

Strong Vibration-Electron Interactions and Vibration Band Enhancement in Vibrational Spectra of C₆₀ Nanofilms and Singlewalled Carbon Nanotubes

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In Raman spectra in nanofilms of fullerene C₆₀ with thickness about 150 – 250 nm it was found the enhancement of vibrational bands Hg (1 ÷ 8) intensity at 2 ÷ 7 times in comparison with the microfilms with thickness 1 – 2 microns. It is shown that the inactive for icosahedral symmetry I_h Raman and IR vibrations Gg, u, Hu, F2g, u, and the lateral spectral components of the bands Hg (1 ÷ 8) increase in 5 – 50 times and more. This is due to an abnormal increasing of the resonant nonlinear interaction of the vibrational modes and the vibrational-electronic interaction, which leads to a change in the electronic states and the appearing of new electronic bands (EB) in the region of the vibrations. The change induced by the polymerization of EB in nanofilms C₆₀ and intense laser pulses have been studied. A nonmonotonic dependence of the EP intensity on the thickness of nanofilms has been established. The lineshape of the overtones 2Ag (2) and 2Hg (7) for fullerene C₆₀ and increasing of overtone 2D in spectra of single-walled carbon nanotubes, as well as unusual changes anharmonicity their 2G and 2D bands varies with the frequency of the laser radiation have been studied.

Keywords: Nanofilm, Nanotube, Fullerene, Vibrational bands enhancement, Vibrational-electronic interaction, Induction of Electronic bands

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1. INTRODUCTION

While the fraction of the surface atoms in any nanoparticulate system is about 50%, the same reaches up to 100% in the case of single-walled carbon nanotubes (SWCNT) and fullerenes). SWCNT and fullerenes exhibit high anharmonicity and nonlinear susceptibilities in vibrational range. However, to date the role of the nonlinear interaction of the vibrational modes (NIVM) in nanostructures, in particular, in typical carbon materials (fullerenes, graphene and nanotubes) remains poorly studied. It should be noted that the efficiency of NIVM significantly increases in the result of the resonant nature of wave processes and spatial accumulation. We point out that the spatial dynamics of nonlinear resonant wave interactions in detail has been studied previously in many publications [3-6].

The great importance for increasing the role of NIVM in nanostructures has a strong vibration-electron interaction (VEI) [1, 2], which leads to the appearance of new electronic states at low frequencies region (in the band gap of semiconductors and dielectrics) and the abnormal increasing of the wave nonlinearities. VEI related to the generation of higher vibrational states (overtones and sum tones) under the nonlinear resonant interaction of thermally excited low-frequency vibrational modes. Excited vibrational states are approaching the electronic states (ES) and interact with them effectively [1, 2]. In this case, the self-consistent with the vibrational excitations change ES promotes abnormal growth of vibrational non-linearity, which makes the phenomena under consideration particularly relevant for the nanostructures. Since the key role of NIVM, VEI, and especially the higher vibrational states were not taken into account in many studies of carbon nanomaterials, the purpose of

this work is the study of changes in ES with the vibrational induction of radically new electronic bands (EB) in vibration region of C₆₀ and SWCNT and the corresponding increase of the vibrational bands and especially the intensity increasing of overtones and sum tones in nanostructures. For this purpose Raman scattering (RS) and infrared absorption (IR) spectra of nanofilms with thickness $d = 150-250$ nm and microfilm ($d = 1,2-2$ mm) of fullerenes C₆₀ have been compared. The influence of laser radiation on the vibrational spectra of fullerenes C₆₀ and SWNTs has been studied. For the first time the structure of the overtone band 2Ag(2) in the IR spectrum of C₆₀ has been analyzed and the anharmonicity changes of SWCNTs as the function of the laser excitation frequency ν_L have been studied.

