within the Hubbard model [11].

A series of our studies [2–5,12–17] used static-fluctuation approximation for the Hubbard model to calculate the energy spectra of fullerenes and CNT [18,19]. The calculation method used to calculate the energy spectra of fullerenes is described in detail in [14]. According to the findings of [2–5,12–17], the intrasite Coulomb interaction in fullerenes and CNT splits π -band into two groups of levels — two Hubbard subbands, „upper“ and „lower“. „Lower“ Hubbard subband states are fully populated, lower subband states are vacant. Due to such splitting, the type of level population in these subbands varies. If each energy level is generally occupied by M electrons with spin „up“ and M electrons with spin „down“, where M is the level degeneracy rate, then thanks to high U , each level, for example, of the „lower“ subband, is occupied only by M electrons with arbitrary spin orientation. The foregoing

results from the fact that repeated occupation of the same level, for example, E_k corresponds to repeated occupation of the site by two electrons and, as a result of Coulomb repulsion, the state of the second electron moves to the „upper“ subband at $E_k + U$ level.

According to [9], π -electron band width $W \approx 6B$, where B is the jump integral. Taking into account the intrasite Coulomb interaction, π -electron band width is equal to $6|B| + U$. It is apparent that at $U > 6|B|$ gap $\Delta = U - W$ will be present between the Hubbard subbands. This, in our opinion, takes place in fullerenes and CNT [17,20]. It has been experimentally found in [21] that π -band width in graphite is $W \approx 12.8$ eV [21]. It has been pointed out in [15] that, according to the finding in [9], this value is approximately equal to $6B$, where the jump integral is generally ~ 2 eV. But taking into account the Coulomb interaction, full width of π -band is written as $W = 6B + U$. The Coulomb integral, including shielding, is equal to $U \approx 7.0$ eV [10]. Then for the jump integral, we get $|B| \approx 1.0$ eV. Finally, it should be noted that $U \approx 7.0$ eV and $|B| \approx 1.0$ eV in various fullerenes and CNT with different chiralities are absolute. They may vary within 10% depending on the arrangement of adjacent atoms, due to different type of shielding. Thus, within our simulation model, described in more detail in [2–5,12–17], these parameters are a kind of adjustable.

3. Energy spectrum and optical absorption spectrum of endohedral fullerene $Sm@C_{80}$

Energy spectrum calculated at the Hubbard model parameters $B \simeq 0.9$ eV and $U \simeq 5.75$ eV by a technique

described in detail in [2–5] is shown in Table (the first number in the cells is the level energy in eV, the second value is the irreducible representation to which the level is applicable). It can be seen that the energy spectrum consists of 160 non-degenerate levels, with 80 levels in each Hubbard subband. Levels with negative energies correspond to the lower Hubbard subband and are fully populated, while the levels with positive energies correspond to the upper Hubbard subband and are vacant. The distance between the subbands, called HOMO–LUMO in the literature written in English, is equal to 0.60 eV, the width of each subband is 5.16 eV. The Table in each cell shows the irreducible representation, after the level energy, to which a particular level belongs. The symmetry analysis carried out using the group theory has shown that the following transitions are allowed in the system with symmetry C_{2v} :

$$\begin{cases} A1 \rightarrow A1, B1, B2 \\ A2 \rightarrow A2, B1, B2 \\ B2 \rightarrow A1, A2, B1 \\ B2 \rightarrow A1, A2, B2 \end{cases} \quad (1)$$

In view of the foregoing, it is apparent that transitions with optical absorption will take place between the energy levels of the „lower“ Hubbard subband to the energy levels of the „upper“ subband, this is applicable to free fullerene, rather than to endohedral one. While in the endohedral fullerene due to transition of the metal valence electrons to π -band of the fullerene, the lower levels of the upper Hubbard subband will be populated with the number of levels equal to the number of transferred electrons. In our case, due to the fact that valence of Sm can be equal to +2 and +3, such levels will be $\{0.1750, A1\}$ and $\{0.3271, A1\}$ for transfer of two electrons, and $\{0.1750, A1\}$, $\{0.3271, A1\}$, $\{0.3374, B1\}$ for transfer of three electrons.

Based on the calculated energy spectrum, OAS of the metallofullerene of interest were determined at different charge transfer values. The calculations were carried out according to the selection rules (1), based on the Fermi rule [22], using equation

$$In(\omega) \sim \sum_{i,k} \frac{M_i M_k \delta}{(\omega - (E_k - E_i)^2 + \delta^2)}. \quad (2)$$

Here, M_i, M_k are degrees of degeneracy of the energy levels participating in the optical transition, E_k, E_i are the energy levels of states of the „upper“ and „lower“ Hubbard subbands, respectively, participating in the optical transition, δ is the phenomenological parameter characterizing attenuation of energy levels of π -electrons. It should be noted that equation (2) is approximate in that it does not consider the dependence of the transition probability on levels i and k participating in a single absorption event. This study approximately considers that this dependence, which is expressed through a matrix element $F_{i,k}$ in the end of

