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# The Chemistry of the Surface of Modified Detonation Nanodiamonds of Different Types

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**Abstract**—The influence of standard chemical treatment used to extract interstellar nanodiamonds from meteorites on the chemical composition of the surface of synthetic nanodiamonds with substantially different properties was studied by thermal desorption mass spectrometry and IR spectroscopy. The chemistry of the surface of nanodiamonds after treatment was substantially different from that of initial particles. The suggestion was made that the chemical structure of the surface of diamond particles in the interstellar space could be reconstructed from the data on meteorite diamonds. Mass spectrometric studies also gave information about possible mechanisms of the release of noble gases from meteorite diamonds at various temperatures.

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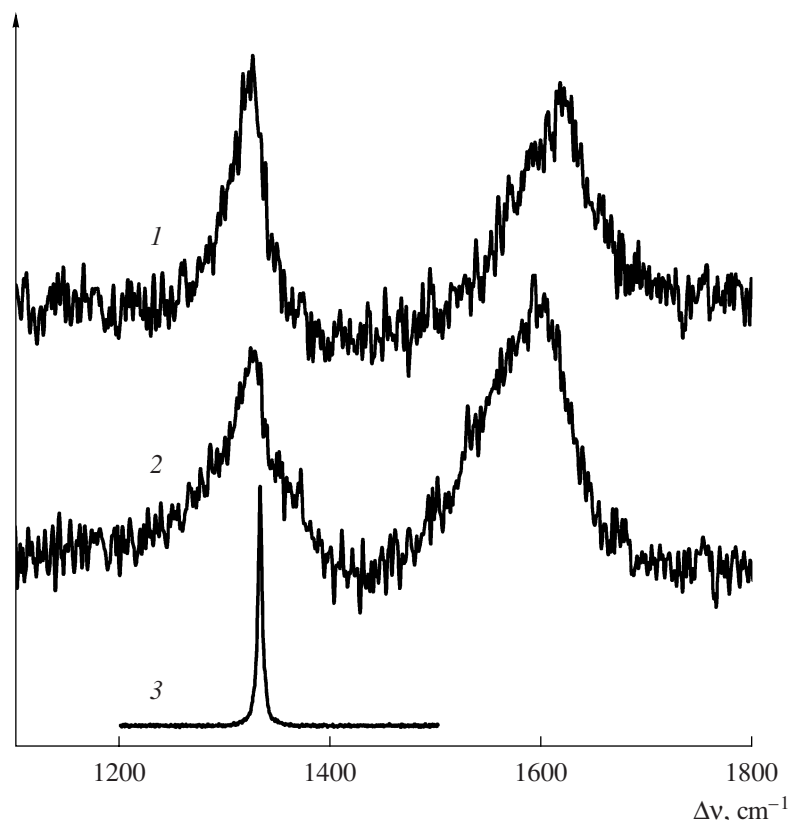
## INTRODUCTION

Diamond nanoparticles of mean size several nanometers were found in explosive detonation products [1] and primitive meteorites [2] about 20 years ago. Ultradisperse detonation diamonds (UDD) are a promising nanomaterial for technological applications [3]. The chemical properties of the surface of UDD to a great extent determine the behavior of nanodiamonds in various processes and are the object of extensive studies [4–8]. Meteorite nanodiamonds (MND) are of interest as the most widespread type of cosmic dust formed before the formation of the Solar system and containing information about processes in stars and circumstellar space [9]. The main efforts in studies of MND were directed toward isotope analysis of impurity elements (mainly, noble gases) [10, 11], which allows suggestions to be made about nuclear synthesis in stars [12, 13].

Much less progress was achieved in studies of the chemistry of the surface of interstellar nanodiamonds. Because of the high specific surface area of nanoparticles, such data would allow us to draw conclusions about physicochemical processes and their differences during the cosmic “life” of nanodiamonds found in various meteorites. The main reason for this is the substantial influence of the “hard” chemical procedure used to extract MND from meteorites on the chemistry of the surface of particles [14–17]. A similar dependence of the composition of the functional coating on the surface of nanodiamonds on the procedure for their technological purification is also characteristic of synthetic UDD [18–21]. With meteorite diamonds, the situation is aggravated by the use of different extraction procedures in different research centers. In one work, equal chem-

ical procedures were applied to two different meteorites, and the details of the IR spectra of the surface groups on extracted MND were different [16]. For this reason, we cannot beforehand exclude the existence of a relation between the surface properties of nanodiamonds before and after chemical extraction (the memory effect).