2. EXPERIMENTAL AND INSTRUMENTAL METHODOLOGY

C₆₀ films were deposited on substrates of crystalline silicon by hot or cold deposition. The Raman spectra were studied using automated spectrometers DFS-24 and Horiba Jobin Yvon T64000, with the cooled photomultiplier and a CCD-detector respectively and a photon counting system. Raman spectra were excited by Ar⁺ laser with a wavelengths $\lambda_L = 514,5; 488$ and 476 nm. To reduce the influence of photopolymerization of C₆₀ the cylindrical focusing of the laser radiation (spot size of 0.3x2,5 mm²) was used, laser intensity was ~ 2 W/cm². With sharp focusing of laser excitation λ_L up to a diameter of ~ 2 microns intensity of the exciting radiation exceeds 10 kW/cm², what allows us to study the impact of light radiation on the Raman spectra and the VEI. Additionally we studied the preliminary laser irradiation of C₆₀ films with doses of 25-30 mJ/cm², and

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the influence of λ_L on SWCNTs anharmonicity. IR spectra of C_{60} have been studied by Fourier spectrometer Nicolet NEXUS-470. Vibrational bands of C_{60} numerically allocated on a broadband background in the Raman and IR spectra and they were associated with the new ES [1] that will be discussed in more detail in the next section. In order to increase the signal/noise ratio the numerical analysis of the spectra was carried out with optimal numerical smoothing. In the numerical decomposition of vibrational and electronic bands on the individual spectral components the method of least squares with the variation of the frequency positions of the components, their intensity, shape and half-width have been used.

3. RESULTS AND DISCUSSION

3.1 The Occurrence of New Electronic States and the Light Influence on Vibration-Electron Interaction

In Raman and IR spectra of nanostructures, as a rule, broadband background that has an electronic origin [1] is observed. The observed vibrational bands is always necessary to allocate from this background, so first analyze the regularities of its change. We have studied in detail the change induced by ES in the band gap of full-erite C_{60} , as shown in Figure 1a, b. Figure 1 shows the overview of the Raman spectra of some of C_{60} nanofilms under study. For nanofilms together with the line Ag (1) 497 cm^{-1} the line $\nu_{Si} = 520\text{ cm}^{-1}$ of crystalline silicon substrate is observed, which is shown in detail in Figure 1a. The ν_{Si} line can be used to classify the C_{60} nanofilms thickness (d) - with decreasing of d the intensity of ν_{Si} increases, and for microfilm C_{60} with thickness about 1.2-2 microns, this line does not appear.

In Raman spectra of nanofilms fabricated by cold deposition process (upper spectrum 3 at Fig. 1a) broad electronic bands (EB) appeared and their intensities several times stronger that in samples prepared by hot method (spectrum 2).

In the original films the low-frequency part of the ES dominates, which is well approximated by exhibitors. After nanofilm polymerization by hydrazine N_2H_4 (2p and 3p spectra) broadband ES can both increase and decrease. But the important fact is that their intensities increases with frequency ν , as well as the intensities in the Raman spectra of EB in C_{60} microfilms (spectrum 1 at Fig.1b). At sharp focusing of the exciting radiation λ_L EB under study enhance more than 100 times and significantly higher than the maximum intensity of the strongest line Ag (2) 1469 cm^{-1} , which is shown in the second inset in Figure 1. The EB maximum moves from the region of the most intense Raman bands Ag (2), Hg (7, 8) to their overtones, that characterizes the increasing of the interaction between the atomic and electronic subsystems (violation of the adiabatic approximation). Such EB also found in the IR spectra of C_{60} films.

For a correct comparison of the intensities of the new EB in various nano- and microfilms of C_{60} Raman spectra were normalized on the intensity of the strongest line Ag (2) at 1469 cm^{-1} , which show at Fig. 1b. One can see that in microfilm ($d=2\text{ m}$, spectrum 1) wide EB is significantly weaker than in nanofilms even obtained by a hot method. After the prior laser irradiation of nanofilms the low-frequency part of the EB (the wing of

