Direct Detection and Quantitation of He@C$_{60}$ by Ultrahigh-Resolution Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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In this paper, we report negative ion microelectrospray Fourier-transform ion cyclotron resonance (FT-ICR) mass spectrometry of C$_{60}$ samples containing ~1% ^{3}He@C$_{60}$ or ^{4}He@C$_{60}$. Resolving ^{3}He@C$_{60}^-$ and ^{4}He@C$_{60}^-$ from C$_{60}$ containing 3 or 4 ^{13}C instead of ^{12}C atoms is technically challenging, because the target species are present in low relative abundance and are very close in mass. Nevertheless, we achieve baseline resolution of ^{3}He@C$_{60}^-$ from ^{13}C$_3^{12}$C$_{57}^-$ and ^{4}He@C$_{60}^-$ from ^{13}C$_4^{12}$C$_{56}^-$ in single-scan mass spectra obtained in broadband mode *without* preisolation of the ions of interest. The results constitute the first *direct* mass spectrometric observation of endohedral helium in a fullerene sample at this (low) level of incorporation. The results also demonstrate the feasibility of determining the extent of He incorporation from the FT-ICR mass spectral peak heights. The present measurements are in agreement with those obtained by the pyrolysis method [1–3]. Although limited in sensitivity, the mass spectral method is faster and easier than pyrolysis. (J Am Soc Mass Spectrom 2002, 13, 1349–1355) © 2002 American Society for Mass Spectrometry

Endohedral fullerene compounds (denoted M@C$_n$ [4]) were observed [5, 6] soon after the discovery of buckminsterfullerene (C$_{60}$) [7]. Following the development of the Krätschmer-Huffman method for preparation of fullerenes [8] (an electrical discharge between graphite electrodes in the presence of 0.2 atm of He gas), Smalley and co-workers produced macroscopic quantities of endohedral metallofullerenes in laser vaporization experiments on graphite doped with metal salts [4]. Weiske et al. [9] observed helium within the fragments of C$_{60}^+$ following high-energy collisions between the cations and the noble gas. Shortly after, the full He@C$_{60}^+$ adduct was observed [10, 11]. Endohedral neon and argon compounds have also been produced by that method [12–14]. Another technique for the preparation of endohedral fullerene compounds is that of ion implantation (the endohedral species is neutralized on implantation). Endohedral species containing lithium and other alkali metals [15–17], the noble gases, He and Ne [18], and nitrogen [19] have been produced by that method.

Endohedral compounds of all the noble gases can be prepared by heating fullerenes under high noble gas pressure [1–3, 20]. Initially, yields of incorporation were approximately 0.1% for He, Ne, Ar and Kr and 0.03% for Xe. Subsequent experiments showed that reiterations of the labeling procedure resulted in higher yields of incorporation (~1%) [21]. ^{3}He@C$_{60}$, an NMR-active molecule, has also been prepared by that method [21, 22]. Recent results have shown that the presence of KCN catalyzes the incorporation of noble gas, giving higher yields of incorporation (~1%) in a single labeling experiment [23]. It is also known that He is trapped inside fullerenes (at about 1 ppm of empty fullerene) prepared by the Krätschmer-Huffman procedure [1, 8]. In a recent finding, it was shown that fullerenes extracted from the Allende and Murchison meteorites contained endohedral helium [24]. The ^{3}He/^{4}He ratio in those fullerenes was very high, ~150 times greater than in the earth's atmosphere and similar to the value estimated for the early solar system. In the above studies, the noble gases were detected and quantified by pyrolyzing the material to release the gas, which was detected in either a quadrupole mass spectrometer [1, 3, 25] or a linear time-of-flight mass spectrometer [24]. It is possible, with sufficient labeling, for the larger noble gas endohedral fullerenes to be detected in standard mass spectra [2]. However, that method is not suitable

for analyzing $He@C_{60}$. At the current yields of incorporation, it is not possible to resolve $^4He@C_{60}$ from the $^{13}C_4^{12}C_{56}$ nuclide of C_{60} with most mass analyzers. In this communication, we report negative-ion electrospray [26–28] FT-ICR mass spectrometry [29] of C_{60} samples containing $^3He@C_{60}$ and $^4He@C_{60}$ prepared by the labeling method. The high mass resolving power and mass accuracy of FT-ICR mass spectrometry make it ideal for application to such a problem. Moreover, the high dynamic range of our instrument (compared to lower field, smaller bore FT-ICR instruments) is particularly advantageous for identifying trace components such as these. We also show that it is possible to calculate yield of incorporation of helium from the FT-ICR MS spectra.

