

OPTICAL PROPERTIES OF FULLERITE C₆₀ NANOSTRUCTURES IN WATER

I.T. Dihor

*Superconductivity & Magnetism Laboratory, State University of Moldova,
MD2009 Chisinau, Moldova*

Abstract

The colloidal solution of fullerene C₆₀ in water has been investigated by UV-VIS spectroscopy. It is shown that the peculiarities of colloidal solution spectrum are similar to UV-VIS spectrum for solid state C₆₀. The direct and indirect optical transitions were found for this colloidal solution of fullerene. The existence of indirect transitions proves the presence of solid state C₆₀ in water. The influence of IR laser irradiation on the colloidal solution of fullerene in water was also investigated. It is shown that under action of high power laser radiation the red shift of the optical line corresponding to $h_u \leftrightarrow t_{1u}$ (HOMO-LUMO) transitions arises. Other transitions are not affected by IR laser.

Since its discovery in 1985 [1], carbon-60 (C₆₀), a newly found all-carbon molecule, has captured the attention of scientists all over the world. The investigation of its physical and chemical properties, as well as the properties of its compounds, became one of the most popular topics of today's research in solid state physics, material science, chemistry and biomedicine.

The main contribution of the present work has been the research of optical properties of fullerite C₆₀ nanostructures in water and changes in the structure of the optical spectra of the fullerene C₆₀ water solution under influence of IR laser irradiation. It is known that the fullerenes are characterized by poor solubility in water. In [2] it has been proposed a method for obtaining the molecular-colloidal dispersions of fullerenes in water without any stabilizers and this resulted in the generation of solutions with fullerene aggregate sizes from several nanometers to 200.

For investigation of fullerene C₆₀ aggregates in water a solution with initial concentration $c=0.3$ mg/ml was used. The parameters of electronic spectrum of this solution were obtained in the 1.6-6.2 eV range using SPECORD M40 UV-VIS spectrometer.

In Fig.1 the absorption spectrum of non-irradiated (○) fullerene C₆₀ aggregates in water is presented. The UV-VIS spectrum of colloidal fullerene water solution does not significantly differ from UV-VIS spectrum of fullerite C₆₀ having the same positions of spectral lines. The similarity of spectra of C₆₀ solid films and C₆₀ in solution suggests the same origin for the transitions in both cases and shows the molecular character of the solid. Four intensive lines of absorption with maxima at 2.92, 3.62, 4.66 and 5.63 eV are caused by dipole allowed transitions. The positions of these lines correspond to data of ellipsometric and optical transparency measurements for crystalline C₆₀ [3-7]. The line of small intensity caused by optical dipolar-forbidden transition $h_u \leftrightarrow t_{1u}$ (HOMO $\leftrightarrow$ LUMO) is also noticed in the range of fundamental absorption edge (~2 eV).

The existence of the direct forbidden transitions $h_u \leftrightarrow t_{1u}$, direct allowed transitions ($h_u \leftrightarrow t_{1g}$, $(h_g + g_g) \leftrightarrow t_{1u}$, $h_u \leftrightarrow h_g$, $(h_g + g_g) \leftrightarrow t_{2u}$), indirect allowed optical transitions ($h_u \leftrightarrow t_{1g}$, $(h_g + g_g) \leftrightarrow t_{1u}$) and indirect forbidden optical transitions ($h_u \leftrightarrow t_{1g}$, $(h_g + g_g) \leftrightarrow t_{1u}$) in the C₆₀ fullerene aggregates in water is shown in Fig.2 and Fig.3 for non-irradiated samples. The

presence of indirect optical transitions is characteristic only of solid state and in the case of C_{60} colloidal water solution existence of such transitions certainly proves the C_{60} crystalline type in water. For transitions $h_u \leftrightarrow h_g$, $(h_g + g_g) \leftrightarrow t_{2u}$ the indirect allowed or forbidden transitions were not identified. The notations for indirect transitions used above are conditional, since the final states at these transitions belong to group of wave vector.

