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C_{60}: Buckminsterfullerene, The Celestial Sphere that Fell to Earth

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In 1975–1978 the long-chained polyynylcyanides, HC_5N, HC_7N, and HC_9N were surprisingly discovered in the cold dark clouds of interstellar space by radioastronomy. The subsequent quest for their source indicated that they were being blown out of red giant, carbon stars. In 1985 carbon-cluster experiments aimed at simulating the chemistry in such stars confirmed these objects as likely sources. During these cluster studies a serendipitous discovery was made; a stable pure-carbon species, C_{60}, formed spontaneously in a chaotic plasma produced by a laser focused on a graphite target. A closed spheroidal cage structure was proposed for this molecule, which was to become the third well-characterized allotrope of carbon and was named buckminsterfullerene. It has taken five years to produce sufficient material to prove the correctness of this conjecture. There may be a timely object lesson in the fact that exciting new and strategically important fields of chemistry and materials science have been discovered overnight due to fundamental research, much of which was unable to attract financial support, and all of which was stimulated by a fascination with the role of carbon in space and stars. In this account, interesting aspects of this discovery, its origins, and its sequel are presented. The story has many facets, some of which relate to the way scientific discoveries are made.

Molecules with Unsaturated Carbon Bonds

In the early 1970s, the chemistry of carbon in unsaturated configurations became the prime research focus for my group at the University of Sussex.[1] We were interested in free unstable species and reaction intermediates containing C-S, C-P, C-Si, or even C-C multiple bonds. The work originated from an abortive attempt to produce thioformaldehyde ($H_2C{=}S$) by photolysis. However, we switched immediately to thermolytic activation after I heard a lecture in which Don Johnson (from the U.S. National Bureau of Standards in Washington, D.C.) described how he and Powell had made this compound[2] by passing MeSSMe vapor through a quartz tube heated simply by a bunsen burner! This approach worked beautifully; we produced numerous other new compounds containing the C=S moiety such as thioethanal and thioketene by thermolysis of specially synthesised precursors, and characterized them mainly by microwave and photoelectron spectroscopy.[1] These sulfur species possessed a distinctive odor, and I for one have sympathy with the citizens of Freiburg who, according to Noller,[3] forced Baumann and Fromm to abandon their work on these compounds. We gave up our work on seleno analogues for similar reasons after detecting selenopropanal! After success with sulfur/carbon compounds we jumped, in the spirit of Mendeleev, to the next element in the second row of the periodic table, phosphorus. The first phosphaalkenes, $CH_2{=}PH$ and $CH_2{=}PCl$,[4] were produced in 1976 in a joint project with John Nixon; several more followed.[1] Simultaneously, Becker in Germany made $PhP{=}C(tBu)OSiMe_3$.[5] At this stage I envisaged a simple possible solution to the problem which had been on my mind

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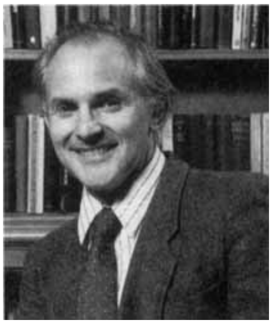
since 1964, namely to ascertain whether derivatives of Gier's beautiful molecule HC≡P[6] could be made. I had been fascinated with HC≡P since the day I arrived as a postdoc at the National Research Council (NRC) laboratory in Ottawa and heard Takeshi Oka (who was then also an NRC postdoc) enthuse over a spectrum of this molecule which Kelvin Tyler (another NRC postdoc) had just obtained.[7] It seemed to me that the chemistry of HC≡P and its analogues must parallel that of the nitriles. Transition-metal complexes could probably be prepared, and cycloadditions to generate phosphorus-containing rings would be feasible.[8, 9] The simple approach worked very well, and we produced the first phosphaacetylene derivative, $CH_3C{\equiv}P$,[10] by thermolysis of $EtPCl_2$ (provided by R. Schmutzler). We followed this breakthrough with the syntheses of other XC≡P species (X = Hal, Ph, N≡C, N≡C−C≡C, etc.[11]). It is most satisfying that, as I had originally conjectured in 1964, the phosphaalkynes (and the phosphaalkenes) have subsequently been exploited by ourselves and other groups as synthetic building blocks.

In parallel with our studies of compounds made up of second-row elements and carbon we probed molecules containing chains with C−C multiple bonds. My fascination with such chains developed very early on in a study of the peculiar molecule, carbon suboxide O=C=C=C=O (one subject of my Ph.D. work at Sheffield in the early 1960s with my supervisor Richard Dixon). This stimulated my curiosity in extended carbon chains and the unusual flexibility which they often exhibited; a preoccupation with such molecules has continued to this day. When I flash-photolyzed C_3O_2 a year or two later at the NRC, I ended up with a cell full of black soot and a magnificent spectrum of the C_3 molecule, whose enigmatic patterns had finally been deciphered by Gausset et al.[11] Almost everything about these carbon chains seemed idiosyncratic, and I stored such observations up for the future. These memories were reawakened in the early 1970s by David Walton's work on polyynes at the University of Sussex. David had developed elegant methods for synthesizing long-chain polyynes, based upon silyl-protection techniques which he pioneered in acetylene chemistry.[12−14] He and his students had made the parent 24 carbon-atom species in minute quantities in solution and even a 32 carbon-atom (silyl-protected) polyyne.[13] These chains were precisely what was needed for a study of vibration–rotation dynamics—a topic which had attracted my interest. In my mind they conjured up an image of a microscopic quantum-mechanical cheerleader tossing a very bendy bamboo baton high into the air—and then attempting to catch the violently flexing and turning baton it as it descended. The obvious first compound for microwave study was the cyanopolyyne, HC_5N, because of its expected enormous dipole moment. Walton devised a synthetic route; Anthony Alexander, a "Chemistry by Thesis" student (editorial comment: for an explanation see the acknowledgements at the end of the review), successfully prepared it and measured its microwave spectrum in 1974.[15] This was a wonderful achievement for an undergraduate and a very important one for me, since it was the first molecule to be characterized on our newly acquired microwave spectrometer.

$$H{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}C{\equiv}C{-}H$$

Fig. 1. The dark clouds in Taurus from Barnards 1927 survey, *Atlas of Selected Regions of the Milky Way*, (Ed.: E. B. Frost, R. Calvert), Carnegie Institute, Washington, D.C., 1927. Heiles's Cloud 2 is in the left-hand bottom corner as indicated by coordinate markers.

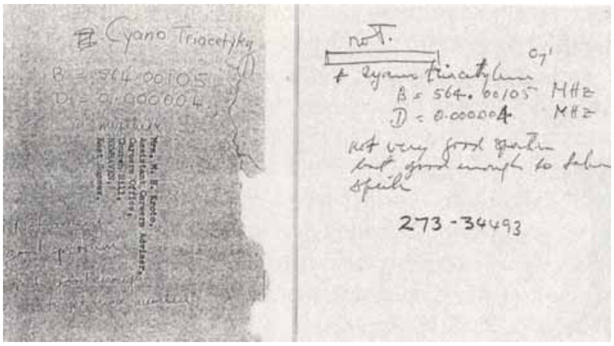
At about this time spectacular advances were being made in molecular radioastronomy. The black clouds which are smeared across our Milky Way galaxy (Fig. 1) were found to possess long-hidden dark secrets. Townes and co-workers[16] opened the Pandora's box in 1968 and revealed that the clouds are full of identifiable molecules. Astronomers suddenly realized what a key role molecules played in the



Harold Kroto, born in 1939, studied in Sheffield from 1958 to 1964 and received his Ph.D. for his research in the electronic spectroscopy of free radicals with R. N. Dixon. After three years of postdoctoral research at the National Research Council in Ottawa and Bell Laboratories, he started his academic career in 1967 at the University of Sussex in Brighton, where he became full professor in 1985. The most recent distinction Kroto has received is a Royal Society Research Professorship (1991). Since 1990 he has been chairman of the editorial board of the Chemical Society Reviews. His research interests include the spectroscopy of unstable species, carbon and metal clusters and microparticles, as well as interstellar molecules and circumstellar dust. Graphic design is his other passion.

intimate gas dynamics involved in the birth of stars and planets. Apart from well-known species such as ammonia, water, and ethanol—enough for 10^{28} bottles of schnapps in Orion alone—Bill Klemperer ingeniously identified the HCO^+ ion (protonated CO)[17] which had not previously been detected in the laboratory. Thus space served not only as a playground reserved for astronomers, but it now presented chemists with a novel piece of apparatus, indeed a colossal new spectroscopic sample cell, containing a plethora of exotic molecules in a wide range of physico-chemical environments.[18] Shortly after Turner[19] had detected HC_3N by microwave frequencies, I wrote to Takeshi Oka at the NRC; my group had recorded the analogous frequencies of HC_5N, and I wanted to search for the molecule in space. Takeshi and I had worked (1964–1966) in the same laboratory at the NRC during the golden years of that research organization.[*] He replied saying that he was "very, very, very, very, very much interested".

In November 1975 the search for radio waves of HC_5N (with Canadian astronomers Lorne Avery, Norm Broten, and John MacLeod) resulted in the successful detection of a signal from Sgr B_2, a giant cloud of molecules near the center of the galaxy.[20] Although we had been hopeful, we were surprised by our discovery since it had seemed such a long shot. In 1975 molecules with more than three or four heavy (C, N, or O) atoms were assumed to be far too rare to be detectable. However, having found HC_5N in space, we thought that HC_7N might also be present. Walton devised a synthesis of HC_7N, and graduate student Colin Kirby managed the very difficult problem of making it and measuring its spectrum.[21]. By the time Colin (in England) finally succeeded in recording the vital frequency, we were actually working on the radio telescope, since our allotted observing session had already started. Colin telephoned my wife, who wrote the value on an envelope (Fig. 2 left). She then telephoned Fokke Creutzberg, a friend in Ottawa, who also noted it carefully (Fig. 2 right) and transmitted it to us at the telescope site in Algonquin park (Fig. 3). The next few hours were high drama. We dashed out to the telescope and tuned the receiver to the predicted frequency range as Taurus (Fig. 1) rose above the horizon (perfect timing). We tracked the extremely weak signals from the cold dark cloud throughout the evening. The computer drove the telescope and stored incoming data, but to our frustration we could not process the data on-line while the telescope was running. The system did, however, display individual ten-minute integrations, and as the run progressed we watched the oscilloscope for the slightest trace of the predicted signal in the receiver's central channel. During the course of these ten-minute snapshots, we gradually concluded that the central channel signal was possibly higher on the average than nearby ones. Desperate for even the faintest scent of success, we carried out a simple statistical analysis in order to determine whether the signal level of the channel was greater than the noise. As the night wore on we became more and more excited, convinced that the signal was significantly more often high than low; we could hardly wait for Taurus to set. By 1:00 a.m. we were too excited and impatient to wait any longer, and shortly before the cloud vanished completely, Avery stopped the run and processed the data. The moment when the trace in Figure 4 appeared on the oscilloscope was one of those that scientists dream about and which, at a stroke, compensate for all the hard work and the disappointments which are endemic in life. The circumstances of this discovery—the arrival of the value of the microwave fre-



Cyano Triacetylene
B = 564.00105
D = 0.000004

+ Cyano triacetylene
B = 564.00105 MHz
D = 0.000004 MHz

273-34493

Fig. 2. The envelope (left) and intermediate note (right) with the precious experimental data from which the frequency of HC_7N in space was determined.

Fig. 3. The 46 m radiotelescope in Algonquin Park, Ontario, Canada with which the long-chain carbon molecules in space were detected.