FT-ICR mass spectrometry offers the highest mass resolving power ($m/\Delta m_{50\%}$, in which $\Delta m_{50\%}$ is mass spectral peak full width at half maximum peak height) and highest mass accuracy for ions of m/z <5000. The literature contains many examples of high resolving power achieved with FT-ICR mass spectrometry [30–35]. Achieving high mass resolution (m_2–m_1 >$\Delta m_{50\%}$, in which m_1 and m_2 are the closest masses that can just be resolved) is far more challenging experimentally for FT-ICR mass spectrometry than obtaining high resolving power for ions of a single mass (or two ions well-separated in mass). Coulomb repulsion between coherently orbiting ion packets of slightly different m/z can result in distortion, shifting and coalescence of the measured cyclotron resonances [36–39]. As ion mass increases, so does the tendency of closely spaced ion resonances to coalesce [36]. Similarly, the smaller the mass difference between the ions, the more likely their cyclotron resonances are to coalesce [36]. Nevertheless, many examples of high resolution have been published [35, 40–42]. Most recently, Marshall and co-workers baseline-resolved two isobaric 900 Da peptides differing in mass by 0.45 mDa [42]. However, that performance required prior stored waveform inverse Fourier transform (SWIFT) [43, 44] dipolar ejection of unwanted ions, followed by digital quadrature heterodyne detection [45]. Reduction of ion density within the cell, e.g., by SWIFT isolation and/or evaporative cooling (by lowering the axial electrostatic trapping potential in a series of steps), is necessary to achieve high resolution, because high ion population density results in significant Coulombic interactions between ions with associated coalescence and distortion of cyclotron resonances. Coalescence is especially prevalent when an ion packet of high ion density (e.g., $^{12}C_{60}$) orbits at a cyclotron frequency close to that of a low-abundance ion packet of interest (e.g $^{13}C_4^{12}C_{56}^-$). High ion population density can also produce a non-quadrupolar variation of the electrostatic field in the ICR trap [34]. If such a variation occurs during acquisition of a long-lasting time-domain ICR signal (a prerequisite for high resolution), a corresponding variation in the cyclotron frequency will broaden, shift, and/or split the FT-ICR mass spectral peaks [46, 47]. Those problems can be minimized by use of higher magnetic field [48] and/or a larger ICR trap, thereby reducing ion density, such as for our instrument (9.4 tesla magnet, 9.4 cm diameter trap).

Experimental

Samples

Neutral C_{60} samples containing approximately 1% $^3He@C_{60}$ and $^4He@C_{60}$ were prepared by the labeling method, in the presence of KCN [1–3, 23]. For comparison, C_{60} (99.5% purity) was purchased from Aldrich (Milwaukee, WI). C_{60}^- and $He@C_{60}^-$ anions were generated on the benchtop by the method described by Wu et al. [49]. ~2–5 mg of the fullerene sample, ~60 mg sodium hydrosulfite, and ~180 mg of sodium hydroxide were placed in a conical flask inside a glove bag. The glove bag was purged with nitrogen. 10 mL of tetrahydrofuran (THF) was added with stirring. The reactants did not dissolve in the THF. 2.5 mL of deoxygenated water was added. The sodium hydroxide pellet dissolved in the water and the fullerene and sodium hydrosulfite were suspended between the organic and caustic layers. Reduction occurred rapidly and the red-purple anions diffused into the THF layer. The THF layer was separated and used directly for negative ion electrospray mass spectrometry.

A number of other species are generated during this procedure as a result of reaction of the fullerene anion with oxygen and subsequent reaction with THF [49, 50]. Examples include $C_{60}O^-$, $C_{60}O_2^-$, $C_{60}(O_2H)^-$ (from dioxygen coupling to C_{60}^- followed by hydrogen abstraction from THF) and $C_{60}(C_4H_7O)^-$ (from coupling the THF radical to the fullerene anion). Although attempts were made to keep such products to a minimum (to ensure high signal-to-noise ratio for the C_{60}^-/$He@C_{60}^-$ peaks), they proved useful in providing internal calibrants (see below).

Water (HPLC grade) was purchased from J. T. Baker (Philipsburg, NJ) and degassed under vacuum with sonication. Tetrahydrofuran, distilled and stored under argon, was purchased from Aldrich (Milwaukee, WI) as was sodium hydrosulfite. Sodium hydroxide was purchased from Fisher Scientific (Fair Lawn, NJ).

