

The influence of boron doped nanodiamonds on hydrogen bonds in suspensions of protic solvents

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ABSTRACT

This work presents the results of study of the influence of BDND on hydrogen bonds of protonic solvents. In addition, the comparative analysis of the interactions of BDND and DND-COOH with solvents molecules was carried out. The analysis of temperature dependences of the quantitative characteristics of the stretching bands of OH groups of the solvents and the suspensions of NDs has shown that the BDND and DND differently weaken the hydrogen bonds in water and in water-ethanol solution with 70 vol. % ethanol content. In water-ethanol solution with 20 vol. % of ethanol the both NDs practically does not change the network of hydrogen bonds.

Keywords: Nanodiamonds, boron doped nanodiamonds, protic solvents, Raman spectroscopy

1. INTRODUCTION

The diamonds with nanoscale size are known as a promising material in biomedicine due to their properties such as chemical, mechanical and thermal stability, biocompatibility, high sorption properties and multi-functional surface¹⁻⁴. For the diamond with impurity defects (color centers) the high emission rate, stability and high quantum yield of luminescence were observed⁵⁻⁸. Due to these properties nanodiamonds can be used as optical biomarkers and nanosensors, targeted delivers of drugs in body or as an adsorbent of heavy metals⁹⁻¹⁴. One of the novel types of ND with specific electromagnetic properties is boron doped nanodiamond (BDND), synthesized by the method of HTHP. Boron-doped diamonds have unique properties that provide them a wide range of possible applications. Because of its high mechanical strength, excellent thermal stability, and extended lifetime, BDND is an efficient metal-free catalyst for oxygen reduction reaction, which plays an important role in the creation of biosensor. Recently the superconductivity was found in a diamond heavily doped with boron^{15,16}. It is known that B-doped CVD diamond films have the widest electric potential window what is the outstanding property for the electrochemical electrodes¹⁷⁻¹⁹.

The attempts to create a boron-doped nanodiamond (BDND) were undertaken for many years. So, in 2008 a 100 nm nanodiamond coated with boron-doped nanocrystalline diamond was synthesized²⁰ and in 2013, a 30 nm BDND was created²¹. The production of these materials consists of mechanical grinding of doped bulk diamond obtained by such methods as static synthesis as chemical vapour deposition (CVD) and the high pressure–high temperature (HPHT) technique. To create the smaller BDND, the authors of this publication developed the method of the direct synthesis of doped nanodiamond based on HPHT treatment of a one-component precursor containing the dopant atom(s)²². In [22] the diamond nanoparticles with a variable size down to less than 10 nm, containing a high concentration of substitutional boron (≈1%), have been produced. The HPHT synthesis was carried out from the organoboron compound 9-borabicyclo[3,3,1] nonane dimer (9BBN), C16H30B2 (Fig.1), at a pressure of 8–9 GPa in a temperature range of 1200–2000 K²² (see Fig.1).

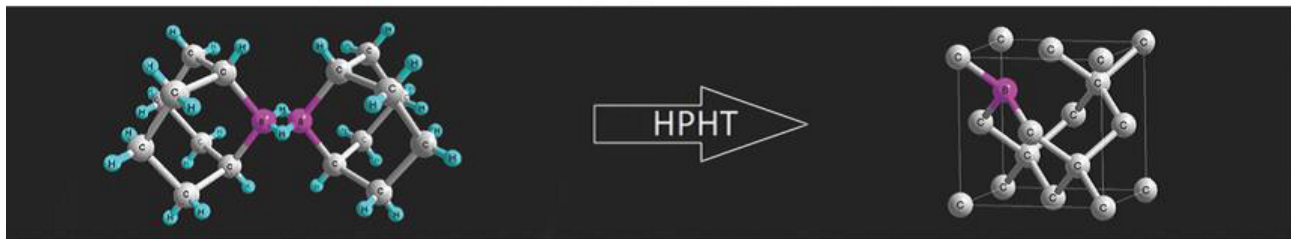


Figure 1. Image of the 9BBN molecule and the diamond lattice with the dopant B.

As it was mentioned before, heavily BDND is of great interest for fundamental science, biomedicine, industrial technologies and electronics. For the prospective applications, BDND powder is foreseen in the use as a support for various catalysts²³ or a conductive ink in screen-printed technologies²⁴, among others. For such applications, especially for biomedicine, it is very important to know how the nanoparticles and surrounding molecules affect the properties of each other.

This work presents the results of the study of the influence of BDND on hydrogen bonds of different protic solvents. The interactions of BDND with solvents molecules were studied using correlation spectroscopy, Raman and IR spectroscopies.

2. EXPERIMENT

2.1 Materials and preparation of suspensions

As objects of research, the suspensions of the BDND were used. BDND were produced by direct HTPT synthesis ($T = 1310^{\circ}\text{C}$, $P = 9 \text{ GPa}$) described in [22]. Initial synthesized BDND powder was purified in the process of boiling in mixture of concentrated nitric/sulfuric (1:3) acids for 3 h. Then the acids were washed out with distilled water in result of 7 washing/centrifugation cycles for 20 min (Centrifuge LMC-3000, BioSan, 1700 g). The resulting precipitate was characterized by the different methods (see below).

