

## DISCOVERING THE FULLERENES

Nobel Lecture, December 7, 1996

by

RICHARD E. SMALLEY

Center for Nanoscale Science and Technology, Rice Quantum Institute, and  
Departments of Chemistry and Physics, Rice University, Houston, Texas  
77005, USA

It is a thrill for me to be here today and to be the first of three speakers discussing the wonders of the fullerenes, an infinite new class of carbon molecules. My colleagues in this famous photograph (Figure 1) are also thrilled to be here in Stockholm this week to see “Bucky get the Prize”. This picture was taken on September 11, 1985, the day before we sent off the manuscript describing the discovery of  $C_{60}$  to the editorial offices of *Nature* (1) (and only a few days after the discovery itself). Every one of the people in that photograph was critically involved in the discovery (with the exception of the one woman walking in the back—we still don’t know who that mystery woman was), so you can understand that there is also some sadness in our hearts today. While the chemistry prize this year is for the discovery of the fullerenes, it is given to individuals, and this individual honor can be shared by no more than three. The Nobel Committee has done as well as they possibly can with this problem. We understand. But the sadness remains.

On the other hand, there are positive aspects to the limit of three. For example, I have asked what happens in those years when there is only one person receiving an award in physics or chemistry. I was told that you just get one lecture for that prize. Now that I am beginning to appreciate the full impact of having a long lecture from each of the three winners this year in each of the two fields, physics and chemistry, all on the same day and in the same room, I can see that one must set limits somewhere.

This discovery was one of the most spiritual experiences that any of us in the original team of five have ever experienced. The main message of my talk today is that this spiritual experience, this discovery of what Nature has in store for us with carbon, is still ongoing. So the title of my talk is not “The Discovery of the Fullerenes” but rather “Discovering the Fullerenes”. Fullerene researchers worldwide are still engaged in this process of discovery.

The sense in which we are still in this process has to do with what the true essence of the 1985 fullerene discovery actually turned out to be. After all, the five people in that happy photograph (Figure 1), brilliant as they all are, were not the ones who first conceived of the truncated icosahedron. That was done several thousand years ago. Archimedes gets the credit for it, although one may reasonably suspect that icosahedra had been truncated long before Archimedes. Nor were we the first people to conceive that if you replaced the

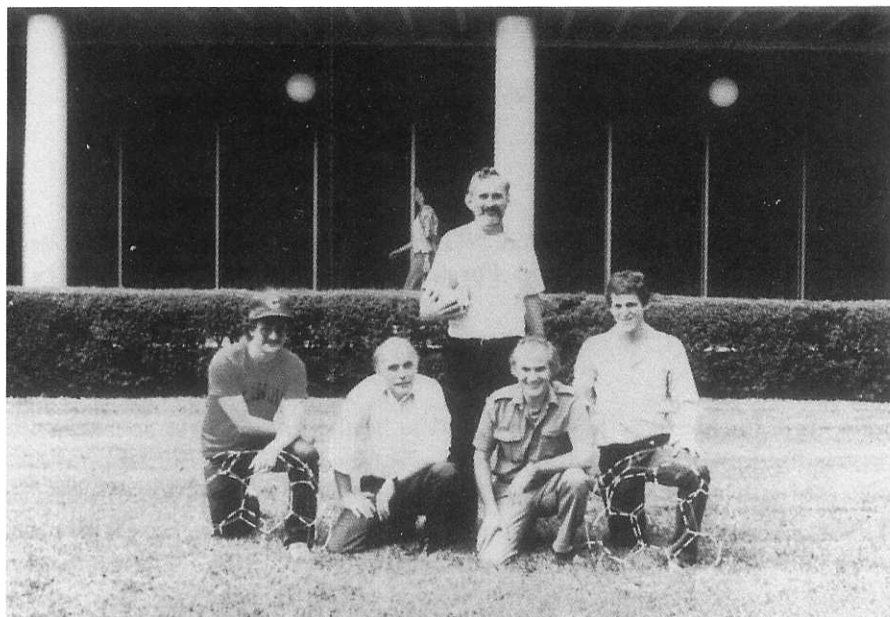


Figure 1. Photograph of the research group that discovered the fullerenes at Rice University in September of 1985. Standing: Curl. Kneeling in front, left to right: O'Brien, Smalley, Kroto, and Heath.

vertices of that pattern with carbon atoms, and let the carbon do what it wanted to do, that that would be an interesting chemical object. That honor had already gone more than a decade before our discovery to E. G. Osawa (2, 3), the Japanese physical organic chemist who had perceived that carbon in that structure would be aromatic and would therefore probably be stable. And a large part of this honor had been earned even before that by David Jones (4), who in a wonderfully imaginative piece, had conceived of closed spheroidal cages made of graphene sheets somehow folded around. A little later, Jones realized that a pentagon would serve nicely as the required defect in an otherwise hexagonal lattice to produce a complex curvature (5). The notion that  $C_{60}$  would be a closed shell molecule with a very large HOMO-LUMO gap, which is a well-appreciated signature of chemical stability, fell to Bochvar, Gal'pern (6) and Stankevich (7) who actually did the relevant Hückel calculations in Russia well over a decade before we ever got into the game.

The conception of carbon being stable in the form of a truncated icosahedron really wasn't the discovery that is being honored this week. If that were, then Archimedes, Osawa, Jones, and/or one or more of these insightful Soviet scientists should have gotten the prize.

Instead, the discovery that garnered the Nobel Prize was the realization that carbon makes the truncated icosahedral molecule, and larger geodesic cages, all by itself. Carbon has wired within it, as part of its birthright ever since the beginning of this universe, the genius for spontaneously assembling into fullerenes. We now realize that all you need to do to generate billions of billions of these objects of such wonderful symmetry is just to make a vapor of

carbon atoms and to let them condense in helium. Now we are still in the process of discovering all of the other consequences of the genius that is wired into carbon atoms. It isn't just a talent to make balls. It can also make tubes such as the short section shown in Figure 2.