Such a possible relation cannot be established experimentally for meteorite diamonds whose initial properties can be different. In the present work, this difficulty was overcome by the use of UDD as synthetic analogues of MND. A similar approach was earlier successfully applied in experiments on ion implantation [22]. The distinguishing feature of this work is a study of the influence of the *same* chemical procedure used to extract diamonds from meteorites on the chemistry of the surface of nanodiamonds of *different types* with substantially *different* and characterized surface properties. This approach allows us to determine whether or not it makes sense to study the chemistry of the surface of extracted MND from the point of view of cosmochemistry and find possible methods for the reconstruction of the initial surface properties formed on the surface of interstellar diamonds in space from the data of laboratory studies of MND. The chemistry of the surface of UDD before and after chemical treatment was studied using the mutually complementary IR spectroscopy and thermal desorption mass spectrometry methods, whose combination was successfully applied to study the surface of disperse diamonds [23], including nanodiamonds [24, 25]. The thermal desorption mass spectrometry data also allowed information to be obtained about possible mechanisms of noble gas release from meteorite diamonds at various temperatures.



**Fig. 1.** Raman spectra of detonation nanodiamonds (1) K-2 and (2) CH-7 and (3) volume diamond;  $\Delta\nu$  is the Raman shift, excitation wavelength is 514 nm.

## EXPERIMENTAL

We used UDD samples of two types (CH-7 and K-2), which differed in details of their explosive synthesis (explosion in frozen water and carbon dioxide, respectively) and purification (the use of chromic and boric anhydrides, respectively). The specific surface area measured from nitrogen adsorption was 290–310 m<sup>2</sup>/g for both samples. The Raman spectra of the samples did not reveal significant differences between their crystal structures (Fig. 1). The width and position of the diamond peak at 1324 cm<sup>-1</sup> (*sp*<sup>3</sup> hybridization) can be used to estimate [26] the mean size of diamond particles (4–5 nm in both samples). This is in agreement with the data of direct mass spectrometric measurements of the mean size of CH-7 particles (3.9 nm) [27]. The intensity of the peak at 1600 cm<sup>-1</sup> (Fig. 1) is indicative of a somewhat higher content of nondiamond carbon (*sp*<sup>2</sup> hybridization) in CH-7 compared with K-2.

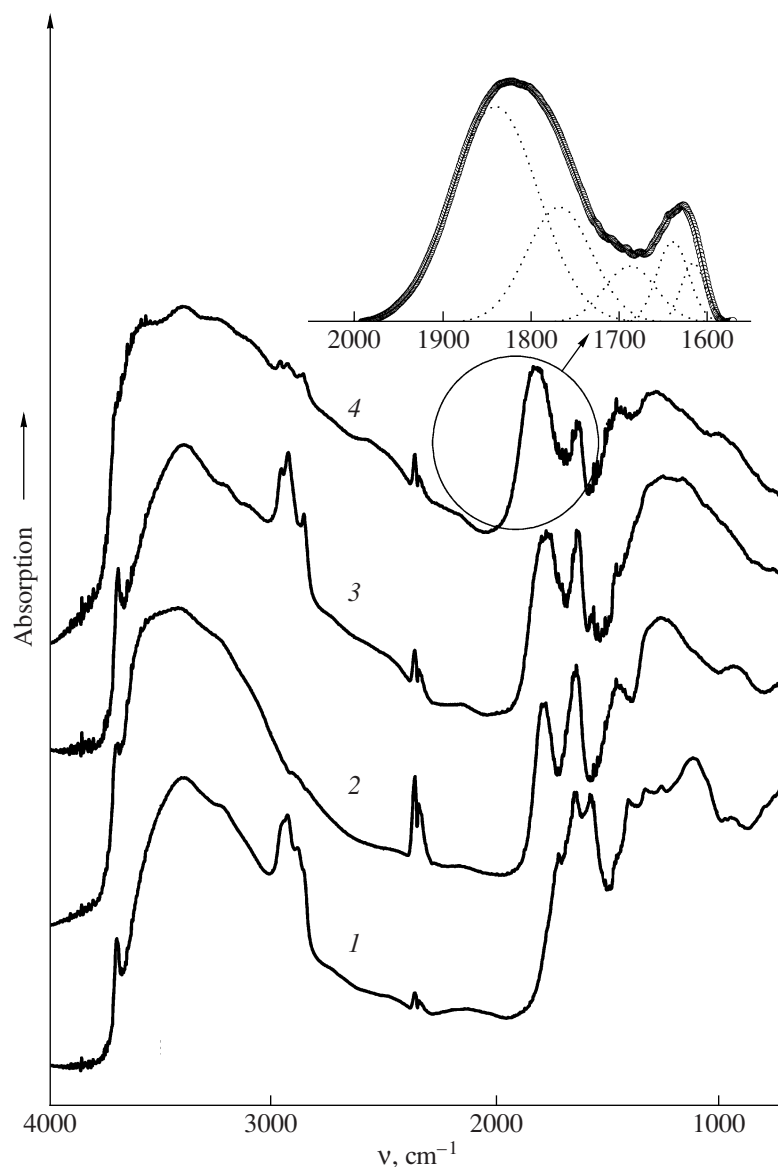
UDD of both types were subjected to identical multistage chemical treatment in acid media used for the extraction of nanodiamonds from meteorites [28]. The composition and structure of the functional surface groups on UDD before and after chemical treatment were studied using Fourier transform IR spectroscopy (4000–700 cm<sup>-1</sup>) under diffuse reflectance conditions and thermal desorption mass spectrometry. The thermal

