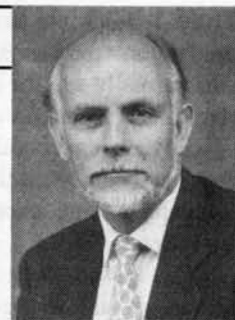Interview: Dr. Richard E. Smalley

Fullerenes: a challenge to the science of chemistry

Dr. Richard E. Smalley, who is a professor of chemistry at Rice University in Houston, and a leading researcher in the field of fullerenes, spoke with Mark Wilsey of 21st Century Science & Technology *on Sept. 20.*

Q: Part of your work involves doping the carbon 60 with various materials; how has this gone so far?
Smalley: There are two kinds of doping we are interested in in getting physical samples of. One is to replace some of the carbons in the fullerene structure with other atoms. Either boron or nitrogen should be virtually perfect substitutions for carbon in the cage.

Q: Because of their similar size or chemical properties?
Smalley: The physical size of the atom, the strengths of the bonds, the bonding desires of these atoms are similar to carbon. The other kind of doping is to put atoms on the inside.

We have demonstrated that we've done both of these things, in small amounts, on the order of a million or so of them at a time. We probe them by levitating them in a magnet and slapping them with lasers, and show that they behave like fullerenes. The next level is to try to make bulk amounts of these, so you can actually have them in a bottle, and you can play with them, touch them, feel them, taste them—if you're stupid enough to try tasting them.

We have a paper that will appear in an October issue of the *Journal of Physical Chemistry,* where we report our first success with putting lanthanum inside and getting a material that actually survives exposure to Houston humidity. This success with lanthanum is poetic justice, because back in 1985, lanthanum was the first thing that we claimed that we had put inside, in small amounts, and that launched quite a controversy at the time. Now, not only do we continue to claim that we put it there, but we have a bottle of stuff that contains lanthanum atoms that are unlike any lanthanum atoms ever seen before.

It turns out that the air-stable lanthanum-containing fullerne is just one out of all possible fullerenes. It is interestingly not LaC_{60}, or LaC_{70}, it turns out to be C_{82}—a C_{82} fullerene with a lanthanum inside.

Q: Is this due to an affinity for the atom's size?

Smalley: We don't know for sure, yet. But it fits a simple quantum mechanical model, which is pretty easy to understand. If you put a lanthanum atom inside of a fullerene cage, it has been calculated already by scientists at Ohio State University that the lanthanum should give up two of its electrons to the cage. If you put it inside a C_{60} cage, the only place to put those two electrons is in a much more loosely bound orbital motion around the ball than the typical 60 electrons of the buckyball ordinarily go into. That makes it a fairly reactive molecule. In fact, we have made that material, too, but it is stable only when it is protected from the air, actually imbedded in a buckyball film.

Doped into that film, we have C_{60} with lanthanum, also some other fullerenes with lanthanum in them. But if you dissolve that film in toluene or benzene, so the molecules are forced to fend for themselves in the solution, the LaC_{60} and LaC_{70} do react and form some solid precipitate. We don't know whether it's actually opened the cage or not—we think it probably hasn't—but we don't have a soluble material surviving that exposure.

On the other hand, one of the clusters, LaC_{82} does survive that exposure and stays in solution. We are now setting about to purify it, to get a pure sample of it. But we have bottles of yellow solutions that contain this LaC_{82} and C_{60}. We have sent samples of this to Minnesota to have what's called x-ray photoelectron spectroscopy done on it, which allows you to probe what the lanthanum is like. It turns out that it is unlike any other kind of lanthanum we've ever seen, which is about what you'd expect, since it's protected inside this cage.

Lanthanum atoms themselves are pyrophoric, and actually burst into flames as these things react with air to form lanthanum oxide, but this lanthanum atom is protected by the carbon cage and is completely immune to air oxidation or water. So this is the first of what we hope will be a long series of metal-containing fullerenes. This technique that we are using should be extendable to a variety of other elements on the periodic table.

Q: Would you describe the electronic structure of C_{60}?
Smalley: If you are just counting the valence electrons for the carbon, there's four for each carbon, so that's $4 \times 60 = 240$. So they are swarming around, glueing the cluster together, and that's basically what holds it in its structure.

