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# On amplification of intensity of absorption spectra of fullerene C60 in long-wave region

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The electron absorption spectra of fullerene C60 and its two dimers in the range of 200−800 nm have been studied. Calculation of the electronic and electron-vibrational spectra of fullerene in the region of 350−400 nm in the Frank–Condon approximation, as well as comparison with experimental spectra, shows that the spectra in the region of 200−400 nm correspond to the structure of only the fullerene C60 monomer, regardless of the concentration of the solution. In the region of 400−800 nm, the experimental absorption spectrum of fullerene C60 measured in *n*-hexane solution agrees well with the calculated electronic absorption spectrum of one of the fullerene dimers, which indicates the spontaneous formation of this dimer in concentrated solutions of fullerene C60. The intensity of the absorption bands of another dimer in this area increases significantly, which makes it possible to use the electronic spectra of fullerene C60 to solve practical problems, for example, in medicine.

**Keywords:** electronic and vibronic spectra, interpretation, fullerene C60 dimers, intensity.

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## Introduction

Fullerenes, the most studied of which is C60 fullerene, have a unique structure and biological activity. It is well known that the lipophilicity of fullerenes determines their membranotropic properties, and electron deficiency leads to the ability to interact with free radicals, which allows fullerenes to exhibit both oxidative and antioxidant properties [1,2]. In addition, the demand in medicine for C60 fullerene, as well as its derivatives, allows not only the creation of effective drugs based on them, but the targeted delivery of active compounds directly into the cell as well [3–5]. At the same time, the Surface Enhanced Raman Spectroscopy (SERS) method is successfully used to monitor and control the delivery process [6]. The application of the traditional and well-proven method of electron spectroscopy in this case is complicated by the fact that fullerenes have weak absorption in the visible and near-UV regions of the spectrum and have virtually no fluorescence.

Let us note that a large number of theoretical and experimental studies have been devoted to the electronic spectra of C60 fullerene [7–9]. First, the absorption spectra were reviewed in different phase states: in the insulating matrix at $T = 4.2\,\mathrm{K}$ [10], in the gas phase, in the film and liquid state [11,12]. Secondly, the influence of solvents, mainly non-polar ones, on the electronic spectra of fullerenes — toluene, polystyrene, polymethyl methacrylate, etc. [13,14] is under study. Since fullerenes are practically insoluble or slightly soluble in polar solvents, and the application of fullerenes in medicine requires their good solubility in water, special attention is paid to the solubility of fullerenes in water, which is usually achieved by functionalizing fullerenes, for example, with amino-acid residues of glycine or phenylalanine [{]15 }. In addition, several spectral ranges of the C60 absorption spectra were studied - these are the ∼ 200−400 and ∼ 400−800 nm regions. The authors of the work [14] explained the absorption in the region of 700−800 nm for concentrated solutions in *n*- hexane at 292 K by the formation of (C60) *n*- clusters.

The goal of this work is to perform a theoretical analysis of the electronic spectra in the region 200−800 nm with the aim of classifying them as a monomer of fullerene C60 or dimer, as well as determining the conditions for increasing the intensity of the long-wave absorption band.

For that, the following tasks were implemented:

1. The electronic and vibronic absorption spectra of C60 fullerene have been calculated and compared with experimental absorption spectra in the region of 200−400 nm. The effect of water as a solvent on the intensity of the electronic absorption spectra of C60 was determined.

2. The electronic absorption spectra of C60 dimers in the region of 400−800 nm were calculated and a comparative analysis with experiment was carried out. The influence of two different structural dimers on the intensity of the long-wave absorption band was determined.

A comparative analysis of the calculated spectra was carried out with experimental absorption spectra measured for concentrated solutions of C60 in hexane [14].

Electronic and vibrational spectra of the ground and electronically excited states were calculated using the DFT/B3LYP/6-31g(d,p) method implemented in the Gaussian-09 [16] program. The vibronic structure of the electronic absorption spectra was calculated in the Franck–Condon approximation.

