Enhanced Raman scattering provided by fullerene nanoclusters

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Observed in crystalline solutions of fullerenes in toluene and carbon tetrachloride, two new nonlinear optic effects are reported. Both are provided by a self-clustering of the solute molecules and are referred to fullerene enhanced Raman scattering (FERS) and solvent enhanced luminescence (SEL). The effects are induced by the excitation of charge transfer states of the fullerene nanoclusters that makes the latter to act as amplifiers of local electric fields.

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Since the first experiments on molecular SERS it has become clear that the resonant excitation of both localised and propagating surface plasmons of metal has stimulated the enhancement of local electric field of both incident and outgoing light that, in its turn, gives rise to nonlinear optical effects for adsorbed molecules (see comprehend reviews in [1]; main concepts have not changed much since). The metal plays the role of an electron-hole (collective electrons around positive atom nuclea) reservoir and/or amplifier subordinated to particular requirements concerning its electron-hole bound state and submicrostructuring which together provide the best conditions for the plasmons excitation. As for the first requirement, it concerns the real part of the metal dielectric function $\varepsilon_1(\omega)$ which should be negative and small by absolute value at resonance frequency ω. The requirement to submicrostructuring occurrs to be rather complicated and dependent on geometrical configuration of the substrate in use with a noticeable preference to nanostructures. Both requirements are well met by such metals as silver and gold and provide a drastic enhancement of both local fields leading to strong nonlinear optical effects for both plasmons themselves and outer molecules adsorbed on the metal substrate. However, if the nonlinear optics of molecules has been well known for a long time as molecular SERS, enhanced generation of the second harmonic [2] and enhanced luminescence [3], a direct evidence of plasmons nonlinear optics has become possible only as sensing to waveguiding [4] while their spectral manifestation has not been obtained since both fluorescence and inelastic scattering of lihgt turned out to be blocked [5]. On the other

hand, no particular limitations, connected with metallicity of the plasmon amplifier, seem to be put on, so that one may expect a similar amplifier existence outside convenient and well known metal nano and submicrom structures. Actually, it occurred to be true and we have succeded in finding such an amplifier formed by nanoclusters of fullerene (hereinafter the word implies both pristine fullerene C_{60} and its derivatives) in frozen molecular solutions in the absence of any metallic additives.

Methods. Samples were prepared by freezing saturated solutions of three fullerenes, namely, 1-methyl-2(4-pyridine)-3,4-C_{60}fulleropyrrolidine (**I**), fullerene C_{60} (**II**), and C_{60}fulleroamid (**III**) (equilibrium structures of the species are shown in Fig.1) in toluene (*tol*) and carbon tetrachloride (*ctcl*). The relevant solutions of the fullerenes will be also marked by **I**, **II**, and **III** pointing to the kind of the solute molecules. The corresponding concentrations are of $\sim 2-3 m$mol/l. Spectroscopic studies were carried out at 80 K on the double grating spectrometer DFS-12 with inverse dispersion of 0.5 nm/mm. Spectra were registered using photo-multiplier-photon-counting system. Different pump lasers providing light emission at 337.1, 476.5, 488.0, 496.5, 514.5, and 632.8 nm were used to excite the solution emission.

