

## CARBON VIBRATION MODES IN C<sub>60</sub> FULLERENES

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The paper reports a study of the spectral dependence of the absorption in the IR domain for C<sub>60</sub> fullerene layers in the interval of temperatures from 78 K till 440 K. The emission spectra of the C<sub>60</sub> molecule formed in the ionized He plasma with the high frequency current, contains two bands located in the domain 245 - 280 nm. On the basis of the spectral dependence of the photo-luminescence at 273 K and 78 K temperatures it is proposed a model for the localized states in the forbidden gap.

(Received October 15, 2001; accepted March 11, 2002)

*Keywords:* Fullerene C<sub>60</sub>, Optical absorption, Vibration modes, Luminescence

In order to study their optical properties, thin layers of C<sub>60</sub> fullerenes have been prepared by the method of thermal sublimation in the quasi-equilibrium volume.

The spectral dependence of the absorption from the infrared domain of the spectrum allows for the identification of the bond types in the molecules with different atoms and vibrational modes. The characteristic transmission spectra for the layers of fullerenes C<sub>60</sub> prepared from the steam phase in the quasi-equilibrium volume at different temperatures in the range 78 K ÷ 440 K are presented in Fig. 1.

The characteristic vibration modes of the sp<sup>3</sup> bonds of the atoms in the C<sub>60</sub> molecule are well known in the literature. Zhizhong Song et al. [1] have shown that in the range of wave numbers of 400 ÷ 1500 cm<sup>-1</sup> five modes with the wave numbers of 525 cm<sup>-1</sup>, 577 cm<sup>-1</sup>, 669 cm<sup>-1</sup>, 1181 cm<sup>-1</sup> and 1428 cm<sup>-1</sup> are active in the IR absorption spectrum.

The measurements evidenced of 13 modes of vibration in the polycrystalline structures with the thickness of 5 ÷ 10 μm, among which the 6 maxima of absorption mentioned in the paper [1], are enough intensives.

The absorption maxima are amplified and simultaneously narrowed when the temperature is decreased from 293 K till 78 K. In the spectrum are seen 10 lines and a band 430 ÷ 400 cm<sup>-1</sup>.

The intensity of fundamental vibration modes are attenuated at the temperatures up to 440 K, but other bands, shown in Table 1, are split into two or three lines. The total number of vibrational modes at 440 K increases till 21.

In accordance with the theoretical calculation, which are confirmed by experiment, the quantum efficiency of fluorescence of C<sub>60</sub> fullerenes is relatively small [2]. The fluorescence of solutions is conditioned by the electron – vibrational transitions and quantum efficiency is of the order of 10<sup>-5</sup>. In the condensed state the quantum efficiency of the C<sub>60</sub> molecules increases and achieves the value of 7 × 10<sup>-4</sup>. This increase is caused by the formation of different defects that lead to the activation of the permitted radiative transition.

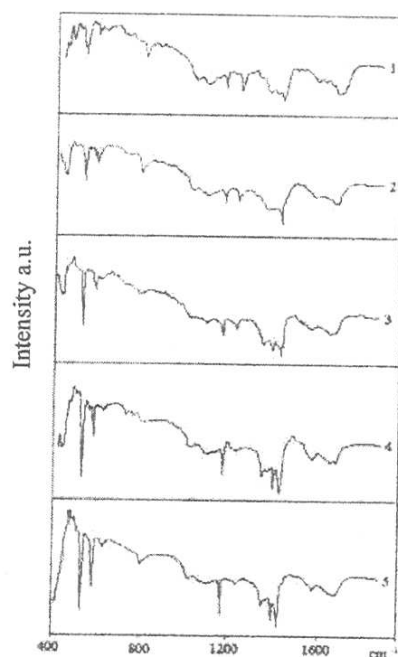


Fig. 1. The spectra of transparency in the IR domain for  $C_{60}$  fullerene layer at the temperatures 1:  $T = 440$  K, 2:  $T = 325$  K, 3:  $T = 270$  K, 4:  $T = 170$  K, 5:  $T = 78$  K.

Table 1. The frequencies of vibrational active modes in the IR spectrum for the  $C_{60}$  fullerene layers.