## 1. Results and discussion

### 1.1. Spectral region 200−400 nm

Figure 1 shows the results of calculating the electronic spectrum of C60 in an isolated state. In the theoretical spectrum, there are three broad absorption bands with maxima at 203, 244 and 315 nm (Fig. 1, *a*). The influence of water leads to a bathochromic shift of the absorption band maxima by ∼ 3−5 nm, and the intensity of the absorption bands increases by ∼ 5−15% (Fig. 1, *b*). To take into account the influence of the aquatic environment, the SCRF method was used (dielectric permittivity of water 78.39). A comparison of the calculated and experimental absorption spectra of C60 measured in a solution of *n*- hexane shows their complete agreement — the maximum absorption values in a solution of *n*- hexane appear at 208, 256 and 328 nm [14].

The long-wave absorption band contains two electronic transitions of weak intensity — these are transitions at 357 (*1*) and 392 nm (*2*) (Fig. 2), which have a fine vibrational structure [9,14]. The calculated vibronic spectra of the *1* and *2* transitions in the Franck–Condon approximation are given below.

It is obvious that the results of calculating the fine structure of electronic spectra will depend on the structural and dynamic models of the molecule in combining electronic states. The molecular structure of two articulated rings of the C60 fullerene with numbering of bond lengths is shown in Fig. 3, and the results of calculating bond lengths in the ground and electronic-vibrational states of the considered transitions *1* and *2* — in Table. 1.

Let us note that, although changes in bond lengths during the transition to electronically excited states do not exceed 0.06 Å, in the second electronically excited state they lead to a change in the multiplicity of bonds in both rings (Fig. 3).

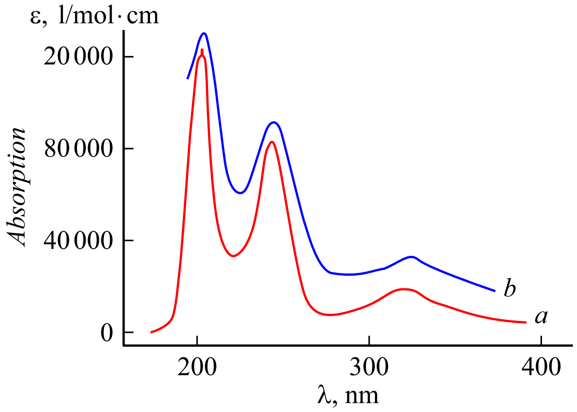

**Figure 1.** Calculated electronic spectra of C60 for the isolated state (*a*) and aqueous solution (*b*) ($\varepsilon$ — molar extinction coefficient; $\lambda$ — wavelength).

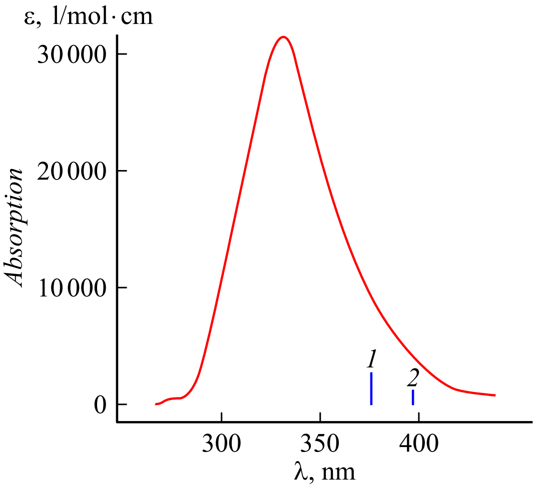

**Figure 2.** Intensities *1* and *2* absorption bands (vertical lines) of C60 in the long-wave spectral region 300−400 nm.

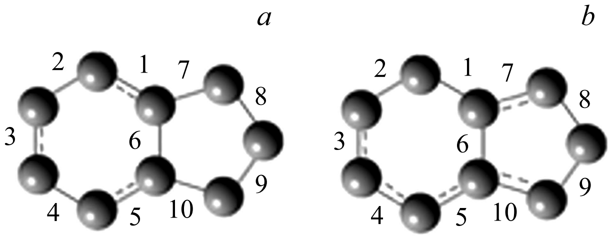

**Figure 3.** Molecular diagrams indicating the bond lengths of two linked C60 rings for the ground (*a*) and second (*b*) electronic states.