desorption mass spectra were obtained on a quadrupole mass spectrometer over the mass interval 2–100 amu during programmed heating of a sample (~1 mg) in a vacuum at a rate of 15 K/min to 1200°C; desorption products were continuously pumped off. In some experiments, samples were heated to 1600°C.

## RESULTS AND DISCUSSION

### IR Spectroscopy

Like the spectra of meteorite diamonds [16], the IR spectra of UDD of both types (Fig. 2) were characterized by the presence of the main absorption bands near 3600–3000 and 1620 cm<sup>-1</sup> (OH groups), 3000–2800 cm<sup>-1</sup> (CH<sub>x</sub>), 1800–1700 cm<sup>-1</sup> (CO), and 1400–700 cm<sup>-1</sup> (N, CN, CO, CH groups, etc.). These bands are typical of the surface functional groups of UDD of other types [4, 19–21]. The main differences between the spectra of CH-7 and K-2 were the difference in the intensity of the 3000–2800 cm<sup>-1</sup> band, the shape of the complex band at 1400–700 cm<sup>-1</sup>, and the position and intensity of the 1800–1700 cm<sup>-1</sup> band characterizing the configuration of surface C–O bonds (ketone groups, carboxyl anhydrides, and lactones [23]). The band at 1570 cm<sup>-1</sup> is only characteristic of CH-7; it is related to unidentified surface groups (possibly, CNH groups



**Fig. 2.** IR spectra of UDD of different types: (1) CH-7 before chemical treatment, (2) K-2 before treatment, (3) CH-7 after treatment, and (4) K-2 after treatment. An example of the deconvolution of part of a spectrum into elementary absorption bands for K-2 after chemical treatment is shown in the inset.

[29]). It follows that the difference between the CH-7 and K-2 samples mainly reduces to differences in the concentration of CH groups and the “degree of surface oxidation” characterized by the peak at 1700–1800  $\text{cm}^{-1}$ .

The IR spectra of CH-7 and K-2 after chemical treatment were closer to each other (Fig. 2), but certain differences persisted. In particular, the absorption band of CH groups (3000–2800  $\text{cm}^{-1}$ ) remained in the spectrum of CH-7 after treatment. In addition, absorption bands of oxygen-containing groups (1715 and 1780  $\text{cm}^{-1}$  for CH-7 and K-2, respectively), although shifted after treatment, did not become identical (1760 and 1810  $\text{cm}^{-1}$  for CH-7 and K-2, respectively). The deconvolution of the band at 1800–1700  $\text{cm}^{-1}$  into

Gauss components showed the presence of several elementary bands with maxima close to 1700, 1750, and 1850  $\text{cm}^{-1}$  (see inset in Fig. 1), which could be assigned to ketone (carbonyl), lactone, and carboxyl anhydride groups, respectively, on the surface of diamond [23]. The results of mathematical processing of this band for samples before and after chemical treatment are presented in Table 1.

