## Robert F. Curl, Jr.: Physical Chemist and Co-Discoverer of Fullerenes

p R. Brooks, R. Bruce Weisman, Bruce R. Johnson Department of Chemistry, Rice University, Houston, TX 77005

Robert F. Curl, Jr. (Bob) passed away on 3 July 2022 in Houston, Texas, at the age of 88. He was born on 23 August 1933 in Alice, Texas, a small town now celebrated as the birthplace of two Nobel Laureates (Curl and James Allison). In 1985, experiments at Rice University led by the team of Bob, Harry Kroto, and Rick Smalley galvanized the scientific world by discovering a novel class of molecules, the fullerenes. These new allotropes of carbon have since led to a broad range of nanocarbon materials and launched the burgeoning field of nanotechnology. This major scientific advance owes much to the remarkable intellect and personal qualities of Bob Curl.

During Bob's childhood, his mother Lessie, and father Robert F. Curl, Sr. (called Floyd) gave him a chemistry set that sparked Bob's interest in science but that nearly destroyed the kitchen stove. As a Methodist minister, Floyd Curl moved frequently with his family until taking an administrative position and settling in San Antonio, Texas, where he played a major role in founding the Methodist Hospital. Bob was fortunate to have a high school teacher who nurtured his scientific interests with special projects. One project he was quite proud of was building a working Cottrell precipitator, a type of electrostatic precipitator for removing fine particles from industrial exhaust smokestacks. To help test it, the non-smoking teacher lit up a cigarette to provide the needed smoke.

After graduating from high school in 1950, Bob entered Rice University (then called Rice Institute) in Houston, Texas. His parents welcomed Bob's enrollment at Rice, not only because of the school's reputation in science and engineering, but because it then had free tuition! Bob thrived in college and his interests evolved toward physical chemistry. Despite his aversion to organic chemistry, in his senior year, he took a mandatory course in Natural Products, taught by Richard B. Turner. Although Turner considered himself a synthetic chemist, he had developed instrumentation that measured the heats of hydrogenation which could reveal subtle conformational changes. Bob became fascinated by how rotation about single chemical bonds could switch steroid molecules between boat and chair conformations and dramatically change their physiological effects. In 1954 Bob graduated from Rice as one of the top two students in his class. He then moved west for graduate work at the University of California, Berkeley, planning to study with Kenneth Pitzer, a pioneer in molecular conformational research.

Pitzer by then apparently considered barriers to internal rotation to be a solved problem and assigned Bob to a thermodynamics project extending the Law of Corresponding States. Bob developed a new approach that yielded improved estimates of thermodynamic properties and enabled the prediction of vaporization entropies to within ≈0.5%. This so-called Curl-Pitzer method was extraordinarily useful in designing chemical plants, and as a result, he and Pitzer were awarded the Clayton Prize of the Institute of Mechanical Engineers in London while Bob

was still a graduate student. Even though Bob had made this substantial theoretical contribution, Berkeley physical chemistry graduate students at the time were expected to do some experimental research. So Bob measured the infrared spectrum of disiloxane,  $(SiH_3)_2O$ , isolated in inert matrices at 20 K. He showed that the Si-O-Si bonding was not linear. This work required the use of hazardous liquid hydrogen as a cryogen, and Bob remained very grateful to the late Dolphus Milligan for helping him to safely handle the hydrogen and avert disaster in the lab.

Bob received his Ph.D. from Berkeley in 1957 (only three years after entering) and moved to Harvard to postdoc with E. B. Wilson on microwave spectroscopic studies of molecular conformations. But early in his time at Harvard, Bob got an unexpected call from Rice University inviting him to apply for a junior faculty position. An opening had arisen because George Bird, a former E. B. Wilson student, was leaving Rice. Bob applied, interviewed, received the job offer, accepted, and came back to Rice as an Assistant Professor in 1958, just four years after he had graduated with a B.A. At Rice, Bob was fortunate to inherit not only Bird's microwave spectrometer but also a brilliant graduate student, Jim Kinsey, who would go on to a distinguished career at M.I.T and later return to Rice as Dean of Natural Sciences.

