Incorporation of Helium, Neon, Argon, Krypton, and Xenon into Fullerenes using High Pressure

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In their first paper on Buckminsterfullerene,[1] Kroto and Smalley et al. proposed a hollow structure. Interest in the inclusion of atoms into the cavity to form "endohedral complexes" has continued. Early work concentrated on incorporating metals,[2] but noble gas atoms were obvious possibilities. Several studies reported that collisions of fullerene cation radicals with helium and neon in a mass spectrometer led to addition of the mass of the noble gas atoms to the ions.[3–7] Many theoretical studies[8–15] have appeared with estimates of the energies of fullerenes containing noble gas atoms, the dynamics of motion inside the cavity, and spectroscopic properties, even though none of these substances has been prepared in quantity.

We have recently shown[16] that fullerene prepared in the standard manner (a graphite arc in a low pressure of helium[17]) contains helium in about one in a million molecules. Heating fullerenes in several atmospheres of ^{3}He or neon at 600 °C led to inclusion of these atoms at similar levels. We proposed that

this process takes place by the reversible breaking of one or more bonds, opening a "window" large enough for entry of atoms. The noble gases were detected by heating samples in the modified mass spectrometer operated by one of us (R.J.P.).[16] We have now incorporated krypton using ∼15 atm at 600 °C for 2 h. An 18.5-mg sample of the resulting fullerene yielded 1.6×10^{-6} cm^3 of ^{84}Kr on heating (1 atom in 410 000 molecules), with a release pattern similar to that reported for helium and neon. Since several theoretical papers predicted that krypton and xenon would not fit into C_{60}, we wanted to try to incorporate xenon.

To investigate the spectroscopic and other properties of these interesting noble gas compounds, it is necessary to increase the fraction of fullerene molecules occupied. We have done this by carrying out the incorporation step at high pressures of the gas. One of us (S.M.) operates a facility with high-pressure steel vessels that can be heated behind appropriate shielding. Usually, a pump is employed to compress the gas into the vessel. Using expensive gases (e.g., ^{3}He), this is a disadvantage since large amounts of gas are required for each run. We wanted to achieve high pressures using small amounts.

We proceded as follows. A 4-in. tube ($^1/_4$-in. o.d.) of oxygen-free copper was thoroughly cleaned and vacuum annealed at 550 °C. One end was sealed using a crimping tool. A 50–100-mg sample of fullerene was introduced and covered with a plug of glass wool. The tube was connected to a vacuum line and carefully evacuated for 30–60 min. Gas was introduced while the copper tube was cooled with liquid nitrogen. When the pressure of the gas in the line was near atmospheric, the open end of the tube was sealed with the crimping tool. The resulting ampule (volume ∼1 mL) was then submerged in water to check for leaks.

The high-pressure vessel used had an internal diameter of $^1/_2$ in. and was 12 in. long. It was first cooled to –70 °C using dry ice, and about $8^1/_2$ in. of it was filled with bars made by compacting powdered dry ice with a hammer and a steel rod in an aluminum "mold" ($^1/_2$-in. i.d., 4-in. long). The ampule was put on top of these bars, and about half of the remaining empty space was filled with powdered dry ice. The vessel was closed using a cap with a pressure gauge. To generate high pressure, it was heated in a furnace to about 600 °C for 5 h (counted after the pyrometer in the furnace reached this temperature, about 2.5 h). We were able to obtain pressures up to 2700 atm (40 000 psi).

When the sealed vessel was heated and the pressure increased, the copper tube collapsed, compressing its contents. We expected the pressure inside the ampule to be approximately the same as that outside it. After the vessel was heated, the furnace was removed and the vessel allowed to cool. The sample was recovered from the copper tube and extracted, usually for 24 h, with toluene or CS$_2$. A Soxhlet extractor can be used for this purpose. Finally, the solvent was removed. Extraction was necessary because some of the fullerene was destroyed by heating and became insoluble.