These results lead us to suggest that carbonyl groups (low degree of oxidation) predominate in initial CH-7. More oxidized K-2 is characterized by the predominance of lactone groups. Chemical treatment increases the degree of surface oxidation and causes the appearance of carboxyl anhydride groups, but the final oxida-

tion state depends on the initial UDD properties. Interestingly, in the spectra of cosmic nanodiamonds extracted from two different meteorites “Allende” and “Murchison” using the same chemical procedure, the IR absorption bands of oxygen-containing groups had different positions (1759 and 1780  $\text{cm}^{-1}$ ) [16]; the authors, however, did not pay attention to this circumstance.

### Mass Spectrometry

The main products of thermal desorption from the surface of UDD are  $\text{H}_2\text{O}$  (100–600°C), hydrocarbons (200–400°C),  $\text{CO}_2$  (200–600°C),  $\text{CO}$  (400–1000°C), and  $\text{H}_2$  (above 800°C). The temperature profiles of desorption and mass spectra of the main volatile products for CH-7 are shown in Fig. 3. Different initial samples had different intensities and shapes of the temperature profiles of the desorption of  $\text{C}_x\text{H}_y$ ,  $\text{CO}_2$ , and  $\text{CO}$  (Fig. 4), in conformity with the IR spectral data on these samples. An increased concentration of hydrocarbons on CH-7 is likely related to the special features of chemical purification (with ion-exchange resins) used by the manufacturer. The  $\text{CO}$  and  $\text{CO}_2$  desorption profiles are formed as a result of the thermal destruction of surface oxygen-containing groups and are determined by their structure [23]. The larger the degree of surface oxidation, the lower the temperature of  $\text{CO}$  desorption maximum and the larger the amount of desorbed carbon oxides. These profiles underwent noticeable changes as a result of chemical treatment (Fig. 4), which was evidence of the additional oxidation of the surface of UDD. In particular, after chemical treatment, the  $\text{CO}$  desorption maxima shifted to lower temperatures, and the total amount of desorbed carbon oxides increased (Table 2). As with the IR spectra, we, however, observed a memory effect with respect to the chemical properties of the surface in the initial state.

Another important observation is the detection of chlorine desorbed in the form of  $\text{HCl}$  over the temperature range 400–700°C (Fig. 4). Chlorine was likely introduced with chlorine-containing acids used in chemical treatment. The contents of chlorine in the treated CH-7 and K-2 samples differed by more than an order of magnitude (Table 2). This is evidence of substantially different chemical activities of nanodiamonds of different types.

The IR spectroscopy and thermal desorption mass spectrometry data show that, although the extraction procedure influences the chemistry of the surface of synthetic nanodiamonds, the degree of modification of certain surface characteristics ( $\text{CH}_x$  and  $\text{CO}$  groups) after chemical treatment depends on the initial properties of untreated UDD. Suppose that the same is true of meteorite nanodiamonds. Our results then show that the real chemistry of interstellar diamonds can in principle be reproduced to a certain degree from the data on chemically extracted meteorite diamonds. Such studies would allow us to determine possible differences in the

**Table 1.** Calculated intensities (areas) of IR spectrum bands at 2000–1650  $\text{cm}^{-1}$  for various UDD samples; the positions of band maxima ( $\text{cm}^{-1}$ ) are given in parentheses

Sample	Ketone and carbonyl groups	Lactone groups	Carboxyl anhydride
CH-7	3.3 (1721)	0.48 (1771)	–
K-2	–	10.8 (1774) 3.1 (1807)	0.26 (1846)
CH-7-chem	1.8 (1701)	2.36 (1744) 9.1 (1790)	1.6 (1841)
K-2-chem	1.35 (1690)	3.5 (1767)	8.6 (1839)

**Table 2.** Parameters characterizing thermal desorption from various UDD samples under linear heating conditions

Sample	$T_{\text{max}}(\text{CO})$	$I_{\text{max}}(\text{CO})$	$I_{\text{total}}$	$I_{\text{max}}(\text{HCl})$
CH-7	750	64	100	–
K-2	570	246	220	–
CH-7-chem	590	108	120	25
K-2-chem	530	310	270	0.3

