A Molecular Dynamics Simulation for the Formation Mechanism of Fullerene

Shigeo Maruyama and Yasutaka Yamaguchi

Abstract

The formation mechanism of fullerene, the new type of carbon molecule with the hollow caged structure, was studied using the molecular dynamics method. Simulated C_{60} with an empirical carbon potential was structurally stable up to 3000 K. For higher temperatures, the isomerization due to the migration of pentagons and the ultimate break-up of the spherical structure were observed. In order to investigate the formation mechanism of fullerene, the clustering process starting from isolated carbon atoms was simulated. Under the certain condition of the temperature control, the simulation yielded the hollow caged carbon network which could be regarded as the imperfect fullerene. Intermediate clusters observed in the clustering process starting from randomly located isolated atoms were dimers trimers, linear chains up to C_{10}, mono-cyclic rings in C_{10}-C_{15}, poly-cyclic rings of about C_{20}, 2 dimensional fragments of network, and the imperfect fullerene. One of the remarkable reaction was the linear chain wrapping the poly-cyclic ring to form a fragment of network. Furthermore, the similar simulation starting from some artificial precursors was tried. Finally, a simulation with thinner density of carbon atoms expected to have more realistic rate of collisions yielded a flat graphitic structure.

KEYWORDS: *Fullerene, Molecular Dynamics Method, C_{60}, Cluster, Condensation, Precursor*

1 Introduction

Existence of soccer ball structured C_{60} [Figure 1(a)] was demonstrated by Kroto et. al. [1] in 1985. They used the laser vaporization supersonic nozzle technique to generate the carbon clusters and measured the time of flight mass spectra. They named the molecule of truncated icosahedron as Buckminsterfullerene since the beautiful network structure resembles the famous geodesic dome designed by Buckminster Fuller. Truncated icosahedron is made of 12 pentagonal faces and 20 hexagonal faces. According to the Euler's rule of geometry, the closed caged structure made from only pentagons and hexagons must have 12 pentagons and n hexagons (n = 0, 2, 3, 4, ...). Then, the number of vertices (number of atoms) is $2n$ + 20. Mass spectra of positive carbon clusters showed only even numbered cluster in the range of C_{30} to at least C_{600} [2,3], suggesting that all of those clusters were closed caged structure. It is common now to call such hollow spherical structures fullerene [Figure 1]. The study of these fascinating molecules was limited to certain mass-spectroscopist who had the supersonic nozzle source until 1990, when the simple technique for macroscopic generation of fullerene [4,5] and isolation [6] were discovered. Then, this new material was open to wide areas of applications. The discovery of the superconductivity [7] at T_c = 19 K of the K doped C_{60} crystal further accelerated the research field. Within a few years, generation of metal containing fullerene [8-10], higher fullerenes [11,12], and bucky tube [13,14] [Figure 1(c)] were made possible.

The most popular technique of the macroscopic generation of fullerene is the arc-discharge method which is simply the arc-discharge of graphite electrodes under certain pressure of helium buffer gas [5,15]. The amount of fullerene compared to the collected soot in such a technique yields 10 ~ 15% under the optimum condition. Usually the generated fullerene consists of 80% C_{60}, 15% C_{70} and a small amount of higher fullerenes like C_{76}, C_{78}, C_{82}, C_{84}, quite interesting magic numbers. It is surprising that once vaporized carbon atoms automatically form the very high symmetric structure like C_{60} in the clustering process in such a high yield. It is also remarkable that such
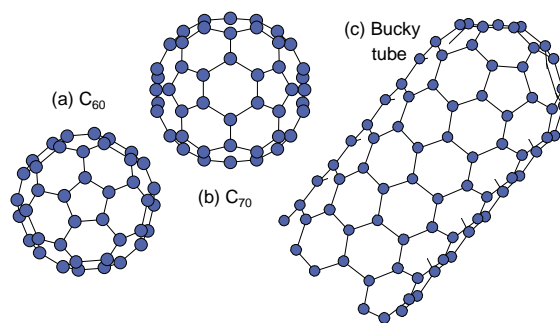

Figure 1 Typical structures of fullerene

molecules had not been found until 1985. Besides these theoretical interests, it is required to clarify the generation mechanism in order to find the more efficient generation method of higher fullerene or metal doped fullerene.