Nearly all of us have long been familiar with the earlier known forms of pure carbon: diamond and graphite. Diamond, for all its great beauty, is not nearly as interesting as the hexagonal plane of graphite. It is not nearly as interesting because we live in a three-dimensional space, and in diamond each atom is surrounded in all three directions in space by a full coordination. Consequently, it is very difficult for an atom inside the diamond lattice to be confronted with anything else in this 3D world because all directions are already taken up. In contrast, the carbon atoms in a single hexagonal sheet of graphite (a "graphene" sheet) are completely naked above and below. In a 3D world this is not easy. I do not think we ever really thought enough about how special this is. Here you have one atom in the periodic table, which can be so satisfied with just three nearest neighbors in two dimensions, that it is largely immune to further bonding. Even if you offer it another atom to bond with from above the sheet—even a single bare carbon atom, for that matter—the only result is a mild chemisorption that with a little heat is easily undone, leaving the graphene sheet intact. Carbon has this genius of making a chemically stable two-dimensional, one-atom-thick membrane in a three-dimensional world. And that, I believe, is going to be very important in the future of chemistry and technology in general.

What we have discovered is that if you just form a vapor of carbon atoms

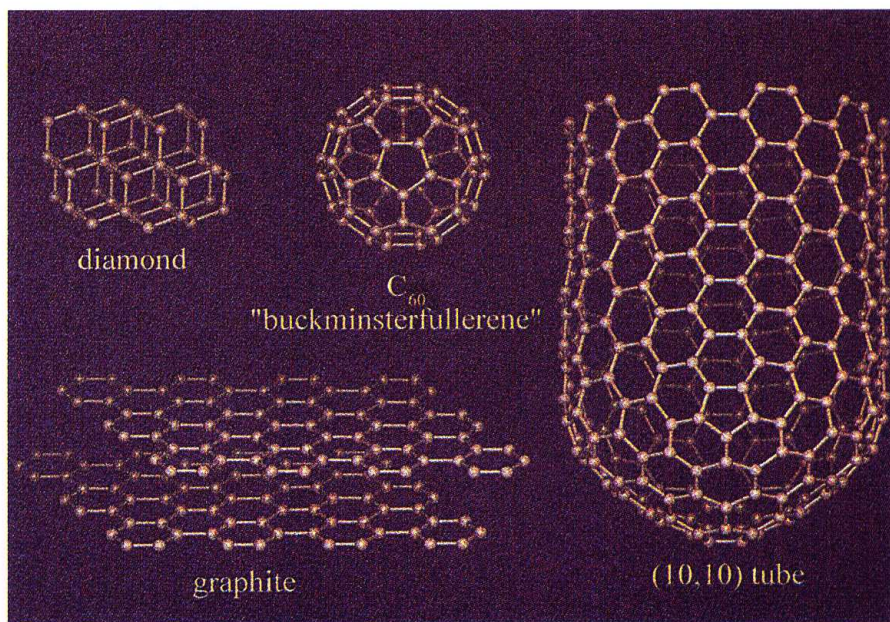


Figure 2. Four perfect crystalline forms of carbon: diamond, graphite, C<sub>60</sub>, and a short length of a (10,10) fullerene nanotube showing the hemi-C<sub>240</sub> end cap.

and let them condense slowly while keeping the temperature high enough so that as the intermediate species grow they can do what it is in their nature to do, there is a path where the bulk of all the reactive kinetics follow that goes to make spheroidal fullerenes. Now it turns out that in addition to this most symmetric of all possible molecules,  $C_{60}$ , and the other fullerene balls, it is possible by adding a few percent of other atoms (nickel and cobalt) to trick the carbon into making tubes. Of all possible tubes there is one tube that is special (8). It is the tube shown in Figure 2, the (10,10) tube. We are beginning to understand that what causes this tube to be the most favorite of all tubes is also wired within the instruction set of what it means to be a carbon atom. The propensity for bonding that causes  $C_{60}$  to be the end point of 30–40% of all the reactive kinetics, leads as well to this (10,10) tube. This detour on the road that otherwise leads to spheroidal fullerenes is taken if you somehow (with cobalt or nickel atoms) frustrate the ability of the open edge to curve in and close. The metal atoms prevent by local annealing the addition of the seventh, eighth, ninth pentagons, and insure by judicious choice of temperature and reaction rate that the growing tublet can anneal to its most energetically favored form.

The object shown in Figure 3 depicts one of the more fascinating new opportunities in the future of the fullerenes. It is a short piece of the (10,10) tube with chemically derivitized ends. One end is closed with a hemifullerene dome (actually one half of a very special fullerene, icosahedral  $C_{240}$ ). The



Figure 3. Derivitized section of a (10,10) fullerene nanotube with one end open.

other end is intentionally left open. Since the closed end contains pentagons and is accordingly more reactive than the smooth, all-hexagon side of the nanotubes, there are techniques such as boiling in nitric acid (9) for heating the closed ends off of these tubes. We also know that if you take such a tube and put it in an oven and heat it to 1200 °C, it will spontaneously close back again. These ends, regardless of whether they are closed or open, are directly amenable to the formation of excellent C-O, C-N, or C-C covalent bonds (10) to attach nearly any molecule, enzyme, membrane, or surface to the end of the tube. You could attach one or several such objects (let's call them A) to the upper end and some other objects on the bottom (B). What is so stunning about this molecule, unlike any other molecule we have ever had before in chemistry, is that with this object "A" and "B" will communicate with each other by true metallic transport along the tube. The (10,10) tube is a quantum waveguide for electrons.

