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Structural Studies of Sc Metallofullerenes by High-resolution Ion Mobility Measurements

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Endohedral metallofullerenes have been extensively studied over the past decade because of their unique structural and electronic properties.[1] Scandium metallofullerenes are especially interesting because they can contain more than two metal atoms ($Sc_3@C_{82}$) which form metal clusters.[2,3] Furthermore, a Sc nitride metallofullerene, $Sc_3N@C_{80}$ has been synthesized recently.[4] The structures of these metallofullerenes have been studied so far by ultrahigh vacuum scanning tunnel microscopy (UHV-STM),[5] NMR,[6]and X-ray diffraction.[3,7] However, these measurements require a large amount (~mg) of purified (>99.9%) samples, which are not always available. It is thus necessary to develop new methods to study the stability and the structures of these novel carbon nanomaterials.

Gas-phase ion mobility measurements have been applied to various species, such as clusters,[8−10] fullerene-related materials,[11] and polypeptides.[12] This method has some favorable features in comparison with STM, NMR, and X-ray measurements. High sensitivity and high selectivity originating from ion mass detection allow us to use only a small amount of mixtures of metallofullerenes. Furthermore, high-speed (~ms) gas-phase detection can provide us structural information on intermediate species.

Here we present the first successful high-resolution ion mobility measurements on $Sc_n@C_m$ ($n = 1\sim3$, $m = 74\sim90$). The results show that all of the metallofullerenes have endohedral structures and that, for some, the carbon cages shrink when exposed to high desorption/ionization laser fluence.

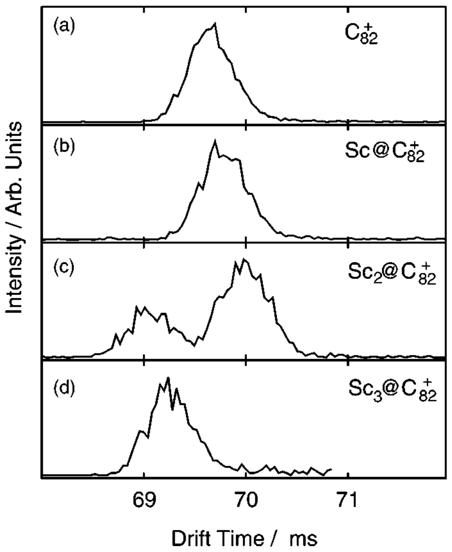

Figure 1. High-resolution ion mobility distributions of C_{82}^{+} and $Sc_n@C_{82}^{+}$ ($n = 1\sim3$) produced from laser desorption/ionization of solvent extractable fullerenes. $Sc_2@C_{82}^{+}$ shows two distinct peaks (details see text).

The Sc metallofullerene samples are prepared by a large-scale DC arc discharge apparatus using Sc graphite composite rods as anodes (Sc 1.6 at %, Toyotanso Inc.). A discharge current of 500 A is employed along with a He buffer gas at 40 Torr.[1,2] The metallofullerenes are extracted from the soot by CS_2. The high-resolution ion-mobility apparatus has been described in detail previously.[13] The apparatus consists of a source region coupled directly to a 63 cm long drift tube. The metallofullerene extracts are drop-coated onto a copper rod and then desorbed/ionized by a focused pulsed excimer laser (XeCl 308 nm). The resulting ions are introduced into the drift tube, which contains helium buffer gas at 500 Torr and has a drift voltage of 10 kV. After traveling through the drift tube, the ions are mass analyzed by a quadrupole mass spectrometer (Extrel Inc.). Drift-time distributions are recorded with a multichannel analyzer (Tennelec/Nucleus Inc. MCS-II).

Figure 1 shows drift time distributions for positive ions of empty fullerenes and metallofullerenes obtained from solvent extractable C_{82} and $Sc_n@C_{82}$ ($n = 1\sim3$). The ions of C_{82}^{+} and $Sc@C_{82}^{+}$ show a single peak, and the drift time is exactly the same as those of previous measurements on $C_{82}{}^{+}$ from other fullerene samples and from well annealed C_{82}^{+} clusters.[10,14] These results are consistent with the endohedral structures determined by X-ray diffraction.[7] However, two structual isomers of $Sc@C_{82}^{+}$ (I, II) existing in the sample[15] are not resolved because as in most cage-isomers they have almost the same ion mobilities. On the other hand, the dimetallofullerene $Sc_2@C_{82}^{+}$ shows two distinct peaks. The main peak with larger drift time corresponds to the peaks measured for C_{82}^{+} and $Sc@C_{82}^{+}$. The other peak has a substantially smaller drift time, which suggests that it has a smaller cage size. The trimetallofullerene $Sc_3@C_{82}^{+}$ shows only one peak which appears to correspond to the $Sc_2@C_{82}^{+}$ peak with the shorter drift time. The high-resolution ion mobility measurements enable us to detect these two structures for the first time.

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(1) Shinohara, H. *Rep. Prog. Phys.* **2000**, *63*, 843−892.

