Determination and refinement of the value of the Urbach energy Eu and the optical energy band gap Eg of C60 and C70 fullerene films based on the analysis their absorption spectra.

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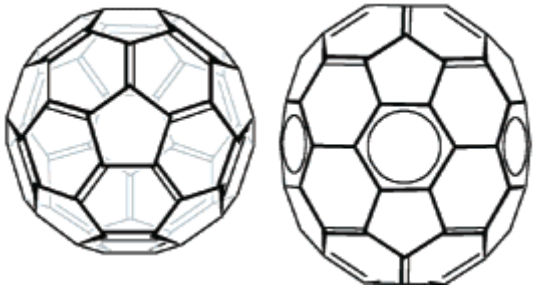
2. The aim of the research paper

C60 and C70 fullerenes are widely used as electron acceptors in organic solar cells [1]. During the synthesis process, mixtures of fullerene molecules with different numbers of carbon atoms are formed. The most stable C60 and C70 molecules are the main components of these mixtures. The absorption edges of C60 and C70 films with a thickness d< 1 μm have not been studied enough.

In our work we did the analysis of the absorption spectra of C60 and C70 films with a thickness from 20 to 5000 nm published by various researchers was carried out in order to determine and clarify the values of Eg and Eu. These studies are relevant and necessary for a deeper understanding of the properties of solar cell films , sensors and other devices based on various composites, which include thin layers of C60 and C70.



C60 C70

[1] L. Benatto, et al.. *Thin Solid Films*. **697**, 137827 (2020).

3. Absorption edge spectra of C60 and C70 fullerene films of different thicknesses.

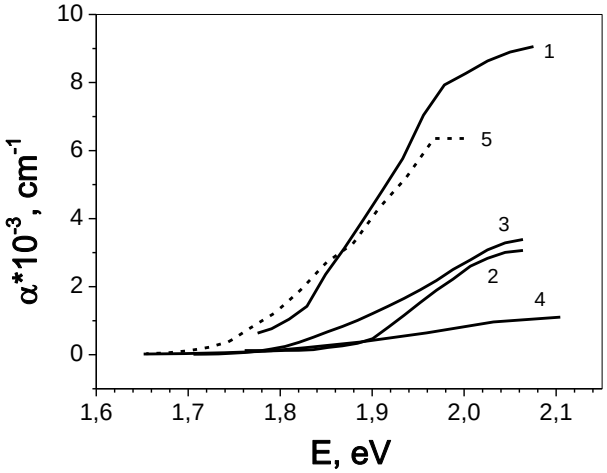


Fig. 1. Absorption edge spectra of 20, 70, 900, (~1000) and 5000nm thick C60 films (graphs 1, 2, 3, 4, and 5, respectively).

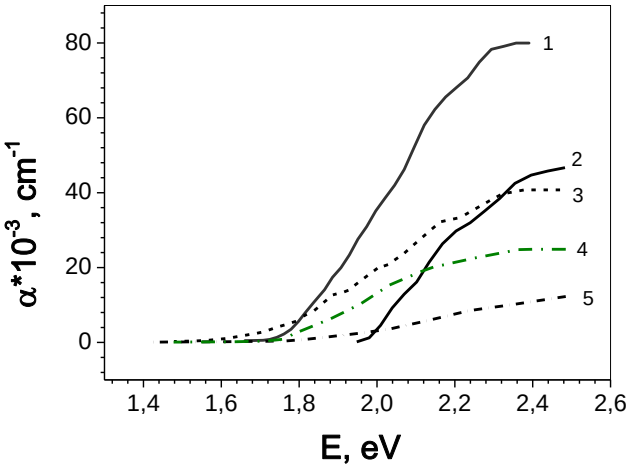


Fig. 2. Absorption edge spectra of 20, 40, 160, 1000 and (~1000) nm thick C70 films (graphs 1, 2, 3, 4 and 5, respectively).

