

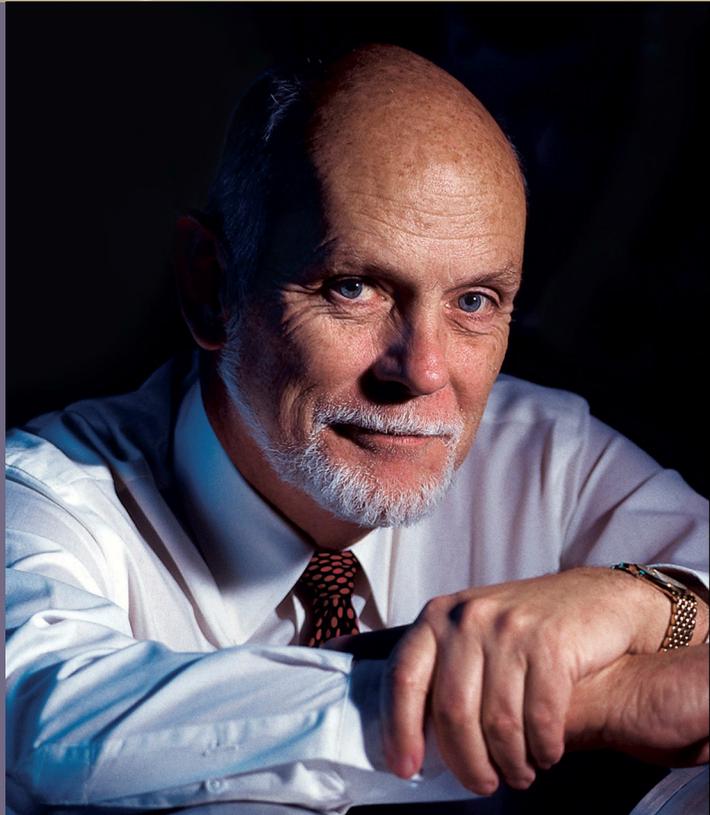


Richard E. Smalley
1943–2005

BIOGRAPHICAL *Memoirs*

A Biographical Memoir by
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RICHARD ERRETT SMALLEY

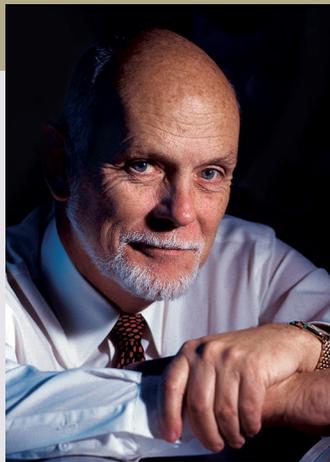
June 6, 1943–October 28, 2005

Elected to the NAS, 1990

Richard Smalley shared the 1996 Nobel Prize in Chemistry for the discovery of the carbon cage compounds called the fullerenes. At that point he had already realized that developments in imaging science would enable the growth of a major new field of basic and applied research called nanotechnology. Leveraging the prestige and visibility of his Nobel award, Smalley began a single-minded effort to persuade the U.S. Congress to fund a multibillion-dollar national program to support this scientific opportunity. This crusade came to fruition in the summer of 2001, when then Pres. George W. Bush signed the bill establishing the National Nanotechnology Initiative. Many other countries, impressed by this development, followed with their own nanotechnology research initiatives. Smalley had “A Charge to Keep” moment in the White House with President Bush when he realized that he had a mission to pursue—energy prosperity for the nation (and the world) by inspiring the next generation of scientists and engineers, developing replacements for dwindling fossil fuel reserves, and finding a solution to global warming.

In addition to the Nobel Prize, Smalley also received the Irving Langmuir Award, the E. O. Lawrence Award, the Welch Award in Chemistry, the American Physical Society International Prize for New Materials, and the American Carbon Society Medal for Achievement in Carbon Research. He was elected to the National Academy of Sciences in 1990.

Richard Errett Smalley was born in Akron, Ohio, on June 6, 1943, the youngest of four children. At an early age, he moved with his family to Kansas City, Missouri, where he grew up. His mother, Esther Virginia Rhoads, was the daughter of a wealthy furniture manufacturer named Errett Stanley Rhoads (hence his unusual middle name). His father, Frank Dudley Smalley, was the son of railroad mail clerk in Kansas City. Smalley’s parents married during the Great Depression, and shortly after the marriage Frank was laid off work. His father started work as a carpenter and later became a printer’s “devil,”



Photography by Tommy LaFegre

*By Robert F. Curl,
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performing a number of tasks such as mixing tubs of ink and fetching type. After a short time at the *Kansas City Star*, he moved to a farm implement trade journal, *Implement and Tractor*. By the time Frank Smalley retired in 1963, he had become CEO of a group of trade journals serving the agricultural industry throughout the Western Hemisphere.

Smalley's interest in science was fostered by his mother, who went back to college after Rick, the youngest child, no longer needed full-time parenting. In college she fell in love with science and transmitted that enthusiasm to Rick, and his father taught Smalley carpentry and electrical and mechanical repair. He also learned drafting from his mother and from courses in high school. This education proved an ideal foundation for his career in physical chemistry, where he imagined, designed, and built powerful new scientific instruments that opened new fields of research.

It was the launch of Sputnik that caused Rick to commit to a career in science. He knew that the U.S. reaction would trigger a new national emphasis on science and technology, and he wanted to be at the center of this new wave. Rick chose chemistry because he had a superb high school chemistry teacher. And it was also the path taken by his aunt Sara Jane Rhoads, who later won the Garvan Medal. In the summer of 1961, Rick worked in her organic chemistry laboratory at the University of Wyoming, and she suggested that he enroll at Hope College. Smalley spent two years studying at Hope but decided to transfer to the University of Michigan in Ann Arbor after his chances for pursuing undergraduate research at Hope were dashed by an unexpected death and a retirement among the faculty.