(2) Shinohara, H.; Sato, H.; Ohkohchi, M.; Ando, Y.; Kodama, T.; Shida, T.; Kato, T.; Saito, Y. *Nature* **1992**, *357*, 52−54.

(3) Takata, M.; Nishibori, E.; Sakata, M.; Inakuma, M.; Yamamoto, E.; Shinohara, H. *Phys. Rev. Lett.* **1999**, *83*, 2214−2217.

(4) Stevenson, S.; Rice, G.; Glass, T.; Harich, K.; Cromer, F.; Jordan, M. R.; Craft, J.; Hadju, E.; Bible, R.; Olmstead, M. M.; Maitra, K.; Fisher, A. J.; Balch, A. L.; Dorn, H. C. *Nature* **1999**, *401*, 55−57.

(5) Hashizume, T.; Wang, X. D.; Nishina, Y.; Shinohara, H.; Saito, Y.; Sakurai, T. *Jpn. J. Appl. Phys.* **1993**, *32*, L132−L134.

(6) Yamamoto, E.; Tansho, M.; Tomiyama, T.; Shinohara, H.; Kawahara, H.; Kobayashi, Y. *J. Am. Chem. Soc.* **1996**, *118*, 2293−2294.

(7) Nishibori, E.; Takata, M.; Sakata, M.; Inakuma, M.; Shinohara, H. *Chem. Phys. Lett.* **1998**, *298*, 79−84.

(8) von Helden, G.; Hsu, M. T.; Kemper, P. R.; Bowers, M. T. *J. Chem. Phys.* **1991**, *95*, 3835−3837.

(9) Hudgins, R. R.; Dugourd, P.; Tenenbaum, J. M.; Jarrold, M. F. *Phys. Rev. Lett.* **1997**, *78*, 4213−4216.

(10) Shvartsburg, A. A.; Hudgins, R. R.; Dugourd, P.; Gutierrez, R.; Frauenheim, T.; Jarrold, M. F. *Phys. Rev. Lett.* **2000**, *84*, 2421−2424.

(11) Shvartsburg, A. A.; Hudgins, R. R.; Gutierrez, R.; Jungnickel, G.; Frauenheim, T.; Jackson, K. A.; Jarrold, M. F. *J. Phys. Chem. A* **1999**, *103*, 5275−5284.

(12) Clemmer, D. E.; Jarrold, M. F. *J. Mass Spectrom.* **1997**, *32*, 577−592.

(13) Dugourd, P.; Hudgins, R. R.; Clemmer, D. E.; Jarrold, M. F. *Rev. Sci. Instrum.* **1997**, *68*, 1122−1129.

(14) Shelimov, K. B.; Jarrold, M. F. *J. Am. Chem. Soc.* **1996**, *118*, 1139−1147.

(15) Inakuma, M.; Shinohara, H. *J. Phys. Chem. B* **2000**, *104*, 7595−7599.

10.1021/ja0039031 CCC: $20.00

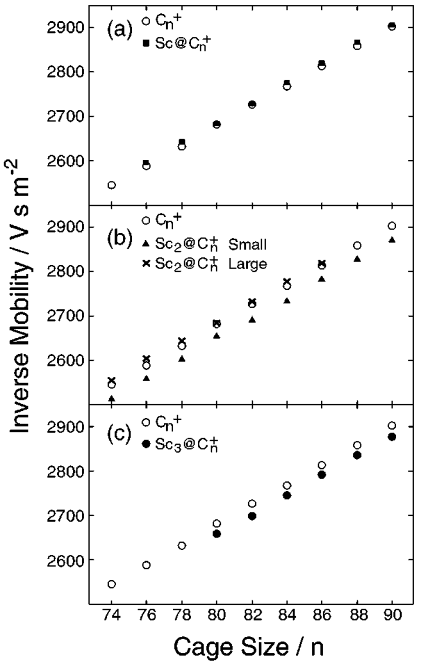

Figure 2. Inverse mobility dependences of $Sc_n@C_m^+$ ($n = 1{\sim}3$) on cage sizes ($m = 74{\sim}90$); (a) $Sc@C_n^+$ vs C_n^+, (b) $Sc_2@C_n^+$ vs C_n^+, (c) $Sc_3@C_n^+$ vs C_n^+. All $Sc@C_n^+$ have inverse mobilities identical to those of C_n^+. Smaller inverse mobilities of $Sc_2@C_n^+$ as well as those of $Sc_3@C_n^+$ are almost the same as those of C_{n-2}^+, suggesting $(Sc_2C_2)@C_{n-2}^+$ and $(Sc_3C_2)@C_{n-2}^+$ structures.