Bob quickly became a key member of the faculty, respected not only for his scientific excellence but also for his commitment to the institution. As an example, in 1961, at the age of just 27, he was instrumental in convincing his former Ph.D. advisor, Kenneth Pitzer, to accept Rice's offer to be its third President. In the lab, Bob explored the microwave spectroscopy of free radicals and later moved into high-resolution laser spectroscopy when the required advanced light sources became available. This work was enhanced by Bob's 45-year collaboration with Frank Tittel, a Rice laser engineering professor.

In the mid 1970s Bob realized that Rick Smalley, a postdoc at the University of Chicago, was revolutionizing the field of molecular spectroscopy by cooling molecules to very low temperatures in pulsed supersonic jets. Bob easily convinced his colleagues to hire Smalley, who proceeded to build a highly advanced apparatus that produced small clusters through laser vaporization, cooled them in a jet expansion, and analyzed their mass spectra. In the mid-1980s, Curl and Smalley used that apparatus for a collaborative project on nanoscale semiconductor clusters. At that time Harry Kroto, a spectroscopist friend at the University of Sussex, UK, was studying small carbon chain molecules that had been detected near red giant stars and that might explain the mysterious diffuse interstellar bands. Bob had also been interested in the origins of these interstellar bands, and the pair realized that Smalley's apparatus would be an ideal tool for studying the carbon chains. Bob persuaded Smalley to undertake the three-way collaboration, although Smalley initially hesitated because a group from Exxon Corporate Research had already published results on carbon clusters using an identical apparatus.

This project became vastly more important than anyone foresaw, because it serendipitously led to the discovery of the fullerenes. With Bob acting as the catalyst in the collaboration, Kroto came to Houston to join a series of intense experiments involving Rice graduate students Jim

Heath, Sean O'Brien, Yuan Liu, and Qingling Zhang. A quick breakthrough came when Heath and O'Brien observed not just the anticipated carbon chains, but large clusters containing between 40 and 90 carbon atoms. At certain pressures in the nozzle, the clusters equilibrated, causing a dramatic peak at mass 720 to grow at the expense of other peaks. This trumpeted the presence of a new, particularly stable, molecule containing exactly 60 carbon atoms. During a four-day frenzy of activity and scientific insight, the team deduced the structure of C60 (a truncated icosahedral cage, like a soccer ball), wrote a short manuscript reporting their discovery, and submitted it to *Nature*. That seminal paper has now been cited approximately 14,000 times. Because the spherical cage structure reminded them of Buckminster Fuller's geodesic domes, the team called the new molecule "Buckminsterfullerene," (nicknamed "Buckyball") and the class became "fullerenes." The beautifully symmetrical proposed structure remained controversial for five years until Donald Huffman and Wolfgang Krätschmer succeeded in producing macroscopic amounts in 1990. With the fullerenes suddenly available in bulk and the cage structure confirmed by detailed chemical analysis, hundreds of labs around the world leaped into this new branch of chemical science. The discovery from Rice earned Curl, Kroto, and Smalley the 1996 Nobel Prize in Chemistry and has led to the publication of more than 100,000 papers.

The hectic pace of early fullerenes research did not appeal to Bob, who was by nature a calm and deep scientific thinker. So he returned to his preferred areas of gas phase molecular spectroscopy, chemical kinetics, and transition-state (or transition-region) spectroscopy, often through collaborations with colleagues Graham Glass and Philip Brooks.

A major theme in Bob Curl's life was selfless service. During his 50 years as a Rice professor and 14 years as an active professor emeritus, he served as Chair of the Chemistry Department, as a valued member of countless panels and committees at the department, university, and national levels, and, with his wife Jonel, as founding Magister (resident faculty mentor) of an undergraduate residence hall. Bob's many contributions to Rice were recognized by the rare honor of appointment as a University Professor. Despite his brilliance and high achievements, Bob remained entirely unassuming and modest. He faithfully attended graduate student presentations until shortly before his death and always had a gentle question or comment for the students. Bob exemplified both scientific excellence and human decency, providing a role model for hundreds of students and colleagues over many decades. As Jim Kinsey commented at Bob's retirement "He's scary smart, but he is also an extraordinarily decent human being." Bob is deeply missed by all who knew him.

Bob Curl is survived by Jonel, his wife of 66 years, his sons Michael and David, and three grandchildren, Colin, Kellie, and Robert.