Upon receiving his bachelor's degree in 1965, Rick decided to work in industry for Shell Oil Company, a decision he never regretted. But after three years as an industrial chemist, he grew eager to expand his skills and return to academia for graduate study. In 1968, however, draft student deferments were eliminated, and Rick chose to stay at Shell to retain his industry deferment. At the time, he was about to marry Judith Grace Sampieri, a coworker at Shell. When Rick's industrial deferment was lost, they decided that he should proceed to pursue a graduate degree. Just as he was about to be drafted and with the Vietnam war raging, Judy became pregnant. Consequently, Rick was reclassified and no longer had to be concerned about the draft.

In 1969, Rick began his graduate career at Princeton University in New Jersey, choosing to work with Elliot Bernstein. Bernstein was interested in studying the Jahn-Teller effect in the E" symmetry excited state of 1,3,5-triazine, a molecule with threefold symmetry. This meant learning about the Jahn-Teller effect, one of the most abstruse areas of

molecular spectroscopy. In order to carry out this work, Smalley had to synthesize high-purity samples of both the normal and deuterated isotopomers. Using crystals of these samples, Smalley then measured the weak UV absorption spectra at liquid helium temperatures and studied the Stark and Zeeman effects in these spectra. Bernstein and Smalley discovered that the crystal field was asymmetric enough to contaminate the Jahn-Teller phenomena. In his efforts to gain a complete understanding of this system, Rick carried out an enormous number of difficult experiments that led to the publication of two papers from his thesis results in 1973. These two papers have received a total of only 18 citations, but Smalley undoubtedly learned important experimental skills in doing this research. The way in which Rick handled this modest recognition of his prodigious efforts may have been the origin of his later comments to his students that there is no such thing as a failed experiment, you can learn something from every experiment.

In the summer of 1973, Smalley, Judy, and young Chad moved to Chicago for his post-doctoral research with Donald Levy at the University of Chicago. Levy had become obsessed, as so many of us were, with understanding the extremely complex visible spectrum of nitrogen dioxide. He was using various new laser-based tools, such as microwave-optical double resonance, to pick apart and analyze spectra.

It happened that when the Smalleys arrived in Chicago, Levy was in Germany for an extended stay. From Rick's point of view, this was good because he still had to dream up and defend three original research proposals for his final oral exam at Princeton. Coming up with ideas for the proposals required many hours of intense reading and thinking in the Chicago chemistry library. Upon reading a paper by Yuan Lee and Stuart Rice about a crossed molecular beam study of the reaction between benzene and fluorine, he realized that the rotational temperature of benzene after its supersonic expansion was only a few degrees above absolute zero. This sort of supersonic expansion would greatly simplify any complex spectrum. Rick's idea could satisfy two needs at once: a research proposal for his Princeton Ph.D. oral and a way to simplify the extremely complex spectrum of NO_2 that Levy was struggling with.

Working with Levy and Lennard Wharton, another faculty member, Rick developed the technology needed to measure the spectra of ultracold molecules. One result of that work was the enormous success of Rick's interview visit to Rice University. His lecture displayed an amazing array of exciting results. In addition to cooled spectra of nitrogen dioxide, Rick showed spectra of cooled tetrazine and of two noble gas van der Waals complexes: HeI_2 and NaAr . After his impressive lecture, the faculty offered Rick an

assistant professor position on the spot with the proviso that only the Rice University president was authorized to officially make the appointment.

The First Eight Years at Rice

When Smalley started at Rice, one of us (RFC) was eager to start collaborating with him but reluctantly decided that it would be best to not complicate his research record by the involvement of a senior colleague before tenure review. Despite his rapid research success, Rick actually took almost the normal time to be promoted because Rice considers teaching seriously before offering tenure, and Rick was far too busy with research to chalk up a good teaching record. He was promoted to associate professor with tenure in 1981. But just one year later he was promoted to professor, and in 1983 he was made the Norman Hackerman Professor of Chemistry. Rice's battles to keep him from being hired away had begun.

As the papers from Chicago continued to roll out, Smalley's first aim after arriving at Rice was to construct a small supersonic jet apparatus that he called AP1 as a tool for his first students to use in their thesis research. The studies he did with this apparatus were extensions of his work at Chicago and, in a new direction, he explored the redistribution of vibrational energy in excited states of isolated alkyl-substituted benzene molecules.

While this research was underway, Rick carefully designed and constructed a larger and more capable version of the apparatus, called AP2. It incorporated a true pulsed supersonic molecular beam coupled to a time-of-flight mass spectrometer, plus UV excimer lasers to ionize molecules in the beam. In order to get funding for this ambitious apparatus, Rick made a deal with the Exxon corporate research laboratories in New Jersey. If Exxon provided the funds, he would build two identical units, keeping one for himself and sending the other to New Jersey for Exxon's use.

The immediate purpose of this powerful new apparatus was to explore the state of matter between molecules and solids. This might at first glance seem like the long-established field of colloid chemistry. The difference was that clusters of atoms could now be characterized by mass to reveal the number of atoms in the cluster. Various laser-based probes could be used to control cluster fragmentation at selected laser wavelengths. Importantly, the reaction of the clusters with various reagents could also be investigated. Through this project, Smalley invented a new field of chemistry that was taken up by many laboratories around the world and is still an active research area.

Smalley and co-workers used AP2 from its completion around 1982 until late 1990, resulting in about seventy publications. This instrument was key to the Nobel Prize-winning discovery of the fullerenes, both in the initial discovery of buckminsterfullerene and in a series of later experiments testing the fullerene structure hypothesis and expanding knowledge of their properties.

In his Nobel autobiography in late 1996, Smalley described the fate of AP2. He writes, “Several years ago AP2 was dismantled and sold off in pieces to other research groups, and the main chamber where the first pulsed nozzle experiments were performed was sold off to a scrap metal dealer along the Houston Ship Channel.”

The great success of AP2 made it much easier for Smalley to build other scientific instruments, starting with a Fourier transform mass spectrometer that allowed studies of reactions between mass-selected cluster ions and low-pressure reactants. This permitted quantitative comparisons of reaction rates and observations of product ions. In addition, a photolyzing laser could be aimed down the solenoid bore to dissociate the trapped ions and gain more information.

The final chapter of Smalley’s 1980s instrument building was his design and construction of a mass-selected negative ion photoelectron spectroscopy system. This powerful instrument could probe the electronic energy levels of a selected cluster referenced to the vacuum.