These 240 fall into two sets, one set with 180 electrons are used to form the bonds that hold it together in the pattern that you normally see for a soccer ball. Each one of those 180 electrons is paired up with another one to make the covalent bonds, the single bonds. In an ordinary molecule, like benzene, you can call it the sigma bonding framework. Here it is much the same, except it is wrapped around the surface of the sphere.

That leaves 60 electrons to be delocalized in, sort of, an almost metallic sea, going around in what would be the π-bonds of benzene, but these are now radially directed carbon orbitals, one sticking out from every carbon, at the vertices, on the radius line. It turns out that 60 is a very special number for those electrons and they again can all find partners to pair up, and it closes what's called an electronic shell. So it's a closed shell molecule, all the electrons are paired up, which is what you need to have to have a really stable molecule.

The next most energetic way of moving electrons around the sphere is quite a distance up. That makes bucky fairly weakly colored in the visible range. If you had a polycyclic aromatic with anything like 60 carbons in it, and you put that in a solution and looked at that in one of these bottles at the concentrations, or even a hundredth of the concentrations that you see these bottles of C_{60}, a typical polycyclic aromatic molecule would be pitch black by that point. So these are not very absorbent molecules: In fact, the color from C_{60} is entirely due to forbidden transitions that wouldn't be true if it weren't vibrating.

The strong absorptions are in the ultraviolet; that's because the structure is so stable, and the next level up is so far away. Now, when you make a crystal of this, and you add alkaline metals to the outside, those alkaline metals have an extra electron associated with a single valence electron, and they don't hold on to them very tightly. C_{60} actually has quite a high affinity for electrons. Electrons can go onto the ball, and they go into this next higher level in the electronic struture, and effectively spin around the outside of the ball.

There's room for six electrons there. If you put six electrons into it, that material will be an insulator, but if you'd put in less than six electrons, you'll have a conducting material. Effectively, each ball becomes metallic. The metallic electrons on the surface of the ball can hop from ball to ball, and therefore, you get a bulk conductivity. This conductivity becomes super when you cool it down. One model for the superconductivity is that each ball is itself a superconducting ball: You just happen to have a close-packed lattice of super-conducting balls where the supercurrent is hopping between balls.

One of the things that makes C_{60} so unusual is that it is so big for a molecule. It behaves in many ways more like a graphite ball than like a big benzene molecule. Also being along the size range of 1 nanometer [1 billionth of a meter] it sits just squarely right where we like to be when we start building structures. One of the things we are hoping is that

this will get organic chemists excited about dealing on this level. They could be in a position to push back the frontiers of nanotechnology rather dramatically.

Q: Another feature of C_{60} is the "free rotation" of these carbon balls in the lattice. It's described to be on the order of billions of revolutions per minute. Is that an unusual feature?
Smalley: Benzene, itself, in the crystal at room temperature is actually spinning around its sixfold axes. Other symmetrical molecules in their crystals often do spin. What is unusual in C_{60} is the broad temperature range over which this happens, and the fact that the spinning is isotropic, or at least it appears to be. There is no preferred direction, because this is a spherical one.

No, it is not by any means unprecedented. Methane, for

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Beginning with benzene

Benzene is a ring of six carbon atoms and is a basic building block in organic chemistry. Benzene was first isolated in 1825 by Michael Faraday, but, of all the proposed structures for this molecule, none seemed to fit. In 1865, German chemist Friedrich August Kekulé came up with a satisfactory structure for benzene. This is how Kekulé recounted his insight in his journal:

"During my stay in Ghent, I resided in elegant bachelor quarters. My study, however, faced a narrow side-alley and no daylight penetrated it. For the chemist who spends his day in the laboratory, this mattered little. I was sitting, writing at my textbook, but the work did not progress; my thoughts were elsewhere. I turned my chair to the fire and dozed. Again atoms were gamboling before my eyes. This time the smaller groups kept modestly in the background. My mental eye, rendered more acute by repeated visions of the kind, could now distinguish larger structures of manifold conformation: long rows, sometimes more closely fitted together, all twining and twisting in snake-like motion. But look! What was that? One of the snakes had seized hold of its own tail, and the form whirled mockingly before my eyes. As if by a flash of lightning, I woke; and this time also I spent the rest of the night in working out the consequences of the hypothesis.

"Let us learn to dream, gentlemen, then perhaps we shall find the truth. But let us beware of publishing our dreams till they have been tested by the waking understanding."

