International Journal of Mass Spectrometry 200 (2000) 253–260

C_{60} and carbon: a postbuckminsterfullerene perspective

Harold Kroto*

CPES University of Sussex, Brighton BN1 9QJ, UK

Received 4 August 2000; accepted 15 August 2000

Abstract

The discovery of the fullerenes and nanotubes has completely changed our perspective on various aspects of carbon chemistry and materials science in quite fundamental ways. The experiments, which uncovered C_{60}, occurred between 1985 and 1990 and there are lessons to be learned of various kinds over the way scientific advances occur and more importantly the way misconceptions can propagate. For instance much of our received wisdom over the behaviour of carbon, in particular graphite on a microscopic scale, was really quite ill-conceived and certainly misleading. Questions might be asked as to why it took almost till the end of the 20th century for the fact to be uncovered that the elegant C_{60} molecule had been lurking in the dark shadows of soot chemistry all the time. After all, mass spectrometric techniques were sufficiently advanced for the discovery to have been made in the 1960's—perhaps even earlier. Some of these issues are addressed here and the discussion gives an insight into the curiously unpredictable way fundamental scientific advances sometimes occur and also highlights the limitations of applied research in this case. (Int J Mass Spectrom 200 (2000) 253–260) © 2000 Elsevier Science B.V.

Keywords: C_{60}; Fullerenes; Carbon; Buckminsterfullerene

1. The discovery of C_{60}

There is no doubt in my mind that when, in the early 1980's, Rick Smalley's group at Rice perfected the laser vapourisation cluster beam apparatus [1,2], C_{60}'s number was essentially up. It was then just a matter of time before this major advance in experimental cluster science came together with the right experiment [3]. Thus if there was a serendipitous aspect to the discovery it lay much more in the events surrounding the particular discovery experiment rather than in the fact that the discovery was made at all [4].

I often went to a symposium that Jim Boggs organised biennially in Austin to bring the spectroscopy and electron diffraction communities together. He had always helped me, and many other young scientists, to participate in this excellent conference. Just after the 1984 conference around Easter time, I had an invitation from Bob Curl to visit Rice, which I accepted. When I arrived, Curl was very excited by the resonant two-photon ionisation (R2PI) study that Smalley's group had just carried out on SiC_2 which had shown that it was a triangular molecule rather than linear one (more-or-less) like the C_3 analogue. I too thought this was an elegant and revealing result and visited the Smalley laboratory. On seeing the cluster beam apparatus I started to wonder whether it could help me to convince some of my colleagues in the interstellar molecule field that the carbon chains that we had discovered in space, by radioastronomy,

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* Corresponding author.

PII S1387-3806(00)00356-0

during the previous decade might have been created in the high temperature/pressure conditions that existed in the expanding plasmas surrounding carbon stars. It seemed to me that laboratory support for my case could be obtained fairly readily by laser-vaporising graphite in the Rice apparatus and reacting the resulting carbon clusters in the nozzle with H_2 and N_2. The goal was to detect the mass spectra of species such as HC_nH, NC_nN and in particular the cyanopolyynes HC_nN, which I was sure would form [5].

These experiments were aimed at producing some circumstantial evidence to add circumstellar-shell chemistry to the two, generally accepted, processes for producing interstellar molecules—the accepted processes being gas phase ion–molecule reactions and interstellar grain surface catalysis. It seemed to me that neither of these two theories satisfactorily explained the existence of interstellar HC_5N, let alone the even larger species such as HC_7N and HC_9N. The ion–molecule reaction schemes had great difficulty producing species with more than 4–5 heavy (non-H atoms) and the latter could not explain how molecules so large could evaporate from the surface of the very cold interstellar grains that provided the creative catalytic surfaces. The experiment I proposed was very simple and could have been carried out essentially immediately. A second even more interesting experiment that came to mind was the possibility of carrying out a R2PI study of the carbon chains, focusing on the possibility that they were responsible for the so-called diffuse interstellar bands (DIBs)—a set of astrophysical optical absorption lines due to some, as-yet, unidentified interstellar material. We could try probing the carbon plasma with a laser tuned to some of the key DIB wavelengths and try to see which mass spectra were affected. Alec Douglas in 1977 [6] had suggested that the carbon chains were good candidates for the DIB carriers. This experiment was a much more difficult proposition and Bob and I had a series of letter correspondences about the problems. In the event it was not till September 1985 that we actually started on the former, more straightforward, experiment. It was during a ten-day period, starting on 1 September 1985, that a 720 u mass spectrum peak was detected and assigned to the C_{60} species [3,4,7]. The experiments were carried out together with graduate students—Jim Heath, Sean O’Brien, and Yuan Liu. Heath, in particular, threw himself into this project and the careful and detailed experimental refinements he made during the discovery period clarified the conditions under which the crucial dominance of the 720 amu signal of the 60-atom carbon molecule was manifested.