Since the macroscopic generation technique was found accidentally, the formation mechanism is not clear yet. Several models have been proposed based on experimental insights. Smalley et al. [5] described the clustering process from dimers and trimers to build the fragments of hexagonal network with a chance to include pentagons as the defect. They claimed that the pentagons was essential to give the curvature and to decrease the number of dangling bonds. On the other hand, two neighbor pentagons resulted too much strain to the network and the Isolated Pentagon Rule (IPR) should obeyed for the stable fullerene. It is interesting to learn that the smallest fullerene satisfying IPR is C_{60} and next smallest is C_{70}. Quite different paths of the formation of fullerene were proposed such as from graphitic sheet [16] or from once grown bucky tube [17]. On the other hand, Heath [18] proposed that the clustering process intermediates were linear chain up to C_{10}, rings in C_{10}-C_{20} range, fullerene at C_{30}. He explained that C_2 addition until the satisfaction of IPR followed. Achiba et al. [19] proposed a special model that fullerene was made of stacking of carbon rings. They could explain the magic numbers of higher fullerene [11,12] and isomers of C_{76}, C_{86} and C_{84} [20]. Recently, the drift

tube ion chromatography experiments of laser vaporized carbon clusters showed the existence of poly-cyclic rings and the possibility of the annealing of such structure to fullerene [21-24].

Although each model explains some experimental results, it is difficult to decide which model is more reliable. The objective of this work is to try the molecular dynamics simulation of clustering process of carbon atoms for the hint of the formation mechanism of fullerene.

2 Description of Calculations

Carbon atoms were expressed by the potential function originally proposed by Brenner [25] for his simulation of the chemical vapor deposition of diamond films. Ignoring the effect of far field force, the total potential energy E_b was expressed as the sum of the bonding energy of each bond between carbon atom i and j.

$$E_b = \sum_i \sum_{j(i>j)} \left[V_R(r_{ij}) - B^*_{ij} V_A(r_{ij}) \right], \qquad (1)$$

where $V_R(r)$ and $V_A(r)$ were repulsive and attractive force terms, respectively. Those terms were expressed by the exponential form with the cut-off function $f(r)$.

$$V_R(r) = f(r) \frac{D^e}{S-1} \exp\left\{ -\beta\sqrt{2S}\left(r - R^e \right) \right\} \qquad (2)$$

$$V_A(r) = f(r) \frac{D^e S}{S-1} \exp\left\{ -\beta\sqrt{2/S}\left(r - R^e \right) \right\} \qquad (3)$$

$$f(r) = \begin{cases} 1 & (r < R^1) \\ \frac{1}{2}\left(1 + \cos\frac{r - R^1}{R^2 - R^1}\pi \right) & (R^1 < r < R^2) \\ 0 & (r > R^2) \end{cases} \qquad (4)$$

The effect of the bonding condition of each atom was taken account through B^*_{ij} term which was the function of angle θ_{ijk} between bond i-j and bond i-k.

$$B^*_{ij} = \frac{B_{ij} + B_{ji}}{2}, \; B_{ij} = \left(1 + \sum_{k(\neq i, j)} \left[G_c(\theta_{ijk}) f(r_{ik}) \right] \right)^{-\delta} \qquad (5)$$

$$G_c(\theta) = a_0 \left(1 + \frac{c_0^2}{d_0^2} - \frac{c_0^2}{d_0^2 + (1 + \cos\theta)^2} \right) \qquad (6)$$

Constants were summarized as follows:

$D^e = 6.325$ eV $S = 1.29$ $\beta = 1.5$ Å^{-1}
$R^e = 1.315$ Å $\delta = 0.80469$
$a_0 = 0.011304$ $c_0 = 19$ $d_0 = 2.5$
$R^1 = 1.7$ Å $R^2 = 2.0$ Å.

Here, we have ignored the term of the compensation for conjugate bonds from the original expression of Brenner [25].

Verlet method was employed to integrate the classical equation of motion with the time step of 0.5 fs. All calculations were performed in a cubic box with periodic boundary conditions in all 3 directions. When temperature control was enforced, the simple velocity scaling was adopted.