Discovery of C₆₀ and the Fullerenes

Harold “Harry” Kroto came from England to Texas in March 1984 to attend a meeting at the University of Texas at Austin. At the meeting, one of us (RFC) invited him to come to Houston and visit. By this time, RFC had joined in experiments using AP2. Harry began pressing to use the apparatus to obtain evidence for his hypothesis that carbon chain molecules (specifically cyanopolyacetylenes) are formed in the clouds surrounding red giant stars. As this project would distract from the work already underway using the apparatus, it was put off until August 1985, when Rick judged that the time had come to rewrite the computer program controlling AP2 and to evaluate carefully the direction of the semiconductor cluster program that was currently underway. Rick invited Harry to come to Rice for the carbon experiments. Then he found a paper published by the Exxon group describing experiments supporting Harry’s belief that carbon chain molecules formed spontaneously in condensing carbon vapor. As the novelty of Harry’s proposed experiments had faded, Rick called Harry again and

suggested that he need not make the trip; the students would proceed to do the experiments and just send the results to him, to which Harry replied that he was coming anyway. Graduate student Yuan Liu would work on the apparatus software, and graduate students James Heath and Sean O'Brien would work with Kroto in the lab to conduct his proposed experiments. The results they found supported Kroto's mechanism for the formation of cyanopolyacetylenes that he had observed using radioastronomy.

Previous studies at Exxon and at Bell Labs had made the curious observation that the only detected clusters had an even number of carbon atoms for masses between thirty-six and about one hundred carbon atoms (the sensitivity of both apparatus began to decrease as the cluster size grew, effectively vanishing at one hundred carbon atoms). In August 1985, Jim, Sean, and Yuan began preparing for Harry's arrival, and in their preliminary experiments testing the apparatus, they noted that the signal for the cluster containing sixty C atoms was more prominent than its neighbors. Such intensity spikes had been observed many times previously for clusters of several elements, and were called, for lack of a ready explanation, "magic numbers." Indeed, for carbon clusters in the range of cluster size near C_{15} , a large variation in signal intensity had been observed by all workers.

The studies performed with Kroto explored a wide range of experimental parameters, and the AP2 group noticed that the intensity of the carbon peak corresponding to sixty carbon atoms varied substantially relative to those of other clusters of similar size as the conditions in the nozzle prior to the expansion were changed. Based on that variation, a logical explanation for the observed behavior seemed to be that the cluster containing sixty carbon atoms must be far less reactive than the others.

Harry was scheduled to return to England on September 10. Therefore, on September 6, the group held a meeting to review the carbon cluster results and discuss any dangling issues. The data supporting Harry's proposal were deemed satisfactory, but just how prominent this C_{60} peak could be made became the critical point. Sean O'Brien and Jim Heath were asked to try to address this question. Each worked individually on trying to generate the most prominent peak. Although both succeeded in enhancing the C_{60} peak, Heath achieved the largest relative prominence, about a 30:1 ratio of C_{60} to C_{62} , so his result was chosen. Harry immediately canceled his return trip to stay and help interpret this exciting finding.

Over the night of September 9, with the aid of an important hint by Kroto, Smalley was able to construct a polyhedral model of a sixty-atom molecule with the atoms located at the vertices of the polyhedron and the chemical bonds corresponding to its edges. This is

most easily pictured as the traditional soccer ball. When Kroto returned home, he immediately verified that the structure he had created pursuing a hobby, and which he was trying to visualize in his hint, was exactly the same structure.

The next two days were spent drafting a letter to the journal *Nature*, and it was submitted on September 12. Many, including the journal's reviewers, were concerned that the evidence for the existence of this first known molecular form of carbon presented in the manuscript was flimsy. One of us (RFC) surmises that the recommendation to publish was based, at least partially, on the reviewers' conviction that if the paper turned out to be wrong, blame would fall on the authors rather than the anonymous reviewers. But if it was rejected and the work proved to be correct, then the reviewers would look very bad indeed.

Because of the healthy skepticism with which our proposal was received, the group carried out several experimental studies aimed at verifying this structure to answer critics. It soon became clear that all of the clusters in the mass region that showed only even numbers of carbon atoms were also polyhedrons involving rings of pentagons and hexagons. Rick dubbed this family of molecules the fullerenes, based on their general resemblance to the geodesic domes devised by the designer and architect Buckminster Fuller.

A serious effort at Rice to make macroscopic samples of C_{60} using sophisticated laser systems failed. But in the early fall of 1990, the group of Wolfgang Kratschmer, Donald Huffman, and their students Fostiropoulos and Lamb reported a simple technique for making macroscopic quantities of C_{60} and C_{70} . Their samples showed properties that were consistent with the structures previously deduced from the Rice molecular beam experiments. With real samples of C_{60} and C_{70} suddenly available, a frenzy of fullerene research was launched in laboratories around the world.

The Birth of Nanotechnology

By 1993, with fullerene research still growing exponentially, Smalley pondered the future and conceived an enormous new research field, nanotechnology. Like all of us, Rick was amazed that molecules as beautifully symmetric as buckminsterfullerene could emerge from the chaos of very hot carbon vapor. Perhaps a similar process to bring order out of chaos might be duplicated in other environments. He became inspired by the short lecture given in 1959 by Richard Feynman, "There's Plenty of Room at the Bottom," which pointed out that physical objects on the nanometer scale had scarcely been

explored. Smalley was also keenly aware of the advances in microscopy that were taking place, led by scanning tunneling microscopy. Now it would be possible to observe and study nanoscale objects on a wide range of surfaces.

Excited by these ideas, Rick set to work convincing others of the importance and promise of these new developments. He began by persuading the Rice administration to support nanotechnology by fundraising and investing \$37,000,000 to build a new laboratory building (Dell Butcher Hall), providing a \$5 million equipment fund, and creating and filling several prestigious new faculty positions spanning various science and engineering departments. This was the origin of Rice's Center for Nanoscale Science and Technology (CNST), the first organized nanotechnology research center in the world. Rice University rewarded Smalley's achievements with a new, richer endowed professorship, the Norman Hackerman/Welch Chair in Chemistry.

