2H and 13C NMR investigation of deuterofullerites C60Dx

1 Introduction

The hydrogenation of fullerenes was initially considered from the standpoint of reversible accumulation of hydrogen (e.g. [1–3]). Later on, it has been shown that the reverse reaction (dehydrogenation) occurs at rather high temperatures (770–820 K) and the reaction products therein contain not only hydrogen, but also methane and some other hydrocarbons [4–6]. However, interest in hydrofullerenes is not waning because of their remarkable properties. For example, hydrofullerite (solid hydrofullerene) can be ferromagnetic at room temperature [7], and its magnetization can be rather high, 1.2 emu/g [8]. Hydro- and deuterofullerenes can be used for obtaining fullerite with an extended fcc lattice [9].

In this paper, we report on the results of NMR study of deuterofullerenes synthesized by reacting the deuterium gas with well-crystallized fullerite C60. As already mentioned, this procedure can lead to deuterofullerenes in which the fcc structure of the pristine fullerite persists, while the lattice constant is noticeably increased [10].

Solid hydrofullerenes have been rather well studied by NMR (e.g. [11–13]). However, to the best of our knowledge, deuterofullerenes have not heretofore been studied by NMR.

2 Experimental

A fullerene C60 with a purity of 99.8% was used. Before deuteration, the fullerene was recrystallized by vacuum sublimation to remove the solvent (toluene) used in the synthesis of fullerene.

The fullerene was deuterated at a pressure of 2.5 ± 0.1 MPa. The temperature was maintained with an accuracy of ±10 K. The sample was preliminarily degassed by heating to 500 K in a vacuum (~ 1 Pa). Deuterium was fed into a reactor directly from a metal hydride accumulator heated to 373 K. To enhance the efficiency of the reaction, it was accomplished under cyclic thermal conditions: a sample under a pressure of deuterium was heated to the required temperature T and kept at this temperature for 1 h; then, the reaction mixture was cooled to room temperature, and all operations were repeated. After three cycles, deuterium was refreshed, namely, the deuterium used was removed, and a new portion of fresh deuterium was taken from the accumulator. This deuteration scheme was repeated n times.

Three samples obtained at different T’s and n’s were studied (1–3, Table 1). To determine the composition of C60Dx, a ~ 4 mg sample was burned in oxygen at 1400 K: C60Dx + (60 + 0.25x) O2 → 60 CO2 + 0.5x D2O. The carbon and deuterium contents of the sample were calculated from the weights of released CO2 and D2O. The x values (x = [D]/[C60]), calculated from the averaged data on the three runs, are listed in Table 1. For all samples, the standard deviation from these x values was ±0.3.

X-ray powder diffraction patterns were taken with a DRON ADP-1 diffractometer (monochromated Cu Kα radiation). The a0 parameter of the fcc lattice was determined from three strongest peaks – (111), (220), and (311) (Fig. 1).

13C NMR spectra were recorded at room temperature (293 ± 3 K) on Bruker AC-200 (50.288 MHz, B0 = 4.69 T) and MSL-300 (75.432 MHz, B0 = 7.04 T) spectrometers. A spin system was excited by means of a one-pulse sequence with a dead time of 10 μs, a pulse width of 3 μs, a sweep width of 125 kHz, and a delay between pulses of 30 s.

Table 1: Deuteration temperature (T), number of cycles (ν), composition (x), and fcc lattice constant (a0) for samples 1–3

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>T, K</th>
<th>ν</th>
<th>x</th>
<th>a0, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>673</td>
<td>3</td>
<td>18.1</td>
<td>1.456</td>
</tr>
<tr>
<td>2</td>
<td>673</td>
<td>30</td>
<td>30.0</td>
<td>1.487</td>
</tr>
<tr>
<td>3</td>
<td>723</td>
<td>30</td>
<td>29.6</td>
<td></td>
</tr>
</tbody>
</table>

* Diffraction peaks are absent.
The 2H NMR spectra (46.077 MHz) were recorded on a Bruker MSL-300 spectrometer in a field of 7.04 T at 293 ± 3 and 390 ± 3 K. A 2H spin system was excited by means of a QUADROECHO two-pulse train \([\theta_x - \tau - \theta_y - \beta] - AQ\), \(\theta_x = \theta_y = 1 \mu s\), \(\tau = 24 \mu s\), and \(\beta = 27 \mu s\). A repetition time of 200 ms and a sweep width of 1 MHz with 4 K points were used. Weighed samples (0.1 g) were placed in spherical ampoules 9 mm in o.d.

### Results and discussion

The 2H NMR spectra of the three samples are of the same type (Fig. 2). Each spectrum shows two pairs of quadrupole doublets. For the stronger outer doublet, the splitting is 128 kHz with the zero asymmetry parameter of the EFG tensor. For the inner doublet, the splitting is 42 kHz. The outer doublet can be assigned to the deuterium atoms bonded to \(sp^3\) carbon. The quadrupole coupling constant (QCC) for these atoms is 171 kHz. Such a QCC value is quite anticipated for deuterium bonded to carbon. The theoretical QCC values for deuterium bonded to differently hybridized carbon are 153.6, 189, and 208.7 kHz for \(sp^3\), \(sp^2\), and \(sp\) carbon, respectively [14]. The experimental QCC of 171 kHz is intermediate between the QCCs for \(sp^3\) and \(sp^2\)-hybridized carbon atoms. This may be a manifestation of the uniqueness of C–C bonding in the fullerene cage as compared to classical hydrocarbons. The emergence of the inner doublet with a small QCC (56 kHz) is an unexpected and inexplicable result. Both the experiment and theory unambiguously show that such small QCCs can be realized only if a deuterium atom serves as a bridge [15, 16]; if so, we can conclude that the deuterofullerites under consideration have two types of carbon–deuterium bonds: terminal bonds (C–D) with a QCC of 171 kHz and bridging bonds (\(-C\cdots D\cdots C\)) with a QCC of 56 kHz. In the latter, the deuterium atom bridges different molecules by a rather strong bond.

Figure 3 shows the \(^{13}\)C NMR spectra of sample 1 (Table 1) in a field of (a) 4.69 and (b) 7.04 T. The spectra show broad overlapping signals with two maxima at 150 and 40 ppm (from TMS). These spectral regions correspond to \(sp^2\) and \(sp^3\) carbon atoms, respectively [11–13]. The \(^{13}\)C NMR line shape depends on the polarizing field strength \(B_0\), which indicates that the spectrum is a superposition of several signals whose shape and width is dominated by magnetic shielding anisotropy. The anisotropy of \(sp^2\) carbon (about 150 ppm) is considerably larger than for \(sp^3\) carbon (about 40 ppm). The anisotropy of shielding on the order of 200 ppm points to a relative rigidity of the crystal lattice on the NMR time scale; i.e., averaging frequencies are smaller than \(1.5 \times 10^4\) Hz [17, 18].

An extra piece of evidence in favor of the lattice rigidity of the samples under consideration was provided by temperature-induced changes in the 2H NMR spectra. As follows from Fig. 4, the line shape and splitting remain unaltered at 390 K. This result also supports the rigidity of the lattice with an averaging frequency below \(4 \times 10^3\) Hz.

Therefore, our findings show that at least two types of D atoms exist in the deuterofullerites: a terminal atom bonded to the carbon cage of a fullerene and a bridging atom.