Results. Emission spectra of the studied fullerenes in *tol* are shown in Fig.1. Arrows mark λ_{ex} positions of the excited light. In spite of a considerable difference in the spectra, all spectra evidently consist of two parts, namely, the red and blue ones below and above $16000\,\text{cm}^{-1}$, respectively. All red spectra are well similar, particularly by total intensity. They involve both the fluorescence and phosphorescence spectra of fullerene
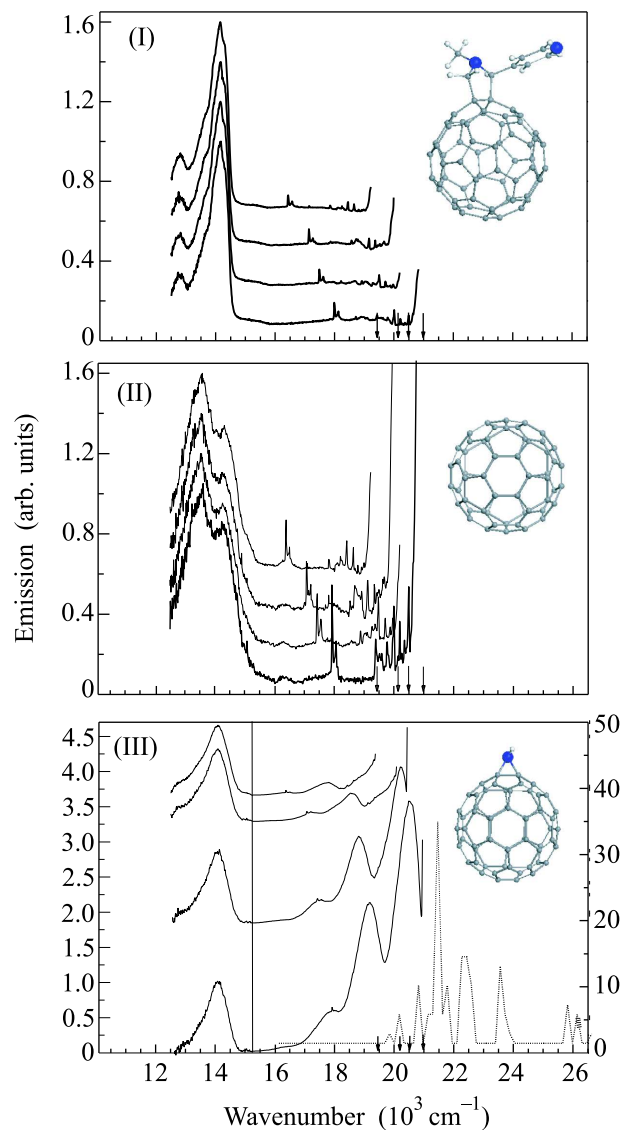
Fig.1. Emission spectra of fullerene solutions in toluene at 80 K. Spectra from bottom to top correspond to λ_{ex} 476.5, 488.0, 496.5, and 514.5 nm, respectively, marked by arrows from right to left. Dotted curve plots the density of CT states of C_{60} crystal courtesy by Dr.A.Eilmes and Dr.B.Pack, Jagiellonian University, Cracow

molecules and for species **I** and **II** are described elsewhere [6] in details. In the current study, they are regarded as internal standards for normalizing the intensity of blue spectra in all series of experiments.

As for blue spectra, there is an evident difference in the spectra intensity and appearance depending on the solute molecules. The spectrum of solution **I** presents normal Raman scattering (NRS) of *tol* and is fully similar to that of pure *tol*. The emission spectrum of the solution as a whole presents a trivial superposition of those of the solute and solvent molecules that is typi-

cal for the case of weak interaction between both solute molecules themselves and solute and solvent molecules.

In the case of fullerene **II**, the blue spectrum still retains a pattern characteristic for NRS of *tol*, but its relative intensity is clearly much higher in the comparison with the previous case and the intensity increases when the excitation wavelength becomes shorter. Therefore, the observed Raman spectrum attains feature characteristic for resonance and/or enhanced Raman scattering (R/ERS).

The most impressive behavior is observed for the blue spectrum of solution **III**. As seen in Fig.1, Raman scattering spectrum of *tol* is hidden under the new one. The latter retains the features characteristic to inelastic scattering (IS) since its position is gradually shifted when the excitation wavelength is changed. But instead of fine-structured NRS and R/ERS spectra of toluene we observe three-broad-band IS spectrum with extremely high intensity (look at different scales of the red and blue spectra in Fig.1). The latter continues to grow when the excitation wavelength decreases. The spectrum is observed when the excitation wavelength fills the region from 514.5 to 476.5 nm. When λ_{ex} is either 632.8 or 337.1 nm, it disappears. Both wavelengths excite red spectrum of the solute fullerene that is a sole spectrum of the solution emission when $\lambda_{ex} = 632.8$ nm but is followed by the luminescence spectrum of *tol* when $\lambda_{ex} = 337.1$ nm.

