**FTIR and DRS – spectroscopy of nanocarbon vibration states**

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Phonon’s structure of amorphous and crystal carbons is investigated in detail with the help of Raman spectroscopy (RS) \([1, 2]\). However, not all vibration states in view of an alternative selection rule are active in Raman spectra.

In the given work on the basis of FTIR reflection spectroscopy and the adapted to absorption media method of the diffuse reflections spectroscopy (DRS) and an original device for the infrared (IR) spectrometer destined for quantitative studying of vibration states in nanocrystal carbon, on an example of pyrolytic carbon (PC) and glassy carbon (GC) are investigated. Research of vibration states in IR-spectra of the condensed carbon is complicated by intensive not selective absorption of free carriers of a charge. The natural surface of the samples was investigated at a corner of reflection 20° on IFS-88 (Bruker) spectrometer in wide spectral region 5000-400 cm\(^{-1}\) with the accuracy 2 cm\(^{-1}\) and in a regime of accumulation up to hundred scans. According to the theoretical-group analysis of fragments of crystal structure in GC and PC IR-spectra, the graphite’s atoms \((D_{6h}^4)\) or fullerenes structures \((I_h)\) should possess the optical activity of intraplane asymmetric vibrations \([1]\). Near central Γ- point of Brillouin zone the following vibration states are active:

\[
D_{6h}^4 : \Gamma_{vibr} = A_{2u} + E_{1u} + 2E_{2g}
\]

\[
I_h : \Gamma_{vibr} = 2A_{2g} + 3T_{1g} + 4T_{2g} + 6G_g + 8H_g + A_u + 4T_{1u} + 5T_{2u} + 6G_u + 7H_u
\]

On the basis of the formula offered by the authors which is similar to Kubelka-Munk relation the influence of initial parameters of samples (concentration, degree of its depressiveness) on the factor of scattering is investigated. In DRS - spectra of specimen the selective absorption in the ranges of 1100-700 cm\(^{-1}\), 1700-1200 cm\(^{-1}\), 3400-1800 cm\(^{-1}\) were found that well enough correlate with the features in a spectrum of function of density phonons states of condensed carbon with graphite’s, fullerenes and carbon’s chains motives. In DRS -spectra of PC and GC the wide bands of absorption in the ranges 900-800 cm\(^{-1}\) and maxima of absorption on 1510 and 1240 cm\(^{-1}\) were registered, and also – the features in the form of curvature in the aria of 1570, 1350, 1020 cm\(^{-1}\) were found \([2]\). In experimental IR-Fourier and DRS spectra of the samples the selective absorption bands of vibration states \(E_{1u}\) and \(T_{1u}\) in the range 1600-1300 cm\(^{-1}\) and \(A_{2u}\) – mode in 900-800 cm\(^{-1}\) were registered. Intensity and position of bands considerably change with the growth of temperature of samples processing and correlates with results of the structural research of Raman and ATR (attenuated total reflection) spectra on the given objects \([2]\).


Photoluminescence of organic semiconductors sensitized by fullerenes $C_{60}$

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Fullerenes $C_{60}$ are the $\pi$-type–acceptor molecules and have a lot of interesting effects in different organic compounds. Sensitizing of amorphous molecular semiconductors as polyvinylcarbazole (PVC) and polyepoxypropylcarbazole (PEPC) by fullerenes $C_{60}$ leads to appearance of new photogeneration centres. The centres are intermolecular complexes with charge transfer (CT), that are formed during accepting by molecule of fullerene few electrons from different polymer macromolecules and can cause transport of excitons and charge carriers. The processes can influence the properties of polymer-fullerene nanocomposites in a different way depending on the concentration of the sensitizer.

In the work we have investigated photoluminescence of concentration dependence of $C_{60}$ in organic semiconductors PVC and PEPC. We also have applied irradiation with Cu ions and with electrons in order to study influence on bonding between $C_{60}$ and PVC, PEPC molecules. The samples were prepared by simultaneous condensation of PVC or PEPC and $C_{60}$ powders on Si substrate from 2 sources at different temperatures of the powders evaporation. Concentration of $C_{60}$ molecules was controlled by rate of deposition. Thickness of the films was 100mn. Irradiation of the films was performed with electrons: energy $E_e=1.8$ MeV and copper ions $E_{Cu}=140$ keV, the fluence $F=4.2\cdot10^{14}$ ion/cm$^2$.

Photoluminescence in the range of singlet excitons radiative recombination is characterised by wide spectral band shifted to the UV region. Depending on the fullerene concentration the band widens and shifts that proves about complicated processes in the systems.