Figure 2 shows the inverse mobilities of mono-, di-, and triscandium fullerenes plotted as a function of cage size. The inverse mobilities are proportional to the cross sections for collisions between the fullerenes and the He buffer gas.[12] Figure 2a shows that Sc monometallofullerenes have almost the same inverse mobilities as the corresponding empty fullerenes, indicating that Sc metallofullerenes are endohedral in this size region. Figure 2b shows, in contrast, that most of $Sc_2@C_n^+$ ($n \leq 86$) have two cage sizes: one corresponds to that of C_n^+ and the other corresponds to that of C_{n-2}^+. These results strongly suggest that $Sc_2@C_n^+$ ions have a "carbide" structure like $(Sc_2C_2)@C_{n-2}^+$ as well as $Sc_2@C_n^+$, the simple endohedral structure. The larger dimetallofullerenes, $Sc_2@C_n^+$ ($n \geq 88$), only have the smaller cage (see Figure 2b). The relative intensity of the carbide structure (carbide/carbide+normal)) shows a minimum of 0.41 at $Sc_2@C_{82}$ and increases to 0.88 and 1.0 at $Sc_2@C_{74}$ and $Sc_2@C_{88}$ as the cage size decreases or increases from $Sc_2@C_{82}$. Sc trimetallofullerenes $Sc_3@C_n^+$ also have smaller cages (see Figure 2c). These Sc trimetallofullerenes may also possess carbide $(Sc_3C_2)@C_{n-2}^+$ structures. In general, the inverse mobilities of the metallofullerenes are slightly larger than those of corresponding empty fullerenes. These differences are probably associated with the electronic properties of the metallofullerenes. Electrons are transferred from the metal atoms to the cage, which results in, for example, $Sc^{2+}@C_{82}^{-2}$.[7] Since the ion mobility is mainly dominated by close interaction between the fullerene cage and He,[12] $(Sc^{2+}@C_{82}^{-2})^+$ and C_{82}^+ are expected to have slightly different mobilities. Parallel differences have been seen in the mobilities of In_n^- and In_n^+ clusters.[16] The inverse mobilities of $(Sc_3C_2)@C_{n-2}^+$ are much larger than those of $(Sc_2C_2)@C_{n-2}^+$ and C_{n-2}^+. The inner hollow space of the carbide structures of $(Sc_3C_2)@C_{n-2}^+$ must be fairly congested, and the C_{n-2}^+ cages may be distorted unlike those of $(Sc_2C_2)@C_{n-2}^+$. However, the inner space of metallofullerenes is large enough to hold these molecules as a Sc tetrametallofullerene $Sc_4@C_{82}$ is stable and has been isolated macroscopically.[1]

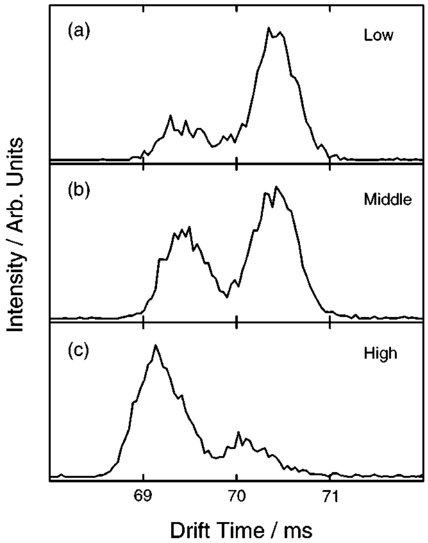

Figure 3. Drift time distribution of $Sc_2@C_{82}^+$ produced under (a) low, (b) middle, and (c) high laser fluence. The shorter drift time peak becomes prominent as the laser fluence increases.

Since the metallofullerenes used in the present study have endohedral structures in the solid state, the carbide structures are probably generated by the laser desorption and ionization processes. Figure 3 shows a laser power dependence of the drift time distributions of $Sc_2@C_{82}^+$. The peak intensities for the shorter drift time increase as the laser power increases. These results clearly suggest that the metallofullerene ions with the smaller (carbide) cages are produced through the desorption/ionization processes. Fullerenes have an even number of carbon atoms in order to eliminate dangling bonds.[17] It is, therefore, natural that two carbon atoms (rather than one) should be encapsulated inside the cage during the shrinkage. This reaction model can explain the low abundance of the carbide structure of $Sc_2@C_{82}$. Since the metallofullerenes with C_{82} cages have been produced with high yield and have shown high stability,[1] some of the $Sc_2@C_{82}$ may survive under the laser irradiation. Although these new carbide structures are observed in gas phase upon desorption/ionization, we have recently produced and characterized $(Sc_2C_2)@C_{84}$ in macroscopic quantities.[18] The results presented here show that the carbide-encapsulated structure are universal. The inner space of fullerenes has much more versatility and flexibility than ever expected.

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Supporting Information Available: A mass spectrum of Sc metallofullerenes (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) Lermé, J.; Dugourd, P.; Hudgins, R. R.; Jarrold, M. F. *Chem. Phys. Lett.* **1999**, *304*, 19–22.

(17) Kroto, H. W. *Nature* **1987**, *329*, 529–531.

(18) Wang, C. R.; Kai, T.; Tomiyama, T.; Yoshida, T.; Kobayashi, Y.; Nishibori, E.; Takata, M.; Sakata, M.; Shinohara, H. *Angew. Chem., Int. Ed.* **2001**, *40*, 397–399.