FT-ICR Mass Spectrometry

The fullerene samples were analyzed with a homebuilt, passively shielded, 9.4 tesla FT-ICR mass spectrometer [51] equipped with an external microelectrospray ionization source [52, 53]. The samples were infused at a flow rate of 300 nL/min through an electrospray emitter consisting of a 50 μm i.d. fused silica capillary which had been mechanically ground to a uniform thin-walled tip [54]. −2.0 kV was applied between the microspray emitter and the capillary entrance. The electrosprayed ions were delivered into the mass spectrometer through a Chait-style atmosphere-to-vacuum interface [55] and externally accumulated [52] for 3–5 s in an rf-only
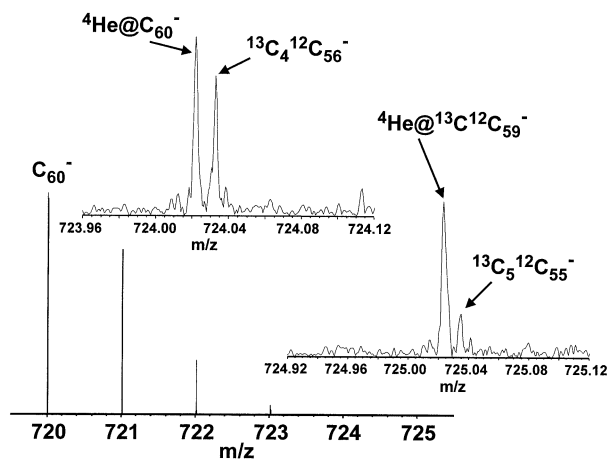
Figure 1. Segment of a single-scan negative ion micro-ESI FT-ICR mass spectrum of C_{60} containing ~1% $^4He@C_{60}$. Mass resolving power, $m/\Delta m_{50\%}$, is ~300,000 at m/z 724. Insets show baseline-resolved $^4He@C_{60}^-$ and $^{13}C_4^{12}C_{56}^-$; and $^4He@^{13}C^{12}C_{59}^-$ and $^{13}C_5^{12}C_{55}^-$.

Figure 2. Segment of a single-scan negative ion micro-ESI FT-ICR mass spectrum of C_{60} containing ~1% $^4He@C_{60}$ showing peaks corresponding to the oxidation product, $C_{60}O^-$. Mass resolving power, $m/\Delta m_{50\%}$, is ~220,000 at m/z 740. Inset shows baseline-resolved $^4He@C_{60}O^-$ and $^{13}C_4^{12}C_{56}O^-$.

octopole. The ions were transferred through multipole ion guides and trapped in an open [56] cylindrical cell (Malmberg-Penning trap [57]).

Ions were frequency-sweep ("chirp") [58] excited (48 to 320 kHz at 150 Hz/μs) and detected in direct mode (4 Mword or 2 Mword time-domain data that was digitized over a period of 3.2 or 1.6 s). Each spectrum shown represents a single-scan mass spectrum, which was Hanning apodized, zero-filled once and subjected to fast Fourier transform (FFT) followed by magnitude calculation. The experimental event sequence was controlled by a modular ICR data acquisition system (MIDAS) [59]. The FT-ICR mass spectra were internally frequency-to-m/z calibrated [60, 61] with respect to the C_{60}^- peak and two of the known oxidation product peaks, e.g., $C_{60}O^-$, $C_{60}O_2^-$, $C_{60}(O_2H)^-$, and $C_{60}(C_4H_7O)^-$. The FT-ICR mass spectra were analyzed by use of the MIDAS analysis software package [62].