Photoluminescence changes also under high-energetic electron irradiation ($E_e>1.8$ MeV) with absorbance doses of 3.0; 4.0 MGr. That proves about change of creation mechanisms of CT complexes due to appearance of donor-acceptor and exchange interaction. During irradiation with Cu ions molecular complexes $Cz^+-C_{60}^-$ undergo to damages that is proved by fall of photoluminescence intensity. Due to that the systems became characterized by segregation and destruction of molecules $C_{60}$ and that causes decrease of number of molecular complexes.
Nanolayers of donor-acceptor systems composed of fullerene and chromophor

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Fullerenes covalently linked to photoactive organic molecules such as e.g. porphyrin and perylene can be very attractive molecular systems for investigations of nature and kinetics of intermolecular interactions upon photoexcitation and can find many applications (e.g. artificial photosynthesis, organic photovoltaics, molecular electronics and photonics [1, 2]). These systems can be used as organic materials in electronic devices where molecular materials is in direct contact with metallic or/and semiconducting electrodes.

In this contribution we have investigated solutions of and Langmuir-Blodgett layers of porphyrin, porphyrin-C_{60}, perylene and perylene-C60 on the gold, In_{2}O_{3} and quartz substrates.

Fullerene covalently linked to the chromophore were studied and analyzed with the use of optical spectroscopy and the measurements were done in the region of UV-Vis. Photoinduced electron transfer in the donor-acceptor dyads was investigated with light induced electron spin resonance spectroscopy (ESR) and photocurrents measurements [3, 4].

The results showed that the presence of C_{60} influences markedly the spectral parameters of the porphyrin and perylene moieties due to the strong interaction which leads to charge redistribution in the systems. Occurrence of intramolecular energy transfer from fullerene to porphyrin and electron transfer between the dye and the fullerene are shown.

A photoelectrochemical used for light-induced photocurrent. It was showed that the linkage of chromophors with C_{60} effects strongly rise of photocurrent.

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Fullerene $C_{60}$ as effective luminescence quencher of Yb (III) phenyltetracyanoporphyrazine complexe

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Novel facile synthetic route to the metal template assembly of a tetrapyrollic framework from tetracyanoethylene (TCNE) structural units by the reaction of TCNE with metal $\pi$-sandwich complexes had been obtained. The reactions occur under extremely mild conditions, the porphyrazine macrocycles being assembled in high yield from TCNE. The formation of a disordered polynuclear coordination polymer network including a macrocyclic structure and metal cations bridged through the nitrile nitrogen atoms (I) is proposed. The complex is readily soluble and is compatible with a variety of polymeric matrices giving doped polymeric glasses, films and solutions which are highly luminescent in the biologically relevant optical window covering the visible and near infrared range.

We investigated luminescent spectra of the toluene solutions of the complexes (I) using $C_{60}$ as the quencher of the fluorescence.

![Figure 1. Excitation (1) and emission (2) spectra of the complex (I) in toluene and quencher of the emission (2) by the fullerene $C_{60}$. $\lambda_{ex}=300$ nm, Slit 5 nm.](image)

The reason of the quencher is the resonance interaction of the complexe (I) with the fullerene $C_{60}$.

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Monte-Carlo model of formation of a swarm of low energy electrons in fullerite C$_{60}$ under electrons in the keV- energy range

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Knowledge about spatial and energy distributions of secondary electrons generated in fullerites by electron beams is important in such applications as electron-beam lithography and coating surfaces by polymeric fullerite films. The Monte-Carlo model of these processes for primary electrons in the keV energy range was developed by the authors on the previous stage of the research and applied to description of the process of fullerite C60 polymerization, in particular for estimation of the number of electronic excitations needed for formation of one intermolecular bond [1]. The model describes the behavior of each of the electrons in cascades generated both by the primary and secondary electrons. Trajectories of all of the electrons are tracked until their energies exceed the minimal energy of HOMO-LUMO transition (2.7 eV). Elastic and inelastic collisions including ionization, single and collective excitations were taken into consideration. The model has been applied to the case of normal incidence angle of the primary electrons in the energy range 150-1500 eV. The mean free path of electrons in fullerite was found to be $\lambda = 1.4; 0.3; 7$ nm correspondingly for the characteristic energies $E = 1500; 50; 4$ eV. It was shown that long mean free path of the extremely low energy electrons results in formation of the swarm of these electrons with huge radius up to 100 nm. The model shows conversion of primary electron into a swarm of low energy secondary electrons after approximately several tens of collisions. At that, the average depth of the penetration of the primary electron into the bulk exceeds the swarm radius up by several times. Low energy electrons generated in thick layer move chaotic and get to behave according to the analytic diffusion model [2]: a part of these electrons can not overpass the surface barrier, are collected in the near surface area and induce polymerization of fullerite. The computer model shows strong energy dependence of the number of electrons with the energy $E < 50$ eV in the studied energy range: from ~20 to several hundreds. It was shown that the energy dependence of the density of low energy electrons in the near surface area is also increasing, which correlate with the energy dependence of the polymerization rate of this area revealed in Ref. [3].

