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Evidence of carbon nanoparticle–solvent molecule interactions in Raman and fluorescence spectra

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Interactions of oxidized detonation nanodiamond and carbon dots with protic solvent molecules in suspensions of water, methanol, and isopropyl alcohol were studied by Raman and fluorescence spectroscopy. The structure of the solvent at the interface with nanoparticles and the strength of the hydrogen bonds between the functional groups on the surface of the nanoparticles and the solvent molecules depend on the type of solvent. The molecules of the solvent affect the fluorescent properties of the nanoparticles. It was found that the more intense fluorescence of nanoparticles corresponds to weaker hydrogen bonding between the surface of the carbon nanoparticles and the surrounding molecules of the solvent. The mechanism of mutual influence of the carbon nanoparticles and the solvent on the properties of each other has been suggested.
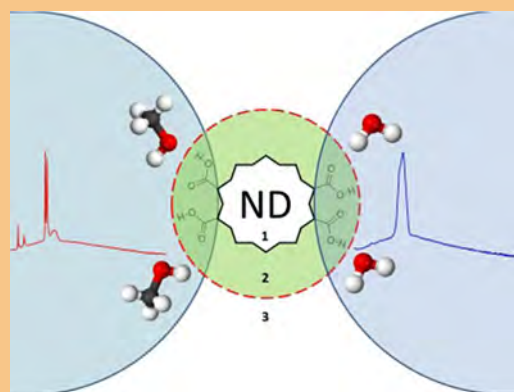
Fluorescence properties of nanodiamonds in the solvents with different hydrogen bonding.

1 Introduction The unique optical and biochemical properties of detonation nanodiamonds (ND) and carbon dots (CD) such as hydrophilicity and dispersivity in water, chemical stability, low photobleaching, biocompatibility, and low toxicity make them an appealing class of luminescent material [1–8]. However, the lack of understanding of the origin of the fluorescence (FL) in the carbon nanoparticles (CNPs) makes the development and use of CNPs with desired FL characteristics very difficult.

Molecular interactions of the surface groups of nanoparticles with the solvent play an important role in optimization of properties of dispersed nanoparticles. Using neutron scattering [9], NMR [10], a synchrotron X-ray scattering study [11], it was found that solvated nanoparticles change the structure of surrounding layers of solvent. It is obvious that the mutual influence of surface groups and solvent molecules is essential for optimization of the fluorescence properties of CNPs and for understanding

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the mechanisms of fluorescence of the nanoparticles. Therefore, studies of the influence of surface modification of CNPs and different solvents on the optical properties of the nanoparticles are very important and are the focus of many research groups. The substantial influence of water molecules on the optical properties of NDs in water suspensions was demonstrated in Refs. [12–14]. In Ref. [14], carbon and oxygen K edges of oxidized detonation NDs in water suspensions at 1 wt.% were specified by XAS and XES. The authors have demonstrated that the π^* transitions from sp^2-hybridized surface states, existing on NDs, disappear at dispersion of the NDs in water. At the same time, valence holes found for NDs in water can be associated with electron transfer from the surface of ND to the surrounding water molecules. Such holes can influence on physical and chemical properties of NDs in water suspensions. In Refs. [15, 16], the substantial influence of surface modification of small NDs with NV centers (20–100 nm) on FL properties was shown theoretically and experimentally. Because of small size of ND, changes of the surface chemical potential modify band bending at the diamond surfaces and intermingle with the electronic NV states. It causes changes in the NV^- and NV° FL ratio. This phenomenon was demonstrated with single crystal diamond containing constructed NV centers and hydrogenated and oxidized ND in physiological buffers for ND particles with different size. It was established that NV^- fluorescence for a hydrogen-terminated ND surface is less intense in comparison with that of oxidized diamond. In Ref. [17], the strength of interactions between NDs and water molecules was first evaluated by the authors of this research. For this estimation, the analysis of position and shape of the water, Raman valence band in water suspensions of NDs was used. It comes as no surprise because as it was shown many times the Raman valence band of vibrations of OH-groups is very sensitive to the presence of different admixtures in water [18, 19] even in small amounts [20]. NDs in water suspensions induce changes in the structure of surrounding water [17]. Different surface functional groups interact with water molecules in different ways affecting the strength of hydrogen bonds. Occurring changes reveal themselves in the change of the position and shape of water vibrational bands, such as the valence band of OH-groups [17] and the fluorescent properties of NDs. The interplay between strength of interactions between functional groups on the surface of NDs and water molecules and intensity of fluorescence was demonstrated.

