# Diamond−Water Coupling Effects in Raman and Photoluminescence Spectra of Nanodiamond Colloidal Suspensions

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**ABSTRACT:** The interaction of nanodiamond (ND) particles produced by detonation synthesis with water molecules in ND water suspensions was studied using Raman and photoluminescence spectroscopy. To address the role of the surface chemistry of ND particles, NDs with heterogeneous surface groups as well as ND particles enriched with carboxyl-, hydroxyl-, and fluorine-containing surface groups were investigated. The influence of the nanodiamond particles on the shape and position of the water valence band in the Raman spectra of ND water suspensions was demonstrated for the first time. Changes in the water band parameters take place up to 1.5 mg/mL of NDs in all studied suspensions and are most pronounced for the ND functionalized with COOH groups. A correlation between increasing ND luminescence intensity and strengthening of hydrogen bonds formed at the interface of ND and water molecules in water suspensions of variously functionalized NDs was found. The most intense ND luminescence was detected for the ND functionalized with OH groups, forming the strongest hydrogen bonds among the studied samples.
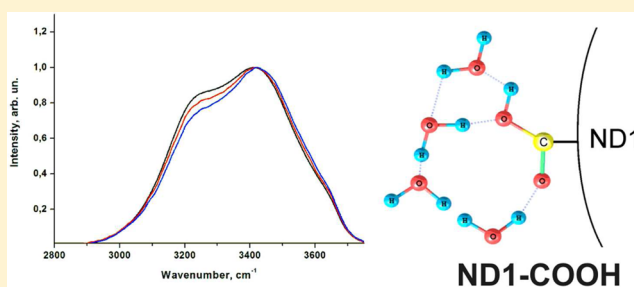
## INTRODUCTION

Interaction of diamond surfaces with water molecules play an important role in a wide variety of practical applications and still remains a challenging problem of fundamental research. Stimulated or spontaneous dissociation of water molecules on a diamond surface at room temperature has been experimentally observed[1] and confirmed by *ab initio* calculations.[2] Water dissociation along with electron exchange between diamond and an aqueous redox couple is expected to be responsible for p-type surface conductivity in diamond as well as for the changes in pH and oxygen concentrations for diamond particles dispersed in aqueous solutions.[3] Some techniques used to study the chemical properties of diamond surfaces are based on a diamond−water interaction. For instance, measuring the water contact angle of a diamond surface allows one to distinguish between hydrophilic and hydrophobic states of the surface and to estimate the degree of the surface hydrogenation or oxidation.[4] Finding efficient ways for a preparation of stable water suspensions consisting of primary nanodiamond particles or their small aggregates opens the door for various nanotechnology applications of nanodiamonds.[5] Water solubility of NDs is a necessary condition for their application in a physiological environment and for production of a biocompatible nanomaterial.

One of the most promising applications for biocompatible NDs is their use as fluorescent labels in targeted drug delivery.[5−13] There are two major sources of fluorescence in diamond particles. One is color centers, such as NV, SiV, and others produced in a diamond core.[14] This type of fluorescence is extremly photostable and has a high quantum yield. However, the problems with the thermodynamic stability and charge stability of most-used NV centers arise[15,16] when the particle size is decreased down to the nanometer scale required for biolabels. Another source of fluorescence is structural defects characteristic of diamond surfaces. The intensity of this type of fluorescence per a volume unit increases with decreasing diamond particle size,[17] in contrast to color center fluorescence. One more advantage of the surface fluorescence is the possibility for its enhancement by various surface functionalizations.[6] The surface fluorescence of the nanoparticles is typically sensitive to the action of the surrounding medium, particularly solvent molecules;[18−24] however, no dependence of fluorescence stability on the environment has been studied up to date for nanodiamond particles.