In retrospect, I know that I was absolutely certain that the basic astrophysically motivated experiment would work and in a sense there seemed no need to do the experiment just to prove I was right. Indeed, a somewhat related study had been published by Rohlfing et al. soon after my Easter 1984 visit to Rice [8]. This study had also revealed that C_n, clusters with n as high as 180, could be produced! However one should always do an experiment, however certain one is that one knows the answer because: (1) you can never be absolutely sure that you really understand things until you have obtained the experimental confirmation; (2) if the experiment does not work as you expected, you actually learn something that you did not know before and correct misconceptions; and (3) as in this case, not only did the pre-conceived experiment work as expected [9], but something quite extraordinary occurred as well—the fullerenes were detected [3,10]. So there is some sort of take-home lesson to be derived from this odd saga.

2. Serendipity

The discovery of C_{60} is often described as a serendipitous discovery—as mentioned above, in some ways yes and in other ways no. Looking back it is interesting to note how serendipitous was my personal involvement with the discovery, even though I had been involved carbon chemistry in some form or other all through my research career. It seems to me that any group which used the Rice-type cluster beam apparatus to carry out a really detailed study of carbon clustering would have discovered C_{60}. Indeed two studies [8,11] had probed this system during 1984–1985 and though they had detected the species they had apparently not varied the clustering conditions sufficiently to uncover the fact that under certain circumstances the C_{60} signal could become totally dominant and “un-missable.” Indeed in our experiments they were so strong that one could not do anything but puzzle over what structural properties could possibly explain the effect. The serendipity was really that an astrophysically motivated experiment, rather than one which directly probed the physicochemical properties of carbon clusters, accidentally uncovered the species.

3. To boldly propose something that had never been proposed before: on the basis of only a single line in the mass spectrum

The basic result can be stated very simply: when a nucleating carbon plasma cools under certain conditions, a stable species consisting of 60 carbon atoms forms in exceptionally high abundance, relative to other (millions of) possible carbon aggregates. Many other aggregates are detectable, some with n as high as 1000 (note that for $n > \sim 30$ n is mainly even). We suggested that this result could be explained by a truncated icosahedral geometry. Some have suggested that we were somewhat out-of-order to suggest such a structure for C_{60} on the basis of simply a single 60-carbon atom mass spectrometric peak. They are quite wrong. It was not just that it was a strong signal—it really did stand out in so dominant a fashion that one could not avoid puzzling over what possible (structural/pattern) explanation might account for such a striking observation.

Certainly (contrary to some claims!) I was just as aware as were my colleagues of the pitfalls into which the unwary can fall by over-interpreting mass spectrometric data. Mass spectra have a long history of requiring care in interpretation. I had good early guidance as I learned much from the papers of and discussions with Fred Lossing at NRC in Canada who was a pioneer in detecting new unstable molecules by carefully analysing mass spectra. In fact his mass spectrometric work in detecting such species as thioformaldehyde $H_2C{=}S$, produced by pyrolysis influenced my early work in detecting unstable species using pyrolytic production methods, together with microwave and photoelectron identification techniques [5]. So when we were confronted with the C_{60} signal I was fully aware of the boldness of the proposal. No one who lived through the amazing few days in early September 1985 and had come, as we had, to the realisation that the truncated icosahedron (buckminsterfullerene) structure might provide a truly elegant explanation of the strength of the 720 u signal could have resisted suggesting this possibility in the article announcing the experimental results. Further, we knew much better than anyone else that the experiment was perfectly valid—the strength of the signal was no flash-in-the-pan as it was repeatable and would not disappear.

My view is that scientists are acting quite responsibly in making a strenuous effort to find a good hypothetical explanation for their results—certainly in the first instance. I also felt that I must make a serious effort to assemble supporting evidence and personally felt somewhat honour-bound to do whatever I could to prove the structure correct—or if it were not, I felt it would be much better if I/we, who had presented the hypothesis, were the ones to disprove it. I do not have much time for those who present wild hypotheses, and feel no compunction to generate the proof themselves, placing the onus on their critics to assemble the falsifying evidence. I consider this to be scientific irresponsibility of the highest order, bordering on the unethical. Furthermore, I am also not that enamoured by hypotheses, which are not amenable to testing by state-of-the-art technology.