This procedure was followed for helium, neon, argon, krypton, and xenon with runs of about 5 h. The pressure varied from run to run since the amount of CO$_2$ was not the same each time. The furnace heats the bottom of the vessel, and the temperature varies at different heights. It is difficult to know the temperature inside the high-pressure vessel accurately. Most of the ampules were heated to ∼620 °C, and about 55–65% of the fullerene was recovered in the latest runs. The decomposition was greater when temperatures over 630 °C were used. The pressures reported are those measured at the end of the experiments. When the bottom of the vessel is at the final temperature, the upper region is still heating up, resulting in an increase in pressure (up to 10%) as the experiment proceeds.

Part-per-million levels of the noble gases produce no measurable effects in the conventional mass spectrum, since the peaks due to ions containing these atoms are well below the noise level. However, samples of fullerene heated in the presence of Ne (38 000 psi, 66% recovery), Ar (40 000 psi, 45% recovery), Kr (24 500

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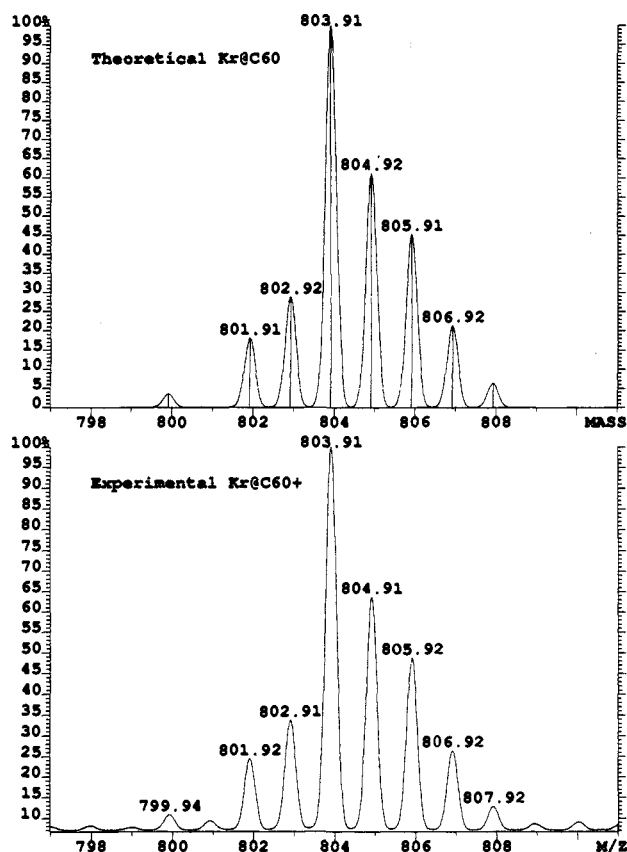
Figure 1. Theoretical mass spectrum for Kr@C$_{60}$ with normal abundances for carbon and krypton isotopes (top) and experimental mass spectrum of krypton-doped sample (bottom).
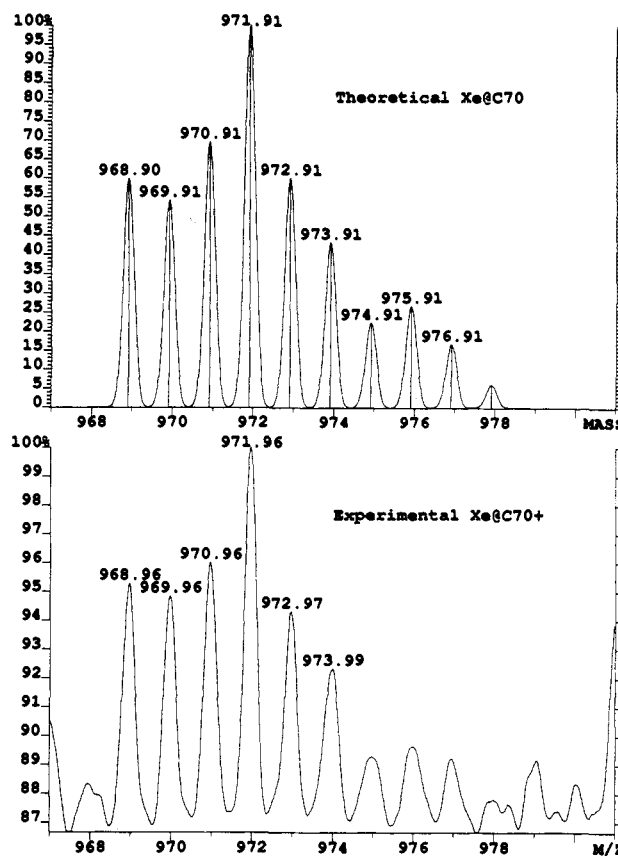