The band structure of graphene, the individual flat sheet of graphite is that of a zero gap semi-conductor. The valence band and conduction band meet at a point at the end of the Brillouin zone. There is a node in the density of states at Fermi energy, and accordingly it is not a very good conductor. In my youth on first hearing that graphite was a poor conductor—more like lead than gold—I had thought that the problem must be due to some sort of original sin that the carbon atom had made. The valence electrons of carbon tended to be localized, and were not freely able to move from one carbon atom to another through an extended sheet. In fact that is not the problem. The  $\pi$  electrons are perfectly itinerant in the graphene sheet, just as they are perfectly itinerant in the aromatic ring of benzene. In fact, it is the freedom of the electrons to move around the ring that gives the special chemical stability to aromatic molecules. The trouble with the electrical conductivity is that when you calculate the band structure of the hexagonal graphene sheet, by symmetry, there is a node in the density of states at the Fermi energy. Even if you were somehow able to replace every one of the carbon atoms in the hexagonal lattice with a gold atom, the band structure would still look the same. It is the symmetry of the hexagonal lattice that is the problem, not the itinerancy of the  $\pi$  electrons of carbon.

But now we realize that there is one (but only one) answer to this problem of making a metal out of pure carbon. If you take the graphene sheet and cut out a thin strip, curl it along its length to form a long cylinder, and seal up the dangling bonds together to form the (10,10) tube as shown in Figure 2, the very symmetry that had been your enemy in preventing metallic behavior from the flat lattice, now becomes your friend. The symmetry of this tubular hexagonal lattice now insists that there will be two bands that cross at the Fermi energy, approximately two thirds of the way across the Brillouin Zone, as shown in the band structure of Figure 4. In addition, the cohesive rigidity of the  $\sigma$ -bond framework of the graphene sheet prevents the metallic  $\pi$  electrons from engendering a Peierls instability that normally plagues all such one-dimensional conductors (11). The (10,10) fullerene tube, and all ( $n,n$ ) tubes in general, will be a molecular wire that is simultaneously a good me-

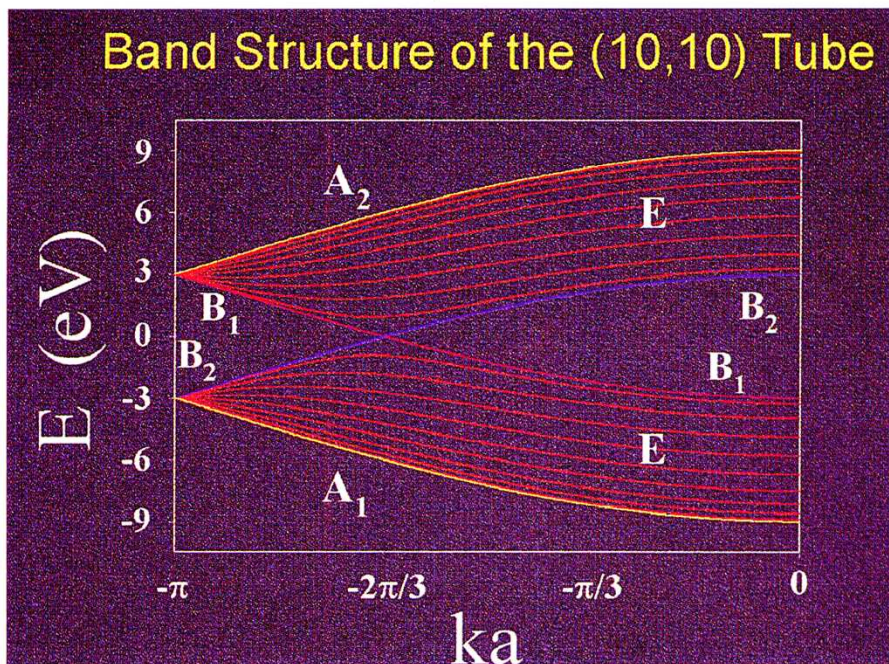


Figure 4. Electronic band structure of a (10,10) fullerene nanotube calculated using tight binding methods, using zone-folding from the band structure of an infinite 2D graphene sheet. The two bands that cross the Fermi energy at  $ka = 2/3$  have different symmetry, and guarantee that the tube will be a metallic conductor.

tallic conductor, and a good molecule, maintaining its structure and conductivity even when exposed to air and water in the real world.

I believe that in the future of chemistry, we are likely to see a vast new set of metallic fullerene molecules such as that shown in Figure 3 readily available from chemical supply houses. Imagine what the impact could be. Essentially, every technology you have ever heard of where electrons move from here to there, has the potential to be revolutionized by the availability of molecular wires made up of carbon. Organic chemists will start building devices. Molecular electronics could become reality.

This is where the fullerenes appear to be leading at the moment. One does not get a feeling that we are over with this discovery process yet. There may be many more wondrous properties of this one little atom in the periodic table than we have yet to appreciate.

Still there was a particular discovery that we celebrate this week. There was something about September of 1985. What was that? How did that happen? Since that original discovery we have been involved in a little bit of what I like to call the archeology of the buckyball: looking back in the written and oral history trying to decide what the roots of the fullerene discovery were. This discovery is principally about the way that carbon condenses, it's genius for forming clusters.