Many papers have been devoted to the influence of the solvents on optical properties of CD and the study of mechanisms of FL of these particles. Zhou et al. [21] and Zhang et al. [22] point out the substantial dependence of quantum yield of CD on the type of solvent and on modification of the CD surface [23, 24]. Kumar and Bohidar [25] carried out a very careful spectroscopic analysis of the specific non-functionalized fluorescent carbon nanoparticles dispersed in 15 organic solvents:

three aromatic solvents, five solvents with hydrogen bonds, seven aprotic solvents. It was established that the position of absorption band did not depend on the polarity of solvent, but the steady-state FL behavior was solvent-dependent with the fluorescence band in the region from 405 to 500 nm. In aromatic solvents, the average measured fluorescence lifetime did not depend considerably on the solvent polarity, with typical values 4–5 ns at 405 nm excitation. In protic solvents (with hydrogen bonding), the FL lifetime decreased with increasing solvent polarity. However, for aprotic solvents, the FL lifetime increased with polarity of solvent. Though many mechanisms of CNPs FL have been proposed, such as for example, based on the particle-size distribution [8, 26], the charge transfer [21], the surface traps [26–28], the radiative recombination of excitons from carbon nanoparticles of various sizes [29], the quantum effect [8], contribution of aromatic molecules [30], presently there is no comprehensive interpretation of the phenomena.

In this paper, the influence of interactions of the surface groups of detonation nanodiamonds and carbon dots with solvent molecules on the fluorescent properties of the nanoparticles was studied by Raman and fluorescence spectroscopy. The major focus of the study was on the dependence of the FL properties of CNPs on the strength of the hydrogen bonds between the surface functional groups and molecules of three protic solvents with different polarity: water, methanol, and isopropyl alcohol. Possible mechanisms of the observed dependence are suggested.

2 Experimental
2.1 Materials
As object of research, the detonation ND from "New Technologies" (Chelyabinsk, Russia) was chosen. They were produced by detonation of a mixture of trinitrotoluene and 1,3,5-trinitro-1,3,5-s-triazine in water cooling media. Purification of the sample from soot was made using a solution of chromic anhydride in H_2SO_4, treatment in H_2O_2/NaOH and ion-exchange resins and fractionating. Obtained sample had different functional groups (carbonyls, ethers, hydroxides) on the surface [31]. ζ-potential of the sample was equal to $+19.6$ mV. Modification of ND surface by COOH groups was produced by air treatment of it at $420\,^\circ$C during 1 h. This sample was characterized in details in Ref. [2]. Carboxylic groups predominated on the surface. The ζ-potential of the sample after treatment became -45 mV.

CDs were produced by oxidation of natural nanographite (400 nm, produced by Nanostructured and Amorphous Materials Inc., Houston, TX) in 3:1 mixture of 95–98% H_2SO_4 to 68% HNO_3 for 2 h [4, 5]. The supernatant and residue were separated by centrifugation. The acidic mixture was evaporated from the supernatant at $350\,^\circ$C and the brownish residue was resuspended in deionized water at a concentration of 5 mg ml^{-1}.

2.2 Preparation and stability of suspensions of carbon nanoparticles
Deionized bidistilled water (specific electrical conductivity 0.1 μSm cm^{-1}, pH = 6.9) was

used for preparation of the CNPs suspensions. The solvents used to prepare the suspensions (methanol, isopropyl alcohol), were supplied by Sigma–Aldrich. Analytical grade chemicals were used.