**Table 1. Size ($z$-Average Diameter for ND, nm), Zeta Potentials (ZP, mV), and Processing Methods for all ND Aggregates Used in the Experiments[a]**

| ND sample | ND processing | pH | ZP, mV | size, nm | $\Delta\nu$, cm$^{-1}$ | $\chi$ | $F_0$ |
|---|---|---|---|---|---|---|---|
| ND1 | wet synthesis; CrO$_3$ in H$_2$SO$_4$; NaOH + H$_2$O$_2$; fractionated | 6.71 | 19.6 ± 3.4 | 46 ± 10 | 8 | 1.32 | 2.2 |
| ND1-F | sample ND1 treated in SF$_6$ plasma | 7.08 | −21.6 ± 1.4 | 54 ± 10 | 7 | 1.30 | 3.3 |
| ND1-OH | sample ND1 reduced with LiAlH$_4$ | 6.97 | +30 | 60 ± 1.75 | 5 | 1.26 | 5.1 |
| ND1-COOH | sample ND1 treated in air at 420 °C | 6.25 | −27.6 ± 17 | 74 ± 10 | 15 | 1.36 | 1.6 |

[a]Changes of characteristics of Raman and fluorescence spectra of water suspensions of initial and modified ND: $\Delta\nu$ (cm$^{-1}$) = shift of water Raman valence band mass center; $\chi$ = a ratio between intensities of the high- and low-frequency components; $F_0$ = a ratio of integral intensity of fluorescence to integral intensity of water Raman valence band. ND concentration in all suspensions is 1 mg/mL.

In this paper the coupling strength of the diamond−water molecule interactions was estimated for the first time from the position and shape of the water Raman valence band in nanodiamond−water suspensions. The influence of different functional groups on the surface photoluminescence (PL) intensity, band shape, and spectral range was studied for detonation nanodiamond−water suspensions. The correlation between diamond functional surface groups−water coupling strength and the surface PL intensity was demonstrated.

### ■ RESULTS

Water suspensions of chemically purified detonation nanodiamonds (ND) as well as ND modified with the functional groups F, OH, and COOH were characterized by different techniques (see Table 1). The starting and modified NDs are denoted as ND1 and ND1-F, ND1-OH, and ND1-COOH, respectively.

Water suspensions of the NDs under study were prepared with concentrations from 0.2 up to 2−3 mg/mL with concentration increments of 0.2 mg/mL. For suspensions with concentrations 1, 2, and 3 mg/mL values of pH and zeta-potential were measured, and the size distributions of ND aggregates were determined. Specified parameters for water suspensions with concentration 1 mg/mL are shown in Table 1. Colloidal stability with time of the samples was monitored (see Experimental Section, Preparation and Stability of ND Water Suspensions).

NDs, as any other substances being dispersed in water, cause structural rearranging of the former. Various molecular functional groups on the ND surface interact with water molecules changing the strength and dynamics of hydrogen bonds. These changes effect the position and shape of water vibrational bands.

The Raman and fluorescence (FL) spectra of all ND water suspensions were measured using a laser Raman spectrometer (see Experimental Section). The spectra of ND1-COOH water suspensions (concentration from 0 up to 3 mg/mL) are shown in Figure 1. Spectra were normalized to the maximum of intensity.

The broad band ranging from 500 to 700 nm with a maximum near 600 nm at 488 nm excitation wavelength dominates the FL spectra of ND1-COOH which are typical for detonation nanodiamond materials. The ND fluorescence intensity monotonously increases with increases of the ND concentration. The Raman portion of the combined spectra reveals two bands characteristic for water and no band characteristic for diamond band in ND−water suspensions. An intense water Raman valence band is observed in the range 570−590 nm. A weak water bending band is present at 530 nm.