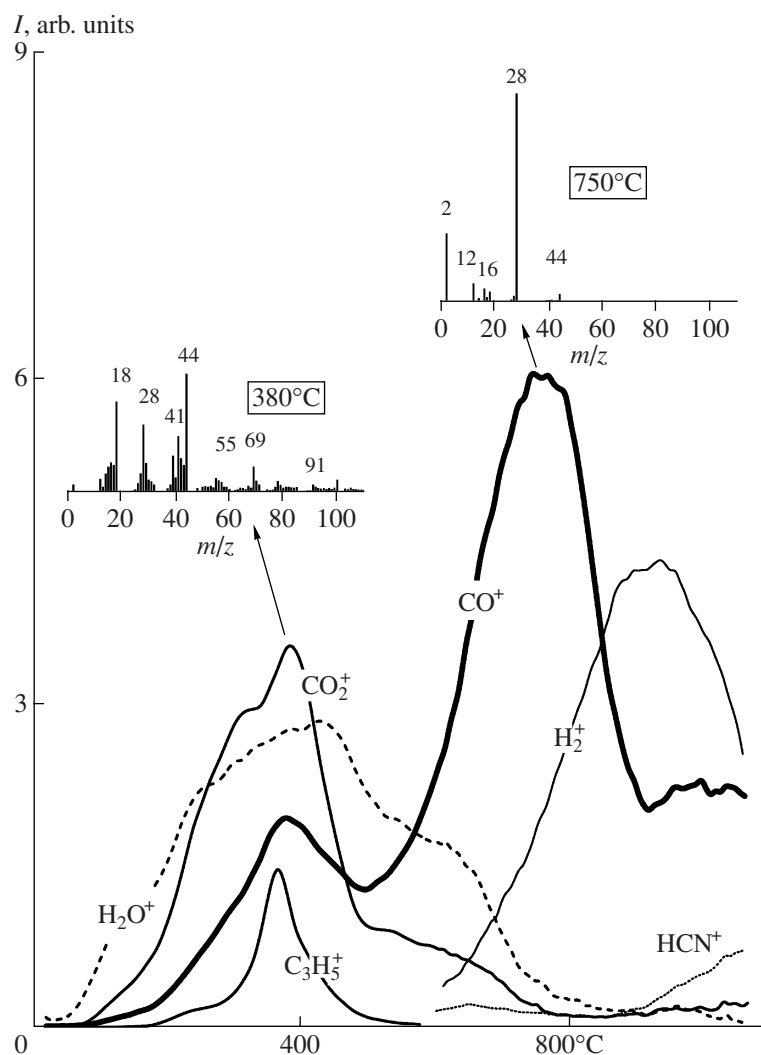
Note:  $T_{\text{max}}(\text{CO})$  is the temperature corresponding to the highest rate of  $\text{CO}$  desorption, °C;  $I_{\text{max}}(\text{CO})$  and  $I_{\text{max}}(\text{HCl})$  are the highest  $\text{CO}$  and  $\text{HCl}$  desorption rates, arb. units; and  $I_{\text{total}}$  is the total amount of volatile products desorbed up to 800°C, arb. units.

chemical properties of meteorite diamonds from different meteorites, which would be evidence of different sources of the formation and different chemical “history” of interstellar diamonds.

Another important consequence of the results obtained is the conclusion of substantially different chemical activities of UDD of different types in reactions with chemical substances used in chemical extraction. CH-7 and K-2 were synthesized under substantially different conditions. The explosive synthesis conditions can influence both the shape [30] and structure [26, 31] of the surface shell of nanodiamonds. On the other hand, the chemical activity of the surface of a diamond in various media depends on the atomic structure of the surface [32, 33]. It can therefore be suggested that the difference in chemical activity between UDD of different types is caused by “inherited” properties formed at the stage of the synthesis of nanodiamonds.

### Thermal Desorption of Active and Noble Gases

The data on the chemical composition of volatile products desorbed from UDD during heating (the thermal desorption mass spectrometry data) were used to establish the role played by the chemistry of surfaces in the thermal desorption of noble gases from nanodiamonds, which was necessary for the determination of thermal desorption mechanisms at low and high tem-



**Fig. 3.** Temperature profiles of the thermal desorption of various components and mass spectra of volatile products at various temperatures for CH-7 in the initial state;  $I$  is the rate of desorption.