Translated by F.R. Japp, Journal of Chemical Education *(1958).*

example, is a tetrahedral arrangement of hydrogens around a carbon atom, and methane down to rather low temperatures as you crystallize it has its molecules spinning around rather speedily, in fact even faster than C_{60}.

Q: Does the C_{60} change axes, or does it tend to stay in a particular one, or does it sort of tumble?
Smalley: Because it is certainly touching the other balls, and at any temperature the balls are vibrating against each other, the rotation will be free for a while, and then it will pick up some energy in a different direction, coupling into the vibrational motion of the lattice. If you really look at one of these balls, you'll find it is rather jerky. It will go for a while and then be kicked off in a different direction, rather chaotically.

Q: Is there a coupling between balls where one spins one direction and another spins another direction?
Smalley: There is a particular direction that would probably be the lowest energy, that has all the balls arranged in a precise orientation relative to each other. However, the difference between that and 43 other different kinds of ways of putting the balls together is so little that, at room temperature, there would be hardly any tendency to find it in a preferred single direction.

Q: As the C_{60} crystal is cooled down, it goes though a transition.
Smalley: It goes through an ordering transition at about 260° Kelvin, but that ordering transition is simply a transition between the free motion of the ball and one where they're in, at one particular moment, one preferred direction and in another moment they'll shift to another one. They end up sort of jittering, shifting rapidly back and forth. You have to get down to near-liquid nitrogen to determine special ordering. The motion becomes slow, on a time scale of a million per second.

Q: Would there be a way of "training" the buckyballs to all spin the same way?
Smalley: No. If you have a pure buckyball film, with nothing else, you will probably never find circumstances where you get all the balls oriented perfectly. So there will always be this intrinsic disorder; even though the ball positions themselves may be perfect, in a f.c.c. [face-centered cubic] lattice or this simple cubic lattice [that] it goes into during the ordering transition, we will probably never get a means of turning each ball so that they're pointed in exactly the same [direction] relative to each other. There is just not enough difference between one direction and another.

On the other hand, when you have these alkali metals in between the balls—in the little gaps in the lattice—that is thought to orient the balls a particular way, this is what the x-ray structure reveals: For example, in the case of the K_3C_{60}

superconductor, what we call the buckide salt, the balls are not rotating and they are all nicely crystalized in a particular orientation.

Q: They try to keep a particular face pointed relative to the crystal.
Smalley: The potassium atoms in this structure are big enough, that unless they, in a sense, sort of poke into the hole in one of the hexagons, there's no room; this tends to give orientation in a particular direction.

Q: Going back to your work and that of others on the formation of the carbon-60 molecule. Is it in the plasma state when it is heated as high as it is to vaporize it?
Smalley: Certainly, when we do it by laser vaporization we generate a plasma, by which we mean a heavily ionized vapor of carbon.

Q: A more simple combustion or resistance heating wouldn't necessarily mean that?
Smalley: It depends on how you do the resistance heating, whether or not you get a plasma. If it really is resistance heating, and there isn't an arc, then at the temperatures necessary to vaporize carbon, which is about 3,500-4,000°C, there wouldn't be very much ionization, so it wouldn't be a plasma. It would be more like a vapor.

Q: Whereas, at the temperatures you're working at, it definitely would be.
Smalley: In fact, it's different even than that, because of the fact that the laser triggers this vaporization. Even before a lot of the carbon is vaporized, it ignites a plasma above the surface of the graphite. As the carbon starts to vaporize, this plasma gets denser and denser, until finally it becomes so dense that the light can't go though it anymore. That's a natural cutoff for how much you're going to vaporize. It is quite convenient in the apparatus to make each pulse a similar length. In our variation of the Huffman-Krätschmer technique, where we used a simple arc welder, we actually set up a real carbon arc, [and] there is certainly a plasma there as well.

We have thought a lot about the mechanism of the formation of C_{60} over the years, and I think we are one of the few laboratories that claims to think we understand it. There's some discussion about what we're suggesting as the model that explains everything we know on how C_{60} and the other fullerenes form, what factors control the yield. The simplest way of saying it is that as carbon clusters begin to grow, we think that by the time they're 35 atoms or so in size, they take the form of open graphite-like sheets, like pieces of chicken wire. The trick is to get these sheets to effectively anneal to their favorite geometry before they grow too big.