I am sure that had we not suggested the buckminsterfullerene structure, then within 60 min of publication there would have been 60 letters winging their ways to the Nature offices suggesting the truncated icosahedral structure. (It might be worth noting—without comment!—that in the case of the discovery of ferrocene, the paper announcing the original experimental observation did not provide the correct structural explanation. Some debate has surrounded the origin of the correct explanation and other aspects of this discovery [12]).

4. Corroborating circumstantial evidence

As it was, a series of studies carried out independently, in collaboration with the Rice group and by the Rice group independently, added a range of excellent support [7,10,13]. My own personal moment of deep satisfaction occurred the day I realised two facts: (1) The C_{60} cage structure, with its 20 hexagons and 12 isolated pentagons, was the smallest cage that could close without abutting pentagons (which is a trivial consequence of Euler's rule which indicates 12 pentagons are required for closure and the fact that $12 \times 5 = 60$ and (2) during a bout of conjecture over when closure might next occur (after C_{60}) without pentagons abutting, the sudden realisation that it might be C_{70} suddenly seemed a plausible result. This conjecture was aided by the knowledge that C_{70} was the next strong signal after C_{60} [3,10]. A phone call to Tom Schmalz in Galveston confirmed the conjecture beyond all reasonable doubt. Thus a nice scientific conclusion could be drawn, and that was that the buckminsterfullerene structure for C_{60} essentially demanded that C_{70} be the next magic number. That moment was not only personally very satisfying but also very consoling, as I never again woke up in the middle of the night feeling that there was the remotest possibility that we might have proposed the wrong structure.

It seemed to me that there was further confirmation of the cage structure to be found. I played with molecular models of small fullerene structures (C_{24}, C_{28}, C_{36}, C_{50}, etc.) on the basis of simple intuitive symmetry principles and a generalisation of the simple single pentagon isolation rule [13] which Klein and co-workers had also suggested [14,15]. The generalisation—the pentagon multiplet isolation rule [13] implied that other smaller cages might show semimagic behaviour and we had strong signals which fitted—two in particular were the signals for C_{28} and C_{50} [4,13,15]. At this time there were no easily accessible computer programmes to draw the fullerene structures so I made molecular models, photographed them with a Polaroid camera, expanded the image on a Xerox copier and then traced the line images. All this took about 30 min for six structures. The resulting images [13] seem to have taken on lives of their own, albeit somewhat metamorphosed, as I find that they have formed the basis for redrawn images published all over the place.

5. Carbon mass spectra in general

The work of David Walton's group at Sussex was one of the first to shed light on what sort of large carbon structures might be possible when they found that linear carbon chain polyynes, with as many as 32 atoms, could form, albeit with end-groups attached to stabilise the species [16]. Microwave spectroscopy also played a role when we discovered the long chain cyanopolyynes in interstellar space [5]. There were other important early experimental and theoretical studies of the pure carbon species which also played important roles [17].

Some of the earliest studies of carbon seem to have been carried out by Otto Hahn and co-workers who detected the mass spectra of carbon species with about a dozen atoms. These studies were followed by others [17] particularly the pioneering studies of Hintenberger and co-workers, in 1961–1963, who detected species with as many as 33 C atoms [18]. Ever since, the structures of these species have remained a fascinating and somewhat enigmatic problem. The species C_2 of course has been known for a long time but the fascinating C_3 molecule has had a fascinating history and exhibits unusual quasilinear behaviour. The very low bending vibration made it a target for special study which took much work to elucidate [19]. Perhaps this observation augured the further fascinating discoveries which were to come, and perhaps future mysterious discoveries on the structures of the numerous carbon species yet to be unequivocally elucidated.

6. Evidence for rings and chains

The particular focus of much speculation was the curious $\Delta n = 4$ effect which was almost always observed in the positive ion carbon mass spectrum for the range $n = 10$–30. This showed $n = 11, 15, 19,$

23 to be strong and $n = 13, 17, 21$ to be particularly weak. This effect has usually been assumed to be an indicator that these species are monocyclic rings. Energetics suggest that ring closure together with the Huckel $4n + 2$ rule for the positive ions is indicative of aromatic ring formation. However there is, as yet, little actual proof. There is another plausible reason for this pattern based on carbon chains, bent or linear. If one consults a Walsh diagram, see Herzberg's books (19 p319), for C_3 and extends this to chains with $n = 5, 7, 9, 11$, etc. one concludes that C_3 should have a very low bending frequency and C_7 also, whereas C_5 should have a relatively normal linear molecule bending frequency. This can be rationalised if one notes that for C_3 and C_7 there is a central node in the highest occupied (pi-type) orbitals which can stabilise the bent configuration. Thus one might expect that for $n = 3, 7, 11, 15, 19, 23$ the species to be bent or quasilinear and for $n = 5, 9, 13, 17, 21$ they are more-or-less normal linear species. There is thus an alternative possible $\Delta n = 4$ alternation to be expected, which is borne out by the work of Saykally's group [20].