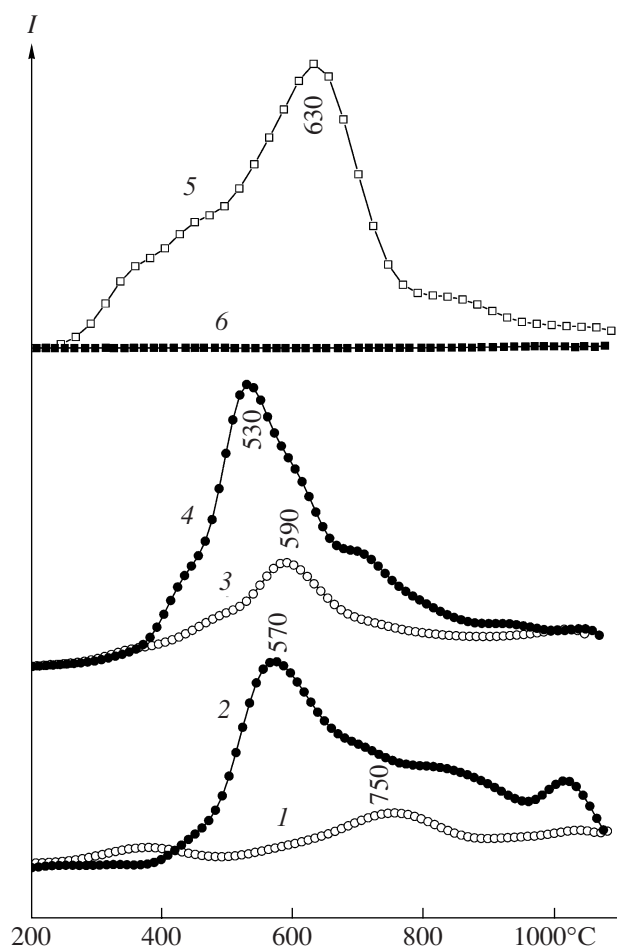
temperatures and interpretation of data obtained by analyzing noble gases in meteorite diamonds [10, 11]. For this purpose, we developed a procedure for simultaneously recording active and noble gases under the conditions of programmed heating up to 1600°C [34]. We studied CH-7o and CH-7x samples with substantially different surface properties. The implantation of argon ions of a 1 keV energy at equal doses was performed as in [22].

The temperature profiles of the release of implanted argon are bimodal and have maxima close to 500–800 and 1200–1500°C (Fig. 5), as with noble gases from meteorite diamonds [10]; they weakly depend on the type of UDD. At the same time, the thermal desorption curves of active gases ( $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{C}_x\text{H}_y$ , etc.) shown in Fig. 5 in the form of the total mass spectrometer ion current are substantially different for the two samples. There is no correlation between the low-temperature desorption of argon and active gases. It follows that the low-temperature desorption of noble gases from nano-

diamonds is not related to the destruction of the surface layer accompanied by the desorption of active gases. At the same time, the high-temperature desorption of argon is accompanied by the desorption of nitrogen (measured in mass spectra in the form of the  $\text{N}^{2+}$  doubly charged ion), which is a bulk impurity in UDD.

Our data substantiate the suggested model of the formation of the temperature profiles of the release of noble gases from meteorite diamonds. According to this model, noble gas atoms are trapped in diamonds by defects of two types with substantially different binding energies [35, 36]. The low-temperature desorption of noble gases is caused by the thermal activation of trapped atoms with a low binding energy. High-temperature desorption is determined by the release of strongly bound noble gas atoms caused by diamond structure destruction (“graphitization”), which develops from the surface toward the center of a diamond nanoparticle [37]. Nitrogen high-temperature desorp-