For correct separation of the valence band from the broad FL band an approximation of the fluorescence background by a
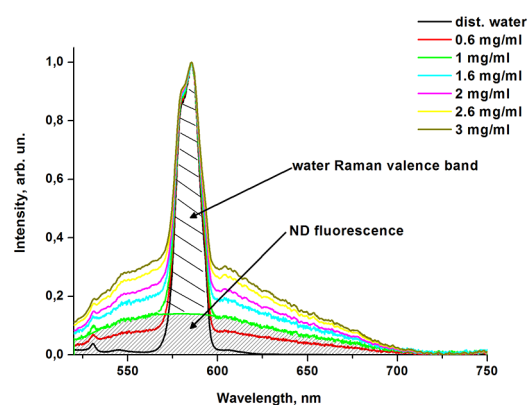


**Figure 1.** Raman and FL spectra of aqueous suspensions of ND1-COOH with concentrations 0.6, 1, 1.6, 2, 2.6, and 3 mg/mL. Excitation wavelength is 488 nm.

second-order polynomial and its subtraction in the 560−610 nm region were used. The water valence bands of ND1 suspensions with different concentrations are shown in Figure 2 after the FL subtraction.
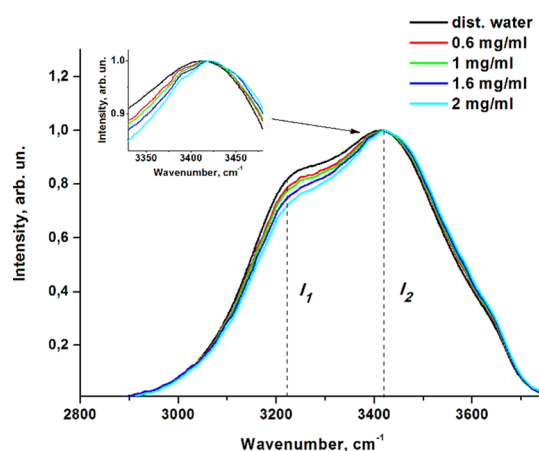


**Figure 2.** Water valence bands in ND1 suspensions with concentrations 0.6, 1, 1.6, and 2 mg/mL (the parameter $\chi$ is defined as $\chi = I(\nu_2)/I(\nu_1) = I_2/I_1$). The inset shows details in the vicinity of the 3400 cm$^{-1}$ peak.

Dependencies of the shape and position of the water valence band on ND concentration C and type of functional groups on the ND surface were analyzed. The shape of the water valence band is complex. The band consists of two main components: a low-frequency component at $\nu_1 \approx 3215$ cm$^{-1}$ and a high-frequency one at $\nu_2 \approx 3415$ cm$^{-1}$ which correspond to vibrations of water molecules with stronger and weaker hydrogen bonds, respectively.[25−27] The changes in the band

shape were estimated by the $\chi$ parameter, which is determined as the ratio between the intensities of the high- and low-frequency components: $\chi = I(\nu_2)/I(\nu_1) = I_2/I_1$ (Figure 2). The position of the band was determined at its "mass center", i.e., at the frequency $\nu_{mc}$ which separates the band into two parts having equal integral intensities. Note that $\chi$ and $\nu_{mc}$ parameters are interrelated: an increase of the $\chi$ value leads to an upshift of $\nu_{mc}$ position.

It was found that the parameter $\chi$ increases (Figure 3a) and the "mass center" $\nu_{mc}$ shifts to high frequencies (Figure 3b)
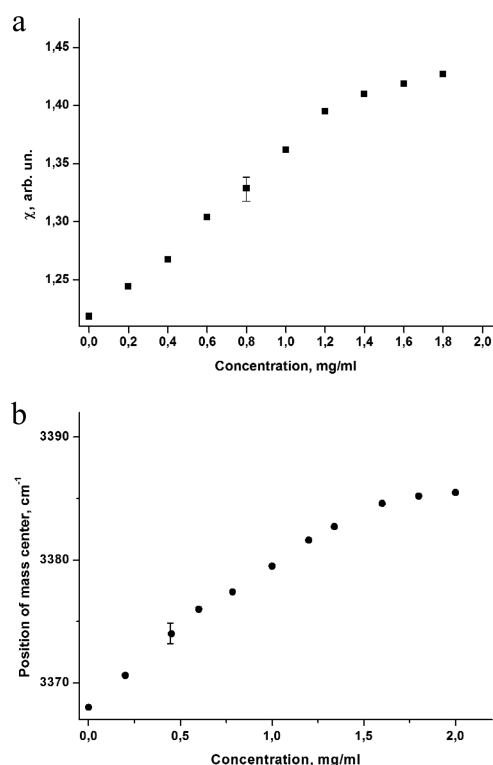