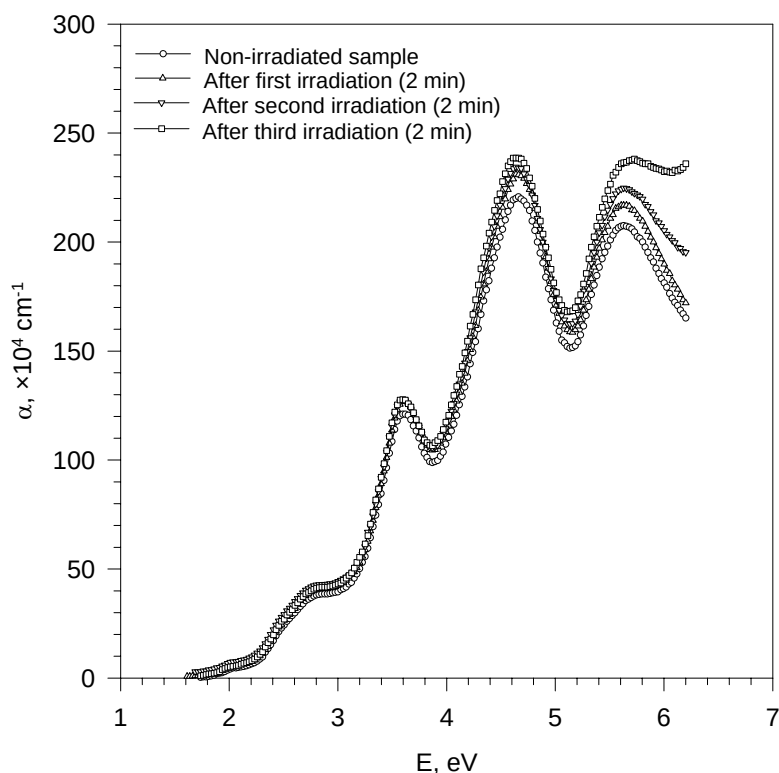


Fig.1 The absorption spectra for non-irradiated ($\circ$) and irradiated (Δ , ∇ , $\square$) by high power IR laser ($P=40$ W) samples of fullerene C_{60} aggregates in water.

The values of E_g for direct and indirect dipole forbidden and dipole allowed transitions, as well as energy of phonons, which participate in indirect optical transitions, are represented in Table 1. Index γ in Table 1 marks the exponent of multiplying $E \cdot \alpha$ of dependence $(E \cdot \alpha)^\gamma = f(E)$.

Table 1.

The energy gaps determined from direct and indirect optical transitions data for the fullerene aggregates C_{60} in water.

Type of transition	Direct forbidden	Direct allowed	Indirect allowed		Indirect forbidden	
	E_g , eV	E_g , eV	E_g , eV	E_{ph} , cm^{-1}	E_g , eV	E_{ph} , cm^{-1}
$h_u \leftrightarrow t_{1u}$	1.77	-	-	-	-	-
$h_u \leftrightarrow t_{1g}$	-	2.37	1.89	879.28	1.71	903.48
$(h_g + g_g) \leftrightarrow t_{1u}$	-	3.27	2.56	1097.098	2.14	1900
$h_u \leftrightarrow h_g$	-	4.02	-	-	-	-
$(h_g + g_g) \leftrightarrow t_{2u}$	-	4.90	-	-	-	-
γ	2/3	2	1/2		1/3	

We see from Table 1 that in the case of indirect forbidden transition ($h_g + g_g \leftrightarrow t_{1u}$) the energy of phonon $E_{ph} = 1900 \text{ cm}^{-1}$ exceeds the limiting energy for “intern” phonons of the fullerite C_{60} . In this transition, probably, two phonons with summary energy equal to 1900 cm^{-1} participate.

