

**SURFACE CHEMISTRY OF CHEMICALLY TREATED DIAMOND NANOGRAINS.** A. P. Koscheev<sup>1</sup>, A. E. Serzhantov<sup>1</sup>, S. Merchel<sup>2\*</sup>, U. Ott<sup>2</sup>, O. Guillois<sup>3</sup>, and C. Reynaud<sup>3</sup>, <sup>1</sup>Karpov Institute of Physical Chemistry, Vorontsovo Pole 10, 105064, Moscow, Russia, (koscheev@cc.nifhi.ac.ru), <sup>2</sup>Max-Planck-Institut für Chemie, Becherweg 27, D-55128 Mainz, Germany, <sup>3</sup>Service des Photons, Atomes et Molécules, CEA-Saclay, 91191 Gif/Yvette Cedex, France. \*present address: BAM, D-12205, Berlin, Germany.

**Introduction:** Diamond nanograins found in meteorites [1] belong to the family of presolar grains and hence can provide a record of nuclear and chemical processes in stars and in the interstellar medium [2]. Main efforts in their study have been directed towards the isotopic analysis of trace elements (primarily, noble gases) [3] and the results allow to draw conclusions regarding stellar nucleosynthesis [2,3]. Much less progress has been achieved in the field of surface chemistry of interstellar diamonds. Such information is important, however, for at least two reasons: 1) Diamond nanograins may be responsible for some of the IR absorption features observed in spectra of the interstellar medium [4,5], mainly due to diamond surface species and defects because pure diamond is inactive in IR region. To determine the location of origin of interstellar diamond present in space using astrophysical observations it is necessary to know their optical properties and, hence, their surface chemistry; 2) Some surface chemical features acquired during the long journey of the diamonds from the stellar source region to the laboratory may have survived and carry a signature of chemical processes in the interstellar medium, just as the noble gases in nanodiamonds are the “fingerprints” of nuclear processes in stars.

Several attempts have been undertaken trying to find a correlation between IR features of the interstellar medium and meteoritic diamonds [6-9]. A main result of these studies is that many of surface IR-active chemical features are modified by the chemical procedure used to extract nanodiamonds from meteorites. This fact can explain differences in the published IR spectra of nanodiamonds extracted from the same meteorite using different extraction methods. However, in one report the same chemical procedure was applied to the two different meteorites and fine details of IR spectra of extracted nanodiamonds were not the identical in the two cases [8]. This fact stimulated us to study in details the effect of chemical extraction procedure on the chemical features of nanodiamond surfaces. Such a study may help to understand if there is a relation between the surface chemistry of nanodiamonds before and after chemical isolation (the memory effect) and, if so, to find a way how to extract the initial chemistry of meteoritic diamonds related to their chemistry in space.

**Experimental:** We used ultradispersed detonation diamonds (UDD) as analogs of meteoritic ones in laboratory simulation experiments - an approach which was successfully applied in earlier studies [10-12]. This allows to eliminate the problems of both the limited available amount of meteoritic diamonds and the characterization of their initial properties. Four samples with different surface chemistry produced in different research centers were used as starting material. All had the same mean size of 3-4 nm and differed mainly in the impurity levels and

in the concentrations and structures of surface functional groups [10]. All samples were treated by the same chemical procedure used to separate meteoritic diamonds including: 1) treatment by concentrated mineral-acids; 2) washing in HCl solution; 3) oxidation in HClO<sub>4</sub>; 4) cycles of washing in HCl; 5) drying. The surface chemistry of the samples both before and after chemical treatment was studied by means of IR spectroscopy and thermodesorption mass spectrometry (TDMS) which are complementary methods to study the surface species on diamond powders [13] including nanodiamonds [10]. FTIR absorption spectra (4000-400 cm<sup>-1</sup>) were measured at room temperature in the reflection mode, in some cases CsJ pellets were used in the transparency mode. Thermodesorption mass spectra of volatiles were measured by quadrupole mass spectrometry during linear heating (15 °C/min) of the sample up to 1200 °C in vacuum under permanent evacuation.

