Fullerenes

Floating Single Hydrogen Molecule in an Open-Cage Fullerene**

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A technique for inserting gaseous or unstable molecules into a molecular cage is a significant problem when researching into molecular capsules for use as hydrogen storage materials or for medicinal applications. We recently succeeded in fully incorporating a H_2 molecule into a derivative of an aza–thia open-cage fullerene (ATOCF). This compound can be regarded as a nanosized container for a single H_2 molecule, with which hydrogen storage can be controlled by pressure and temperature. X-ray diffraction analysis of a single crystal of this fully H_2-encapsulating molecule allowed the successful direct observation of a single H_2 molecule floating inside the hollow cavity of an ATOCF molecule.

Various types of endohedral fullerene complexes are known to date. For example, pure metallofullerenes have been subjected to complete scrutiny as to their structures and properties,[1] but the isolated amounts are generally quite minute. The cages are made of higher fullerenes and the metal atom tends to be located not in the center of the interior space, but close to the carbon cage.[2] These metallofullerenes are generally produced by the arc-discharge method, but the use of such extreme conditions is apparently not suitable for encapsulation of unstable molecules or gases. Rubin et al. reported the synthesis of a fullerene derivative with a 14-membered-ring orifice and succeeded in introducing a He atom and a H_2 molecule inside this fullerene molecule.[3] However, the content of these guest species was so low (1.5 and 5%, respectively) that sufficient information about the encapsulated species could not be obtained, except for NMR data.

We recently succeeded in fully incorporating a H_2 molecule into a derivative of the ATOCF molecule (Figure 1).[4,5] This compound is regarded as a unique model that can provide an opportunity to observe a single molecule of H_2 as a completely isolated species. The extraordinary high-field shift ($\delta = -7.25$ ppm) of the ^{1}H NMR signal of the H_2 molecule surely indicates that H_2 is encapsulated *somewhere* inside the fullerene cage. However, we desired more substantial information about the location of the H_2 molecule within the ATOCF cage, hopefully through direct observation of the molecule. X-ray diffraction analysis with synchrotron radiation appeared most suitable for this purpose.

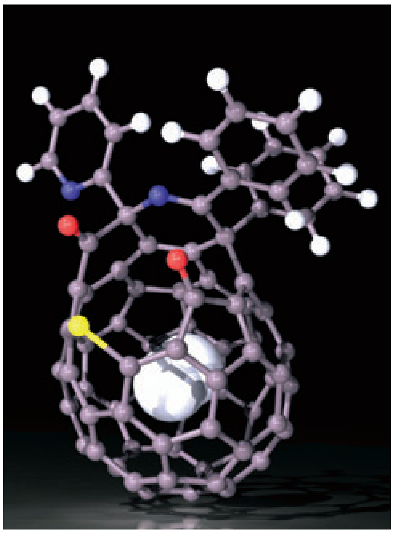

Figure 1. Molecular structure of H_2@ATOCF. The encapsulated H_2 molecule is shown as a space-filling model, and the host molecule is shown as a ball-and-stick model.

Thus, we conducted an X-ray diffraction study of single crystals of H_2-containing ATOCF (H_2@ATOCF) and of empty-cage ATOCF as a matching reference. Accurate X-ray diffraction data were obtained by synchrotron radiation with a Weissenberg-type imaging-plate detector at BL-1A in the Photon Factory at KEK, Japan.[6] The results showed good agreement with those of a previous report on the crystal structure of ATOCF.[5] According to the results of differential-Fourier calculations, there were clearly observed electron-density peaks with a height of 0.46 electrons Å^{-3} in the cages of H_2@ATOCF in the unit cell, while no such electron density was observed in the case of the empty ATOCF cage. Thus, the direct observation of the H_2 molecule encapsulated in the cage of ATOCF was achieved for the first time.