**Figure 3.** Dependences of the parameter $\chi$ (a) and the mass center $\nu_{mc}$ (b) of the water valence band on ND1 concentration. Error bars typical for all data points are shown for selected points at both graphs.

with increase of ND1 concentration in water. These changes in the shape and the position of water valence band indicate that water molecules with weaker hydrogen bonds increases with ND concentration. Increase of the parameter $\chi$ from 1.16 (for distilled water) to 1.32 at increased ND1 concentration up to 1 mg/mL means significant rearrangement of hydrogen bonds in water due to the influence of dispersed ND1. For example, for water solutions of potassium iodide, KI (it is one of the most chaotropic salts), the parameter $\chi$ changes from 1.16 to 1.21 as the concentration is increased from 0 to 1 mg/mL.[27,28] This influence reaches saturation at ND concentrations of 1.5−2 mg/mL. We relate the saturation in the $\chi$ and $\nu_{mc}$ with increased agglomeration of the ND particles in water which starts at these ND concentrations and leads to instability of ND suspensions at concentrations higher than 3 mg/mL. The ND agglomeration prevents further increase in the amount of water molecules interacting with ND particles.

The changes in the $\chi$ and $\nu_{mc}$ parameters for 1 mg/mL water suspensions of initial ND1 and ND1 modified with the functional groups F, OH, COOH as compared against pure water are shown in Table 1. Up-frequency shifts of $\nu_{mc}$ ($\Delta\nu$) and increases of $\chi$ values ($\Delta\chi$) with ND concentration are

observed for all samples studied. The suspension of ND1 with carboxylic groups (COOH) demonstrate the largest shift of the "mass center", $\Delta\nu = 15$ cm$^{-1}$, and the largest increase of the $\chi$ parameter, $\Delta\chi = 0.2$. The lowest change of $\Delta\nu$ and $\chi$, $\Delta\nu = 5$ cm$^{-1}$ and $\Delta\chi = 0.1$, respectively, were determined for the ND1-OH suspension. The dependencies of the $\chi$ parameter on the concentration of nanodiamond particles in ND1, ND1-F, ND1-OH, and ND1-COOH in water suspensions are shown in Figure 4. Saturation in the $\chi$ increase is observed for all curves when the ND concentration reaches 2 mg/mL.
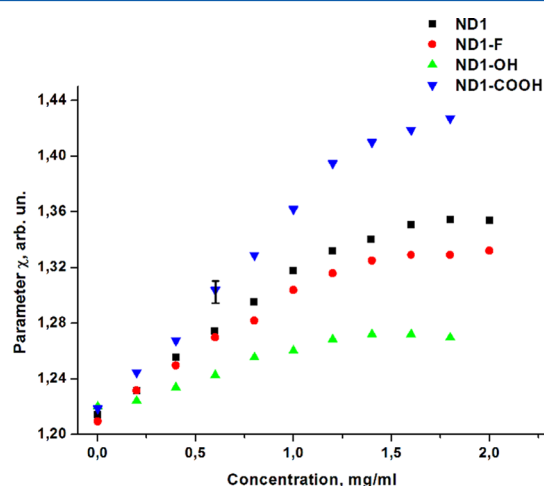


**Figure 4.** Dependencies of the parameter $\chi$, the ratio of the water valence band intensities, on the concentration of initial ND1, ND1-F, ND1-OH, and ND1-COOH in water suspensions.