These graphs are based on original spectra taken from references: [2] W. Krätschmer et al. *Nature* **347**, 354 (1990); [3] Scumanich. *Mat. Res. Symp. Proc.* **270**, 299 (1992); [4] W. Zhou et al. *J. Appl. Phys.* **80**(1), 489 (1996); [5] T. Gotoh et al. Phys. Rev. B 58(15), 10060 (1998) and [6] S. Pfuetzner et al. *Appl. Phys. Lett.* **97**(22), 223307 (2009).

4. Absorption spectra of C60 and C70 fullerene films of different thicknesses (intermediate conclusions).

1) *It was established that the value of the effective absorption coefficient* ***α*** *decreases with an increase in the thickness of C60 and C70 films.*
2) *2). It can be assumed that the observed deviations from the Bouguer–Lambert law are mainly caused by the different precision of films thickness measurement. We believe that the thickness value ~1000 nm of C60 and C70 films in [3] is exaggerated. Our estimates show that thickness of these films in accordance with the Bouguer-Lambert law should be 303 and 418 nm, respectively.*

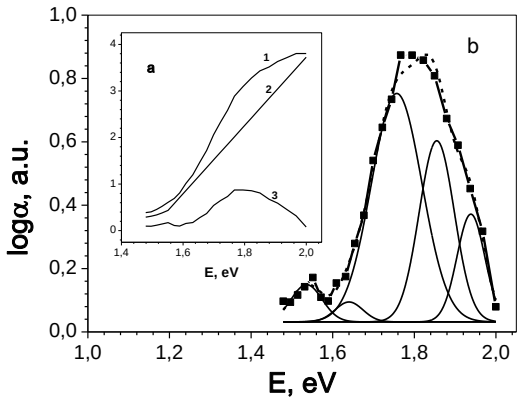


Fig.3. Edge absorption spectra of the C60 film with a thickness of 5000 nm in a semi-logarithmic scale: a) in the inset on the left, graphs 1, 2, and 3 correspond to the original spectrum, the baseline, and their difference, respectively; b) The Gaussian fitting of graph 3. The name of the ordinate axis is the same for all graphs.

3) Considering these data, it can be assumed, that the vibronic progression bands 1.536, 1.640, 1.757, 1.855 and 1.939 eV of the triplet exciton and the singlet exciton band 1.999 eV are superimposed on the long-wavelength absorption edge of C60 films.

5. Determination of the Urbach energy Eu value based on the absorption spectra of C60 and C70 films.

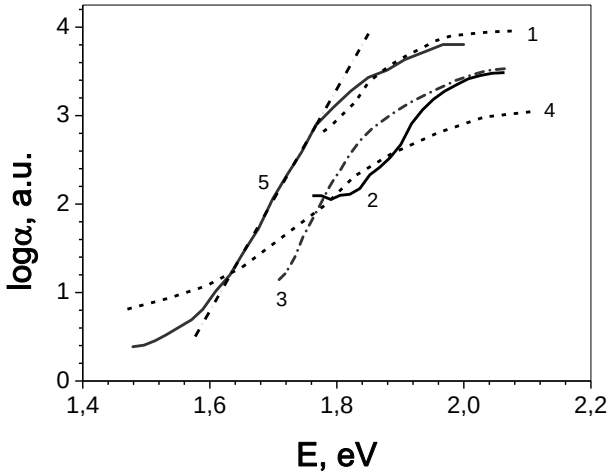


Fig. 4. Edge absorption spectra of 20, 70, 900, (~1000) and 5000 nm thick C60 films in a semi-logarithmic scale (graphs 1, 2, 3, 4 and 5, respectively).