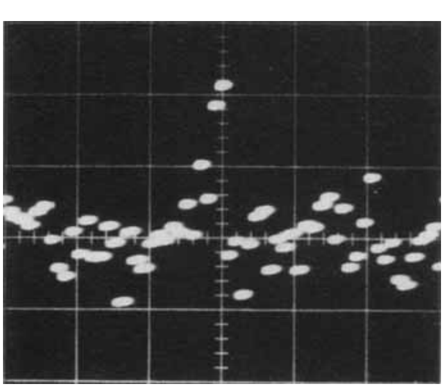


Fig. 4. The first oscilloscope trace of the radio signal emitted by interstellar HC_7N in Heiles's Cloud 2 in the constellation of Taurus (see the coordination markers in Fig. 1).

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[*] Under the guidance of Gerhard Herzberg the NRC had become the Mecca for spectroscopists, and it was here that Cec Costain introduced me to the delights of microwave spectroscopy.

quency from the UK just in the nick of time, the gradual growth of the conviction that there might be a signal in that central channel of the receiver, and then finally the revelation that we (Fig. 5) had detected an enormous molecule in space[22]—made for a truly cathartic scientific experience. (Modern on-line data processing would have diminished the experience). Obviously, the next candidate was HC_9N, but its synthesis was a daunting task. Fortunately, Oka developed a beautifully simple extrapolation technique with which he predicted the radio frequencies of HC_9N. Almost unbelievably, we detected this molecule as well![23] Bell et al. later detected even $HC_{11}N$.[24]

Fig. 5. The team at the NRC laboratory just after the detection of HC_7N in space (from left): Avery, Oka, Broten, MacLeod, and Kroto.

The Search for the Source of Carbon Chains in Space

It is not so obvious today, but in 1975–1978 such long-chain molecules were a totally new and unexpected component of the interstellar medium. How such species came to be present was not at all clear. I felt that it was not sufficient just to have co-discovered them; I really wanted to solve the puzzle of how they got there in the first place, and indeed what they were doing there anyway. After all, everything in nature seems to have some role to play. The search for the source of these compounds became something of a preoccupation (even an obsession). By the early 1980s I was convinced that the ion–molecule reactions which Eric Herbst and Bill Klemperer,[25] and Alex Dalgarno and John Black[26] had devised, and which accounted beautifully for almost all other interstellar molecules, really could not explain the origins of chain molecules.[1, 18] It gradually became clear to me that red giant, carbon stars must hold the key. Particularly interesting was the spectacular infrared object IRC+10216, discovered by Eric Becklin and his colleagues,[27] which pumps vast quantities of chains and grains out into space. I wondered about this red giant and the fact that it was shrouded in grains and chains, which were formed at roughly the same time,[1, 18] and whether "the long chains may be an intermediate form of carbon, between atoms and small molecules such as C, C_2, and C_3, which are well known, and particles with high carbon content such as soot".[1] Perhaps some symbiotic chain/dust chemistry was involved.

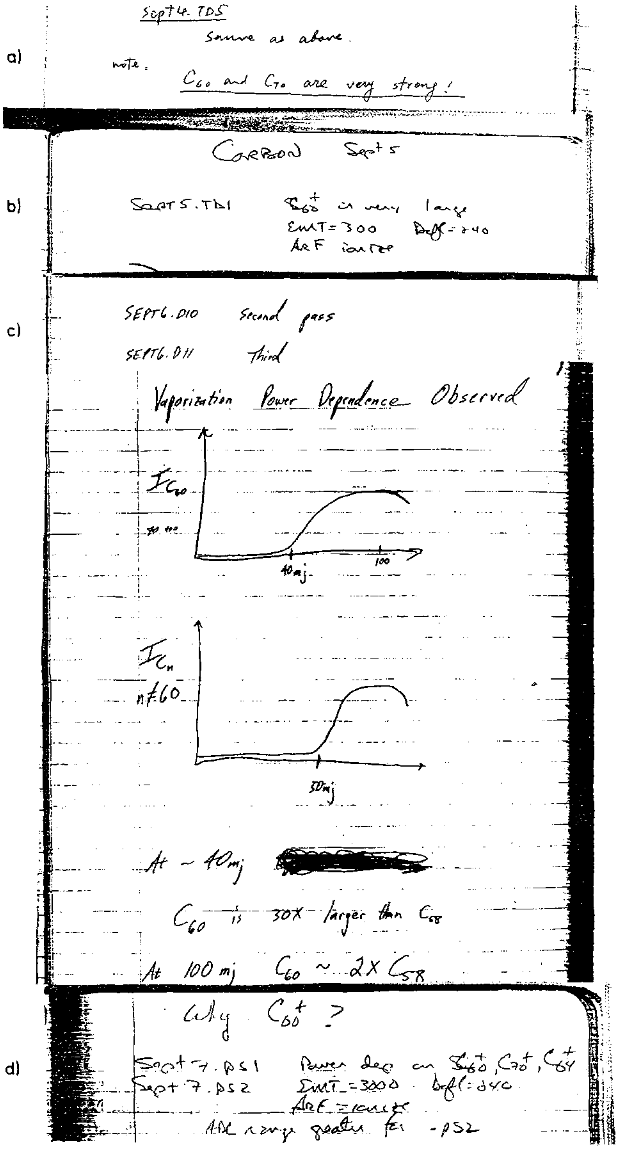
The First Visit to Rice University (Easter 1984)

The foregoing account sets out the background for my thoughts about the role of carbon in space prior to my trip to Rice University in Texas during Easter 1984 to visit Bob Curl. Almost the first thing that Curl told me was that I should visit his colleague, Rick Smalley. He enthused over a very recent result obtained by Smalley and his co-workers, who had analyzed the spectrum of the SiC_2 and had shown the molecule not to be linear, as some might have expected, but triangular.[28] (The analogous C_3 species is linear, although only just.[11]) I visited Smalley's laboratory and saw the laser vaporization cluster-beam apparatus which he and his co-workers had recently developed. This powerful technique enabled the mass-spectrometric study of stable clusters formed in a helium-entrained plasma, produced by a pulsed laser focused on a solid target. In this particular experiment silicon carbide was vaporized and the electronic spectrum of SiC_2 observed.[28] I was much impressed by the result but even more by the experimental technique.[29] This method was clearly a major breakthrough in cluster science, since it made refractory clusters accessible for detailed study for the first time. I had already heard of it, but to see the apparatus in operation was quite fascinating. The result of the SiC_2 experiment was particularly interesting to me, because it was consistent with some unusual theoretical results for $>Si=C<$ species[30] obtained at Sussex in collaboration with John Murrell some years earlier. What excited me most, however, was the thought that by simply replacing silicon carbide with graphite, it should be possible to simulate the type of chemistry which takes place in the atmosphere of a carbon star and produce the long carbon chains. As the day wore on I became more and more convinced that the technique was perfect for this purpose and that evening discussed it with Curl. Because of his interest in microwave spectroscopy, he was immediately enthusiastic, and we made plans for a joint project in the hope that Smalley would also be interested. Perhaps we could detect chains with as many as 24–32 carbon atoms related to Walton's polyynes or Hintenberger's equally amazing pure-carbon species (C_{33} etc.), which were detected by mass spectrometry in the early 1960s in a carbon arc.[31] I dreamt that one day it might be possible to detect a chain molecule such as $HC_{33}N$ (which is as long as the chains that Walton had made in a test tube) in space. Curl was particularly excited by the prospect that we could check out an interesting idea of the late Alec Douglas,[32] namely, that carbon chains might be carriers of the famous Diffuse Interstellar Bands—a set of absorption features[33] which have puzzled astronomers and spectroscopists for more than six decades. Because the project was not considered a priority by the cluster group at Rice University at that stage, it had to await a convenient slot in their program.

In the interim, a group at Exxon carried out the basic graphite-vaporization experiment. In the summer of that year (1984) they published a fascinating result: the discovery of a totally new family of carbon clusters C_{30}–C_{190}[34]—

much larger species than those prepared by Walton et al.[12–14] or observed by Hintenberger.[31] This exciting discovery was peculiar because only even-numbered clusters were detected. It is important to note that at this juncture no specific cluster was perceived to be special. In August 1985 (almost 18 months after my visit) Curl telephoned to say that carbon experiments were at long last imminent. He asked whether I wanted to come to Houston to participate or if they should carry out the experiments and send the data to me. One thing was certain in my mind: I had not waited this long to have my experiments carried out by others in my absence; I wanted to do them myself and to direct the operation personally. Therefore I packed my bags and at my wife Marg's expense arrived at Rice University within days.

Second Visit to Rice University—The Discovery of C_{60}



Sept4. TDS
Same as above.
note: C_{60} and C_{70} are very strong!

CARBON Sept 5
SEPT5.TD1 C_{60}^+ is very large
EMT = 300 Defl = 240
ArF ionize

SEPT6.D10 Second pass
SEPT6.D11 Third
Vaporization Power Dependence Observed

At ~ 40mj
C_{60} is 30X larger than C_{58}
At 100 mj C_{60} ~ 2X C_{58}

Why C_{60}^+?
Sept 7.PS1 Power dep on C_{60}^+, C_{70}^+, C_{64}^+
Sept 7.PS2 EMT = 3000 Defl = 240
ArF ionize
ArF range greater for .PS2

Fig. 7. Entries by Heath, Liu, and O'Brien in the Cluster Laboratory Notebook from the period September 4–7, 1985 when key experiments were carried out at Rice University. a) September 4th: First recorded note that C_{60} and C_{70} were very strong (see also Fig. 6). b) September 5th: C_{60} signal again very strong. c) September 6th: Record of first experiments which specifically aimed at optimization of the conditions for production of a dominant C_{60} signal ("C_{60} is 30 × larger than C_{58}.") d) September 7th: Further power-dependence studies.

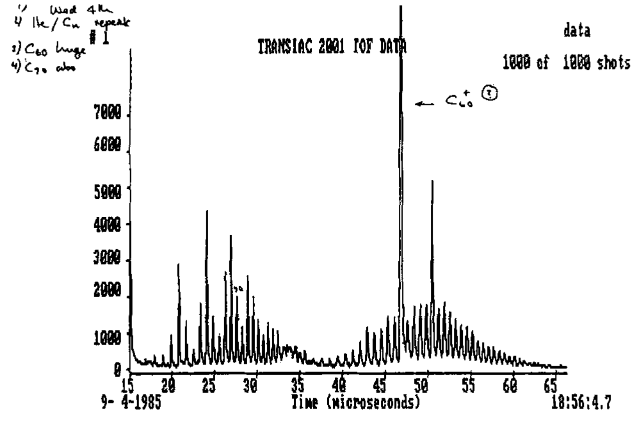


Fig. 6. Annotated time-of-flight (TOF) mass spectrum of carbon clusters produced on Wednesday, September 4th, 1985, the day on which the dominance of the C_{60} signal was first recorded (see also Fig. 7a).