Combined Raman−FL spectra of all studied suspensions (Table 1) were measured in the range of 500−800 nm. The spectra of suspensions with a ND1 concentration of 1 mg/mL are shown in Figure 5. As one can see, the wide bands of ND fluorescence differ not only by intensity but also by their maximum position for various samples.

The parameter $F_0$ was used for a quantitative characterization of the fluorescence bands. It is the ratio of integral intensity of fluorescence to integral intensity of water Raman valence band[29] (Figure 1). Values of $F_0$ were determined for all studied suspensions; the corresponding spectra are shown in Figure 5 (Table 1). The obtained results reveal a decent correlation of
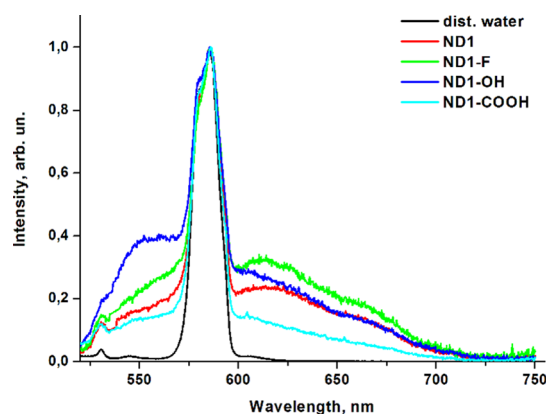


**Figure 5.** Raman and FL spectra of water and water suspensions of NDs with concentration 1 mg/mL. All spectra were obtained under the same conditions. Excitation wavelength is 488 nm.

the fluorescence properties of ND with the shape of water valence band in the ND suspensions. In a set of variously functionalized ND suspensions an increase of $F_0$ corresponds to a decrease of $\chi$ (Figure 6).
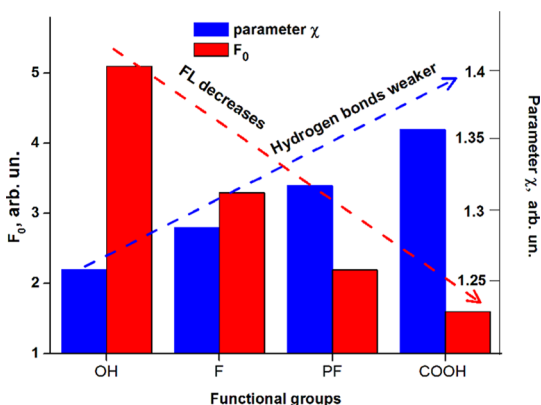


**Figure 6.** Dependences of the parameters $\chi$ and $F_0$ on the type of functional groups on the ND surface. Abbreviation "PF" corresponds to the polyfunctional surface of ND.

We expect that this result could be related to a quenching effect of the solvent (water) on the surface fluorescence of nanoparticles dispersed in the solvent.[30] Strong hydrogen bonds can contribute to deactivation of nonradiative channels so that the role of radiative channels in the recombination of photogenerated charges is enhanced—the stronger the H-bonds, stronger the influence of the presence of the solvent.

Note that results obtained at 514, 476, and 457 nm excitation wavelengths (not shown in the text) were similar to those obtained at 488 nm. This reveals an independence of observed effects in Raman and photoluminescence spectra of nano-diamond colloidal suspensions on excitation energy.