Rick then turned his attention to the U.S. government, urging Congress to support the emerging field. He spearheaded the effort that culminated in the 2001 law establishing the National Nanotechnology Initiative and appropriating about \$6 billion of funding. In recognition of his leading role in nanotechnology research and advocacy, Smalley was the only academic invited to the White House to witness President Bush's signing of the landmark bill. Rick then began to think locally again—that Houston needed an initiative in medical nanotechnology, building on the vast medical expertise and research in the Texas Medical Center. This effort resulted in the creation and funding of a new entity, the Alliance for Nano Health.

Single-Wall Conducting Carbon Nanotubes

In 1993, Sumio Iijima at NEC Corporation in Japan and Donald Bethune at IBM in the United States simultaneously reported the preparation of single-wall carbon nanotubes. Mildred Dresselhaus (at the Massachusetts Institute of Technology) and coworkers had already developed a theory of the electronic energy structure of such tubes. To Smalley, the crucial pieces of information were that carbon nanotubes would be the strongest imaginable material for their weight and that a special nanotube structure called the "armchair" would have very high electrical conductivity. Smalley decided to redirect all of his research efforts to the synthesis, study, and potential applications of such nanotubes. He loved to remark, "If it ain't tubes, we don't do it."

The demonstration that carbon atoms could actually form nanotubes with potentially high electrical conductivity was astonishing to the materials science world. The strength

and electrical properties of this new kind of carbon nanotube introduced a wide-open arena for researchers worldwide to explore. Smalley quickly devised several methods to grow single-wall carbon nanotubes, as discussed below. And he did something unusual for a scientist of high stature—he freely sent nanotube samples to many other researchers around the world. In this way he advanced the understanding of this new nanomaterial and also benefited personally from the many interactions and collaborations that his generosity fostered.

Smalley imagined many uses for single-wall carbon nanotubes (hereafter called SWCNTs). He calculated that cables made of them would have the strongest tensile strength of any possible material and could be used to reinforce materials such as concrete or plastics, which are strong in compression but not in tension. Smalley envisioned that nanotube cables could be used to lift supplies to orbiting satellite stations and that the special highly conducting armchair nanotubes could replace heavier copper and aluminum in high-tension power lines.

Rick realized that many of the world's problems could not be solved without abundant supplies of energy, and the only energy source large enough would be captured solar radiation. Because sunlight is available only eight hours per day on average, long transmission lines would be needed to export the harvested electrical power to distant time zones. To make this a reality would require finding a way to synthesize long enough SWCNTs cheaply and abundantly, and then to devise a method to spin these tubes into cables. For the maximum electrical conductivity, only tubes of the armchair type would be required.

Bringing these ideas to fruition might require a lifetime of research, but unfortunately Smalley would have only about a decade to work on them. His first task was to make SWCNT tubes of many types. Additionally, they would need to be produced on a fairly large scale because he intended to supply other laboratories with nanotubes. If the properties and uses of SWCNTs were to be rapidly explored, the required research could not all be done in his laboratory. All that was known at the start was that synthesis of nanotubes seemed to require the combination of carbon vapor and catalytic nanoparticles of mid-first row transition metals, iron, cobalt, or nickel.

Inspired by his longtime use of pulsed lasers, Smalley's first nanotube growth successes used laser vaporization of graphite rods impregnated with one of these metals. Although this laser vaporization method was quite successful in growing high-quality SWCNTs, it was not practical for producing them in the large quantities that were required. His

next scheme used the disproportionation reaction at about 1000 °C of carbon monoxide to produce elemental carbon and carbon dioxide. The other requirement of a transition metal catalyst was provided by the quick decomposition at this temperature of iron carbonyl vapor into iron nanoparticles. With careful engineering and development, this production scheme worked well and was scalable. The so-called Rice HiPco reactor (for high-pressure CO) became the main source of SWCNTs for researchers around the world.

This apparatus continued Smalley's intrinsic desire to build large, complex laboratory machines that would enable him to make discoveries. To develop it he hired a couple of talented undergrad Rice students to help build a chamber that could heat a flowing gas to 1000 °C and inject the catalyst precursor, all at high pressure. Furthermore, the apparatus needed to allow collection of the nanotube product while still maintaining the high temperature and pressure in the reaction zone.

Eventually, all of these challenges were met with an automated system that could run continuously for months at a time without failure. It occupied a full laboratory and was a source of pride for Rick, even if its large compressor tended to shake that end of the building a bit. It produced about a single gram of SWCNTs per hour, hence the need for continuous and automatic operation. This large HiPCo reactor could make about a kilogram of high quality SWCNTs in about forty days and could operate for up to nine months. As a side activity, Rick worked with another Rice faculty member, Ken Smith, to launch a new company, Carbon Nanotechnologies, Inc. (CNI), with the goal of producing HiPCo SWCNTs on a much larger scale. CNI built a two-story version of the reactor, which did scale up the production but only by a factor of ten instead of the planned hundredfold. The company was ultimately purchased by the California-based Unidym, Inc.

It quickly became apparent that, as synthesized, the individual nanotubes self-assembled into 10- to 20-nm diameter "ropes" containing about 100 SWCNTs. Some ropes were more than 100 μm long with individual tubes extending over the entire length. A four-point measurement of resistance on an individual rope indicated that its resistivity was about six hundred times that of copper.

Saito and Dresselhaus had predicted that SWCNTs could be formed in a variety of chiral structures, about two-thirds of which have diameter-dependent band gaps and the other one-third of which have no band gap and show metallic conductivity. A crucial first step would be the experimental verification of the Saito and Dresselhaus model. Working

with Cees Dekker's group at the Delft University of Technology, Smalley verified that SWCNTs are actually produced in a variety of chiralities.

Although the simple Saito-Dresselhaus model of electronic structure indicated that one-third of the nanotubes would conduct electricity like a metal, more sophisticated theories predicted that only a subset of those structures (the "armchairs") would actually conduct ideally. As a rope might contain a random collection of different nanotube structures, it was still possible that a single "armchair tube" could have room temperature conductivity better than copper, and these conducting tubes would have the advantage of weighing far less than the amount of copper (or aluminum) needed to carry the same current.

It appeared to be a formidable challenge to synthesize only armchair nanotubes in lengths long enough to make strong and high-conductivity cables, and then to align them well enough to spin into a macroscopic cable. But this did not trouble Rick much; he loved challenges.

