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^{129}Xe NMR Spectrum of Xenon Inside C_{60}

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Abstract: Xenon was inserted into C_{60} by heating C_{60} in 3000 atm of xenon gas at 650 °C. The Xe@C_{60} was separated from the empty C_{60} by using HPLC. The ^{13}C resonance for Xe@C_{60} is shifted downfield by 0.95 ppm (192 Hz). ^{129}Xe NMR showed a line 179.2 ppm downfield from xenon gas.

Introduction

In 1994, we were able to put enough ^{3}He inside the cage molecule, buckminsterfullerene (C_{60}), to make it possible to obtain its helium NMR spectrum.[1] This result has had many consequences. The chemical shift of the very sharp helium peak inside the cage compared with the helium shift outside the cage yielded a precise value for the change of the magnetic field inside caused by the diamagnetism of the fullerene. This shift compared favorably with that calculated using ab initio theory.[2] Study of the higher fullerenes showed that helium was incorporated in these molecules by our high-temperature, high-pressure method and that the helium NMR chemical shifts covered a very wide range.[3] The number of helium peaks for each fullerene indicated how many isomers there were. The shifts, again, agree reasonably well with theoretical results.

When ^{3}He-labeled fullerene is subject to any of the many different known chemical transformations, very substantial shifts of the helium peak occur.[4] In the helium NMR spectra of reaction mixtures, peaks can be readily assigned to the starting material, the products, and isomers of the products of multiple reactions. So far, no two different products have been found to have the same helium shift. At this time, this helium NMR methodology is one of the most useful and powerful ways to follow fullerene chemistry. Reversible Diels−Alder addition with dimethylanthracene, which goes to equilibrium at room temperature, was also readily followed with helium NMR.[5] Adducts, including isomers of products of multiple additions of up to four addends could be enumerated and accurate constants could be obtained for the equilibria involving them. Reduction of C_{60} and C_{70} by adding electrons resulted in enormous changes in the helium chemical shifts, which we related to altering aromaticity and antiaromaticity.[6]

Aside from ^{3}He, the only other noble gas isotope with the NMR favorable spin $= {}^{1}/_{2}$ is ^{129}Xe. In contrast with helium, xenon is very polarizable. It interacts strongly with other atoms and molecules, and its chemical shift is markedly affected by these interactions. We expect that these interactions will make the xenon shifts very different from the helium shifts and that they might change differently as a result of chemical reactions or reduction. A few of these results might be predicted theoretically. However, the many electrons of the xenon and the nonbonded nature of the interaction make these calculations very difficult and the results uncertain. It is necessary to have the experimental results.

Obtaining an NMR spectrum of xenon inside C_{60} has been very much more difficult than for helium. The lower gyromagnetic ratio of ^{129}Xe makes its spectroscopy much less sensitive than that of ^{3}He. Also, ordinary xenon is only 26% ^{129}Xe. In addition, our high-temperature, high-pressure method results in an incorporation level 3 to 5 times lower for xenon than we get for helium, probably because the size of xenon is approaching

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the size of the cavity.[7] We have made several attempts in the past to detect the NMR signal of $^{129}Xe@C_{60}$ without success.

To overcome these difficulties, we have now done several things. We have purchased xenon enriched with ^{129}Xe (86%) and used it for the labeling. We have used an improved method for our noble gas labeling process involving grinding C_{60} with KCN before the high-temperature, high-pressure step. This results in an increase in the incorporation of xenon and other noble gases of about an order of magnitude.

Nevertheless, the fraction of incorporation was still not enough for us to see the xenon NMR in a saturated solution. We therefore worked on separating the small amount of $^{129}Xe@C_{60}$ from the empty C_{60}. We have previously reported that we could use HPLC to isolate $Kr@C_{60}$.[8] We used a mass spectrometer to find where the $^{129}Xe@C_{60}$ eluted from the column, since the amount was far too small to give a separate peak in the elution spectrum. We then made hundreds of injections, collecting the last part of the peak for C_{60}. This was then reinjected to further enrich the material.

Experimental Details

Labeling of C_{60} with ^{129}Xe. In a typical run, 100 mg of C_{60} fullerene is ground up together with 30 mg of potassium cyanide in a ball mill for 8 min, and it becomes a uniform, finely powdered mixture. This is put into a 4 in. long tube made of OFHC (oxygen-free high-conductivity) copper that has been crimped shut at one end to form a vacuum seal. The tube is evacuated overnight, filled with Xe gas that contains 86 atom % of ^{129}Xe at a pressure of 3 atm, and then crimp sealed at the other end. The sealed ampule is then placed in a high-pressure vessel and heated to 650 °C and 3000 atm, as in our high-temperature, high-pressure method reported earlier.[1] At the end of the run, the fullerene is taken out of the tube, ground in the ball mill for a minute, extracted with carbon disulfide, and filtered with a 0.2 μm filter. Evaporation of the solvent gives about 40 mg of fullerene where roughly 0.3% of the C_{60} molecules contain xenon.