3 High Temperature Stability of C_{60}

In order to check the characteristics of the potential function when applied to fullerene, we calculated high temperature stability of the structure of C_{60}. Locating 60 carbon atoms at the equilibrium position of truncated icosahedron C_{60} structure, we gave the vibrational temperature discarding the total translational and rotational energy. With the temperature control at the certain temperature T for initial 15 ps, we calculated the vibration for 100 ps.
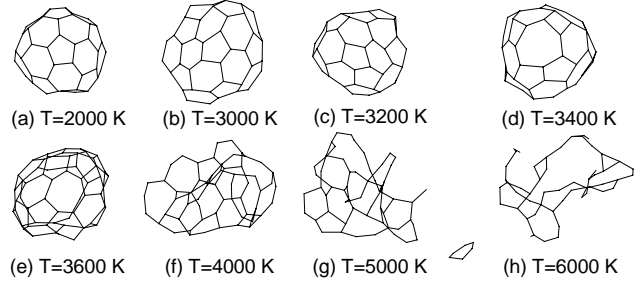

(a) T=2000 K   (b) T=3000 K   (c) T=3200 K   (d) T=3400 K

(e) T=3600 K   (f) T=4000 K   (g) T=5000 K   (h) T=6000 K

Figure 2 High temperature stability of C_{60}

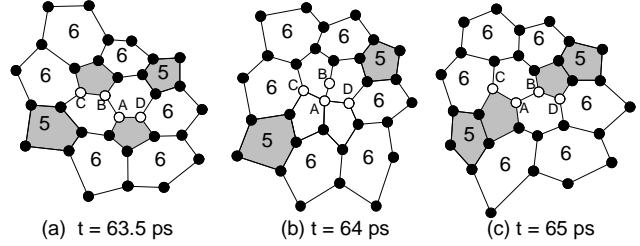(a) t = 63.5 ps   (b) t = 64 ps   (c) t = 65 ps

Figure 3 Migration of pentagons observed for $T = 3200$ K

Figure 2 summarizes the observed structure after 100 ps in each temperature. When the temperature is below 3000 K, no change of carbon network was observed within 100 ps. The indication of the deformation of the network structure was observed at $T = 3200$ K. Here, the isomerization of C_{60} by migrations of pentagon was demonstrated as shown in Figure 3. Until 63.5 ps the structure is perfect C_{60} with isolated pentagons [Figure 3(a)]. During 63.5 ps to 64 ps, a bond B-C was broken and A-C was formed leaving atom B very unstable position [Figure 3(b)]. Then, at t = 65 ps, atom B chose atom D as the new partner [Figure 3(c)]. The whole process can be regarded as the twist of bond A-B and consequent migration of two pentagons. Whether this isomerization occurs in practice is not certain, however, such a freedom of transformation is the essential for the annealing of the imperfect fullerene. At $T=3400$ K the previous transformation occurred one after another, and some heptagons appeared. At $T = 4000$ K, the cage was open as shown in Figure 3(f), and at $T = 6000$ K the dissociation of a part of the cluster was observed. Unfortunately we could not observed the C_2 loss dissociation [3, 26] that is supposed to be observed when a strong laser is irradiated to a fullerene.

4 Formation of Fullerene Structure

4.1 Assembly of fullerene from random atoms

The most interesting point of the formation mechanism of fullerene is how such a hollow caged structure can be self-assembled. We first tried the possibility of constructing the caged structure by using the carbon atom potential. As seen in the last section, C_{60} is extraordinary stable at high temperature, though 3000 K might be the over-estimation since a tiny error in the atomic potential may be amplified in the view of the vibrational temperature. We supposed that this stability at high temperature was the key of the selection of fullerene structure rather than graphite or diamond.

Locating 200 carbon atoms at random positions in a 80 Å cubic box with the full periodic boundary condition, we controlled the carbon temperature at 3000 K for every 0.25 ps. Several snapshots of the simulation are shown in Figure 4. At

about 120 ps [Figure 4(a)], most of clusters were smaller than C_3 but several linear chain clusters as large as C_9 were observed. Then, at about 180 ps [Figure 4(b)], some of clusters grew to rings or chains with about 12 atoms and a fragment of flat network with about 30 atoms were observed. Finally at 400 ps [Figure 4(c)], two large clusters of almost closed caged structure were observed. Figure 4(d) shows the enlarged view of the largest cluster (70 carbon atoms). This structure can be regarded as the imperfect fullerene basically made of pentagons and hexagons, though there observed 8-membered rings and a small hole. Picking up this cluster with 70 atoms, we continued the simulation more 150 ps after this stage. However, it was not clear whether this cluster was annealing toward the perfect fullerene structure or not.