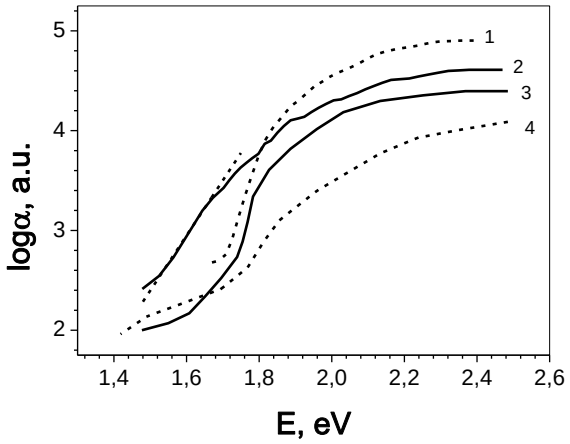


Fig. 5. Edge absorption spectra of 20, 160, 1000, and (~1000) nm thick C70 films in a semi-logarithmic scale (graphs 1, 2, 3, and 4, respectively).

The Eu values of C60 and C70 films were determined by the tangent of the angle of inclination of a straight-linear sections, obtained by a computer fitting. For 20 nm thick C60 and C70 films were received *Eu* 59 and 43 meV, respectively. *Eu* values of C60 and C70 films of other thicknesses are listed below in Table 1.

6. Determination of the optical band gap *Eg* for first indirect electronic transitions of C60 and C70 films.

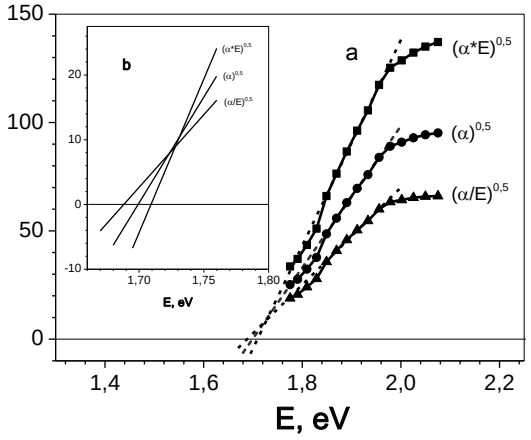


Fig. 6.: a) dependencies of the $(\alpha*E)^{0.5}$, $(\alpha)^{0.5}$and $(\alpha/E)^{0.5}$ on the energy *E* of incident photons for the absorption edge spectrum of the 20 nm thick C60 film. The ordinate axis is common to the three graphs; b) the inset on the left shows an enlarged fragment of the extrapolated straight-linear sections of these graphs to the zero value of the ordinate.

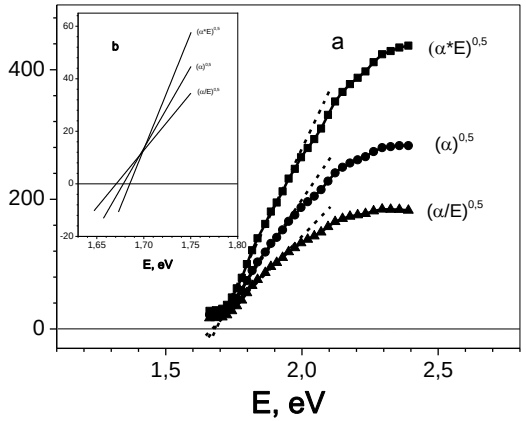


Fig. 7. Dependencies of the $(\alpha*E)^{0.5}$, $(\alpha)^{0.5}$, and $(\alpha/E)^{0.5}$ on the energy *E* of incident photons for the edge absorption spectrum of the 20 nm thick C70 film. All designations are the same as in fig. 6.

The largest value of E_g is given by Tauc method, the intermediate one by the classical method, and the smallest by the Cody method. The E_g values of C60 and C70 films are listed below in Table 1.