Water and methanol suspensions of ND-COOH were prepared in the concentration range from 0 up to 1.8 mg/ml with an increment 0.1 mg ml^{-1}. ND suspensions were treated for 180 min in an ultrasonic bath (Bandelin Sonorex RK-31). ND suspensions were characterized by different methods. The size of ND in the suspensions was measured by DLS (ALV-CGS 5000/6010), ζ-potential was measured using a ζ-sizer (Malvern Instruments). The stability of suspensions was checked during 3 months. The size and pH of the NDs in the suspensions were measured every month. Measurements of these parameters showed a good stability of ND-COOH suspensions: during 3 months, the size of particles changed in the following way: ND-COOH in water within limits of 9%, ND-COOH in methanol –13%, CD in water within limits of 11%, CD in methanol and isopropyl alcohol 12.5% (see Supporting Information, online at www.pss-a.com). Characteristic parameters for water and methanol suspensions of ND-COOH with concentration 1 mg ml^{-1} are presented in Table 1. Water, methanol, and isopropyl alcohol solutions of CDs were prepared in concentration range of 0.01–0.1 mg ml^{-1} with increment of 0.01 mg ml^{-1}. CD suspensions were characterized by the same methods as NDs suspensions (Table 1).

2.3 Laser Raman spectroscopy The Raman and fluorescence spectra of studied CNPs suspensions were obtained using setup described in Ref. [17]. Argon laser (wavelength 488 nm, operating power density 10 W cm^{-2} on the sample) was used for excitation of signal. Spectra used for calculation of quantitative characteristics of the FL parameter F_0 (explained in the next section) were measured by PMT coupled with monochromator (Acton, focal distance 500 mm). For precise analysis of the change of the valence bands of OH groups in the suspensions, CCD

camera (Jobin Yvon, Synapse BIUV) was used as detector. The temperature of samples was stabilized at $22.0 \pm 0.2\,^{\circ}$C.

3 Results and discussion
3.1 ND-COOH in different solvents The spectra of the ND-COOH water suspensions and ND-COOH methanol suspensions with different concentrations are shown in Fig. 1a and b, respectively. The band in the region 500–700 nm with a maximum at 580 nm is the FL spectra of ND-COOH.

As it can be seen from the obtained data, the ND-COOH FL intensity increases with growth of the ND concentration. The parameter $F_0 = S_{FL}/S_R$ (S_{FL}, integral intensity of ND fluorescence, S_R, integral intensity of Raman valence band of OH-groups for water (Fig. 2a) or integral intensity of Raman valence bands of CH and OH groups for methanol (Fig. 2b)) was used to specify the intensity of ND fluorescence (Table 1).

For water suspensions the contribution of Raman scattering into the total spectra is the following: the intense band with maximum at 585 nm (corresponding to valence vibrations of OH-groups) and weak band with maximum at 530 nm (band of bending vibrations of OH-groups).

The valence band of OH-groups is very sensitive to changes of the strength and number of hydrogen bonds in water and in other solvents containing hydrogen bonds [18, 19]. It is obvious that the frequency of valence vibrations for OH-groups bound by weak hydrogen bonds is higher than that for OH-groups bound by strong hydrogen bonds. That is why the intensity of the high-frequency region of the valence band I_2 (near 3410 cm^{-1}, inset in Fig. 1a) is caused by the number of weak hydrogen bonds, while the intensity of low-frequency region I_1 (near 3260 cm^{-1}, inset in Fig. 1a), by the number of strong hydrogen bonds. Thus, the parameter $\chi_{21} = I_2/I_1$ (Fig. 1a) determines the relation between strong and weak hydrogen bonds in the solution. Wavenumbers of points of water valence bands with intensities I_1 and I_2 were determined as singular points of

Table 1 Characteristics of the ND-COOH and CD suspensions in different solvents. Changes of the parameters of Raman and fluorescence spectra of ND-COOH and CD suspensions are summarized (parameters χ_{21}, F_0, and $\Delta\nu_{mc}$).