The time history of the bonding characteristics are compared with the snapshots in Figure 4. Here, we considered that two carbon atoms had a bond when they were nearer than 1.8 Å, and plotted the transition of the number of carbon atoms N_{Nx} having a coordination number x. Hence, N_{N0} represents the number of isolated atoms and N_{N2} the atoms with sp^2 bondings. The number of isolated atoms N_{N0} decreased and N_B and N_{N3} increased monotonously. On the other hand, N_{N1} and N_{N2} had the maximum at certain time. Atoms contributing N_{N1} and N_{N2} were atoms at the ends of chains and atoms inside of chains or rings, respectively.

4.2 Precursors in the reaction process

Figure 5 shows the outline of the clustering process yielding to the imperfect fullerene C_{70} shown in Figure 4. One of the major piece was irregular three dimensional cluster C_{43} which had grown rather irregularly by additions of small clusters to the irregular poly-cyclic ring C_{26}. This irregular feature was almost kept after growing to C_{70}. Another piece was the fragment of flat network C_{25} which had been regularly grown by successive additions of poly-cyclic ring C_{12}, mono-cyclic ring C_7 and linear chain C_6. Seven solid atoms in C_{19} represent atoms originally from the C_7 ring structure. It can be said that no original rings were kept after the merge of C_7 and C_{12}. On the other hand, 6 solid atoms in C_{25} cluster originally from C_6 linear chain kept the original bondings, suggesting an organized process of the addition.

The details of this process is shown in Figure 6. At a glance, the C_{19} poly-cyclic cluster captured the C_6 chain and the chain wrapped the poly-cyclic cluster to add two hexagons. However, there were considerable number of bond alternations during these process. The thin lines in Figure 6 mark the new bondings and the cross marks are the breaking bonds. Anyway, it is clear that a chain cluster is a very convenient source of the growth of the network structure. This process is quite similar to the part of the model proposed by Hunter et al. [24]. The key precursor in their model consisted of two hexagons and a long chain whose ends were connected to each hexagons. They proposed that the chain would spirally wrap the fragment until completely close to the fullerene. Though our chain is short and one end is open, this similarity is remarkable.

4.3 Artificial precursors

Learning the chain-wrapping transformation in Figure 6, we speculated that this might be the key mechanism of the network growth. Then, we tried a simulation which could enhance this feature. We prepared a seed fragment made of 2 hexagons [see top left C_{10} in Figure 7] and five C_{10} linear chains as the initial condition. This configuration of the fragment C_{10} is the same as the initial cup precursor used in the ring-stacking model [19].
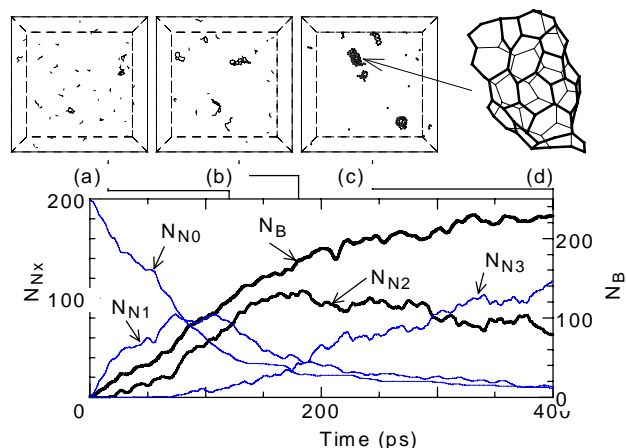

Figure 4 Assemble of fullerene structure from randomly distributed 200 carbon atoms
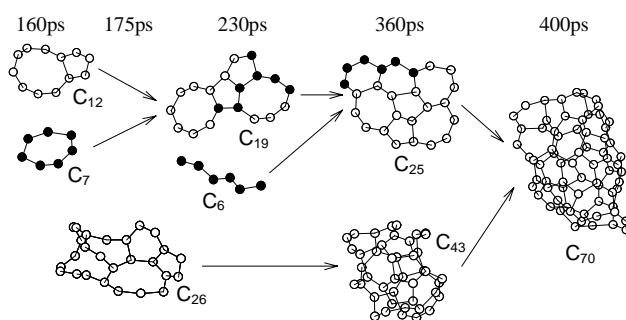