T.K	The wave number of the vibrational modes, $cm^{-1}$													
78	1466	1438	1376	1269	1190	831	816		627	580		525	430	
170	1464	1429	1380	1258	1190		812	670	620	577		525	435	400
293	1464	1427	1380	1260	1190		800	720	620	577		525	430	
325	1456	1425	1382	1256	1187		800	710	670	577		525	435	
400	1460 1451	1420	1388 1380 1335	1256	1187		820 811 790	720	675	577	636 624 612	525	438	

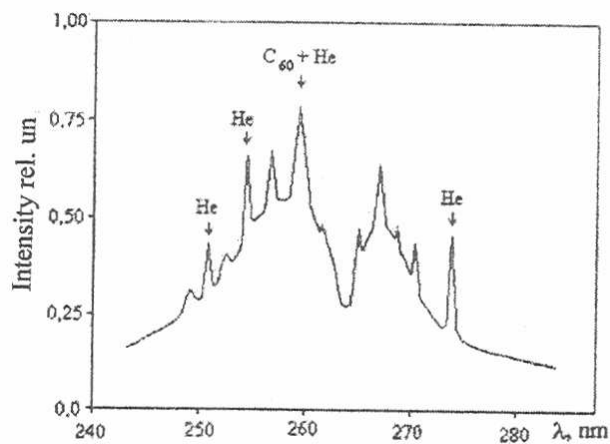


Fig. 2. The emission spectra of the  $C_{60}$  molecules excited in the He plasma ionized in the high frequency current.

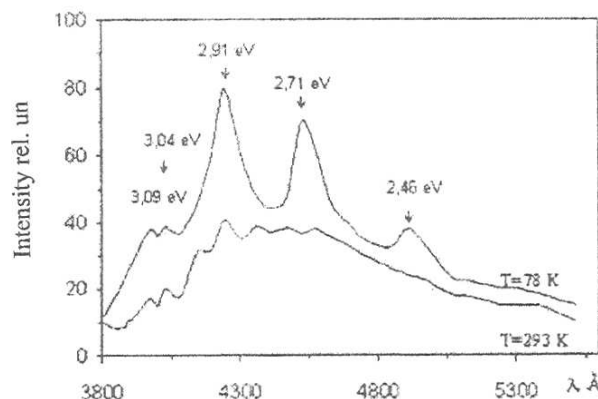


Fig. 3. The spectral dependence of toluene photoluminescence at the temperatures of 78 K and 293 K.

The emission spectra of the C<sub>60</sub> molecules which are excited in the plasma ionized in the current of high frequency contains only a large band located in the domain from 245 nm till 280 nm wavelengths (Fig. 2).

The emission spectra of the C<sub>60</sub> molecules have a characteristic form for electronic spectra of the molecule with many atoms at the transitions with the emission of the photon between the vibrational levels of the two electronic state and a fundamental electronic state [3].

The luminescence spectrum presented in the Fig. 2 is in a good correlation with the absorption band "a" with the maximum at 5.58 eV at the transmission spectrum. This concordance allows us to suppose that the absorption spectrum and the emission spectrum of the fullerene molecules is conditioned by the molecular transitions between two electronic states, one of those is fundamental. In order to study the peculiarities of the luminescence in C<sub>60</sub> fullerene dissolved in toluene solution the spectral dependence of the pure toluene photoluminescence at 78 and 293 K, has been measured (Fig. 3).

The luminescence of toluene has been excited with the radiation of N<sub>2</sub> molecular laser. The density of the exciting beam was 1.5 MW/cm<sup>2</sup>. The photoluminescence spectrum of the toluene in the range 3.3 eV ÷ 2.2 eV at 78 K exhibits pronounced bands at 3.09 eV and 3.04 eV and remains practically unchanged with temperature, the intense bands with the maxima situated at 2.92 eV and 2.7 eV diminish their intensity with the increase of temperature from 78 K, and, at the room temperature, practically do not differ from the continuum background.

From spectral dependence of the photo-luminescence of C<sub>60</sub> solution in toluene at the temperature of 78 K (Fig. 4) it is concluded that the presence of fullerene molecules in the solution attenuates the toluene luminescence bands. The excitation energy of toluene molecules is scattered with the contribution of C<sub>60</sub> fullerene molecule, and consequently the C<sub>60</sub> fullerene molecules stop the photoluminescence of the solution.

