^{13}C NMR STUDY OF Ca@C_{74}: CAGE STRUCTURE AND DYNAMICS OF A Ca ATOM INSIDE THE CAGE

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So far the isolation of mono-metallofullerenes with C_{74} cage, Ca@C_{74}[1], Eu@C_{74}[2], and Sm@C_{74}[3,4], has been reported. However, there is little experimental information about their cage structures. Thus we isolated Ca@C_{74} and measured its ^{13}C NMR spectrum to determine its cage structure experimentally.

The soot containing Ca@C_{74} was produced by direct current (40A) arc discharge of Ca/C composite rod under a 500 Torr He atmosphere. The fullerenes were extracted by refluxing for 6h with 1,2,4-trichlorobenzene. The isolation of Ca@C_{74} was accomplished by three-stage high performance liquid chromatography. The ^{13}C NMR spectra were measured at 125 MHz in CS_2 solvent with 5% 1,1,2,2-tetrachloroethane-d_2 as an internal lock, or in o-dichlorobenzene-d_4 solvent. Chromium acetylacetonate was used as a relaxant.

Figure 1 shows the temperature-dependent ^{13}C NMR spectra of Ca@C_{74}. The symmetry of the C_{74} cage was found to be D_{3h} because the integrated intensity ratio of the peaks marked with an open circle, a solid circle, and an open square is 6:3:1 and the numbers of them are 4, 4, and 1, respectively. Moreover, inside the cage, the Ca atom should be jumping between some equivalent sites displaced from the center of D_{3h} cage, because the several ^{13}C NMR lines sharpened at higher temperature as shown in figure 1. In addition, the activation energy of the jumping motion was determined by analyzing the temperature-dependent ^{13}C NMR spectra.

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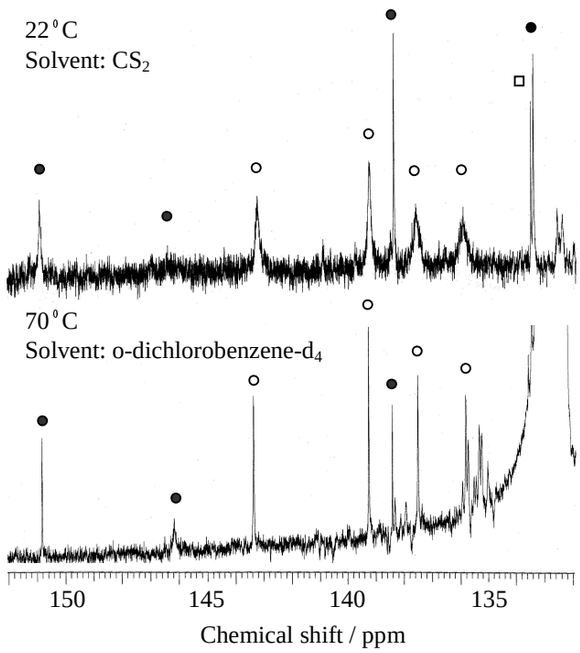

Figure 1. Temperature-dependent ^{13}C NMR spectra of Ca@C_{74}. The integrated intensity ratio of the peaks marked with an open circle, a solid circle, and an open square is 6:3:1.