**Results and Discussion:** IR spectra of four different samples of UDD before treatment bear a general resemblance to known spectra of meteoritic diamonds [8]. The main bands appear near 3600-3000 cm<sup>-1</sup> (OH-groups), 3000-2800 cm<sup>-1</sup> (CH<sub>x</sub>), 1850-1700 cm<sup>-1</sup> (CO), 1620 cm<sup>-1</sup> (OH), and as a wide complex band at 1400-700 cm<sup>-1</sup> (N, CN, CO, CH etc.).

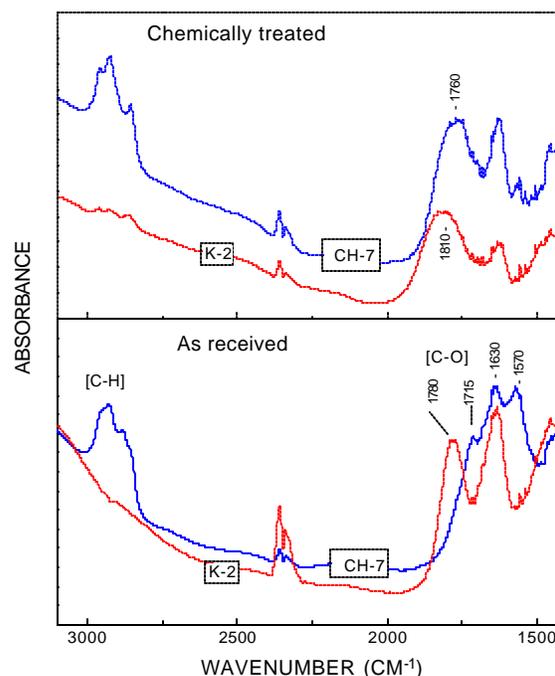


Fig. 1. The parts of IR spectra of various UDD (CH-7 and K-2) before and after chemical treatment.

The main differences between the various samples of UDD were the intensity of the 3000-2800  $\text{cm}^{-1}$  band, the shape of the complex 1400-700  $\text{cm}^{-1}$  band and pronounced differences in intensity and position of the 1800-1700  $\text{cm}^{-1}$  band related to the configuration of the surface C-O bonds (ketone, lactone or carboxylic anhydride structure [13]) and hence to the oxidation state of the surface. Fig. 1 shows 1400-3100  $\text{cm}^{-1}$  region of IR spectra of two different UDD samples. Note that the band at 1570  $\text{cm}^{-1}$  of sample CH-7 was not observed in other samples of UDD and may be caused by some unidentified impurity. (This band was sharply reduced when measuring the spectra of UDD CH-7 in CsJ pellet).

Some of these differences between IR spectra of different samples became less pronounced but were still observable after chemical treatment. Specifically, the intensity of the  $\text{CH}_x$ -band at 3000-2800  $\text{cm}^{-1}$  in CH-7 sample survived the chemical treatment although slightly changed in shape (Fig. 1). We suggest, therefore, that at least some of the C-H bonds in nanodiamonds can survive the chemical attack.

The other important feature is that the positions of CO-bands near 1800-1700  $\text{cm}^{-1}$  (1715 and 1780  $\text{cm}^{-1}$  for CH-7 and K-2, resp.) while being displaced to the higher wavenumbers after chemical treatment, nevertheless were not identical for different samples (after treatment: 1760 and 1810  $\text{cm}^{-1}$  for CH-7 and K-2, resp.). In other words, the chemical treatment caused additional oxidation of diamond surfaces but the final state seems to depend on the initial one.

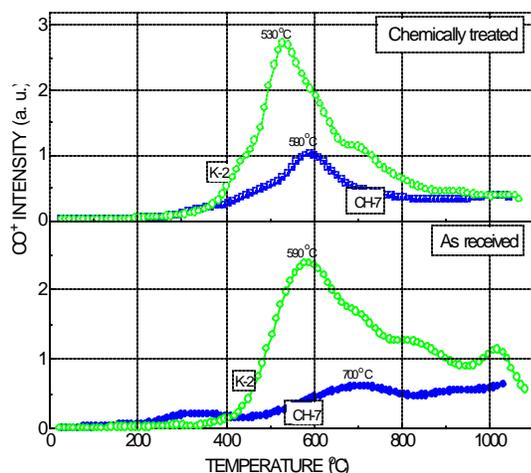


Fig. 2. The effect of chemical treatment on the TDMS pattern of CO ( $m/e=28$ ) release from UDD of various types.