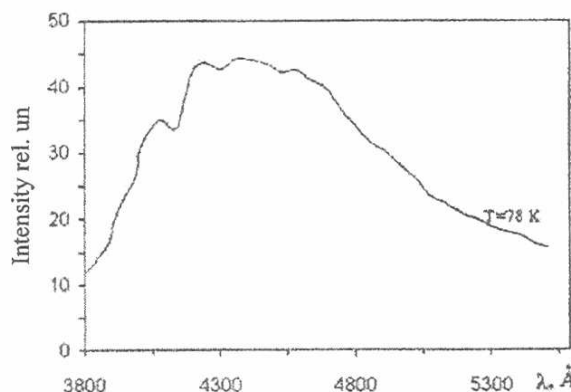


Fig. 4. The spectral dependence of photoluminescence of C<sub>60</sub> toluene solution at the temperature of 78 K.

The luminescence of polycrystalline layers of  $C_{60}$  fullerenes have been excited with the He-Ne laser radiation with  $\lambda = 0.6328 \mu\text{m}$ . The radiation density did not overcome  $100 \text{ W/cm}^2$ . The spectral dependence of photoluminescence of  $C_{60}$  fullerene layers at 78 and 293 K is shown in Fig. 5.

The maximum of irradiative luminescence situated at 1.806 eV is explained as a radiative recombination between neighboring bands with the participation of optical longitudinal photons or as a donor – acceptor luminescence.

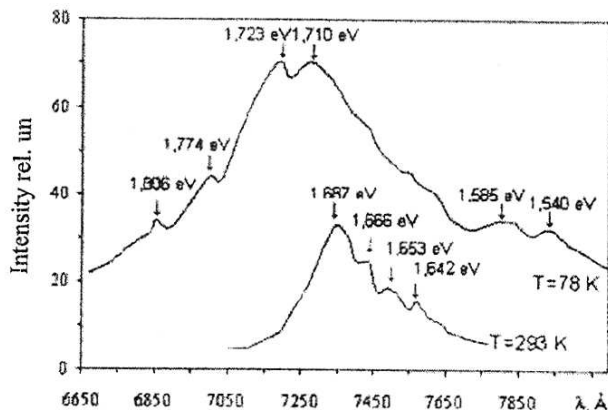


Fig. 5. The spectral dependence of  $C_{60}$  fullerene layer at 78 and 293 K.

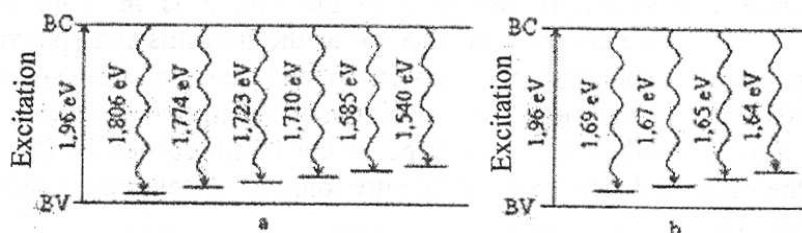


Fig. 6. The probable model of the energetic location of the impurity states. a)  $T = 78 \text{ K}$ , b)  $T = 293 \text{ K}$ .

The photoluminescence spectrum represents a broad band with the absolute maximum in the vicinity of 1.69 eV. In the neighborhood of the fundamental absorption limit of the  $C_{60}$  fullerene layers appears a row of weakly pronounced maxima near the impurity band at low temperature, whose intensities depend on the nature of the support where the layer [4] is grown. As far as is shown in the Fig. 5, the luminescence spectrum of the  $C_{60}$  fullerene layer prepared from the steam phase in the quasi-equilibrium volume at the temperatures of 293 K and 78 K is characterized by a several distinct maxima. These maxima of the photoluminescence are located at the energies of 1.806 eV, 1.774 eV, 1.723 eV, 1.710 eV, 1.585 eV, 1.540 eV at 78 K and 1.69 eV, 1.67 eV, 1.65 eV and 1.64 eV at 293 K. Since the spectrum peculiarities are located at the photons energies  $\hbar\omega < E_g$ , one can conclude that the photo-luminescence of the  $C_{60}$  fullerene thin layers is due to impurities. The energetic levels of the active radiative impurities are located between  $E_v$  and  $E_c$ .

Based on the spectral dependence of photo-luminescence (Fig. 5) we propose in Fig. 6 a model for the location of the impurity states.

## References

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