The first step was to clean up the messy tangle of ropes into material that was free of metallic impurities and soot. This was achieved by breaking the ropes into smaller fragments by sonication in *aqua regia* followed by the addition of anionic surfactants to prevent flocculation. Removal of the solvents produced a papery material named "bucky paper," which when torn revealed remarkably well-ordered material at the torn edges.

In two early publications involving several institutions, the Raman spectroscopy of SWCNTs produced by laser vaporization was explored and interpreted entirely in terms of armchair and zigzag nanotubes, as chiral tubes were not yet understood to be Raman active. The presence of Raman lines of three armchair structures indicated that they were being produced in abundance.

With a target of making SWCNT fibers containing only armchair SWCNTs, it was important to characterize the electronic composition of SWCNT samples. In 2001, Smalley began a collaboration with Bruce Weisman's group at Rice to explore the optical spectroscopy of HiPCo nanotubes. This soon led to the discovery and interpretation of near-infrared SWCNT fluorescence, which is emitted only by the semiconducting nanotubes that should be excluded from armchair SWCNT fibers. Because the wavelengths of SWCNT fluorescence vary systematically with nanotube structure, near-IR fluorescence and absorption spectroscopy has become a powerful and widely used research tool.

The electrical resistance of a nanotube cable is lowest if the cable contains only long, overlapping armchair nanotubes. The straightforward way to achieve the goal of synthesizing only a particular type of SWCNT is to create a template for the growth of the desired nanotube. Copies of this template could then be distributed over a surface and individual “cloned” nanotubes grown from the templates. To achieve this, there are three problems to overcome. First, one must selectively grow only the desired type of SWCNT. Second, it is necessary to grow the tubes to lengths approaching 10 millimeters. The feasibility of making tubes long enough was demonstrated for untemplated seeds of random chirality in 2004 by Li, Yu, Rutherglen, and Burke, but extending this to growth in the gas phase had not been demonstrated. Moreover, in this prior work, many of the seeds did not grow or grew only to short lengths. Third, it is necessary somehow to align the SWCNTs into ropes and then assemble the ropes into a cable.

At the time of his untimely death in October 2005, Rick Smalley had made significant progress towards solving the first problem by demonstrating growth from the seed template while maintaining the desired chirality. In pursuing this goal, Smalley created a team at Rice involving several other faculty members. One who played a key role was Robert Hauge, whose experimental talents and productive interactions with students and postdocs led to co-authorship with Smalley on 114 nanotube papers. CNST director Wade Adams took the lead in finding continued financial support for the ambitious project. The research aimed at producing cables of armchair nanotubes was pursued at Rice until about 2018. It still continues in several other laboratories around the world, because success would have a revolutionary impact on electrical power transmission.

Although Smalley had undergone treatment for lymphoma since the late 1990s, he continued to work so intensely, fearlessly, and optimistically as to appear invincible to his co-workers and colleagues. But in the fall of 2005, Rick’s health deteriorated sharply, and he succumbed to the disease. The death of this larger-than-life figure was a great shock and loss to his group, to Rice University, and to the entire scientific community.

Personal Reminiscences

Robert Curl

I actively collaborated with Rick for about a decade starting in 1982. Rick, Frank Tittel, and I began collaborating in 1982 on research in clusters of semiconductor materials, specifically Si, Ge, and GaAs, supported by the Army Research Office. The shrinkage of the features on computer chips provided the motivation for this research. We proposed that there had to be a change in the fundamental properties of the semiconductors on a

chip when the feature size became so small that most atoms would be on the surface of the feature. Thus, a study of the properties of small semiconductor clusters to anticipate such effects could provide valuable information. This gave me a vantage point to observe the interactions between Rick and his students and postdocs.

Rick drove himself to push his research forward; he expected his group members to do the same, with mixed results. One of Jim Heath's favorite stories is about an evening just after he started research. At the end of the workday, he was in the lab with another student in the early days of AP2. The other student left at some point in the evening, but Jim continued to work until about 3 a.m. when he decided to quit and go home. Then Jim realized that he did not know how to turn the apparatus off. In fear and trembling, he called Rick at home for instructions. Instead of the chewing out that Jim expected, Rick was delighted that Jim was still working at such a late hour.

For me, the most impressive thing I observed in student interactions was what happened at group meetings. In the fullerene days, these took place every morning. The format was always the same. Each student or postdoc was asked to describe what they had accomplished the previous day. If they had data, they were expected to bring the data/charts that resulted. These were discussed in a very interactive manner with participation by everyone present until a consensus was achieved on the meaning of the results and a target for what was to be done that very day emerged, with Rick making it clear what he expected each student to do. It struck me that this experience was part of a perfect education on how to succeed as an assistant professor at a research university.

The other aspect of Rick was his creative ability to find untouched areas to work in. Rick's pattern was to work quietly at home thinking of a new field, working through all the snags, and then to design a new instrument capable of exploring the field. I would hear about it when actual construction of the instrument started. At that point, it was normally six months from the beginning of the research until the instrument started producing data.

By 1992, it was clear to both of us that there were too many people working worldwide on research on the fullerenes. Consequently, I devoted all my attention to my ongoing research on free radical spectroscopy and kinetics. For his part, Rick discovered Mildred Dresselhaus' work on carbon nanotubes and the discovery of how to make them, described above, and decided that these were the next big thing. For reasons that remain somewhat unclear to me, I was not interested in working in this area.

Because of Dresselhaus' research on nanotubes, we were both aware of and understood the almost ancient (1940s) theoretical work on graphene, but neither of us chose to pursue graphene research.

After 1992, Rick and I remained friends and had very frequent discussions, but we never collaborated again. In my opinion, he was the smartest person I have ever worked with.

