# Solution-phase $^{13}$C NMR Spectroscopy of Detonation Nanodiamond

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Solution-phase $^{13}$C NMR spectroscopy of detonation nanodiamond has been developed to give the resonance of diamond carbons. This novel and convenient analytical method is promising for quantitative and structure-informative analysis of the surface chemical structure of nanodiamond as has been used for the analysis of organic molecules.

Diamonds have attracted much attention because of a variety of outstanding properties including high thermal conductivity, hardness, chemical inertness, wide band gap, high refraction index, and so on. These properties make diamonds promising candidates for many applications ranging from mechanical use to optical and electrical devices. Since fine applications sometimes require precise control of their properties, strict control of the surface termination is desirable, in particular, for nanosize crystals of diamonds called "nanodiamonds (NDs)" owing to their large specific surface area. Therefore, chemical and biochemical surface modification have been extensively reported for both films[1–4] and powders[5–10] of diamonds. Although many functional groups were incorporated into the surface via solid- and liquid-phase reactions, they were not fully identified because the analytical methods for the surface chemical structure are limited mostly to the following three ones; infrared,[4–10] X-ray photoelectron[2–4,8,10] and solid-state NMR spectroscopies.[8,11–13] Herein, we report very convenient analysis of detonation nanodiamonds (*d*-NDs) with solution-phase $^{13}$C NMR spectroscopy, which have been frequently used for quantitative and structure-informative analysis of organic compounds.

Aqueous *d*-ND colloidal solution (≈10 wt %), Nano-Amando®, prepared by stirred-media milling with microsized ceramic beads,[14] was purchased from NanoCarbon Research Institute Ltd. After addition of small amounts of $D_2O$ as an internal lock and 1,4-dioxane as an internal standard, the solution in a NMR tube (5-mm diameter) was subjected to $^{13}$C NMR measurement. $^{13}$C NMR (67.5 MHz) spectra of the *d*-ND suspensions were recorded by JEOL JNM-GX270.

In the spectra of *d*-ND suspension (Figure 1a), a broad peak was observed at 33 ppm after 30000 times accumulation with 90° pulse (7.4 μs) and enough recycle delay (11.0 s) as compared to the previously reported value for solid-state $^{13}$C NMR of *d*-ND solid (0.72 s).[12] The peak is due to the resonance of $sp^3$ diamond carbon, because the chemical shift in the solution-phase $^{13}$C NMR spectrum of the *d*-ND suspension is similar to those reported in solid-state $^{13}$C NMR spectra as shown in Table 1.[11–13,15–17]

In order to determine the parameters of the solution-phase $^{13}$C NMR precisely, spin-lattice relaxation time ($T_1$) was determined by an inversion-recovery method (5000 scans), in which the pulse sequence is 180° pulse (14.8 μs)–$\tau$ (10–1000 ms)–90° pulse (7.4 μs)–recycle delay (3.0 s). As a result, the null point ($T_{1/2}$) was found to be 0.2 s, and the $T_1$ of the *d*-ND in solution is calculated to be 0.3 s. As compared with the $T_1$ values reported previously in solid-state $^{13}$C NMR of various diamonds (Table 1), the present $T_1$ value in solution (Run 1) is similar to that of *d*-ND in solid (Run 2),[12] and much smaller than those of the gem diamond (Run 3)[15] and synthetic diamonds by high-temperature and high-pressure (HTHP) method (Runs 4 and 5),[16,18] shock compression method (Run 6)[11] and CVD method (Run 7).[17] The much smaller $T_1$ values of *d*-ND in both solution and solid (Runs 1 and 2) are considered to be attributed to the inherent contamination of paramagnetic metals and/or the electric spin in the defect.[12]

**Table 1.** Chemical shift and $T_1$ of diamond carbon in solution-phase and solid-state $^{13}$C NMR spectroscopies

| Run | Type of diamond[a] | Method | Chemical shift (ppm) | $T_1$ |
|---|---|---|---|---|
| 1[b] | *d*-ND | solution | 33 | 0.3 s |
| 2[12] | *d*-ND | solid | 35 ± 3 | 0.14–0.17 s |
| 3[15] | gem diamond | solid | 39 | 3.5 days |
| 4[16] | HTHP | solid | 33 ± 3 | 220 ± 20 s |
| 5[18] | HTHP | solid | not reported | 14–17 s |
| 6[11] | shock compression | solid | 36–38 | 12–45 s |
| 7[17] | CVD | solid | 36 ± 5 | 8–67 s |

[a]*d*-ND: detonation nanodiamond, HTHP: diamond synthesized under high-temperature and high-pressure conditions, CVD: diamond film prepared by chemical vapor deposition. [b]This work.