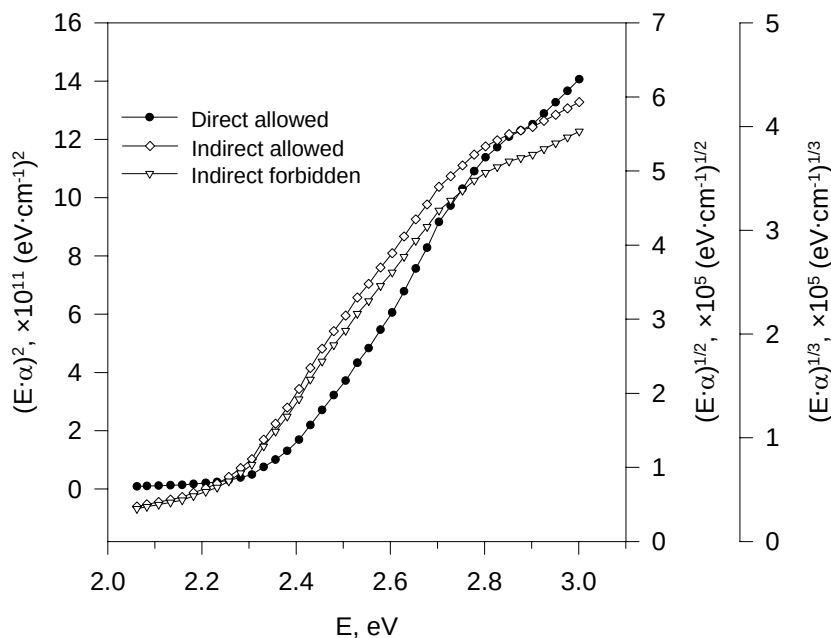


Fig.2 The direct allowed transitions (●), indirect allowed transitions (◇) and indirect forbidden transitions (▽) in the C_{60} fullerene aggregates in water in (2-3.1) eV range.

The solution of fullerene aggregates C_{60} in water was irradiated by IR laser type LTN-101 with wavelength $\lambda = 1064.1 \text{ nm}$ (emitted power $\approx 40 \text{ W}$) for 3 times, every time being with 2 min duration. The absorption optical spectra for irradiated samples (Δ , ∇ , $\square$) are presented in Fig.1. The increasing of optical absorption with increasing of irradiation dose is caused by evaporation of the water with increasing of fullerene aggregate concentration during the irradiation processes. In the case of irradiated samples the change of E_g occurs. Namely, for the direct forbidden transitions $h_u \leftrightarrow t_{1u}$ the decrease of E_g after IR laser irradiation was found. This decreasing depends on irradiation dose: 1.77 eV before irradiation, 1.68 eV after the first irradiation, 1.62 eV after the second irradiation, 1.57 eV after the third irradiation (Fig.4). The influence of high power IR laser irradiation on $h_u \leftrightarrow t_{1u}$ (HOMO $\leftrightarrow$ LUMO) transitions in C_{60} thin films was also examined. But in this case no change of E_g value was observed. Thereby the red shift of HOMO $\leftrightarrow$ LUMO E_g only for fullerite C_{60} nanostructures in water occurs. The decreasing of E_g during the high power irradiation of fullerene C_{60} aggregates in water is linear type dependence in the first approximation.

In [8] the effect of energy blue shift of star-like $C_{60}PS_n$ macromolecule (PS polystyrene, $n=1, 2, 3, 4$) photoluminescence spectra was observed. This shift is assumed to HOMO-LUMO gap increasing. According to [8] the increasing of HOMO $\leftrightarrow$ LUMO gap is caused by formation of new covalent bonds between fullerene C_{60} and polystyrene chains. The type of such bonds can affect the values of Hamiltonian matrix elements W_1 and W_2 of states mixing