Bruce Weisman

I first met Rick Smalley in 1973, when he came to the University of Chicago for post-doctoral research with Don Levy. At the time, I was a third-year graduate student in Stuart Rice's physical chemistry laboratory, but both groups were housed in the Research Institutes building and communication between groups was a strong tradition. Rick stood out as being a bit older than other new postdocs and also was notably more intense and scientifically ambitious. Don Levy later admiringly recalled Rick's research style as "fierce." When Don was out of the country for a period, I remember Rick happily (if temporarily) lounging with his feet on the desk in Levy's faculty office, a preview of his future status. Before long, Smalley's project successfully demonstrated the now-famous method for measuring spectra of molecules cooled to nearly absolute zero in beams of supersonic gases. In an early conference presentation of this work, Rick (then still a postdoc) wowed the audience with his results, poise, and wit by showing the stunningly simplified spectrum of cooled NO₂, a famously frustrating molecule to spectroscopists that he described as "absorbing in the brown." (Some specialized background may be needed to appreciate the wit here.) The huge impact of supersonic beam spectroscopy in physical chemistry was immediately obvious and made Smalley a star candidate in his academic job search. He accepted an offer from Rice University and began as an assistant professor in the Department of Chemistry in 1976.

Our paths crossed again in 1979, when I joined Rick on the Rice faculty and was assigned lab space adjacent to his. Despite Rick's awesome prior achievements and ambitious plans, Rice allotted him only very modest startup funds and just a corner of another faculty member's lab as his research space! But he quickly overcame these obstacles by attracting talented graduate students, writing successful proposals, and publishing leading-edge research enabled by the construction of his AP1 instrument. Smalley's rapid rise to academic fame is well documented.

Although Rick Smalley was widely known for his scientific intensity, focus, and vision, I think his most distinctive characteristic was research courage. By this I mean his willingness to halt research in a promising, productive, and "safe" area in order to explore

a new and uncertain topic. Over and over again through the years, he pioneered a new field (such as supersonic beam spectroscopy), led it as it exploded in popularity, and then moved on even though he could clearly have enjoyed a productive and respected career just by continuing. Nearly all scientists would choose that easier path, but Rick was always eager to find and confront the next big challenge. Rather than stay in fullerene research as a venerated founder and leader, he dove headlong into the emerging but risky area of carbon nanotube research and quickly became a leader there. His colleagues watched in amazement as Smalley literally dismantled his custom-built, state-of-the-art instruments to support new research ventures in areas in which he had no prior credentials or certainty of funding. Following this pattern, Smalley tackled larger and larger problems, culminating in his efforts to find a solution to the world's need for abundant renewable energy. I think one of the main values Rick conveyed to those around him was the importance of identifying the most significant problems and having the courage to tackle them.

Rick Smalley had remarkable personal presence and charisma that made him an inspiring advisor and a natural scientific celebrity. He seemed to thrive on the attention that came with the Nobel Prize, using that platform to advance public and government support for nanotechnology and energy research. Although Rick could be very charming in personal interactions, he was also at times quite blunt and unconcerned with others' feelings. But this did not dissuade talented students and postdocs from choosing to work with him, and there is a long and impressive list of Smalley protégés who have gone on to distinguished scientific careers.

The most exciting research in my career is linked to Rick Smalley. Although I played no part in the discovery of C_{60} , I turned from gas-phase molecular photophysics to studies of fullerene triplet states in solution in the early 1990s, shortly after macroscopic samples became available. This research showed me the appeal of exploring the properties of new materials. Then in 2001, Rick invited my group to collaborate with his on the spectroscopy of single-wall carbon nanotubes. I was flattered, because Rick was of course an accomplished spectroscopist who could easily have led such an effort himself. But his nanotube research program was by then so broad and ambitious that he wanted someone to focus on the spectroscopy problems. As part of his effort to drive nanotube research rapidly forward, Rick was cultivating numerous collaborations and sending samples of high-quality nanotubes around the world, which led to co-authorship on many publications in the quickly growing field. He once joked that in the early days of nanotube research, he tried to read all of the papers that appeared. Then that became an over-

whelming task, so he just read all of the papers in his special areas of interest. Finally, he said, that too became impossible, “so now I only read the papers that have my name in the author list.”

Our collaboration soon led to the discovery of near-infrared nanotube fluorescence and then to the challenging spectroscopic assignment of particular emission bands to specific nanotube structures. Those results have transformed my research career because of their substantial value to basic and applied nanotube investigators. In 2002, when this work was completed but not yet published, Rick was scheduled to be first and keynote speaker at the NT02 nanotube conference in front of hundreds of researchers. In an act of great generosity, Rick spoke for only a few minutes before letting me take the stage for the rest of his keynote slot to present our results to the international nanotube community, who previously had no idea who I was. I remain very grateful for the good fortune of having Rick Smalley as a colleague for twenty-six years.

Wade Adams

I first interacted with Richard Smalley on September 21, 2000, when I invited him to Dayton, Ohio, where I was the Chief Scientist of the Materials and Manufacturing Directorate of the Air Force Research Laboratory. He gave a lecture in a series I created called MMETS (Materials, Manufacturing and Enabling Technology Seminars)—the first speaker in the series (in January 1998) was Steven Chu, who had just won the 1997 Nobel Prize in Physics for laser cooling atoms. Smalley was very impressed with the tour of our lab, calling it the best he had seen anywhere in the world, and he then proceeded to completely wow the Air Force senior executives (some hundred colonels, generals, and senior executive service members) at a Top Issues Day luncheon at Wright-Patterson Air Force Base. Using only a blank 8-½-by-11-inch sheet of paper, he mesmerized these VIPs, showing them what a marvelous molecule a nanotube was as he walked among the tables, describing the amazing properties of this new form of carbon. He was an incredible teacher!

Next, we went to the Engineers Club of Dayton (of which I happened to be the president), housed in a beautiful, nearly 100-year-old building downtown on the Miami River that was created by Charles Kettering and Colonel Edward Deeds (with Orville Wright as an early President). Smalley gave his MMETS and Dayton Section ACS co-sponsored talk on “Buckytubes and Fibers” following a shorter, less-formal discussion with some fifty sixth-grade students in the auditorium, which he pointed out had a graphene motif in the old carpet! We capped the day with a nice dinner, then he and I

stood at the bar in the Canal Street Tavern drinking good microbrew beer, and he was totally enthralled by a performance featuring one of the best fingerstyle guitarists in the world and his wife, a wonderful cellist, my daughter Julie. I don't know which of these experiences made the biggest impression on Rick, but he began to ask me when I could leave my Air Force career and join him at Rice University. It took more than a year, but I did retire from my 38-year career and joined his team. In December 2001, I retired from the Wright-Patterson laboratory on materials research to become director of the Rice University CNST. By then he had decided that I should take over the leadership of the CNST, and he would work for me!