It is not possible to precisely locate the electron density of a species as small as a H_2 molecule by conventional least-squares refinement. However, we were able to picture an

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image, which enabled us to construct a three-dimensional electron-density map from the diffraction data by using the maximum entropy method (MEM). The MEM analysis was carried out with the Enigma program[7] at a resolution of 128 × 128 × 128 pixels. The R factors of the final MEM charge density were 0.028 and 0.024 for H_2@ATOCF and empty ATOCF, respectively. Three-dimensional representations of the final MEM charge densities of H_2@ATOCF and empty ATOCF are shown in Figure 2. The equal-density levels are at 0.4 electrons Å^{-3}. The MEM charge-density maps clearly show an area of electron density, which is colored red in Figure 2, floating at the center of the cage in the H_2@ATOCF molecule. In sharp contrast, no such electron density was observed in the case of the empty ATOCF cage. These characteristic density features are also shown as contour maps in Figure 3.

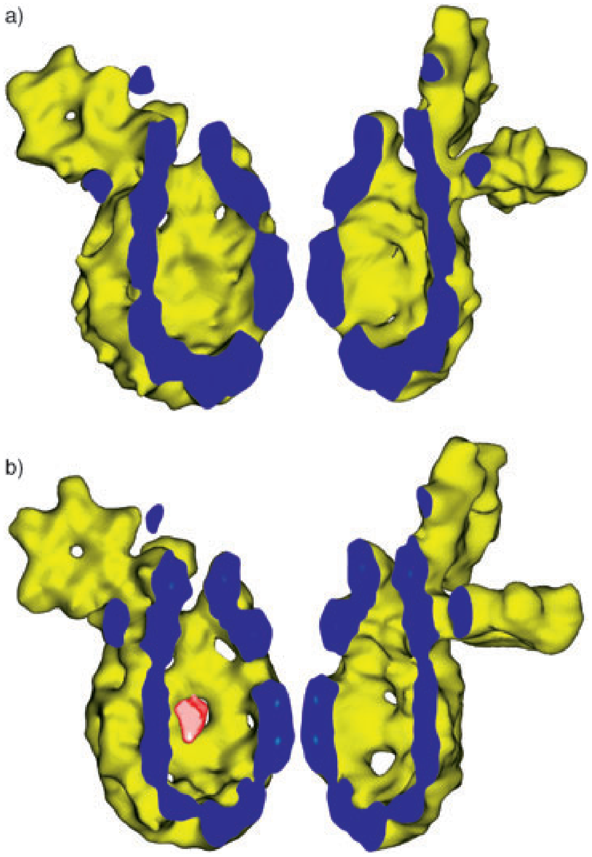

Figure 2. MEM electron densities of a) empty ATOCF and b) H_2@ATOCF as an equal-density contour surface and as a vertical division. The equicontour level is at 0.4 eÅ^{-3}. The electron density of the encapsulated H_2 molecule is colored red in (b).

The main charge density within the fullerene cage is condensed almost at the center of the cage, and a much lower density seems to exist in the area between the center and the inside wall of the cage (Figure 3: vertical division, map 2). However, it is difficult to determine whether the shape of the encapsulated charge density is spherical or elliptical. This ambiguity is most probably caused by the motion of the H_2 molecule, because there is no chemical bond between the trapped H_2 and the carbon cage. Very recently, Carravetta et al. investigated the rotational motion of encapsulated H_2 in H_2@ATOCF by low-temperature solid-state NMR measurements.[8] Their results show that the motional anisotropy of the H_2 molecule inside the ATOCF cage is very small, and that the orifice in the ATOCF molecule only slightly perturbs the rotational motion. In the contour vertical division map (Figure 3) there is no electron density along the neck of the ATOCF molecule, which indicates that the H_2 molecule is electronically segregated from the outside of the cage. Therefore, this H_2 molecule is considered to be completely isolated from the outside. In that sense, the environment of the encapsulated H_2 is assumed to be similar to that of the H_2 molecule incorporated in the pristine C_{60} itself, that is, H_2@C_{60}.