C$_{60}$H$_{42}$ Oxidation in Air

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We experimentally studied the changes C$_{60}$H$_x$ (36$<x<$60) undergo when exposed to atmospheric air. It has been previously known [1] that C$_{60}$H$_{36}$ oxidizes in air changing its colour from white to orange. The oxidation causes characteristic changes in C$_{60}$H$_{36}$ vibrational and electronic spectra [1].

We found that higher hydrogenated fullerenes demonstrated similar change of colour in air. For detailed experimental study we prepared samples with average formula C$_{60}$H$_{42}$. C$_{60}$ was hydrogenated at 500°C and at a pressure of 50 kbar H$_2$ (see [2] for the details).

Fresh white powder samples consisted of microcrystals with a size of a few µm. A change of their colour caused by oxidation could be seen after several months exposure in air. In [1] the colour changed just after 1 hour. It is the diffusion of O$_2$ into the volume of samples that determines the speed of the oxidation. Evidently, the diffusion was much slower in our microcrystals than in C$_{60}$H$_{36}$ of [1]. Probably in [1] the particles of C$_{60}$H$_{36}$ formed rather porous conglomerates. The samples kept in distilled water showed the same behaviour as the samples kept in open air. The oxidation could not be reversed by annealing in vacuum at 200°C during 2 hours.

The fresh and aged samples were characterized by infra-red and visible spectroscopy and Raman spectroscopy. In aged samples, we detected the changes in the infra-red and visible regions similar to the changes reported in [1]: there appear broad bands at about 3400 cm$^{-1}$ (OH stretching), 1705 cm$^{-1}$ (ketonic groups), and 1010 cm$^{-1}$ (C-OH bending). However, changes in the 1100-1550 cm$^{-1}$ region (vibrations of the fullerene cage, mostly) in our samples were much less pronounced than in [1].

We did not find any new lines for aged samples in the region of C-H stretchings, just original lines substantially broadened.

In aged samples, Raman spectra revealed a strong luminescence under 632.8 nm irradiation, its intensity increasing with the oxidation. The luminescence can be easily seen even in slightly oxidized samples which look perfectly white. It can probably be used as a probe of oxidation degree.


High temperature depolymerization of the 2D(R) C$_{60}$ polymer studied by Raman spectroscopy

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Raman spectra of single crystalline two-dimensional rhombohedral \{2D(R)\} C$_{60}$ polymer were measured at ambient conditions after its high temperature treatment (HTT) in order to study the depolymerization process. The HTT was performed for 30 minutes at various temperatures up to 300°C using a high temperature cell with a quartz window and protection against microscope objective overheating. The cell is equipped with a temperature controller unit that maintains temperatures up to 400°C with an accuracy of ±2°C.

Raman spectra were recorded by means of a triple monochromator DILOR XY system equipped with a nitrogen cooled CCD detector system. The laser beam of a Ti:sapphire tunable laser operating at 780 nm was focused on the sample by means of a long working distance 20× objective in a spot of ~3 µm diameter, while the beam intensity on the sample was less than 0.1 mW in order to prevent sample overheating and/or damage.

Raman spectra were measured at a fixed site of a small piece of the 2D(R) polymer of C$_{60}$ after successive HTT runs up to 300°C. The spectra were measured at 25°C to avoid the sample damage that was observed within the laser spot for T≥150 °C even at laser intensity as low as 0.005 mW. The typical Raman spectra in the region of the A$_g$(2) (PP-mode) are shown in Fig.1. The data obtained show that the 2D(R) polymer is stable up to ~240°C while at higher temperature a material transformation takes place. The Raman spectrum after HTT at 250°C shows new Raman modes related to the 2D tetragonal and 1D orthorhombic polymers, as well as to the C$_{60}$ dimers and monomers, that coexist with the 2D(R) PP-mode. The intermediate state of the partially depolymerized 2D(R) polymer was observed up to 275°C where the material changes drastically its composition resulting in the domination of C$_{60}$ monomers with some inclusion of C$_{60}$ dimers {as it follows from the splitting of the low energy H$_g$(1) Raman mode (not shown)}.

The support by the Russian Foundation for Basic Research, grant № 08-02-00890, and the hospitality of the Aristotle University of Thessaloniki (Greece) are greatly acknowledged.
Correlation of plasmon and Auger energies and its use for diagnostic of irradiated and degraded fullerite C$_{60}$