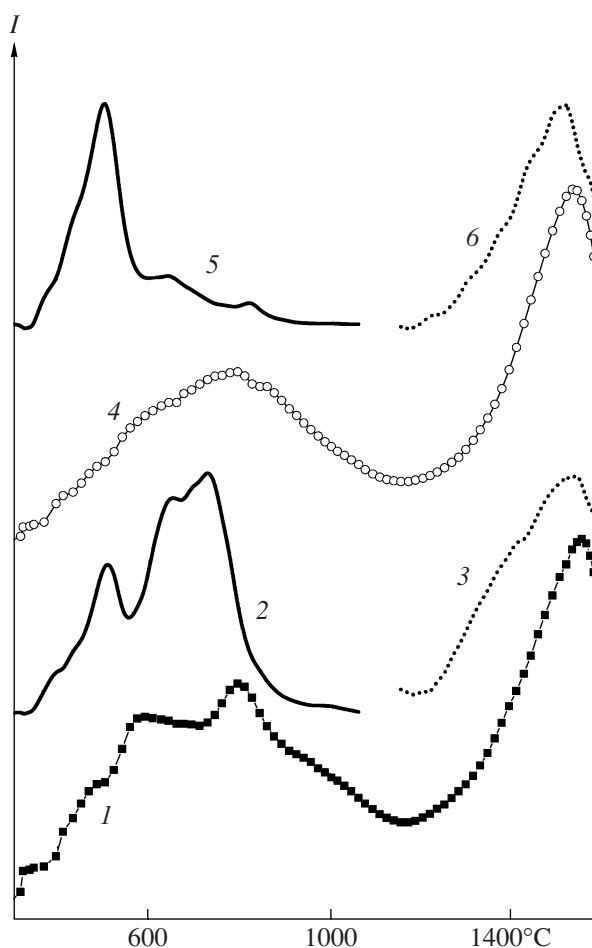


**Fig. 4.** Influence of chemical treatment on the temperature profiles of (1–4) CO ( $m/z = 28$ ) and (5, 6) HCl ( $m/z = 36$ ) thermal desorption from (1, 3, 5) CH-7 and (2, 4, 6) K-2 (1, 2) before treatment and (3, 5, 4, 6) after treatment.

tion profiles can be used to quantitatively estimate the effectiveness of this process. This model can be used to evaluate the energies of ions introduced into cosmic nanodiamonds in the circumstellar space from the laboratory analysis data on meteorite diamonds [36].

## CONCLUSIONS

To summarize, although the chemical procedure used in the extraction of cosmic nanodiamonds from meteorites modifies the composition and structure of surface functional groups, some special features can in part remain unchanged ( $\text{CH}_x$  groups). Changes in the chemistry of the surface (CO and Cl groups) as a result of the extraction procedure are controlled by the initial properties of the surface. This means that the extraction procedure does not completely wipe off information about the chemical properties of the surface of nanodiamonds in interstellar space. The use of a special set of synthetic UDD with different chemical properties in



**Fig. 5.** Thermal desorption of implanted argon (1 keV) and active gases from UDD CH-7o and CH-7x; (1) Ar from CH-7x, (2) total release of active gases from CH-7x, (3) nitrogen from CH-7x, (4) Ar from CH-7o, (5) total release of active gases from CH-7o, and (6) nitrogen from CH-7o.

such experiments allows “calibration curves” to be constructed, which can be used to reconstruct some special features of the chemical structure of the surface of diamond particles in interstellar space. This in turn can be used to draw conclusions about chemical processes in circumstellar space. In addition, it was shown that simultaneous study of the thermal desorption of noble and active (nitrogen) gases allows the energy of ionic implantation of noble gases into nanodiamonds to be estimated.