### ■ DISCUSSION

According to the IUPAC definition, the hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X−H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation.[31] The larger the difference in electronegativity between the H atom and the X fragment, the stronger the H-bond.[31] The electronegative oxygen involved in the OH and COOH functional groups on the ND surfaces interacts with surrounding water molecules by H-bonding (Figure 7). However, the observed increase in $\chi$ for ND1-OH and ND1-COOH suspensions against $\chi$ in pure water means that $H_2O$ is more electronegative than OH and COOH groups on the ND1 surface. Therelationship between the electronegativities of these O-containing fragments and $H_2O$ molecule holds in general.[32,33]

The increase of the $\chi$ parameter for suspension ND1-F against pure water provides evidence that hydrogen bonds between surface fluorine and water molecules are weaker than those among water molecules themselves. It has been shown[25−27] that single F ions in water form stronger hydrogen bonds with water molecules as compared to hydrogen bonds in pure water. However, covalently bounded fluorine (in contrast to anionic fluoride) hardly acts as a hydrogen-bond acceptor.[34] In our case, F atoms covalently bounded with carbon atoms
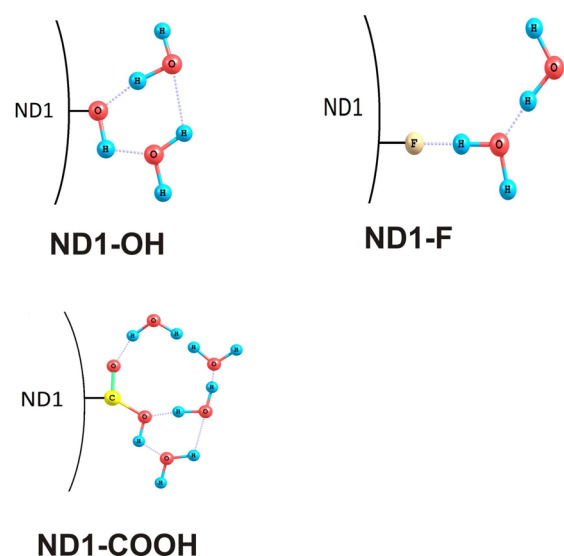


**Figure 7.** Schematic representation of hydrogen bonding between water molecules and functional groups on the ND1 surface.

weaken the hydrogen bonds in the ND1-F−water suspension. The $\chi$ parameter in ND1-F suspensions increases more strongly with concentration than in ND1-OH suspensions but weaker than in ND1-COOH suspensions (Figure 4).

According to the IR absorption study of detonation NDs after their purification with acids, the surface of the material is polyfunctional (PF).[35] Among the large variety of functional groups on the ND surface, the OH and the COOH are the most typical for the purified NDs. It explains why the $\chi$ parameter in the suspensions of initial ND1 reaches a value that is in between those measured for ND1-OH and ND1-COOH suspensions at the same ND1 concentrations (Table 1 and Figure 4).

Thus, the produced functional groups on ND surfaces are suggested to be arranged in the order according with an increase in their electronegativity: COOH, PF, F, and OH. This arrangement reveals the correlation of the strength of the hydrogen bonds formed at the interface of ND particles with specific surface groups and surrounding water molecules, with the fluorescence of ND particles in the suspension (Figure 6). As the strength of the hydrogen bonds at the interface is decreased, the structural luminescence for the ND suspensions is also decreased.

### ■ CONCLUSION

In the current work we have studied the diamond−water coupling effects by using Raman and photoluminescence spectroscopy of nanodiamond colloidal suspensions. For the first time the influence of the ND concentration and the specific ND surface groups on the shape and position of the water valence band in Raman spectra of ND−water suspensions was demonstrated. The influence is explained through changes of the hydrogen bond strength in the suspensions. This finding opens up new possibilities in study of functional state of ND surface by mean of an analysis of water valence band.

The observed dependence of ND luminescence intensity on the type of functional groups on the ND surface demonstrated a relationship between the broadband luminescence typical for NDs and the chemical state of ND surface. The increase in the PL intensity of ND was found to correlate with the hydrogen

bonds strengthening in water suspension. This finding could be important in a study of still unexplained mechanisms of the ND surface PL.