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Research and characterization of electron structure and optic properties of fullerite films modified by electron irradiation seems to be an important task for electron lithography [1], the problem of natural degradation of fullerite films [2] and other applications in which fullerite films are used. The technique of characterization of the band gap, density of states, $\pi$-plasmon energy, extent of polymerization and amorphization of fullerite under irradiation and in the course of degradation has been developed earlier on the bases of high resolution electron energy loss spectroscopy [1]. Unfortunately, this technique is rather complicated and needs special low dispersion electron gun and high resolution energy analyzer. We present here much easier approach with the use of ordinary Auger spectroscopy and correlation between $\mathrm{C}_{K\mathrm{VV}}$ Auger and $\pi$-plasmon energies revealed in this work and shown in Fig.1. Diagnostic of fullerite film can be performed by measuring $\mathrm{C}_{K\mathrm{VV}}$ Auger energy and obtaining $\pi$-plasmon energy shift through which all the information mentioned above can be deduced. The correlation between Auger and plasmon energies was obtained by their parallel measurements in the course of irradiation of in situ grown fullerite films by electrons with the energy $E_o = 1500$ eV. Commercial LHS-11 electron spectrometer was used. Dose dependences of Auger and $\pi$-plasmon energy shifts were obtained in the range of doses $Q \sim 0 \div 2$ C/cm$^2$ corresponding to the polymerization and initial stages of amorphization of fullerite where the modification parameter is $I_m \sim 0.5$ [1]). Fig.1 shows that $\mathrm{C}_{K\mathrm{VV}}$ Auger energy before the irradiation was $E_{\mathrm{AF}} = 273.1$ eV (relative to the Fermi level) or $E_{\mathrm{AV}} = 268.4$ eV (relative to the vacuum level), which evidences for high quality of pristine fullerite film [3]. Auger and $\pi$-plasmon energies undergo correlated blue and red shifts under irradiation correspondingly. The reason of the first one is decreasing the binding energies of occupied states due to creation of the conductivity electronic states resulting in increasing the relaxation energy. The $\pi$-plasmon red shift seems to be a result of completely different reasons. Therefore the practically liner correlation of these shifts looks surprisingly and demands further investigation. As a practical result, the large dynamic diapason of the Auger energy shift provides for high sensitivity of diagnostics. The research was supported by the Russian Academy of Sciences (Program “Quantum physics of condensed matter”).


Figure 1. Relationship between $\pi$-plasmon and $\mathrm{C}_{K\mathrm{VV}}$ Auger energies. Auger energy scale is counted out of the Fermi level.
Electronic structure and radiation instability of $C_{60}F_{48}$

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Fluorination is known to be an effective way of manipulation of the electric and optic properties of fullerenes. The band gap of $C_{60}F_x$ rises radically on enlargement of the number of attached fluorine atoms. Though, the mechanism of the transformation of the valence electron structure has not been clear. Shift of the highest occupied electron levels (HOMO) out of the Fermi level was revealed in [1], on the contrary, disappearance of the upper HOMO levels was observed in [2]. The aim of this work was obtaining the valence band photoemission spectrum of the highly fluorinated fullerenes $C_{60}F_{48}$, its comparison with that of ordinary fullerenes and clarifying the discussed mechanism of the band gap widening. Electrostatic charging and possible radiation instability of the $C_{60}F_x$ films was expected to complicate solving the task. Therefore, conductive organic thing films MnPc were used as a solid solvent of fluorinated fullerenes $C_{60}F_{48}$ to prevent charging of these wide band gap dielectric molecules. Extremely low radiation stability of $C_{60}F_{48}$ molecules was revealed. Visible shift of F1s line and removal of fluorine atoms were observed after irradiation by diagnostic x-ray beam during several minutes (Fig. 1). Therefore the photoemission spectra were recorded during short expositions. The values of the binding energies $E_b$ (C1s, C-F) = 288.5 eV and $E_b$ (F1s) = 687.1 eV corresponding to carbon and fluorine atoms bound to each other proved to be very close (within 0.2 eV) to the corresponding values obtained by us earlier for $C_{60}F_{36}$ film [3]. The valence band spectrum of $C_{60}F_{48}$ molecules was obtained as a difference between the spectra of the composite film and solvent. It was shown that the band gap of fullerene becomes wider in fluorination due to disappearance of molecular levels starting from the highest ones, which takes place due to participation of $\pi$-electrons in creation of C-F bonds. The research was supported by the bilateral program “Russian-German Laboratory at BESSY” and by the Russian Academy of Sciences (Program “Quantum physics of condensed matter”).

![Fig.1. F1s photoelectron spectra of $C_{60}F_{48}$ measured after 3, 15 and 60 min of irradiation by diagnostic x-ray beam ($h\nu \sim 850$ eV).](image)

Diffuence of solid C\textsubscript{60} film due to high rate surface diffusion of fullerenes