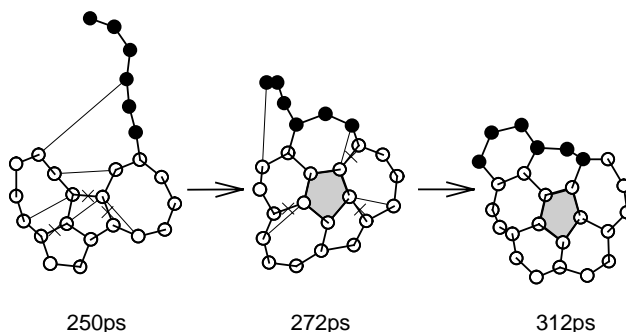Figure 5 Clustering process yielding to the imperfect fullerene.

Figure 6 Chain wrapping transformation.

Keeping the temperature at 3000 K, the same simulation as the case of the random position was performed. Observed clustering process outlined in Figure 7 shows that the final structure of C_{60} was the flat graphitic sheet. The growth of the network fragment was systematic and organized as seen in Figure 7. Chains or small rings worked as the nice feed stock of the network growth. However, we should notice that the initial configuration of the C_{10} was completely lost when it was grown to C_{30}. The solid atoms in Figure 7 represent 10 atoms initially located as the precursor C_{10}. Probably this result implies that the systematic organized growth of the network fragment is not a good choice to formulate a fullerene.

4.4 Thinner System

In order to reduce the computational time, the density of initial carbon atoms used in the previous calculations was probably a few orders higher than the physical conditions of

experimental fullerene generation. The largest discrepancy from the physical phenomena is in the collisional frequency. With such a simulation of compressed time scale, small clusters collided each other before they were fully annealed. So, we tried about 30 times thinner density system with 100 carbon atoms in a 200 Å cubic box. As the result, the clustering process shown in Figure 8 was very systematic and yielded the graphitic sheet structure. Again the organized growth of the network fragment yielded the graphitic structure. Since we know that the graphite is more stable than fullerene, these results may be straightforward.

5 conclusions

The molecular dynamics simulation of the clustering process staring from the random position and random velocity of carbon atoms yielded the imperfect fullerene at certain temperature and density conditions. The simplified potential function of the carbon atoms and the unrealistic dense carbon for the sake of the computational limitations, make it difficult to compare the calculational condition with the real physical phenomena. However, since we could calculate the some imperfect fullerene structure from the completely random configuration, we could imagine that the self assembly of carbon atoms might be calculated by simulations. We have traced some of the precursors appeared in the simulations. Some of the transformations observed in the simulations were remarkable similar to a proposed model.

Acknowledgment

Figure 7 Simulation from artificial precursors
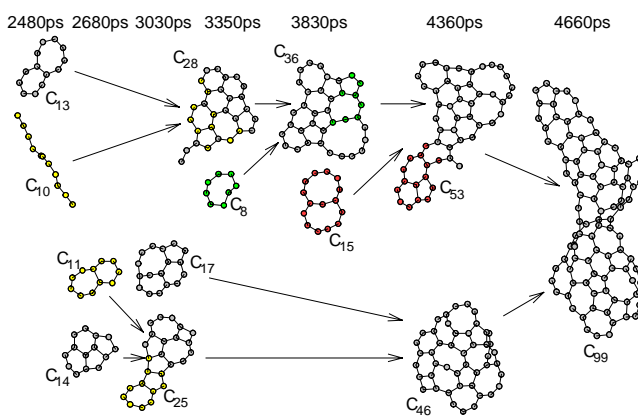
Figure 8 Clustering process observed for thinner density system.

References

[1] H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley: *Nature*, **318**, 162 (1985).

[2] E. A. Rohlfing, D. M. Cox and A. Kalder: *J. Chem. Phys.*, **81**, 3322 (1984).

[3] S. Maruyama, M. Y. Lee, R. E. Haufler, Y. Chai and R. E. Smalley: *Z. Phys. D*, **19**, 409 (1991).

[4] W. Krätschmer, L. D. Lamb, K. Fostiropoulos and D. R. Huffman: *Nature*, **347**, 354 (1990).

[5] R. E. Haufler, Y. Chai, L. P. F. Chibante, J. Conceicao, C. Jin, L.-S. Wang, S. Maruyama and R. E. Smalley: *Mat. Res. Soc. Symp. Proc.*, **206**, 627 (1991).