The observed peculiarities of the blue spectra of the studied solutions are practically fully reproduced when *tol* is substituted by *ctcl* with the only difference of lower intensity of the spectra in the latter case. Fig.2 demonstrates the observation for the emission spectra
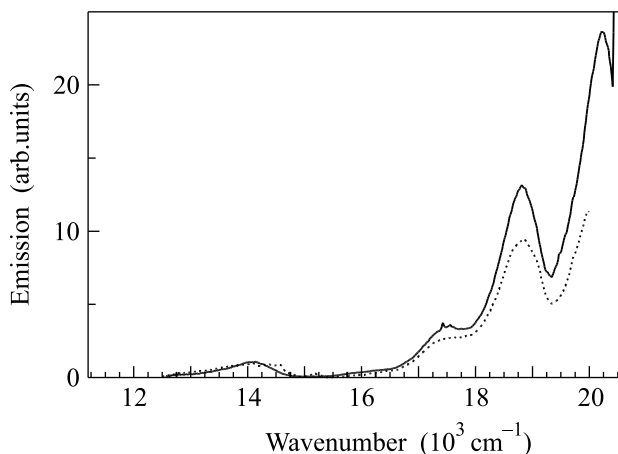

Fig.2. Emission spectra of fullerene **III** solutions in toluene (solid curve) and carbon tetrachloride (dotted curve) at 80 K, $\lambda_{ex} = 476.5$ nm

of fullerene **III** in both solutions. As previously, the spectra are normalized by equal total intensity of the respective red spectra.

Discussion. The obtained results have hilighted a new optical phenomenon in fullerene solutions. That consists in the intense inelastic scattering of the excited light that accompanies the luminescence of the solute molecules and changes its appearance when changing the solute molecule. The scattering intensity increases when the excitation wavelength shortens from 514.5 to 476.5 nm and goes to zero when λ_{ex} is either 337.1 or 632.8 nm. Obviously, the explanation of this emission should be looked for in peculiarities of the studied solutions.

Fullerene solutions differ from convenient molecular ones by a considerable contribution of donor-acceptor (DA) interaction into intermolecular interaction (IMI) between the molecules. This is caused by an exclusively high both donor (low ionization potential, I) and acceptor (high electron affinity, ε) abilities of the molecule. Even two fullerene molecules are enough for the IMI potential to be transformed into a two-well one [7] providing the formation of either a weakly bound charge-transfer complex (CTC) at equilibrium distances > 3.2 Å or tightly bound dimer at distances < 1.55 Å [8]. The feature affects the spectrum of excited states of the molecule pair. Thus, the dimer spectrum is evidently molecular, or nonpolar, by origin while the CTC spectrum consists of two branches, one of which is nonpolar and is attributed to an individual molecule while the other is polar one (these polar and nonpolar components introduced in [9] are forerunners of Frenkel and charge transfer excitons of bulk crystal). Usually, when speaking about molecular solutions of fullerenes, it is implied that no tightly bound dimers or higher oligomers are formed and solute molecules are randomly distributed over the solvent. Actually, only the first suggestion is true while the second is violated due to a strong tendency of the solute molecules to form CTCs. Additionally, since some solvents exhibit rather high donor activity (*tol* etc.), new DA pairs full+M_{solv} should be added to the original full+full pairs. As a consequence, a new polar branch appears in the energy spectrum. The said above can be applied to the majority of the C_{60} derivatives (including studied in the paper) that preserve high DA efficacy.