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Films of condensed fullerenes (fullerites) and their derivatives are widely used in different applications. Fullerite films are usually considered to be easily fabricated, stable and comprehensively studied. Nevertheless, degradation of thin fullerite films depending on time has been recently revealed in conditions of the absence of oxygen and radiation [1]. The mechanism of diffusion of fullerenes away of film and enrichment of the near surface layers of film by defected molecules and polymeric clusters deposed together with normal fullerenes during the film growth was assumed. To confirm the suggested hypothesis, the experiment devoted to study of the time dependence of the thickness of fullerite films has been performed. Thin films of fullerite C\textsubscript{60} with thickness of about several monolayers (ML) were grown on the atomically clean surface of GaAs directly in the analytic chamber of the electron spectrometer LHS-11 at high vacuum conditions. Sublimation source was used. Ga \textit{LMM} (E\textsubscript{A}=1064 eV) Auger line of the substrate was controlled together with C \textit{KVV} line of the film. Fig.1 shows radical increasing intensity of Ga \textit{LMM} line during 20 min after the film deposition. This fact evidences reducing thickness of the film which was estimated by the formula: \( h = \lambda \ln(I_o/I) \), where \( I_o \) and \( I \) are intensities of Ga \textit{LMM} line before and after the film deposition and \( \lambda \approx 2.4 \text{ nm} \) is the mean free path of Auger electron in fullerite. The effective thickness of the film decreased at room temperature by approximately 1.5 ML: from \( \approx 4 \) to \( \approx 2.5 \) ML. The observed fact can be explained by high rate diffusion of the fullerenes of the upper layer out of the film. Taking into account the average diffusion length \( L \approx 2 \text{ mm} \) connected with the sample sizes, the diffusion coefficient can be estimated: \( D \approx L^2/t = 4 \times 10^{-9} \text{ m}^2/\text{c} \). Earlier efficient diffusion of fullerenes C\textsubscript{60} was observed at room temperature in polyimid films [2] and polyimid films heavily irradiated by ions [3]. Comparison of diffusion coefficients reported in these references, \( D = 10^{-22} \text{ m}^2/\text{c} \) and \( D = 10^{-17} \text{ m}^2/\text{c} \) correspondingly, shows that mobility of fullerenes drastically increases when internal transport surfaces arise. Thus the conducted experiment confirms the high surface mobility of fullerenes which can result in diffuence of thing fullerite films and can be accompanied by enrichment of the film by defected molecules and polymeric clusters. The research was supported by the Russian Academy of Sciences (Program “Quantum physics of condensed matter”).

New photovoltaic materials based on composites of conjugated polymer with tetra-substituted metallophthalocyanines and [60]fullerene

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The design and synthesis of the new materials for the organic photovoltaic (PV) cells based on the composites of a conjugated polymer and fullerene or its derivatives are intensively investigated nowadays for application. In this work we present the results of the investigations of the three-component composites as active layer in PV cells: fullerene, the conjugated polymer MEH-PPV (poly(2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene) or P3HT (Poly(3-hexylthiophene)) and tetra-substituted metallophthalocyanines (PcM, where M = Cu, Zn).

We have measured the dependence of polymer photoluminescence in the composites on the concentration of additives (fullerene and metallophthalocyanine) in order to evaluate the ability of such additives as the acceptors in the process of photoinduced electron transfer. We have found that some of our systems are the effective quenchers of polymer photoluminescence. We have also studied the photovoltaic properties of the three-component bulk-heterojunction systems: MEH-PPV:C\textsubscript{60}:PcM and P3HT:C\textsubscript{60}:PcM and compare them with that of polymer:fullerene composites.

The results of the present work show that the three-component bulk-heterojunction systems based on a conjugated polymer and a fullerene-phthalocyanine complex may be rather effective materials for photovoltaic devices. Adding of phthalocyanine into the two-component system polymer:fullerene may lead to an increase in the acceptor ability of the non-polymer components and in the higher photovoltaic efficiency of the composite at the same fullerene contents.
The FT-IR spectroscopic studies of the destruction of the fullerites $C_{60}$ and $C_{70}$ under heating in the air

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In the present work the behavior of the powders of the fullerenes $C_{60}$, $C_{70}$ and their solvate forms under heating in the temperature range from 200 to 400°C in the air have been studied by the FT-IR spectroscopy.

It has been shown that fullerene $C_{60}$ under heating forms the oxides with single C-O bonds and then subsequent heating results in the destruction of the carbon cage, with forming double C=O bonds on the ends of C-C loose bonds. In under the same conditions, the destruction of the $C_{70}$ molecule occurs with the oxidation along double bonds without intermediate formation of the oxides and dimers.

It has been revealed that oxidation of the solvate form of the $C_{60}$ (crystallization from the toluene solution at room temperature) begins at lower temperature than that of the “non-solvate” form (crystallization in a rotating evaporator at 96°C, P=10^{-1}-10^{-2} Torr). In the latter case toluene “seals” between the microcrystals of fullerite without forming crystal solvates.

It have been established that a solvent evacuates from the crystalline lattice of the fullerene’s solvate forms (both $C_{60}$ and $C_{70}$) at the lower temperature than without any solvate.