To study the influence of dispersed NDs on the properties of solvents we prepared several model solvents with different strength of hydrogen bonds. We used the fact that the self-organization of ethanol and water molecules is observed near ethanol concentration around of 20 vol. % in water. It leads to the effect of stabilization of water structure: strengthening of hydrogen bonds in the solution in comparison with pure water and with water-ethanol solutions with the other concentrations of ethanol²⁵⁻³⁰. This effect was confirmed by theoretical calculations and by calorimetric methods, NMR, FTIR and Raman spectroscopy²⁵⁻³⁰. To explain such strengthening of hydrogen bonds the authors of [26,28,30] supposed that at the ethanol concentration of 20 vol. % the ethanol and water molecules form clathrate-like structures.

Thus, to create the media with different strength of hydrogen bonds the water-ethanol solutions with three concentrations of ethanol were prepared: 0, 20 and 70 vol. %. In the solution with ethanol concentration of 20 vol. % the hydrogen bonds are stronger than that in pure water and water-ethanol solution with 70 vol. % of ethanol. In the solution with 70 vol. % of ethanol the hydrogen bonds are much weaker than that in water.

In this work we prepared the following samples: 1) 3 solvents – the water-ethanol solutions with ethanol concentrations of 20 and 70 vol. % and pure water; 2) 3 suspensions of BDND with concentration 0.5 g/l in water and water-ethanol suspensions with ethanol concentrations of 20 and 70 vol. %. Deionized bidistilled water with specific electrical conductivity 0.1 $\mu\text{Sm/cm}$ and ethanol (96%, Sigma-Aldrich) were used to prepare all samples.

2.2 Experimental setup

The size of BDND dispersed in water was measured using DLS method (analyzer ALV-CGS-5000/6010 Langen, Germany).

Raman spectrum of the BDND powder was obtained using a Horiba LABRAM HR800 spectrometer equipped with the diode-pumped solid-state laser Ciel-473 (Laser Quantum). The laser radiation (473 nm, 0.1 mW) was focused in a 2 μm spot on the surface of the BDND powder on a Si substrate. The spectrometer was operated in a confocal mode; a backscattering geometry was used for the Raman spectra recording.

IR spectrum of the BDND powder was obtained using Bruker Vertex 70v FTIR spectrometer.

Raman spectra of the solvents and the ND suspensions were obtained using the laser Raman spectrometer. Raman spectra were excited by the radiation of the argon laser (with wavelength 488 nm, power 250 mW, power density in cuvette 10 W/cm²). The registration system consist of the monochromator (Acton 2500i, focal length 500 mm, grade 900 grooves/mm) and CCD-camera (Horiba Jobin Yvon, Synapse 1024*128 BIUV, width of entrance slit 25 μm , resolution 2 cm⁻¹). Integral spectra were measured in 90-degree scattering geometry and were corrected to the laser power, spectrum accumulation time, spectral and channel sensitivity of the receiver. To measure and maintain the temperature of the samples, the special thermostabilization system KRIO-VT-01 was used. It allows us to control samples temperatures in a wide range with the accuracy better than 0.1°C.

3. RESULTS

3.1 Characterization of BDND suspensions

After purification the BDND has been characterized using Raman spectroscopy, IR spectroscopy and correlation spectroscopy.

The Raman spectrum of the BDND powder dried from the water suspension are characteristic for a heavily boron-doped diamond (Fig.2). The diamond line of the zone-center phonon mode is shifted from 1332 cm⁻¹ (observed for undoped diamond) to 1310 cm⁻¹. According to the empirical dependence of the diamond line shift on the concentration of substitutional boron atoms in the diamond lattice³¹, the boron concentration in BDND is at the level of 1 %. The lines positioned below 1300 cm⁻¹ are caused by the vibration modes of C and B in diamond lattice³². The line with low intensity at 1600 cm⁻¹ corresponds to the sp²-bonded carbon that was not completely removed from the sample during its purification.

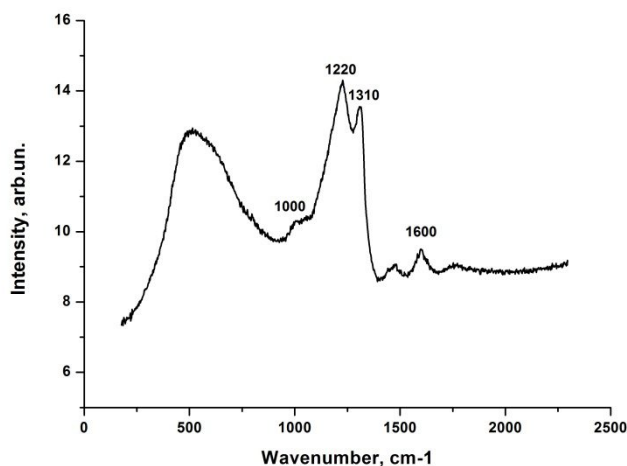


Figure 2. Raman spectrum of the BDND powder dried from the water suspension.

To study the interactions of NDs with solvent molecules it is important to know the functional cover of nanoparticles. To determine the functional groups on the BDND surface the IR spectrum of the BDND powder was measured (Fig.3). As

can be seen from IR spectrum the surface of BDND has C-C, COO⁻, C=O, C-O-C, O-H groups. Therefore, the BDND surface has many carboxyl groups -COOH and hydroxyl groups -OH.

