

¹²⁹Xe NMR of Xenon Inside in C₆₀

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For the past several years we have developed methods to put noble gas atoms into fullerenes, where they remain trapped. (1) While there is no chemical bond between the gas atom and the carbon cage, the atom cannot escape unless several C-C bonds are broken. We have made ³He@C₆₀ and studied its ³He NMR spectroscopy. (1-3) Because of the "ring currents" in the π -electron system, the NMR resonance of ³He is shifted upfield by 6.3 ppm from that in free ³He. Making derivatives of ³He@C₆₀ changes the π -electrons and hence the chemical shift. The NMR lines are sharp, and each derivative gives a separate, well-resolved line. Making the hexa-anion of C₆₀ causes the chemical shift to go from -6.3 ppm to -48.7 ppm. (4) C₇₀ and the higher fullerenes also give unique and distinct lines. Good agreement is obtained with *ab initio* theoretical calculations of the chemical shift. (5) According to the theory, the ³He is very slightly bound inside the C₆₀ and effectively samples the magnetic field inside without interacting with the π -electrons of the C₆₀.

The only other noble gas isotope with spin 1/2 and reasonable natural abundance is ¹²⁹Xe. We expect that ¹²⁹Xe@C₆₀ will behave quite differently from ³He@C₆₀. A xenon atom fits tightly inside C₆₀, so that the outer electrons on the xenon atom interact with the π -electrons in C₆₀. Making derivatives of C₆₀ involves changing the π -electron structure and distorting the C₆₀ cage. These changes are expected to have negligible effects on the reaction rates or the equilibrium constants if a ³He atom is inside. But, because of the tight fit of a xenon atom, the rates and equilibrium constants might be very different with a xenon atom inside.

Measuring the NMR spectrum of ¹²⁹Xe@C₆₀ is far more difficult than the corresponding experiment with ³He@C₆₀. Natural xenon is only 29% ¹²⁹Xe. Our high-pressure method of making noble-gas labeled fullerenes gives an incorporation of xenon only a third of that for the other noble gases. Finally, the gyromagnetic ratio for ¹²⁹Xe is much smaller than for ³He, and therefore the sensitivity is much lower. We overcame the first difficulty by using isotopically enriched ¹²⁹Xe. We overcame the second by using our new cyanide catalyzed method, which increases the incorporation by an order of magnitude. We increased the sensitivity by separating the Xe@C₆₀ using HPLC.

The HPLC separation is similar to the one previously used for Kr@C₆₀. (6) Because the initial labeled C₆₀ contains only ~0.3% xenon, it is impossible to see the UV signal from the Xe@C₆₀, as it elutes from the chromatograph. We used a mass spectrometer to determine when the peak eluted. About 800 μ g of Xe labeled C₆₀ was injected into our PYE column in 100 μ L of o-dichlorobenzene, and the fullerene eluting out of the column between 12 and 16 min was collected in 8 equal fractions of 30 sec each. The fractions were analyzed by our mass spectrometer for ¹²⁹Xe content. It was found that Xe@C₆₀ eluted from the column between 13 min and 15 min. The procedure was repeated with a dilute sample containing 300 μ g of Xe labeled fullerene in 100 μ L of o-dichlorobenzene. The fullerene which eluted was

collected every 15 sec between 12.5-14.5 min in 8 fractions. This revealed that Xe@C₆₀ eluted between 13.25 and 14.25 min with the peak at 13.8 min.

We repeatedly injected the labeled material into the HPLC and collected the fraction eluting between 13-16 min. We combined the fractions, evaporated the toluene and reinjected the material. After four rounds of injections we obtained 320 μ g of product that contained 50% Xe@C₆₀. ¹³C NMR of the mixture gave two peaks: one at 143.52, due to C₆₀ and one at 144.48 ppm due to Xe@C₆₀. Thus the xenon gives a downfield shift of 0.95 ppm or 192 Hz. Using *ab initio* methods, Bühl et al. (5) predicted the shift for xenon to be 1 ppm, in very good agreement with our result.

The ¹²⁹Xe NMR was done on a Varian 800 spectrometer running at a Xe frequency of 221 MHz. The sample was dissolved in a 50-50 mixture of benzene and benzene-d₆, using the deuterium signal as a frequency lock. The figure shows the spectrum.

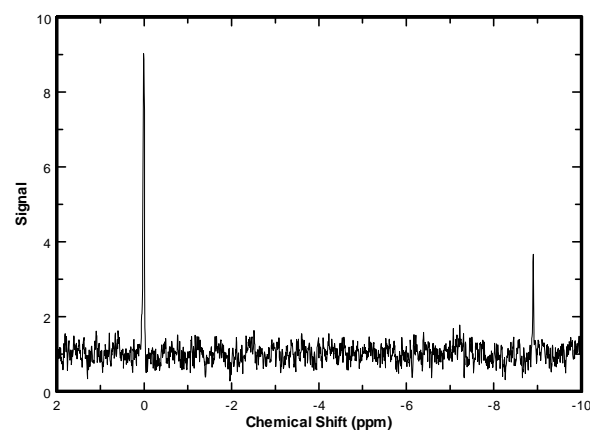


Fig. 1. ¹²⁹Xe NMR of ¹²⁹Xe@C₆₀ (dissolved ¹²⁹Xe is the reference at 0 ppm).

We find the resonance for ¹²⁹Xe@C₆₀ to be -8.89 ppm (upfield) from the resonance for ¹²⁹Xe dissolved in benzene. Bühl et al. (5) calculated the chemical shift as +70 ppm relative to ¹²⁹Xe gas. Using a capillary containing xenon gas, we measured the shift of xenon in benzene to be +188.14 ppm relative to xenon gas. The chemical shift of ¹²⁹Xe@C₆₀ relative to ¹²⁹Xe gas based on our experiment is then +179.24 ppm.

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