The fraction of C_{60} containing xenon was determined with a mass spectrometer. About 1 mg of the Xe-labeled C_{60} was sealed in a fused silica tube under vacuum and pyrolized in an oven at 1000 °C for 2 h to destroy the C_{60} and release the xenon. The ampule was broken open under vacuum. A getter pump (SAES) removed all gases, other than noble gases. The amount of ^{129}Xe that was released was then measured by a quadrupole mass spectrometer (Ametek Dycor). By comparing the amount of ^{129}Xe released by a known amount of a standard sample it was concluded that the C_{60} labeled by the cyanide method contained roughly 0.3% of $^{129}Xe@C_{60}$.

HPLC Procedure. A semipreparative PYE [2-(1-pyrenyl)ethylsilyl] column (10 × 250 mm) was used for the separation of $^{129}Xe@C_{60}$ with toluene as the eluent at a flow rate of 2 mL/min. To determine the extent of separation of $^{129}Xe@C_{60}$ from C_{60}, the following procedure was adopted. *o*-Dichlorobenzene (100 μL) containing 800 μg of Xe-labeled C_{60} was injected into the PYE column and the fullerene eluting out of the column between 12 and 16 min was collected in eight equal fractions of 30 s each. This was repeated four times and the respective fractions were combined, evaporated, and analyzed by our mass spectrometer for ^{129}Xe content. It was found that $Xe@C_{60}$ eluted from the column between 13 and 15 min.

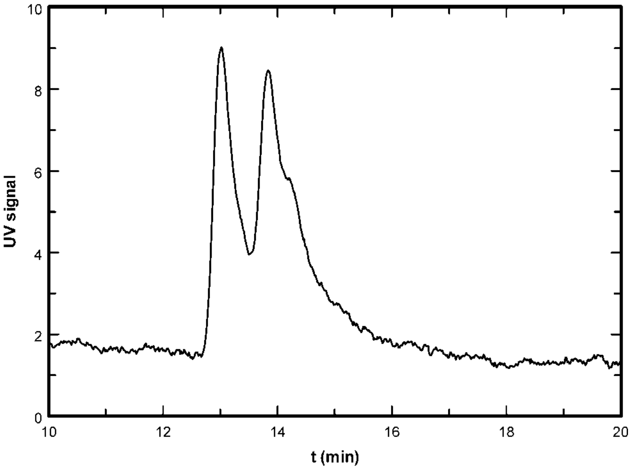

Figure 1. Chromatogram of a mixture of C_{60} and $Xe@C_{60}$ on a PYE column. The first peak is due to C_{60} and the second to $Xe@C_{60}$.

The procedure was repeated with a dilute sample containing 300 μg of Xe-labeled fullerene in 100 μL of *o*-dichlorobenzene. The fullerene which eluted was collected every 15 s between 12.5 and 14.5 min in eight fractions. This revealed that $Xe@C_{60}$ eluted between 13.25 and 14.25 min with the peak at 13.8 min.

Preparative HPLC. Using the information given above, it was possible to separate the $Xe@C_{60}$ from the empty C_{60} in several stages. The same PYE column was used for preparative purposes. Typically, we dissolved 150 mg of Xe-labeled C_{60} in 20 mL of *o*-dichlorobenzene and injected it in 0.1 mL portions. We collected the fraction eluting between 13 and 16 min at a flow rate of 2 mL/ min. We combined all the fractions and evaporated the solvent on a rotavap to get 17 mg of enriched material after the first stage. In the second stage of separation, each injection of 100 μL consisted of 300 μg of fullerene to yield 6 mg. The third stage, in a similar manner, yielded 2 mg. After each stage, the enriched fullerene was treated with triphenylphosphine at 45 °C for 2 h to reduce the C_{60} epoxide, since this has an interfering retention time around 14 min. At the end of the third stage a definite shoulder could be seen at the HPLC at 13.8 min. The fourth stage of separation gave 320 μg of 50%-enriched material. Figure 1 shows the UV trace of a mixture of 69% C_{60} and 31% $Xe@C_{60}$.