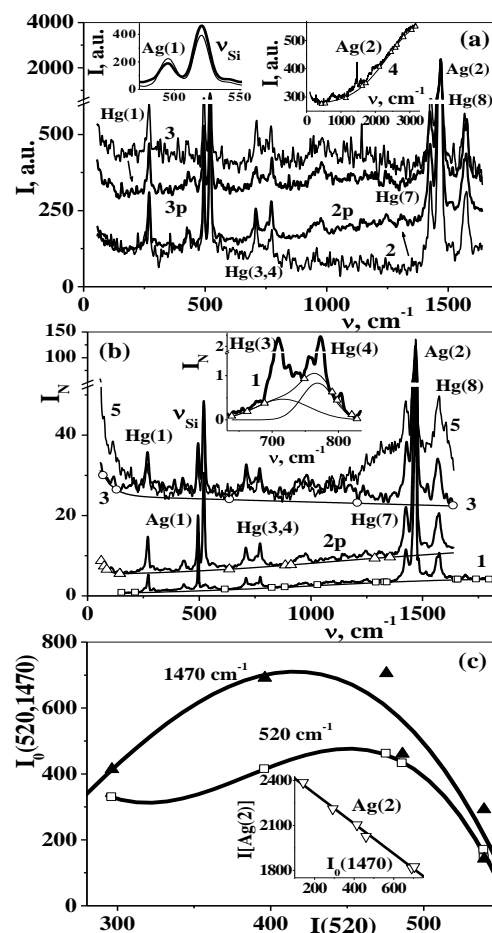


Fig. 1 – Manifestation of new EB in the Raman spectra of initial C_{60} nanofilms (2,3), and after polymerization (2p, 3p) and the strong focusing the laser radiation (4, inset) (a); comparison of wide electronic band in the normalized Raman spectra of different C_{60} films and the appearing of "island" EB in the vicinity of Hg (3,4) vibration (inset)(b) and non-monotonic change in the EB intensity I_0 at 520 and 1470 cm^{-1} from the line intensity $\nu_{Si} = 520\text{ cm}^{-1}$ (the thickness of nanofilms d) (c).

the Rayleigh line) can increase as well as their high-frequency part near the most intense Raman bands Ag (2) and Hg (7,8), as shown at spectrum 5 on Fig.1b. From Fig.1b one can see great increasing of Hg (7,8) intensities with an increase of EB intensity I_0 . Established that all the EB in the region of vibrational states are well approximated by the Gauss functions with half-widths $\delta\nu \sim (1-2) \cdot 10^3$. Localization of their maxima in areas of intense vibrations confirms the vibrational induction of new ES.

In addition to broadband ES with half-widths $\delta\nu > 10^3\text{ cm}^{-1}$ in the vicinity of the vibrations the "islet" EB with $\delta\nu \sim 10^2\text{ cm}^{-1}$ have been observed, which is due to their non-linear vibrational origin. For the region of Hg (3,4) vibrations the local EB are shown in the inset in Figure 1b. The peak intensities of these local EB approaching to the maxima of narrow vibrational bands of C_{60} , and the integral intensity of EB are significantly greater. The non-monotonic dependence of the broad EB from the thickness of nanofilms d (Fig.1c) have been established, that is confirm their non-linear

nature. Here the dependence of I_0 at 520 and 1470 cm^{-1} from the intensity of line ν_{Si} , which is uniquely related to the thickness of nanofilms d have been shown. In Fig.1c shown how the experimental points approach cubic polynomials. The sharp decrease I_0 for thin films is connected with insufficient spatial accumulation of nonlinear wave processes. The existence of optimal nanofilm thickness, at which the intensities of the new EB reach a maximum, is also associated with a decrease in the vibrational nonlinearity with increasing of thickness d . This clearly demonstrates the important role of NIVM just for nanostructures. The role of the VEI is also confirmed by the strong linear weakening of the intensity of the Ag (2) line with I_0 (1470 cm^{-1}) increasing as shown in the inset in Fig.1c. In strengthening EB intensity of the vibrational bands are reduced.

The increasing role of VEI is associated with increased non-linear resonant interaction of vibrational modes in nanostructures. The efficiency of nonlinear processes in nanofilms of C_{60} abnormally increases due to a number of serial vibrational resonances of the Hg (1) + Hg (2) = Hg (3), Hg (1) Ag + (1) = Hg (4), 2Hg (3) = Hg (7), Hg (3) + Hg (4) \approx Ag (2), 2Hg (4) \approx Hg (7) etc., number of which with taking into account a plurality of the inactive vibrations exceeds one hundred and coherent changes of ES.