It has long been known that the carbon has a special ability to cluster in the

gas phase at high temperatures. Unlike every other refractory element in the periodic table, the vapor of carbon in equilibrium with its solid at temperatures in the 3000–4000 K range is dominated by clusters,  $C_n$ , with substantial abundance of species as high as  $C_{15}$ . The first evidence of this extends back to early research on nuclear fission products by Hahn and Strassman in Germany (12). They noticed that carbon cluster ions up to  $C_{15}^+$  were produced in a high frequency arc with a graphite electrode, the arc being used for elemental analysis by mass spectrometry (13); Similar observations were made in the US about this same time in research associated with the Manhattan Project during the Second World War (14). By the early 1950's it was clear that there were sufficient numbers of small carbon clusters at equilibrium in the vapor to have a major affect on the measurement (15,16) of the heat of formation of C(gas), one of the most important constants in chemical thermodynamics. In 1959 Pitzer and Clementi (17,18) made the first serious quantum calculations of the structures responsible for this behavior in the vapor up to about 20 atoms, and concluded that they had the form of linear chains for  $C_2$  up to about  $C_{10}$ , and above that they took the form of monocyclic rings—little ‘Hoola Hoops’ of pure carbon.

Although it was not commented on at the time, this is quite a remarkable result. Here carbon is able to make clusters that are so stable that they are the dominant species—substantially more abundant than  $C_1$ —in the gas phase even at a temperature of 3000–4000 K, and they do this with only a coordination number of two! All other refractory elements such as platinum, tungsten, or tantalum achieve their high cohesive energy by a close packing arrangement within the bulk crystal or liquid, with coordination number of 8 to 12. Even though the clusters of these metals in the gas phase also adopt compact structures (19), arranging as many atoms around each other in three dimensions as possible, they still do not have a sufficiently high cohesive energy to be abundant in the equilibrium vapor. Instead the vapor of these metals is almost completely monatomic. Above 1000 K the vapor in equilibrium with pure condensed phase of every element in the periodic table—except carbon—is dominantly either monatomic or diatomic. But here is carbon making so many of these large clusters that it throws off the measures of heat of formation, and in a show of chemical bonding chutzpah, doing this with two of it's three available dimensions for bonding “tied behind its back”.

Looking back now at the data available in the literature on gas-phase clusters of pure carbon up to mid-1984, it is clear that there was no suggestion in the experiments of anything more interesting going on than these one-dimensional clusters (20,21). All the data appeared to be well-explained by the model of linear chains and monocyclic rings, and the cluster abundance dropped off so severely by the time the clusters were in the mid-twenty-atom size that no one was led to speculate what would happen as the clusters grew larger. In light of what we now know about the fullerenes, this would have been a very fruitful line of speculation. After all, at some point as the clusters grew larger they would certainly have to start trying structures that were two- or three-dimensional. What would these look like? Consideration of the dang-

ling bond energies could reasonably have led to the speculation that graphene sheets would form but curl up to closed cages.

But, as far as we can determine, no such speculation ever occurred. While in the mid 1960's Jones (4) had the notion that graphene sheets could curl up to make "hollow molecules," Osawa (2) had already conjured up the notion of carbon in a soccer ball structure in early 1970, and Gal'pern (6) had completed the first of many Hückel calculations showing that it would be a closed shell molecule with a large HOMO-LUMO gap in 1973, but no one ever suggested these objects could form spontaneously in a condensing carbon vapor. The mystery of the buckyball was never so much that it would be a stable molecule once formed. After all, it violates no rules of organic chemistry. The secret laying there to be discovered is that part of carbon's "birth right" is the genius to form a chemically passive two-dimensional surface, to self-assemble fullerenes in general, and C<sub>60</sub> in particular and in sensationally high yield, out of the chaos of a carbon vapor at thousands of degrees.

To trigger this realization, new data turned out to be necessary. Data on what happened when you allowed a carbon vapor to become supersaturated, allowed it to begin to condense, and the small clusters that were in equilibrium with the solid began to grow larger. That data had to wait for the invention of a new technique, something that would enable one to study the properties of carbon clusters in detail as they grow through the size range of 40 to 100 atoms where the dimensionality of the bonding does, in fact, increase from 1 to 2. It had to wait for the laser-vaporization cluster beam methods of the 1980's.

The laser-vaporization supersonic cluster beam technique was originally developed at Rice University in 1980–1981 as a means of studying clusters of virtually any element in the periodic table, including highly refractory metals (22–26) and semiconductors such as silicon (27) and gallium arsenide (28). The objective of this line of research was to explore the behavior of matter intermediate in size between atoms and bulk crystals. It grew out of decades of development of atomic and molecular beams, and in particular the development of seeded supersonic molecular beams as a means of "freezing out" the vast number of rotational and vibrational excitations which otherwise preclude detailed study of polyatomic molecules (29–32). In addition to enabling the study of common chemically stable polyatomic molecules, it was possible to generate supercold van der Waals clusters of these molecules with each other, and with other species, including at these ultralow temperatures even helium (33). By the use of intense pulsed laser irradiation within the supersonic nozzle it was possible to study highly reactive fragments of molecules, free radicals (34). Extension of the supersonic beam technique to seeded beams of refractory atoms and clusters was a direct outgrowth of this early free radical work.

Once beams of refractory clusters were available, a vast new area of research was opened, for each cluster may be thought of as a nanoscale crystalline particle that has a surface (in fact, most of it is surface). Supersonic metal cluster beams thereby provided a route to a new sort of surface science



(35). In my research group at Rice we were very heavily engaged in developing this new science. We developed and applied new methods for studying the electronic structure of the clusters by one- and two-photon laser photoionization with time-of-flight mass spectral detection (25, 36, 37), photodissociation, and photodepletion spectroscopy (38–40), and ultraviolet photoelectron spectroscopy (41). In order to study the surface chemistry of the nanoscale clusters, we developed techniques using a fast flow reactor attached to the end of the supersonic nozzle (42–44). We developed a variety of methods involving charged ions of the clusters levitated in a magnetic field and probed by ion cyclotron resonance spectroscopy (45–47), etc. The early 1980's were a very busy, very fruitful time in this research group at Rice University, and much was learned.