TDMS study of as received samples showed release of  $\text{H}_2\text{O}$  (100-600  $^{\circ}\text{C}$ ),  $\text{CO}_2$  (200-600  $^{\circ}\text{C}$ ), CO (400-1000  $^{\circ}\text{C}$ ) and  $\text{H}_2$  (above 800  $^{\circ}\text{C}$ ) as main components. No straight correlation was observed between the amount of released hydrogen and the intensity of the CH-band in the IR spectra suggesting that much of the hydrogen in dia-

monds is not IR active [14]. Different samples differed mainly in the temperature profiles (both intensity and shape) of CO (Fig. 2) and  $\text{CO}_2$  release, in accordance with IR data. The higher the oxidation level of the surface is, the lower is the temperature of maximum of  $\text{CO}_x$  release and the larger is the amount of released gas.

The profiles were modified substantially by chemical treatment indicating additional oxidation of the surface, but again - as in the case of the CO-band in IR-spectra, but even more pronounced - there was a "memory" of the initial surface properties (Fig. 2). The IR and TDMS studies of UDD CH-7 thermally oxidized in oxygen showed that the chemical treatment was equivalent to the heating of the sample in air at 370-380  $^{\circ}\text{C}$  for 30 min, except that in the latter case the CH-band was reduced substantially.

**Conclusions:** Our results strongly indicate that, even though the chemical extraction procedure affects the surface chemistry of synthetic diamond nanograins, some surface features can either survive partially ( $\text{CH}_x$ -groups) or vary in a manner controlled by the initial state (CO-groups). If this is also true in the case of meteoritic nanodiamonds, our observations may open a way to reproduce to some extent the real surface chemistry of presolar diamonds from data on chemically separated meteoritic diamonds. Specifically, assuming that the effect of the chemical treatment is the same in our work and in [8], our data suggest that the observed difference in the position of the CO-band in IR spectra of diamonds extracted from the Allende and Murchison meteorites (1759 and 1780  $\text{cm}^{-1}$ , resp.; [8]) may be caused by different initial oxidation states of these grains and even may allow to estimate the initial positions of these bands ( $\sim 1720$  and  $\sim 1740$   $\text{cm}^{-1}$ , resp.).

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**References:** [1] Lewis R. S. et al. (1987) *Nature*, 326, 160-162. [2] Ott U. (1993) *Nature*, 364, 25-33. [3] Huss G. R. and Lewis R. S. (1994) *Meteoritics*, 29, 791-810. [4] Allamandola L. et al. (1993) *Science*, 260, 64-66. [5] Guillois O. et al. (1999) *Astrophys. J.*, 521, L133-L136. [6] Mutschke H. et al. (1995) *Astrophys. J.*, 454, L157-L160. [7] Hill H. G. M. et al. (1997) *Meteoritics & Planet. Sci.*, 32, 713-718. [8] Braatz A. et al. (2000) *Meteoritics & Planet. Sci.*, 35, 75-84. [9] Andersen A. C. (1998) *Astron. Astrophys.*, 330, 1080-1090. [10] Koscheev A. P. et al. (1998) *Meteoritics & Planet. Science*, 33, A88. [11] Koscheev A. P. and Ott U. (2000) *Meteoritics & Planet. Sci.*, 35, A92. [12] Koscheev A. P. et al. (2001) *Nature*, 412, 615-617. [13] Ando T. et al. (1993) *J. Chem. Soc. Farad. Trans.*, 89, 3635-3640. [14] Sweeney R. J. et al. (1999) *Nucl. Instr. Meth.*, 158, 582-587.