**Table 1.** Calculated values of bond lengths of isolated C60 fullerene in the ground state $l_{basic}$ (Å) and electronically excited states of the first ($l_1$, Å) and second ($l_2$, Å) transitions

| Number of the bond | $l_{basic}$ | $l_1$ | $l_2$ | Number of the bond | $l_{basic}$ | $l_1$ | $l_2$ |
|---|---|---|---|---|---|---|---|
| 1 | 1.40 | 1.39 | 1.45 | 6 | 1.45 | 1.46 | 1.45 |
| 2 | 1.45 | 1.45 | 1.47 | 7 | 1.45 | 1.45 | 1.39 |
| 3 | 1.40 | 1.39 | 1.40 | 8 | 1.45 | 1.45 | 1.42 |
| 4 | 1.45 | 1.45 | 1.40 | 9 | 1.45 | 1.45 | 1.44 |
| 5 | 1.40 | 1.41 | 1.39 | 10 | 1.45 | 1.44 | 1.39 |

The vibronic absorption spectra calculated in the Franck–Condon approximation for both electronic-vibrational transitions are shown in Fig. 4.

A comparison of the vibrational structure of the experimental spectrum in the region 390−410 nm with the calculated vibronic spectra shows that the electronic vibrational spectra exhibit fully symmetric vibrations corresponding to vibrations of the unassociated C60 fullerene [14].

Thus, the theoretical calculation and interpretation of the electronic and vibronic spectra of the C60 fullerene, as well as comparison with the corresponding experimental spectra of the C60 fullerene measured in *n*-hexane at 292 K, showed

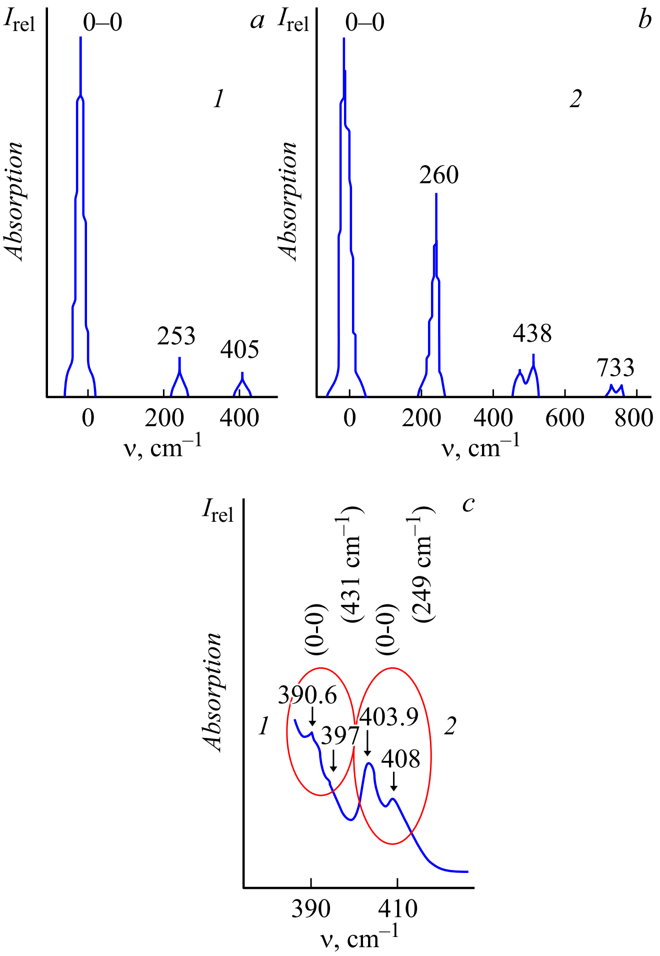

**Figure 4.** Calculated electronic-vibrational absorption spectra *1* (*a*) and *2* (*b*) electronic transitions; experimental vibronic spectra (*c*) (based on [9,14]).

that in the region of 200–400 nm the electronic spectrum is an absorption spectrum C60 fullerene monomer, regardless of the concentration of the solution.