Thus the larger fullerenes are now well characterised and a few chains also, but the rest of the carbon species are still an enigma, though great progress has been made there is still a long way to go. The work of the groups of Maier [21] and Saykally and co-workers [20] as well as the radioastronomy/laboratory experiments of Thaddeus and co-workers [22] all show that long linear carbon chain species can be produced in the laboratory and are floating around in space, just as our original laboratory and radioastronomy studies on the cyanoployynes implied over 20 years ago [5]. As it is, apart from the larger fullerenes, only linear carbon chain species have been structurally characterised so far [20–22]. That is probably mainly because they are easier to detect and study by high resolution vibration–rotation spectroscopy. This is because each J rotational line may be split into anything up to $2J + 1$ components for a nonlinear molecule and for an asymmetric top molecule the pattern of rotational lines might be very complicated and difficult to interpret.

The work of the Bowers group [23] has added totally new dimensions to the problems as it clearly shows that there are several different families of carbon clusters. These observations, and related ones, serve only to whet the appetite for future studies that will eventually result in the elucidation of the structures of all types of carbon clusters from chains at one extreme, through rings of various kinds, to the fullerene cages.

7. Why did it take so long to discover C_{60}?

An interesting question arises as to why C_{60} was not discovered much earlier in the 20th century. In retrospect it still seems incredible that it took so long to discover the third well-characterised form of carbon. It might be seen as a shining example of the way fundamental science often uncovers the unexpected and some sort of argument to show that strategic science has limitations, indeed we see that basic and applied research actually complement each other.

In one of our studies we conjectured over whether the carbon nucleation process that led to C_{60} might be telling us something about the soot formation process. It seemed to us that as soot particles are spheroidal carbonaceous particles, then we might have inadvertently uncovered some knowledge of real value for a deeper understanding of the mechanism of soot formation. We made what we thought was a rather imaginative proposal—that a hypothetical, partly closing, fullerene-related cage structure might serve as a key nucleation intermediate. Such a partly closing object might be prevented from perfect closure by the presence of H atoms and wrap itself up in some aggregating chaotic 3d spiral type process [24,25,10]. Although this suggestion found little favour among some in the soot research community (to put it mildly) it is still interesting to note that Homann's group found a highly dominant C_{60} signal when they studied soot formation using a mass spectrometer capable of detecting the 720 u signal [26]. Amazing as it may now seem, this appears to have been the first time that a mass spectrometer, capable of detecting species with masses greater than 400 amu, had been applied to a soot-forming system. In retrospect this is very surprising as mass spectrometers capable of detecting C_{60} have been available for a long time. Indeed the magnets used during the War to separate uranium have since been used to study C_{60}. Certainly any study of soot formation carried out with a mass spectrometer capable of detecting masses up to 800 could hardly have failed to detect dominant signals for C_{60} and C_{70}. This observation together with some attempt to find a possible structural explanation of this signal would surely have uncovered the species within a few days. Howard's group [27] subsequently showed that the soot collected from combustion of a hydrocarbon flame, premixed with oxygen, contains some 10%, by weight, of fullerenes which can be readily extracted. Perhaps scientists studying soot had routinely washed away all evidence of C_{60} in separating the soot from the various contaminating hydrocarbons for further study. Interestingly a Bunsen burner flame produces C_{60}, so almost all chemists have at some time or other made the species. The molecule is formed in the cooler, inner part of the yellow sooting flame; in fact the yellow colour is continuum emission from incandescent hot soot particles. However, the reason it was not detected previously from this source is that the hot C_{60} is destroyed immediately on contact with oxygen in the air—the outer surfaces of the soot particles are burnt off but as they are macroscopic some remnants of the particles survive.