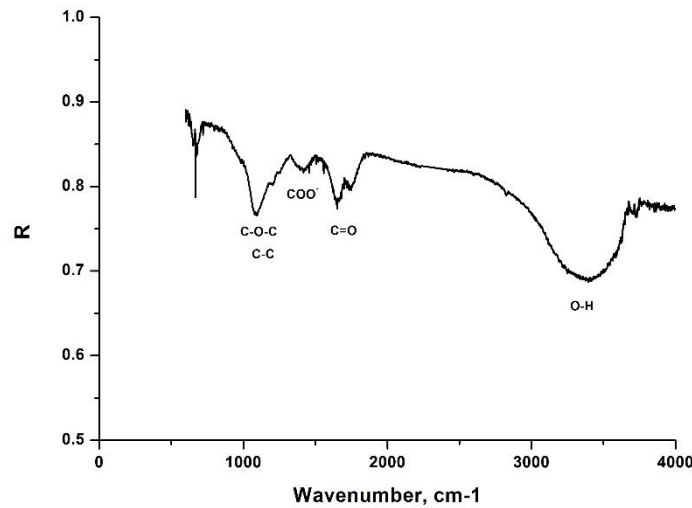


Figure 3. IR spectrum of BDND powder dried from the water suspension.

The size of BDND particles in water was measured by the DLS method. It showed that the most of nanoparticles have the size of 11 nm (see Fig.4).

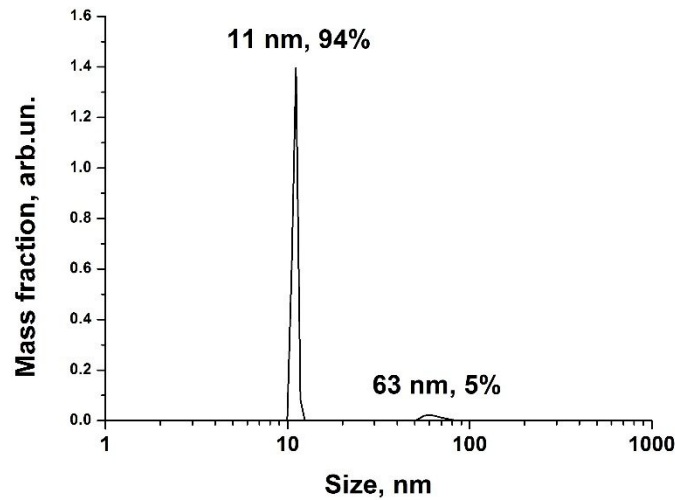


Figure 4. Particle size distribution of BDND water suspension.

3.2 Temperature dependencies of Raman spectra of NDs suspensions

To study the influence of BDND on the hydrogen bonds of protic solvents the temperature dependencies of Raman spectra of the BDND suspensions in water and water-ethanol solvents with ethanol concentration of 20 and 70 vol. % were obtained. All spectra were obtained under the five temperatures: 0.5°C, 10°C, 25°C, 45°C, 60°C. Thus, we had the suspensions of the BDND in three solvents: with weak, medium and strong hydrogen bonds. In all of these BDND

suspensions and solvents we changed the strength of hydrogen bonds in the same way: when samples are heated, the hydrogen bonds in the solvents become weaker. These changes are manifested in the Raman spectra of solutions and suspensions. This allows to carry out the comparative analysis and to make the conclusions about the influence of BDND on hydrogen bonds in the studied samples.

In Fig.5 one can see the temperature dependencies of Raman spectra of water (Fig.5a) and water suspension of BDND (Fig.5b).

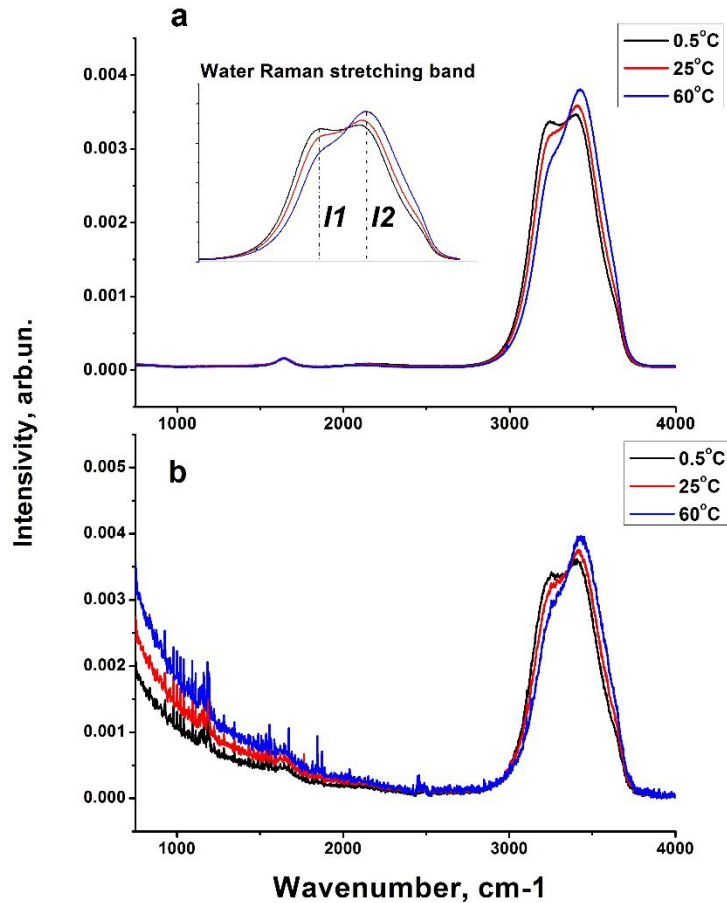


Figure 5. Raman spectra of water (a) and of water suspension of BDND (b) at different temperatures. In the inset, one can see the illustration of calculation of the parameter $\chi_{21} = I2/I1$.