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“Windows” in 1s shell photoemission from 1D crystalline structures encapsulated in carbon nanotubes

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X-ray absorption and inner-shell photoemission studies provide a sensitive probe of local electronic and atomic structures in matter. In the present work spectral dependence of inner-shell photoemission from composite systems such as one-dimensional crystalline structures encapsulated in single-wall-carbon-nanotubes (1D@SWCNT) is examined and discussed. Strong anisotropy of 1s-shell photoemission in directions perpendicular and parallel to the translation vector <001> specifies these spectra. Resonance photoemission in directions perpendicular to the vector attracts our main attention.

The double barrier optical potential approach successfully applied earlier to X-ray absorption in molecular units in van-der-Waals clusters [1,2] is used. The internal and external potential barriers describe respectively scattering of 1s-photoelectron on atoms in the crystalline structure and carbon atoms embodied in the nanotube. Applicability of this approach to 1s photoemission from 1D@SWCNT is examined.

The performed calculations predict appearance of new window-like resonance features. They in addition to the shape and confined resonances as well as multielectron excitations dominate in inner-shell photoemission near the threshold. The predicted „windows“ are associated with resonance tunneling of the photoelectron through the composite system in directions <0-11> and <011>. The computed and experimental data are compared to reveal the „windows“.

The link of the „windows“ with electronic and atomic structures of 1D@SWCNT is discussed in more detail.

Dependence of nanophotonics of fullerene solutions on molecular structure

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The fullerene ability to form clusters in diluted solutions causes exciting spectral properties of these matrices providing an enhancement of both the emission spectra and nonlinear optical response [1-3]. Hereinafter, “fullerene” is related to both C₆₀ and its derivatives. Being common for solutions, the molecule clusterization and, as a consequence, a potential ability to use the solution as an active nonlinear optical (NLO) matrix depends crucially from the fullerene molecule chemical structure. When pursuing a goal of a selection of an NLO matrix with required NLO characteristics, a researcher faces the problem of sorting a great number of derivatives, both already available and newly to be synthesized. Obviously, the lack of a priori criteria results in a considerable finance and time expenses. That is why the availability of a reliable and, even more, a priori testing is of extreme importance.

The paper presents two ways of the problem solution based on empirical and computational investigations [1-3]. In the first case, the testing reduces the problem to looking for an extra blue emission in the visible part of spectra. The intense emission witnesses reliably good NLO properties of the tested matrix. The second approach is based on quantum-chemical calculations and can serve as a priori testing which can be followed afterwards by a synthesis of the fullerene with required properties. The testing is based on the fact that the formation of stable clusters is fully determined by the energy of pairwise interaction \(E_{cpl}\) of fullerene molecules (sol-sol clusters) and the fullerene and solvent molecule (sol-solv clusters). Stable clusters which enable to provide the enhancement of the local electric field of both incoming and outgoing light are formed if only \(E_{cpl}\) is negative and large by absolute value. The latter directly correlates with the efficacy of the NLO response of the matrix considered. The two approaches are proven by testing a set of matrices with different derivatives of fullerene C₆₀, both already available and purposely synthesized for the current study.

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Shpolskii effect in optical spectra of frozen toluene solutions of organic C$_{60}$-fullerene derivative


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Optical spectra of toluene solution of ethyl ester of the fulleroacetic acid (C$_{60}$EEAA) have been studied. This molecule possesses high nonlinear optical parameters and is of great interest in the view of its potential application. Quantum-chemical analysis show that C$_{60}$EEAA molecules in toluene matrix interact with each other and with toluene molecules much more actively than that of fullerene C$_{60}$ leading to formation of clusters of different size and composition.

Absorption spectra of C$_{60}$EEAA toluene solution at T = 80K exhibit a superposition of intense structureless background, caused by clusters – charge transfer complexes, and a weak structure of fullerene molecular absorption. A relatively high intensity of the band corresponding to molecular pure electron 0-0 transition takes place for C$_{60}$EEAA, whereas for C$_{60}$ the probability of 0-0 transition is known to be very small. This could be attributed to lower symmetry of the molecule due to joined molecular group. At T = 2K the bands in the molecular absorption structure transform into multiplets of narrow lines with the width of ~5 cm$^{-1}$. The lines in the multiplet correspond to optical excitation of molecules in different nonequivalent positions in the matrix. The same structure is observed in luminescence spectra of C$_{60}$EEAA at T = 2K and structured absorption and luminescence spectra exhibit mirror symmetry. The energies of optical transitions and the frequencies of the corresponding molecular vibrations were determined. The allowed character of dissymmetrical spectra and total conformity of frequencies that form the spectra give the evidence in favour of Frank-Condon mechanism of vibronic interaction in the molecule.

Along with vibronic molecular structure the additional bands in the visible region is observed in the emission spectra. The spectrum in visible region has the components with short and long decay times. The visible light emission is attributed to emission of clusters formed of only fullerene and both fullerene and solvent molecules. The origin of this emission is associated with complicated processes of electromagnetic field enhancement on fullerene nanoclusters due to excitation of localized charged transfer excitons [1] and attests high nonlinear optical activity of the solution under study.