CNP sample	solvent	conc. (mg ml^{-1})	pH	size (nm)	$\Delta\nu_{mc}$ (cm^{-1})	χ_{21}	F_0
–	water	–	6.90 ± 0.01	–	0 ± 1	1.19 ± 0.02	0–0.15
–	methanol	–	8.10 ± 0.01	–	0 ± 3	1.27 ± 0.03	0
–	isopropyl alcohol	–	6.09 ± 0.01	–	0 ± 3	1.31 ± 0.03	0
ND-COOH	water	1	6.25 ± 0.01	10 ± 1	4 ± 1	1.23 ± 0.02	1.4 ± 0.18
ND-COOH	methanol	1	8.32 ± 0.01	11 ± 1	14 ± 3	1.5 ± 0.03	2.7 ± 0.23
CD	water	0.1	2.51 ± 0.01	7.1 ± 0.8	–[a]	1.22 ± 0.03	72 ± 5
CD	methanol	0.1	1.91 ± 0.01	7.2 ± 0.8	–	1.44 ± 0.04	264 ± 7
CD	isopropyl alcohol	0.1	1.85 ± 0.01	7.1 ± 0.9	–	1.64 ± 0.04	299 ± 9

Error of determination of parameters $\Delta\nu_{mc}$, χ_{21}, and F_0 was calculated using set of 7–8 spectra of CNP suspensions with one of the large concentrations of CNP for each solvent (see Supporting Information).
[a]Magnitude of the shift of position of mass center for solutions of CD turned out to be within the limits of experimental error (because of low concentrations of CD) and that is why it is not shown in Table 1.
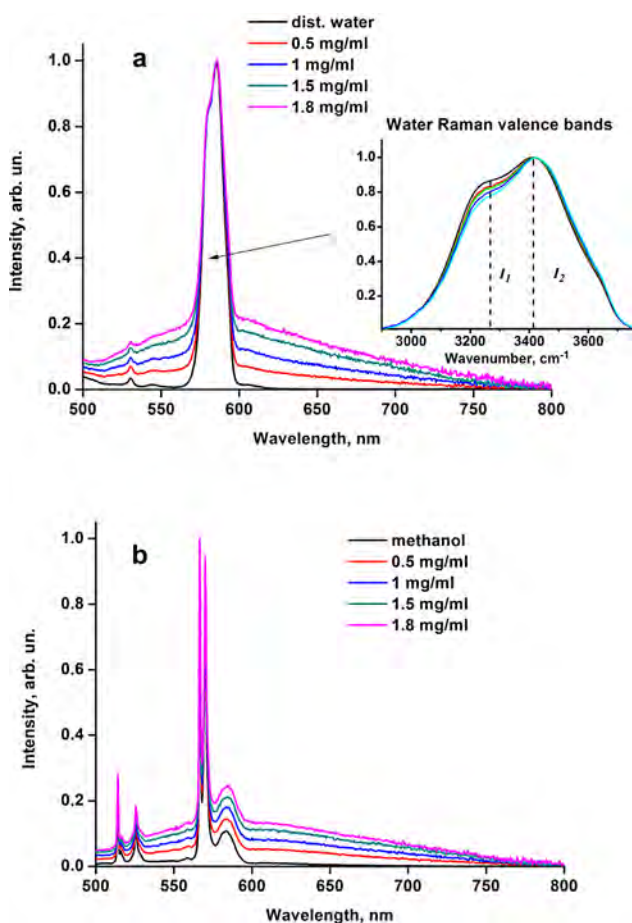
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Figure 1 Spectra of water suspensions (a) and methanol suspensions (b) with different concentrations of ND-COOH (normalized to maximum of intensity).