Silicon and germanium cluster studies were on the Rice plate in August 1985 because of their implications for semiconductors. Such experiments were considered to be important because the results might have useful applications (!) The carbon project, on the other hand, was thought to have no possible application (other than for astronomy) and was to be completed quickly, causing as little delay to the semiconductor study as possible. Preliminary measurents on carbon had already been carried out, and the Exxon spectra had been reproduced; nothing untoward was noticed. As soon as I arrived (August 28th) I presented a lengthy informal seminar on everything I knew about carbon in space, stars, and soot. My experiments started on Sunday, September 1st, 1985. I worked in the laboratory alongside two research students, Jim Heath and Sean O'Brien—an exhilarating experience; Yuan Liu was also involved. We toiled late into the night, varying the clustering conditions and monitoring the reactions of the carbon clusters with hydrogen, oxygen, and ammonia—gases which I thought would give rise to polyynylcyanides and other chain molecules. They did! The experiments thus immediately confirmed that the chemistry in red giant stars could be responsible for interstellar carbon chains. Curl and Smalley paid frequent visits to the laboratory. As the experiments progressed it gradually became clear that something quite remarkable was taking place: As we varied the conditions from one run to the next, we noticed that a peak at 720 amu[*] (corresponding to a C_{60} species) behaved in a most peculiar fashion. Sometimes it was completely off-scale; at other times it was quite unassuming. The spectrum recorded on Wednesday, September 4th, 1985 was astounding (Fig. 6). Our reactions were noted in the laboratory record book (Fig. 7a), and I annotated my copy of the printout (Fig. 6). From that point onwards the idiosyncratic behavior of this peak was followed very, very closely (Fig. 7b). When this result appeared, the carbon project—

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[*] Editorial note: amu = atomic mass unit. According to *Quantities, Units and Symbols in Physical Chemistry* (Ed.: Int. Union of Pure and Applied Chemistry), Blackwell, Oxford, **1989** (Chapter 2.10), amu is the symbol for the unified atomic mass unit m_u and the unit u. In this review the unit amu which is still encountered frequently is used.

for the first time—engendered general interest, and by mutual agreement continuation of the semiconductor program was delayed so that we could concentrate on the remarkable phenomenon which we had uncovered. As the weekend approached our actions, thoughts, and conversations turned more and more to the phenomenon. What might this special "wadge" of carbon be? Smalley had never come across this British term for a cluster and liked it so much that he started to refer to C_{60} as the "Mother Wadge"; the omnipresence of the cluster led me to call it the "Godwadge". On Friday, September 6 during a group meeting, Curl suggested that we should concentrate on identifying the conditions under which the 720 amu peak was most prominent. O'Brien and Heath agreed to work shifts during the weekend. Experiments aimed specifically at optimizing the signal were carried out that same evening, and conditions were immediately found under which C_{60} peak was 30 times stronger than the adjacent C_{58} signal (Fig. 7c). After further optimization (Fig. 7d) the striking spectrum (Fig. 8) was finally obtained. C_{70} is also prominent!

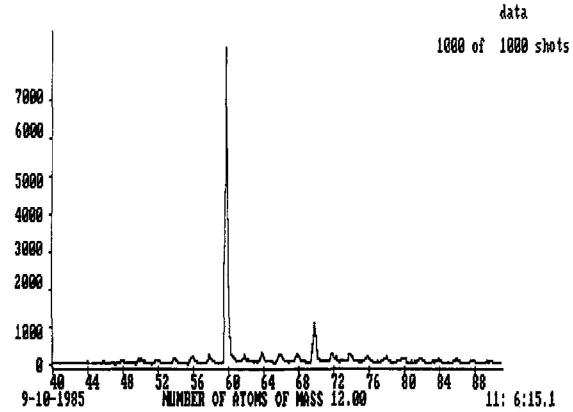

Fig. 8. TOF mass spectrum of carbon clusters under the optimum conditions for the observation of a dominant C_{60} signal.

The Structure of C_{60}(?)

What on earth could C_{60}(?) be? In the days following our discovery of C_{60} (Fig. 6), the signal began gradually to dominate our results as well as our thoughts and conversation. The quest for a structure which could account for this precocious wadge of carbon led to numerous, synergistic [Editorial comment: R. Buckminster Fuller's architectural constructions were based on a vectoral geometry which he called energetic—synergetic geometry. This was founded on a natural philosophy, according to which nature constructs systems of forces such that the maximal strength can be obtained from the minimum effort in construction.] discussions among all five members of the team during those days. The deliberations were particularly intense on Monday, September 9th. As this day wore on and all the ideas which had surfaced during the period were assessed and reassessed, a consensus grew that C_{60} might be some sort of spheroid. One possibility we considered was that the laser had blasted flakes of hexagonal carbon from the graphite surface, and that these hot graphite-like networks had somehow wrapped themselves up into closed cages, thus eliminating the dangling edge bonds and making the cage unreactive. This idea had instant appeal for all. For me this concept brought back vivid memories of Buckminster Fuller's geodesic dome at EXPO '67 in Montreal (Figs. 9 and 10). I had actually been inside this remarkable structure at that time and remembered pushing my small son in his pram along the ramps and up the escalators, high up among the exhibition stands and close to the delicate network of struts from which the edifice was primarily constructed. This experience had left an image in my mind which could never be erased. I had collected numerous photographs of the dome from magazines over

Fig. 9. Photograph (by Michel Proulx) of the geodesic dome designed by Buckminster Fuller for the U.S. exhibit at EXPO '67 in Montreal (taken from *Graphis* **1967**, *132* 379). One of the pentagons necessary for closure is discernable in this photograph.

Fig. 10. Photograph (by Robin Whyman) of the inside of the EXPO '67 dome in Montreal. One of the pentagons necessary for closure is clearly visible in the middle section, as is the way in which the strut lengths have been adjusted to achieve a smooth round shape.

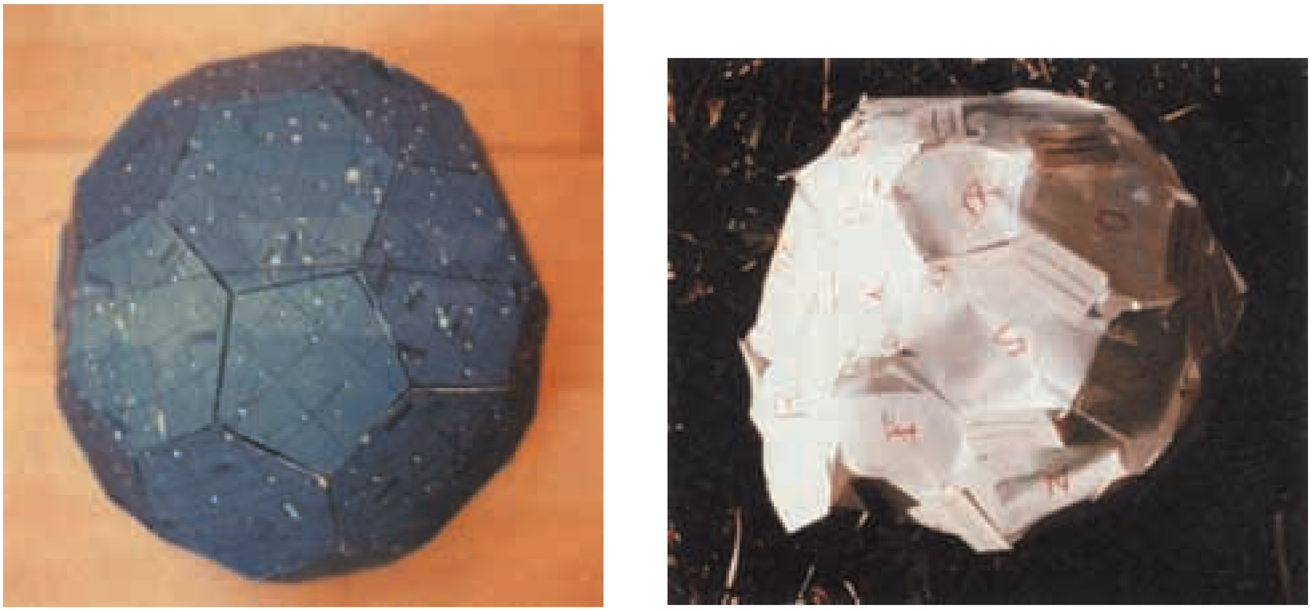

Fig. 11. The two cardboard polyhedra which played key roles in our search for the structure of C_{60} (see text). Left) stardome map of the sky (Buckminster Fuller patented t-icosahedral and other polyhedral world-map projections); right) Smalley's model with 60 vertices and 12 pentagonal and 20 hexagonal faces.

the years from Life, Paris Match, and Graphis. Particularly striking were those in my favorite graphic art and design magazine, Graphis, to which I had subscribed since my university days. As I remembered it, the Graphis pictures (Fig. 9) showed that the dome consisted of a plethora of hexagonally interconnected struts. Indeed, the dome had actually initiated my interest in some of Buckminster Fuller's other projects; I had even been in the process of writing to him with a view to working with him on the organized growth of massive urban structures. However, I did not pursue this, because I was offered a permanent academic position at Sussex at just that time.

As far as C_{60} was concerned, I wondered whether Buckminster Fuller's domes might provide some clue. Smalley also strongly favored some sort of spheroidal structure and suggested that we borrow a book from the Rice University library. We obtained a book by Marks[35] in which geodesic domes of all kinds were described. In addition I had one or two other structural proposals which intrigued me: One was a four-deck model 6:24:24:6 (two coronene-like sheets sandwiched between two benzenoid ones) with a roughly spheroidal shape. It contained 60 atoms, and its symmetry suggested that the dangling bonds might be somewhat deactivated. However, I really could see no reason why this species would be as unreactive as C_{60} appeared to be; a closed-cage solution would certainly be more stable. A second image came to mind several times, most vividly on this particular Monday. This was of a polyhedral cardboard stardome (Fig. 11 left) which I had constructed many years before when my children were young. This map of the stars in the sky was tucked away in a cardboard box (that universal quantum of storage) downstairs in my home far away in England. I itched to get my hands on it and even described its features to Curl at lunch time. I remembered cutting out not only hexagons but also pentagons. I wondered whether I should telephone my wife to ask her to count the vertices in order to ascertain whether, as I half-suspected, they totaled sixty.

The Mexican Restaurant

I was due to return to the UK the next day, so that evening (Monday, September 9th) I thought we should celebrate our extraordinary discovery. I invited the group out to dinner at what had become our favorite Mexican restaurant. During the meal the conversation was naturally dominated by C_{60}(?). We again considered all the ideas which had come up in our deliberations during the days that had passed since the signal had first been noticed. We agreed unanimously on a *closed cage* structure. We talked about Buckminster Fuller's domes, Smalley, about chicken-wire cages, and I reiterated the essentials of the stardome—its spheroidal shape, hexagonal faces, and, in particular, the pentagonal faces. Smalley expressed an interest. After the meal other members of the group went home; I returned to the laboratory in order to study the Marks' book on Buckminster Fuller, but I could not find it. I again considered telephoning home about the number of vertices in the stardome. But it was now far too late since it was well after midnight in the UK.

Very early the next morning Curl telephoned to say that Smalley had experimented with paper models based on the stardome characteristics I had mentioned the previous day. Smalley had come up with something bigger than anything he (Curl) had ever been involved with before. When I got to the laboratory and saw the paper model (Fig. 11 right) which Smalley had constructed during the night I was ecstatic and overtaken by its beauty. It seemed identical to the stardome as I remembered it, and I was quietly pleased that my conjecture had been right all along. Heath and his wife Carmen had also experimented with a geodesic structure modeled out of jelly beans and toothpicks; it was not quite so convincing.[36]

In summary, the quest for a rational explanation of the dominant line in the mass spectrum had reached a climax on Monday, September 9th. Ideas were suggested, refined, or critized in earnest throughout that final day. Buckminster Fuller's domes were invoked, Marks' book was consulted, and the stardome's pentagonal faces introduced at midday and again in the evening; Smalley and the Heaths experimented further with models during the night after our meal. All this took place in a matter of hours, leaving no time for anything important—other than perhaps Marks' book—to "slip through the cracks".[37] It was most satisfying that synergistic (a Fullerism) teamwork had been involved in the experimental observation as well as in the positing of the structure.