## EXPERIMENTAL SECTION

**Materials.** Detonation NDs (DND) were produced by detonation of a mixture of trinitrotoluene (TNT) and 1,3,5-trinitro-1,3,5-s-triazine (RDX) in water cooling media. DNDs were purified from nondiamond carbon using liquid oxidizers. With purification, removal of metallic impurities and oxidation of nondiamond carbon was achieved. Additional processing methods were used to further reduce the nondiamond carbon content and provide intentional alternation to the ND's surface group content and composition.

The sample ND1 ("New Technologies", Chelyabinsk, Russia) was purified from soot using a solution of chromic anhydride in sulfuric acid, followed by treatment in $H_2O_2$/NaOH and ion-exchange resins and fractionating. The incombustible impurity content of the materials was 0.6 wt %. This sample has a positive zeta potential and a variety of surface groups: carbonyls, ethers, hydroxides.[35] Sample ND1-F was obtained by treatment of the ND1 sample in a $SF_6$ plasma;[36] it contains ~6 atom % F. Sample ND1-OH was obtained by reduction of the sample ND1 using $LiAlH_4$.[35] Sample ND1-COOH was obtained by air treatment of ND1 at 420 °C for 1 h. Characterization of the surface groups for this sample (prevalence of carboxylic acid groups and carboxylic acid anhydrides) is reported in ref 37.

**Preparation and Stability of ND–Water Suspensions.** Water suspensions of ND1 with concentrations 1, 2, and 3 mg/mL were prepared. Deionized bidistilled water was used for preparation of the suspensions. ND1 suspensions were treated 180 min in an ultrasonic bath. For 3 months the stability of the prepared suspensions was examined—size of ND aggregates in the suspensions and zeta-potential (by zeta-sizer Malvern Instruments) were measured monthly. Measurements of mentioned characteristics demonstrated good stability of all solutions. For example, the size of main portion of ND1 nanoparticles increased from 38 up to 52 nm; a little amount (about 4%) of aggregates with size 146 nm appears. But, in general, ND1 water suspension reveals fully successful time stability.

Using $F_0$, we estimated the stability of the spectroscopic features of the prepared ND1 suspensions. For this, Raman and FL spectra of ND1 suspensions with concentrations 1 and 2 mg/mL were measured every week for 3 months. Results demonstrated that water–ND1 suspensions are stable enough, and they have stable fluorescence. Mean values of parameter $F_0$ for all measurements for ND1 suspensions are the following: $F_0$ = 2.8 ± 0.4 for concentration 2 mg/mL; $F_0$ = 2.2 ± 0.3 for 1 mg/mL.

**Experimental Laser Raman Spectrometer.** The laser spectrometer was adjusted for Raman and fluorescence spectroscopy of ND water suspensions. Excitation of Raman and fluorescence spectra was performed by argon laser operating at 488, 514, 476, and 457 nm wavelengths. The last three wavelengths were used to check independence of the results obtained at 488 nm on excitation energy. The output power was 500 mW, and the real power density in cuvette was 10 $W/cm^2$ at 488 nm excitation. For suppression of the elastic scattering, an edge filter (Semrock) was used. It allowed measurement of spectra separated by 200 $cm^{-1}$ from the laser excitation. The system of registration consisted of mono-

chromator (Acton, grades 900 and 1800 grooves/mm, focal length 500 nm, spectral resolution 1 $cm^{-1}$) and two detectors (PMT and CCD camera). Panoramic spectra in the range 500–800 nm were measured by PMT in the mode of step-by-step registration. Registration of spectra was performed by a CCD camera in a parallel detection mode (Jobin Yvon, Synapse1024*128 BIUV-SYN). The temperature of the samples during experiment was maintained constant equal to 22.0 ± 0.2 °C in thermostabilized cuvette from fused quartz. The spectra were normalized to the power of laser radiation and to the spectrum accumulation time.

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**Author Contributions**
The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

**Notes**
The authors declare no competing financial interest.

## ABBREVIATIONS

ND, nanodiamond; PL, photoluminescence; FL, fluorescence; DND, detonation nanodiamonds.

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