Multi-branch character of the solution both ground and excited states spectrum originates a peculiar photonics. Thus, nonpolar component of the absorption spectrum covers vibronic series related to series of singlet-singlet transitions in the fullerene molecules that provides fine structure of the spectrum that is largely

discussed in [10]. Oppositely, broad-band structureless polar absorption forms the pedestal, or background, for the previous one. The analysis of the absorption spectrum structure from this viewpoint for the fullerene solutions in *tol* has been firstly performed in [6]. Similarly, a specularly symmetric nonpolar component in the emission spectra involves fluorescence and phosphorescence spectra of the solute molecules [6]. These spectra are positioned over a broad-band spectrum of polar component related to transitions from the lowest CT states to the ground state of the solution and form all together the red spectra discussed above. Within the framework of this viewpoint, solutions of all studied fullerenes are to behave in a common way that has been observed indeed.

As turned out, the peculiarities of the blue spectra are also connected with CT states of the solutions. Thus, the observed dependence of the R/ERS and IS spectra intensity on the excitation wavelength clearly witnesses the presence of a particular zone in the excited-state energy spectrum of the solutions in the region of 2.40–2.60 eV. Obviously, the spectrum is additional to the molecular excitation spectrum of solute molecules since the direct excitation of molecular excited states by either λ_{ex} 337.1 or 632.8 nm does not cause any inelastic scattering of the excitation light. As known for pristine C_{60} crystals [11], the energy spectrum of CT states covers the above region and extends towards higher energy. Dotted curve in Fig.1c plots the density of states of the spectrum over the whole Brillouin zone of the crystal [12], thus tagging the position of CT states in the energy spectrum. According to performed quantum-chemical (QCh) calculations (for calculation details see [6]), the ionization potentials and electron affinities of fullerenes **I** and **III** are similar to those of C_{60}, so that the plotted curve positions the CT energy spectrum for all studied solutions with acceptable accuracy.

Therefore, there is a strong point to connect the peculiarities in the R/ERS and IS spectra with the excitation of CT states of the solutions. But why does the spectra behavior depend on the molecular moiety? Since DA interaction between the fullerenes is expected in all three cases, the matter may be connected with its contribution into IMI. Performed QCh calculations have proven the suggestion. The obtained results, listed in Table, are related to the IMI minimum related to the formation of charge transfer complexes. Equilibrated structures of clusters **III** and partially **II** are showm in Fig.3. Photoexcitation of any complex is accompanied by the electron transfer from one molecule to another.

As seen from the table, the IMI, which provides the CTCs formation, does not result in coupling molecules **I** in stable cluster at any mutual disposition of the latter.

Ionization potentials and electron affinities of fullerenes and coupling energy of fullerene clusters*

Fullerenes	I, eV	ε, eV	$E_{cpl}\{(X)_n\}$, kcal/mol				
			2**	3	4	5	6
I	9.68	2.48	2.21; 1.16; 1.06	–	–	–	–
II	9.87	2.66	−0.52	–	–	–	−2.74
III	9.79	2.57	−0.09; −1.26	−2.73	−4.32	−7.94	−8.42

*QCh calculations have been performed in semiempirical approach by using AM1 version of the CLUSTER-Z1 software (see details in [6]). The data for ionization potentials are traditionally somewhat overestimated while electron affinities well suit experimental data. The coupling energy $E_{cpl}\{(X)_n\}$ of $(X)_n$ cluster was determined following the relationship $E_{cpl}\{(X)_n\} = \Delta H\{(X)_n\} - n\Delta H\{X\}$ where $\Delta H\{(X)_n\}$ and $\Delta H\{X\}$ are heats of formation of $(X)_n$ cluster and fullerene X ($X = $ **I, II, III**), respectively.