I delayed my flight home for one extra day (until Wednesday, September 11th) in order to help to write the publication. At one point Heath was sitting at Smalley's desk when the telephone rang. A mathematician, whom Smalley had consulted earlier to ask about the structure, informed Heath, "Tell Rick—it's a soccerball!" Almost unbelievably, until that moment, none of us had realized that the C_{60} structure we were proposing had the same symmetry as the modern soccer-(USA) or football (rest of the world). I do not know how I could have been so blind—my only (feeble) excuse was that the modern football was introduced after I ended my serious soccer-playing days. The other members of the team could be excused, since a structure related to the American football really was an unlikely contender, at least at that stage. We immediately purchased a real football and our five-a-side team posed for a photograph (Fig. 12). I also photographed Smalley's paper ball (Fig. 11 right), but when I queried the whereabouts of the Heath model in order to photograph it for posterity, I was informed that it no longer existed because Mary-Joe (another Rice graduate student) had eaten it. So all tangible record of a truly remarkable edifice was lost for all time.

Fig. 12. The five-a-side Rice/Sussex football team (from left): O'Brien, Smalley, Curl, Kroto, and Heath.

Since the geodesic dome concepts had played such an important part in helping us to arrive at the solution (at least as far as I was concerned), I suggested that we name the compound buckminsterfullerene. Smalley and Curl fortunately agreed, accepting that though the name was long, it did indeed roll smoothly off the tongue. Thus we avoided the fearful international conflict over terminology which would have raged had we named it after a certain well-known ball game. Smalley could not resist putting some alternative suggestions for names at the end of the publication. The name engendered the occasional mild criticism[38] which was dispatched with a little help from Shakespeare.[39] Now that some time has passed, it is satisfying to note how instructive (about geodesy) others have found the name and how flexible it has turned out to be. The whole family of closed cages can be appropriately named—fullerenes.[40] The paper[41] was dispatched by Federal Express to the journal *Nature* on the afternoon of Wednesday, September 11th, 1985.

Five Long Years in the Desert

The ten-hour nonstop flight home to England was a physical and psychological high for me. My first action upon entering the house was to open the cardboard box and take out the stardome which had influenced my deliberations during the search for the structure of C_{60}. It had always looked beautiful; now it positively glowed. When the news of our result spread, Martyn Poliakoff at Nottingham wrote that his friend, David Jones, had already thought of hollow carbon cages. In 1966 Jones had written a delightful article under the pseudonym Daedalus in the journal *New Scientist*[42, 43] in which he had suggested that the high-temperature process in the production of graphite might be modified to generate graphite balloons. This was a typical example of the presciently "crazy" ideas of Jones. I thus learned about the Euler principle, which says that 12 pentagons are needed to close a network and that hexagons alone just will not do. I was introduced to D'Arcy Thompson's elegant book[44] and learned that one could close an even-numbered carbon cage with any number of hexagons (except one, I subsequently learned) provided 12 pentagons were included in the network. The beautiful Aulonia (Fig. 13 photograph from Tibor Tarnai) already knew more than we about these simple (pentagonal) facets of (its) life. This was all fun and truly fascinating, because it became clear that there might even be other (even-numbered) carbon cages—there were certainly other (even-numbered) peaks (Fig. 6), in particular C_{70}. O'Brien and Smalley reached the same conclusions independently. Particularly important were a series of reactivity ex-

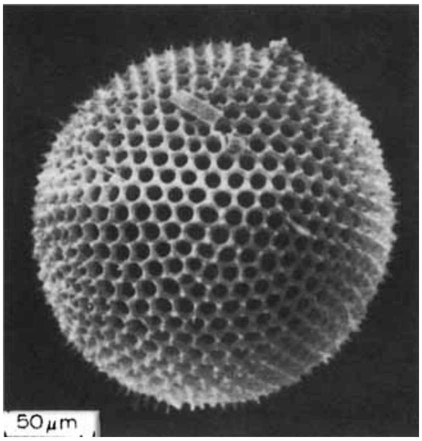

Fig. 13. A siliceous sea creature, *Aulonia hexagona*, appears at first glance to possess a skeleton composed completely of hexagons. Pentagonal structural elements are discernable, however (photograph supplied by Tibor Tarnai).

periments carried out by O'Brien, which showed that all the even-numbered carbon species were totally unreactive, a result neatly commensurate with closed structures for all the even-numbered cages.[45]

I met David Jones, a most fascinating individual, who epitomizes so much of what the spirit of science should be about. We also learned that Osawa and Yoshida had already thought of C_{60} in 1970 and had even suggested that it might be superaromatic.[46,47] In 1973 Bochvar and Gal'pern[48] also published a theoretical paper on the molecule. Thus it transpired that although there were some most imaginative scientists around, few—other than Orville Chapman at the University of California at Los Angeles (UCLA)[49]—had noticed these pioneering flights of imagination.

Circumstantial Evidence for the Identity of the "Third Man"

The first question stimulated by the realization that we might have found a "third form of carbon" with a hollow, cage structure was obvious: is it possible to trap an atom inside the cage? My early Sheffield background led me to wonder whether iron might form an intriguing ferrocene-like analogue. The day I left, Heath tried to encapsulate iron without success, but the next day he succeeded in detecting a stable $C_{60}La$ complex.[50] This experiment provided the first convincing piece of evidence to support our proposal of the cage structure. Then began what was to become a truly exhausting schedule for me: Every four to six weeks I flew to Houston, and after two to three weeks' work with the group at Rice I returned to the UK and my commitments in Sussex. As soon as I arrived in Houston I would present a group seminar based on ideas which I had developed while in the UK. This schedule continued until April 1987. From the outset the joint Rice/Sussex follow-up program had two clear objectives. First, to make enough C_{60} to prove beyond doubt that our structure was correct and second, to measure the optical spectrum of C_{60} which we had surmised might in some way be responsible for the Diffuse Interstellar Bands.[41] These astronomical features had of course been partly responsible for the carbon-cluster experiment in the first place. These goals were all-consuming and we often talked about "the little yellow (Smalley's guess) or pink (my guess) vial" of C_{60}.

During the late 70s and early 80s I felt that it was simply not enough just to detect the carbon chains; the source must be tracked down. This obsession with the source led ultimately to the discovery of C_{60}. After 1985 I developed a similar attitude to C_{60}. Our discovery of a species which probably had a truncated icosahedral structure was "not enough", and as months and then years passed, confirmation of the structure and its identification in space also became somewhat of an obsession. We (the Rice group and myself) were convinced from the outset that our proposed structure was correct; surely it was too beautiful and perfect to be wrong. However, if for once aesthetics were misleading us, it would be much better if we proved our model wrong ourselves. It is certainly fair to say that the proposed structure was greeted with scepticism by some, though many loved C_{60} and were convinced that we were right from the start. During this period (1985–1990) I examined the problem independently at Sussex, as well as in collaboration with the Rice group, who also made independent studies. In time all these efforts resulted in a mass of convincing evidence in support of our proposal.

From the moment we discovered that C_{60} was stable I had one all-consuming dream: I wanted so solve the molecule's structure by NMR spectroscopy. Because all 60 carbon atoms in buckminsterfullerene are equivalent, the ^{13}C NMR spectrum should consist of a single line. Proof of our radical proposal in such an exquisitely simple manner was to remain elusive for some five years; this goal was almost like a holy grail—far, far beyond reach. I was quite convinced that a clever young organic chemist would accomplish this task. I had one consoling thought, namely that we had been rather successful in the past with a series of molecules whose identifications were based on spectra consisting of single lines: Phosphaethene, $CH_2{=}PH$ (the first phosphaalkene made) had been assigned by its $J = 1 - 0$ microwave line[1,4] and HC_5N and also HC_7N had both been originally single radio-line detections in space.[20,22] Then there was, of course, the 720 amu peak in the mass spectrum of C_{60}.[41] How fitting it would be to round it all off by *proving* by another *single* line that C_{60} was buckminsterfullerene.

C_{70} and the Fullerene Family

It is fair to say that I (and perhaps also my colleagues at Rice University) occasionally woke up in the middle of the night and wondered whether I should have to commit suicide if our idea turned out to be wrong. Had we stuck our necks out too far? These thoughts only lasted seconds. I would reassess all the evidence, realize that everything fitted, and go back to sleep convinced more than ever that C_{60} had to be a geodesic cage. Time pased, we made several advances,[51,52] and each time the cage concept clarified our observations. That was important. I remembered hearing Richard Feynman on BBC radio say that it seemed to him that if a radical new theory were right, it would allow the solution of previously unsolved puzzles. I quantified this: If an idea fitted 80–90% of the observations, it was almost certainly right; if more than 10–20% of the details had to be bent to fit, it was almost certainly wrong. Buckminsterfullerene was well up in the first category.

I remember vividly the day on which all my lingering doubts vanished. I was sitting at my desk thinking about the reasons why C_{60} might be stable. The missing piece of evidence in this personal jigsaw puzzle turned out to be so simple, it was almost child's play; indeed it evolved from my playing with molecular models of various conceivable cages. The solution was related to the C_{70} signal which always popped up prominently when C_{60} was strong. I used to call the two species "the Lone Ranger and Tonto"[*] because

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[*] The Lone Ranger und Tonto were a famous cowboy and Indian duo from the movies. As a child I saw them every week fighting crime in the Wild West. Bob Dylan immortalized them in the following blues text:
Well the Lone Ranger and Tonto
They are ridin' down the line
Fixin' ev'rybody's troubles
Ev'rybody's 'cept mine.
Somebody must a tol' 'em that I was doin' fine.

they were so inseparable and because C_{60} was always dominant (Figs. 6 and 8). As far as C_{60} was concerned, it seemed no accident that the modern soccerball with the same layout is one of the most, if not *the* most, resilient of constructs, able to survive being kicked around the world (and perhaps around the galaxy). Maybe the football held a simple clue. When I looked carefully at a football, I was struck by the fact that all the (black) pentagons are isolated, whereas all the (white) hexagons are linked. It is known that unsaturated compounds composed of abutting pentagons (the pentalene configuration, Type **II**, Fig. 14), without substituents which allow extended conjugation, tend to be unstable. Curiously, a compound with just such a structure appeared on the cover of *Angewandte Chemie* (July 1987) that very week.

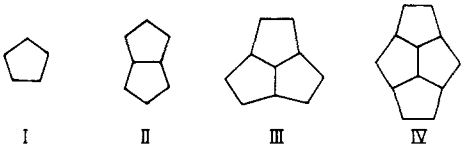


Fig. 14. Isolated and abutting pentagons: **I**, isolated; **II**, fused pair (pentalene configuration); **III**, symmetrically fused triplet (triquinacene configuration); **IV**, directly fused quartet [53].

Since Euler's law requires 12 pentagons for closure, it was also clear that C_{60} was the smallest carbon cage for which all the pentagons could be isolated. O'Brien's reactivity experiments had convinced us that closure was possible, even probable, for all the even clusters. I conjectured that a *pentagon isolation rule* could be formulated to account for the stability[53]; then I began to wonder which was the next cage for which pentagon isolation was feasible.

By playing with the models I saw immediately that it was not C_{62}, and as I added more atoms, try as I would, I could not find cage structures for C_{64}, C_{66}, or C_{68} without abutting pentagons. We had already proposed a structure for C_{70},[50] after Smalley had shown that by splitting C_{60} into two C_{30} hemispheres a ring of ten extra carbons could be neatly inserted, producing a most elegant, symmetric, egg-shaped structure (Fig. 15 right). Suddenly I realized that perhaps this C_{70} cage was the next structure after C_{60} which could close and which also had *isolated* pentagons (Fig. 15). This surprised me. Perhaps closure *necessitated* that 70 be the second magic number! We had stuck our necks out with the C_{60} hypothesis on the basis of a single peak in the mass spectrum, but it now seemed that the cage concept positively insisted that C_{70} *as well as* C_{60} are special.[53] That would be wonderful. A second solution which required both of these particular magic numbers was impossible to conceive, especially since 70 would be an unusual number to be deduced as magic at all, let alone the second in order. I knew that nature would not be that perverse, and thus for first time my conviction that our structure was corrrect became absolute, and I never again doubted that one day we would be vindicated. Indeed in my opinion this result meant that we were home and dry.