Carbon-13 NMR. The NMR spectrum was taken on a Varian 800 instrument running at a ^{13}C frequency of 200 MHz. A 50:50 mixture of benzene and benzene-d_6 was used as the solvent with no added relaxation agent. The benzene-d_6 triplet was used as reference at 128.3 ppm. A total of 54 592 pulses were used with a width of 4.5 μs and a pulse delay of 0.5 s. A line broadening of 0.1 Hz was used for processing the data. Figure 2 shows the spectrum.

^{129}Xe NMR Spectroscopy. A Varian 800 spectrometer running at a Xe frequency of 221 MHz was used for the ^{129}Xe NMR spectroscopy. A 50:50 mixture of benzene and benzene-d_6 was used as the solvent with no added relaxation agent. Dissolved Xe gas containing 86 atom % of ^{129}Xe was used as reference. A total of 33 344 pulses were acumulated. A 45° pulse was used with a 2 s delay between pulses. The pulse width was 6 μs. A line broadening of 1 Hz was used while processing the data. Figure 3 shows the ^{129}Xe spectrum.

Results and Discussion

Our improved method of labeling fullerenes with noble gases using a finely powdered mixture of C_{60} with potassium cyanide enabled us to put in more xenon (0.3%) than we could using pure C_{60}. We are not sure why the KCN improves the yield.

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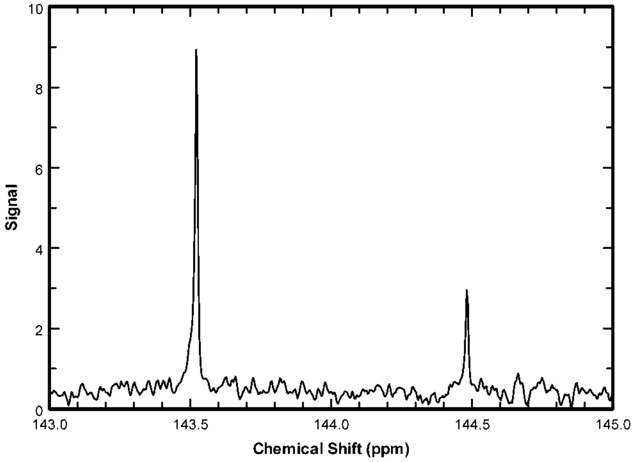

Figure 2. ^{13}C NMR of a mixture of C_{60} and Xe@C_{60}. The large peak to the left is due to C_{60}, and the smaller peak is due to Xe@C_{60}.

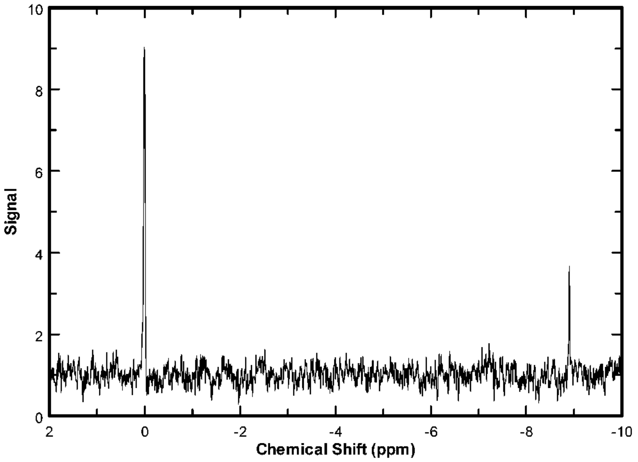

Figure 3. ^{129}Xe NMR of ^{129}Xe@C_{60} (dissolved ^{129}Xe is the reference at 0 ppm).

Cyanide is a nucleophile that adds readily to the double bonds in fullerenes.[9] We feel that the addition weakens the bonds next to the carbon where the cyanide has added. Breaking one bond opens a "window" but it is not nearly large enough to permit the entry of xenon. Several additional bonds must break to unzip an entryway large enough for the xenon atom to enter. The process must then reverse and eliminate the cyanide to make the product.

A systematic analysis of the Xe content of the various HPLC fractions with a quadrupole mass spectrometer enabled us to locate the Xe-containing C_{60} as it eluted from the column. Repeated injections resulted in almost pure Xe@C_{60}. In general, the separation of the peaks for C_{60} and Xe@C_{60} was slightly larger than the separation we observed previously for Kr@C_{60}. This, in turn, was larger than the separation for Ar@C_{60} observed by DiCamillo et al.[8c]

After every stage the mixture had to be reduced with triphenylphosphine to prevent the loss of Xe-containing C_{60} in the form of $C_{60}O$, which is formed in small amounts by the exposure of the C_{60} solution to light and air. The HPLC retention time of the C_{60} epoxide under the present conditions was found to be 14.2 min, which interferes with theXe@C_{60} eluting out at 13.8 min and therefore has to be removed for efficient separation to take place. The retention time of $C_{60}O$ was verified by conducting the ozonolysis[8d] of C_{60} under mild conditions and injecting the oxidized mixture through the PYE column under the same conditions of HPLC separation. Figure 1 shows the chromatogram containing C_{60}, Xe@C_{60} , and the epoxide[10] that appears as a shoulder to the Xe@C_{60}.