As it can be seen in Fig.5 the band of stretching vibrations of O–H groups (3000-3800 cm^{-1}) changes with the changing of the temperature. With decreasing temperature the intensity of high-frequency region of stretching band decreases and the band's center of mass shifts to low frequencies³³⁻³⁵. With temperature increasing the changes in the stretching O–H band are opposite. This effect is explained by changes of strength of hydrogen bonds. The high-frequency region of the stretching band (around 3420 cm^{-1}) is caused by the vibrations of O–H groups with weak hydrogen bonds, and the low-frequency region (around 3200 cm^{-1}) is caused by the vibrations of that with strong hydrogen bonds³³⁻³⁵. With decreasing temperature the hydrogen bonds in water become stronger, the frequency of stretching vibrations of O–H decreases, that is why the stretching band shifts to low frequencies and the intensity of low-frequency region of band increases. To characterize the change of the strength of hydrogen bonds we used the parameter $\chi_{21} = I2/I1$ (see Fig.5a), which is equal

to the ratio of the intensity of the high-frequency region of the stretching band to the intensity of the low frequency region. In accordance with the above, the increase of parameter χ_{21} means weakening hydrogen bonds in water.

In Fig.6 one can see the temperature dependencies of Raman spectra of the water-ethanol solvent with 70 vol. % of ethanol (Fig.6a) and of the BDND suspension in this solvent (Fig.6b). As it can be seen, with changing the temperature of water-ethanol solutions (Fig.6) the significant changes occur only in the Raman stretching band of hydroxyl groups O–H. The vibrational bands of molecular groups C–H of ethanol (2800-3100 cm^{-1}) undergo only small changes in intensity with changes in temperature, because in water-ethanol solutions only hydroxyl groups O–H can create hydrogen bonds.

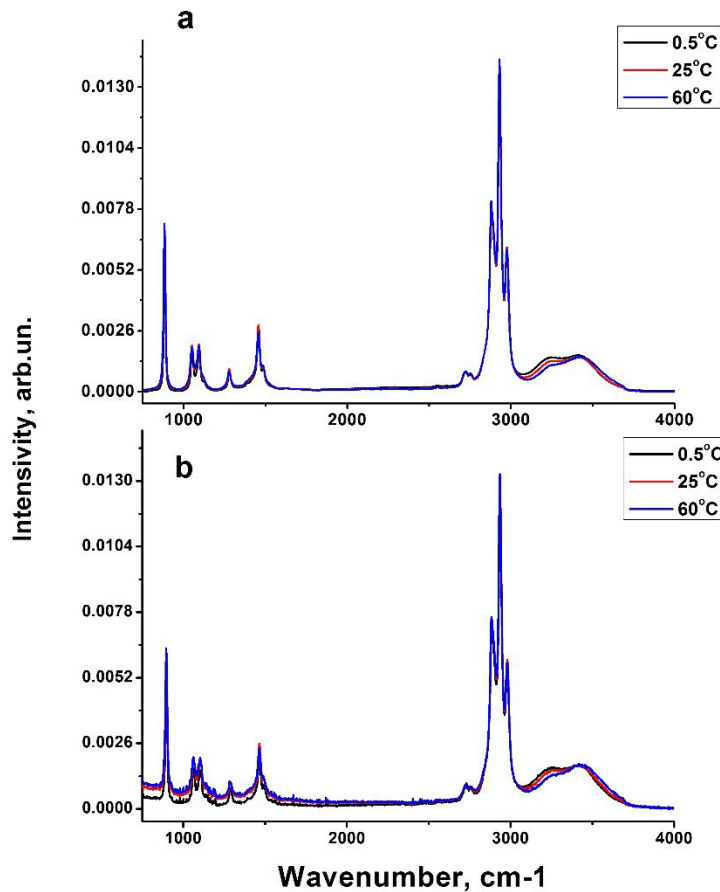


Figure 6. Raman spectra of water-ethanol solution with concentration of ethanol 70 vol. % (a) and of suspension of BDND in this solvent (b) at different temperatures.

For the Raman spectra of all the investigated solvents and BDND suspensions the temperature dependencies of the parameter χ_{21} were obtained. The values of the parameter χ_{21} obtained at temperatures 0.5°C, 10°C, 25°C, 45°C, 60°C are presented in Fig.7. The error of determination of the value of parameter χ_{21} is 0.02 arb. un.