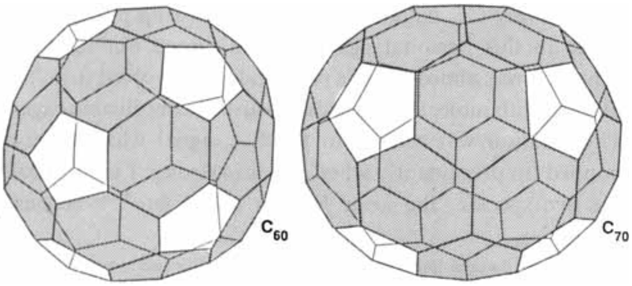


Fig. 15. For species with less than 72 atoms these two structures are the only ones which can be constructed without abutting pentagons. Thus on the basis of the *pentagon isolation principle* and geodesic considerations C_{60} and C_{70} are predicted to be the first and second magic fullerenes. This result together with Figure 8 provided the simplest and strongest circumstantial evidence supporting the closed-cage concept.

I was elated by this line of reasoning, but I really needed proof. I remembered that Tom Schmalz and his colleagues, Klein and Hite, in nearby Galveston had published some elegant graph-theoretical studies on the fullerenes. I contacted him and asked him what he thought about my idea. I was amazed and delighted when he told me that they had been looking at this same problem and had proven that cages composed of 62, 64, 66, and 68 atoms cannot be constructed without abutting pentgagons.[54] So it was true! I told him that I wondered whether the semimagic C_{50} might be the smallest cage able to avoid abutting triplets of pentagons (Type **III**, Fig. 14, Lit.[53]). Schmalz et al. subsequently showed this also to be correct.[54] One Sunday afternoon, sitting in front of the molecular models strewn all over our coffee table at home, I decided to investigate other semimagic numbers. I wondered about C_{32} which had been shown by the group at Rice University to be the first cage relatively stable towards photolysis. I toyed with the idea that it might be the smallest cage able to avoid fused quartets of pentagons (Type **IV**, Fig. 14). I tried to make the smallest model containing such a structure, and as I counted up the atoms I suddenly realized, that it was not C_{32} but a delightfully symmetric C_{28} cage (Fig. 16). I became excited because I knew, that during the Rice/Sussex collaboration period we had occasionally obtained mass spectra in which C_{28} was almost as dominant as C_{60}. At this point it seemed that essentially all the magic numbers would fall into place if these clusters were *all* cages. In particular, I found that I could explain the fascinating spectrum (Fig. 17) published by the Exxon group.[55] Here was all the proof I needed to convince myself that a whole family of cage molecules was sitting around waiting to be discovered. The first somewhat

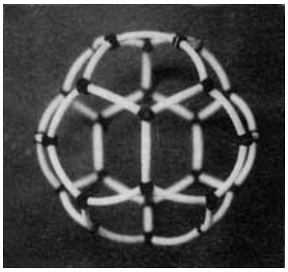


Fig. 16. Molecular model of C_{28}, one of several fullerenes (with 24, 28, 32, 50, and 70 atoms) predicted to be stable on the basis of geodesic and chemical considerations [53]. These magic-number predictions fitted almost perfectly the observations made under certain clustering conditions [51, 55] (see Fig. 17).

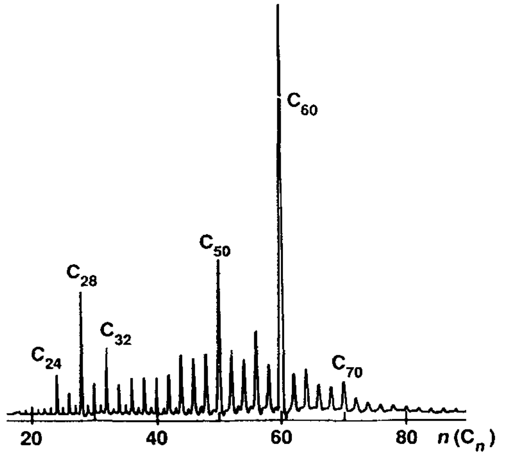


Fig. 17. The particularly interesting mass spectrum of C_n clusters obtained by Cox et al. [55]. The correspondence with the magic fullerene sequence 24, 28, 32, 50, 60, and 70 [53] was the most convincing evidence for the existence of the fullerene *family* prior to the extraction breakthrough. The sharp cut-off at 24 is articularly convincing, since no C_{22} fullerene can exist.

stable member of the family appeared to be C_{24}. This can be explained by the fact that C_{22} cannot exist (I am indebted to Patrick Fowler for pointing out this fact to me) and that C_{20} is the smallest cage and as it has no hexagons at all, almost certainly the least stable. To some extent C_{28} (Fig. 16) became my own personal favorite, because regardless of which of the four threefold axes one views this tetrahedral molecule along, it looks uncannily like Gomberg's famous free radical, triphenylmethyl; this also just had to be right. I knew about Moses Gomberg's discovery from my favorite organic text (Fieser and Fieser[56] which Harry Heaney, my chemistry teacher in school, had encouraged me to buy and read so long ago). It had always amused me to think that on attempting to make the rather mundane compound hexaphenylethane, Gomberg failed (miserably), produced the triphenylmethyl radical, and had to be consoled with becoming known as the father of free radical chemistry instead. This was the sort of "failure" that really appealed to me. If C_{28} is relatively stable, then $C_{28}H_4$ should be a fairly stable hydrofullerene. This seemed not at all farfetched; after all, dodecahedrane which Paquette and co-workers first made[57] is basically the perhydrofullerene of dodecahedrene (fullerene-20), the simplest and probably the least stable of all the fullerenes since it contains no hexagons. At this time I had a telephone conversation about nomenclature with Alex Nickon in which we came to the conclusion that the name "fullerenes" would work well for the family of carbon cages.[40, 53] I gained much satisfaction from the refined concept which was even more appropriate, because Buckminster Fuller had patented constructs of all shapes and sized based on the 5/6 ring principle;[58] some were very similar to the elongated framework of C_{70}. Nickon was just finishing his entertaining book with Silversmith on the origins of the trivial names of compounds.[40]

In Houston a particularly important series of experiments was carried out by Curl, Smalley, and their co-workers which offered further overwhelming evidence for closed cages.[52] One of these was a photofragmentation experiment which provided even-numbered products. Curl had worked out a neat way of explaining how the cages might "spit out" even-numbered (2, 4, 6, ...) carbon chains and then reseal. Another most convincing study showed that when the encapsulation of atoms of various sizes appeared to be successful, the smallest caged species detectable had diameters commensurate with the known sizes of the encapsulated atoms.

C_{60} and Soot

During one of my eight visits to Rice University between August 1985 and April 1987 we considered carefully the reactivity results and developed a hypothetical mechanism for the formation of C_{60}.[45] Heath, O'Brien, and I spent hours in the library digging through an excellent selection of books and journals on carbon. The final version of the mechanism grew out of intense synergistic group discussion. It was also clear that the mechanism might explain soot formation as well. After all in a review on soot, Harris and Weiner[59] had pointed out the complete absence of knowledge of the chemistry involved in soot formation. Thus a fresh idea probably would be welcome. Our mechanism implied C_{60} should be a by-product of soot formation. Curl was apprehensive about introducing the word soot, especially in the title. How prescient were his worries! However, Smalley and I decided to throw caution to the wind—after all, when you have gone as far as you can go (in postulating C_{60} formation in a chaotic plasma), you might as well go further. Our paper met with some criticism.[60] To our delight, however, in 1987 we heard that Klaus Homann's group in Darmstadt discovered that C_{60} was a dominant ion in a sooting flame.[61] (Note: Very recently, a careful study by Howard's group at the Massachusetts Institute of Technology has shown that up to 7% of the soot from a benzene flame consists of fullerenes.[62])

The Giant Fullerenes

One day I decided to spend £300 on ten-thousand sp^2 carbon atoms (molecular models!) The odd eyebrow was raised at Sussex when I said that I was buying them just because I wanted to see what giant fullerenes such as C_{6000} (with a diameter ten times that of C_{60}) looked like. Ken McKay (a graduate student) obtained Coxeter's book[63] and Goldberg's paper[64] and set to work. When he came into my room with models of C_{240} and C_{540} (Fig. 18), I was delighted but perplexed—they were beautiful, but not at all what I had expected. C_{540}, in particular, was not round like Buckminster Fuller's domes, but in fact much more interesting: It was essentially a monosurface which swept between cusps in the vicinity of the pentagons; it had icosahedral symmetry, but was not an icosahedron.[65] Then we realized that its shape might explain[65] the polyhedral patterns in graphite microparticle electron microscope pictures published by Iijima (Fig. 19).[66] The structure of these microparticles could be nicely explained as concentric shells of graphitic carbon in which the shells had giant fullerene shapes. Few of our discoveries have delighted me more than these objects, partly because they are so elegant, but also because the exercise, which was started *purely* for fun and with no serious aim, had yielded such an apparently important result. It was also an object lesson, since I had assumed

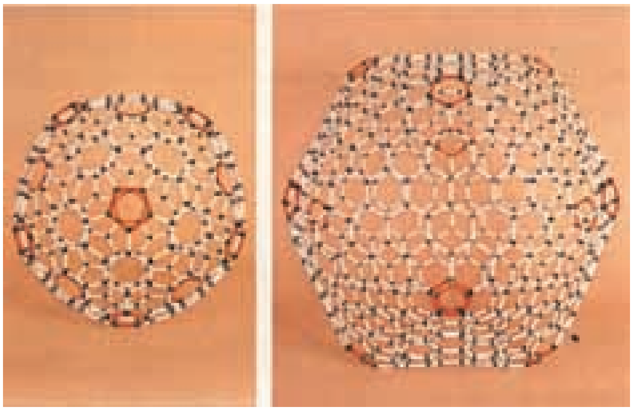


Fig. 18. Molecular models of the giant fullerenes C_{240} (left) and C_{560} (right). The models possess icosahedral shapes rather than perfectly spheroidal ones similar to the geodesic domes. Each of these structures can be considered as an initially flat hexagonal network which has warped into a closed monosurface (of icosahedral symmetry) by 12 pentagonal disclinations giving rise to the cusps.

that the giant fullerenes would be spherical like Buckminster Fuller's domes and had not looked carefully at Iijima's images. Even the most spheroidal giant fullerene (Fig. 19 a) was clearly polyhedral (Fig. 19 b). To see what one wants to see rather than what is, is a cardinal sin for a scientist and the temptation is to be resisted at all costs.