Figure 2 Illustration of calculation of the parameter $F_0 = S_{FL}/S_R$ for the spectra of suspensions ND-COOH in water (a) and in methanol (b).

concentration, the FL intensity increases in both suspensions. However, for an equal change of ND concentration, the fluorescence increases more strong in solvent with weaker hydrogen bonding, in methanol (Fig. 4).

Thus, the substantial dependence of FL properties of ND on the strength of hydrogen bonds between their surface groups and molecules of solvent was shown. The more intense FL of nanoparticles corresponds to the weaker hydrogen bonds between the ND surface and surrounding molecules.

derivative of this curve (see Supporting Information). Parameter χ_{21} increases with weakening hydrogen bonds and the valence band mass center ν_{mc} shifts to higher frequencies. Calculation of ν_{mc} is given in the Supporting Information.

In this study, the parallel analysis of the change of fluorescent properties of ND-COOH in different solvents (parameter F_0) and the change of the strength of hydrogen bonds (parameters χ_{21} and $\Delta\nu_{mc}$) with a change of ND concentration was carried out.

The obtained values of parameters χ_{21} and $\Delta\nu_{mc}$ and their concentration dependencies (Fig. 3, Table 1) allow making the following conclusions: 1. in pure methanol, hydrogen bonds are weaker than in pure water; 2. the presence of ND-COOH makes hydrogen bonds weaker both in water and in methanol; 3. weakening of hydrogen bonds depends on concentration of ND-COOH. When the concentration of ND-COOH increases, these bonds are weakening faster in methanol than in water.

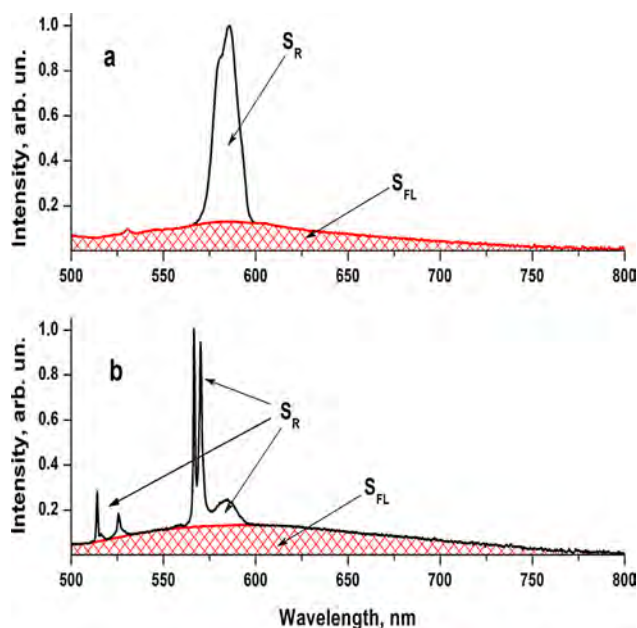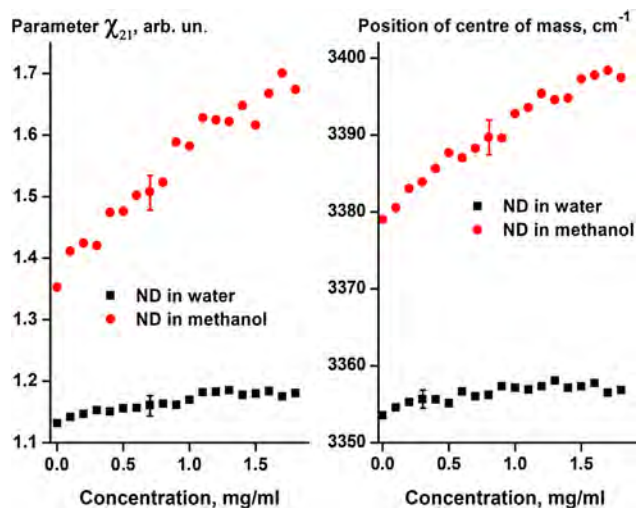Analysis of the FL properties of ND-COOH in the solvents demonstrated that with increasing ND