**Data present the largest and smallest energy coupling values that depend on mutual disposition of molecules in a pair.
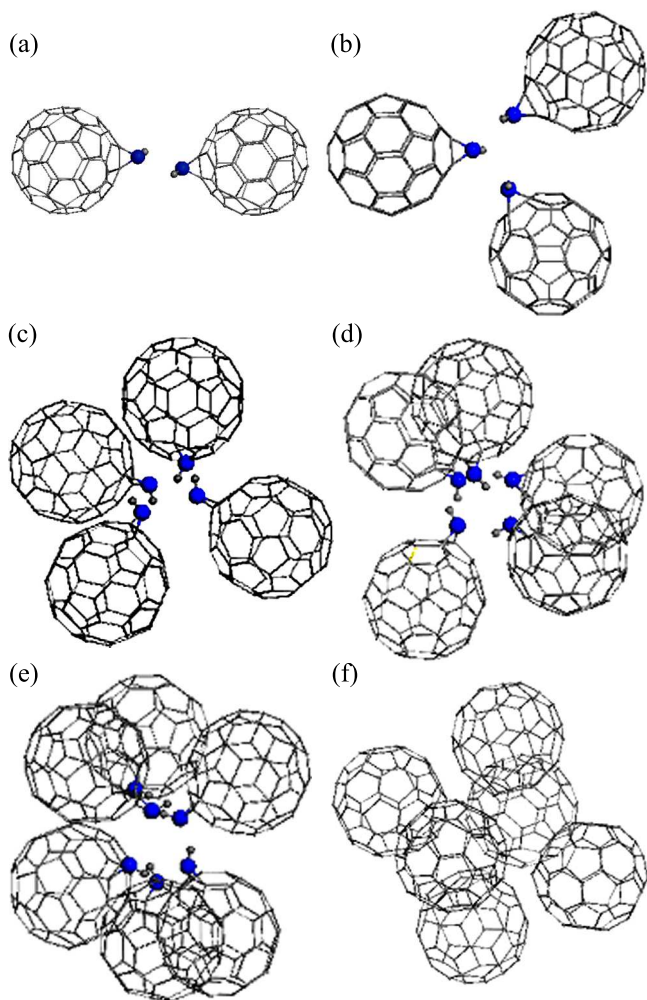

Fig.3. (a)–(e). Equilibrium structures of **(III)**$_n$ ($n = 2, 3, 4, 5, 6$) clusters obtained in due course of total optimization of the cluster configurations when seeking the energy minimum. (f) The same but for **(II)**$_6$ cluster

The coupling energy is positive that points to a dominant repulsive interaction between the units. As for fullerene C_{60}, the coupling energy of the pair molecule is negative and thus attractive. Enlarging the cluster results in an approximate multiplication of the energy with respect to the number of the molecules involved. Therefore, C_{60} molecules form clusters in solutions, albeit not very tightly coupled. As for fullerene **III**, the interaction between the molecules is the strongest among the studied. That depends on mutual orientation of NH units and is the largest for the compositions whose equilibrium structures are shown in Fig.3. The cluster growing is followed by increasing the total coupling energy. The latter is quite considerable indicating the formation of stable configurations. Therefore, the calculations have shown that effects connected with DA interaction are strengthening when going from fullerene **I** to fullerene **III**.

Coming back to experimental data, we see a strong correlation between the computation predictions and optical spectra behavior. Thus, the IMI between fullerene molecule in solution **I** has no coupling effects both for fullerenes themselves and for them and solvent molecules in both solutions (QCh calculations show a repulsive interaction in the latter cases as well) that is why the emission spectra of fullerene **I** in *tol* (Fig.1a) and *ctcl* present a trivial superposition of the red luminescence spectra of solute and NRS spectra of the solvents. The total intensity of the latter constitutes about 5% of the red spectrum intensity.