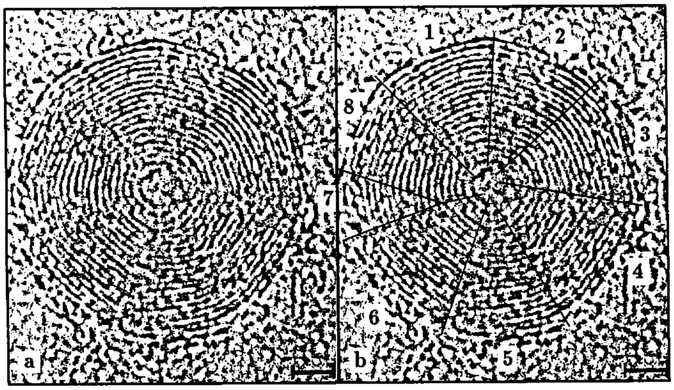


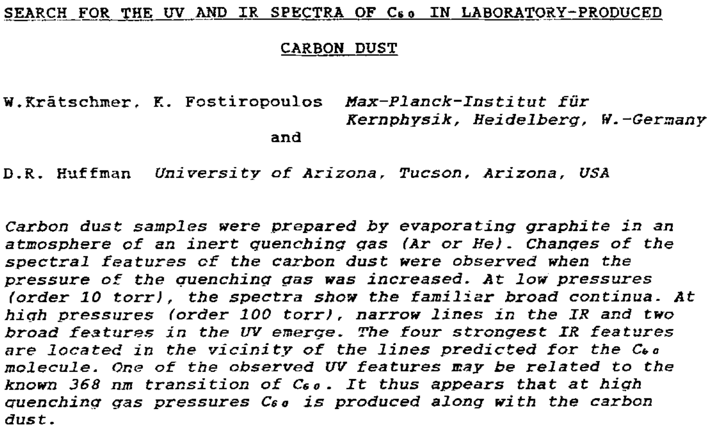
Fig. 19. The image obtained by electron microscopy of an onionlike graphite microparticle observed by Iijima [66] which appears superficially to be spheroidal (a). Careful scrutiny of this image, however, indicates that the object has a polygonal outline consistent with a set of concentric quasi-icosahedral fullerene-like shells (b) [65]. The marker indicates a scale of 20 Å.

The Quest for C_{60}

Until late 1989 the evidence in support of our structure proposal was, to my mind, very convincing, but it could not be deemed anything other than circumstantial. Clearly a macroscopic sample of C_{60} was needed—not just a whisper in a supersonic helium wind, detectable only by that ultrasensitive sensor, the mass spectrometer. At Sussex we sought more tangible evidence. The Science and Engineering Research Council (SERC) funded the construction of a cluster-beam apparatus, which was assembled with Tony Stace; Steve Wood helped us to obtain financial support from British Gas in the form of Collaborative Award in Science and Engineering (CASE) studentship for combustion-related studies. It was this assistance which was ultimately our salvation (vide infra). In a third project conducted with Ken McKay, we probed (by electron microscopy) the films produced by a carbon arc under helium in an old bell jar evaporator. We found that the film microstructure changed as the helium pressure was increased (to ca. 50 mmHg). The quadrupole mass spectrometer, with which I sought to monitor whether C_{60} was produced in this experiment, was the integral part of a modest carbon materials research project which failed to attract support from any funding source (including chemical companies). Because Stace and I had been quite generously funded by the SERC solely for the cluster-beam studies, another application (and indeed a rather applied one) to that source was difficult. Time slipped by and this program faltered even though I had put a great deal of effort into trying to obtain financial support.

The First Paper by Krätschmer, Fostiropoulos, and Huffman

In September 1989 Michael Jura (UCLA Astronomy Department) sent me a copy of a thought-provoking paper[67] (Fig. 20) presented by Krätschmer, Fostiropoulos, and Huffman at a symposium on interstellar dust. This research group from Heidelberg and Tucson had observed four weak but distinct infrared absorptions in a film of arc-processed graphite, which were tantalizingly consistent with the expected spectrum of buckminsterfullerene. From theoretical studies[68] it was known that C_{60} should exhibit only four lines. What was more, the observed frequencies agreed quite well with those predicted. I had long followed the work of this group and knew that they had developed great expertise in studying carbon by spectroscopy. We had occasionally tried related studies, and I was only too aware of how tricky they were. I was sceptical about their result and also rather cha-



SEARCH FOR THE UV AND IR SPECTRA OF C_{60} IN LABORATORY-PRODUCED

CARBON DUST

W.Krätschmer, K. Fostiropoulos   *Max-Planck-Institut für*
Kernphysik, Heidelberg, W.-Germany
and
D.R. Huffman   *University of Arizona, Tucson, Arizona, USA*

Carbon dust samples were prepared by evaporating graphite in an atmosphere of an inert quenching gas (Ar or He). Changes of the spectral features of the carbon dust were observed when the pressure of the quenching gas was increased. At low pressures (order 10 torr), the spectra show the familiar broad continua. At high pressures (order 100 torr), narrow lines in the IR and two broad features in the UV emerge. The four strongest IR features are located in the vicinity of the lines predicted for the C_{60} molecule. One of the observed UV features may be related to the known 368 nm transition of C_{60}. It thus appears that at high quenching gas pressures C_{60} is produced along with the carbon dust.

Fig. 20. Annotated copy of the key paper presented by Krätschmer, Fostiropoulos, and Huffman at the conference *Dusty Objects in the Universe* in Capri (1989) [67]. This paper with the appended query was sent to me by Michael Jura (UCLA) who attended this conference.

grined, for had not Ken McKay and I made soot in a bell jar in exactly the same way three years before during the project, which we were forced to abandon through lack of funds?

I decided to resurrect the old and decrepit bell jar and with Jonathan Hare (holder of the British Gas CASE graduate studentship) tried to reproduce the infrared features obtained by Krätschmer et al. Michael Jura's missive arrived around September 1989, just before the start of the Sussex academic year, a time when third year undergraduate projects are needed. It does not matter whether these projects yield results; they should imbue the student with the flavor and excitement of genuine research, that is, the experience of working in the dark, not—as all too often happens—the frantic scramble for results at all costs! I had often initiated the most speculative of projects in this way, and my experience had shown time and time again that important and exciting studies could often start from such inauspicious beginnings. It seemed perfect for Amit Sarkar's third-year project, and he joined Hare on this wildly speculative project. Fairly soon these students succeeded in obtaining the IR bands (Fig. 21), which, although always very weak and highly irreproducible, confirmed the observations of the group from Heidelberg and Tucson. The obsolete apparatus then promptly fell to pieces! After rebuilding it almost completely from scratch, Hare tried to repeat the earlier observations, but consistent results eluded him. Sometimes he obtained the characteristic spectral features, sometimes they disappeared for days or weeks at a time. In retrospect, I suspect that the original discovery of the IR features by Krätschmer et al. could have been made by few other groups. Hare carefully varied every experimental parameter he could think of and finally developed the expertise to produce films which exhibited the telltale infrared features consistently. He wrote to Krätschmer about his efforts and received an encouraging reply containing useful advice. This certainly helped, because it was quite difficult to make films amenable to analysis.

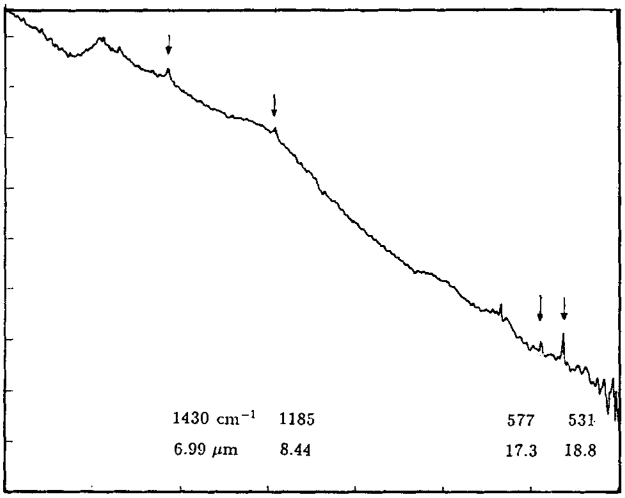


Fig. 21. Infrared spectrum of a film of arc-processed carbon obtained by Hare and Sarkar at Sussex which shows weak but clear (and confirmatory) evidence that the features first observed by Krätschmer et al. [67] (see Fig. 20) and tentatively assigned to C_{60} were real and repeatable.

The Dimerization of C_{30}

I spent about one month in the UCLA Astronomy Department around Easter 1990. One day, Mark Morris brought François Diederich from the Chemistry Department to see me. Diederich appeared excited and exhorted me to come to his office because he had something to show me. In response to his manner I somewhat disdainfully quipped, "You've not made C_{60}?" When he replied, "How do you know?". I was startled and suddenly became apprehensive since there was genuine surprise in his voice. When we arrived at his office he showed me an astonishing mass spectrum. In their attempts to make a pure carbon ring of 30 atoms Diederich, Rubin, Whetton, and their co-workers, had found that the molecule spontaneously dimerized to form C_{60} with almost unbelievable efficiency.[69] This staggering result seemed to answer, almost at a stroke, many puzzling questions that had been on my mind for years about carbon chains, their relationship with C_{60}, and soot. But I became even more apprehensive when I comprehended that the UCLA group might be on the verge of obtaining the coveted C_{60} NMR line. Subsequent discussions with David Walton, with whom I had probed aspects of the C_{60} formation mechanism,[70] alleviated my worries; he convinced me that scaling up the UCLA experiment so as to produce sufficient C_{60} for the key NMR measurement presented an anormous challenge.

Mass Spectrometry

I returned to Sussex and by early summer 1990 started to believe for the first time that C_{60} really might be in our sooty deposit. We therefore decided to probe the material by solid-state magic-angle-spinning (MAS) NMR. Indeed Ken Seddon (a Sussex colleague) had encouraged me to do this some years before. Perhaps the single ^{13}C NMR line was close at hand in the black soot, which at least we could now touch. I considered buying the most isotopically pure ^{13}C graphite, but that would have been very expensive, and we had no

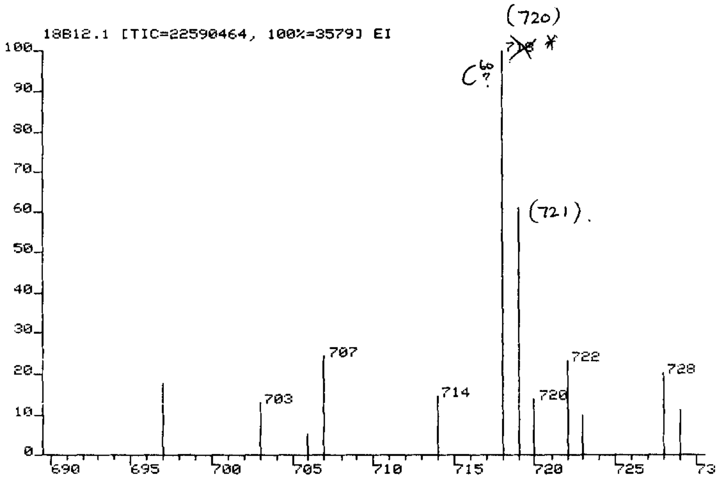
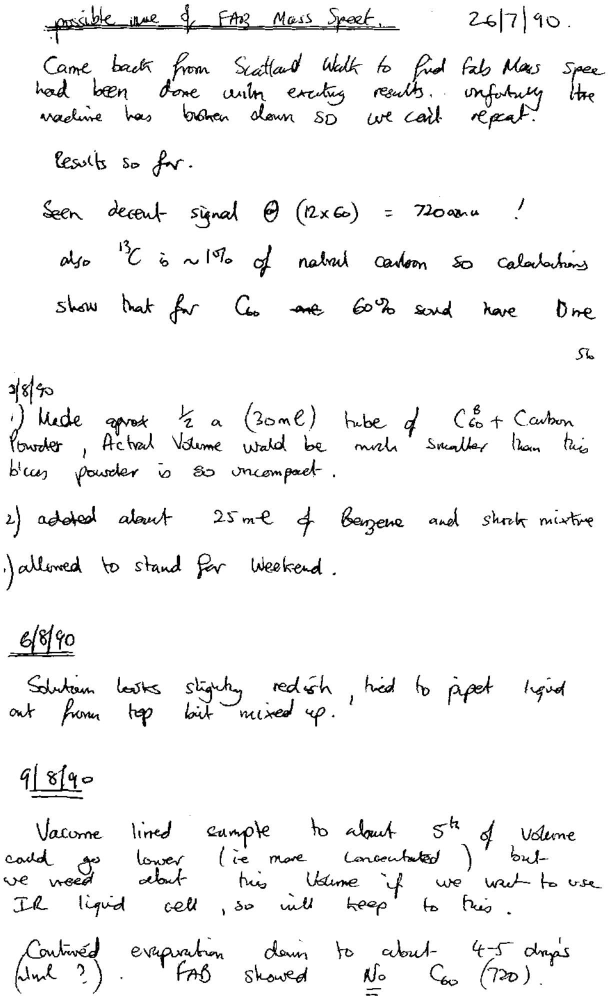


Fig. 22. Part of the FAB mass spectrum of a deposit of arc-processed soot obtained by Abdul-Sada on July 23rd, 1990 at Sussex. The calibration was off by 2 amu; however, the isotope pattern was convincing since the peaks are close to the intensity ratio 1.0/0.66/0.44 expected for $^{12}C_{60}/^{12}C_{59}/^{12}C_{58}\,^{13}C_2$.

money anyway. The problem of generating enough material for solid-state NMR from the scrapings of thin sooty films, seemed insurmountable, especially since it was so difficult to produce the films in the first place, let alone analyze them. We really needed another way to monitor the samples, so we tried Fast Atom Bombardment (FAB) mass spectrometry. Ala'a Abdul-Sada helped us, and finally we obtained the mass spectrum shown in Figure 22. The signal containing the ^{13}C satellites was really quite convincing, but I wanted the result confirmed. The entry in Jonathan Hare's laboratory notebook on July 26th, 1990 (Fig. 23 top, second sentence) epitomizes many of our problems and requires little further comment.