The laser vaporization supersonic beam source and the associated probe techniques that we developed to study the 2–200 atom metal and semiconductor clusters was effectively a new sort of microscope. It allowed one to “see” something of the nature of nanoscopic aggregates of atoms in a way that was entirely new, and very poignant. Whatever we measured for the cluster in the supersonic beam, we knew that it was the true property of that cluster traveling free in space. We developed the technique in order to bring a sort of intellectual tension to surface science: to make measurements so fundamental that theorists stayed awake at night trying to understand them. Although we had no notion of it at the time we were engaged in this enterprise in the early 1980's, we were building the instrument and the line of research that would discover the fullerenes. All one had to do is put carbon in this new “microscope”, adjust the focus a little, and “see” the fullerenes revealed plainly for the first time.

As it happened, we at Rice were not the first to put carbon into the new microscope. In 1984 a group headed by Andrew Kaldor at Exxon used such an apparatus (actually one that had been designed and built at Rice) in a study of carbon clusters that was motivated by the desire to study coke buildup on reforming catalyst. Now, in a famous mass spectrum reproduced here as Figure 5, carbon clusters were evident extending out beyond 100 atoms (48), and it was immediately clear that a whole new world of interesting carbon clusters could exist that had never been seen before.

Three distinct regions characterized the mass spectrum: first the small clusters, containing fewer than 25 atoms, consisting of the chains and monocyclic rings (49) so well known from the earlier studies; second a new region between about 25 and 35 atoms in which few species of any sort were observed—a region that the Rice group came to call the “forbidden zone”; and, third, an even-numbered clusters distribution extending from the high 30's to well over 150 atoms. By early 1984 the laser-vaporization supersonic cluster beam technique had been used to study clusters broadly throughout the periodic table, and many “magic number” cluster distributions had been found and studied (35), but nothing remotely like this even-numbered distribution of carbon had ever been seen for any other element. Today this is still true: carbon is unique.

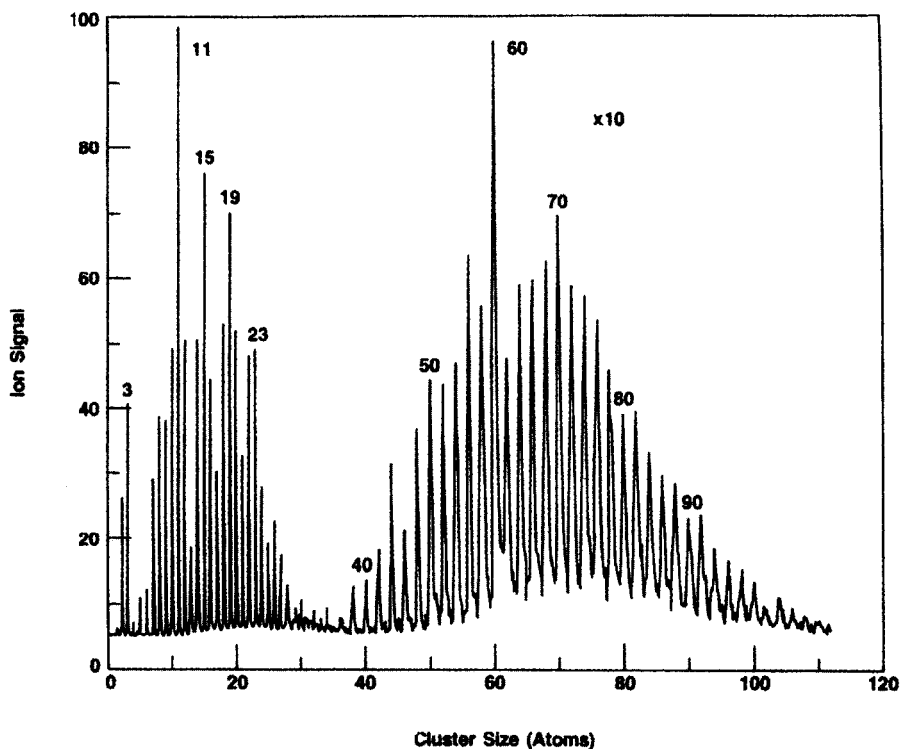


Figure 5. Mass spectrum of carbon clusters in a supersonic beam produced by laser vaporization of a carbon target in a pulsed supersonic nozzle operating with a helium carrier gas. The long distribution of even-numbered carbon clusters starting near  $C_{40}$  and extending to over  $C_{100}$  is due the fullerenes. This was the first published experiment that revealed the fullerene cluster distribution, although it was not appreciated as such at the time. Reproduced with permission of the authors, reference (48).

The even-numbered distribution seen by the Exxon group was due to the fullerenes. I suspect the members of that original group at Exxon still regret that they did not consider in more depth why the peak for  $C_{60}$  appeared to be about 20% more intense than its neighbors. But to be fair, at the time neither did we. This result of the Exxon group was widely known in the burgeoning metal and semiconductor cluster research world by the summer of 1984. I saw the result at a meeting, and discussed it with Andy Kaldor at some length. Bob Curl saw it. Harry Kroto saw it. Wolfgang Krätschmer and Donald Huffman saw it. None of us stopped to think just what might be the reason  $C_{60}$  was a little more prominent than the other even-numbered clusters. It did not stand out sufficiently above its neighbors to attract notice. As it turned out, the Exxon group simply had not “focussed” the new cluster beam microscope carefully enough.

At nearly the same time another research group, including one of my former graduate students, Michael Geusic, had built a supersonic cluster beam apparatus as well, and was engaged in early experiments with mass-selected semiconductor cluster ions (50). Having heard about the Exxon work, they put carbon in the apparatus, also observed the mysterious even-numbered large cluster distribution, and even selected out  $C_{60}^+$  for a photofragmenta-

tion experiment. But they, too, failed to experiment sufficiently with the nozzle conditions to appreciate the potential preeminence of  $C_{60}$ .