3.2 The Enhancing of active vibrational bands in the Raman spectra of C_{60} Nanofilms

A comparison of the intensities of various VB in the Raman and IR spectra of C_{60} films was conducted with the normalization of dedicated lanes on the intensities of the strongest lines of Ag (2) and F1u (1) (527 cm^{-1}), as shown in Figure 2a ($I_N = I_j / I_{\text{max}}$). In the Raman spectra of C_{60} nanofilms it was found a large intensity increasing active in the RS vibrational bands Hg(j), where $j = 1 \div 8$ at the relative weakening of the most intense Raman band Ag (1,2), as shown in Figure 2a, b. It can be seen that the low frequency Raman bands Hg (1,2), and the medium frequency band Hg (3,4) as well as Hg(7,8) amplified by 2 - 7 times comparing with 2 μm microfilm. Should be noted the weakening of Hg(3) band and increasing of Hg(4) band after the polymerization of 2 and 3 Nanofilms by diamine N_2H_4 (spectra 2p on Figure 2b) and the observation of several inactive vibrations e.g., Gu (2) Gg (1,3). On Fig.2c there are shown the ratio of the Raman bands Hg (1-8) and Ag (1) maxima for nanofilms of fullerene C_{60} 2 and 3 and microfilm with thickness $d = 2 \mu\text{m}$ (1).

The greater enhancement of vibrational band Hg (j) have been observed in the micro-RS spectra with strong focusing radiation $\lambda_L = 488 \text{ nm}$, even for microfilm $d = 1,2 \mu\text{m}$ (ratio 4/1). For polymerized by N_2H_4 nanofilms (films 2p and 3p) the observed enhancement of VBP became weaker (see attitude 3p/1 to 2c), which is associated with a decrease in the vibrational nonlinearity and is consistent with the EB weakening in Figure 1a. The obtained results open the way to understanding the significant differences between experimental results and the results of quantum chemical calculations (QCC) the observed bands Hg (3) and Hg (7) 8-10 times stronger than in theory, and the bands Hg (5,6) is reduced by more than an order of magnitude, as shown in the inset 2c. We also note that the calculated activity of Raman vibration Hg (4) is approx-

imately 6 times higher than the activity of Hg (3), and in the experiment they have similar intensities. When loosening nonlinearity as in the case of polymerization of nanofilms, band Hg (3) is weakened, and Hg (4) – increased (2p spectrum in Figure 2b), i.e. approaching QCC results. It shows that the differences under discussion NEVM and strong VEI, which is not taken into account in QCC.

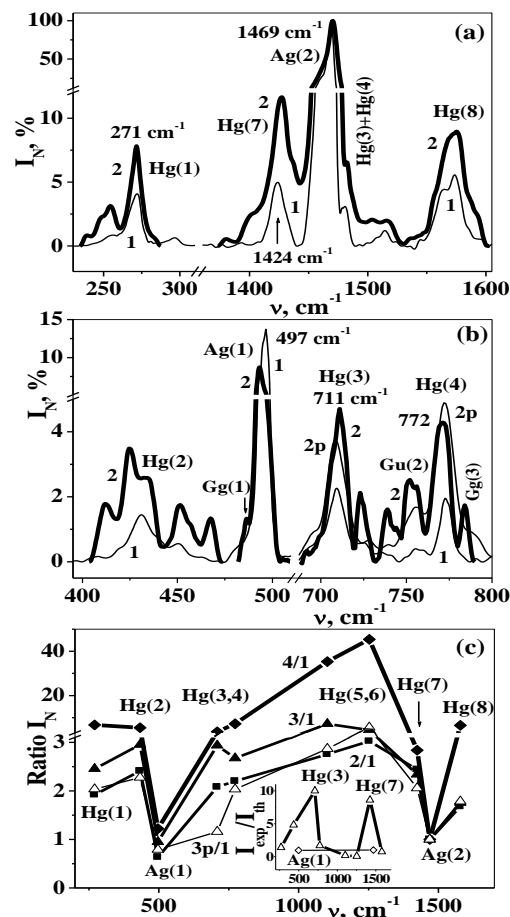


Fig.2 – Comparison the normalized on line Ag (2) in the Raman spectra of micro (1) and nanofilms (2) of fullerene C_{60} (a, b) and the enhancement of Raman-active Hg (1-8) vibrations in nanofilms over microfilm (s).