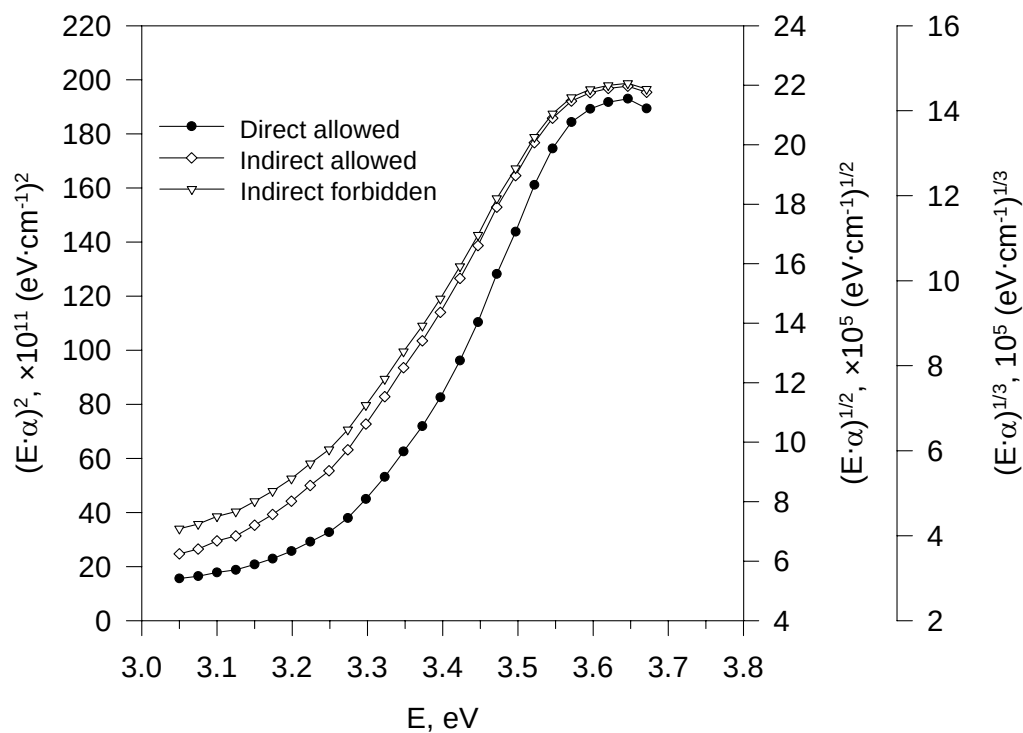


Fig.3 The direct allowed transitions (●), indirect allowed transitions (◇) and indirect forbidden transitions (▽) in the C_{60} fullerene aggregates in water in (3-3.8) eV range.

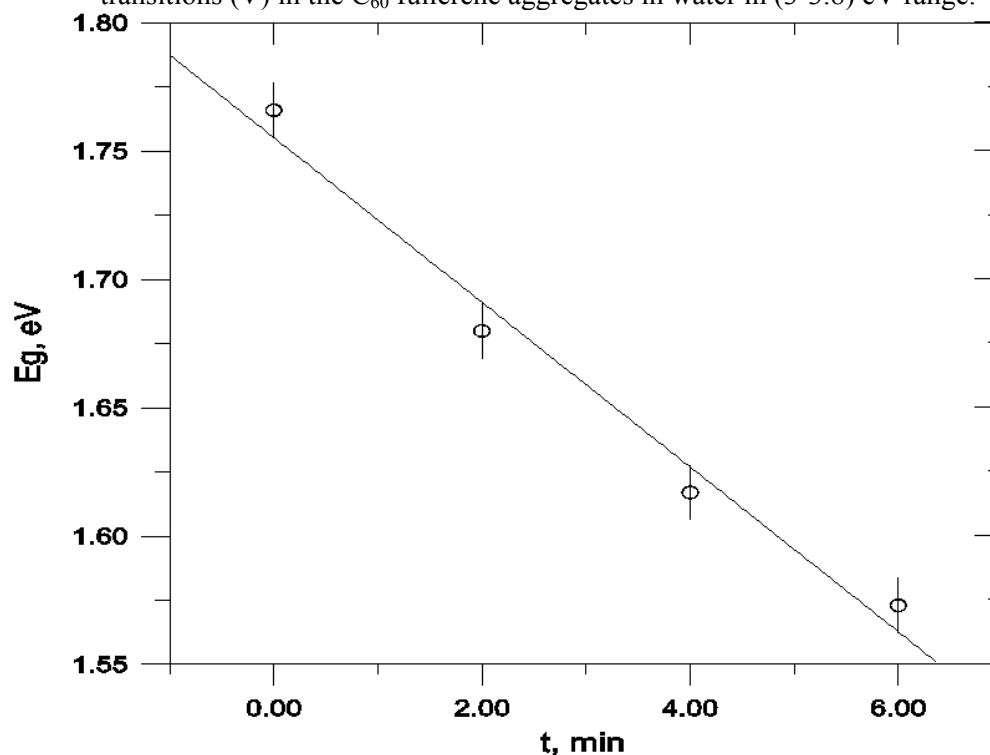


Fig.4. The decreasing of E_g corresponding to $h_u \leftrightarrow t_{lu}$ ($\text{HOMO} \leftrightarrow \text{LUMO}$) direct dipole forbidden transitions under action of high power IR laser irradiation vs. irradiation time

for cases of C-C and C-H bond formation, respectively. These matrix elements determine the following dependence of the HOMO $\leftrightarrow$ LUMO transition quantum [9]