Figure 3 Dependencies of characteristics of valence band of OH-groups of the solvents on the concentration of ND-COOH.
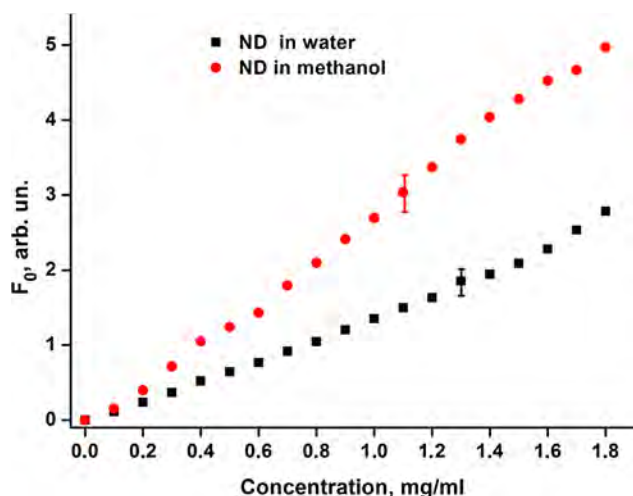
Figure 4 Dependence of the parameter F_0 on the concentration of ND-COOH for different solvents.

Figure 6 Dependence of the parameter χ_{21} on the CD concentration.

3.2 CDs in different solvents Similar studies of water, methanol, and isopropyl alcohol solutions of CDs in the concentration range of 0.01–0.1 mg ml^{-1} were carried out using Raman and fluorescence spectroscopy. The Raman and FL spectra of CDs solutions in hydrogen-bonded solvents are shown in Fig. 5. The analysis of the dependence of parameter χ_{21} of valence band of OH-groups of solvents on the concentration of CDs has demonstrated that for pure solvents the strength of hydrogen bonds decreases in accordance with the following order: water > methanol > isopropyl alcohol; with an increase of CD concentration these bonds weaken faster in accordance with the order: isopropyl alcohol > methanol > water (Fig. 6).
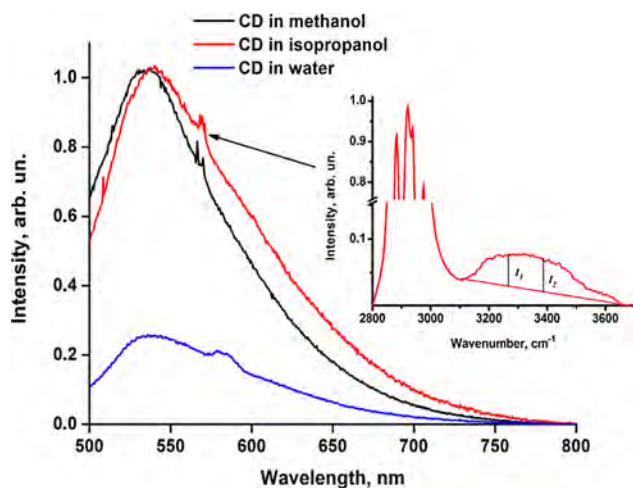
Calculation of the parameters χ_{21} and F_0 is explained in the Supporting Information.

The substantial dependence of FL properties of CD on the strength of hydrogen bonds between their surface groups and molecules of the solvent was also demonstrated. Analysis of FL properties of CD in solvents has demonstrated that with increasing CD concentration, the FL intensity increases in all solvents. But for equal changes of CD concentration, the fluorescence of nanoparticles increases more strongly in the solvent with weaker hydrogen bonding in isopropyl alcohol (Fig. 7).