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Chemiluminescent test for oxofullerenecarbonyl oxides generated by fullerenes ozonolysis

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Epoxides, ketones, esters and secondary ozonides are the stable products of C\textsubscript{60} and C\textsubscript{70} ozonolysis in solutions. In spite of the great success in identification of the products of fullerenes ozonolysis, the mechanism of their generation has been poorly understood. In this work the influence of carbonyl oxide traps ROH (R =Me, Et, Ac) and pyridine on the chemiluminescence (CL) upon C\textsubscript{60} and C\textsubscript{70} ozonolysis in CCl\textsubscript{4} has been studied to prove the carbonyl oxide nature of the intermediates of fullerene ozonolysis.

Addition of 0.48 mol dm\textsuperscript{-3} MeOH, EtOH or AcOH into the C\textsubscript{60}+O\textsubscript{3} system leads to the decrease of CL intensity (I\textsubscript{max}) by about 50, 30 or 20%, respectively. The dependence of I\textsubscript{max} on [ROH] is characterized with the threshold concentration of ROH (~0.75 mol dm\textsuperscript{-3}). Addition of larger amounts of ROH does not cause the further decrease in I\textsubscript{max}. The IR spectra of the products show chemical binding between the modified fullerene framework and RO group. These allow us to conclude that the CL observed in C\textsubscript{60} ozonolysis is generated not only in bimolecular reactions (1) and (2) of oxofullerenecarbonyl oxides (OFCO-60 1) but also in unimolecular processes (3).

In the case of C\textsubscript{70} ozonolysis in the presence of ROH, the decrease of I\textsubscript{max} is <10% and there no changes in IR spectra of the products, that suggests lower reactivity of OFCO-70 toward ROH. Quantum-chemical modelling shows that in the case of OFCO-70, carbonyl group is closer to carbonyl oxide moiety therefore two-centre coordination of OFCO-70 and ROH which is necessary for their interaction, has an obstacle. To prove this proposition, fullerene ozonolysis in the presence of pyridine has been performed. The reaction between OFCOs and pyridine needs one-centre coordination of reactants and leads to pyridine-N-oxide formation. In both cases of C\textsubscript{60} and C\textsubscript{70}, I\textsubscript{max} decreases by the same value (~80%) when pyridine is added into the reaction system.

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Photospectroscopy revealing of interface organization of fullerol molecule and molecular metal ion complex with protein amino-acid molecule as novel fullerene derivative for single molecular biosensor

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Qualitative and rapid half-quantitative analysis of the protein amino-acids is one of great value in the amino-acid studies. Therefore we start to build structural models for interface of fullerol (immobilized fullerene C\textsubscript{60}), metal ion (Cu\textsuperscript{+}) complex and amino-acid (glycine, alanine, methionine, histidine) molecules taking in account that donor-acceptor pair formation may increase the photoactivity and the biocompatibility to this carbon molecule counterpart. The interface designing concept as the base for fullerol single molecular sensor and molecular ion metal complex sensor development will be discussed in general terms.

Based on well established rationale of interface organization in biological macromolecules (nucleic acids, proteins), driven by non-covalent interactions (hydrogen bonding, hydrophobic effect and electrostatic interaction) in living cells, we selected biomolecules for non-covalent interaction with a core of fullerol molecule and a molecule of organic ligand in ion metal complex – amino acids. Then we revealed molecular interface organization in colloidal solutions by photospectroscopy.

From first experimental results we revealed specific interface formation between molecule of a ligand in molecular (Cu\textsuperscript{2+}:ligand) complex and histidine molecule for organic specially synthesized ligand with the same coordination nature as amino-acid. A special structure of a ligand and histidine molecules, when the presence of Nim and Nan atoms gives more coordination geometry to molecular complexes, determines specific interface formation at supramolecule. Selective coordination of such supramolecule in solutions with the 2.7 – 12.91 pH range by histidine molecule was confirmed by absorbance spectra with the intensive band (600-800nm) and it is assigned to the d – d transition of Cu\textsuperscript{2+}. In the case of CuCl\textsubscript{2} * 2H\textsubscript{2}O (0.1 mol/l), ligand (0.025 mol/l) and histidine (0.1 mol/l) solution maximum position shifted from 753 to 615 nm, depending on pH. Histidine concentration effect was also determined.