The dimer C_{120}, which has a retention time of 22.6 min under the present HPLC conditions,[8a] was removed during the first stage of separation. A shoulder at 13.8 min corresponding to Xe@C_{60} started appearing after the second stage of separation and after four stages the area under this shoulder was approximately 30% of the mixture (Figure 1). This was in good agreement with the NMR integration values for the C_{60} and the Xe@C_{60} in the ^{13}C NMR spectrum of the same mixture (Figure 2).

^{13}C NMR Spectroscopy. As Figure 2 shows, we get two peaks in the ^{13}C NMR spectrum of C_{60} containing 30% Xe@C_{60} in benzene, one for C_{60} at 143.52 ppm and one due to Xe@C_{60} at 144.48 ppm with respect to the benzene triplet at 128.3 ppm as reference. Thus, the presence of Xe inside the C_{60} produces a downfield shift of 0.95 ppm or 192 Hz. This is a far larger shift than in the krypton case where there is a downfield shift of 0.39 ppm, presumably due to greater interaction of Xe with the fullerene π electrons. Using ab initio methods, Bühl et al.[11] predicted the shift for xenon to be 1 ppm, in very good agreement with our result. The lack of splitting in the Xe@C_{60} signal (both in the ^{13}C spectrum and in the ^{129}Xe spectrum) shows that the spin−spin coupling of the ^{13}C to the xenon is less than ~2 Hz.

^{129}Xe Spectroscopy. As Figure 3 shows, we find the resonance for ^{129}Xe@C_{60} to be −8.89 ppm (upfield) from the resonance when it is dissolved in benzene. Bühl et al.[11] calculated the chemical shift in the gas phase as +71.7 ppm relative to ^{129}Xe gas. To make a comparison between theory and experiment we needed to know the chemical shift of ^{129}Xe dissolved in benzene relative to that for free xenon. We inserted a capillary tube filled with ^{129}Xe gas at 1 atm into the center of the solution of ^{129}Xe in benzene and measured this shift to be +188.14 ppm. This compares with the previous value of 195 ppm obtained by Miller et al. for the ^{129}Xe chemical shift of Xe in benzene with reference to Xe gas at zero pressure.[12] The chemical shift of ^{129}Xe@C_{60} relative to ^{129}Xe gas based on our experiment is then 179.24 ppm. The difficult calculation of Bühl et al.[11] used no electron correlation. They did a test calculation using correlation with a benzene ring and concluded that correlation will shift the result upfield, improving it. We have no way of estimating the effect of the solvent on the chemical shift of ^{129}Xe@C_{60}. It may seem surprising that the chemical shift of xenon inside C_{60} is so close to that in benzene. It is well-known that xenon chemical shifts vary widely depending on the solvent. Miller et al.[12] found that they range from 153 ppm in CH_3OH to 335 ppm in CH_2I_2. However, the ^{129}Xe chemical shifts in simple aromatic solvents were all clustered within 10 ppm around 190 ppm.

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(10) In the case of Kr@C_{60} we reported a longer retention time for the epoxide, namely, 15.1 min under similar HPLC conditions. Work is in progress to sort out the difference in the oxidized species in the two cases.

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In the case of ^{3}He inside of various fullerenes and their adducts, Bühl et al.[2] are generally able to predict the chemical shifts to a few ppm. It is not surprising that their agreement is not as good in the case of ^{129}Xe. Helium is much smaller than the cavity in C_{60}, and the helium electrons are tightly bound to the nucleus. Therefore, there is little interaction between these electrons and the π-electrons of the fullerene. The helium nucleus effectively samples the magnetic field inside the fullerene cavity. In the case of xenon, the 5p electrons of the xenon are much closer to and interact much more strongly with the π-electrons of the fullerene. In addition, it is much more difficult to do a calculation on a system with so many electrons.

We are now in a position to measure the NMR spectra of adducts of Xe@C_{60}. We anticipate that the spectra will be quite different from those of the corresponding helium adducts.

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