The $^{13}$C NMR of the *d*-ND solution was carried out under the conditions of 1.5 s recycle delay ($5T_1$ value), 7.4 μs 90° pulse and 30000 scans at 296 K. A very decent spectrum was obtained for only 12.5 h accumulation as shown in Figure 1c. When the recycle delay was changed to 0.5, 1.0, and 3.0 s, quite similar spectra to those of 1.5 and 11.0 s recycle delay mentioned above were obtained as shown in Figure 1. No influence of recycle delay to spectra indicates that carbon atoms around the surface and inside the core have similar $T_1$ values. This observation is in contrast with that of the solid-state $^{13}$C NMR spectra of ND prepared by shock compression;[11] two peaks with different $T_1$ values, 14–17 s and 39–45 s, were observed at 36 and 38 ppm, respectively. Therefore, the short recycle delay relatively decreased the peak intensity of the carbon at 38 ppm because of the longer $T_1$ value.[11] In this case, core and surface diamond carbons are considered to exhibit different $T_1$ value, while the $T_1$ values of both core and surface diamond carbons in *d*-ND are remarkably reduced by the presence of the paramagnetic metals and/or the defects,[11] giving no influence of recycle delay to the

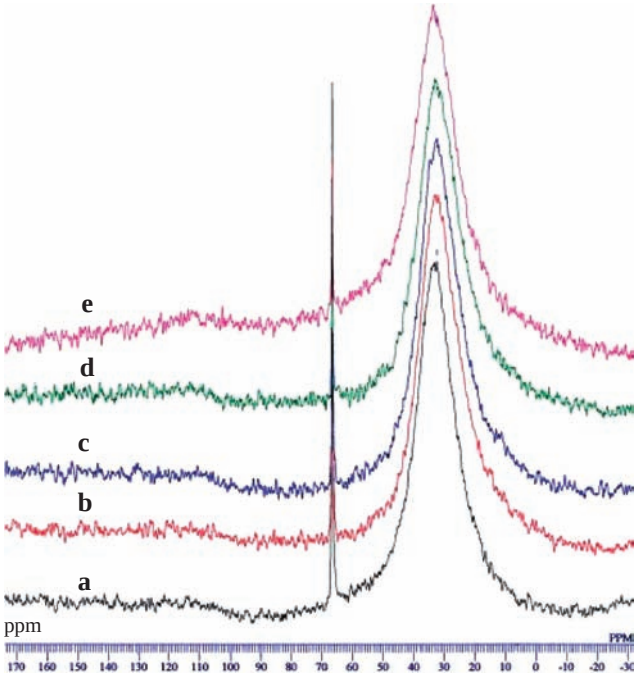


**Figure 1.** $^{13}$C NMR spectra of detonation nanodiamond (NanoAmando®) with recycle delay of 11.0 s (**a**), 3.0 s (**b**), 1.5 s (**c**), 1.0 s (**d**), and 0.5 s (**e**). The sharp peaks at 66.0 ppm are due to dioxane as an internal standard.

shape of the NMR peak.

Although $sp^2$ carbons are reported to be observed in *d*-ND by solid-state $^{13}$C NMR analysis,[13] any clear resonance was not observed in the lower magnetic region of 100–150 ppm in the present solution-phase $^{13}$C NMR spectra as shown in Figure 1. This is probably because the *d*-ND colloidal solution used in this experiment (NanoAmando®) contains much less amount of $sp^2$ carbons; that is, the purity of diamond may increase through the process of disintegration.[14]

Other than *d*-ND, we examined $^{13}$C NMR of larger size ND (30 nm in average diameter) synthesized under HTHP conditions. The resonance of diamond carbons was observed at 34 ppm under similar conditions to those of *d*-ND (see Supporting Information).[19] However, the intensity of the resonance of HTHP-ND is much lower than that of *d*-ND probably because HTHP-ND is expected to have much larger $T_1$ as HTHP diamond (Runs 4 and 5 in Table 1) and lower dispersibility than *d*-ND.