Figure 5 Fluorescence spectra of CDs suspensions with the same concentration 0.1 mg ml^{-1} (measured by PMT). In the inset, one can see the valence bands of CH and OH groups of isopropyl alcohol (measured by CCD).
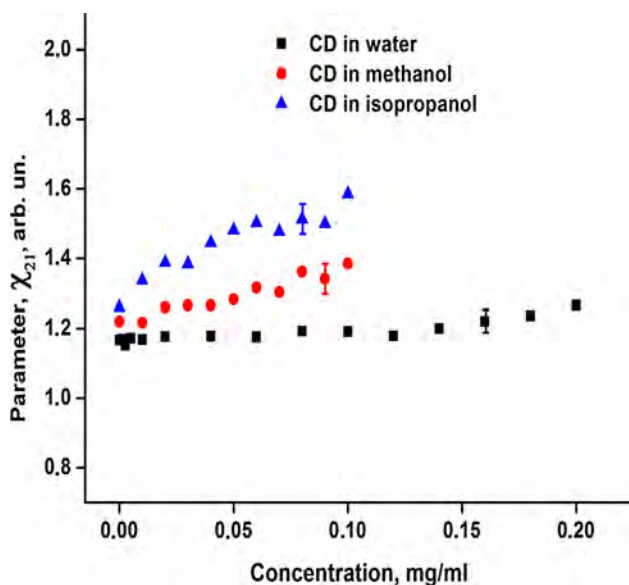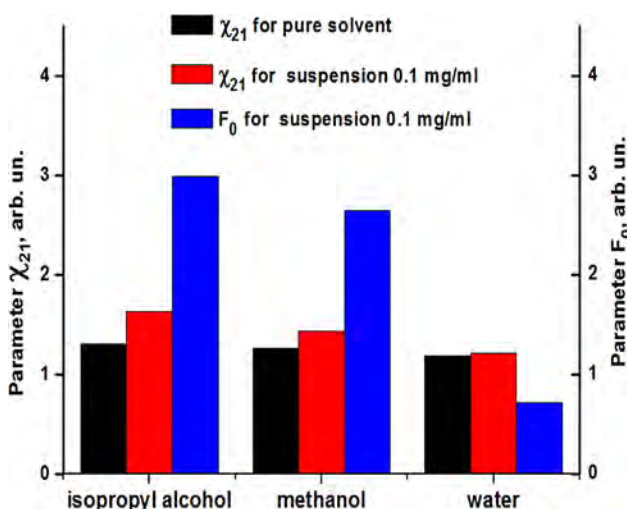

Figure 7 Correlation between the CD fluorescence and the strength of hydrogen bonds in the solvent. The values of parameter F_0 were divided by 100.
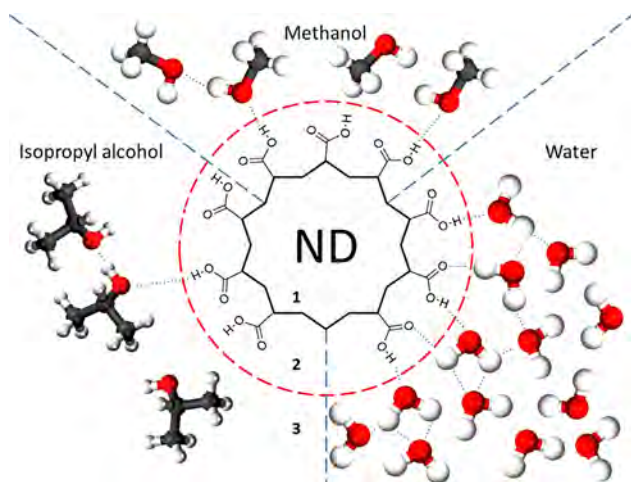
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Figure 8 A particle of ND-COOH in different solvents.