Soon after I arrived at Rice, Smalley took me to see Rice University president Malcolm Gillis in his office—my first meeting with him. He was on the phone and motioned us to sit down on the low couch in his very cluttered office. When he finished his call, he came over and sat on a chair opposite us, and after Rick introduced me, he immediately excitedly said to Rick, “You have got to get me a nanotube sword! I had an adventure dream last night—I was in Hell and I was slaying hundreds of demons and devils with ease. My sword was indestructible, and I killed everything that came at me! I woke up feeling great, not tired at all—so Rick, you have got to get me a nanotube sword!” I thought, this was fantastic—the president of Rice is dreaming about the technology that I am going to be leading the development for. It doesn't get better than this!

Rick later said to me, “I hope Malcolm didn't scare me off as a lunatic,” and Malcolm also told me later that he thought about the possible danger of being too personal with a new guy from the military! I of course became pretty close to Malcolm, which I think benefitted the CNST. Upon his retirement from Rice in 2004, we presented him with his dream gift—a two-handed broadsword made from heavy plastic but coated with carbon nanotubes that rendered it pitch black. (It was made in Rick Barrera's lab by his grad students.) Malcolm told us at this ceremony that he had another adventure dream in which he had on black nanotube armor that was impenetrable. We who knew Malcolm well really missed his open style of leadership!

This story gives a wonderful example of Rick's vision. One morning, a couple of months after I arrived at Rice, Rick looked into my office and asked the question I will never forget: “Got a minute?” The two of us met for two hours and proceeded to outline what later became known as the “Be a Scientist, Save the World” campaign, aimed at stopping and likely reversing the predicted effects of global warming (climate change) and creating

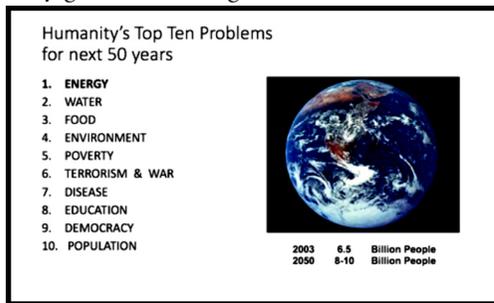
the Armchair Quantum Wire (AQW)—THE answer to most of the dire issues still being confronted today. (Note: this article was prepared in 2021!)

In our conversation, Rick recalled how in 1957 Sputnik convinced him that he wanted to become a scientist. He felt that the oncoming global challenges required alerting young people that the need for scientists was greater than ever, and times called for a similar wake up cry. Henceforth, at every occasion where young people were present, he said “Be a scientist or an engineer and save the world!”

Our conversation included considering the world’s likely greatest challenges, which are distilled in the associated figure. As the conversation developed, it became clear that solving the energy problem could help solve problems 2 to 10.

Smalley proposed a series of three workshops for as many international scientists/engineers and any other people who were interested. They would be held and co-sponsored by Rice’s Baker Institute for Public Policy, and they succeeded as Smalley had foreseen. This tie to the Baker Institute has continued to contribute not only to Rice’s Energy Program but also more broadly to science-based thinking about policy issues related to energy.

The first of the three workshops was held from May 1–3, 2003, was entitled “Energy and Nanotechnology: Strategy for the Future,” and for it Rick assembled many experts in both fields. Texas senator Kay Bailey Hutchison, who was a long-time supporter of Rice and Smalley, spoke. The meeting included a perspective on the energy challenges facing the country and the world provided by Smalley and several high-level government speakers, followed by various prominent speakers and soon-to-be authors of books on relevant topics that included Jeremy Rifkin (*The Hydrogen Economy*), Matt Simmons (*Twilight in the Desert*), and Martin Hoffert, one of the world’s leading experts on climate change. Experts on oil and natural gas provided their perspectives, a path forward was discussed, and various alternatives were presented by experts in carbon sequestration, nuclear fission and fusion, solar energy from space and on Earth, and hydrogen efficiency. Finally, the grid and its efficiency, stability and reliability, and transportation



Humanities Top 10 Problems for the next 50 years.

(Richard Smalley/Wade Adams)

issues were presented and discussed. This first workshop pointed out that among the most important technical challenges facing the world in the twenty-first century is providing clean, affordable energy whose supply is sustainable and universally available. The meeting is available on YouTube and a position paper resulting from this meeting is available from the Baker Institute.

A second workshop (October 16–17, 2004) addressed the narrower topic of “Prospects for Solar Energy in the 21st Century.” The second workshop focused on converting the ample solar flux on the Earth of 165,000 terawatts per day to the needed 30–60 terawatts per day as the world population increases from about six billion in 2000 to perhaps ten billion by 2050. Speakers included representatives from companies such as Konarka, Shell, and British Petroleum, the National Renewable Energy Lab, and two European and seven faculty members from the United States, and one from the U.S. Department of Energy. The participants covered current and possible thermal, photocatalytic, and photovoltaic technologies in mostly optimistic presentations of the available opportunities and growing interest in funding from both domestic and foreign agencies.

The third workshop was entitled “Energy and Nanotechnology: Storage and the Grid,” and was scheduled for November 15–16, 2005. Unfortunately, Rick Smalley passed away on October 28 of that year. Rick helped plan the workshop, but he could not enjoy the fruits of his labor. The workshop was dedicated to him, and many of the speakers included remarks about the man’s greatness. The Baker Institute included his lecture on “Our Energy Challenge” in the notes for the second workshop (actually added in December 2005), which reflects how the great thinker decided that the “new oil” needed was really electricity, and how distributed storage would make the new grid robust.

Imagining 100 million individual storage devices, one for every electrical user, would enable a robust and efficient system that would encourage continuing innovation for profit at the storage sites, but the grid would have to be capable of handling much larger power levels than at present.