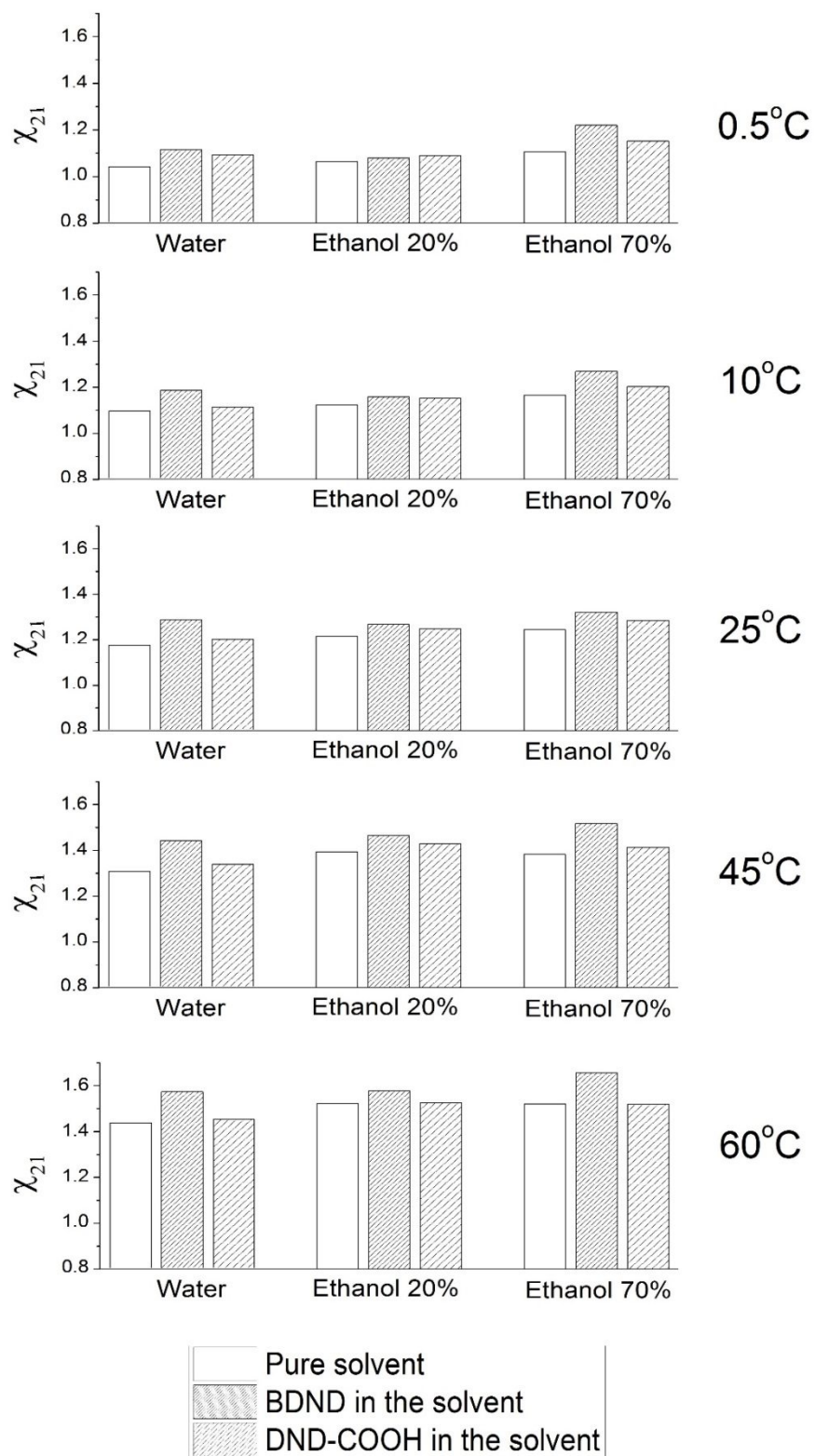


Figure 7. The values of the parameter χ_{21} obtained at different temperatures in the solvents with different concentration of ethanol.

In Fig.7 for comparison the values of parameter χ_{21} calculated for the Raman spectra of water and water-ethanol suspensions of detonation nanodiamond coated carboxyl groups (DND-COOH) and described in [36,37] are added. The data for water and water-ethanol suspensions of DND-COOH (size 10 nm, concentration 2 g/l) at different temperatures were obtained by us earlier; they are presented in publication [38].

According to the obtained results, the parameter χ_{21} increases with the increasing temperature for all solvents and NDs suspensions. This is understandable, because when water samples are heated the hydrogen bonds are weakened. However, in the presence of NDs in suspension the behavior of the dependence $\chi_{21}(T)$ is changed compared to that of the dependence $\chi_{21}(T)$ in the solvents. The weakening of hydrogen bonds in all NDs suspensions occurs faster: the values of χ_{21} at the same temperatures in the Raman spectra of NDs suspensions are higher than that in the Raman spectra of the solvents (Fig.7). It means that when NDs are injected into the solvent the orientation of OH groups is changed because of interactions of NDs with solvent molecules³⁹⁻⁴³, resulting the hydrogen bonds between them are weakened^{39,43}. However, the DND-COOH and BDND in water and water-ethanol solution with an ethanol content of 70 vol. % influence hydrogen bonds differently. If at the initial moment when NDs are injected into pointed solvents the both NDs weaken the hydrogen bonds at the same degree (Fig.7, 0.5°C, 10°C, 25°C), then under increasing the temperature in the DND-COOH suspensions the weakening of hydrogen bonds due to the interactions of DND-COOH with solvent molecules decreases. And in BDND suspensions the weakening of hydrogen bonds due to the interaction of BDND with solvent molecules, continues with the same degree. We explain this by significant difference between Zeta potentials of DND-COOH (-45 mV) and BDND (+7 mV). Due to the high Zeta potential the DND-COOH particles in protonic solvent form around themselves the thick shell of the hydroxyl groups of the solvent, which prevents a substantial impact of surface groups on the remaining volume of solvent and, consequently, prevents weakening of the hydrogen bonds in the remaining volume. A further weakening of hydrogen bonds (Fig.7) occurs only due to the heating of the sample. The BDND particles with the lower Zeta potential does not form around themselves a thick shell of the hydroxyl groups of the solvent, so their influence extends over a greater volume of solvent, providing a constant contribution of interactions of BDND with solvent molecules into the weakening of hydrogen bonds with increasing temperature (Fig.7). Noteworthy, that despite the fact that the concentration of BDND four times lower than the concentration of DND-COOH (0.5 against 2 g/l), the weakening of the hydrogen bonds caused by BDND is remarkably stronger.