We suppose that this favorite geometry is one that obeys what we call the pentagon rule. The rule is to incorporate as
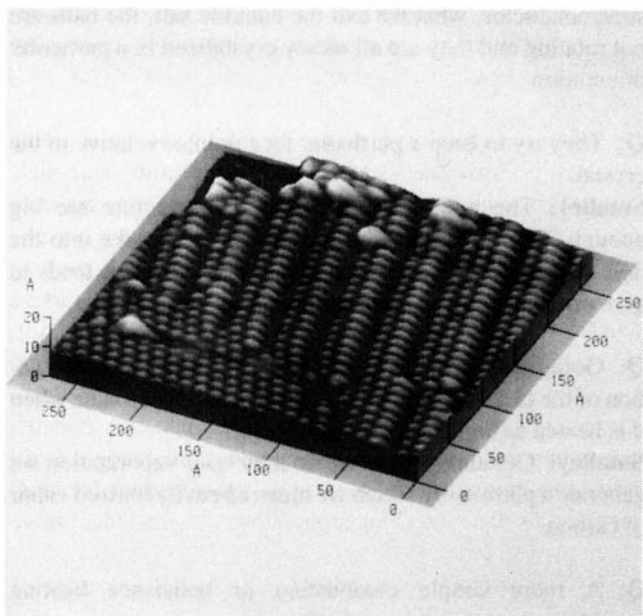
Image from a scanning tunnelling microscope of C_{60}. The flat region, toward the lower left, shows clearly the close-packed structure. The uneven region above that shows C_{60} growth in a different orientation.

Courtesy of Li, et al. [Science 253,429, (1991)].

many pentagons into the sheet as possible with the provision that no two pentagons be adjacent to each other. Structures of that sort, as they grow, will form uniquely C_{60}, which is the virtue of this mechanism. There must be thousands of different ways that you can put carbon atoms together and quite by accident get C_{60}; the real question is how do you contrive to have—it's been reported—as much as 40% of all the condensed carbon vapor make C_{60}. How could that possibly be? Then you look at every mechanism that you can think of and ask, how could this mechanism get me such a high yield? If there's no way, then you throw it out. For every mechanism we've heard of, none of them can explain such high yields except this one, what we call the pentagon road in reactive kinetics.

One aspect of this theory is that it is a firm, testable theory. It could be wrong. One way to prove it wrong is that you can look at the calculations of all possible structures for an open sheet, and see if you can find one that violates the pentagon rule and is more stable. When you do that, you will find there is one more stable than the open sheet, and that is, in fact, the closed fullerene structure.

The major contender for the alternative explanation is that the clusters close to form fullerenes quite early, but until they're C_{60}, they keep on opening up, and growing, and then closing again. The trouble with that mechanism is that we don't understand why C_{60} wouldn't open and grow larger, at least some of the time. Because calculations reveal quite uniformly that the larger fullerenes are actually more stable than C_{60}. There is no particular reason to stop at 60.

So we presume that, in the reactive kinetics, open sheets are formed, but that you don't spend long enough at high enough temperatures to anneal them into the closed fullerene before you get to C_{60}. It's really a matter of an open sheet curving and closing. It's a test of all hypotheses, in that it predicts that you will improve the yield by protracting the time the clusters are growing in the size range smaller than 60, and by increasing the temperature of this reignon, so that they'll have a chance to anneal. That is the thinking that led us to modify our laser vaporization conditions, to doing it in an oven at 1,200°C, which changed the laser vaporization method we had been dealing with, over all the time up till Huffman-Krätschmer, from making buckyballs, but not enough to really see, to a method now that makes buckyballs in very high yields. You just put it in an oven; everything is the same, that's all that was necessary.

That, in turn, is the method that we're now using to get macroscopic amounts of metal-containing fullerenes. Instead of just vaporizing graphite, we laser vaporize a composite of graphite and the metal of interest, and off comes touchable, feelable, smellable versions of metal-containing ones.

Q: Returning to superconductivity: A feature of the alkaline-doped C_{60} superconductor is that it is sensitive to pressure, such that conductivity goes down with increased pressure. What mechanism would be involved in that? The opposite seems to be true in other metals.

Smalley: The rationalization that has been offered, is that, what one is trying to do is to get the density of conducting states to be very high in order to get the critical temperature high. In the theory of superconductivity, that sometimes makes sense, apparently. As you squeeze these balls together you broaden out this band of states that's doing the conduction. That makes the density of states per given energy range lower. That's the rationale, or at least the one that's most discussed.