The Red Solution

During this period we had considered the properties of C_{60}. What form would the compound take? Would it be a high-melting solid or a liquid? Would it be soluble? Benzene was an obvious solvent, since C_{60} should look like benzene from every side (or at least from 20 sides). I remembered the little pink (or yellow) vial of liquid we used to talk about and wondered if the compound might even be volatile. In addition I had often discussed (with Smalley, Rohlfing, and others) how much C_{60} was being made in our experiments. The rough proportion which always seemed to arise was $< 1/10\,000$ of the total amount of carbon. At this level, given the amount of soot available, only a supreme optimist would attempt solvent extraction. Fortunately Hare is one—perhaps partly because he is a physicist working among chemists. On Friday, August 3rd Hare made up a mixture of the soot and benzene in a small vial, which he set aside over the weekend (Fig. 23, second entry). When he came in on Monday morning (August 6th) he noted (Fig. 23, third entry) that the solution looked "slightly red(d)ish" (Fig. 24). The generation of a red solution from pure carbon was scarcely believable. Hare made more material during the next few days and attempted mass spectrometric measurements on extracted material for the first time on Thursday, August 9th (Fig. 23, fourth entry).



possible use of FAB Mass Spect. 26/7/90.

Came back from Scotland Walk to find Fab Mass Spec had been done with exciting results. unfortunatly the machine has broken down so we can't repeat.

Results so far.

Seen decent signal @ (12x60) = 720amu !

also ^{13}C is ~1% of natural carbon so calculations show that for C_{60} ~~one~~ 60% should have One

5h

3/8/90

1) Made aprox ½ a (30ml) tube of C_{60}^{B} + Carbon Powder, Actual Volume would be much smaller than this b'cos powder is so uncompact.

2) added about 25ml of Benzene and shook mixture

3) allowed to stand for Weekend.

6/8/90

Solution looks slightly redish, tried to pipet liquid out from top but mixed up.

9/8/90

Vacume lined sample to about 5th of Volume could go lower (ie more concentrated) but we need about this Volume if we want to use IR liquid cell, so will keep to this.

(Continued evaporation down to about 4-5 drops (1ml ?)). FAB showed No C_{60} (720).

Fig. 23. Entries by Hare in his laboratory notebook: July 26th, 1990; August 3rd, 1990; August 6th, 1990; August 9th, 1990.

Fig. 24. Original reddish extract obtained on Monday, September 6th, 1990 (see Fig. 23).

About 10 o'clock the next morning (Friday, August 10th) I received a telephone request from the journal *Nature* to referee a paper by the Heidelberg/Tucson group which I accepted. I was totally unprepared for the bombshell which arrived minutes later by telefax. Following up their own earlier work, Krätschmer, Lamb, Fostiropoulos, and Huffman had successfully sublimed from their carbon deposit a volatile brown material, which dissolved in benzene to give a RED SOLUTION (!!!!!).[71] Crystals obtained from this solution yielded X-ray and electron-diffraction data commensurate with material composed of arrays of spheroidal molecules 7 Å in diameter separated by 3 Å, just as expected for buckminsterfullerene. This beautiful paper even contained photographs of crystals. I was convinced that they had isolated C_{60}, and we had been pipped at the post. Somewhat stunned, I pondered our demise and faxed my report back to *Nature* after lunch. I recommended that the paper be published without delay and requested the editor to convey my sincere congratulations to Krätschmer and his associates.

This was what the British call a difficult moment, but as I slowly surveyed the damage I realized that all was not quite lost. It gradually dawned on me that there was not a single(!) NMR line to be seen in the manuscript (nor was there a mass spectrum. We later learned that they had the mass spectrum, but certain problems had arisen which precluded its inclusion in the manuscript.) At this point we had spent nearly a year struggling independently learning how to make the arc-processed material; we had made our own soot, we had confirmed the presence of C_{60} mass spectrometrically, and we had solvent-extracted the red materal—and all this *before* the manuscript arrived. I decided that we were not going to abandon our efforts now after we had achieved all this. We still had a lot going for us, and I thought we might be able to obtain the desired NMR result. However, now that the Heidelberg/Tucson study was essentially in the public domain it would be transmitted around the world by telefax within hours. I had studiously tried to avoid such situations in science—competition—all my life; my philosophy is to probe areas in which few others, preferably no one, work. That is where, it seems to me, the most unexpected discoveries are likely to be made.

We had to act very quickly if five years of effort were not to be completely in vain. A race must be on because the material was now so easy to make, and it could not be long before other groups, far better equipped than we, recognized that there was one last exquisite prize remaining in the story of the discovery of C_{60}—the NMR line. Our one priceless advantage was that Hare had already made a reasonable quantity of material, and that, at that moment, only the Heidelberg/Tucson group had any at all. We needed help and fast. Roger Taylor, an organic chemist, provided the desperately needed expertise; he separated the material quickly and efficiently. Since our mass spectrometer had broken down again, Hare rushed by train to Manchester with a sample of the precious extract. Numerous frantic telephone calls passed between Sussex and Manchester, because the sample refused to respond to analysis. Then with a key piece of advice from Taylor about solubility, the Manchester operators (at Kratos) managed to dissolve the material in the FAB matrix and obtained the FABulous mass spectrum shown in Figure 25. It was hard to believe, but besides C_{60} other fullerenes with 56 to 72 atoms were detected; in particular, C_{70} was abundant. The whole family of fullerenes appeared to be present in the soot, not just C_{60}!

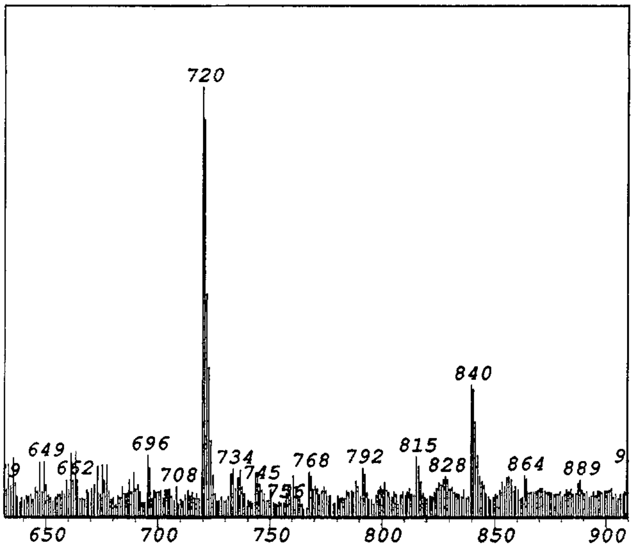


Fig. 25. Part of the FAB mass spectrum of the red extract which confirmed that it consisted mainly of C_{60} and C_{70}. The spectrum also indicates the presence of other fullerenes [72].

C_{60} is Magenta (Pink?) in Solution

Taylor noted that the extract was soluble in hexane and recognized that he might be able to separate the fullerenes chromatographically. To his delight he found that on an alumina column resolution into two bands, one red, the other magenta, could be achieved. The magenta fraction, (Fig. 26) was a delight to the eye in the delicacy of its color. Its mass spectrum showed a peak at 720 amu, and we sent the sample to Tony Avent for NMR analysis. We were summoned to see our single line (Fig. 27), which Avent assured

Fig. 26. Chromatographic separation of the red extract by Taylor resulted in a magenta C_{60} fraction (left) and a red C_{70} fraction (right).

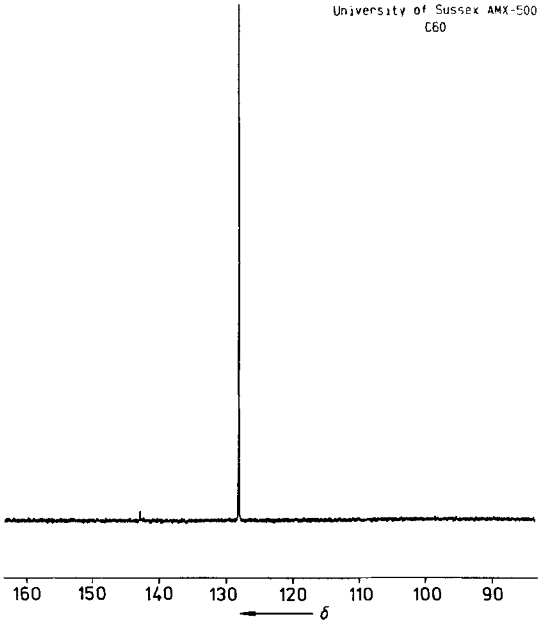


Fig. 27. The first NMR spectrum in which the C_{60} resonance (at $\delta = 143$ ppm) was first identified (barely). The strong line at $\delta = 128$ ppm is (rather appropriately) the resonance of benzene.

us was present. So this was it: a line so small I needed a microscope to see it! Could this insignificant little blip really be the line I had dreamed about for five years? Further work confirmed beautifully that this was the result which we had sought for so long.[72] The joy alleviated almost all the despair I had first felt on reading the paper by Krätschmer et al. One might have thought, as some said, that I should have been pleased to have been proven right when so many had been sceptical. That was not my feeling, probably because I had known ever since the recognition of C_{70} as the second magic fullerene[51] that our structure could not possibly be wrong. I know that my colleagues at Rice University also had no doubts.