3.3 The Enhancing of "silent" vibrations in the Raman and IR spectra of C_{60} Nanofilms

The abnormally strong increasing of many inactive for icosahedral symmetry I_h vibrations Gg, u, Hu, F2g, u, etc. have been also observed in Raman and IR spectra, as illustrated in Figure 3a-c. In the Raman spectrum between vibrations Hg (1) and Hg (2), the bands of inactive vibrations F2u (1), Gu (1) and Hu (1), with position consistent with the results of QCC have been also observed. Some of the identified spectral components of these vibrations are shown in Figure 3a. We point out that the classification of these vibrations in [7, 8] is not consistent with the data QCC. Essential that in nanofilms inactive vibrations are enhanced in 5–25 times, and at a strong laser pulses - in 50–300 times. The side components of the vibrations Hg (2) and Hg (1) (inset) enhanced significantly stronger than the central component. This may be due to the exist-

ence of vibrational states near the Brillouin zone boundary. The enhancement exactly the high-frequency edge of bands Hg (1,2) indicates the positive dispersion $\omega(k)$ of corresponding phonon branches. Similar regularities are also observed in the region of Hg(3,4) bands. At Fig.3b a significant increasing of side spectral components (SC) in the vicinity of the most high band Hg (8) is shown.

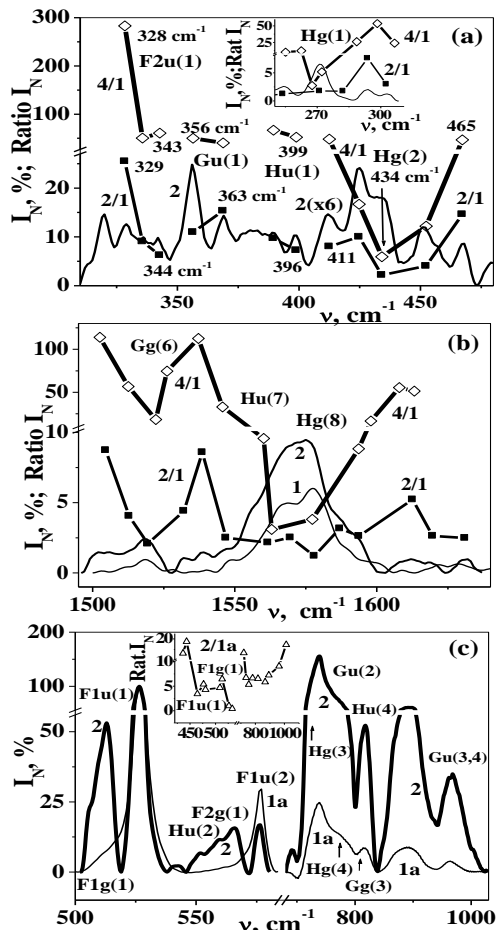


Fig.3 – The enhancement of vibrations in C60 nanofilms: low- (a) and highfrequency (b) parts of Raman and IR (c) spectra and enhancement of active and “silent” vibrations in Raman (a,b) and IR (c) spectra in nanofilms compared with microfilms

Here the maximum of I_N relations in the region 1530-1550 cm^{-1} are associated with the "silent" Gg (6) and Hu (7) vibrations [7,8]. In the IR spectrum of C60 nanofilms an enormous enhancement of some vibrations compared with microfilm 1a with thickness of 1.2 μm also have been found, as shown in Fig. 3.

3.4 Spectral studies of the overtones of the fundamental vibrations of C60 and SWCNTs

In contrast to [7,8], where a series of high-frequency vibrational bands have been observed we have performed a detailed analysis of these spectra with taking into account the 2nd order vibrational states near the Brillouin zone boundary, which is not taken into account in [7,8]. Dedicaded in the IR spectra of C60 micro- and nanofilms vibrational bands in the region of overtones 2Hg (7) and 2Ag (2) are shown in Figure 4.