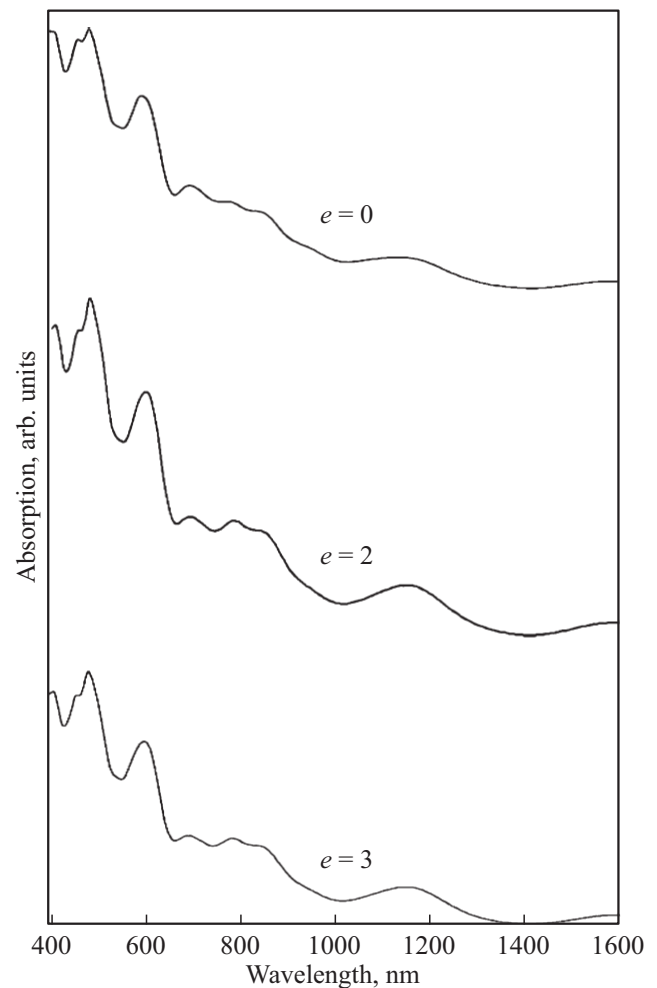


Figure 2. Optical absorption spectrum of Sm@C₈₀ calculated at different charge transfer values.

the section on page 190 in [22], is weak. This is confirmed by the fact that OAS curves calculated in [12–18,19] taking into account the weak dependence of $F_{i,k}$ on i and k agree with the experiment at a good quality level. However, we still believe it necessary to address this issue in more detail in our further studies. Equation (2), taking into account the probability of transition from i and k without involving the symmetry aspects, may be derived within the Kubo equation [23,24] through Green’s two-particle function. Our first results in this area show that, for simple molecular systems such as, for example, benzene atom, transition probabilities between the contributing levels actually do not depend on i and k . The foregoing by no means compromises the necessity of a more correct calculation of $In(\omega)$.

Curves plotted at different charge transfer values are shown in Figure 2 (charge transfer value is shown in the diagram). It is apparent that the theoretical curves plotted for different charge transfer values have strongly pronounced absorption bands with peaks at 500 nm and 600 nm. Diffused absorption bands are also present at 720 nm (corresponding to the peak at 730 nm on the experimental curve)

and 1200 nm. A flat segment approximately in the same wavelength region on the experimental curve corresponds, in our opinion, to low peaks in the wavelength region from 750 nm to 900 nm. It should be noted that the absorption intensity on the experimental curve at $\lambda \rightarrow 400$ nm grows and poorly agrees with the theoretical curve near this value. This is highly likely attributable to the contribution of a hydrosulphuric solvent used in [6] to the absorption. According to our calculations, the absorption band with strongly pronounced peak at 500 nm, that is present in the test compound during Sm@C₈₀ OAS measurement, is washed away by the solvent contribution. Therefore, there is only a small „swelling“ on the experimental curve at $\lambda \approx 500$ nm. Thus, poor agreement of the experimental and theoretical curves in the short wave region is apparently associated with the solvent contribution to the measured absorption. Unfortunately, our calculations cannot consider this contribution. Finally, it should be noted that the charge transfer value cannot be determined from the optical absorption spectra by comparison of the experimental and theoretical curves. Close agreement of absorption band peaks at 500 nm, 600 nm and 1200 nm and agreement of the theoretical and experimental OAS curve behavior suggest that our understanding of the electronic structure of endohedral metallofullerenes described in the first two sections herein is correct and may be used to study all carbon nanosystems where carbon is in sp^2 -hybridized state.

4. Conclusion

Optical absorption spectra of Sm@C₈₀ have been obtained herein. The calculations have been made using the energy spectrum of this isomer calculated using the Hubbard model within our understanding of the electronic structure of carbon nanosystems with sp^2 -hybridization. The obtained optical absorption spectra closely agree with the appropriate experimental data [6] confirming the adequacy of our understanding of the electronic structure of carbon nanosystems with sp^2 -hybridization that is discussed in the series of our studies [2–5,12–17].

Conflict of interest

The authors declare that they have no conflict of interest.

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