[6] R. Talor, J. P. Hare, A. K. Abdul-Sada and H. W. Kroto: *J. Chem. Soc. Chem. Communications*, **1423**, 1425 (1990).

[7] A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez and A. R. Kortan: *Nature*, **350**, p. 600 (1991).

[8] Y. Chai, T. Guo, C. Jin, R. E. Haufler, L. P. F. Chibante, J. Fure, L. Wang, J. M. Alford and R. E. Smalley: *J. Phys. Chem.*, **95**, 7564 (1991).

[9] H. Shinohara, H. Sato, Y. Saito, M. Ohkohchi and Y. Ando: *J. Phys. Chem.*, **96**, 3571 (1992).

[10] K. Kikuchi, S. Suzuki, Y. Nakao, N. Nakahara, T. Wakabayashi, H. Shiromaru, K. Saito, I. Ikemoto and Y. Achiba: *Chem. Phys. Lett.*, **216**, 67 (1993).

[11] K. Kikuchi, N. Nakahara, T. Wakabayashi, M. Honda, S. Suzuki, K. Saito, H. Shiromaru, K. Yamauchi, I. Ikemoto, T. Kuramochi, S. Hino and Y. Achiba: *Chem. Phys. Lett.*, **188**, 177 (1992).
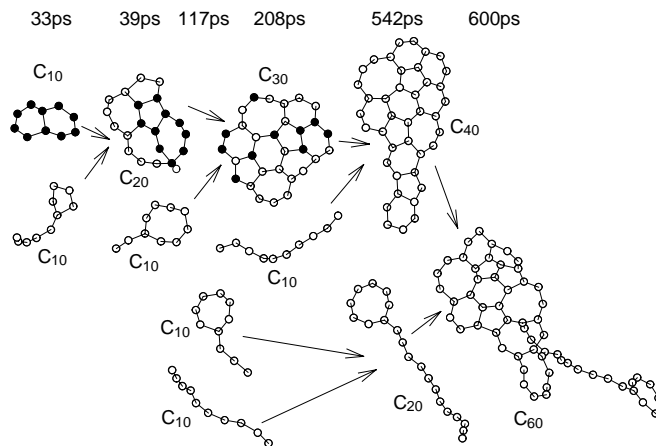
[12] Y. Achiba and T. Wakabayashi: *Z. Phys. D*, **26**, 69 (1993).

[13] S. Iijima: *Nature*, **354**, 56 (1991); T. W. Ebbesen and P. M. Ajayan: *Nature*, **358**, 220 (1992).

[14] R. E. Smalley: *Materials Science and Engineering*, **B19**, 1 (1993).

[15] S. Maruyama, T. Takagi, H. Kinbara and M. Inoue: *Proc. 31th National Heat Transfer Conf.*, 943 (1994).

[16] D. H. Robertson, D. W. Brenner and C. T. White: *J. Phys. Chem.*, **96**, 6133 (1992).

[17] V. P. Dravid, X. Lin, Y. Wang, X. K. Wang, A. Lee, J. B. Ketterson and R. P. H. Chang: *Science*, **259**, 1601 (1993).

[18] J. R. Heath: *Fullerenes*, Ed. G. S. Hammand & V. J. Kuck, American Chemical Society (Washington, D. C.), 1 (1992).

[19] T. Wakabayashi and Y. Achiba: *Chem. Phys. Lett.*, **190**, 465 (1992).

[20] T. Wakabayashi, H. Shiromaru, K. Kikuchi and Y. Achiba: *Chem. Phys. Lett.*, **201**, 470 (1993).

[21] G. Helden, N. G. Gotts and M. T. Bowers: *Nature*, **363**, 60 (1993).

[22] J. Hunter, J. Fye and M. F. Jerrold: *Science*, **260**, 784 (1993).

[23] D. E. Clemmer, K. B. Shelimov and M. F. Jarrold: *Nature*, **367**, 718 (1994).

[24] J. M. Hunter, J. L. Fye, E. J. Roskamp and M. F. Jarrold: *J. Phys. Chem.*, **98**, 1810 (1994).

[25] D. W. Brenner: *Phys. Rev. B*, **42**, 9458 (1990).

[26] S. C. O'Brien, J. R. Heath, R. F. Curl and R. E. Smalley: *J. Chem. Phys.*, **88**, 220 (1988).