Results and Discussion

$^4He@C_{60}^-$

The mass [63] of $^4He@C_{60}^-$ is 724.003152 Da and the mass of $^{13}C_4^{12}C_{56}^-$ is 724.013968 Da, a mass difference, Δm, of 10.8 mDa. Figure 1 shows a segment of a single-scan micro-ESI FT-ICR broadband mass spectrum of a C_{60} sample containing ~1% $^4He@C_{60}$. Two Mword time-domain data were collected. The absence of signals at non-integral m/z values confirms that all ionic species are singly charged [64]. The spectrum was internally calibrated with respect to $^{12}C_{60}^-$ (theoretical ion mass, 720.000549 Da), $^{12}C_{60}O^-$ (theoretical ion mass, 735.995464 Da), and $^{12}C_{60}(C_4H_7O)^-$ (theoretical ion mass, 791.050239 Da). The RMS error was 0.91 ppm from 720–791 Da. Peaks corresponding to $^4He@C_{60}^-$ and $^{13}C_4^{12}C_{56}^-$ species (see inset of Figure 1), were baseline-resolved (mass resolving power, $m/\Delta m_{50\%}$, ~300,000) and the calculated mass difference was 10.9 mDa, in
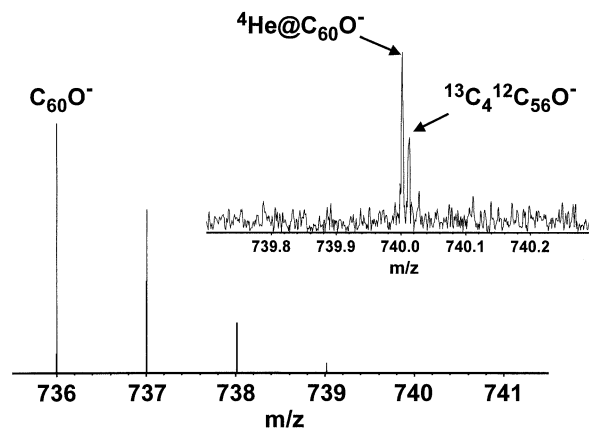
excellent agreement with the theoretical 10.8 mDa value. It was also possible to resolve (see inset, Figure 1) the peaks corresponding to the species, $^4He@^{13}C^{12}C_{59}^-$ and $^{13}C_5^{12}C_{55}^-$ ($m/\Delta m_{50\%} \approx 200,000$). The increased relative abundance of the endofullerene in the latter mass doublet reflects the increased probability that a molecule comprising sixty C atoms contains *one* rather than *five* ^{13}C atoms. The theoretical abundances of $^4He@^{12}C_{60}^-$ relative to $^4He@^{13}C^{12}C_{59}^-$ and $^{13}C_4^{12}C_{56}^-$ relative to $^{13}C_5^{12}C_{55}^-$ are 1:0.67 and 1:0.12, respectively, in qualitative agreement with the experimental FT-ICR mass spectral relative abundance ratios, 1:0.85 and 1:0.32. The deviation may be explained by Coulomb distortions that occur between closely spaced resonances. Although doubly-charged anions of C_{60} are stable and have been observed experimentally by laser desorption/ionization, no doubly-charged anions [64, 65] were observed here by electrospray, in agreement with the prior findings of Wu et al. [49].

Peaks corresponding to the incorporation of helium in the fullerene oxidation products were also observed. Figure 2 shows a segment of a single-scan mass spectrum of the $C_{60}/^4He@C_{60}$ sample, in which peaks corresponding to the oxidation product, $C_{60}O^-$, are clearly evident. The species, $^4He@C_{60}O^-$ and $^{13}C_4^{12}C_{56}O^-$, are baseline resolved ($m/\Delta m_{50\%} \approx 220,000$). The calculated mass difference, Δm, is 10.8 mDa, in perfect agreement with the theoretical value. Analysis of commercially available C_{60} analyzed under the same conditions yielded unsplit peaks, thereby eliminating the possibility of peak splitting arising from ion redistribution during the long trapping period. In each case, single peaks were observed (see Figure 3).

$^3He@C_{60}^-$

The masses of $^3He@C_{60}^-$ and $^{13}C_3^{12}C_{57}^-$ are 723.016578 Da and 723.010614 Da: a mass difference, Δm, of 5.96 mDa. Figure 4 shows segments of a single-scan ESI FT-ICR
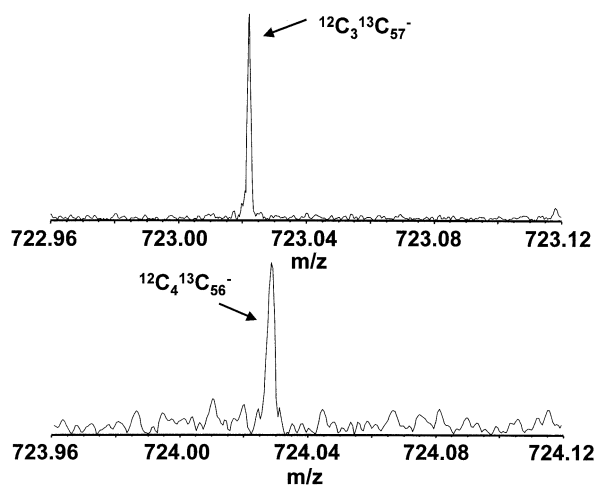
Figure 3. Segments of single-scan negative ion micro-ESI FT-ICR mass spectra of pure C_{60} showing (top) $^{13}C_3^{12}C_{57}^-$ (mass resolving power, $m/\Delta m_{50\%} \approx 650{,}000$ at m/z 723, 4 Mword data set) and (bottom) $^{13}C_4^{12}C_{56}^-$ ($m/\Delta m_{50\%} \approx 260{,}000$ at m/z 724, 2 Mword data set).