What about C_{70}? It turned out to be the icing on the cake, although not without attendent trauma. The wine-red fraction which had masked the pale magenta of C_{60} yielded a mass spectral peak at 840 amu and was clearly C_{70}. According to the expected structure (Fig. 15 right) this compound should exhibit a ^{13}C NMR spectrum with five lines. On Sunday, September 2nd, 1990 I entered the laboratory at the same time as Avent who told me the C_{70} measurement should have just been completed. The spectrum we plotted was sensational—or almost so. There were indeed five lines, but one was in the same position as the C_{60} peak. Could it be that one line was underneath the C_{60} signal? After repeated chromatography to remove the last vestiges of C_{60}, further NMR studies showed the fifth line to be rather different from the others. The resonance of the ten atoms in the waist (Fig. 28c) is more "benzenoid" than the other four resonances.[72] Indeed this line lies dangerously close to the benzene solvent line; had it been a little closer to the benzene signal it would have been swamped and missed altogether. In many ways the five lines of C_{70} are (arguably) more important and significant than the C_{60} singlet. For one thing, they confirm that fullerene carbon atoms are not fluxional; for another, they show that the atoms are not on the perimeter of a monocyclic ring. Both of these cases would lead to a spectrum with a single resonance. Even more important was the fact that the NMR results confirmed the family concept for fullerene cages. It was now clear that a host of stable fullerenes were just waiting to be discovered, as we had long suspected.[53]

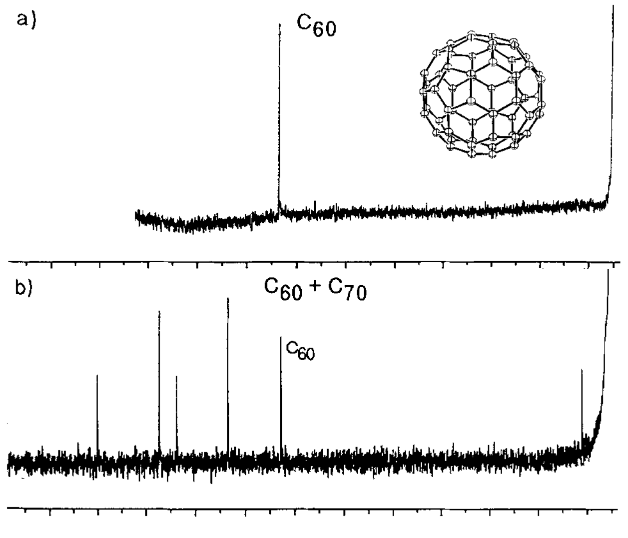


Fig. 28. ^{13}C NMR spectra obtained from chromatographed samples of soluble material extracted from arc-processed graphite: a) spectrum of purified C_{60} (magenta fraction); b) mixed C_{60}/C_{70} sample; c) spectrum of purified C_{70} (red fraction) showing five lines as expected for the symmetric egg-shaped molecule (see Fig. 15).

"The Third Man" is as Elusive as Ever in Space

The elusiveness of C_{60} and my belief that it has been lurking in that blackest of black materials, soot, since time immemorial often reminded me of the role played by Orson Welles in the film "The Third Man". The spirit of this antihero pervades the whole movie although he is seldom seen. Indeed he makes his first appearance late on in the movie in the black shadows of a dark street in Vienna when his face is suddenly illuminated by a light being switched on. For five years C_{60} played a very similar shadowy role—at least as far as I was concerned. My part in the buckminsterfullerene story really started out in space, and this celestial sphere has come down to earth with more of a bounce than a bump; but will it bound back up into space? Is this third form of carbon distributed ubiquitously in space as we surmised the day we found it in the laboratory?[41] Now that we know something about fullerene-60, we should be able to study all its optical properties. It is clear that the UV radiation density in the optically observable interstellar medium is such that the species will be ionized.[73] The possible existence of encapsulated complex ions[73, 74] is quite interesting. However, even with buckminsterfullerene in our hands, we find that this "third man" is as elusive as he ever was in the space between the stars. Perhaps the interstellar form is related to protonated carbon monoxide (HCO^+), which Bill Klemperer identified about 20 years ago.[17] If there are any C_{60} molecules in space there can be little doubt that most will have a proton or some other atom adhering to their surface.[74] $C_{60}H^+$ could probably survive for eons. Other abundant elements, particularly alkali and alkaline-earth metals, must also stick to the surface. Such species will have fascinating optical spectra. For instance, the energy and wavelength of the charge-transfer transition $(C_{60}^+)X \rightarrow (C_{60})X^+$ can be estimated to a first approximation as simply the difference between the ionization potentials of the separated species. For $(C_{60}H)^+$ this transition lies at about 2200 Å. For $(C_{60}Na)^+$ and $(C_{60}K)^+$ the transitions lie in the region of the Diffuse Interstellar Bands[33] and for $(C_{60}Mg)^+$ near zero frequency(!) These observations imply that this and related species will have unusual electrical properties. These processes are probably related to the recently observed superconductivity of metal-doped fullerene-60 materials.[75] This conjecture is supported by an important new result which comes not from work with bulk material but from cluster-beam studies by McElvaney and Callahan.[76] They found that the gas-phase proton affinity of C_{60} is similar to that of ammonia—a remarkable result! I like to put my trust in intuition; when all else fails it is, after all, our only guide: It is curious to note that some important spectral features of space (the Diffuse Bands) have been visible for decades, yet we do not know what causes them. Now we have discovered that an unexpected molecule, C_{60}, has been under our noses on earth since time immemorial and was invisible until now. It seems to me highly likely that these two observations will turn out to be connected.

Epilogue

Since the time that graphite balloons and C_{60} were twinkles in the eyes of David Jones, Eiji Osawa, and a few other imaginative scientists,[42, 43, 46–48] there have been many significant contributions, both experimental and theoretical, to the first chapter of the buckminsterfullerene story which has just been completed. These have recently been comprehensively reviewed.[77] Figure 12 shows the Rice/Sussex team and Figure 29, the Sussex Buckaneers. These two teams together with the Heidelberg/Tucson team scored many of the goals in the football match which has just ended. Many new teams have now started to play an exciting, but different, ball game. The important difference is that the players can now see what they are kicking.

Fig. 29. The Sussex Buckaneers football team. From left: Kroto, Abdul-Sada, Taylor, Hare, and Walton.

Apart from the successful observation of the "lone" NMR line, two other matters give me a sense of deep pleasure: one was the beautiful color of C_{60} and, furthermore, that it was seen first at Sussex. The second was that apparently no one else appeared to have followed up the early IR results obtained by the group from Heidelberg and Tucson (September 1989). In retrospect I find this astounding; perhaps it was because the work appeared in the astronomy literature, but more likely it was because research today is carried out under such pressure, and our fear of failure is so great (and exacerbated by funding procedures). Few groups enjoy the luxury of working in the dark—a condition which I feel lies at the heart of true scientific endeavor. I have a videotape of a marvellous BBC documentary on Richard Feynman (the greatest lecturer I had ever heard) from the series "Horizon". In one part he talks on essentially this topic. This 50 minute program had the most profound effect on me. At one point Feynmann described how, when he was hired at Cornell, Bob Wilson had told him that it was the university's responsibility whether he accomplished anything—it was their risk(!) It was not for Feynman to worry about, he should amuse himself. In this way he was freed from the psychological burden of doing anything "important", and he was able to relax and do what he most enjoyed—physics and mathematics—just for the fun of it. How lucky he was. I know of few professional scientists today, certainly no young ones, who are in such a utopian scientific environment. What a sad reflection on today's research, especially since we know in our hearts that human beings achieve most when they are free of pressure. We know that small children learn and discover the joys of nature most efficiently during their play.

News of the breakthroughs spread like wildfire during September 1990, and the method of production developed by the Heidelberg/Tucson group was immediately improved upon[78] at Rice University. As soon as it was known that fullerenes are chromatographically separable and that solution NMR is feasible, other groups confirmed these measurements.[79, 80] Don Huffman remarked laconically at a recent symposium, "Everyone is able to repeat these experiments".

A new postbuckminsterfullerene world of round organic chemistry and materials science has been discovered overnight. Almost every day a new paper appears on some novel aspect of fullerene behavior. The group from Rice University has shown that C_{60} forms species such as $C_{60}H_{36}$.[78] Hawkins et al. have made an osmium complex in which the spinning of the fullerene ball is stopped and has enabled accurate bond lengths to be determined.[81] NMR studies by Yannoni et al. have also yielded accurate bond lengths.[82] The radical anion has been polymethylated by Olah's group;[83] platinum complexes have been prepared at DuPont.[84] At AT&T it has been found that the metal-doped material now holds the temperature record for molecular superconductivity.[75] Fascinating differences in the crystal structure of C_{60} have been found which depend upon how the crystals are produced.[77] Foote and co-workers at UCLA have shown that C_{60} transfers light energy efficiently to generate singlet oxygen.[85] Diederich, Whetten, and co-workers have evidence for oxides such as $C_{70}O$.[86] C_{60} is decomposed by light under circumstances which still need to be fully identified.[87] Also interesting is the fact that more fullerenes, such as C_{76} and C_{84}, are being extracted and characterized.[86] The fullerene family has arrived in force, and there are balls of all shapes and sizes for everyone to play with.

This advance is an achievement of fundamental science, not applied science, and serves as a timely reminder that fundamental science can achieve results of importance for strategic and applied areas. The origin of the whole program lay in an interest in aspects of molecular dynamics, allied with the quest for an understanding of the origin of the carbon chains in space and their possible relationship to circumstellar and interstellar grains as well as soot.[1] These ideas welded together beautifully with the major advance in cluster science brought about by the experimental techniques developed by Smalley and co-workers at Rice University. Krätschmer and Huffman and co-workers were originally motivated by an interest in space dust and, in their recent breakthrough, by astrophysical implications of C_{60}. The C_{60} story has many facets, but more than anything else it is yet another archetypal lesson on the benefits to be gained by supporting pure fundamental science. The field has exploded, and its applications in chemistry and the science of materials are only just starting to be explored. Finally it is worth noting that C_{60} might have been detected 20–40 years ago, perhaps in a sooting flame; one wonders why it took so long.

Another lesson may be learned from these acknowledgements. Important contributions were made in research programs at the University of Sussex (Brighton, UK), the National Research Council (Ottawa, Canada), Rice University (Houston, Texas, USA), the Max-Planck-Institut für Kernphysik (Heidelberg, Germany) and the University of Arizona (Tucson, USA). The discovery of C_{60} is a tribute to not only the international nature of science but also the necessity of interdisciplinary cooperation. The contribution from the University of Sussex to the story started as a consequence of the "Chemistry by Thesis" degree course initiated by Colin Eaborn, which enabled undergraduates (such as Anthony Alexander) to carry out research with supervisors from more than one field. It could only have been successful in the interdisciplinary scientific research and teaching environment which the university pioneered when Sussex was founded in the "optimistic 60s". Sadly this and other courses have been "regulated" out of existence by bureaucrats who have little understanding of how student research expertise is brought to maturity and no awareness of the dire consequences for our future scientific capability. The first part the story could also not have been achieved had chemistry at Sussex been divided into those traditional subsections of organic, inorganic, and physical chemistry. I also had close contacts with astronomers at Sussex, particularly Bill McCrea and Robert Smith. The carbon discoveries resulted from a free-wheeling research program which started with synthetic chemistry (with David Walton, Anthony Alexander, and Colin Kirby) and moved via spectroscopy and quantum mechanics to radioastronomy (with Takeshi Oka, Lorne Avery, Norm Broten, and John MacLeod at the NRC). It moved back to the laboratory and chemical physics (with Jim Heath, Sean O'Brien, Bob Curl, and Rick Smalley at Rice University). In the last phase, key advice came from Michael Jura (an astronomer) which initiated some basic chemistry (with Jonathan Hare, Amit Sarkar, Ala'a Abdul Sada, Roger Taylor, and David Walton). Apart from those mentioned in the text who played direct (and sometimes crucial parts) such as Steve Wood of British Gas, I also acknowledge greatly the help of many others who played indirect parts, particularly graduate students and post-doctoral fellows as well as colleagues such as Tony Stace, Roger Suffolk, and Mike Lappert. Finally I wish to thank Ed Wasserman for some invaluable advice and David Walton in particular for his unfailing help throughout the period of this story and his painstaking assistance in preparing this account.

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