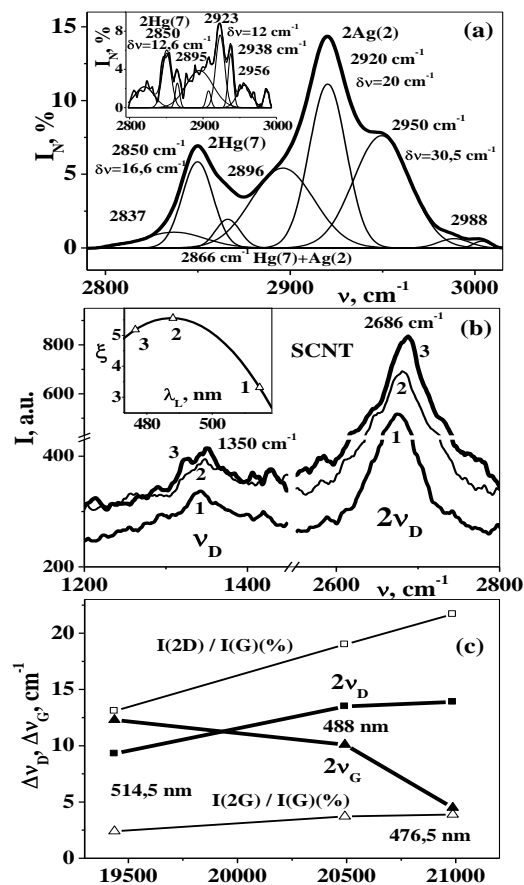


Fig. 4 – The structure of the bands of overtones 2Hg (7) and 2Ag (2) in the IR spectra of C60 micro- and nanofilms (inset) (a), the enhancement of bands of overtones 2D SWCNT when changing the laser excitation $\lambda_L = 514,5 \text{ nm}$ (1), 488 nm (2) and 476 nm (3) (b) and changes in the relative intensities of the 2D and 2G (open symbols) and anharmonic frequency shifts of these harmonics (solid symbols) with increasing ν_L (s)

Characteristically, in the area between the maxima of overtones 2850 2920 cm^{-1} the sum band Hg (7) + Ag (2) at 2896 cm^{-1} have been observed, as well as high satellites 2866 and 2950 cm^{-1} of band overtones. These high-frequency (HF) components we assign to the edge of the Brillouin zone, which confirms the positive phonon dispersion $\omega(k)$ of corresponding phonon branches. Interestingly, the high-frequency component of C60 nanofilms the overtone 2Ag (2) 2956 cm^{-1} is shifted to higher frequencies, and the additional narrow lines 2865 and 2938 cm^{-1} with half-widths $\delta\nu = 6-7 \text{ cm}^{-1}$ appear (see inset in Fig.4a). This suggests the possibility of the phonon dispersion enhancing in nanostructures due to the increased interparticle interactions, as well as the phonon branches folding as a result of increasing the unit cell size.

For the of SWCNTs the essential growth the intensity of the overtones 2vD and 2vG of D and G modes near 2680 and 3180 cm^{-1} with the growth of laser excitation frequency ν_L have been detected, that is shown Fig.4b. Seen that the overtone 2vD increased stronger than bany vD and the ratio of the intensities of the bands and 2v and vD $\xi > 5$, and reaches its maximum at 488 nm (see

inset in Fig. 4b). It is similar to Fig. 1c the optimal value λ_L close to 488 nm have been observed, where the value of ξ was maximal. Note that a similar behavior of these bands is also observed for graphene [9]. Intensities of overtone bands I (2D), I (2G) for SWCNTs normalized to a maximum intensity of G band increases approximately linearly with ν_L , as shown in 4c, and reach values of about 20 and 4% respectively. It is established that the anharmonicity of D mode, as well as sum tone $\nu_D + \nu_G$ increases with ν_L , while the anharmonicity of the G-mode decreases (4c) [10]. This indicates a different sensitivity of the different vibrational modes of SWCNTs under high-frequency laser radiation.

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4. SUMMARY

The observed anomalous enhancement of the vibrational bands in nanostructures is associated with significant change in the electrophysical parameters of nanostructured objects as a result of the weakening of symmetry and enhancing anharmonicity and NEVM. This leads the VEI increasing and the change of the electronic states, which plays a significant role in nanostructures, but until now practically has not been studied. This opens up a new fundamental direction in the study of nanostructured materials. The obtained results, including the study of changes of new electronic states in vibrational spectra form the basis of a new method of spectroscopy, which in addition to the vibrational dynamics provides information about the nonlinear vibration-electron dynamics and nonlinear changes in the quantum properties of the material media.