8. What a difference a name makes

There is, as I have noted previously, no doubt that C_{60} would have been discovered within months had we not found it and the field would now be, much as it is today, perhaps delayed by at most 6 months or so. The only small difference that I feel that my involvement with the discovery made involves the name Buckminsterfullerene. I suspect that had I not suggested this name it would have been called something totally mundane such as soccerene or footballene. As it is, the name has been quite successful in a wider context. Kids love calling C_{60} "Buckyball" and others like to draw analogies with architectural structures through the association with the geodesic domes of Buckminster Fuller. I felt somewhat personally affected when, as often occurred in those early days, complaints were made about the name and I felt moved to defend it. Indeed a plethora of alternative suggestions surfaced during the early years between the discovery and the amazing Krätschmer et al. paper [28] in which the extraction was announced. When Krätschmer et al. used the term "fullerite" I think the decision on the name was finalised. Among those who were less than enthusiastic about the name were my friends Jack Dunitz and Edgar Heilbronner who somewhat humourously mused over whether the discoverers of molecules should be allowed, as are parents, to name their offspring. My view is that the name, though long, does roll of the (English) tongue as smoothly as a football rolls on turf, either Wembley turf or Texas turf [29].

9. What have we learned

We have learned how little we understood about carbon previously in that the hypothetical isolated single crystals of carbon, so often illustrated in basic chemistry textbooks as flat single graphene sheets or little multideck graphite sandwiches are probably just that—hypothetical and do not exist in isolation. Perhaps the nearest we can get are the planar, polycyclic, aromatic hydrocarbons, of which the simplest archetypes are molecules such as naphthalene, anthracene and coronene etc. However they all have H atoms tying down the electrons at the edge, which would be dangling bond electrons in the case of a pure carbon sheet. I look upon the closure of a sheet into C_{60} as a sort of edge reconstruction process, *i.e.* the planar analogue of surface reconstruction that reorganises the atoms in the surface layers in three-dimensional crystals such as silicon.

It is worth pointing out that mass spectrometry was absolutely crucial in the discovery and although numerous cages have now been isolated it might have taken a very long time to deduce that the fullerene species existed had not the C_{60} species been so dominant and given such a thought-provoking clue. In fact it is conceivable that we still might not have come to this conclusion had the (still not obvious!) spontaneous self-assembly mechanism that created C_{60} in so much higher abundance than the rest of the fullerenes taken place.

I must also comment on the brilliant detective work of Wolfgang Krätschmer, Don Huffman, and their young colleagues Kostas Fostiropoulos and Lowell Lamb [28]. To truly appreciate the story of the birth of fullerene science one must also learn about their beautiful contribution in extracting C_{60} and obtaining a definitive x-ray structure. Further, there were highly imaginative theoretical contributions by David Jones, Eiji Osawa, and Zenichi Yoshida as well as Bochvar and Gal'pern and Davidson which all predated the discovery [10].

10. So you thought you knew why graphite is a lubricant

My last observation on the lessons learned from the C_{60} saga relates to the only experiment I have done in recent years all by myself with no help from anyone! In September 1990 when I first had a sample of C_{60} in my hands, I put a small amount on a glass slide and squeezed it with a spatula to test the prediction we made in the discovery article [3]—that perhaps C_{60} would be a superlubricant. To my great disappointment the sample behaved like a lump of grit. So, the obvious conclusion, that as graphite is a lubricant, round pieces of graphite should surely be even better lubricants, is wrong. My "experiment" suggested that pure buckminsterfullerene was an infinitely poorer lubricant than graphite. I thought about this result and its implications and started to wonder why graphite was a lubricant. As time passed and I occasionally mentioned this observation I discovered that numerous scientists were aware of the fact that the standard textbook explanation of graphite's lubricating behaviour is not correct. It appears that during WWII fighter aircraft, such as Spitfires, were developed which could fly at higher and higher altitudes and as they did so the brushes in the electric motors and dynamos started to wear out more and more quickly. It was then discovered that as the pressure dropped, graphite outgases and loses its lubricating properties which are due to intercalated air and water which appears to separate the layers and weaken the inter-graphene layer forces [30]. In fact pure graphite is not used by NASA on the Space Shuttle. Molybdenum sulphide however does have very weak forces between the layers and can be used as a lubricant without additives in a vacuum. There is much food for thought in the fact that this behaviour has been known for over 50 years and yet almost every chemistry textbook has propagated an incorrect explanation. It is especially disturbing as the lubricating behaviour, together with the simple (incorrect) explanation—are the first things that most of us associate with graphite.

Acknowledgements

I wish to thank many colleagues for many fruitful discussions over the years, in particular, David Walton and Tony Cheetham during the completion of this article. Note that most of the key references in this article are to be found in the review paper ref (10), which is as complete an inventory as possible on fullerene publications prior to Dec 31st 1990.

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