Contrary to the case, fullerene C_{60} (**II**) willingly forms clusters that possess properties of CTCs so that their photoexcitation is followed by the creation of electron-hole pairs. The Coulomb interaction within the pairs leads to the creation of CT excitons in a bulk crystal and localized CT excitons in space-limited clusters. Similarly to plasmons, the CT excitons cause considerable polarization effects that must lead to the enhancement of the local field of incident and outgoing electro-magnetic waves. Therefore, the solutions con-

taining clusters of C_{60} might be expected to act as solutions with colloidal metallic particles.

The theory of light-scattering efficiency of small metal particles [13] shows that the enhancement of the local electric field E_1 due to the polarization of the metal with respect to the electric field of the incident light E_0 is described by the relation

$$E_1 = \frac{E_0}{(\varepsilon_1(\omega) + 2\varepsilon_m)}, \qquad (1)$$

where $\varepsilon_1(\omega)$ is the real part of the dielectric function of the metal at the frequency of incident light ω and ε_m is the dielectric constant of the embedding medium. As follows from the equation, the dielectric function $\varepsilon_1(\omega)$ of $\sim -2\varepsilon_m$ by value provides a strong nonlinear optical effect both within and outside the particle. Similar effect can be expected for CTC clusters as well. Unlike to the majority of molecular species for which function $\varepsilon_1(\omega)$ is positive and large, in case of fullerene C_{60} crystal the function changes from $+3$ to -5 in the energy interval of 2.6–2.8 eV [14] which corresponds to frequencies of the used pump lasers. This means that one can expect considerable nonlinear optical effects caused by the polarization of C_{60} clusters at incident light filling by frequency the mentioned interval. Coming back to Fig.1b, we evidently see such effect as enhanced Raman scattering of toluene molecules surrounding the C_{60} clusters. The enhancement coefficient cannot be obtained accurately since the evaluation of the SERS total intensity by its relation to that of the fullerene red luminescence cannot exclude the luminescence enhancement due to high local field of the fullerene clusters. But even under this complication, the relative intensity of SERS spectrum (at $\lambda_{ex} = 476.5$ nm) constitutes $\sim 13\%$ in solution **II** and shows ~ 3 times increasing with respect to NRS of toluene in solution **I**. Similarly to *tol* solution, SERS of the solvent is observed in the *ctcl* solution as well, albeit of much less intensity ($\sim 4\%$). The difference in the relative intensities of SERS in the two solutions clearly evidences the role of the DA interaction between the solute and solvent molecules that is characterized by the coupling energy of -0.014 kcal/mol in *tol* and repulsive interaction in *ctcl*.

As shown [15], the electronic structure of fullerene **III** does not differ much from that of **II**. This suggests, in particular, that the dielectric functions of fullerene **II** and **III** media should be very close as well and, consequently, the resonance condition (1) for achieving the enhancement of the local field in clusters of both fullerenes is fulfilled for the same pump laser frequencies. Obviously, clusters of fullerene **III** provide suitable conditions, if not better, as in the previous case, for the ob-

servation of SERS spectrum of solvents. Nevertheless, the spectrum is absolutely hidden under new IS one and only small fine structure features (see Fig.1) reveal its presence. Since only two vibrating systems in the studied solution may cause inelastic scattering we must assign the observed IS spectrum to the Raman scattering of fullerenes **III** configured in CTC clusters.

The observed IS spectrum is shown in Fig.4 in a scale of Raman shift with respect to the excitation band. Its
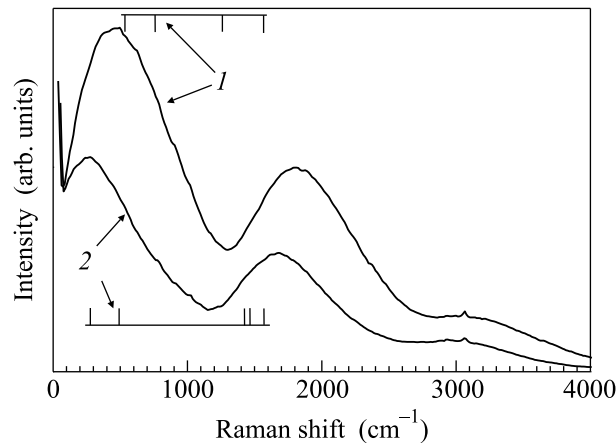