broadband mass spectrum of a C_{60} sample containing ~1% $^3He@C_{60}$. The mass difference between the species of interest is smaller here than for endohedral $^4He@C_{60}$; hence higher resolution is required and it is necessary to extend the time-domain data acquisition period (from 1.6 to 3.2 s). The spectrum was internally calibrated with respect to $^{12}C_{60}^-$, $^{12}C_{60}O^-$, and $^{12}C_{60}(C_4H_7O)^-$. The RMS error was 0.22 ppm from 720–791 Da. The $^3He@C_{60}^-$ and $^{13}C_3^{12}C_{57}^-$ species are clearly resolved ($m/\Delta m_{50\%} \approx 650{,}000$), as are the $^3He@^{13}C^{12}C_{59}^-$ and $^{13}C_4^{12}C_{56}^-$ species. The calculated mass differences, Δm, are 5.99 mDa ($^{13}C_3^{12}C_{57}^-/^3He@C_{60}^-$) and 5.89 mDa ($^{13}C_4^{12}C_{56}^-/^3He@^{13}C^{12}C_{59}^-$), in excellent agreement with the theoretical value of 5.96 mDa. As for $^4He@C_{60}$, the relative abundances between these pairs of species are explained by the relative abundances of ^{13}C and $^{13}C_5$.

Endohedral helium was also observed in the oxida-

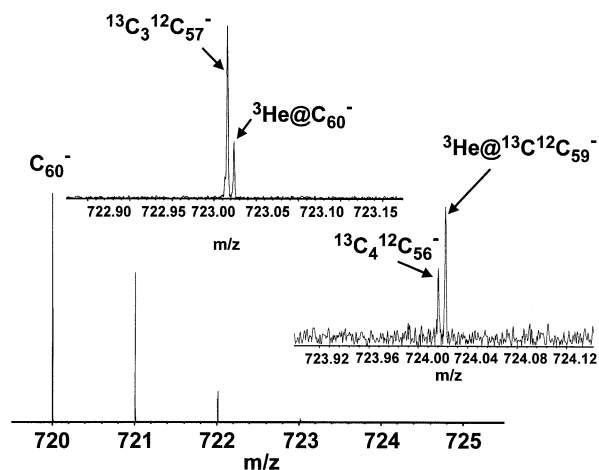**Figure 4.** Segment of a single-scan negative ion micro-ESI FT-ICR mass spectrum of C_{60} containing ~1% $^3He@C_{60}$. Mass resolving power, $m/\Delta m_{50\%}$, is ~650,000 at m/z 723. Insets show baseline-resolved $^3He@C_{60}^-$ and $^{13}C_3^{12}C_{57}^-$; and $^3He@^{13}C^{12}C_{59}^-$ and $^{13}C_4^{12}C_{56}^-$.
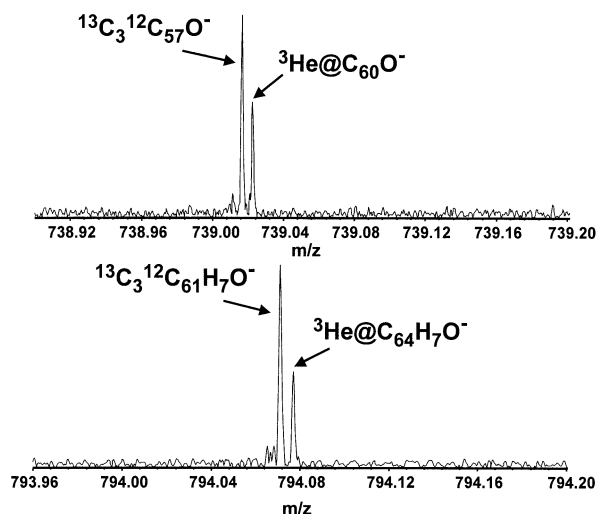