7. Determination of the parameter α_0 of C60 films.

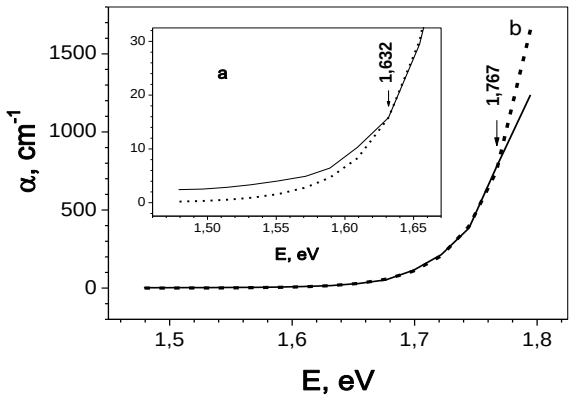


Fig.8. **The absorption spectrum of the 5000nm thick C60 film (solid graph) and its approximation by an exponential line (dashed graph): a) in the region of 1.5–1.65 eV (inset, left); b) in the region of 1.5–1.8 eV.**

The edge spectra of $\alpha\ (E)$ were approximated by exponential lines with parameters $<\alpha_0>$, $<E_g>$ and E_u. It was established that for all C60 and C70 films, at photon energies $E < E_1$ and $E > E_2$, the approximate exponential line passes below and above the spectrum $\alpha(E)$, respectively.

8. Table 1. Values of optical band gap Eg, Urbach energy Eu, and parameter <α0> for C60 and C70 fullerene films of different thicknesses.

Fullerene		C_{60}					C_{70}			
***d*, nm**		**20**	**70**	**900**	**~1000**	**5000**	**20**	**160**	**1000**	**~1000**
E_g, eV	$(\alpha*E)^{0,5}$	1.709	1.828	1.722	1.672	1.681	1.685	1.620	1.650	1.679
	$(\alpha)^{0.5}$	1.700	1.825	1.715	1.660	1.678	1.679	1.607	1.627	1.673
	$(\alpha/E)^{0,5}$	1.689	1.822	1,707	1.646	1.675	1,671	1.591	1.601	1.666
$<E_g>$, eV		***1.699***	***1.825***	***1.715***	***1.659***	***1,678***	***1.678***	***1.606***	***1.626***	***1.673***
E_u, meV		59	49	36	76	35	43	107	50	78
$log\alpha_1$, a.u.		2.883	2.175	1.630	1.290	1.199	2.903	3.328	2.668	2.706
$log\alpha_2$, a.u.		3.494	3.186	2.713	2.571	2.889	4.027	4.104	3.514	3.355
E_1, eV		1.791	1,836	1.747	1.652	1.632	1.725	1.673	1.720	1.774
E_2, eV		1.870	1.952	1.836	1.831	1.767	1.837	1.887	1.820	1.890
$<\alpha_0>$, cm^{-1}		163.38	113.78	17.98	20.90	59.21	302.52	1020.48	69.30	139.67

Note. In the photon energy range $E_1<E<E_2$, the approximate exponential line coincides with the absorption spectrum of C60 or C70 films.

9. Conclusions.

1. It was established that the Urbach energy *Eu* decreases from 59 to 35 meV when the thickness of C60 films increases from 20 to 5000 nm, except for the C60 film with a thickness of (~1000) nm, for which *Eu* = 76 meV. This may indicate an increase in the degree of ordering of the C60 films structure as their thickness increases. In C70 films with a thickness of 20, 160, 1000, and (~1000) nm, the value of Eu is 43, 107, 50, and 78 meV, respectively. This may indicate the unequal degree of ordering of the structure of C70 films of different thicknesses.

2. For C60 and C70 films, the largest, intermediate, and smallest values of the optical band gap *Eg* were obtained by methods of Tauc, classical, and Cody, respectively. The average value of <*Eg*> coincides with the value of *Eg* for the classical method. At the same thicknesses, a slightly larger <*Eg*> value was observed for C60 films. If the thicknesses of these films are 20 nm, then <*Eg*> is 1.699 and 1.678 eV for C60 and C70, respectively.

3. Long-wavelength edge spectra $\alpha\ (E)$ were approximated by exponential lines with parameters $<\alpha_0>$, $<E_g>$ and E_u. It was established that for all C60 and C70 films, at photon energies $E < E_1$ and $E > E_2$, the approximate exponential line passes below and above the spectrum $\alpha(E)$, respectively.

Thanks for your attention