Fig.4. FERS spectrum of fullerene **III** solution in toluene at 80 K and $\lambda_{ex} = 476.5$ (*1*) and 488.0 nm (*2*), respectively. Bars mark positions of the main peaks in HREELS [18] (*1*) and SERS [20] (*2*) spectra

total intensity at $\lambda_{ex} = 476.5$ nm is ~ 70 times larger that that of the reference red spectrum. At first glance the suggested assignment seems doubtful since the spectrum differs from other known vibrational spectra of fullerene C_{60} too drastically. (Speaking about vibrational spectrum of fullerene **III** we can refer to the spectra of C_{60} since those are quite similar as can be judged from the close similarity of the vibronic series pattern of their absorption and luminescence spectra [15]). As well known, the appearance of the vibrational spectrum of C_{60} depends on the spectroscopic technique in use due to a particular, both dense and quasi-regular, distribution of the vibrational states density (VDOS) $g(\omega)$ consisting of a large set of rather narrow fractions [16]. That is why IR absorption and Raman scattering spectra [17] differ from each other and both of them differ from HREELS [18], INS [19] and SERS [20] spectra quite considerably. However, in spite of the difference, all these spectra are rather fine structured due to well structured $g(\omega)$ of the objects under study (crystal, thin films and adsorbed molecules) with the band width determined mainly by the resolution function of the spectroscopic apparatus in use. Oppositely to the case, we have observed ill-structured spectrum consisting of three broad

bands of $\sim 600\,\mathrm{cm}^{-1}$ in width, forming a shape typical to, say, the luminescence Frank-Condon series with a totally symmetric vibration of $\sim 1320\,\mathrm{cm}^{-1}$ as the main repetition pattern. None of previously observed vibrational spectrum is similarly shaped. The other noticeable difference is that the position of the series determining by the position of the head band, depends on the pump light λ_{ex} and proceeds to lower Raman shift when λ_{ex} increases.

We believe that these peculiarities are connected with the fact that the molecules emit the light being configured in rather tightly coupled clusters. This can explain: 1) the band breadth by both obvious statistical inhomogeneity of clusters by size and a confining effect to the vibrational spectrum caused by the cluster nanodimensions [5, 21] and 2) the series head band shift when λ_{ex} increases. If the former is quite obvious, the latter may evidence changing the mechanism of the vibration participation in the emitted light. The vertical bars related to spectra 1 and 2 in Fig.4 mark main features shown in HREELS spectrum of thin C_{60} film deposited on Si (100) surface [18] and SERS spectrum of thin C_{60} film deposited on gold nanorods [20], respectively. It should be noted that in both HREELS and SERS spectra the low-frequency part is the most intense similarly to the discussed IS spectrum. As seen in Fig.4, the IS spectrum is moved just from the HREELS to SERS position when λ_{ex} increases and the spectrum intensity decreases. The intensity decreasing means that λ_{ex} gradually goes out of the resonance zone that, in its turn, causes lowering of the local field enhancement. The shape of the vibrational assistance of the emitting wave can be roughly described via amplitude-weighted VDOS $a(\omega)g(\omega)$ where $a(\omega)$ is determined by the derivatives of the third order nonlinear susceptibility $\chi^{(3)}(\omega)$ over normal coordinates $\{Q_i\}$. The derivatives are evidently ω-dependent, where ω is pump laser frequency, showing that dipole active vibrations, similar to those active in HREELS, are the most efficient in the close-to-resonance region (Spectrum 1) while molecular polarizability stimulated by the enhanced local field produced inside the fullerene clusters is responsible for Spectrum 2 thus shifting it towards the SERS spectrum of thin C_{60} film. Peculiar is a role of a totally symmetric vibration of $1320\,\mathrm{cm}^{-1}$, which is active in the luminescence and absorption spectra of solutions II and III [6, 15], in the observed spectra. Obviously, these vibration repetitions of the head band prevail in both spectra albeit the participation of other vibrations from the extended VDOS spectrum cannot be excluded as well. The observed features clearly point to an urgent necessity in a theoretical consideration of vibrationally-assisted nonlinear effects.