The next step is the development of controlled by light excitation interface between fullerol, ion metal and many protein-acid molecules organization for their photospectroscopy recognition and single molecular biosensor design.
Design and testing of fullerene photoprobes for ds-, ss-DNA molecules

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Designed photoprobes are nanofluids, which contain hydrated C\textsubscript{60} aggregates or hydrated C\textsubscript{60} derivative aggregates in aqueous suspensions (1,2). Their photosresponse under UV-vis excitation depends from electronic features of biomolecular surrounding. These photoprobes, used for ds-, ss-DNA molecule detection by UV-vis absorption and photoluminescence spectroscopy of fluids, show features in absorption spectra at (275-380) and (235-290)nm ranges and in photoluminescence spectra at (490-635) and (525-635)nm ranges, caused by the absorption and photoluminescence at interface between C\textsubscript{60}, C\textsubscript{60} derivative core and ds-, ss-DNA molecules, respectively. The analysis of spectra is based on models of electrostatic and/or hydrophobic interactions of C\textsubscript{60} and C\textsubscript{60} derivatives with negatively charged phosphate groups and/or DNA bases of DNA molecules in aqueous fluids. These models result from our investigations of the role of electrostatic and hydrophobic interactions between fullerene core and DNA molecule in aqueous suspensions.

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Spin relaxation of fullerene $C_{70}$ photoexcited triplets in glassy matrices

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The dynamic Yahn-Teller effect for photoexcited fullerenes in triplet state results in pseudorotations of distorted molecules of fullerenes. The pseudorotations affect spin relaxation and make triplet fullerenes to be high sensitive spin probe of surrounding matrix. The photoexcited fullerene $C_{70}$ in glassy solutions in this work was investigated by pulse electron paramagnetic resonance (EPR) spectroscopy.

It was found that longitudinal spin relaxation of $^3C_{70}$ at different organic glassy matrices is anisotropic while transversal spin relaxation anisotropy is small. A sharp rise of the transversal relaxation rates of $^3C_{70}$ in glassy $\alpha$-terphenyl, decaline, $\alpha$-methylnaphthalene and polystyrene with temperature increase was found at temperatures in the range of $105K \div 115K$.

We suppose that pseudorotations of $^3C_{70}$ molecule along its symmetry axis is affected by motion processes of surrounding molecules. So the sharp increasing of relaxation rate may be interpreted as arising from interaction of the pseudorotation with uniaxial cooperative molecular librations in the matrix, which may become thermally excited at these temperatures.

Shungite carbon as a material for optical limiting of high intensity laser radiation in the visible and near infrared region

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The application of shungite carbon (ShC), a natural fossil being mined in Karelia, for the optical limiting has been examined. Shungite carbon is considered as a fullerene-like nanostructured material with two-level organization: a BSU (basic structural unit) – of about 1 nm and a large globular unit – less than 100 nm. The aqueous dispersion of ShC was prepared by the sonication procedure and without the use of the surfactants. An average particle diameter was about 96 nm, measured by DLS (dynamic light scattering). Such dispersion was found to be stable up to the concentration of 0.1 mg/ml. This dispersion system was studied in the light transmission experiments. The samples were exposed to the focused laser radiation of wide energy range up to 25 mJ in nano- and picosecond ranges of pulse duration at wavelength - 532 nm. In both time scales the samples displayed a nonlinear optical response comparable to that for an aqueous dispersion system of fullerene. The transmission of the samples decreased from 50% to 3% in the picosecond range and to 0.5 % in the nanosecond range, with the energy threshold of nonlinearity at the 10⁻⁶ J. In addition, experiments were carried out at the wavelength of 1064 nm. In the infrared region ShC dispersion also showed considerable decrease of the optical transmission up to 3.3 %, with the energy threshold of nonlinearity at the 10⁻⁵ J. The values of the dynamic range of energy were about 10⁴ for the visible range and 10³ for the infrared range of the wavelengths.
Nonlinear optical properties of fullerene-porphyrin complexes

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We have studied nonlinear optical properties in solutions and thin films of MTPP and C_{60}-MTPP complexes (M=Zn, Cu, FeCl; TPP – tetraphenylporphyrin). Among the fullerene-containing dyads, the ones with porphyrin display improved nonlinear responses. We have developed the vacuum deposition technique for producing thin films of these compounds and shown that the enhancement of optical nonlinearity is not necessarily connected with the formation of covalent bonds between the components. Our ab initio calculations have shown that a pair C_{60} and MTPP forms a stable charge transfer complex. The linear polarizability and first and second order hyperpolarizabilities of the both components and C_{60}-MTPP complex were calculated using DFT/B3LYP method. It was found that the formation of the complex gives rise to a giant enhancement of the nonlinear response. We have measured the absorption profile in the range 2·10^{-5}-1 J/cm^2 at the wavelength of 532 nm, which corresponds to slope of the Q-band absorption of porphyrin. A comparative study is made for toluene solutions of: (i) C_{60} with 2·10^{-4} mol/1 concentration; (ii) MTPP with 5·10^{-5} mol/1 concentration; (iii) joint solution C_{60}-MTPP (1:1); (iii) C_{60}-MTPP complexes with (1-5)·10^{-5} mol/1 concentration. Similar study has been performed for the thin films of pristine components and the mentioned complexes, which were grown by in the quasiequilibrium conditions on the CaF_2 substrates. A large increase of the absorption intensity (darkening) is found on the formation of the charge transfer complex.

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