In conclusion, solution-phase $^{13}$C NMR spectroscopy has been developed as a facile analytical method for nanodiamond instead of solid-state $^{13}$C NMR spectroscopy frequently used so far. In future, we might be able to elucidate the chemical structure of nanodiamond by solution-phase NMR technique just like organic compounds.

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**References and Notes**

1 S. Wenmackers, P. Christiaens, M. Daenen, K. Haenen, M. Nesládek, M. v. deVen, V. Vermeeren, L. Michiels, M. Ameloot, P. Wagner, *Phys. Status Solidi* **2005**, *202*, 2212.
2 A. Härtl, E. Schmich, J. A. Garrido, J. Hernando, S. C. R. Catharino, S. Walter, P. Feulner, A. Kromka, D. Steinmüller, M. Stutzmann, *Nat. Mater.* **2004**, *3*, 736.
3 W. Yang, O. Auciello, J. E. Butler, W. Cai, J. A. Carlisle, J. Gerbi, D. M. Gruen, T. Knickerbocker, T. Lasseter, J. N. Russell, Jr., L. M. Smith, R. J. Hamers, *Nat. Mater.* **2002**, *1*, 253.
4 T. Nakamura, M. Suzuki, M. Ishihara, T. Ohana, A. Tanaka, Y. Koga, *Langmuir* **2004**, *20*, 5846.
5 K. Ushizawa, Y. Sato, T. Mitsumori, T. Machinami, T. Ueda, T. Ando, *Chem. Phys. Lett.* **2002**, *351*, 105.
6 T. Ando, M. Ishii, M. Kamo, Y. Sato, *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1783.
7 T. Saito, Y. Ikeda, S. Egawa, K. Kusakabe, S. Morooka, H. Maeda, Y. Taniguchi, Y. Fujiwara, *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 929.
8 T. Nakamura, M. Ishihara, T. Ohana, Y. Koga, *Chem. Commun.* **2003**, 900.
9 T. Tsubota, S. Tanii, S. Ida, M. Nagata, Y. Matsumoto, *Phys. Chem. Chem. Phys.* **2003**, *5*, 1474.
10 Y. Liu, Z. Gu, J. L. Margrave, V. N. Khabashesku, *Chem. Mater.* **2004**, *16*, 3924.
11 T. M. Alam, *Mater. Chem. Phys.* **2004**, *85*, 310.
12 A. I. Shames, A. M. Panich, W. Kempinski, A. E. Alexenskii, M. V. Baidakova, A. T. Dideikin, V. U. Osipov, V. I. Siklitski, E. Osawa, M. Ozawa, A. Y. Vul', *J. Phys. Chem. Solids* **2002**, *63*, 1993.
13 J.-B. Donnet, E. Fousson, L. Delmotte, M. Samirant, C. Baras, T. K. Wang, A. Eckhardt, *C. R. Acad. Sci., Ser. IIc: Chim.* **2000**, *3*, 831.
14 A. Krüger, F. Kataoka, M. Ozawa, T. Fujino, Y. Suzuki, A. E. Aleksenskii, A. Ya. Vul', E. Ōsawa, *Carbon* **2005**, *43*, 1722.
15 P. M. Henrichs, M. L. Cofield, R. H. Young, J. M. Hewitt, *J. Magn. Reson.* **1984**, *58*, 85.
16 M. J. Duijvestijn, C. V. D. Lugt, J. Smidt, R. A. Wind, K. W. Zilm, D. C. Staplin, *Chem. Phys. Lett.* **1983**, *102*, 25.
17 M. Pruski, D. P. Lang, S.-J. Hwang, H. Jia, J. Shinar, *Phys. Rev. B* **1994**, *49*, 10635.
18 K. Lefmann, B. Buras, E. J. Pedersen, E. S. Shabanova, P. A. Thorsen, F. B. Rasmussen, J. P. F. Sellschop, *Phys. Rev. B* **1994**, *50*, 15623.
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