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## REFERENCES

1. A. I. Lyamkin, E. A. Petrov, A. P. Ershov, et al., Dokl. Akad. Nauk SSSR **302** (3), 611 (1988).

2. R. S. Lewis, T. Ming, J. F. Wacker, et al., *Nature (London)* **326**, 160 (1987).
3. V. Yu. Dolmatov, *Usp. Khim.* **70** (7), 607 (2001).
4. I. I. Kulakova, *Fiz. Tverd. Tela (St. Petersburg)* **46** (4), 621 (2004) [*Phys. Solid State* **46** (4), 636 (2004)].
5. Y. Liu, Zh. Gu, J. L. Margrave, and V. N. Khabashesku, *Chem. Mater.* **16**, 3924 (2004).
6. B. V. Spitsyn, J. L. Davidson, M. N. Gradoboev, et al., *Diamond Relat. Mater.* **15**, 296 (2006).
7. M. A. Ray, O. Shenderova, W. Hook, et al., *Diamond Relat. Mater.* **15**, 1809 (2006).
8. G. V. Lisichkin, V. V. Korol'kov, B. N. Tarasevich, et al., *Izv. Akad. Nauk, Ser. Khim.*, No. 12, 2130 (2006).
9. U. Ott, *Nature (London)* **364**, 25 (1993).
10. G. R. Huss and R. S. Lewis, *Meteoritics* **29**, 791 (1994).
11. A. V. Fisenko and L. F. Semenova, *Geokhimiya*, No. 2, 131 (2005) [*Geochem. Int.* **43** (2), 105 (2005)].
12. D. D. Clayton, *Astrophys. J.* **340**, 613 (1989).
13. U. Ott, *Astrophys. J.* **463**, 344 (1996).
14. H. Mutschke, J. Dorschner, Th. Henning, et al., *Astrophys. J.* **454**, L157 (1995).
15. H. G. M. Hill, L. B. d'Hendecourt, C. Perron, and A. P. Jones, *Meteorit. Planet. Sci.* **32**, 713 (1997).
16. A. Braatz, U. Ott, Th. Henning, et al., *Meteorit. Planet. Sci.* **35**, 75 (2000).
17. A. C. Andersen, U. G. Jrgensen, F. M. Nicolaisen, et al., *Astron. Astrophys.* **330**, 1080 (1998).
18. V. L. Kuznetsov, M. N. Aleksandrov, I. V. Zagoruiko, et al., *Carbon* **29**, 665 (1991).
19. T. Jiang and K. Xu, *Carbon* **33**, 1663 (1995).
20. E. Mironov, A. Koretz, and E. Petrov, *Diamond Relat. Mater.* **11**, 872 (2002).
21. D. Mitev, R. Dimitrova, M. Spassova, et al., *Diamond Relat. Mater.* **16**, 776 (2007).
22. A. P. Koscheev, M. D. Gromov, R. K. Mohapatra, and U. Ott, *Nature (London)* **412**, 615 (2001).
23. T. Ando, K. Yamamoto, M. Ishii, et al., *J. Chem. Soc., Faraday Trans.* **89**, 3635 (1993).
24. A. P. Koscheev, I. A. Panin, and U. Ott, *Meteorit. Planet. Sci.* **33**, A88 (1998).
25. Yu. V. Butenko, V. L. Kuznetsov, E. A. Paukshtis, et al., *Fullerenes, Nanotubes, Carbon Nanostructures* **14**, 557 (2006).
26. A. E. Aleksenskii, M. V. Baidakova, A. Ya. Vul', et al., *Fiz. Tverd. Tela (St. Petersburg)* **39**, 1125 (1997).
27. J. Maul, E. Marosits, Ch. Sudek, et al., *Phys. Rev. B: Condens. Matter* **72**, 245401 (2005).
28. S. Merchel, U. Ott, S. Herrmann, et al., *Geochim. Cosmochim. Acta* **67**, 4949 (2003).
29. T. Jiang, K. Xu, and S. Ji, *J. Chem. Soc., Faraday Trans.* **92**, 3401 (1996).
30. P. Chen, F. Huang, and Sh. Yun, *Carbon* **41**, 2093 (2003).
31. K. Iakoubovskii, M. V. Baidakova, B. H. Wouters, et al., *Diamond Relat. Mater.* **9**, 861 (2000).
32. C.-L. Cheng, H.-C. Chang, J.-C. Lin, et al., *Phys. Rev. Lett.* **78**, 3713 (1997).
33. F. K. de Theije, O. Roy, N. J. van der Laag, and W. J. P. van Enckevort, *Diamond Relat. Mater.* **9**, 929 (2000).
34. A. P. Koscheev, M. D. Gromov, N. V. Zaripov, and U. Ott, *Meteorit. Planet. Sci.* **39**, A55 (2004).
35. A. P. Koscheev and U. Ott, *Meteorit. Planet. Sci.* **35**, A92 (2000).
36. A. P. Koscheev, M. D. Gromov, P. V. Gorokhov, et al., *Meteorit. Planet. Sci.* **40**, A87 (2005).
37. V. L. Kuznetsov, A. L. Chuvilin, Yu. V. Butenko, et al., *Chem. Phys. Lett.* **222**, 343 (1994).