Figure 2. Theoretical mass spectrum for Xe@C$_{70}$ with normal abundances for carbon and xenon isotopes (top) and experimental mass spectrum of xenon-doped sample (bottom).

psi, 25% recovery), and Xe (18 000 psi, 45% recovery) show distinct and reproducible peaks (electron impact ionization) for fullerene ions containing the noble gases. The theoretical mass spectra of the corresponding adducts were calculated using the natural isotopic abundance of the involved atoms. Theoretical spectra and the corresponding regions of the experimental spectrum for Kr@C$_{60}$ are shown in Figure 1, and for Xe@C$_{70}$ in Figure 2. Agreement between calculated and experimental curves provides convincing evidence that Ne@C$_{60}$, Ar@C$_{60}$, Kr@C$_{60}$, Xe@C$_{60}$, Ne@C$_{70}$, Ar@C$_{70}$, Kr@C$_{70}$, and Xe@C$_{70}$ have been synthesized. We determined the fraction of molecules incorporating noble gas atoms from the heights of the largest peak corresponding to X@C$_{60}$ in relation to the 720 peak in C$_{60}{}^{+}$, correcting for relative isotope abundance. The results are Ne, 0.2%; Ar, 0.3%; Kr, 0.3%; and Xe, detected but difficult to quantify because of interferences ($\sim$0.008%). In a similar way, the fractions of X@C$_{70}$ relative to the abundance of the m/z 840 ion were found to be Ne, 0.2%; Ar, 0.2%; Kr, 0.2%; Xe, 0.04%. The yields were measured by signal averaging over 100 spectra and are preliminary until we are able to signal average over the volatilization of an entire sample. The data trends, including the significantly lower yields of Xe@C$_{70}$ and still lower yield of Xe@C$_{60}$, should be valid. We have probably not achieved equilbrium in the labeling. The equilibrium amounts are likely to be greater in all cases.

It was more difficult to measure incorporation of helium at high pressure in the manner described above because the natural abundance of C$_{60}$ and C$_{70}$ with four ^{13}C atoms is high enough to interfere with the peaks of ^{4}He@C$_{60}{}^{+}$ and ^{4}He@C$_{70}{}^{+}$. We *do* see an increase of the intensity of the m/z 725 peak over that predicted for C$_{60}$ with five ^{13}C's which we believe is due to ions with ^{4}He and one ^{13}C. Additional, compelling evidence for increased helium incorporation was obtained. ^{3}He has spin = $^{1}/_{2}$, allowing its observation in the NMR. The ^{3}He NMR spectra

of ^{3}He@C$_{60}$ and ^{3}He@C$_{70}$ in collaboration with Anet and Freedberg[18] show that the incorporation fraction is about 0.1%.

We previously used a simple hard-sphere model[17] to estimate the amount of helium to be expected inside C$_{60}$. A carbon atom size was used to estimate the size of the "cavity" in C$_{60}$. The equilibrium probability of a noble gas atom to be in that cavity was assumed to be a function of gas density and the "free volume" of the cavity. As the atom size increases, the predicted equilibrium incorporation fraction falls, rapidly approaching zero as the atom size approaches the size of the cavity. The usual hard-sphere radii for krypton and xenon lead to a prediction of little or no incorporation of these gases at equilibrium. To rationalize the substantial incorporation of krypton and (less) of xenon, one must include a van der Waals-type attractive interaction between the noble gas atom and the carbons. The favorable interaction energy is greater for these larger atoms. Furthermore, as the size of an included atom increases, it is able to interact favorably with more of the carbons of C$_{60}$ at the same time. An atom of ideal size at the center of C$_{60}$ should be able to interact optimally with all 60 carbon atoms at once. Xenon appears to be so large that repulsion becomes important.

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