In water-ethanol solution with an ethanol content of 20 vol. %, in which the hydrogen bonds are stronger than that in the other two investigated solvents, the both NDs behave in the same. The values of $\chi_{21}(T)$ for the solvent and suspensions of the DND-COOH and BDND are very close to each other (Fig.7). This means that the interactions of the NDs particles with molecules of water-ethanol solution with ethanol concentration 20 vol. % is not so strong to weaken the hydrogen bonds of the solvent. Therefore, suspended in water-ethanol solution with an ethanol content of 20 vol. % NDs not change the network of the hydrogen bonds in it.

4. CONCLUSIONS

In this work the influence of dispersed BDND on the hydrogen bonds in the protonic solvents was studied using Raman spectroscopy. The comparative analysis of the interactions of BDND and DND-COOH with solvents molecules was carried out.

The Raman spectra of water, water-ethanol solutions with the concentration of ethanol of 20 and 70 vol. % and of suspensions of BDND in these solvents (with the concentration of BDND 0.5 g/l) at the temperatures of 0.5°C, 10°C, 25°C, 45°C and 60°C were obtained experimentally. The analysis of temperature dependences of the quantitative characteristics of the stretching bands of OH groups of the solvents and the suspensions of BDND has shown that the BDND particles significantly weaken the hydrogen bonds in water and in water-ethanol solution with 70 vol. % ethanol content. In water-ethanol solution with 20 vol. % of ethanol in which the hydrogen bonds are stronger than that in water (the enthalpy of weakening/formation of hydrogen bonds in water-ethanol solution with 20 vol. % of ethanol on average by 6-7 % larger than that in water³⁰), BDND practically does not change the network of hydrogen bonds.

The obtained results were compared with similar results obtained for the suspensions of DND-COOH with concentration 2 g/l in the same solvents³⁸. It turned out that the DND-COOH particles in water and in water-ethanol solution with 70

vol. % of ethanol also weaken the hydrogen bond of solvents. However, their influence on the hydrogen bonds, even when DND-COOH concentration 4 times higher compared to the concentration of BDND, is much weaker than that of BDND. Moreover, the influence of DND-COOH decreases with increasing temperature. We explain this difference in the effect of the both NDs on the hydrogen bonds of solvents by the differences in their Zeta potentials. DND-COOH as BDND, change the network of the hydrogen bonds in water-ethanol solution with 20 vol. % ethanol content incidentally.