3.3 Discussion Strong dependence of the fluorescent properties of dispersed detonation ND and CD on the molecular interactions with surrounding molecules confirms one more time the hypothesis about the surface mechanisms of FL of the CNPs [26–28]. Surface groups, such as, e.g., C–O, C=O, and O=C–OH, can introduce trapping surface states with different energy levels (Fig. 9). As a result of interactions between surface groups and solvent molecules (the interaction between layers 2↔3, Fig. 8), including interactions under the influence of hydrogen bonding between them due to their electrostatic nature, the shift of the electron-excited states of these surface groups occurs in solvents owing to the charge transfer (Fig. 9). Moreover, (i) bonds different in strength induce shift of levels different by value, what causes different shift of the maximum of FL of CNP; (ii) bonds different in strength induce different
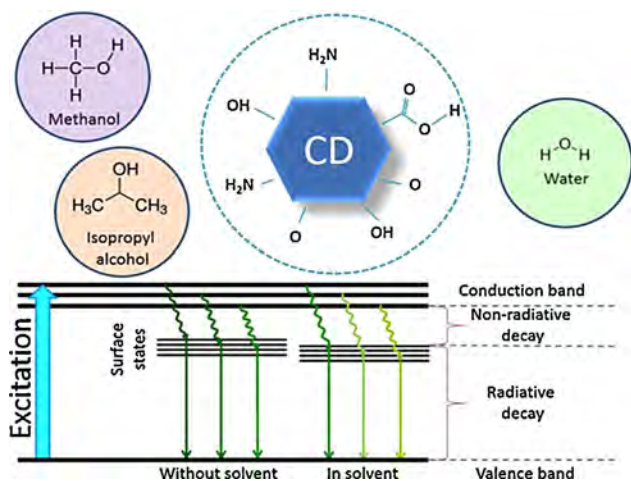
changes of the population of the upper excited levels, what causes different changes in the intensity of FL of CNP.

The obtained results demonstrated that with the increase of the ND and CD concentrations, the intensity of CNPs FL increased in all studied solvents. However, the intensity of CNPs FL in solvents with stronger hydrogen bonds increases more slowly in comparison with the solvents with weaker hydrogen bonds, i.e., FL is quenched by strong hydrogen bonds more actively. The solvents that we studied are differed by the fact that in water around CNPs, a uniform network of strong hydrogen bonds is formed. In methanol and isopropyl alcohol, the hydrogen bonds are much weaker, and hydrogen bonding network formed by the solvent molecules with surface functional groups is loose and non-uniform (Fig. 8). As a result, in all solvents one can observe not only different shifts of maximum of CNPs FL (Fig. 5), but also different CNPs FL quenching. It can be assumed that uniform network of strong hydrogen bonds of water induces stronger depletion of the population of upper excited levels of surface traps than non-regular networks of weaker hydrogen bonds of methanol and isopropanol. As a result, with increasing concentration of CNPs, the increase of FL intensity goes smaller in the row: isopropanol, methanol, water. That is why the intensity of FL in water suspensions at the same concentration of CNPs is lower.

4 Conclusions Using Raman and fluorescence spectroscopy, the substantial influence of the interactions of detonation ND-COOH and carbon dots with different solvent molecules in suspensions on the properties of each other was ascertained. The nanoparticles change the structure of the solvent, specifically, the strength of the hydrogen bonds between surface functional groups and the solvent molecules, while the strength of these hydrogen bonds affect the fluorescent properties of the nanoparticles. As a result of comparative analysis of Raman and FL spectra of suspensions of ND-COOH and CD in water, methanol, and isopropyl alcohol, it was found that the more intense fluorescence of nanoparticles in suspensions corresponds to weaker hydrogen bonding between CNP and solvent molecules. Stronger hydrogen bonds are quenching FL of CNP in suspensions at equal concentrations (and equal sizes) of nanoparticles more actively. The authors explain the revealed effects with different degree of change in populations of the upper excited levels of surface groups of nanoparticles under the influence of hydrogen bonding: uniform network of strong hydrogen bonds of water induces stronger depletion of the population of upper excited levels of surface traps than non-regular networks of weaker hydrogen bonds of methanol and isopropanol. This finding could be important in study of the still unexplained mechanisms of the surface FL of CNP.

Supporting Information
Additional supporting information may be found in the online version of this article at the publisher's website.

Figure 9 A schematic of the proposed mechanism of the influence of solvents on the FL of carbon nanoparticles in suspensions.

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