The necessary "focussing" of the new supersonic cluster beam "microscope" was finally performed in my laboratory at Rice in the September of 1985 (1, 51). Now the supremacy of  $C_{60}$ , was made clear. In thinking about what this all meant, we finally saw that  $C_{60}$  must be a closed spheroidal cage. No other explanation was consistent with the observed facts. The realization that all the even-numbered carbon cluster distribution was due to carbon in the form of hollow geodesic domes (fullerenes) came within a month, as a result of reactivity studies of these clusters (52) using the fast flow reactor on the end of the supersonic nozzle. Soccer ball  $C_{60}$  quickly became a sort of "Rosetta Stone" leading to the discovery of a new world of geodesic structures of pure carbon built on the nanometer scale.

This discovery episode has by now been so extensively covered in articles (53, 54), monographs (55, 56), and television documentaries, that there is little reason to repeat the details here. We succeeded where two other groups had failed for at least two reasons. First, we had evolved a better version of the "microscope". We had been the group to develop the supersonic cluster beam technique in the first place, and we were still leading the subsequent development and elaboration of its capabilities. The original apparatus, known affectionately by the students as "AP2" and shown in Figure 6, was able to handle much larger gas flows, and had a more advanced supersonic nozzle design than the machines of either of the other groups. Particularly important was the development of the rotating disc design for the cluster beam source that we had just recently completed for our semiconductor cluster

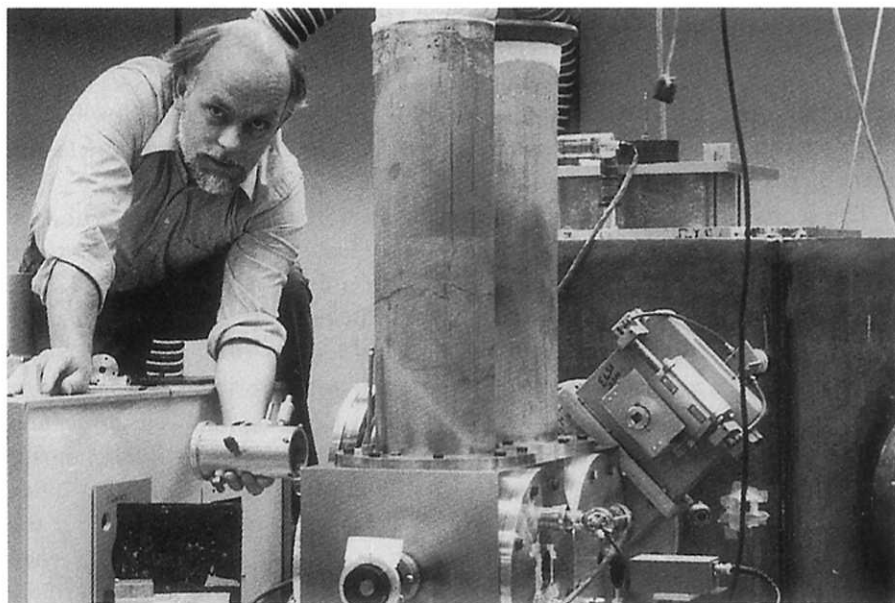


Figure 6. Photograph of the author climbing around on the top of a section of AP2, the supersonic laser vaporization cluster beam apparatus that discovered  $C_{60}$  and the fullerenes in the fall of 1985.

work with silicon, germanium (27), and gallium arsenide (28). As part of this project, it was necessary to anneal the semiconductor clusters in the supersonic nozzle source as much as possible. To simplify interpretation we need conditions so that the most energetically stable geometrical form would dominate the cluster distribution. For this reason the nozzle was fitted with a variety of down-stream flow restrictors to form what we called the “integrating cup”, as shown in Figure 7.

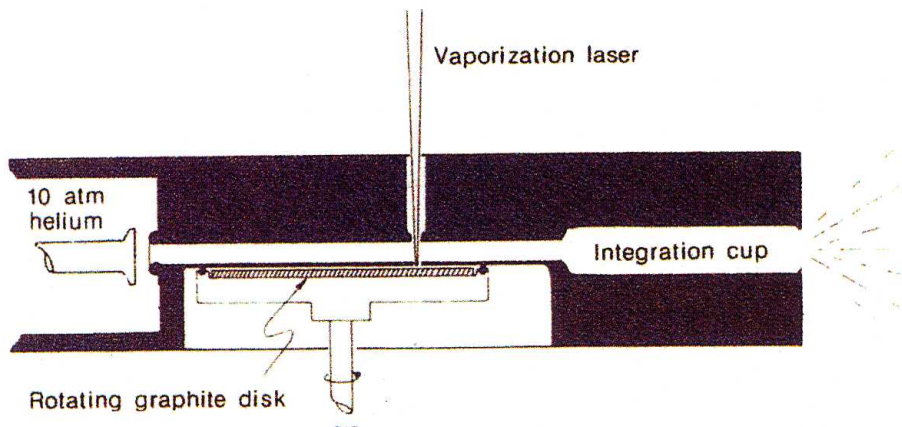


Figure 7. Schematic cross-sectional drawing of the supersonic laser-vaporization nozzle source used in the discovery of the fullerenes. Note the section labeled “integrating cup”. Cluster “cooking” reactions in this zone were responsible for the  $C_{60}$  cluster becoming over 50 times more intense than any other cluster in the nearby size range. These up-clustering reactions with small carbon chains and rings reacted away nearly all clusters except for  $C_{60}$ , which because of its perfect symmetry survived.