## 1.2. Spectral region 400–800 nm

The intensity of the experimental absorption bands of C60 in the region over 400 nm is significantly less than the intensity of the absorption bands in the region of 200–400 nm. At the same time, measurements performed by the authors of the work [14] for concentrated solutions of C60 fullerene show a well-structured absorption spectrum and a low-intensity fluorescence spectrum in the region of 400–800 nm. Taking into account that these spectra can be caused by the formation of (C60) *n* clusters, electronic absorption spectra were calculated for two types of dimers I and II. When dimer I is formed, short bonds between hexagons on neighboring molecules are broken and transformed into a four-membered ring (symmetry $D_{2h}$); in the case of dimer II, only one intermolecular covalent bond CC is formed (symmetry $C_{2h}$) (Fig. 5).

**Table 2.** Experimental ($\lambda_{exper}$, nm) and calculated ($\lambda_{calc}$, nm) values of the wavelengths of absorption band maxima and oscillator strengths ($f_{osc}$) for dimer I of C60 fullerene

| $\lambda_{exper}$ | $\lambda^*_{calc}$ | $f_{osc}$ | $\lambda_{exper}$ | $\lambda^*_{calc}$ | $f_{osc}$ |
|---|---|---|---|---|---|
| 760.6 | 890.1 | 0.0002 | 569 | 651.83 | 0.0016 |
| 745.9 | 843.95 | 0.0008 | | 633.99 | 0.0008 |
| 620.2 | 762.55 | 0.0013 | | 623.34 | 0.0001 |
| 609 | 723.22 | 0.0003 | | 621.07 | 0.0006 |
| 597.6 | 702.61 | 0.0021 | | 617.28 | 0.0001 |
| | 676.87 | 0.0001 | | 609.20 | 0.0004 |
| | 670.14 | 0.0004 | 541 | 602.17 | 0.0020 |
| | 653.98 | 0.0001 | 529 | 599.74 | 0.0013 |
| 590 | 653.08 | 0.0013 | | 597.79 | 0.0011 |

Figure 6 shows the experimental spectrum and calculated absorption spectra of dimers I and II of C60 fullerene.

A comparison of the experimental (Fig. 6, *a*) and calculated spectra (Fig. 6, *b*, *c*) shows, firstly, a good agreement between the experimental absorption spectrum with the calculated dimer spectrum I (using a scaling factor 1.15). Table 2 and Fig. 6 show the corresponding values of the wavelengths of the maxima of the experimental and theoretical absorption spectra, as well as the strength of the oscillators.

Secondly, for a dimer of type II there is an increase in the intensity of the absorption bands of the electronic spectrum compared to the intensity of the absorption bands of dimer I by a factor of $\sim 2$.