ACKNOWLEDGMENTS

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REFERENCES

- [1] Badziag, P., Verwoerd, W. S., Ellis, W. P. and Greiner, N. R., “Nanometer-sized diamonds are more stable than graphite”, *Nature* 343, 244 (1990).
- [2] Prabhakar, N., Nareoja, T., E. von Haartman, Karaman, D. S., Jiang, H., Koho, S., Dolenko, T., Hanninen, P., Vlasov, D. I., Ralchenko, V. G., Hosomi, S., Vlasov, I. I., Sahlgren, C. and Rosenholm, J. M., “Core-shell designs of photoluminescent nanodiamonds with porous silica coatings for bioimaging and drug delivery II: Application”, *Nanoscale* 5 (9), 3713-3722 (2013).
- [3] Rosenholm, J. M., Vlasov, I. I., Burikov, S. A., Dolenko, T. A. and Shenderova, O. A., “Nanodiamond-Based Composite Structures for Biomedical Imaging and Drug Delivery (Review)”, *J. of Nanoscience and Nanotechnology* 15, 959-971 (2015).
- [4] Krueger, A., “The structure and reactivity of nanoscale diamond”, *J. Mater. Chem.* 18, 1485 (2008).
- [5] Doherty, M. W., Manson, N. B., Delaney, P., Jelezko, F., Wrachtrup, J. and Hollenberg, L. C. L., “The Nitrogen-Vacancy Colour Centre in Diamond”, *Phys. Rep.* 528, 1–45 (2013).
- [6] Neu, E., Arend, C., Gross, E., Guldner, F., Hepp, C., Steinmetz, D., Zscherpel, E., Ghodbane, S., Sternschulte, H., Steinmüller-Nethl, D., et al., “Narrowband Fluorescent Nanodiamonds Produced from Chemical Vapor Deposition Films”, *Appl. Phys. Lett.* 98, 243107 (2011).
- [7] Aharonovich, I., Castelletto, S., Simpson, D. A., Su, C.-H., Greentree, A. D. and Praver, S., “Diamond-Based Single-Photon Emitters”, *Rep. Prog. Phys.* 74, 076501 (2011).
- [8] Vlasov, I. I., Shiryayev, A. A., Rendler, T., Steinert, S., Lee, S.-Y., Antonov, D., Voeroes, M., Jelezko, F., Fisenko, A. V., Semjonova, L. F., et al., “Molecular-Sized Fluorescent Nanodiamonds”, *Nat. Nanotechnol.* 9, 54–58 (2014).
- [9] Mochalin, V., Shenderova, O., Ho, D. and Gogotsi, Y., “The properties and applications of nanodiamonds”, *Nature Nanotech.* 7(1), 11-23 (2011).
- [10] Schrand, A. M., Ciftan Hens, S. A. and Shenderova, O. A., “Nanodiamonds Particles: Properties and Perspectives for Bioapplications”, *Crit. Rev. Solid State Mater. Sci.* 34 (1-2), 18-74 (2009).
- [11] Chen, M., Pierstorff, E. D., Lam, R., Li, S. Y., Huang, H., Osawa, E. and Ho, D., “Nanodiamond-mediated delivery of water-insoluble therapeutics”, *ASC Nano* 7 (3), 2012 (2009).
- [12] Liu, K. K., Zheng, W. W., Wang, C. C., Chiu, Y. C., Cheng, C. L., Lo, Y. S., Chen, C. and Chao, J. I., “Covalent linkage of nanodiamond-paclitaxel for drug delivery and cancer therapy”, *Nanotechnol.* 21, 315106 (2010).
- [13] Huang, L.-C. L. and Chang, H.-C., “Adsorption and immobilization of cytochrome c on nanodiamonds”, *Langmuir* 20 (14), 5879–5884 (2004).

- [14] Dolenko, T. A., Burikov, S. A., Laptinskiy, K. A., Laptinskaya, T. V., Rosenholm, J. M., Shiryaev, A. A., Sabirov, A. R. and Vlasov, I. I., "Study of adsorption properties of functionalized nanodiamonds in aqueous solutions of metal salts using optical spectroscopy", *J. Alloys Compd.* 586, S436-S439, (2014).
- [15] Ekimov, E. A., Sidorov, V. A., Bauer, E. D., Mel'nik, N. N., Curro, N. J., Thompson, J. D. and Stishov, S. M., "Superconductivity in diamond", *Nature* 428, 542-545 (2004).
- [16] Zhang, G., Turner, S., Ekimov, E. A., Vanacken, J., Timmermans, M., Samuely, T., Sidorov, V. A., Stishov, S. M., Lu, Y., Deloof, B., Goderis, B., Tendeloo, G., Vondel, J. and Moshchalkov, V. V., "Global and local superconductivity in boron-doped granular diamond", *Adv. Mater.* 26(13), 2034-2040 (2014).
- [17] Kim, D. Y., Yang, J. C., Kim, H. W. and Swain, G. M., "Heterogeneous Electron-Transfer Rate Constants for Ferrocene and Ferrocene Carboxylic Acid at Boron-Doped Diamond Electrodes in a Room Temperature Ionic Liquid", *Electrochim. Acta* 94, 49-56 (2013).
- [18] Channon, R. B., Newland, J. C., Bristow, A. W. T., Ray, A. D. and Macpherson, J. V., "Selective Detection of Hydrazine in the Presence of Excess Electrochemically Active Pharmaceutical Ingredients Using Boron Doped Diamond Metal Nanoparticle Functionalised Electrodes", *Electroanalysis* 25, 2613-2619 (2013).
- [19] Kato, H., Hees, J., Hoffmann, R., Wolfer, M., Yang, N., Yamasaki, S. and Nebel, C. E., "Diamond Foam Electrodes for Electrochemical Applications", *Electrochem. Commun.* 33, 88-91 (2013).
- [20] Ay, A., Swope, V. M. and Swain, G. M., "The Physicochemical and Electrochemical Properties of 100 and 500 nm Diameter Diamond Powders Coated with Boron-Doped Nanocrystalline Diamond", *J. Electrochem. Soc.* 155, B1013-B1022 (2008).
- [21] Neu, E., Guldner, F., Arend, C., Liang, Y., Ghodbane, S., Sternschulte, H., Nethl, D. S., Krueger, A. and Becher, C., "Low temperature investigations and surface treatments of colloidal narrowband fluorescent nanodiamonds", *J. Appl. Phys.* 113, 203507 (2013).
- [22] Ekimov, E. A., Kudryavtsev, O. S., Khomich, A. A., Lebedev, O. I., Dolenko, T. A. and Vlasov, I. I., "High-Pressure Synthesis of Boron-Doped Ultrasmall Diamonds from an Organic Compound", *Advanced Materials* 27(37), 5518-5522 (2015).
- [23] Salazar-Banda, G. R., Eguiluz, K. I. B. and Avaca, L. A., "Boron-doped diamond powder as catalyst support for fuel cell applications", *Electrochem. Commun.* 9(1), 59-64 (2007).
- [24] Kondo, T., Horitani, M., Sakamoto, H., Shitanda, I., Hoshi, Y., Itagaki, M. and Yuasa, M., "Screen-printed Modified Diamond Electrode for Glucose Detection Chem", *Lett.* 42(4), 352-354 (2013).
- [25] Mizuno, K., Miyashita, Y., Shindo, Y. and Ogawa, H., "NMR and FT-IR Studies of Hydrogen Bonds in Ethanol-Water Mixtures", *J. Phys. Chem.* 99 (10), 3225-3228 (1995).
- [26] Nishi, N., Takahashi, S., Matsumoto, M., Tanaka, A., Muraya, K., Takamuku, T. and Yamaguchi, T., "Hydrogen-Bonded Cluster Formation and Hydrophobic Solute Association in Aqueous Solutions of Ethanol", *J. Phys. Chem.* 99 (1), 462-468 (1995).
- [27] Wakisaka, A. and Matsuura, K., "Microheterogeneity of ethanol-water binary mixtures observed at the cluster level", *J. Mol. Liq.* 129 (1-2), 25-32 (2006).
- [28] Burikov, S., Dolenko, T., Patsaeva, S., Starokurov, Yu. and Yuzhakov, V., "Raman and IR spectroscopy research on Hydrogen bonding in waterethanol systems", *Mol. Phys.* 108 (18), 2427-2436 (2010).
- [29] Yang, D. and Wang, H., "Effects of Hydrogen Bonding on the Transition Properties of Ethanol-Water Clusters: A TD-DFT Study", *J. Clust. Sci.* 24, 485-495 (2013).