Figure 5. Two segments of a single-scan negative ion micro-ESI FT-ICR mass spectrum of C_{60} containing ~1% $^3He@C_{60}$ showing peaks corresponding to the oxidation products (**a**) $C_{60}O^-$ ($m/\Delta m_{50\%}, \approx 640{,}000$ at m/z 739) and (**b**) $C_{64}H_7O^-$ ($m/\Delta m_{50\%}, \approx 480{,}000$ at m/z 794).

tion products, as shown in Figure 5. Peaks corresponding to the species $^{13}C_3^{12}C_{57}O^-$ and $^3He@C_{60}O^-$, and the species $^{13}C_3^{12}C_{61}H_7O^-$ and $^3He@C_{64}H_7O^-$, are baseline-resolved. Commercially available C_{60} analyzed under the same conditions exhibited no mass doublets.

Extent of He Incorporation

Previous measurements by the pyrolysis method suggested that He incorporation in the samples provided was approximately 1%. Because we are able to resolve $He@C_{60}$ from the ^{13}C-containing nuclides of C_{60}, and because the relative abundance of ^{13}C versus ^{12}C is well known (0.0111), it is possible to calculate the extent of He incorporation from the abundance of the all ^{12}C endohedral fullerene relative to its adjacent ^{13}C-containing fullerene nuclide. [Although space charge effects can severely distort the observed abundance ratio of ions of widely different relative abundance, the observed abundance ratio of ions of comparable relative abundance (as in the present data) should be more accurate.] The underlying assumption of this method of calculation is that both unoccupied C_{60} and the endohedral fullerene have similar electron affinities. That assumption appears eminently reasonable based on the prior work of DiCamillo et al. [20]. The abundance of $^{13}C_4^{12}C_{56}$ relative to $^{12}C_{60}$ is $(60)(59)(58)(57)(0.9889)^{56}$ $(0.0111)^4/(4)(3)(2)(0.9889)^{60} = 0.77\%$. Thus, from the abundance of $^4He@C_{60}^-$, x, relative to $^{13}C_4^{12}C_{56}^-$, we obtain the abundance of $^4He@C_{60}$ relative to C_{60} as $x(0.77)$. The mean value for x, based on thirteen experiments, was 1.8. ^4He incorporation was calculated as $(1.8)(0.77) = 1.4$ $(\pm 0.6)\%$. ^4He incorporation was also calculated for the oxidation products $C_{60}O^-$ and $C_{60}(C_4H_7O)^-$ and found to be $2.0 \pm 0.4\%$ and $2.7 \pm 0.6\%$ respectively. Finally, He incorporation in the $^3He@C_{60}$ sample was calculated to

be 1.7 ± 0.3% for C_{60}, 2.2 ± 0.3% for $C_{60}O^-$ and 1.4 ± 0.4% for $C_{60}(C_4H_7O)^-$. The extents of incorporation of ^{4}He and ^{3}He in C_{60}, calculated by this method, are in close agreement with the ~1% values estimated by the pyrolysis method. The observed difference between apparent He incorporation in the oxidation products versus C_{60} itself may reflect different reactivities of C_{60} and He@C_{60} toward oxidation.

Conclusion

Negative ion microelectrospray ionization FT-ICR mass spectrometry can baseline resolve endohedral fullerenes containing ~1% ^{4}He or ^{3}He from adjacent ^{13}C-containing nuclides of C_{60} itself: Namely, ^{4}He@C_{60}^- and $^{13}C_4^{12}C_{56}^-$, or ^{3}He@C_{60}^- and $^{13}C_3^{12}C_{57}^-$. It is worth noting that such resolution has been achieved *without* preisolation, e.g., ejecting unwanted ions by use of SWIFT excitation. The experiment is thus more difficult because the target species are present at low abundance relative to $^{12}C_{60}^-$. High mass resolution under such high dynamic range conditions is made possible by the combination of high magnetic field (9.4 T) and large (9.4 cm diameter) ICR trap.

Resolution of the above species enables the *direct* determination of the extent of incorporation of trace levels of helium into a fullerene. Previously, it has not been possible to confirm the presence of He@C_{60}, *at this level of incorporation*, by direct mass spectrometric analysis of the fullerene sample. In that respect, this work represents a significant advance.

We calculate the extent of incorporation of helium, based on relative abundances of species distinguishable only at ultrahigh mass resolving power. Measurements made by this method are in agreement with those made by the pyrolysis method. Although the present method is faster and simpler than the pyrolysis method, it is limited in sensitivity. It is unlikely that an extent of incorporation <0.3% could be determined.

Acknowledgments

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