The observed enhanced inelastic scattering related to fullerene clusters, which both provide a large enhancement of the local field and emit light, is a particular new nonlinear phenomenon and following to the tendency to discriminate the effect from the convenient SERS, similarly to TERS [22], can be called FERS outlining the governing role of fullerene in the phenomenon.

As known, enhanced Raman scattering can be phenomenologically described by a macroscopic polarization $P(\omega)$ that combines a number of nonlinear optical effects. The value is determined as [2]

$$P(\omega) = L'(\omega)\chi^{(1)}L(\omega)E(\omega) +$$

$$+ L'(\omega)\chi^{(2)}L(\omega_1)L(\omega_2)E(\omega_1)E(\omega_2) +$$

$$+ L'(\omega)\chi^{(3)}L(\omega_1)L(\omega_2)L(\omega_3)E(\omega_1)E(\omega_2)E(\omega_3) + \ldots \tag{2}$$

Local field factors L' and L are introduced to describe the amplification of the incident and outgoing field E, respectively, $\chi^{(i)}$ determines the susceptibility of the i-th order (see details in [2]). Important to note that if the third-order effect is strong (SERS, TERS, FERS) one may expect the enhancement of both linear (photoluminescence) and the second order (the second harmonic generation) effects as well when the incident and outgoing fields meet some requirements. When metal particles are considered as amplifiers, the enhancement of the adsorbed molecules fluorescence is expected to occur when the emission wavelengths lie within the plasma particle resonance [2]. As shown in Fig.5, this requirement is also
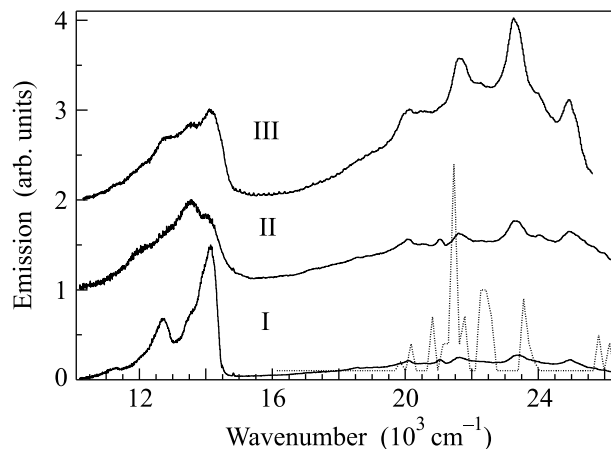
Fig.5. Emission spectra of fullerene solutions I, II, and III at 80 K. $\lambda_{\mathrm{ex}} = 337.1\,\mathrm{nm}$. Dotted curve plots the density of CT states of C_{60} crystal [10, 11]

met when the solvent fluorescence wavelengths lie within the CT resonances of the studied solutions. And again, a strong dependence of the fluorescence enhancement

on the strength of the DA interaction between fullerene molecules is observed. Thus, the relative intensity of the toluene spectrum with respect to the red-reference one increases ~ 4.3 times when going from solution **I** to solution **III**. Therefore, the figure presents another nonlinear phenomenon of the *solvent enhanced luminescence* (SEL) provided by nanosize fullerene clusters. The enhancement effect is not too drastic. However, a simultaneous observation of both nonlinear effects, namely, FERS and SEL, undoubtedly proves the amplifier behavior of the fullerene clusters resulting in the amplification of local fields both inside and outside of the clusters.

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