$$h\nu = [\Delta^2 + n(W_1^2 + W_2^2)]^{1/2},$$

where Δ is initial HOMO-LUMO gap of unperturbed fullerene and n is number of new formed chemical bond pairs. The dependence of HOMO $\leftrightarrow$ LUMO gap vs. n at $n < 9$ is linear function in accordance with experimental data (blue HOMO $\leftrightarrow$ LUMO transition shift) [8]. Moreover, this behavior weakly depends on peculiarities of full polymer chain or other ligands attached to fullerene, but strongly depends on the nearest neighbors of C₆₀ linked to fullerene by covalent bonds. In contrast to the fullerene C₆₀PS_{*n*} blue HOMO $\leftrightarrow$ LUMO shift at decreasing of n the red shift of HOMO $\leftrightarrow$ LUMO transitions must be observed. This effect was observed in our experiments at action of high power IR laser irradiation on the fullerite C₆₀ in water.

The fullerene water solution consists of isolated C₆₀ molecules in hydrated state, C₆₀@{H₂O}_{*n*} complexes and of their small spherical clusters. The complexes C₆₀@{H₂O}_{*n*} are surrounded by spherical layers of interconnected water molecules and can be noticed as [C₆₀@{H₂O}_{*n*}]_{*m*} [10]. In such a structure the carbon atoms are centers of electron-deficiency and capable of interacting with electrons donated by extra water molecules. Under action of the high power IR laser irradiation the breaking of these bonds takes places. This leads to decreasing of HOMO $\leftrightarrow$ LUMO gap. The high power IR laser irradiation leads also to breaking of the bonds between C₆₀@{H₂O}_{*n*} complexes in spherical fractal clusters of hydrated fullerenes. However at these breakings the HOMO-LUMO gap remains unchanged.

According to our experiments, unlike HOMO-LUMO transitions, the value of E_g corresponding to direct allowed optical transitions ($h_u \leftrightarrow t_{1g}$, $(h_g + g_g) \leftrightarrow t_{1u}$, $h_u \leftrightarrow h_g$, $(h_g + g_g) \leftrightarrow t_{2u}$), indirect allowed optical transitions ($h_u \leftrightarrow t_{1g}$, $(h_g + g_g) \leftrightarrow t_{1u}$) and indirect forbidden optical transitions ($h_u \leftrightarrow t_{1g}$, $(h_g + g_g) \leftrightarrow t_{1u}$) for fullerene C₆₀ aggregates in water is not affected by high power IR laser irradiation.

References

- [1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl, and R. E. Smalley, Space, stars, C60 and soot, *Nature* (London), 318:162-163, 1985.
- [2] G.V. Andrievsky, M.V. Kosevich, O.M. Vovk, V.S. Shelkovsky, L.A. Vashchenko, *J.Chem.Soc. Chem.Comm.*, 1995, 12, 1281.
- [3] S.L. Ren, Y. Wang, A.M. Lee, H.F. Ni, J. Selegne, P.C. Eklund, *Appl. Phys. Lett.*, 1991, 59, 2678.
- [4] V.I. Srdanov, C.H. Lee, N.S. Sariciftci, *Thin Solid Films*, 1995, 257, 233.
- [5] E. Sohmen, J. Fink, *Phys. Rev. B.*, 1993, 47, 14532.
- [6] S. Modesti, S. Gerasari, P. Rudolf, *Phys. Rev. Lett.*, 1993, 71, 2469.
- [7] G. Gensterblum, J.J. Pireaux, P.A. Thiry, R. Caudano, J.P. Vigneron, P. Lambin, A.A. Lucas, W. Kratschmer, *Phys. Rev. Lett.*, 1991, 67, 2171.
- [8] A. N. Aleshin, Yu. F. Biryulin, N. B. Mironkov, L. V. Sharonova, E. N. Fadeeva, V.N. Zgonnik, *Fullerene Science and Technology* 1998, 6, 3, 545.
- [9] Yu. F. Biryulin, V. S. Vihnin, V.N. Zgonnik, *FTT*, 2000, 42, 188.
- [10] G. V. Andrievsky, V. K. Klochkov, A. Bordyuh and G. I. Dovbeshko, *Chem. Phys. Lett.* 364 (2002).