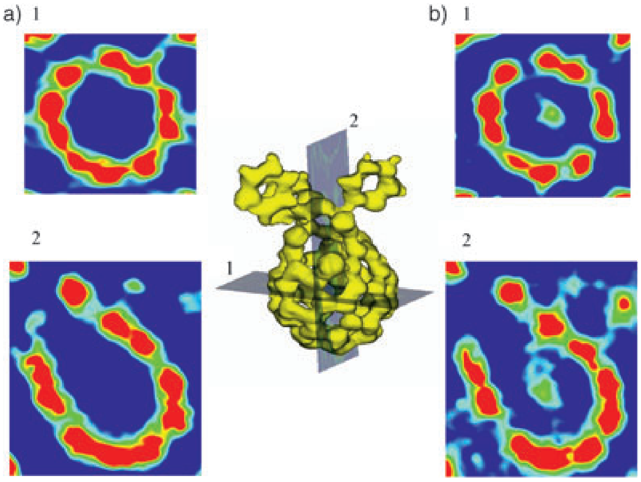

Figure 3. MEM electron-density distributions of a) empty ATOCF and b) H_2@ATOCF for 1) horizontal division and 2) vertical division. The center figure shows the positions of division for (1) and (2). The contour maps are drawn from 0.01 to 0.11 eÅ^{-3}.

Is there any charge-transfer interaction between the encapsulated H_2 molecule and the cage? In the case of metallofullerenes M@C_{82}, the presence of significant charge-transfer interaction between the encapsulated metal and the cage has been reported, which also causes the selection of cage symmetry according to the stability of different isomers.[9,10] In striking contrast, there is no difference in cage structure between H_2@ATOCF and empty ATOCF. Thus, we conclude that there is no appreciable charge transfer between the encapsulated H_2 and the cage.

The precise electron-density profile obtained by the MEM analysis is visualized by the dependence of the electron density on the radius (r), or distance from the center of the cage (Figure 4). The filled and open circles represent the profiles for H_2@ATOCF and empty ATOCF, respectively. The maximum peaks at around $r \approx 3.6$ Å apparently correspond to the cage frame of the ATOCF molecule itself. In the case of an empty ATOCF cage, no charge density is observed in the region of $r < 1.8$ Å. In contrast, the electron density of H_2@ATOCF, which appears to show a local maximum at

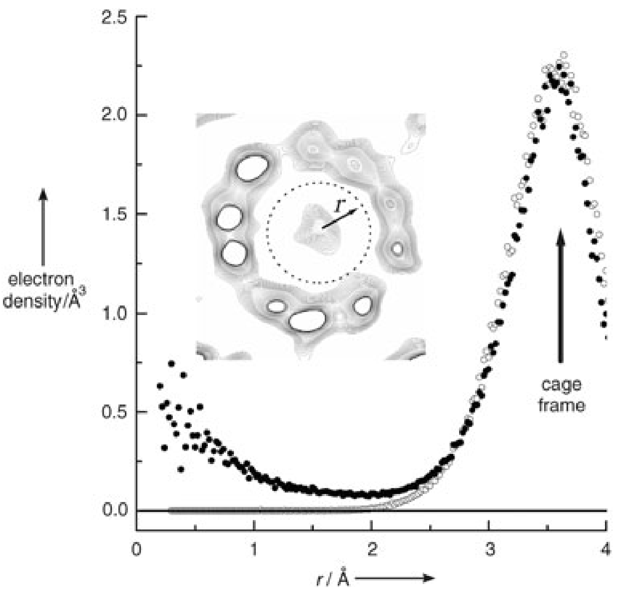

Figure 4. Dependence of electron density on the radius *r* from the center of the cage for endohedral (●) and empty (○) ATOCF molecules. The inset picture demonstrates the determination of the radius (*r*). The electron-density peak for H_2@ATOCF shows a floating H_2 molecule.

the center ($r = 0$ Å), gradually decreases as the distance from the center increases until *r* reaches about 2 Å, but the minimum value for the electron density is not exactly zero. This electron-distribution profile involving nonzero electron density seems to reflect the unsteady motion of the encapsulated H_2. The number of electrons belonging to this H_2 molecule, which was estimated by integration from the center of the cage to the minimum point of electron density, turned out to be 2.0 ± 0.1. This result exactly corresponds to the presence of one H_2 molecule at the center of the hollow cage of the ATOCF molecule, which is in excellent agreement with the ^{1}H NMR result.[4]