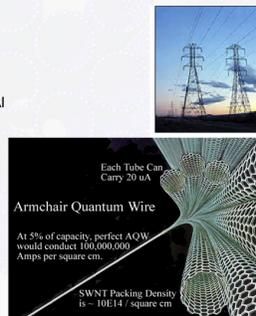
For the grid, Rick envisioned that the current would be carried by a special type of single-wall nanotube, the armchair. The figure on the right shows his vision.

My final meeting with Rick Smalley was in his hospital room at M.D. Anderson Cancer Center on

- Expected Features**
- 1–10x Copper Conductivity
 - 6x Less Mass
 - Stronger Than Steel
 - Zero Thermal Expansion
 - 30x Power Density vs. Cu/Al

- Key Grid Benefits**
- Reduced Power Loss
 - Low-to-No Sag
 - Reduced Mass
 - Higher Power Density

- SWNT Technology Needs**
- Type & Class Specific
 - Higher Purity
 - Lower Cost
 - Polymer Dispersible



SWNT Quantum Wire Project.
(Richard Smalley/Wade Adams)

the Saturday before he passed away. He was in good spirits, anxious to hear about plans for the upcoming workshop at the Baker Institute, and happy to have Paul Cherukuri diligently but quietly working at the desk in his room to get his email online. I brought with me a set of plans for a new “Smalley Building” on the Rice University campus. We had worked on it with a local design company friend in secret because we knew that Rice was very stringent about having ALL building programs go through a process that was lengthy and usually produced beautiful but not so functional results. Rick was truly pleased with the plans, and he thanked the architect and me for doing this great honor for him. I remember he sighed and said he would do his best to beat the disease so he could enjoy its fruition. I left the room after the two hours of happy discussion only to be devastated by his passing on that next dark Thursday morning.

Note: After his passing, a few weeks later, the Dean gave me a terrible chewing out about not following protocol on building design; then a few weeks later asked me to bring her the building designs so she could show the other deans; then a few months later, the new Dean of Engineering made the same request. Maybe we’ll someday see the AQW in reality on the front of a new building at Rice University, no doubt in honor of Richard E. Smalley.

We had a marvelous almost four years together before he tragically lost his seven-year battle with cancer. Rick is gone, but his vision of using science and technology to benefit all people on earth lives on!

SELECTED BIBLIOGRAPHY

- 1985 With H. W. Kroto, J. R. Heath, S. C. O'Brien, and R. F. Curl. C_{60} ; Buckminsterfullerene. *Nature* 318:162–163.
- With J. R. Heath et al. Lanthanum complexes of spheroidal carbon shells. *J. Am. Chem. Soc.* 107:7779–7780.
- 1990 With R. E. Haufler et al. Efficient production of C_{60} (buckminsterfullerene), $C_{60}H_{36}$, and the solvated buckide ion. *J. Phys. Chem.* 94:8634–8636.
- 1991 With Y. Chai et al. Fullerenes with metals inside. *J. Phys. Chem.* 95:7564–7568.
- 1995 With A. G. Rinzler et al. Unraveling nanotubes: Field emission from an atomic wire. *Science* 269:1550–1553.
- With T. Guo, P. Nikolaev, A. Thess, and D. T. Colbert. Catalytic growth of single-walled nanotubes by laser vaporization. *Chem. Phys. Lett.* 243:49–54
- 1996 With A. Thess et al. Crystalline ropes of metallic carbon nanotubes. *Science* 273:483–487.
- With H. J. Dai, J. H. Hafner, A. G. Rinzler, and D. T. Colbert. Nanotubes as nanoprobe in scanning probe microscopy. *Nature* 384:147–150.
- With H. J. Dai, A. G. Rinzler, Nikolaev, A. Thess, and D. T. Colbert. Single-wall nanotubes produced by metal-catalyzed disproportionation of carbon monoxide. *Chem. Phys. Lett.* 260:471–475.
- 1997 With A. M. Rao et al. Diameter-selective Raman scattering from vibrational modes in carbon nanotubes. *Science* 275:187–191.
- With S. J. Tans et al. Individual single-wall carbon nanotubes as quantum wires. *Nature* 386:474–477.
- 1997 With M. Bockrath et al. Single-electron transport in ropes of carbon nanotubes. *Science* 275:1922–1925.
- With A. M. Rao, P. C. Eklund, S. Bandow, and A. Thess. Evidence for charge transfer in doped carbon nanotube bundles from Raman scattering. *Nature* 388:257–259.

- 1998 With J. Liu et al. Fullerene pipes. *Science* 280:1253–1256.
- With J. W. G. Wildoer, L. C. Venema, A. G. Rinzler, and C. Dekker. Electronic structure of atomically resolved carbon nanotubes. *Nature* 391:59–62.
- With A. G. Rinzler et al. Large-scale purification of single-wall carbon nanotubes: Process, product, and characterization. *Appl. Phys. A Materials Science and Processing*. 67:29–37.
- 1999 With P. Nikolaev et al. Gas-phase catalytic growth of single-walled carbon nanotubes from carbon monoxide. *Chem. Phys. Lett.* 313:91–97.
- With M. Bockrath et al. Luttinger-liquid behaviour in carbon nanotubes. *Nature* 397:598–601.
- 2001 With M. J. O’Connell et al. Reversible water-solubilization of single-walled carbon nanotubes by polymer wrapping. *Chem. Phys. Lett.* 342:265–271.
- With J. L. Bahr, J. P. Yang, D. V. Kosynkin, M. J. Bronikowski, and J. M. Tour. Functionalization of carbon nanotubes by electrochemical reduction of aryl diazonium salts: A bucky paper electrode. *J. Am. Chem. Soc.* 123:6536–6542
- 2002 With M. J. O’Connell et al. Band gap fluorescence from individual single-walled carbon nanotubes. *Science* 297:593–596.
- With S. M. Bachilo, M. S. Strano, C. Kittrell, R. H. Hauge, and R. B. Weisman. Structure-assigned optical spectra of single-walled carbon nanotubes. *Science* 298:2361–2366.
- 2003 With M. S. Strano et al. Electronic structure control of single-walled carbon nanotube functionalization. *Science* 301:1519–1522.
- With V. C. Moore et al. Individually suspended single-walled carbon nanotubes in various surfactants. *Nano Lett.* 3:1379–1382.

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