

ON THE FINE STRUCTURE OF NMR ^{13}C SPECTRUM OF FULLERITE C_{60} INTERCALATED WITH MOLECULAR OXYGEN

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Introduction

Interactions in $\text{C}_{60} - \text{O}_2$ system are very important to understanding of properties of fullerite (solid state fullerene) because as it well known oxygen molecules are easy penetrate in fullerite, which contacts with air. It follows from large diameter of octahedral site in the face-centered cubic lattice of C_{60} solid (0.41 nm [1]) and small van der Waals diameter of O_2 [2]. It was established that oxygen content in the fullerite, which is stored during 1 month in air, are correspond to formula $(\text{O}_2)_{0.004}\text{C}_{60}$ [3]. More high content $((\text{O}_2)_{0.20}\text{C}_{60})$ can be obtained in fullerite treated with oxygen at 0.15 kbar (room temperature, 7 days) [4,5].

It well known that all atoms in fullerite C_{60} are equivalent. At room temperature C_{60} molecules rotate with high speed (more than 10^9 cycles per second) and, as result, NMR ^{13}C spectrum of fullerite C_{60} at room temperature consists of a single peak (see, for example, [6]). At doping of fullerite with alkali metal atoms electrons transfer from metal atoms to fullerene sub-lattice. The charge transfer leads to shift NMR ^{13}C resonance in more low magnetic fields in compare with the resonance for clear fullerite. Transfer of 1 electron per 1 molecule C_{60} corresponds to shift of approximately 2 ppm [7].

Satellite structure appease in spectrum of NMR ^{13}C of fullerite intercalated with molecular oxygen. This structure consists of 6 peaks and lies in site of more high ppm relative to position of the peak of non- intercalated fullerite. Satellite peaks are placed approximately 0.7 ppm apart [1, 3-5]. Authors of work [1] explain the appearance of the satellite structure by means of paramagnetic interaction of nuclear spin of ^{13}C atom and spin of O_2 molecule. First satellite appears then one in every six octahedral sites is filled by oxygen molecule. Second satellite, which is separated by 1.4 ppm from resonance of clear fullerite, appears

then two in every six octahedral sites are filled by oxygen molecule. And so on. If we denote the intensity of n peak as I_n ($0 \leq n \leq 6$), the part of C_{60} molecules surrounded by i molecules of O_2 will be expressed as $f_i = I_i / \sum I_n$, (summing to made for all n from 0 to 6). In this case the oxygen content (the numerical value x in formula $(\text{O}_2)_x\text{C}_{60}$) in the sample under study will be expressed by simple equation $x = \sum n f_n / 6$.

In this work we set ourselves the task to obtain fullerite with greatest possible oxygen content, to investigate it's with help of high resolution NMR spectroscopy, to analyze the fin structure of ^{13}C spectrum and to evaluate the distance between ^{13}C atom and O_2 molecule.

Sample preparation

Fullerite C_{60} intercalated with O_2 $((\text{O}_2)_x\text{C}_{60})$ was prepared in accordance with park [8]. The solution of the fullerene (5 mg C_{60} per 1 ml 1,2-dichlorobenzene) was saturated with O_2 by bubbling during 10 hours. After that the isopropyl alcohol in five times higher volume was slowly added to the solution. Isopropyl alcohol was also previously saturated with O_2 . The mixture was then kept at room temperature as long as it was necessary to clear up the solution. The black crystals of fullerite precipitated from the solution were finally separated by filtration and dried on air during 3 hours. The yield of intercalated fullerite with a size $>0.2 \mu\text{m}$ was about 60%.

The oxygen content (2.3 ± 0.2 mass.%) was measured by Vario-MICRO "CUBE" (Elementar, Germany).

NMR spectra ^1H and ^{13}C were registered with help of Varian Unity Inova 500 WB spectrometer at room temperature.

Results and discussion

NMR investigation is not revealed a same ^1H resonance which intensity is exceeding

substantially level of noise. Hence the solvents used in the synthesis are absent in the sample under study.

^{13}C spectrum of the sample is present on Fig. 1. One can see 7 peaks, which are placed approximately equidistantly. The position of the peak 0 is correspondent to the position of ^{13}C resonance in the spectrum of clean fullerite. The positions of other peaks are nearly to the positions of satellite peaks in the spectrum of $(\text{O}_2)_{0.20}\text{C}_{60}$ [4,5], but the relative intensities of the peaks 1-6 are much higher than that in the spectrum of $(\text{O}_2)_{0.20}\text{C}_{60}$.

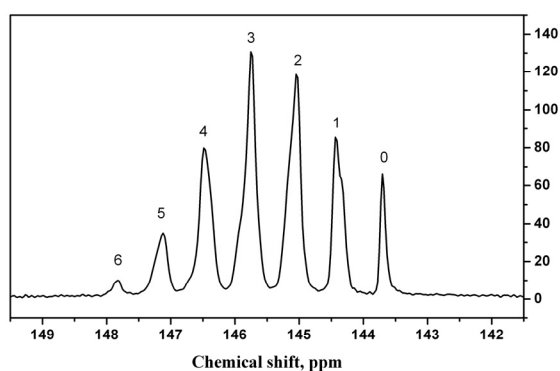


Fig. 1. NMR ^{13}C spectrum of sample under study.

The numerical values of intensities and full-widths at half maximum (FWHM) of the peaks in the spectrum of our sample are present in Table 1. It is interesting to note that value of FWHM for peak 0 is approximately twice lower than that for other peaks. As it was written in Introduction peak 0 corresponds to C_{60} molecules, which are not have O_2 molecules in nearest octahedral sites. Appearance of one paramagnetic molecule O_2 in nearest octahedral site corresponds to appearance peak 1. Interaction between nuclear spin of ^{13}C atoms and spin O_2 molecule leads increase in width of correspondent resonance. It is interesting to evaluate the effective distance l between ^{13}C and O_2 . Evaluation can be done in accordance with formula $l = (\mu/\Delta FWHM)^{1/3}$, where μ is magnetic moment of oxygen molecule, and $\Delta FWHM$ is rise in half-width in going from peak 0 to peak 1. At $\Delta FWHM = 0,009$ Gauss we derive $l = 1.4 \text{ \AA}$. Such short distance at random initial relative positions of ^{13}C and O_2 may be obtained

only at very fast rotation of C_{60} molecule around its center of mass.

Table 1. Positions (δ), half-widths (FWHM) and intensities (I_p) of the peaks in NMR ^{13}C spectrum of sample under study.

Peak number	δ , ppm	FWHM, Hz	I_p , %
0	143,7	12.4	12,2
1	144,426	24.9	16,3
2	145,037	27.5	22,5
3	145,744	22.3	24,8
4	146,477	28.6	15,0
5	147,122	29.6	6,5
6	147,825	23	2,6

In accordance with formula $x = \Sigma n f_n / 6$ numeric value of x is equal to 0.442. This value is close to value 0.53 obtained from data of elemental analysis.

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