It was our experience with the extra “chemical cooking” achieved by this device that made us appreciate that it was cluster chemistry that differentiated  $C_{60}$  from the others. The relative absence of further up-clustering reactions is, we realized, what ultimately makes the  $C_{60}$  peak stand out over 50 times more intensely than any other. And it is in thinking about how 60 carbon atoms can possibly avoid reactive edges, that one is led to the conclusion that  $C_{60}$  is a truncated icosahedron.

The second reason I believe we succeeded was, in a word, karma. With Bob Curl in our collaboration on semiconductor clusters, we had evolved one of the most intellectually demanding and penetrating styles of research I have ever witnessed in any research group. Sean O’Brien had evolved just the right version of the cluster nozzle to handle the difficulties of dealing with semiconductor discs, and Jim Heath had developed an amazing talent for making “science happen” on the machine. When Harry Kroto came, his intensity and scientific background blended in perfectly. Working with the students mostly in late afternoons and at night, and in daily marathon conversations with me, he kept the focus of our minds on the results coming out of AP2, under the hot hands of Heath and O’Brien. One way or another, over the years, each member of the team had paid the dues required to deserve to be there for the discovery of the fullerenes during those wonderful days in September 1985.

Contrary to most written accounts, I do not believe the discovery of the fullerenes had much to do with questions of astrophysics such as the mechanism of formation of interstellar carbon molecules. While this was certainly what brought Kroto to Texas, and this was without contest the reason we first put carbon into AP2 in preparation for his visit, in the end the connection of this line of research (57, 58) to the fullerene discovery was casual, not causal. The discovery of  $C_{60}$  and the fullerenes would have been made by AP2 or some other such instrument within a year or two in any event. Two other groups had already put carbon in a supersonic cluster beam machine for reasons that were much more mundane. At Exxon, as mentioned earlier, their principal concern was to understand carbon buildup on catalysts, while at AT&T Bell Laboratories the motivation derived from their long-term interest in semiconductors and the nanometer scale.

The notion that the discovery of the fullerenes came out of research into the nature of certain molecules in space is highly appealing to scientists. It is hard to think of any line of research that is less likely than interstellar chemistry to have some practical, technological impact back here on Earth. So if fullerenes turn out to lead to the technological wonders that some people (like me) believe are in our future, then perhaps one can argue that any research project could get lucky too, no matter how irrelevant to worldly problems it may currently seem. I have argued this way in the past, and I still believe there is some sense to it—but only a little. In fact, the fullerenes were discovered as a result of decades of research and development of methods to study first atoms, then polyatomic molecules, and ultimately nanometer-scale aggregates. It was well-funded research that at nearly every stage was justified by its perceived relevance to real world technological problems. To a great extent, many of these earlier bets as to the worldly significance of fundamental research actually paid off.

While it is fun to think about the wonderful role of serendipity in the story, one should also spend a bit of time comprehending the inevitability of the discovery as well. The only character of true genius in the story is carbon. Fullerenes are made wherever carbon condenses. It just took us a little while to find out.

## REFERENCES

1. Kroto, H.W., Heath, J.R., O'Brien, S.C., Curl, R.F. & Smalley, R.E. *Nature* 318, 162–163 (1985).
2. Osawa, E. *Kagaku* 25, 854–863 (1970).
3. Osawa, E. *Philosophical Transactions of the Royal Society of London Series A – Physical Sciences and Engineering* 343, 1–8 (1993).
4. Jones, D.E.H. *New Scientist* 32, 245 (1966).
5. Jones, D.E.H. *The Inventions of Daedalus* (W. H. Freeman, Oxford, 1982).
6. Bochvar, D.A. & Gal'pern, E.G. *Proc. Acad. Sci. USSR* 209, 610–612 (1973).
7. Stankevich, I.V., Nikerov, M.V. & Bochvar, D.A. *Russian Chemical Reviews* 53, 640–655 (1984).
8. Thess, A., et al. *Science* 273, 483–487 (1996).
9. Tsang, S.C., Chen, Y.K., Harris, P.J.F. & Green, M.L.H. *Nature* 372, 159–162 (1994).