The preference of the H_2 molecule to be located at the center of the cage is considered to be the result of van der Waals interaction between the H_2 molecule and the 60 sp^2-hybridized carbon atoms that have an inward curvature in the ATOCF molecule. A preliminary theoretical calculation by density functional theory conducted for $H_2@C_{60}$ revealed that the total energy loss caused by shifting the H_2 molecule from the center of the cage is 0.02, 0.2, and 1.0 eV for a H_2 shift of 0.5, 1, and 1.5 Å from the center, respectively.[11] This result suggests that the encapsulated H_2 molecule is confined to the spherical space at the center of the cage, and strongly supports the results of the MEM analysis.

In summary, we have observed a single H_2 molecule encapsulated in the fullerene cage of ATOCF with synchrotron X-ray diffraction experiments and MEM analysis. The H_2@ATOCF molecule is regarded as an excellent system to examine the important issues characteristic of a single isolated H_2 molecule, for example, *ortho*-H_2 to *para*-H_2 conversion, and the quantum motion of the H_2 molecule at low temperatures in a tiny space. At present H_2@ATOCF is the only molecule which can allow us to discuss the electronic state of a H_2 molecule that is entirely isolated from the atmosphere.

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[1] a) H. Shinohara, *Rep. Prog. Phys.* **2000**, *63*, 843–892; b) *Endofullerenes: A New Family of Carbon Clusters* (Eds.: T. Akasaka, S. Nagase), Kluwer, Dordrecht, **2002**.

[2] For examples, see: a) M. Tanaka, B. Umeda, E. Nishibori, M. Sakata, Y. Saito, M. Ohno, H. Shinohara, *Nature* **1995**, *377*, 46–49; b) C.-R. Wang, T. Kai, T. Tomiyama, T. Yoshida, Y. Kobayashi, E. Nishibori, M. Takata, M. Sakata, H. Shinohara, *Nature* **2000**, *408*, 426–427.

[3] Y. Rubin, T. Jarrosson, G.-W. Wang, M. D. Bartberger, K. N. Houk, G. Schick, M. Saunders, R. J. Cross, *Angew. Chem.* **2001**, *113*, 1591–1594; *Angew. Chem. Int. Ed.* **2001**, *40*, 1543–1546.

[4] Y. Murata, M. Murata, K. Komatsu, *J. Am. Chem. Soc.* **2003**, *125*, 7152–7153.

[5] Y. Murata, M. Murata, K. Komatsu, *Chem. Eur. J.* **2003**, *9*, 1600–1609.

[6] The X-ray wavelength was 1.0 Å. The intensity of the Bragg reflections was measured in a half-sphere of reciprocal space in the range $2\theta < 120°$. The sample was cooled at 200 K by a N_2-gas flow-type refrigerator. The Rapid-Auto program by MSC Corporation was used for two-dimensional image processing; the Sir2002 program was used for the direct method. The number of observed reflections with $I > 5\sigma(I)$ was 9449 for the H_2@ATOCF crystal and 9302 for the empty ATOCF crystal. The Shelx97 program was used for refinements. After full refinement, the *R* factor was 0.09 for the H_2@ATOCF crystal and 0.08 for the empty one.

[7] H. Tanaka, M. Takata, E. Nishibori, K. Kato, T. Iishi, M. Sakata, *J. Appl. Crystallogr.* **2002**, *35*, 282–286.

[8] M. Carravetta, Y. Murata, M. Murata, I. Heinmaa, R. Stern, A. Tontcheva, A. Samoson, Y. Rubin, K. Komatsu, M. H. Levitt, *J. Am. Chem. Soc.* **2004**, *126*, 4092–4093.

[9] K. Kobayashi, S. Nagase, *Chem. Phys. Lett.* **1998**, *282*, 325–329.

[10] S. Nagase, K. Kobayashi, *Chem. Phys. Lett.* **1994**, *231*, 319–324.

[11] S. Tsuneyuki, K. Akagi, private communication. The calculation is done within the generalized gradient approximation (PW91) with Gaussian basis functions 6-31G(d,p).