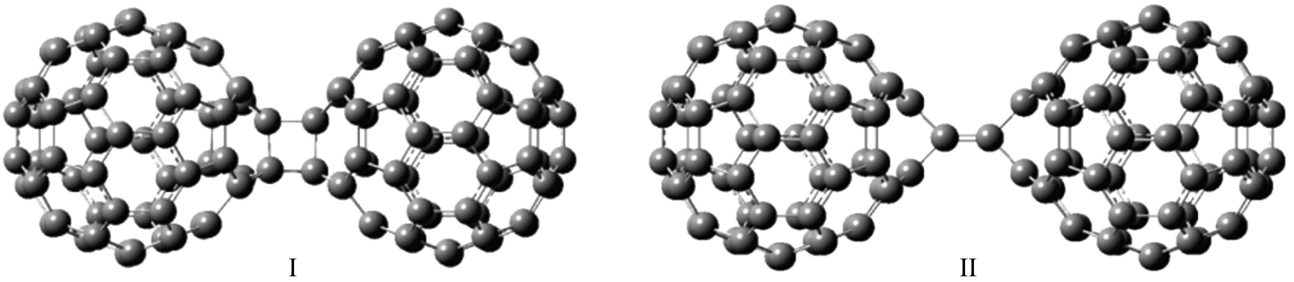

**Figure 5.** Molecular diagrams of two C60 fullerene dimers I and II.

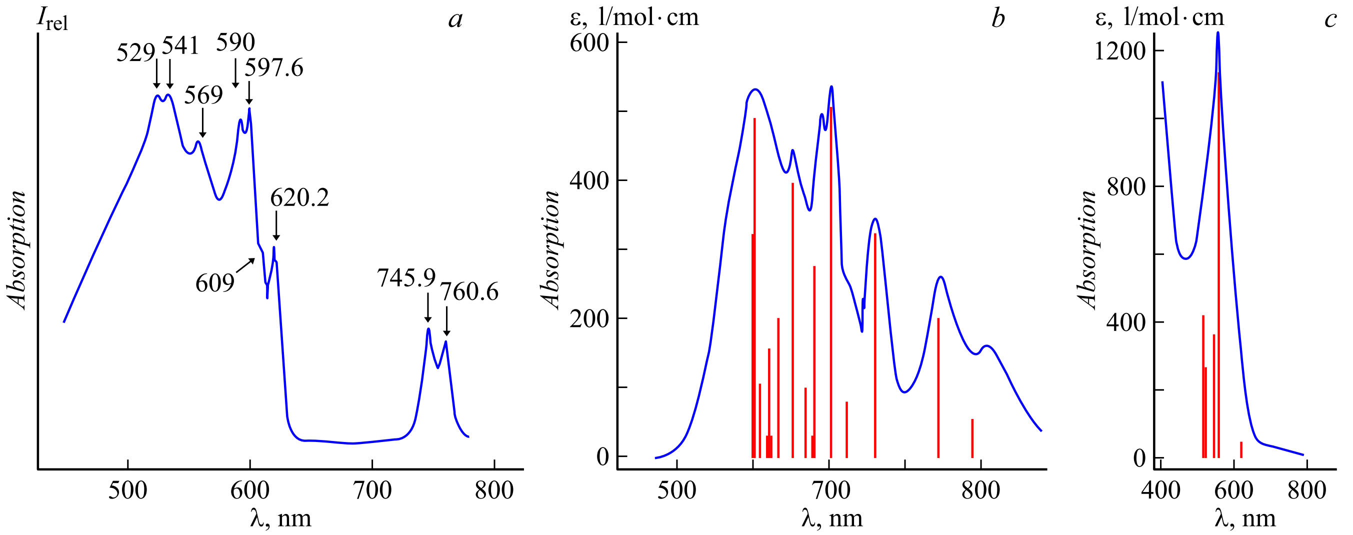

**Figure 6.** Experimental absorption spectra of C60 fullerene in a concentrated solution in the region of 400−800 nm (*a*). Calculated absorption spectra of dimers I (*b*) and II (*c*).

## Conclusion

In the work, in order to determine the conditions under which it is possible to increase the intensity of the long-wave absorption band and, accordingly, fluorescence, which is important for the use of fullerenes and their diagnostics in medicine, the electronic absorption spectra of C60 and its dimers in the region 200−800 nm were calculated and analyzed.

It was shown that in the region of 200−400 nm there is a slight increase in the intensity of absorption bands in an aqueous solution, and the calculation of the electronic and vibronic spectra confirms their agreement with the experimental electronic-vibrational spectra of the C60 fullerene monomer.

The calculation of the electronic absorption spectra of two types of C60 dimers in the region of 400−800 nm showed good agreement with the experimental spectrum for only one of the dimers. The influence of dimers on the intensity of the long-wave absorption band was determined. It was shown that the intensity of the absorption bands for dimer II increases by a factor of $\sim 2$ compared to the intensity of the absorption spectrum of dimer I. Thus, II dimers of C60 fullerene can be successfully used for monitoring and diagnostics in medicine.

## Conflict of interest

The author declares that he has no conflict of interest.

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