10. Hirsch, A. *Chemistry of the Fullerenes* (1995).
11. Mintmire, J.W., Dunlap, B.I. & White, C.T. *Physical Review Letters* 68, 631–634 (1992).
12. Hahn, O., Strassman, F., Mattauch, J. & Ewald, H. *Naturwiss* 30, 541–542 (1942).
13. Mattauch, J., Ewald, H., Hahn, O. & Strassman, F. *Zeitschrift für Physik* 120, 598–617 (1943).
14. Brewer, L., Gilles, P.W. & Jenkins, F.A. J. *Chem. Phys.* 16, 797 (1948).
15. Chupka, W.A. & Inghram, M.G. *Journal of Chemical Physics* 21, 1313 (1953).
16. Chupka, W.A. & Inghram, M.G. *Journal of Physical Chemistry* 59, 100–104 (1955).
17. Pitzer, K.S. & Clemente, E. *Journal of the American Chemical Society* 81, 4477 (1959).
18. Strickler, S.J. & Pitzer, K.S. in *Molecular Orbitals in Chemistry, Physics, and Biology* (eds. Lowdin, P.O. & Pullman, B.) 281 (Academic Press, New York, 1964).
19. Jarrold, M.F. *Journal of Physical Chemistry* 99, 11–21 (1995).
20. Dornenburg, E. & Hintenberger, H. Z. *Naturforsch.* 14A, 765–767 (1959).
21. Dornenburg, E. & Hintenberger, H. Z. *Naturforsch.* 16A, 532–534 (1961).
22. Diez, T.G., Duncan, M.A., Powers, D.E. & Smalley, R.E. *Journal of Chemical Physics* 74, 6511–6512 (1981).
23. Michalopoulos, D.L., Geusic, M.E., Hansen, S.G., Powers, D.E. & Smalley, R.E. *The Journal of Physical Chemistry* 86, 3914–3916 (1982).
24. Powers, D.E., et al. *The Journal of Physical Chemistry* 86, 2556–2560 (1982).
25. Powers, D.E., Hansen, S.G., Geusic, M.E., Michalopoulos, D.L. & Smalley, R.E. *Journal of Chemical Physics* 78, 2866–2881 (1983).
26. Hopkins, J.B., Langridge-Smith, P.R.R., Morse, M.D. & Smalley, R.E. *Journal of Chemical Physics* 78, 1627–1637 (1983).
27. Heath, J.R., et al. *Journal of Chemical Physics* 83, 5520–5526 (1985).
28. O'Brien, S.C., et al. *Journal of Chemical Physics* 84, 4074–4079 (1986).
29. Smalley, R.E., B, L.R., Levy, D.H. & Wharton, L. *The Journal of Chemical Physics* 61, 4363–4364 (1974).
30. Smalley, R.E., Wharton, L. & Levy, D.H. *The Journal of Chemical Physics* 63, 4977–4989 (1975).
31. Smalley, R.E., Wharton, L. & Levy, D.H. in *Chemical and Biochemical Applications of Lasers* (ed. Moore, C.B.) 1–43 (Academic Press, 1977).
32. Smalley, R.E., Wharton, L. & Levy, D.H. *Accounts of Chemical Research* 10, 139–145 (1977).
33. Smalley, R.E., Levy, D.H. & Wharton, L. *The Journal of Chemical Physics* 64, 3266–3276 (1976).
34. Powers, D.E., Hopkins, J.B. & Smalley, R.E. *The Journal of Physical Chemistry* 85, 2711–2713 (1981).
35. Smalley, R.E. in *Comparison of Ab Initio Quantum Chemistry with Experiment for Small Molecules* (ed. Bartlett, R.J.) 53–65 (D. Reidel Publishing Company, Boston, 1985).
36. Dietz, T.G., Duncan, M.A., Liverman, M.G. & Smalley, R.E. *Journal of Chemical Physics* 73, 4816–4821 (1980).
37. Michalopoulos, D.L., Geusic, M.E., Langridge-Smith, P.R.R. & Smalley, R.E. *Journal of Chemical Physics* 80, 3556–3560 (1984).
38. Morse, M.D., Hopkins, J.B., Langridge-Smith, P.R.R. & Smalley, R.E. *Journal of Chemical Physics* 79, 5316–5328 (1983).
39. Brucat, P.J., Zheng, L.-S., Pettiette, C.L., Yang, S. & Smalley, R.E. *Journal of Chemical Physics* 84, 3078–3088 (1986).
40. Brucat, P.J., et al. *Journal of Chemical Physics* 85, 4747–4748 (1986).
41. Cheshnovsky, O., et al. in *International Symposium on the Physics and Chemistry of Small Clusters* (eds. Jena, P., Kanna, S. & Rao, B.) 1–14 (Plenum Press, Richmond, Virginia, 1986).
42. Morse, M.D., Geusic, M.E., Heath, J.R. & Smalley, R.E. *Journal of Chemical Physics* 83, 2293–2304 (1985).
43. Geusic, M.E., Morse, M.D. & Smalley, R.E. *Journal of Chemical Physics* 82, 590–591 (1985).

44. Geusic, M.E., Morse, M.D., O'Brien, S.C. & Smalley, R.E. *Review of Scientific Instruments* 56, 2123–2130 (1985).
45. Alford, J.M., Williams, P.E., Trevor, D.J. & Smalley, R.E. *International Journal of Mass Spectrometry and Ion Processes* 72, 33–51 (1986).
46. Alford, J.M., Weiss, F.D., Laaksonen, R.T. & Smalley, R.E. *Journal of Physical Chemistry* 90, 4480–4482 (1986).
47. Elkind, J.L., Weiss, F.D., Alford, J.M., Laaksonen, R.T. & Smalley, R.E. *Journal of Chemical Physics* 88, 5215–5224 (1988).
48. Rohlfiing, E.A., Cox, D.M. & Kaldor, A. *Journal of Chemical Physics* 81, 3322–3330 (1984).
49. Yang, S., et al. *Chemical Physics Letters* 144, 431–436 (1988).
50. Bloomfield, L.A., Geusic, M.E., Freeman, R.R. & Brown, W.L. *Chemical Physics Letters* 121, 33–37 (1985).
51. Curl, R.F. & Smalley, R.E. *Science* 242, 1017–1022 (1988).
52. Zhang, Q.L., et al. *The Journal of Physical Chemistry* 90, 525–528 (1986).
53. Hargittai, I. in *The Chemical Intelligencer* 6–54 (1995).
54. Smalley, R.E. *The Sciences* 22–28 (1991).
55. Baggott, J. *Perfect Symmetry, The Accidental Discovery of Buckminsterfullerene* 1–315 (Oxford University Press, Oxford, 1994).
56. Aldersey-Williams, H. *The Most Beautiful Molecule, The Discovery of the Buckyball* 1–340 (John Wiley & Sons, Inc., New York, 1995).
57. Heath, J.R., et al. *Journal of the American Chemical Society* 109, 359–363 (1987).
58. Kroto, H.W., Heath, J.R., O'Brien, S., Curl, R.F. & Smalley, R.E. *Astrophysics J* 314, 352–(1987).
59. Dresselhaus, M.S., Dresselhaus, G. & Eklund, P.C. *Science of Fullerenes and Carbon Nanotubes* 1–985 (Academic Press, San Diego, 1996).

## Erratum

Page 15, line 8 should read as:

Cox and Kaldor<sup>26</sup> in an essentially the same apparatus. In the Rohlfiing, Cox, and