- [30] Dolenko, T. A., Burikov S. A., Dolenko, S. A., Efitorov, A. O., Plastinin, I. V., Yuzhakov, V. I. and Patsaeva, S. V., "Raman Spectroscopy of Water-Ethanol Solutions: the Estimation of Hydrogen Bonding Energy and the Evidence of Clathrate-like Structures", *J. of Phys. Chem. A* 119(44), 10806-10815 (2015).
- [31] Zhang, R. J., Lee, S. T. and Lam, Y. W., "Characterization of heavily boron-doped diamond films", *Diamond Relat. Mater.* 5, 1288-1294 (1996).
- [32] Bourgeois, E., Bustarret, E., Achatz, P., Omnès, F. and Blasé, X., "Impurity dimers in superconducting B-doped diamond: Experiment and first-principles calculations", *Phys. Rev. B* 74(9), 094509 (2006).
- [33] Chaplin, M., "Water structure and science", http://www1.lsbu.ac.uk/water/water_structure_science.html
- [34] Walrafen, G. E., Fisher, M. R., Hokmabadi, M. S. and Yang, W.-H., "Temperature dependence of the low- and high-frequency Raman scattering from liquid water", *J. Chem. Phys.* 85 (12), 6970-6982 (1986).
- [35] Dolenko, T. A., Churina, I. V., Fadeev, V. V. and Glushkov, S. M., "Valence band of liquid water Raman scattering: some peculiarities and applications in the diagnostics of water media", *J. Raman Spectrosc.* 31, 863-870 (2000).
- [36] Shenderova, O., Panich, A. M., Moseenkov, S., Hens, S. C., Kuznetsov, V. and Vieth, H.-M., "Hydroxylated Detonation Nanodiamond: FTIR, XPS, and NMR Studies", *J. Phys. Chem.* 115, 19005-19011 (2011).
- [37] Shenderova, O., Koscheev, A., Zaripov, N., Petrov, I., Skryabin, Y., Detkov, P., Turner, S. and Van Tendeloo, G.J., "Surface Chemistry and Properties of Ozone-Purified Detonation Nanodiamonds", *J. Phys. Chem. C* 115, 9827 (2011).
- [38] Dolenko, T., Burikov, S., Vervald, A., Shenderova, O., Podkopaev, D. and Vlasov, I., "Laser spectroscopy of molecular interactions of nanodiamonds with solvents", *J. of Phys. Chem. C*, 2015, submitted.
- [39] Dolenko, T. A., Burikov, S. A., Rosenholm, J. M., Shenderova, O. A. and Vlasov, I. I., "Diamond-water coupling effects in Raman and Photoluminescence spectra of nanodiamond colloidal suspensions", *J. Phys. Chem. C* 116, 24314-24319 (2012).
- [40] Zobel, M., Neder, R.B. and Kimber, S. A. J., "Universal solvent restructuring induced by colloidal nanoparticles", *Science* 347(6219), 292-294 (2015).
- [41] Petit, T., Pflüger, M., Tolksdorf, D., Xiao, J. and Aziz, E. F., "Valence holes observed in nanodiamonds dispersed in water", *Nanoscale* 7, 2987-2991 (2015).
- [42] Petit, T., Yuzawa, H., Nagasaka, M., Yamanoi, R., Osawa, E., Kosugi, N. and Aziz, E. F., "Probing Interfacial Water on Nanodiamonds in Colloidal Dispersion", *J.Phys.Chem.Lett.* 6, 2909 –2912 (2015).
- [43] Dolenko, T. A., Burikov, S. A., Laptinskiy, K. A., Rosenholm, J. M., Shenderova, O. A., Vlasov, I. I., "Carbon nanoparticles – solvent molecules interactions in Raman and Fluorescence spectra", *Phys. Status Solidi A* 212(11), 2512-2518 (2015).