On the other hand, I think it's fair to say that nobody really has much of a clue of what the superconducting mechanism is in buckyballs. So it's a little glib to say we understand why, when you press on it, the value of T_c [critical temperature at which superconducting begins] goes down, since we can't really predict in any sort of intellectually honest way what that value of T_c is.

Simply put nobody really knows what the mechanism of superconductivity of these balls is yet. For that matter they're pretty unsure about all of the practical superconducting materials, even the ones currently used are not very well understood. They're not BCS materials, at least not very well handled by BCS theory. [Bardeen-Cooper-Schreiffer theory of superconducting, which doesn't explain high-temperature superconductivity—ed.] Superconductivity theory is not in a very good situation, has not been for years. That's one of the all-time bugs in the bonnet of solid-state physicists.

It might be that one of the most important aspects of C_{60}

buckide superconductors is that it may be a happier hunting ground to get at the new concepts necessary to get a firm theory for superconductivity.

Q: Carbon-60 comes out of research into atomic clusters. How has the work in C_{60} affected this research?
Smalley: I'm not quite sure what the answer is going to be. It is certainly going to have a big effect on it. In one sense it is the sort of thing we hoped to find, something really completely new, because we were dealing with a new cluster that no one ever looked at before, and of course, one always hopes there's something there.

But carbon is really quite special, and I don't anticipate we'll find things like this again roaming through the periodic table, for the simple reason that carbon is the only element that's content to have just three nearest neighbors, three other carbon atoms, which allows it to make a two-dimensional sheet. These molecules are basically a two-dimensional sheet wrapped around on itself to form a closed sphere. Silicon, for example, is never content with just three nearest neighbors: It insists on having four, sometimes more. So, in exactly the same apparatus, you make silicon clusters, and they're not like this at all: They always start with a couple of atoms in the center and just keep on building out; there is never a point where they stop building. There is no cluster of silicon that is so happy with itself that, when offered another silicon atom, wouldn't say, "Thank you very much, that feels good." But these carbon clusters are different. C_{60} carbon, when it's offered other carbon atom, says, "No thanks, I'm happy, I'm pleased with this." They're molecules, closed shell, and behave like molecules, that's why we have them in bottles.

The long-term future for the fullerenes may be very rich because they are molecules, which means you can manipulate them while they are still nanometer-scale objects. You can build architectures with them. With the other materials, like silicon, and germanium, and gallium-arsenide, and the transition metals, in order to have a cluster that is content to not grow bigger, you have to passivate the surface in some fashion.

A little bit of success has been had along these lines, by a group at Bell Labs, led by Lou Bruse and Mike Steigerwald, who have learned to make little nanometer-size particles of cadmium-sulfide and a variety of other semiconducting materials. A member of that group, Paul Alivisatos, now at [the University of California at] Berkeley, has succeeded in finding ways of making gallium-arsenide nanometer particles and having them passivated on the surface. With transition metals, there are a class of clusters that are passivated on the surface by carbon monoxide.

This business of actually making nanometer particles, and making structures with them, is only part of the reason why we got into the game to begin with. The main reason was to develop a fundamental understanding of the chemistry and physics of materials, when they weren't molecules, when the surfaces were not saturated, when you have this ragingly reactive metallic surface, like you have in a transition metal surface; to understand in more detail the processes involved in heterogeneous catalysis, corrosion, and reactions at electrodes.

When you actually get down to thinking about machining materials on a nanometer scale, and you want to manipulate and control what's going on at that scale, you're going to have to be able to understand the chemistry of such objects. The reason we built these machines, and have been pushing this field is to develop, in a sense, this tinker-toy surface science, where these clusters are the tinker-toys. We do it, not because they are easy to understand, but because they are hard. It may be in this environment, where we finally learn the concepts necessary to understand the chemistry of stuff, rather than the chemistry of molecules. That challenge still pretty much remains. We've gone a long way down that road, but there's still a much longer path down the road than we've gone down so far.

For my own scientific career I'm going to have to decide whether I'm going to keep on going down that road. I must admit that fullerenes constitutes a real tantalizing fork in the road here, and I'm not quite sure how many more years we can keep straddling this line. At some point I'll have to decide on which path to take; right now, I don't know which it will be.